A Convenient Allylation of 1,*n*-Dicarbonyl Compounds Using Organoindium Reagents

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The chemoselective reactions of 1,*n*-dicarbonyl compounds with allyl halides using indium metal were investigated. α-Ketoesters such as ethyl pyruvate, ethyl 3-methyl-2-oxobutyrate and ethyl benzoylformate reacted with a variety of allyl halides in the presence of indium to afford hydroxy unsaturated carbonyl compounds in good to excellent yields in MeOH/HCl at 25 °C. For the allyl bromide, the presence of various substituents at the α or γ position exhibited little effects on both the reaction rates and yields. Ethyl acetoacetate or ethyl levulinate was treated with allylindium reagent to give hydroxy unsaturated carbonyl compounds in good yield. These results mean that both reactivity and selectivity are independent of the distance between carbonyl groups. 2,3-Butanedione or 1-phenyl-1,2-propanedione reacted with allylindium to produce monoallylation product as major compound.

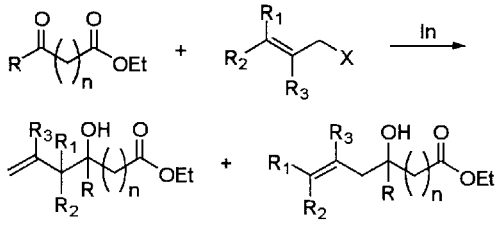
Keywords : Indium, Allylindium reagent, Hydroxy unsaturated carbonyl compounds, Chemoselectivity.

Introduction

Metal-mediated addition of allyl halides to aldehydes or ketones, which is a well established method for the synthesis of homoallylic alcohols, is one of the fundamental reactions in carbon-carbon bond formations.[1] The reactions of carbonyl compounds with allyl- and crotyl-metal reagents derived from a variety of metals, in particular, have been widely investigated.[2] Recently, it has been reported that indium-mediated allylation of carbonyl compounds in aqueous media afforded the corresponding homoallylic alcohols.[3] Those reactions in aqueous media are of especially interest because they offer the possibility of environmentally benign reaction conditions by reducing the burden of organic solvent disposal. Although lots of examples on the indium-mediated allylation in aqueous media of simple aldehydes and ketones have been reported,[4] additives such as sodium iodide[4h] were needed and allylindium reagents were not diverse.[4g,4i] As part of our continuing effort to expand the synthetic utility of indium,[5] we now report that indium metal is highly effective for the chemoselective allylation of 1,*n*-dicarbonyl compounds to afford hydroxy unsaturated carbonyl compounds (Scheme 1).[6]

Results and Discussion

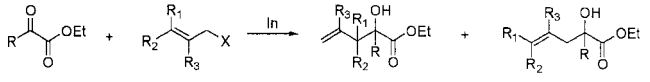
To find optimum conditions for indium-mediated allylation, ethyl pyruvate was chosen as a standard substrate and it reacted with allyl bromide in the presence of indium in various solvents. The results are summarized in Table 1. Of the solvents tested, the best results were obtained in MeOH/0.1 N HCl (1 : 4) and THF/H_2O (1 : 4). The indium-mediated reaction of ethyl pyruvate with allyl bromide in MeOH/0.1 N HCl (1 : 4) or THF/H_2O (1 : 4) afforded ethyl 2-hydroxy-2-methyl-4-pentenoate in 90% yield (Table 1, entry 1). However, the yields were decreased in other solvents under the identical conditions despite longer reaction times. Also, ethyl 3-methyl-2-oxobutyrate (entry 2) and ethyl benzoylformate (entry 3) reacted with allyl bromide under the identical conditions to produce the desired compound **2** and **3** in 94% and 92% yields, respectively. The reactions are completely chemoselective and no addition to the ester group is observed by ^{1}H NMR spectroscopy of the crude reaction mixture.

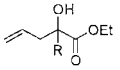
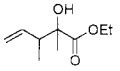
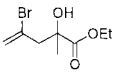
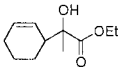
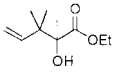
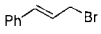
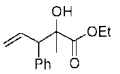
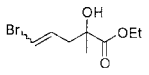
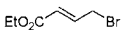
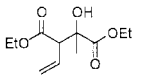
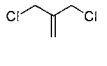
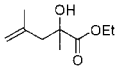
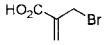
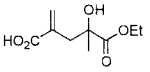
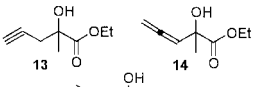
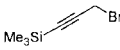
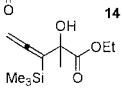
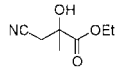
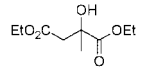
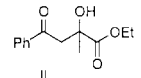
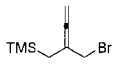
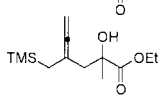


Scheme 1

Table 1 summarizes the experimental results and illustrates the efficiency and scope of the present method.[7] For the allyl bromide, the presence of various substituents at the γ position, such as methyl (entry 4), dimethyl (entry 7), phenyl (entry 9), bromo (entry 10) or ethoxycarbonyl (entry 11) exhibited little effects on both the reaction rates and yields. Also, good to excellent yields were obtained in reactions of various α-substituted allyl bromide such as 3-bromocyclohexene (entry 6). However, 2,3-dibromopropene reacted with ethyl pyruvate to give the desired product in 10% yield (entry 5). In case of prenyl bromide, cinnamy bromide and ethyl bromocrotonate, the products resulting from γ attack were obtained selectively. Reaction of allylindium with methallyl dichloride produced the dechlorinated compound **11** which was obtained by allylation followed by reduction of allyl chloride (entry 12). It is especially noteworthy that indium reagent having an acidic hydrogen such as 2-(bromomethyl)acrylic acid reacted with ethyl pyruvate to provide the corresponding α-hydroxy-γ,δ-unsaturated esters **12** in 67% yield (entry 13). In case of propargyl bromide (entry 14), regioisomeric products **13** and **14** were produced.

Table 1. Reaction of α-keto esters with a variety of allyl halides using indium metal

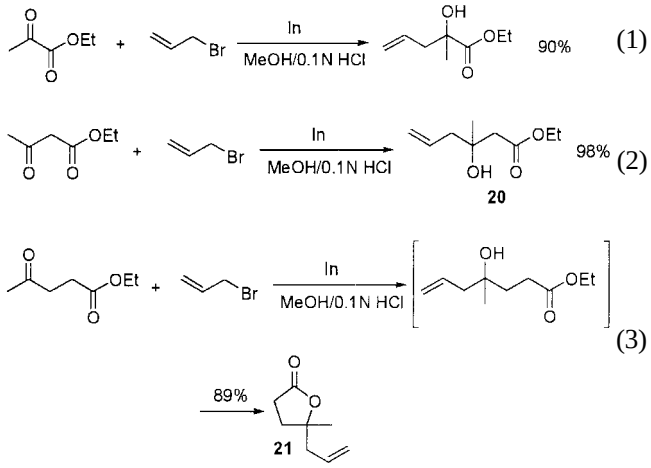


Entry	R	Allyl halide	Product	Isolate yield (%)
1	CH_3			**1** 90[a,b]
2	$(CH_3)_2CH$			**2** 94
3	Ph			**3** 92
4	CH_3			**4** 79[b](1.2:1)[e]
5	CH_3			**5** 10[a,c]
6	CH_3			**6** 68[c](4.5:1)[e]
7	CH_3			**7** 68[b]
8				0[c]
9	CH_3			**8** 85[c](100:0)[e]
10	CH_3			**9** 61[a](1.2:1)[f]
11	CH_3			**10** 85[c](100:0)[e]
12	CH_3			**11** 72[c]
13	CH_3			**12** 67[d]
14	CH_3			**13** **14** 71[c](2.7:1)[g]
15	CH_3			**15** 72[b]
16	CH_3			**16** 89[h]
17				0[c]
18	CH_3			**17** 84[i]
19				0[c]
20	CH_3			**18** 38[i]
21	CH_3			**19** 77[b]

[a]solvent: MeOH : 0.1 N HCl = 1 : 4. [b]solvent: THF : H_2O = 1 : 4. [c]solvent: MeOH : 0.2 N HCl = 1 : 4. [d]solvent: H_2O. [e]diastereomeric ratios which were determined by ^1H NMR integration ratio of methyl groups of α-position. [f]*cis*/*trans* ratio and configuration of 1,3-dibromo-1-propene was retained. [g]regioisomeric ratio. [h]solvent: THF. TMSCl was used as additive. [i]solvent: DMF.

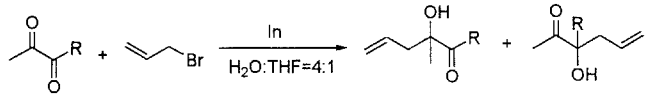
However, 3-bromo-1-(trimethylsilyl)-1-propyne gave regioselectively the allenylated compound **15** in 72% yield (entry 15). Organoindium reagents derived from the reaction of indium with bromoacetonitrile and ethyl bromoacetate reacted with ethyl pyruvate to afford the desired compound in 89% and 84% yields, respectively (entry 16 and 18). Treatment of ethyl pyruvate with organoindium reagent derived from phenacyl bromide gave the addition product **18** in 38% yield (entry 20). The protocol developed here could also be applied to a reaction with allenyl bromide. For example, ethyl pyruvate reacted with 4-bromo-3-[(trimethylsilyl)-methyl]-1,2-butadiene[8] under the identical conditions to give the desired compound **19** in 77% yield (entry 21).

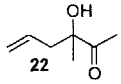
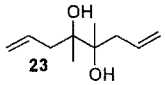
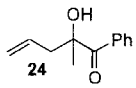
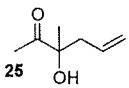
On the basis of theses results, ethyl acetoacetate which is 3-ketoester was treated with allylindium reagent in MeOH/HCl at 25 °C to give the desired compound **20** in 98% yield (eq. 2).[4g] In case of ethyl levulinate which is 4-ketoester, γ-butyrolactone **21** which was produced by addition of allylindium to ketone followed by esterification, was obtained in 89% yield (eq. 3). These results mean that both reactivity and selectivity are independent of the distance between carbonyl groups.



2,3-Butanedione reacted with allylindium in H_2O/THF to produce monoallylation **22** and diallylation compound **23** in 12% and 29% yields, respectively. Dropwise addition of allylindium to 2,3-butanedione increased the selectivity (entry 2, Table 2). Treatment of 1-phenyl-1,2-propanedione with allylindium afforded 2-benzoyl-4-penten-2-ol (**24**) and

Table 2. Reaction of 1,2-diketones with allyl halide using indium metal



Entry	R	Product	
	CH_3	 **22**	 **23**
1		12%	29%
2		23%	6%
3	Ph	 **24**	 **25**
		38%	31%

3-hydroxy-3-phenyl-5-hexen-2-one (**25**) in 38% and 31% yields, respectively (entry 3).

In conclusion, the chemoselective reactions of 1,*n*-dicarbonyl compounds with allyl halides using indium metal were investigated. α-Ketoesters such as ethyl pyruvate, ethyl 3-methyl-2-oxobutyrate and ethyl benzoylformate reacted with a variety of allyl halides in the presence of indium to afford hydroxy unsaturated carbonyl compounds in good to excellent yields in MeOH/HCl at 25 °C. For the allyl bromides, the presence of various substituents at the α or γ position exhibited little effects on both the reaction rates and yields. Ethyl acetoacetate or ethyl levulinate was treated with allylindium reagent to give hydroxy unsaturated carbonyl compounds in good yield. These results mean that both reactivity and selectivity are independent of the distance between carbonyl groups. 2,3-Butanedione or 1-phenyl-1,2-propanedione reacted with allylindium to produce mono-allylation product as major compound. The present method may serve as an alternative to the existing synthetic methods of α-hydroxy ester because of mild reaction condition and some advantages of indium metal such as ease of handling, high reactivity and selectivity, low toxicity and operational simplicity.

Experimental Section

The ^{1}H NMR and ^{13}C NMR spectra were recorded on Brucker IFS 48 (400 MHz) spectrometer. Proton chemical shifts (δ) were reported in ppm downfield from tetramethylsilane (TMS), and ^{13}C resonances were recorded using the 77.0 ppm $CDCl_3$ resonance peak of the solvent as internal reference. Fourier transform infrared (FTIR) spectra were recorded on a JASCO IR 100 spectrophotometer. Mass spectra were obtained on a Autospec, M363 series. Column chromatography was performed on silica gel (Merck, 230-400 mesh). The gas chromatograms were obtained on HP 5890.

Typical experimental procedures: Ethyl 2-hydroxy-2-methyl-4-pentenoate (1). To a solution of ethyl pyruvate (116.0 mg, 1.0 mmol) and allyl bromide (181.0 mg, 1.5 mmol) in 5 mL of MeOH/0.1 N HCl (1 : 4) was added indium (115.0 mg, 1.0 mmol : indium power (99.99%) purchased from Aldrich Chem Co.) in one portion. The reaction mixture was stirred vigorously at room temperature for 2 hr. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution. The aqueous layer was extracted with ether (3 25 mL) and the combined organic layer washed with water (20 mL) and brine (20 mL) and dried with $MgSO_4$, filtered and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (hexane/EtOAc = 10/1) leading to ethyl 2-hydroxy-2-methyl-4-pentenoate (142.0 mg, 90%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.65-5.92 (m, 1H), 5.14 (m, 2H), 4.22 (q, *J* = 7.32 Hz, 2H), 2.99 (s, 1H), 2.15-2.42 (m, 2H), 1.41 (s, 3H), 1.29 (t, *J* = 7.02 Hz, 3H); ^{13}C NMR (100 HMz, $CDCl_3$) δ 176.61, 132.52, 119.07, 74.30, 61.86, 44.71, 25.54, 14.26; IR (film) 3490, 3010, 2960, 1700, 1430, 1360, 1240, 1200, 1150 cm^{-1}; MS (CI) calcd for $C_8H_{15}O_3$ $[M+H]^+$ 159, found 159.

Ethyl 2-hydroxy-2-isopropyl-4-pentenoate (2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92-5.65 (m, 1H), 5.10 (d, *J* = 7.82 Hz, 1H), 5.06 (s, 1H), 4.23 (q, *J* = 7.13 Hz, 2H), 3.17 (s, 1H), 2.53, 2.50 (dd, *J* = 6.34, 13.79 Hz, 1H), 2.40, 2.36 (dd, *J* = 8.19, 13.70 Hz, 1H), 2.15-1.82 (m, 1H), 1.29 (t, *J* = 7.14 Hz, 3H), 0.97 (d, *J* = 6.83 Hz, 3H), 0.85 (d, *J* = 6.83 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.33, 133.08, 118.47, 79.68, 61.75, 41.55, 35.09, 17.42, 15.91, 14.31; IR (film) 3500, 3020, 2940, 1700, 1420, 1400, 1240 cm^{-1}; MS (CI) calcd for $C_{10}H_{19}O_3$ $[M+H]^+$ 187, found 187.

Ethyl 2-hydroxy-2-phenyl-4-pentenoate (3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.72 Hz, 2H), 7.36 (t, *J* = 7.08 Hz, 2H), 7.12-7.42 (m, 1H), 5.95-5.79 (m, 1H), 5.17, 5.14 (dd, *J* = 17.08, 9.76 Hz, 2H), 4.41-4.19 (m, 2H), 3.77 (s, 1H), 2.99, 2.96 (dd, *J* = 7.76, 13.99 Hz, 1H), 2.78, 2.74 (dd, *J* = 6.49, 14.00 Hz, 1H), 1.27 (t, *J* = 7.16 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.62, 141.42, 132.40, 128.25, 127.78, 125.35, 119.30, 77.89, 62.50, 44.17, 14.10; IR (film) 3480, 3020, 2960, 1710, 1430, 1410, 1240 cm^{-1}; MS (CI) calcd for $C_{13}H_{17}O_3$ $[M+H]^+$ 221, found 221.

Ethyl 2-hydroxy-2,3-dimethyl-4-pentenoate (4). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.92-7.65 (m, 1H), 5.14-4.99 (m, 2H), 4.24 (m, 2H), 3.15 (s, 1H), 2.46 (m, 1H), 1.32 (t, *J* = 3.66 Hz, 3H), 1.08 (d, *J* = 6.72 Hz, 3H), 0.96 (d, *J* = 6.72 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.18, 177.06, 139.34, 138.60, 116.87, 116.09, 76.41, 76.14, 65.98, 61.99, 61.93, 46.32, 46.16, 24.37, 23.59, 15.36, 15.30, 14.30, 13.58; IR (film) 3520, 3020, 2960, 1700, 1430, 1410, 1240 cm^{-1}; MS (CI) calcd for $C_9H_{17}O_3$ $[M+H]^+$ 173, found 173.

Ethyl 4-bromo-2-hydroxy-2-methyl-4-pentenoate (5). ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.73 (s, 1H), 5.61 (d, *J* = 1.53 Hz 1H), 4.28 (q, *J* = 7.32 Hz, 2H), 3.38 (s, 1H), 3.00 (d, *J* = 14.65 Hz, 1H), 2.85 (d, *J* = 14.65 Hz, 2H), 1.48 (s, 3H), 1.35 (t, *J* = 7.02 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.25, 140.11, 136.23, 128.62, 128.42, 127.22, 118.40, 76.74, 61.97, 58.10, 24.77, 14.11; IR (film) 3500, 3020, 2960, 1700, 1410, 1360, 1250 cm^{-1}; MS (CI) calcd for $C_8H_{13}BrO_3$ $[M+H]^+$ 238, found 238.

Ethyl 2-(2′-cyclohexenyl)-2-hydroxy-2-methylpropanoate (6). ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.90-5.85 (m, 1H), 5.83-5.37 (m, 1H), 4.26 (q, *J* = 7.02 Hz, 2H), 2.68 (s, 1H), 1.99 (m, 1H), 1.89-1.82 (m, 2H), 1.52-1.41 (m, 2H), 1.39 (s, 3H), 1.31 (t, *J* = 7.02, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.12, 176.93, 130.97, 130.36, 126.35, 125.29, 76.48, 61.92, 61.80, 43.88, 43.81, 25.02, 24.11, 23.59, 22.95, 22.44, 21.97, 21.84, 14.28; IR (film) 3520, 3030, 2960, 2940, 1710, 1440, 1420, 1250 cm^{-1}; MS (CI) calcd for $C_{11}H_{19}O_3$ $[M+H]^+$ 199, found 199.

Ethyl 2-hydroxy-2,3,3-trimethyl-4-pentenoate (7). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.94, 5.90 (dd, *J*= 10.96, 16.00 Hz, 1H), 5.00 (d, *J* = 3.35 Hz, 1H), 4.96 (d, *J* = 9.71 Hz, 1H), 4.17 (m, 2H), 3.41 (s, 1H), 1.28 (s, 3H), 1.24 (t, *J* = 7.19, 3H), 1.02 (s, 3H), 1.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.80, 144.22, 113.56, 78.80, 62.20, 43.82, 22.79, 22.33, 21.11, 14.62; IR (film) 3490, 3020, 2950, 1690, 1410, 1360, 1240, 1120 cm^{-1}; MS (CI) calcd for $C_{10}H_{19}O_3$ $[M+H]^+$ 187,

found 187.

Ethyl 2-hydroxy-2-methyl-3-phenyl-4-pentenoate (8). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.42-7.15 (m, 5H), 6.49-6.21 (m, 1H), 5.28 (d, J = 3.97, 1H), 5.24 (d, J =11.60, 1H), 4.21-3.96 (m, 2H), 3.58 (d, J = 9.77, 1H), 3.29 (s, 1H), 1.50 (s, 3H), 1.20 (t, J = 6.71, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.25, 140.12, 136.23, 128.62, 128.42, 127.22, 118.40, 76.74, 61.97, 58.10, 24.77, 14.11; IR (film) 3500, 3020, 2940, 1700, 1440, 1410, 1240, 1140 cm^{-1}; MS (CI) calcd for $C_{14}H_{19}O_3$ [M+H]$^+$ 235, found 235.

***trans*-Ethyl 5-bromo-2-hydroxy-2-methyl-4-pentenoate (9-*trans*)**. ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.92-5.63 (m, 1H), 5.26-4.98 (m, 1H), 4.60 (d, J = 10.07 Hz, 1H), 4.41-4.18 (m, 2H), 2.59-2.18 (m, 2H), 1.43 (s, 3H), 1.31 (t, J = 7.33 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.64, 132.52, 119.14, 74.32, 61.91, 44.73, 25.58, 14.29; IR (film) 3500, 3020, 2960, 1720, 1420, 1400, 1240 cm^{-1}; MS (CI) calcd for $C_8H_{14}BrO_3$ [M+H]$^+$ 237, found 237.

***cis*-Ethyl 5-bromo-2-hydroxy-2-methyl-4-pentenoate (9-*cis*)**. ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.21-5.99 (m, 1H), 5.24 (d, J = 27.45 Hz, 1H), 5.31-5.19 (m, 1H), 4.42-4.14 (m, 2H), 2.59-2.31 (m, 2H), 1.53 (s, 3H), 1.33 (t, J = 7.33 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.42, 135.02, 119.02, 74.32, 61.54, 44.73, 24.88, 14.22; IR (film) 3500, 3020, 2960, 1720, 1420, 1400, 1240 cm^{-1}; MS (CI) calcd for $C_8H_{14}BrO_3$ [M+H]$^+$ 237, found 237.

Diethyl 2-hydroxy-2-methyl-3-vinylsuccinate (10). ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.18-5.94 (m, 1H), 5.38 (d, J = 10.07 Hz, 1H), 5.30 (d, J = 17.09 Hz, 1H), 4.26 (q, J = 7.33 Hz, 2H), 4.16 (q, J = 7.02 Hz, 2H), 3.47 (d, J = 9.77 Hz, 1H), 1.35 (s, 3H), 1.31 (t, J = 7.33 Hz, 3H), 1.26 (t, J = 7.32 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.84, 172.49, 130.85, 121.61, 74.94, 61.97, 61.30, 57.35, 23.91, 14.15, 14.08; IR (film) 3500, 3020, 2960, 1710, 1430, 1410, 1240 cm^{-1}; MS (CI) calcd for $C_{11}H_{19}O_5$ [M+H]$^+$ 231, found 231.

Ethyl 2-hydroxy-2,4-dimethyl-4-pentenoate (11). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.81 (s, 1H), 4.68 (s, 1H), 4.31-4.02 (m, 2H), 2.55 (d, J = 13.72 Hz, 1H), 2.39 (d, J = 13.57 Hz, 1H), 1.69 (s, 3H), 1.36 (s, 3H), 1.24 (t, J = 7.22 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.18, 141.67, 115.36, 74.89, 62.18, 48.19, 26.86, 24.27, 14.56; IR (film) 3500, 3020, 2940, 1700, 1430, 1350, 1440 cm^{-1}; MS (CI) calcd for $C_9H_{17}O_3$ [M+H]$^+$ 173, found 173.

4-Ethoxycarbonyl-4-hydroxy-2-methylenylpentanoic acid (12). ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.44 (s, 1H), 5.82 (s, 1H), 4.38-4.19 (m, 2H), 2.86 (d, J = 14.04 Hz, 1H), 2.69 (d, J = 14.04 Hz, 1H) 1.47 (s, 3H), 1.30 (t, J = 7.02 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.10, 172.37, 135.03, 131.67, 74.30, 62.14, 41.20, 25.56, 14.13; IR (film) 3010, 3940, 1700, 1670, 1610, 1420, 1400, 1140, 950 cm^{-1}; MS (CI) calcd for $C_9H_{15}O_5$ [M+H]$^+$ 203, found 203.

Ethyl 2-hydroxy-2-methyl-4-pentynoate (13). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23 (q, J = 3.58, 2H), 3.16 (s, 1H), 2.63 (d, J = 16.59 Hz, 1H), 2.52 (d, J = 16.59 Hz, 1H) 2.29-1.98 (m, 1H), 1.43 (s, 3H), 1.28 (t, J = 5.04, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.55, 79.34, 73.93, 71.71, 62.50, 31.21, 25.44, 14.51; MS (CI) calcd for $C_8H_{13}O_3$ [M+H]$^+$ 157, found 157.

Ethyl 2-hydroxy-2-methyl-3,4-pentadienoate (14). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32 (t, J = 6.79, 1H), 5.13-4.86 (m, 2H), 4.23 (q, J = 3.58, 2H), 3.16 (s, 1H), 1.49 (s, 3H), 1.26 (t, J = 7.36, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.91, 175.48, 96.36, 79.34, 72.87, 62.54, 25.24, 14.51; MS (CI) calcd for $C_8H_{13}O_3$ [M+H]$^+$ 157, found 157.

Ethyl 2-hydroxy-2-methyl-3-trimethylsilyl-3,4-pentadienoate (15). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.55 (s, 2H), 4.26 (q, J = 6.83 Hz, 2H), 1.56 (s, 3H), 1.31 (t, J = 7.19, 3H), 0.16 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.03, 176.21, 101.42, 75.31, 71.82, 62.12, 26.65, 14.28, 0.03; IR (film) 3480, 3020, 2940, 1910, 1700, 1430, 1400, 1240, 1120 cm^{-1}; MS (CI) calcd for $C_{11}H_{21}O_3Si$ [M+H]$^+$ 229, found 229.

Ethyl 3-cyano-2-hydroxy-2-methylpropanoate (16). ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.32 (q, J = 7.02 Hz, 2H), 3.33 (s, 1H), 2.79 (s, 1H), 2.72 (s, 1H), 1.54 (s, 3H), 1.34 (t, J = 7.02 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.02, 116.25, 72.12, 63.14, 29.18, 25.62, 14.11; IR (film) 3490, 3020, 2960, 2260, 1700, 1430, 1400, 1230 cm^{-1}; MS (CI) calcd for $C_7H_{11}NO_3$ [M+H]$^+$ 158, found 158.

Ethyl 3-ethoxycarbonyl-3-hydroxybutanoate (17). ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.25 (q, J = 7.02 Hz, 2H), 4.14 (q, J = 7.32 Hz, 2H), 3.47 (s, 1H), 2.97 (d, J = 16.48 Hz, 1H), 2.65 (d, J = 16.48 Hz, 1H), 1.43 (s, 3H), 1.29 (t, J = 7.94 Hz, 3H), 1.25 (t, J = 7.02 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.68, 171.07, 72.51, 62.00, 60.89, 44.26, 26.35, 14.13; IR (film) 3500, 3010, 2940, 1700, 1710, 1240, 1170 cm^{-1}; MS (CI) calcd for $C_9H_{16}O_5$ [M+H]$^+$ 205, found 205.

Ethyl 2-hydroxy-2-phenacylpropanoate (18). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.97 (d, J = 14.00 Hz, 2H), 7.56-7.44 (m, 3H), 4.25 (q, J = 7.02 Hz, 2H), 3.69 (d, J = 17.70 Hz, 1H), 3.36 (d, J = 17.70 Hz, 1H), 1.53 (s, 3H), 1.27 (t, J = 7.32 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.00, 176.07, 133.80, 128.80, 128.26, 72.73, 61.83, 47.99, 26.52, 14.16; IR (film) 3520, 3020, 2940, 1720, 1660, 1430, 1400, 1230, 1200 cm^{-1}; MS (CI) calcd for $C_{13}H_{16}O_4$ [M+H]$^+$ 237, found 237.

Ethyl 2-hydroxy-2-methyl-4-[(trimethylsilyl)methyl]-4,5-hexadienoate (19). ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.73-4.51 (m, 2H), 4.49-4.13 (m, 2H), 3.33 (s, 1H), 2.52-2.21 (m, 2H), 1.43 (s, 3H), 1.35 (s, 2H), 1.30 (t, J = 7.02 Hz, 3H), 0.03 (s, 9H); ^{13}C NMR (100 Mz, $CDCl_3$) δ 207.18, 176.43, 143.04, 96.37, 75.75, 74.93, 61.67, 44.51, 26.67, 26.13, 22.58, 14.20, -1.16; IR (film) 3450, 3020, 2940, 1700, 1400, 1260, 1140 cm^{-1}; MS (CI) calcd for $C_{13}H_{25}O_3Si$ [M+H]$^+$ 257, found 257.

4-Allyl-4-methyl-γ-butyrolactone (21). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.97-5.71 (m, 1H), 5.19, 5.16 (dd, 9.78, 6.92 Hz, 2H), 2.85-2.51 (m, 2H), 2.42 (d, J = 6.92 Hz, 2H), 2.42-1.65 (m, 2H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.69, 132.04, 119.79, 85.96, 45.26, 32.15, 29.16, 26.14; IR (film) 3460, 3040, 2960, 1750, 1410, 1380, 1150 cm^{-1}; MS (CI) calcd for $C_8H_{12}O_2$ [M+H]$^+$ 141, found 141.

3-Hydroxy-3-methyl-5-hexen-2-one (22). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92-5.69 (m, 1H), 5.24-4.97 (m, 2H), 3.82

(s, 1H), 2.47 (d, J = 7.63 Hz, 2H), 2.22 (s, 3H), 1.39 (s, 3H); GCMS (CI) calcd for $C_7H_{12}O_2$ $[M+H]^+$ 129, found 129.

4,5-Dihydroxy-4,5-dimethyl-1,7-octadiene (23). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.24-5.91 (m, 2H), 5.19-5.08 (m, 4H), 2.56-2.45 (m, 2H), 2.24 (s, 4H), 1.16 (s, 6H); GCMS (CI) calcd for $C_{10}H_{18}O_2$ $[M+H]^+$ 171, found 171.

2-Benzoyl-4-penten-2-ol (24). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 7.02 Hz, 2H), 7.62-7.26 (m, 4H), 5.89-5.71 (m, 1H), 5.27-4.96 (m, 2H), 4.05 (s, 1H), 2.99-2.93 (m, 1H), 2.89-2.57 (m, 2H), 1.63 (s, 3H); GCMS (CI) calcd for $C_{12}H_{14}O_2$ $[M+H]^+$ 191, found 191.

3-Hydroxy-3-phenyl-5-hexen-2-one (25). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.02 (d, J = 7.02 Hz, 2H), 7.62-7.26 (m, 4H), 5.74 (m, 1H), 5.27-4.96 (m, 2H), 4.27 (s, 1H), 2.99-2.93 (m, 1H), 2.89-2.57 (m, 2H), 2.09 (s, 3H); GCMS (CI) calcd for $C_{12}H_{14}O_2$ $[M+H]^+$ 191, found 191.

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7. All new compounds have satisfactory analytical data including ^{1}H, ^{13}C-NMR, MS, and IR spectroscopy.
8. 4-Bromo-3-[(trimethylsilyl)methyl]-1,2-butadiene was prepared from 2-butyn-1,4-diol according to the following scheme.