A New Reaction System for Horner–Wadsworth–Emmons Olefination of Optically Active 4-Hydroxy-2-oxo-alkylphosphonates and 4-Hydroxy-1-chloro-2-oxo-alkylphosphonates with Aliphatic Aldehydes

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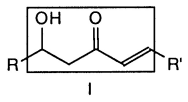
Abstract: A new and convenient reaction system is described for the synthesis of chiral β′-hydroxy-α,β-unsatuarated ketones based on the Horner–Wadsworth–Emmons olefination of optically active 4-hydroxy-2-oxo-alkylphosphonates and 4-hydroxy-1-chloro-2-oxo-alkylphosphonates with aliphatic aldehydes.

Key words: 2′-hydroxy-1,2-unsatuarated ketones, Horner–Wadsworth–Emmons reaction, 4-hydroxy-2-oxo-alkylphosphonates, 4-hydroxy-1-chloro-2-oxo- alkylphosphonates

β′-Hydroxy-α,β-unsatuarated ketones (**I**, Figure 1) are structure units that are frequently found in the molecule of natural products, such as pentamycin,[1] yashabushitriol,[2] and 1α, 25-dihydrovitamin D_3[3] etc. For the preparation of those compounds, several synthetic routes were reported in the literature including Mukaiyama aldol reaction,[4] $LnCl_3$-mediated α′-alkylations of enone and aldehydes,[5] reductive transformation of α,β-epoxy ketones to β-hydroxy ketones promoted through a photoinduced electron transfer process with 1,3-dimethyl-2-phenylbenzimidazoline (DMPBI),[6] vanadium-catalyzed aldol additions of allenic alcohols and aldehydes,[7] boron trifluoride-promoted reaction of dithio-substituted allylic anions and cyclic ethers,[8] and the reaction of α,β-unsaturated and α-phenyl acetals with expoxides promoted by lithium-potassium mixed base LICKOR [butylithium and potassium butoxide (so called 'Schlosser reagent')].[9]



I

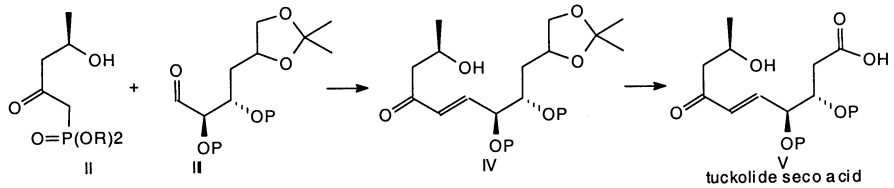
Figure 1

The disadvantages of the above synthetic routes are significant, consisting of harsh reaction conditions, expensive reagents, low chemical yields and even low optical purity.[4–9] Development of a new procedure leading to the preparation of the β′-hydroxy-α,β-unsaturated ketones (**I**) seems necessary. It is reasonable to predict that the Horner–Wadsworth–Emmons (HWE) reaction will offer better results, since this method is usually applied under mild conditions.

Diethyl 4-hydroxy-2-oxo-4-aryl (or alkyl) butylphosphonates and diethyl 4-hydroxy-1-chloro-2-oxo-4-aryl (or alkyl) butylphosphonates are an important kind of compounds, which could react with aldehydes or ketones to provide key building blocks of α,β-unsatuarated ketones through HWE reaction.[10] They could also be transformed into 2-oxo-3-alkenylphosphonates and in the following reacting with vinyl ethers by hetero-Diels–Alder reactions leading to 5-substituted 2-phosphoryl-2-cyclohexen-1-ones.[11] Recently, we transformed this kind of compounds into a new series of tetrahydrofuran units through an intramoleular O–H insertion reaction catalyzed by rhodium acetate [$Rh_2(OAc)_2$].[12]

Very recently, our group has exploited *Candia Antarctic* lipase B (*CALB*) and crude *Candia Rugosa* lipase (*CRL*) to resolve hydroxyphosphonates and aminophosphonates.[10a,b,12,13] One of the resulting optically active hydroxyphosphonates (**II**) is a useful intermediate for the synthesis of tuckolide seco acid (**V**) that is an inhibitor of HMGCoA reductase (Scheme 1).[14]

In this paper, we describe a new and facile reaction system for the HWE olefination of chiral 4-hydroxy-2-oxo-alkylphosphonates and 4-hydroxy-1-chloro-2-oxo-alkylphosphonates with aliphatic aldehydes.



Scheme 1

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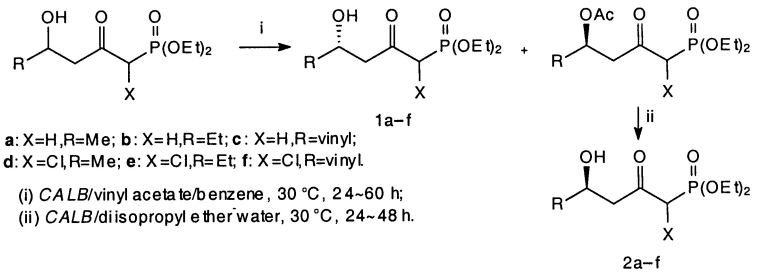
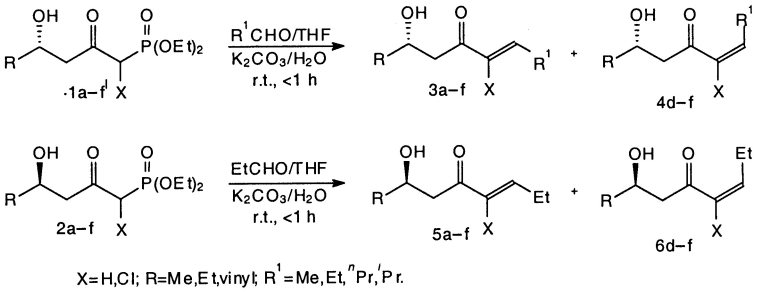


Scheme 2

According to our previous papers,[10a,b] we prepared the optically active 4-hydroxy-2-oxo-alkylphosphonates (**1a**–**c**, **2a**–**c**) and 4-hydroxy-1-chloro-2-oxo-alkylphosphonates (**1d**–**f**, **2d**–**f**) (Scheme 2).

In the first part of this paper, we demonstrate that the HWE reaction of chiral compounds **1a**–**f** and **2a**–**f** obtained from *CALB* kinetic resolution, underwent normal olefination with benzaldehyde with good enantiomeric excess. To our surprise, these optically active substrates gave only low chemical yields and even racemization products in the HWE reaction with aliphatic aldehydes using a DBU/LiBr system due to long reaction times and strong alkaline conditions.[11] By careful examination of the reaction conditions, however, we developed a new reaction system consisting of RCHO/THF/H_2O/K_2CO_3 to provide olefination products with aliphatic aldehydes (Scheme 3, Table 1).



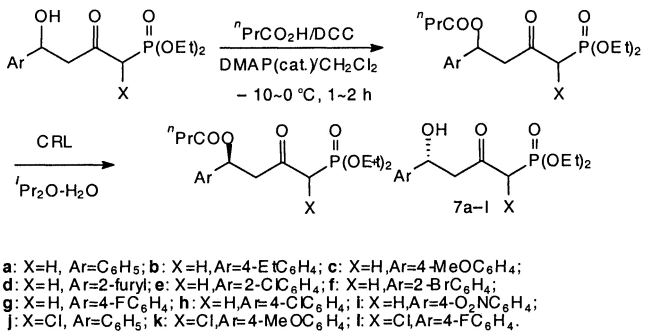
Scheme 3

Table 1 HWE Reaction of Compounds **1a**–**f** and **2a**–**f** with Aliphatic Aldehydes

Substrate	X	R	R^1	**3**		**4**		**5**		**6**	
				Yield (%)[a]	ee (%)[b]	Yield (%)[a]	ee (%)[c]	Yield (%)[a]	ee (%)[b]	Yield (%)[a]	ee (%)[c]
a	H	Me	Et	95	99	–	–	94	99	–	–
b	H	Et	Et	96	95	–	–	95	96	–	–
b(1)	H	Et	Me	92	>99	–	–	–	–	–	–
b(2)	H	Et	*n*-Pr	94	96	–	–	–	–	–	–
b(3)	H	Et	*i*-Pr	95	96	–	–	–	–	–	–
c	H	Vinyl	Et	96	99	–	–	97	99	–	–
d	Cl	Me	Et	83	99	7	99	84	99	7	99
e	Cl	Et	Et	81	97	7	97	–	–	–	–
e(1)	Cl	Et	Me	86	>99	7	>99	–	–	–	–
e(2)	Cl	Et	*n*-Pr	79	97	8	97	–	–	–	–
e(3)	Cl	Et	*i*-Pr	85	92	7	92	85	95	7	95
f	Cl	Vinyl	Et	82	95	7	95	86	98	7	98

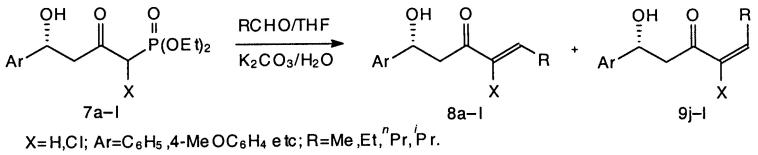
[a] Isolated yields.
[b] The ee values were determined by chiral HPLC (CHIRALPAK AD, OD, AS *n*-hexane–*i*-PrOH = 8:2 to 9:1).
[c] The *E* and *Z* isomers were obtained from the same substrate in one reaction, so the ee values of *E* and *Z* isomers were considered to be identical.

Based on our experimental data, we found that 4-hydroxy-2-oxo-alkylphosphonates **1a–c** and **2a–c** reacted with aliphatic aldehydes only to give the respective *E* isomer, which was identical to the results of the reaction with benzaldehyde (X = H). However, the reaction time was shortened by about 50% and the overall yield was dramatically increased. We also obtained the same results for the 4-hydroxy-1-chloro-2-oxo-alkylphosphonates **1d–f** and **2d–f** under analogous reaction conditions. In the latter case a mixture of *E* and *Z* isomers was obtained, which was identical to the corresponding results of the reaction with benzaldehyde, while the *E*/*Z* ratio was greater than 1:10 and the *E* isomer could slowly convert into the thermodynamically more favorable *Z* isomer (X = Cl). The *E* and *Z* iso-



a: X=H, Ar=C_6H_5; **b**: X=H,Ar=4-EtC_6H_4; **c**: X=H,Ar=4-MeOC_6H_4;
d: X=H, Ar=2-furyl; **e**: X=H,Ar=2-ClC_6H_4; **f**: X=H,Ar=2-BrC_6H_4;
g: X=H, Ar=4-FC_6H_4; **h**: X=H,Ar=4-ClC_6H_4; **i**: X=H,Ar=4-O_2N-C_6H_4;
j: X=Cl, Ar=C_6H_5; **k**: X=Cl,Ar=4-MeOC_6H_4; **l**: X=Cl,Ar=4-FC_6H_4.

Scheme 4



Scheme 5

Table 2 HWE Reaction of Compounds **7a–l** with Aliphatic Aldehydes

Substrate	X	Ar	R	**8**		**9**	
				Yield (%)[a]	ee (%)[b]	Yield (%)[a]	ee (%)[c]
a	H	C_6H_5	Et	94	>99	–	–
a(1)	H	C_6H_5	Me	90	97	–	–
a(2)	H	C_6H_5	*n*-Pr	96	97	–	–
a(3)	H	C_6H_5	*i*-Pr	94	98	–	–
b	H	4-EtC_6H_4	Et	95	>99	–	–
c	H	4-MeOC_6H_4	Et	95	99	–	–
d	H	2-furyl	Et	93	88	–	–
e	H	2-ClC_6H_4	Et	96	>99	–	–
f	H	2-BrC_6H_4	Et	95	99	–	–
g	H	4-FC_6H_4	Et	94	>99	–	–
h	H	4-ClC_6H_4	Et	96	–[d]	–	–
i	H	4-O_2N-C_6H_4	Et	93	96	–	–
j	Cl	C_6H_5	Et	86	98	4	98
j(1)	Cl	C_6H_5	Me	85	98	5	98
j(2)	Cl	C_6H_5	*n*-Pr	86	98	5	98
j(3)	Cl	C_6H_5	*i*-Pr	83	98	8	98
k	Cl	4-MeOC_6H_4	Et	88	>99	5	>99
l	Cl	4-FC_6H_4	Et	85	97	4	97

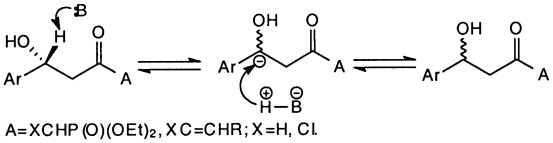
[a] Isolated yields.
[b] The ee values were determined by chiral HPLC (CHIRALPAK AD, OD, AS *n*-hexane–*i*-PrOH = 8:2 to 9:1).
[c] The *E* and *Z* isomers were obtained from the same substrates in one reaction, so the ee values of *E* and *Z* isomers were considered to be identical.
[d] The ee values could not be determined by chiral HPLC.

mers could be determined based on steric effects and ^{1}H NMR spectra.

Since the results of the HWE reactions with aliphatic aldehydes of *CALB*-catalyzed products **1a–f** and **2a–f** were encouragable, it was therefore interesting to examine the HWE reaction of *CRL*-catalyzed products (**7a–l**, Scheme 4).

It is quite exciting that aliphatic aldehydes/THF/K_2CO_3/H_2O systems performed these experiments successfully (Scheme 5, Table 2).

The substrates **7a–i**, reacted with aliphatic aldehydes, also provided only the *E* isomer, as in the case of benzaldehyde (X = H) while compounds **7j–l** also yielded the mixture of *E* and *Z* isomers with the ratio *E*/*Z* greater than 1:10. Also in these cases, the *E* isomers could be converted slowly into the corresponding *Z* isomers. Those two isomers could be determined based on steric effects and ^{1}H NMR spectra. These reactions were completed within one hour and the yields were higher than 90%. Because compounds **7a–l** could be partly racemized under basic conditions and long reaction times (Scheme 6), the ee values of compounds **8a–l** were higher than that of the products obtained from benzaldehyde.[10a,b]



Scheme 6

A new facile reaction system for the Horner–Wadsworth–Emmons olefination was realized by treatment of chiral 4-hydroxy-2-oxo-alkylphosphonates and 4-hydroxy-1-chloro-2-oxo-alkylphosphonates with aliphatic aldehydes.

IR spectra were recorded on a Shimadzu IR-440 spectrometer. EI mass spectra (MS) were run on a HP-5989A mass spectrometer at 70 eV. ^{1}H NMR spectra were recorded on a Bruker AMX-330 (300 MHz) spectrometer in $CDCl_3$ and chemical shifts were reported in ppm downfield relative to TMS (internal standard); ^{31}P NMR spectra were taken on the same spectrometer using 80% phosphorus acid as external standard.

CALB (Novozym 435) was provided from Novo Norvodisk Co. *CRL* (901units/mg) was purchased from Sigma Chemical Co.

The chiral liquid chromatography system: Waters 515 HPLC pump; UV Waters 2487 Dual λ Absorbance Detector, 254 nm; Penelson Network chromatography interface NCI 900, Turbohrom Navigator data station software; column dimensions: 0.46cm × 25cm; the flow rate: 0.7mL/min; eluent: hexane–*i*-PrOH = 9:1 to 8:2 (v/v).

HWE Reaction of Chiral Compounds 1 and 2 with Aliphatic Aldehydes; General Procedure

A mixture of substrates (50 mg), THF (1 mL), aliphatic aldehyes (0.4 mL), H_2O (1 mL) and K_2CO_3 (150 mg) was stirred until the starting materials disappeared (generally within 1 h) as monitored by TLC. Then Et_2O (5 mL) and a sat. aq solution of NH_4Cl (3 mL) was added, the aqueous layer was extracted with Et_2O (3 × 5 mL). After drying over anhyd Na_2SO_4, the solvent was removed under reduced pressure and the residues were subjected to flash chromatography (EtOAc–*n*-hexane, ca. 1:10). The yields of the products are listed in Table 1.

(2*S*,5*E*)-2-Hydroxyoct-5-en-4-one (3a)

Colorless oil; $[\alpha]_{Na}^{20}$ = +51.2 (*c* 1.0, $CHCl_3$).

IR (neat): 3434, 2971, 2935, 1663, 1626, 1375, 1192, 979, 946 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.86 (dt, 1 H, *J* = 6.3, 16.2 Hz, COCH=C*H*CH$_2$), 6.02 (d, 1 H, *J* = 16.2 Hz, COC*H*=CHCH$_2$), 4.21–4.08 (m, 1 H, COCH$_2$C*H*OH), 3.46 (s, 1 H, OH), 2.69 (dd, 1 H, *J* = 3.0, 17.1 Hz, COC*H*$_2$CHOH), 2.57 (dd, 1 H, *J* = 8.4, 17.1 Hz, COC*H*$_2$CHOH), 2.24–2.15 (m, 2 H, CH=CHC*H*$_2$CH$_3$), 1.15 (d, 3 H, *J* = 7.2 Hz, C*H*$_3$CHOH), 1.01 (t, 3 H, *J* = 7.8 Hz, CH=CHCH$_2$C*H*$_3$).

MS (EI, 70 eV): *m*/*z* (%) = 143 (M$^+$ + 1, 26), 125 (15), 113 (15), 101 (10), 98 (9), 83 (100), 55 (35), 45 (11), 43 (20), 39 (10).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.43; H, 10.13.

(2*R*,53*E*)-2-Hydroxyoct-5-en-4-one (5a)

Colorless oil; $[\alpha]_{Na}^{20}$ = –50.7 (*c* 0.7, $CHCl_3$).

IR (neat): 3440, 2971, 2935, 1663, 1626, 1375, 1192, 1054, 979, 946 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.86 (dt, 1 H, *J* = 6.3, 16.5 Hz, COCH=C*H*CH$_2$), 6.02 (d, 1 H, *J* = 16.5 Hz, COC*H*=CHCH$_2$), 4.22–4.09 (m, 1 H, COCH$_2$C*H*OH), 3.46 (s, 1 H, OH), 2.69 (dd, 1 H, *J* = 3.3, 17.1 Hz, COC*H*$_2$CHOH), 2.57 (dd, 1 H, *J* = 8.4, 17.1 Hz, COC*H*$_2$CHOH), 2.25–2.15 (m, 2 H, CH=CHC*H*$_2$CH$_3$), 1.15 (d, 3 H, *J* = 6.9 Hz, C*H*$_3$CHOH), 1.01 (t, 3 H, *J* = 7.5 Hz, CH=CHCH$_2$C*H*$_3$).

MS (EI, 70 eV): *m*/*z* (%) = 143 (M$^+$ + 1, 30), 125 (17), 113 (14), 101 (9), 98 (8), 83 (100), 55 (35), 45 (11), 43 (20), 39 (10).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.33; H, 10.13.

(3*E*,7*S*)-7-Hydroxynon-3-en-5-one (3b)

Colorless oil; $[\alpha]_{Na}^{20}$ = +35.3 (*c* 1.4, $CHCl_3$).

IR (neat): 3446, 2969, 2937, 1660, 1625, 1463, 1187, 1114, 977 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.93 (dt, 1 H, *J* = 6.3, 15.9 Hz, COCH=C*H*CH$_2$), 6.10 (d, 1 H, *J* = 15.9 Hz, COC*H*=CHCH$_2$), 4.08–3.95 (m, 1 H, COCH$_2$C*H*OH), 3.41 (d, 1 H, *J* = 2.7 Hz, OH), 2.77 (dd, 1 H, *J* = 3.0, 17.4 Hz, COC*H*$_2$CHOH), 2.63 (dd, 1 H, *J* = 9.6, 17.4 Hz, COC*H*$_2$CHOH), 2.30–2.23 (m, 2 H, CH=CHC*H*$_2$CH$_3$), 1.59–1.46 (m, 2 H, CH$_3$C*H*$_2$CHOH), 1.10 (t, 3 H, *J* = 7.2 Hz, CH=CHCH$_2$C*H*$_3$), 0.97 (t, 3 H, *J* = 7.2 Hz, C*H*$_3$CH$_2$CHOH).

MS (EI, 70 eV): *m*/*z* (%) = 156 (M$^+$, 1), 127 (12), 101 (6), 98 (8), 83 (100), 70 (4), 57 (11), 55 (35), 43 (17).

Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.36; H, 10.39.

(2*E*,6*S*)-6-Hydroxyoct-2-en-4-one [3b(1)][15]

Colorless oil; $[\alpha]_{Na}^{20}$ = +57.2 (*c* 1.2, $CHCl_3$).

IR (neat): 3448, 2967, 2937, 1664, 1630, 1443, 1378, 1292, 1190, 973 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.97–6.84 (m, 1 H, COCH=C*H*CH$_3$), 6.13 (d, 1 H, *J* = 15.6 Hz, COC*H*=CHCH$_3$), 4.07–3.95 (m, 1 H, COCH$_2$C*H*OH), 3.33 (s, 1 H, OH), 2.76 (dd, 1 H, *J* = 2.7, 17.4 Hz, COC*H*$_2$CHOH), 2.61 (dd, 1 H, *J* = 9.0, 17.4 Hz, COC*H*$_2$CHOH), 1.92 (d, 3 H, *J* = 7.2 Hz, CH=CHC*H*$_3$), 1.61–1.43 (m, 2 H, CHC*H*$_2$CH$_3$), 0.96 (t, 3 H, *J* = 7.5 Hz, C*H*$_3$CH$_2$CHOH).

MS (EI, 70 eV): *m*/*z* (%) = 124 (M$^+$ – H_2O, 2), 113 (10), 87 (5), 84 (9), 69 (100), 57 (9), 43 (16), 41 (49).

(6*E*,3*S*)-3-Hydroxydec-6-en-5-one [3b(2)]
Colorless oil; $[\alpha]_{Na}^{20}$ = +50.5 (*c* 0.7, $CHCl_3$).

IR (neat): 3447, 2964, 2934, 2877, 1663, 1627, 1464, 1380, 1186, 1114, 978 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.88 (dt, 1 H, *J* = 6.9, 16.2 Hz, COCH=C*H*CH_2), 6.10 (dt, 1 H, *J* = 1.5, 15.9 Hz, COC*H*=$CHCH_2$), 4.04–3.95 (m, 1 H, $COCH_2CHOH$), 3.32 (m, 1 H, OH), 2.77 (dd, 1 H, *J* = 3.0, 17.4 Hz, $COCH_2CHOH$), 2.62 (dd, 1 H, *J* = 9.6, 17.4 Hz, $COCH_2CHOH$), 2.26–2.18 (m, 2 H, CH=$CHCH_2CH_2$), 1.61–1.43 (m, 4 H, CH=$CHCH_2CH_2CH_3$, CH_3CH_2CHOH), 1.00–0.92 (m, 6 H, CH=$CHCH_2CH_3$, CH=$CHCH_2CH_2CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 152 ($M^+ - H_2O$, 3), 141 (14), 112 (8), 97 (100), 70 (9), 55 (62), 43 (17), 41 (26).

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.53; H, 10.65.

(3*E*,7*S*)-7-Hydroxy-2-methylnon-3-en-5-one [3b(3)]
Colorless oil; $[\alpha]_{Na}^{20}$ = +46.5 (*c* 0.8, $CHCl_3$).

IR (neat): 3449, 2966, 2935, 2876, 1686, 1662, 1626, 1466, 1366, 1190, 980 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.84 (dd, 1 H, *J* = 6.9, 15.9 Hz, COCH=C*H*CH), 6.05 (dd, 1 H, *J* = 1.5, 15.9 Hz, COC*H*=CHCH), 4.06–3.92 (m, 1 H, $COCH_2CHOH$), 3.29 (m, 1 H, OH), 2.78 (dd, 1 H, *J* = 2.7, 17.1 Hz, $COCH_2CHOH$), 2.61 (dd, 1 H, *J* = 9.0, 17.1 Hz, $COCH_2CHOH$), 2.55–2.43 [m, 1 H, CH=CHC*H*$(CH_3)_2$], 1.62–1.41 (m, 2 H, CH_3CH_2CHOH), 1.08 [t, 6 H, *J* = 6.6 Hz, CH=CHCH$(CH_3)_2$], 1.00 (t, 3 H, *J* = 7.5 Hz, CH_3CH_2CHOH).

MS (EI, 70 eV): *m*/*z* (%) = 152 ($M^+ - H_2O$, 1), 141 (8), 127 (9), 112 (7), 97 (100), 69 (22), 55 (14), 43 (29), 41 (48).

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.61; H, 10.71.

(3*E*,7*R*)-7-Hydroxynon-3-en-5-one (5b)
Colorless oil; $[\alpha]_{Na}^{20}$ = –35.6 (*c* 1.0, $CHCl_3$).

IR (neat): 3445, 2969, 2937, 2879, 1659, 1626, 1463, 1188, 1024, 978 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.94 (dt, 1 H, *J* = 6.3, 16.2 Hz, COCH=C*H*CH_2), 6.10 (d, 1 H, *J* = 16.5 Hz, COC*H*=$CHCH_2$), 4.07–3.96 (m, 1 H, $COCH_2CHOH$), 3.41 (d, 1 H, *J* = 2.4 Hz, OH), 2.77 (dd, 1 H, *J* = 3.0, 17.4 Hz, $COCH_2CHOH$), 2.63 (dd, 1 H, *J* = 9.0, 17.4 Hz, $COCH_2CHOH$), 2.32–2.23 (m, 2 H, CH=$CHCH_2CH_3$), 1.59–1.48 (m, 2 H, CH_3CH_2CHOH), 1.09 (t, 3 H, *J* = 7.8 Hz, CH=$CHCH_2CH_3$), 0.97 (t, 3 H, *J* = 7.5 Hz, CH_3CH_2CHOH).

MS (EI, 70 eV): *m*/*z* (%) = 156 (M^+, 1), 127 (18), 101 (8), 98 (9), 83 (100), 70 (7), 57 (11), 55 (27), 43 (13).

Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.36; H, 10.39.

(3*R*,6*E*)-3-Hydroxynona-1,6-dien-5-one (3c)
Colorless oil; $[\alpha]_{Na}^{20}$ = +25.2 (*c* 1.4, $CHCl_3$).

IR (neat): 3434, 2970, 2935, 2879, 1661, 1626, 1423, 1186, 978, 923 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.94 (dt, 1 H, *J* = 6.3, 15.6 Hz, COCH=C*H*CH_2), 6.11 (d, 1 H, *J* = 15.6 Hz, COC*H*=$CHCH_2$), 5.95–5.84 (m, 1 H, CH_2=C*H*CHOH), 5.24 (d, 1 H, *J* = 15.6 Hz, C*H*$_2$=CHCHOH), 5.14 (d, 1 H, *J* = 10.2 Hz, C*H*$_2$=CHCHOH), 4.67–4.58 (m, 1 H, $COCH_2CHOH$), 3.39 (s, 1 H, OH), 2.86–2.72 (m, 2 H, $COCH_2CHOH$), 2.32–2.22 (m, 2 H, CH=$CHCH_2CH_3$), 1.09 (t, 3 H, *J* = 7.5 Hz, CH=$CHCH_2CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 137 (M^+ – OH, 7), 126 (15), 111 (10), 99 (16), 98 (22), 83 (100), 71 (42), 57 (71), 55 (60), 43 (66).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.09; H, 9.45.

(3*S*,6*E*)-3-Hydroxynona-1,6-dien-5-one (5c)
Colorless oil; $[\alpha]_{Na}^{20}$ = –25.3 (*c* 1.1, $CHCl_3$).

IR (neat): 3443, 2970, 2935, 2879, 1661, 1626, 1423, 1187, 979, 923 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.94 (dt, 1 H, *J* = 6.0, 15.9 Hz, COCH=C*H*CH_2), 6.07 (d, 1 H, *J* = 15.9 Hz, COC*H*=$CHCH_2$), 5.95–8.84 (m, 1 H, CH_2=C*H*CHOH), 5.31 (d, 1 H, *J* = 17.1 Hz, C*H*$_2$=CHCHOH), 5.14 (d, 1 H, *J* = 10.8 Hz, C*H*$_2$=CHCHOH), 4.68–4.59 (m, 1 H, $COCH_2CHOH$), 3.40 (s, 1 H, OH), 2.88–2.70 (m, 2 H, $COCH_2CHOH$), 2.32–2.22 (m, 2 H, CH=$CHCH_2CH_3$), 1.09 (t, 3 H, *J* = 7.8 Hz, CH=$CHCH_2CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 125 ($M^+ - C_2H_5$, 7), 98 (16), 97 (7), 83 (100), 79 (5), 57 (14), 55 (44), 43 (18).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15%. Found: C, 70.04; H, 9.25.

(2*R*,5*Z*)-5-Chloro-2-hydroxyoct-5-en-4-one (3d)
Colorless oil; $[\alpha]_{Na}^{20}$ = +42.8 (*c* 1.0, $CHCl_3$).

IR (neat): 3429, 2974, 2936, 2881, 1687, 1615, 1376, 1187, 1116, 950, 720 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.99 (t, 1 H, *J* = 7.2 Hz, COC=C*H*CH_2), 4.38–4.22 (m, 1 H, $COCH_2CHOH$), 3.09 (s, 1 H, OH), 2.94 (dd, 1 H, *J* = 3.0, 18.0 Hz, $COCH_2CHOH$), 2.83 (dd, 1 H, *J* = 8.7, 18.0 Hz, $COCH_2CHOH$), 2.48–2.38 (m, 2 H, C=$CHCH_2CH_3$), 1.26 (d, 3 H, *J* = 6.6 Hz, CH_3CHOH), 1.14 (t, 3 H, *J* = 7.5 Hz, C=$CHCH_2CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 177 (M^+ + 1, 13), 159 (14), 132 (11), 117 (50), 97 (13), 89 (12), 53 (55), 45 (67), 43 (100).

Anal. Calcd for $C_8H_{13}ClO_2$: C, 54.40; H, 7.42%. Found: C, 54.51; H, 7.40.

(2*S*,5*E*)-5-Chloro-2-hydroxyoct-5-en-4-one (4d)
Colorless oil; $[\alpha]_{Na}^{20}$ = +30.0 (*c* 0.4, $CHCl_3$).

IR (neat): 3423, 2974, 2936, 2881, 1687, 1615, 1460, 1187, 1116, 949, 720 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.30 (t, 1 H, *J* = 7.8 Hz, COC=C*H*CH_2), 4.30–4.21 (m, 1 H, $COCH_2CHOH$), 2.96 (dd, 1 H, *J* = 3.0, 18.6 Hz, $COCH_2CHOH$), 2.82 (dd, 1 H, *J* = 8.7, 18.3 Hz, $COCH_2CHOH$), 2.58–2.48 (m, 2 H, C=$CHCH_2CH_3$), 1.25 (d, 3 H, *J* = 6.9 Hz, CH_3CHOH), 1.07 (t, 3 H, *J* = 7.5 Hz, C=$CHCH_2CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 176 (M^+, 4), 158 (18), 147 (16), 132 (36), 119 (35), 117 (100), 97 (23), 89 (15), 53 (22), 43 (20).

Anal. Calcd for $C_8H_{13}ClO_2$: C, 54.40; H, 7.42%. Found: C, 54.31; H, 7.29.

(2*R*,5*Z*)-5-Chloro-2-hydroxyoct-5-en-4-one (5d)
Colorless oil; $[\alpha]_{Na}^{20}$ = –42.6 (*c* 1.0, $CHCl_3$).

IR (neat): 3410, 2972, 2929, 2819, 1687, 1615, 1187, 950, 721 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.99 (t, 1 H, *J* = 7.2 Hz, COC=C*H*CH_2), 4.37–4.21 (m, 1 H, $COCH_2CHOH$), 3.08 (s, 1 H, OH), 2.95 (dd, 1 H, *J* = 3.0, 18.0 Hz, $COCH_2CHOH$), 2.84 (dd, 1 H, *J* = 8.7, 18.0 Hz, $COCH_2CHOH$), 2.48–2.38 (m, 2 H, C=$CHCH_2CH_3$), 1.26 (d, 3 H, *J* = 7.2 Hz, CH_3CHOH), 1.13 (t, 3 H, *J* = 7.2 Hz, C=$CHCH_2CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 176 (M^+, 2), 158 (13), 147 (13), 141 (12), 132 (32), 119 (34), 117 (100), 53 (37), 43 (54).

HRMS (EI): *m*/*z* [M^+] calcd for $C_8H_{13}ClO_2$, 176.0604; found, 176.0580.

(2*R*,5*E*)-5-Chloro-2-hydroxyoct-5-en-4-one (6d)
Colorless oil; $[\alpha]_{Na}^{20}$ = –30.1 (*c* 0.4, $CHCl_3$).

IR (neat): 3406, 2972, 2929, 2819, 1687, 1615, 1461, 1120, 950, 721 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.30 (t, 1 H, *J* = 7.8 Hz, COC=C*H*CH_2), 4.30–4.22 (m, 1 H, $COCH_2CHOH$), 2.96 (dd, 1 H, *J* = 3.3, 18.6 Hz, $COCH_2CHOH$), 2.82 (dd, 1 H, *J* = 8.7, 18.3 Hz, $COCH_2CHOH$), 2.58–2.48 (m, 2 H, $C=CHCH_2CH_3$), 1.25 (d, 3 H, *J* = 7.2 Hz, CH_3CHOH), 1.07 (t, 3 H, *J* = 7.5 Hz, $C=CHCH_2CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 177 (M^+ + 1, 23), 159 (18), 141 (7), 132 (19), 117 (66), 97 (19), 71 (22), 57 (32), 53 (48), 43 (100).

HRMS (EI): *m*/*z* [M^+] calcd for $C_8H_{13}ClO_2$, 176.0604; found, 176.0586.

(3*Z*,7*S*)-4-Chloro-7-hydroxynon-3-en-5-one (3e)
Colorless oil; $[\alpha]_{Na}^{20}$ = +29.6 (*c* 1.0, $CHCl_3$).

IR (neat): 3419, 2973, 2939, 2881, 1733, 1625, 1463, 978, 740 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.99 (t, 1 H, *J* = 6.9 Hz, COC=C*H*CH_2), 4.11–4.02 (m, 1 H, $COCH_2CHOH$), 3.02 (s, 1 H, OH), 2.94 (dd, 1 H, *J* = 3.0, 17.4 Hz, $COCH_2CHOH$), 2.85 (dd, 1 H, *J* = 9.0, 18.0 Hz, $COCH_2CHOH$), 2.48–2.38 (m, 2 H, $C=CHCH_2CH_3$), 1.59–1.51 (m, 2 H, CH_3CH_2CHOH), 1.13 (t, 3 H, *J* = 7.8 Hz, $C=CHCH_2CH_3$), 0.99 (t, 3 H, *J* = 7.5 Hz, CH_3CH_2CHOH).

MS (EI, 70 eV): *m*/*z* (%) = 190 (M^+, 7), 172 (11), 143 (40), 132 (50), 117 (53), 97 (82), 83 (100), 76 (21), 55 (49), 43 (14).

Anal. Calcd for $C_9H_{15}ClO_2$: C, 56.69; H, 7.93. Found: C, 56.99; H, 7.65.

(2*Z*,6*S*)-3-Chloro-6-hydroxyoct-2-en-4-one [3e(1)]
Colorless oil; $[\alpha]_{Na}^{20}$ = +23.5 (*c* 1.0, $CHCl_3$).

IR (neat): 3427, 2970, 2937, 2881, 1687, 1625, 1379, 1155, 979 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.11 (q, 1 H, *J* = 6.6 Hz, COC=C*H*CH_3), 4.14–3.90 (m, 1 H, $COCH_2CHOH$), 3.09–2.78 (m, 3 H, $COCH_2CHOH$,O*H*), 2.02 (d, 3 H, *J* = 6.6 Hz, $COC=CHCH_3$), 1.40–1.21 (m, 2 H, CH_3CH_2CHOH), 0.99 (t, 3 H, *J* = 7.2 Hz, CH_3CH_2CHOH).

MS (EI, 70 eV): *m*/*z* (%) = 176 (M^+, 1), 158 (11), 147 (28), 118 (19), 103 (100), 83 (12), 75 (24), 59 (20), 43 (29).

Anal. Calcd for $C_8H_{13}ClO_2$: C, 54.40; H, 7.52. Found: C, 54.27; H, 7.78.

(3*S*,6*Z*)-6-Chloro-3-hydroxydec-6-en-5-one [3e(2)]
Colorless oil; $[\alpha]_{Na}^{20}$ = +33.3 (*c* 1.0, $CHCl_3$).

IR (neat): 3438, 2965, 2935, 2877, 1686, 1616, 1464, 1182, 980 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.02 (t, 1 H, *J* = 7.2 Hz, COC=C*H*CH_2CH_3), 4.04–3.97 (m, 1 H, $COCH_2CHOH$), 3.07 (s, 1 H, OH), 2.92–2.78 (m, 2 H, $COCH_2CHOH$), 2.39 (q, 2 H, *J* = 7.2 Hz, $C=CHCH_2CH_2CH_3$), 1.63–1.48 (m, 4 H, $C=CHCH_2CH_2CH_3$, CH_3CH_2CHOH), 0.98 (t, 6 H, *J* = 7.5 Hz, $C=CHCH_2CH_2CH_3$, CH_3CH_2CHOH).

MS (EI, 70 eV): *m*/*z* (%) = 204 (M^+, 1), 186 (10), 175 (18), 143 (13), 131 (100), 104 (28), 89 (26), 67 (20), 57 (45), 43 (19).

Anal. Calcd for $C_{10}H_{17}ClO_2$: C, 58.68; H, 8.37. Found: C, 58.76; H, 8.44.

(3*Z*,7*S*)-4-Chloro-7-hydroxy-2-methylnon-3-en-5-one [3e(3)]
Colorless oil; $[\alpha]_{Na}^{20}$ = +29.2 (*c* 1.0, $CHCl_3$).

IR (neat): 3442, 2968, 2935, 2876, 1687, 1613, 1466, 1386, 1166, 980 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.80 [d, 1 H, *J* = 9.0 Hz, $COC=CH(CH_3)_2$], 4.06–3.97 (m, 1 H, $COCH_2CHOH$), 3.02–2.77 (m, 3 H, $COCH_2CHOH$,O*H*), 1.59–1.51 (m, 2 H, CH_3CH_2CHOH), 1.11 [d, 6 H, *J* = 6.6 Hz, $C=CHC(CH_3)_2$], 0.96 (t, 3 H, *J* = 6.9 Hz, CH_3CH_2CHOH).

MS (EI, 70 eV): *m*/*z* (%) = 204 (M^+, 2), 175 (14), 146 (48), 131 (100), 111 (27), 103 (26), 95 (40), 67 (54), 57 (41), 43 (38).

Anal. Calcd for $C_{10}H_{17}ClO_2$: C, 58.68; H, 8.37. Found: C, 58.59; H, 8.36.

(3*E*,7*S*)-4-Chloro-7-hydroxynon-3-en-5-one (4e)
Colorless oil; $[\alpha]_{Na}^{20}$ = +16.0 (*c* 0.4, $CHCl_3$).

IR (neat): 3446, 2972, 2937, 2881, 1732, 1623, 1463, 979 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.30 (t, 1 H, *J* = 7.5 Hz, COC=C*H*CH_2), 4.06–3.98 (m, 1 H, $COCH_2CHOH$), 2.98 (dd, 1 H, *J* = 2.7, 18.6 Hz, $COCH_2CHOH$), 2.81 (dd, 1 H, *J* = 9.0, 18.6 Hz, $COCH_2CHOH$), 2.59–2.49 (m, 2 H, $C=CHCH_2CH_3$), 1.64–1.49 (m, 2 H, CH_3CH_2CHOH), 1.08 (t, 3 H, *J* = 7.2 Hz, $C=CHCH_2CH_3$), 0.99 (t, 3 H, *J* = 7.5 Hz, CH_3CH_2CHOH).

MS (EI, 70 eV): *m*/*z* (%) = 190 (M^+, 1), 161 (17), 143 (14), 132 (15), 119 (33), 117 (100), 97 (15), 89 (15), 57 (24), 43 (13).

Anal. Calcd for $C_9H_{15}ClO_2$: C, 56.69; H, 7.93. Found: C, 56.70; H, 7.99.

(2*E*,6*S*)-3-Chloro-6-hydroxyoct-2-en-4-one [4e(1)]
Colorless oil; $[\alpha]_{Na}^{20}$ = +24.7 (*c* 0.5, $CHCl_3$).

IR (neat): 3427, 2970, 2937, 2881, 1686, 1625, 1379, 1155, 1108, 979 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.41 (q, 1 H, *J* = 7.8 Hz, COC=C*H*CH_3), 4.08–3.97 (m, 1 H, $COCH_2CHOH$), 3.02–2.77 (m, 3 H, $COCH_2CHOH$,O*H*), 2.09 (d, 3 H, *J* = 7.8 Hz, $COC=CHCH_3$), 1.62–1.39 (m, 2 H, CH_3CH_2CHOH), 0.99 (t, 3 H, *J* = 7.2 Hz, CH_3CH_2CHOH).

MS (EI, 70 eV): *m*/*z* (%) = 176 (M^+, 1), 158 (11), 147 (28), 118 (20), 103 (100), 83 (12), 75 (22), 57 (45), 43 (45).

Anal. Calcd for $C_8H_{13}ClO_2$: C, 54.40; H, 7.52. Found: C, 54.37; H, 7.55.

(3*S*,6*E*)-6-Chloro-3-hydroxydec-6-en-5-one [4e(2)]
Colorless oil; $[\alpha]_{Na}^{20}$ = +16.0 (*c* 0.6, $CHCl_3$).

IR (neat): 3439, 2965, 2935, 2877, 1686, 1616, 1464, 1182, 980 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.30 (t, 1 H, *J* = 7.5 Hz, COC=C*H*CH_2CH_3), 4.06–4.01 (m, 1 H, $COCH_2CHOH$), 3.01–2.76 (m, 3 H, $COCH_2CHOH$, OH), 2.49 (q, 2 H, *J* = 7.5 Hz, $C=CHCH_2CH_2CH_3$), 1.65–1.26 (m, 4 H, $C=CHCH_2CH_2CH_3$, CH_3CH_2CHOH), 1.03–0.98 (m, 6 H, $C=CHCH_2CH_2CH_3$, CH_3CH_2CHOH).

MS (EI, 70 eV): *m*/*z* (%) = 204 (M^+, 1), 186 (10), 175 (19), 143 (12), 131 (100), 104 (27), 89 (24), 67 (18), 57 (33), 43 (14).

Anal. Calcd for $C_{10}H_{17}ClO_2$: C, 58.68; H, 8.37%. Found: C, 58.70; H, 8.41.

(3*E*,7*S*)- 4-Chloro-7-hydroxy-2-methylnon-3-en-5-one [4e(3)]
Colorless oil; $[\alpha]_{Na}^{20}$ = +33.5 (*c* 0.6, $CHCl_3$).

IR (neat): 3442, 2968, 2935, 2876, 1687, 1613, 1466, 1166, 1114, 980 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.06 [d, 1 H, *J* = 9.9 Hz, $COC=CH(CH_3)_2$], 4.03–3.95 (m, 1 H, $COCH_2CHOH$), 2.97–2.73 (m, 3 H, $COCH_2CHOH$,O*H*), 1.55–1.47 (m, 2 H, CH_3CH_2CHOH), 1.06 [d, 6 H, *J* = 6.6 Hz, $C=CHC(CH_3)_2$], 0.96 (t, 3 H, *J* = 6.9 Hz, CH_3CH_2CHOH).

MS (EI, 70 eV): *m*/*z* (%) = 204 (M^+, 3), 175 (14), 146 (47), 131 (100), 111 (26), 103 (27), 95 (38), 71 (39), 67 (59), 57 (52), 43 (74).

Anal. Calcd for $C_{10}H_{17}ClO_2$: C, 58.68; H, 8.37%. Found: C, 58.42; H, 8.37.

(3*Z*,7*R*)-4-Chloro-7-hydroxynon-3-en-5-one (5e)
Colorless oil; $[\alpha]_{Na}^{20}$ = –29.8 (*c* 1.0, $CHCl_3$).

IR (neat): 3410, 2967, 2928, 1687, 1465, 1119, 976 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.99 (t, 1 H, *J* = 6.9 Hz, COC=C*H*CH_2), 4.08–4.00 (m, 1 H, $COCH_2CHOH$), 3.02 (s, 1 H, OH), 2.95 (dd, 1 H, *J* = 3.3, 18.0 Hz, $COCH_2CHOH$), 2.85 (dd, 1 H, *J* = 9.0, 18.0 Hz, $COCH_2CHOH$), 2.48–2.35 (m, 2 H, C=CHCH_2CH_3), 1.63–1.46 (m, 2 H, CH_3CH_2CHOH), 1.13 (t, 3 H, *J* = 7.5 Hz, C=$CHCH_2CH_3$), 0.99 (t, 3 H, *J* = 7.5 Hz, CH_3CH_2CHOH).

MS (EI, 70 eV): *m*/*z* (%) = 191 (M^+ + 1, 65), 173 (79), 161 (20), 143 (17), 132 (15), 117 (100), 99 (21), 71 (23), 57 (64), 53 (45), 43 (57).

Anal. Calcd for $C_9H_{15}ClO_2$: C, 56.69; H, 7.93. Found: C, 56.87; H, 7.72.

(3*E*,7*R*)-4-Chloro-7-hydroxynon-3-en-5-one (6e)
Colorless oil; $[\alpha]_{Na}^{20}$ = –16.0 (*c* 0.5, $CHCl_3$).

IR (neat): 3418, 2970, 2935, 2880, 1688, 1615, 1153, 1463, 976 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.29 (t, 1 H, *J* = 7.8 Hz, COC=C*H*CH_2), 4.06–3.98 (m, 1 H, $COCH_2CHOH$), 2.98 (dd, 1 H, *J* = 2.7, 18.6 Hz, $COCH_2CHOH$), 2.81 (dd, 1 H, *J* = 9.0, 18.6 Hz, $COCH_2CHOH$), 2.59–2.49 (m, 2 H, C=CHCH_2CH_3), 1.63–1.46 (m, 2 H, CH_3CH_2CHOH), 1.08 (t, 3 H, *J* = 7.2 Hz, C=$CHCH_2CH_3$), 0.98 (t, 3 H, *J* = 7.5 Hz, CH_3CH_2CHOH).

MS (EI, 70 eV): *m*/*z* (%) = 190 (M^+, 1), 172 (9), 161 (22), 143 (16), 132 (15), 117 (100), 99 (33), 70 (69), 59 (49), 57 (70), 43 (66).

HRMS (EI): *m*/*z* [M^+] calcd for $C_9H_{15}ClO_2$, 190.0706; found, 190.0769.

(3*R*,6*Z*)-6-Chloro-3-hydroxynona-1,6-dien-5-one (3f)
Colorless oil; $[\alpha]_{Na}^{20}$ = +11.5 (*c* 1.0, $CHCl_3$).

IR (neat): 3447, 2970, 2927, 2800, 1689, 1615, 1463, 1110, 992, 927 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.00 (t, 1 H, *J* = 7.2 Hz, COC=C*H*CH_2), 5.93–5.86 (m, 1 H, CH_2=C*H*CHOH), 5.35 (d, 1 H, *J* = 17.1 Hz, CH_2=CHCHOH), 5.18 (d, 1 H, *J* = 13.5 Hz, CH_2=CHCHOH), 4.69–4.63 (m, 1 H, $COCH_2CHOH$), 3.02–2.95 (m, 3 H, $COCH_2CHOH$), 2.48–2.38 (m, 2 H, C=CHCH_2CH_3), 1.13 (t, 3 H, *J* = 7.5 Hz, C=$CHCH_2CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 189 (M^+ + 1, 3), 171 (15), 159 (9), 132 (28), 117 (56), 97 (24), 70 (40), 57 (98), 55 (69), 53 (88), 43 (100).

Anal. Calcd for $C_9H_{13}ClO_2$: C, 57.30; H, 6.95. Found: C, 57.55; H, 7.23.

(3*R*,6*E*)-6-Chloro-3-hydroxynona-1,6-dien-5-one (4f)
Colorless oil; $[\alpha]_{Na}^{20}$ = +9.0 (*c* 0.3, $CHCl_3$).

IR (neat): 3432, 2971, 2927, 2856, 1689, 1614, 1462, 1110, 992 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.30 (t, 1 H, *J* = 7.8 Hz, COC=C*H*CH_2), 5.97–5.85 (m, 1 H, CH_2=C*H*CHOH), 5.33 (d, 1 H, *J* = 17.1 Hz, CH_2=CHCHOH), 5.17 (d, 1 H, *J* = 10.5 Hz, CH_2=CHCHOH), 4.54–4.52 (m, 1 H, $COCH_2CHOH$), 3.07–2.91 (m, 2 H, $COCH_2CHOH$), 2.87 (s, 1 H, OH), 2.59–2.48 (m, 2 H, C=CHCH_2CH_3), 1.10 (t, 3 H, *J* = 7.8 Hz, C=$CHCH_2CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 189 (M^+ + 1, 1), 171 (5), 159 (9), 132 (30), 117 (59), 97 (28), 89 (18), 79 (15), 57 (95), 55 (64), 53 (100), 43 (92).

Anal. Calcd for $C_9H_{13}ClO_2$: C, 57.30; H, 6.95. Found: C, 57.45; H, 7.03.

(3*S*,6*Z*)-6-Chloro-3-hydroxynona-1,6-dien-5-one (5f)
Colorless oil; $[\alpha]_{Na}^{20}$ = –12.0 (*c* 1.0, $CHCl_3$).

IR (neat): 3415, 2967, 2929, 2856, 1693, 1465, 1150, 975 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.00 (t, 1 H, *J* = 7.2 Hz, COC=C*H*CH_2), 5.94–5.86 (m, 1 H, CH_2=C*H*CHOH), 5.35 (d, 1 H, *J* = 16.8 Hz, CH_2=CHCHOH), 5.18 (d, 1 H, *J* = 13.5 Hz, CH_2=CHCHOH), 4.68–4.65 (m, 1 H, $COCH_2CHOH$), 3.03–2.96 (m, 3 H, $COCH_2CHOH$), 2.50–2.38 (m, 2 H, C=CHCH_2CH_3), 1.13 (t, 3 H, *J* = 7.2 Hz, C=$CHCH_2CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 170 ($M^+ - H_2O$, 2), 171 (15), 145 (9), 126 (9), 99 (39), 87 (8), 70 (40), 70 (100), 58 (48), 55 (51), 43 (54).

HRMS (EI): *m*/*z* [$M^+ - H_2O$] calcd for $C_9H_{11}ClO$, 170.0498; found, 170.0534.

(3*S*,6*E*)-6-Chloro-3-hydroxynona-1,6-dien-5-one (6f)
Colorless oil; $[\alpha]_{Na}^{20}$ = –9.2 (*c* 0.4, $CHCl_3$).

IR (neat): 3425, 2966, 2928, 2856, 1691, 1465, 1120, 975 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.30 (t, 1 H, *J* = 7.8 Hz, COC=C*H*CH_2), 5.96–5.85 (m, 1 H, CH_2=C*H*CHOH), 5.33 (d, 1 H, *J* = 16.8 Hz, CH_2=CHCHOH), 5.17 (d, 1 H, *J* = 10.5 Hz, CH_2=CHCHOH), 4.65–4.61 (m, 1 H, $COCH_2CHOH$), 3.05–2.91 (m, 2 H, $COCH_2CHOH$), 2.87 (s, 1 H, OH), 2.59–2.48 (m, 2 H, C=CHCH_2CH_3), 1.07 (t, 3 H, *J* = 7.5 Hz, C=$CHCH_2CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 171 (M^+ – OH, 3), 145 (11), 132 (7), 117 (10), 99 (42), 85 (12), 70 (100), 57 (69), 55 (55), 43 (70).

HRMS (EI): *m*/*z* [$M^+ - H_2O$] calcd for $C_9H_{11}ClO$, 170.0498; found, 170.0511.

HWE Reaction of Chiral Compounds 7 with Aliphatic Aldehydes; General Procedure
The procedures were similar to that used for the aliphatic counterparts. The yields of the products were listed in Table 2.

(1*R*,4*E*)-1-Hydroxy-1-phenylhept-4-en-3-one (8a)
Colorless oil; $[\alpha]_{Na}^{20}$ = +68.0 (*c* 0.9, $CHCl_3$).

IR (neat): 3448, 2970, 2936, 1660, 1625, 1455, 1058, 977, 759, 701 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.40–6.96 (m, 5 H, C_6H_5), 6.91 (dt, 1 H, *J* = 6.3, 16.2 Hz, COCH=C*H*CH_2), 6.09 (d, 1 H, *J* = 16.2 Hz, COC*H*=$CHCH_2$), 5.22–5.17 (m, 1 H, $COCH_2CHOH$), 3.64 (d, 1 H, *J* = 3.0 Hz, OH), 2.95 (d, 2 H, *J* = 6.0 Hz, $COCH_2CHOH$), 2.28–2.20 (m, 2 H, CH=CHCH_2CH_3), 1.07 (t, 3 H, *J* = 7.5 Hz, CH=$CHCH_2CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 204 (M^+, 2), 187 (9), 175 (12), 120 (19), 105 (90), 83 (100), 77 (51), 55 (42), 43 (34).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{13}H_{16}O_2$, 204.1150; found, 204.1141.

(1*R*,4*E*)-1-Hydroxy-1-phenylhex-4-en-3-one [8a(1)][16]
Colorless oil; $[\alpha]_{Na}^{20}$ = +84.5 (*c* 1.0, $CHCl_3$).

IR (neat): 3449, 3.33, 2973, 1656, 1629, 1442, 1193, 1057, 970, 757, 701 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.25 (m, 5 H, C_6H_5), 6.95–6.83 (m, 1 H, COCH=C*H*CH_3), 6.13 (d, 1 H, *J* = 15.9 Hz, COC*H*=$CHCH_2$), 5.22–5.17 (m, 1 H, $COCH_2CHOH$), 3.64 (d, 1 H, *J* = 2.4 Hz, OH), 2.94 (d, 2 H, *J* = 6.0 Hz, $COCH_2CHOH$), 1.91 (d, 3 H, *J* = 6.9 Hz, CH=CHCH_3).

MS (EI, 70 eV): *m*/*z* (%) = 190 (M^+, 9), 162 (19), 120 (23), 105 (94), 77 (60), 69 (100), 51 (26), 41 (64), 39 (55).

(1*R*,1*E*)-1-Hydroxy-1-phenyloct-4-en-3-one [8a(2)]
Colorless oil; $[\alpha]_{Na}^{20}$ = +54.1 (*c* 1.0, $CHCl_3$).

IR (neat): 3449, 3032, 2962, 2933, 1662, 1625, 1454, 1058, 978, 757, 701 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.26 (m, 5 H, C_6H_5), 6.86 (dt, 1 H, *J* = 6.9, 16.2 Hz, COCH=C*H*CH_2), 6.10 (d, 1 H, *J* = 16.2 Hz, COC*H*=$CHCH_2$), 5.20 (d, 1 H, *J* = 6.3 Hz, $COCH_2CHOH$), 3.65 (s, 1 H, OH), 2.96 (d, 2 H, *J* = 6.3 Hz, $COCH_2CHOH$), 2.24–2.16 (m, 2 H, CH=$CHCH_2CH_2CH_3$), 1.55–1.43 (m, 2 H, CH=$CHCH_2CH_2CH_3$), 0.93 (t, 3 H, *J* = 7.2 Hz, CH=$CHCH_2CH_2CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 218 (M^+, 5), 200 (11), 175 (21), 157 (19), 120 (90), 107 (73), 78 (85), 70 (75), 51 (73), 39 (100).

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.77; H, 8.60,

(1*R*,43*E*)-1-Hydroxy-6-methyl-1-phenylhept-4-en-3-one [8a(3)]
Colorless oil; $[\alpha]_{Na}^{20}$ = +54.9 (*c* 1.0, $CHCl_3$).

IR (neat): 3449, 3064, 2966, 2873, 1656, 1624, 1454, 1387, 1364, 1203, 1057, 983, 758, 701 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.26 (m, 5 H, C_6H_5), 6.82 (dd, 1 H, *J* = 6.6, 16.2 Hz, COCH=C*H*CH_2), 6.05 (d, 1 H, *J* = 15.9 Hz, COC*H*=CHCH), 5.22–5.18 (m, 1 H, $COCH_2CHOH$), 3.65 (d, 1 H, *J* = 3.0 Hz, OH), 2.97 (d, 2 H, *J* = 6.3 Hz, $COCH_2CHOH$), 2.49–2.44 [m, 1 H, CH=CHC*H*$(CH_3)_2$], 1.05 [t, 6 H, *J* = 6.6 Hz, CH=CHCH$(CH_3)_2$].

MS (EI, 70 eV): *m*/*z* (%) = 218 (M^+, 1), 175 (42), 120 (12), 105 (63), 97 (66), 79 (34), 71 (41), 55 (54), 43 (100).

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.65; H, 8.65.

(1*R*,4*E*)-1-(4-Ethylphenyl)-1-hydroxyhept-4-en-3-one (8b)
Colorless oil; $[\alpha]_{Na}^{20}$ = +84.6 (*c* 1.1, $CHCl_3$).

IR (neat): 3433, 2968, 2936, 2878, 1661, 1626, 1462, 976, 833 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.30 (d, 2 H, *J* = 8.1 Hz, C_6H_4), 7.18 (d, 2 H, J = 7.8 Hz, C_6H_4), 6.91 (dt, 1 H, *J* = 6.3, 16.2 Hz, COCH=C*H*CH_2), 6.10 (d, 1 H, *J* = 16.2 Hz, COC*H*=$CHCH_2$), 5.20–5.13 (m, 1 H, $COCH_2CHOH$), 3.59 (d, 1 H, *J* = 3.0 Hz, OH), 2.96 (t, 2 H, *J* = 3.9 Hz, $COCH_2CHOH$), 2.64 (q, 2 H, *J* = 7.5 Hz, $C_6H_5CH_2CH_3$), 2.27–2.22 (m, 2 H, CH=$CHCH_2CH_3$), 1.23 (t, 3 H, *J* = 7.5 Hz, $C_6H_5CH_2CH_3$), 1.07 (t, 3 H, *J* = 7.2 Hz, CH=$CHCH_2CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 232 (M^+, 4), 205 (6), 185 (4), 148 (10), 133 (62), 99 (42), 70 (100), 59 (31), 55 (49), 43 (43).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{15}H_{20}O_2$, 232.1463; found, 232.1485.

(1*R*,4*E*)-1-Hydroxy-1-(4-methoxyphenyl)hept-4-en-3-one (8c)
Colorless oil; $[\alpha]_{Na}^{20}$ = +69.1 (*c* 0.7, $CHCl_3$).

IR (neat): 3453, 2968, 2937, 1662, 1615, 1515, 1249, 1177, 1035, 833 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.30 (d, 2 H, *J* = 6.6 Hz, C_6H_4), 6.96–6.87 (m, 3 H, C_6H_4, COCH=C*H*CH_2), 6.10 (d, 1 H, *J* = 15.9 Hz, COC*H*=$CHCH_2$), 5.15–5.12 (m, 1 H, $COCH_2CHOH$), 3.80 (s, 3 H, OCH_3), 3.58 (d, 1 H, *J* = 2.7 Hz, OH), 2.94 (t, 2 H, *J* = 2.1 Hz, $COCH_2CHOH$), 2.28–2.23 (m, 2 H, CH=$CHCH_2CH_3$), 1.07 (t, 3 H, *J* = 7.5 Hz, CH=$CHCH_2CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 234 (M^+, 3), 217 (4), 201 (5), 150 (9), 137 (33), 135 (100), 109 (14), 83 (36), 77 (26), 55 (32), 43 (25).

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.66; H, 7.95.

(1*R*,4*E*)-1-(2-Furyl)-1-hydroxyhept-4-en-3-one (8d)
Colorless oil; $[\alpha]_{Na}^{20}$ = +38.9 (*c* 1.3, $CHCl_3$).

IR (neat): 3437, 2970, 2937, 2879, 1663, 1626, 1370, 1147, 1012, 979, 740 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.37 (m, 1 H, C_4H_3), 6.97 (dt, 1 H, *J* = 6.3, 16.8 Hz, COCH=C*H*CH_2), 6.34–6.33 (m, 1 H, C_4H_3), 6.29–6.27 (m, 1 H, C_4H_3), 6.12 (d, 1 H, *J* = 15.9 Hz, COC*H*=$CHCH_2$), 5.24–5.19 (m, 1 H, $COCH_2CHOH$), 3.61 (d, 1 H, *J* = 4.2 Hz, OH), 3.17 (dd, 1 H, *J* = 8.4, 17.7 Hz, $COCH_2CHOH$), 3.05 (dd, 1 H, *J* = 3.3, 17.7 Hz, $COCH_2CHOH$), 2.32–2.22 (m, 2 H, CH=$CHCH_2CH_3$), 1.09 (t, 3 H, *J* = 7.2 Hz, CH=$CHCH_2CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 194 (M^+, 4), 176 (6), 165 (12), 147 (9), 121 (8), 110 (78), 97 (46), 95 (46), 83 (100), 69 (14), 55 (84), 43 (47).

Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 67.73; H, 7.49.

(1*R*,1*E*)-1-(2-Chlorophenyl)-1-hydroxyhept-4-en-3-one (8e)
Colorless oil; $[\alpha]_{Na}^{20}$ = +97.0 (*c* 1.1, $CHCl_3$).

IR (neat): 3443, 2970, 2937, 2880, 1662, 1625, 1440, 1034, 976, 757 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.70–7.64 (m, 1 H, C_6H_4), 7.35–7.21 (m, 3 H, C_6H_4), 6.94 (dt, 1 H, *J* = 6.3, 16.2 Hz, COCH=C*H*CH_2), 6.11 (d, 1 H, *J* = 16.2 Hz, COC*H*=$CHCH_2$), 5.55–5.51 (m, 1 H, $COCH_2CHOH$), 3.89 (d, 1 H, *J* = 3.6 Hz, OH), 3.15 (dd, 1 H, *J* = 2.1, 17.7 Hz, $COCH_2CHOH$), 2.76 (dd, 1 H, *J* = 9.3, 17.7 Hz, $COCH_2CHOH$), 2.29–2.24 (m, 2 H, CH=$CHCH_2CH_3$), 1.07 (t, 3 H, *J* = 7.2 Hz, CH=$CHCH_2CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 238 (M^+, 1), 203 (28), 185 (18), 154 (11), 141 (50), 139 (94), 111 (21), 98 (18), 83 (100), 77 (55), 55 (65), 43 (46).

Anal. Calcd for $C_{13}H_{15}ClO_2$: C, 65.41; H, 6.33. Found: C, 65.11; H, 6.46.

(1*R*,4*E*)-1-(2-Bromophenyl)-1-hydroxyhept-4-en-3-one (8f)
Colorless oil; $[\alpha]_{Na}^{20}$ = +105.8 (*c* 0.9, $CHCl_3$).

IR (neat): 3446, 2970, 2937, 2879, 1662, 1625, 1467, 1071, 1020, 976, 756 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.65 (d, 1 H, *J* = 7.2 Hz, C_6H_4), 7.52 (d, 1 H, *J* = 7.2 Hz, C_6H_4), 7.36 (t, 1 H, *J* = 7.2 Hz, C_6H_4), 7.14 (t, 1 H, *J* = 7.5 Hz, C_6H_4), 6.94 (dt, 1 H, *J* = 6.3, 16.2 Hz, COCH=C*H*CH_2), 6.12 (d, 1 H, *J* = 16.2 Hz, COC*H*=$CHCH_2$), 5.50–5.46 (m, 1 H, $COCH_2CHOH$), 3.87 (d, 1 H, *J* = 3.0 Hz, OH), 3.16 (dd, 1 H, *J* = 2.7, 17.4 Hz, $COCH_2CHOH$), 2.73 (dd, 1 H, *J* = 9.3, 17.9 Hz, $COCH_2CHOH$), 2.29–2.22 (m, 2 H, CH=$CHCH_2CH_3$), 1.07 (t, 3 H, *J* = 7.8 Hz, CH=$CHCH_2CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 283 (M^+, 2), 203 (71), 185 (57), 183 (35), 157 (9), 145 (10), 99 (44), 83 (65), 70 (100), 55 (74), 43 (62).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{13}H_{15}BrO_2$, 282.0255; found, 282.0289.

(1*R*,4*E*)-1-(4-Fluorophenyl)-1-hydroxyhept-4-en-3-one (8g)
Colorless oil; $[\alpha]_{Na}^{20}$ = +52.9 (*c* 0.9, $CHCl_3$).

IR (neat): 3447, 2972, 2938, 1663, 1625, 1511, 1223, 978, 838 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.34 (dd, 2 H, *J* = 5.4, 9.0 Hz, C_6H_4), 7.02 (t, 2 H, *J* = 6.9 Hz, C_6H_4), 6.92 (dt, 1 H, *J* = 6.6, 15.9 Hz, COCH=C*H*CH_2), 6.09 (d, 1 H, *J* = 15.9 Hz, COC*H*=$CHCH_2$), 5.18–5.14 (m, 1 H, $COCH_2CHOH$), 3.79 (d, 1 H, *J* = 3.3 Hz, OH), 2.92 (d, 2 H, *J* = 6.3 Hz, $COCH_2CHOH$), 2.30–2.20 (m, 2 H, CH=$CHCH_2CH_3$), 1.07 (t, 3 H, *J* = 7.5 Hz, CH=$CHCH_2CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 222 (M^+, 2), 205 (14), 193 (8), 138 (11), 123 (47), 99 (16), 83 (100), 75 (8), 55 (23), 43 (18).

Anal. Calcd for $C_{13}H_{15}FO_2$: C, 70.25; H, 6.80. Found: C, 70.15; H, 7.01.

(1*R*,4*E*)-1-(4-Chlorophenyl)-1-hydroxyhept-4-en-3-one (8h)
Colorless oil; $[\alpha]_{Na}^{20}$ = +60.7 (*c* 0.8, $CHCl_3$).

IR (neat): 3451, 3062, 2902, 1652, 1608, 1451, 1176, 757, 700 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.28 (m, 4 H, C_6H_4), 6.92 (dt, 1 H, *J* = 6.3, 16.2 Hz, COCH=C*H*CH_2), 6.09 (d, 1 H, *J* = 16.2 Hz, COC*H*=CHCH_2), 5.20–5.09 (m, 1 H, $COCH_2CHOH$), 3.74 (s, 1 H, OH), 2.92 (d, 2 H, *J* = 6.0 Hz, $COCH_2CHOH$), 2.36–2.21 (m, 2 H, CH=CHCH_2CH_3), 1.07 (t, 3 H, *J* = 7.2 Hz, CH=$CHCH_2CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 238 (M^+, 2), 209 (11), 191 (5), 165 (6), 154 (24), 141 (50), 139 (100), 111 (25), 83 (71), 77 (49), 55 (54), 43 (36).

Anal. Calcd for $C_{13}H_{15}ClO_2$: C, 65.41; H, 6.33. Found: C, 65.33; H, 6.52.

(1*R*,4*E*)-1-Hydroxy-1-(4-nitrophenyl)hept-4-en-3-one (8i)
Colorless oil; $[\alpha]_{Na}^{20}$ = +50.8 (*c* 1.3, $CHCl_3$).

IR (neat): 3446, 2971, 2938, 1663, 1625, 1521, 1348, 979, 857 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.21 (d, 2 H, *J* = 7.2 Hz, C_6H_4), 7.56 (d, 2 H, *J* = 8.1 Hz, C_6H_4), 6.95 (dt, 1 H, *J* = 6.3, 15.9 Hz, COCH=C*H*CH_2), 6.12 (d, 1 H, *J* = 15.9 Hz, COC*H*=CHCH_2), 5.32–5.29 (m, 1 H, $COCH_2CHOH$), 3.96 (d, 1 H, *J* = 3.0 Hz, OH), 3.01 (dd, 1 H, *J* = 3.9, 17.7 Hz, $COCH_2CHOH$), 2.93 (dd, 1 H, *J* = 8.7, 17.7 Hz, $COCH_2CHOH$), 2.304–2.22 (m, 2 H, CH=CHCH_2CH_3), 1.08 (t, 3 H, *J* = 7.5 Hz, CH=$CHCH_2CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 249 (M^+, 4), 220 (39), 205 (9), 165 (29), 150 (36), 117 (16), 99 (17), 83 (100), 77 (17), 55 (44), 43 (24).

Anal. Calcd for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.07; N, 5.62. Found: C, 62.34; H, 6.31; N, 5.39.

(1*R*,4*Z*)-4-Chloro-1-hydroxy-1-phenylhept-4-en-3-one (8j)
Colorless oil; $[\alpha]_{Na}^{20}$ = +43.6 (*c* 1.0, $CHCl_3$).

IR (neat): 3448, 2974, 2880, 1685, 1616, 1456, 1110, 1059, 761, 700 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.26 (m, 5 H, C_6H_5), 6.98 (t, 1 H, *J* = 7.2 Hz, COC=C*H*CH_2), 5.23 (dd, 1 H, *J* = 3.9, 8.4 Hz, $COCH_2CHOH$), 3.35 (s, 1 H, OH), 3.16 (ddd, 2 H, *J* = 4.2, 8.7, 17.7 Hz, $COCH_2CHOH$), 2.46–2.36 (m, 2 H, C=CHCH_2CH_3), 1.10 (t, 3 H, *J* = 7.5 Hz, C=$CHCH_2CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 238 (M^+, 5), 203 (4), 132 (10), 117 (11), 107 (28), 105 (100), 79 (39), 77 (34), 53 (14), 43 (9).

Anal. Calcd for $C_{13}H_{15}ClO_2$: C, 65.41; H, 6.33. Found: C, 65.14; H, 6.63.

(1*R*,4*Z*)-4-Chloro-1-hydroxy-1-phenylhex-4-en-3-one [8j(1)]
Colorless oil; $[\alpha]_{Na}^{20}$ = +81.9 (*c* 0.6, $CHCl_3$).

IR (neat): 3483, 3063, 3033, 2914, 1685, 1624, 1495, 1453, 1293, 1182, 1059, 761, 701 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.37–7.25 (m, 5 H, C_6H_5), 7.07 (q, 1 H, *J* = 6.9 Hz, COC=C*H*CH_3), 5.20 (dd, 1 H, *J* = 3.0, 8.1 Hz, $COCH_2CHOH$), 3.37 (s, 1 H, OH), 3.21–3.04 (m, 2 H, $COCH_2CHOH$), 2.00 (d, 3 H, *J* = 6.6 Hz, C=CHCH_3).

MS (EI, 70 eV): *m*/*z* (%) = 224 (M^+, 5), 189 (5), 131 (4), 118 (13), 105 (100), 79 (52), 77 (48), 51 (16), 43 (19), 39 (21).

Anal. Calcd for $C_{12}H_{13}ClO_2$: C, 64.15; H, 5.82. Found: C, 63.95; H, 6.00.

(1*R*,4*Z*)-4-Chloro-1-hydroxy-1-phenyloct-4-en-3-one [8j(2)]
Colorless oil; $[\alpha]_{Na}^{20}$ = +18.6 (*c* 0.8, $CHCl_3$).

IR (neat): 3479, 3033, 2963, 2934, 2874, 1687, 1615, 1454, 1180, 760, 700 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.26 (m, 5 H, C_6H_5), 6.99 (t, 1 H, *J* = 6.9 Hz, COC=C*H*CH_3), 5.23 (dd, 1 H, *J* = 3.6, 8.1 Hz, $COCH_2CHOH$), 3.34 (s, 1 H, OH), 3.21–3.04 (m, 2 H, $COCH_2CHOH$), 2.38 (q, 2 H, *J* = 7.2 Hz, C=CHC$H_2CH_2CH_3$), 1.59–1.47 (m, 2 H, C=$CHCH_2CH_2CH_3$), 0.97 (t, 3 H, *J* = 7.2 Hz, C=$CHCH_2CH_2CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 252 (M^+, 5), 235 (7), 217 (4), 131 (19), 105 (100), 79 (36), 77 (36), 51 (10), 43 (9), 39 (11).

Anal. Calcd for $C_{14}H_{17}ClO_2$: C, 66.53; H, 6.78. Found: C, 66.47; H, 7.03.

(1*R*,4*Z*)-4-Chloro-1-hydroxy-6-methyl-1-phenylhept-4-en-3-one [8j(3)]
Colorless oil; $[\alpha]_{Na}^{20}$ = +52.8 (*c* 0.8, $CHCl_3$).

IR (neat): 3425, 2966, 2874, 1694, 1470, 1363, 1101, 1025, 747, 700 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.26 (m, 5 H, C_6H_5), 6.78 (d, 1 H, *J* = 9.0 Hz, COC=C*H*CH), 5.22 (t, 1 H, *J* = 4.2 Hz, $COCH_2CHOH$), 3.37 (d, 1 H, *J* = 3.0 Hz, OH), 3.22–3.07 (m, 2 H, $COCH_2CHOH$), 2.97–2.89 [m, 1 H, C=CHC*H*$(CH_3)_2$], 1.08 [d, 6 H, *J* = 6.6 Hz, C=CHCH$(CH_3)_2$].

MS (EI, 70 eV): *m*/*z* (%) = 252 (M^+, 7), 209 (15), 173 (7), 131 (21), 105 (100), 98 (27), 83 (42), 79 (50), 71 (69), 43 (66).

Anal. Calcd for $C_{14}H_{17}ClO_2$: C, 66.53; H, 6.78. Found: C, 66.47; H, 7.06.

(1*R*,4*E*)-4-Chloro-1-hydroxy-1-phenylhept-4-en-3-one (9j)
Colorless oil; $[\alpha]_{Na}^{20}$ = +78.0 (*c* 0.2, $CHCl_3$).

IR (neat): 3449, 2974, 2880, 1686, 1615, 1455, 1110, 761, 701 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.26 (m, 5 H, C_6H_5), 6.30 (t, 1 H, *J* = 7.5 Hz, COC=C*H*CH_2), 5.21 (dd, 1 H, *J* = 4.2, 9.6 Hz, $COCH_2CHOH$), 3.24–3.13 (m, 3 H, $COCH_2CHOH$), 2.60–2.49 (m, 2 H, C=CHCH_2CH_3), 1.07 (t, 3 H, *J* = 7.5 Hz, C=$CHCH_2CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 238 (M^+, 6), 203 (4), 132 (11), 117 (11), 105 (100), 79 (42), 77 (39), 53 (17), 43 (12).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{13}H_{15}ClO_2$, 238.0761; found, 238.0790.

(1*R*,4*E*)-4-Chloro-1-hydroxy-1-phenylhex-4-en-3-one [9j(1)]
Colorless oil; $[\alpha]_{Na}^{20}$ = +33.2 (*c* 0.2, $CHCl_3$).

IR (neat): 3483, 3063, 3033, 2915, 1686, 1624, 1495, 1453, 1293, 1182, 1060, 761, 701 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.09 (m, 5 H, C_6H_5), 6.43 (q, 1 H, *J* = 7.8 Hz, COC=C*H*CH_3), 5.22 (t, 1 H, *J* = 4.8 Hz, $COCH_2CHOH$), 3.30–3.12 (m, 3 H, $COCH_2CHOH$), 2.09 (d, 3 H, *J* = 7.5 Hz, C=CHCH_3).

MS (EI, 70 eV): *m*/*z* (%) = 224 (M^+, 10), 189 (8), 171 (4), 118 (22), 105 (100), 79 (74), 77 (70), 51 (20), 43 (17), 39 (21).

Anal. Calcd for $C_{12}H_{13}ClO_2$: C, 64.15; H, 5.82. Found: C, 63.94; H, 5.87.

(1*R*,4*E*)-4-Chloro-1-hydroxy-1-phenyloct-4-en-3-one [9j(2)]
Colorless oil; $[\alpha]_{Na}^{20}$ = +15.9 (*c* 0.2, $CHCl_3$).

IR (neat): 3480, 3033, 2963, 2934, 2875, 1686, 1615, 1455, 1058, 761, 701 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.26 (m, 5 H, C_6H_5), 6.32 (t, 1 H, *J* = 8.4 Hz, COC=C*H*CH_2), 5.24 (dd, 1 H, *J* = 3.0, 6.0 Hz, $COCH_2CHOH$), 3.25 (s, 1 H, OH), 3.18–3.16 (m, 2 H, $COCH_2CHOH$), 2.52 (q, 2 H, *J* = 6.9 Hz, C=CHC$H_2CH_2CH_3$),

1.61–1.47 (m, 2 H, C=CHCH$_2$C*H*$_2$CH$_3$), 0.98 (t, 3 H, *J* = 7.2 Hz, C=CHCH$_2$CH$_2$C*H*$_3$).

MS (EI, 70 eV): *m*/*z* (%) = 252 (M^+, 7), 217 (7), 131 (16), 105 (100), 79 (51), 77 (45), 51 (11), 43 (8), 39 (9).

Anal. Calcd for $C_{14}H_{17}ClO_2$: C, 66.53; H, 6.78. Found: C, 66.50; H, 7.03.

(1*R*,4*E*)-4-Chloro-1-hydroxy-6-methyl-1-phenylhept-4-en-3-one [9j(3)]

Colorless oil; $[\alpha]_{Na}^{20}$ = +51.0 (*c* 0.2, $CHCl_3$).

IR (neat): 3434, 2966, 2874, 1694, 1470, 1363, 1100, 1025, 747, 700 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.26 (m, 5 H, C_6H_5), 6.11 (d, 1 H, *J* = 10.2 Hz, COC=C*H*CH), 5.22–5.18 (m, 1 H, COCH$_2$C*H*OH), 3.53–3.47 (m, 3 H, COC*H*$_2$CHO*H*), 3.18–3.12 [m, 1 H, C=CHC*H*(CH$_3$)$_2$], 1.09 [d, 6 H, *J* = 6.9 Hz, C=CHCH(C*H*$_3$)$_2$].

MS (EI, 70 eV): *m*/*z* (%) = 252 (M^+, 1), 173 (8), 144 (11), 127 (50), 98 (72), 83 (100), 72 (97), 55 (33), 43 (60).

Anal. Calcd for $C_{14}H_{17}ClO_2$: C, 66.53; H, 6.78. Found: C, 66.63; H, 6.97.

(1*R*,4*Z*)-4-Chloro-1-hydroxy-1-(4-methoxyphenyl)hept-4-en-3-one (8k)

Colorless oil; $[\alpha]_{Na}^{20}$ = +21.0 (*c* 0.8, $CHCl_3$).

IR (neat): 3456, 2971, 1687, 1614, 1515, 1250, 1036, 832 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31 (d, 2 H, *J* = 7.5 Hz, C_6H_4), 6.98 (t, 1 H, *J* = 7.2 Hz, COC=C*H*CH$_2$), 6.90 (d, 2 H, *J* = 6.6 Hz, C_6H_4), 5.17 (dd, 1 H, *J* = 3.6, 8.4 Hz, COCH$_2$C*H*OH), 3.81 (s, 3 H, OCH$_3$), 3.35 (s, 1 H, OH), 3.13 (ddd, 2 H, *J* = 3.9, 8.4, 17.4 Hz, COC*H*$_2$CHOH), 2.49–2.38 (m, 2 H, C=CHC*H*$_2$CH$_3$), 1.10 (t, 3 H, *J* = 7.2 Hz, C=CHCH$_2$C*H*$_3$).

MS (EI, 70 eV): *m*/*z* (%) = 268 (M^+, 3), 251 (17), 161 (6), 137 (56), 135 (100), 117 (10), 109 (21), 94 (11), 77 (23), 53 (15), 43 (21).

Anal. Calcd for $C_{14}H_{17}ClO_3$: C, 62.58; H, 6.38. Found: C, 62.62; H, 6.68.

(1*R*,4*E*)-4-Chloro-1-hydroxy-1-(4-methyoxyphenyl)hept-4-en-3-one (9k)

Colorless oil; $[\alpha]_{Na}^{20}$ = +30.8 (*c* 0.4, $CHCl_3$).

IR (neat): 3493, 2973, 2911, 1685, 1614, 1515, 1250, 1035, 832 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31 (d, 2 H, *J* = 7.2 Hz, C_6H_4), 6.90 (d, 2 H, *J* = 6.9 Hz, C_6H_4), 6.30 (t, 1 H, *J* = 7.2 Hz, COC=C*H*CH$_2$), 5.20–5.03 (m, 1 H, COCH$_2$C*H*OH), 3.82 (s, 3 H, OCH$_3$), 3.22–3.03 (m, 3 H, COC*H*$_2$CHO*H*), 2.59–2.42 (m, 2 H, C=CHC*H*$_2$CH$_3$), 1.12 (t, 3 H, *J* = 7.2 Hz, C=CHCH$_2$C*H*$_3$).

MS (EI, eV): *m*/*z* (%) = 268 (M^+, 3), 224 (8), 153 (7), 137 (67), 135 (100), 126 (27), 109 (20), 98 (25), 77 (18), 70 (40), 55 (28), 43 (19).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{14}H_{17}ClO_3$, 268.0866; found, 268.0904.

(1*R*,4*Z*)-4-Chloro-1-(4-fluorophenyl)-1-hydroxyhept-4-en-3-one (8l)

Colorless oil; $[\alpha]_{Na}^{20}$ = +31.2 (*c* 1.0, $CHCl_3$).

IR (neat): 3429, 2972, 2939, 1688, 1608, 1512, 1224, 1156, 837 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36 (dd, 2 H, *J* = 5.7, 9.0 Hz, C_6H_4), 7.08–6.96 (m, 3 H, C_6H_4, COC=C*H*CH$_2$), 5.24–5.20 (m, 1 H, COCH$_2$C*H*OH), 3.84 (s, 1 H, OH), 3.21–3.05 (m, 2 H, COC*H*$_2$CHOH), 2.42–2.39 (m, 2 H, C=CHC*H*$_2$CH$_3$), 1.11 (t, 3 H, *J* = 7.8 Hz, C=CHCH$_2$C*H*$_3$).

MS (EI, 70 eV): *m*/*z* (%) = 256 (M^+, 3), 221 (17), 149 (13), 125 (49), 123 (100), 117 (16), 97 (61), 77 (19), 53 (21), 43 (23).

Anal. Calcd for $C_{13}H_{14}ClFO_2$: C, 60.83; H, 5.50. Found: C, 60.88; H, 5.72.

(1*R*,4*E*)-4-Chloro-1-(4-fluorophenyl)-1-hydroxyhept-4-en-3-one (9l)

Colorless oil; $[\alpha]_{Na}^{20}$ = +25.6 (*c* 0.3, $CHCl_3$).

IR (neat): 3425, 2970, 2930, 2881, 1688, 1608, 1512, 1225, 1156, 836 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37 (dd, 2 H, *J* = 5.1, 8.1 Hz, C_6H_4), 7.06 (t, 2 H, *J* = 8.7 Hz, C_6H_4), 6.34 (t, 1 H, *J* = 7.8 Hz, COC=C*H*CH$_2$), 5.19 (t, 1 H, *J* = 6.0 Hz, COCH$_2$C*H*OH), 3.24 (s, 1 H, OH), 3.15 (d, 2 H, *J* = 6.3 Hz, COC*H*$_2$CHOH), 2.61–2.52 (m, 2 H, C=CHC*H*$_2$CH$_3$), 1.09 (t, 3 H, *J* = 7.5 Hz, C=CHCH$_2$C*H*$_3$).

MS (EI, 70 eV): *m*/*z* (%) = 256 (M^+, 4), 221 (3), 132 (6), 125 (35), 123 (100), 117 (10), 97 (38), 95 (15), 77 (13), 53 (15), 43 (15).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{13}H_{14}ClFO_2$, 256.0666; found, 256.0673.

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