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A Stereoselective Synthesis of α-(1-Hydroxyalkyl)-β-Substituted Acrylic Acid Esters

Taïcir Ben Ayed,[a] Jean Villiéras[b] and Hassen Amri[c,*]

[a]*INSAT, B.P. 676 Tunis-1080 Cedex, Tunisia*

[b]*Laboratoire de Synthèse Organique, UMR CNRS 6513, Faculté des Sciences et des Techniques, BP 922082, rue de la Houssinière, F44322 Nantes Cedex 3, France*

[c]*Laboratoire de Chimie Organique et Organométallique, Faculté des Sciences Campus Universitaire-1060, Tunis, Tunisia*

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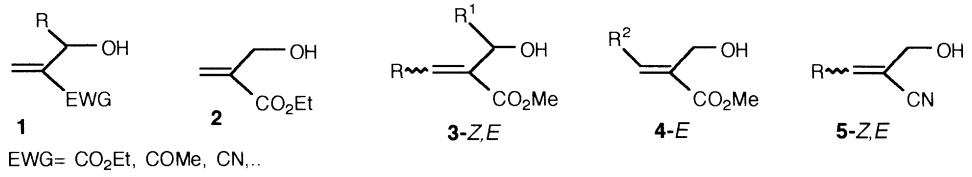
Abstract—Nucleophilic substitution of vinylic iodide of methyl 2-(1-hydroxyalkyl)-3-iodo prop-2-enoates **8** in the presence of magnesium dialkyl cuprates generated in situ provided a stereoselective methodology for the synthesis of infrequent β-substituted Baylis–Hillman products.

Since their first synthesis in 1972, α-(1-hydroxyalkyl) acrylic acid derivatives **1** commonly called Baylis–Hillman products[1] have been used by numerous researchers as particularly useful intermediates.[2] Although the α-hydroxymethylated analogues **2**[3] (R=H) have recently been described, the α-substitution of 2-alkenoic esters providing β-branched Baylis–Hillman adducts **3**[4] is difficult to obtain and has serious limitations. To overcome this problem several chemical solutions have been reported, most of them involving the generation of α-carbanion of α-silyl their derivatives,[8] Tantalum-acetylenic complex[9] and Reformatsky-type reaction[10] using Cerium metal, have also been reported. As part of our research program on the synthesis and the reactivity of α-functional acrylic substrates **1**, we have recently reported the first examples of successful tandem: bromination–formylation–hydrolysis of readily available Baylis–Hillman products **1** giving rise to the preparation of (*E*)-2-(hydroxymethyl) alk-2-enoates **4**[11] and (*E*,*Z*)-2-(hydroxymethyl) alk-2-enenitriles **5**[11,12] in good yields (Scheme 1).



Scheme 1.

t-butyl alk-2-enoates[5] or substituted acetylenic esters[6] by conjugated addition of mixed alkyl cuprates followed by addition of appropriate electrophiles (aldehyde or ketone). Some analogous α-(1-hydroxyalkyl) acrylic acid esters **1** have been obtained from the reaction coupling of reactive α,β-unsaturated vinyl moieties[7] which can be generated from hydroalumination of α,β-acetylenic esters or ketones with carbonyl compounds. Alternatively, attempts to use vinyl carbanions derived from acrylic esters and

To complete this series, it was therefore of interest to find a new synthetic way for the preparation of α-(1-hydroxyalkyl)-β-substituted acrylic esters **3**. As reported in the literature, nucleophilic substitution of vinylic halide using organometallic species[13] is a useful pathway for C–C bond formation. In this area, it occurred to us that the Baylis–Hillman derivatives **5** are ideal candidates for this target but our procedure which serves to prepare dialkyl (*E*)-2-bromomethylene glutarates **7**,[14] failed and yielded epoxides **9**[15] when applied to esters **1** (Scheme 2).

As alternative method, we have applied Lu's technique[16] in which low-valent zirconium (derived from $ZrCl_4$ as Lewis acid) mediates conjugated addition of halide ion to the C–C

Keywords: Baylis–Hillman products; cuprates; nucleophilic substitution; stereoselectivity.

* Corresponding author. Fax: +216-1-88-50-08; e-mail: hassen.amri@fst.rnu.tn

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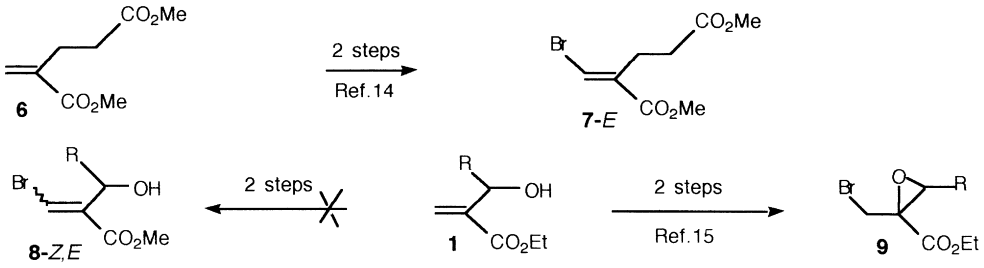
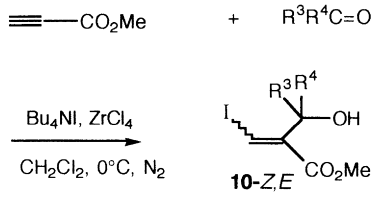


Scheme 2.

triple bond of methyl propiolate. The arised vinyl anion was trapped with varied aldehydes or ketones as electrophiles leading to a stereoselective synthesis of methyl (*Z*,*E*)-2-(1-hydroxyalkyl)-3-iodo acrylates **10** (Table 1, Scheme 3).



Scheme 3.

Table 1. Synthesis of methyl 2-(1-hydroxyalkyl)-3-iodo acrylates **10**

Entry	R^3	R^4	Product **10**[17]	Yield (%)[a]	Ratio *Z*:*E*[b]
1	*n*-pentyl	H	**10a**	80	72:28
2	*i*-propyl	H	**10b**	78	78:22
3	Methyl	H	**10c**	47	70:30
4	Methyl	Methyl	**10d**	43	100:0

[a] Isolated yields of products **8a**–**d** after column chromatography (silica gel, 2% AcOEt in hexane).
[b] All the assigned structures have been confirmed by spectroscopic data

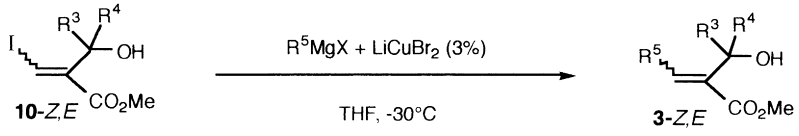
The interesting paper of Guigen Li[17] and co-workers which have investigated a new stereoselective synthesis of compounds **3** via the formation of vinyl anion of β-substituted propiolate using drastic conditions (DIBAH, HMPA, *n*-Bu_2BOTf as catalyst in THF at −78°C), prompts us to report here a convenient method to accomplish a one step synthesis of β-substituted allylic alcohols **3** in high yields involving conjugate addition of organocuprates prepared in situ in THF at low temperature to α-functional-β-iodo acrylic esters **10** (Scheme 4, Table 2).

β-Halo-α-substituted vinylic systems undergo cuprous salt promoted conjugated addition of Grignard reagents and lithium dialkyl cuprates. Analogue compounds β-substituted by an halogen as a leaving group and bearing α,α-disubstituted strongly electron withdrawing groups like adducts **3** are ambident electrophiles and their reactivity toward nucleophilic reagents has also been documented.[18] In this context, preliminary experiments involved the treatment of functional iodo vinylic products **10** with lithium dialkyl cuprates in varying equivalents. The best results were obtained when cuprates are generated in situ from Grignard reagents (2.2 to 2.7 equiv.) in the presence of $LiCuBr_2$ as catalyst (3%). As reported in Table 2, the substitution reactions provided α,β-unsaturated esters **3** in high (*Z*)-stereoselectivity (% *Z*/*E*: 55–88/45–12) when applied to a mixture of 3-iodo acrylic esters **10**-(*Z*/*E*) while the substitution of pure **10**-(*Z*) or **10**-(*E*) was stereospecificly leading respectively to **3**-(*Z*) or **3**-(*E*) isomers.

In conclusion, we have demonstrated that Grignard reagents in the presence of 0.1 equiv. of $LiCuBr_2$ undergo facile reaction with β-iodo-α-functional acrylic esters **10** to provide a substitute method for the hitherto resistant Baylis–Hillman reaction of β-substituted acrylic acid esters.

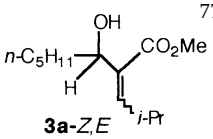
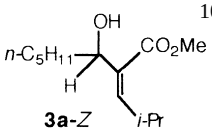
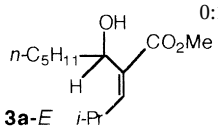
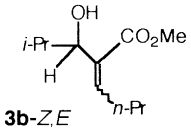
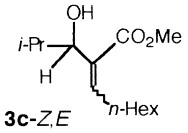
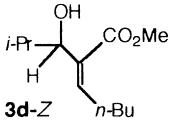
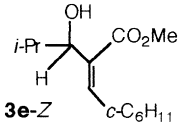
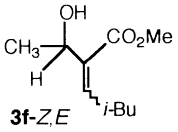
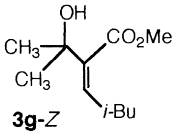
Experimental

All reactions involving anhydrous conditions were conducted in dry glassware under a nitrogen atmosphere. Solvents were distilled under nitrogen immediately prior to use. Grignard reagents were prepared by the known procedures and stored under inert atmosphere. They were titrated prior to use,[19] i.e. with 1 M solution of benzyl alcohol in toluene and 2,2′-biquinoline as indicator. Reactions were monitored with an Intersmat 20 M gas chromatograph using a 3 m column packed with 10% SE 30 and by TLC on silica gel plates (Fluka Kieselgel 60 F_{254}). For column chromatography, Fluka Kieselgel 70–230 mesh was used. The infrared (IR) spectra were determined on a Perkin–Elmer Paragon 1000 PC spectrophotometer. ^1H and ^{13}C NMR (fully decoupled) and spectra were recorded on Bruker AMX 300 in $CDCl_3$ as solvent and TMS as the internal. GC–MS spectra were obtained using a HP 5890 chromatograph fitted with HP 1 (0.33 μ×12 m) and HP 5889A quadripolar spectrometer in Electronic Impact (70 eV) or in Chemical Ionization (500 eV) with NH_3 gas. The fragmentation peaks are given in relative intensity (%).



Scheme 4.

Table 2. Synthesis of α-(1-hydroxyalkyl)-α,β-unsaturated esters **3** (all reactions were carried out in 10 mmol scale of methyl 2-(1-hydroxalkyl)-3-iodo prop-2-enoates **10**)

Substrate **10**	R^3	R^4	R^5MgX (equiv.)	Time (min)	Product **3a**–**g**	Ratio (*Z*:*E*)[a]	Yield (%)[b]
10a-*Z*,*E*	*n*-Pentyl	H	*i*-PrMgCl (2.2)	10	 **3a**-*Z*,*E*	77:23	93
10a-*Z*	*n*-Pentyl	H	*i*-PrMgCl (2.2)	10	 **3a**-*Z*	100:0	94
10a-*E*	*n*-Pentyl	H	*i*-PrMgCl (2.2)	10	 **3a**-*E*	0:100	94
10b-*Z*,*E*	*i*-Propyl	H	*n*-PrMgCl (2.7)	15	 **3b**-*Z*,*E*	88:12	93
10b-*Z*,*E*	*i*-Propyl	H	*n*-C_6H_{13}MgBr (2.5)	15	 **3c**-*Z*,*E*	86:14	95
10b-*Z*	*i*-Propyl	H	*n*-BuMgBr (2.5)	15	 **3d**-*Z*	100:0	93
10b-*Z*	*i*-Propyl	H	*c*-C_6H_{11}MgCl (2.6)	15	 **3e**-*Z*	100:0	96
10c-*Z*,*E*	Methyl	H	*i*-BuMgBr (2.5)	15	 **3f**-*Z*,*E*	55:45	86
10d-*Z*	Methyl	Me	*i*-BuMgBr (2.7)	30	 **3g**-*Z*	100:0	88

[a] Stereochemistry of products was refered to the pure corresponding 3-iodo vinylic ester **10**-*Z* or **10**-*E* previously separated from the mixture.
[b] Yields of isolated alcohols **3a**–**g** after silica gel chromatography (10% AcOEt in hexane).

Synthesis of methyl (*Z*,*E*)-2-(1-hydroxyalkyl)-3-iodo prop-2-enoates 10

Typical procedure. To a mixture of methyl propiolate (0.84 g, 10 mmol), hexanal (1.2 g, 12 mmol) and Bu_4NI (4 g, 11 mmol) in anhydrous CH_2Cl_2 (50 mL) was added $ZrCl_4$ (2.8 g, 12 mmol) at 0°C. After stirring at 0°C under N_2 for 5 h, the reaction was complete as monitored by TLC. Water (5 mL) was then added and followed by extraction with CH_2Cl_2 (3×50 mL). The combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure. The resulting residue was separated by chromatography on silca gel (2% AcOEt in hexane) to give **10a-*Z*,*E*** (80%). IR (neat): 1210, 1590, 1720, 3448 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ_H 0.90 (t, 3H, *J*=7.1 Hz, C*H*$_3$(CH$_2$)$_4$); 1.2–1.6 (m, 8H, CH$_3$(C*H*$_2$)$_4$); 3.6 (br, 1H); 3.80 (s, 3H, OCH$_3$); 4.36 (m, 1H); 7.10 (s, 1H). *m*/*z* (C.I.) 313 (M^+-OH, 4%); 241 (100).

Synthesis of methyl 2-(1-hydroxyalkyl) alk-2-enoates 3

General procedure. An ether or THF solution of alkylmagnesium halide RMgX (2.2 to 2.7 equiv.) was added dropwise over a period of 15–20 min to a mixture of 2-(1-hydroxyalkyl)-3-iodo acrylate ***10*** (10 mmol) and $LiCuBr_2$ (0.3 mL) in dry THF (40 mL) at −30°C under N_2. After a few minutes (TLC) at −30°C, the reaction mixture was quenched with a saturated NH_4Cl solution (20 mL), extracted with ether (3×30 mL) and subjected to standard workup. The crude methyl 2-(1-hydroxyalkyl) alk-2-enoates ***3*** were chromatographed on silica gel with 10% ethyl acetate in hexane as eluent.

Methyl (*Z*,*E*)-2-(1-hydroxyhexyl)-4-methyl pent-2-enoate 3a-*Z*,*E*. IR (neat): 1642, 1709, 3448 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ_H 0.88 (t, 3H, *J*=6.6 Hz, C*H*$_3$CH$_2$); 1.10 (m, 6H, (C*H*$_3$)$_2$CH); 1.28 (m, 6H, CH$_3$(C*H*$_2$)$_3$CH$_2$); 1.59 (m, 2H, CH$_2$C*H*$_2$CHOH); 2.70 (s br, 1H, O*H*); 3.07 (m, 1H, =CHC*H*(CH$_3$)$_2$); 3.77 (s, 3H, C*H*$_3$O); 4.19 (t, 1H, *J*=6.7 Hz, CH$_2$C*H*OH); 5.87 (d, 1H, *J*=9.9 Hz, CHC*H*=C, *Z*); 6.56 (d, 1H, *J*=10.4 Hz, CHC*H*=C, *E*). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 13.9 (*C*H$_3$CH$_2$); 22.2, 22.4 (CH$_3$*C*H$_2$); 22.5 (*C*H$_3$)$_2$CH); 25.5, 25.7 (*C*H$_2$CH$_2$CH$_3$); 27.2, 28.3 (*C*H$_2$CH$_2$CHOH); 31.4, 31.5 (*C*H$_3$O); 36.4, 37.1 (CH$_2$*C*H$_2$CHOH); 51.2 (*C*HC=C); 69.0, 74.0 (*C*HOH); 130.6, 131.8 (HC=*C*); 148.2, 150.2 (*C*H=C); 168.1 (*C*OO). *m*/*z* (C.I.) 157 (M^+-n-C_5H_{11}, 58%); 125 (100).

Methyl (*Z*)-2-(1-hydroxyhexyl)-4-methyl pent-2-enoate 3a-*Z*. IR (neat): 1646, 1712, 3447 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ_H 0.88 (t, 3H, *J*=6.8 Hz, C*H*$_3$CH$_2$); 1.01 (2d, 6H, *J*=6.6 Hz, (C*H*$_3$)$_2$CH); 1.28 (m, 6H, CH$_3$(C*H*$_2$)$_3$CH$_2$); 1.59 (m, 2H, CH$_2$C*H*$_2$CHOH); 2.70 (s br, 1H, O*H*); 3.07 (m, 1H, =CHC*H*(CH$_3$)$_2$); 3.77 (s, 3H, C*H*$_3$O); 4.19 (t, 1H, *J*=6.7 Hz, CH$_2$C*H*OH); 5.87 (d, 1H, *J*=9.9 Hz, CHC*H*=C). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 13.7 (*C*H$_3$CH$_2$); 22.2 (CH$_3$*C*H$_2$); 22.3 (*C*H$_3$)$_2$CH; 25.5 (*C*H$_2$CH$_2$CH$_3$); 28.3 (*C*H$_2$CH$_2$CHOH); 31.4 (*C*H$_3$O); 36.4 (*C*H$_2$CHOH); 51.2 (*C*HC=C); 74.0 (*C*HOH); 131.8 (HC=*C*); 148.2 (*C*H=C); 168.1 (*C*OO). *m*/*z* (C.I.) 157 (M^+-n-C_5H_{11}, 58%); 125 (100).

Methyl (*E*)-2-(1-hydroxyhexyl)-4-methyl pent-2-enoate 3a-*E*. IR (neat): 1642, 1712, 3448 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ_H 0.88 (t, 3H, *J*=6.7 Hz, C*H*$_3$CH$_2$); 1.05 (2d, 6H, *J*=10.2 Hz, (C*H*$_3$)$_2$CH); 1.26–1.51 (m, 8H, CH$_3$(C*H*$_2$)$_4$); 1.84 (s br, 1H, CHO*H*); 2.75 (m, 1H, =CHC*H*(CH$_3$)$_2$); 3.75 (s, 3H, C*H*$_3$O); 4.19 (t, 1H, *J*=6.7 Hz, CH$_2$C*H*OH); 6.56 (d, 1H, *J*=10.5 Hz, CHC*H*=C). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 13.9 (*C*H$_3$CH$_2$); 22.1 (CH$_3$*C*H$_2$), 22.5 ((*C*H$_3$)$_2$CH); 25.7 (*C*H$_2$CH$_2$CH$_3$); 27.2 (*C*H$_2$CH$_2$CHOH); 31.5 (*C*H$_3$O); 37.1 (*C*H$_2$CHOH); 51.2 (*C*HC=C); 69.0 (*C*HOH); 130.6 (HC=*C*); 150.2 (*C*H=C); 168.1 (*C*OO). *m*/*z* (C.I.) 157 (M^+-n-C_5H_{11}, 57%); 125 (100).

Methyl (*Z*,*E*)-2-[(1-hydroxy-2-methyl) propyl] hex-2-enoate 3b-*Z*,*E*. IR (neat): 1638, 1709, 3448 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ_H 0.93–1.08 (m, 9H, (C*H*$_3$)$_2$CH, C*H*$_3$CH$_2$); 1.45 (m, 2H, CH$_3$C*H*$_2$CH$_2$); 1.81 (m, 1H, (CH$_3$)$_2$C*H*CHOH); 2.37 (td, 2H, *J*=7.4, 7.4 Hz, CH$_2$C*H*$_2$CH=); 3.00 (s br, 1H, O*H*); 3.76 (s, 3H, C*H*$_3$O); 3.88 (d, 1H, *J*=7.4 Hz, (CH$_3$)$_2$CHC*H*OH); 6.07 (t, 1H, *J*=7.4 Hz, CH$_2$C*H*=C, *Z*); 6.87 (t, 1H, *J*=7.4 Hz, CH$_2$C*H*=C, *E*). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 13.6 (*C*H$_3$CH$_2$); 18.0, 19.3 ((*C*H$_3$)$_2$CH); 22.3 (CH$_2$*C*H$_2$CH$_3$); 31.2 (*C*H$_3$O); 32.8 (*C*HCHOH); 51.1, 51.4 (C=CH*C*H$_2$CH$_2$); 79.7, 80.6 (*C*HOH); 131.8, 133.2 (HC=*C*); 142.5, 144.9 (*C*H=C); 168.1 (*C*OO). *m*/*z* (C.I.) 157 (M^+-i-C_3H_7, 57%); 125 (100).

Methyl (*Z*,*E*)-2-[(1-hydroxy-2-methyl) propyl] non-2-enoate 3c-*Z*,*E*. IR (neat): 1638, 1708, 3467 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ_H 0.74–0.87 (m, 9H, (C*H*$_3$)$_2$CH, C*H*$_3$CH$_2$); 1.19 (m, 6H, CH$_3$(C*H*$_2$)$_3$CH$_2$); 1.34 (m, 2H, CH$_2$C*H*$_2$CH$_2$); 1.74 (m, 1H, (CH$_3$)$_2$C*H*CHOH); 2.31 (td, 2H, *J*=7.2, 7.2 Hz, CH$_2$C*H*$_2$CH=); 3.15 (s br, 1H, O*H*); 3.69 (s, 3H, C*H*$_3$O); 3.82 (d, 1H, *J*=7.2 Hz, CHC*H*OH); 6.00 (t, 1H, *J*=7.5 Hz, CH$_2$C*H*=C, *Z*); 6.75 (t, 1H, *J*=7.5 Hz, CH$_2$C*H*=C, *E*). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 13.7 (*C*H$_3$(CH$_2$)$_5$); 17.7, 19.2 ((*C*H$_3$)$_2$CH); 22.3 (CH$_2$*C*H$_2$CH$_3$); 29.0, 29.1, 29.3 ((CH$_2$(*C*H$_2$)$_3$CH$_2$); 31.3 (*C*H$_3$O); 32.7 (*C*HCHOH); 50.8, 51.2 (C=CH*C*H$_2$); 79.2, 80.5 (*C*HOH); 131.6, 133.1 (HC=*C*); 142.3, 145.0 (*C*H=C); 168.0 (*C*OO). *m*/*z* (C.I.) 199 (M^+-i-C_3H_7, 81%); 167 (100).

Methyl (*Z*)-2-[(1-hydroxy-2-methyl) propyl] hept-2-enoate 3d-*Z*. IR (neat): 1642, 1709, 3448 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ_H 0.82–0.96 (m, 9H, (C*H*$_3$)$_2$CH, C*H*$_3$CH$_2$); 1.30–1.42 (m, 4H, CH$_3$(C*H*$_2$)$_2$CH$_2$); 1.82 (m, 1H, (CH$_3$)$_2$C*H*CHOH); 2.40 (td, 2H, *J*=7.1, 7.1 Hz, CH$_2$C*H*$_2$CH=); 3.09 (s br, 1H, O*H*); 3.75 (s, 3H, C*H*$_3$O); 3.89 (d, 1H, *J*=7.3 Hz, CHC*H*OH); 6.08 (t, 1H, *J*=7.5 Hz, CH$_2$C*H*=C). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 13.6 (*C*H$_3$CH$_2$); 17.9, 19.3 ((*C*H$_3$)$_2$CH); 22.1 (*C*H$_2$CH$_3$); 28.9 (*C*H$_2$CH$_2$CH$_3$); 31.1 (*C*H$_3$O); 32.8 (*C*HCHOH); 51.0 (C=CH*C*H$_2$); 79.6 (*C*HOH); 133.0 (HC=*C*); 142.5 (*C*H=C); 168.1 (*C*OO). *m*/*z* (C.I.) 171 (M^+-i-C_3H_7, 60%); 139 (100).

Methyl (*Z*)-2-[(1-hydroxy-2-methyl) propyl]-3-cyclohexyl prop-2-enoate 3e-*Z*. IR (neat): 1638, 1718, 3448 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ_H 0.83, 0.94 (2d, 6H, *J*=6.6 Hz, (C*H*$_3$)$_2$CH); 1.20–1.28 (m, 6H, cC_6H_{11}); 1.71 (m, 4H, cC_6H_{11}); 1.79 (m, 1H, (CH$_3$)$_2$C*H*CHOH); 2.72 (m, 1H, cC_6H_{11}); 2.93 (s br, 1H, O*H*); 3.75 (s, 3H, C*H*$_3$O); 3.85 (d,

1H, J=7.3 Hz, $(CH_3)_2CHCHOH$); 5.86 (d, 1H, J=9.9 Hz, $c(C_6H_{11})CH$=C). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 17.9, 19.3 ($(CH_3)_2CH$); 25.2, 25.3, 25.6, 32.4, 32.8, 51.0 (cC_6H_{11}); 32.3 (CH_3O); 38.0 (*C*HCHOH); 79.6 (*C*HOH); 133.0 (HC=*C*); 147.4 (*C*H=C); 168.2 (*C*OO). *m*/*z* (C.I.) 197 ($M^+ - i\text{-}C_3H_7$, 59%); 165 (100).

Methyl (*Z*,*E*)-2-(1-hydroxyethyl)-5-methyl hex-2-enoate 3f-*Z*,*E*. IR (neat): 1640, 1707, 3447 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 0.92, 0.95 (2d, 6H, J=6.8 Hz, $(CH_3)_2CH$); 1.33, 1.39 (2d, 3H, J=6.4 Hz, CH_3CHOH); 1.72 (m, 1H, $(CH_3)_2CHCH_2$); 2.12, 2.31 (2m, 2H, $CHCH_2CH$=); 3.3 (s br, 1H, O*H*); 3.76 (s, 3H, CH_3O); 4.62, 4.71 (2q, 1H, J=7.2 Hz, CH_3CHOH); 6.19 (t, 1H, J=7.5 Hz, CH_2CH=C, *Z*); 6.74 (t, 1H, J=7.5 Hz, CH_2CH=C, *E*). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 22.1, 22.2 ($(CH_3)_2CH$; 22.6, 22.9 (*C*HCH_2CH=); 28.1, 28.4 (CH_3O); 36.6, 36.9 (CH_3CHOH); 51.0 (CH_2CH=C); 64.7, 68.6 (*C*HOH); 134.1, 135.9 (HC=*C*); 139.6, 142.1 (*C*H=C); 167.4, 169.9 (*C*OO). *m*/*z* (C.I.) 171 ($M^+ - CH_3$, 27%); 43 (100).

Methyl (*Z*)-2-[(1-hydroxy-1-methyl) ethyl]-5-methyl hex-2-enoate 3g-*Z*. IR (neat): 1654, 1725, 3448 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 0.9 (d, 6H, J=6.7 Hz, $(CH_3)_2CH$); 1.41 (s, 6H, $(CH_3)_2COH$); 1.69 (m, 1H, $(CH_3)_2CHCH_2$); 2.07 (dd, 2H, J=7.2, 7.2 Hz, $CHCH_2CH$=); 3.12 (s br, 1H, O*H*); 3.79 (s, 3H, CH_3O); 5.98 (t, 1H, J=7.5 Hz, CH_2CH=C). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 22.2 ($(CH_3)_2CH$; 28.4 (*C*HCH_2CH=); 29.3 (CH_3O); 38.4 ($(CH_3)_2COH$; 51.2 (CH_2CH=C); 71.6 (*C*HOH); 133.1 (HC=*C*); 140.3 (*C*H=C); 169.7 (*C*OO). *m*/*z* (C.I.) 185 ($M^+ - CH_3$, 51%); 153 (100).

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