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Ketalised α- and β-Lithiated α,β-Unsaturated Ketones: New Masked Acylvinyl Anion Equivalents

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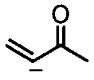
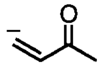
Abstract: The reaction of chloroketals **1**, **5** and **10** with an excess of lithium powder and a catalytic amount of DTBB (4-5%) in THF at -78 or -90°C leads to the corresponding functionalised organolithium compounds **2**, **6** and **11**, respectively, resulting from a chlorine/lithium exchange; treatment of these intermediates with different electrophiles [H_2O, D_2O, Me_3SiCl, Bu^{t}CHO, PhCHO, Me_2CO, $(CH_2)_4CO$, $(CH_2)_5CO$, PhCOMe] affords, after hydrolysis with water, the corresponding products **3**, **7** and **12**, respectively. Careful acidic hydrolysis of these ketalised products with a 10% aqueous solution of oxalic acid leads to the expected ketones **4**, **9** and **13**, respectively. © 1997 Elsevier Science Ltd.

INTRODUCTION

α- or β-Acylvinyl anion equivalents of the types **I** or **II**, respectively, are versatile intermediates in synthetic organic chemistry because they can transfer the α,β-unsaturated acyl functionality to electrophilic reagents.[1] Intermediates of the type **I** and **II** can also be considered as sp^2-hybridised enolate or homoenolate equivalents,[2,3] respectively, as well as d^2- and d^3-reagents, following Seebach's nomenclature.[4] Comparing both these intermediates, the corresponding β-acylvinyl equivalents **II** have been more widely studied than the corresponding α-derivatives **I**. Thus, lithium compounds of the general type **III** have been prepared normally by deprotonation of the corresponding activated precursors containing either a carboxylic acid derivative[5] or a carbonyl functionality.[6] Non-stabilised naked lithium derivatives cannot be prepared by direct deprotonation and are therefore rare species; in fact, to the best of our knowledge only the intermediates **IV**[6b] and **V**,[6g,h] prepared by bromine/lithium exchange, have been described in the literature. On the other hand, in the last few years we have developed a methodology based on an arene-catalysed lithiation,[7] which allows the preparation under very mild reaction conditions, of very reactive organolithium compounds. For instance, using this methodology we were able to prepare organolithium compounds starting from non-halogenated materials,[8a] very reactive functionalised organolithium intermediates[5b] by chlorine/lithium exchange[8b] or by reductive opening of saturated heterocycles[8c] and polylithiated synthons.[8d] In this paper we describe the direct, regio and stereoselective preparation of ketalised synthons of types **I** and **II** derived from α,β-unsaturated ketones by a 4,4'-di-*tert*-butylbiphenyl (DTBB) catalysed lithiation of the corresponding chlorinated precursors at low temperature.[7,9]


I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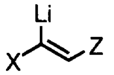
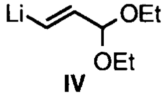
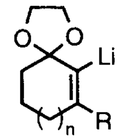

III

[X = R, RO, RS, R_2N, Cl, Br, ArSO, Ts
Z = PhCO, $RC(OR)_2$, CONLiR, $CONR_2$, CN]

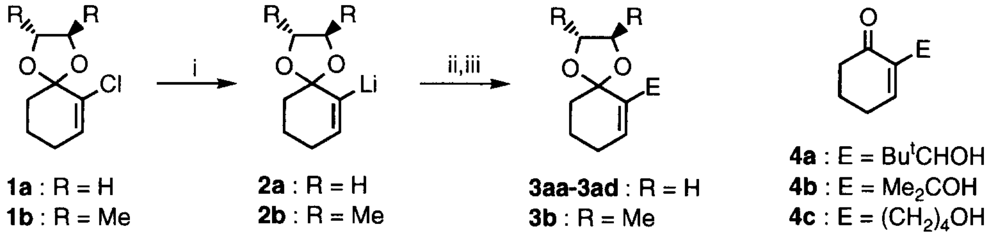

IV


V

[R = H, Me
n = 0, 1]

RESULTS AND DISCUSSION

The reaction of the α-chloroketal **1a** with an excess of lithium powder (*ca.* 1:15 molar ratio) and a catalytic amount of DTBB (*ca.* 1:0.1 molar ratio; 5 mol %) in THF at -78°C led in 1 h to a solution of the corresponding ketalised organolithium compound **2a**, which by reaction with different electrophiles [Me_3SiCl, Bu^tCHO, Me_2CO, $(CH_2)_4CO$] at the same temperature for 10 min followed by final hydrolysis with water led to the expected products **3aa-3ad** (Scheme 1 and Table 1, entries 1-4). The same reaction was applied to the chiral chloroketal and pivalaldehyde as the electrophilic component in order to study a possible asymmetric induction: the 300 MHz ^1H NMR analysis of the reaction crude indicated that a *ca.* 1:1 diastereoisomers mixture (**3b**) was obtained, which was separated by column chromatography giving the enantiomerically pure diastereoisomers (Scheme 1 and Table 1, entry 5).



Scheme 1. *Reagents and conditions*: i, Li, DTBB cat. (5%), THF, -78°C; ii, E^+ = Me_3SiCl, Bu^tCHO, Me_2CO, $(CH_2)_4CO$, -78°C; iii, H_2O, -78 to 20°C.

Compounds **3ab-3ad** were easily deprotected under controlled conditions (silica gel, CH_2Cl_2, 10% aqueous solution of oxalic acid).[10] Thus, compounds **4a-c** were obtained in almost quantitative isolated yield (>95%; Scheme 1 and Table 2, entries 1-3). The same treatment applied to the silylated compound **3aa** did not work affording destruction of the expected final product of type **4** (E = Me_3Si).

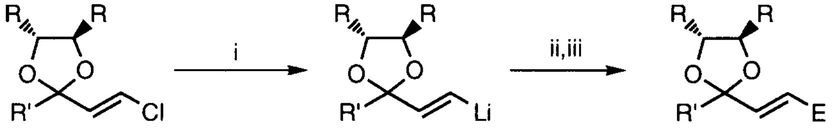
We then considered the acyclic (*E*)-β-chloroketals **5a** and **5b**. Their lithiation using the same procedure shown in Scheme 1 but working at -90°C led, after 1.5 h, to the formation of the corresponding intermediates **6a** and **6b**, respectively, which by treatment with different electrophiles [H_2O, D_2O, Bu^tCHO, PhCHO, Me_2CO, $(CH_2)_4CO$, PhCOMe] at temperatures ranging between -90 and -60°C afforded, after hydrolysis with water, the expected products **7aa-7ag** and **7ba-7bg**, respectively (Scheme 2 and Table 1, entries 6-19). All these

Table 1. Preparation of Compounds **3**, **7** and **11**

Entry	Starting material	Intermediate	Electrophile E^+	Product[a]				
				No.	R	E^+	Yield (%)[b]	R_f[c]
1	**1a**	**2a**	Me_3SiCl	**3aa**	H	Me_3Si	98	0.44[d]
2	**1a**	**2a**	Bu^tCHO	**3ab**	H	Bu^tCHOH	69	0.57
3	**1a**	**2a**	Me_2CO	**3ac**	H	Me_2COH	62	0.52
4	**1a**	**2a**	$(CH_2)_4CO$	**3ad**	H	$(CH_2)_4COH$	51	0.55
5	**1b**	**2b**	Bu^tCHO	**3b**	Me	Bu^tCHOH	69[e]	0.54,0.56[e]
6	**5a**	**6a**	H_2O	**7aa**	H	H	90	0.93
7	**5a**	**6a**	D_2O	**7ab**	H	D	88[f]	0.93
8	**5a**	**6a**	Bu^tCHO	**7ac**	H	Bu^tCHOH	55	0.53
9	**5a**	**6a**	PhCHO	**7ad**	H	PhCHOH	52	0.64
10	**5a**	**6a**	Me_2CO	**7ae**	H	Me_2COH	65	0.23
11	**5a**	**6a**	$(CH_2)_4CO$	**7af**	H	$(CH_2)_4COH$	52	0.36
12	**5a**	**6a**	PhCOMe	**7ag**	H	PhC(OH)Me	53	0.45
13	**5b**	**6b**	H_2O	**7ba**	H	H	90	0.86
14	**5b**	**6b**	D_2O	**7bb**	H	D	67[f]	0.86
15	**5b**	**6b**	Bu^tCHO	**7bc**	H	Bu^tCHOH	53	0.45
16	**5b**	**6b**	PhCHO	**7bd**	H	PhCHOH	43	0.60
17	**5b**	**6b**	Me_2CO	**7be**	H	Me_2COH	63	0.44
18	**5b**	**6b**	$(CH_2)_4CO$	**7bf**	H	$(CH_2)_4COH$	62	0.57
19	**5b**	**6b**	PhCOMe	**7bg**	H	PhC(OH)Me	55	0.56
20	**5c**	**6c**	Bu^tCHO	**7ca**	Me	Bu^tCHOH	70[e]	0.61[g]
21	**5c**	**6c**	PhCHO	**7cb**	Me	PhCHOH	72[e]	0.57[g]
22	**5c**	**6c**	$(CH_2)_5CO$	**7cc**	Me	$(CH_2)_5COH$	62	0.66
23	**10**	**11**	Bu^tCHO	**12a**	-	Bu^tCHOH	67	0.47
24	**10**	**11**	Me_2CO	**12b**	-	Me_2COH	80	0.31[h]
25	**10**	**11**	$(CH_2)_4CO$	**12c**	-	$(CH_2)_4COH$	75	0.45[h]

[a] All products **3**, **7** and **11** were >94% pure (GLC and/or 300 MHz ^1H NMR). [b] Isolated yield after column chromatography (silica gel, Hexane/ethyl acetate) based on the starting chloroketals **1**, **5** or **9**. [c] Silica gel, hexane/ethyl acetate: 2/1. [d] Silica gel, hexane/ethyl acetate: 5/1. [e] A *ca.* 1:1 diastereoisomers mixture was obtained (300 MHz ^1H NMR). [f] >90% Deuterium incorporation (mass spectrometry). [g] Both distereoisomers, which could not be separated by column chromatography, gave the same R_f value. [h] Silica gel, hexane/ethyl acetate; 1/1.

compounds show an *E*-geometry [>95% *E* from 300 MHz ^{1}H NMR ($J_{CH=CH}$ = 15.4-17.2 Hz) and GLC], so a retention in both the lithiation and the S$_E$ steps took place.[11] The temperature should be kept at *ca.* -90°C in order to avoid side-reactions; for instance, working at -78°C acetylenic compounds **8a** and **8b** were isolated, together with the corresponding expected compounds **7**, in 14 and 13% yield in the reaction of intermediates **6a** and **6b** with cyclopentanone and acetone, respectively. The formation of side-products **8** can be rationalised by an initial dehydrochlorination of starting materials **5a** and **5b** followed by lithiation of the corresponding ketalised alkyne prior to the final condensation with the electrophile.

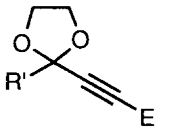


5a : R = H; R' = Pr^n
5b : R = H; R' = Pr^i
5c : R = Me, R' = Pr^n

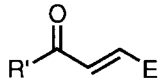
6a : R = H; R' = Pr^n
6b : R = H; R' = Pr^i
6c : R = Me, R' = Pr^n

7aa-7ag : R = H; R' = Pr^n
7ba-7bg : R = H; R' = Pr^i
7ca-7cc : R = Me; R' = Pr^n

Scheme 2. *Reagents and conditions*: i, Li, DTBB cat. (4%), THF, -90°C; ii, E$^+$ = H_2O, D_2O, Bu^{t}CHO, PhCHO, Me_2CO, $(CH_2)_4CO$, PhCOMe, -90 to -60°C; iii, H_2O, -60 to 20°C.



8a : R' = Pr^n; E = $(CH_2)_4COH$
8b : R' = Pr^i; E = Me_2COH

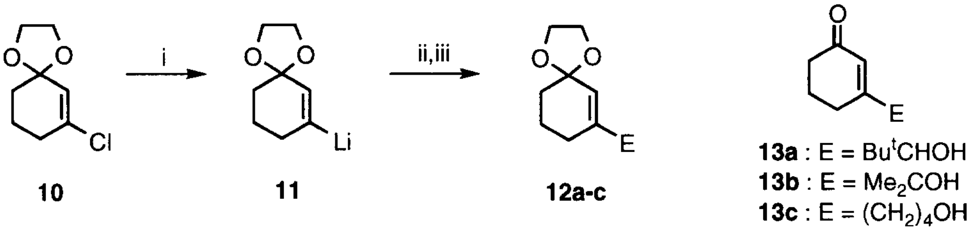


9a : R' = Pr^n; E = Bu^{t}CHOH
9b : R' = Pr^n; E = PhCHOH
9c : R' = Pr^n; E = Me_2COH
9d : R' = Pr^n; E = $(CH_2)_4COH$
9e : R' = Pr^n; E = PhC(OH)Me
9f : R' = Pr^i; E = PhC(OH)Me

Also in the case of compounds **5**, the corresponding chiral derivative **5c** was prepared and submitted to the same reaction shown in Scheme 2: as it happened for compound **3b** a *ca.* 1:1 mixtures of diastereoisomers **7ca** and **7cb** was obtained when prochiral aldehydes (Bu^{t}CHO, PhCHO) were used as electrophiles (Scheme 2 and Table 1, entries 20 and 21), which could not be separated by column chromatography. The use of a non-prochiral ketone, such as cyclohexanone, afforded the enantiopure compound **7cc** (Table 1, entry 22).

Representative compounds **7ac-ag**, **7bg** were carefully hydrolysed as it was above described for compounds **3** giving the expected products **9a-f** almost in quantitative yield (Table 2, entries 4-9).

In the final part of this work we studied the DTBB-catalysed lithiation of the cyclic β-chlorinated ketal **10**, under the reaction conditions shown in Scheme 1, to give the intermediate **11**, which was submitted to the reaction with different electrophiles [Bu^{t}CHO, Me_2CO, $(CH_2)_4CO$] to afford, after hydrolysis with water, the expected products **12a-c** (Scheme 3 and Table 1, entries 23-25). In this case, and considering the bad results obtained with chiral starting materials **1b** and **5c**, we did not try the reaction with the corresponding chiral ketal of type **10**.



13a : E = Bu^tCHOH
13b : E = Me_2COH
13c : E = $(CH_2)_4OH$

Scheme 3. *Reagents and conditions*: i, Li, DTBB cat. (5%), THF, -78°C; ii, E^+ = Bu^tCHO, Me_2CO, $(CH_2)_4CO$, -78°C; iii, H_2O, -78 to 20°C.

Table 2. Preparation of Compounds **4**, **9** and **13**

Entry	Starting material	Product[a]			
		No.	R'	E	R_f[b]
1	**3ab**	**4a**	-	Bu^tCHOH	0.49
2	**3ac**	**4b**	-	Me_2COH	0.39
3	**3ad**	**4c**	-	$(CH_2)_4COH$	0.38
4	**7ac**	**9a**	Pr^n	Bu^tCHOH	0.47
5	**7ad**	**9b**	Pr^n	PhCHOH	0.41
6	**7ae**	**9c**	Pr^n	Me_2COH	0.46
7	**7af**	**9d**	Pr^n	$(CH_2)_4COH$	0.42
8	**7ag**	**9e**	Pr^n	PhC(OH)Me	0.50
9	**7bg**	**9f**	Pr^i	PhC(OH)Me	0.51
10	**12a**	**13a**	-	Bu^tCHOH	0.26
11	**12b**	**13b**	-	Me_2COH	0.29[c]
12	**12c**	**13c**	-	$(CH_2)_4COH$	0.25[c]

[a] All products **4**, **9** and **13** were >95% pure (GLC and/or 300 MHz ^1H NMR); isolated yields were almost quantitative (>95%) in all cases. [c] Silica gel, hexane/ethyl acetate: 2/1. [c] Silica gel, hexane/ethyl acetate: 1/1.

Careful hydrolysis of compounds **12** under the reaction conditions used for the preparation of compounds **4** and **9** gave the expected products **13** almost in quantitative isolated yield (>95%; Scheme 3 and Table 2, entries 10-12).

Starting chloroketals **1** and **10** were prepared by ketalisation of the corresponding chloroketones by the standard procedure (the corresponding diol, *p*-toluenesulfonic acid cat., benzene reflux). In the case of the starting materials **5**, 1,2-(trimethylsilyloxy)ethane or the corresponding di-*O*-silylated chiral diol were used under trimethylsilyl triflate catalysis.[12]

From the results described in this paper we conclude that this methodology represents an adequate and direct way to prepare lithiated α- or β-acylvinyl anion intermediates in a regio- and stereo-selective manner from easily available precursors; the reaction of these species with different electrophiles is a convenient route for the preparation of ketalised functionalised α,β-unsaturated ketones, which after deprotection under mild reaction conditions afford the corresponding ketones.

EXPERIMENTAL SECTION

General.- M.p.s are uncorrected and were measured on a Reichert Thermovar apparatus. IR spectra were determined with a FT-IR Nicolet 400 D spectrometer. ^1H and ^{13}C NMR spectra were recorded in a Brucker AC-300 using $CDCl_3$ as solvent and $SiMe_4$ as internal standard; chemical shifts are given in δ (ppm) and the coupling constants (*J*) are measured in Hz. MS (EI) were recorded with a Shimazdu QP-5000 spectrometer. Thin layer chromatography (TLC) was carried out on Scheleicher & Schnell F1500/LS 254 plates coated with a &f0.2 mm layer of silica gel, using hexane or a mixture of hexane/ethyl acetate as eluant; R_f values are given under these conditions. Specific rotations were determined with a Jasco DIP-1000 Digital Polarimeter. High resolution mass spectra were performed by the corresponding service at the University of Zaragoza. Solvents were dried by standard procedures.[13] Starting chloroketones [2-chloro-2-cyclohexenone,[14a] (*E*)-propyl and (*E*)-isopropyl 2-chloro-vinyl ketones[14b], 3-chloro-2-cyclohexanone[14c]], precursors of compounds **1**, **5** and **10**, were prepared according to the literature procedures.[14] All reagents were commercially available (Aldrich or Fluka) and were used as received.

Preparation of Chloroketals **1** *and* **10**. *General Procedure.-* A stirred benzene solution (50 ml) of the corresponding chloroketone (5.0 mmol), 1,2-diol (10.0 mmol) and *p*-toluenesulfonic acid (0.01 mmol) was refluxed in a Dean-Stark apparatus for 4 h in the case of compounds **1a-b** and for 8 h in the case of compound **10**. Then it was hydrolysed with a $NaHCO_3$ saturated aqueous solution and extracted with ethyl acetate (3x40 ml). The organic layer was dried over anhydrous sodium carbonate and evaporated (15 Torr). The resulting residue was then purified by column chromatography (silica gel; hexane/ethyl acetate) to yield pure products **1a-b** and **10**. Yields, physical, analytical and spectroscopic data follow.

6-Chloro-1,4-dioxaspiro[4,5]dec-6-ene (**1a**): (80%) $R_f = 0.49$ (hexane/ethyl acetate, 5/1); ν (film) 3040, 1643 (HC=C), 1179, 1094 cm^{-1} (CO); δ_H 1.73-1.82 (2H, m, $CH_2CH_2CO_2$), 1.86-1.92 (2H, m, CH_2CO_2), 2.10-2.16 (2H, m, CH_2CH), 3.95-4.05 (2H, m, CH_2O), 4.13-4.23 (2H, m, CH_2O), 6.09 (1H, t, $J = 4.1$, $CHCH_2$); δ_C 20.4 ($CH_2CH_2CO_2$), 26.15 (CH_2CH), 35.7 (CH_2CO_2), 65.9 ($2xCH_2O$), 105.7 (CO_2), 131.4 (CH), 132.7 (CCl); *m/z* 174 (M$^+$, 6%), 148 (42), 146 (100), 139 (22), 102 (46), 99 (78), 79 (24), 55 (56), 42 (23) (Found: M$^+$, 174.0450. $C_8H_{11}ClO_2$ requires M, 174.0469).

*(2*R*,3*R*)-6-Chloro-2,3-dimethyl-1,4-dioxaspiro[4,5]dec-6-ene* (**1b**): (78%) $R_f = 0.30$ (hexane/ethyl acetate, 5/1); ν (film) 3030, 1610 (HC=C), 1109, 1080 cm^{-1} (CO); δ_H 1.25 (3H, d, $J = 5.8$, CH_3CH), 1.31 (3H, d, $J = 5.8$, CH_3CH), 1.75-2.13 (4H, m, $2xCH_2$), 2.46-2.52 (1H, m, CHHCH), 2.58-2.63 (1H, m, CHHCH), 3.53-3.69 (1H, m, $CHCH_3$), 3.94-4.02 (1H, m, $CHCH_3$), 6.07 (1H, t, $J = 4.0$, CHCCl); δ_C 15.75 ($CH_2CH_2CO_2$), 20.3 ($2xCH_3$), 26.15 (CH_2CH), 36.95 (CH_2COO), 78.35 ($2xCHCH_3$), 80.2 (CO_2), 104.75 (CCl), 131.2 (CHCCl); *m/z* 202 (M$^+$, 3%), 176 (28), 174 (85), 127 (33), 104 (25), 102 (82), 79 (47), 77 (24),

67 (22), 55 (100), 43 (51) (Found: M^+, 202.0760. $C_{10}H_{15}ClO_2$ requires M, 202.0782). $[\alpha]_D^{25}$ = -24.5 [c = 1.09 (CH_2Cl_2)].

7-Chloro-1,4-dioxaspiro[4,5]dec-6-ene (**10**): (59%) R_f = 0.44 (hexane/ethyl acetate, 5/1); ν (film) 3040, 1605 (HC=C), 1085, 1025 cm^{-1} (CO), 1350; δ_H 1.70-1.81 (2H, m, CH_2CH_2COO), 1.83-1.91 (2H, m, CH_2COO), 2.33 (2H, dt, J = 6.1, 1.8, CH_2CCl), 3.92-4.02 (4H, m, 2xCH_2O), 5.75 (1H, s, CH); δ_C 21.05 (CH_2CH_2CCl), 32.55 (CH_2CO_2), 32.65 (CH_2CCl), 64.55 (2xCH_2O), 106.5 (CO_2), 125 25 (CH), 138.45 (CCl); *m/z* 174 (M^+ , 35%), 146 (94), 139 (61), 111 (99), 86 (100), 79 (39), 77 (40), 67 (56), 65 (33), 55 (23), 53 (23), 51 (36), 43 (47), 42 (62) (Found: M^+, 174.0440. $C_8H_{11}ClO_2$ requires M, 174.0469).

Preparation of Chloroketals **5**. *General Procedure*.- To a stirred dichloromethane (10 mmol) solution of the starting chloroketone (5.0 mmol) was added the corresponding di-*O*-silylated diol (6.0 mmol) and trimethylsilyl triflate (0.2 mmol) at -78°C. The reaction mixture was stirred at the same temperature for 8 h and kept at -5°C for 12 h, then it was hydrolysed with a $NaHCO_3$ saturated aqueous solution and extracted with dichloromethane (3x5 ml). The organic layer was dried over anhydrous sodium sulfate and evaporated (15 Torr). The resulting residue was purified by destillation to yield pure products **5**. Yields, physical, analytical and spectroscopic data follow.

*(*E*)-2-(Chlorovinyl)-2-propyl-1,3-dioxolane* (**5a**):[15] (55%) b.p. 44-46°C (1.0 Torr); ν (film) 3060, 1610 cm^{-1} (HC=C); δ_H 0.89 (3H t, J = 7.4, CH_3), 1.33-1.37 (2H, m, CH_2CH_3), 1.62-1.68 (2H, m, $CH_2CH_2CH_3$), 3.82-3.93 (4H, m, 2xCH_2O), 5.82 (1H, d, J = 13.2, CH=CHCl), 6.28 (1H, d, JJ = 13.2, CHCl); δ_C 14.1 (CH_3), 16.6 (CH_2CH_3), 40.6 ($CH_2CH_2CH_3$), 64.6 (2xCH_2O), 108.4 (CO_2), 120.75 (CH=CHCl), 133.5 (CHCl); *m/z* 133 (M^+-C_3H_7, 100%), 135 (37), 115 (11), 91 (23), 89 (67), 87 (12), 71 (32), 69 (18), 61 (16), 43 (40), 41 (29).

*(*E*)-2-(2-Clorovinyl)-2-(isopropyl)-1,3-dioxolane-* (**5b**):[15] (68%) b.p. 48-50°C (1.0 Torr); ν (film) 3060, 1610 (HC=C), 1155, 1130 cm^{-1} (CO); δ_H 0.87 [6H, d, J = 6.8, $(CH_3)_2C$], 1.75-1.87 [1H, m, $CH(CH_3)_2$], 3.78-3.88 (4H, m, 2xCH_2O), 5.78 (1H, d, J = 13.2, CH=CHCl), 6.21 (1H, d, J = 13.2, CHCl); δ_C 16.75 [$(CH_3)_2C$], 35.9 [$CH(CH_3)_2$], 64.8 (2xCH_2O), 110.65 (CO_2), 121.1 (CHCl), 132.00 (CH=CHCl); *m/z* 133 (M^+-C_3H_7, 100%), 135 (37), 91 (20), 89 (59).

*(*E*,4*R*,5*R*)-2-(2-Chlorovinyl)-4,5-dimethyl-2-propyl-1,3-dioxolane* (**5c**):[15] (72%) b.p. 50-52°C (1.0 Torr); ν (film) 3000, 1600 (HC=C), 1130, 1090 cm^{-1} (CO); δ_H 0.80 (3H, t, J = 7.3, CH_3CH_2), 1.12 (3H, d, J = 7.3, CH_3CH), 1.14 (3H, d, J = 5.2, CH_3CH), 1.15-1.34 (2H, m, CH_2CH_3), 1.51-1.57 (2H, m, $CH_2CH_2CH_3$), 3.46-3.52 (2H, m, 2x$CHCH_3$), 5.82 (1H, d, J = 13.1, $CHCHCl$), 6.24 (1H, d, J = 13.1, CHCl); δ_C 14.1 (CH_3CH_2), 15.9 (CH_3CH), 16.45 (CH_3CH), 16.8 (CH_2CH_3), 41.65 ($CH_2CH_2CH_3$), 77.85 (2x$CHCH_3$), 107.42 (COO), 120.35 (CHCl), 135.15 ($CHCHCl$); *m/z* 161 (M^+-C_3H_7, 63%), 125 (15), 91 (30), 89 (100), 81 (10), 71 (12), 55 (24), 43 (36). $[\alpha]_D^{25}$ = -8.75 [c = 1.37 (CH_2Cl_2)].

Preparation of Compounds **3**, **7**, **8** *and* **12**. *General Procedure*.- To a blue suspension of lithium powder (0.105 g, 15.0 mmol) in THF (10 ml) at -78°C was added the corresponding chloroketal **1** or **10** under argon and the mixture was stirred for 1 h at the same temperature. In the case of chloroketals **5** the stirring was performed at -90°C for 1.5 h. Then, the corresponding electrophile (1.2 mmol) was added and hydrolysed with water after 10 min. The resulting mixture was extracted with ethyl acetate (3x25 ml). The organic layer was dried over anhydrous sodium sulfate and evaporated (15 Torr). The resulting residue was then purified by column chromatography (silica gel; hexane/ethyl acetate) to yield pure products **3**, **7**, **8** and **12**. Yields and physical data are included in Table 1 or given in the text; other physical, analytical and spectroscopic data follow.

6-Trimethylsilyl-1,4-dioxaspiro[4,5]dec-6-ene (**3aa**):[16] ν (film) 3093, 1595 (HC=C), 1160, 1105 cm^{-1} (CO); δ_H 0.09 [9H, s, $(CH_3)_3Si$], 1.66-1.77 (4H, m, 2xCH_2), 2.05-2.10 (2H, m, CH_2CH), 3.95-4.05 (2H, m, CH_2O), 4.01-4.03 (2H, m, CH_2O), 6.28 (1H, t, J = 3.5, $CHCH_2$); δ_C 0.3 [$(CH_3)_3Si$], 20.0 ($CH_2CH_2CO_2$), 26.6 (CH2CH), 31.85 (CH_2CO_2), 63.7 (2xCH_2O), 108.85 (CO_2), 139 (CSi), 143.65 (CH); *m/z* 212 (M^+, 10%), 184 (88), 153 (51), 125 (34), 99 (100), 85 (20), 75 (88), 73 (41), 55 (28), 45 (52), 43 (41).

6-(1-Hydroxy-2,2-dimethylpropyl)-1,4-dioxaspiro[4,5]dec-6-ene (**3ab**):[15] ν (film) 3650-3200 (OH), 3030, 1645 (HC=C), 1173, 1120 cm^{-1} (CO); δ_H 0.96 [9H, s, $(CH_3)_3C$], 1.66-1.80 (4H, m, $2xCH_2$), 2.09-2.17 (2H, m, CH_2CH), 2.20 (1H, br s, OH), 3.88 (1H, s, CHOH), 3.96-4.04 (4H, m, $2xCH_2O$), 6.18 (1H, t, J = 3.8, $CHCH_2$); δ_C 20.1 ($CH_2CH_2CO_2$), 25.05 (CH_2CH), 26.75 [$(CH_3)_3C$], 33.05 (CH_2COO), 35.55 [$C(CH_3)]_3$, 64.1 (CH_2O), 64.5 (CH_2O), 76.6 (CHOH), 107.8 (CO_2), 133.1 (CH), 139.5 (CCO_2); *m/z* 208 (M^+-H_2O, 3%), 169 (43), 141 (22), 125 (100), 55 (23), 43 (23).

6-(1-Hydroxy-1-methylethyl)-1,4-dioxaspiro[4,5]dec-6-ene (**3ac**):[15] ν (film) 3670-3050 (OH), 3080, 1605 (HC=C), 1115, 1085 cm^{-1} (CO); δ_H 1.40 [6H, s, $(CH_3)_2C$], 1.73-1.74 (4H, m, $2xCH_2$), 2.09-2.15 (2H, m, CH_2CH), 4.02 (1H, br s, OH), 4.03-4.08 (2H, m, CH_2O), 4.10-4.16 (2H, m, CH_2O), 6.08 (1H, t, J = 4.0 $CHCH_2$); δ_C 19.5 ($CH_2CH_2CO_2$), 25.05 (CH_2CH), 30.1 [$(CH_3)_2C$], 32.8 (CH_2CO_2), 63.3 ($2xCH_2O$), 72.7 (COH), 109.75 (CO_2), 129.8 (CH), 139.75 (CCOH); *m/z* 174 (M^+ -CH_3, 7%), 155 (21), 99 (59), 55 (33), 44 (100), 43 (59).

6-(1-Hydroxycyclopentyl)-1,4-dioxaspiro[4,5]dec-6-ene (**3ad**):[15] ν (film) 3650-3100 (OH), 3030, 1653 (HC=C), 1150, 1090 cm^{-1} (CO); δ_H 1.64-1.83 (12H, m, $6xCH_2$), 2.11-2.13 (2H, m, CH_2CH), 3.70 (1H, br s, OH), 4.02-4.15 (4H, m, $2xCH_2O$), 6.10 (1H, t, J = 3.7, $CHCH_2$); δ_C 19.6 ($CH_2CH_2CO_2$), 22.6 ($2xCH_2CH_2COH$), 25.1 (CH_2CH), 32.25 (CH_2CO_2), 38.3 ($2xCH_2COH$), 63.45 ($2xCH_2O$), 83.1 (COH), 109.45 (CO_2), 130.3 (CH), 138.7 (CCOH); *m/z* 224 (M^+, 0.5%), 206 (14), 99 (100), 91 (16), 55 (33).

*(2*R*,3*R*)-6-(1-Hydroxy-2,2-dimethylpropyl)-2,3-dimethyl-1,4-dioxaspiro[4,5]dec-6-ene* (**3b**):[15] First diastereoisomer, ν (film) 3690-3130 (OH), 3035, 1650 (HC=C), 1107, 1091 cm^{-1} (CO); δ_H 0.97 [9H, s, $(CH_3)_3C$], 1.25 (1H, d, J = 5.8, CH_3CH), 1.31 (1H, d, J = 5.5, CH_3CH), 1.68-1.84 (4H, m, $2xCH_2$), 1.86 (1H, br s, OH), 2.06-2.11 (2H, m, CH_2CH), 3.63-3.77 (2H, m, $2xCHCH_3$), 3.90 (1H, s, CHOH), 6.17 (1H, t, J = 3.7, $CHCH_2$); δ_C 16.25 (CH_3CH), 18.2 (CH_3CH), 20.4 ($CH_2CH_2CO_2$), 24.85 (CH_2CH), 26.9 [$(CH_3)_3C$], 35.2 (CH_2CO_2), 35.7 [$C(CH_3)_3$], 75.9 (CHOH), 77.2 ($CHCH_3$), 79.8 ($CHCH_3$), 107.05 (CO_2), 132.05 ($CHCH_2$), 140.9 (CCO_2); *m/z* 236 (M^+-H_2O, 1%), 197 (20), 169 (20), 125 (100), 57 (20), 55 (51), 44 (28), 43 (53). $[\alpha]_D^{25}$ = -35.0 [c = 0.48 (CH_2Cl_2)]. Second diastereoisomer, ν (film) 3690-3130 (OH), 3035, 1650 (HC=C), 1107, 1091 cm^{-1} (CO); δ_H 0.97 [9H, s, $(CH_3)_3C$], 1.25 (1H, d, J = 5.8, CH_3CH), 1.29 (1H, d, J = 5.4, CH_3CH), 1.30-1.85 (4H, m, $2xCH_2$), 1.90 (1H, br s, OH), 2.08-2.10 (2H, m, CH_2CH), 3.65-3.93 (2H, m, $2xCHCH_3$), 3.96 (1H, s, CHOH), 6.18 (1H, t, J = 4.0, $CHCH_2$); δ_C 16.25 (CH_3CH), 18.25 (CH_3CH), 20.1 ($CH_2CH_2CO_2$), 25.1 (CH_2CH), 26.95 [$(CH_3)_3C$], 35.5 (CH_2CO_2), 35.55 [$C(CH_3)_3$], 75.35 (CHOH), 77.8 ($CHCH_3$), 79.65 ($CHCH_3$), 106.85 (CO_2), 132.05 ($CHCH_2$), 140.8 (CCO_2); *m/z* 236 (M^+ -H_2O, 1%), 197 (19), 169 (17), 125 (100), 57 (16), 55 (45), 43 (42). $[\alpha]_D^{25}$ = -22.9 [c = 0.97 (CH_2Cl_2)].

*(*E*)-2-Propyl-2-vinyl-1,3-dioxolane* (**7aa**):[15] ν (film) 3040, 1645 (HC=C), 1030, 1050 cm^{-1} (CO); δ_H 0.92 (3H, t, J = 7.3, CH_3CH_2), 1.37-1.46 (2H, m, CH_2CH_3), 1.62-1.71 (2H, m, $CH_2CH_2CH_3$), 3.84-3.97 (4H, m, $2xCH_2O$), 5.15 (1H, dd, J = 10.6, 1.9, $CHCH_2$), 5.35 (1H, dd, J = 17.2, 1.9, CHHCH), 5.73 (1H, dd, J = 17.2, 10.6, CHHCH); δ_C 14.25 (CH_3CH_2), 16.75 (CH_2CH_3), 40.25 ($CH_2CH_2CH_3$), 64.45 ($2xCH_2O$), 109.1 (CO_2), 115.2 (CH_2CH), 137.75 ($CHCH_2$); *m/z* 99 (M^+-C_3H_7, 100%), 115 (42), 71 (10), 55 (49), 43 (12).

*(*E*)-2-(2-Deuteriovinyl)-2-propyl-1,3-dioxolane* (**7ab**):[15] ν (film) 3040, 1645 (HC=C), 1030, 1050 cm^{-1} (CO); δ_H 0.92 (3H, t, J = 7.3, CH_3CH_2), 1.37-1.46 (2H, m, CH_2CH_3), 1.62-1.71 (2H, m, $CH_2CH_2CH_3$), 3.84-3.97 (4H, m, $2xCH_2O$), 5.29 (1H, d, J = 17.0, CHCHD), 5.52 (1H, d, J = 17.0, CHDCH); δ_C 14.25 (CH_3CH_2), 16.75 (CH_2CH_3), 40.25 ($CH_2CH_2CH_3$), 64.45 ($2xCH_2O$), 109.1 (CO_2), 115.4 (t, J_{CD} = 24.3), 137.75 (CHCHD); *m/z* 100 (M^+-C_3H_7, 100%), 115 (38), 71 (12).

*(*E*)-2-(3-Hydroxy-4,4-dimethyl-1-pentenyl)-2-propyl-1,3-dioxolane* (**7ac**):[15] ν (film) 3600-3000 (OH), 3110 (HC=C), 1150, 1090 cm^{-1} (CO); δ_H 0.91 [9H, s, $(CH_3)_3C$], 0.93 (3H, t, J = 7.4, CH_3CH_2), 1.29-1.44 (2H, m, CH_2CH_3), 1.60 (1H, br s, OH), 1.66-1.72 (2H, m,$CH_2CH_2CH_3$), 3.79 (1H, dd, J = 6.7, 1.1, CHOH), 3.85-3.97 (4H, m, $2xCH_2O$), 5.57 (1H, dd, J = 15.5, 1.1, CHCOO), 5.89 (1H, dd, J = 15.5, 6.7,

$CHCHOH$); δ_C 14.25 [$(CH_3)_3C$], 16.85 (CH_3CH_2), 25.25 (CH_2CH_3), 34.95 ($CH_2CH_2CH_3$), 40.55 [$C(CH_3)_3$], 64.5 ($2xCH_2O$), 79.8 (COH), 109.0 (CO_2), 130.95 ($CHCO_2$), 131.75 ($CHCHOH$); *m/z* 185 (M^+-C_3H_7, 48%), 129 (15), 115 (49), 99 (64), 71 (26), 57 (100), 43 (64), 41 (90).

(E)-2-(3-Hydroxy-3-phenyl-1-propenyl)-2-propyl-1,3-dioxolane (**7ad**):[15] ν (film) 3700-3100 (OH), 3025, 1580 (HC=C), 1050, 1010 cm^{-1} (CO); δ_H 0.91 (3H, t, *J* = 7.3, CH_3CH_2), 1.33-1.46 (2H, m, CH_2CH_3), 1.67-1.72 (2H, m, CH_2CH_2CH3), 3.81-3.92 (4H, m, $2xCH_2O$), 5.23 (1H, d, *J* = 5.9, $CHOH$), 5.71 (1H, d, *J* = 15.5, $CHCO_2$), 6.01 (1H, dd, *J* = 15.5, 5.9, $CHCHOH$), 7.27-7.93 (5H, m, ArH); δ_C 16.75 (CH_3CH_2), 20.95 (CH_2CH_3), 40.55 ($CH_2CH_2CH_3$), 64.5 ($2xCH_2O$), 74.05 (CHOH), 108.85 (CO_2), 126.3, 127.7, 128.55, 130.2, 133.1, 142.4 (CH=CH, ArC); *m/z* 205 (M^+-C_3H_7, 100%), 115 (33), 105 (26), 79 (15), 77 (43), 55 (21), 43 (55), 41 (36).

(E)-2-(3-Hydroxy-3-methyl-1-butenyl)-2-propyl-1,3-dioxolane (**7ae**):[15] ν (film) 3600-3100 (OH), 3020, 1650 (HC=C), 1050, 1140 cm^{-1} (CO); δ_H 0.92 (3H, t, *J* = 7.4, CH_3CH_2), 1.32 [6H, s, $(CH_3)_2COH$], 1.34-1.42 (2H, m, CH_2CH_3), 1.52 (1H, br s, OH), 1.51-1.71 (2H, m, $CH_2CH_2CH_3$), 3.86-3.94 (4H, m, $2xCH_2O$), 5.55 (1H, d, *J* = 15.6, CH=CHCOH), 5.94 (1H, d, *J* = 15.6, $CHCOH$); δ_C 14.25 (CH_3CH_2), 16.85 (CH_2CH_3), 29.8 [$(CH_3)_2COH$], 40.7 ($CH_2CH_2CH_3$), 64.5 ($2xCH_2O$), 70.5 (COH), 109.05 (CO_2), 126.25 (CHCOH), 138.85 (CH=CHCOH); *m/z* 157 (M^+-C_3H_7, 72%), 115 (23), 73 (22), 71 (13), 59 (14), 55 (14), 45 (11), 43 (100).

(E)-2[2-(1-Hydroxycyclopentyl)vinyl]-2-propyl-1,3-dioxolane (**7af**):[15] ν (film) 3600-3100 (OH), 3000, 1650 (HC=C), 1150, 1130 cm^{-1} (CO); δ_H 0.92 (3H, t, *J* = 7.4, CH_3CH_2), 1.25-1.33 (2H, m, CH_2CH_3), 1.36-1.44 (4H, m, $2xCH_2CH_2COH$), 1.6 (1H, br s, OH), 1.62-1.76 (4H, m, $2xCH_2COH$), 1.82-1.89 (2H, m, $CH_2CH_2CH_3$), 3.84-3.96 (4H, m, $2xCH_2O$), 5.61 (1H, d, *J* = 15.6, CH=CHCOH), 5.96 (1H, d, *J* = 15.6, $CHCOH$); δ_C 14.25 (CH_3CH_2), 16.85 (CH_2CH_3), 27.75 ($2xCH_2CH_2COH$), 40.65 ($2xCH_2COH$), 40.7 ($CH_2CH_2CH_3$), 64.5 ($2xCH_2O$), 81.5 (COH), 109.15 (CO_2), 126.6 ($CHCOH$), 137.25 (CH=CHCOH); *m/z* 183 (M^+-C_3H_7, 100%), 121 (10), 115 (33), 73 (23), 69 (14), 67 (12), 55 (44), 45 (17), 43 (68), 41 (88).

(E)-2-[3-Hydroxy-3-phenyl-1-butenyl)-2-propyl-1,3-dioxolane (**7ag**):[15] ν (film) 3700-3100 (OH), 3020, 1655 (HC=C), 1050, 1010 cm^{-1} (CO); δ_H 0.91 (3H, t, *J* = 7.4, CH_3CH_2), 1.36-1.44 (2H, m, CH_2CH_3), 1.64 (s, 3H, CH_3COH), 1.67-1.73 (2H, m, $CH_2CH_2CH_3$), 2.01 (1H, br s, OH), 3.82-3.94 (4H, m, $2xCH_2O$), 5.64 (1H, d, *J* = 15.6, $CHCHCOH$), 6.13 (1H, d, *J* = 15.6, $CHCOH$), 7.21-7.29 (1H, m, ArH), 7.30-7.42 (2H, m, ArH), 7.44-7.46 (2H, m, ArH); δ_C 14.25 (CH_3CH_2), 16.8 (CH_2CH_3), 29.85 (CH_3COH), 40.65 ($CH_2CH_2CH_3$), 64.55 ($2xCH_2O$), 74.05 (COH), 109.05 (CO_2), 125.05, 127.0, 127.75, 128.25, 137.75, 146.55 (CH=CH, ArC); *m/z* 219 (M^+-C_3H_7, 50%]) 131 (13), 115 (31), 105 (31), 77 (24), 43 (100).

(E)-2-Isopropyl-2-vinyl-1,3-dioxolane (**7ba**):[16] ν (film) 3060, 1630 (HC=C), 1080, 1025 cm^{-1} (CO); δ_H 0.94 [6H, d, *J* = 6.9, $(CH_3)_2CH$], 1.81-1.94 [1H, m, $CH(CH_2)_2$], 3.84-3.98 (4H, m, $2xCH_2O$), 5.21 (1H, dd, *J* = 10.6, 2.0, $CHCH_2$), 5.34 (1H, dd, *J* = 17.2, 2.0, $CHHCH$), 5.72 (1H, dd, *J* = 17.2, 10.6, $CHHCH$) ; δ_C 16.85 [$(CH_3)_2CH$], 35.45 [$CH(CH_3)_2$], 64.6 ($2xCH_2O$), 111.15 (CO_2), 116.05 (CH_2=CH), 136.1 (CH=CH_2); *m/z* 99 (M^+-C_3H_7, 100%), 115 (27), 100 (12), 55 (78), 43 (24),41 (12).

(E)-2(2-Deuteriovinyl)-2-isopropyl-1,3-dioxolane (**7bb**):[15] ν (film) 3020, 1625 (HC=C), 1070, 1010 cm^{-1} (CO); δ_H 0.94 [6H, d, *J* = 7.0, $(CH_3)_2CH$], 1.86-1.95 [1H, m, $CH(CH_3)_2$], 3.84-3.98 (4H, m, $2xCH_2O$), 5.33 (1H, d, *J* = 17.1, CH=CHD), 5.71 (1H, d, *J* = 17.1, $CDHCH$) ; δ_C 16.85 [$(CH_3)_2CH$], 35.5 [$CH(CH_3)_2$], 64.6 ($2xCH_2O$), 111.2 (CO_2), 115.8 (t, J_{CD} = 24.4), 136.00 (CH=CHD); *m/z* 100 (M^+ - C_3H_7, 100%), 115 (12), 56 (28).

(E)-2-(3-Hydroxy-4,4-dimethyl-1-pentenyl)-2-isopropyl-1,3-dioxolane (**7bc**):[15] ν (film) 3600-3100 (OH), 3010, 1620 (HC=C), 1080, 1040 cm^{-1} (CO); δ_H 0.92 [9H, s, $(CH_3)_3C$], 0.95 [6H, d, *J* = 6.9, $(CH_3)_2CH$], 1.60 (1H, br s, OH), 1.87-1.96 [1H, m, $CH(CH_3)_2$], 3.81 (1H, d, *J* = 6.7, $CHOH$), 3.86-3.96 (4H, m, $2xCH_2O$), 5.56 (1H, d, *J* = 15.6, $CHCO_2$), 5.89 (1H, dd, *J* = 15.6, 6.7, $CHCOH$); δ_C 17.0 [$(CH_3)_3C$], 25.7

$[(CH_3)_2CH]$, 34.95 $[C(CH_3)_3]$, 35.85 $[CH(CH_3)_2]$, 64.65 ($2xCH_2O$), 79.95 (CHOH), 111.1 (COO), 130.05 ($CHCO_2$), 131.85 (CHCHOH); *m/z* 185 (M^+-C_3H_7, 100%), 171 (19), 129 (32), 115 (27), 99 (95), 57 (44), 43 (31).

*(*E*)-2-(3-Hydroxy-3-phenyl-1-propenyl)-2-isopropyl-1,3-dioxolane* (**7bd**):[15] ν (film) 3600-3100 (OH), 3015, 1600 (HC=C), 1090, 1020 cm^{-1} (CO); δ_H 0.93 [6H, d, J = 6.8, $(CH_3)_2CH$], 1.86-1.93 [1H, m, $CH(CH_3)_2$], 3.02 (1H, br s, OH), 3.84 (1H, d, J = 5.9, CHOH), 3.80-3.91 (4H, m, $2xCH_2O$), 5.69 (1H, d, J = 15.4, $CHCO_2$), 6.00 (1H, dd, J = 15.4, 5.9, CHCHOH), 7.23-7.35 (5H, m, ArH); δ_C 16.95 $[(CH_3)_2CH]$, 35.85 $[CH(CH_3)_2]$, 64.65 ($2xCH_2O$), 79.1 (CHOH), 110.95 (CO_2), 126.25, 127.7, 128.55, 128.85, 133.9, 142.8 (CH=CH, ArC); *m/z* 205 (M^+-C_3H_7, 100%), 115 (19), 105 (25), 77(14).

*(*E*)-2-(3-Hydroxy-3-methyl-1-butenyl)-2-isopropyl-1,3-dioxolane* (**7be**):[15] ν (film) 3680-3040 (OH), 3010, 1630 (HC=C), 1085, 1015 cm^{-1} (CO); δ_H 0.86 [6H, d, J = 7.0, $(CH_3)_2CH$], 1.26 [6H, s, $(CH_3)_2COH$], 1.65 (1H, br s, OH), 1.79-1.88 [1H, m,$CH(CH_3)_2$], 3.76-3.89 (4H, m, $2xCH_2O$), 5.46 (1H, d, J = 15.8, CH=CHCOH), 5.87 (1H, d, J = 15.8, CHCOH); δ_C 16.95 $[(CH_3)_2CH]$, 29.9 $[(CH_3)_2COH]$, 35.85 $[CH(CH_3)_2]$, 64.6 ($2xCH_2O$), 70.6 (C-OH), 111.15 (CO_2), 124.5 (CH=CHCOH), 139.75 (CHCOH); *m/z* 157 (M^+-C_3H_7, 100%), 115 (13), 113 (11), 73 (11), 43 (24).

*(*E*)-2-[2-(1-Hydroxycyclopentyl)vinyl]-2-isopropyl-1,3-dioxolane-* (**7bf**):[15] ν (film) 3600-3100 (OH), 3000, 1640 (HC=C), 1080, 1010 cm^{-1} (CO); δ_H 0.98 [6H, d, J = 6.9, $(CH_3)_2CH$], 1.25-1.36 (4H, m, $2xCH_2CH_2OH$), 1.62-1.88 (5H, m, $2xCH_2COH$, OH), 2.25-2.3 [1H, m, $CH(CH_3)_2$], 3.94-4.01 (4H, m, $2xCH_2O$), 5.31 (1H, d, J = 13.4, CH=CHCOH), 5.6 (1H, d, J = 13.4, CHCOH); δ_C 16.9 $[(CH_3)_2CH]$, 23.9 $[CH(CH_3)_2]$, 36.25 ($2xCH_2CH_2COH$), 42.0 ($2xCH_2COH$), 64.7 ($2xCH_2O$), 83.00 (COH), 112.00 (CO_2), 128.45 (CH=CHCOH), 139.9 (CHCOH); *m/z* 183 (M^+-C_3H_7, 100%), 165 (15), 155 (31), 139 (33), 121 (38), 115 (32), 111 (35), 73 (36), 55 (51), 43 (79).

*(*E*)-2-(3-Hydroxy-3-phenyl-1-butenyl)-2-isopropyl-1,3-dioxolane* (**7bg**):[15] ν (film) 3600-3100 (OH), 3015, 1590 (HC=C), 1070, 1010 cm^{-1} (CO); δ_H 0.86 [6H, d, J = 6.9, $(CH_3)_2CH$], 1.59 (3H, s, CH_3COH), 1.80-1.89 [1H, m,$CH(CH_3)_2$], 1.88 (1H, br s, OH), 3.73-3.86 (4H, m, $2xCH_2O$), 5.56 (1H, d, J = 15.6, CH=CHCOH), 6.05 (1H, d, J = 15.6, CHCOH), 7.14-7.19 (1H, m, ArH), 7.26 (2H, t, J = 7.0, ArH), 7.35-7.4 (2H, m, ArH); δ_C 17.00 $[(CH_3)_2CH]$, 29.85 (CH_3COH), 35.95 $[CH(CH_3)_2]$, 64.65 ($2xCH_2O$), 74.2 (COH), 111.15 (CO_2), 125.05, 126.15, 127.0, 128.25, 138.6, 146.9 (CH=CH, ArC); *m/z* 219 (M^+-C_3H_7, 58%), 115 (20), 105 (41), 77 (22), 43 (100).

*(*E*,4*R*,5*R*)-2-(3-Hydroxy-4,4-dimethyl-1-pentenyl)-4,5-dimethyl-2-propyl-1,3-dioxolane* (**7ca**):[15] First diastereoisomer, ν (film) 3550-3000 (OH), 3020, 1660 (HC=C), 1150, 1080 cm^{-1} (CO); δ_H 0.91 [9H, s, $(CH_3)_3C$], 0.92 (3H, t, J = 7.3, CH_3CH_2), 1.23 (3H, d, J = 6.8, CH_3CH), 1.25 (3H, d, J = 6.4, CH_3CH), 1.39-1.93 (2H, m, CH_2CH_3), 1.63-1.69 (2H, m, $CH_2CH_2CH_3$), 1.72 (1H, br s, OH), 3.56-3.63 (2H, m, $2xCHCH_3$), 3.77 (1H, dd, J = 6.4, 2.5, CHOH), 5.65 (1H, dd, J = 15.5, 2.5, $CHCO_2$), 5.92 (1H, dd, J = 15.5, 6.4, CHCHOH); δ_C 14.25 (CH_3CH_2), 16.1 (CH_3CH), 16.6 (CH_3CH), 17.05 (CH_2CH_3), 25.7 $[(CH_3)_3C]$, 34.95 $[C(CH_3)_3]$, 41.75 ($CH_2CH_2CH_3$), 77.7 (CHOH), 79.8 ($CHCH_3$), 80.0 ($CHCH_3$), 108.0 (CO_2), 130.0 (CHCHOH), 133.85 ($CHCO_2$); *m/z* 213 [M^+-C_3H_7, 49%], 143 (24), 128 (14), 84 (15), 71 (27), 57 (100), 43 (44), 41 (64). Second diastereoisomer, ν (film) 3550-3000 (OH), 3020, 1660 (HC=C), 1150, 1080 cm^{-1} (CO); δ_H 0.91 [9H, s, $(CH_3)_3C$], 0.92 (3H, t, J = 7.3, CH_3CH_2), 1.23 (3H, d, J = 6.8, CH_3CH), 1.25 (3H, d, J = 6.4, CH_3CH), 1.39-1.43 (2H, m, CH_2CH_3), 1.63-1.69 (2H, m, $CH_2CH_2CH_3$), 1.72 (1H, br s, OH), 3.56-3.63 (2H, m, $2xCHCH_3$), 3.77 (1H, dd, J = 6.4, 2.5, CHOH), 5.65 (1H, dd, J = 15.5, 2.5, CHCOO), 5.93 (1H, dd, J = 15.5, 6.4, CHCHOH); δ_C 14.25 (CH_3CH_2), 16.1 (CH_3CH), 16.6 (CH_3CH), 17.1 (CH_2CH_3), 25.7 $[(CH_3)_3C]$, 35.05 $[C(CH_3)_3]$, 41.75 ($CH_2CH_2CH_3$), 79.35 (CHOH), 79.8 ($CHCH_3$), 80.0 ($CHCH_3$), 107.8 (CO_2), 130.1 (CHCHOH), 133.55 ($CHCO_2$); *m/z* 213 (M^+-C_3H_7, 49%), 199 (7), 143 (24), 128 (14), 84 (15), 71 (27), 57 (100), 43 (44), 41 (64). Diastereomeric mixture : $[\alpha]_D^{25}$ =

+10.2 [c = 0.90 (CH_2Cl_2)].

(E,4R,5R)-2-(3-Hydroxy-3-phenyl-1-propenyl)-4,5-dimethyl-2-propyl-1,3-dioxolane (**7cb**):[15] First diastereoisomer, ν (film) 3700-3100 (OH), 3025, 1595 (HC=C), 1170, 1090 cm^{-1} (CO); δ_H 0.90 (3H, t, J = 7.3, CH_3CH_2), 1.19 (3H, d, J = 5.2, CH_3CH), 1.22 (3H, d, J = 5.5, CH_3CH), 1.36-1.45 (2H, m, CH_2CH_3), 1.60-1.69 (2H, m, $CH_2CH_2CH_3$), 3.54-3.62 (2H, m, 2x$CHCH_3$), 5.23 (1H, dd, J = 6.1, 2.2, CHOH), 5.80 (1H, dd, J = 15.6, 2.2, $CHCO_2$), 6.10 (1H, dd, J = 15.6, 6.1, CHCHOH), 7.26-7.36 (5H, m, ArH); δ_C 14.2 (CH_3CH_2), 16.1 (CH_3CH), 16.55 (CH_3CH), 17.0 (CH_2CH_3), 41.6 ($CH_2CH_2CH_3$), 74.1 (CHOH), 77.75 ($CHCH_3$), 79.35 ($CHCH_3$), 107.85 (CO_2), 126.35, 127.65, 128.3, 132.2, 132.25, 142.75 (CH=CH, ArC); *m/z* 233 (M^+-C_3H_7, 100%), 161 (96), 143 (21), 133 (12), 125 (16), 115 (10), 105 (37), 77 (20), 71 (11), 55 (13). 43 (15). Second diastereoisomer, ν (film) 3700-3100 (OH), 3025, 1595 (HC=C), 1170, 1090 cm^{-1} (CO); δ_H 0.90 (3H, t, J = 7.3, CH_3CH_2), 1.19 (3H, d, J = 5.2, CH_3CH), 1.23 (3H, d, J = 5.8, CH_3CH), 1.36-1.45 (2H, m, CH_2CH_3), 1.60-1.69 (2H, m, $CH_2CH_2CH_3$), 3.54-3.62 (2H, m, 2x$CHCH_3$), 5.23 (1H, dd, J = 6.1, 2.2, CHOH), 5.79 (1H, dd, J = 15.6, 2.2, $CHCO_2$), 6.04 (1H, dd, J = 15.6, 6.1, CHCHOH), 7.27-7.36 (5H, m, ArH); δ_C 14.2 (CH_3CH_2), 16.7 (CH_3CH), 16.45 (CH_3CH), 17.1 (CH_2CH_3), 41.6 ($CH_2CH_2CH_3$), 72.6 (CHOH), 77.8 ($CHCH_3$),80.5 ($CHCH_3$), 107.1 (CO_2), 126.3, 127.9, 128.45, 132.3, 132.35, 142.75 (CH=CH, ArC); *m/z* 233 (M^+-C_3H_7, 100%), 161 (91), 143 (17), 133 (23), 125 (19), 115 (23), 105 (33), 77 (22), 71 (10), 55 (14). 43 (23). Diastereomeric mixture : $[\alpha]_D^{25}$ = -20.8 [c = 1.05 (CH_2Cl_2)].

(E,4R,5R)-2-[2-(1-Hydroxycyclohexyl)viniyl]-4,5-dimethyl-2-propyl-1,3-dilxalane (**7cc**):[15] ν (film) 3600-3100 (OH), 3005, 1650 (HC=C), 1110, 1080 cm^{-1} (CO); δ_H 0.91 (3H, t, J = 7.3, CH_3CH_2), 1.22 (3H, d, J = 5.8, CH_3CH), 1.25 (3H, d, J = 5.8, CH_3CH), 1.42-1.48 (14H, m, 7xCH_2), 1.90 (1H, br s, OH), 3.56-3.61 (2H, m, 2x$CHCH_3$), 5.67 (1H, d, J = 15.7, CHCHCOH), 5.96 (1H, d, J = 15.7, CHCOH); δ_C 14.2 (CH_3CH_2), 16.15 (CH_3CH), 16.6 (CH_3CH), 17.15 (CH_2CH_3), 22.05 (2xCH_2CH_2COH), 25.45 ($CH_2CH_2CH_2COH$), 37.9 (CH_2COH), 37.95 (CH_2COH), 41.75 ($CH_2CH_2CH_3$), 71.2 (COH), 77.6 ($CHCH_3$), 79.3 ($CHCH_3$), 108.25 (CO_2), 128.8 (CHCOH), 138.0 (CHCHCOH); *m/z* 225 [M^+-C_3H_7, 100%], 153 (36), 143 (26), 81 (13), 71 (11), 55 (20), 43 (13). $[\alpha]_D^{25}$ = -14.4 [c = 1.00 (CH_2Cl_2)].

(E)-2-(1-Hydroxycyclohexylethynyl)-2-propyl-1,3-dioxolane (**8a**):[15] R_f = 0.38 (hexane/ethyl acetate, 2/1); ν (film) 3650-3050 cm^{-1} (OH), 2200 cm^{-1} (C≡C); δ_H 0.96 (3H, t, J = 7.4, CH_3CH_2), 1.26-1.97 (13H, m, 6xCH_2, OH), 3.94-4.09 (4H, m, 2xCH_2O); δ_C 14.0 (CH_2CH_3), 17.4 (CH_3CH_2), 23.4 (2xCH_2CH_2COH), 41.4 ($CH_2CH_2CH_3$), 42.4 (2xCH_2COH), 64.5 (2xCH_2O), 74.3 (COH), 80.7 (CCO_2), 87.6 (CCOH), 103.35 (CO_2); ; *m/z* 181 [M^+-C_3H_7, 100%], 119 (13), 113 (41), 69 (23), 67 (15), 45 (23), 41 (89).

(E)-2-(3-Hydroxy-3-methylbutynyl)-2-isopropyl-1,3-dioxolane (**8b**):[15] R_f = 0.41 (hexane/ethyl acetate, 2/1); ν (film) 3600-3000 (OH), 2200 cm^{-1} (C≡C); δ_H 0.98 [6H, d, J = 7.0, $(CH_3)_2CH$], 1.46 [6H, s, $(CH_3)_2COH$], 1.87 (1H, br s, OH), 1.89-1.93 [1H, m, $CH(CH_3)_2$], 3.95-3.99 (4H, m, 2xCH_2O); δ_C 17.1 [$(CH_3)_2CH$], 31.3 [$(CH_3)_2COH$], 36.7 [$CH(CH_3)_2$], 64.75 (2xCH_2O), 77.2 (C-OH), 78.7 (CCO_2), 89.1 (CCOH), 106.5 (CO_2); *m/z* 155 (M^+-C_3H_7, 13%), 97 (10), 53 (30), 43 (100), 41 (31).

7-(1-Hydroxy-2,2-dimethylpropyl)-1,4-dioxaspiro[4,5]dec-6-ene (**12a**):[16] ν (film) 3680-3100 (OH), 3090, 1645 (HC=C), 1085 cm^{-1} (CO); δ_H 0.94 [9H, s, $(CH_3)_3C$], 1.68-1.88 (4H, m, 2xCH_2), 1.70 (1H, br s, OH), 1.95-2.35 (1H, m, CHHCCHOH), 2.38-2.46 (1H, m, CHHCCHOH), 3.72 (1H, s, CHOH), 3.92-4.02 (4H, m, 2xCH_2O), 5.52 (1H, s, $CHCO_2$); δ_C 21.3 ($CH_2CH_2CO_2$), 23.0 [$C(CH_3)_3$], 26.35 [$(CH_3)_3C$], 27.9 (CH_2CCHOH), 37.95 (CH_2CO_2), 63.65 (2xCH_2O), 82.35 (CHOH), 107.05 (CO_2), 124.8 ($CHCO_2$), 127.2 (CCHOH); *m/z* 226 (M^+, 5%), 170 (65), 169 (65), 126 (59), 125 (24), 99 (99), 97 (47), 79 (29), 73 (67), 67 (20), 57 (88), 55 (40), 45 (37), 44 (100), 43 (73), 42 (33).

7-(1-Hydroxy-1-methylethyl)-1,4-dioxaspiro[4,5]dec-6-ene (**12b**): ν (film) 3670-3099 (OH), 3100, 1659 (HC=C), 1170, 1120 cm^{-1} (CO); δ_H 1.33 [6H, s, $(CH_3)_2C$], 1.76-1.77 (4H, m, 2xCH_2), 2.07 (1H, br s, OH), 2.09-2.10 (2H, m, CH_2CCOH), 3.95-4.02 (4H, m, 2xCH_2O), 5.65 (1H, s, CH); δ_C 21.25 ($CH_2CH_2CO_2$), 24.55 (CH_2CO_2), 28.5 [$(CH_3)_2C$], 33.4 (CH_2CCOH), 64.45 (2xCH_2O), 72.5 (COH), 106.6 (CO_2), 119.35 (CH), 151.05 (CCOH); *m/z* 198 (M^+, 1%), 170 (46), 139 (28), 111 (100), 99 (22), 73 (24), 67 (23), 55 (27), 43 (86) (Found: M^+, 198.1260. $C_{11}H_{18}O_3$ requires M, 198.1256).

7-(1-Hydroxycyclopentyl)-1,4-dioxaspiro[4,5]dec-6-ene (**12c**): ν (film) 3700-3140 (OH), 3053, 1647 (HC=C), 1115, 1095 cm^{-1} (CO); δ_H 1.62-1.89 (12H, m, 6xCH_2), 1.90 (1H, br s, OH), 2.04-2.12 (2H, m, CH_2CCOH), 3.95-4.02 (4H, m, 2xCH_2O), 5.67 (1H, s, CH); δ_C 21.3 ($CH_2CH_2CO_2$), 23.6 (2xCH_2CH_2COH), 25.1 (CH_2CCOH), 33.5 (CH_2CO_2), 38.2 (2xCH_2COH), 64.5 (2xCH_2O), 83.7 (COH), 106.6 (CO_2), 120.1 (CH), 149.05 (CCOH); *m/z* 224 (M^+, 5%), 206 (57), 178 (47), 134 (46), 112 (72), 106 (32), 105 (30), 99 (77), 91 (100), 86 (56), 79 (40), 77 (46), 67 (59), 65 (37), 55 (87), 51 (35), 44 (80), 43 (54), 42 (43) (Found: M^+, 224.1403. $C_{13}H_{20}O_3$ requires M, 224.1412).

Preparation of Compounds **4**, **9** *and* **13**. *General Procedure*.- To a suspension of silica gel (0.3 g) in dichloromethane (1 ml) was added 2 drops of 10% aqueous oxalic acid and a dichloromethane solution (0.5 ml) of the corresponding ketal **3**, **7** or **12** at 20°C. The reaction mixture was stirred at the same temperature for 3 h, then Na_2CO_3 (0.1 g) is added and stirring is continued for 30 min and after that, ethyl acetate (10 ml) is also added to the reaction mixture. After filtration, the solvents were evaporated (15 Torr) to yield pure compounds **4**, **9** and **13**. Yields and physical data are included in Table 2; analytical and spectroscopic data follow.

2-(1-Hydroxy-2,2-dimethylpropyl)-2-cyclohexenone (**4a**): ν (film) 3700-3150 (OH), 3010, 1664 (HC=C), 1665 cm^{-1} (CO); δ_H 0.86 [6H, s, $(CH_3)_3C$], 1.94-2.04 (2H, m, CH_2CH_2CO), 2.41-2.46 (4H, m, 2xCH_2), 3.32 (1H, br s, OH), 4.15 (1H, s, CHOH), 6.85 (1H, t, J = 4.3, $CHCH_2$); δ_C 22.4 (CH_2CH_2CO), 25.85 (CH_2CH), 26.0 [$(CH_3)_3C$], 36.05 [$C(CH_3)_3$], 38.75 (CH_2CO), 79.1 (CHOH), 138.2 (CCO), 148.85 (CH), 202.9 (CO); *m/z* 182 (M^+, 1%), 126 (77), 125 (100), 111 (30), 97 (39), 83 (32), 57 (41), 43 (34) (Found: M^+, 182.1300 $C_8H_{18}O_2$ requires M, 182.1307).

2-(1-Hydroxy-1-methyl)cyclohexenone (**4b**):[15] ν (film) 3680-3110 (OH), 3050, 1656 (CO), 1172, 1161 cm^{-1} (CO); δ_H 1.39 [6H, s, $(CH_3)_2C$], 1.93-2.02 (2H, m, CH_2CH_2CO), 2.38-2.48 (4H, m, 2xCH_2), 4.42 (1H, br s, OH), 6.93 (1H, t, J = 4.3, $CHCH_2$); δ_C 22.5 (CH_2CH_2CO), 25.8 (CH_2CH), 28.95 [$(CH_3)_2C$], 39.4 (CH_2CO), 71.82 (COH), 143.9 (CCO), 144.3 (CH), 202.0 (CO); *m/z* 174 (M^+-CH_3, 15%), 97 (20), 79 (20), 59 (22), 55 (38), 43 (100).182.1300.

2-(1-Hydroxycyclopentyl)-2-cyclohexenone (**4c**):[15] ν (film) 3640-3140 cm^{-1} (OH), 3040, 1750 (CO), 1660 (HC=C), 1160, 1120 cm^{-1} (CO); δ_H 1.64-2.02 (12H, m, 6xCH_2), 2.37-2.51 (2H, m, CH_2CO), 3.81 (1H, br s, OH), 6.92 (1H, t, J = 4.0, $CHCH_2$); δ_C 22.5 (2xCH_2CH_2COH), 23.1 (CH_2CH_2CO), 25.75 (CH_2CH), 38.4 (2xCH_2COH), 39.2 (CH_2CO), 81.9 (COH), 131.25 (CCO), 143.45 (CH), 202.05 (CO); *m/z* 182 (M^+-H_2O, 50%), 157 (57), 134 (15), 123 (72), 110 (31), 109 (40), 106 (33), 105 (27), 96 (38), 95 (34), 91 (54), 81 (22), 79 (28), 77 (30), 68 (24), 67 (50), 65 (25), 55 (100), 53 (33), 51 (24), 43 (51).

(E)-7-Hydroxy-8,8-dimethyl-5-nonen-4-one (**9a**):[15] ν (film) 3650-3250 (OH), 1700 cm^{-1}(CO); δ_H 0.89 [9H, s, $(CH_3)_3C$], 0.89 (3H, t, J = 7.3, CH_3CH_2), 1.52 (1H, br s, OH), 1.56-1.66 (3H, m, CH_2CH_3, CHOH), 2.48 (2H, t, J = 7.0, CH_2CO), 6.26 (1H, d, J = 15.9, CHCO), 6.82 (1H, dd, J = 15.9, 5.5, CHCHOH); δ_C 13.8 (CH_3CH_2), 17.6 (CH_2CH_3), 25.6 [$(CH_3)_3C$], 35.6 [$C(CH_3)_3$], 42.8 (CH_2CO), 79.2 (CHOH), 129.2 (CHCO), 145.0 (CHCOH), 200.4 (CO); *m/z* 128 (M^+-C_4H_9, 81%), 99 (17), 71 (79), 57 (100), 55 (25), 43 (67), 41 (67).

(E)-1-Hydroxy-1-phenyl-2-hepten-4-one (**9b**):[16] ν (film) 3600-3200 (OH), 1700 cm^{-1} (CO); δ_H 0.93 (3H, t, J = 7.3, CH_3CH_2), 1.58-1.67 (3H, m, CH_2CH_3, CHOH), 2.19 (1H, br s, OH), 2.55 (2H, t, J = 7.3, CH_2CO), 6.42 (1H, d, J = 15.9, CHCO), 6.89 (1H, dd, J = 15.9, 4.9, CHCHOH), 7.29-7.41 (5H, m, ArH); δ_C 13.75 (CH_3), 17.5 (CH_2CH_3), 42.6 (CH_2CO), 73.8 (CHOH), 126.5, 126.6, 126.75, 128.4, 128.9, 145.95 (CH=CH, ArC), 200.55 (CO); *m/z* 204 (M^+, 2%), 175 (28), 133 (26), 115 (19), 105 (100), 115 (13), 91 (16), 77 (78), 55 (34), 43 (68), 41 (44).

(E)-7-Hydroxy-7-methyl-5-octen-4-one (**9c**):[15] ν (film) 3650-3150 (OH), 1680 cm^{-1} (CO); δ_H 0.94 (3H, t, J =

7.6, CH_3CH_2), 1.38 [6H, s, $(CH_3)_2COH$], 1.57 (1H, br s, OH), 1.61-1.69 (2H, m, CH_2CH_3), 2.54 (2H, t, J = 7.3, CH_2CO), 6.3 (1H, d, J = 15.9, CHCO), 6.86 (1H, d, 1H, J = 15.9, CHCOH); δ_C 13.75 (CH_3CH_2), 17.55 (CH_2CH_3), 29.4 [$(CH_3)_2COH$], 42.9 (CH_2CO), 70.85 (COH), 125.75 (CHCO), 152.6 (CHCOH), 200.6 (CO); *m/z* 157 (M^+-C_3H_7, 21%), 71 (32), 70 (26), 57 (87), 55 (35), 43 (100), 41 (86).

(E)-1-(1-Hydroxycyclopentyl)-1-hexen-3-one (**9d**):[15] ν (film) 3700-3200 (OH), 1680 cm^{-1} (CO); δ_H 0.94 (3H, t, J = 7.6, CH_3CH_2), 1.62 (1H, br s, OH), 1.58-1.94 (10H, m, CH_2CH_3, 4xCH_2), 2.54 (2H, t, J = 7.0, CH_2CO), 6.39 (1H, d, J = 15.6, CHCHCO), 6.9 (1H, d, J = 15.6, CHCO); δ_C 13.8 (CH_3), 17.6 (CH_2CH_3), 24.00 (2xCH_2COH), 40.8 (2xCH_2CH_2COH), 43.1 (CH_2CO), 81.8 (COH), 126.00 (CHCO), 151.2 (CHCOH), 200.65 (CO); *m/z* 139 [M^+-C_3H_7, 2%], 111 (22), 97 (14), 83 (15), 79 (12), 69 (20), 55 (50), 43 (56), 41 (100).

(E)-7-Hydroxy-7-phenyl-5-octen-4-one (**9e**):[15] ν (film) 3700-3200 (OH), 1700 cm^{-1} (CO); δ_H 0.92 (3H, t, J = 7.3, CH_3CH_2), 1.55-1.66 (2H, m, CH_2CH_3), 1.68 (1H, br s, OH), 1.72 (3H, s, CH_3COH), 2.53 (2H, t, J = 7.3, CH_2CO), 6.38 (1H, d, J = 15.9, CHCO), 6.99 (1H, d, J = 15.9, CHCOH), 7.26-7.53 (5H, m, ArH); δ_C 13.7 (CH_3CH_2), 17.45 (CH_2CH_3), 29.0 (CH_3COH), 42.8 (CH_2CO), 74.0 (COH), 125.1, 126.1, 127.5, 128.5, 144.8, 150.7 (CH=CH, ArC), 200.9 (CO); *m/z* 175 (M^+-C_3H_7, 43%), 147 (14), 129 (16), 105 (15), 77 (23), 71 (13), 51 (13), 43 (100), 41 (21).

(E)-6-Hydroxy-2-methyl-6-phenyl-4-hepten-3-one (**9f**):[15] ν (film) 3700-3200 (OH), 1700 cm^{-1} (CO); δ_H 1.12 [6H, d, J = 6.7, $(CH)_3CH)$], 1.73 (3H, s, CH_3COH), 2.08 (1H, br s, OH), 2.79-2.84 [1H, m, $CH(CH_3)_2$], 6.48 (1H, d, J = 15.8, CHCO), 7.06 (1H, d, J = 15.8, CHCOH), 7.27-7.47 (5H, m, ArH); δ_C 18.25 [$(CH_3)_2CH$], 29.2 (CH_3COH), 39.35 [$CH(CH_3)_2$], 74.4 (COH), 124.2, 125.1, 127.5, 128.5, 144.85, 150.7 (CH=CH, ArC), 204.05 (CO); *m/z* 175 [M^+-C_3H_7, 47%], 147 (16), 131 (36), 129 (32), 128 (10), 115 (13), 105 (46), 103 (15), 91 (22), 78 (14), 77 (43), 51 (17), 43 (100), 41 (38).

3-(1-Hydroxy-2,2-dimethylpropyl)-2-cyclohexenone (**13a**):[15] ν (film) 3650-3140 (OH), 1650 cm^{-1} (CO); δ_H 0.97 [9H, s, $(CH_3)_3$], 1.93-2.03 (2H, m, CH_2CH_2CO), 2.01 (1H, br s, OH), 2.28-2.54 (4H, m, 2xCH_2), 3.92 (1H, s, CHOH), 5.98 (1H, s, CHCO); δ_C 23.0 (CH_2CH_2CO), 26.35 [$(CH_3)_3C$], 27.9 (CH_2CCHOH), 36.0 [$C(CH_3)_3$], 38.0 (CH_2CO), 82.4 (CHOH), 127.3 (CHCO), 166.15 (CCHCO), 199.75 (CO); *m/z* 164 (M^+-H_2O, 1%), 126 (100), 97 (54), 57 (67), 55 (21), 43 (30).

3-(1-Hydroxy-1-methylethyl)-2-cyclohexenone (**13b**): ν (film) 3630-3100 (OH), 1656 cm^{-1} (CO); δ_H 1.33 [6H, s, $(CH_3)_2C$], 1.88-1.97 (2H, m, CH_2CH_2CO), 2.27-2.34 (4H, m, CH_2CO, CH_2CCOH), 2.89 (1H, br s, OH), 6.09 (1H, s, CHCO); δ_C 22.95 (CH_2CH_2CO), 25.6 (CH_2CCOH), 28.3 [$(CH_3)_2C$], 37.3 (CH_2CO), 72.5 (COH), 122.3 (CH), 171.35 (CCOH), 200.85 (CO); *m/z* 154 (M^+, 3%), 139 (13), 111 (68), 59 (55), 55 (23), 43 (100) (Found: M^+, 154.0999. $C_9H_{14}O_2$ requires M, 154.0994).

3-(1-Hydroxycyclopentyl)-2-cyclohexenone (**13c**): ν (film) 3690-3050 (OH), 1656 cm^{-1} (CO); δ_H 1.61-2.07 (10H, m, 5xCH_2), 2.23 (1H, br s, OH), 2.36-2.40 (4H, m, CH_2CCOH, CH_2CO), 6.20 (1H, s, CH); δ_C 23.1 (2xCH_2CH_2COH), 24.0 (2xCH_2COH), 26.2 (CH_2CH_2CO), 37.55 (CH_2CCOH), 38.9 (CH_2CO), 83.6 (COH), 122.95 (CH), 169.3 (CCOH), 200.6 (CO); *m/z* 180 (M^+, 13%), 162 (35), 152 (25), 134 (28), 124 (52), 123 (100), 119 (21), 110 (82), 109 (23), 95 (43), 91 (44), 81 (23), 79 (27), 77 (25), 68 (41), 67 (83), 66 (22), 65 (28), 55 (89), 53 (34), 51 (24), 44 (61), 43 (56) (Found: M^+, 180.1150. $C_{11}H_{16}O_2$ requires M, 180.1150).

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16. For compounds **3aa**, **9b** and **12a** it was not possible to obtain the corresponding HRMS due to their instability.

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