

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 (H₂O, D₂O, Me₃SiCl, Bu^tCHO, PhCHO, Me₂CO, (CH₂)₄CO, (CH₂)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

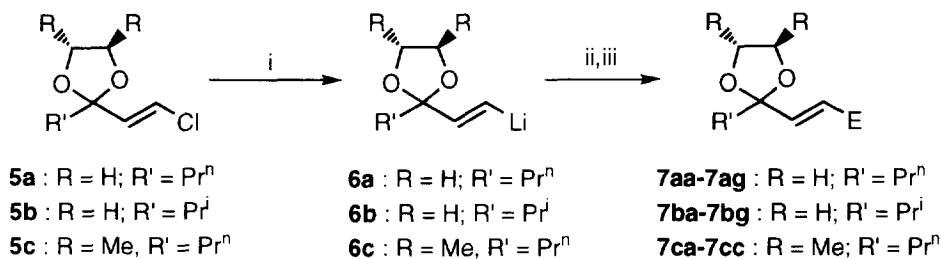
α - or β -Acylvinyl anion equivalents of the types **I** or **II**, respectively, are versatile intermediates in synthetic organic chemistry because they can transfer the α,β -unsaturated acyl functionality to electrophilic reagents.¹ Intermediates of the type **I** and **II** can also be considered as sp²-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 derivative⁵ 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**^{6a} 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 polyolithiated 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}

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

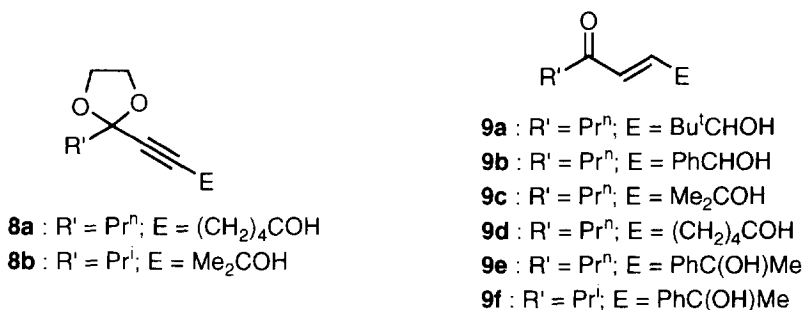
Entry	Starting material	Intermediate	Electrophile E ⁺	Product ^a				
				No.	R	E ⁺	Yield (%) ^b	R _f ^c
1	1a	2a	Me ₃ SiCl	3aa	H	Me ₃ Si	98	0.44 ^d
2	1a	2a	Bu ^t CHO	3ab	H	Bu ^t CHOH	69	0.57
3	1a	2a	Me ₂ CO	3ac	H	Me ₂ COH	62	0.52
4	1a	2a	(CH ₂) ₄ CO	3ad	H	(CH ₂) ₄ COH	51	0.55
5	1b	2b	Bu ^t CHO	3b	Me	Bu ^t CHOH	69 ^e	0.54,0.56 ^e
6	5a	6a	H ₂ O	7aa	H	H	90	0.93
7	5a	6a	D ₂ O	7ab	H	D	88 ^f	0.93
8	5a	6a	Bu ^t CHO	7ac	H	Bu ^t CHOH	55	0.53
9	5a	6a	PhCHO	7ad	H	PhCHOH	52	0.64
10	5a	6a	Me ₂ CO	7ae	H	Me ₂ COH	65	0.23
11	5a	6a	(CH ₂) ₄ CO	7af	H	(CH ₂) ₄ COH	52	0.36
12	5a	6a	PhCOMe	7ag	H	PhC(OH)Me	53	0.45
13	5b	6b	H ₂ O	7ba	H	H	90	0.86
14	5b	6b	D ₂ O	7bb	H	D	67 ^f	0.86
15	5b	6b	Bu ^t CHO	7bc	H	Bu ^t CHOH	53	0.45
16	5b	6b	PhCHO	7bd	H	PhCHOH	43	0.60
17	5b	6b	Me ₂ CO	7be	H	Me ₂ COH	63	0.44
18	5b	6b	(CH ₂) ₄ CO	7bf	H	(CH ₂) ₄ COH	62	0.57
19	5b	6b	PhCOMe	7bg	H	PhC(OH)Me	55	0.56
20	5c	6c	Bu ^t CHO	7ca	Me	Bu ^t CHOH	70 ^e	0.61 ^g
21	5c	6c	PhCHO	7cb	Me	PhCHOH	72 ^e	0.57 ^g
22	5c	6c	(CH ₂) ₅ CO	7cc	Me	(CH ₂) ₅ COH	62	0.66
23	10	11	Bu ^t CHO	12a	-	Bu ^t CHOH	67	0.47
24	10	11	Me ₂ CO	12b	-	Me ₂ COH	80	0.31 ^h
25	10	11	(CH ₂) ₄ CO	12c	-	(CH ₂) ₄ COH	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 ^1H NMR ($J_{\text{CH}=\text{CH}} = 15.4\text{-}17.2$ 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.



Scheme 2. Reagents and conditions: i, Li, DTBB cat. (4%), THF, -90°C ; ii, $\text{E}^+ = \text{H}_2\text{O}$, D_2O , Bu^tCHO , PhCHO , Me_2CO , $(\text{CH}_2)_4\text{CO}$, PhCOMe , -90 to -60°C ; iii, H_2O , -60 to 20°C .

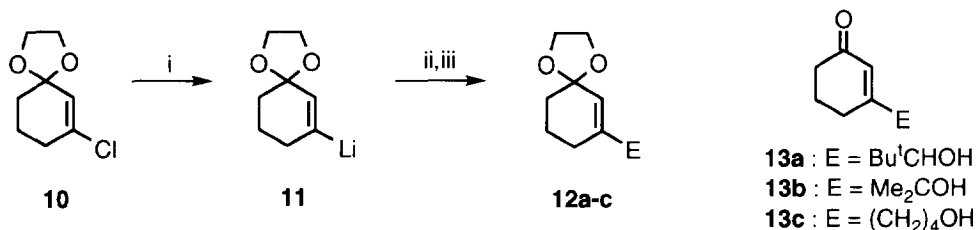


Also in the case of compounds **5**, the corresponding chiral derivative **5c** was prepared and submitted to the same reaction shown in Scheme 2: as it happened for compound **3b** a *ca.* 1:1 mixtures of diastereoisomers **7ca** and **7cb** was obtained when prochiral aldehydes (Bu^tCHO , PhCHO) were 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^tCHO , Me_2CO , $(\text{CH}_2)_4\text{CO}$] 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**.



Scheme 3. Reagents and conditions: i, Li, DTBB cat. (5%), THF, -78°C;
 ii, E⁺ = Bu^tCHO, Me₂CO, (CH₂)₄CO, -78°C; iii, H₂O, -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 ^t CHOH	0.49
2	3ac	4b	-	Me ₂ COH	0.39
3	3ad	4c	-	(CH ₂) ₄ COH	0.38
4	7ac	9a	Pr ⁿ	Bu ^t CHOH	0.47
5	7ad	9b	Pr ⁿ	PhCHOH	0.41
6	7ae	9c	Pr ⁿ	Me ₂ COH	0.46
7	7af	9d	Pr ⁿ	(CH ₂) ₄ COH	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 ^t CHOH	0.26
11	12b	13b	-	Me ₂ COH	0.29 ^c
12	12c	13c	-	(CH ₂) ₄ COH	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 ¹³C NMR spectra were recorded in a Bruker AC-300 using CDCl₃ as solvent and SiMe₄ 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 Shimadzu QP-5000 spectrometer. Thin layer chromatography (TLC) was carried out on Scheleicher & Schnell F1500/LS 254 plates coated with a ÷0.2 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 NaHCO₃ 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, CH₂CH₂CO₂), 1.86-1.92 (2H, m, CH₂CO₂), 2.10-2.16 (2H, m, CH₂CH), 3.95-4.05 (2H, m, CH₂O), 4.13-4.23 (2H, m, CH₂O), 6.09 (1H, t, *J* = 4.1, CHCH₂); δ_{C} 20.4 (CH₂CH₂CO₂), 26.15 (CH₂CH), 35.7 (CH₂CO₂), 65.9 (2xCH₂O), 105.7 (CO₂), 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. C₈H₁₁ClO₂ requires M, 174.0469).

(2R,3R)-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, CH₃CH), 1.31 (3H, d, *J* = 5.8, CH₃CH), 1.75-2.13 (4H, m, 2xCH₂), 2.46-2.52 (1H, m, CHHCH), 2.58-2.63 (1H, m, CHHCH), 3.53-3.69 (1H, m, CHCH₃), 3.94-4.02 (1H, m, CHCH₃), 6.07 (1H, t, *J* = 4.0, CHCCl); δ_{C} 15.75 (CH₂CH₂CO₂), 20.3 (2xCH₃), 26.15 (CH₂CH), 36.95 (CH₂COO), 78.35 (2xCHCH₃), 80.2 (CO₂), 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, $2 \times CH_2O$), 5.75 (1H, s, CH); δ_C 21.05 (CH_2CH_2CCl), 32.55 (CH_2CO_2), 32.65 (CH_2CCl), 64.55 ($2 \times CH_2O$), 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 $-78^\circ C$. The reaction mixture was stirred at the same temperature for 8 h and kept at $-5^\circ C$ 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 distillation 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. $44-46^\circ C$ (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, $2 \times CH_2O$), 5.82 (1H, d, $J = 13.2$, $CH=CHCl$), 6.28 (1H, d, $J = 13.2$, CHCl); δ_C 14.1 (CH_3), 16.6 (CH_2CH_3), 40.6 ($CH_2CH_2CH_3$), 64.6 ($2 \times CH_2O$), 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-Chlorovinyl)-2-(isopropyl)-1,3-dioxolane- (5b):¹⁵ (68%) b.p. $48-50^\circ C$ (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, $2 \times CH_2O$), 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 ($2 \times CH_2O$), 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,4R,5R)-2-(2-Chlorovinyl)-4,5-dimethyl-2-propyl-1,3-dioxolane (5c):¹⁵ (72%) b.p. $50-52^\circ C$ (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, $2 \times CHCH_3$), 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 ($2 \times CHCH_3$), 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 $-78^\circ C$ 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 $-90^\circ C$ 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, $2 \times CH_2$), 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 (CH_2CH), 31.85 (CH_2CO_2), 63.7 ($2 \times CH_2O$), 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, $(\text{CH}_3)_3\text{C}$], 1.66-1.80 (4H, m, $2\times\text{CH}_2$), 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, $2\times\text{CH}_2\text{O}$), 6.18 (1H, t, $J = 3.8$, CHCH_2); δ_{C} 20.1 ($\text{CH}_2\text{CH}_2\text{CO}_2$), 25.05 (CH_2CH), 26.75 [$(\text{CH}_3)_3\text{C}$], 33.05 (CH_2COO), 35.55 [$\text{C}(\text{CH}_3)_3$], 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 ($\text{M}^+-\text{H}_2\text{O}$, 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 v (film) 3670-3050 (OH), 3080, 1605 (HC=C), 1115, 1085 cm^{-1} (CO); δ_{H} 1.40 [6H, s, $(\text{CH}_3)_2\text{C}$], 1.73-1.74 (4H, m, $2\times\text{CH}_2$), 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 ($\text{CH}_2\text{CH}_2\text{CO}_2$), 25.05 (CH_2CH), 30.1 [$(\text{CH}_3)_2\text{C}$], 32.8 (CH_2CO_2), 63.3 ($2\times\text{CH}_2\text{O}$), 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 v (film) 3650-3100 (OH), 3030, 1653 (HC=C), 1150, 1090 cm^{-1} (CO); δ_{H} 1.64-1.83 (12H, m, $6\times\text{CH}_2$), 2.11-2.13 (2H, m, CH_2CH), 3.70 (1H, br s, OH), 4.02-4.15 (4H, m, $2\times\text{CH}_2\text{O}$), 6.10 (1H, t, $J = 3.7$, CHCH_2); δ_{C} 19.6 ($\text{CH}_2\text{CH}_2\text{CO}_2$), 22.6 ($2\times\text{CH}_2\text{CH}_2\text{COH}$), 25.1 (CH_2CH), 32.25 (CH_2CO_2), 38.3 ($2\times\text{CH}_2\text{COH}$), 63.45 ($2\times\text{CH}_2\text{O}$), 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).

(2R,3R)-6-(1-Hydroxy-2,2-dimethylpropyl)-2,3-dimethyl-1,4-dioxaspiro[4,5]dec-6-ene (3b):¹⁵ First diastereoisomer, v (film) 3690-3130 (OH), 3035, 1650 (HC=C), 1107, 1091 cm^{-1} (CO); δ_{H} 0.97 [9H, s, $(\text{CH}_3)_3\text{C}$], 1.25 (1H, d, $J = 5.8$, CH_3CH), 1.31 (1H, d, $J = 5.5$, CH_3CH), 1.68-1.84 (4H, m, $2\times\text{CH}_2$), 1.86 (1H, br s, OH), 2.06-2.11 (2H, m, CH_2CH), 3.63-3.77 (2H, m, $2\times\text{CHCH}_3$), 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 ($\text{CH}_2\text{CH}_2\text{CO}_2$), 24.85 (CH_2CH), 26.9 [$(\text{CH}_3)_3\text{C}$], 35.2 (CH_2CO_2), 35.7 [$\text{C}(\text{CH}_3)_3$], 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 ($\text{M}^+-\text{H}_2\text{O}$, 1%), 197 (20), 169 (20), 125 (100), 57 (20), 55 (51), 44 (28), 43 (53). $[\alpha]_{\text{D}}^{25} = -35.0$ [$c = 0.48$ (CH_2Cl_2)]. Second diastereoisomer, v (film) 3690-3130 (OH), 3035, 1650 (HC=C), 1107, 1091 cm^{-1} (CO); δ_{H} 0.97 [9H, s, $(\text{CH}_3)_3\text{C}$], 1.25 (1H, d, $J = 5.8$, CH_3CH), 1.29 (1H, d, $J = 5.4$, CH_3CH), 1.30-1.85 (4H, m, $2\times\text{CH}_2$), 1.90 (1H, br s, OH), 2.08-2.10 (2H, m, CH_2CH), 3.65-3.93 (2H, m, $2\times\text{CHCH}_3$), 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 ($\text{CH}_2\text{CH}_2\text{CO}_2$), 25.1 (CH_2CH), 26.95 [$(\text{CH}_3)_3\text{C}$], 35.5 (CH_2CO_2), 35.55 [$\text{C}(\text{CH}_3)_3$], 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 ($\text{M}^+-\text{H}_2\text{O}$, 1%), 197 (19), 169 (17), 125 (100), 57 (16), 55 (45), 43 (42). $[\alpha]_{\text{D}}^{25} = -22.9$ [$c = 0.97$ (CH_2Cl_2)].

(E)-2-Propyl-2-vinyl-1,3-dioxolane (7aa):¹⁵ v (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, $\text{CH}_2\text{CH}_2\text{CH}_3$), 3.84-3.97 (4H, m, $2\times\text{CH}_2\text{O}$), 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 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 64.45 ($2\times\text{CH}_2\text{O}$), 109.1 (CO_2), 115.2 (CH_2CH), 137.75 (CHCH_2); m/z 99 ($\text{M}^+-\text{C}_3\text{H}_7$, 100%), 115 (42), 71 (10), 55 (49), 43 (12).

(E)-2-(2-Deuteriovinyl)-2-propyl-1,3-dioxolane (7ab):¹⁵ v (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, $\text{CH}_2\text{CH}_2\text{CH}_3$), 3.84-3.97 (4H, m, $2\times\text{CH}_2\text{O}$), 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 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 64.45 ($2\times\text{CH}_2\text{O}$), 109.1 (CO_2), 115.4 (t, $J_{\text{CD}} = 24.3$), 137.75 (CHCHD); m/z 100 ($\text{M}^+-\text{C}_3\text{H}_7$, 100%), 115 (38), 71 (12).

(E)-2-(3-Hydroxy-4,4-dimethyl-1-pentenyl)-2-propyl-1,3-dioxolane (7ac):¹⁵ v (film) 3600-3000 (OH), 3110 (HC=C), 1150, 1090 cm^{-1} (CO); δ_{H} 0.91 [9H, s, $(\text{CH}_3)_3\text{C}$], 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, $\text{CH}_2\text{CH}_2\text{CH}_3$), 3.79 (1H, dd, $J = 6.7$, 1.1, CHOH), 3.85-3.97 (4H, m, $2\times\text{CH}_2\text{O}$), 5.57 (1H, dd, $J = 15.5$, 1.1, CHCOO), 5.89 (1H, dd, $J = 15.5$, 6.7,

CHCHOH); δ_C 14.25 [(CH₃)₃C], 16.85 (CH₃CH₂), 25.25 (CH₂CH₃), 34.95 (CH₂CH₂CH₃), 40.55 [C(CH₃)₃], 64.5 (2xCH₂O), 79.8 (COH), 109.0 (CO₂), 130.95 (CHCO₂), 131.75 (CHCHOH); m/z 185 (M⁺-C₃H₇, 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 v (film) 3700-3100 (OH), 3025, 1580 (HC=C), 1050, 1010 cm⁻¹ (CO); δ_H 0.91 (3H, t, $J = 7.3$, CH₃CH₂), 1.33-1.46 (2H, m, CH₂CH₃), 1.67-1.72 (2H, m, CH₂CH₂CH₃), 3.81-3.92 (4H, m, 2xCH₂O), 5.23 (1H, d, $J = 5.9$, CHOH), 5.71 (1H, d, $J = 15.5$, CHCO₂), 6.01 (1H, dd, $J = 15.5, 5.9$, CHCHOH), 7.27-7.93 (5H, m, ArH); δ_C 16.75 (CH₃CH₂), 20.95 (CH₂CH₃), 40.55 (CH₂CH₂CH₃), 64.5 (2xCH₂O), 74.05 (CHOH), 108.85 (CO₂), 126.3, 127.7, 128.55, 130.2, 133.1, 142.4 (CH=CH, ArC); m/z 205 (M⁺-C₃H₇, 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 v (film) 3600-3100 (OH), 3020, 1650 (HC=C), 1050, 1140 cm⁻¹ (CO); δ_H 0.92 (3H, t, $J = 7.4$, CH₃CH₂), 1.32 [6H, s, (CH₃)₂COH], 1.34-1.42 (2H, m, CH₂CH₃), 1.52 (1H, br s, OH), 1.51-1.71 (2H, m, CH₂CH₂CH₃), 3.86-3.94 (4H, m, 2xCH₂O), 5.55 (1H, d, $J = 15.6$, CH=CHCOH), 5.94 (1H, d, $J = 15.6$, CHCOH); δ_C 14.25 (CH₃CH₂), 16.85 (CH₂CH₃), 29.8 [(CH₃)₂COH], 40.7 (CH₂CH₂CH₃), 64.5 (2xCH₂O), 70.5 (COH), 109.05 (CO₂), 126.25 (CHCOH), 138.85 (CH=CHCOH); m/z 157 (M⁺-C₃H₇, 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 v (film) 3600-3100 (OH), 3000, 1650 (HC=C), 1150, 1130 cm⁻¹ (CO); δ_H 0.92 (3H, t, $J = 7.4$, CH₃CH₂), 1.25-1.33 (2H, m, CH₂CH₃), 1.36-1.44 (4H, m, 2xCH₂CH₂COH), 1.6 (1H, br s, OH), 1.62-1.76 (4H, m, 2xCH₂COH), 1.82-1.89 (2H, m, CH₂CH₂CH₃), 3.84-3.96 (4H, m, 2xCH₂O), 5.61 (1H, d, $J = 15.6$, CH=CHCOH), 5.96 (1H, d, $J = 15.6$, CHCOH); δ_C 14.25 (CH₃CH₂), 16.85 (CH₂CH₃), 27.75 (2xCH₂CH₂COH), 40.65 (2xCH₂COH), 40.7 (CH₂CH₂CH₃), 64.5 (2xCH₂O), 81.5 (COH), 109.15 (CO₂), 126.6 (CHCOH), 137.25 (CH=CHCOH); m/z 183 (M⁺-C₃H₇, 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 v (film) 3700-3100 (OH), 3020, 1655 (HC=C), 1050, 1010 cm⁻¹ (CO); δ_H 0.91 (3H, t, $J = 7.4$, CH₃CH₂), 1.36-1.44 (2H, m, CH₂CH₃), 1.64 (s, 3H, CH₃COH), 1.67-1.73 (2H, m, CH₂CH₂CH₃), 2.01 (1H, br s, OH), 3.82-3.94 (4H, m, 2xCH₂O), 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 (CH₃CH₂), 16.8 (CH₂CH₃), 29.85 (CH₃COH), 40.65 (CH₂CH₂CH₃), 64.55 (2xCH₂O), 74.05 (COH), 109.05 (CO₂), 125.05, 127.0, 127.75, 128.25, 137.75, 146.55 (CH=CH, ArC); m/z 219 (M⁺-C₃H₇, 50%) 131 (13), 115 (31), 105 (31), 77 (24), 43 (100).

(E)-2-Isopropyl-2-vinyl-1,3-dioxolane (**7ba**):¹⁶ v (film) 3060, 1630 (HC=C), 1080, 1025 cm⁻¹ (CO); δ_H 0.94 [6H, d, $J = 6.9$, (CH₃)₂CH], 1.81-1.94 [1H, m, CH(CH₂)₂], 3.84-3.98 (4H, m, 2xCH₂O), 5.21 (1H, dd, $J = 10.6, 2.0$, CHCH₂), 5.34 (1H, dd, $J = 17.2, 2.0$, CHHCH), 5.72 (1H, dd, $J = 17.2, 10.6$, CHHCH); δ_C 16.85 [(CH₃)₂CH], 35.45 [CH(CH₃)₂], 64.6 (2xCH₂O), 111.15 (CO₂), 116.05 (CH₂=CH), 136.1 (CH=CH₂); m/z 99 (M⁺-C₃H₇, 100%), 115 (27), 100 (12), 55 (78), 43 (24), 41 (12).

(E)-2-(2-Deuteriovinyl)-2-isopropyl-1,3-dioxolane (**7bb**):¹⁵ v (film) 3020, 1625 (HC=C), 1070, 1010 cm⁻¹ (CO); δ_H 0.94 [6H, d, $J = 7.0$, (CH₃)₂CH], 1.86-1.95 [1H, m, CH(CH₃)₂], 3.84-3.98 (4H, m, 2xCH₂O), 5.33 (1H, d, $J = 17.1$, CH=CHD), 5.71 (1H, d, $J = 17.1$, CDHCH); δ_C 16.85 [(CH₃)₂CH], 35.5 [CH(CH₃)₂], 64.6 (2xCH₂O), 111.2 (CO₂), 115.8 (t, $J_{CD} = 24.4$), 136.00 (CH=CHD); m/z 100 (M⁺-C₃H₇, 100%), 115 (12), 56 (28).

(E)-2-(3-Hydroxy-4,4-dimethyl-1-pentenyl)-2-isopropyl-1,3-dioxolane (**7bc**):¹⁵ v (film) 3600-3100 (OH), 3010, 1620 (HC=C), 1080, 1040 cm⁻¹ (CO); δ_H 0.92 [9H, s, (CH₃)₃C], 0.95 [6H, d, $J = 6.9$, (CH₃)₂CH], 1.60 (1H, br s, OH), 1.87-1.96 [1H, m, CH(CH₃)₂], 3.81 (1H, d, $J = 6.7$, CHOH), 3.86-3.96 (4H, m, 2xCH₂O), 5.56 (1H, d, $J = 15.6$, CHCO₂), 5.89 (1H, dd, $J = 15.6, 6.7$, CHCOH); δ_C 17.0 [(CH₃)₃C], 25.7

[(CH₃)₂CH], 34.95 [C(CH₃)₃], 35.85 [CH(CH₃)₂], 64.65 (2xCH₂O), 79.95 (CHOH), 111.1 (COO), 130.05 (CHCO₂), 131.85 (CHCHOH); *m/z* 185 (M⁺-C₃H₇, 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 v (film) 3600-3100 (OH), 3015, 1600 (HC=C), 1090, 1020 cm⁻¹ (CO); δ_H 0.93 [6H, d, *J* = 6.8, (CH₃)₂CH], 1.86-1.93 [1H, m, CH(CH₃)₂], 3.02 (1H, br s, OH), 3.84 (1H, d, *J* = 5.9, CHOH), 3.80-3.91 (4H, m, 2xCH₂O), 5.69 (1H, d, *J* = 15.4, CHCO₂), 6.00 (1H, dd, *J* = 15.4, 5.9, CHCHOH), 7.23-7.35 (5H, m, ArH); δ_C 16.95 [(CH₃)₂CH], 35.85 [CH(CH₃)₂], 64.65 (2xCH₂O), 79.1 (CHOH), 110.95 (CO₂), 126.25, 127.7, 128.55, 128.85, 133.9, 142.8 (CH=CH, ArC); *m/z* 205 (M⁺-C₃H₇, 100%), 115 (19), 105 (25), 77(14).

(*E*)-2-(3-Hydroxy-3-methyl-1-butenyl)-2-isopropyl-1,3-dioxolane (**7be**):¹⁵ v (film) 3680-3040 (OH), 3010, 1630 (HC=C), 1085, 1015 cm⁻¹ (CO); δ_H 0.86 [6H, d, *J* = 7.0, (CH₃)₂CH], 1.26 [6H, s, (CH₃)₂COH], 1.65 (1H, br s, OH), 1.79-1.88 [1H, m, CH(CH₃)₂], 3.76-3.89 (4H, m, 2xCH₂O), 5.46 (1H, d, *J* = 15.8, CH=CHCOH), 5.87 (1H, d, *J* = 15.8, CHCOH); δ_C 16.95 [(CH₃)₂CH], 29.9 [(CH₃)₂COH], 35.85 [CH(CH₃)₂], 64.6 (2xCH₂O), 70.6 (C-OH), 111.15 (CO₂), 124.5 (CH=CHCOH), 139.75 (CHCOH); *m/z* 157 (M⁺-C₃H₇, 100%), 115 (13), 113 (11), 73 (11), 43 (24).

(*E*)-2-[2-(1-Hydroxycyclopentyl)vinyl]-2-isopropyl-1,3-dioxolane- (**7bf**):¹⁵ v (film) 3600-3100 (OH), 3000, 1640 (HC=C), 1080, 1010 cm⁻¹ (CO); δ_H 0.98 [6H, d, *J* = 6.9, (CH₃)₂CH], 1.25-1.36 (4H, m, 2xCH₂CH₂OH), 1.62-1.88 (5H, m, 2xCH₂COH, OH), 2.25-2.3 [1H, m, CH(CH₃)₂], 3.94-4.01 (4H, m, 2xCH₂O), 5.31 (1H, d, *J* = 13.4, CH=CHCOH), 5.6 (1H, d, *J* = 13.4, CHCOH); δ_C 16.9 [(CH₃)₂CH], 23.9 [CH(CH₃)₂], 36.25 (2xCH₂CH₂COH), 42.0 (2xCH₂COH), 64.7 (2xCH₂O), 83.00 (COH), 112.00 (CO₂), 128.45 (CH=CHCOH), 139.9 (CHCOH); *m/z* 183 (M⁺-C₃H₇, 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 v (film) 3600-3100 (OH), 3015, 1590 (HC=C), 1070, 1010 cm⁻¹ (CO); δ_H 0.86 [6H, d, *J* = 6.9, (CH₃)₂CH], 1.59 (3H, s, CH₃COH), 1.80-1.89 [1H, m, CH(CH₃)₂], 1.88 (1H, br s, OH), 3.73-3.86 (4H, m, 2xCH₂O), 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 [(CH₃)₂CH], 29.85 (CH₃COH), 35.95 [CH(CH₃)₂], 64.65 (2xCH₂O), 74.2 (COH), 111.15 (CO₂), 125.05, 126.15, 127.0, 128.25, 138.6, 146.9 (CH=CH, ArC); *m/z* 219 (M⁺-C₃H₇, 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, v (film) 3550-3000 (OH), 3020, 1660 (HC=C), 1150, 1080 cm⁻¹ (CO); δ_H 0.91 [9H, s, (CH₃)₃C], 0.92 (3H, t, *J* = 7.3, CH₃CH₂), 1.23 (3H, d, *J* = 6.8, CH₃CH), 1.25 (3H, d, *J* = 6.4, CH₃CH), 1.39-1.93 (2H, m, CH₂CH₃), 1.63-1.69 (2H, m, CH₂CH₂CH₃), 1.72 (1H, br s, OH), 3.56-3.63 (2H, m, 2xCHCH₃), 3.77 (1H, dd, *J* = 6.4, 2.5, CHOH), 5.65 (1H, dd, *J* = 15.5, 2.5, CHCO₂), 5.92 (1H, dd, *J* = 15.5, 6.4, CHCHOH); δ_C 14.25 (CH₃CH₂), 16.1 (CH₃CH), 16.6 (CH₃CH), 17.05 (CH₂CH₃), 25.7 [(CH₃)₃C], 34.95 [C(CH₃)₃], 41.75 (CH₂CH₂CH₃), 77.7 (CHOH), 79.8 (CHCH₃), 80.0 (CHCH₃), 108.0 (CO₂), 130.0 (CHCHOH), 133.85 (CHCO₂); *m/z* 213 [M⁺-C₃H₇, 49%], 143 (24), 128 (14), 84 (15), 71 (27), 57 (100), 43 (44), 41 (64). Second diastereoisomer, v (film) 3550-3000 (OH), 3020, 1660 (HC=C), 1150, 1080 cm⁻¹ (CO); δ_H 0.91 [9H, s, (CH₃)₃C], 0.92 (3H, t, *J* = 7.3, CH₃CH₂), 1.23 (3H, d, *J* = 6.8, CH₃CH), 1.25 (3H, d, *J* = 6.4, CH₃CH), 1.39-1.43 (2H, m, CH₂CH₃), 1.63-1.69 (2H, m, CH₂CH₂CH₃), 1.72 (1H, br s, OH), 3.56-3.63 (2H, m, 2xCHCH₃), 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 (CH₃CH₂), 16.1 (CH₃CH), 16.6 (CH₃CH), 17.1 (CH₂CH₃), 25.7 [(CH₃)₃C], 35.05 [C(CH₃)₃], 41.75 (CH₂CH₂CH₃), 79.35 (CHOH), 79.8 (CHCH₃), 80.0 (CHCH₃), 107.8 (CO₂), 130.1 (CHCHOH), 133.55 (CHCO₂); *m/z* 213 (M⁺-C₃H₇, 49%), 199 (7), 143 (24), 128 (14), 84 (15), 71 (27), 57 (100), 43 (44), 41 (64). Diastereomeric mixture : [α]_D²⁵ =

+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 ($\text{HC}=\text{C}$), 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, $\text{CH}_2\text{CH}_2\text{CH}_3$), 3.54-3.62 (2H, m, $2\times\text{CHCH}_3$), 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 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 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 ($\text{CH}=\text{CH}$, ArC); m/z 233 ($\text{M}^+-\text{C}_3\text{H}_7$, 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 ($\text{HC}=\text{C}$), 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, $\text{CH}_2\text{CH}_2\text{CH}_3$), 3.54-3.62 (2H, m, $2\times\text{CHCH}_3$), 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 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 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 ($\text{CH}=\text{CH}$, ArC); m/z 233 ($\text{M}^+-\text{C}_3\text{H}_7$, 100%), 161 (91), 143 (17), 133 (23), 125 (19), 115 (23), 105 (33), 77 (22), 71 (10), 55 (14), 43 (23). Diastereomeric mixture : $[\alpha]_{\text{D}}^{25} = -20.8$ [$c = 1.05$ (CH_2Cl_2)].

(*E*,*4R*,*5R*)-2-[2-(1-Hydroxycyclohexyl)vinyl]-4,5-dimethyl-2-propyl-1,3-dioxolane (**7cc**):¹⁵ ν (film) 3600-3100 (OH), 3005, 1650 ($\text{HC}=\text{C}$), 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, $7\times\text{CH}_2$), 1.90 (1H, br s, OH), 3.56-3.61 (2H, m, $2\times\text{CHCH}_3$), 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 ($2\times\text{CH}_2\text{CH}_2\text{COH}$), 25.45 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{COH}$), 37.9 (CH_2COH), 37.95 (CH_2COH), 41.75 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 71.2 (COH), 77.6 (CHCH_3), 79.3 (CHCH_3), 108.25 (CO_2), 128.8 (CHCOH), 138.0 (CHCHCOH); m/z 225 [$\text{M}^+-\text{C}_3\text{H}_7$, 100%], 153 (36), 143 (26), 81 (13), 71 (11), 55 (20), 43 (13). $[\alpha]_{\text{D}}^{25} = -14.4$ [$c = 1.00$ (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} ($\text{C}\equiv\text{C}$); δ_{H} 0.96 (3H, t, $J = 7.4$, CH_3CH_2), 1.26-1.97 (13H, m, $6\times\text{CH}_2$, OH), 3.94-4.09 (4H, m, $2\times\text{CH}_2\text{O}$); δ_{C} 14.0 (CH_2CH_3), 17.4 (CH_3CH_2), 23.4 ($2\times\text{CH}_2\text{CH}_2\text{COH}$), 41.4 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 42.4 ($2\times\text{CH}_2\text{COH}$), 64.5 ($2\times\text{CH}_2\text{O}$), 74.3 (COH), 80.7 (CCO_2), 87.6 (CCOH), 103.35 (CO_2); m/z 181 [$\text{M}^+-\text{C}_3\text{H}_7$, 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} ($\text{C}\equiv\text{C}$); δ_{H} 0.98 [6H, d, $J = 7.0$, $(\text{CH}_3)_2\text{CH}$], 1.46 [6H, s, $(\text{CH}_3)_2\text{COH}$], 1.87 (1H, br s, OH), 1.89-1.93 [1H, m, $\text{CH}(\text{CH}_3)_2$], 3.95-3.99 (4H, m, $2\times\text{CH}_2\text{O}$); δ_{C} 17.1 [$(\text{CH}_3)_2\text{CH}$], 31.3 [$(\text{CH}_3)_2\text{COH}$], 36.7 [$\text{CH}(\text{CH}_3)_2$], 64.75 ($2\times\text{CH}_2\text{O}$), 77.2 (C-OH), 78.7 (CCO_2), 89.1 (CCOH), 106.5 (CO_2); m/z 155 ($\text{M}^+-\text{C}_3\text{H}_7$, 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 ($\text{HC}=\text{C}$), 1085 cm^{-1} (CO); δ_{H} 0.94 [9H, s, $(\text{CH}_3)_3\text{C}$], 1.68-1.88 (4H, m, $2\times\text{CH}_2$), 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, $2\times\text{CH}_2\text{O}$), 5.52 (1H, s, CHCO_2); δ_{C} 21.3 ($\text{CH}_2\text{CH}_2\text{CO}_2$), 23.0 [$\text{C}(\text{CH}_3)_3$], 26.35 [$(\text{CH}_3)_3\text{C}$], 27.9 (CH_2CCHOH), 37.95 (CH_2CO_2), 63.65 ($2\times\text{CH}_2\text{O}$), 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 ($\text{HC}=\text{C}$), 1170, 1120 cm^{-1} (CO); δ_{H} 1.33 [6H, s, $(\text{CH}_3)_2\text{C}$], 1.76-1.77 (4H, m, $2\times\text{CH}_2$), 2.07 (1H, br s, OH), 2.09-2.10 (2H, m, CH_2CCOH), 3.95-4.02 (4H, m, $2\times\text{CH}_2\text{O}$), 5.65 (1H, s, CH); δ_{C} 21.25 ($\text{CH}_2\text{CH}_2\text{CO}_2$),

24.55 (CH₂CO₂), 28.5 [(CH₃)₂C], 33.4 (CH₂CCOH), 64.45 (2xCH₂O), 72.5 (COH), 106.6 (CO₂), 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. C₁₁H₁₈O₃ requires M, 198.1256).

7-(1-Hydroxycyclopentyl)-1,4-dioxaspiro[4,5]dec-6-ene (12c): *v* (film) 3700-3140 (OH), 3053, 1647 (HC=C), 1115, 1095 cm⁻¹ (CO); δ_{H} 1.62-1.89 (12H, m, 6xCH₂), 1.90 (1H, br s, OH), 2.04-2.12 (2H, m, CH₂CCOH), 3.95-4.02 (4H, m, 2xCH₂O), 5.67 (1H, s, CH); δ_{C} 21.3 (CH₂CH₂CO₂), 23.6 (2xCH₂CH₂COH), 25.1 (CH₂CCOH), 33.5 (CH₂CO₂), 38.2 (2xCH₂COH), 64.5 (2xCH₂O), 83.7 (COH), 106.6 (CO₂), 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. C₁₃H₂₀O₃ 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 Na₂CO₃ (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): *v* (film) 3700-3150 (OH), 3010, 1664 (HC=C), 1665 cm⁻¹ (CO); δ_{H} 0.86 [6H, s, (CH₃)₃C], 1.94-2.04 (2H, m, CH₂CH₂CO), 2.41-2.46 (4H, m, 2xCH₂), 3.32 (1H, br s, OH), 4.15 (1H, s, CHOH), 6.85 (1H, t, *J* = 4.3, CHCH₂); δ_{C} 22.4 (CH₂CH₂CO), 25.85 (CH₂CH), 26.0 [(CH₃)₃C], 36.05 [C(CH₃)₃], 38.75 (CH₂CO), 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 C₈H₁₈O₂ requires M, 182.1307).

2-(1-Hydroxy-1-methyl)cyclohexenone (4b):¹⁵ *v* (film) 3680-3110 (OH), 3050, 1656 (CO), 1172, 1161 cm⁻¹ (CO); δ_{H} 1.39 [6H, s, (CH₃)₂C], 1.93-2.02 (2H, m, CH₂CH₂CO), 2.38-2.48 (4H, m, 2xCH₂), 4.42 (1H, br s, OH), 6.93 (1H, t, *J* = 4.3, CHCH₂); δ_{C} 22.5 (CH₂CH₂CO), 25.8 (CH₂CH), 28.95 [(CH₃)₂C], 39.4 (CH₂CO), 71.82 (COH), 143.9 (CCO), 144.3 (CH), 202.0 (CO); *m/z* 174 (M⁺-CH₃, 15%), 97 (20), 79 (20), 59 (22), 55 (38), 43 (100).182.1300.

2-(1-Hydroxycyclopentyl)-2-cyclohexenone (4c):¹⁵ *v* (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, 6xCH₂), 2.37-2.51 (2H, m, CH₂CO), 3.81 (1H, br s, OH), 6.92 (1H, t, *J* = 4.0, CHCH₂); δ_{C} 22.5 (2xCH₂CH₂COH), 23.1 (CH₂CH₂CO), 25.75 (CH₂CH), 38.4 (2xCH₂COH), 39.2 (CH₂CO), 81.9 (COH), 131.25 (CCO), 143.45 (CH), 202.05 (CO); *m/z* 182 (M⁺-H₂O, 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 *v* (film) 3650-3250 (OH), 1700 cm⁻¹(CO); δ_{H} 0.89 [9H, s, (CH₃)₃C], 0.89 (3H, t, *J* = 7.3, CH₃CH₂), 1.52 (1H, br s, OH), 1.56-1.66 (3H, m, CH₂CH₃, CHOH), 2.48 (2H, t, *J* = 7.0, CH₂CO), 6.26 (1H, d, *J* = 15.9, CHCO), 6.82 (1H, dd, *J* = 15.9, 5.5, CHCHOH); δ_{C} 13.8 (CH₃CH₂), 17.6 (CH₂CH₃), 25.6 [(CH₃)₃C], 35.6 [C(CH₃)₃], 42.8 (CH₂CO), 79.2 (CHOH), 129.2 (CHCO), 145.0 (CHCOH), 200.4 (CO); *m/z* 128 (M⁺-C₄H₉, 81%), 99 (17), 71 (79), 57 (100), 55 (25), 43 (67), 41 (67).

(E)-1-Hydroxy-1-phenyl-2-hepten-4-one (9b):¹⁶ *v* (film) 3600-3200 (OH), 1700 cm⁻¹ (CO); δ_{H} 0.93 (3H, t, *J* = 7.3, CH₃CH₂), 1.58-1.67 (3H, m, CH₂CH₃, CHOH), 2.19 (1H, br s, OH), 2.55 (2H, t, *J* = 7.3, CH₂CO), 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 (CH₃), 17.5 (CH₂CH₃), 42.6 (CH₂CO), 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 *v* (film) 3650-3150 (OH), 1680 cm⁻¹ (CO); δ_{H} 0.94 (3H, t, *J* =

7.6, CH_3CH_2), 1.38 [6H, s, $(\text{CH}_3)_2\text{COH}$], 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 [$(\text{CH}_3)_2\text{COH}$], 42.9 (CH_2CO), 70.85 (COH), 125.75 (CHCO), 152.6 (CHCOH), 200.6 (CO); m/z 157 ($\text{M}^+ - \text{C}_3\text{H}_7$, 21%), 71 (32), 70 (26), 57 (87), 55 (35), 43 (100), 41 (86).

(E)-1-(1-Hydroxycyclopentyl)-1-hexen-3-one (**9d**):¹⁵ v (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 , $4\times\text{CH}_2$), 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 ($2\times\text{CH}_2\text{COH}$), 40.8 ($2\times\text{CH}_2\text{CH}_2\text{COH}$), 43.1 (CH_2CO), 81.8 (COH), 126.00 (CHCO), 151.2 (CHCOH), 200.65 (CO); m/z 139 [$\text{M}^+ - \text{C}_3\text{H}_7$, 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 v (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 ($\text{CH}=\text{CH}$, ArC), 200.9 (CO); m/z 175 ($\text{M}^+ - \text{C}_3\text{H}_7$, 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 v (film) 3700-3200 (OH), 1700 cm^{-1} (CO); δ_{H} 1.12 [6H, d, $J = 6.7$, $(\text{CH})_3\text{CH}$], 1.73 (3H, s, CH_3COH), 2.08 (1H, br s, OH), 2.79-2.84 [1H, m, $\text{CH}(\text{CH}_3)_2$], 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 [$(\text{CH}_3)_2\text{CH}$], 29.2 (CH_3COH), 39.35 [$\text{CH}(\text{CH}_3)_2$], 74.4 (COH), 124.2, 125.1, 127.5, 128.5, 144.85, 150.7 ($\text{CH}=\text{CH}$, ArC), 204.05 (CO); m/z 175 [$\text{M}^+ - \text{C}_3\text{H}_7$, 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 v (film) 3650-3140 (OH), 1650 cm^{-1} (CO); δ_{H} 0.97 [9H, s, $(\text{CH}_3)_3$], 1.93-2.03 (2H, m, $\text{CH}_2\text{CH}_2\text{CO}$), 2.01 (1H, br s, OH), 2.28-2.54 (4H, m, $2\times\text{CH}_2$), 3.92 (1H, s, CHOH), 5.98 (1H, s, CHCO); δ_{C} 23.0 ($\text{CH}_2\text{CH}_2\text{CO}$), 26.35 [$(\text{CH}_3)_3\text{C}$], 27.9 (CH_2CCHOH), 36.0 [$\text{C}(\text{CH}_3)_3$], 38.0 (CH_2CO), 82.4 (CHOH), 127.3 (CHCO), 166.15 (CCHCO), 199.75 (CO); m/z 164 ($\text{M}^+ - \text{H}_2\text{O}$, 1%), 126 (100), 97 (54), 57 (67), 55 (21), 43 (30).

3-(1-Hydroxy-1-methylethyl)-2-cyclohexenone (**13b**): v (film) 3630-3100 (OH), 1656 cm^{-1} (CO); δ_{H} 1.33 [6H, s, $(\text{CH}_3)_2\text{C}$], 1.88-1.97 (2H, m, $\text{CH}_2\text{CH}_2\text{CO}$), 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 ($\text{CH}_2\text{CH}_2\text{CO}$), 25.6 (CH_2CCOH), 28.3 [$(\text{CH}_3)_2\text{C}$], 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. $\text{C}_9\text{H}_{14}\text{O}_2$ requires M , 154.0994).

3-(1-Hydroxycyclopentyl)-2-cyclohexenone (**13c**): v (film) 3690-3050 (OH), 1656 cm^{-1} (CO); δ_{H} 1.61-2.07 (10H, m, $5\times\text{CH}_2$), 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 ($2\times\text{CH}_2\text{CH}_2\text{COH}$), 24.0 ($2\times\text{CH}_2\text{COH}$), 26.2 ($\text{CH}_2\text{CH}_2\text{CO}$), 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. $\text{C}_{11}\text{H}_{16}\text{O}_2$ 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.