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γ-Functionalised β-Methylene Organolithium Compounds from 3-Chloro-2-(chloromethyl)propene: Synthetic Applications

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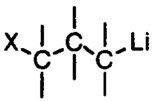
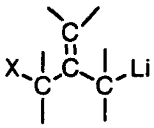
Abstract: **The reaction of functionalised methallylic chlorides 1 with an excess of lithium powder and a catalytic amount of naphthalene (8 mol %) in the presence of a carbonyl compound (Barbier-type conditions) at -78°C leads, after hydrolysis with water, to the corresponding polyfunctionalised compounds 2. Starting materials 1 are easily available from 3-chloro-2-(chloromethyl)propene by nucleophilic substitution.**

INTRODUCTION

γ-Functionalised sp^3-hybridised organolithium compounds[1] of the general type **I** are interesting intermediates as three-carbon homologating agents[2] in reactions with electrophiles. These d^3-reagents[3] have been prepared by deprotonation[4], bromine-[5], chlorine-[6] or sulphur-lithium[7] exchange, tin-lithium transmetallation[8], and other methods such as reductive opening of oxetanes[9] or addition of organolithium reagents to allyl alcohol or amine derivatives[10]. A special class of intermediates of the type **I** are the γ-functionalised organolithium compounds **II**, bearing an isobutylene skeleton, because they have been used as multicoupling reagents in cyclization reactions[11,12]. The preparation of the corresponding derivatives of the type **II** with X=OR or NR$_2$ has been accomplished, to the best of our knowledge, only by direct deprotonation at the activated allylic position[4b,c,13]. We report here an alternative general route to functionalised intermediates of the type **II**, bearing an oxygen-, nitrogen-, sulphur- or silicon-containing functional group by direct chlorine-lithium exchange from the appropriate chlorinated precursors by a naphthalene-catalysed lithiation[14,15], which represents an extension of our previous work[14f].



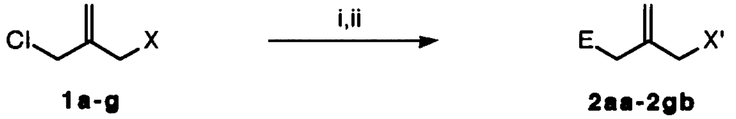
I (X=OR, NR$_2$, SR)



II

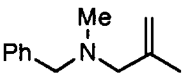
RESULTS AND DISCUSSION

The reaction of different functionalised methallylic chlorides **1** with an excess of lithium powder (1:5.5 molar ratio) and a catalytic amount of naphthalene (1:0.06 molar ratio; 8 mol %) in the presence of a carbonyl compound as electrophilic component, under Barbier-type reaction conditions, in tetrahydrofuran at -78°C led, after hydrolysis with water, to the corresponding polyfunctionalised compounds **2** (Scheme 1 and Table 1).

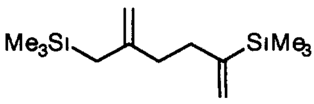


Scheme 1. *Reagents and conditions*: i, E^+=Bu^tCHO, Et_2CO, $(CH_2)_5CO$, Li powder, $C_{10}H_8$ cat. (8 %), THF, -78°C; ii, H_2O.

Some interesting features about the reaction shown in Scheme 1 are: (a) The reaction of the benzylic starting material **1b** under the above described reaction conditions yielded directly the alcohols **2ba** and **2bb** resulting from the expected process together with the benzylic ether cleavage[16] (Table 1, entries 3 and 4). (b) The same behaviour was observed starting from the benzylic sulphide **1e** (Table 1, entry 9) but it did not happen when the benzylic amine **1d** was used as starting material (Table 1, entries 7 and 8). (c) The reaction did not work with *tert*-butyl sulphide **1f** and pivalaldehyde or 3-pentanone giving only decomposition products. (d) All starting materials **1**, except the silylated compound **1g** which is commercially available, have been easily prepared from 3-chloro-2-(chloromethyl)propene **3**, commercially available, by a nucleophilic substitution process using the appropriate deprotonated nucleophile under 1,2-dimethoxyethane (DME) reflux (Scheme 2 and Table 2). (e) When the lithiation reaction was carried out in the absence of the electrophile the yields were poor or the reaction failed due to the instability of the intermediate of the type **II**; thus, the lithiation of compound **1d** under the above described reaction conditions for 30 min followed by hydrolysis with water gave the expected product **2dc** in only 33% isolated yield (compare to Table 1, entries 7 and 8); on the other hand, the same treatment as for compound **2dc** but starting from **1g** gave the dimer **4g** in 87% isolated yield[17].



2dc

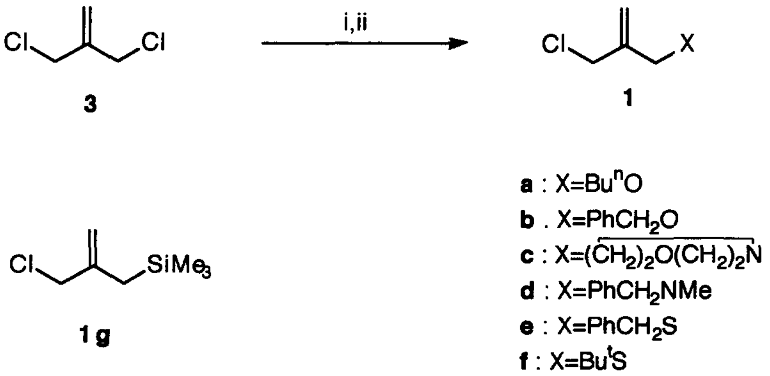


4g

Table 1. Obtention of Compounds **2**

Entry	Starting material 1	Electrophile E^+	Product[a] no.	X'	E	yield (%)[b]
1	**1a**	Et_2CO	**2aa**	Bu^nO	Et_2COH	54
2	**1a**	$(CH_2)_5CO$	**2ab**	Bu^nO	$(CH_2)_5COH$	55
3	**1b**	Et_2CO	**2ba**	OH	Et_2COH	61
4	**1b**	$(CH_2)_5CO$	**2bb**	OH	$(CH_2)_5COH$	59
5	**1c**	Et_2CO	**2ca**	-[c]	Et_2COH	46
6	**1c**	$(CH_2)_5CO$	**2cb**	-[c]	$(CH_2)_5COH$	21
7	**1d**	Et_2CO	**2da**	$PhCH_2NMe$	Et_2COH	74
8	**1d**	$(CH_2)_5CO$	**2db**	$PhCH_2NMe$	$(CH_2)_5COH$	63
9	**1e**	Bu^tCHO	**2ec**	SH	Bu^tCHOH	31
10	**1g**	Et_2CO	**2ga**	Me_3Si	Et_2COH	69
11	**1g**	$(CH_2)_5CO$	**2gb**	Me_3Si	$(CH_2)_5COH$	62

[a] All isolated products **2** were >95% pure by GLC and 300 MHz ^1H NMR. [b] Isolated yield after flash chromatography (silica gel, hexane/ethyl acetate) based on the starting material **1**. [c] X= morpholino.



3

1

1g

a : $X=Bu^nO$
b . $X=PhCH_2O$
c : $X=(CH_2)_2O(CH_2)_2N$
d : $X=PhCH_2NMe$
e : $X=PhCH_2S$
f : $X=Bu^tS$

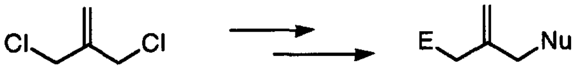
Scheme 2 *Reagents and conditions*: i, HX-NaH, DME reflux; ii, HCl-H_2O.

Table 2. Preparation of Starting Materials 1

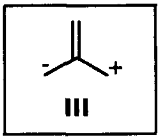
Entry	Nucleophile HX	Product 1[a] no.	Product 1[a] X	Product 1[a] yield (%)[b]
1	Bu^nOH	**1a**	Bu^nO	56
2	$PhCH_2OH$	**1b**	$PhCH_2O$	66
3	-[c]	**1c**	$\overline{(CH_2)_2O(CH_2)_2N}$	57
4	$PhCH_2NHMe$	**1d**	$PhCH_2NMe$	57
5	$PhCH_2SH$	**1e**	$PhCH_2S$	20
6	Bu^tSH	**1f**	Bu^tS	78

[a] All products were >95% pure by GLC and 300 MHz ^1H NMR. [b] Isolated yield after flash chromatography (silica gel, hexane) based on the starting material **3**. [c] Morpholine was used as nucleophile.

From the results described in this paper we conclude that the commercially available starting material **3** is an adequate precursor for the successive introduction of a nucleophile (**3**→**1**) an an electrophile (**1**→**2**) after the corresponding lithiation, behaving as a synthon of the type **III**[11] and being a useful method for preparing functionalised homoallylic aolcohols **2**.



3



III

EXPERIMENTAL PART

General.- For general information see reference 14f. High resolution mass spectra were performed by the corresponding service at the University of Zaragoza. Starting materials **1g** and **3** and the other reagents were commercially available (Aldrich) and were used as received.

Preparation of Chlorinated Starting Materials 1. General Procedure.- To a suspension of NaH (11 mmol) in ethylene glycol dimethyl ether (DME, 10 ml) was added dropwise and with stirring a solution of the starting alcohol, amine or thiol (HX, see Scheme 2) (10 mmol) in DME (10 ml). After refluxing for 1 h, the reaction mixture was cooled to room temperature. 3-Chloro-2-(chloromethyl)-1-propene (**3**, 11 mmol) was added and the reaction mixture was heated under reflux for 1 h. After cooling, the mixture was hydrolysed with water (20 ml), neutralized with 2 N HCl and extracted with diethyl ether (3x20 ml). The organic layer was dried over anhydrous Na_2SO_4 and evaporated (15 Torr). The resulting residue was then purified by flash chromatography (silica gel, hexane) to afford the title compounds. Yields are included in Table 2. Physical and spectral data follow.

3-Butoxy-2-(chloromethyl)-1-propene (**1a**): t_r=7.28 min, R_f=0.67 (hexane/ethyl acetate: 9/1); ν_{max} (film) 3040, 3020, 1630 (CH_2=C) and 1090 cm^{-1} (C-O); δ_H 0.92 (3 H, t, J=7.3, CH_3), 1.30-1.45, 1.50-1.80 (4 H, 2 m, $(CH_2)_2CH_2O$), 3.43 (2 H, t, J=6.5, CH_2CH_2O), 4.05, 4.10 (4 H, 2 s, CH_2CCH_2), 5.22 and 5.28 (2 H, 2 s, CH_2=C); δ_C 13.85, 19.3, 31.75, 45.15, 70.35, 70.8, 116.3 and 142.35; m/z 127 (M$^+$-35, 32%), 91 (13), 89 (38), 71 (100), 55 (56), 56 (16), 55 (25), 43 (23) and 41 (60).

3-Benzyloxy-2-(chloromethyl)-1-propene (**1b**)[18]: t_r=11.37 min, R_f=0.58 (hexane/ethyl acetate: 9/1); ν_{max} (film) 3060, 3020, 1640 (CH=C), 1080 and 1060 cm^{-1} (C-O); δ_H 4.08 (4 H, s, OCH_2CCH_2Cl), 4.48 (2 H, s, CH_2Ph), 5.23, 5.27 (2 H, 2 d, J=0.9, CH_2=C) and 7.23-7.33 (5 H, m, Ph); δ_C 45.05, 70,05, 72.15, 116.55, 116.6, 127.5 (2C), 128.25 (2C), 137.9 and 141.9; m/z 195 (M$^+$, <1%), 107 (31), 105 (14), 92 (37), 91 (100), 79 (20), 77 (14), 65 (23) and 51 (10).

2-(Morpholinomethyl)-3-chloro-1-propene (**1c**): t_r=9.08 min, R_f=0.39 (hexane/ethyl acetate: 9/1); ν_{max} (film) 3060, 1640 (CH_2=C) and 1100 cm^{-1} (C-O); δ_H 2.37-2.42 (4 H, m, 2xNCH_2CH_2), 3.03 (2 H, s, CCH_2N), 3.65-3.75 (4 H, m, 2xCH_2O), 4.11 (2 H, s, CH_2Cl), 5.15 and 5.27 (2 H, 2 s, CH_2=C); δ_C 46.05, 53.45 (2C), 61.25, 67.0 (2C), 117.35 and 141.9; m/z 177 (M$^+$+2, 7%), 175 (M$^+$, 21), 140 (29), 110 (85), 100 (100), 86 (15), 82 (40), 80 (10), 56 (27), 55 (19), 54 (13), 53 (37), 42 (26) and 41 (17) (Found: M$^+$, 175.075974. $C_8H_{14}{}^{35}ClNO$ requires 175.076392).

*3-(*N*-Benzyl-*N*-methylamino)-2-(chloromethyl)-1-propene* (**1d**): t_r=11.82 min, R_f=0.56 (hexane/ethyl acetate: 9/1); ν_{max} (film) 3040, 3060, 1630 and1590 cm^{-1} (CH=C); δ_H 2.13 (3 H, s, CH_3), 3.08 (2 H, s, $NCH_2C{=}CH_2$), 3.48 (2 H, s, CH_2Ph), 4.15 (2 H, d, J=1.0, CH_2Cl), 5.19, 5.27 (2 H, q and d respectively, J=1.0, CH_2=C) and 7.20-7.35 (5 H, m, Ph); δ_C42.0, 46.15, 60.25, 61.9, 116.8, 126.95, 128.2 (2C), 128.75 (2C), 139.1 and 143.35; m/z 211 (M$^+$+2, 3%), 209 (M$^+$, 9), 134 (58), 91 (100), 65 (11) and 42 (19) (Found: M$^+$, 211.092779. $C_{12}H_{16}{}^{37}ClN$ requires 211.094177).

2-(Benzylthiomethyl)-3-chloro-1-propene (**1e**): t_r=12.86 min, R_f=0.66 (hexane/ethyl acetate: 9/1); ν_{max} (film) 3070, 3040. 3020, 1630 and 1600 cm^{-1} (CH=C); δ_H 3.18 (2 H, s, $SCH_2C{=}CH_2$), 3.60 (2 H, s, CH_2Ph), 4.19 (2 H, s, CH_2Cl), 5.05, 5.25 (2 H, 2 s, CH_2=C) and 7.20-7.35 (5 H, m, Ph); δ_C 34.0, 35.3, 45.9, 117.35, 127.0, 128.4 (2C), 128.95 (2C), 137.8 and 140.85; m/z 214 (M$^+$+2, 1%), 212 (M$^+$, 5), 121 (30), 92 (12), 91 (100), 85 (18) and 45 (18) (Found: M$^+$. 212.042568. $C_{11}H_{13}{}^{35}ClS$ requires 212.042650).

*2-(*tert*-Butylthiomethyl)-3-chloro-1-propene* (**1f**): t_r=8.35 min, R_f=0.78 (hexane/ethyl acetate: 9/1); ν_{max} (film) 3060 and 1600 cm^{-1} (CH_2=C); δ_H 1.34 (9 H, s, 3xCH_3), 3.36 (2 H, s, CH_2S), 4.22 (2 H, s, CH_2Cl) and 5.20 (2 H, s, CH_2=C); δ_C 30.8 (3C), 31.55, 42.85, 46.52, 117 2 and 142.4; m/z 180 (M$^+$+2, 2%), 178 (M$^+$, 5), 59 (18), 57 (100), 53 (22), 45 (22) and 41 (56).

*Catalytic Lithiation of Precursors **1**. Isolation of Compounds **2** and **4g**. General Procedure*.- To a suspension of lithium (100 mg, 14 mmol), carbonyl compound (2.6 mmol)[19] and naphthalene (20 mg, 0.16 mmol) in THF (5 ml) was added a solution of the chlorinated precursor **1** (2.5 mmol) in THF (5 ml) at -78°C under an argon atmosphere. The reaction mixture was stirred for *ca.* 30 min[19] at the same temperature, appearing the typical green colour of lithium naphthalenide. Then, the resulting mixture was warmed to 20°C for *ca.* 2 h, hydrolyzed with water (20 ml), acidified with 2 N HCl and extracted with diethyl ether (2x20 ml)[20]. The organic layer was dried over anhydrous Na_2SO_4 and evaporated (15 Torr). The resulting residue was then purified by flash chromatography (silica gel, hexane/ethyl acetate) to afford the corresponding compounds. Yields are included in Table 1 and text. Physical and spectral data follow.

2-Butoxymethyl-4-ethyl-1-hexen-4-ol (**2aa**): t_r=11.04 min, R_f=0.47 (hexane/ethyl acetate: 4/1); ν_{max} (film) 3420 (OH), 3040, 1630 (CH_2=C), 1110 and 1080 cm^{-1} (C-O); δ_H 0.86, 0.87, 0.92 (9 H, 3 t, J=5.6, 7.5 and 7.3 respectively, 3xCH_3), 1.30-1.65 (8 H, m, 3xCH_2CH_3 and OCH_2CH_2), 2.29 (2 H, s, CCH_2CO), 3.45 (2 H, t, J=6.65, OCH_2CH_2), 3.65 (1 H, s, OH), 3.95 (2 H, s, CCH_2O), 4.98 and 5.16 (2 H, 2 s, CH_2=C); δ_C 7.95 (2C), 13.7, 19.2, 30.75 (2C), 31.45, 44.6, 70.3, 73.25, 75.54, 118.05 and 142.4; m/z 185 (M$^+$-29, 5%), 128 (25), 111 (45), 87 (84), 72 (40), 69 (13), 57 (100), 56 (17), 55 (22), 54 (23), 45 (27), 43 (20) and 41 (31).

1-(3-Butoxy-2-methylene)propylcyclohexanol (**2ab**): t_r=12.62 min, R_f=0.49 (hexane/ethyl acetate: 4/1); ν_{max} (film) 3400 (OH), 3040, 1620 (CH_2=C) and 1070 cm^{-1} (C-O); δ_H 0.92 (3 H, t, *J*=7.3, CH_3), 1.20-1.70 [14 H, m, $(CH_2)_5$ and $(CH_2)_2CH_3$], 2.30 (2 H, d, *J*=0.8, CCH_2CO), 3.45 (2 H, t, *J*=6.7, OCH_2CH_2), 3.65 (1 H, s, OH), 3.93 (2 H, d, *J*=0.9, CCH_2O), 4.95-4.98 and 5.14-5.17 (2 H, 2 m, CH_2=C); δ_C 13.75, 19.2, 22.25 (2C), 25.8, 31.45, 37.85 (2C), 47.7, 69.9, 70.35, 75.6, 118.2 and 141.95; *m/z* 226 (M$^+$, <1%), 128 (29), 109 (17), 99 (100), 81 (57), 79 (12), 72 (35), 57 (28), 56 (12), 55 (41), 54 (19), 53 (11), 43 (19) and 41 (38).

4-Ethyl-2-(hydroxymethyl)-1-hexen-4-ol (**2ba**)[13a]: t_r=9.27 min, R_f=0.56 (hexane/ethyl acetate: 1/4), m.p. 65-67°C (hexane/ethyl acetate); ν_{max} (melted) 3240 (OH), 3060, 1630 (CH_2=C), 1040 and 1020 cm^{-1} (C-O); δ_H 0.87 (6 H, t, *J*=7.5, 2xCH_3), 1.51 (4 H, q, *J*=7.5, 2xCH_2CH_3), 2.30 (2 H, s, CCH_2CO), 3.6 (1 H, br s, OH), 4.08 (2 H, s, CH_2O), 4.60 (1 H, br s, OH), 4.90 and 5.13 (2 H, 2 d, *J*=0.9, CH_2=C); δ_C 7.95 (2C), 30.7 (2C), 44.0, 67.1, 74.5, 116.3 and 145.15; *m/z* 141 (M$^+$-17, <1%), 111 (22), 87 (100), 69 (25), 57 (78), 55 (19), 53 (11), 45 (53), 43 (25) and 41 (29).

1-(3-Hydroxy-2-methylene)propylcyclohexanol (**2bb**)[13a]: t_r=10.91 min, R_f=0.60 (hexane/ethyl acetate: 1/4); ν_{max} (film) 3280 (OH), 3040, 1630 (CH_2=C), 1060 and 1020 cm^{-1} (C-O); δ_H 1.25-1.65 [10 H, m, $(CH_2)_5$], 2.04 (1 H, s, OH), 2.30 (2 H, d, *J*=0.9, CCH_2CO), 3.20 (1 H, br s, OH), 4.06 (2 H, s, CH_2O), 4.88 and 5.13 (d, dt, *J*=1.9 and 1.9, 0.9 respectively, CH_2=C); δ_C 22.2 (2C), 25.55, 37.5 (2C), 46.75, 66.75, 70.7, 116.15 and 144.45; *m/z* 127 (M$^+$-43, 1%), 99 (100), 81 (57), 79 (12), 55 (23), 43 (16) and 41 (23).

4-Ethyl-2-(morpholinomethyl)-1-hexen-4-ol (**2ca**): t_r=12.38 min, R_f=0.39 (hexane/ethyl acetate: 3/2); ν_{max} (film) 3140 (OH), 3040, 1630 (CH_2=C), 1100 and 1000 cm^{-1} (C-O); δ_H 0.87 (6 H, t, *J*=7.5, 2xCH_3), 1.41, 1.43 (4 H, 2 q, *J*=7.5, 2xCH_2CH_3), 2.31 (2 H, s, CCH_2CO), 2.45-2.60 (4 H, m, 2xCH_2CH_2N), 2.92 (2 H, s, NCH_2C), 3.60-3.75 (4 H, m, 2xCH_2O), 5.00, 5.02 (2 H, 2 d, *J*=2.3, CH_2=C) and 6.71 (1 H, s, OH); δ_C 8.0 (2C), 30.7 (2C), 47.5, 52.95 (2C), 65.75, 66.25 (2C), 72.1, 120.5 and 140.8; *m/z* 227 (M$^+$, 1%), 198 (34), 141 (23), 140 (17), 111 (22), 110 (15), 100 (100), 96 (11), 88 (10), 87 (26), 86 (39), 85 (10), 82 (11), 57 (32), 56 (19), 55 (19), 45 (18), 43 (14), 42 (13) and 41 (18) (Found: M$^+$, 227.188270. $C_{13}H_{25}NO$ requires 227.188529).

1-(3-Morpholino-2-methylene)propylcyclohexanol (**2cb**): t_r=13.89 min, R_f=0.43 (hexane/ethyl acetate: 3/2); ν_{max} (film) 3140 (OH), 3040, 1630 (CH_2=C), 1100 and 1000 cm^{-1} (C-O); δ_H 1.20-1.80 [10 H, m, $(CH_2)_5$], 2.34 (2 H, s, CCH_2CO), 2.50-2.65 (4 H, m, 2xCH_2CH_2N), 2.91 (2 H, s, NCH_2C), 3.60-3.75 (4 H, m, 2xCH_2O), 4.99, 5.02 (2 H, 2 d, *J*=2.2, CH_2=C) and 7.28 (1 H, s, OH); δ_C 22.35 (2C), 26.0, 38.25 (2C), 50.0, 53.15 (2C), 66.00, 66.45 (2C), 69.85, 120.85 and 140.85; *m/z* 239 (M$^+$, 4%), 196 (18), 141 (28), 140 (22), 138 (16), 110 (14), 100 (100), 96 (13), 86 (37), 82 (10), 81 (22), 57 (10), 56 (19), 55 (33), 43 (14), 42 (19) and 41 (25).

*3-(*N*-Benzyl-*N*-methylamino)methyl-4-ethyl-1-hexen-4-ol* (**2da**): t_r=14.48 min, R_f=0.36 (hexane/ethyl acetate: 4/1); ν_{max} (film) 3140 (OH), 3040, 3020, 1630 (CH=C) and 1010 cm^{-1} (C-O); δ_H 0.89 (6 H, t, *J*=7.5, 2xCH_3CH_2), 1.40-1.55 (4 H, m, 2xCH_2CH_3), 2.11 (3 H, s, CH_3N), 2.30 (2 H, s, CCH_2CO), 2.97 (2 H, s, NCH_2CCH_2), 3.54 (2 H, s, CH_2Ph), 4.99, 5.04 (2 H, 2 s, CH_2=C), 6.84 (1 H, br s, OH), and 7.20-7.35 (5 H, m, Ph); δ_C 8.2 (2C), 31.05 (2C), 41.1, 46.85, 61.45, 65.1, 72.1, 119.9, 127.2, 128.25 (2C), 129.2 (2C), 137.15 and 142.35; *m/z* 261 (M$^+$, <1%), 232 (10), 174 (10), 134 (57), 121 (10), 120 (25), 91 (100), 65 (10), 57 (13) and 42 (10) (Found: M$^+$, 261.211182. $C_{17}H_{27}NO$ requires 261.209265).

*1-[3-(*N*-Benzyl-*N*-methylamino)methyl-2-methylene]propylcyclohexanol* (**2db**): t_r=15.85 min, R_f=0.38 (hexane/ ethyl acetate: 4/1); ν_{max} (film) 3130 (OH), 3040, 3020, 1630 (CH=C) and 1010 cm^{-1} (C-O); δ_H 1.20-1.80 [10 H, m, $(CH_2)_5$], 2.11 (3 H, s, CH_3), 2.32 (2 H, s, CCH_2CO), 2.96 (2 H, s, NCH_2C=CH_2), 3.54 (2 H, s, CH_2Ph), 5.00, 5.01 (2 H, 2 s, CH_2=C), 6.95 (1 H, br s, OH) and 7.20-7.35 (5 H, m, Ph); δ_C 22.5 (2C), 25.95, 38.25 (2C), 41.15, 49.95, 61.25, 65.2, 68.8, 120.15, 127.15, 128.25 (2C), 129.15 (2C), 137.05 and 141.7; *m/z* 273 (M^+, 1%), 175 (11), 174 (12), 134 (59), 120 (33), 91 (100), 55 (10) and 42 (10) (Found: M^+, 273.209183. $C_{18}H_{27}NO$ requires 273.209265).

2-(Mercaptomethyl)-5,5-dimethyl-1-hexen-4-ol (**2ec**): t_r=11.65 min, R_f=0.71 (hexane/ethyl acetate: 3/2); ν_{max} (film) 3420 (OH and SH), 3060, 1630 (CH_2=C) and 1000 cm^{-1} (C-O); δ_H 0.93 (9 H, s, 3xCH_3), 1.90-2.10 (2 H, m, CH_2CO), 2.30-2.50 (2 H, m , CH_2S), 3.38-3.44 (1 H, m, CHO), 5.02, 5.15 (2 H, 2 s, CH_2=C) and 7.1 (2 H, br s, OH and SH); δ_C 25.7 (3C), 34.75, 39.15, 76.3, 78.15, 114.05 and 146.65; *m/z* 174 (M^+, <1%), 135 (16), 109 (79), 95 (16), 87 (86), 83 (17), 82 (34), 71 (17), 89 (83), 87 (17), 57 (100), 56 (12), 55 (25), 45 (22), 43 (44) and 41 (98).

3-Ethyl-2-(trimethylsilylmethyl)-1-hexen-4-ol (**2ga**): t_r=9.87 min, R_f=0.50 (hexane/ethyl acetate: 9/1); ν_{max} (film) 3430, 1620 (CH_2=C), 1240 (CH_3Si) and 980 cm^{-1} (C-O); δ_H 0.01 (9 H, s, 3xCH_3Si), 0.85 (6 H, t, *J*=7.4, 2xCH_3C), 1.23 (1 H, br s, OH), 1.45 (4 H, q, *J*=7.4, 2xCH_2CH_3), 1.63 (2 H, s, CH_2Si), 2.08 (2 H, s, CCH_2CO), 4.62 and 4.69 (2 H, 2 s, CH_2=C); δ_C -1.45 (3C), 8.1 (2C), 29.25, 30.8 (2C), 46.15, 74.1, 111.4 and 144.55; *m/z* 199 (M^+-15, <1%), 185 (11), 159 (14), 87 (45), 75 (25), 73 (100), 69 (12), 57 (30), 45 (50), 43 (17) and 41 (10).

1-(3-Trimethylsilyl-2-methylene)propylcyclohexanol (**2gb**): t_r=11.50 min, R_f=0.54 (hexane/ethyl acetate: 9/1); ν_{max} (film) 3440 (OH), 3040, 1610 (CH_2=C), 1240 (CH_3Si) and 1000 cm^{-1} (C-O); δ_H 0.03 (9 H, s, 3xCH_3), 1.20-1.60 [10 H, m, $(CH_2)_5$] , 1.65 (2 H, s, CH_2Si), 1.80 (1 H, s, OH), 2.11 (2 H, s, CCH_2CO), 4.64 and 4.71(2 H, 2 s, CH_2=C); δ_C -1.5 (3C), 22.3 (2C), 25.8, 29.45, 37.9 (2C), 50.05, 70.7, 111.25 and 144.25; *m/z* 225 (M^+-1, <1%), 171 (25), 99 (39), 81 (41), 75 (25), 73 (100), 55 (16), 45 (16), 43 (15) and 41 (11).

N-*Benzyl*-N-*methyl-2-methylallylamine* (**2dc**): t_r=9.38 min, R_f=0.64 (hexane/ethyl acetate: 4/1); ν_{max} (film) 3040, 3020 and 1630 cm^{-1} (CH=C); δ_H 1.78 (3 H, s, CH_3C), 2.13 (3 H, s, CH_3N), 2.89 (2 H, s, CH_2C=CH_2), 3.44 (2 H, s, CH_2Ph), 4.85, 4.91 (2 H, 2 s, CH_2=C) and 7.15-7.40 (5 H, m, Ph); δ_C 20.7, 42.2, 61.7, 64.6, 112.65, 126.75, 128.1 (2C), 128.7 (2C), 139.55 and 143.75; *m/z* 176 (M^++1, 2%), 175 (M^+, 17), 134 (58), 92 (12), 91 (100), 65 (18) and 42 (18).

2,5-Bis(trimethylsilylmethyl)hexan-1,5-diene (**4g**): t_r=10.88 min, R_f=0.79 (hexane); ν_{max} (film) 3060, 1630 (CH_2=C) and 1240 cm^{-1} (CH_3Si); δ_H 0.02 (18 H, s, 6xCH_3), 1.53 (4 H, s, 2xCH_2Si), 2.08 (4 H, s, CH_2CH_2), 4.51 and 4.59 (4 H, 2 s, 2xCH_2=C); δ_C -1.25 (6C), 27.0 (2C), 36.75 (2C), 106.85 (2C) and 147.55 (2C); *m/z* 254 (M^+, 1%), 74 (11), 72 (100) and 45 (26) (Found: M^+, 254.188211. $C_{14}H_{30}Si_2$ requires 254.188608).

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20. In the case of using nitrogenated compounds (**1c** or **1d**) as starting material, the acidic organic layers were refused and the aqueous layer was basified with a saturated solution of Na_2CO_3, extracted with ether (3x20 ml), following the above protocol.