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DTBB-Catalysed Lithiation of 4-Functionalised 1-Chloro-2-Butenes

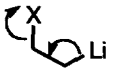
Fernando F. Huerta, Cecilia Gómez and Miguel Yus*

Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Alicante, Apdo. 99, 03080 Alicante, Spain

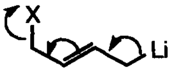
Abstract: The reaction of *N,N*-disubstituted (*E*)-4-amino-1-chloro-2-butenes **1** with an excess of lithium and a catalytic amount of DTBB in the presence of an electrophile [$E^+ = Bu^tCHO$, PhCHO, Me_2CO, $(CH_2)_5CO$, $(c\text{-}C_3H_5)_2CO$, Me_3SiCl] in THF at -78°C leads, after hydrolysis with water, to the expected mixture of 1,2- and 1,4- disubstituted compounds (**2** and **3**, respectively), which could be easily separated by flash chromatography. When the reaction was applied either to the corresponding (*Z*)-starting materials or to (*Z*)- or (*E*)-oxygen or sulfur containing chlorinated 2-butenes the yields are poorer than for nitrogenated precursors. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

One important problem to be overcome, concerning functionalised organolithium compounds,[1,2] is the instability of these species due to elimination process depending on the relative position of the lithium atom and the functionality. Thus β-substituted intermediates of type I are very unstable species, which decompose by β-elimination even at very low temperature giving olefins;[3] however, they have been stabilised at low temperature by locating a negative charge on the functionality at the β position (alkoxide, amide, ...).[4] Similarly δ-elimination from the corresponding vinilogous species of type **II** would generate a dienic system. Also in this case, the existence of a negative charge on the heteroatom can avoid a δ-elimination. Thus, to the best of our knowledge, the only example of an intermediate of the type II described in the literature was prepared by direct double deprotonation of crotyl alcohol using the Bu^nLi/Bu^tOK combination, the reaction with carbonyl compounds being also studied.[5] In this paper we report the preparation of neutral intermediates of type **II** starting from the corresponding chlorinated materials and using as a trick the combination of a powerful lithiation methodology (arene-catalysed lithiation at low temperature)[6,7] with performing the reaction under Barbier type reaction conditions[8] (lithiation in the presence of the electrophile).[9]



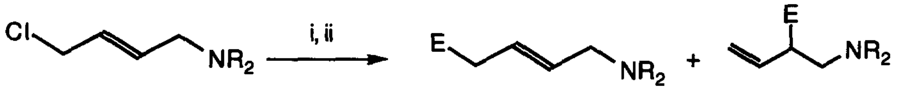
I



II

RESULTS AND DISCUSSION

The reaction of chloro butenamines **1** with an excess of lithium powder (1:7 molar ratio) and a catalytic amount of 4,4'-di-*terc*-butylbiphenyl (DTBB; 1:0.1 molar ratio, 5 mol %) in the presence of an electrophile [E+= Bu^tCHO, PhCHO, Me_2CO, $(CH_2)_5CO$, $(c\text{-}C_3H_5)_2CO$, Me_3SiCl, 1:1 molar ratio] in THF at -78°C led, after hydrolysis with water at the same temperature, to the corresponding mixture of 1,4 and 1,2 substituted products, **2** and **3**, respectively (Scheme 1 and Table 1). In general, the major component of the mixture is the 1,2 product, except for the silylated compounds **2/3af** and **2bf**, in which the 1,4-one is the most abundant or the only one (Table 1 entries 6 and 9). Although the **2/3** mixture was almost always obtained, pure products **2** and **3** could be obtained by flash chromatography. With dicyclopropyl ketone as electrophile, the starting material **1a**[10] produced *Z/E*-isomerisation: a *ca*. 1:1 mixture of both diastereoisomers **2ae** was isolated (Table 1, entry 5). For prochiral carbonyl compounds, the expected mixture of diastereoisomers was isolated for the corresponding 1,2-reaction products (Table 1, entries 1, 2, 7 and 10).



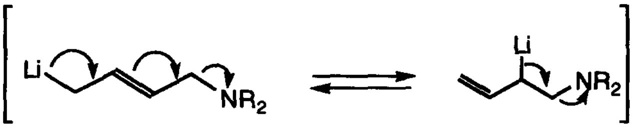
1a: R-R = $[(CH_2)_2]_2O$
1b: R = $CH_2{=}CHCH_2$
1c: R = $PhCH_2$

2aa-2cd

3aa-3cd

Scheme 1. *Reagents and conditions*: i, Li, DTBB cat. (5 mol %), E+= Bu^tCHO, PhCHO, Me_2CO, $(CH_2)_5CO$, $(c\text{-}C_3H_5)_2CO$, Me_3SiCl, THF, -78°C, 2.5 h; ii, H_2O, -78 to 20°C.

It is essential that the reaction shown in the Scheme 1 is performed under Barbier-type reaction conditions: when the corresponding two-step process was carried out no reaction products were isolated after the addition of different electrophiles, even at very low temperatures (< -100°C): either the 1,4- or the 1,2 intermediates (**III** or **IV**) suffer rapid elimination in the absence of the electrophile.



III

IV

Table 1. DTBB-Catalysed Lithiation of Chlorobutenamines **1** in the Presence of Electrophile E^+.

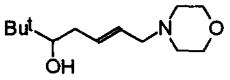
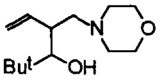
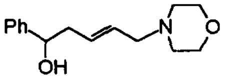
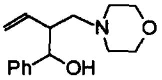
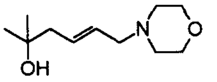
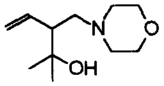
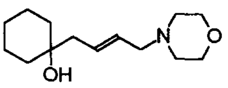
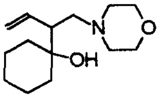
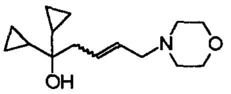
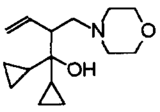
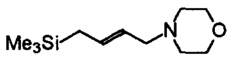
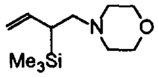
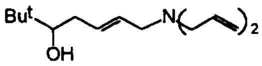
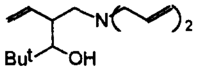
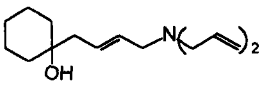
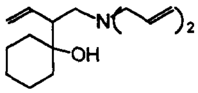
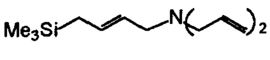
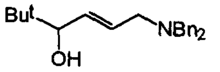
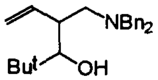
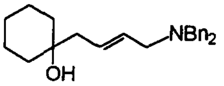
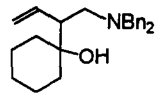
Entry	Starting Material	Electrophile E^+	Product[a]		
			Structure (no.)[b]	Yield (%)[c]	2/3[d]
1	**1a**	$\mathrm{Bu^tCHO}$	 **2aa** +  **3aa** (2.1/1)	70	2.2/1
2	**1a**	PhCHO	 **2ab** +  **3ab** (2.1/1)	30	1/2
3	**1a**	Me_2CO	 **2ac** +  **3ac**	69	1/6.1
4	**1a**	$(CH_2)_5CO$	 **2ad** +  **3ad**	40	1/2.7
5	**1a**	$(c\text{-}C_3H_5)_2CO$	 **2ae** (1.2/1) +  **3ae**	69	1/19
6	**1a**	Me_3SiCl	 **2af** +  **3af**	88	11.5/1
7	**1b**	$\mathrm{Bu^tCHO}$	 **2ba** +  **3ba**(2.6/1)	46	2/1
8	**1b**	$(CH_2)_5CO$	 **2bd** +  **3bd**	36	1/1.5

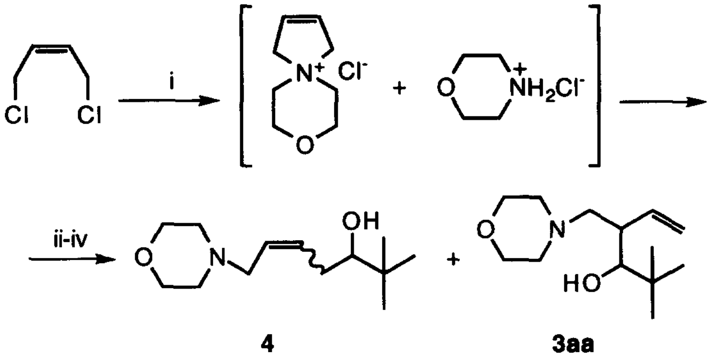
Table 1. (Cont.)

	Starting	Electrophile	Product[a]			
Entry	Material	E^+	Structure (no.)[b]		Yield (%)[c]	2/3[d]
9	**1b**	Me_3SiCl	 **2bf**	--	51	--
10	**1c**	Bu^tCHO	 **2ca**	+  **3ca**(1.9/1)	30	1.1/1
11	**1c**	$(CH_2)_5CO$	 **2cd**	+  **3cd**	42	1/1

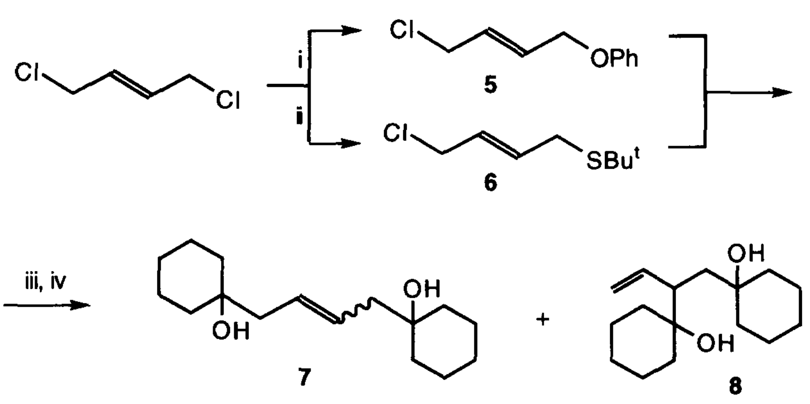
[a] All isolated products **2** and **3** were >94% pure (GLC and 300 MHz ^{1}H NMR). [b] In parenthesis diastereoisomers ratio (GLC). [c] Global isolated yield after flash chromatography (silica gel, hexane/ethyl acetate) based on the starting chloroamine **1**.[d] Determined by GLC.

Starting chlorobutenamines **1a-c** were easily prepared by reaction of commercially available (*E*)-1,4-dichlorobut-2-ene and the corresponding amine (1:2 molar ratio) in THF. When this process was applied to the corresponding (*Z*)-dichlorinated material and morpholine, instead of the expected chloroamine, the corresponding ammonium salts mixture was formed. The *in situ* treatment of this mixture with *n*-butyllithium (1:2 molar ratio) followed by DTBB catalysed lithiation in the presence of pivalaldehyde at -50°C (see above), yielded, after hydrolysis, a mixture of 1,4- and 1,2-substitution products (**3aa** and **4** respectively) in only *ca.* 20% yield (Scheme 2). We conclude that this methodology is not appropiate for *cis*-derivatives.

In the last part of this study we used oxygen and sulfur containing chlorinated materials **5**[11] and **6** prepared from the same dichlorinated compound used to prepared chloroamines **1**. When they were submitted to the same procedure described in the Scheme 1 with cyclohexanone as electrophile, even at lower temperatures the corresponding mixture of diols **7** and **8** was obtained in very poor yield (*ca.* 10%). So in this case a double lithiation took place, not only the chlorine atom but also the oxygenated and sulfur containing moiety acting as leaving groups in the lithiation step. Anyhow, the elimination process is the main process giving 1,3-butadiene as the major product (Scheme 3). On the other hand products **7**/**8** were the same as the corresponding ones resulting from the application of our methodology to 1,2 or 1,4-dichlorobutenes.[12]

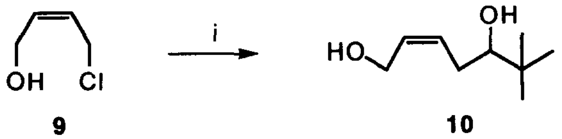


Scheme 2. *Reagents and conditions*: i, morpholine, THF, 24 h; ii, 2 Bu^nLi, -50°C, 30 min; iii, Li, DTBB cat.(5 mol %), Bu^tCHO, -78°C, 1 h; iv, H_2O, -78 to 20°C.



Scheme 3. *Reagents and conditions*: i, NaH, PhOH, DMF, 30 min; ii, Bu^nLi, Bu^tSH, 15 min; iii, Li, DTBB cat.(5 mol %), $(CH_2)_5CO$, THF, -90 to -110°C, 1-2 h; iv, H_2O, -90 or -110 to 20°C.

Finally, we studied the catalysed lithiation of the (*Z*)-oxygenated materials: chloroalcohol **9**[13] was submitted to the same procedure described in Scheme 1 using pivalaldehyde as electrophile giving the expected product **10** with 33% isolated yield (24% at -78°C) (Scheme 4).



Scheme 4. *Reagents and conditions*: i, Li, DTBB cat. (5 mol %), Bu^tCHO, THF, -40°C; iii, H_2O, -40 to 20°C.

As a conclusion, 4-heteroatom-substituted chloro-2-butenes can be lithiated catalytically in the presence of an electrophile (Barbier type conditions) avoiding so elimination process, which would destroy the corresponding intermediates. The reaction, as expected, gives a mixture of both 1,2- and 1,4-disubstituted products easily separated chromatographically, being the best results obtained for the *trans* nitrogenated derivatives.[14]

EXPERIMENTAL SECTION

General.- For general information, see references 9b and 12.

Preparation of Chloroamines **1**. *General procedure.*- To a solution of 1,4-dichloro-2-butene (0.21 ml, 2 mmol) in THF (5 ml) was added the corresponding amine (4 mmol). After 5 h stirring at room temperature the reaction mixture was hydrolysed with water (5 ml), neutralised with 4M NaOH and extracted with ethyl acetate (3x10 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/ethyl acetate) to afford the title compounds. Yields, physical, spectroscopic and analytical datas, as well as literature references for known compounds follow.

(E)-1-Chloro-4-morpholino-2-butene (**1a**):[10] (54% yield) R_f 0.3 (hexane/diethyl ether: 2/1); ν (film) 1454 (C=C) and 1117 cm^{-1} (C-O); δ_H 2.45 (4H, t, J = 4.6, CH_2NCH_2), 3.01 (2H, dd, J = 0.9, 4.3, CH_2N), 3.72 (4H, t, J = 4.6, CH_2OCH_2), 4.06 (2H, dd, J = 4.9, 0.9, CH_2Cl), 5.81 (2H, m, HC=CH); δ_C 44.4, 53.5 (3xCH_2N), 60.1 (CH_2Cl), 66.8 (CH_2OCH_2), 129.5, 131.1 (HC=CH); *m/z* 177 (M^++2, 4%), 175 (M^+, 11), 174 (10), 140 (67), 110 (89), 100 (30), 91 (15), 89 (47), 88 (32), 87 (100), 86 (67), 82 (29), 81 (38), 80 (17), 68 (23), 57 (25), 56 (56), 55 (70), 54 (48), 53 (77), 51 (17), 44 (12), 43 (17), 42 (78), 41 (70).

*(E)-4-Chloro-*N,N*-diallyl-2-butenamine* (**1b**): (51% yield) R_f 0.5 (hexane/diethyl ether: 3/1);ν (film) 3078, 1643 and 920 cm^{-1} (C=CH); δ_H 3.06-3.10 (6H, m, 3xCH_2N), 4.05, 4.07 (2H, 2m, H_2CCl), 5.12-5.21 (4H, m, 2xHC=CH_2), 5.71-5.90 (4H, m, 2xHC=CH_2 and HC=CH); δ_C 44.6 (CH_2Cl), 53.3, 56.3 (3xCH_2N), 117.6 (2x H_2C=CH), 128.7, 132.3 (HC=CH), 135.3 (2x H_2C=CH); *m/z* 187 (M^++2, 1.3%), 185 (M^+, 4), 160 (13), 158 (40), 150 (46), 110 (31), 97 (23), 96 (13), 94 (12), 91 (12), 89 (27), 82 (34), 81 (23), 80 (14), 79 (17), 70 (50), 69 (10), 68 (57), 67 (19), 56 (26), 55 (37), 54 (26), 53 (65), 51 (10), 43 (14), 42 (56), 41 (100), 40 (14).

*(E)-*N,N*-Dibenzyl-4-chloro-2-butenamine* (**1c**): (54% yield) R_f 0.7 (hexane/diethyl ether: 2/1); ν (film) 3084, 3061, 3026, 1601, 1494 and 1453 cm^{-1} (C=CH); δ_H 3.06 (2H, d, J = 5.2, CH_2Cl), 3.56 (4H, s, 2xCH_2Ph), 4.02 (2H, d, J = 5.5, CH_2N), 5.69-5.90 (2H, m, HC=CH), 7.18-7.37 (10H, m, 2xArH); δ_C 44.7 (CH_2Cl), 54.5 (CH_2N), 57.9 (2xCH_2Ph), 126.9, 128.1, 128.2, 128.7, 139.35 (2xArC and HC=CH); *m/z* 287 (M^++2, 0.7%), 285 (M^+, 2.1), 250 (11), 210 (10), 197 (24), 106 (24), 92 (18), 91 (100), 65 (22).

Catalytic Lithiation of Chloroamines **1** *and Reaction with Electrophiles. Isolation of Compounds* **2** *and* **3**. *General Procedure.*- To a cooled suspension of lithium (100 mg, 14 mmol) and DTBB (52 mg, 0.2 mmol) in THF (5 ml) at -78°C was slowly added (*ca.* 1 h) a solution of the corresponding electrophile (2 mmol) and the chloroamine **1** (2 mmol) in THF (3 ml). The resulting mixture was stirred for 1.5 h at the same temperature and then it was hydrolysed with water (5 ml) allowing the temperature to rise to 20°C. The resulting mixture was extracted with ethyl acetate (3x10 ml) being then acidified with 0.1N HCl and extracted with ethyl acetate. The aqueous layer was basified with 4N NaOH and extracted again with ethyl acetate (3x10 ml). The organic layer was dried over anhydrous Na_2SO_4 and evaporated (15 Torr) to give a residue, which was purified by flash chromatography (silica gel, hexane/ethyl acetate) to afford the title compounds **2** and **3**. Yields as well as diastereoisomers ratios are included in Table 1. Physical, spectroscopic and analytical data follow.

(E)-2,2-Dimethyl-7-morpholino-5-hepten-3-ol (**2aa**): R_f 0.5 (hexane/ethyl acetate: 1/2); ν (film) 3441 (OH) and

1652 cm^{-1} (C=C); δ_H 0.91 [9H, s, $(CH_3)_3C$], 2.00, 2.34 (2H, 2m, $HOCHCH_2$), 2.45 (4H, m, CH_2NCH_2), 2.98 (2H, d, J = 6.1, CH_2N), 3.24 (1H, dd, J = 10.7, 2.1, $CHOH$), 3.72 (4H, m, CH_2OCH_2), 5.54-5.74 (2H, m, HC=CH); δ_C 25.7 [$(CH_3)_3C$], 34.7 (CH_2CHOH), 35.0 [$(CH_3)_3C$], 43.45, 53.5 (3xCH_2N), 61.1 (CH_2OCH_2), 78.5 (CHOH), 128.8, 132.5 (HC=CH); *m/z* 228 (M$^+$+1, 1%), 227 (M$^+$, 4), 140 (20), 126 (15), 110 (38), 100 (42), 88 (28), 87 (100), 86 (46), 82 (16), 69 (22), 68 (11), 57 (52), 56 (29), 55 (43), 54 (18), 45 (21), 44 (16), 43 (39), 42 (32), 41 (70), 40 (11) (Found M$^{+\cdot}$ 227.1873. $C_{13}H_{25}NO_2$ requires M, 227.1885).

(E)-1-Phenyl-5-morpholino-3-pentenol (**2ab**):[15] R_f 0.3 (hexane/ethyl acetate: 1/1); ν (film) 3403 (OH), 3028, 1642, 1603, 1493, 1454 (C=CH) and 1117 cm^{-1} (C-O); δ_H 2.32 (4H, t, J = 4.6, CH_2NCH_2), 2.51 (2H, m, $HOCHCH_2$), 2.73 (1H, br s, OH), 2.90 (2H, m, CH_2N), 3.64 (4H, m, CH_2OCH_2), 4.71 (1H, t, J = 6.6, HOC*H*), 5.48-5.64 (2H, m, HC=CH), 7.24-7.34 (5H, m, ArH); δ_C 42.2 ($HOCHCH_2$), 53.3, 61.0 (3xCH_2N), 66.8 (CH_2OCH_2), 73.6 (HOCH), 125.9, 127.5, 128.3, 129.3, 130.4, 144.0 (ArC and HC=CH); *m/z* 248 (M$^+$+1, 1%), 247 (M$^+$, 7), 140 (40), 110 (55), 107 (37), 105 (46), 100 (34), 88 (44), 87 (100), 86 (45), 82 (12), 81 (10), 79 (57), 77 (46), 57 (28), 56 (32), 55 (36), 54 (31), 53 (14), 51 (16), 43 (10), 42 (37), 41 (34).

(E)-2-Methyl-6-morpholino-4-hexen-2-ol (**2ac**): R_f 0.5 (hexane/methyl alcohol: 1/1); ν (film) 3442 (OH) and 1652 cm^{-1} (C=C); δ_H 1.22 (6H, s, 2xCH_3), 2.22 (2H, d, J = 7.0, CH_2COH), 2.46 (4H, m, CH_2NCH_2), 3.00 (2H, d, J = 6.7, CH_2N), 3.73 (4H, m, CH_2OCH_2), 5.47-5.75 (2H, m, HC=CH); δ_C 29.1 (2xCH_3), 46.7 (CCH_2), 53.4, 61.2 (3xCH_2N), 66.8 (CH_2OCH_2), 70.4 (HOC), 126.9, 130.4 (HC=CH); *m/z* 200 (M$^+$+1, 1%), 199 (M$^+$, 10), 184 (12), 140 (33), 126 (22), 110 (55), 100 (27), 88 (22), 87 (100), 86 (59), 82 (15), 81 (12), 68 (11), 59 (96), 57 (38), 56 (35), 55 (39), 54 (33), 53 (12), 44 (14), 43 (87), 42 (45), 41 (58), 40 (11) (Found M$^+$, 199.1580. $C_{11}H_{21}NO_2$ requires M, 199.1572).

(E)-1-(4-Morpholino-2-butenyl)cyclohexanol (**2ad**): R_f 0.3 (hexane/ethyl acetate: 1/1); ν (film) 3450 (OH), 3030 and 1668 cm^{-1} (C=CH); δ_H 1.37-1.61 (10H, m, 5xring CH_2), 2.20 (2H, d, J = 7.0, $HOCCH_2$), 2.45 (4H, m, CH_2NCH_2), 2.99 (2H, d, J = 6.4, CH_2N), 3.72 (4H, t, J = 4.6, CH_2OCH_2), 5.57, 5.71 (2H, 2xdef dt, J = 15.2, 7.2, HC=CH); δ_C 22.1, 25.7, 37.4 (5xring CH_2), 37.5 ($HOCCH_2$), 53.4, 61.2 (3xCH_2N), 66.9 (CH_2OCH_2), 71.0 (HOC), 129.6, 129.8 (HC=CH); *m/z* 240 (M$^+$+1, 0.2%), 239 (M$^+$, 0.2), 101 (19), 100 (100), 87 (53), 86 (17), 81 (10), 70 (12), 57 (34), 56 (40), 55 (35), 54 (16), 53 (11), 43 (18), 42 (35), 41 (38) (Found M$^+$, 239.1881. $C_{14}H_{25}NO_2$ requires M, 239.1885).

(Z/E)-1,1-Dicyclopropyl-5-morpholino-3-butenol (**2ae**): this compound was identified by tandem GLC-mass spectrometry; *m/z* (first isomer) 251 (M$^+$, 1%, 140 (12), 126 (20), 111 (68), 110 (12), 100 (15), 91 (15), 87 (78), 86 (20), 79 (10), 69 (100), 67 (11), 57 (22), 56 (19), 55 (32), 54 (13), 53 (10), 44 (15), 43 (13), 42 (20), 41 (72), 40 (40). *m/z* (second isomer) 233 (M$^+$-18, 4.6%), 190 (19), 147 (13), 139 (13), 131 (14), 126 (100), 119 (16), 118 (10), 117 (24), 113 (21), 105 (43), 100 (32), 98 (21), 93 (15), 92 (11), 91 (73), 88 (13), 86 (13), 81 (12), 79 (39), 78 (13), 77 (34), 69 (10), 67 (41), 65 (23), 57 (19), 56 (39), 55 (44), 53 (16), 51 (12), 44 (23), 43 (16), 42 (35), 41 (86), 40 (63).

(E)-4-Trimethylsilyl-1-morpholino-2-butene (**2af**): R_f 0.5 (hexane/diethyl ether: 3/1); ν (film) 1660, 1003, 971 (C=CH), 1120 (C-O) and 854 cm^{-1} (Si-C); δ_H 0.20 [9H, s, $(CH_3)_3Si$], 1.68 (2H, d, J = 8.0, CH_2Si), 2.63 (4H, m, CH_2NCH_2), 3.14 (2H, d, J = 6.9, CH_2N), 3.92 (4H, m, CH_2OCH_2), 5.51 (1H, dt, J = 15.1, 6.9, HC=C*H*), 5.79 (1H, dt, J = 15.1, 8.O, *H*C=CH); δ_C -2.0 [$(CH_3)_3Si$], 22.7 (CH_2Si), 53.4, 61.6 (3xCH_2N), 67.0 (CH_2OCH_2), 124.2, 131.2 (CH=CH); *m/z* 213 (M$^+$, 22%), 144 (25), 140 (33), 126 (48), 113 (17), 112 (12), 110 (37), 101 (11), 100 (65), 88 (12), 87 (90), 86 (69), 75 (20), 74 (31), 73 (100), 59 (48), 58 (15), 57 (47), 56 (52), 55 (47), 54 (32), 53 (16), 45 (68), 44 (25), 43 (49), 42 (46), 41 (44) (Found M$^+$, 213.1562. $C_{11}H_{23}NOSi$ requires M, 213.1549).

(E)-7-(N,N-Diallylamino)-2,2-dimethyl-5-hepten-3-ol (**2ba**): R_f 0.5 (hexane/ethyl acetate: 1/2); ν (film) 3416 (OH), 3077 and 1643 cm^{-1} (C=CH); δ_H 0.92 [9H, s, $(CH_3)_3C$], 1.26 (1H, br s, OH), 2.00, 2.35 (2H, 2m, $HOCHC\mathit{H}_2$), 3.10 (6H, m, 3xCH_2N), 3.23 (1H, dd, J = 10.5, 2.0, $C\mathit{H}OH$), 5.17 (4H, m, 2xH_2C=CH), 5.62 (2H, m, HC=CH), 5.79-5.93 (2H, m, 2x$\mathit{H}C=CH_2$); δ_C 25.7 [$(\mathit{C}H_3)_3C$], 34.6 [$(CH_3)_3\mathit{C}$], 35.1 ($HOCH\mathit{C}H_2$), 55.2, 56.2 (3xCH_2N), 78.5 (CHOH), 117.9 (2x$H_2\mathit{C}$=CH), 129.7, 132.0 (HC=CH), 135.2 (2x$H_2C=\mathit{C}H$); *m/z* 237 (M^+, 1.7%), 150 (18), 136 (10), 110 (27), 96 (15), 87 (14), 70 (30), 69 (15), 68 (21), 57 (17), 56 (13), 55 (18), 45 (10), 43 (21), 42 (17), 41 (100) (Found M^+, 237.2088. $C_{15}H_{27}NO$ requires M, 237.2093).

(E)-1-[4-(N,N-Diallylamino)-2-butenyl]cyclohexanol (**2bd**): R_f 0.5 (hexane/ethyl acetate: 1/2); ν (film) 3395 (OH), 3077 and 1643 cm^{-1} (C=CH); δ_H 1.37-1.66 (12H, m, 5xring CH_2 and $HOCC\mathit{H}_2$), 2.21 (2H, d, J = 7.3, $HC=CHC\mathit{H}_2N$), 3.18 (4H, m, 2xCH_2N), 5.22 (4H, m, 2x$HC=C\mathit{H}_2$), 5.58 (1H, def dt, J = 15.4, 6.3, $\mathit{H}C=CHCH_2N$), 5.74 (1H, def dt, J = 15.4, 7.3, $HC=C\mathit{H}CH_2N$), 5.89 (2H, m, 2x$\mathit{H}C=CH_2$); δ_C 21.0, 22.1, 25.7 (5xring CH_2), 37.4 ($\mathit{C}H_2CH=CH$), 54.65, 55.5 (2xCH_2N), 71.1 (HOC), 119.2 (2x$HC=\mathit{C}H_2$), 128.7, 130.9 (HC=CH), 133.5 (2x$H\mathit{C}=CH_2$); *m/z* 250 (M^++1, 1%), 249 (M^+, 2), 150 (73), 136 (21), 123 (23), 122 (14), 110 (49), 108 (27), 99 (53), 97 (21), 96 (47), 94 (15), 82 (44), 81 (68), 80 (14), 79 (26), 70 (56), 69 (23), 68 (59), 67 (31), 57 (16), 56 (38), 55 (58), 54 (23), 53 (22), 43 (49), 42 (56), 41 (100) (Found M^+, 249.2075. $C_{16}H_{27}NO$ requires M, 249.2093).

(E)-N,N-Diallyl-4-trimethylsilyl-2-butenamine (**2bf**):[15] R_f 0.7 (hexane/diethyl ether: 3/1); ν (film) 3077 and 1643 cm^{-1} (C=CH); δ_H 0.02 [9H, s, $(CH_3)_3Si$], 1.49 (2H, dd, J = 7.9, 0.9, CH_2Si), 3.04 (2H, dd, J = 6.7, 0.6, CH_2N), 3.09 (4H, dt, J = 6.4, 1.2, 2xCH_2N), 5.11-5.21 (4H, m, 2x$HC=C\mathit{H}_2$), 5.32 (1H, dtt, J = 15.1, 7.9, 1.2, $HC=C\mathit{H}CH_2Si$), 5.57 (1H, dtt, J = 15.1, 6.7, 1.2, $\mathit{H}C=CHCH_2Si$), 5.80-5.94 (2H, m, 2x$\mathit{H}C=CH_2$); δ_C -1.95 [$(CH_3)Si$], 22.8 (CH_2Si), 55.6, 56.1 (3xCH_2N), 117.4 (2x$H_2\mathit{C}$=CH), 124.9, 130.6 (HC=CH), 135.8 (2x$H_2C=\mathit{C}H$); *m/z* 223 (M^+, 3%), 222 (M^+-1, 5), 154 (10), 150 (19), 136 (11), 110 (24), 108 (16), 97 (11), 96 (10), 82 (14), 74 (13), 73 (100), 68 (25), 59 (13), 45 (30), 43 (12), 42 (18), 41 (67).

(E)-7-(N,N-Dibenzylamino)-2,2-dimethyl-5-hepten-3-ol (**2ca**):[15] R_f 0.6 (hexane/ethyl acetate: 7/3); ν (film) 3454 (OH), 3061, 3026, 1691, 1653 and 1494 cm^{-1} (C=CH); δ_H 0.92 [9H, s, $(CH_3)_3C$], 1.97, 2.33 (2H, 2m, $HOCHC\mathit{H}_2$), 3.05 (2H, m, CH_2N), 3.20 (1H, dd, J = 10.4, 1.8, $HOC\mathit{H}$), 3.57 (4H, br s, 2x$NC\mathit{H}_2Ph$), 5.64 (2H, m, HC=CH), 7.22-7.38 (10H, 2xArH); δ_C 25.7 [$(\mathit{C}H_3)_3C$], 34.6 [$(CH_3)_3\mathit{C}$], 35.2 (HOCH), 55.4 (CH_2N), 57.8 (2x$\mathit{C}H_2Ph$), 80.4 (HOCH), 126.8, 128.2, 128.7, 130.7, 131.2, 139.7 (2xArC and HC=CH); *m/z* 338 (M^++1, 1.4%), 337 (M^+, 5.7), 280 (16), 250 (10), 246 (20), 236 (11), 211 (14), 210 (76), 197 (21), 196 (13), 181 (14), 160 (15), 123 (17), 120 (22), 118 (10), 106 (77), 92 (41), 91 (100), 87 (16), 69 (19), 65 (35), 57 (36), 55 (19), 45 (14), 43 (28), 42 (12), 41 (44).

(E)-1-(N,N-Dibenzyl-2-buten-4-amino)cyclohexanol (**2cd**): R_f 0.3 (hexane/ethyl acetate: 9/1); ν (film) 3402 (OH), 3061, 3027, 1595 and 1453 cm^{-1} (C=CH); δ_H 1.39-1.59 (10H, m, 5xring CH_2), 2.19 (2H, d, J = 6.1, $HOCC\mathit{H}_2$), 3.06 (2H, d, J = 4.9, CH_2N), 3.57 (4H, br s, 2x$C\mathit{H}_2Ph$), 5.60 (1H, def dd, J = 15.4, 4.9, $HC=C\mathit{H}CH_2N$), 5.69 (1H, def dd, J = 15.4, 6.1, $\mathit{H}C=CHCH_2N$), 7.22-7.38 (10H, m, 2xArH); δ_C 21.0, 22.1, 25.7 (5xring CH_2), 37.4 ($\mathit{C}H_2CH=CH$), 55.5 (CH_2N), 57.8 (2x$\mathit{C}H_2Ph$), 71.1 (HOC), 126.8, 128.2, 128.8, 129.4, 131.5, 139.6 (2xArC and HC=CH); *m/z* 350 (M^++1, 1.3%), 349 (M^+, 5), 236 (11), 226 (20), 106 (41), 99 (10), 92 (17), 91 (100), 81 (14), 65 (11), 55 (14), 41 (11) (Found M^+, 349.2396. $C_{24}H_{31}NO$ requires M, 349.2406).

2,2-Dimethyl-4-morpholinomethyl-5-hexen-3-ol (**3aa**):[16] Diastereomers mixture 2/1. R_f (major) 0.4 (hexane/diethyl ether: 1/2), R_f (minor) 0.3 (hexane/diethyl ether: 1/2); ν (film) 3471 (OH), 3064, 1650 (C=CH) and 1119 cm^{-1} (C-O); δ_H (major) 0.93 [9H, s, $(CH_3)_3C$], 1.25 (1H, br s, OH), 2.44-2.68 (7H, m, $CHCH_2N$ and CH_2NCH_2), 3.53 (1H, br s, $C\mathit{H}OH$), 3.70 (4H, m, CH_2OCH_2), 5.08 (2H, 2d, J = 16.8, 11.0, H_2C=CH), 6.17 (1H, m, $H_2C=C\mathit{H}$); δ_H (minor) 0.92 [9H, s, $(CH_3)_3C$], 1.57 (1H, s br, OH), 2.04-2.80 (7H, m, $CHCH_2N$ and CH_2NCH_2), 3.42 (1H, d, *J* = 9.0, C*H*OH), 3.72 (4H, m, CH_2OCH_2), 5.04 (2H, m, $H_2C=C\mathit{H}$), 5.64 (1H, dt, *J* = 17.1, 10.0, $H_2C=C\mathit{H}$); δ_C (major) 26.8 [$(\mathit{C}H_3)_3C$], 29.7 [$(CH_3)_3\mathit{C}$], 35.45 ($\mathit{C}HCH_2N$), 43.6, 55.0 ($3xCH_2N$), 66.0 (CH_2OCH_2), 80.8 (CHOH), 115.7 ($H_2\mathit{C}=CH$), 138.5 ($H_2C=\mathit{C}$); δ_C (minor) 26.5 [$(\mathit{C}H_3)_3C$], 26.8 [$(CH_3)_3\mathit{C}$], 36.4 ($\mathit{C}HCH_2N$), 41.3, 53.6 ($3xCH_2N$), 66.7 (CH_2OCH_2), 83.8 (CHOH), 115.4 ($H_2\mathit{C}=CH$), 139.95 ($H_2C=\mathit{C}$); *m/z* 170 (M^+-Bu^t, 1%), 100 (100), 57 (11), 56 (18), 42 (15), 41 (20).

1-Phenyl-2-morpholinomethyl-3-butenol (**3ab**): Diastereomers mixture 1/1. Identified by tandem GLC-mass spectrometry identification: *m/z* (t_R= 13.17 min) 247 (M^+, 1%), 101 (31), 100 (100), 87 (49), 86 (20), 79 (24), 77 (35), 72 (10), 70 (22), 57 (34), 56 (55), 55 (33), 54 (25), 53 (13), 51 (17), 44 (14), 43 (16), 42 (47), 41 (38). *m/z* (t_R= 13.24 min) 247 (M^+, 0.6%), 101 (24), 100 (100), 87 (54), 86 (20), 79 (18), 77 (28), 70 (18), 57 (36), 56 (53), 55 (26), 54 (20), 53 (10), 51 (14), 44 (11), 43 (12), 42 (41), 41 (40).

2-Methyl-3-morpholinomethyl-4-penten-2-ol (**3ac**): R_f 0.4 (diethyl ether); ν (film) 3265 (OH), 3077, 1639 (C=CH) and 1121 cm^{-1} (CO); δ_H 1.14, 1.16 (6H, 2s, $2xCH_3$), 2.37 (1H, dd, *J* = 13.0, 3.7, C*H*HN), 2.40 (2H, m, CH_2N), 2.52 (1H, ddd, *J* = 12.0, 9.0, 3.7, CHC), 2.73 (2H, m, CH_2N), 2.78 (1H, dd, *J* = 13.0, 12.0, CH*H*N), 3.71 (4H, m, $2xCH_2O$), 5.06 (1H, m, *H*HC=CH), 5.10 (1H, ddd, *J* = 6.3, 1.8, 0.9, H*H*C=CH), 5.47-5.59 (1H, m, $H_2C=C\mathit{H}$); δ_C 24.4, 29.7 ($2xCH_3$), 49.2 (*C*HC), 53.9, 61.0, ($3xCH_2N$), 66.9 (CH_2O), 73.0 (COH), 117.4 ($\mathit{C}H_2=CH$), 136.8 ($CH_2=\mathit{C}H$); *m/z* 184 (M^+-15, 2%), 101 (25), 100 (100), 87 (62), 86 (33), 72 (10), 70 (23), 59 (30), 57 (50), 56 (55), 55 (32), 54 (27), 53 (14), 44 (15), 43 (52), 42 (52), 41 (50) (Found M^+, 184.1342. $C_{10}H_{18}NO_2$ requires M, 184.1338).

1-(1-Morpholinomethyl-2-propenyl)cyclohexanol (**3ad**):[15] R_f 0.4 (hexane/diethyl ether: 1/2); ν (film) 3255 (OH), 3079, 1610 (C=CH) and 1119 cm^{-1} (C-O); δ_H 1.08-1.78 (10H, m, 5xring CH_2), 2.31 (1H, dd, *J* = 12.8, 3.6, C*H*HN), 2.45 (3H, m, ring CH_2N and $C\mathit{H}CH_2N$), 2.70 (2H, m, ring CH_2N), 2.82 (1H, dd, *J* = 12.8, 11.9, CH*H*N), 3.71 (4H, m, CH_2OCH_2), 5.04 (1H, m, *H*HC=CH), 5.09 (1H, m, $H_2C=C\mathit{H}$), 5.58 (1H, ddd, *J* = 16.6, 10.8, 9.0, H*H*C=CH); δ_C 21.3, 21.4, 26.1, 32.0, 37.5 (5xring CH_2), 49.6 ($\mathit{C}HCH_2$), 53.9, 60.4 ($3xCH_2N$), 66.8 (CH_2OCH_2), 73.4 (CHOH), 117.4 ($H_2\mathit{C}=C$), 137.0 ($H_2C=\mathit{C}$); *m/z* 240 ($M^{+}+1$, 2%), 239 (M^+, 11), 141 (10), 140 (47), 126 (34), 113 (11), 110 (70), 100 (42), 99 (50), 96 (12), 88 (24), 87 (100), 86 (78), 82 (21), 81 (71), 79 (17), 69 (17), 68 (16), 67 (16), 58 (10), 57 (59), 56 (44), 55 (69), 54 (39), 53 (22), 44 (14), 43 (57), 42 (63), 41 (75).

1,1-Dicyclopropyl-2-morpholinomethyl-3-butenol (**3ae**): R_f 0.4 (hexane/diethyl ether: 2/1); ν (film) 3199 (OH), 3084, 1642 (C=CH) and 1120 cm^{-1} (C-O); δ_H 0.17-0.55 (8H, m, 4xring CH_2), 0.78-0.95 (2H, m, 2xring CH), 2.31 (1H, dd, *J* = 12.5, 3.4, C*H*HN), 2.32-2.40 (2H, m, NCH_2), 2.67 (1H, ddd, *J* = 12.5, 9.1, 3.4, $C\mathit{H}CH_2N$), 2.62-2.71 (2H, m, CH_2N), 3.13 (1H, t, *J* = 12.5, CH*H*N), 3.68 (4H, m, CH_2OCH_2), 5.11 (1H, dd, *J* = 10.4, 1.8, *H*HC=CH), 5.14 (1H, m, H*H*C=CH), 5.82 (1H, ddd, *J* = 17.2, 10.4, 8.7, $H_2C=C\mathit{H}$); δ_C -1.4, -1.2 , -0.3, 0.9 (4xring CH_2), 14.9, 20.2 (2xring CH), 48.9 (HOC*C*H), 53.7, 60.6 ($3xCH_2N$), 66.8 ($2xCH_2O$), 72.1 (COH), 117.0 ($\mathit{C}H_2=CH$), 136.7 ($CH_2=\mathit{C}H$); *m/z* 210 (M^+-41, 5%), 141 (17), 111 (10), 101 (22), 100 (100), 87 (78), 86 (38), 70 (16), 69 (42), 57 (52), 56 (44), 55 (34), 54 (19), 53 (14), 44 (12), 43 (19), 42 (41), 41 (64) (Found M^+, 251.1897. $C_{15}H_{25}NO_2$ requires M, 251.1885).

4-Morpholino-2-trimethylsilyl-1-butene (**3af**): *m/z* 213 (M^+, 14%), 144 (17), 140 (21), 126 (24), 113 (10), 110 (22), 100 (43), 87 (92), 86 (53), 75 (12), 74 (19), 73 (100), 59 (32), 58 (10), 57 (17), 56 (37), 55 (32), 53 (10), 55 (32), 53 (10), 45 (61), 44 (11), 43 (29), 42 (28), 41 (25).

*4-(*N,N*-Diallylaminomethyl)-2,2-dimethyl-5-hexen-3-ol* (**3ba**):[16] Diastereomers mixture. R_f 0.5 (hexane/ethyl acetate: 1/1); ν (film) 3371 (OH), 3074 and 1635 cm^{-1} (C=CH); δ_H (mixture) 0.92 [18H, s, $(CH_3)_3C$)], 2.22 (1H, m, C*H*OH), 2.55 (2H, m, CH_2N), 2.90 (1H, m, C*H*OH), 3.05 (6H, m, $3xCH_2N$), 3.15 (4H, m, $2xCH_2N$), 3.40 (1H, d, *J* = 8.9, C*H*CHOH), 3.50 (1H, br s, C*H*CHOH), 4.95-5.22 (12H, m, $6x\mathit{H}_2C=CH$), 5.61 (1H, ddd, *J* = 19.2, 9.5, 9.0, H$_2$C=C*H*), 5.85 (4H, m, 4xNCH$_2$C*H*), 6.15 (1H, ddd, *J* = 19.2, 10.0, 9.7, H$_2$C=C*H*); δ_C (mixture) 26.6, 26.9 [2x(*C*H$_3$)$_3$C], 35.3, 35.4 [2x(CH$_3$)$_3$*C*], 42.2, 42.25 (2x*C*HCHOH), 56.4 (2xCH$_2$NCH$_2$), 57.75, 57.8 (2xCH$_2$N), 77.2 (2xHOCH), 115.1, 115.5, 118.0, 118.1, 118.9, 133.9, 140.3 (6xH$_2$C=CH); *m/z* (First diastereomer) 180 (M$^+$-Bu^t, 1.7%), 111 (12), 110 (100), 68 (14), 42 (26), 41 (75). *m/z* (Second diastereomer) 180 (M$^+$-Bu^t, 12%), 110 (100), 68 (12), 42 (19), 41 (73).

*1-[1-(*N,N*-Diallylaminomethyl)-2-propenyl]cyclohexanol* (**3bd**): *R*$_f$ 0.7 (hexane/ethyl acetate: 7/3); ν (film) 3250 (OH), 3076 and 1643 cm^{-1} (C=CH); δ_H 1.20-1.77 (10H, m, 5xring CH$_2$), 2.26 (1H, dd, *J* = 13.1, 3.7, CHC*H*HN), 2.45 (1H, m, C*H*CH$_2$N), 2.85 (2H, dd, *J* = 13.7, 8.2, 2xNC*H*H), 2.97 (1H, t, *J* = 13.1, CHCH*H*N), 3.40 (2H, dd, *J* = 13.7, 5.2, 2xNCH*H*), 5.04, 5.18 (6H, 2m, 3xHC=C*H*$_2$), 5.55, 5.85 (3H, 2m, 3x*H*C=CH$_2$); δ_C 21.4, 26.2, 31.8, 37.7 (5xring CH$_2$), 50.5 (*C*HCH$_2$N), 54.9, 56.8 (3xNCH$_2$), 73.4 (HOC), 117.2, 118.7 (3xHC=*C*H$_2$), 134.3, 137.3 (3xH*C*=CH$_2$); *m/z* 250 (M$^+$+1, 0.5%), 111 (30), 110 (100), 97 (12), 82 (26), 81 (31), 79 (21), 70 (33), 69 (14), 68 (40), 67 (14), 56 (14), 55 (36), 54 (15), 53 (18), 43 (27), 42 (43), 41 (70) (Found M$^+$, 249.2085. C$_{16}$H$_{27}$NO requires M, 249.2093).

*4-(*N,N*-Dibenzylaminomethyl)-2,2-dimethyl-5-hexen-3-ol* (**3ca**):[16] Diastereomers mixture. *R*$_f$ 0.6 (hexane/ethyl acetate: 8:2); ν (film) 3224 (OH), 3064, 3028, 1640, 1602 and 1463 cm^{-1} (C=CH); δ_H (Major diastereomer) 0.85 [9H, s, (CH$_3$)$_3$C], 1.65 (1H, br s, OH), 2.36 (1H, dd, *J* = 12.2, 4.6, CHC*H*HN), 2.50 (1H, m, C*H*CHHN), 2.61 (1H, dd, *J* = 12.2, 8.6, CHCH*H*N), 3.46 (1H, m, C*H*OH), 3.55 (4H, s, 2xC*H*$_2$Ph), 5.00 (2H, m, HC=C*H*$_2$), 5.95 (1H, m, *H*C=CH$_2$), 7.10-7.36 (10H, m, 2xArH); δ_H (Minor diastereomer) 0.90 [9H, s, (CH$_3$)$_3$C], 2.30 (1H, dd, *J* = 12.7, 2.9, CHC*H*HN), 2.63 (1H, m, C*H*CHHN), 2.90 (1H, dd, *J* = 12.7, 1.4, CHCH*H*N), 3.27 (1H, d, *J* = 8.9, C*H*OH), 3.30 (2H, d, *J* = 13.3, 2xNC*H*HPh), 3.93 (2H, d, *J* = 13.3, 2xNCH*H*Ph), 4.96 (2H, m, *H*$_2$C=CH), 5.54 (1H, m, H$_2$C=C*H*), 7.26-7.34 (10H, m, 2xArH); *m/z* (major) 280 (M$^+$-Bu^t, 1%), 211 (41), 210 (100), 181 (22), 106 (12), 92 (32), 91 (84), 65 (31), 57 (19), 42 (22), 41 (28); *m/z* (minor) 281 (M$^+$-58, 1%), 280 (M$^+$-Bu^t, 6.4), 211 (41), 210 (91), 181 (10), 106 (10), 92 (17), 91 (100), 65 (14), 57 (13), 42 (10), 41 (14).

*1-[1-(*N,N*-Dibenzylaminomethyl)-2-propenyl)cyclohexanol* (**3cd**):[15] *R*$_f$ 0.6 (hexane/ethyl acetate: 8/2); ν (film) 3250 (OH), 3061, 3027, 1495 and 1452 cm^{-1} (C=CH); δ_H 1.19-1.67 (10H, m, 5xring CH$_2$), 2.23 (1H, dd, *J* = 13.1, 3.4, C*H*CH$_2$N), 2.56 (1H, m, C*H*HN), 2.98 (1H, m, CH*H*N), 3.11 (2H, d, *J* = 13.0, CH$_2$Ph), 3.56 (1H, br s, OH), 4.02 (2H, d, *J* = 13.0, C*H*$_2$Ph), 5.05 (2H, m, HC=C*H*$_2$), 5.45 (1H, m, *H*C=CH$_2$), 7.24-7.33 (10H, m, 2xArH); δ_C 21.15, 26.0, 30.7 (5xring CH$_2$), 37.5 (*C*HCH$_2$N), 50.7 (CH$_2$N), 58.9 (2xCH$_2$Ph), 73.6 (HOC), 117.2 (H$_2$*C*=CH), 127.4, 128.4, 129.7, 137.4, 137.6 (H$_2$C=*C*H and ArC); *m/z* 258 (M$^+$-Bn, 0.5%), 211 (20), 210 (100), 106 (18), 92 (18), 91 (100), 65 (13), 55 (10), 42 (10).

Reaction of (Z)-1,4-Dichloro-2-butene with Morpholine and Further Lithiation in the Presence of Pivalaldehyde.- A solution of the starting dichlorobutene (0.21 ml, 2 mmol) and morpholine in dry THF (5 ml) was stirred for 24 h at room temperature. The white precipitate formed was filtered and washed with THF (3x5 ml). The resulted solid was suspended in THF and cooled to -50°C. To the resulting suspension was added Bu^{n}Li (4 mmol) and it was stirred for 30 min at the same temperature. Then the mixture was cooled at -90°C and to the suspension was slowly added pivalaldehyde (2 mmol) and a suspension of lithium (120 mg, 17 mmol), and DTBB (52 mg) in THF (3-4 ml). The mixture was stirred for 1h at the same temperature being then hydrolysed with water and worked up as for compound **1**, giving the mixture of compound **3aa** and **4** in *ca.* 20% yield in 3/1 **3aa/4** molar ratio (GLC). Compound **3aa** was characterised by comparation to the same material obtained before from starting material **1a**. Compound **4** was tentatively characterised by tandem GC-mass spectrometry [*m/z* 227 (M$^+$, 6%), 171 (15), 170 (100), 141 (13), 126 (14), 123 (34), 116 (21), 112 (11), 100 (12), 97 (39), 88 (15), 86 (12), 85 (13), 83 (17), 81 (13), 70 (26), 69 (12), 57 (40), 56 (23), 55 (40), 54 (11), 44 (11), 43 (39), 42 (33), 41 (48)].

*Preparation of (*E*)-1-Chloro-4-phenoxy-2-butene* **5**[11].- Phenol (1.77 ml, 20 mmol) was added to a suspension of sodium hydride (0.94 g, 22 mmol) in DMF (6 ml). The mixture was stirred for 30 min. Then (*E*)-1,4-dichloro-2-butene (2.36 ml) was added and the mixture was stirred for 5 additional hours. The resulting mixture was hydrolysed with water (10 ml) and extracted with ethyl acetate (3x20 ml). The organic layer was dried over anhydrous Na_2SO_4 and evaporated (15 Torr) giving a residue, which was purified by flash chromatography (silica gel, hexane/eathyl acetate) to give the title compound (51% yield): R_f 0.6 (hexane/ethyl acetate: 8/2); ν (film) 3039, 1599, 1587 and 1495 cm^{-1} (C=CH); δ_H 4.08, 4.53 (4H, 2m, $2xCH_2$), 6.00 (2H, m, HC=CH), 6.94, 7.26 (5H, 2m, ArH); δ_C 44.1, 67.1 ($2xCH_2$), 114.6, 121.0, 128.8, 129.4, 158.3 (ArC and HC=CH); *m/z* 184 (M^++2, 12.3%), 182 (M^+,38.5), 147 (27), 95 (34), 94 (100), 91 (22), 89 (36), 88 (11), 77 (44), 66 (41), 65 (44), 64 (11), 63 (26), 55 (10), 54 (34), 53 (67), 52 (67), 51 (44), 50 (24), 49 (10), 43 (21), 41 (16), 40 (23).

*Preparation of (*E*)-4-*tert*-Butylmercapto-1-chloro-2-butene* (**6**).- To a solution of 1,1-dimethylethanethiol (0.65 ml, 5 mmol) in THF (5 ml) was added Bu^nLi (5.4 mmol). After 15 min stirring at room temperature the resulting solution was slowly added (20 min) to a solution of (*E*)-1,4-dichloro-2-butene (0.54 ml, 5 mmol) in THF (5 ml). The resulting mixture was stirred for 1.5h, hydrolysed with water (10 ml) and extracted with ethyl acetate (3x10 ml). The organic layer was dried over anhydrous Na_2SO_4 and evaporate (15 Torr) giving the title compound essentially pure (>95% from GLC) which was used for the lithiation reaction without further purification: R_f 0.6 (hexane/ethyl acetate: 9/1); ν (film) 1615 cm^{-1} (C=C); δ_H 1.33 [9H, s, $(CH_3)_3C$], 3.23, 4.05 (4H, 2m, $2xCH_2$), 5.81 (2H, m, HC=CH); δ_C 30.9 [$(CH_3)_3C$], 42.75 [$(CH_3)_3C$], 43.5, 44.5 ($2xCH_2$), 127.8, 129.2 (HC=CH); *m/z* 180 (M^++2, 10%), 178 (M^+, 28), 143 (10), 90 (25), 89 (30), 88 (55), 87 (44), 86 (21), 85 (24), 75 (17), 59 (24), 58 (33), 57 (100), 55 (23), 54 (10), 53 (39), 51 (12), 49 (12), 47 (10), 45 (37).

DTBB-Catalysed Lithiation of Compound **5** *and* **6**.- Compound **5** and **6** were submited to the same procedure as it was above described for the starting material **1** giving a mixture of dioles **7** and **8** in *ca.* 10% yield (2/1, **7**/**8** mixture from GLC), which were identified by comparation of their spectroscopy data with authentic samples.[17]

*Preparation of (*Z*)-2-Chloro-2-butenol* (**9**).- Compound **9** was obtained according to the literature procedure:[13] ν (film) 3371 (OH) and 1018 cm^{-1} (C-O); δ_H 2.88 (1H, s, OH), 4.13 (2H, d, J = 7.0, CH_2Cl), 4.26 (2H, d, J = 4.9, CH_2OH), 5.70-5.84 (2H, m, HC=CH); δ_C 38.9 (CH_2Cl), 57.8 (CH_2OH), 127.3, 133.0 (HC=CH); *m/z* 90 (M^+-16, 3%), 88 (M^+-18, 9), 71 (20), 70 (44), 69 (16), 57 (87), 53 (28), 51 (20), 50 (16), 49 (14), 44 (47), 43 (81), 42 (100), 41 (78).

DTBB-Catalysed Lithiation of Chloroalcohol **9**. *Isolation of (*Z*)-6,6-Dimethyl-2-hepten-1,5-diol* (**10**)[15].- When the procedure described above for compounds **2** + **3** was applied to the starting material **9** at -40°C compound **10** was isolated. Yield is included in the text: ν (film) 3346 (OH), 1645 cm^{-1} (C=C); δ_H 0.93 [9H, s, $(CH_3)_3$]C, 1.25 (1H, s, OH), 2.20-2.33 (3H, m, $CHCH_2$ and OH), 3.23 (1H, dd, J = 9.8, 2.7, CHOH), 4.03 (1H, dd, J = 12.2, 6.4, C*H*H), 4.25 (1H, dd, J = 12.2, 7.45, CH*H*), 5.68, 5.89 (2H, 2m, HC=CH); δ_C 25.7 [$(CH_3)_3C$], 29.7 ($CHCH_2$), 34.9 [$(CH_3)_3C$], 57.5 (CH_2OH), 78.3 (CHOH), 131.0, 131.5 (HC=CH); *m/z* 85 (M^+-73, 15%), 83 (24), 71 (13), 70 (10), 69 (20), 57 (100), 55 (49), 54 (66), 53 (21), 45 (14), 44 (17), 43 (57), 42 (11), 41 (95).

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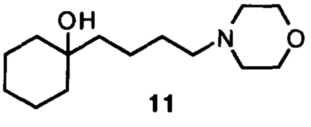

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15. For this product was not possible to obtain HRMS spectra due its decomposition.
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