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Naphthalene-Catalysed Lithiation of Carbamoyl and Thiocarbamoyl Chlorides under Barbier-Type Reaction Conditions

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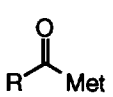
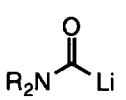
Abstract: The reaction of different carbamoyl or thiocarbamoyl chlorides **1** with carbonyl compounds or imines **2** in the presence of an excess of lithium powder and a catalytic amount of naphthalene (3 mol %) in THF at -78°C leads, after hydrolysis with water, to the expected α-hydroxy or α-amino amides **3**, respectively. In the case of allylic or benzylic derivatives **1a,c**, when longer reaction times are used, the corresponding products **4** resulting from a deallylation or debenzylation are obtained. The use of DMF or phenyl isocyanate as electrophiles affords substituted oxamides **5**. Finally, when previously to the hydrolysis an excess of an alkyl chloride is added to the reaction mixture, 1,2-diols **6** are formed, resulting from a final double addition of the *in situ* generated alkyllithium to the α-hydroxy amide initially formed. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

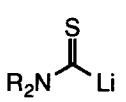
Acyl metal intermediates[1] derived from electropositive metals[2] (**I** with Met = Li, MgX, ..), which show umpolung reactivity,[3] are important species in synthetic organic chemistry because they are able to transfer the acyl moiety to the electrophile in only one step by reaction with electrophilic reagents. In the case of the corresponding carbamoyllithium intermediates **II**,[4] they are accesible at low temperatures through three methodologies: (a) carbonylation of lithium amides;[5] (b) direct deprotonation of formamides;[6] (c) mercury-lithium,[7] tellurium-lithium[8] or tin-lithium[9] transmetallation. Thiocarbamoyllithium analogue of type **III** have been prepared following the route (b) by deprotonation of the corresponding thioformamides.[10] To the best of our knowledge, the samarium derivative **IV** is the only carbamoyl intermediate postulated in the literature[11] prepared starting from a carbonyl chloride. We describe in this paper the preparation of intermediates of types **II** and **III** starting from the corresponding chlorides by a naphthalene-catalysed lithiation[12] at low temperature and the *in situ* reaction of these organolithium species with electrophilic reagents.[13, 14]



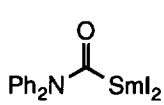
I



II



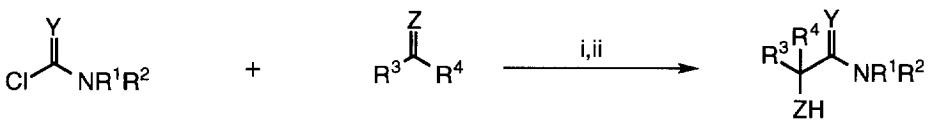
III



IV

RESULTS AND DISCUSSION

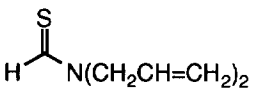
The reaction of carbamoyl chlorides **1a** or **1b** with different carbonyl compounds (1:1.2 molar ratio) and an excess of lithium powder (1:5.8 molar ratio) in the presence of a catalytic amount of naphthalene (1:0.06 molar ratio; 3 mol %) in THF at temperatures ranging between -78 and 0°C (Table 1, footnote b) led, after hydrolysis with water, to the corresponding α-hydroxy amides **3aa,ab** and **3ba-bj**, respectively (Scheme 1 and Table 1, entries 1, 2 and 4-13). The use of benzylideneaniline as electrophile under the same reaction conditions afforded the expected α-amino amides **3ac** and **3bk** (Table 1, entries 3 and 14). We considered then the same reaction starting from a chiral carbonyl chloride, such as compound **1c**, in order to study the possible asymmetric induction in the final products **3**, when a prochiral carbonyl compound derivative was used: with aldehydes or the above mentioned imine the corresponding diastereoisomer ratio was poor (1:1-3.1:1; Table 1, entries 15-17 and footnotes h-k) for the obtained products **3ca-cc**.[15] We finally extended the reaction with carbamoyl chlorides to thiocarbamoyl derivatives such as compound **1d**, which using the same methodology described above allowed the isolation of α-hydroxy thioamides **3da-3dd** (Scheme 1 and Table 1, entries 18-21). Only with thiocarbonyl chloride **1e** the reaction failed: after lithiation in the presence of different electrophiles [Bu^tCHO, PhCHO, Et_2CO, $(CH_2)_5CO$] only the corresponding "reduced" product **3e** was isolated with poor yield after hydrolysis; in this case, the corresponding intermediate of the type **III** seems to be very unstable under the reaction conditions tried (-78°C) and abstracts a proton from the reaction medium[16] before reacting with the electrophile present. However, when the reaction was carried out in the absence of the electrophile and was hydrolysed after 1 h, the expected product **3e** was obtained with 74% isolated yield.



1a: Y = O, $R^1 = R^2 = CH_2{=}CHCH_2$
1b: Y = O, $R^1 = R^2 = Pr^i$
1c: Y = O, R^1 = (*R*)-PhCH(Me), R^2 = Me
1d: Y = S, $R^1 = R^2$ = Me
1e: Y = S, $R^1 = R^2 = CH_2{=}CHCH_2$

2

3aa-3dd



3e (74%)

Scheme 1. *Reagents and conditions*: i, Li, $C_{10}H_8$ cat. (3 mol %), THF, -78 to 20°C, 45 min to 2 h; ii, H_2O.

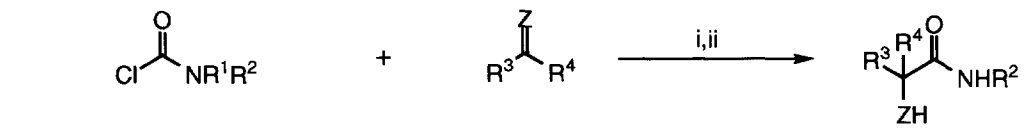
One important remark about the reaction described in Scheme 1 is that the process has to be carried out at low temperature and in the presence of the electrophile (Barbier-type reaction conditions)[17] in order to get the best results. For instance, when the catalytic lithiation of **1b** was carried out in the absence of the electrophile for 30 min at -78°C [the starting material was consumed (GLC)] followed by treatment with benzaldehyde, the expected compound **3be** was isolated, after hydrolysis, in only 42% yield (compare to Table 1, entry 8). In addition, the same process using 4,4'-di-*tert*-butylbiphenyl (DTBB) as electron carrier[18] at 0°C led to compound **3be** in only 30% isolated yield. In both cases a partial decomposition of the intermediate of the type **II** took place before reacting with the carbonyl compound present in the reaction medium. When the starting materials

Table 1. Preparation of Compounds **3**

Entry	Starting material	Electrophile **2**	Reaction conditions[b]	Product **3**[a] No.	R1	R2	R3	R4	Y	Z	Yield(%)[c]	Mp (°C)[d] or R_f[e]
1	**1a**	Bu^nCHO	A	**3aa**	CH_2=$CHCH_2$	CH_2=$CHCH_2$	Bu^n	H	O	O	40	0.71[f]
2	**1a**	Bu^tCHO	A	**3ab**	CH_2=$CHCH_2$	CH_2=$CHCH_2$	Bu^t	H	O	O	82	0.69[f]
3	**1a**	PhCH=NPh	B	**3ac**	CH_2=$CHCH_2$	CH_2=$CHCH_2$	Ph	H	O	PhN	28	0.53[f]
4	**1b**	EtCHO	C	**3ba**	Pr^i	Pr^i	Et	H	O	O	71	0.51[g]
5	**1b**	Pr^iCHO	C	**3bb**	Pr^i	Pr^i	Pr^i	H	O	O	76	0.68[f]
6	**1b**	Bu^nCHO	C	**3bc**	Pr^i	Pr^i	Bu^n	H	O	O	61	0.60[f]
7	**1b**	Bu^iCHO	C	**3bd**	Pr^i	Pr^i	Bu^i	H	O	O	48	0.48[f]
8	**1b**	PhCHO	C	**3be**	Pr^i	Pr^i	Ph	H	O	O	79	94-96
9	**1b**	4-$MeOC_6H_4CHO$	C	**3bf**	Pr^i	Pr^i	4-$MeOC_6H_4$	H	O	O	71	116-118
10	**1b**	Me_2CO	C	**3bg**	Pr^i	Pr^i	Me	Me	O	O	62	81-83
11	**1b**	Bu^iCOMe	C	**3bh**	Pr^i	Pr^i	Bu^i	Me	O	O	42	41-43
12	**1b**	PhCOMe	C	**3bi**	Pr^i	Pr^i	Ph	Me	O	O	79	118-120
13	**1b**	$(CH_2)_5CO$	C	**3bj**	Pr^i	Pr^i	-$(CH_2)_5$-		O	O	78	138-140
14	**1b**	PhCH=NPh	C	**3bk**	Pr^i	Pr^i	Ph	H	O	PhN	50	153-155
15	**1c**	Bu^tCHO	A	**3ca**	(*R*)-PhCH(Me)	Me	Bu^t	H	O	O	48[h]	0.48/0.60[f]
16	**1c**	PhCHO	A	**3cb**	(*R*)-PhCH(Me)	Me	Ph	H	O	O	56[i]	0.56[f,j]
17	**1c**	PhCH=NPh	B	**3cc**	(*R*)-PhCH(Me)	Me	Ph	H	O	PhN	43[k]	0.67[f,j]
18	**1d**	EtCHO	C	**3da**	Me	Me	Et	H	S	O	83	0.51[g]
19	**1d**	PhCHO	C	**3db**	Me	Me	Ph	H	S	O	70	94-96
20	**1d**	Me_2CO	C	**3dc**	Me	Me	Me	Me	S	O	84	0.47[g]
21	**1d**	PhCOMe	C	**3dd**	Me	Me	Ph	Me	S	O	40	0.47[l]

[a] All products **3** were >95 % pure (GLC and 300 MHz ^{1}H NMR). [b] Method A: -78°C, 2 h, then hydrolysis; Method B: -78°C, 1 h, then hydrolysis; Method C: -78°C, 45 min, then -78 to 20°C, 2 h, then hydrolysis. [c] Isolated yield after flash chromatography (silica gel, hexane/ethyl acetate) based on the starting material **1**. [d] Hexane/ethyl acetate. [e] Silica gel. [f] Hexane/ethyl acetate: 7/3. [g] Hexane/ethyl acetate: 3/2. [h] 1.3:1 diastereoisomers mixture (GLC and 300 MHz ^{1}H NMR). [i] 1:1 diastereoisomers mixture (GLC and 300 MHz ^{1}H NMR). [j] Both diastereoisomers could not be separated by TLC. [k] 3.1:1 diastereoisomers mixture (GLC and 300 MHz ^{1}H NMR). [l] Hexane/ethyl acetate 4:1.

1a and **1c** were used, even the reaction time played an interesting role due to deallylation or debenzylation processes. Thus, when the reaction was performed using **1a** or **1c** as starting materials and under the reaction conditions shown in Scheme 1, but increasing the reaction time up to 4 or 6 hours (Table 2, footnote b), monoallylated compounds **4aa**, **4ab** or debenzylated product **4ca** were isolated, respectively (Scheme 2 and Table 2).[19]



1a: $R^1 = R^2 = CH_2{=}CHCH_2$ **2** **4aa-4ca**
1c: R^1 = (*R*)-PhCH(Me), R^2 = Me

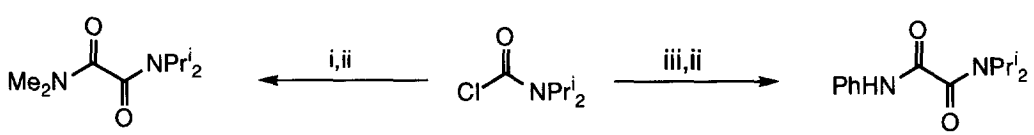
Scheme 2. *Reagents and conditions*: i, Li, $C_{10}H_8$ cat. (3 mol %), THF, -78°C, 4-6 h; ii, H_2O.

Table 2. Preparation of Compounds **4**

Entry	Starting material	Electrophile **2**	Reaction conditions[b]	Product **4**[a] No	R^2	R^3	R^4	Z	Yield (%)[c]	R_f[d]
1	**1a**	BuiCHO	A	**4aa**	$CH_2{=}CHCH_2$	Bui	H	O	41	0.11[e]
2	**1a**	PhCHO	A	**4ab**	$CH_2{=}CHCH_2$	Ph	H	O	59	0.22[f]
3	**1a**	PhCH=NPh	B	**4ca**	Me	Ph	H	PhN	51	0.12[e]

[a] All products **4** were > 96% pure (GLC and 300 MHz ^1H NMR). [b] Method A: -78°C, 4h, then hydrolysis; Method B: -78°C, 6h, then hydrolysis. [c] Isolated yield after flash chromatography (silica gel, hexane/ethyl acetate) based on the starting material **1**. [d] Silica gel. [e] Hexane/ethyl acetate: 7/3. [f] Hexane/ethyl acetate : 1/1.

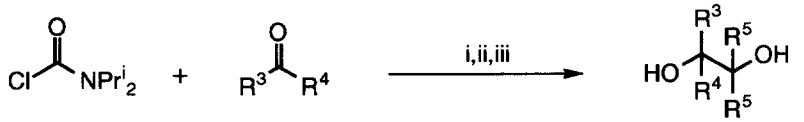
Scheme 3 shows the results obtained when the starting chloroamide **1b** was allowed to react with DMF or phenyl isocyanate as electrophiles under the reaction conditions shown in Scheme 1: the substituted oxamides **5ba** and **5bb** were isolated. In case of the first product, the unexpected result could be explained considering that the initially formed intermediate of the type **II** can deprotonate DMF giving the corresponding acyl anion, which condenses with the starting material **1b** giving the final product **5ba**.



5ba (42%) **1b** **5bb** (21%)

Scheme 3. *Reagents and conditions*: i, Li, $C_{10}H_8$ cat. (3 mol %), $HCONMe_2$, THF, -78°C; ii, H_2O; iii, Li, $C_{10}H_8$ cat (3 mol%), PhNCO, THF, -78°C.

Finally, we introduced a modification in the reaction shown in Scheme 1: since the final product is an amide and we work with an excess of lithium powder it should be possible to add an alkyl chloride, which through the corresponding *in situ* generated alkyllithium could afford the corresponding diol. This possible synthetic route was confirmed using **1b** as starting material and an excess of *n*-butyl or *n*-octyl chloride as coreagents: as expected, 1,2-diols **6ba-bc** were isolated (Scheme 4 and Table 3).



1b **2** **6ba-bc**

Scheme 4. *Reagents and conditions*: i, Li, $C_{10}H_8$ cat. (3 mol %), THF, -78 to 0°C; ii, R^5Cl excess (1:8 molar ratio), 0 to 25°C; iii, H_2O.

Table 3. Preparation of Compounds **6**

Entry	Electrophile **2**	R^5Cl	Product **6**[a] No.	R^3	R^4	R^5	Yield (%)[b]	R_f[c]
1	EtCHO	Bu^nCl	**6ba**	Et	H	Bu^n	44	0.67
2	EtCHO	*n*-$C_8H_{17}Cl$	**6bb**	Et	H	*n*-C_8H_{17}	38	0.66
3	$(CH_2)_5CO$	Bu^nCl	**6bc**	-$(CH_2)_5$-		Bu^n	50	0.67

[a] All products **6** were >95% pure (GLC and 300 MHz ^1H NMR). [b] Isolated yield after flash chromatography (silica gel, hexane/ethyl acetate) based on the starting material **1**. [c] Silica gel, hexane/ethyl acetate: 7/3.

Starting materials **1b** and **1d** are commercially available. The other systems **1a**,[20] **1c** and **1e** were prepared according to the literature general procedures.[21, 22]

As a conclusion, we think that the methodology described in this paper is a versatile way to the *in situ* generation of carbamoyl or thiocarbamoyllithium reagents, which are able to transfer the amide functionality to different electrophiles in a Barbier type process.

EXPERIMENTAL PART

General.- For general information see reference 23. Starting chloroamides **1b** and **1d** were commercially available (Aldrich).

Preparation of Starting Carbamoyl and Thiocarbamoyl Chlorides **1a,c,e**.- These compounds were prepared following the literature procedures:[21, 22] *N,N-Diallylcarbamoyl Chloride* (**1a**):[20] (80% yield) bp 72-77°C (0.1 Torr); ν (film) 3081, 3008 (HC=C), 1732 cm^{-1} (C=O); δ_H 3.95-4.10 (4H, m, 2xCH_2N), 5.10-5.30 (4H, m, 2xCH_2=C), 5.70-5.90 (2H, m, 2xCH=C); δ_C 50.95, 52.30, 117.95, 118.55, 131.05, 131.3, 149.05; *m/z* 161 (M^++2, 1%), 159 (M^+, 4), 144 (14), 124 (54), 118 (14), 96 (19), 94 (11), 82 (44), 81 (10), 76 (11), 75 (11), 75 (17), 70 (49), 68 (22), 67 (10), 63 (14), 56 (60), 55 (21), 54 (34), 44 (28), 42 (28), 41 (100), 40

(40).

(R)-N-Methyl-N-(1-phenylethyl)carbamoyl Chloride (**1c**): (76% yield) bp 150-155°C (0.1 Torr); $[\alpha]_D^{25}$ +139.7 [c=2.93 ($CHCl_3$)]; ν (film) 3093, 3087 (HC=C), 1728 cm^{-1} (C=O); δ_H 1.58 (3H, d, *J*=7.0, CH_2CH_3), 2.78 (3H, s, NCH_3), 5.68 (2H, q, *J*=7.0, CH_2CH_3), 7.25-7.40 (5H, m, Ph); δ_C 15.7, 32.65, 55.8, 127.05, 127.9, 128.6, 138.6, 150.3; *m/z* 197 (M^+, 1%), 161 (54), 146 (15), 125 (26), 118 (16), 105 (100), 104 (22), 103 (25), 79 (27), 78 (22), 77 (49), 65 (10), 63 (20), 58 (11), 57 (10), 56 (18), 51 (39), 50 (16), 42 (27).

N,N-*Diallylthiocarbamoyl Chloride* (**1e**): (74% yield) bp 110-115°C (0.1 Torr); ν (film) 3092, 3019, 1642 (HC=C), 1489 (C-N), 1242 cm^{-1} (C=S); δ_H 4.37, 4.54 (2 and 2H, respectively, 2d, *J*=5.5 and 5.8, respectively, 2xNCH_2), 5.20-5.40 (4H, m, 2xCH_2=C), 5.75-6.00 (2H, m, 2xCH=C); δ_C 56.5, 57.0, 118.85, 119.4, 129.2, 129.85, 175.25; *m/z* 177 (M^++2, 5%), 175 (M^+, 15), 162 (35), 160 (93), 140 (27), 135 (19), 133 (52), 102 (11), 99 (21), 98 (100), 81 (48), 79 (93), 75 (23), 73 (78), 72 (48), 71 (13), 54 (11), 45 (53), 44 (15), 42 (20).

Naphthalene-Catalysed Lithiation of Chloroamides **1** *in the Presence of Electrophile* **2**. *Isolation of Compounds* **3**. *General Procedure. Method A*.- To a suspension of lithium (100 mg, 14 mmol), the corresponding carbonyl compound **2** (3.0 mmol) and naphthalene (20 mg, 0.16 mmol) in THF (5 ml), was added a mixture of the chlorinated precursor **1** (2.5 mmol) in THF (10 ml) at -78°C under an argon atmosphere. The reaction mixture was stirred for 2 h, and then, hydrolysed with water (20 ml), neutralised with 2 M hydrochloric acid and extracted with ethyl acetate (3x20 ml). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed (15 Torr). *Method B*.- As method A but the reaction mixture was stirred at -78°C for 1 h. *Method C*.- As method A but the reaction mixture was stirred at -78°C for 45 min, then the temperature was allowed to rise to 0°C (2 h) and the resulting mixture was hydrolysed as above. The resulting residue was then purified by flash chromatography (silica gel, hexane/ethyl acetate) to afford the corresponding compounds **3**. Yields and mp's or R_f values are included in Table 1. Spectroscopic and analytical data as well as literature references for known compounds follow.

N,N-*Diallyl-2-hydroxyhexanamide* (**3aa**): ν (film) 3427 (OH), 3085, 3015 (HC=C), 1630 (C=O), 1079, 993 cm^{-1} (C-O); δ_H 0.91 (3H, t, *J*=7.2, CH_3), 1.20-1.75 [6H, m, $(CH_2)_3$], 3.60-3.65, 3.75-4.00, 4.10-4.20, 4.25-4.35 (1, 3, 1 and 1H, respectively, 4m, CHOH, 2xNCH_2), 5.05-5.35 (4H, m, 2xCH_2=C), 5.65-5.85 (2H, m, 2xCH=C); δ_C 13.9, 22.4, 27.05, 35.05, 47.75, 48.2, 68.1, 117.7, 117.9, 132.1, 132.3, 174.65; *m/z* 194 (M^+ -17, <1%), 125 (13), 124 (32), 84 (20), 70 (12), 69 (17), 56 (20), 55 (19), 44 (14), 43 (14), 42 (11), 41 (100), 40 (15).

N,N-*Diallyl-2-hydroxy-3,3-dimethylbutanamide* (**3ab**): ν (film) 3450 (OH), 3081 (HC=C), 1635 (C=O), 1076, 925 cm^{-1} (C-O); δ_H 0.98 (9H, s, 3xCH_3), 3.28 (1H, d, *J*=9.8, OH), 3.59, 3.78, 4.05-4.20, 4.47 (1, 1, 2 and 1H, respectively, dd, dd, m, dd, respectively, *J*=7.0, 14.9; 4.9, 17.1; 5.2, 14.9, respectively, CHO, 2xNCH_2), 5.10-5.30 (4H, m, 2xCH_2=C), 5.65-5.85 (2H, m, 2xCH=C); δ_C 25.85 (3C), 36.05, 47.65, 49.2, 74.05, 117.75, 117.85, 132.25, 132.6, 173.6; *m/z* 211 (M^+, 3%), 155 (18), 154 (31), 125 (33), 124 (59), 96 (18), 87 (13), 84 (37), 82 (19), 81 (12), 70 (27), 69 (26), 68 (16), 57 (31), 56 (37), 55 (30), 45 (22), 44 (16), 43 (28), 42 (19), 41 (100), 40 (15) (Found: M^+, 211.1565. $C_{12}H_{21}NO_2$ requires M, 211.1572).

N,N-*Diallyl-2-phenylamino-2-phenylacetamide* (**3ac**): ν (film) 3390 (OH), 3084, 3061, 3027 (HC=C), 1650 cm^{-1} (C=O); δ_H 3.70-3.80, 3.90-4.05, 4.10-4.20 (2, 1 and 1H, respectively, 3m, 2xNCH_2), 5.00-5.30 (6H, m, NHCH, 2xCH_2=C), 5.45-5.75 (2H, m, 2xCH=C), 6.60-6.70, 7.05-7.15, 7.20-7.30, 7.40-7.45 (3, 2, 3 and 2H, respectively, 4m, 2xPh); δ_C 48.05, 48.65, 58.15, 113.6 (2C), 117.25, 117.45, 117.65, 127.7 (2C), 127.95, 128.8(2C), 128.95 (2C), 132.25, 132.3, 138.25, 146.25, 170.75; *m/z* 306 (M^+, 2%), 183 (15), 182

(100), 104 (13), 77 (25), 41 (12), 40 (11) (Found: M+: 306.1736. $C_{20}H_{22}N_2O$ requires M, 306.1732).

N,N-*Diisopropyl-2-hydroxybutanamide* (**3ba**):[6e] ν (film) 3380 (OH), 1620 (C=O), 1030 cm^{-1} (C-O); δ_H 0.97 (3H, t, *J*=7.4, CH_2CH_3), 1.21, 1.22 (6H, 2d, *J*=6.6, 2xCHCH_3), 1.39, 1.44 (6H, 2d, *J*=6.8, 2xCHCH_3), 1.60-1.80 (2H, m, CH_2CO), 3.44, 3.85 (1 and 1H, respectively, 2sept, *J*=6.8 and 6.6, respectively, 2xCHN), 4.08 (1H, d, *J*=7.0, OH), 4.24 (1H, dt, *J*=7.0, 3.2, CHO); δ_C 8.75, 20.15 (2C), 20.5, 20.8, 27.95, 46.2, 47.65, 69.05, 172.65; *m/z* 187 (M+, 2%), 128 (19), 86 (100), 70 (11), 59 (16), 58 (15), 44 (25), 43 (83), 42 (15), 41 (37).

N,N-*Diisopropyl-2-hydroxy-3-methylbutanamide* (**3bb**):[24] ν (film) 3388 (OH), 1629 (C=O), 1041 cm^{-1} (C-O); δ_H 0.77, 1.07, 1.21, 1.23, 1.39, 1.45 (3, 3, 3, 3, 3 and 3H, respectively, 6d, *J*=6.7, 6xCH_3), 1,75-1.90 (1H, m, C*H*CHO), 3.44, 3.87 (1 and 1H, respectively, 2sept, *J*=6.7, 2xCHN), 4.05 (1H, s, OH), 4.17 (1H, m, CHO); δ_C 14.3, 19.85, 20.0, 20.15, 20.5, 20.8, 31.2, 46.15, 47.65, 72.1, 172.3; *m/z* 201 (M+, <1%), 158 (20), 128 (20), 116 (11), 86 (95), 83 (15), 74 (21), 73 (16), 72 (42), 58 (19), 57 (14), 55 (28), 44 (48), 43 (100), 42 (30), 41 (68).

N,N-*Diisopropyl-2-hydroxyhexanamide* (**3bc**): ν (film) 3404 (OH), 1633 (C=O), 1138, 1042 cm^{-1} (C-O); δ_H 0.91 (3H, t, *J*=7.0, CH_2CH_3), 0.95-1.40 (18H, m, 3xCH_2, 4CHCH_3), 3.45, 3.85 (1 and 1H, respectively, 2sept, *J*=7.2, 2xCHN), 4.10 (1H, t, *J*=7.0, CHO), 4.27 (1H, s, OH); δ_C 13.75, 19.9, 19.95, 20.35, 20.65, 22.3, 26.65, 34.6, 45.95, 47.5, 68.05, 172.75; *m/z* 215 (M+, 5%), 129 (10), 128 (35), 114 (11), 87 (12), 86 (100), 74 (15), 72 (20), 70 (21), 58 (29), 57 (12), 44 (60), 43 (95), 42 (38), 41 (68), 40 (18) (Found: M+, 215.1888. $C_{12}H_{25}NO_2$ requires M, 215.1885).

N,N-*Diisopropyl-2-hydroxy-4-methylpentanamide* (**3bd**): ν (film) 3404 (OH), 1634 (C=O), 1077 cm^{-1} (C-O); δ_H 0.95, 0.98, 1.21, 1.23 (3, 3, 3 and 3H, respectively, 4d, *J*=6.7, 4xNCHCH_3), 1.25-1.35 (2H, m, CH_2), 1.39, 1.43 (3 and 3H, 2d, *J*=7.0, 2xCCHCH_3), 1.85-2.05 (1H, m, CC*H*CH_3), 3.44, 3.81 (1 and 1H, respectively, 2sept, *J*=7.8, 2xCHN), 3.99 (1H, d, *J*=7.35, OH), 4.29 (1H, t, *J*=7.8, CHO); δ_C 19.9, 19.95, 20.35, 20.65, 21.25, 23.6, 24.5, 44.45, 46.0, 47.45, 66.8, 173.4; *m/z* 216 (M++1, 1%), 159 (22), 158 (14), 130 (11), 129 (11), 128 (36), 116 (13), 114 (13), 87 (14), 86 (100), 74 (18), 72 (24), 70 (13), 69 (20), 58 (36), 57 (10), 45 (24), 44 (60), 43 (86), 42 (47), 41 (68), 40 (10).

N,N-*Diisopropyl-2-hydroxy-2-phenylacetamide* (**3be**):[6e] ν (melted) 3340 (OH), 3040 (HC=C), 1630 (C=O), 1030 cm^{-1} (C-O); δ_H 0.45, 1.23, 1.39, 1.47 (3, 3, 3 and 3H, respectively, 4d, *J*=6.8, 4xCH_3), 3.28, 3.74 (1 and 1H, respectively, 2sept, *J*=6.8, 2xCHN), 5.12, 5.13 (1 and 1H, respectively, 2s, CHOH), 7.25-7.37 (5H, m, Ph); δ_C 18.4, 19.4, 20.3 (2C), 46.15, 47.75, 71.6, 127.2 (2C), 128.0, 128.7 (2C), 140.0, 170.45; *m/z* 236 (M++1, <1%), 128 (57), 107 (28), 86 (100), 79 (50), 77 (52), 51 (11), 43 (75), 42 (12), 41 (28).

N,N-*Diisopropyl-2-hydroxy-2-(4-methoxyphenyl)acetamide* (**3bf**): ν (melted) 3366 (OH), 3001, 1512 (HC=C), 1634 (C=O), 1250, 1062 cm^{-1} (C-O); δ_H 0.50, 1.13, 1.39, 1.47 (3, 3, 3 and 3H, respectively, 4d, *J*=6.7, 6xCCH_3), 3.53, 3.78 (1 and 1H, respectively, 2sept. *J*=6.7, 2xCHN), 3.77 (3H, s, CH_3O), 5.08 (2H, s, CHOH), 6.86, 7.21 (2 and 2H, respectively, 2d, *J*=8.5, Ph); δ_C 18.5, 19.4, 20.25, 20.3, 46.05, 47.75, 55.0, 70.95, 114.05 (2C), 128.45 (2C), 132.3, 159.25, 170.7; *m/z* 237 (M+-28, 5%), 138 (12), 137 (100), 135 (11), 130 (18), 128 (16), 109 (26), 101 (21), 94 (23), 86 (75), 77 (33), 66 (15), 44 (26), 43 (70), 42 (27), 41 (45) (Found: C, 68.03; H, 8.79; N, 4.84. $C_{15}H_{23}NO_3$ requires: C, 67.90; H, 8.74; N, 5.28).

N,N-*Diisopropyl-2-hydroxy-2-methylpropionamide* (**3bg**):[6e] ν (melted) 3600 (OH), 3040 (HC=C), 1600 (C=O), 1030 cm^{-1} (C-O); δ_H 1.22, 1.41 (6 and 6H, respectively, 2d, *J*=6.65, 6.75, respectively, 4xCHCH_3),

1.47 (6H, s, 2xOCCH$_3$), 3.42, 4.18 (1 and 1H, respectively, 2sept, *J*=6.75, 6.65, respectively, 2xCH), 4.30 (1H, br s, OH); δ_C 20.3, 20.35, 27.45 (4C), 46.95, 49.0, 70.9, 175.15; *m/z* 188 (M$^+$+1, <1%), 129 (24), 114 (18), 86 (100), 72 (41), 70 (15), 59 (67), 58 (14), 44 (19), 43 (86), 41 (20), 41 (43).

N,N-*Diisopropyl-2,4-dimethyl-2-hydroxypentanamide* (**3bh**): ν (melted) 3344 (OH), 1622 (C=O), 1035 cm^{-1} (C-O); δ_H 0.87, 0.96, 1.21, 1.23 (3, 3, 3 and 3H, respectively, 4d, *J*=6.7, 4xC*H*$_3$CHN), 1.41, 1.43 (3 and 3H, respectively, 2d, *J*=6.1, 2xCCHC*H*$_3$), 1.44 (3H, s, CH$_3$CO), 1.66 (2H, d, *J*=6.4, CH$_2$), 1.76-1.90 (1H, m, CH$_2$C*H*), 3.44, 4.16 (1 and 1H, respectively, 2sept, *J*=6.7, 2xCHN), 5.31 (1H, s, OH); δ_C 19.85, 19.9, 20.25, 20.55, 23.8, 24.0, 24.55, 27.6, 46.95, 48.75, 48.9, 73.45, 174.8; *m/z* 214 (M$^+$-15, <1%), 130 (23), 129 (32), 114 (39), 101 (25), 100 (13), 86 (87), 72 (46), 70 (10), 59 (30), 58 (32), 57 (53), 45 (23), 44 (40), 43 (100), 41 (69) (Found: C, 68.12; H, 11.80; N, 5.91. $C_{13}H_{27}NO_2$ requires: C, 68.08; H, 11.87; N, 6.11).

N,N-*Diisopropyl-2-hydroxy-2-phenylpropionamide* (**3bi**): ν (melted) 3360 (OH), 3040 (HC=C), 1610 (C=O), 1020 cm^{-1} (C-O); δ_H 0.46, 1.01 (3 and 3H, respectively, 2d, *J*=6.6, 2xCHC*H*$_3$), 1.44 (6H, d, *J*=6.9, 2xCHC*H*$_3$) 1.78 (3H, s, CH$_3$CO), 3.31, 3.75 (1 and 1H, respectively, 2sept, *J*=6.9, 6.6, respectively, 2xCHN), 5.77 (1H, s, OH), 7.20-7.40 (5H, m, Ph); δ_C 18.3, 19.75, 19.9, 20.1, 24.15, 46.65, 48.9, 74.2, 125.45 (2C), 127.45, 128.5 (2C), 143.4, 173.65; *m/z* 221 (M$^+$-28, <1%), 121 (20), 86 (40), 77 (11), 43 (100), 41 (15) (Found: C, 72.00; H, 9.20; N, 5.30. $C_{15}H_{23}NO_2$ requires: C, 72.25; H, 9.29; N, 5.61).

N,N-*Diisopropyl-1-hydroxycyclohexanecarboxyamide* (**3bj**): ν (melted) 3337 (OH), 1601 (C=O), 1026 cm^{-1} (C-O); δ_H 1.22, 1.39 (6 and 6H, respectively, 2d, *J*=6.1, 4xCH$_3$), 1.60-2.00 (10H, m, 5xCH$_2$), 3.40 (1H, s, OH), 4.45-4.65 (2H, m, 2xCH); δ_C 20.35, 21.75 (2C), 25.15 (2C), 34.25 (4C), 46.85, 48.55, 73.8, 174.55; *m/z* 209 (M$^+$-18, <1%), 130 (13), 129 (39), 114 (38), 100 (24), 99 (59), 86 (100), 81 (57), 72 (43), 70 (13), 58 (26), 57 (10), 55 (34), 44 (44), 43 (82), 42 (42), 41 (70) (Found: C, 69.07; H, 11.20; N, 6.42. $C_{13}H_{25}NO_2$ requires: C, 68.67; H, 11.09; N, 6.16).

N,N-*Diisopropyl-2-phenyl-2-phenylaminoacetamide* (**3bk**): ν (melted) 3380 (NH), 3050, 3000 (HC=C), 1636 cm^{-1} (C=O); δ_H 0.56, 1.19, 1.31, 1.42 (3, 3, 3 and 3H, respectively, 4d, *J*=6.4, 4xCH$_3$), 3.30, 4.15 (1 and 1H, respectively, 2sept, *J*=6.4, 2xC*H*CH$_3$), 5.1 (1H, s, CHCO), 5.65 (1H, s, NH), 6.00-6.70, 7.00-7.50 (3 and 7H, respectively, 2m, 2xPh); δ_C 19.25, 19.5, 20.7, 20.75, 46.25, 48.15, 58.9, 113.40 (2C), 117.25, 127.6, 127.75 (2C), 128.7 (2C), 129.0 (2C), 139.25, 146.5, 168.8; *m/z* 310 (M$^+$, 2%), 183 (27), 182 (100), 180 (11), 77 (38), 51 (12), 43 (33), 41 (17) (Found: C, 77.39; H, 8.53; N, 9.15. $C_{20}H_{26}N_2O$ requires: C, 77.38; H, 8.44; N, 9.02).

(1'R, 2R)-2-Hydroxy*-N-*(1'-phenylethyl)*-N,*33-trimethylbutanamide* (**3ca**): First diastereomer: $[\alpha]_D^{25}$ +185.6 [c=3.15 (CHCl$_3$)]; ν (film) 3455 (OH), 3075, 3032 (HC=C), 1631 (C=O), 1061 cm^{-1} (C-O); δ_H 1.01 [9H, s, C(CH$_3$)$_3$], 1.52 (3H, d, *J*=7.3, 3H, CHC*H*$_3$), 2.69 (3H, s, NCH$_3$), 3.42 (1H, d, *J*=79.5, OH), 4.17 (1H, d, *J*=9.5, CHO), 6.15 (1H, q, *J*=7.3, CHN), 7.25-7.40 (5H, m, Ph); δ_C 15.75, 25.95 (3C), 29.95, 36.7, 51.0, 74.3, 127.3 (2C), 127.4, 128.45 (2C), 139.6, 173.85; *m/z* 249 (M$^+$, 4%), 162 (23), 144 (18), 106 (22), 105 (100), 91 (10), 88 (23), 87 (15), 79 (12), 77 (16), 69 (11), 58 (13), 57 (17), 45 (10), 42 (13), 41 (23), 40 (16) (Found: M$^+$, 249.1722. $C_{15}H_{23}NO_2$ requires M, 249.1728). Second diastereomer: $[\alpha]_D^{25}$ +87.1 [c=3.13 (CHCl$_3$)]; ν (film) 3454 (OH), 3093, 3061, 3030 (HC=C), 1631 (C=O), 1061 cm^{-1} (C-O); δ_H 0.97 [9H, s, C(CH$_3$)$_3$], 1.51 (3H, d, *J*=7.0, CHC*H*$_3$), 2.65 (3H, s, NCH$_3$), 3.45 (1H, d, *J*=8.8, OH), 4.16 (1H, d, *J*=8.8, CHO), 6.05 (1H, q, *J*=7.0, CHN), 7.20-7.40 (5H, m, Ph); δ_C 14.5, 26.0 (3C), 29.95, 36.8, 51.75, 74.4, 126.05, 127.5 (2C), 128.45 (2C), 139.75, 173.75; *m/z* 249 (M$^+$, 4%), 162 (25), 144 (18), 106 (22), 105

(100), 88 (22), 87 (14), 79 (12), 77 (15), 69 (10), 58 (13), 57 (16), 45 (10), 42 (12), 41 (22), 40 (20) (Found: M+, 249.1734. $C_{15}H_{23}NO_2$ requires M, 249.1728).

(1'R, 2R)-2-Hydroxy*-N-*methyl*-N-*(1'-phenylethyl)-phenylacetamide* (**3cb**): ν (film) 3442 (OH), 3028 (HC=C), 1611 (C=O), 1034 cm^{-1} (C-O); δ_H 1.04, 1.31 (3 and 3H, respectively, 2d, *J*=7.0, 2xCHCH_3), 2.90-3.15 (2H, m, 2xCHCH$_3$), 3.75, 3.80 (3 and 3H, respectively, 2s, 2xNCH$_3$), 3.85-4.00 (2H, m, 2xOH), 4.60, 4.73 (1 and 1H, respectively, 2d, *J*=8.85, 6.1, respectively, 2xCHO), 7.00-7.40 (20H, m, 4xPh); δ_C 15.4, 18.35, 47.2, 48.1, 55.15, 55.25, 78.4, 79.2, 113.2, 113.25 (2C), 113.65 (2C), 126.3, 126.8, 127.45 (4C), 128.0, 128.05 (4C), 128.1 (2C), 128.6 (2C), 134.65, 135.0, 143.55 (2C), 158.65, 159.15; *m/z* 225 (M+-44, 2%), 224 (12), 138 (10), 137 (100), 109 (17), 94 (13), 77 (22), 40 (13).

(1'R, 2R)*-N-*Methyl-2-phenyl-2-phenylamino*-N-*(1'-phenylethyl)acetamide* (**3cc**): ν (film) 3390 (NH), 3060, 3028 (HC=C), 1637 cm^{-1} (C=O); δ_H 1.28, 1.44 (3 and 3H, respectively, 2d, *J*=7.0, 2xCHCH_3), 2.55 (6H, s, 2xNCH$_3$), 5.20-5.50 (4H, m, 2xCHNH), 6.0-6.15 (2H, m, 2xCHN), 6.50-7.50 (30H, m, 6xPh); δ_C 14.95, 153, 28.3, 29.0, 29.05, 51.05, 53.6, 126.4, 126.6, 126.75, 126.9, 127.0, 127.05, 127.2, 127.7, 127.8, 128.1, 128.3, 128.35, 128.5, 128.6, 128.8, 128.9, 138.45, 139.6, 139.75, 170.5, 170.7; *m/z* 344 (M+, 1%), 183 (16), 182 (100), 104 (15), 77 (30) (Found: M+, 344.1887. $C_{23}H_{24}N_2O$ requires M, 344.1888).

N,N-*Dimethyl-2-hydroxythiobutanamide* (**3da**):[10a] ν (film) 3260 (OH), 1520, 1380, 1130 (S=CN), 1040 cm^{-1} (C-O); δ_H 1.05 (3H, t, *J*=7.4, CH_3CH$_2$), 1.40-1.55, 1.60-1.70 (1 and 1H, respectively, 2m, CH$_2$), 3.29, 3.50 (3 and 3H, respectively, 2s, 2xCH$_3$N), 4.22 (1H, d, *J*=8.5, OH), 4.36 (1H, dt, *J*=8.5, 5.5, CHO); δ_C 9.8, 30.3, 40.45, 44.75, 72.4, 206.65; *m/z* 148 (M++1, 8%), 147 (M+, 95), 118 (60), 89 (33), 88 (100), 74 (77), 73 (15), 46 (26), 45 (13), 44 (30), 42 (23).

N,N-*Dimethyl-2-hydroxy-2-phenylthioacetamide* (**3db**):[10a] ν (melted) 3240 (OH), 3040, 3020, 1590 (HC=C), 1520, 1360, 1180 (S=CN), 1030 cm^{-1} (C-O); δ_H 3.09, 3.50 (3 and 3H, respectively, 2s, 2xCH$_3$), 5.29, 5.34 (1 and 1H, respectively, 2d, *J*=7.0, CHOH), 7.25-7.45 (5H, m, Ph); δ_C 41.05, 45.5, 73.8, 127.3 (2C), 128.35, 128.9 (2C), 139.75, 203.5; *m/z* 197 (M++2, 2%), 195 (M+, 21), 105 (15), 90 (16), 89 (49), 88 (100), 79 (38), 78 (17), 77 (76), 74 (32), 73 (26), 72 (11), 51 (39), 50 (18), 46 (15), 45 (15), 44 (23), 42 (41).

2-Hydroxy-N,N,*2-trimethylthiopropionamide* (**3dc**):[10a] ν (film) 3380, 3200 (OH), 1510, 1360, 1130 (S=CN), 1030 cm^{-1} (C-O); δ_H 1.49 (6H, s, 2xCCH$_3$), 3.42 (6H, s, 2xNCH$_3$), 5.29 (1H, br s, OH); δ_C 28.65 (2C), 44.0, 47.9, 73.8, 209.7; *m/z* 148 (M++1, 4%), 147 (M+, 52), 132 (17), 90 (20), 89 (100), 88 (65), 74 (60), 73 (15), 59 (46), 46 (17), 45 (10), 44 (36), 43 (18), 42 (77).

N,N-*Dimethyl-2-hydroxy-2-phenylthiopropionamide* (**3dd**):[10a] ν (film) 3360, 3160 (OH), 3040, 3020, 1590 (HC=C), 1520, 1380, 1100 (S=CN), 1010 cm^{-1} (C-O); δ_H 1.86 (3H, s, CH$_3$CO), 2.87, 3.51 (3 and 3H, respectively, 2s, 2xCH$_3$N), 6.02 (1H, br s, OH), 7.15-7.40 (5H, m, Ph); δ_C 25.75, 43.6, 47.6, 76.6, 125.35 (2C), 127.65, 128.85 (2C), 143.9, 208.2; *m/z* 209 (M+, 1%), 120 (33), 105 (100), 89 (63), 88 (27), 77 (81), 74 (22), 51 (37), 50 (20), 44 (23), 43 (35), 42 (33).

N,N-*Diallylthioformamide* (**3e**): ν (film) 3083, 3013, 1642 (HC=C), 1498, 1229 cm^{-1} (S=CN); δ_H 4.08, 4.46 (2 and 2H, respectively, 2d, *J*=5.8, 6.1, respectively, 2xNCH$_2$), 5.15-5.35 (4H, m, 2xCH$_2$=C), 5.70-5.90 (2H, m, 2xCH=C), 9.32 (1H, s, CHS); δ_C 49.4, 57.5, 119.15, 119.95, 129.9, 131.35, 188.65; *m/z* 141 (M+, 9%), 126 (67), 73 (34), 68 (11), 56 (100), 45 (61), 44 (15), 43 (18), 42 (16).[25]

Naphthalene-Catalysed Lithiation of Chloroamides **1a,c** *in the Presence of Electrophile* **2** *using Longer Reaction Times. Isolation of Compounds* **4**. *General Procedure.*- The reaction was carried out as it was

described above for compounds **3** (method A), but using 6 mmol of carbonyl compound **2**, and 4-6 h as reaction time (see Table 2, footnote b), affording the title compound **4**. Yields and R_f values are included in Table 2. Spectroscopic and analytical data as well as literature references for known compounds follow.

N-*Allyl-2-hydroxy-3-methylbutanamide* (**4aa**): ν (film) 3344 (OH, NH), 3013 (HC=C), 1657 (C=O), 925 cm^{-1} (C-O); δ_H 0.85, 1.01 (3 and 3H, respectively, 2d, *J*=6.7, 7.0, respectively, 2xCH_3), 2.10-2.20 (1H, m, CHCO), 3.80-4.20 (4H, m, CH_2N, CHOH), 5.10-5.25 (2H, m, CH_2=C), 5.75-5.90 (1H, m, CH=C), 7.05 (1H, s, NH); δ_C 14.0, 15.35, 19.1, 20.9, 31.6, 41.2, 60.35, 76.05, 116.2, 133.85, 173.9; *m/z* 157 (M^+, 5%), 115 (67), 114 (26), 86 (22), 85 (44), 84 (41), 83 (14), 74 (19), 73 (76), 69 (13), 58 (38), 57 (69), 56 (82), 55 (83), 45 (21), 44 (26), 43 (63), 42 (44), 41 (100), 40 (15) (Found: M^+, 197.1408. $C_{11}H_{19}NO_2$ requires M, 197.1415).

N-*Allyl-2-hydroxy-2-phenylacetamide* (**4ab**):[26] ν (film) 3327 (NH, OH), 3085, 3065, 3032 (HC=C), 1660 (C=O), 1062 cm^{-1} (C-O); δ_H 3.65-3.75 (2H, m, CH_2N), 4.84 (1H, s, OH), 4.95-5.15 (3H, m, CHO, CH_2=C), 5.60-5.73 (1H, m, C*H*CH_2), 7.05 (1H, s, NH), 7.20-7.30 (5H, m, Ph); δ_C 41.15, 73.65, 115.95, 126.4, 127.9, 128.15, 133.35, 139.5, 172.6; *m/z* 191 (M^+, 2%), 108 (74), 107 (100), 105 (18), 85 (27), 79 (90), 77 (58), 57 (45), 56 (31), 51 (22), 44 (23), 41 (84), 40 (36).

N-*Methyl-2-phenyl-2-phenylaminoacetamide* (**4ca**):[27] $[\alpha]_D^{25}$ +68.3 [c=0.61 ($CHCl_3$)]; ν (film) 3318 (NH), 3087, 3053, 3030 (HC=C), 1652 cm^{-1} (C=O); δ_H 2.73, 2.74 (3H, 2s, CH_3), 4.65 (1H, s, N*H*Ph), 4.73 (1H, s, CHN), 6.55-6.65, 6.70-6.90, 7.10-7.20, 7.25-7.45 (2, 1, 1 and 7H, respectively, 4m, 2xPh, NHCO); δ_C 26.15, 63.65, 113.6 (2C), 118.7, 127.2 (2C), 128.3, 129.0 (2C), 129.15 (2C), 138.75, 146.5, 171.8; *m/z* 240 (M^+, 6%), 183 (18), 182 (100), 180 (11), 104 (25), 77 (40), 51 (14).

Naphthalene-Catalysed Lithiation of Compound **1b** *in the Presence of DMF or Phenyl isocyanate. Isolation of Compounds* **5**. *General Procedure.*- Following the same procedure described above for compounds **3** (method C), the title compounds **5** were isolated. Yields are included in Scheme 3. Physical, spectroscopic and analytical data follow.

N,N-*Diisopropyl*-N',N'-*dimethyloxamide* (**5ba**): R_f= 0.68 (hexane/ethyl acetate: 7/3); ν (film) 1646 cm^{-1} (C=O); δ_H 1.27 (12H, d, *J*=6.7, 4xCHC*H*$_3$), 2.72 (6H, s, 2xNCH_3), 3.59 (2H, sept, *J*=6.7, 2xNCH); δ_C 21.35 (4C), 38.75 (2C), 47.2 (2C), 164.75, 174.05; *m/z* 172 (M^+-28, 9%), 157 (31), 115 (11), 86 (37), 84 (20), 73 (11), 72 (100), 58 (10), 46 (10), 45 (10), 44 (45), 43 (74), 42 (46), 41 (41).

N,N-*Diisopropyl*-N'-*phenyloxamide* (**5bb**): mp 166-168°C ($CHCl_3$/hexane), R_f= 0.73 (hexane/ethyl acetate: 7/3); ν (melted) 3264 (NH), 3139, 3088 (HC=C), 1617, 1608 cm^{-1} (C=O); δ_H 1.26, 1.46 (6 and 6H, respectively, 2d, *J*=6.7, 4xCH_3), 3.56, 4.79 (1 and 1H, respectively, 2sept, *J*=6.7, 2xCHN), 7.05-7.15, 7.20-7.40, 7.60-7.70 (1, 2 and 2H, respectively, 3m, Ph), 9.54 (1H, s, NH); δ_C 20.0 (2C), 20.75 (2C), 46.7, 49.9, 119.8 (2C), 124.5, 128.85 (2C), 137.35, 160.65, 162.95; *m/z* 249 (M^++1, 3%), 248 (M^+, 18), 120 (11), 119 (15), 100 (78), 93 (22), 92 (15), 77 (30), 72 (13), 66 (12), 65 (17), 58 (50), 51 (12), 44 (38), 43 (100), 42 (30), 41 (51) (Found: M^+, 248.1521. $C_{14}H_{20}N_2O_2$ requires M, 248.1524).

Naphthalene-Catalysed Lithiation of Compound **1b** *in the Presence of Electrophiles* **2** *and Further Reaction with Alkyl Chlorides. Isolation of Compounds* **6**. *General Procedure.*- Once the reaction was carried out as it was described for compounds **3** (method C), and before the hydrolysis, an excess of *n*-butyl or *n*-octyl chloride (1:8 molar ratio) was added at 0°C allowing the temperature to rise to 20°C during *ca.* 24 h. The resulting mixture was hydrolysed and worked up as it was described above for compound **3** affording the title compounds **6**. Yields and R_f values are included in Table 3. Spectroscopic and analytical data follow.

5-(2-Hydroxypropyl)-5-nonanol (**6ba**): ν (film) 3300 (OH), 1024, 977 cm^{-1} (C-O); δ_H 0.91, 1.03 (6 and 3H,

respectively, 2t, *J*=6.6, 7.3, respectively, 3xCH_3), 1.25-1.60 (14H, m, 7xCH_2), 1.84, 1.99 (2H, 2s, 2OH), 3.39 (1H, dd, *J*=4.6, 10.0, CHO); δ_C 11.2, 14.05 (2C), 23.4, 23.5 (2C), 23.8, 25.4, 25.5, 34.25, 35.9, 76.1, 77.55; *m/z* 185 (M^+-17, <1%), 145 (28), 144 (12), 143 (100), 87 (15), 85 (44), 83 (30), 73 (10), 71 (18), 69 (66), 59 (20), 58 (30), 57 (85), 55 (61), 45 (16), 43 (58), 42 (12), 41 (70).

9-(1-Hydroxypropyl)-9-heptadecanol (**6bb**): ν (film) 3416 (OH), 1117, 973 cm^{-1} (C-O); δ_H 0.84, 0.98 (6 and 3H, respectively, 2t, *J*=6.7, 7.3, respectively, 3xCH_3), 1.15-1.60 (30H, m, 15xCH_2), 1.96, 2.20 (1 and 1H, respectively, 2s, 2xOH), 3.30-3.35 (1H, m, CHO); δ_C 11.2, 14.0 (2C), 22.6 (2C), 23.2, 23.25, 23.75, 25.7, 29.25 (2C), 29.5, 29.55, 30.35, 30.4, 31.85 (2C), 34.5, 36.15, 76.15, 77.5; *m/z* 278 (M^+-36, 1%), 255 (53), 201 (20), 141 (11), 97 (14), 95 (12), 85 (17), 83 (25), 82 (11), 81 (15), 71 (34), 69 (37), 67 (11), 58 (18), 57 (100), 56 (12), 55 (51), 44 (15), 43 (74).

5-(1-Hydroxycyclohexyl)-5-nonanol (**6bc**): ν (film) 3456 (OH), 1131, 1018 cm^{-1} (C-O); δ_H 0.92 (6H, t, *J*=7.0, 2xCH_3), 1.20-1.40, 1.45-1.70 (10 and 12H, respectively, 2m, 11xCH_2), 2.03 (2H, s, 2xOH); δ_C 14.05 (2C), 21.8 (2C), 23.7 (2C), 25.8, 26.7 (2C), 31.45 (2C), 34.3 (2C), 76.25, 77.9; *m/z* 206 (M^+-36. 3%), 167 (16), 143 (100), 142 (13), 99 (48), 98 (19), 85 (61), 83 (32), 81 (41), 79 (14), 70 (11), 69 (71), 67 (15), 58 (30), 57 (71), 56 (12), 55 (82), 44 (30), 43 (59), 42 (27) .

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