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Reductive Deprotection of Allyl, Benzyl and Sulfonyl Substituted Alcohols, Amines and Amides Using a Naphthalene-Catalysed Lithiation†

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Abstract: The reaction of different protected alcohols, amines and amides with lithium and a catalytic amount of naphthalene (4 mol %) in THF at low temperature leads to their deprotection under very mild reaction conditions, the process being in many cases chemoselective. © 1997 Elsevier Science Ltd.

INTRODUCTION

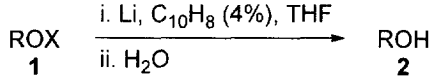
Protective groups play a decisive role in synthetic organic chemistry, above all in multi-step processes.[1,2] Concerning alcohols and amines, their protection through alkylation or acylation processes has been extensively used. Allyl or benzyl groups have the advantage of being deprotected by reductive procedures, including catalytic hydrogenation or dissolving metals.[3,4] In the case of acylated derivatives, esters and amides, the most usual way to deprotect them consists in the corresponding hydrolysis under a variety of reaction conditions.[1c] On the other hand, in the last few years we have developed a new methodology consisting in using a catalytic amount of an arene for the lithiation with lithium powder of different substrates under very mild reaction conditions.[5] Using this procedure we have been able to prepare for the first time organolithium reagents from non-halogenated materials[6a] as well as very reactive functionalised organolithium compounds[7] (from chlorinated starting materials[6b] or heterocyclic systems[6c]) and polylithium synthons.[6d] In this paper we report on the application of the arene-catalysed chemoselective lithiation for the deprotection of different *O*- and *N*-substituted compounds, such as ethers, amines or amides under very mild reaction conditions. Our interest in this chemistry is focused on the study on the chemoselective deprotection of one group in the presence of other protecting ones.

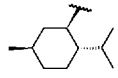
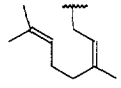
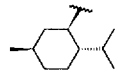
†This paper is dedicated to Professor Teruaki Mukaiyama on occasion of his 70th birthday.

RESULTS AND DISCUSSION

The reaction of different allylic or benzylic ethers **1** with an excess of lithium powder (1:14 molar ratio) in the presence of a catalytic amount of naphthalene (1:0.08 molar ratio, 4 mol %) in THF at temperatures ranging between -78 and 20°C (see Table 1) led, after hydrolysis with water, to the expected deprotected alcohols **2** (Table 1).[8] Some remarks on this reaction are: (a) only allyl or benzyl groups can be deprotected; for instance, in the case of the alkyl derivative **1c** only starting material was isolated after work-up (Table 1, entry 3). (b) In general, deprotection of benzyl derivatives worked better than of allyl ones (compare Table 1, entries 1 and 2 or 6 and 9). (c) Phenylsilyl ethers can be also deprotected; however the process worked for the dimethylphenyl derivative **1d** but not for the *tert*-butyldiphenyl one **1e** (Table 1, entries 4 and 5). We do not have any explanation for this last behaviour.

Table 1. Deprotection of Ethers **1**.



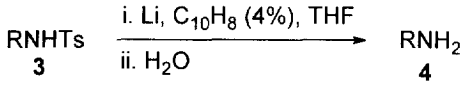
	Compound **1**			Reaction Conditions		Product **2**	
Entry	No.	R	X	T (°C)	t (h)	No.	Yield (%)[a]
1	**1a**	Ph	CH_2=$CHCH_2$	-78	1	**2a**	51 (90)
2	**1b**	Ph	$PhCH_2$	-78	3.5	**2a**	68 (91)
3	**1c**	Ph	$CH_3(CH_2)_{24}$	-78 to 20	12	**2a**	0[b]
4	**1d**	$CH_3(CH_2)_{21}$	$PhSiMe_2$	0	4	**2d**	80
5	**1e**	$CH_3(CH_2)_{21}$	Ph_2SiBu^t	20	12	**2d**	0[b]
6	**1f**		CH_2=$CHCH_2$	-78 to 20	12	**2f**	(25)
7	**1g**	$CH_3(CH_2)_{21}$	$PhCH_2$	-78 to 20	2	**2d**	71
8	**1h**		$PhCH_2$	-78 to -10	5	**2h**	97
9	**1i**		$PhCH_2$	-78 to -10	5	**2f**	99

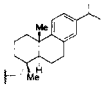
[a] Crude isolated yield (> 90% pure by GLC or/and 300 MHz ^{1}H NMR) based on the starting materials **1**; in parenthesis GLC yields. [b] Starting material **1** was quantitatively recovered.

We then studied the deprotection of different *N*-substituted sulfonamides to give the corresponding amines using the same methodology as for ethers **1**. Thus, tosylamides **3** were easily transformed into the corresponding amines **4** when submitted to reductive cleavage using lithium and a catalytic amount of

naphthalene in THF at low temperature followed by hydrolysis (Table 2). When the same procedure was applied to mesylamides [*N*-cyclohexyl (**3f**) or *N*-benzyl (**3g**) derivatives] the reaction failed. It is worthy to note that the reaction with tosylamide **3** worked nicely for aliphatic compounds **3a**, **3e** (Table 2, entries 1 and 5) as well as for the aromatic one **3d** (Table 2, entry 4), and that the process is chemoselective, so benzylic derivatives **3b** and **3c** yielded the corresponding amine without any cleavage of the benzylic moiety (Table 2, entries 2 and 3).[9]

Table 2. Deprotection of *N*-Substituted Tosylamides **3**



	Compound **3**		Reaction Conditions		Product **4**	
Entry	No.	R	T (°C)	t (h)	No.	Yield (%)[a]
1	**3a**	$CH_3(CH_2)_7$	-78 to 20	12	**4a**	95
2	**3b**	$PhCH_2$	-78	2	**4b**	81
3	**3c**	PhCHMe	-78 to 20	3	**4c**	65
4	**3d**	2,6-$Me_2C_6H_3$	-78 to 20	12	**4d**	99
5	**3e**		-78	2	**4e**	99

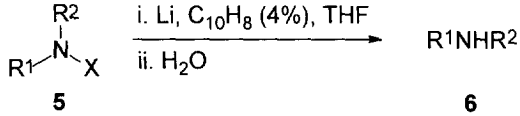
[a] Crude isolated yield (> 95% pure by GLC or/and 300 MHz ^{1}H NMR) based on the starting materials **3**.

N,*N*-Disubstituted sulfonamides or carboxamides **5** behave in a different manner to the corresponding *N*-substituted ones **3**. In this case, and applying the same protocol as before, the mesyl derivatives **5a**, **5c**, **5f** and **5g** could be easily deprotected (Table 3, entries 1, 3, 6 and 7): in all cases the expected amines **6** were isolated. However, for the allyl derivative **5h**, allylic cleavage was preferred to the mesyl one, so sulfonamide **6h** was the only product isolated after work-up. This behaviour contrasts with that observed for the benzylic derivative **5a**, in which demesylation was achieved in the presence of the benzylic group (Table 3, entry 1). Tosyl derivatives **5b**, **5d** and **5i** behave similarly to the corresponding mesyl ones (Table 3, entries 2, 4 and 9). Finally, while the reaction of the aliphatic carboxamide **5e** failed, the process with the benzylic one **5j** or **5k** (a carbamate derivative) worked with variable yield (Table 3, entries 5, 10 and 11).

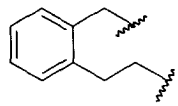
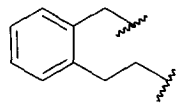
In the last part of this study, we considered different disubstituted carboxamides **7**, which were submitted to the above described methodology, using naphthalene as electron carrier, isolating the corresponding monosubstituted amides **8** (Table 4).[10] Some interesting features about this reaction are: (a) the desulfonylation reaction can be carried out with enolizable amides such as compounds **7a** and **7b** (Table 4,

entries 1 and 2); as expected, when no α-hydrogens are present the reaction worked nicely (Table 4, entries 4, 7, 8 and 10). (b) Sulfonyl groups are preferentially cleaved compared to benzyl or allyl ones (Table 4, entries 1, 2, 4, 7, 8 and 10). (c) *N*-Benzylic amides are debenzylated only if they are not enolizable (Table 4, entries 3, 5, 9 and 11), the only exception being *N*-benzyl-*N*-methylformamide (**7l**); for instance, the reaction failed for *N*-benzyl-*N*-methylacetamide (**7m**). (d) When both substituents at the nitrogen atom are benzyl and allyl, the first one is preferentially cleaved, although with low yield (Table 4, entry 5). (e) Finally, in the case of the glycine ester derivative **7f**, the loss of the corresponding stabilised enolate occurred instead of the benzylic cleavage, this behaviour being in principle unexpected (Table 4, entry 6).

Table 3. Deprotection of *N,N*-Disubstituted Amides **5**

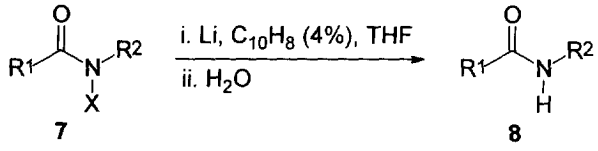


5 **6**

					Reaction Conditions			
	Compound **5**						Product **6**	
Entry	No.	R^1	R^2	X	T (°C)	t (h)	No.	Yield (%)[a]
1	**5a**	Me	$PhCH_2$	Ms	-30 to 20	2	**6a**	30
2	**5b**	Me	$PhCH_2$	Ts	-78 to 20	12	**6a**	31
3	**5c**	Bu^n	Bu^n	Ms	20	12	**6b**	75
4	**5d**	Bu^n	Bu^n	Ts	-78	2	**6b**	68
5	**5e**	Bu^n	Bu^n	Bu^tOCO	-78 to 20	12	**6b**	0[b]
6	**5f**	$Me(CH_2)_7$	$Me(CH_2)_7$	Ms	20	24	**6f**	77
7	**5g**	$Me(CH_2)_5CHEt$	$Me(CH_2)_5CHEt$	Ms	20	48	**6g**	75
8	**5h**	$Me(CH_2)_7$	Ms	$CH_2{=}CHCH_2$	-78 to 20	12	**6h**	99
9	**5i**	$PhCH_2$	EtO_2CCH_2	Ts	-78	2	**6i**	21
10	**5j**			Bu^tCO	-78 to 20	4	**6j**	30
11	**5k**			Bu^tOCO	-78 to 20	4	**6j**	84

[a] Crude isolated yield (> 90% pure by GLC or/and 300 MHz ^{1}H NMR) based on the starting materials **5**. [b] Starting material **5e** was quantitatively recovered.

Table 4. Deprotection of Carboxamides 7.

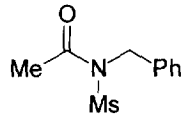


7 **8**

	Compound 7				Reaction Conditions		Product 8	
Entry	No.	R^1	R^2	X	T (°C)	t (h)	No.	Yield (%)[a]
1	**7a**	Me	$PhCH_2$	Ts	-78	2	**8a**	97
2	**7b**	Pr^i	$PhCH_2$	Ms	-78 to 20	2	**8b**	99
3	**7c**	Bu^t	Me	PhCHMe	-78 to 20	12	**8c**	33
4	**7d**	Bu^t	Me	Ts	-78 to 20	4	**8c**	98
5	**7e**	Bu^t	CH_2=$CHCH_2$	$PhCH_2$	-78	3	**8e**	22
6	**7f**	Bu^t	$PhCH_2$	EtO_2CCH_2	-78 to 20	12	**8f**	53
7	**7g**	Bu^t	$PhCH_2$	Ms	-78	1.5	**8f**	99
8	**7h**	Bu^t	$PhCH_2$	Ts	-78	2.5	**8f**	99
9	**7i**	Bu^tO	Me	$PhCH_2$	-78 to 20	12	**8i**	98
10	**7j**	Bu^tO	$PhCH_2$	Ts	-78	2	**8j**	99
11	**7k**	Pr^i_2N	Me	$PhCH_2$	-78 to 20	12	**8k**	86

[a] Crude isolated yield (> 90% pure by GLC or/and 300 MHz ^{1}H NMR) based on the starting materials 7.

Compared to the behaviour of compound **7a** (Table 4, entry 1), the corresponding mesyl derivative **7n** gave a mixture of compounds **8a** and **3g** (3 : 2 molar ratio) in 90% isolated yield, when it was submitted to the procedure described above.



7n

As a conclusion, we report here a new methodology for deprotection of alcohol and amide derivatives based on a naphthalene-catalysed lithiation using lithium powder, which permits carring out the process under very mild reaction conditions and, in many cases, in a chemoselective manner.

EXPERIMENTAL SECTION

General.- For general information, see reference 11. All starting alcohols or amines were commercially available (Acros, Aldrich, Fluka) and were used as received. Compounds **1a**,**b**, **2**, **4** and **6a**,**b**,**f**,**g**,**j**, which are commercially available, were fully characterised by comparison of their physical (GLC) and spectroscopic (300 MHz ^{1}H NMR and MS) data with authentic samples.

Preparation of Pentacosyl Phenyl Ether (**1c**)[12].- A mixture of phenol (10 mmol, 0.92 ml), pentacosyl bromide (10 mmol, 3.0 g), potassium carbonate (12 mmol, 1.46 g) and acetone (20 ml) was refluxed for 24 h. Then, water (10 ml) was added and the mixture was extracted with ethyl acetate (2 x 20 ml), washed with 2N NaOH solution (2 x 10 ml) and dried over anhydrous Na_2SO_4. Solvents were evaporated (15 Torr) to give the pure title compound: Yield 80%; t_r 16.64, R_f 0.50 (hexane); mp 41-42°C (ethyl acetate); ν (melted) 3060, 3039, 1601, 1473 cm^{-1} (HC=C); δ_H 0.88 (3H, t, *J*=6.6, CH_3), 1.15-1.50, 1.65-1.85 [44 and 2H, respectively, 2m, $(CH_2)_{23}CH_3$], 3.93 (2H, t, *J*=6.6, CH_2O), 6.85-6.95, 7.20-7.30 (3 and 2H, respectively, 2m, Ph); δ_C 14.1 (CH_3), 22.7, 26.05, 29.3, 29.35, 29.4, 29.65, 29.7, 31.95 [$(CH_2)_{23}CH_3$], 67.8 (CH_2O), 114.45, 120.4, 129.35, 159.0 (Ph); *m/z* 304 (M^+-140, 8%), 95 (12), 94 (100), 69 (11), 57 (23), 55 (29), 43 (41) (Found: C, 81.25; H, 11.95. $C_{31}H_{56}O{\cdot}3/4\ H_2O$ requires: C, 81.24; H, 12.65).

Preparation of Starting O-*Silyl Alcohols* **1d** *and* **1e**. *General Procedure*[13].- To a solution of the corresponding alcohol (10 mmol) and triethylamine (10 mmol, 1.4 ml) in THF (20 ml) was dropwise added the corresponding chlorosilane (10 mmol) at 0°C. After 1h stirrring at temperatures ranging between 0 and 20°C the resulting mixture was hydrolysed with water (10 ml) and extracted with ether (2 x 20 ml). The organic layer was washed with water (10 ml) and dried over anhydrous Na_2SO_4. Solvents were evaporated (15 Torr) and the resulting residue containing the title compounds **1d** or **1e** was submitted to lithiation without further purification. Yields, physical, analytical and spectroscopic data follow.

Docosyloxydimethylphenylsilane (**1d**): Yield 85%; t_r 24.14, R_f 0.26 (hexane); ν (film) 3069, 3050 (HC=C), 1251 ($SiCH_3$), 1117 cm^{-1} (SiO); δ_H 0.37 (6H, s, 2xCH_3Si), 0.85 (3H, t, *J*=6.7, CH_2CH_3), 1.15-1.60 [40H, m, $(CH_2)_{20}CH_3$], 3.55-3.65 (2H, m, CH_2O), 7.30-7.40, 7.55-7.60 (3 and 2H, respectively, 2m, Ph); δ_C -2.0 (2xCH_3Si), 14.05 (CH_3CH_2), 22.65, 25.7, 29.35, 29.4, 29.55, 29.65, 30.8, 31.9, 32.55 [$(CH_2)_{20}CH_3$], 63.15 (CH_2O), 127.7, 129.45, 133.4, 138.0 (Ph); *m/z* 448 (M^++2, 1%), 447 (M^++1, 6), 446 (M^+, 23), 445 (64), 382 (12), 367 (29), 143 (23), 138 (12), 137 (90), 135 (41), 129 (21), 123 (13), 121 (15), 97 (21), 91 (12), 85 (12), 83 (26), 75 (28), 71 (23), 69 (31), 61 (14), 57 (65), 55 (51), 45 (10), 44 (11), 43 (100).

Docosyloxy(tert-*butyldiphenyl)silane* (**1e**): Yield 85%; t_r 13.60, R_f 0.39 (hexane/ethyl acetate: 6/1); mp 63-64°C (ethyl acetate); ν (melted) 3071, 3048 (HC=C), 1113 cm^{-1}(SiO); δ_H 0.85-0.95 (3H, m, CH_3CH_2), 1.25 [9H, s, $(CH_3)_3C$], 1.20-1.60 [40H, m, $(CH_2)_{20}CH_3$], 3.60 (2H, t, *J*=6.7, CH_2O), 7.30-7.40, 7.65-7.75 (5 and 5H, respectively, 2m, Ph); δ_C 14.1 (CH_3CH_2), 19.0 [$C(CH_3)_3$], 22.65, 25.7, 29.35, 29.4, 29.6, 29.65, 29.7 (12C), 31.9, 32.75 [$(CH_2)_{20}CH_3$], 26.5 [$C(CH_3)_3$], 63.05 (CH_2O), 127.65 (2C), 129.55 (2C), 134.8 (2C), 135.25 (2C) (Ph); *m/z* 507 (M^+-57, <1%), 308 (12), 199 (18), 112 (10), 111 (29), 98 (14), 97 (73), 96 (14), 85 (21), 84 (21), 83 (81), 82 (32), 81 (10), 71 (43), 70 (29), 69 (77), 68 (28), 67 (18), 57 (80), 56 (34), 55 (95), 43 (100), 42 (22), 41 (68) (Found: C, 77.97; H, 11.28. $C_{38}H_{64}OSi{\cdot}H_2O$ requires: C, 78.28; H, 11.41).

Preparation of Starting Protected Alcohols **1f-i**. *General Procedure*[14].- To a suspension of sodium hydride (12 mmol, 0.47 g) in THF (10 ml) was slowly added (*ca.* 10 min) a solution of the corresponding alcohol (10 mmol) in THF (5 ml) at room temperature. Stirring was continued for 30 min at the same temperature. Then, the corresponding bromide (12 mmol) was slowly added and the reaction was stirred for 6 h (in the cases **1g** and **1i** the mixture was refluxed for 12h). Then, water (5 ml) was added and the mixture was extracted with ether (2 x 20 ml). The organic layer was washed with water (10 ml) and dried over anhydrous Na_2SO_4. Solvents were evaporated (15 Torr) and the resulting residue containing the title compounds **1f-i** was submitted to lithiation without further purification. Yields, physical, analytical and spectroscopic data, as well as literature references for known compounds, follow.

(1S,2R,4R)-2-Allyloxy-1-isopropyl-4-methylcyclohexane (**1f**):[15] Yield 80%; t_r 8.24, R_f 0.42 (hexane); ν (film) 3095, 1652, 1456 (HC=C), 1086 cm^{-1} (CO); δ_H 0.77 (3H, d, *J*=7.0, CH_3CH), 0.80-1.00 (9H, m with 2d at 0.89, 0.92, *J*=7.0, 2xCH_3CH, 3x*CH*H ring), 1.15-1.40, 1.50-1.70, 2.00-2.15, 2.20-2.35 (2, 2, 1 and 1H, respectively, 4m, 3x*CH*H ring, 2x*CH*CH_3, CHCO), 3.08 (1H, td, *J*=10.5, 4.1, CHO), 3.80-3.95, 4.05-4.20 (2H, 2m, CH_2O), 5.10-5.30 (2H, m, CH_2=CH), 5.85-6.05 (1H, m, *CH*CH_2); δ_C 16.2, 20.95, 22.3 (3xCH_3), 23.35, 34.55, 40.45 (3xCH_2 ring), 25.5, 31.5, 48.25 (3xCH ring), 69.5 (CH_2O), 78.65 (CHO), 116.25, 135.7 (CH=CH_2); *m/z* 181 (M^+-15, 1%), 138 (37), 123 (11), 111 (68), 95 (33), 83 (33), 82 (23), 81 (61), 80 (13), 69 (100), 67 (23), 57 (32), 56 (11), 55 (81), 43 (57), 42 (10).

1-Docosyloxymethylbenzene (**1g**): Yield 80%; t_r 23.70, R_f 0.20 (hexane); mp 39-40°C (ethyl acetate); ν (melted) 3086, 3062, 3028 (HC=C), 1101 cm^{-1} (CO); δ_H 0.88 (3H, t, *J*=6.6, CH_3), 1.15-1.40, 1.50-1.60 [38 and 2H, respectively, 2m, $(CH_2)_{20}CH_3$], 3.46 (2H, t, *J*=6.6, CH_2CH_2O), 4.49 (2H, s, CH_2Ph), 7.20-7.35 (5H, m, Ph); δ_C 14.1 (CH_3), 22.7, 26.2, 29.35, 29.5, 29.6, 29.7, 29.75, 31.9 [$(CH_2)_{20}CH_3$], 70.5, 72.85 (2xCH_2O), 127.4, 127.6, 128.3, 138.7 (Ph); *m/z* 416 (M^+, <1%), 111 (12), 97 (26), 92 (100), 91 (99), 85 (13), 83 (26), 82 (11), 71 (24), 69 (24), 57 (52), 55 (32), 43 (57) (Found: C, 83.85; H, 12.72. $C_{29}H_{52}O$ requires: C, 83.58; H, 12.58).

[(2E)-3,7-Dimethyl-2,6-octadienyloxy]methylbenzene (**1h**):[16] Yield 70%; t_r 12.92, R_f 0.17 (hexane); ν (film) 3087, 3063, 3029, 1669, 1496 (HC=C), 1069 cm^{-1} (CO); δ_H 1.60, 1.64, 1.68 (3, 3 and 3H, respectively, 3s. 3xCH_3), 2.00-2.15 (4H, m, CH_2CH_2), 4.03 (2H, d, *J*=7.0, $CHCH_2O$), 4.49 (2H, s, CH_2Ph), 5.05-5.15, 5.35-5.45 (1 and 1H, respectively, 2m, 2xCH=C), 7.20-7.40 (5H, m, Ph); δ_C 16.4, 17.6, 25.65 (3xCH_3), 26.3, 39.55 (CH_2CH_2), 66.5, 71.85 (2xCH_2O), 120.8, 123.95, 127.45, 127.75, 128.3, 131.55, 138.55, 140.3 (Ph, CH=C); *m/z* 244 (M^+, <1%), 136 (12), 123 (25), 121 (14), 108 (28), 107 (31), 95 (24), 94 (13), 93 (67), 92 (37), 91 (100), 81 (17), 80 (28), 79 (55), 77 (43), 70 (12), 69 (79), 68 (42), 67 (33), 65 (28), 55 (16), 53 (27), 51 (23), 43 (24).

(1S,2R,4R)-2-Benzyloxy-1-isopropyl-4-methylcyclohexane (**1i**):[17] Yield 96%; t_r 12.56, R_f 0.34 (hexane); ν (film) 3089, 3064, 3030, 1497 (HC=C), 1109 cm^{-1} (CO); δ_H 0.71 (3H, d, *J*=6.7, CH_3CH), 0.80-1.05 (9H, m with 2d at 0.89, 0.93, *J*=7.3, 6.4, respectively, 2xCH_3CH, 3x*CH*H ring), 1.15-1.40, 1.55-1.65, 2.10-2.20, 2.25-2.40 (2, 2, 1 and 1H, respectively, 4m, 3x*CH*H ring, 2x*CH*CH_3, CHCO), 3.16 (1H, td, *J*=10.5, 4.2, CHO), 4.38, 4.64 (1 and 1H, respectively, 2d, *J*=11.6, CH_2O), 7.20-7.35 (5H, m, Ph); δ_C 15.95, 20.95, 22.35 (3xCH_3), 23.15, 34.5, 40.25 (3xCH_2 ring), 25.4, 31.5, 48.25 (3xCH ring), 70.35 (CH_2O), 78.65 (CHO), 127.3, 127.75, 128.2, 139.1 (Ph); *m/z* 221 (M^+-25, 2%), 155 (13), 138 (31), 137 (12), 95 (25), 92 (25), 91 (100), 81 (52), 69 (39), 67 (11), 65 (20), 57 (17), 55 (37), 43 (34).

Preparation of Starting Amides **3**, **5a-d**, **5f**, **5g**, **5j**,**7f**, **7k** *and* **7m**. *General Procedure*[18].- To a solution of the corresponding amine (10 mmol) [in the case of compound **7f** the corresponding amine was prepared according to literature procedure[19] from a mixture of benzyl amine (10 mmol, 1.1 ml), ethyl bromoacetate (12 mmol, 1.4 ml) and K_2CO_3 (20 mmol, 2.12 g) stirred under argon at room temperature for 12h] and triethylamine (12 mmol, 1.68 ml) in CH_2Cl_2 (20 ml) was dropwise added the corresponding acid chloride at 0°C. After 2h stirring at 20°C the resulting mixture was hydrolysed with water (10 ml), extracted with ethyl acetate (2 x 20 ml) and sucessively washed with 2N HCl solution (2 x 20 ml) and saturated $NaHCO_3$ (2 x 20 ml). The organic layer was dried over anhydrous Na_2SO_4. Solvents were evaporated (15 Torr) and the resulting residue containing the title compounds was submitted to lithiation without further purification. Yields, physical, analytical and spectroscopic data, as well as literature references for known compounds, follow.

N-*Octyl-4-methylbenzenesulfonamide* (**3a**):[20] Yield 92%; t_r 16.21, R_f 0.56 (hexane/ethyl acetate: 2/1); mp 53-54°C (ethyl acetate) (lit.: mp 53-54°C); δ_C 13.95 (CH_3CH_2), 21.4 (CH_3Ar), 22.5, 26.4, 28.9, 29.0, 29.4, 31.6 [$(CH_2)_6CH_3$], 43.1 (CH_2N), 127.0, 129.55, 136.95, 143.15 (ArC); *m/z* 284 (M^++1, <1%), 283 (M^+, 2), 184 (88), 172 (34), 156 (10), 155 (100), 128 (40), 92 (12), 91 (88), 69 (19), 65 (34), 55 (16), 44 (10), 43 (23).

N-*Benzyl-4-methylbenzenesulfonamide* (**3b**):[21] Yield 88%; t_r 16.18, R_f 0.43 (hexane/ethyl acetate: 2/1); mp 113-114°C (ethyl acetate) (lit.: mp 116-117°C); ν (melted) 3268 (NH), 3089, 3065, 3033, 1598, 1495 (HC=C), 1324, 1310, 1162 cm^{-1} (SO); δ_H 2.41 (3H, s, CH_3), 4.08 (2H, d, *J*=5.5, CH_2), 5.05 (1H, br s, NH), 7.15-7.30, 7.73 (7 and 2H, respectively, m and d with *J*=7.9, ArH); δ_C 21.45 (CH_3), 47.1 (CH_2), 127.05,

127.7, 127.75, 128.55, 129.6, 136.25, 136.75, 143.35 (ArC); *m/z* 263 (M^++2, <1%), 262 (M^++1, 4), 261 (M^+, 13), 260 (74), 155 (66), 120 (72), 105 (26), 104 (19), 92 (16), 91 (100), 79 (14), 78 (11), 77 (32), 65 (43), 51 (23), 42 (39).

N-*(1-Phenylethyl)-4-methylbenzenesulfonamide* (**3c**):[22] Yield 95%; t_r 15.88, R_f 0.54 (hexane/ethyl acetate: 2/1); mp 81-82°C (ethyl acetate) (lit.: mp 101-102°C for the corresponding enantiomerically pure compound); *m/z* 260 (M^+-15, 63%), 155 (57), 120 (61), 105 (23), 104 (18), 92 (14), 91 (100), 79 (13), 78 (11), 77 (30), 65 (40), 51 (22), 42 (35).

N-*2,6-Dimethylphenyl-4-methylbenzenesulfonamide* (**3d**):[23] Yield 75%; t_r 15.63, R_f 0.54 (hexane/ethyl acetate: 2/1); mp 125-126°C (ethyl acetate) (lit.: mp 135-137°C); ν (melted) 3268 (NH), 1596, 1472 (HC=C), 1325, 1158 cm^{-1} (SO); δ_H 2.05 [6H, s, $(CH_3)_2Ar$], 2.41 (3H, s, $CH_3C_6H_4$), 6.35 (1H, br s, NH), 7.00-7.10 (3H, m, C_6H_3), 7.23, 7.60 (2 and 2H, respectively, 2d, *J*=7.6, C_6H_4S); δ_C 18.65 [$(CH_3)_2Ar$], 21.5 ($CH_3C_6H_4$), 127.1, 127.65, 128.65, 129.5, 132.55, 137.7 (2C), 143.55 (ArC); *m/z* 277 (M^++2, 2%), 276 (M^++1, 6), 275 (M^+, 31), 121 (17), 120 (100), 91 (34), 77 (23), 65 (20).

N-*Dehydroabietyl-4-methylbenzenesulfonamide* (**3e**):[24] Yield 70%; R_f 0.63 (hexane/ethyl acetate: 2/1); mp 152-155°C (ethyl acetate) (lit.: mp 152-155°C); δ_C 18.45, 21.45, 23.9, 23.95, 25.15 (5xCH_3), 18.5, 18.6, 29.8, 35.65, 38.1, 53.7 (6xCH_2), 36.85, 37.3 (2xCH_2CCH_3), 33.35, 44.7 ($CHCH_2$, $CHCH_3$), 123.7, 124.05, 126.75, 126.9, 129.65, 134.6, 137.05, 143.15, 145.45, 146.9 (ArC); *m/z* 441 (M^++2, 2%), 440 (M^++1, 4), 439 (M^+, 13), 259 (15), 257 (14), 255 (30), 254 (10), 253 (37), 239 (16), 185 (23), 184 (20), 177 (10), 174 (12), 173 (100), 172 (10), 155 (32), 91 (40).

N-*Cyclohexylmethanesulfonamide* (**3f**):[25] Yield 70%; t_r 10.29, R_f 0.25 (hexane/ethyl acetate: 2/1); mp 103-104°C (ethyl acetate); ν (melted) 3260 (NH), 1333, 1317, 1153 cm^{-1} (SO).

N-*Benzylmethanesulfonamide* (**3g**):[26] Yield 91%; t_r 11.51, R_f 0.20 (hexane/ethyl acetate: 2/1); mp 63-64°C (ethyl acetate); ν (melted) 3237 (NH), 3088, 3064, 3021, 1635, 1496 (HC=C), 1306, 1156 cm^{-1} (SO); δ_H 2.87 (3H, s, CH_3), 4.33 (2H, d, *J*=6.1, CH_2), 4.63 (1H, br s, NH), 7.30-7.40 (5H, m, Ph); δ_C 41.15 (CH_3), 47.2 (CH_2), 127.9, 128.15, 128.95, 136.6 (Ph); *m/z* 185 (M^+, <1%), 106 (86), 105 (19), 104 (45), 91 (29), 81 (13), 79 (34), 78 (15), 77 (28), 65 (15), 51 (25), 50 (10), 44 (100), 43 (28).

N-*Benzyl*-N-*methylmethanesulfonamide* (**5a**):[27] Yield 95%; t_r 11.25, R_f 0.26 (hexane/ethyl acetate: 2/1); ν (film) 3087, 3064, 3030, 1605, 1587, 1496 (HC=C), 1366, 1329, 1151 cm^{-1} (SO); δ_H 2.76 (3H, s, CH_3N), 2.83 (3H, s, CH_3S), 4.30 (2H, s, CH_2), 7.25-7.45 (5H, m, Ph); δ_C 30.0 (CH_3N), 35.55 (CH_3S), 53.55 (CH_2N), 127.7, 128.05, 128.45, 135.35 (Ph); *m/z* 199 (M^+, 1%), 120 (37), 119 (41), 118 (90), 92 (11), 91 (100), 65 (22), 51 (12), 44 (30), 42 (57).

N-*Benzyl*-N-*methyl-4-methylbenzenesulfonamide* (**5b**):[28] Yield 95%; t_r 15.05, R_f 0.57 (hexane/ethyl acetate: 2/1); mp 94-95°C (ethyl acetate); ν (melted) 1652, 1595 (HC=C), 1340, 1162 cm^{-1} (SO); δ_H 2.44 (3H, s, CH_3Ar), 2.57 (3H, s, CH_3N), 4.11 (2H, s, CH_2), 7.30-7.40, 7.72 (7 and 2H, respectively, m and d with *J*=8.2, ArH); δ_C 21.45 (CH_3Ar), 34.25 (CH_3N), 54.05 (CH_2), 127.4, 127.75, 128.25, 128.5, 129.65, 134.15, 135.6, 143.4 (ArC); *m/z* 275 (M^+, 2%), 155 (12), 121 (11), 120 (100), 119 (24), 118 (75), 92 (17), 91 (100), 77 (13), 65 (45), 51 (13), 42 (63).

N,N-*Dibutylmethanesulfonamide* (**5c**):[29] Yield 92%; t_r 9.20, R_f 0.26 (hexane/ethyl acetate: 4/1); ν (film) 1332, 1144 cm^{-1} (SO); δ_H 0.94 (6H, t, *J*=7.3, 2xCH_3CH_2), 1.25-1.40, 1.55-1.60 [4 and 4H, respectively, 2m, 2x$(CH_2)_2CH_3$], 2.82 (3H, s, CH_3S), 3.10-3.20 (4H, m, 2xCH_2N); δ_C 13.45 (2xCH_3CH_2), 19.65 (2xCH_2CH_3), 30.6 (2xCH_2CH_2N), 37.8 (CH_3S), 47.35 (2xCH_2N); *m/z* 208 (M^++1, <1%), 208 (M^+, 4), 164 (39), 122 (100), 108 (30), 57 (31), 56 (13), 44 (38), 43 (21), 42 (40).

N,N-*Dibutyl-4-methylbenzenesulfonamide* (**5d**):[30] Yield 90%; t_r 14.77, R_f 0.43 (hexane/ethyl acetate: 4/1); ν (film) 1339, 1156 cm^{-1} (SO); δ_H 0.89 (6H, t, *J*=7.3, 2xCH_3CH_2), 1.20-1.35, 1.45-1.55 [4 and 4H, respectively, 2m, 2x$(CH_2)_2CH_3$], 2.40 (3H, s, CH_3Ar), 3.10 (4H, t, *J*=7.6, 2xCH_2N), 7.28, 7.68 (2 and 2H, respectively, 2d, *J*=7.6, ArH); δ_C 13.55 (2xCH_3CH_2), 19.75 (2xCH_2CH_3), 21.25 (CH_3Ar), 30.65 (2xCH_2CH_2N), 47.85 (2xCH_2N), 126.9, 129.35, 136.95, 142.7 (ArC); *m/z* 284 (M^++1, 1%), 283 (M^+, 4), 241 (15), 240 (100), 198 (58), 155 (91), 92 (12), 91 (92), 65 (31), 57 (12), 44 (12), 43 (20), 42 (41).

N,N-*Dioctylmethanesulfonamide* (**5f**):[31] Yield 96%; t_r 16.14, R_f 0.68 (hexane/ethyl acetate: 2/1); ν (film) 1335, 1149 cm^{-1} (SO); δ_H 0.88 (6H, t, *J*=6.6, 2xCH_3CH_2), 1.20-1.40, 1.50-1.60 [20 and 4H, respectively, 2m, 2x$(CH_2)_6CH_3$], 2.81 (3H, s, CH_3S), 3.15 (4H, t, *J*=7.6, 2xCH_2N); δ_C 13.9 (2xCH_3CH_2), 22.45 (2C), 26.55

(2C), 28.6 (2C), 29.05 (4C), 31.6 (2C), [2x(CH_2)$_6$$CH_3$], 38.0 ($CH_3S$), 47.7 (2x$CH_2N$); *m/z* 319 ($M^+$, 1%), 220 (46), 122 (100), 84 (15), 71 (11), 69 (24), 57 (33), 55 (24), 44 (38), 43 (48), 42 (26).

N,N-*Di-(2-ethylhexyl)methanesulfonamide* (**5g**):[17] Yield 90%; t_r 14.85, R_f 0.84 (hexane/ethyl acetate: 2/1); ν (film) 1377, 1334, 1151 cm^{-1} (SO); δ_H 0.85-0.95 (12H, m, 4xCH_3CH_2), 1.20-1.60, [18H, m, 2x(CH_2)$_3$$CH_3$, 2x$CHCH_2$], 2.80 (3H, s, CH_3S), 2.85-3.10 (4H, m, 2xCH_2N); δ_C 10.3 (2C), 13.85 (2C) (4xCH_3), 22.8 (2C), 23.3 (2C), 28.4 (2C), 30.05 (2C) [2x(CH_2)$_3$$CH_3$, 2x$CH_3CH_2CH$], 36.85, 36.9 (2xCH), 37.4 (CH_3S), 52.55, 52.6 (2xCH_2N); *m/z* 220 (M^+-99, 26%), 122 (100), 108 (12), 71 (23), 69 (17), 57 (45), 55 (21), 44 (24), 43 (47), 42 (31).

2-Pivaloyl-1,2,3,4-tetrahydroisoquinoline (**5j**):[32] Yield 96%; t_r 13.42, R_f 0.54 (hexane/ethyl acetate: 2/1); mp 63-64°C (ethyl acetate) (lit.: mp 65°C); δ_C 28.2 [(CH_3)$_3$C], 38.85 [C(CH_3)$_3$], 38.7, 43.3 (CH_2CH_2), 47.3 (NCH_2Ar), 126.2 (2C), 126.4, 128.55, 133.45, 134.25 (ArC), 176.55 (CO).

N-*Benzyl*-N-*(ethoxycarbonyl)methyl-2,2-dimethylpropanamide* (**7f**):[17] Yield 50%; t_r 14.40, R_f 0.35 (hexane/ethyl acetate: 6/1); ν (film) 3065, 3030 (HC=C), 1747, 1636 (C=O), 1178, 1028 cm^{-1} (CO); δ_H 1.25 (3H, t, *J*=7.1, CH_3CH_2), 1.35 [9H, s, (CH_3)$_3$C], 3.90 (2H, s, CH_2CO), 4.17 (2H, s, CH_2CH_3), 4.82 (2H, s, CH_2Ph), 7.20-7.40 (5H, m, Ph); δ_C 14.0 (CH_3CH_2), 28.3 [(CH_3)$_3$C], 38.8 [C(CH_3)$_3$], 48.55 (CH_2CO), 60.85 (CH_2Ph), 126.9, 127.55, 128.75, 136.45 (Ph), 169.45, 178.4 (2xC=O); *m/z* 232 (M^+-51, 3%), 193 (12), 192 (92), 120 (11), 92 (12), 91 (100), 85 (19), 65 (14), 57 (98), 42 (11).

N-*Benzyl*-N-*methyl*-N',N'-*diisopropylurea* (**7k**): Yield 90%; t_r 13.09, R_f 0.65 (hexane/ethyl acetate: 2/1); ν (film) 3086, 3063, 3027, 1449 (HC=C), 1646 cm^{-1} (C=O); δ_H 1.28, 1.30 [6 and 6H, respectively, 2s, 2x(CH_3)$_2$CH], 2.63 (3H, s, CH_3N), 3.55-3.70 [2H, m, 2xCH(CH_3)$_2$], 4.25 (2H, s, CH_2), 7.20-7.35 (5H, m, Ph); δ_C 21.55 [2x(CH_3)$_2$CH], 36.8 (CH_3N), 47.3 [2xCH(CH_3)$_2$], 54.55 (CH_2), 126.8, 127.4, 128.3, 138.25 (Ph), 164.0 (C=O); *m/z* 249 (M^++1, 4%), 248 (M^+, 19), 233 (22), 205 (26), 148 (31), 121 (11), 119 (67), 117 (15), 100 (63), 92 (34), 91 (100), 86 (60), 84 (40), 65 (33), 58 (29), 44 (35), 43 (54), 42 (45), 41 (42) (Found M^+, 248.1889. $C_{15}H_{24}N_2O$ requires M, 248.1889).

N-*Benzyl*-N-*methylacetamide* (**7m**):[33] Yield 95%; t_r 9.80, R_f 0.29 (hexane/ethyl acetate: 2/1); ν (film) 3089, 3064, 3033 (HC=C), 1698 cm^{-1} (C=O); δ_H 2.14 (3H, s, CH_3CO), 2.90, 2.92 (3H, 2s, CH_3N), 4.51, 4.57 (2H, 2s, CH_2), 7.10-7.40 (5H, m, Ph); δ_C 21.15, 21.55 (CH_3CO), 33.45, 35.25 (CH_3N), 50.3, 53.95 (CH_2), 126.05, 127.05, 127.35, 127.7, 128.3, 128.7, 136.3, 137.1 (Ph), 170.5, 170.8 (CO); *m/z* 165 (M^++2, 1%), 164 (M^++1, 12), 163 (M^+, 100), 162 (15), 120 (67), 106 (97), 92 (14), 91 (82), 79 (15), 77 (14), 72 (20), 65 (36), 63 (10), 51 (21), 44 (89), 43 (89), 42 (76).

Preparation of Starting Boc-Derivatives **5e**, **5k** *and* **7i**. *General Procedure*[34].- To a solution of the corresponding amine (1 mmol) in acetonitrile (6 ml) was added di-*tert*-butyl dicarbonate (1.5 mmol, 0.34 g) and 4-(dimethylamino)pyridine (0.36 mmol, 0.045 g). The reaction mixture was stirred for 12h and the solvent was evaporated (15 Torr). To the resulting residue was added water (10 ml) and was extracted with ethyl acetate (2 x 20 ml). The organic layer was successively washed with 1N HCl, saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4 and evaporated (15 Torr) to provide the pure title crude compounds. Yields, physical, analytical and spectroscopic data, as well as literature references for known compounds, follow.

tert-*Butyl* N,N-*Dibutylcarbamate* (**5e**): Yield 80%; t_r 9.48, R_f 0.54 (hexane/ethyl acetate: 4/1); ν (film) 1696 (C=O), 1156 cm^{-1} (CO); δ_H 0.90-0.95 (6H, m, 2xCH_3CH_2), 1.20-1.40 (4H, m, 2xCH_2CH_3), 1.45-1.55 [13H, m, 2xCH_2CH_2N, (CH_3)$_3$C], 3.15 (4H, br s, 2xCH_2N); δ_C 13.7 (2xCH_3CH_2), 19.9 (2xCH_2CH_3), 28.3 [(CH_3)$_3$C], 30.5 (2xCH_2CH_2N), 46.6 (2xCH_2N), 78.65 (2xCO), 155.5 (C=O); *m/z* 230 (M^++1, 1%), 229 (M^+, 5), 173 (10), 156 (12), 130 (96), 88 (64), 86 (91), 58 (17), 57 (100), 56 (25), 55 (14), 44 (66), 43 (25), 42 (27) (Found M^+, 229.2042. $C_{13}H_{27}NO_2$ requires M, 229.2042).

2-tert-*Butoxycarbonyl-1,2,3,4-tetrahydroisoquinoline* (**5k**):[17] Yield 90%; t_r 12.83, R_f 0.34 (hexane/ethyl acetate: 2/1); ν (film) 3023, 1455 (HC=C), 1695 cm^{-1} (C=O); δ_H 1.48 [9H, s, (CH_3)$_3$C], 2.78, 3.61 (2 and 2H, respectively, 2t, *J*=5.6, CH_2CH_2N), 4.55 (2H, s, NCH_2Ph), 7.00-7.15 (4H, m, ArH); δ_C 28.2 [(CH_3)$_3$C], 40.4, 41.6, 45.6 (3xCH_2), 79.35 (CO), 125.9 (2C), 126.05, 128.4, 133.4, 134.4 (ArC), 154.55 (CO); *m/z* 177 (M^+-58, 45%), 176 (M^+-57, 100), 160 (27), 133 (16), 132 (82), 130 (11), 117 (13), 105 (17), 104 (64), 103 (15), 78 (14), 77 (15), 65 (10), 58 (12), 57 (73), 56 (22), 51 (13), 44 (34).

tert-*Butyl* N-*Benzyl*-N-*methylcarbamate* (**7i**):[35] Yield 75%; t_r 11.01, R_f 0.65 (hexane/ethyl acetate: 2/1); ν (film) 3087, 3064, 3030, 1606, 1496 (HC=C), 1697 (C=O), 1145 cm^{-1} (CO); δ_H 1.48 [9H, s, $(CH_3)_3C$], 2.81 (3H, s, CH_3N), 4.40 (2H, s, CH_2), 7.20-7.35 (5H, m, Ph); δ_C 28.2 [$(CH_3)_3C$], 33.65 (CH_3N), 51.95 (CH_2), 79.3 (CO), 126.95, 127.0, 128.25, 137.85 (Ph), 155.0 (C=O); *m/z* 165 (M^+-56, 73%), 121 (12), 120 (64), 92 (23), 91 (85), 65 (16), 57 (100), 56 (23), 51 (10).

Preparation of Starting Protected Amides **5h**, **5i**, **7a**,**7b**, **7d**, **7g**, **7h**, **7j**, **7n**. *General Procedure*.- To a solution of the corresponding amine or amide (1 mmol) in dry THF (5 ml) was added a 1.6 M solution of *n*-butyllithium (1.2 mmol, 0.75 ml) in hexane at -78°C. The reaction mixture was allowed to warm up to 0°C for 30 min. Then, the corresponding alkylating or acylating reagent (allyl bromide for compound **5h**, ethyl bromoacetate for compound **5i**, acetyl chloride for compounds **7a** and **7n**, 2-methylpropanoyl chloride for compound **7b**, pivaloyl chloride for compounds **7d**, **7g** and **7h**, and di-*terc*-butyldicarbonate for compound **7j**) (1 mmol) was added at -78°C, allowing the temperature to rise to room temperature overnight. The resulting mixture was hydrolysed with water (10 ml), extracted with ethyl acetate (2 x 20 ml) and washed with saturated $NaHCO_3$ (2 x 20 ml). The organic layer was dried over anhydrous Na_2SO_4. Solvents were evaporated (15 Torr) to give a residue, which was purified by column chromatography (silica gel, hexane/ethyl acetate) affording the pure title compounds. Yields, physical, analytical and spectroscopic data, as well as literature references for known compounds, follow.

N-*Allyl*-N-*octylmethanesulfonamide* (**5h**):[17] Yield 55%; t_r 13.01, R_f 0.56 (hexane/ethyl acetate: 2/1); ν (film) 3081, 3012, 1643, 1465 (HC=C), 1333, 1147 cm^{-1} (SO); δ_H 0.88 (3H, t, *J*=6.4, CH_3CH_2), 1.20-1.30, 1.55-1.60 [10 and 2H, respectively, 2m, $(CH_2)_6CH_3$], 2.84 (3H, s, CH_3S), 3.17 (2H, t, *J*=7.3, CH_2CH_2N), 3.84 (2H, d, *J*=6.1, NCH_2CH), 5.20-5.35, 5.75-5.90 (2 and 1H, respectively, 2m, CH_2=CH); δ_C 13.95 (CH_3CH_2), 22.5, 26.5, 28.15, 29.05 (2C), 31.65 [$(CH_2)_6CH_3$], 38.95 (CH_3S), 46.95, 49.75 (2xCH_2N), 118.85, 132.8 (CH_2=CH); *m/z* 232 (M^+-15, 1%), 188 (67), 124 (36), 70 (71), 69 (12), 68 (15), 67 (11), 57 (15), 56 (26), 55 (100), 53 (10), 44 (15), 43 (39), 42 (31).

N-*Benzyl*-N-*(ethoxycarbonyl)methyl-4-methylbenzenesulfonamide* (**5i**):[17] Yield 60%; t_r 17.83, R_f 0.58 (hexane/ ethyl acetate: 2/1); ν (film) 3064, 3030, 1598, 1496 (HC=C), 1748 (C=O), 1341, 1159 cm^{-1} (SO); δ_H 1.13 (3H, t, *J*=7.1, CH_3CH_2), 2.43 (3H, s, CH_3Ar), 3.90 (2H, s, CH_2N), 3.99 (2H, q, *J*=7.1, CH_2O), 4.49 (2H, s, CH_2Ph), 7.25-7.35, 7.78 (7 and 2H, respectively, m and d with *J*=8.2, ArH); δ_C 13.85 (CH_3CH_2), 21.45 (CH_3Ar), 46.55 (CH_2CO), 51.15 (CH_2Ph), 61.0 (CH_2O), 127.35, 128.0, 128.55, 128.6, 129.45, 134.9, 136.85, 143.4 (ArC), 168.55 (C=O); *m/z* 274 (M^+-73, 16%), 193 (12), 192 (84), 118 (17), 92 (22), 91 (100), 65 (35).

N-*Acetyl*-N-*benzyl-4-methylbenzenesulfonamide* (**7a**):[36] Yield 80%; t_r 16.54, R_f 0.48 (hexane/ethyl acetate: 2/1); mp 92-93°C (ethyl acetate) (lit.: 95°C); ν (melted) 3089, 3065, 3033, 1597, 1496 (HC=C), 1700 (C=O), 1354, 1167 cm^{-1} (SO); *m/z* 239 (M^+-64, 1%), 149 (11), 148 (83), 107 (21), 106 (100), 92 (17), 91 (73), 79 (30), 77 (21), 65 (43), 51 (17), 43 (61).

N-*Benzyl*-N-*(2-methylpropanoyl)methanesulfonamide* (**7b**):[17] Yield 90%; t_r 12.25, R_f 0.56 (hexane/ethyl acetate: 4/1); ν (film) 3089, 3064, 3033, 1734 (HC=C), 1698 (C=O), 1387, 1353, 1299, 1164 cm^{-1} (SO); δ_H 1.13 (6H, d, *J*=6.7, 2xCH_3CH), 2.85-3.05 (1H, m, $CHCH_3$), 3.17 (3H, s, CH_3S), 5.01 (2H, s, CH_2), 7.25-7.40 (5H, m, Ph); δ_C 13.9 (2xCH_3CH), 33.6 ($CHCH_3$), 42.55 (CH_3S), 48.45 (CH_2), 126.65, 127.6, 128.65, 136.35 (Ph), 178.55 (CO); *m/z* 184 (M^+-71, 1%), 176 (58), 107 (13), 106 (100), 104 (11), 91 (65), 79 (18), 78 (12), 77 (18), 71 (44), 65 (24), 51 (16), 43 (85).

N-*(2,2-Dimethylpropanoyl)*-N,*4-dimethylbenzenesulfonamide* (**7d**): Yield 50%; t_r 13.70, R_f 0.47 (hexane/ ethyl acetate: 2/1); mp 104-105°C (ethyl acetate); ν (melted) 1682 (C=O), 1594, 1451 (HC=C), 1347, 1165 cm^{-1} (SO); δ_H 1.27 [9H, s, $(CH_3)_3C$], 2.42 (3H, s, CH_3Ar), 3.47 (3H, s, CH_3N), 7.31, 7.86 (2 and 2H, respectively, 2d with *J*=8.4, ArH); δ_C 21.5 (CH_3Ar), 27.35 [$(CH_3)_3C$], 34.45 (CH_3N), 41.3 [$C(CH_3)_3$], 128.3, 129.0, 136.2, 144.15 (ArC), 179.1 (CO); *m/z* 254 (M^+-15, 1%), 186 (10), 155 (52), 98 (92), 92 (22), 91 (86), 65 (49), 58 (15), 57 (100), 56 (16), 42 (65) (Found: C, 58.50; H, 7.28; N, 5.02; S, 11.47. $C_{13}H_{19}NO_3S$ requires: C, 57.97; H, 7.11; N, 5.20; S, 11.90).

N-*Benzyl*-N-*(2,2-dimethylpropanoyl)methanesulfonamide* (**7g**): Yield 65%; t_r 12.92, R_f 0.24 (hexane/ethyl acetate: 4/1); mp 96-97°C (ethyl acetate); ν (melted) 3089, 3062, 3033, 1497 (HC=C), 1660 (C=O), 1366, 1342, 1308, 1161 cm^{-1} (SO); δ_H 1.35 [9H, s, $(CH_3)_3C$], 3.02 (3H, s, CH_3S), 5.05 (2H, s, CH_2), 7.25-7.40 (5H,

m, Ph); δ_C 28.05 [(CH_3)$_3$C], 42.25 [C(CH$_3$)$_3$], 42.6 (CH_3S), 50.3 (CH_2), 127.0, 127.85, 128.75, 135.95 (Ph), 181.75 (C=O); *m/z* 214 (M^+-55, 1%), 190 (44), 106 (40), 91 (68), 85 (12), 79 (12), 78 (10), 77 (13), 65 (19), 58 (17), 57 (100), 51 (12) (Found: C, 56.97; H, 6.90; N, 5.51; S, 12.39. $C_{13}H_{19}NO_3S$·1/4 H_2O requires: C, 57.02; H, 7.18; N, 5.11; S, 11.71).

N-*Benzyl*-N-*(2,2-dimethylpropanoyl)-4-methybenzenesulfonamide* (**7h**): Yield 60%; t_r 17.07, R_f 0.63 (hexane/ethyl acetate: 2/1); mp 124-125°C (ethyl acetate); ν (melted) 3057, 3065, 3033, 1596, 1497 (HC=C), 1666 (C=O), 1334, 1309, 1166 cm^{-1} (SO); δ_H 1.19 [9H, s, (CH$_3$)$_3$C], 2.40 (3H, s, CH_3Ar), 4.94 (2H, s, CH$_2$), 7.20-7.30, 7.62 (7 and 2H, respectively, m and d with J=8.0, ArH); δ_C 21.4 (CH_3Ar), 27.75 [(CH_3)$_3$C], 42.4 [C(CH$_3$)$_3$], 50.9 (CH$_2$), 127.3, 127.5, 128.4, 128.6, 128.95, 135.95, 136.1, 144.05 (ArC), 181.85 (C=O); *m/z* 260 (M^+-85, 5%), 190 (38), 174 (29), 155 (15), 107 (10), 106 (65), 92 (33), 91 (100), 77 (11), 65 (38), 57 (84), 51 (11) (Found: C, 66.01; H, 6.83; N, 4.06; S, 8.99. $C_{19}H_{23}NO_3S$ requires: C, 66.06; H, 6.71; N, 4.05; S, 9.28).

tert-*Butyl* N-*Benzyl*-N-*tosylcarbamate* (**7j**):[37] Yield 75%; t_r 16.18, R_f 0.64 (hexane/ethyl acetate: 2/1); mp 117-118°C (ethyl acetate) (lit.: mp 116-116.5°C); ν (film) 3065, 3033, 1598, 1496 (HC=C), 1731 (C=O), 1369, 1356, 1154 cm^{-1} (SO); δ_C 21.5 (CH_3Ar), 27.75 [(CH_3)$_3$C], 49.65 (CH$_2$), 84.35 (CO), 127.55, 127.95, 128.05, 128.4, 129.05, 137.0, 144.0 (ArC), 151.05 (C=O); *m/z* 196 (M^+-155, 1%), 107 (18), 106 (100), 92 (24), 91 (63), 79 (34), 77 (23), 65 (39), 51 (20).

N-*Acetyl*-N-*benzylmethanesulfonamide* (**7n**):[17] Yield 95%; t_r 12.19, R_f 0.29 (hexane/ethyl acetate: 2/1); ν (film) 3089, 3064, 3033 (HC=C), 1698 (C=O), 1348, 1161 cm^{-1} (SO); δ_H 2.34 (3H, s, CH$_3$C=O), 3.13 (3H, s, CH$_3$S), 5.00 (2H, s, CH$_2$), 7.30-7.40 (5H, m, Ph); δ_C 24.5 (CH_3CO), 42.45 (CH$_3$S), 49.1 (CH$_2$N), 127.15, 127.8, 128.75, 136.05 (Ph), 171.0 (CO); *m/z* 184 (M^+-43, <1%), 148 (53), 107 (12), 106 (100), 104 (12), 91 (30), 79 (35), 78 (11), 77 (22), 65 (19), 51 (22), 43 (85).

Preparation of Starting Protected Amides **7c** *and* **7e**. *General Procedure*[38].- Methyl iodide or allyl bromide (13 mmol) in toluene (20 ml) was added to a mixture of the corresponding amide (10 mmol) (prepared from the corresponding amine and pivaloyl chloride)[18], finely powdered sodium hydroxide (50 mmol, 2 g), potassium carbonate (18.86 mmol, 2 g), tetra-*n*-butylamonium hydrogen sulfate (1 mmol, 0.35 g) and toluene (10 ml) at 40-50°C. After the addition was completed (*ca.* 1h), stirring was continued for 24 h at reflux. The resulting mixture was then cooled to room temperature and filtered off with a plug of celite. The filtered was washed with water (3 x 20 ml), dried over anhydrous Na_2SO_4 and evaporated (15 Torr) and the resulting residue was purified by column chromatography (silica gel, hexane/ethyl acetate) to give the pure title compound. Yields, physical, analytical and spectroscopic data follow.

N,*2,2-Trimethyl*-N-*(1-phenylethyl)propanamide* (**7c**): Yield 80%; t_r 12.09, R_f 0.55 (hexane/ethyl acetate: 2/1); ν (film) 3086, 3059, 3029, 1495 (HC=C), 1624 cm^{-1} (C=O); δ_H 1.33 [9H, s, (CH$_3$)$_3$C], 1.45-1.60 (3H, m, CH_3CH), 2.70 (3H, s, CH$_3$N), 5.75-6.00 (1H, m, CHCH$_3$), 7.20-7.35 (5H, m, Ph); δ_C 15.7 (CH_3CH), 28.25 [(CH_3)$_3$C], 30.45 (CH$_3$N), 38.95 [C(CH$_3$)$_3$], 52.25 (CHN), 126.7, 126.8, 128.25, 140.65 (Ph), 177.4 (C=O); *m/z* 220 (M^++1, 4%), 219 (M^+, 24), 204 (14), 120 (14), 106 (16), 105 (100), 104 (13), 79 (13), 77 (18), 58 (15), 57 (86), 51 (10), 42 (19) (Found M^+, 219.1625. $C_{14}H_{21}NO$ requires M, 219.1623).

N-*Allyl*-N-*benzyl-2,2-dimethylpropanamide* (**7e**): Yield 82%; t_r 12.9, R_f 0.69 (hexane/ethyl acetate: 2/1); ν (film) 3085, 3065 (HC=C), 1634 cm^{-1} (C=O); δ_H 1.32 [9H, s, (CH$_3$)$_3$C], 3.90-4.00 (2H, m, CH_2CH), 4.64 (2H, s, CH_2Ph), 5.05-5.25 (2H, m, CH$_2$=C), 5.65-5.85 (1H, m, CH=CH$_2$), 7.10-7.40 (5H, m, Ph); δ_C 28.6 [(CH_3)$_3$C], 39.0 [C(CH$_3$)$_3$], 49.15 (CH$_2$CH=C), 60.3 (CH$_2$Ph), 117.3, 127.05, 127.15, 128.5, 133.25, 137.5 (Ph, HC=CH$_2$), 177.65 (CO); *m/z* 231 (M^+, 1%), 190 (26), 106 (12), 92 (11), 91 (100), 57 (82), 41 (38) (Found M^+, 231.1627. $C_{15}H_{21}NO$ requires M, 231.1623).

Preparation of N-*Benzyl*-N-*methylformamide* (**7l**)[39a].- To a cold solution of acetic formic anhydride [wich was prepared according literature procedure[39b] from a mixture of sodium formate (15 mmol, 1.03 g), in dry diethyl ether (10 ml) and acetyl chloride (17.4 mmol, 1.25 ml) after stirring for 12h at room temperature] was added benzyl methyl amine (18 mmol, 2.4 ml) over 5 min, stirring being continued at room temperature for 12h. Water (5 ml) was added and the mixture was extracted with diethyl ether (2 x 10 ml), the organic layer was washed with water (2 x 10 ml) and dried over anhydrous Na_2SO_4. Solvents were removed in vacuo

(15 Torr) and the resulting residue was purified by column chromatography (silica gel, hexane/ethyl acetate) to give the pure title compound:[40] Yield 50%; t_r 9.68, R_f 0.15 (hexane/ethyl acetate: 1/1); δ_C (*ca.* 1:1 rotamer mixture) 29.4, 34.0 (CH_3), 47.7, 53.4 (CH_2), 127.3, 127.6, 128.05, 128.15, 128.6, 128.8, 135.65, 135.95 (Ph), 162.55, 162.7 (CHO); *m/z* 151 (M^++2, 1%), 150 (M^++1, 15), 149 (M^+, 100), 148 (50), 134 (15), 120 (11), 107 (11), 106 (37), 92 (23), 91 (76), 79 (42), 77 (18), 65 (37), 63 (13), 51 (25), 50 (11), 44 (37), 43 (11), 42 (52), 41 (12).

Naphthalene-Catalysed Reductive Deprotection of Alcohols, Amines and Amides. Isolation of Compounds **2**, **4**, **6, 8** *and* **3g**. *General Procedure.*- To a green suspension of lithium powder (14 mmol, 100 mg), and naphthalene (0.08 mmol, 10 mg) in THF (5 ml) was slowly added (*ca.* 10 min) a solution of the corresponding protected compound (1 mmol) in THF (2 ml) at -78, -30, 0°C or room temperature (see Tables 1, 2, 3 and 4). Stirring was continued for several hours (see Table 1, 2, 3 and 4). The resulting mixture was then hydrolysed with water (5 ml) and extracted with diethyl ether (2 x 20 ml). Phenol was isolated by basic/acid extraction and the amines **4a-4d** were isolated by acid/basic extraction, in both cases using 2N HCl and 2N NaOH. The organic layer was dried over anhydrous Na_2SO_4. Solvents were evaporated (15 Torr) giving a residue which contained the expected pure (>90%) compounds. Yields are included in Tables 1, 2, 3 and 4. Compounds **2**, **4** and **6a,b,f,g,j** were fully characterised by comparison of their physical (GLC) and spectroscopic (300 MHz ^{1}H NMR and MS) data with those of commercially available authentic samples. Physical, analytical and spectroscopic data, as well as literature references for known compounds, follow.

N-*Octylmethanesulfonamide* (**6h**):[41] t_r 11.88, R_f 0.28 (hexane/ethyl acetate: 2/1); ν (film) 3291 (NH), 1321, 1152 cm^{-1} (SO); δ_H 0.88 (3H, t, *J*=6.4, CH_3CH_2), 1.15-1.60 [12H, m, $(CH_2)_6CH_3$], 2.95 (3H, s, CH_3S), 3.12 (2H, t, *J*=7.0, CH_2N); δ_C 14.0 (CH_3CH_2), 22.55, 26.5, 29.05, 29.1, 30.05, 31.65 [$(CH_2)_6CH_3$], 40.1 (CH_3S), 43.25 (CH_2N); *m/z* 128 (M^+-79, 13%), 108 (100), 95 (21), 84 (12), 79 (12), 70 (13), 69 (24), 57 (11), 56 (16), 55 (23), 43 (25), 42 (13).

Ethyl Benzylaminoacetate (**6i**): t_r 9.50, R_f 0.18 (hexane/ethyl acetate: 2/1); ν (film) 3362 (NH), 3067, 3025 (HC=C), 1683 (C=O), 1021 cm^{-1} (CO); δ_H 1.27 (3H, t, *J*=7.2, CH_3), 2.50 (1H, br s, NH), 3.42 (2H, s, CH_2CO), 3.81 (2H, s, CH_2Ph), 4.19 (2H, q, *J*=7.2, CH_2O), 7.25-7.35 (5H, m, Ph); δ_C 14.2 (CH_3), 49.85, 53.15 (2xCH_2N), 60.8 (CH_2O), 127.25, 128.35, 128.45, 139.05 (Ph), 172.2 (C=O); *m/z* 193 (M^+, 1%), 120 (28), 106 (25), 91 (100), 65 (15) (Found M^+-1, 192.1026. $C_{11}H_{14}NO_2$ requires M-1, 192.1024).

N-*Benzylacetamide* (**8a**):[42] t_r 10.65, R_f 0.13 (hexane/ethyl acetate: 2/1); mp 54-55 °C (ethyl acetate); ν (melted) 3296 (NH), 3063, 3030, 1555 (HC=C), 1645 cm^{-1} (C=O); δ_H 2.00 (3H, s, CH_3), 4.41 (2H, d, *J*=5.8, CH_2), 5.94 (1H, br s, NH), 7.05-7.40 (5H, m, Ph); δ_C 20.95 (CH_3), 43.55 (CH_2), 127.65, 128.55, 129.7, 138.15 (Ph), 170.05 (CO); *m/z* 151 (M^++2, <1%), 150 (M^++1, 8), 149 (M^+, 72), 107 (22), 106 (100), 91 (41), 79 (29), 77 (23), 65 (17), 51 (24), 50 (10), 43 (70).

N-*Benzyl-2-methylpropanamide* (**8b**):[43] t_r 10.17, R_f 0.22 (hexane/ethyl acetate: 2/1); mp 75-76°C (ethyl acetate); ν (melted) 3286 (NH), 3066, 3033, 1543, 1456 (HC=C), 1641 cm^{-1} (C=O); δ_H 1.17 (6H, d, *J*=7.0, 2xCH_3), 2.30-2.45 (1H, m, $CHCH_3$), 4.41 (2H, d, *J*=5.8, CH_2), 5.97 (1H, br s, NH), 7.20-7.35 (5H, m, Ph); δ_C 19.4 (2xCH_3), 32.25 ($CHCH_3$), 43.05 (CH_2), 127.05, 127.35, 128.35, 138.5 (Ph), 176.95 (C=O); *m/z* 178 (M^++1, 5%), 177 (M^+, 37), 107 (13), 106 (21), 92 (20), 91 (100), 65 (16), 43 (52).

N,*2,2-Trimethylpropanamide* (**8c**):[33] t_r 4.27, R_f 0.53 (hexane/ethyl acetate 2/1); mp 49-50°C (ethyl acetate); ν (melted) 3333 (NH), 1636 cm^{-1} (C=O); δ_H 1.20 [9H, s, $(CH_3)_3C$], 4.20 (3H, d, *J*=4.9, CH_3N), 5.75 (1H, br s, NH); δ_C 26.4 [$(CH_3)_3C$], 27.5 [$C(CH_3)_3$], 38.5 (CH_3N), 179.1 (CO); *m/z* 116 (M^++1, 1%), 115 (15), 73 (12), 60 (35), 58 (58), 57 (100), 56 (10), 41 (65).

N-*Allyl-2,2-dimethylpropanamide* (**8e**):[44] t_r 6.09, R_f 0.28 (hexane/ethyl acetate: 2/1); ν (film) 3344 (NH), 3082, 1532 (HC=C), 1641 cm^{-1} (C=O); δ_H 1.22, 1.23 [9H, 2s, $(CH_3)_3C$], 3.85-3.95 (2H, m, CH_2N), 5.10-5.25 (2H, m, CH_2=C), 5.75-5.95 (1H, m, CH=CH_2); δ_C 27.4 [$(CH_3)_3C$], 38.85 [$C(CH_3)_3$], 41.65 (CH_2), 115.65, 134.4 (HC=CH_2), 178.1 (CO); *m/z* 142 (M^++1,<1%), 141 (M^+, 6), 84 (13), 81 (10), 57 (100), 56 (14), 55 (10).

N-*Benzyl-2,2-dimethylpropanamide* (**8f**):[45] t_r 10.88, R_f 0.77 (hexane/ethyl acetate: 2/1); δ_C 27.3 [$(CH_3)_3C$], 38.55 [$C(CH_3)_3$], 60.25 (CH_2), 127.2, 127.45, 128.5, 138.55 (Ph), 178.25 (CO); *m/z* 193 (M^++2, <1%), 192 (M^++1, 7), 191 (M^+, 47), 106 (12), 92 (31), 91 (100), 65 (21), 57 (91), 51 (11).

tert-*Butyl* N-*Methylcarbamate* (**8i**):[46] t_r 4.20, R_f 0.54 (hexane/ethyl acetate: 2/1); ν (film) 3353 (NH), 1698 (C=O), 1174 cm^{-1} (CO); δ_H 1.44 [9H, s, $(CH_3)_3C$], 2.73 (3H, d, *J*=5.2, CH_3N), 4.51 (1H, br s, NH); δ_C 28.15 [$(CH_3)_3C$], 53.2 (CH_3N), 78.65 (CO), 156.55 (C=O); *m/z* 116 (M^+-15, 2%), 76 (93), 59 (94), 58 (54), 57 (100), 56 (44), 55 (21), 44 (31), 43 (35), 42 (13).

tert-*Butyl* N-*Benzylcarbamate* (**8j**):[47] t_r 10.61, R_f 0.78 (hexane/ethyl acetate: 2/1); δ_C 28.3 [$(CH_3)_3C$], 44.55 (CH_2), 79.35 (CO), 127.15, 128.45, 129.7, 138.85 (Ph), 155.84 (C=O); *m/z* 152 (M^+-55, 5%), 151 (44), 150 (57), 107 (13), 106 (48), 105 (16), 91 (58), 79 (21), 77 (17), 65 (14), 59 (33), 57 (100), 56 (29), 55 (13), 51 (21), 50 (11), 44 (47).

N-*Methyl*-N',N'-*diisopropylurea* (**8k**):[48] t_r 8.17, R_f 0.32 (hexane/ethyl acetate: 4/1); mp 88-89°C (ethyl acetate) (lit.: 99-101°C); ν (melted) 3318 (NH), 1626 cm^{-1} (C=O); δ_H 1.22, 1.25 [6 and 6H, respectively, 2s, $2x(CH_3)_2C$], 2.17 (1H, s, NH), 2.80 (3H, d, *J*=4.9, CH_3N), 3.75-3.95 (2H, m, 2xCH); δ_C 21.35 [$2x(CH_3)_2C$], 27.25 (CH_3N), 45.0 (2xCH), 157.95 (CO); *m/z* 159 (M^++1, 1%), 158 (M^+, 10), 143 (15), 86 (75), 58 (45), 44 (100), 43 (39), 42 (23), 41 (25).

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