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α -Nitrogenated Organolithium Compounds from α -Amidomethyl and α -Aminomethyl Sulfones[†]

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Abstract: Successive reaction of α -amidomethyl sulfones 7a,b, derived from primary amides, with *n*butyllithium and primary alkyl bromides (CH₂=CHCH₂Br, CH₂=CMeCH₂Br, CH₂=CBrCH₂Br, CH=CCH₂Br, PhCH₂Br, Bu¹O₂CCH₂Br) at -90°C yields, after hydrolysis, enamides 11. The same procedure applied to α -amidomethyl sulfones 7c,d derived from secondary amides and using different electrophiles [AcOD, D₂O, Et], CH₂=CHCH₂Br, BuⁿI, PhCH₂Br, Bu¹O₂CCH₂Br, Bu¹CHO, PhCHO, (CH₂)₄CO, EtOCOCI, CH₃COCI, PhCOCI] gives substituted α -amidomethyl sulfones 13. Representative compounds 13 are desulfonated (Na·Hg, Na₂S₂O₄ or Mg-MeOH) affording the amides 15. Lithiated sulfones 13 are methylenated to the corresponding acyl enamines 16 or 17 with *in situ* generated chloromethylmagnesium chloride. Naphthalene-catalysed lithiation of α -aminomethyl sulfone 19 in the presence of electrophiles [Bu¹CHO, PhCHO, Et₂CO, Pri₂CO, (CH₂)₅CO, PhCOMe] at -78 to 0°C leads, after hydrolysis with water, to the expected aminoalcohols 20. The application of this method to α -amidomethyl sulfones 7c,d using electrophiles [Bu¹CHO, PhCHO, Et₂CO, (CH₂)₄CO, (CH₂)₅CO, PhCOMe, Me₃SiCI] yields fuctionalised amides 22. Representative examples of compounds 22 were hydrolysed (HCI-EtOAc or CF₃CO₂H), reduced (LiAlH₄) or cyclised (NaH) to give aminoalcohols 24, 25 or oxazolidinones 26, respectively. () 1997 Elsevier Science Lid.

INTRODUCTION

 α -Nitrogenated alkyl sulfones have been widely used as α -amido-¹ and α -amino-alkylating² agents of different type of nucleophiles. Acyclic α -amidoalkyl sulfones $1^{1a,b}$ suffer direct substitution of the arylsulfonyl group with thiolates, ^{1a,b} primary amines, ^{1b} sodium malonate, ^{1b} Grignard reagents ^{1a} and tributyltin anions.^{1c} Cyclic α -amidoalkyl sulfones $2^{1d,e}$ derived from pyrrolidine and piperidine or lactams $3^{1f,g}$ can also be substituted by Grignard reagents in the presence of a zinc halide or by silyl enol ethers, silyl ketene acetals, allylsilanes and trimethylsilyl cyanide in the presence of a Lewis acid. This methodology has been applied to the synthesis of alkaloids norruspoline and ruspoline^{1e} and 4-substituted β -lactams.^{1g} α -Arylaminomethyl sulfones 4 have been used as precursors of cationic 2-azabutadienes in $[4\pi^++2\pi]$ cycloadditions for the synthesis of tetrahydroquinolines.² According to the ability of the sulfone group to stabilise carbanions³ and to be transformed reductively into organolithium compounds,⁴ α -nitrogenated alkyl sulfones should be appropriate precursors of the corresponding "umpoled" d^1 -reagents⁵ of the type 5⁶ and 6, respectively. Versatile α -

[†] This paper is dedicated to Professor D. Seebach on occasion of his 60th birthday.

nitrogen-substituted organolithium compounds of type 6 have been previously prepared by direct α -lithiation mainly of *N*-Boc protected amines,⁷ by tin-lithium exchange⁸ and by reductive carbon-sulfur⁹ or carbonchloride¹⁰ bond cleavage by means of lithium napthalenide or DTBB-catalysed lithiation, respectively. We report here on the use of α -amidomethyl and α -aminomethyl sulfones as precursors of two types of α nitrogenated organolithium compounds either substituted by the sulfone group of type 5, or of type 6.¹¹



RESULTS AND DISCUSSION

The required α -amidomethyl sulfones 7 were synthesised in good yields from sodium *p*-toluenesulfinate, formaldehyde and the corresponding amide or carbamate in the presence of formic acid.¹²

Sulfones **7a,b** derived from primary amides were lithiated with *n*-butyllithium (2 equiv) in the presence of N,N'-dimethylpropyleneurea (DMPU, 2 equiv) at -90°C for *ca*. 2 min to afford dilithiated intermediates **8**, which were characterised by deuterolysis to give the deuterated derivatives **9** (Scheme 1).



Scheme 1. Reagents and conditions: i, 2 BuⁿLi, 2 DMPU, THF, -90°C; ii, D₂O; iii, R²CH₂Br, -90 to -20 or -60°C; iv, NH₄Cl.

Intermediates 8 are very unstable and alkylation with reactive alkyl bromides led the formation of N-acylenamines and dienamines 11, probably resulting from an intramolecular dehydrosulfinylation of alkylated products 10 (Scheme 1 and Table 1). Compounds 11 were obtained with moderate yields as Z/E diastereomers mixture in the case of allyl, benzyl and propargyl bromides, which were separated by flash chromatography. However, in the case of methallyl bromide only the (E)-N-acyldienamines 11 were isolated probably due to the much greater stability of conformation A than B in intermediates 10; the corresponding enaminoesters 11ae and 11be were also obtained with E-configuration for the above mentioned reasons.



Table 1.	Preparation	of N-Acy	vlenamines	11
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	Starting	Electrophile	Product						
Entry	Entry sulfone	Electrophile E+	No.	R ²	Yield (%)a	Rf ^b	Z/E Ratioc		
1	7a	CH ₂ =CHCH ₂ Br	11aa	CH ₂ =CH	45	0.77ª/0.71ª	1/1e		
2	7 b	CH2=CHCH2Br	11ba	CH ₂ =CH	59	0.55f/0.42f	1/1e		
3	7 b	CH ₂ =CMeCH ₂ Br	11bb	CH ₂ =CMe	33	0.47f	-/1		
4	7 b	CH ₂ =CBrCH ₂ Br	11bc	CH≡C	30	0.51d	-/1		
5	7a	CH≡CCH ₂ Br	11ac	CH≡C	31	0.83d/0.74d	1/3e		
6	7a	PhCH ₂ Br	11ad	Ph	20	0.82d/0.69d	1/2e		
7	7 b	PhCH ₂ Br	11bd	Ph	39	0.67f/0.50f	1/2e		
8	7a	EtO_2CCH_2Brg	11ae	EtO ₂ C	52	0.73 ^{d,h}	-/1		
9	7 b	EtO2CCH2Brg	11be	EtO ₂ C	62	0.90i.j	-/1		

^a Based on starting sulfone 7 after column chromatography (silica gel, hexane/EtOAc). ^b Silica gel, values for Z and E-diastereomers, respectively. ^c From ¹H NMR (300 MHz). ^d EtOAc. ^e Separated by flash chromatography (silica gel, hexane/EtOAc). ^f Hexane/ether: 1/1. ^g Without DMPU. ^h Mp 84-85°C (hexane/EtOAc). ⁱ Ether. ^j Mp 144-145°C (hexane/EtOAc).

When 2,3-dibromopropene was allowed to react with intermediate 8b compound 11bc (the same as when propargyl bromide was used as electrophile) was isolated with *E*-configuration, as in the case of methallyl bromide. It means, that once dehydrosulfinylation occurred, the corresponding intermediate suffered dehydrobromination (Table 1 entry 4). On the other hand, the reaction of dianions 8 with other electrophiles such as carbonyl compounds, acyl chlorides or electrophilic olefins failed.

The lithiation of sulfones **7c**,**d**, derived from pyrrolidinone and *O*-tert-butyl *N*-methylcarbamate, at -90°C for 5 min furnished intermediates **12**, which were characterised by deuterolysis and reacted with different electrophiles (alkyl halides, carbonyl compounds and acyl chlorides) to give products **13** (Scheme 2 and Table 2). The dehydrosulfinylation process was only observed in the reaction of **12c** with *tert*-butyl bromoacetate to give a mixture of compounds **13cf** and **14cf** (Table 2, entry 10).

	Storting	Electrophile	Product					
Entry	sulfone	Electrophine . E+	No.	X	Yield(%) ^a	Mp (°C) ^b or R_f^c		
1	7 c	CH ₃ CO ₂ D	13ca	D	65 ^d	117-118		
2	7 d	D_2O	13da	D	82 ^d	102-103		
3	7 c	Etl	13cb	Et	41	92-93		
4	7 c	CH2=CHCH2Br	13cc	CH ₂ =CHCH ₂	67	115-116		
5	7 d	CH ₂ =CHCH ₂ Br	13dc	CH ₂ =CHCH ₂	61	0.57		
6	7 c	BunI	13cd	Bun	50	102-103		
7	7 d	BunI	13dd	Bun	42	0.64		
8	7 c	PhCH ₂ Br	13ce	PhCH ₂	64	0.84e		
9	7 d	PhCH ₂ Br	13de	PhCH ₂	66	0.53		
10	7 c	ButO2CCH2Br	13cf	ButO2CCH2	59f	111-112		
11	7 c	ButCHO	13cg	Bu ^t CHOH	53g	0.88h/0.79i		
12	7 c	PhCHO	13ch	PhCHOH	62i	0.79k/0.83l		
13	7 d	(CH ₂) ₄ CO	13di	(CH ₂) ₄ COH	63	0.43		
14	7 c	EtOCOCI	13cj	EtOCO	72	0.81e		
15	7d	EtOCOC 1	13dj	EtOCO	66	0.55		
16	7 c	CH ₃ COCl	13ck	CH ₃ CO	40	0.63		
17	7 c	PhCOC1	13cl	PhCO	56	0.49		

Table 2. Preparation of Compounds 13

^a Based on starting sulfone 7 after flash chromatography (silica gel, hexane/EtOAc). ^b Hexane/ether. ^c Hexane/ EtOAc: 2/1. ^d >92% of deuterium incorporation. ^e EtOAc. ^f 10% of **14cf** was also obtained. ^g Erythro/threo: 1/2. ^h Erythro. ⁱ Threo: mp 96-97°C. ^j Erythro/threo: 1/1. ^k Erythro: mp 122-123°C. ¹ Threo.

The enamine 14cf was mainly obtained in 56% isolated yield when sulfone 7c was treated with LDA followed by reaction with *tert*-butyl bromoacetate (Scheme 3).



Scheme 2. Reagents and conditions: i, Bu^nLi , DMPU, THF, -90°C; ii, $E^+ = CH_3CO_2D$, D_2O , EtI, $CH_2=CHCH_2Br$, Bu^nI , $PhCH_2Br$, $Bu^tO_2CCH_2Br$, Bu^tCHO , PhCHO, $(CH_2)_4CO$, EtOCOCl, CH_3COCl , PhCOCl, -90 to 20°C; iii, NH_4Cl .



Scheme 3. Reagents and conditions: i, LDA, THF, -90°C; ii, BrCH₂CO₂Bu^t; iii, NH₄Cl.

In the reaction of 12d with *tert*-butyl bromoacetate a 3/2 mixture of 13df and 14df was obtained, which was treated with potassium *tert*-butoxide in THF at room temperature for 30 min to give compound 14df in 60% yield (Scheme 4).



Scheme 4. Reagents and conditions: i, BrCH2CO2But; ii, NH4Cl; iii, KOBut, THF, 20°C.

Representative sulfones 13 were desulfonylated with sodium amalgam¹³ in the case of 13ce, with sodium dithionite¹⁴ in the case of 13cl or with magnesium in methanol¹⁵ for 13dj to give compounds 15ce, 15cl and 15dj, respectively (Scheme 5). In the first case 8% of enamine 14ce was also obtained due to a competitive dehydrosulfinylation process.



Scheme 5. Reagents and conditions: i, Na·Hg, Na₂HPO₄, MeOH, 0 to 20° C; ii, Na₂S₂O₄, NaHCO₃, DMF, H₂O, 100° C; iii, Mg, MeOH, 20° C.

Alkylated amido sulfones 13ce and 13dc suffered methylenation by means of Julia's methodology:¹⁶ lithiation with *n*-butyllithium at -78°C and *in situ* reaction with chloromethylmagnesium chloride provided enamines 16ce and 16dc in 55 and 56% yield, respectively (Scheme 6). Compound 16dc isomerised quantitatively in the NMR tube to give stereoselectively the corresponding conjugated dienic carbamate 17. The substitution of the tosyl group by means of a Grignard reagent ^{1d} has been performed with compound 13dc and phenylmagnesium bromide in the presence of zinc bromide to afford the carbamate 18 (Scheme 6).

When the methodology described above (α -lithiation of α -amidomethyl sulfones) was applied to α aminomethyl sulfones the reaction failed, only decomposition of the starting material¹⁷ being observed. Thus, α -lithiation of compound **19** under different reaction conditions did not work.

In the second part of this study, we studied the reductive desulfonylation of α -aminomethyl sulfone 19 or the corresponding α -amidomethyl sulfones of type 7.

Treatment of *N*-methyl-*N*-(tosylmethyl)aniline (**19**) with an excess of lithium powder (1:14 molar ratio) and a catalytic amount of naphthalene (1:0.08 molar ratio; 4 mol %) in the presence of different carbonyl compounds as electrophiles (Barbier-type reaction conditions)¹⁸ in THF at temperatures ranging between -78 and 0°C led, after hydrolysis with water, to the corresponding aminoalcohols **20** in moderate yields,

intermediate **21** being probably involved in the process (Scheme 7 and Table 3). In absence of electrophile (twostep reaction) the process failed.



Scheme 6. Reagents and conditions: i, BuⁿLi, THF, -78°C; ii, ClCH₂I, PrⁱMgCl, -78 to 0°C; iii, NH₄Cl; iv, PhMgBr, ZnBr₂, THF, 20°C.



Scheme 7. Reagents and conditions: i, Li, $C_{10}H_8$ cat. (4 mol%), E⁺ = Bu¹CHO, PhCHO, Et₂CO, Pri₂CO, (CH₂)₅CO, PhCOMe, THF, -78 to 0°C; ii, H₂O.

		Product						
Entry	Electrophile E+	No.	R1	R ²	Yield (%) ^a	$R_{f^{b}}$		
1	ButCHO	20a	But	Н	54	0.49		
2	PhCHO	20b	Ph	н	43	0.27		
3	Et ₂ CO	20c	Et	Et	48	0.35		
4	Pri ₂ CO	20d	Pri	Pri	25	0.57		
5	(CH ₂) ₅ CO	20e	-(CH	[₂) ₅ -	51	0.37		
6	PhCOMe	20 f	Ph	Me	53	0.34		
	÷							

Table 3. Preparation of Compounds 20

^a Isolated yield after column chromatography (silica gel, hexane/ EtOAc) based on the starting amino sulfone **19**. ^b Silica gel, hexane/EtOAc: 6/1.

The application of the methodology shown in Scheme 7 to the α -amidomethyl sulfones 7c and 7d using carbonyl compounds and chlorotrimethylsilane as electrophiles led to the expected functionalised amides 22 in moderate yields (Scheme 8 and Table 4). In this case the probable intermediate of type 23 is stabilised by intramolecular coordination of the lithium atom by the amide group (CIPE effect).¹⁹ Also in this case the reaction has to be performed under Barbier-type reaction conditions in order to avoid decomposition of carbenoid 23.



Scheme 8. Reagents and conditions: i, Li, $C_{10}H_8$ cat. (4 mol%), E⁺ = Bu⁴CHO, PhCHO, Et₂CO, (CH₂)₄CO, (CH₂)₅CO, PhCOMe, Me₃SiCl, THF, -78 to 0°C; ii, H₂O.

Finally, we studied some transformations of compounds 22 in order to explore their synthetic applications Thus, hydrolysis of hydroxy carbamates 22db and 22df with either hydrogen chloride in ethyl acetate (method A)²⁰ or trifluoroacetic acid in dichloromethane (method B)²¹ gave, after basic treatment, the expected aminoalcohols 24 (Scheme 9 and Table 5, entries 1 and 2). Reduction of starting materials 22da, 22db and 22df with lithium aluminum hydride under DME reflux²² yielded the corresponding aminoalcohols 25 (Scheme 9 and Table 5, entries 3-5). Cyclisation of carbamates 22da and 22df with sodium hydride under THF reflux afforded oxazolidinones 26 (Scheme 9 and Table 5, entries 6 and 7).

	Starting	Electrophile E+	Product					
Entry	sulfone		No.	X	Yield (%) ^a	R _f b		
1	7 đ	ButCHO	22da	ButCHOH	50	0.45		
2	7 d	PhCHO	22db	PhCHOH	45	0.30		
3	7 c	Et ₂ CO	22cc	Et ₂ COH	37	0.50c		
4	7d	Et ₂ CO	22dc	Et ₂ COH	20	0.43		
5	7d	(CH ₂) ₄ CO	22dd	(CH ₂) ₄ COH	30	0.27		
6	7 c	(CH ₂) ₅ CO	22ce	(CH ₂) ₅ COH	31	0.36¢		
7	7d	PhCOMe	22df	PhC(OH)Me	43	0.41		
8	7d	Me ₃ SiCl	22dg	Me ₃ Si	28	0.81		

Table 4. Preparation of Compounds 22

^a Isolated yield after column chromatography (neutral alumina, hexane/ EtOAc) based on the starting amido sulfone **7**. ^b Silica gel, hexane/EtOAc: 4/1. ^c Silica gel, EtOAc.



Scheme 9. Reagents and conditions: i, HCl-EtOAc (Method A) or CF₃CO₂H, CH₂Cl₂ (Method B) 20°C; ii, NaOH (3 M); iii, LiAlH₄, DME reflux; iv, H₂O; v, NaH, THF reflux.

	Starting material	Product						
Entry		No.	R1	R ²	Yield (%) ^a	R _f b		
1	22db	24db	Ph	Н	93° (98)d	0.32e		
2	22df	24d f	Ph	Me	95°	0.26e		
3	22da	25da	But	Н	69	0.32f		
4	22db	25db	Ph	Н	93	0.73f		
5	22df	25df	Ph	Me	82	0.52f		
6	22da	26da	But	Н	80	0. 2 9s		
7	22df	26df	Ph	Me	99	0. 4 0g		

Table 5. Preparation of Compounds 24-26

a Isolated yield based on the starting carbamate **22**. ^b Silica gel. ^c Method A (see text). ^d Method B (see text). ^e CH₂Cl₂/MeOH: 4/1. ^f Hexane/EtOAc: 3/1. ^g Hexane/EtOAc: 6/1.

From the results described in this paper we conclude that α -aminomethyl and α -amidomethyl sulfones, which are easily prepared by a Mannich reaction, are available substrates to be lithiated either by deprotonation

or by reductive desulfonylation giving α -nitrogenated organolithium intermediates; these d^{l} -reagents react with different electrophiles to yield polyfunctionalised organic molecules bearing or not the sulfone functionality.

EXPERIMENTAL SECTION

General.- Melting points were obtained with a Reichert Thermovar apparatus and are uncorrected. FT-IR spectra were obtained on a Nicolet Impact 400D spectrophotometer. NMR spectra were recorded on a Brucker AC-300 (300 MHz for 1H and 75 MHz for 13C) using CDCl₃ as solvent and TMS as internal standard; chemical shifts are given in δ (ppm). ¹³C NMR assignments were made on the basis of DEPT experiments. Mass spectra (EI) were obtained on a Hewlett-Packard 5988A or a Shimazdu OP-5000 spectrometers. High resolution mass spectra were measured in the Mass Spectrometry Service at the University of Zaragoza. Elemental analyses were performed by the Microanalyses Service at the University of Alicante. The purity of volatile products and the chromatographic analyses (GLC) were determined with a Hewlett Packard HP-5890 instrument equipped with a flame ionisation detector and a 12 m capillary column (0.2 mm diam, 0.33 µm film thickness), using nitrogen (2 ml/min) as the carrier gas, $T_{injector} = 275^{\circ}$ C, $T_{column} = 60^{\circ}$ C (3 min) and 60-270°C (15°C/min); t_r values are given under these conditions. Thin layer chromatography (TLC) was carried out on Schleicher & Schuell F1400/LS 254 plates coated with a 0.2 mm layer of silica gel and UV, iodine or phosphomolybdic acid visualisation; R_f values are given under these conditions. Column chromatography was performed using silica gel 60 of 35-70 or 70-230 mesh or neutral alumina of 70-290 mesh. All starting materials were commercially available (Acros, Aldrich, Fluka) of the best grade and were used without further purification. THF was dried over benzophenone ketyl under an argon atmosphere and distilled before use.

Synthesis of α -Amidomethyl and α -Aminomethyl Sulfones. General Procedure.- To a stirred solution of sodium *p*-toluenesulfinate (20 mmol), formaldehyde (22 mmol) and the corresponding nitrogenated compound (20 mmol) in water (20 ml) (9 ml of MeOH were added as cosolvent in the case of compound **7d**), a formic acid concentrated solution (5 ml, 85%) was added. Then, the reaction mixture was stirred at 80°C for 5 h (in the case of carbamate **7d** the reaction was carried out at room temperature for 24 h). The crystals of the corresponding sulfones were directly obtained from the reaction mixture, were filtered off and washed with water (15 ml) and ether (15 ml). Then, compounds **7** and **19**¹⁷ were dried *in vacuo* (0.1 Torr) to afford the corresponding amido and amino sulfones. Yields are included in the text, physical, spectroscopic and analytical data, as well as literature referces for known compounds follow.

N-(*Tosylmethyl*)acetamide (**7a**):^{12b} mp 137-138°C; v (KBr) 3400-3100 (NH), 1666 (C=O), 1324, 1296, 1273 and 1145 cm⁻¹ (SO₂); $\delta_{\rm H}$ 1.92 (s, 3H, CH₃CO), 2.44 (s, 3H, CH₃Ar), 4.70 (d, *J*=6.7 Hz, 2H, CH₂S), 7.23 (br t, *J*=6.7 Hz, 1H, NH), 7.36 and 7.79 (2d, *J*=8.2 Hz, 4H, ArH); $\delta_{\rm C}$ 21.5 (*C*H₃Ar), 22.4 (*C*H₃CO), 61.1 (CH₂S), 129.6, 130.5, 136.1, 145.6 (ArC) and 170.0 (C=O); *m/z* 228 (*M*++1, <1%), 227 (*M*+, <1), 91 (16), 72 (75), 65 (17) and 43 (100).

N-(*Tosylmethyl*)-2,2-*dimethylpropanamide* (**7b**): mp 89-90°C; v (KBr) 3388 (NH), 1683 (C=O), 1317, 1306, 1284 and 1140 cm⁻¹ (SO₂); $\delta_{\rm H}$ 1.07 [s, 9H, (CH₃)₃C], 2.44 (s, 3H, CH₃Ar), 4.72 (d, *J*=6.7 Hz, 2H, CH₂S), 6.55 (m, 1H, NH), 7.34 and 7.77 (2d, *J*=8.0 Hz, 4H, ArH); $\delta_{\rm C}$ 21.6 (CH₃Ar), 27.1 [(CH₃)₃C], 38.6 [(CH₃)₃C], 60.3 (CH₂S), 128.7, 129.6, 133.8, 145.2 (ArC) and 177.6 (C=O); *m*/z 269 (*M*+, 1%), 114 (27), 91 (11), 85 (35), 57 (100) and 41 (16) (Found: C, 51.50; H, 8.19; N, 6.02; S, 13.15. Calcd. for C₁₃H₁₉NO₃S: C, 51.48; H, 8.21; N, 6.00 and S, 13.34%).

tert-Butyl N-Methyl-N-(tosylmethyl)carbamate (7c): mp 101-102°C; v (KBr) 1686 (C=O), 1321, 1292 and 1147 cm⁻¹ (SO₂); $\delta_{\rm H}$ 1.11, 1.24 [2s, 18H, 2x(CH₃)₃C], 2.41, 2.45 (2s, 6H, 2xCH₃Ar), 3.08 (s, 6H, 2xCH₃N), 4.61, 4.63 (2s, 4H, 2xCH₂S), 7.31-7.38 and 7.75-7.78 (2m, 8H, 2xArH); $\delta_{\rm C}$ 21.4 (2xCH₃Ar), 27.5, 27.7 [2x(CH₃)₃C], 35.2, 35.5 (2xCH₃N), 69.3, 70.2 (2xCH₂S), 80.8, 81.0 [2x(CH₃)₃C], 128.8, 128.9, 129.5, 129.8, 134.3, 134.6, 144.8, 145.1 (ArC), 153.4 and 154.2 (2xC=O); *m*/z 299 (*M*+, <1%), 144 (24), 139 (11), 91 (14), 57 (100), 44 (53) and 41 (16) (Found: C, 56.66; H, 4.77; N, 7.22; S, 10.61. Calcd. for C₁₄H₂₁NO₄S: C, 56.17; H, 4.68; N, 7.07 and S, 10.71%).

l-(*Tosylmethyl*)-2-*pyrrolidinone* (**7d**): mp 117-118°C; v (KBr) 1692 (C=O), 1319, 1312, 1289 and 1140 cm⁻¹ (SO₂); δ_H 2.04 (q, *J*=7.0 Hz, 2H, CH₂CO), 2.22 (t, *J*=7.0 Hz, 2H, CH₂CO), 2.44 (s, 3H, CH₃Ar), 3.72

(t, J=7.0 Hz, 2H, CH₂CH₂N), 4.65 (s, 2H, CH₂S), 7.35 and 7.76 (2d, J=8.2 Hz, 4H, ArH); $\delta_{\rm C}$ 18.1 (CH₂CH₂CO), 21.6 (CH₃Ar), 29.7 (CH₂CO), 47.4 (CH₂CH₂N), 63.8 (CH₂S), 128.5, 129.8, 134.0, 145.3 (ArC) and 174.7 (C=O); *m/z* 253 (*M*+, <1%), 98 (100), 70 (20) and 41 (13) (Found: C, 57.06; H, 5.57; N, 6.02; S, 12.49, Calcd, for C₁₂H₁₅NO₃S: C, 56.90; H, 5.97; N, 5.53 and S, 12.66%).

N-Methyl-N-(tosylmethyl)aniline (19):2 mp 91-92°C; v (KBr) 3067, 3043, 1599, 1509 (HC=C), 1316, 1269 and 1135 cm⁻¹ (SO₂); $\delta_{\rm H}$ 2.36 (s, 3H, CH₃Ar), 2.94 (s, 3H, CH₃N), 4.71 (s, 2H, CH₂), 6.60-6.75, 7.05-7.25 and 7.65-7.75 (3m, 9H, ArH); $\delta_{\rm C}$ 21.4 (CH₃Ar), 39.1 (CH₃N), 75.9 (CH₂), 112.9, 118.7, 128.7, 128.8, 129.7, 135.5, 144.8 and 146.7 (ArC); *m/z* 275 (*M*+, 1%), 121 (12), 120 (100), 105 (13), 91 (12) and 77 (13).

Lithiation of α -Amidomethyl Sulfones **7a-d**. Reaction with Electrophiles. General Procedure.- To a solution of the corresponding sulfone **7** (0.35 mmol) and DMPU (0.39 or 0.77 mmol; see Scheme 1 and 2) (in the case of compound **7d** DMPU was not used) in dry THF (3 or 6 ml; see Scheme 1 and 2) at -90°C, was added a 1.6M solution of *n*-butyllithium (0.39 or 0.77 mmol; see Scheme 1 and 2) in hexane. After 2 or 5 min stirring, the corresponding electrophile was added (0.39 mmol), the reaction mixture was warmed up to room temperature (in the case of sulfones **7a** and **7b** the reaction was warmed up to -20 and -60°C, respectively). The reaction mixture was hydrolyzed with a saturated aqueous solution of NH₄Cl and extracted with EtOAc (3x10 ml). The organic layer was dried over Na₂SO₄, evaporated and the residue was purified by column chromatography (silica gel or alumina, hexane/EtOAc) and/or recrystallisation to afford the corresponding products. Yields and physical data are included in Tables 1 and 2; spectral and analytical data, as well as literature references for known compounds follow.

N-(*Tosyldeuteriomethyl*)acetamide (**9a**): v (KBr) 3400-3100 (NH), 1666 (C=O), 1324, 1296, 1273 and 1145 cm⁻¹ (SO₂); $\delta_{\rm H}$ 1.92 (s, 3H, CH₃CO), 2.44 (s, 3H, CH₃Ar), 4.67-4.71 (m, 1H, CHD), 7.11 (d, *J*=6.4 Hz, 1H, NH), 7.36 and 7.78 (2d, *J*=8.2 Hz, 4H, ArH); $\delta_{\rm C}$ 21.6 (CH₃Ar), 22.5 (CH₃CO), 60.2 (t, *J*=22.4 Hz, CHD), 128.6, 129.9, 133.8, 145.4 (ArC) and 169.8 (C=O); *m/z* 229 (*M*++1, <1%), 228 (*M*+, <1), 92 (10), 91 (17), 73 (79), 65 (18) and 43 (100) (Found: C, 52.80; H/D, 5.01; N, 6.25; S, 13.87. Calcd. for C₁₀H₁₂DNO₃S: C, 52.63; H/D, 5.26; N, 6.14 and S, 14.04%).²³

N-(*Tosyldeuteriomethyl*)-2,2-*dimethylpropanamide* (**9b**): v (KBr) 3388 (NH), 1683 (C=O), 1317, 1306, 1284 and 1140 cm⁻¹ (SO₂); $\delta_{\rm H}$ 1.07 [s, 9H, (CH₃)₃C], 2.44 (s, 3H, CH₃Ar), 4.70 (m, 1H, CHD), 6.72 (br s, 1H, NH), 7.33 and 7.76 (2d, *J*=8.2 Hz, 4H, ArH); $\delta_{\rm C}$ 21.6 (CH₃Ar), 27.1 [(CH₃)₃C], 38.7 [(CH₃)₃C], 60.0 (t, *J*=23 Hz, CHD), 128.8, 129.7, 133.8, 145.3 (ArC) and 177.5 (C=O); *m*/*z* 270 (*M*+, <1%), 115 (29), 85 (41), 58 (17), 57 (100), 43 (43) and 41 (37) (Found: C, 57.90; H/D, 6.40; N, 5.15; S, 11.70. Calcd. for C₁₃H₁₈DNO₃S: C, 57.78; H/D, 6.67; N, 5.19 and S, 11.85%).²³

N-[(1Z)-1,3-Butadienyl]acetamide (Z-11aa): v (film) 3294 (NH) and 1648 cm⁻¹ (C=O); $\delta_{\rm H}$ 2.11 (s. 3H, CH₃CO), 5.09 (d, J=10.1 Hz, 1HxCH₂=CH), 5.23 (d, J=16.5 Hz, 1HxCH₂=CH), 5.41 (dd, J=11.3, 9.2 Hz, 1H, NCH=CH), 6.45 (dt, J=16.5, 10.5 Hz, 1H, CH₂=CH), 6.71 (t, J=10.2 Hz, 1H, NCH=CH) and 7.46 (m, 1H, NH); $\delta_{\rm C}$ 23.3 (CH₃CO), 110.3, 116.8, 121.5, 128.8 (C=C) and 167.2 (C=O); *m*/z 112 (*M*++1, 2%), 111 (*M*+, 34), 69 (83), 68 (50), 54 (22), 43 (100), 42 (26) and 41 (40) (Found: *M*+ 111.0684. Calcd. for C₆H₉NO, 111.0684).

N-(1,3-butadienyl)-2,2-dimethylpropanamide (**11ba**): v (film) 3339 (NH), 3085, 1645, 960 (HC=C) and 1665 cm⁻¹ (C=O); $\delta_{\rm H}$ 1.24, 1.26 [s, 18H, 2x(CH₃)₃C], 4.93-5.46, 5.80-5.89, 6.24-6.46, 6.70-6.77, 6.98-7.06 (5m, 10H, olefinic H), 7.38 and 7.51 (2m, 2H, NH); $\delta_{\rm C}$ 27.3, 27.4 [2x(CH₃)₃C], 38.7, 39.0 [2x(CH₃)₃C], 110.3, 113.6, 114.1, 116.6, 122.0, 126.3, 128.7, 134.6 (2xC=C), 175.2 and 175.6 (2xC=O); *m*/*z* (*Z*) 154 (*M*++1, 2%), 153 (*M*+, 26), 69 (43), 68 (17), 57 (100), 43 (25), 42 (10) and 41 (59); *m*/*z* (*E*) 154

 $(M^{++1}, 2\%)$, 153 $(M^{+}, 22)$, 69 (39), 68 (15) and 57 (100) (Found: M^{+} 153.1150. Calcd. for C₉H₁₅NO, 153.1154).

N-[(E)-1-Buten-3-ynyl]-2,2-dimethylpropanamide (11bc): v (film) 3303 (NH) and 1668 cm⁻¹ (C=O); $\delta_{\rm H}$ 1.24 [s, 9H, (CH₃)₃C], 2.85 (d, J=2.1 Hz, 1H, HC≡C), 5.20 (dd, J=14.3, 2.1 Hz, 1H, CH=CHN), 7.38 (dd, J=14.3, 11.0 Hz, 1H, CH=CHN) and 7.58 (m, 1H, NH); $\delta_{\rm C}$ 27.2 [(CH₃)₃C], 38.9 [(CH₃)₃C], 77.3, 80.7 (HC≡C), 90.3, 135.7 (CH=CH) and 175.5 (C=O); *m*/*z* 152 (*M*++1, 1%), 151 (*M*+, 11), 128 (27), 85 (15), 67 (15), 57 (67), 44 (47), 43 (33), 42 (33), 41 (38) and 40 (100) (Found: *M*+ 151.0990. Calcd. for C₉H₁₃NO, 151.0997).

N-[(Z)-1-Buten-3-ynyl]acetamide (Z-11ac): v (film) 3500-3150 (NH), 3096, 1631 (HC=C), 2090 (C≡C) and 1681 cm⁻¹ (C=O); $\delta_{\rm H}$ 2.14 (s, 3H, CH₃CO), 3.33 (d, J=2.1 Hz, 1H, CH≡C), 4.80 (dd, J=8.9, 2.1 Hz, 1H, CH=CHN), 7.25 (dd, J=11.6, 8.9 Hz, 1H, C=CHN) and 7.68 (m, 1H, NH); $\delta_{\rm C}$ 23.3 (CH₃CO), 78.2 (CH≡C), 84.7 (C≡CH), 87.2 (CH=CHN), 133.7 (CH=CHN) and 167.2 (C=O); *m*/z 110 (*M*++1, 2%), 109 (*M*+, 31), 67 (100), 43 (99), 42 (10), 41 (19) and 40 (60) (Found: *M*+ 109.0527. Calcd. for C₆H₇NO, 109.0528).

N-[(E)-1-Buten-3-ynyl]acetamide (E-11ac): v (film) 3307 (NH), 3150, 3080, 1635 (HC=C), 2106 (C≡C) and 1679 cm⁻¹ (C=O); $\delta_{\rm H}$ 2.09 (s, 3H, CH₃CO), 2.86 (d, J=2.4 Hz, 1H, CH≡C), 5.17 (dd, J=14.7, 2.4 Hz, 1H, CH=CHN), 7.34 (dd, J=14.7, 11.1 Hz, 1H, C=CHN) and 7.95 (m, 1H, NH); $\delta_{\rm C}$ 23.2 (CH₃CO), 77.5 (CH≡C), 80.5 (CH≡C), 90.3 (CH=CHN), 135.0 (C=CHN) and 167.2 (C=O); *m*/*z* 110 (*M*++1, 1%), 109 (*M*+, 28), 67 (91), 43 (100), 41 (15) and 40 (47).

 $\begin{array}{l} \text{N-}[(Z)-2-Phenyl-1-ethenyl]acetamide~(Z-11ad):}^{24} \text{ v~(film)} 3290~(\text{NH}), 1660~(\text{C=O})~\text{and}~1645~\text{cm}^{-1}~(\text{C=C});~\delta_{\text{H}} \\ \text{2.06~(s, 3H, CH_{3}\text{CO}), 5.75~(d, J=9.8~\text{Hz}, 1H, CH=CHN), 6.93-7.00, 7.24-7.42~(2m, 6H, ArH, CH=CHN) \\ \text{and}~7.56~(m, 1H, \text{NH});~\delta_{\text{C}}~23.5~(CH_{3}\text{CO}), 109.7~(CH=CHN), 122.0~(CH=CHN), 127.0, 127.9, 129.1, \\ 135.7~(\text{ArC})~\text{and}~167.5~(\text{C=O});~m/z~162~(M^{+}+1,~4\%), 161(M^{+},~36), 120~(10), 119~(100), 118~(77), 117~(14), \\ 91~(33),~90~(10),~89~(13),~65~(20),~63~(14),~51~(15),~43~(85),~42~(11)~\text{and}~40~(15). \end{array}$

N-[(E)-2-Phenyl-1-ethenyl]acetamide (E-11ad):²⁴ v (film) 3290 (NH), 1660 (C=O) and 1645 cm⁻¹ (C=C); $\delta_{\rm H}$ 2.11 (s, 3H, CH₃CO), 6.09 (d, J=14.7 Hz, 1H, CH=CHN) and 7.14-7.53 (m, 7H, NH, ArH, CH=CHN); $\delta_{\rm C}$ 23.3 (CH₃CO), 112.4 (CH=CHN), 122.6 (CH=CHN), 125.5, 126.6, 128.6, 134.0 (ArC) and 167.4 (C=O); *m*/z 162 (*M*++1, 5%), 161(*M*+, 39), 120 (10), 119 (100), 118 (72), 117 (12), 91 (32), 89 (13), 65 (16), 63 (12), 51 (12) and 43 (79).

N-[(Z)-2-Phenyl-1-ethenyl]-2,2-dimethylpropanamide (Z-11bd): v (film) 3336 (NH) and 1668 cm⁻¹ (C=O); $\delta_{\rm H}$ 1.23 [s, 9H, (CH₃)₃C], 5.76 (d, J=9.5 Hz, 1H, CH=CHN), 6.99 (t, J=9.5 Hz, 1H, CH=CHN), 7.17-7.43 (m, 5H, ArH) and 7.96 (m, 1H, NH); $\delta_{\rm C}$ 27.3 [(CH₃)₃C], 38.9 [(CH₃)₃C], 109.8, 122.5, 126.9, 127.7, 129.1, 135.9 (ArC, C=C) and 175.7 (C=O); *m*/*z* 204 (*M*++1, 9%), 203 (*M*+, 57), 119 (66), 118 (37), 91 (16), 58 (11) and 57 (100).

N-[(E)-2-Phenyl-1-ethenyl]-2,2-dimethylpropanamide (E-11bd): v (film) 3336 (NH) and 1668 cm⁻¹ (C=O); $\delta_{\rm H}$ 1.28 [s, 9H, (CH₃)₃C], 6.13 (d, J=14.3 Hz, 1H, CH=CHN), 7.26-7.42 (m, 6H, PhH, NH) and 7.54 (dd, J=14.3, 10.8 Hz, 1H, CH=CHN); $\delta_{\rm C}$ 27.4 [(CH₃)₃C], 38.8 [(CH₃)₃C], 112.5, 123.2, 125.5, 125.6, 128.4, 136.2 (ArC, C=C) and 175.7 (C=O); *m*/z 204 (*M*++1, 8%), 203 (*M*+, 55), 119 (67), 118 (38), 91 (16), 58 (11) and 57 (100) (Found: *M*+ 203.1306. Calcd. for C₁₃H₁₇NO, 203.1310).

tert Butyl (E)-3-Methylcarboxamido-2-propenoate (**11ae**): v (KBr) 3289 (NH), 1715 and 1686 cm⁻¹ (C=O); $\delta_{\rm H}$ 1.48 [s, 9H, (CH₃)₃C], 2.12 (s, 3H, CH₃CO), 5.37 (dd, J=14.0, 2.1 Hz, 1H, CH=CHCO₂), 7.90 (dd, J=14.0, 11.6 Hz, 1H, CH=CHN) and 8.91 (br d, J=11.6 Hz, 1H, NH); $\delta_{\rm C}$ 23.2 (CH₃CO), 28.2 [(CH₃)₃C], 80.4 [(CH₃)₃C], 103.2 (CH=CHCO), 137.0 (CH=CHN), 167.2 and 168.8 (C=O); *m/z* 185 (*M*⁺, 2%), 129

(23), 112 (20), 87 (100), 84 (11), 70 (62), 69 (30), 57 (45), 43 (99) and 41 (55) (Found: C, 58.32; H, 8.18; N, 7.57. Calcd. for $C_9H_{15}NO_3$: C, 58.36; H, 8.16 and N, 7.56%).

tert-*Butyl* (E)-3-(tert-*Butylcarboxamido*)-2-*propenoate* (11be): v (KBr) 3308 (NH), 1691 (C=O), 1151 and 1135 cm⁻¹ (C-O); $\delta_{\rm H}$ 1.25, 1.47 [2s, 18H, 2x(CH₃)₃C], 5.44 (d, *J*=14.0 Hz, 1H, CH=CHN), 7.94 (dd, *J*=14.0, 11.6 Hz, 1H, CH=CHN) and 8.10 (br d, *J*=11.6 Hz, 1H, NH); $\delta_{\rm C}$ 27.1, 28.2 [2x(CH₃)₃C], 39.1 [(CH₃)₃CC=O], 80.1 [(CH₃)₃CO], 103.5, 137.3 (CH=CH), 166.8 and 176.5 (C=O); *m/z* 227 (*M*+, 3%), 171 (27), 154 (19), 126 (23), 114 (13), 87 (50), 85 (52), 70 (26), 69 (23), 58 (16), 57 (100), 56 (24), 55 (13), 44 (16), 43 (12) and 42 (17) (Found: C, 63.37; H, 9.32; N, 6.18. Calcd. for C₁₂H₂₁NO₃: C, 63.41; H, 9.31 and N, 6.16%).

1-(Tosyldeuteriomethyl)-2-pyrrolidinone (**13ca**): v (KBr) 1692 (C=O), 1319, 1312, 1289 and 1140 cm⁻¹ (SO₂); $\delta_{\rm H}$ 2.04 (q, *J*=7.6 Hz, 2H, CH₂CH₂CO), 2.23 (t, *J*=7.6 Hz, 2H, CH₂CO), 2.44 (s, 3H, CH₃Ar), 3.72 (t, *J*=7.0 Hz, 2H, CH₂CH₂N), 4.63 (s, 1H, CHD), 7.35 and 7.77 (2d, *J*=8.2 Hz, 4H, ArH); $\delta_{\rm C}$ 18.2 (CH₂CH₂CO), 21.6 (CH₃Ar), 29.7 (CH₂CO), 47.6 (CH₂CH₂N), 64.0 (t, *J*=23.2 Hz, CHD), 128.5, 129.8, 134.0, 145.4 (ArC) and 174.8 (C=O); *m/z* 254 (*M*+, <1%), 100 (27), 99 (100), 98 (97), 91 (12), 71 (26), 70 (24), 69 (32), 65 (20), 44 (13), 43 (31), 42 (37) and 41 (62) (Found: C, 56.40; H/D, 5.70; N,5.75; S, 12.30. Calcd. for C₁₂H₁₄DNO₃S: C, 56.69; H/D, 5.51; N, 5.51 and S, 12.60%).²³

tert-Butyl N-Methyl-N-(tosyldeuteriomethyl)carbamate (13da): v (KBr) 1686 (C=O), 1321, 1292 and 1147 cm⁻¹ (SO₂); $\delta_{\rm H}$ 1.11, 1.24 [2s, 18H, 2x(CH₃)₃C], 2.41, 2.44 (2s, 6H, 2xCH₃Ar), 3.08 (s, 6H, 2xCH₃N), 4.59-4.64 (m, 2H, 2xCHD), 7.31-7.39 and 7.75-7.78 (2m, 8H, 2xArH); $\delta_{\rm C}$ 21.3 (2xCH₃Ar), 27.4, 27.6 [2x(CH₃)₃C], 35.0, 35.4 (2xCH₃N), 68.9, 69.8 (2t, *J*=21.1 Hz, 2xCHD), 80.7, 80.9 [2x(CH₃)₃C], 128.7, 128.8, 129.4, 129.7 134.2, 134.5, 144.7, 145.0 (ArC), 153.3 and 154.1 (2xC=O); *m/z* 300 (*M*⁺, <1%), 91 (16), 65 (11), 57 (100), 46 (17), 45 (30), 44 (12), 43 (12) and 41 (24) (Found: C, 56.25; H/D, 6.79; N, 4.50; S, 10.50. Calcd. for C₁₄H₂₀DNO₄S: C, 56.00; H/D, 6.67; N, 4.67 and S, 10.67%).²³

1-(1-Tosylpropyl)-2-pyrrolidinone (13cb): v (KBr) 1695 (C=O), 1314, 1306, 1282 and 1148 cm⁻¹ (SO₂); $\delta_{\rm H}$ 0.94 (t, *J*=7.6 Hz, 3H, CH₃CH₂), 1.92-2.18, 2.20-2.34 [2m, 6H, CH₃CH₂, (CH₂)₂CO], 2.43 (s, 3H, CH₃Ar), 3.34-3.42 (m, 1HxCH₂N), 3.75-3.83 (m, 1HxCH₂N), 5.18 (dd, *J*=11.6, 3.7 Hz, 1H, CHS), 7.33 and 7.76 (2d, *J*=7.9 Hz, 4H, ArH); $\delta_{\rm C}$ 10.0 (CH₃CH₂), 16.8, 18.4 (CH₂CH₃, CH₂CH₂CON), 21.6 (CH₃Ar), 30.1 (CH₂CO), 42.5 (CH₂N), 72.3 (CHS), 128.6, 129.6, 134.0, 145.1 (ArC) and 175.4 (C=O); *m/z* 281 (*M*+, <1%), 126 (100), 69 (17) and 41 (21) (Found: C, 59.75; H, 6.80; N, 4.99; S, 11.43. Calcd. for C₁₄H₁₉NO₃S: C, 59.76; H, 6.81; N, 4.98 and S, 11.39%).

I-(*I*-Tosyl-3-butenyl)-2-pyrrolidinone (**13cc**): v (KBr) 3080, 3065 (HC=C), 1705 (C=O), 1301, 1286, 1275 and 1140 cm⁻¹ (SO₂); $\delta_{\rm H}$ 1.88-2.01, 2.03-2.09, 2.14-2.25 [3m, 4H, (CH₂)₂CO], 2.43 (s, 3H, CH₃Ar), 2.70-2.82, 2.95-3.04 (2m, 2H, CH₂CO), 3.40 (dt, J=9.9, 7.0 Hz, 1HxCH₂N), 3.78 (dt, J=9.9, 6.7 Hz, 1HxCH₂N), 5.13 (d, J=11.3 Hz, 1HxCH₂=CH), 5.18 (d, J=18.6 Hz, 1HxCH₂=CH), 5.37 (dd, J=11.9, 3.7 Hz, 1H, CHS), 5.56-5.70 (m, 1H, CH=CH₂), 7.33 and 7.75 (2d, J=8.2 Hz, 4H, ArH); $\delta_{\rm C}$ 18.5 (CH₂CH₂CO), 21.5 (CH₃Ar), 27.5, 29.7 (CH₂CO, CH₂C=), 42.5 (CH₂N), 69.8 (CHS), 118.9 (CH₂=C), 128.5, 129.6, 131.0, 133.5, 145.1 (ArC, CH₂=C) and 175.1 (C=O); *m*/z 188 (*M*+-105, <1%), 139 (10), 138 (100), 91 (11), 70 (10), 69 (18), 65 (11) and 41 (24) (Found: C, 61.44; H, 6.55; N, 4.75; S, 10.90. Calcd. for C₁₅H₁₉NO₃S: C, 61.41; H, 6.53; N, 4.77 and S, 10.93%).

tert-*Butyl* N-*Methyl*-N-(*1*-tosyl-3-butenyl)carbamate (**13dc**):²⁵ v (film) 3082 (HC=C), 1703 (C=O), 1317, 1291 and 1143 cm⁻¹ (SO₂); $\delta_{\rm H}$ 1.11, 1.19 [2s, 18H, 2x(CH₃)₃C], 2.40, 2.44 (2s, 6H, 2xCH₃Ar), 2.69-2.83 (m, 4H, 2xCHSCH₂), 2.88, 2.96 (2s, 6H, 2xCH₃N), 5.12-5.27 (m, 4H, 2xCH₂=CH), 5.52-5.74 (m, 4H, 2xCH=CH₂, 2xCH₂S), 7.30-7.37 and 7.72-7.78 (2m, 8H, 2xArH); $\delta_{\rm C}$ 21.4, 21.5 (2xCH₃Ar), 27.5 (2xCHSCH₂), 27.6, 27.8 [2x(CH₃)₃C], 28.2, 28.9 (2xCH₃N), 73.0, 74.6 (2xCHS), 80.7, 81.0 [2x(CH₃)₃C], 118.8, 119.0 (CH₂=C), 128.9, 129.0, 129.4, 129.7, 131.1, 131.4, 134.1, 144.7, 145.0 (2xArC, 2xCH=CH₂), 153.9 and 154.9 (2xC=O); *m/z* 266 (*M*+-BuⁱO, <1%), 156 (16), 128 (56), 92 (48), 91 (50), 84 (31), 65 (30), 57 (100), 44 (21), 43 (20), 42 (26) and 41 (46).

1-(1-Tosylpentyl)-2-pyrrolidinone (13cd): v (KBr) 1671 (C=O), 1317, 1307, 1280 and 1150 cm⁻¹ (SO₂); $\delta_{\rm H}$ 0.90 (t, J=7.0 Hz, 3H, CH₃CH₂), 1.19-1.47, 2.00-2.30 [2m, 10H, CH₃(CH₂)₃, (CH₂)₂CO], 2.43 (s, 3H, CH₃CH₂) (CH₂) (CH₂)₂CO], 2.43 (s, 3H, CH₃CH₂) (CH₂) (CH₂

CH₃Ar), 3.33-3.41, 3.75-3.83 (2m, 2H, CH₂N), 5.24 (dd, J=11.6, 3.4 Hz, 1H, CHS), 7.33 and 7.75 (2d, J=8.2 Hz, 4H, ArH); $\delta_{\rm C}$ 13.7 (CH₃CH₂), 18.4 (CH₂CH₂CON), 21.6 (CH₃Ar), 21.9, 22.7, 27.5 [(CH₂)₃CH₃], 30.1 (CH₂CO), 42.6 (CH₂N), 70.9 (CHS), 128.6, 129.6, 133.9, 145.1 (ArC) and 175.2 (C=O); *m*/z 309 (*M*⁺, <1%), 154 (100), 124 (18), 98 (38), 91 (11), 86 (11) and 69 (11) (Found: C, 62.15; H, 7.51; N, 4.49; S, 10.34. Calcd. for C₁₆H₂₃NO₃S: C, 62.11; H, 7.49; N, 4.53 and S, 10.36%).

tert-*Butyl* N-*Methyl*-N-(*1-tosylpentyl*)*carbamate* (**13dd**):²⁵ v (film) 1703 (C=O), 1317, 1289 and 1142 cm⁻¹ (SO₂); $\delta_{\rm H}$ 0.89-0.94 (m, 6H, 2xCH₃CH₂), 1.11, 1.20 [2s, 18H, 2x(CH₃)₃C], 1.22-1.50 [m, 8H, 2xCH₃(CH₂)₂], 2.01-2.26 (m, 4H, 2xCHSCH₂), 2.40, 2.43 (2s, 6H, 2xCH₃Ar), 2.87, 2.95 (2s, 6H, 2xCH₃N), 5.63 (dd, *J*=11.6, 3.7 Hz, 1H, CHS), 5.96 (dd, *J*=11.6, 4.0 Hz, 1H, CHS), 7.28-7.36 and 7.72-7.77 (2m, 8H, 2xArH); $\delta_{\rm C}$ 13.7 (2xCH₃CH₂), 21.5 (2xCH₃Ar), 21.7, 21.9, 22.5, 22.6 [2xCH₃(CH₂)₂], 27.2, 27.4 (2xCHSCH₂), 27.6, 27.8 [2x(CH₃)₃C], 28.0, 28.7 (2xCH₃N), 73.8, 75.1 (2xCHS), 80.7, 80.9 [2x(CH₃)₃C], 128.9, 129.0, 129.4, 129.6, 134.5, 144.5, 144.9 (2xArC), 154.1 and 155.0 (2xC=O); *m/z* 282 (*M*+-BuⁱO, <1%), 144 (100), 139 (13), 114 (14), 100 (62), 92 (13), 91 (26), 70 (17), 65 (14), 57 (79), 42 (16) and 41 (18).

1-(1-Tosyl-2-phenylethyl)-2-pyrrolidinone (**13ce**):²⁵ v (film) 1697 (C=O), 1305, 1287, 1268 and 1148 cm⁻¹ (SO₂); $\delta_{\rm H}$ 1.66-1.97 [3m, 4H, (CH₂)₂CO], 2.42 (s, 3H, CH₃Ar), 3.29 (dd, *J*=15.0, 12.2 Hz, 1HxCH₂Ph), 3.32-3.40 (m, 1HxCH₂N), 3.64 (dd, *J*=15.0, 4.0 Hz, 1HxCH₂Ph), 3.76-3.84 (m, 1HxCH₂N), 5.68 (dd, *J*=12.2, 4.0 Hz, 1H, CHS), 7.14-7.35 (m, 7H, 2xp-Tol, PhH) and 7.78 (d, *J*=8.2 Hz, 2H, 2xp-Tol); $\delta_{\rm C}$ 18.3 (CH₂CH₂CON), 21.6 (CH₃Ar), 29.3, 29.8 (CH₂CO, CH₂Ph), 42.7 (CH₂N), 70.8 (CHS), 127.0, 128.2, 128.6, 128.7, 129.6, 133.6, 134.4, 145.2 (ArC) and 175.0 (C=O); *m/z* 188 (*M*+-Ts, 100%), 187 (36), 139 (13), 132 (50), 131 (10), 130 (31), 117 (15), 115 (10), 105 (11), 103 (16), 102 (10), 92 (25), 91 (89), 90 (13), 89 (21), 77 (36), 69 (35), 65 (69), 63 (29), 51 (31), 50 (17), 42 (28) and 41 (79).

tert-*Butyl* N-*Methyl*-N-(*1*-tosyl-2-phenylethyl)carbamate (**13de**):²⁵ v (film) 1705 (C=O), 1318 and 1147 cm⁻¹ (SO₂); $\delta_{\rm H}$ 0.97, 1.10 [2s, 18H, 2x(CH₃)₃C], 2.39, 2.42 (2s, 6H, 2xCH₃Ar), 2.84, 2.95 (2s, 6H, 2xCH₃N), 3.17-3.29, 3.59-3.67 (2m, 4H, 2xCH₂CHS), 5.56 (dd, *J*=11.9, 3.4 Hz, 1H, CHS), 5.87 (dd, *J*=11.9, 4.0 Hz, 1H, CHS), 7.16-7.36 and 7.76-7.81 (2m, 18H, 2xArH); $\delta_{\rm C}$ 21.4 (2xCH₃Ar), 27.4, 27.6 [2x(CH₃)₃C], 28.3, 29.0 (2xCH₃N), 29.2, 29.3 (2xCH₂CHS), 73.8, 75.9 (2xCHS), 80.6, 80.7 [2x(CH₃)₃C], 126.8, 127.0, 128.4, 128.5, 128.6, 128.8, 128.9, 129.4, 129.7, 134.1, 134.2, 135.0, 135.2, 144.7, 145.0 (ArC), 153.6 and 154.8 (2xC=O); *m/z* 388 (*M*+-1, <1%), 387 (*M*+-2, <1), 172 (56), 108 (19), 107 (38), 105 (14), 92 (16), 91 (100), 90 (13), 89 (18), 79 (16), 77 (33), 65 (42), 63 (22), 51 (18) and 50 (12).

tert-*Butyl 3-Tosyl-3-*(2-*oxotetrahydro-1*H-*1-pyrrolyl)propanoate* (**13cf**):²⁵ v (film) 1732, 1682 (C=O), 1292, 1276 and 1145 cm⁻¹ (SO₂); δ_{H} 1.40 [s, 9H, (CH₃)₃C], 1.91-2.24 [m, 4H, (CH₂)₂CO], 2.44 (s, 3H, CH₃Ar), 2.93 (dd, *J*=15.6, 11.6 Hz, 1HxCH₂CO), 3.19 (dd, *J*=15.6, 4.0 Hz, 1HxCH₂CO), 3.42-3.56, 3.74-3.82 (2m, 2H, CH₂N), 5.64 (dd, *J*=11.6, 4.0 Hz, 1H, CHS), 7.34 and 7.75 (2d, *J*=8.0 Hz, 4H, ArH); δ_{C} 17.2 (CH₂CH₂CON), 21.6 (CH₃Ar), 27.7 [(CH₃)₃C], 29.9, 30.7 (2xCH₂CO), 42.8 (CH₂N), 68.0 (CHS), 82.1 [(CH₃)₃C], 128.7, 129.7, 133.0, 136.3 (ArC), 167.2 and 174.5 (2xC=O); *m/z* 294 (*M*+-Bu⁴O, 2%), 212 (28), 156 (31), 155 (36), 139 (23), 138 (45), 137 (12), 113 (10), 112 (22), 110 (55), 100 (19), 91 (13), 82 (41), 70 (13), 69 (13), 57 (100), 56 (20), 43 (27) and 41 (47).

erythro-1-(2-Hydroxy-3,3-dimethyl-1-tosylbutyl)-2-pyrrolidinone (erythro-13cg):²⁵ R_f 0.88 (EtOAc); v (film) 3526 (OH), 1698 (C=O), 1302, 1287, 1265 and 1144 cm⁻¹ (SO₂); δ_H 0.93 [s, 9H, (CH₃)₃C], 1.71-2.27 [m, 4H, (CH₂)₂CO], 2.45 (s, 3H, CH₃Ar), 3.35 (br s, 1H, OH), 3.87-3.94, 3.99-4.13 (2m, 2H, CH₂N), 4.28 (br s, 1H, CHO), 5.52 (br s, 1H, CHS), 7.36 and 7.79 (2d, J=8.2 Hz, 4H, ArH); δ_C 19.0 (CH₂CH₂N), 21.7 (CH₃Ar), 26.0 [(CH₃)₃C], 29.5 (CH₂CO), 35.6 [(CH₃)₃C], 46.8 (CH₂N), 71.0, 75.3 (CHO, CHS), 128.6, 129.9, 133.5, 145.6 (ArC) and 176.0 (CO); *m/z* 278 (*M*+61, <1%), 107 (11), 105 (33), 98 (100), 92 (21), 91 (52), 84 (44), 77 (40), 70 (47), 69 (23), 65 (35), 63 (13), 51 (36), 43 (20), 42 (36) and 41 (58).

threo-1-(2-Hydroxy-3,3-dimethyl-1-tosylbutyl)-2-pyrrolidinone (threo-13cg): v (KBr) 3526 (OH), 1699 (C=O), 1302, 1287, 1269 and 1144 cm⁻¹ (SO₂); $\delta_{\rm H}$ 0.91 [s, 9H, (CH₃)₃C], 1.89-2.05, 2.20-2.29 [2m, 4H, (CH₂)₂CO], 2.43 (s, 3H, CH₃Ar), 2.47 (br s, 1H, OH), 3.52-3.59, 3.80-3.88 (2m, 2H, CH₂N), 4.00 (d,

J=9.2 Hz, 1H, CHO), 5.50 (d, J=9.2 Hz, 1H, CHS), 7.33 and 7.77 (2d, J=8.2 Hz, 4H, ArH); $\delta_{\rm C}$ 18.4 (CH₂CH₂N), 21.6 (CH₃Ar), 25.5 [(CH₃)₃C], 30.0 (CH₂CO), 36.0 [(CH₃)₃C], 44.4 (CH₂N), 73.6, 74.6 (CHO, CHS), 128.1, 129.6, 137.0, 144.6 (ArC) and 175.6 (CO); *m*/*z* 278 (*M*+-61, <1%), 107 (11), 105 (33), 98 (100), 92 (21), 91 (52), 84 (44), 77 (40), 70 (47), 69 (23), 65 (35), 63 (13), 51 (36), 43 (20), 42 (36) and 41 (58) (Found: C, 60.12; H, 7.40; N, 4.13; S, 9.48. Calcd. for C₁₇H₂₅NO₄S: C, 60.15; H, 7.42; N, 4.13 and S, 9.44%).

erythro-*1*-(2-*Hydroxy*-*1*-*tosyl*-2-*phenylethyl*)-2-*pyrrolidinone* (*erythro*-**13ch**): v (KBr) 3600-3100 (OH), 1700 (C=O), 1315, 1300, 1284 and 1143 cm⁻¹ (SO₂); $\delta_{\rm H}$ 1.78-2.01 [m, 4H, (C*H*₂)₂CO], 2.43 (s, 3H, C*H*₃Ar), 3.78 (br s, 1H, OH), 3.94 (m, 2H, CH₂N), 5.53, 5.74 (2m, 2H, CHO, CHS), 7.24-7.32 (m, 7H, 2*xp*-Tol, PhH) and 7.74 (d, *J*=7.6 Hz, 2H*xp*-Tol); $\delta_{\rm C}$ 18.9 (*C*H₂CH₂N), 21.7 (*C*H₃Ar), 29.3 (*C*H₂CO), 46.0 (CH₂N), 70.4, 74.4 (CHO, CHS), 125.7, 128.1, 128.4, 128.5, 129.8, 134.1, 138.1, 145.5 (ArC) and 176.0 (CO); *m/z* 281 (*M*+-PhH, <1%), 139 (23), 112 (27), 107 (15), 106 (10), 105 (68), 98 (100), 92 (26), 91 (61), 85 (12), 84 (54), 79 (12), 77 (66), 70 (34), 69 (25), 65 (30), 63 (12), 51 (41), 50 (18), 49 (11), 43 (13), 42 (26) and 41 (38) (Found: C, 63.50; H, 5.88; N, 3.93; S, 8.91. Calcd. for C ₁₉H₂₁NO₄S: C, 63.97; H, 5.78; N, 4.00 and S, 9.10%).

threo-1-(2-Hydroxy-1-tosyl-2-phenylethyl)-2-pyrrolidinone (threo-13ch):²⁵ R_f 0.83 (EtOAc); v (film) 3600-3100 (OH), 1700 (C=O), 1315, 1300, 1284 and 1143 cm⁻¹ (SO₂); $\delta_{\rm H}$ 1.39-1.49, 1.71-1.99 [2m, 4H, (CH₂)₂CO], 2.43 (s, 3H, CH₃Ar), 3.11-3.19, 3.69-3.73 (2m, 2H, CH₂N), 3.95 (m, 1H, OH), 5.45, 5.75 (2br s, *J*=9.5 Hz, 2H, CHO, CHS), 7.28-7.34 (m, 7H, 2x*p*-Tol, PhH) and 7.80 (d, *J*=8.2 Hz, 2Hx*p*-Tol); $\delta_{\rm C}$ 18.6 (CH₂CH₂N), 21.7 (CH₃Ar), 29.3 (CH₂CO), 44.0 (CH₂N), 71.5, 74.8 (CHO, CHS), 127.2, 128.4, 128.7, 129.0, 129.7, 135.2, 138.0, 145.3 (ArC) and 175.1 (CO): *m*/*z* 281 (*M*+-PhH, <1%), 139 (23), 112 (27), 107 (15), 106 (10), 105 (68), 98 (100), 92 (26), 91 (61), 85 (12), 84 (54), 79 (12), 77 (66), 70 (34), 69 (25), 65 (30), 63 (12), 51 (41), 50 (18), 49 (11), 43 (13), 42 (26) and 41 (38).

tert-*Butyl* N-*[(1-Hydroxycyclopentyl)*-N-*methylcarbamate* (**13di**): v (KBr) 3525 (OH), 1693 (C=O), 1319, 1302 and 1137 cm⁻¹ (SO₂); $\delta_{\rm H}$ 1.19, 1.27 [2s, 18H, 2x(CH₃)₃C], 1.34-2.16 [m, 9H, OH, (CH₂)₄], 2.41, 2.44 (2s, 6H, 2xCH₃Ar), 3.16, 3.17 (2s, 6H, 2xCH₃N), 5.21, 5.48 (2s, 2H, 2xCHS), 7.29-7.37 and 7.75-7.82 (2m, 8H, 2xArH); $\delta_{\rm C}$ 21.4, 21.5 (2xCH₃Ar), 22.2, 22.3, 24.0, 24.3, 38.6, 40.6, 41.0 [2x(CH₂)₄], 27.8, 27.9 [2x(CH₃)₃C], 31.4, 32.0 (2xCH₃N), 79.0, 80.3 (2xCHS), 80.9, 81.3, 84.3, 84.4 [2x(CH₃)₃C, 2xCOH], 128.4, 128.5, 129.5, 129.7, 135.9, 136.2, 142.1, 144.7, 145.1 (2xArC), 153.9 and 155.7 (2xC=O); *m*/z 239 (*M*+-144, <1%), 172 (83), 108 (25), 107 (47), 92 (10), 91 (100), 79 (18), 77 (25), 65 (42), 63 (20) and 51 (10) (Found: C, 59.70; H, 7.40; N, 3.66; S, 8.40. Calcd. for C₁₉H₂₉NO₅S: C, 59.51; H, 7.62; N, 3.65 and S, 8.36%).

Ethyl 2-Tosyl-2-(2-oxotetrahydro-1H-1-pyrrolyl)acetate (**13cj**): v (film) 1750, 1708 (C=O), 1325, 1291 and 1147 cm⁻¹ (SO₂); $\delta_{\rm H}$ 1.28 (t, *J*=7.0 Hz, 3H, CH₃CH₂), 2.02-2.12, 2.25-2.42 [2m, 4H, (CH₂)₂CO], 2.46 (s, 3H, CH₃Ar), 3.83-3.91, 4.01-4.13 (2m, 2H, CH₂N), 4.20-4.34 (m, 2H, CH₂CH₃), 6.07 (s, 1H, CHS), 7.37 and 7.81 (2d, *J*=8.2 Hz, 4H, ArH); $\delta_{\rm C}$ 13.7 (CH₃CH₂), 18.6 (CH₂CH₂N), 21.6 (CH₃Ar), 29.6 (CH₂CO), 45.0 (CH₂N), 62.6 (CH₂O), 73.3 (CHS), 128.8, 129.6, 135.0, 145.5 (ArC), 162.7 and 176.1 (2xCO); *m/z* 325 (*M*+, <1%), 170 (100), 142 (60), 114 (16), 91 (13), 86 (12), 69 (23), 68 (12), 65 (12), 42 (14) and 41 (25) (Found: *M*++1 326.1062. Calcd. for C₁₅H₂₀NO₅S, 326.1062).

tert-*Butyl* N-*[(Ethoxycarbonyl)tosylmethyl]*-N-*methylcarbamate* (**13dj**):²⁵ v (film) 1752, 1705 (C=O), 1325, 1305 and 1144 cm⁻¹ (SO₂); $\delta_{\rm H}$ 1.25-1.35 [m, 24H, 2x(CH₃)₃C, 2xCH₃CH₂], 2.43, 2.45 (2s, 6H, 2xCH₃Ar), 3.09, 3.12 (2s, 6H, 2xCH₃N), 4.24-4.37 (m, 4H, 2xCH₂CH₃), 5.85, 6.22 (2s, 2H, 2xCHS), 7.33-7.39 and 7.76-7.84 (2m, 8H, 2xArH); $\delta_{\rm C}$ 13.9 (2xCH₃CH₂), 21.5 (2xCH₃Ar), 27.8, 27.9 [2x(CH₃)₃C], 32.3, 32.6 (2xCH₃N), 62.5, 62.8 (2xCH₂CH₃), 76.8 (2xCHS), 81.6, 82.0 [2x(CH₃)₃C], 128.9, 129.1, 129.5, 129.7, 135.3, 135.4, 145.1, 145.4 (2xArC), 153.4, 155.2 (2xCO₂N), 162.9 and 163.3 (2xCO₂Et); *m/z* 371 (*M*+, <1%), 216 (14), 160 (12), 157 (12), 144 (17), 139 (22), 116 (100), 92 (15), 91 (30), 88 (11), 65 (13), 57 (80), 42 (16) and 41 (14).

l-(*l*-Tosyl-2-oxopropyl)-2-pyrrolidinone (**13ck**): v (film) 1718, 1699 (C=O), 1318, 1305, 1290 and 1146 cm⁻¹ (SO₂); $\delta_{\rm H}$ 1.51-2.26 [m, 4H, (CH₂)₂CO], 2.45 (s, 3H, CH₃Ar), 2.55 (s, 3H, CH₃CO), 3.71-3.79,

3.88-3.96 (2m, 2H, CH₂N), 6.11 (s, 1H, CHS), 7.37 and 7.81 (2d, J=8.2 Hz, 4H, ArH); $\delta_{\rm C}$ 18.9 (CH₂CH₂N), 21.7 (CH₃Ar), 29.5 (CH₂CO), 30.7 (CH₃CO), 44.8 (CH₂N), 77.9 (CHS), 128.6, 129.9, 134.1, 146.0 (ArC), 175.6 (CON) and 195.6 (PhCO); m/z 296 (M++1, <1%), 295 (M+, <1), 140 (100), 70 (11), 69 (12), 43 (17), 42 (13) and 41 (18) (Found: M+ 295.0867. Calcd. for C₁₄H₁₇NO₄S, 295.0879).

 $\begin{array}{l} 1-(1-Tosyl-2-oxo-2-phenylethyl)-2-pyrrolidinone (13cl):^{25} v \text{ (film) 1735, 1689 (C=O), 1300, 1287, 1263 and 1148 cm^{-1} (SO_2); \\ \delta_{\rm H} 2.02 (m, 2H, CH_2CH_2CO), 2.26 (t, J=7.6 Hz, 2H, CH_2CO), 2.44 (s, 3H, CH_3Ar), 3.62-3.70, 4.03-4.10 (2m, 2H, CH_2N), 6.88 (s, 1H, CHS) and 7.31-7.88 (m, 9H, ArH); \\ \delta_{\rm C} 18.8 (CH_2CH_2CON), 21.7 (CH_3Ar), 29.7 (CH_2CO), 45.2 (CH_2N), 72.4 (CHS), 128.8, 128.9, 129.1, 129.9, 134.5, 134.6, 135.2, 145.7 (ArC), 175.3 (CON) and 189.3 (PhCO); m/z 357 (M⁺, <1%), 202 (65), 105 (100), 91 (30), 77 (85), 69 (27), 65 (24), 51 (31), 42 (40) and 41 (99). \end{array}$

tert-*Butyl* (E)-3-(2-Oxotetrahydro-1H-1-pyrrolyl)-2-propenoate (14cf): R_f 0.75 (EtOAc); v (film) 3082, 1600, 981 (HC=C), 1732 and 1699 cm⁻¹ (C=O); δ_H 1.49 [s, 9H, (CH₃)₃C], 2.17 (q, *J*=7.0 Hz, 2H, CH₂CH₂CO), 2.54 (t, *J*=7.6 Hz, 2H, CH₂CO), 3.54 (t, *J*=7.3 Hz, 2H, CH₂N), 5.14 and 7.99 (2d, *J*=14.3 Hz, 2H, CH=CH); δ_C 17.3 (*C*H₂CH₂CO), 28.1 [(*C*H₃)₃C], 30.8 (*C*H₂CO), 44.9 (CH₂N), 80.0 [(CH₃)₃C], 102.6, 136.3 (C=C), 166.4 and 174.0 (2xC=O); *mlz* 212 (*M*++1, <1%), 211 (*M*+, 6), 155 (61), 154 (12), 138 (63), 137 (18), 113 (16), 110 (100), 109 (15), 100 (32), 83 (11), 82 (78), 70 (26), 69 (13), 68 (12), 57 (33), 56 (32), 55 (25), 54 (14), 53 (11), 44 (14), 43 (13) and 42 (20).

Reaction of Compound 13df with Potassium tert-Butoxide. Isolation of tert-Butyl N-(2-tert-Butoxycarbonylethenyl)-N-methylcarbamate (14df).- To a solution of crude compound 13df (0.16 mmol) in dry THF (4 mL) was added potassium tert-butoxide (ca. 5 equiv), the reaction mixture was stirred at room temperature for 20 min. Then the mixture was poured into water and extracted with EtOAc (2x10 ml). The organic layer was dried over Na₂SO₄, evaporated (15 Torr) and the residue was purified by flash chromatography (silica gel, hexane/EtOAc) to yield pure compound 14df: R_f 0.79 (hexane/EtOAc: 2/1); v (film) 1725, 1709 (C=O), 1143 and 1133 cm⁻¹ (CO); δ_H 1.49, 1.52 [2s, 18H, 2x(CH₃)₃C], 3.04 (s, 3H, CH₃N), 5.06 and 8.17 (2d, J=14.0 Hz, 2H, CH=CH); δ_C 28.1, 28.3 [2x(CH₃)₃C], 31.0 (CH₃N), 79.7, 82.9 [2x(CH₃)₃C], 99.2 (CH=CHN), 142.7 (CH=CHN), 152.2 (CO₂CH=CH) and 167.1 (NCO₂); m/z 258 (M++1, <1%), 257 (M+, 6), 184 (17), 128 (53), 102 (14), 101 (100), 84 (34), 83 (57), 58 (26), 57 (89), 56 (51), 55 (41), 44 (45), 43 (19) and 42 (58) (Found: M+257.1633. Calcd. for C₁₃H₂₃NO₄, 257.1627).

Reduction of Sulfone 13ce with Sodium Amalgam.- To a suspension of anhydrous Na_2HPO_4 (251 mg, 1.75 mmol) and *ca*. 6% sodium amalgam (1.70 g, 4.4 mmol) in dry methanol (5 ml) was dropped at 0°C a solution of the sulfone (0.44 mmol) in methanol (1.5 ml). The reaction mixture was stirred at room temperature until the reduction was complete (monitored by TLC and GLC). Then, the reaction mixture was hydrolyzed with water and extracted with dichloromethane (3x15 ml). The organic layer was dried over Na_2SO_4 , concentrated in vacuo (15 Torr) and the residue was purified by flash chromatography (silica gel, hexane/EtOAc) to yield the desulfonylated compounds 15ce and 14ce. Yields are included in Scheme 5; physical and spectroscopic data, as well as literature references for known compounds follow:

1-Phenylethyl-2-pyrrolidinone (**15ce**):²⁶ *t*, 12.28 min; v (film) 1678 cm⁻¹ (C=O); $\delta_{\rm H}$ 1.95 (m, 2H, CH₂CH₂CO), 2.34 (t, J=7.6 Hz, 2H, CH₂CO), 2.84 (t, J=7.6 Hz, 2H, CH₂Ar), 3.24 (t, J=7.0 Hz, 2H, ArCH₂CH₂N), 3.53 (t, J=7.3 Hz, 2H, CO(CH₂)₂CH₂N) and 7.18-7.37 (m, 5H, ArH); $\delta_{\rm C}$ 18.0 (CH₂CH₂CO), 30.9, 33.8 (CH₂CO, CH₂Ph), 44.0, 47.6 (2xCH₂N), 126.4, 128.5, 128.6, 138.3 (ArC) and 174.8 (C=O); *m/z* 190 (*M*++1, 5%), 189 (*M*+, 37), 104 (36), 99 (16), 98 (100), 91 (16), 77 (15), 70 (50), 69 (30), 68 (14), 65 (14), 51 (13), 43 (32) and 42 (33).

1-[(E)-2-Phenyl-1-ethenyl]-2-pyrrolidinone (14ce):²⁷ t_r 13.95 min; δ_H 2.16 (m, 2H, CH₂CH₂N), 2.55 (t, *J*=7.9 Hz, 2H, CH₂CO), 3.66 (t, *J*=7.0 Hz, 2H, CH₂N), 5.89, 7.63 (2d, *J*=15.0 Hz, 2H, CH=CH), and 7.18-7.37 (m, 5H, ArH); δ_C 17.4 (*C*H₂CH₂N), 31.2 (CH₂CO), 45.2 (CH₂N), 111.7, 123.6, 125.6, 126.5, 128.5, 136.3 (CH) and 172 (C=O); *m/z* 188 (*M*++1, 11%), 187 (*M*+, 88), 133 (10), 132 (100), 130 (51), 117 (24), 115 (19), 103 (14), 102 (11), 91 (12), 77 (28), 65 (28) and 51 (21).

Reduction of Compound 13cl with Sodium Dithionite. Isolation of N-(2-Phenyl-2-oxoethyl)-2pyrrolidinone (15cl)²⁸.- Sodium dithionite (0.34 mmol), sodium hydrogen carbonate (28 mg) were added to a solution of compound 13cl (48 mg, 0.13 mmol) in DMF (3 ml) and water (2 ml). The mixture was heated to 100°C for 24 h and then poured into water (15 ml), extracted with EtOAc (3x15 ml). The organic layer was dried over Na₂SO₄ and evaporated (15 Torr), the residue was column chromatographied (silica gel, hexane/EtOAc) to afford pure compound 15cl:²⁵ R_f 0.27 (EtOAc); v (film) 1701 and 1681 cm⁻¹ (C=O); δ_H 2.12 (m, J=7.0 Hz, 2H, CH₂CH₂N), 2.49 (t, J=7.9 Hz, 2H, CH₂CO), 3.51 (t, J=7.0 Hz, 2H, CH₂CH₂N), 4,74 (s, 2H, NCH₂CO), 7.46-7.63 and 7.95-7.98 (2m, 5H, PhH); δ_C 18.0 (CH₂CH₂N), 30.4 (CH₂CO), 47.9, 49.1 (2xCH₂N), 128.0, 128.8, 133.8, 134.9 (ArC), 178.8 (CON) and 193.0 (CO); m/z 204 (M⁺⁺¹, <1%), 203 (M⁺, 5), 105 (41), 98 (100), 84 (67), 77 (31), 70 (42), 69 (16), 51 (19), 43 (11) and 42 (18).

Reduction of Amido Sulfone **13dj** *with Magnesium in Methanol. Isolation of Ethyl* N-(tert-*Butoxy-carbonyl*)-N-*methyl-2-aminoacetate* (**15dj**).- A mixture of substrate **13dj** (2.0 mmol), magnesium powder (146 mg, 6.0 mmol), a few crystals of HgCl₂ in dry MeOH (10 ml) was stirred for 6 h at room temperature. The reaction mixture was poured into water and extracted with CH₂Cl₂ (3x10 ml). The organic layer was dried over Na₂SO₄, concentrated *in vacuo* (15 Torr) to give crude product which was purified by flash chromatography to afford pure compound **15dj**:²⁵ *R*_f 0.34 (hexane/EtOAc: 1/1); v (film) 1755, 1702 (C=O) and 1148 cm⁻¹ (CO); δ_H 1.43, 1.47 [2s, 18H, 2x(CH₃)₃C], 2.92, 2.94 (2s, 6H, 2xCH₃N), 3.73, 3.74 (2s, 6H, 2xCH₃O), 3.91 and 3.99 (2s, 4H, 2xCH₂N); δ_C 28.2, 28.3 [2x(CH₃)₃C], 35.5 (2xCH₃N), 50.1, 50.9 (2xCH₂N), 51.9 (CH₃O), 80.1 [2x(CH₃)₃C], 155.1, 155.4 (2xNCO₂) and 170.4 (*CO*₂Me); *m/z* 149 (*M*+-54, 3%), 148 (17), 147 (10), 144 (11), 130 (11), 104 (14), 103 (17), 102 (45), 88 (19), 59 (13), 58 (22), 57 (95), 56 (32), 55 (14), 45 (16), 44 (100), 43 (48) and 42 (63).

Reaction of α -Sulfonyl Carbanions Derived from Sulfones 13ce and 13dc with Chloromethylmagnesium Chloride.- To a solution of (chloromethyl)magnesium chloride at -78°C in THF (2 mmol) [prepared from reaction of chloroiodomethane (2 mmol), isopropylmagnesium chloride (2 mmol) at -78°C]¹⁶ was transferred via cannula a solution of the corresponding lithiated sulfone (1 mmol) at -78°C, allowing the reaction mixture to warm to 0°C. Then, the reaction was quenched with water and extracted with EtOAc (3x10 ml). The organic layer was dried over Na₂SO₄ and evaporated (15 Torr) to give the corresponding crude product which was then purified by column chromatography (silica gel, hexane/EtOAc) to afford pure compounds 16ce and 17. Yields are included in the text; physical, spectroscopic and analytical data follow:

 $\begin{aligned} &I-(I-Benzylvinyl)-2-pyrrolidinone \ (16ce): R_f \ 0.51 \ (\text{ether}); \ v \ (\text{film}) \ 3084 \ (\text{HC=C}) \ \text{and} \ 1691 \ \text{cm}^{-1} \ (\text{C=O}); \ \delta_{\text{H}} \\ &I-92 \ (\text{m}, \ 2\text{H}, \ \text{CH}_2\text{CH}_2\text{CO}), \ 2.39 \ (\text{t}, \ J=7.9 \ \text{Hz}, \ 2\text{H}, \ \text{CH}_2\text{CO}), \ 3.49 \ (\text{t}, \ J=7.0 \ \text{Hz}, \ 2\text{H}, \ \text{CH}_2\text{Ar}), \ 3.92 \ (\text{s}, \ 2\text{H}, \ \text{CH}_2\text{Ph}), \ 4.61, \ 4.81 \ (2\text{s}, \ 2\text{H}, \ \text{CH}_2\text{=C}) \ \text{and} \ 7.20\text{-}7.31 \ (\text{m}, \ 5\text{H}, \ \text{ArH}); \ \delta_{\text{C}} \ 18.0 \ (\text{CH}_2\text{CH}_2\text{CO}), \ 32.6 \ (\text{CH}_2\text{CO}), \ 39.6 \ (\text{CH}_2\text{C=}), \ 49.5 \ (\text{CH}_2\text{N}), \ 103.2 \ (\text{CH}_2\text{=C}), \ 126.3, \ 128.3, \ 128.8, \ 138.5, \ 144.9 \ (\text{ArC}, \ \text{CH}_2\text{=C}) \ \text{and} \ 174.1 \ (\text{C=O}); \ m/z \ 203 \ (M^++2, \ 1\%), \ 202 \ (M^++1, \ 15), \ 201 \ (M^+, \ 100), \ 172 \ (11), \ 146 \ (35), \ 144 \ (33), \ 131 \ (11), \ 129 \ (24), \ 117 \ (16), \ 116 \ (65), \ 115 \ (88), \ 96 \ (13), \ 91 \ (27), \ 89 \ (12), \ 86 \ (72), \ 82 \ (52), \ 77 \ (10), \ 68 \ (11), \ 65 \ (20), \ 55 \ (10), \ 54 \ (14), \ 51 \ (18), \ 44 \ (18) \ \text{and} \ 42 \ (32) \ (Found: \ M^+ \ 201.1153. \ Calcd. \ for \ C_{13}H_{15}\text{NO}, \ 201.1154). \end{aligned}$

tert-Butyl N-(1-Methyl-1,3-butadienyl)-N-methylcarbamate (17): R_f 0.85 (hexane/EtOAc: 1/1); v (film) 3086, 1650 (HC=C) and 1702 cm⁻¹ (C=O); δ_H 1.46 [s, 9H, (CH₃)₃C], 3.04 (s, 3H, CH₃N), 5.10 (d, J=10.0 Hz, 1HxCH₂=CH), 5.18 (d, J=17.4 Hz, 1HxCH₂=C), 5.87 (d, J=11.0 Hz, 1H, CH=CN) and 6.42-6.54 (m, 1H, CH=CH₂); δ_C 16.4 (CH₃C=CH), 28.3 [(CH₃)₃C], 36.3 (CH₃N), 79.9 [(CH₃)₃C], 116.8 (CH₂=CH), 124.5, 132.4 (CH=CH), 140.3 (CH₃C=CH) and 154.5 (CO); m/z 197 (M+, 1%), 141 (48), 140 (31), 124 (13), 97 (17), 96 (90), 82 (43), 67 (21), 66 (11), 58 (27), 57 (100), 56 (56), 55 (44), 54 (18), 44 (39) and 42 (36) (Found: M+ 197.1412. Calcd. for C₁₁H₁₉NO₂, 197.1416).

Reaction of Amido Sulfone 13dc with Phenylmagnesium Bromide. Isolation of tert-Butyl N-(1-Phenyl-3- butenyl)-N-methylcarbamate (18).- Phenylmagnesium bromide (405 μ l, 1.22 mmol) was added to a solution of anhydrous zinc chloride (165 mg, 0.73 mmol) in dry THF (4 ml), the mixture was stirred at room temperature under argon for 30 min to afford the organozinc species. Then, a solution of the sulfone (206 mg, 0.61 mmol) was added and stirring continued at room temperature for 24 h. The reaction was then quenched with water and extracted with EtOAc (3x10 ml), the organic layer was dried over Na₂SO₄, evaporated (15 Torr). The crude product was purified by column chromatography (silica gel, hexane/EtOAc) to afford pure compound **18**²⁵ as an oil: R_f 0.54 (hexane/EtOAc: 1/1); v (film) 1690 (C=O) and 1147 cm⁻¹ (C-O); δ_H 1.48 [s, 9H, (CH₃)₃C], 2.55-2.75 (m, 6H, CH₃N, CH₂CHN), 5.08 (d, *J*=10.1 Hz, 1HxCH=CH₂), 5.15 (d, *J*=17.1 Hz, 1HxCH=CH₂), 5.76-5.89 (m, 1H, CH=CH₂) and 7.23-7.36 (m, 5H, PhH); δ_C 28.4 (CH₃N), 28.5 [(CH₃)₃C], 34.7 (CH₂CH=CH₂), 56.1, 57.5 (2br s, NCH₂Ph), 79.5 [(CH₃)₃C], 117.1 (CH₂=CH), 127.2, 127.3, 128.3, 134.9, 140.2 (ArC, CH₂=CH) and 156.2 (CO); *m*/z 220 (*M*+-CH₂CHCH₂, 23%), 165 (18), 164 (100), 131 (36), 120 (96), 118 (20), 91 (27), 77 (19), 58 (15), 57 (63), 51 (14), 44 (25) and 42 (52).

Naphthalene-catalysed Lithiation of N-Methyl-N-(tosylmethyl)aniline **19** and α -Amidomethyl Sulfone **7c** and **7d**. Isolation of Compounds **20** and **22**. General Procedure.-To a green suspension of lithium powder (100 mg, 14 mmol) and naphthalene (10 mg, 0.08 mmol) in THF (5 ml) was slowly added (ca. 10 min) a solution of compound **19**, **7c** or **7d** (1 mmol) and the electrophile (1.2 mmol) in THF (2 ml) at -78°C under an argon atmosphere. Stirring was continued for 2 h allowing the temperature to rise to 0°C for compound **19**; for compound **7c** the temperature was allowing to rise to 20°C overnight; for compound **7d** the reaction mixture was stirred for 2 h at -78°C. Then, the resulting mixture was hydrolysed with water (5 ml) and extracted with EtOAc (2x20 ml). The organic layer was dried over anhydrous Na₂SO₄ and the solvents evaporated (15 Torr) to give a residue, which was purified by column chromatography (silica gel or neutral alumina for derivatives of **7d**, hexane/EtOAc) affording pure title compounds **20** or **22**. Yields and R_f values are included in Tables 3 and 4. Spectral and analytical data as well as literature data for known compounds follow.

3.3-Dimethyl-1-(N-methylanilino)-2-butanol (**20a**): t_r 11.81 min: v (film) 3417 (OH), 3101, 3063, 3018, 1600 and 1506 cm⁻¹ (HC=C): $\delta_{\rm H}$ 1.00 [s, 9H, (CH₃)₃C], 2.92 (s, 4H, CH₃N, OH), 3.23 (dd, *J*=14.2, 10.4 Hz, 1H, 1xCH₂), 3.34 (dd, *J*=14.2, 3.0 Hz, 1H, 1xCH₂), 3.58 (dd, *J*=10.4, 3.0 Hz, 1H, CHO), 6.75-6.85 and 7.20-7.30 (2m, 2 and 3H, ArH): $\delta_{\rm C}$ 25.7 [(CH₃)₃C], 33.8 [C(CH₃)₃], 39.1 (CH₃N), 56.5 (CH₂), 75.8 (CO), 114.0, 117.8, 129.1, and 151.0 (ArC); *m/z* 208 (*M*++1, 4%), 207 (*M*+, 25), 150 (11), 121 (35), 120 (100), 107 (10), 106 (12), 105 (14), 104 (15), 77 (27), 57 (12), 51 (12) and 42 (13) (Found: *M*+ 207.1621. Calcd. for C₁₃H₂₁NO, 207.1623).

2-(N-*Methylanilino*)-*1*-phenylethanol (**20b**):²⁹ t 14.19 min; v (film) 3417 (OH), 3099, 3061, 3027, 1599 and 1506 cm⁻¹ (HC=C); $\delta_{\rm H}$ 2.52 (br s, 1H, OH), 2.94 (s, 3H, CH₃), 3.43 (dd, *J*=14.6, 4.6 Hz, 1H, 1xCH₂), 3.51 (dd, *J*=14.6, 8.6 Hz, 1H, 1xCH₂), 5.00 (dd, *J*=8.6, 4.6 Hz, 1H, CHO), 6.75-6.85 and 7.20-7.45 (2m, 3 and 7H, respectively, ArH); $\delta_{\rm C}$ 39.4 (CH₃N), 62.0 (CH₂), 71.7 (CO), 113.3, 117.6, 125.9, 127.8, 128.5, 129.2, 141.9 and 149.9 (ArC); *m/z* 228 (*M*++1, 1%), 227 (*M*+, 5), 209 (10), 121 (14), 120 (100), 106 (13), 105 (16), 104 (11), 77 (30), 51 (16) and 42 (15).

2-*Ethyl-1*-(N-*methylanilino*)-2-*butanol* (**20**c): t_r 12.19 min; v (film) 3458 (OH), 3097, 3066, 3040, 1674, 1600 and 1506 cm⁻¹ (HC=C); $\delta_{\rm H}$ 0.94 (t, *J*=7.6 Hz, 6H, 2xCH₃CH₂), 1.58 (q, *J*=7.6 Hz, 4H, 2xCH₂CH₃), 1.74 (br s, 1H OH), 2.99 (s, 3H, CH₃N), 3.30 (s, 2H, CH₂N), 6.70-6.75, 6.85-6.90 and 7.20-7.25 (3m, 5H, Ph); $\delta_{\rm C}$ 7.8 (2xCH₃CH₂), 29.2 (2xCH₂CH₃), 41.1 (CH₃N), 61.3 (CH₂N), 76.2 (CO), 112.9, 117.1, 129.0 and 151.5 (ArC); *m/z* 208 (*M*++1, 2%), 207 (*M*+, 9), 121 (25), 120 (100), 107 (11), 77 (20), 57 (13), 44 (17), 43 (16) and 42 (13) (Found: *M*+ 207.1624. Calcd. for C₁₃H₂₁NO, 207.1623).

2,4-Dimethyl-3-(N-methylanilinomethyl)-3-pentanol (**20d**): t_r 12.57 min; v (film) 3515 (OH), 3061, 1600 and 1505 cm⁻¹ (HC=C); $\delta_{\rm H}$ 0.99 (d, J=7.0 Hz, 6H, 2xCH₃C), 1.05 (d, J=6.7 Hz, 6H, 2xCH₃C), 1.85-2.10 (m, 2H, 2xCHCH₃), 2.95 (s, 3H, CH₃N), 3.37 (s, 2H, CH₂), 6.75-6.80, 6.90-6.95 and 7.20-7.30 (3m, 5H, ArH); $\delta_{\rm C}$ 17.5, 17.7, 18.2, 18.3 (4xCH₃C), 33.7 (CH₃N), 42.0 (2xCCH₃), 57.0 (CH₂), 77.3 (CO), 114.2, 117.7, 128.9 and 152.1 (ArC); m/z 236 (M^{+} +1, 1%), 235 (M^{+} , 3), 121 (27), 120 (100), 77 (12) and 43 (28) (Found: M^{+} 235.1937. Calcd. for C₁₅H₂₅NO, 235.1936).

l-(N-*Methylanilino*)*methylcyclohexanol* (**20e**): R_f 0.37 (hexane/EtOAc: 6/1); t_r 13.17 min; ν (film) 3441 (OH), 3099, 3060, 3022, 1599 and 1505 cm⁻¹ (HC=C); δ_H 1.20-1.75 [m, 11H, (CH₂)₅, OH], 3.00 (s, 3H,

CH₃), 3.27 (s, 2H, CH₂N), 6.70-6.75, 6.85-6.90 and 7.20-7.25 (3m, 1, 2 and 3H, respectively, ArH); $\delta_{\rm C}$ 21.7, 25.8, 36.0 (CH₂)₅, 41.3 (CH₃), 64.5 (CH₂N), 73.1 (CO), 112.8, 116.9, 129.0, and 151.2 (ArC); *m*/z 220 (*M*++1, 4%), 219 (*M*+, 23), 121 (54), 120 (100), 107 (14), 105 (14), 104 (15), 91 (11), 77 (28), 55 (14), 51 (12), 44 (13) and 42 (19).

1-(N-*Methylanilino*)-2-*phenyl*-2-*propanol* (**20f**):³⁰ t_r 14.50 min; v (film) 3461 (OH), 3058, 3024, 1598 and 1505 cm⁻¹ (HC=C); $\delta_{\rm H}$ 1.62 (s, 3H, CH₃C), 2.65 (s, 4H, CH₃N, OH), 3.51, 3.60 (2d, *J*=14.6 Hz, 2H, CH₂), 6.70-6.90 and 7.15-7.50 (2m, 10H, ArH); $\delta_{\rm C}$ 27.9 (CH₃C), 40.1 (CH₃N), 66.1 (CH₂), 75.1 (CO), 113.1, 117.5, 124.9, 126.8, 128.2, 129.0, 146.8 and 151.2 (ArC); *m/z* 242 (*M*++1, <1%), 241 (*M*+, 2), 121 (10), 120 (100), 77 (17), 43 (22) and 42 (11).

tert-Butyl N-(3,3-Dimethyl-2-hydroxybutyl)-N-methylcarbamate (**22da**):²⁵ t_r 10.17 min; v (film) 3477 (OH), 1681 (C=O) and 1147 cm⁻¹ (CO); $\delta_{\rm H}$ 0.93 [s, 9H, (CH₃)₃CCH], 1.46 [s, 9H, (CH₃)₃CO], 2.91 (s, 3H, CH₃N), 3.10 (s, 1H, OH) and 3.40-3.55 (m, 3H, CH₂N, CH); δ_c 25.5, 28.3 [(CH₃)₃C], 34.1 [(CH₃)₃C], 35.5 (CH₃N), 51.5 (CH₂), 78.4 (CHO), 80.0 [(CH₃)₃CO] and 158.1 (C=O); m/z 158 (M+-ButO, 1%), 118 (12), 90 (22), 89 (46), 88 (25), 74 (11), 57 (79), 56 (11), 45 (14), 44 (100), 43 (16) and 42 (12).

tert-Butyl N-(2-Hydroxy-2-phenylethyl)-N-methylcarbamate (**22db**):³¹ t_r 13.10 min; v (film) 3420 (OH), 1694 (C=O) and 1172 cm⁻¹ (CO); $\delta_{\rm H}$ 1.47 [s, 9H, (CH₃)₃C], 2.75-2.90 (br s, 3H, CH₃N), 3.40-3.55 (br s, 2H, CH₂), 4.20 (br s, 1H, CHO), 4.92 (br s, 1H, OH) and 7.25-7.40 (m, 5H, ArH); $\delta_{\rm C}$ 28.3 [(CH₃)₃C], 36.3 (CH₃N), 57.5 (CH₂), 73.6 (CHO), 80.2 [(CH₃)₃C), 125.7, 127.4, 128.3, 142.2 (ArC) and 158.0 (C=O); m/z 195 (*M*+-56, 2%), 144 (11), 107 (30), 90 (12), 89 (15), 79 (16), 77 (16), 57 (70), 56 (14), 45 (12), 44 (100), 43 (23) and 42 (22).

1-(2'-Ethyl-2'-hydroxybutyl)-2-pyrrolidinone (**22cc**):²⁵ t_r 10.40 min; v (film) 3435 (OH) and 1668 cm⁻¹ (C=O); $\delta_{\rm H}$ 0.92, 0.93 (2t, *J*=7.3 Hz, 6H, 2xCH₃), 1.20-1.35, 1.40-1.50, 1.60-1.85 (3m, 1, 2 and 3H, respectively, 2xCH₂CH₃ and CH₂CH₂N), 2.73 (t, *J*=9.8 Hz, 2H, CH₂C=O), 2.86 (s, 2H, NCH₂CO), 3.20-3.35 (m, 2H, CH₂CH₂N) and 4.62 (s, 1H, OH); $\delta_{\rm C}$ 7.3, 7.6 (2xCH₃), 20.5 (*C*H₂CH₂N), 28.5, 29.2, 29.5 (*C*H₂CH₃, *C*H₂C=O), 47.2, 47.4 (2xCH₂N) and 177.1 (C=O); *m/z* 167 (*M*+-18, 30%), 156 (100), 100 (28), 99 (99), 98 (85), 81 (10), 69 (13), 58 (11), 57 (75), 56 (12), 55 (24), 45 (22), 44 (70), 43 (60) and 42 (42).

tert-Butyl N-(2-Ethyl-2-hydroxybutyl)-N-methylcarbamate (**22dc**) ${}^{25}t_r$ 10.44 min; v (film) 3429 (OH), 1675 (C=O) and 1162 cm⁻¹ (CO); $\delta_{\rm H}$ 0.89 (t, J=7.5 Hz, 6H, 2xCH₃CH₂), 1.47 [s, 9H, (CH₃)₃C], 1.40-1.55 (m, 4H, 2xCH₂CH₃), 1.50 (br s, 1H, OH), 2.95 (s, 3H, CH₃N) and 3.26 (s, 2H, CH₂N); $\delta_{\rm C}$ 7.75 (2xCH₃CH₂), 28.3 [(CH₃)₃C], 29.0 (2xCH₂CH₃), 37.9 (CH₃N), 57.2 (CH₂N), 76.0 (CHO), 80.2 [(CH₃)₃C] and 158.4 (C=O); *m/z* 175 (*M*+-56, 1%), 145 (12), 102 (36), 90 (56), 89 (100), 88 (68), 87 (85), 69 (15), 57 (94), 46 (11), 45 (87), 44 (92), 43 (58), 42 (60) and 41 (91).

tert-Butyl N-(1-Hydroxycyclopentylmethyl)-N-methylcarbamate (**22dd**):²⁵ t_r 11.03 min; v (film) 3451 (OH), 1698, 1673 (C=O) and 1157 cm⁻¹ (CO); $\delta_{\rm H}$ 1.47 [s, 9H, (CH₃)₃C], 1.45-1.70, 1.75-1.90 [2m, 4 and 2H, (CH₂)₄], 2.97 (s, 3H, CH₃N), 3.37 (s, 2H, CH₂N) and 3.74 (br s, 1H, OH); $\delta_{\rm C}$ 23.4, 38.1 [(CH₂)₄], 28.3 [(CH₃)₃C], 37.5 (CH₃N), 58.2 (CH₂N), 80.1 [(CH₃)₃C], 83.5 (CHO) and 158.1 (C=O); m/z 173 (M^{+-56} , 2%), 90 (36), 89 (92), 88 (42), 85 (53), 67 (26), 57 (88), 56 (14), 55 (18), 46 (11), 45 (69), 44 (100), 43 (39), 42 (36) and 41 (78).

1-(1'-Hydroxycyclohexylmethyl)-2-pyrrolidinone (**22ce**): t_r 12.57 min; v (film) 3415 (OH) and 1668 cm⁻¹ (C=O); δ_H 1.05-1.85 (m, 12H, CH₂CH₂N), 2.00-2.20 (m, 1H, 1xCH₂C=O), 2.85 (t, *J*=9.8 Hz, 1H, 1xCH₂C=O), 2.85 (s, 2H, CH₂NC=O), 3.25-3.35 (m, 2H, CH₂CH₂N) and 4.50 (s, 1H, OH); δ_C 20.8, 21.1, 21.2, 25.8, 29.5, 31.4, 36.0 [(CH₂)₅, CH₂CH₂N], 47.5, 51.0 (CH₂N), 72.2 (COH) and 176.2 (C=O); m/z 197 (*M*+, 3%), 179 (27), 154 (21), 141 (13), 99 (100), 98 (62), 55 (12), 44 (12) and 42 (12) (Found: *M*+ 197.1413. Calcd. for C₁₁H₁₉NO₂, 197.1416).

tert-*Butyl* N-(2-*Hydroxy*-2-*phenylpropyl*-N-*methylcarbamate* (**22df**):²⁵ t_r 14.04 min; v (film) 3435 (OH), 1694 (C=O) and 1163 cm⁻¹ (CO); δ_H 1.45 [s, 9H, (CH₃)₃C], 1.55 (s, 3H, CH₃COH) 2.55-2.80 (m, 3H, CH₃N), 3.31, 3.67 (2d, *J*=14.7 Hz, 2H, CH₂), 5.15 (s, 1H, OH) and 7.25-7.50 (m, 5H, ArH); δ_C 27.2 (CH₃COH), 28.2 [(CH₃)₃C], 37.5 (CH₃N), 61.9 (CH₂), 75.8 (CHO), 80.4 [(CH₃)₃C], 125.2, 126.5, 127.9, 146.2 (ArC)

and 158.6 (C=O); m/z 209 (M+-56, 1%), 121 (36), 105 (10), 90 (12), 89 (16), 77 (12), 57 (52), 56 (16), 45 (16), 44 (100), 43 (89) and 42 (30).

tert-Butyl N-Methyl-N-(trimethylsilyl)methylcarbamate (22dg):²⁵ t_r 7.90 min; v (film) 1696 (C=O), 1249 (SiC) and 1173 cm⁻¹ (CO); δ_H 0.90 [s, 9H, (CH₃)₃Si], 1.58 [s, 9H, (CH₃)₃C], 2.89 (s, 2H, CH₂) and 2.98 (s, 3H, CH₂N); δ_C -1.7 [(CH₃)₃Si], 28.4 [(CH₃)₃C], 36.4 (CH₃N), 40.1 (CH₂N), 78.9 [(CH₃)₃C] and 155.7 (C=O); m/z 162 (M+-56, 2%), 161 (11), 147 (10), 146 (97), 144 (15), 116 (20), 102 (36), 73 (80), 61 (12), 59 (22), 57 (100), 45 (23), 44 (78), 43 (32), 42 (14) and 41 (56).

Hydrolysis of Hydroxy Carbamates **22da** and **22df**. Isolation of Compounds **24**. Method A: A solution of the corresponding starting carbamate (1 mmol) in EtOAc saturated with hydrogen chloride (10 ml) was stirred at 20°C for 2 h. The resulting mixture was basified with a 3M NaOH solution and extracted with EtOAc (2x20 ml). The organic layer was dried over anhydrous Na₂SO₄ and the solvent evaporated (15 Torr) to give the essentially pure (>95% by 300 Mz ¹H NMR) title compounds. Method B: A solution of the corresponding carbamate (1 mmol) and trifuoroacetic acid (4 mmol) in CH₂Cl₂ (2 ml) was stirred at 20°C for 12 h. Then, the resulting mixture was basified and worked-up as described in Method A. Yields and R_f values are included in Table 5. Spectral and analytical data as well as literature data for known compounds follow.

2-(*Methylamino*)-1-phenylethanol (**24db**):³¹ t_r 9.39 min; v (film) 3318 (OH), 3084, 3061, 3028 and 1629 cm⁻¹ (HC=C); $\delta_{\rm H}$ 2.40 (s, 3H, CH₃), 2.65-2.80 (m, 2H, CH₂), 3.32 (br s, 2H, NH, OH), 4.75 (dd, *J*=8.1, 4.5 Hz, 1H, CHO) and 7.25-7.40 (m, 5H, ArH); $\delta_{\rm C}$ 35.7 (CH₃), 59.0 (CH₂), 71.3 (CO), 125.7, 127.4, 128.3 and 142.7 (ArC); *m*/z 151 (*M*+, 1%), 134 (11), 105 (14), 91 (12), 79 (18), 78 (11), 77 (34), 71 (23), 56 (15), 51 (29), 50 (13), 45 (34), 44 (100), 43 (18) and 42 (34).

1-Methyl-2-(*methylamino*)-*1-phenylethanol* (**24df**):³² t_r 8.59 min; v (film) 3402 (OH, NH), 3091, 3060, 3021, 1600 and 1493 cm⁻¹ (HC=C); δ_H 1.48 (s, 3H, CH₃CO), 2.36 (s, 3H, CH₃N), 2.69, 3.02 (2d, *J*=11.9 Hz, 2H, CH₂), 2.95 (br s, 1H, OH) and 7.15-7.50 (m, 5H, ArH); δ_C 28.2 (CH₃CO), 36.5 (CH₃N), 62.6 (CH₂), 72.6 (CO), 124.8, 126.5, 128.1 and 146.7 (ArC); *m/z* 165 (*M*+, 1%), 121 (10), 105 (19), 91 (11), 78 (13), 77 (36), 51 (34), 50 (12), 45 (77), 44 (100), 43 (90) and 42 (53).

Reduction of Hydroxy Carbamates 22da, 22ab and 22df. Isolation of Compounds 27. General Procedure.- A suspension of lithium aluminum hydride (9 mmol) and the corresponding carbamate (1 mmol) in DME (20 ml) was refluxed for 12 h under an argon atmosphere. The resulting mixture was carefully hydrolysed with water (5 ml) and extracted with EtOAc (2x20 ml). The organic layer was dried over anhydrous Na₂SO₄ and the solvent evaporated (15 Torr) to give the essentially pure (>95% by 300 Mz ¹H NMR) title compounds. Yields and R_f values are included in Table 5. Spectral and analytical data as well as literature data for known compounds follow.

3,3-Dimethyl-1-(dimethylamino)-2-butanol (**25da**):³³ t_r 4.15 min; v (film) 3402 cm⁻¹ (OH); δ_H 0.91 (s, 9H, [(CH₃)₃C], 2.20-2.45 (m with s at 2.34, 8H, CH₂, 2xCH₃N) and 3.33 (dd, J=11.0, 3.0 Hz, 1H, CH); δ_C 25.6 [(CH₃)₃C], 33.3 [C(CH₃)₃], 45.2 (2xCH₃N), 60.5 (CH₂) and 73.6 (CO); m/z 145 (M+, 1%), 58 (100), 45 (42), 44 (35), 43 (27) and 42 (14).

2-(*Dimethylamino*)-1-phenylethanol (**25db**):³⁴ t_r 8.71 min; v (film) 3415 (OH), 3091, 3053, 3028, 1494 and 1454 cm⁻¹ (HC=C); δ_H 2.30-2.40 (m, 7H, 2xCH₃, 1xCH₂), 2.48 (dd, *J*=12.3, 10.4 Hz, 1H, 1xCH₂), 3.82 (br s, 1H, OH), 4.69 (dd, *J*=10.4, 3.4 Hz, 1H, 1xCHO) and 7.20-7.40 (m, 5H, ArH); δ_C 45.2 (2xCH₃), 67.5 (CH₂), 69.5 (CO), 125.8, 127.3, 128.2 and 142.2 (ArC); *m/z* 147 (*M*+-H₂O, 2%), 105 (11), 91 (11), 78 (11), 77 (40), 59 (52), 58 (100), 56 (12), 52 (10), 51 (38), 50 (14), 44 (55), 43 (39) and 42 (68).

1-Methyl-2-(dimethylamino)-1-phenylethanol (**25df**):³² t_r 7.94 min; v (film) 3404 (OH), 3091, 3060, 3025, 1601 and 1492 cm⁻¹ (HC=C); δ_H 1.45 (s, 3H, CH₃CO), 2.10 (s, 6H, 2xCH₃N), 2.63, 2.74 (2d, *J*=12.8 Hz, 2H, CH₂), 3.63 (br s, 1H, OH) and 7.15-7.50 (m, 5H, ArH); δ_C 29.7 (CH₃CO), 47.2 (2xCH₃N), 70.4 (CH₂), 71.6 (CO), 124.7, 126.2, 128.0 and 148.1 (ArC); *m/z* 164 (*M*+-CH₃, 6%), 105 (11), 77 (20), 59 (30), 58 (100), 51 (18), 44 (28), 43 (43) and 42 (37).

Cyclisation of Hydroxy Carbamates **22da** and **22df**. Isolation of Compounds **26**. General Procedure.- A suspension of sodium hydride (1.5 mmol) and the corresponding carbamate (1 mmol) in THF (5 ml) was refluxed under an argon atmosphere for 1 h. The resulting mixture was hydrolysed with water (5 ml) and extracted with EtOAc (2x20 ml). The organic layer was dried over anhydrous Na₂SO₄ and the solvent evaporated (15 Torr) to give the essentially pure (>95% by 300 Mz ¹H NMR) title compounds. Yields and R_f values are included in Table 5. Spectral and analytical data as well as literature data for known compounds follow.

5-(tert-Butyl)-3-methyl-1,3-oxazolin-2-one (**26da**): t_r 8.96 min; v (film) 1745 cm⁻¹ (C=O); $\delta_{\rm H}$ 0.94 [s, 3H, (CH₃)₃C], 2.88 (s, 3H CH₃N), 3.28, 3.46 (2t, J=8.5 Hz, 2H, CH₂) and 4.17 (t, J=8.5 Hz, 1H, CH); $\delta_{\rm C}$ 24.2 [(CH₃)₃C], 30.8 [(CH₃)₃C], 33.5 (CH₃N), 47.9 (CH₂), 80.3 (CHO) and 158.4 (C=O); m/z 157 (M+, 8%), 101 (55), 100 (25), 57 (36), 56 (34), 44 (100), 43 (58) and 42 (69) (Found: M+ 157.1101. Calcd. for C₈H₁₅NO₂, 157.1103).

3,5-Dimethyl-5-phenyl-1,3-oxazolin-2-one (**26df**):³⁵ t_r 11.61 min; v (film) 3056, 3030 (HC=C) and 1748 cm⁻¹ (C=O); δ_H 1.75 (s, 3H, CH₃C), 2.88 (s, 3H, CH₃N), 3.64 (s, 2H, CH₂) and 7.25-7.40 (m, 5H, ArH); δ_C 28.7 (*C*H₃C), 31.0 (CH₃N), 60.1 (CH₂), 79.6 (CO), 123.9, 127.8, 128.6, 143.9 (ArC) and 157.6 (C=O); m/z 192 (M++1, 1%), 191 (M+, 9), 176 (20), 146 (15), 121 (20), 105 (16), 91 (12), 77 (17), 51 (17), 44 (24), 43 (100) and 42 (65).³⁶

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