Pergamon

Tetrahedron, Vol. 53, No. 13, pp. 4835-4856, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00166-X

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

Diego A. Alonso, Emma Alonso, Carmen Nájera*, Diego J. Ramón and Miguel Yus*

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

Fax: + 34-6-5903549; E-mail: cnajera@ua.es, yus@ua.es

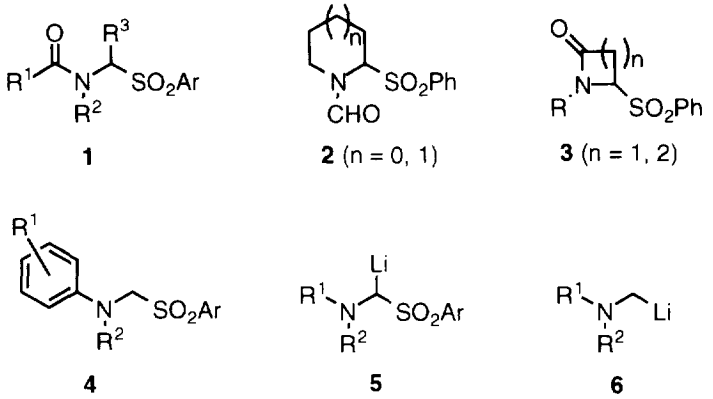
Abstract: Successive reaction of α-amidomethyl sulfones **7a,b**, derived from primary amides, with *n*-butyllithium and primary alkyl bromides (CH_2=$CHCH_2Br$, CH_2=$CMeCH_2Br$, CH_2=$CBrCH_2Br$, CH≡CCH_2Br, $PhCH_2Br$, $Bu^tO_2CCH_2Br$) at -90°C yields, after hydrolysis, enamides **11**. The same procedure applied to α-amidomethyl sulfones **7c,d** derived from secondary amides and using different electrophiles [AcOD, 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] gives substituted α-amidomethyl sulfones **13**. Representative compounds **13** are desulfonated (Na·Hg, $Na_2S_2O_4$ 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 [Bu^tCHO, PhCHO, Et_2CO, Pr^i_2CO, $(CH_2)_5CO$, 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 [Bu^tCHO, PhCHO, Et_2CO, $(CH_2)_4CO$, $(CH_2)_5CO$, PhCOMe, Me_3SiCl] yields fuctionalised amides **22**. Representative examples of compounds **22** were hydrolysed (HCl-EtOAc or CF_3CO_2H), reduced ($LiAlH_4$) or cyclised (NaH) to give amino-alcohols **24**, **25** or oxazolidinones **26**, respectively. © 1997 Elsevier Science Ltd.

INTRODUCTION

α-Nitrogenated alkyl sulfones have been widely used as α-amido-[1] and α-amino-alkylating[2] 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 [4π⁺+2π] cycloadditions for the synthesis of tetrahydroquinolines.[2] According to the ability of the sulfone group to stabilise carbanions[3] and to be transformed reductively into organolithium compounds,[4] α-nitrogenated alkyl sulfones should be appropriate precursors of the corresponding "umpoled" *d*[1]-reagents[5] of the type **5**[6] and **6**, respectively. Versatile α-

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

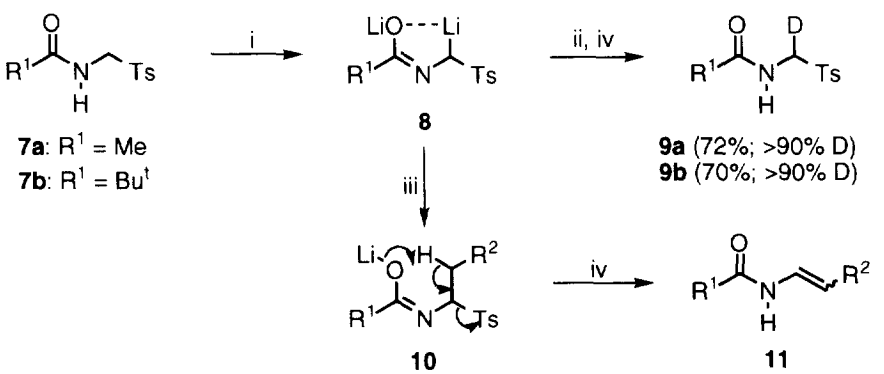
nitrogen-substituted organolithium compounds of type **6** have been previously prepared by direct α-lithiation mainly of *N*-Boc protected amines,[7] by tin-lithium exchange[8] and by reductive carbon-sulfur[9] or carbon-chloride[10] bond cleavage by means of lithium napthalenide or DTBB-catalysed lithiation, 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

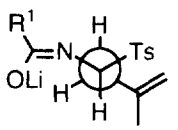
The required α-amidomethyl sulfones **7** were synthesised in good yields from sodium *p*-toluenesulfinate, formaldehyde and the corresponding amide or carbamate in the presence of formic acid.[12]

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).

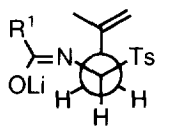


Scheme 1. *Reagents and conditions*: i, 2 Bu^nLi, 2 DMPU, THF, -90°C; ii, D_2O; iii, R^2CH_2Br, -90 to -20 or -60°C; iv, NH_4Cl.

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.



A



B

Table 1. Preparation of *N*-Acylenamines **11**

Entry	Starting sulfone	Electrophile E^+	Product				
			No.	R^2	Yield (%)[a]	R_f[b]	*Z*/*E* Ratio[c]
1	**7a**	CH_2=$CHCH_2Br$	**11aa**	CH_2=CH	45	0.77[d]/0.71[d]	1/1[e]
2	**7b**	CH_2=$CHCH_2Br$	**11ba**	CH_2=CH	59	0.55[f]/0.42[f]	1/1[e]
3	**7b**	CH_2=$CMeCH_2Br$	**11bb**	CH_2=CMe	33	0.47[f]	-/1
4	**7b**	CH_2=$CBrCH_2Br$	**11bc**	CH≡C	30	0.51[d]	-/1
5	**7a**	CH≡CCH_2Br	**11ac**	CH≡C	31	0.83[d]/0.74[d]	1/3[e]
6	**7a**	$PhCH_2Br$	**11ad**	Ph	20	0.82[d]/0.69[d]	1/2[e]
7	**7b**	$PhCH_2Br$	**11bd**	Ph	39	0.67[f]/0.50[f]	1/2[e]
8	**7a**	EtO_2CCH_2Br[g]	**11ae**	EtO_2C	52	0.73[d,h]	-/1
9	**7b**	EtO_2CCH_2Br[g]	**11be**	EtO_2C	62	0.90[i,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.

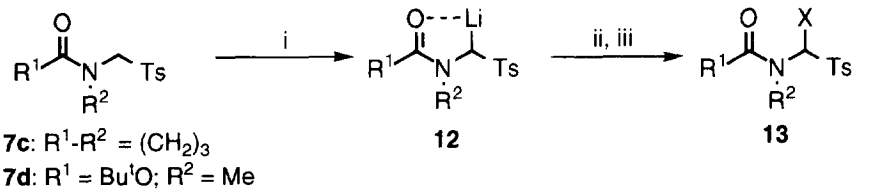
The lithiation of sulfones **7c,d**, derived from pyrrolidinone and *O-tert*-butyl *N*-methylcarbamate, at -90°C for 5 min furnished intermediates **12**, which were characterised by deuterolysis and reacted with different electrophiles (alkyl halides, carbonyl compounds and acyl chlorides) to give products **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).

Table 2. Preparation of Compounds **13**

Entry	Starting sulfone	Electrophile E+	Product			
			No.	X	Yield(%)[a]	Mp (°C)[b] or R_f[c]
1	**7c**	CH_3CO_2D	**13ca**	D	65[d]	117-118
2	**7d**	D_2O	**13da**	D	82[d]	102-103
3	**7c**	EtI	**13cb**	Et	41	92-93
4	**7c**	CH_2=$CHCH_2Br$	**13cc**	CH_2=$CHCH_2$	67	115-116
5	**7d**	CH_2=$CHCH_2Br$	**13dc**	CH_2=$CHCH_2$	61	0.57
6	**7c**	Bu^nI	**13cd**	Bu^n	50	102-103
7	**7d**	Bu^nI	**13dd**	Bu^n	42	0.64
8	**7c**	$PhCH_2Br$	**13ce**	$PhCH_2$	64	0.84[e]
9	**7d**	$PhCH_2Br$	**13de**	$PhCH_2$	66	0.53
10	**7c**	$Bu^tO_2CCH_2Br$	**13cf**	$Bu^tO_2CCH_2$	59[f]	111-112
11	**7c**	Bu^tCHO	**13cg**	Bu^tCHOH	53[g]	0.88[h]/0.79[i]
12	**7c**	PhCHO	**13ch**	PhCHOH	62[j]	0.79[k]/0.83[l]
13	**7d**	$(CH_2)_4CO$	**13di**	$(CH_2)_4COH$	63	0.43
14	**7c**	EtOCOCl	**13cj**	EtOCO	72	0.81[e]
15	**7d**	EtOCOCl	**13dj**	EtOCO	66	0.55
16	**7c**	CH_3COCl	**13ck**	CH_3CO	40	0.63
17	**7c**	PhCOCl	**13cl**	PhCO	56	0.49

[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. [l] *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).

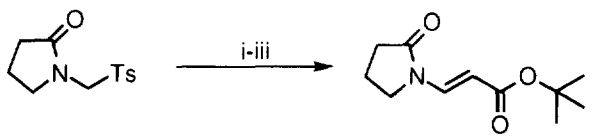


7c: R^1-R^2 = $(CH_2)_3$
7d: R^1 = Bu^tO; R^2 = Me

12

13

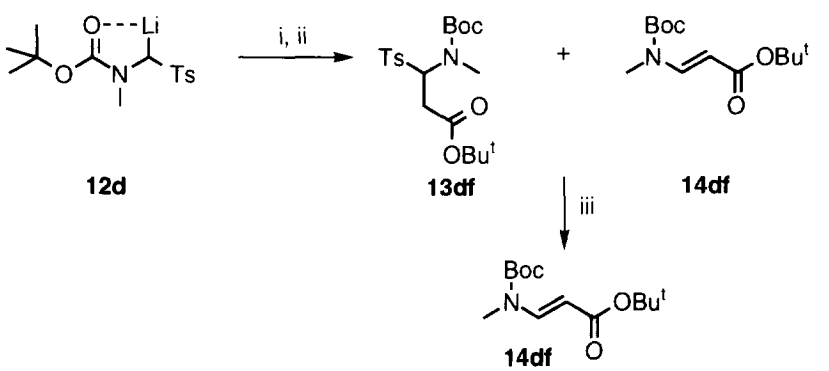
Scheme 2. *Reagents and conditions*: i, Bu^nLi, DMPU, THF, -90°C; ii, E^+ = CH_3CO_2D, D_2O, EtI, CH_2=$CHCH_2Br$, Bu^nI, $PhCH_2Br$, $Bu^tO_2CCH_2Br$, Bu^tCHO, PhCHO, $(CH_2)_4CO$, EtOCOCl, CH_3COCl, PhCOCl, -90 to 20°C; iii, NH_4Cl.



7c **14cf**

Scheme 3. *Reagents and conditions*: i, LDA, THF, -90°C; ii, $BrCH_2CO_2Bu^t$; iii, NH_4Cl.

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).

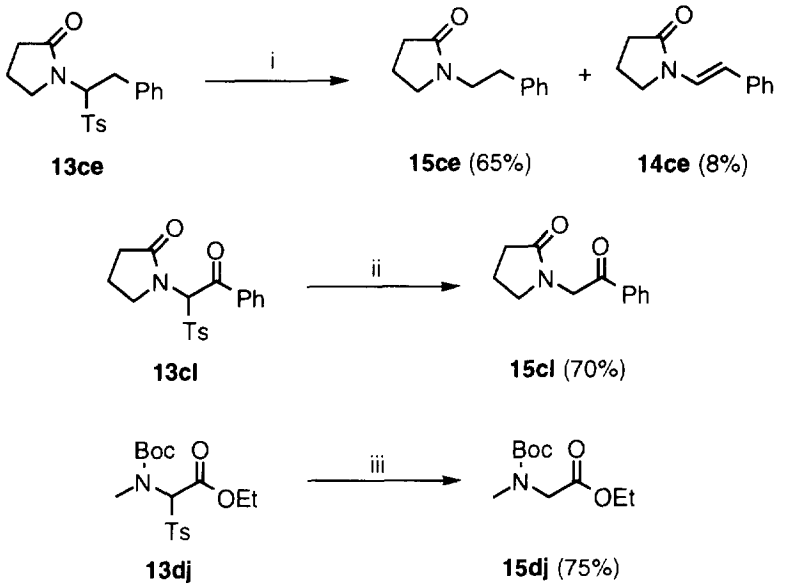


12d **13df** **14df**

14df

Scheme 4. *Reagents and conditions*: i, $BrCH_2CO_2Bu^t$; ii, NH_4Cl; iii, $KOBu^t$, THF, 20°C.

Representative sulfones **13** were desulfonylated with sodium amalgam[13] in the case of **13ce**, with sodium dithionite[14] in the case of **13cl** or with magnesium in methanol[15] 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, Na_2HPO_4, MeOH, 0 to 20°C; ii, $Na_2S_2O_4$, $NaHCO_3$, DMF, H_2O, 100°C; iii, Mg, MeOH, 20°C.

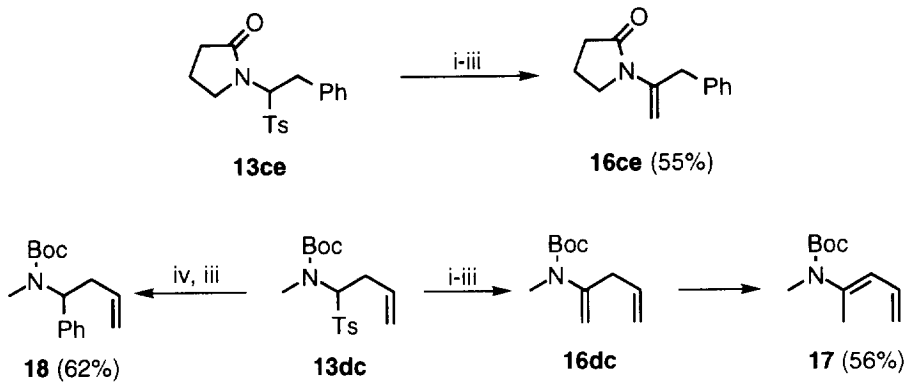
Alkylated amido sulfones **13ce** and **13dc** suffered methylenation by means of Julia's methodology:[16] lithiation with *n*-butyllithium at -78°C and *in situ* reaction with chloromethylmagnesium chloride provided enamines **16ce** and **16dc** in 55 and 56% yield, respectively (Scheme 6). Compound **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 material[17] being observed. Thus, α-lithiation of compound **19** under different reaction conditions did not work.

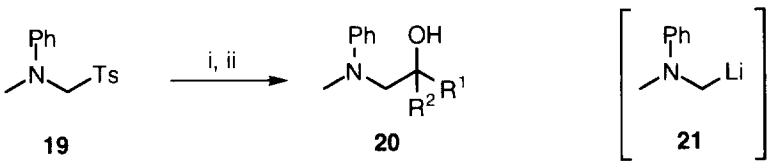
In the second part of this study, we studied the reductive desulfonylation of α-aminomethyl sulfone **19** or the corresponding α-amidomethyl sulfones of type **7**.

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 (two-step reaction) the process failed.



Scheme 6. *Reagents and conditions*: i, Bu^nLi, THF, -78°C; ii, $ClCH_2I$, Pr^iMgCl, -78 to 0°C; iii, NH_4Cl; iv, PhMgBr, $ZnBr_2$, THF, 20°C.



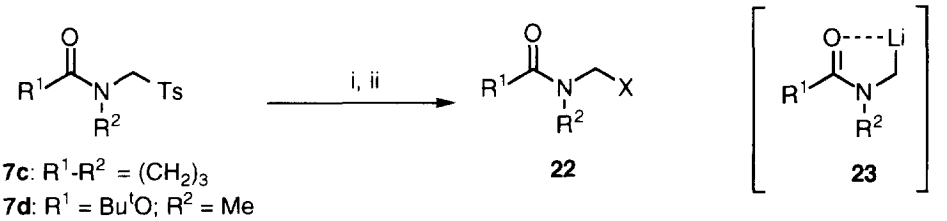
Scheme 7. *Reagents and conditions*: i, Li, $C_{10}H_8$ cat. (4 mol%), E^+ = Bu^tCHO, PhCHO, Et_2CO, Pr^i_2CO, $(CH_2)_5CO$, PhCOMe, THF, -78 to 0°C; ii, H_2O.

Table 3. Preparation of Compounds **20**

Entry	Electrophile E^+	Product No.	R^1	R^2	Yield (%)[a]	R_f[b]
1	Bu^tCHO	**20a**	Bu^t	H	54	0.49
2	PhCHO	**20b**	Ph	H	43	0.27
3	Et_2CO	**20c**	Et	Et	48	0.35
4	Pr^i_2CO	**20d**	Pr^i	Pr^i	25	0.57
5	$(CH_2)_5CO$	**20e**	$-(CH_2)_5-$		51	0.37
6	PhCOMe	**20f**	Ph	Me	53	0.34

[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**.



7c: R^1-R^2 = $(CH_2)_3$
7d: R^1 = Bu^tO; R^2 = Me

22 **23**

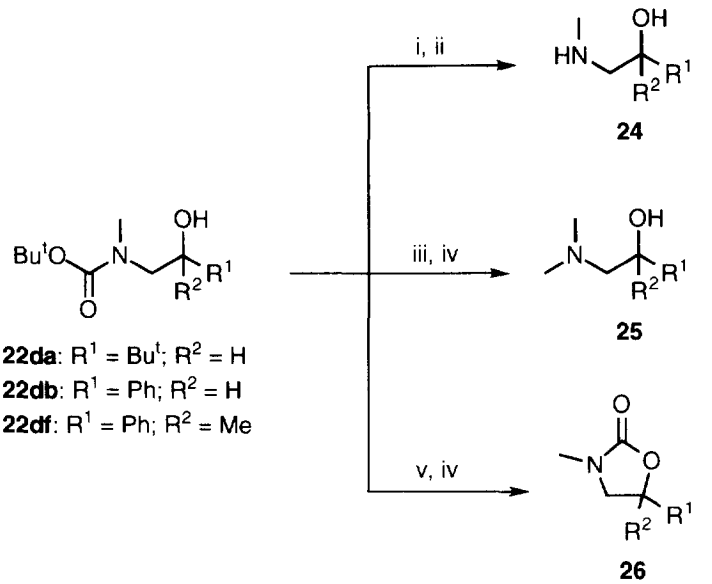
Scheme 8. *Reagents and conditions*: i, Li, $C_{10}H_8$ cat. (4 mol%), E^+ = Bu^tCHO, PhCHO, Et_2CO, $(CH_2)_4CO$, $(CH_2)_5CO$, PhCOMe, Me_3SiCl, THF, -78 to 0°C; ii, H_2O.

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 reflux[22] 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).

Table 4. Preparation of Compounds **22**

Entry	Starting sulfone	Electrophile E^+	Product			
			No.	X	Yield (%)[a]	R_f[b]
1	**7d**	Bu^tCHO	**22da**	Bu^tCHOH	50	0.45
2	**7d**	PhCHO	**22db**	PhCHOH	45	0.30
3	**7c**	Et_2CO	**22cc**	Et_2COH	37	0.50[c]
4	**7d**	Et_2CO	**22dc**	Et_2COH	20	0.43
5	**7d**	$(CH_2)_4CO$	**22dd**	$(CH_2)_4COH$	30	0.27
6	**7c**	$(CH_2)_5CO$	**22ce**	$(CH_2)_5COH$	31	0.36[c]
7	**7d**	PhCOMe	**22df**	PhC(OH)Me	43	0.41
8	**7d**	Me_3SiCl	**22dg**	Me_3Si	28	0.81

[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 CF_3CO_2H, CH_2Cl_2 (Method B), 20°C; ii, NaOH (3 M); iii, $LiAlH_4$, DME reflux; iv, H_2O; v, NaH, THF reflux.

Table 5. Preparation of Compounds **24-26**

Entry	Starting material	Product				
		No.	R^1	R^2	Yield (%)[a]	R_f[b]
1	**22db**	**24db**	Ph	H	93[c] (98)[d]	0.32[e]
2	**22df**	**24df**	Ph	Me	95[c]	0.26[e]
3	**22da**	**25da**	But	H	69	0.32[f]
4	**22db**	**25db**	Ph	H	93	0.73[f]
5	**22df**	**25df**	Ph	Me	82	0.52[f]
6	**22da**	**26da**	But	H	80	0.29[g]
7	**22df**	**26df**	Ph	Me	99	0.40[g]

[a] Isolated yield based on the starting carbamate **22**. [b] Silica gel. [c] Method A (see text). [d] Method B (see text). [e] CH_2Cl_2/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^1-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 ^{1}H and 75 MHz for ^{13}C) using $CDCl_3$ as solvent and TMS as internal standard; chemical shifts are given in δ (ppm). ^{13}C NMR assignments were made on the basis of DEPT experiments. Mass spectra (EI) were obtained on a Hewlett-Packard 5988A or a Shimazdu QP-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°C, T_{column} = 60°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 refences for known compounds follow.

N-*(Tosylmethyl)acetamide* (**7a**):[12b] mp 137-138°C; ν (KBr) 3400-3100 (NH), 1666 (C=O), 1324, 1296, 1273 and 1145 cm^{-1} (SO_2); δ_H 1.92 (s, 3H, CH_3CO), 2.44 (s, 3H, CH_3Ar), 4.70 (d, *J*=6.7 Hz, 2H, CH_2S), 7.23 (br t, *J*=6.7 Hz, 1H, NH), 7.36 and 7.79 (2d, *J*=8.2 Hz, 4H, ArH); δ_C 21.5 (CH_3Ar), 22.4 (CH_3CO), 61.1 (CH_2S), 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; ν (KBr) 3388 (NH), 1683 (C=O), 1317, 1306, 1284 and 1140 cm^{-1} (SO_2); δ_H 1.07 [s, 9H, $(CH_3)_3C$], 2.44 (s, 3H, CH_3Ar), 4.72 (d, *J*=6.7 Hz, 2H, CH_2S), 6.55 (m, 1H, NH), 7.34 and 7.77 (2d, *J*=8.0 Hz, 4H, ArH); δ_C 21.6 (CH_3Ar), 27.1 [$(CH_3)_3C$], 38.6 [$(CH_3)_3C$], 60.3 (CH_2S), 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 $C_{13}H_{19}NO_3S$: 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; ν (KBr) 1686 (C=O), 1321, 1292 and 1147 cm^{-1} (SO_2); δ_H 1.11, 1.24 [2s, 18H, 2x$(CH_3)_3C$], 2.41, 2.45 (2s, 6H, 2xCH_3Ar), 3.08 (s, 6H, 2xCH_3N), 4.61, 4.63 (2s, 4H, 2xCH_2S), 7.31-7.38 and 7.75-7.78 (2m, 8H, 2xArH); δ_C 21.4 (2xCH_3Ar), 27.5, 27.7 [2x$(CH_3)_3C$], 35.2, 35.5 (2xCH_3N), 69.3, 70.2 (2xCH_2S), 80.8, 81.0 [2x$(CH_3)_3C$], 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 $C_{14}H_{21}NO_4S$: C, 56.17; H, 4.68; N, 7.07 and S, 10.71%).

1-(Tosylmethyl)-2-pyrrolidinone (**7d**): mp 117-118°C; ν (KBr) 1692 (C=O), 1319, 1312, 1289 and 1140 cm^{-1} (SO_2); δ_H 2.04 (q, *J*=7.0 Hz, 2H, CH_2CH_2CO), 2.22 (t, *J*=7.0 Hz, 2H, CH_2CO), 2.44 (s, 3H, CH_3Ar), 3.72

(t, *J*=7.0 Hz, 2H, CH_2CH_2N), 4.65 (s, 2H, CH_2S), 7.35 and 7.76 (2d, *J*=8.2 Hz, 4H, ArH); δ_C 18.1 (CH_2CH_2CO), 21.6 (CH_3Ar), 29.7 (CH_2CO), 47.4 (CH_2CH_2N), 63.8 (CH_2S), 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 $C_{12}H_{15}NO_3S$: C, 56.90; H, 5.97; N, 5.53 and S, 12.66%).

N-*Methyl*-N-*(tosylmethyl)aniline* (**19**):[2] mp 91-92°C; ν (KBr) 3067, 3043, 1599, 1509 (HC=C), 1316, 1269 and 1135 cm^{-1} (SO_2); δ_H 2.36 (s, 3H, CH_3Ar), 2.94 (s, 3H, CH_3N), 4.71 (s, 2H, CH_2), 6.60-6.75, 7.05-7.25 and 7.65-7.75 (3m, 9H, ArH); δ_C 21.4 (CH_3Ar), 39.1 (CH_3N), 75.9 (CH_2), 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 NH_4Cl and extracted with EtOAc (3x10 ml). The organic layer was dried over Na_2SO_4, 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**): ν (KBr) 3400-3100 (NH), 1666 (C=O), 1324, 1296, 1273 and 1145 cm^{-1} (SO_2); δ_H 1.92 (s, 3H, CH_3CO), 2.44 (s, 3H, CH_3Ar), 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); δ_C 21.6 (CH_3Ar), 22.5 (CH_3CO), 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 $C_{10}H_{12}DNO_3S$: C, 52.63; H/D, 5.26; N, 6.14 and S, 14.04%).[23]

N-*(Tosyldeuteriomethyl)-2,2-dimethylpropanamide* (**9b**): ν (KBr) 3388 (NH), 1683 (C=O), 1317, 1306, 1284 and 1140 cm^{-1} (SO_2); δ_H 1.07 [s, 9H, $(CH_3)_3C$], 2.44 (s, 3H, CH_3Ar), 4.70 (m, 1H, CHD), 6.72 (br s, 1H, NH), 7.33 and 7.76 (2d, *J*=8.2 Hz, 4H, ArH); δ_C 21.6 (CH_3Ar), 27.1 [$(CH_3)_3C$], 38.7 [$(CH_3)_3C$], 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 $C_{13}H_{18}DNO_3S$: C, 57.78; H/D, 6.67; N, 5.19 and S, 11.85%).[23]

N-*[(1Z)-1,3-Butadienyl]acetamide* (*Z*-**11aa**): ν (film) 3294 (NH) and 1648 cm^{-1} (C=O); δ_H 2.11 (s, 3H, CH_3CO), 5.09 (d, *J*=10.1 Hz, 1HxCH_2=CH), 5.23 (d, *J*=16.5 Hz, 1HxCH_2=CH), 5.41 (dd, *J*=11.3, 9.2 Hz, 1H, NCH=C*H*), 6.45 (dt, *J*=16.5, 10.5 Hz, 1H, CH_2=C*H*), 6.71 (t, *J*=10.2 Hz, 1H, NC*H*=CH) and 7.46 (m, 1H, NH); δ_C 23.3 (CH_3CO), 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 C_6H_9NO, 111.0684).

N-*[(1E)-1,3-Butadienyl]acetamide* (*E*-**11aa**): ν (film) 3294 (NH) and 1648 cm^{-1} (C=O); δ_H 2.07 (s, 3H, CH_3CO), 4.97 (d, *J*=10.1 Hz, 1HxCH_2=CH), 5.09 (d, *J*=16.8 Hz, 1HxCH_2=CH), 5.78 (dd, *J*=14.0, 10.5 Hz, 1H, NCH=C*H*), 6.29 (dt, *J*=16.8, 10.5 Hz, 1H, CH_2=C*H*), 7.00 (dd, *J*=14.0, 10.9 Hz, 1H, NC*H*=CH), and 7.21 (m, 1H, NH); δ_C 23.3 (CH_3CO), 113.5, 114.5, 125.7, 134.4 (C=C) and 167.3 (C=O); *m/z* 112 (*M*+1, 2%), 111 (*M*+, 33), 69 (81), 68 (45), 59 (19), 43 (100), 42 (23) and 41 (37).

N-*(1,3-butadienyl)-2,2-dimethylpropanamide* (**11ba**): ν (film) 3339 (NH), 3085, 1645, 960 (HC=C) and 1665 cm^{-1} (C=O); δ_H 1.24, 1.26 [s, 18H, 2x$(CH_3)_3C$], 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); δ_C 27.3, 27.4 [2x$(CH_3)_3C$], 38.7, 39.0 [2x$(CH_3)_3C$], 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 $C_9H_{15}NO$, 153.1154).

N-*[(1E)-3-Methyl-1,3-butadienyl]-2,2-dimethylpropanamide* (**11bb**): ν (film) 3310 (NH), 3081, 1643, 961 (HC=C) and 1662 cm^{-1} (C=O); δ_H 1.24 [s, 9H, $(CH_3)_3C$], 1.87 (s, 3H, CH_3), 4.84 (br s, 2H, CH_2=C), 5.92 (d, J=14.4 Hz, 1H, C*H*=CHN), 7.01 (dd, J=14.3, 11.0 Hz, CH=C*H*N) and 7.23 (m, 1H, NH); δ_C 18.7 (CH_3C), 27.4 [$(CH_3)_3C$], 38.8 [$(CH_3)_3C$], 113.9, 115.9, 123.2, 140.5 (C=C) and 175.7 (C=O); *m/z* 168 (M^++1, 4%), 167 (M^+, 37), 83 (53), 82 (28), 68 (29), 57 (100), 55 (10), 43 (41), 42 (12) and 41 (65) (Found: M^+ 167.1313. Calcd. for $C_{10}H_{17}NO$, 167.1310).

N-*[(E)-1-Buten-3-ynyl]-2,2-dimethylpropanamide* (**11bc**): ν (film) 3303 (NH) and 1668 cm^{-1} (C=O); δ_H 1.24 [s, 9H, $(CH_3)_3C$], 2.85 (d, J=2.1 Hz, 1H, HC≡C), 5.20 (dd, J=14.3, 2.1 Hz, 1H, C*H*=CHN), 7.38 (dd, J=14.3, 11.0 Hz, 1H, CH=C*H*N) and 7.58 (m, 1H, NH); δ_C 27.2 [$(CH_3)_3C$], 38.9 [$(CH_3)_3C$], 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 $C_9H_{13}NO$, 151.0997).

N-*[(Z)-1-Buten-3-ynyl]acetamide* (*Z*-**11ac**): ν (film) 3500-3150 (NH), 3096, 1631 (HC=C), 2090 (C≡C) and 1681 cm^{-1} (C=O); δ_H 2.14 (s, 3H, CH_3CO), 3.33 (d, J=2.1 Hz, 1H, CH≡C), 4.80 (dd, J=8.9, 2.1 Hz, 1H, C*H*=CHN), 7.25 (dd, J=11.6, 8.9 Hz, 1H, C=CHN) and 7.68 (m, 1H, NH); δ_C 23.3 (CH_3CO), 78.2 (*C*H≡C), 84.7 (*C*≡CH), 87.2 (*C*H=CHN), 133.7 (CH=C*H*N) 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 C_6H_7NO, 109.0528).

N-*[(E)-1-Buten-3-ynyl]acetamide* (*E*-**11ac**): ν (film) 3307 (NH), 3150, 3080, 1635 (HC=C), 2106 (C≡C) and 1679 cm^{-1} (C=O); δ_H 2.09 (s, 3H, CH_3CO), 2.86 (d, J=2.4 Hz, 1H, CH≡C), 5.17 (dd, J=14.7, 2.4 Hz, 1H, C*H*=CHN), 7.34 (dd, J=14.7, 11.1 Hz, 1H, C=CHN) and 7.95 (m, 1H, NH); δ_C 23.2 (CH_3CO), 77.5 (CH≡*C*), 80.5 (*C*H≡C), 90.3 (*C*H=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).

N-*[(Z)-2-Phenyl-1-ethenyl]acetamide* (*Z*-**11ad**):[24] ν (film) 3290 (NH), 1660 (C=O) and 1645 cm^{-1} (C=C); δ_H 2.06 (s, 3H, CH_3CO), 5.75 (d, J=9.8 Hz, 1H, C*H*=CHN), 6.93-7.00, 7.24-7.42 (2m, 6H, ArH, CH=C*H*N) and 7.56 (m, 1H, NH); δ_C 23.5 (CH_3CO), 109.7 (*C*H=CHN), 122.0 (CH=*C*HN), 127.0, 127.9, 129.1, 135.7 (ArC) and 167.5 (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) and 40 (15).

N-*[(E)-2-Phenyl-1-ethenyl]acetamide* (*E*-**11ad**):[24] ν (film) 3290 (NH), 1660 (C=O) and 1645 cm^{-1} (C=C); δ_H 2.11 (s, 3H, CH_3CO), 6.09 (d, J=14.7 Hz, 1H, C*H*=CHN) and 7.14-7.53 (m, 7H, NH, ArH, CH=C*H*N); δ_C 23.3 (CH_3CO), 112.4 (*C*H=CHN), 122.6 (CH=*C*HN), 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**): ν (film) 3336 (NH) and 1668 cm^{-1} (C=O); δ_H 1.23 [s, 9H, $(CH_3)_3C$], 5.76 (d, J=9.5 Hz, 1H, C*H*=CHN), 6.99 (t, J=9.5 Hz, 1H, CH=C*H*N), 7.17-7.43 (m, 5H, ArH) and 7.96 (m, 1H, NH); δ_C 27.3 [$(CH_3)_3C$], 38.9 [$(CH_3)_3C$], 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**): ν (film) 3336 (NH) and 1668 cm^{-1} (C=O); δ_H 1.28 [s, 9H, $(CH_3)_3C$], 6.13 (d, J=14.3 Hz, 1H, C*H*=CHN), 7.26-7.42 (m, 6H, PhH, NH) and 7.54 (dd, J=14.3, 10.8 Hz, 1H, CH=C*H*N); δ_C 27.4 [$(CH_3)_3C$], 38.8 [$(CH_3)_3C$], 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 $C_{13}H_{17}NO$, 203.1310).

tert *Butyl (E)-3-Methylcarboxamido-2-propenoate* (**11ae**): ν (KBr) 3289 (NH), 1715 and 1686 cm^{-1} (C=O); δ_H 1.48 [s, 9H, $(CH_3)_3C$], 2.12 (s, 3H, CH_3CO), 5.37 (dd, J=14.0, 2.1 Hz, 1H, CH=C*H*CO_2), 7.90 (dd, J=14.0, 11.6 Hz, 1H, CH=C*H*N) and 8.91 (br d, J=11.6 Hz, 1H, NH); δ_C 23.2 (CH_3CO), 28.2 [$(CH_3)_3C$], 80.4 [$(CH_3)_3C$], 103.2 (CH=*C*HCO), 137.0 (CH=*C*HN), 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**): ν (KBr) 3308 (NH), 1691 (C=O), 1151 and 1135 cm^{-1} (C-O); δ_H 1.25, 1.47 [2s, 18H, 2x$(CH_3)_3C$], 5.44 (d, *J*=14.0 Hz, 1H, C*H*=CHN), 7.94 (dd, *J*=14.0, 11.6 Hz, 1H, CH=C*H*N) and 8.10 (br d, *J*=11.6 Hz, 1H, NH); δ_C 27.1, 28.2 [2x$(CH_3)_3$C], 39.1 [$(CH_3)_3CC$=O], 80.1 [$(CH_3)_3CO$], 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 $C_{12}H_{21}NO_3$: C, 63.41; H, 9.31 and N, 6.16%).

1-(Tosyldeuteriomethyl)-2-pyrrolidinone (**13ca**): ν (KBr) 1692 (C=O), 1319, 1312, 1289 and 1140 cm^{-1} (SO_2); δ_H 2.04 (q, *J*=7.6 Hz, 2H, CH_2CH_2CO), 2.23 (t, *J*=7.6 Hz, 2H, CH_2CO), 2.44 (s, 3H, CH_3Ar), 3.72 (t, *J*=7.0 Hz, 2H, CH_2CH_2N), 4.63 (s, 1H, CHD), 7.35 and 7.77 (2d, *J*=8.2 Hz, 4H, ArH); δ_C 18.2 (CH_2CH_2CO), 21.6 (CH_3Ar), 29.7 (CH_2CO), 47.6 (CH_2CH_2N), 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 $C_{12}H_{14}DNO_3S$: C, 56.69; H/D, 5.51; N, 5.51 and S, 12.60%).[23]

tert-*Butyl* N-*Methyl*-N-*(tosyldeuteriomethyl)carbamate* (**13da**): ν (KBr) 1686 (C=O), 1321, 1292 and 1147 cm^{-1} (SO_2); δ_H 1.11, 1.24 [2s, 18H, 2x$(CH_3)_3C$], 2.41, 2.44 (2s, 6H, 2xCH_3Ar), 3.08 (s, 6H, 2xCH_3N), 4.59-4.64 (m, 2H, 2xCHD), 7.31-7.39 and 7.75-7.78 (2m, 8H, 2xArH); δ_C 21.3 (2xCH_3Ar), 27.4, 27.6 [2x$(CH_3)_3$C], 35.0, 35.4 (2xCH_3N), 68.9, 69.8 (2t, *J*=21.1 Hz, 2xCHD), 80.7, 80.9 [2x$(CH_3)_3C$], 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 $C_{14}H_{20}DNO_4S$: C, 56.00; H/D, 6.67; N, 4.67 and S, 10.67%).[23]

1-(1-Tosylpropyl)-2-pyrrolidinone (**13cb**): ν (KBr) 1695 (C=O), 1314, 1306, 1282 and 1148 cm^{-1} (SO_2); δ_H 0.94 (t, *J*=7.6 Hz, 3H, CH_3CH_2), 1.92-2.18, 2.20-2.34 [2m, 6H, CH_3CH_2, $(CH_2)_2CO$], 2.43 (s, 3H, CH_3Ar), 3.34-3.42 (m, 1HxCH$_2$N), 3.75-3.83 (m, 1HxCH$_2$N), 5.18 (dd, *J*=11.6, 3.7 Hz, 1H, CHS), 7.33 and 7.76 (2d, *J*=7.9 Hz, 4H, ArH); δ_C 10.0 (CH_3CH_2), 16.8, 18.4 (CH_2CH_3, CH_2CH_2CON), 21.6 (CH_3Ar), 30.1 (CH_2CO), 42.5 (CH_2N), 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 $C_{14}H_{19}NO_3S$: C, 59.76; H, 6.81; N, 4.98 and S, 11.39%).

1-(1-Tosyl-3-butenyl)-2-pyrrolidinone (**13cc**): ν (KBr) 3080, 3065 (HC=C), 1705 (C=O), 1301, 1286, 1275 and 1140 cm^{-1} (SO_2); δ_H 1.88-2.01, 2.03-2.09, 2.14-2.25 [3m, 4H, $(CH_2)_2CO$], 2.43 (s, 3H, CH_3Ar), 2.70-2.82, 2.95-3.04 (2m, 2H, CH_2CO), 3.40 (dt, *J*=9.9, 7.0 Hz, 1HxCH_2N), 3.78 (dt, *J*=9.9, 6.7 Hz, 1HxCH_2N), 5.13 (d, *J*=11.3 Hz, 1HxCH_2=CH), 5.18 (d, *J*=18.6 Hz, 1HxCH_2=CH), 5.37 (dd, *J*=11.9, 3.7 Hz, 1H, CHS), 5.56-5.70 (m, 1H, C*H*=CH$_2$), 7.33 and 7.75 (2d, *J*=8.2 Hz, 4H, ArH); δ_C 18.5 (CH_2CH_2CO), 21.5 (CH_3Ar), 27.5, 29.7 (CH_2CO, CH_2C=), 42.5 (CH_2N), 69.8 (CHS), 118.9 (CH_2=C), 128.5, 129.6, 131.0, 133.5, 145.1 (ArC, CH_2=*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 $C_{15}H_{19}NO_3S$: 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] ν (film) 3082 (HC=C), 1703 (C=O), 1317, 1291 and 1143 cm^{-1} (SO_2); δ_H 1.11, 1.19 [2s, 18H, 2x$(CH_3)_3C$], 2.40, 2.44 (2s, 6H, 2xCH_3Ar), 2.69-2.83 (m, 4H, 2xCHSCH_2), 2.88, 2.96 (2s, 6H, 2xCH_3N), 5.12-5.27 (m, 4H, 2xCH_2=CH), 5.52-5.74 (m, 4H, 2xC*H*=CH$_2$, 2xCH$_2$S), 7.30-7.37 and 7.72-7.78 (2m, 8H, 2xArH); δ_C 21.4, 21.5 (2xCH_3Ar), 27.5 (2xCHSCH_2), 27.6, 27.8 [2x$(CH_3)_3C$], 28.2, 28.9 (2xCH_3N), 73.0, 74.6 (2xCHS), 80.7, 81.0 [2x$(CH_3)_3C$], 118.8, 119.0 (CH_2=C), 128.9, 129.0, 129.4, 129.7, 131.1, 131.4, 134.1, 144.7, 145.0 (2xArC, 2x*C*H=CH$_2$), 153.9 and 154.9 (2xC=O); *m/z* 266 (*M*+-BuᵗO, <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**): ν (KBr) 1671 (C=O), 1317, 1307, 1280 and 1150 cm^{-1} (SO_2); δ_H 0.90 (t, *J*=7.0 Hz, 3H, CH_3CH_2), 1.19-1.47, 2.00-2.30 [2m, 10H, $CH_3(CH_2)_3$, $(CH_2)_2CO$], 2.43 (s, 3H,

CH_3Ar), 3.33-3.41, 3.75-3.83 (2m, 2H, CH_2N), 5.24 (dd, *J*=11.6, 3.4 Hz, 1H, CHS), 7.33 and 7.75 (2d, *J*=8.2 Hz, 4H, ArH); δ_C 13.7 (CH_3CH_2), 18.4 (CH_2CH_2CON), 21.6 (CH_3Ar), 21.9, 22.7, 27.5 [$(CH_2)_3CH_3$], 30.1 (CH_2CO), 42.6 (CH_2N), 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 $C_{16}H_{23}NO_3S$: C, 62.11; H, 7.49; N, 4.53 and S, 10.36%).

tert-*Butyl* N-*Methyl*-N-*(1-tosylpentyl)carbamate* (**13dd**):[25] ν (film) 1703 (C=O), 1317, 1289 and 1142 cm^{-1} (SO_2); δ_H 0.89-0.94 (m, 6H, 2xCH_3CH_2), 1.11, 1.20 [2s, 18H, 2x$(CH_3)_3C$], 1.22-1.50 [m, 8H, 2x$CH_3(CH_2)_2$], 2.01-2.26 (m, 4H, 2xCHSCH_2), 2.40, 2.43 (2s, 6H, 2xCH_3Ar), 2.87, 2.95 (2s, 6H, 2xCH_3N), 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); δ_C 13.7 (2xCH_3CH_2), 21.5 (2xCH_3Ar), 21.7, 21.9, 22.5, 22.6 [2x$CH_3(CH_2)_2$], 27.2, 27.4 (2xCHSCH_2), 27.6, 27.8 [2x$(CH_3)_3C$], 28.0, 28.7 (2xCH_3N), 73.8, 75.1 (2xCHS), 80.7, 80.9 [2x$(CH_3)_3C$], 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*+-Bu^{t}O, <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] ν (film) 1697 (C=O), 1305, 1287, 1268 and 1148 cm^{-1} (SO_2); δ_H 1.66-1.97 [3m, 4H, $(CH_2)_2CO$], 2.42 (s, 3H, CH_3Ar), 3.29 (dd, *J*=15.0, 12.2 Hz, 1HxCH_2Ph), 3.32-3.40 (m, 1HxCH_2N), 3.64 (dd, *J*=15.0, 4.0 Hz, 1HxCH_2Ph), 3.76-3.84 (m, 1HxCH_2N), 5.68 (dd, *J*=12.2, 4.0 Hz, 1H, CHS), 7.14-7.35 (m, 7H, 2x*p*-Tol, PhH) and 7.78 (d, *J*=8.2 Hz, 2H, 2x*p*-Tol); δ_C 18.3 (CH_2CH_2CON), 21.6 (CH_3Ar), 29.3, 29.8 (CH_2CO, CH_2Ph), 42.7 (CH_2N), 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] ν (film) 1705 (C=O), 1318 and 1147 cm^{-1} (SO_2); δ_H 0.97, 1.10 [2s, 18H, 2x$(CH_3)_3C$], 2.39, 2.42 (2s, 6H, 2xCH_3Ar), 2.84, 2.95 (2s, 6H, 2xCH_3N), 3.17-3.29, 3.59-3.67 (2m, 4H, 2xCH_2CHS), 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); δ_C 21.4 (2xCH_3Ar), 27.4, 27.6 [2x$(CH_3)_3C$], 28.3, 29.0 (2xCH_3N), 29.2, 29.3 (2xCH_2CHS), 73.8, 75.9 (2xCHS), 80.6, 80.7 [2x$(CH_3)_3C$], 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] ν (film) 1732, 1682 (C=O), 1292, 1276 and 1145 cm^{-1} (SO_2); δ_H 1.40 [s, 9H, $(CH_3)_3C$], 1.91-2.24 [m, 4H, $(CH_2)_2CO$], 2.44 (s, 3H, CH_3Ar), 2.93 (dd, *J*=15.6, 11.6 Hz, 1HxCH_2CO), 3.19 (dd, *J*=15.6, 4.0 Hz, 1HxCH_2CO), 3.42-3.56, 3.74-3.82 (2m, 2H, CH_2N), 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 (CH_2CH_2CON), 21.6 (CH_3Ar), 27.7 [$(CH_3)_3C$], 29.9, 30.7 (2xCH_2CO), 42.8 (CH_2N), 68.0 (CHS), 82.1 [$(CH_3)_3C$], 128.7, 129.7, 133.0, 136.3 (ArC), 167.2 and 174.5 (2xC=O); *m/z* 294 (*M*+-Bu^{t}O, 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); ν (film) 3526 (OH), 1698 (C=O), 1302, 1287, 1265 and 1144 cm^{-1} (SO_2); δ_H 0.93 [s, 9H, $(CH_3)_3C$], 1.71-2.27 [m, 4H, $(CH_2)_2CO$], 2.45 (s, 3H, CH_3Ar), 3.35 (br s, 1H, OH), 3.87-3.94, 3.99-4.13 (2m, 2H, CH_2N), 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 (CH_2CH_2N), 21.7 (CH_3Ar), 26.0 [$(CH_3)_3C$], 29.5 (CH_2CO), 35.6 [$(CH_3)_3C$], 46.8 (CH_2N), 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**): ν (KBr) 3526 (OH), 1699 (C=O), 1302, 1287, 1269 and 1144 cm^{-1} (SO_2); δ_H 0.91 [s, 9H, $(CH_3)_3C$], 1.89-2.05, 2.20-2.29 [2m, 4H, $(CH_2)_2CO$], 2.43 (s, 3H, CH_3Ar), 2.47 (br s, 1H, OH), 3.52-3.59, 3.80-3.88 (2m, 2H, CH_2N), 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); δ_C 18.4 (CH_2CH_2N), 21.6 (CH_3Ar), 25.5 [$(CH_3)_3C$], 30.0 (CH_2CO), 36.0 [$(CH_3)_3C$], 44.4 (CH_2N), 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 $C_{17}H_{25}NO_4S$: 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**): ν (KBr) 3600-3100 (OH), 1700 (C=O), 1315, 1300, 1284 and 1143 cm^{-1} (SO_2); δ_H 1.78-2.01 [m, 4H, $(CH_2)_2CO$], 2.43 (s, 3H, CH_3Ar), 3.78 (br s, 1H, OH), 3.94 (m, 2H, CH_2N), 5.53, 5.74 (2m, 2H, CHO, CHS), 7.24-7.32 (m, 7H, 2x*p*-Tol, PhH) and 7.74 (d, *J*=7.6 Hz, 2Hx*p*-Tol); δ_C 18.9 (CH_2CH_2N), 21.7 (CH_3Ar), 29.3 (CH_2CO), 46.0 (CH_2N), 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 $C_{19}H_{21}NO_4S$: 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); ν (film) 3600-3100 (OH), 1700 (C=O), 1315, 1300, 1284 and 1143 cm^{-1} (SO_2); δ_H 1.39-1.49, 1.71-1.99 [2m, 4H, $(CH_2)_2CO$], 2.43 (s, 3H, CH_3Ar), 3.11-3.19, 3.69-3.73 (2m, 2H, CH_2N), 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); δ_C 18.6 (CH_2CH_2N), 21.7 (CH_3Ar), 29.3 (CH_2CO), 44.0 (CH_2N), 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**): ν (KBr) 3525 (OH), 1693 (C=O), 1319, 1302 and 1137 cm^{-1} (SO_2); δ_H 1.19, 1.27 [2s, 18H, 2x$(CH_3)_3C$], 1.34-2.16 [m, 9H, OH, $(CH_2)_4$], 2.41, 2.44 (2s, 6H, 2xCH_3Ar), 3.16, 3.17 (2s, 6H, 2xCH_3N), 5.21, 5.48 (2s, 2H, 2xCHS), 7.29-7.37 and 7.75-7.82 (2m, 8H, 2xArH); δ_C 21.4, 21.5 (2xCH_3Ar), 22.2, 22.3, 24.0, 24.3, 38.6, 40.6, 41.0 [2x$(CH_2)_4$], 27.8, 27.9 [2x$(CH_3)_3C$], 31.4, 32.0 (2xCH_3N), 79.0, 80.3 (2xCHS), 80.9, 81.3, 84.3, 84.4 [2x$(CH_3)_3C$, 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 $C_{19}H_{29}NO_5S$: C, 59.51; H, 7.62; N, 3.65 and S, 8.36%).

*Ethyl 2-Tosyl-2-(2-oxotetrahydro-1*H*-1-pyrrolyl)acetate* (**13cj**): ν (film) 1750, 1708 (C=O), 1325, 1291 and 1147 cm^{-1} (SO_2); δ_H 1.28 (t, *J*=7.0 Hz, 3H, CH_3CH_2), 2.02-2.12, 2.25-2.42 [2m, 4H, $(CH_2)_2CO$], 2.46 (s, 3H, CH_3Ar), 3.83-3.91, 4.01-4.13 (2m, 2H, CH_2N), 4.20-4.34 (m, 2H, CH_2CH_3), 6.07 (s, 1H, CHS), 7.37 and 7.81 (2d, *J*=8.2 Hz, 4H, ArH); δ_C 13.7 (CH_3CH_2), 18.6 (CH_2CH_2N), 21.6 (CH_3Ar), 29.6 (CH_2CO), 45.0 (CH_2N), 62.6 (CH_2O), 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 $C_{15}H_{20}NO_5S$, 326.1062).

tert-*Butyl* N-*[(Ethoxycarbonyl)tosylmethyl]*-N-*methylcarbamate* (**13dj**):[25] ν (film) 1752, 1705 (C=O), 1325, 1305 and 1144 cm^{-1} (SO_2); δ_H 1.25-1.35 [m, 24H, 2x$(CH_3)_3C$, 2xCH_3CH_2], 2.43, 2.45 (2s, 6H, 2xCH_3Ar), 3.09, 3.12 (2s, 6H, 2xCH_3N), 4.24-4.37 (m, 4H, 2xCH_2CH_3), 5.85, 6.22 (2s, 2H, 2xCHS), 7.33-7.39 and 7.76-7.84 (2m, 8H, 2xArH); δ_C 13.9 (2xCH_3CH_2), 21.5 (2xCH_3Ar), 27.8, 27.9 [2x$(CH_3)_3C$], 32.3, 32.6 (2xCH_3N), 62.5, 62.8 (2xCH_2CH_3), 76.8 (2xCHS), 81.6, 82.0 [2x$(CH_3)_3C$], 128.9, 129.1, 129.5, 129.7, 135.3, 135.4, 145.1, 145.4 (2xArC), 153.4, 155.2 (2xCO_2N), 162.9 and 163.3 (2xCO_2Et); *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).

1-(1-Tosyl-2-oxopropyl)-2-pyrrolidinone (**13ck**): ν (film) 1718, 1699 (C=O), 1318, 1305, 1290 and 1146 cm^{-1} (SO_2); δ_H 1.51-2.26 [m, 4H, $(CH_2)_2CO$], 2.45 (s, 3H, CH_3Ar), 2.55 (s, 3H, CH_3CO), 3.71-3.79,

3.88-3.96 (2m, 2H, CH_2N), 6.11 (s, 1H, CHS), 7.37 and 7.81 (2d, *J*=8.2 Hz, 4H, ArH); δ_C 18.9 (CH_2CH_2N), 21.7 (CH_3Ar), 29.5 (CH_2CO), 30.7 (CH_3CO), 44.8 (CH_2N), 77.9 (CHS), 128.6, 129.9, 134.1, 146.0 (ArC), 175.6 (CON) and 195.6 (Ph*C*O); *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 $C_{14}H_{17}NO_4S$, 295.0879).

1-(1-Tosyl-2-oxo-2-phenylethyl)-2-pyrrolidinone (**13cl**):[25] ν (film) 1735, 1689 (C=O), 1300, 1287, 1263 and 1148 cm^{-1} (SO_2); δ_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); δ_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 (Ph*C*O); *m/z* 357 (*M*+, <1%), 202 (65), 105 (100), 91 (30), 77 (85), 69 (27), 65 (24), 51 (31), 42 (40) and 41 (99).

tert-*Butyl (E)-3-(2-Oxotetrahydro-1H-1-pyrrolyl)-2-propenoate* (**14cf**): R_f 0.75 (EtOAc); ν (film) 3082, 1600, 981 (HC=C), 1732 and 1699 cm^{-1} (C=O); δ_H 1.49 [s, 9H, $(CH_3)_3C$], 2.17 (q, *J*=7.0 Hz, 2H, CH_2CH_2CO), 2.54 (t, *J*=7.6 Hz, 2H, CH_2CO), 3.54 (t, *J*=7.3 Hz, 2H, CH_2N), 5.14 and 7.99 (2d, *J*=14.3 Hz, 2H, CH=CH); δ_C 17.3 (CH_2CH_2CO), 28.1 [$(CH_3)_3C$], 30.8 (CH_2CO), 44.9 (CH_2N), 80.0 [$(CH_3)_3C$], 102.6, 136.3 (C=C), 166.4 and 174.0 (2xC=O); *m/z* 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 Na_2SO_4, 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); ν (film) 1725, 1709 (C=O), 1143 and 1133 cm^{-1} (CO); δ_H 1.49, 1.52 [2s, 18H, 2x$(CH_3)_3C$], 3.04 (s, 3H, CH_3N), 5.06 and 8.17 (2d, *J*=14.0 Hz, 2H, CH=CH); δ_C 28.1, 28.3 [2x$(CH_3)_3C$], 31.0 (CH_3N), 79.7, 82.9 [2x$(CH_3)_3C$], 99.2 (CH=CHN), 142.7 (CH=CHN), 152.2 (CO_2CH=CH) and 167.1 (NCO_2); *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 $C_{13}H_{23}NO_4$, 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_r 12.28 min; ν (film) 1678 cm^{-1} (C=O); δ_H 1.95 (m, 2H, CH_2CH_2CO), 2.34 (t, *J*=7.6 Hz, 2H, CH_2CO), 2.84 (t, *J*=7.6 Hz, 2H, CH_2Ar), 3.24 (t, *J*=7.0 Hz, 2H, $ArCH_2CH_2N$), 3.53 (t, *J*=7.3 Hz, 2H, $CO(CH_2)_2CH_2N$) and 7.18-7.37 (m, 5H, ArH); δ_C 18.0 (CH_2CH_2CO), 30.9, 33.8 (CH_2CO, CH_2Ph), 44.0, 47.6 (2xCH_2N), 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, CH_2CH_2N), 2.55 (t, *J*=7.9 Hz, 2H, CH_2CO), 3.66 (t, *J*=7.0 Hz, 2H, CH_2N), 5.89, 7.63 (2d, *J*=15.0 Hz, 2H, CH=CH), and 7.18-7.37 (m, 5H, ArH); δ_C 17.4 (CH_2CH_2N), 31.2 (CH_2CO), 45.2 (CH_2N), 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)-2-pyrrolidinone* (**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 Na_2SO_4 and evaporated (15 Torr), the residue was column chromatographied (silica gel, hexane/EtOAc) to afford pure compound **15cl**:[25] R_f 0.27 (EtOAc); ν (film) 1701 and 1681 cm^{-1} (C=O); δ_H 2.12 (m, *J*=7.0 Hz, 2H, CH_2CH_2N), 2.49 (t, *J*=7.9 Hz, 2H, CH_2CO), 3.51 (t, *J*=7.0 Hz, 2H, CH_2CH_2N), 4,74 (s, 2H, NCH_2CO), 7.46-7.63 and 7.95-7.98 (2m, 5H, PhH); δ_C 18.0 (CH_2CH_2N), 30.4 (CH_2CO), 47.9, 49.1 (2xCH_2N), 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-*Butoxycarbonyl)*-N-*methyl-2-aminoacetate* (**15dj**).- A mixture of substrate **13dj** (2.0 mmol), magnesium powder (146 mg, 6.0 mmol), a few crystals of $HgCl_2$ in dry MeOH (10 ml) was stirred for 6 h at room temperature. The reaction mixture was poured into water and extracted with CH_2Cl_2 (3x10 ml). The organic layer was dried over Na_2SO_4, 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); ν (film) 1755, 1702 (C=O) and 1148 cm^{-1} (CO); δ_H 1.43, 1.47 [2s, 18H, 2x$(CH_3)_3C$], 2.92, 2.94 (2s, 6H, 2xCH_3N), 3.73, 3.74 (2s, 6H, 2xCH_3O), 3.91 and 3.99 (2s, 4H, 2xCH_2N); δ_C 28.2, 28.3 [2x$(CH_3)_3C$], 35.5 (2xCH_3N), 50.1, 50.9 (2xCH_2N), 51.9 (CH_3O), 80.1 [2x$(CH_3)_3C$], 155.1, 155.4 (2xNCO_2) 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 Na_2SO_4 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:

1-(1-Benzylvinyl)-2-pyrrolidinone (**16ce**): R_f 0.51 (ether); ν (film) 3084 (HC=C) and 1691 cm^{-1} (C=O); δ_H 1.92 (m, 2H, CH_2CH_2CO), 2.39 (t, *J*=7.9 Hz, 2H, CH_2CO), 3.49 (t, *J*=7.0 Hz, 2H, CH_2Ar), 3.92 (s, 2H, CH_2Ph), 4.61, 4.81 (2s, 2H, CH_2=C) and 7.20-7.31 (m, 5H, ArH); δ_C 18.0 (CH_2CH_2CO), 32.6 (CH_2CO), 39.6 (CH_2C=), 49.5 (CH_2N), 103.2 (CH_2=C), 126.3, 128.3, 128.8, 138.5, 144.9 (ArC, CH_2=*C*) and 174.1 (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) and 42 (32) (Found: *M*$^+$ 201.1153. Calcd. for $C_{13}H_{15}NO$, 201.1154).

tert-*Butyl* N-*(1-Methyl-1,3-butadienyl)*-N-*methylcarbamate* (**17**): R_f 0.85 (hexane/EtOAc: 1/1); ν (film) 3086, 1650 (HC=C) and 1702 cm^{-1} (C=O); δ_H 1.46 [s, 9H, $(CH_3)_3C$], 3.04 (s, 3H, CH_3N), 5.10 (d, *J*=10.0 Hz, 1HxCH_2=CH), 5.18 (d, *J*=17.4 Hz, 1HxCH_2=C), 5.87 (d, *J*=11.0 Hz, 1H, CH=CN) and 6.42-6.54 (m, 1H, CH=CH_2); δ_C 16.4 (CH_3C=CH), 28.3 [$(CH_3)_3C$], 36.3 (CH_3N), 79.9 [$(CH_3)_3C$], 116.8 (CH_2=CH), 124.5, 132.4 (CH=CH), 140.3 (CH_3C=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 $C_{11}H_{19}NO_2$, 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 μl, 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 Na_2SO_4, 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); ν (film) 1690 (C=O) and 1147 cm^{-1} (C-O); δ_H 1.48 [s, 9H, $(CH_3)_3C$], 2.55-2.75 (m, 6H, CH_3N, CH_2CHN), 5.08 (d, *J*=10.1 Hz, 1HxCH=CH_2), 5.15 (d, *J*=17.1 Hz, 1HxCH=CH_2), 5.76-5.89 (m, 1H, C*H*=CH_2) and 7.23-7.36 (m, 5H, PhH); δ_C 28.4 (CH_3N), 28.5 [(CH_3)$_3$C], 34.7 (CH_2CH=CH_2), 56.1, 57.5 (2br s, NCH_2Ph), 79.5 [$(CH_3)_3C$], 117.1 (CH_2=CH), 127.2, 127.3, 128.3, 134.9, 140.2 (ArC, CH_2=*C*H) and 156.2 (CO); *m/z* 220 (*M*$^+$-CH_2CHCH_2, 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 compond **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 Na_2SO_4 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; ν (film) 3417 (OH), 3101, 3063, 3018, 1600 and 1506 cm^{-1} (HC=C); δ_H 1.00 [s, 9H, $(CH_3)_3C$], 2.92 (s, 4H, CH_3N, OH), 3.23 (dd, *J*=14.2, 10.4 Hz, 1H, 1xCH_2), 3.34 (dd, *J*=14.2, 3.0 Hz, 1H, 1xCH_2), 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); δ_C 25.7 [(CH_3)$_3$C], 33.8 [*C*(CH_3)$_3$], 39.1 (CH_3N), 56.5 (CH_2), 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 $C_{13}H_{21}NO$, 207.1623).

2-(N-Methylanilino)-1-phenylethanol (**20b**):[29] t_r 14.19 min; ν (film) 3417 (OH), 3099, 3061, 3027, 1599 and 1506 cm^{-1} (HC=C); δ_H 2.52 (br s, 1H, OH), 2.94 (s, 3H, CH_3), 3.43 (dd, *J*=14.6, 4.6 Hz, 1H, 1xCH_2), 3.51 (dd, *J*=14.6, 8.6 Hz, 1H, 1xCH_2), 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); δ_C 39.4 (CH_3N), 62.0 (CH_2), 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 (**20c**): t_r 12.19 min; ν (film) 3458 (OH), 3097, 3066, 3040, 1674, 1600 and 1506 cm^{-1} (HC=C); δ_H 0.94 (t, *J*=7.6 Hz, 6H, 2xCH_3CH_2), 1.58 (q, *J*=7.6 Hz, 4H, 2xCH_2CH_3), 1.74 (br s, 1H OH), 2.99 (s, 3H, CH_3N), 3.30 (s, 2H, CH_2N), 6.70-6.75, 6.85-6.90 and 7.20-7.25 (3m, 5H, Ph); δ_C 7.8 (2xCH_3CH_2), 29.2 (2xCH_2CH_3), 41.1 (CH_3N), 61.3 (CH_2N), 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 $C_{13}H_{21}NO$, 207.1623).

2,4-Dimethyl-3-(N-methylanilinomethyl)-3-pentanol (**20d**): t_r 12.57 min; ν (film) 3515 (OH), 3061, 1600 and 1505 cm^{-1} (HC=C); δ_H 0.99 (d, *J*=7.0 Hz, 6H, 2xCH_3C), 1.05 (d, *J*=6.7 Hz, 6H, 2xCH_3C), 1.85-2.10 (m, 2H, 2xC*H*CH_3), 2.95 (s, 3H, CH_3N), 3.37 (s, 2H, CH_2), 6.75-6.80, 6.90-6.95 and 7.20-7.30 (3m, 5H, ArH); δ_C 17.5, 17.7, 18.2, 18.3 (4xCH_3C), 33.7 (CH_3N), 42.0 (2x*C*CH_3), 57.0 (CH_2), 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 $C_{15}H_{25}NO$, 235.1936).

1-(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, $(CH_2)_5$, OH], 3.00 (s, 3H,

CH_3), 3.27 (s, 2H, CH_2N), 6.70-6.75, 6.85-6.90 and 7.20-7.25 (3m, 1, 2 and 3H, respectively, ArH); δ_C 21.7, 25.8, 36.0 (CH_2)$_5$, 41.3 (CH_3), 64.5 (CH_2N), 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; ν (film) 3461 (OH), 3058, 3024, 1598 and 1505 cm^{-1} (HC=C); δ_H 1.62 (s, 3H, CH_3C), 2.65 (s, 4H, CH_3N, OH), 3.51, 3.60 (2d, *J*=14.6 Hz, 2H, CH_2), 6.70-6.90 and 7.15-7.50 (2m, 10H, ArH); δ_C 27.9 (*C*H_3C), 40.1 (CH_3N), 66.1 (CH_2), 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; ν (film) 3477 (OH), 1681 (C=O) and 1147 cm^{-1} (CO); δ_H 0.93 [s, 9H, (*CH*$_3$)$_3$CCH], 1.46 [s, 9H, (CH_3)$_3$CO], 2.91 (s, 3H, CH_3N), 3.10 (s, 1H, OH) and 3.40-3.55 (m, 3H, CH_2N, CH); δ_C 25.5, 28.3 [(*C*H_3)$_3$C], 34.1 [(CH_3)$_3$*C*], 35.5 (CH_3N), 51.5 (CH_2), 78.4 (CHO), 80.0 [(CH_3)$_3$*C*O] and 158.1 (C=O); *m/z* 158 (*M*+-Bu^{t}O, 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; ν (film) 3420 (OH), 1694 (C=O) and 1172 cm^{-1} (CO); δ_H 1.47 [s, 9H, (CH_3)$_3$C], 2.75-2.90 (br s, 3H, CH_3N), 3.40-3.55 (br s, 2H, CH_2), 4.20 (br s, 1H, CHO), 4.92 (br s, 1H, OH) and 7.25-7.40 (m, 5H, ArH); δ_C 28.3 [(*C*H_3)$_3$C], 36.3 (CH_3N), 57.5 (CH_2), 73.6 (CHO), 80.2 [(CH_3)$_3$*C*), 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; ν (film) 3435 (OH) and 1668 cm^{-1} (C=O); δ_H 0.92, 0.93 (2t, *J*=7.3 Hz, 6H, 2xCH_3), 1.20-1.35, 1.40-1.50, 1.60-1.85 (3m, 1, 2 and 3H, respectively, 2xCH_2CH_3 and CH_2CH_2N), 2.73 (t, *J*=9.8 Hz, 2H, CH_2C=O), 2.86 (s, 2H, NCH_2CO), 3.20-3.35 (m, 2H, CH_2CH_2N) and 4.62 (s, 1H, OH); δ_C 7.3, 7.6 (2xCH_3), 20.5 (*C*H_2CH_2N), 28.5, 29.2, 29.5 (*C*H_2CH_3, *C*H_2C=O), 47.2, 47.4 (2xCH_2N) 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; ν (film) 3429 (OH), 1675 (C=O) and 1162 cm^{-1} (CO); δ_H 0.89 (t, *J*=7.5 Hz, 6H, 2x*CH*$_3$CH$_2$), 1.47 [s, 9H, (CH_3)$_3$C], 1.40-1.55 (m, 4H, 2x*CH*$_2$CH$_3$), 1.50 (br s, 1H, OH), 2.95 (s, 3H, CH_3N) and 3.26 (s, 2H, CH_2N); δ_C 7.75 (2x*C*H$_3$CH$_2$), 28.3 [(*C*H_3)$_3$C], 29.0 (2x*C*H$_2$CH$_3$), 37.9 (CH_3N), 57.2 (CH_2N), 76.0 (CHO), 80.2 [(CH_3)$_3$*C*] 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; ν (film) 3451 (OH), 1698, 1673 (C=O) and 1157 cm^{-1} (CO); δ_H 1.47 [s, 9H, (CH_3)$_3$C], 1.45-1.70, 1.75-1.90 [2m, 4 and 2H, (CH_2)$_4$], 2.97 (s, 3H, CH_3N), 3.37 (s, 2H, CH_2N) and 3.74 (br s, 1H, OH); δ_C 23.4, 38.1 [(CH_2)$_4$], 28.3 [(*C*H_3)$_3$C], 37.5 (CH_3N), 58.2 (CH_2N), 80.1 [(CH_3)$_3$*C*], 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; ν (film) 3415 (OH) and 1668 cm^{-1} (C=O); δ_H 1.05-1.85 (m, 12H, *CH*$_2$CH$_2$N), 2.00-2.20 (m, 1H, 1xCH_2C=O), 2.85 (t, *J*=9.8 Hz, 1H, 1xCH_2C=O), 2.85 (s, 2H, CH_2NC=O), 3.25-3.35 (m, 2H, CH_2CH_2N) and 4.50 (s, 1H, OH); δ_C 20.8, 21.1, 21.2, 25.8, 29.5, 31.4, 36.0 [(CH_2)$_5$, *C*H_2CH_2N], 47.5, 51.0 (CH_2N), 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 $C_{11}H_{19}NO_2$, 197.1416).

tert-*Butyl* N-*(2-Hydroxy-2-phenylpropyl*-N-*methylcarbamate* (**22df**):[25] t_r 14.04 min; ν (film) 3435 (OH), 1694 (C=O) and 1163 cm^{-1} (CO); δ_H 1.45 [s, 9H, (CH_3)$_3$C], 1.55 (s, 3H, *CH*$_3$COH) 2.55-2.80 (m, 3H, CH_3N), 3.31, 3.67 (2d, *J*=14.7 Hz, 2H, CH_2), 5.15 (s, 1H, OH) and 7.25-7.50 (m, 5H, ArH); δ_C 27.2 (*C*H$_3$COH), 28.2 [(*C*H$_3$)$_3$C], 37.5 (CH_3N), 61.9 (CH_2), 75.8 (CHO), 80.4 [(CH_3)$_3$*C*], 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; ν (film) 1696 (C=O), 1249 (SiC) and 1173 cm^{-1} (CO); δ_H 0.90 [s, 9H, $(CH_3)_3Si$], 1.58 [s, 9H, $(CH_3)_3C$], 2.89 (s, 2H, CH_2) and 2.98 (s, 3H, CH_2N); δ_C -1.7 [$(CH_3)_3Si$], 28.4 [$(CH_3)_3C$], 36.4 (CH_3N), 40.1 (CH_2N), 78.9 [$(CH_3)_3C$] 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 Na_2SO_4 and the solvent evaporated (15 Torr) to give the essentially pure (>95% by 300 Mz ^{1}H NMR) title compounds. *Method B*: A solution of the corresponding carbamate (1 mmol) and trifuoroacetic acid (4 mmol) in CH_2Cl_2 (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; ν (film) 3318 (OH), 3084, 3061, 3028 and 1629 cm^{-1} (HC=C); δ_H 2.40 (s, 3H, CH_3), 2.65-2.80 (m, 2H, CH_2), 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); δ_C 35.7 (CH_3), 59.0 (CH_2), 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; ν (film) 3402 (OH, NH), 3091, 3060, 3021, 1600 and 1493 cm^{-1} (HC=C); δ_H 1.48 (s, 3H, CH_3CO), 2.36 (s, 3H, CH_3N), 2.69, 3.02 (2d, *J*=11.9 Hz, 2H, CH_2), 2.95 (br s, 1H, OH) and 7.15-7.50 (m, 5H, ArH); δ_C 28.2 (CH_3CO), 36.5 (CH_3N), 62.6 (CH_2), 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 Na_2SO_4 and the solvent evaporated (15 Torr) to give the essentially pure (>95% by 300 Mz ^{1}H 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; ν (film) 3402 cm^{-1} (OH); δ_H 0.91 (s, 9H, $[(CH_3)_3C]$, 2.20-2.45 (m with s at 2.34, 8H, CH_2, 2xCH_3N) and 3.33 (dd, *J*=11.0, 3.0 Hz, 1H, CH); δ_C 25.6 [$(CH_3)_3C$], 33.3 [$C(CH_3)_3$], 45.2 (2xCH_3N), 60.5 (CH_2) 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; ν (film) 3415 (OH), 3091, 3053, 3028, 1494 and 1454 cm^{-1} (HC=C); δ_H 2.30-2.40 (m, 7H, 2xCH_3, 1xCH_2), 2.48 (dd, *J*=12.3, 10.4 Hz, 1H, 1xCH_2), 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 (2xCH_3), 67.5 (CH_2), 69.5 (CO), 125.8, 127.3, 128.2 and 142.2 (ArC); *m/z* 147 (*M*+-H_2O, 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; ν (film) 3404 (OH), 3091, 3060, 3025, 1601 and 1492 cm^{-1} (HC=C); δ_H 1.45 (s, 3H, CH_3CO), 2.10 (s, 6H, 2xCH_3N), 2.63, 2.74 (2d, *J*=12.8 Hz, 2H, CH_2), 3.63 (br s, 1H, OH) and 7.15-7.50 (m, 5H, ArH); δ_C 29.7 (CH_3CO), 47.2 (2xCH_3N), 70.4 (CH_2), 71.6 (CO), 124.7, 126.2, 128.0 and 148.1 (ArC); *m/z* 164 (*M*+-CH_3, 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 Na_2SO_4 and the solvent evaporated (15 Torr) to give the essentially pure (>95% by 300 Mz ^{1}H 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; ν (film) 1745 cm^{-1} (C=O); δ_H 0.94 [s, 3H, $(CH_3)_3C$], 2.88 (s, 3H CH_3N), 3.28, 3.46 (2t, *J*=8.5 Hz, 2H, CH_2) and 4.17 (t, *J*=8.5 Hz, 1H, CH); δ_C 24.2 [$(CH_3)_3C$], 30.8 [$(CH_3)_3C$], 33.5 (CH_3N), 47.9 (CH_2), 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 $C_8H_{15}NO_2$, 157.1103).

3,5-Dimethyl-5-phenyl-1,3-oxazolin-2-one (**26df**):[35] t_r 11.61 min; ν (film) 3056, 3030 (HC=C) and 1748 cm^{-1} (C=O); δ_H 1.75 (s, 3H, CH_3C), 2.88 (s, 3H, CH_3N), 3.64 (s, 2H, CH_2) and 7.25-7.40 (m, 5H, ArH); δ_C 28.7 (CH_3C), 31.0 (CH_3N), 60.1 (CH_2), 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]

REFERENCES AND NOTES

1. (a) Uchino, M.; Suzuki, K.; Sekiya, M. *Synthesis* **1977**, 794-796. (b) Morton, J.; Rahim, A.; Walker, E. R. H. *Tetrahedron Lett.* **1982**, *23*, 4123-4126. (c) Pearson, W. H.; Lindbeck, A. C.; Kampf, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 2622-2636. (d) Brown, D. S.; Hansson, T.; Ley, S. V. *Synlett* **1990**, 48-49. (e) Brown, D. S.; Charreau, P.; Hansson, T.; Ley, S. V. *Tetrahedron* **1991**, *47*, 1311-1328. (f) Brown, D. S.; Charreau, P.; Ley, S. V. *Synlett* **1990**, 749-750. (g) Basak, A.; Khamrai, U. K. *Tetrahedron Lett.* **1996**, *37*, 2475-2478.
2. Beiffuss, U.; Kunz, O.; Ledderhose, S.; Taraschewski, M.; Tonko, C. *Synlett* **1996**, 34-36.
3. For recent contributions from our laboratory about functionalised lithiated sulfones, see: (a) Alonso, D. A.; Favello, L. R.; Mancheño, B.; Nájera, C.; Tomás, M. *J. Org. Chem.* **1996**, *61*, 5004-5012. (b) Caturla, F; Nájera, C. *Tetrahedron Lett.* **1996**, *37*, 4787-4790.
4. (a) Guijarro, D.; Yus, M. *Tetrahedron Lett.* **1994**, *35*, 2965-2968. (b) Alonso, E.; Guijarro, D.; Yus, M. *Tetrahedron* **1995**, *51*, 2699-2708. (c) For a recent review on arene-catalysed lithiation, see: Yus, M. *Chem. Soc. Rev.* **1996**, 155-161.
5. (a) For a review on "umpolung" reactivity, see: Seebach, D. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 239-258. (b) For a review on functionalised organolithium compounds, see: Nájera, C.; Yus, M. *Trends Org. Chem.* **1991**, *2*, 155-181.
6. To the best of our knowledge, only one example on the lithiation of a α-amido sulfone and the subsequent reaction with methyl iodide has been described (reference 1c).
7. For recent leading references, see: (a) Park, Y. S; Beak, P. *Tetrahedron* **1996**, *52*, 12333-12350. (b) Kopach, M. E.; Meyers, A. I. *J. Org. Chem.* **1996**, *61*, 6764-6765. (c) Park, Y. S.; Boys, M. L.; Beak, P. *J. Am. Chem. Soc.* **1996**, *118*, 3757-3758. (d) Wu, S.; Lee, S.; Beak, P. *J. Am. Chem. Soc.* **1996**, *118*, 715-721. (e) Kise, N.; Kashiwagi, K.; Watanabe, M.; Yoshida, J. *J. Org. Chem.* **1996**, *61*, 428-429.
8. (a) See, for instance reference 1c. (b) For a recent paper, see: Coldham, I.; Hutton, R.; Snowden, D. J. *J. Am. Chem. Soc.* **1996**, *118*, 5322-5323 and references cited therein.

9. Strohmann, C.; Abele, B. C. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2378-2380.
10. Guijarro, A.; Ortíz, J.; Yus, M. *Tetrahedron Lett.* **1996**, *37*, 5597-5600.
11. Preliminary communication: Alonso, D. A.; Alonso, E.; Nájera, C.; Yus, M. *Synlett* **1997**, in the press.
12. (a) Engberts, J. B. F. N.; Strating, J. *Recl. Trav. Chim. Pays-Bas* **1964**, *83*, 733-736. (b) Olijnsma, T.; Engberts, J. B. F. N.; Strating, J. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 463-473.
13. Trost, B. M.; Arndt, H. C.; Strege, P. E.; Verhoeven, T. R. *Tetrahedron Lett.* **1976**, 3477-3478.
14. Harris, A. R.; Mason, T. J.; Hanna, G. R. *J. Chem. Res. (S)* **1990**, 218-219.
15. Lee, G. H.; Choi, E. B.; Lee, E.; Pak, C. S. *Tetrahedron Lett.* **1993**, *34*, 4541-4542.
16. De Lima, C.; Julia, M.; Verpeaux, J.-M. *Synlett* **1992**, 133-134.
17. This compound was prepared by reaction of *p*-toluenesulfinic acid with aqueous formaldehyde and *N*-methylaniline in methanol in 80% yield (see reference 2).
18. For a review, see: Blomberg, C. *The Barbier Reaction and Related One-Pot Processes*; Springer-Verlag: Berlin, 1993.
19. (a) Beak, P.; Snieckus, V. *Acc. Chem. Res.* **1982**, *15*, 306-312. (b) Beak, P.; Meyers, A. I. *Acc. Chem. Res.* **1986**, *19*, 356-363.
20. Stahl, G. L.; Walter, R.; Smith, C. W. *J. Org. Chem.* **1978**, *43*, 2285-2288.
21. Lundt, B. F.; Johansen, N. L.; Vølund, A.; Markussen, J. *Int. J. Pept. Protein Res.* **1978**, *12*, 258-268.
22. Cran, G. A.; Gibson, C. L.; Handa, S. *Tetrahedron:Asymmetry* **1995**, *6*, 1553-1556.
23. The microanalysis method (sample weighed but $D_2O + H_2O$ content measured by gas chromatography) does not allow the determination of %D. Thus, calculated %H/D values are corrected considering this fact.
24. Brettle, R.; Shibib, S. M.; Wheeler, K. J. *J. Chem. Soc., Perkin Trans. 1* **1985**, 831-836.
25. For compounds **13dc**, **13dd**, **13ce**, **13de**, **13cf**, *erythro*-**13cg**, *threo*-**13ch**, **13dj**, **13cl**, **15cl**, **15dj**, **18**, **22da**, **22cc**, **22dc**, **22dd**, **22df** and **22dg**, it was not possible to obtain the corresponding HRMS due to the low intensity or the absence of the M^+ signal.
26. Malawska, B; Gorczyca, M. *Acta Pol. Pharm.* **1985**, *42*, 359-366; *Chem. Abstr.* **1987**, *106*, 18292p.
27. Couture, A.; Deniau, E.; Grandclaudon, P. *Tetrahedron Lett.* **1993**, *34*, 1479-1482.
28. Ouazzani-Chadi, L.; Quirion, J.-C.; Troin, Y.; Gramain, J. C. *Tetrahedron* **1990**, *46*, 7751-7762.
29. Davidson, R. S.; Orton, S. P. *J. Chem. Soc., Chem. Commun.* **1974**, 209-210.
30. Komeyoshi, Y.; Suzukamo, T.; Konya, N. **Jpn. Kokai Tokkyo Koho JP 63 02,935**, 1988; *Chem. Abstr.* **1988**, *109*, 149050t.
31. Coote, S. J.; Davies, S. G.; Middlemiss, D.; Nayler, A. *J. Chem. Soc., Perkin Trans. 1* **1989**, 2223-2228.
32. Meyers, A. I.; Hoeve, W. T. *J. Am. Chem. Soc.* **1980**, *102*, 7125-7126.
33. Hayashi, M.; Okamura, F.; Toba, T.; Oguni, N.; Sharpless, K. B. *Chem. Lett.* **1990**, 547-548.
34. Tomioka, K.; Okuda, M. *Tetrahedron Lett.* **1994**, *35*, 4585-4586.
35. Tsujimoto, Y.; Nakahara, A.; Nishimura, Y.; Miyamoto, T.; Odaira, Y. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3705-3706;*Chem. Abstr.* **1977**, *86*, 155555j.

36. This work was supported by DGICYT from the Spanish Ministerio de Educación y Ciencia (MEC; projects no. PB94-1514 and PB94-1515). D. A. A., E. A. and D. J. R. thank the MEC for grants.

(*Received in UK* 23 *January* 1997; *accepted* 13 *February* 1997)