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# Lithiated β-Aminoalkyl Sulfones as Mono and Dinucleophiles in the Preparation of Nitrogen Heterocycles: Application to the Synthesis of Capsazepine

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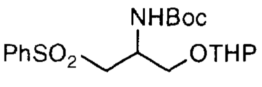
***Abstract:*** The lithiation of *N*-benzyl-β-tosylethanamine (**10a**) and *N*-benzyl-α-phenyl-β-tosylethanamine (**10b**) with *n*-butyllithium at -78°C leads to monoanions **11a** and **11b**, respectively. Intermediates **11** react with different monoelectrophiles ($D_2O$, alkyl halides, and carbonyl compounds) at the α-position with respect to the sulfone, and with dielectrophiles (1,3-, 1,4-dihalides, α-bromoacetates, and α-chloroketones) to afford the corresponding 6, 7, and 5-membered nitrogen heterocycles. The benzoazepine derivative **13ae**, obtained by reaction of **11a** with 4,5-bis(chloromethyl)-1,2-dimethoxybenzene, are transformed into the inmediate precursor **24** of capsazepine **25** an antagonist of the sensory neuron excitants capsaicin and resiniferatoxin. Cyclic β-amino sulfone: *N*-benzyl-3-tosylpiperidine (**13aa**) suffers lithiation at the axial position reacting with electrophiles to give compounds **27**. In the case of the Michael addition to methyl crotonate the corresponding adducts are converted into 1-azabicyclo[3.3.1]nonan-2-one derivatives. Finally, base-induced dehydrosulfinylation, reductive desulfonylation, and Julia's methylenation are studied with some representative derivatives.

## INTRODUCTION

Lithiated β-aminoalkyl sulfones are interesting $d^2$ reagents[1] stabilized by the sulfonyl group. The first examples of the lithiation of β-aminoalkyl sulfones (and alkylation with methyl iodide) were described by Eisch and Galle[2] as an alternative strategy for the direct lithiation of vinyl sulfones.[3] (*R*) and (*S*) Sasaki's reagents **1** derived from serine have been used as chiral precursors of the corresponding dianions in the synthesis of α-amino acids[4] and chiral 2,5-disubstituted pyrrolidines.[5] Other recent examples used the dianions of β-aminoalkyl sulfones in the Julia-Paris-Kocienski (JPK) strategy: coupling reaction with carbonyl compounds followed by reductive desulfonylation.[6] This JPK methodology has been applied to the synthesis of: (a) *trans*-alkene isosteres of dipeptides (sulfones **2**[7] and **3**[8]), (b) a precursor of HIV protease inhibitors (sulfone **3**[9]), (c) the indolizidine (-)-slaframine (sulfone **4**[10]), and (d) (*E*)-allylamines (sulfone **5**[11]). Sulfones derived from tertiary amines **6** and **7** have been used as monoanions into the synthesis of vinyl sulfones[12] and indolizidines,[13] respectively.



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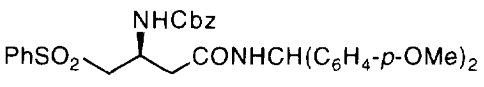

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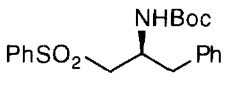

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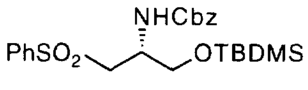

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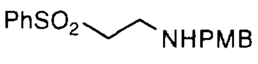

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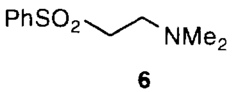
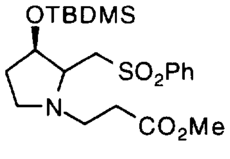


**6**



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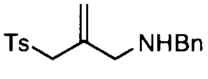

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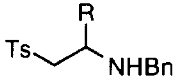
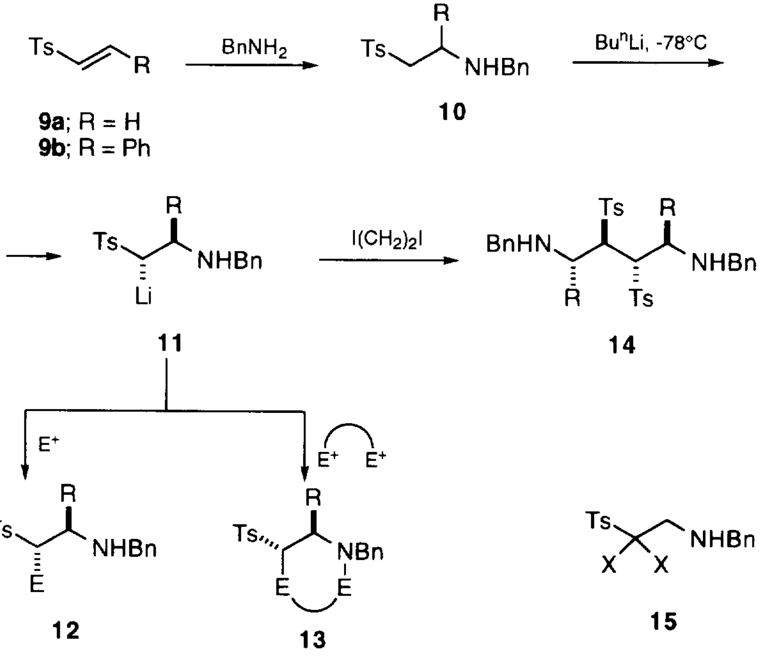


**10**

In connection with our studies on the application of organolithium compounds of γ-aminomethallyl sulfone **8**,[14] specially as 1,4-dinucleophile in annelation reactions in the synthesis of nitrogen-containing heterocycles,[15] we describe here the use of the generated monoanions from secondary β-aminoalkyl sulfones **10** as mono and 1,3-dinucleophiles and their utility for the synthesis of nitrogen-containing heterocycles, capsazepine[16] and bicyclic lactams such as 1-azabicyclo[3.3.1]nonan-2-ones.

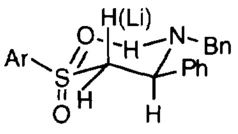
## RESULTS AND DISCUSSION

The starting β-aminoalkyl sulfones **10a**[17] and **10b** were prepared by Michael addition of benzylamine to the corresponding vinyl sulfone **9a**[18] and **9b**[19] in 73 and 79% yield, respectively. The monolithiation of compounds **10** with *n*-butyllithium at -78°C in THF afforded intermediates **11** which were characterized by deuterolysis with $D_2O$ to furnish compounds **12aa** and **12ba** up to 90% of deuterium incorporation (Scheme 1 and Table 1, entries 1 and 2). It means that the thermodynamic and kinetic acidities of the α-sulfone hydrogens are greater than the NH ones. Both organolithium compounds reacted with alkyl halides to give monoalkylated products **12ab**-**12ae** (Table 1, entries 3-8). Intermediate **11b** reacted stereoselectively with electrophiles to afford mainly the *anti*-diastereomers[20] (Table 1, entries 2, 4, and 6). Stereoselective dimerization of anions **11** took place by treatment with 1,2-diiodoethane to furnish 1,4-diamines **14** with an *anti* relative configuration as well (Scheme 1 and Table 1, entries 10 and 11).

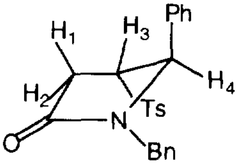


Scheme 1.

In the case of the reaction of **11b** with ethyl bromoacetate the alkylation at the α-position of the sulfone followed by intramolecular lactamization occurred very easily even at -78 °C to afford stereoselectively the expected *trans*-lactam **16b** resulting from the monoalkylated *anti*-diastereomer. It means that the proton abstraction in the lithiation step occurred mainly at the axial position, due to a possible chelation with the nitrogen, in the chair conformation of the starting β-aminoalkyl sulfone **10b** which is *cis* or *anti* (in the cyclic or acyclic structure, respectively) bearing the phenyl group at the equatorial position. The *trans*-pseudoaxial configuration for lactam **16b** seems to be more stable than the corresponding pseudoequatorial[21] as was deduced from $^1$H NMR studies of the coupling constants ($J_{H3\text{-}H4}$ = 3.4; $J_{H1\text{-}H3}$ = 9.8; $J_{H2\text{-}H3}$ = 4.9 Hz) and NOE difference experiments.

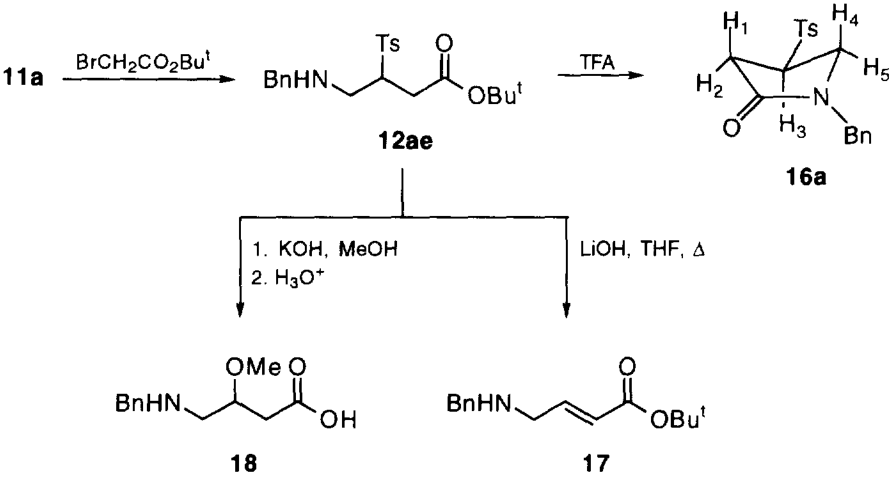


**10b(11b)**



**16b**

In thereaction of **11a** with *tert*-butyl bromoacetate the alkylation product **12ae** was obtained even when the reaction was allowed to rise to room temperature, and it was quantitatively transformed into the corresponding lactam **16a**[22] after hydrolysis with trifluoroacetic acid followed by heating of the resulting amino acid under THF reflux for 20 h. Attempts to carry out the corresponding dehydrosulfinylation of lactam **16a** with DBU failed. This behaviour is in agreement with the pseudoequatorial position of the tosyl group as it has been deduced from the $J$ values 9.8 and 8.9 Hz for $H_1$-$H_3$ and $H_3$-$H_4$, respectively (Scheme 2). Compound **12ae** was also quantitatively transformed into the α,β-unsaturated γ-aminobutyric ester **17**[23] by treatment with LiOH. Other basic elimination conditions such as methanolic potassium hydroxide produced subsequent Michael addition of methanol and hydrolysis of the ester giving the GABA derivative **18** in 70% yield (Scheme 2).



**Scheme 2.**

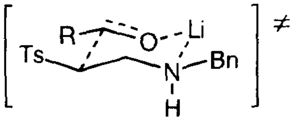
The reactivity of intermediate **11b** is much lower than the less substituted **11a**. Thus, only **11a** reacted with carbonyl compounds to give 3-aminoalcohols **12af-al** (Scheme 1 and Table 1). In the case of aldehydes

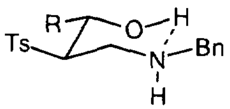
**Table 1**. Reaction of Lithiated β-Aminoalkyl Sulfones **11** with Electrophiles.

| | | | product | | | | |
|---|---|---|---|---|---|---|---|
| entry | starting sulfone | electrophile | no. | R | E | yield (%)[a] | mp (°C)[b] or $R_f$[c] |
| 1 | **10a** | $D_2O$ | **12aa** | H | D | 60[d] | 29-30 |
| 2 | **10b** | $D_2O$ | **12ba** | Ph | D | 78[d] | 0.84 |
| 3 | **10a** | $BrCH_2CHCH_2$ | **12ab** | H | $CH_2CHCH_2$ | 76[e] | 0.71 |
| 4 | **10b** | $ICH_2CHCH_2$ | **12bb** | Ph | $CH_2CHCH_2$[f] | 34 | 0.65 |
| 5 | **10a** | $BrCH_2Ph$ | **12ac** | H | $PhCH_2$ | 53 | 0.83 |
| 6 | **10b** | $BrCH_2Ph$ | **12bc** | Ph | $PhCH_2$[g] | 30 | 0.60 |
| 7 | **10a** | $ICH_2SiMe_3$ | **12ad** | H | $Me_3SiCH_2$ | 40 | 95-96 |
| 8 | **10a** | $BrCH_2CO_2Bu^t$ | **12ae** | H | $Bu^tO_2CCH_2$ | 71 | 112-113 |
| 9 | **10b** | $BrCH_2CO_2Et$ | **16b** | Ph | | 45 | 122-123 |
| 10 | **10a** | $I(CH_2)_2I$ | **14a** | H | | 33 | 0.75 |
| 11 | **10b** | $I(CH_2)_2I$ | **14b** | Ph | | 52 | 102-103[h] |
| 12 | **10a** | $Pr^iCHO$ | **12af** | H | $Pr^iCHOH$[i] | 75 | 77-78[j] |
| 13 | **10a** | $Bu^tCHO$ | **12ag** | H | $Bu^tCHOH$[k] | 97 | 153-154[j] |
| 14 | **10a** | PhCHO | **12ah** | H | PhCHOH[l] | 75 | 0.61[j] |
| 15 | **10a** | *p*-$MeOC_6H_4CHO$ | **12ai** | H | *p*-$MeOC_6H_4CHOH$[k] | 70 | 0.54[j] |
| 16 | **10a** | $(CH_2)_4CO$ | **12aj** | H | $(CH_2)_4CHOH$ | 82 | 102-103 |
| 17 | **10a** | $(CH_2)_5CO$ | **12ak** | H | $(CH_2)_5CHOH$ | 65 | 109-110 |
| 18 | **10a** | PhCOMe | **12al** | H | PhMeCHOH[m] | 66 | 0.66[j] |

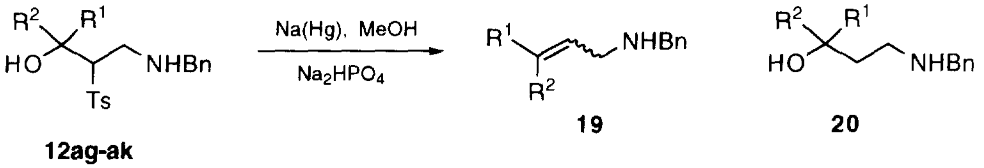
[a] Isolated yield after column chromatography on silica gel, based on starting sulfone **10**. [b] Hexane/ether. [c] Ether. [d] >90% of deuterium incorporation ( $^{13}C$ NMR). [e] 23% of dialkylated compound **15ab** was also obtained. [f] *Anti/syn*: 15/1. [g]. *Anti/syn* :3/1 [h] Hexane/EtOAc. [i] *Erythro/threo* : 3/1. [j] For both diastereomers. [k] *Erythro/threo* : 4/1. [l] *Erythro/threo* : 9/1. [m] *Erythro/threo* : 1/1.

compounds **12af-ai** (Table 1, entries 12-15) were obtained as mixture of diastereomers the *erythro* being the major isomer.[24] The observed diasteroselectivity can be explained by participation of an intramolecular chelation between the alcoholate and the amino group in the transition state, which favoures the formation of the *erythro*-diastereomer with the tosyl and the R group of the aldehyde in the *trans*-diequatorial position in a chair conformation. In the final 3-aminoalcohol the intramolecular hydrogen bond would also be the reason for a





greater stability of the *erythro* than for the *threo*-diastereomer. According to the JPK methodology further reduction of these β-hydroxy sulfones **12ag-ak** by sodium amalgam[25] gave exclusively the corresponding allyl amines **19** in the case of aldehydes. 3-Aminoalcohols **20** were obtained as minor products in the case of ketones derivatives (Scheme 3 and Table 2). The reductive elimination to give compounds **19** was completly stereoselective for compound **19a**, which was obtained with *E*-configuration. The reduction of molecule **12ai** gave **19b** as a 1/2 mixture of *Z/E* diastereomers independ-ently of the *erythro/threo* ratio of starting **12ai**.[26]



**Scheme 3.**

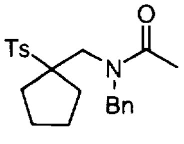
**Table 2.** Reductive Desulfonylation of β-Hydroxy Sulfones.

| starting sulfone | | | product | | | |
|---|---|---|---|---|---|---|
| no. | $R^1$ | $R^2$ | no. | yield (%)[a] | configuration[b] | $R_f$[c] |
| **12ag** | $Bu^t$ | H | **19a** | 98 | *E* | 0.40 |
| **12ai** | *p*-$MeOC_6H_4$ | H | **19b** | 61 | *Z/E*[d] | 0.57 |
| **12aj** | -$(CH_2)_4$- | | **19c** | 52[e] | | 0.50 |
| **12ak** | -$(CH_2)_5$- | | **19d** | 48[f] | | 0.52 |

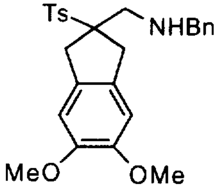
[a] Isolated yield after column chromatography on silica gel, based on starting sulfone **12**. [b] Deduced by $^1H$ NMR 300 MHz. [c] Ether. [d] 1/2 ratio. [e] 20% of compound **20c** ($R_f$ = 0.13) was also obtained. [f] 14% of compound **20d** ($R_f$ = 0.14) was also isolated.

The ability of monoanions **11** as 1,3-dinucleophiles was studied with other different dielectrophiles (Scheme 1 and Table 3). 1,3-Dihalides such as 1,3-diiodopropane and 2-iodomethyl-3-iodo-1-propene gave the corresponding piperidine derivatives **13aa,ba,ab** (Table 3, entries 1-3). The phenyl substituted piperidine *trans*-**13ba** derived from sulfone **10b** was obtained stereoselectively with both substituents at the equatorial position as deduced from the pattern of coupling constants pattern in the $^1H$ NMR spectrum in $d^6$-benzene.[21] When 1,4-dihalides: 1,4-diiodobutane, α,α'-dibromo-*o*-xylene and 4,5-bis(chloromethyl)-1,2-dimethoxybenzene were allowed to react as dielectrophiles with **11a**, the corresponding perhydroazepine derivatives

**13ac,ad,ae** (Table 3, entries 4-6) were synthesized. In these last cases the cyclopentane derivatives **21** were obtained as by-products as a result of a dialkylation process at the α-position with respect to the sulfone group. Compound **13ac** was separated from the cyclopentane derivative by transforming the latter into its acetamide **21ac**.

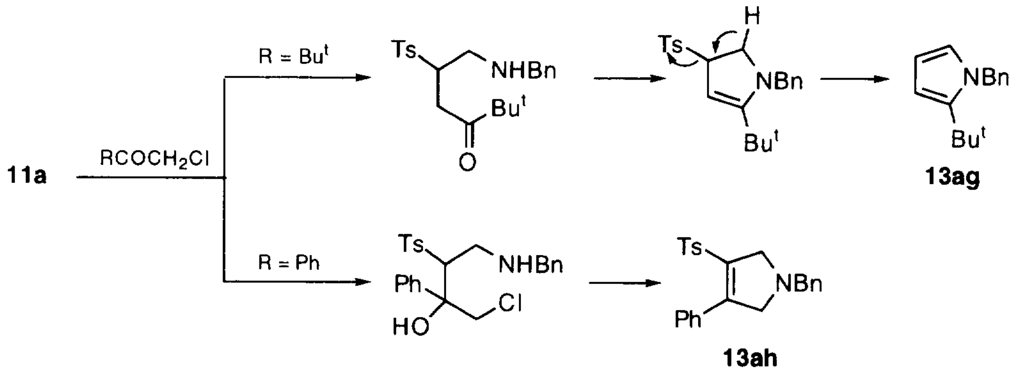


**21ac**



**21ae**

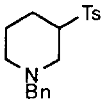
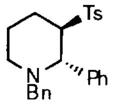
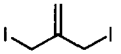
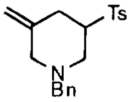
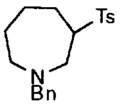
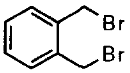
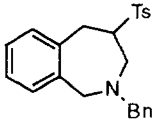
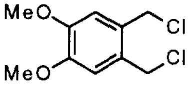
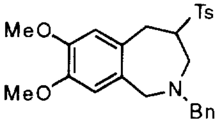
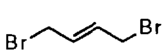
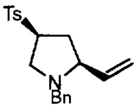
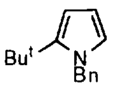
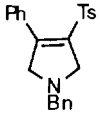
Five-membered heterocycles were prepared with *E*-1,4-dibromo-2-butene and α-chloroketones (Table 3, entries 7-9). Compound **13af**, which was obtained by reaction of **11a** with *E*-1,4-dibromo-2-butene, was stereoselectively obtained with the more stable *cis*-configuration[20] as deduced by $^1$H NMR studies (coupling constants and NOE experiments, see Figure 1). The reaction with *tert*-butyl chloromethyl ketone gave 2-*tert*-butylpyrrol **13ag** resulting from a substitution reaction followed by condensation of the carbonyl and amino groups and final dehydrosulfinylation. However, in the case of α-chloroacetophenone the first step was the addition to a less hindered carbonyl group followed by $S_N$ reaction to afford the 3-pyrroline **13ah** (Scheme 4).



Scheme 4.

This methodology has been applied to the synthesis of the amine **24** precursor of capsazepine **25**.[27] The reduction of benzoazepine derivative **13ae** with sodium amalgam[25] afforded a mixture in 55/45 ratio of the cyclic **22** and the open product **23** in 90% overall yield. The benzoazepine **22** was debenzylated with ammonium formate and palladium on carbon in methanol[28] to give the di-*O*-methylated capsazepine **24** in 80% yield, which has been previously transformed into capsazepine by deprotection with HBr of the hydroxy groups and reaction with 2-(4-chlorophenyl)ethyl isothiocyanate[16] (Scheme 5).

**Table 3**. Reaction of Lithiated β-Aminoalkyl Sulfones **10** with Dielectrophiles.

| | | | product | | | |
|---|---|---|---|---|---|---|
| entry | starting sulfone | electrophile | no. | structure | yield (%)[a] | mp (°C)[b] or $R_f$[c] |
| 1 | **10a** | $I(CH_2)_3I$ | **13aa** |  | 43[d] | 0.76 |
| 2 | **10b** | $I(CH_2)_3I$ | **13ba** |  | 43 | 0.84 |
| 3 | **10a** |  | **13ab** |  | 32 | 0.83 |
| 4 | **10a** | $I(CH_2)_4I$ | **13ac** |  | 31[e] | 0.69 |
| 5 | **10a** |  | **13ad** |  | 47 | 163-164 |
| 6 | **10a** |  [f] | **13ae** |  | 22[g] | 169-170 |
| 7 | **10a** |  | **13af** |  | 44 | 0.71 |
| 8 | **10a** | $Bu^tCOCH_2Cl$ | **13ag** |  | 27 | 0.89 |
| 9 | **10a** | $PhCOCH_2Cl$ | **13ah** |  | 24 | 0.44 |

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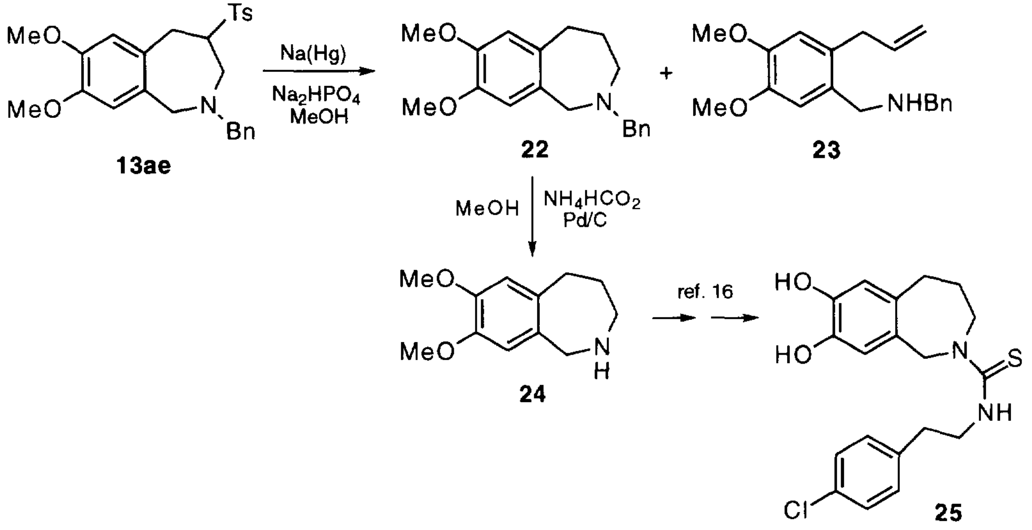
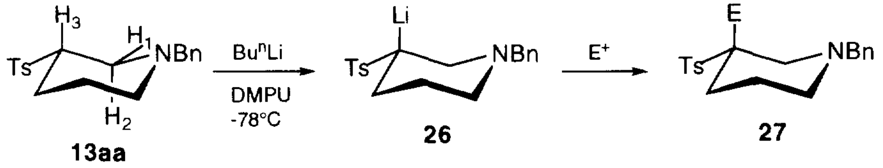
[a] Isolated yield after column chromatography on silica gel, based on starting sulfone **10**. [b] Hexane/ether. [c] Ether. [d] 26% of *N*-allyl-*N*-benzyl-2-tosylethanamine was also obtained. [e] 26% of compound **21ac** isolated as acetamide was also obtained. [f] See ref. 16. [g] 20% of compound **21ae** was also obtained.



**Scheme 5.**

Conformational analysis based on $^1H$-$^1H$ COSY and NOE experiments of the 3-tosylpiperidine **13aa** showed that the tosyl group in the chair occupied the equatorial position[21] ($H_2$ apears as t, $J$ = 11.6 Hz). This fact prompted us to prepare the corresponding organolithium derivative **26**, by deprotonation with *n*-butyllithium at -78°C in the presence of DMPU, a stable intermediate derived from a tertiary amine in which the C-Li and C-N bonds are not in an *anti* position avoiding a decomposition through an β-elimination reaction. The versatility of intemediate **26** as monoanion was much better than **11**, it also reacted with acyl chlorides and electrophilic olefins to give compounds **27** (Scheme 6 and Table 4).



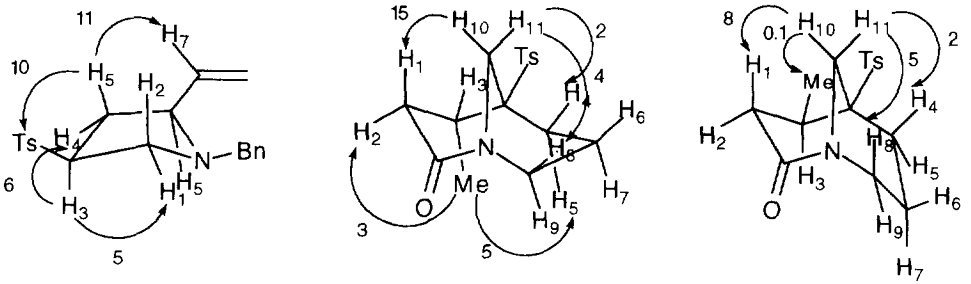
**Scheme 6.**

Compound **27h**, obtained by Michael addition of intermediate **26** to methyl crotonate as mixture 2/1 of diastereomers, was choosen as starting material for preparing 1-azabicyclo[3.3.1]nona-2-ones.[29] Debenzylation of compound **27h** as previouly described, with ammonium formate and Pd/C in methanol,[28] gave quantitavely a mixture of the *endo*-**29** (35% yield) and the open diastereomer (3*S**, 3*S*'*)-**28** (65%). Compound (3*S**, 3*S*'*)-**28** cyclized slowly after deprotonation with LDA at -78°C to room temperature for 2d to afford the other bicyclic lactam *exo*-**29** (60% yield) (Scheme 7). Spectroscopic data, IR: $\nu_{C=O}$ 1680 $cm^{-1}$ and $^1H$ NMR coupling constants and NOE experiments (Fig. 1) for lactams are in agreement with the expected chair-boat conformation as it has been previously assigned for 1-azabicyclo[3.3.1]nona-2-one.[29] However, in the *endo*-isomer the chair was deformed to a twist or quasi boat conformation due to the interaction between the methyl group and the hydrogen at C7 located at the axial position in the chair-boat one (Scheme 7, see also Fig 1).

**Table 4**. Reaction of Lithiated *N*-Benzyl-3-tosylpiperidine **26** with Electrophiles.

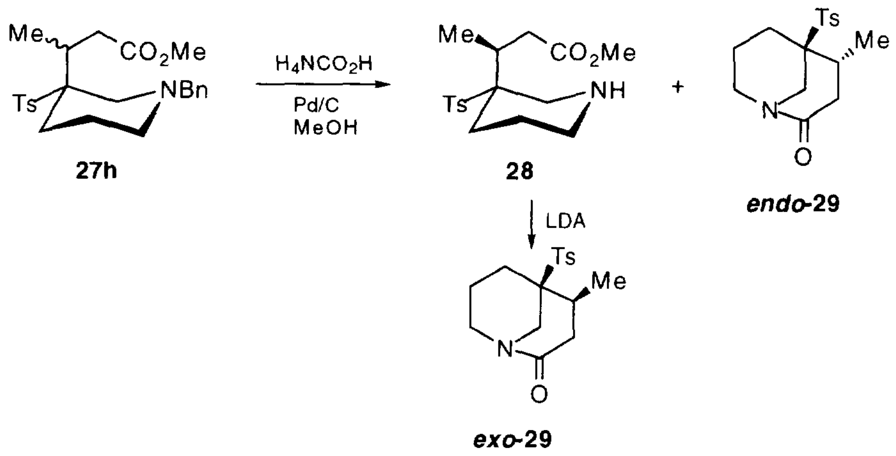
| electrophile | product<br>no. | E | yield (%)[a] | $R_f$[b] |
|---|---|---|---|---|
| $D_2O$ | **27a** | D | 70[c] | 0.76[d] |
| $Pr^iCH_2I$ | **27b** | $Pr^iCH_2$ | 72 | 0.63 |
| $Me_3SiCH_2I$ | **27c** | $Me_3SiCH_2$ | 53 | 0.59 |
| $Bu^tO_2CCH_2Br$ | **27d** | $Bu^tO_2CCH_2$ | 66 | 0.50 |
| PhCHO | **27e** | PhCHOH | 77[e] | 0.88[d] |
| PhCOCl | **27f** | PhCO | 95 | 0.59 |
| $CH_2{=}CHCO_2Me$ | **27g** | $CH_2CH_2CO_2Me$ | 53 | 0.83[d] |
| (*E*)-$MeCH{=}CHCO_2Me$ | **27h** | $MeCHCH_2CO_2Me$ | 75[f] | 0.38[g] |

[a] Isolated yield after column chromatography on silica gel, based on starting sulfone **13aa**. [b] 1/1: hexane/ether. [c] 99% of deuterium incorporation (MS). [d] Ether. [e] *Erythro/threo* : 1/1. [f] 2/1 Diastereomers ratio. [g] Mp 96-97°C (hexane/ether).



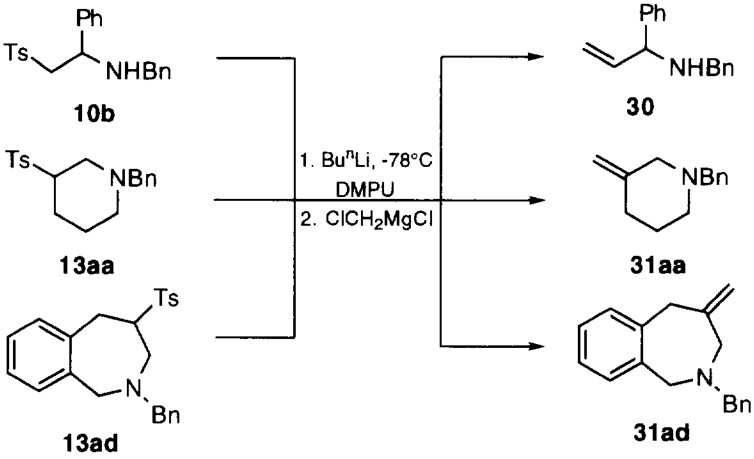
**13af** *endo-***29** *exo-***29**

**Figure 1.** Selected NOE (%) observed.



**Scheme 7.**

Some representative compounds **10b**, **13aa** and **13ad** have been also desulfonylated by means of the Julia's methylenation methodology.[30] The corresponding organolithium derivatives were generated at -78°C with Bu$^n$Li in the presence of DMPU and allowed to react with chloromethylmagnesium chloride, prepared *in situ* by reaction of chloroiodomethane and isopropylmagnesium chloride, to yield the corresponding allylamine **30** and the exo-methylene substituted heterocycles **31aa** and **31ad** in 52, 62 and 85% yield, respectively (Scheme 8). The 3-methylenepiperidine **31aa** was also prepared from compound **27c** through β-elimination of tosyltrimethylsilane induced by tetrabutylammonium fluoride[31] in 46% yield from **13aa**.



**Scheme 8.**

In conclusion, monoanions derived from acyclic and cyclic β-aminosulfones are versatile intermediates in synthesis, specially for the preparation in moderate yields of nitrogen-containing heterocycles (5 to 7-membered rings) and 1-azabicyclo[3.3.1]nona-2-ones. This methodology has been also applied to the synthesis of a benzoazepine inmediate precursor of capsazepine.

## EXPERIMENTAL SECTION

**General.** Melting points were obtained with a Reichert Thermovar apparatus and are uncorreted. FT-IR spectra were obtained on a Nicolet Impact 400D spectrophotometer as neat liquids. 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 assignements were made on the basis of DEPT experiments. Mass spectra (EI, 70 eV) were obtained on a Hewlett-Packard 5988A spectrometer. 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. 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 visualization. Column chromatography was performed using silica gel 60 of 35-70 and 70-230 mesh. All starting materials were commercially available (Aldrich, Fluka, Across) 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 *N*-Benzyl-β-tosylethanamine (10a).** A solution of *p*-tolyl vinyl sulfone (5 g, 27.5 mmol), prepared from 1-bromo-2-chloroethane (see ref. 18) and benzylamine (3.80 ml, 33 mmol) in THF (40 ml), was refluxed during 6 h. The reaction mixture was cooled to rt and extracted with EtOAc (3x30 ml) and water. The organic layer was dried ($Na_2SO_4$) and evaporated (15 Torr) and the residue was purified by flash chromatography (hexane/EtOAc) to give 6.4 g of compound **10a** (80%): $R_f$ 0.45 (ether); mp 29-30°C (hexane/ether); ν (KBr) 3320 (NH), 1300 and 1140 cm$^{-1}$ ($SO_2$); $\delta_H$ 1.78 (br s, 1H, NH), 2.44 (s, 3H, C*H*$_3$Ar), 2.99 (t, *J*=6.3 Hz, 2H, $CH_2N$), 3.28 (t, *J*=6.3 Hz, 2H, $CH_2S$), 3.74 (s, 2H, C*H*$_2$Ph), 7.24-7.35 (m, 7H, PhH, 2x*p*-Tol), 7.74 (d, *J*=8.2 Hz, 2Hx*p*-Tol); $\delta_C$ 21.5 (*C*H$_3$Ar), 42.3 ($CH_2N$), 53.3 ($CH_2$Ph), 55.9 ($CH_2S$), 127.0, 127.6, 127.8, 128.3, 129.8, 136.0, 139.3 and 144.7 (ArC); *m/z* 289 ($M^+$, <1%), 132 (12), 106 (63), 104 (11), 92 (11), 91 (100), 77 (10) and 65 (32); Found: C, 66.50; H, 6.50; N, 4.85; S, 11.18. Calcd. for $C_{16}H_{19}NO_2S$: C, 66.41; H, 6.62; N, 4.80 and S, 11.12%.

**Synthesis of *N*-Benzyl-α-phenyl-β-tosylethanamine (10b).** A solution of β-tosylstyrene (see ref. 19) (2.4 g, 9.3 mmol) and benzylamine (2.5 ml, 23 mmol) in 1,4-dioxane (20 ml) was refluxed during 24 h. The reaction mixture was cooled at rt and the solvent was evaporated at reduced pressure (15 Torr). Then, the residue was purified by flash chromatography (hexane/EtOAc) to give 2.35 g of compound **10b** (77%): $R_f$ 0.86 (ether); ν 3334 (NH), 1313, 1301, 1289 and 1145 cm$^{-1}$ ($SO_2$); $\delta_H$ 2.16 (s, 3H, C*H*$_3$Ar), 3.00 (br s, 1H, NH), 3.01 (dd, *J*=14.3, 2.4 Hz, 1HxC*H*$_2$S), 3.24, 3.45 (2d, *J*=14.3 Hz, 2H, C*H*$_2$Ph), 3.29 (dd, *J*=14.3, 10.0 Hz, 1HxC*H*$_2$S), 3.96 (dd, *J*=10.0, 2.4 Hz, 1H, CHN), 7.00-7.22 (m, 12H, ArH) and 7.43 (d, *J*=8.2 Hz, 2Hx*p*-Tol); $\delta_C$ 21.1 (*C*H$_3$Ar), 50.4 ($CH_2N$), 56.2 (CHPh), 62.5 ($CH_2S$), 126.5, 126.7, 127.4, 127.5, 127.8, 127.9, 128.4, 129.4, 135.7, 139.3, 140.5 and 144.2 (ArC); *m/z* 365 ($M^+$, <1%), 209 (11), 208 (29), 196 (32), 106 (36), 104 (13), 92 (11), 91 (100), 77 (11) and 65 (22); Found: $M^+$ 365.14391. Calcd for $C_{22}H_{23}NO_2S$, 365.14495.

**Lithiation of *N*-Benzyl-β-tosylethanamine (10a) and *N*-Benzyl-α-phenyl-β-tosylethanamine (10b). Reaction with Monoelectrophiles. General Procedure.** To a solution of the corresponding sulfone **10** (100 mg, 0.35 mmol) and DMPU (51μl, 0.39 mmol) in dry THF (3 ml) cooled at -78°C, was added a 1.6M solution of n-butyllithium (238 μl, 0.39 mmol) in hexanes. After 10 min stirring, the corresponding electrophile was added (0.39 mmol) and the reaction mixture was warmed up to room temperature (in the case of alkyl halides and carbonyl compounds the reaction was warmed up to -70 and -40°C respectively). The reaction mixture was hydrolyzed with a saturated aqueous solution of NaCl and extracted with EtOAc (3x10 ml). The organic layer was dried ($Na_2SO_4$), evaporated and the residue was purified by column chromatography (hexane/EtOAc) and/or recrystallization to afford the corresponding sulfones **12**, **14**, **15** and **16b**. Yields and physical data are included in Table 1, spectral and analytical data follow:

***N*-Benzyl-2-deuterio-2-tosyl-1-ethanamine (12aa):** ν (KBr) 3320 (NH), 1300 and 1140 cm$^{-1}$ ($SO_2$); $\delta_H$ 1.89 (br s, 1H, NH), 2.43 (s, 3H, C*H*$_3$Ar), 2.89 (m, 2H, $CH_2N$), 3.26 (m, 1H, CHD), 3.74 (s, 2H, C*H*$_2$Ph), 7.23-7.34 (m, 7H, PhH, 2x*p*-Tol) and 7.73 (d, *J*=8.2 Hz, 2Hx*p*-Tol); $\delta_C$ 21.5 (*C*H$_3$Ar), 42.4 ($CH_2N$), 53.4 ($CH_2$Ph), 55.8 (t, *J*=21.1 Hz, CHD), 127.1, 127.9, 128.0, 128.4, 129.9, 136.2, 139.4 and 144.7 (ArC); *m/z* 290 ($M^+$, 1%), 289 ($M^+$-1, 1), 134 (15), 133 (38), 106 (95), 104 (23), 92 (23), 91 (100), 89 (10), 77 (12), 65 (51) and 51 (13); Found: C, 66.05; H, 6.15; N, 4.80; S, 11.10. Calcd. for $C_{16}DH_{18}NO_2S$: C, 66.12; H, 6.21; N, 4.84 and S, 11.03%.

**(1*R**,2*S**)-*N*-Benzyl-1-phenyl-2-deuterio-2-tosyl-1-ethanamine (12ba):** ν 3334 (NH), 1313, 1301, 1289 and 1145 cm$^{-1}$ ($SO_2$); $\delta_H$ 2.42 (s, 3H, C*H*$_3$Ar), 3.18 (br s, 1H, CHS), 3.46, 3.70 (2d, *J*=13.4 Hz, 2H, C*H*$_2$Ph), 4.15 (br s, 1H, C*H*Ph), 7.22-7.64 (m, 14H, ArH); $\delta_C$ 21.6 (*C*H$_3$Ar), 51.0 ($CH_2N$), 56.6 (*C*HPh), 62.8 (t, *J*=21.2 Hz, CHD), 127.0, 127.2, 127.9, 128.0, 128.2, 128.4, 128.8, 129.9, 136.2, 139.7, 141.0 and 144.7 (ArC); *m/z* 367 ($M^+$+1, <1%), 366 ($M^+$, <1), 365 ($M^+$-1, <1), 210 (10), 209 (35), 196 (46), 106 (42), 105 (13), 104 (10), 92 (14), 91 (100) and 65 (21).

***N*-Benzyl-2-tosyl-4-penten-1-amine (12ab):** ν 3310 (NH), 3080, 3060, 1630 (C=C), 1300 and 1140 $cm^{-1}$ ($SO_2$); $\delta_H$ 2.00 (br s, 1H, NH), 2.22-2.33, 2.55-2.61 (2m, 2H, $CHSC\textit{H}_2C=$), 2.44 (s, 3H, $C\textit{H}_3Ar$), 2.56 (dd, *J*=13.4, 3.7 Hz, 1Hx$CH_2N$), 2.97 (dd, *J*=13.4, 7.0 Hz, 1Hx$CH_2N$), 3.14-3.22 (m, 1H, CHS), 3.69, 3.77 (2d, *J*=13.1 Hz, 2H, $C\textit{H}_2Ph$), 5.02-5.08 (m, 2H, $C\textit{H}_2=CH$), 5.61-5.74 (m, 1H, $C\textit{H}=CH_2$), 7.22-7.34 (m, 7H, PhH, 2x*p*-Tol) and 7.69 (d, *J*=8.2 Hz, 2Hx*p*-Tol); $\delta_C$ 21.6 ($\textit{C}H_3Ar$), 31.4 ($\textit{C}H_2CS$), 46.2 ($CH_2N$), 53.7 ($\textit{C}H_2Ph$), 64.2 (CHS), 118.5 ($\textit{C}H_2=CH$), 133.2 ($\textit{C}H=CH_2$), 127.0, 128.1, 128.3, 128.8, 129.8, 134.5, 139.7 and 144.8 (ArC); *m/z* 174 ($M^+$-Ts, <1%), 92 (13), 91 (100), 89 (11), 65 (39) and 41 (15).

***N*-Benzyl-2-allyl-2-tosyl-4-penten-1-amine (15ab):** $R_f$ 0.79 (ether); ν 3320 (NH), 3080, 1630 (C=C), 1290 and 1140 $cm^{-1}$ ($SO_2$); $\delta_H$ 1.90 (br s, 1H, NH), 2.40-2.47 (m with s at 2.43, 5H, $C\textit{H}_3Ar$, $C\textit{H}_2CH=$), 2.60 (dd, *J*=15.0, 6.9 Hz, 2H, $C\textit{H}_2CH$), 2.74 (s, 2H, $CH_2N$), 3.73 (s, 2H, $C\textit{H}_2Ph$), 4.98-5.11 (m, 4H, 2x$C\textit{H}_2=CH$), 5.88-5.90 (m, 2H, 2x$C\textit{H}=CH_2$), 7.23-7.36 (m, 7H, PhH, 2x*p*-Tol) and 7.65 (d, *J*=8.2 Hz, 2Hx*p*-Tol); $\delta_C$ 21.6 ($\textit{C}H_3Ar$), 35.7 (2x$\textit{C}H_2CH=$), 50.7, 54.2 ($CH_2N$, $\textit{C}H_2Ph$), 68.2 (CS), 119.2 (2x$\textit{C}H_2=CH$), 132.3 (2x$\textit{C}H=CH_2$), 126.9, 128.1, 128.2 128.3, 129.4, 130.2, 140.1 and 144.7 (ArC); *m/z* 279 ($M^+$-Bn, <1%), 120 (11), 92 (12), 91 (100), 65 (29) and 41 (14).

**(1*R**,2*S**)-*N*-Benzyl-2-tosyl-1-phenyl-4-penten-1-amine (12bb):** ν 3340 (NH), 3082, 1640 ($CH_2=CH$), 1314, 1301, 1288 and 1144 $cm^{-1}$ ($SO_2$); $\delta_H$ 1.25 (br s, 1H, NH), 2.44 (s, 3H, $C\textit{H}_3Ar$), 2.61-2.71 (m, 1Hx$C\textit{H}_2CHS$), 2.78-2.82 (m, 1Hx$C\textit{H}_2CHS$), 3.11-3.13 (m, 1H, CHS), 3.45, 3.73 (2d, *J*=13.4 Hz, 2H, $C\textit{H}_2Ph$), 4.27 (brs, 1H, $C\textit{H}Ph$), 4.70 (d, *J*=17.7 Hz, 1Hx$C\textit{H}_2=CH$), 4.72 (d, *J*=10.1 Hz, 1Hx$C\textit{H}_2=CH$), 5.32-5.43 (m, 1H, $C\textit{H}=CH_2$), 7.26-7.61 (m, 14H, ArH); $\delta_C$ 21.7 ($\textit{C}H_3Ar$), 26.4 ($\textit{C}H_2CHS$), 51.1 ($CH_2N$), 59.0, 70.8 (CHS, CHN), 117.0 ($\textit{C}H_2=CH$), 127.0, 127.5, 127.6, 128.3, 128.4, 128.6, 128.7, 129.8, 135.2, 139.6, 140.0 and 144.7 (ArC and $\textit{C}H=CH_2$); *m/z* 250 ($M^+$-Ts, 16%), 196 (64), 106 (10), 92 (10), 91 (100) and 65 (12).

***N*-Benzyl-2-tosyl-3-phenyl-1-propanamine (12ac):** ν 3335 (NH), 1310, 1300, 1288, and 1143 $cm^{-1}$ ($SO_2$); $\delta_H$ 2.00 (br s, 1H, NH), 2.44 (s, 3H, $C\textit{H}_3Ar$), 2.76-2.92 (m, 3H, $CSC\textit{H}_2Ph$, 1x$CH_2N$), 3.19 (dd, *J*=13.8, 3.4 Hz, 1Hx$CH_2N$), 3.37 (m, 1H, CHS), 3.56, 3.65 (2d, *J*=13.4 Hz, 2H, $C\textit{H}_2Ph$), 7.04-7.33 (m, 12H, PhH, 2x*p*-Tol) and 7.73 (d, *J*=8.2 Hz, 2Hx*p*-Tol); $\delta_C$ 21.6 ($\textit{C}H_3Ar$), 32.6 ($\textit{C}H_2CHS$), 45.6, 53.5 (2x$CH_2N$), 66.0 (CHS), 126.8, 126.9, 128.0, 128.3, 128.6, 128.7, 129.0, 129.8 134.6, 136.9, 139.7 and 144.8 (ArC); *m/z* 224 ($M^+$-Ts, 2%), 120 (25), 117 (13), 106 (34), 92 (11), 91 (100) and 65 (17).

**(1*R**,2*S**)-*N*-Benzyl-2-tosyl-1,3-diphenyl-1-propanamine (12bc):** ν 3335 (NH), 1312, 1301, 1289 and 1143 $cm^{-1}$ ($SO_2$); $\delta_H$ 2.38 (s, 3H, $C\textit{H}_3Ar$), 3.00 (br s, 1H, NH), 3.15 (dd, *J*=16.5, 7.6 Hz, 1Hx$CHC\textit{H}_2Ph$), 3.39-3.46 (m, 2H, 1x$CHC\textit{H}_2Ph$, CHS), 3.53, 3.79 (2d, *J*=13.4 Hz, 2H, $NC\textit{H}_2Ph$), 4.39 (br s, 1H, $C\textit{H}Ph$), 6.48-7.49 (m, 19H, ArH); $\delta_C$ 21.6 ($\textit{C}H_3Ar$), 27.7 ($CH\textit{C}H_2Ph$), 51.0 ($Ph\textit{C}H_2N$), 59.1 ($\textit{C}HPh$), 72.5 (CHS), 125.8, 127.0, 127.6, 127.7, 128.0, 128.3, 128.4, 128.5, 128.8, 129.7, 135.1, 139.3, 139.5, 140.0 and 144.5 (ArC); *m/z* 300 ($M^+$-Ts, 2%), 197 (14), 196 (100), 193 (15), 91 (91) and 65 (10).

***N*-Benzyl-2-tosyl-3-trimethylsilyl-1-propanamine (12ad):** ν (KBr) 3432 (NH), 1289, 1281, 1267, 1136 ($SO_2$) and 844 $cm^{-1}$ ($SiMe_3$); $\delta_H$ -0.05 [s, 9H, $(CH_3)_3Si$], 0.79 (dd, *J*=14.3, 12.2 Hz, 1Hx$CH_2Si$), 1.07 (dd, *J*=14.3, 2.5 Hz, 1Hx$CH_2Si$), 2.14 (br s, 1H, NH), 2.42 (s, 3H, $C\textit{H}_3Ar$), 2.71 (dd, *J*=13.6, 2.8 Hz, 1Hx$CH_2N$), 2.86 (dd, *J*=13.6, 7.4 Hz, 1Hx$CH_2N$), 3.15-3.23 (m, 1H, CHS), 3.72 (s, 2H, $C\textit{H}_2Ph$), 7.21-7.33 (m, 7H, PhH, 2x*p*-Tol) and 7.66 (d, *J*=8.2 Hz, 2Hx*p*-Tol); $\delta_C$ -1.3 [$(CH_3)_3Si$], 14.0 ($CH_2Si$), 21.5 ($\textit{C}H_3Ar$), 48.4, 53.6 (2x$CH_2N$), 62.6 (CHS), 126.9, 128.1, 128.2, 128.9, 129.5, 134.0, 139.6 and 144.4 (ArC); *m/z* 375 ($M^+$ <1%), 128 (10), 120 (77), 106 (33), 91 (100), 73 (33) and 65 (10); Found: C, 64.00; H, 7.75; N, 3.74; S, 8.50. Calcd. for $C_{20}H_{29}NO_2SSi$: C, 63.95; H, 7.78; N, 3.73 and S, 8.52%.

***tert*-Butyl 4-(Benzylamino)-3-tosylbutanoate (12ae):** ν (KBr) 3434 (NH), 1727 (C=O), 1312, 1303, 1292 and 1146 $cm^{-1}$ ($SO_2$); $\delta_H$ 1.38 [s, 9H, $(CH_3)_3C$], 1.80 (br s, 1H, NH), 2.43 (s, 3H, $C\textit{H}_3Ar$), 2.60 (dd, *J*=16.8, 8.2 Hz, 1HxCH$_2$CO), 2.80 (dd, *J*=16.8, 4.9 Hz, 1HxCH$_2$CO), 2.83 (dd, *J*=13.1, 5.3 Hz, 1HxCH$_2$N), 3.03 (dd, *J*=13.1, 6.1 Hz, 1HxCH$_2$N), 3.65-3.74 (m with s at 3.72, 3H, C*H*$_2$Ph, CHS), 7.20-7.33 (m, 7H, PhH, 2x*p*-Tol) and 7.71 (d, *J*=8.2 Hz, 2Hx*p*-Tol); δ$_C$ 21.5 (*C*H$_3$Ar), 27.9 [(*C*H$_3$)$_3$C], 32.8 (*C*H$_2$CO), 46.8, 53.4 (CH$_2$N, *C*H$_2$Ph), 60.8 (CHS), 81.4 [(CH$_3$)$_3$*C*], 127.0, 128.0, 128.3, 128.8, 129.8, 134.4, 139.7, 144.9 (ArC) and 169.5 (C=O); *m/z* 404 (*M*$^+$+1, <1%), 192 (15), 146 (21), 120 (39), 106 (54), 92 (19), 91 (100), 65 (22), 57 (41) and 41 (36); Found: C, 65.47; H, 7.25; N, 3.45; S, 7.94. Calcd. for $C_{22}H_{29}NO_4S$: C, 65.48; H, 7.24; N, 3.47 and S, 7.95%.

***trans*-*N*-Benzyl-4-tosyl-5-phenyl-2-pyrrolidinone (16b)**: ν 1699 (C=O), 1319, 1303, 1291 and 1147 cm$^{-1}$ (SO$_2$); δ$_H$ 2.44 (s, 3H, C*H*$_3$Ar); 2.92 (ddd, *J*=17.7, 8.9, 0.9 Hz, 1HxCH$_2$CO), 3.02 (dd, *J*=17.7, 4.8 Hz, 1HxCH$_2$CO), 3.46, 5.10 (2d, *J*=14.7 Hz, 2H, C*H*$_2$Ph), 3.57-3.63 (m, 1H, CHS), 4.77 (d, *J*=3.4 Hz, 1H, C*H*Ph), 6.88-7.59 (m, 14H, ArH); δ$_C$ 22.6 (*C*H$_3$Ar), 32.0 (*C*H$_2$CO), 45.6 (CH$_2$N), 61.6, 64.7 (CHS, CHN), 127.2, 128.7, 129.5, 129.8, 130.3, 131.0, 134.5, 135.7, 139.0, 146.4 (ArC) and 171.6 (C=O); *m/z* 405 (*M*$^+$, 1%), 250 (26), 249 (36), 117 (15), 115 (13), 106 (24), 91 (100) and 65 (12); Found: C, 71.04; H, 5.70; N, 3.45; S, 7.90. Calcd. for $C_{24}H_{23}NO_3S$: C, 71.01; H, 5.72; N, 3.45 and S, 7.91%.

**(2*S**,3*R**)-*N*′-Dibenzyl-2,3-ditosyl-1,4-butanediamine (14a)**: ν 3339 (NH), 1320, 1304, 1293 and 1149 cm$^{-1}$ (SO$_2$); δ$_H$ 1.91 (br s, 2H, 2xNH), 2.46 (s, 6H, 2xC*H*$_3$Ar), 3.11 (dd, *J*=14.3, 7.8 Hz, 2H, CHSC*H*$_2$N), 3.18 (dd, *J*=14.3, 5.5 Hz, 2H, CHSC*H*$_2$N) 3.72, 3.79 (2d, *J*=13.4 Hz, 4H, 2xC*H*$_2$Ph), 5.12 (dd, *J*=7.8, 5.5 Hz, 2H, 2xCHS), 7.23-7.35 (m, 14H, 2xPhH, 4x*p*-Tol) and 7.78 (d, *J*=8.5 Hz, 4H, 4x*p*-Tol); δ$_C$ 21.7 (*C*H$_3$Ar), 44.9 (CHS), 51.3, 52.5 (2xCH$_2$N), 127.2, 128.1, 128.5, 129.6, 129.7, 132.2, 139.1 and 145.6 (ArC); *m/z* 416 (*M*$^+$-TsH, <1%), 139 (13), 127 (13), 120 (35), 106 (36), 104 (12), 92 (10), 91 (100), 77 (12) and 65 (17).

**(1*R**,2*S**,3*R**,4*S**)-*N*,*N*′-Dibenzyl-2,3-ditosyl-1,4-diphenyl-1,4-butanediamine (14b)**: ν 3640-3142 (NH), 1324, 1304 and 1148 cm$^{-1}$ (SO$_2$); δ$_H$ 2.46 (s, 6H, 2xC*H*$_3$Ar), 3.00 (br s, 2H, 2xNH), 3.42 (br s, 2H, 2xCHS), 3.50, 3.80 (2d, *J*=13.7 Hz, 4H, 2xC*H*$_2$Ph), 4.90 (br s, 2H, 2xC*H*Ph), 7.21-7.57 (m, 28H, ArH); δ$_C$ 21.7 (*C*H$_3$Ar), 50.3 (CH$_2$N), 56.7, 57.8 (CHS, *C*HPh), 127.1, 127.6, 128.3, 128.4, 128.7, 129.3, 129.8, 132.3, 138.5, 139.8 and 145.4 (ArC); *m/z* 364 (*M*$^+$-TsCHCHPhNHBn, 2%), 196 (50), 91 (100) and 65 (15).

***erythro*-1-(Benzylamino)-4-methyl-2-tosyl-3-pentanol (12af)**: ν (KBr) 3521, 3323 (OH, NH), 1311, 1300, 1287 and 1144 cm$^{-1}$ (SO$_2$); δ$_H$ 0.71, 0.93 [2d, *J*=6.4 Hz, 6H, (C*H*$_3$)$_2$CH], 1.56-1.72 [m, 1H, C*H*(CH$_3$)$_2$], 2.44 (s, 3H, C*H*$_3$Ar), 1.90 (br s, 1H, NH), 3.09 (dd, *J*=13.5, 5.5 Hz, 1HxCSCH$_2$N), 3.17 (m, 1H, CHS), 3.30 (dd, *J*=13.5, 2.0 Hz, 1HxCSCH$_2$N), 3.57 (br s, 1H, OH), 3.71 (dd *J*=7.9, 2.4 Hz, 1H, CHO), 3.74 (s, 2H, C*H*$_2$Ph), 7.23-7.35 (m, 7H, PhH, 2x*p*-Tol) and 7.76 (d, *J*=8.2 Hz, 2Hx*p*-Tol); δ$_C$ 18.5, 20.0 [(*C*H$_3$)$_2$CH], 21.6 (*C*H$_3$Ar), 32.6 [(CH$_3$)$_2$*C*H], 43.8, 53.9 (2xCH$_2$N), 65.5 (CHS), 74.4 (CHO), 127.3, 128.2, 128.5, 128.6, 129.9, 134.9, 138.7 and 145.0 (ArC); *m/z* 361 (*M*$^+$, <1%), 162 (12), 120 (23), 107 (11), 106 (32), 92 (11), 91 (100), 65 (18), 43 (20) and 41 (13); Found: C, 66.43; H, 7.55; N, 3.85; S, 8.86. Calcd. for $C_{21}H_{29}NO_3S$: C, 66.45; H, 7.53; N, 3.87 and S, 8.87%.

***threo*-1-(Benzylamino)-4-methyl-2-tosyl-3-pentanol (12af)**:*R*$_f$ 0.71 (ether); ν 3521, 3323 (OH, NH), 1311, 1300, 1287 and 1144 cm$^{-1}$ (SO$_2$); δ$_H$ 0.91, 0.95 [2d, *J*=6.7 Hz, 6H, (C*H*$_3$)$_2$CH], 1.90 (br s, 1H, NH), 2.08 [m, 1H, C*H*(CH$_3$)$_2$], 2.44 (s, 3H, C*H*$_3$Ar), 2.78 (dd, *J*=13.7, 5.8 Hz, 1HxCSCH$_2$N), 3.00 (dd, *J*=13.7, 3.4 Hz, 1HxCSCH$_2$N), 3.30 (m, 1H, CHS), 3.57 (br s, 1H, OH), 3.69 (s, 2H, C*H*$_2$Ph), 3.89 (t, *J*=5.8 Hz, 1H, CHO), 7.23-7.35 (m, 7H, PhH, 2x*p*-Tol) and 7.70 (d, *J*=8.6 Hz, 2Hx*p*-Tol); δ$_C$ 18.7, 20.0 [(*C*H$_3$)$_2$CH], 21.6 (*C*H$_3$Ar), 30.3 [(CH$_3$)$_2$*C*H], 46.6, 53.9 (2xCH$_2$N), 67.1 (CHS), 75.1 (CHO), 127.2, 128.1, 128.4, 128.5, 129.8, 136.2, 139.2 and 144.8 (ArC); *m/z* 361 (*M*$^+$, <1%), 162 (12), 120 (23), 107 (11), 106 (32), 92 (11), 91 (100), 65 (18), 43 (20) and 41 (13).

***erythro*-1-(Benzylamino)-4,4-dimethyl-2-tosyl-3-pentanol (12ag)**: ν (KBr) 3418, 3167 (OH, NH), 1299, 1288, 1259 and 1143 cm$^{-1}$ (SO$_2$); δ$_H$ 0.77 [s, 9H, (CH$_3$)$_3$C], 2.00 (br s, 1H, NH), 2.42 (s, 3H, C*H*$_3$Ar), 2.50 (br s, 1H, OH), 3.09 (dd, *J*=13.4, 5.3 Hz, 1HxCH$_2$N), 3.21 (m, 1H, CHS), 3.29 (dd, *J*=13.4, 2.1 Hz, 1HxCH$_2$N), 3.70, 3.77 (2d *J*=13.1 Hz, 2H, C*H*$_2$Ph), 3.95(d, *J*=1.5 Hz, 1H, CHO), 7.23-7.34 (m, 7H, PhH, 2x*p*-Tol) and 7.72 (d, *J*=8.2 Hz, 2Hx*p*-Tol); $\delta_C$ 21.5 (*C*H$_3$Ar), 25.7 [(*C*H$_3$)$_3$C], 36.1 [(*C*(CH$_3$)$_3$], 44.7, 53.8 (2xCH$_2$N), 64.4 (CHS), 75.1 (CHO), 127.2, 128.1, 128.4, 128.6, 129.8, 134.6, 138.5 and 144.9 (ArC); *m/z* 318 ($M^+$-Bu$^t$, 1%), 162 (14), 120 (29), 108 (10), 106 (36), 91 (100), 57 (14) and 41(11); Found: C, 67.19; H, 7.81; N, 3.67; S, 8.54. Calcd. for $C_{21}H_{29}NO_3S$: C, 67.17; H, 7.78; N, 3.73 and S, 8.54%.

***threo*-1-(Benzylamino)-4,4-dimethyl-2-tosyl-3-pentanol (12ag)**: *R*$_f$ 0.76 (ether); ν 3418, 3167 (OH, NH), 1299, 1288, 1259 and 1143 cm$^{-1}$ (SO$_2$); $\delta_H$ 0.86 [s, 9H, (CH$_3$)$_3$C], 2.00 (br s, 1H, NH), 2.41 (s, 3H, C*H*$_3$Ar), 2.50 (br s, 1H, OH), 2.81 (dd, *J*=13.7, 3.7 Hz, 1HxCH$_2$N), 2.89 (dd, *J*=13.7, 6.4 Hz, 1HxCH$_2$N), 3.41 (m, 1H, CHS), 3.62 (d, *J*=5.2 Hz, 1H, CHO), 3.70 (s, 2H, C*H*$_2$Ph), 7.23-7.34 (m, 7H, PhH, 2x*p*-Tol), 7.73 (d, *J*=8.2 Hz, 2Hx*p*-Tol); $\delta_C$ 21.5 (*C*H$_3$Ar), 25.7 [(*C*H$_3$)$_3$C], 36.0 [(*C*(CH$_3$)$_3$], 48.9, 53.6 (2xCH$_2$N), 66.5 (CHS), 78.1 (CHO), 127.0, 128.1, 128.3, 128.4, 129.4, 136.8, 139.4 and 144.4 (ArC); *m/z* 318 ($M^+$-Bu$^t$, 1%), 162 (14), 120 (29), 108 (10), 106 (36), 91 (100), 57 (14) and 41(11).

***erythro*-3-(Benzylamino)-1-phenyl-2-tosyl-1-propanol (12ah)**: ν 3500, 3310 (OH, NH), 1300 and 1140 cm$^{-1}$ (SO$_2$); $\delta_H$ 1.30, 2.40 (2 br s, 2H, NH, OH), 2.44 (s, 3H, C*H*$_3$Ar), 2.88 (dd, *J*=13.8, 4.6 Hz, 1HxCH$_2$N), 3.18 (m, 1H, CHS), 3.23-3.29 (m, 1HxCH$_2$N), 3.60, 3.65 (2d, *J*=13.3 Hz, 2H, CH$_2$Ph), 5.35 (br s, 1H, CHO), 7.36-7.50 (m, 12H, PhH, 2x*p*-Tol) and 7.84 (d, *J*=8.2 Hz, 2Hx*p*-Tol); $\delta_C$ 21.6 (*C*H$_3$Ar), 43.0 (CH$_2$N), 53.9 (*C*H$_2$Ph), 68.8, 71.5 (CHS, CHO), 125.2, 127.3, 127.4, 128.3, 128.4, 128.5, 128.6, 130.0, 134.7, 138.4, 141.5 and 145.2 (ArC); *m/z* 239 ($M^+$-TsH, <1%), 122 (22), 106 (34), 105 (11), 92 (13), 91 (100), 79 (15), 77 (17) and 65 (19).

***threo*-3-(Benzylamino)-1-phenyl-2-tosyl-1-propanol (12ah)**: *R*$_f$ 0.61 (ether); ν 3500, 3310 (OH, NH), 1300 and 1140 cm$^{-1}$ (SO$_2$); $\delta_H$ 1.30, 2.40 (2 br s, 2H, NH, OH), 2.42 (s, 3H, C*H*$_3$Ar), 2.67 (dd, *J*=13.7, 4.9 Hz, 1HxCH$_2$N), 2.76 (dd, *J*=13.7, 5.2 Hz, 1HxCH$_2$N), 3.40-3.45 (m, 3H, C*H*$_2$Ph, CHS), 5.30 (d, *J*=7.6 Hz, 1H, CHO), 6.97-7.50 (m, 12H, PhH, 2x*p*-Tol) and 7.70 (d, *J*=8.2 Hz, 2Hx*p*-Tol); $\delta_C$ 21.6 (*C*H$_3$Ar), 45.8 (CH$_2$N), 53.4 (*C*H$_2$Ph), 69.9, 72.5 (CHS, CHO), 125.2, 126.9, 127.0, 127.2, 127.9, 128.4, 128.7, 129.8, 135.6, 139.0, 139.6 and 144.9 (ArC); *m/z* 239 ($M^+$-TsH, <1%), 122 (22), 106 (34), 105 (11), 92 (13), 91 (100), 79 (15), 77 (17) and 65 (19).

***erythro/threo*-3-(Benzylamino)-1-*p*-methoxyphenyl-2-tosyl-1-propanol (12ai)**: ν 3493, 3320 (OH, NH), 1311, 1301, 1288 and 1142 cm$^{-1}$ (SO$_2$); $\delta_H$ 1.80 (br s, 2H, NH), 2.10 (br s, 2H, OH), 2.41 (s, 6H, 2xC*H*$_3$Ar), 2.66 (dd, *J*=13.4, 4.9 Hz, 1HxCSCH$_2$N$_{threo}$), 2.71 (dd, *J*=13.4, 5.1 Hz, 1HxCSCH$_2$N$_{threo}$), 2.92 (dd, *J*=13.7, 4.9 Hz, 1HxCSCH$_2$N$_{erythro}$), 3.16 (m, 1H, CHS$_{erythro}$), 3.20-3.26 (m, 1HxCSCH$_2$N$_{erythro}$), 3.41-3.54 (m with s at 3.42, 3H, CHS, C*H*$_2$Ph$_{threo}$), 3.58, 3.64 (2d, *J*=13.1 Hz, 2H, C*H*$_2$Ph$_{erythro}$), 3.73 (s, 3H, CH$_3$O$_{erythro}$), 3.75 (s, 3H, CH$_3$O$_{threo}$), 5.20 (d, *J*=7.9 Hz, 1H, CHO$_{threo}$), 5.31 (d, *J*=1.4 Hz, 1H, CHO$_{erythro}$), 6.74-7.82 (m, 28H, ArH$_{erythro,\ threo}$); $\delta_C$ (*erythro*) 21.5 (*C*H$_3$Ar), 42.8, 53.7 (2xCH$_2$N), 55.1 (CH$_3$O), 68.8, 70.9 (CHS, CHO), 113.7, 126.3, 127.1, 128.2, 128.4, 128.5, 129.8, 133.3, 134.7, 138.4, 145.0 and 158.7 (ArC); $\delta_C$(*threo*) 21.5 (*C*H$_3$Ar), 45.5, 53.2 (2xCH$_2$N), 55.1 (CH$_3$O), 69.9, 71.9 (CHS, CHO), 113.6, 126.8, 127.8, 128.0, 128.2, 128.4, 129.6, 131.7, 135.6, 138.9, 144.7 and 159.3 (ArC); *m/z* 300 ($M^+$-H$_2$O-*p*-MeOPh, <1%), 163 (12), 135 (17), 120 (26), 108 (17), 107 (15), 106 (38), 92 (14), 91 (100), 77 (15) and 65 (18).

**1-[2-(Benzylamino)-1-tosylethyl]-1-cyclopentanol (12aj)**: ν (KBr) 3404, 3085 (OH, NH), 1300, 1289, 1284, 1271 and 1140 cm$^{-1}$ (SO$_2$); $\delta_H$ 1.42-1.96 [m, 9H, (CH$_2$)$_4$CO, NH], 2.40 (br s, 1H, OH), 2.43 (s, 3H, C*H*$_3$Ar), 3.06 (dd, *J*=14.0, 5.2 Hz, 1HxCH$_2$N), 3.14 (dd, *J*=14.0, 2.6 Hz, 1HxCH$_2$N), 3.19 (dd, *J*=5.2, 2.6 Hz, 1H, CHS), 3.66 (s, 2H, C*H*$_2$Ph ), 7.20-7.34 (m, 7H, PhH, 2x*p*-Tol) and 7.76 (d, *J*=8.2 Hz, 2Hx*p*-Tol); $\delta_C$ 21.6 (*C*H$_3$Ar), 22.3, 24.0, 39.2, 40.4 [(*C*H$_2$)$_4$CO], 46.9, 53.9 (2xCH$_2$N), 72.0 (CHS), 82.9 (CO), 127.2, 128.1, 128.4, 128.5, 129.7, 137.2, 139.0 and 144.6 (ArC); *m/z* 374 ($M^+$+1, <1%), 197

(11), 120 (26), 106 (30), 92 (12), 91 (100), 65(22), 55 (15) and 41 (11); Found: C, 67.55; H, 7.33; N, 3.73; S, 8.55. Calcd. for $C_{21}H_{29}NO_3S$: C, 67.53; H, 7.29; N, 3.75 and S, 8.57%.

**1-[2-(Benzylamino)-1-tosylethyl]-1-cyclohexanol (12ak)**: ν (KBr) 3507, 3329 (OH, NH), 1311, 1300, 1286 and 1142 cm$^{-1}$ ($SO_2$); $\delta_H$ 1.18-2.00 [m, 12H, $(CH_2)_5C$, NH, OH], 2.42 (s, 3H, C*H*$_3$Ar), 2.97 (m, 2H, $CH_2N$), 3.20 (t, *J*=4.4 Hz, 1H, CHS), 3.56, 3.61 (2d *J*=13.4 Hz, 2H, C*H*$_2$Ph), 7.14-7.29 (m, 7H, PhH, 2x*p*-Tol) and 7.70 (d, *J*=8.2 Hz, 2Hx*p*-Tol); $\delta_C$ 21.5 (*C*H$_3$Ar), 21.4, 21.6, 25.3, 35.7, 36.4 [(*C*H$_2$)$_5$CO], 45.2, 53.5 (2x$CH_2N$), 71.9 (CO), 74.5 (CHS), 127.1, 128.0, 128.1, 128.3, 129.6, 137.4, 138.8 and 144.4 (ArC); *m/z* 388 (*M*$^+$, <1%), 197 (11), 188 (10), 120 (43), 107 (15), 106 (38), 92 (10), 91 (100) and 65 (12); Found: C, 68.20; H, 7.52; N, 3.60; S, 8.28. Calcd. for $C_{21}H_{29}NO_3S$: C, 68.18; H, 7.54; N, 3.61 and S, 8.27%.

***erythro/threo* 4-(Benzylamino)-2-phenyl-3-tosyl-2-butanol (12al)**: ν 3700-3300 (OH, NH), 1310, 1302, 1292 and 1136 cm$^{-1}$ ($SO_2$); $\delta_H$(*erythro*) 1.30 (br s, 1H, NH), 1.83 (s, 3H, $CH_3CO$), 2.40 (br s, 1H, OH), 2.41 (s, 3H, C*H*$_3$Ar), 2.55 (dd, *J*=14.0, 4.6 Hz, 1Hx$CH_2N$), 2.89 (dd, *J*=14.0, 2.7 Hz, 1Hx$CH_2N$), 3.30, 3.40 (2d, *J*=13.3 Hz, 2H, C*H*$_2$Ph), 3.48 (dd, *J*=4.6, 2.7 Hz, 1H, CHS), 7.03-7.39 (m, 12H, PhH, 2x*p*-Tol), 7.77 (d, *J*=8.2 Hz, 2Hx*p*-Tol); $\delta_H$(*threo*) 1.30 (br s, 1H, NH), 1.75 (s, 3H, $CH_3CO$), 2.38 (s, 3H, C*H*$_3$Ar), 2.40 (br s, 1H, OH), 3.07 (dd, *J*=14.2, 4.9 Hz, 1Hx$CH_2N$), 3.14 (dd, *J*=14.2, 4.0 Hz, 1Hx$CH_2N$), 3.54 (br s, 2H, C*H*$_2$Ph), 3.65 (dd, *J*=4.9, 4.0 Hz, 1H, CHS), 7.11-7.18, 7.23-7.33 (2m, 12H, PhH, 2x*p*-Tol) and 7.45 (d, *J*=8.2 Hz, 2Hx*p*-Tol); $\delta_C$ (*erythro*, *threo*) 21.5 (*C*H$_3$Ar), 28.6, 29.9 (*C*H$_3$CO), 45.6, 46.1, 53.5, 53.6 (4x$CH_2N$), 71.2, 73.1 (2xCHS) 75.9, 77.2 (2xCO), 124.3, 125.3, 126.9, 127.0, 127.1, 127.2, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 129.4, 129.7, 137.2, 137.4, 138.5, 138.9, 144.1, 144.5, 144.7 and 147.3 (ArC); *m/z* 289 (*M*$^+$-120, <1%), 139 (17), 120 (45), 107 (20), 106 (52), 105 (35), 91 (100), 77 (26), 65 (12) and 43 (12).

**Synthesis of *N*-Benzyl-4-tosyl-2-pyrrolidinone (16a)**: A solution of compound **12ae** (24 mg, 0.06 mmol) and 30% trifluoroacetic acid (0.07 mmol) in $CH_2Cl_2$ (3 ml) was stirred at rt during 4 h. Then $CH_2Cl_2$ was evaporated (15 Torr) and the residue was dissolved in THF. The reaction mixture was heated under reflux during 20 h. The cooled reaction was poured into water and extracted with EtOAc (3x10 ml). The organic layer was dried ($Na_2SO_4$) and evaporated (15 Torr) to afford 20 mg of pure compound as a white solid (100%): $R_f$ 0.17 (ether); mp 137-138°C (hexane/EtOAc); ν (KBr) 1674 (C=O), 1317, 1305, 1293 and 1148 cm$^{-1}$ ($SO_2$); $\delta_H$ 2.45 (s, 3H, C*H*$_3$Ar), 2.70 (dd, *J*=17.7, 9.8 Hz, 1Hx$CH_2CO$), 2.93 (dd, *J*=17.7, 6.4 Hz, 1Hx$CH_2CO$), 3.46 (dd, *J*=11.1, 8.9 Hz, 1Hx$CH_2N$), 3.69 (dd, *J*=11.1, 5.5 Hz, 1Hx$CH_2N$), 3.76-3.86 (m, 1H, CHS), 4.32, 4.47 (2d, *J*=14.6 Hz, 2H, C*H*$_2$Ph), 7.17-7.44 (m, 7H, PhH, 2x*p*-Tol) and 7.71 (d, *J*=8.5 Hz, 2Hx*p*-Tol); $\delta_C$ 21.7 (*C*H$_3$Ar), 32.1 (*C*H$_2$CO), 45.7, 46.6 ($CH_2N$, *C*H$_2$Ph), 55.7 (CHS), 127.9, 128.2, 128.7, 128.8, 130.3, 133.7, 135.2, 145.7 (ArC) and 170.2 (C=O); *m/z* 329 (*M*$^+$, <1%), 173 (45), 146 (16), 92 (10), 91 (100) and 65 (15); Found: C, 65.65; H, 5.82; N, 4.26; S, 9.68. Calcd. for $C_{18}H_{19}NO_3S$: C, 65.63; H, 5.81; N, 4.25 and S, 9.73%.

**Synthesis of *tert*-Butyl (*E*)-4-(Benzylamino)-2-butenoate (17)**: A solution of compound **12ae** (38 mg, 0.09 mmol) and $LiOH.H_2O$ (14 mg, 0.32 mmol) in THF (4 ml), was refluxed for 6 h. Then the reaction mixture was cooled at room temperature and extracted with brine (10 ml) and EtOAc (2x10 ml). The organic layer was dried ($Na_2SO_4$) and evaporated (15 Torr) to obtain pure crude compound **17** (26 mg, 100%): $R_f$ 0.39 (ether/hexane: 3/1); ν 3336 (NH), 3086, 3062, 3028, 982 (C=C) and 1713 (C=O); $\delta_H$ 1.48 [s, 9H, $(CH_3)_3C$], 1.59 (br s, 1H, NH), 3.40 (dd, *J*=5.5, 1.8 Hz, 2H, CHC*H*$_2$N), 3.82 (s, 2H, C*H*$_2$Ph), 5.93 (dt, *J*=15.9, 1.8 Hz, 1H, CHCO), 6.91 (dt, *J*=15.9, 5.5 Hz, 1H, C*H*CH$_2$N) and 7.33 (s, 5H, PhH); $\delta_C$ 28.1 [(*C*H$_3$)$_3$C], 49.5, 53.3 (2x$CH_2N$), 80.3 [(CH$_3$)$_3$*C*], 123.5, 127.1, 128.1, 128.5, 139.5, 145.3 (ArC, CH=CH) and 165.8 (C=O); *m/z* 190 (*M*$^+$-Bu$^t$, 10%), 146 (20), 100 (73), 91 (100), 68 (11), 65 (15), 57 (37), 43 (16) and 41 (34).

**Synthesis of 4-(Benzylamino)-3-methoxybutanoic Acid (18):** To a solution of compound **12ae** (65 mg, 0.16 mmol) in MeOH (4 mL) was added a 1.0 M solution of KOH in MeOH (0.19 mmol) and the mixture was stirred at rt during 12 h. Then the reaction mixture was poured into water and extracted with EtOAc (2x10 ml). The organic layer was dried ($Na_2SO_4$) and evaporated (15 Torr) to afford 25 mg of pure compound **18** (70%): $\nu$ 3470 (OH) and 1687 cm$^{-1}$ (C=O); $\delta_H$ 1.86 (br s, 1H, NH), 2.51 (dd, *J*=17.3, 3.1 Hz, 1Hx$CH_2CO_2$), 2.67 (dd, *J*=17.3, 6.7 Hz, 1Hx$CH_2CO_2$), 3.24 (dd, *J*=11.0, 2.9 Hz, 1HxCHOC$H_2$N), 3.28 (s, 3H, $CH_3O$), 3.45 (dd, *J*=11.0, 6.1 Hz, 1HxCHOC$H_2$N), 4.00 (m, 1H, CHO), 4.44, 4.50 (2d, *J*=15.0 Hz, 2H, C$H_2$Ph), 7.22-7.36 (m, 5H, PhH) and 10.0 (br s, 1H, OH); $\delta_C$ 37.7 ($CH_2CO_2$), 42.2, 52.5 ($CH_2$N, $CH_2$Ph), 56.3 ($CH_3O$), 73.0 (CHO), 127.6, 128.0, 128.7, 136.1 (ArC) and 172.4 (C=O); *m/z* 205 ($M^+$-18, 63%), 146 (31), 132 (17), 118 (12), 104 (29), 92 (17), 91 (100), 65 (30), 59 (10), 58 (41), 43 (13) and 42 (13).

**Reduction of Hydroxy Sulfones with Sodium Amalgam. General Procedure.** 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 corresponding 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 ($Na_2SO_4$), concentrated in vacuo (15 Torr) and the residue was purified by flash chromatography (hexane/EtOAc) to yield the corresponding compounds **19**. Yields and physical data are included in Table 2, spectral and analytical data follow:

**(*E*)-*N*-Benzyl-4,4-dimethyl-2-penten-1-amine (19a):**[32] $\nu$ 3315 (NH), 3087, 3063, 3027 and 974 cm$^{-1}$ (C=C); $\delta_H$ 1.00 [s, 9H, $(CH_3)_3C$], 1.69 (br s, 1H, NH), 3.21 (dd, *J*=6.1, 1.2 Hz, 2H, =C$CH_2$N), 3.77 (s, 2H, C$H_2$Ph), 5.45 (dt, *J*=15.6, 6.1 Hz, 1H, CH=C*H*$CH_2$N), 5.62 (dt, *J*=15.6, 1.2 Hz, 1H, C*H*=CH$CH_2$N) and 7.21-7.32 (m, 5H, PhH); $\delta_C$ 29.6 [$(CH_3)_3C$], 32.8 [$C(CH_3)_3$], 51.3, 53.2 (2x$CH_2$N), 122.7, 126.8, 128.2, 128.3, 140.3 and 143.9 (ArC, C=C); *m/z* 203 ($M^+$, 7%), 146 ($M^+$-Bu$^t$, 42), 108 (12), 106 (12), 92 (14), 91 (100), 65 (15), 55 (23) and 41 (26).

**(*E*/*Z*)-*N*-Benzyl-3-(4-methoxyphenyl)-2-propen-1-amine (19b):**[32] $\nu$ 3307 (NH), 3027 and 968 cm$^{-1}$ (C=C); $\delta_H$ (*E*) 1.76 (br s, 1H, NH), 3.42 (dd, *J*=6.4, 1.2 Hz, 2H, $CH_2$N), 3.80 (s, 3H, $CH_3O$), 3.81 (s, 2H, C$H_2$Ph), 6.18 (dt, *J*=15.9, 6.4 Hz, 1H, CH=C*H*$CH_2$N), 6.48 (d, *J*=15.9 Hz, 1H, C*H*=CH$CH_2$), 6.82-7.35 (m, 9H, PhH); $\delta_H$ (*Z*) 1.76 (br s, 1H, NH), 3.56 (dd, *J*=6.7, 1.8 Hz, 2H, $CH_2$N), 3.80 (s, 3H, $CH_3O$), 3.83 (s, 2H, C$H_2$Ph), 5.71 (dt, *J*=11.6, 6.7 Hz, 1H, CH=C*H*$CH_2$N), 6.48 (d, *J*=11.6 Hz, 1H, C*H*=CH$CH_2$), 6.83-7.33 (m, 9H, PhH); $\delta_C$ 47.1, 53.4 (2x$CH_2$N, *Z*), 51.3, 53.3 (2x$CH_2$N, *E*), 55.2 ($CH_3O$, *Z*), 55.3 ($CH_3O$, *E*), 113.6 (*C*H=CHAr, *Z*), 114.0 (*C*H=CHAr, *E*), 126.1, 127.0, 127.4, 128.2, 128.3, 128.4, 128.5, 129.2, 129.7, 129.9, 130.0, 130.2, 131.0, 140.1, 140.2, 158.5 and 159.1 (ArC, CH=*C*HAr, *Z*,*E*); *m/z* (*E*) 253 ($M^+$, 14%), 162 (46), 147 (14), 138 (18), 132 (85), 118 (13), 105 (13), 91 (100), 77 (13), 65 (19) and 51 (10); *m/z* (*Z*) 253 ($M^+$, 9%), 162 (44), 147 (12), 135 (16), 132 (81), 118 (12), 105 (13), 92 (10), 91 (100), 77 (12), 65 (21), 51 (10), 43 (12) and 41 (11).

***N*-Benzyl-2-cyclopentylidene-1-ethanamine (19c) and 1-(2-Benzylaminoethyl)-1-cyclopentanol (20c):** $\nu$ 3311 (NH), 3093, 3062 and 1495 cm$^{-1}$ (C=C); $\nu$ 3600-3100 cm$^{-1}$ (OH, NH); $\delta_H$ 1.25-1.88, 2.16-2.25 [3m, 19H, 2xNH, OH, 2x$(CH_2)_4$], 2.94 (t, *J*=5.8 Hz, 2H, $CH_2N_{alcohol}$), 3.22 (tq, *J*=7.0, 1.3 Hz, 2H, $NCH_2C{=}_{olef.}$), 3.78 (s, 4H, 2xNC$H_2$Ph), 5.39 (m, 1H, CH=C), 7.22-7.32 (m, 10H, 2xPhH); $\delta_C$ 23.7, 26.1, 26.3, 28.7, 33.6, 38.5, 39.9 [2x$(CH_2)_4$, $CH_2$CO], 46.8, 48.2, 53.4, 53.8 (4x$CH_2$N), 82.8 (CO), 118.2 (*C*H=C), 126.8, 127.1, 128.1, 128.2, 128.3, 128.4, 139.3, 140.4 and 146.0 (ArC and CH=*C*); $m/z_{olef.}$ 201 ($M^+$, 6%), 172 (15), 132 (19), 118 (11), 110 (10), 108 (69), 106 (28), 95 (10), 94 (30), 92 (18), 91 (100), 79 (59), 77 (14), 67 (20), 65 (32), 55 (11), 51 (11) and 41 (45); $m/z_{\mathrm{alcohol}}$ 201 ($M^+$-18, 1%), 121 (11), 120 (97), 107 (10), 106 (46), 92 (13), 91 (100), 65 (17), 43 (10), 42 (10) and 41 (16); Found: $M^+$ 201.15123. Calcd. for $C_{14}H_{19}N$, 201.15175.

***N*-Benzyl-2-cyclohexylidene-1-ethanamine (19d):** $\nu$ 3308 (NH), 3027 and 820 cm$^{-1}$ (C=C); $\delta_H$ 1.40-1.60 [m, 6H, $CH_2(C\textit{H}_2)_3CH_2$], 2.10-2.13 (m, 4H, 2x$CH_2C\textit{H}_2C$=), 2.51 (br s, 1H, NH), 3.24 (d, *J*=7.0 Hz, 2H, =$CCH_2N$), 3.78 (s, 2H, $NC\textit{H}_2Ph$), 5.23 (br t, *J*=7.0 Hz, 1H, CH=C), 7.22-7.32 (m, 5H, PhH); $\delta_C$ 26.8, 27.8, 28.5, 28.9, 37.1 [$(\textit{C}H_2)_5C$=], 45.6, 53.2 (2x$CH_2N$), 119.3 (*C*H=C), 126.9, 128.2, 128.3, 140.2 and 142.8 (ArC, CH=*C*); *m/z* 215 ($M^+$, 2%), 108 (87), 106 (20), 93 (34), 92 (11), 91 (100), 80 (14), 79 (59), 78 (15), 67 (23), 65 (23), 55 (14) and 41 (36).

**1-(2-Benzylaminoethyl)-1-cyclohexanol (20d):** $\nu$ 3450-3100 cm$^{-1}$ (NH, OH); $\delta_H$ 1.34 (br s, 1H, OH), 1.28-1.70 [m, 10H, $(C\textit{H}_2)_5CO$], 1.62 (t, *J*=5.8 Hz, 2H, $COCH_2$), 2.51 (br s, 1H, NH), 2.90 (t, *J*=5.8 Hz, 2H, $CH_2C\textit{H}_2N$), 3.77 (s, 2H, $NC\textit{H}_2Ph$), 7.22-7.33 (m, 5H, PhH); $\delta_C$ 21.6, 22.3, 26.0, 26.2, 40.5 [$(\textit{C}H_2)_5CO$], 40.5, 45.5, 50.7 ($CH_2CH_2NCH_2$), 71.6 (CO), 127.2, 128.2, 128.4 and 140.2 (ArC); *m/z* 233 ($M^+$, <1%), 215 (20), 120 (97), 106 (26), 91 (100), 65 (10) and 41 (12).

**Reaction of Intermediates 11a and 11b with Dielectrophiles. General Procedure**. The reaction conditions and the reaction work-up were the same as outlined for the synthesis and reaction of the monoanions with monoelectrophiles, except that 10 ml of THF were added. Yields and physical data of the corresponding sulfones **13** are included in Table 3; spectral and analytical data follow:

***N*-Benzyl-3-tosylpiperidine (13aa):** $\nu$ 1300 and 1150 cm$^{-1}$ ($SO_2$); $\delta_H$ 1.41-1.56 (m, 2H, 1x$C\textit{H}_2CH_2N$, 1x$CH_2C\textit{H}_2CHS$), 1.70-1.87 (m, 2H, 1x$CH_2C\textit{H}_2N$, 1x$C\textit{H}_2CH_2N$), 2.01-2.05 (m, 1Hx$CH_2C\textit{H}_2CS$), 2.14 (t, *J*=11.6 Hz, 1Hx$NC\textit{H}_2CS$), 2.44 (s, 3H, $C\textit{H}_3Ar$), 2.75-2.81 (m, 1Hx$CH_2C\textit{H}_2N$), 3.13-3.23 (m, 2H, 1x$NC\textit{H}_2CHS$, CHS), 3.44, 3.55 (2d, *J*=13.1 Hz, 2H, $C\textit{H}_2Ph$), 7.20-7.35 (m, 7H, PhH, 2x*p*-Tol) and 7.72 (d, *J*=8.2 Hz, 2Hx*p*-Tol); $\delta_C$ 21.6 ($\textit{C}H_3Ar$), 24.0, 24.2 ($CS\textit{C}H_2\textit{C}H_2$), 52.3, 52.4, 63.0 (3x$CH_2N$), 61.6 (CHS), 127.1, 128.2, 127.8, 128.9, 129.7, 134.4, 137.5 and 144.6 (ArC); *m/z* 329 ($M^+$, <1%), 174 (19), 173 (69), 172 (14), 92 (11), 91 (100) and 65 (21).

***trans*-*N*-Benzyl-2-phenyl-3-tosylpiperidine (13ba):** $\nu$ 1317, 1307, 1283 and 1142 cm$^{-1}$ ($SO_2$); $\delta_H$ 1.60-1.80 (m, 3H, $C\textit{H}_2CH_2N$, 1x$C\textit{H}_2CHS$), 2.01 (td, *J*=11.9, 2.4 Hz, 1Hx$CH_2C\textit{H}_2N$), 2.32 (s, 3H, $C\textit{H}_3Ar$), 2.39-2.42 (m, 1Hx$C\textit{H}_2CHS$), 2.71, 3.51 (2d, *J*=13.4 Hz, 2H, $C\textit{H}_2Ph$), 2.90 (d, *J*=11.3 Hz, 1Hx$CH_2C\textit{H}_2N$), 3.53-3.59 (m, 2H, CHS, CHN), 7.00-7.31 (m, 14H, ArH); $\delta_C$ 21.4 ($\textit{C}H_3Ar$), 24.4, 25.3 ($CS\textit{C}H_2\textit{C}H_2$), 52.0, 58.1 (2x$CH_2N$), 67.4, 68.3 (CHS, CHN), 126.7, 127.7, 128.0, 128.1, 128.2, 128.5, 129.1, 129.6, 137.0, 139.2 and 143.1 (ArC); *m/z* 405 ($M^+$, 1%), 250 (19), 249 (66), 248 (26), 194 (12), 92 (12), 91 (100) and 65 (13). Found: $M^+$-1 404.16722. Calcd. for $C_{25}H_{26}NO_2S$, 404.16843.

**1-Benzyl-3-methylene-5-tosylpiperidine (13ab):** $\nu$ 3062, 1658 (C=C), 1316, 1301, 1290 and 1146 cm$^{-1}$ ($SO_2$); $\delta_H$ 2.26-2.42, 2.58-2.65 (2m, 4H, $NCH_2CS$, C=$CCH_2CS$), 2.46 (s, 3H, $C\textit{H}_3Ar$), 3.18, 3.25 (2d, *J*=12.8 Hz, 2H, =$CCH_2N$), 3.19-3.30 (m, 1H, CHS), 3.49, 3.59 (2d, *J*=13.1 Hz, 2H, $C\textit{H}_2Ph$), 4.80, 4.82 (2br s, 2H, $CH_2$=C), 7.20-7.36 (m, 7H, PhH, 2x*p*-Tol) and 7.73 (d, *J*=8.3 Hz, 2Hx*p*-Tol); $\delta_C$ 21.6 ($\textit{C}H_3Ar$), 32.3 (=$C\textit{C}H_2CS$), 51.6, 58.3, 61.7 (3x$CH_2N$), 60.9 (CHS), 112.4 ($\textit{C}H_2$=C), 127.3, 128.3, 128.8, 129.0, 129.8, 134.2, 137.1, 139.7 and 144.9 (ArC, *C*=$CH_2$); *m/z* 341 ($M^+$, 1%), 250 (39), 185 (21), 184 (34), 94 (32), 92 (10), 91 (100) and 65 (15).

**1-Benzyl-3-tosylazepane (13ac):** $\nu$ 1297, 1285 and 1132 cm$^{-1}$ ($SO_2$); $\delta_H$ 1.50-1.92, 2.12-2.20 [2m, 6H, $(CH_2)_3CS$], 2.43 (s, 3H, $C\textit{H}_3Ar$), 2.46-2.69 (m, 2H, $CH_2C\textit{H}_2N$), 2.84 (dd, *J*=13.4, 8.9 Hz, 1Hx$CSC\textit{H}_2N$), 3.04 (dd, *J*=13.4, 3.4 Hz, 1Hx$CSC\textit{H}_2N$), 3.14-3.25 (m, 1H, CHS), 3.52, 3.64 (2d, *J*=13.4 Hz, 2H, $C\textit{H}_2Ph$), 7.13-7.24 (m, 7H, PhH, 2x*p*-Tol) and 7.63 (d, *J*=8.2 Hz, 2Hx*p*-Tol); $\delta_C$ 21.6 ($\textit{C}H_3Ar$), 24.3, 26.6, 28.1 [$(\textit{C}H_2)_3CHS$], 52.8, 55.8, 62.4 (3x$CH_2N$), 64.5 (CHS), 126.8, 128.1, 128.5, 128.6, 129.6, 134.8, 138.9 and 144.2 (ArC); *m/z* 343 ($M^+$, 1%), 188 (25), 187 (34), 160 (10), 120 (12), 96 (15), 92

(10), 91 (100) and 65 (14). Found: $M^+$ 343.15983. Calcd. for $C_{20}H_{25}NO_2S$, 343.16060.

***N*-Benzyl-*N*-(1-tosylcyclopentylmethyl)acetamide (21ac):** $R_f$ 0.49 (ether); ν 3468 (NH), 1654 (C=O), 1298, 1285 and 1138 cm$^{-1}$ ($SO_2$); $\delta_H$ 1.28-1.98 [m, 8H, $(CH_2)_4$], 2.14 (s, 3H, $CH_3CO$), 2.43 (s, 3H, $CH_3$Ar), 3.89 (s, 2H, $NCH_2$Ph), 4.87 (s, 2H, $CSCH_2$), 7.13-7.40 (m, 7H, PhH, 2x*p*-Tol) and 7.70 (d, *J*=8.2 Hz, 2Hx*p*-Tol); $\delta_C$ 21.6 ($CH_3$Ar), 22.0 ($CH_3CO$), 25.6, 32.8 [$(CH_2)_4CS$], 48.9, 53.3 (2x$CH_2N$), 74.3 (CS), 126.1, 127.5, 128.9, 129.6, 130.4, 133.3, 136.9, 144.7 (ArC) and 173.3 (C=O); *m/z* 342 ($M^+$-$CH_3CO$, <1%), 230 (11), 130 (11), 120 (40), 106 (11), 92 (10), 91 (100), 68 (12), 65 (14), 57 (35), 43 (18) and 41 (15).

**2-Benzyl-2,3,4,5-tetrahydro-1*H*-benzo[c]azepin-4-yl 4-Methylphenyl Sulfone (13ad):** ν (KBr) 1298, 1289 and 1142 cm$^{-1}$ ($SO_2$); $\delta_H$ 2.44 (s, 3H, $CH_3$Ar), 3.12-3.32, 3.39-3.53 (2m, 7H, $CH_2CHSCH_2N$, $CCH_2N$), 3.72, 4.02 (2d, *J*=14.8 Hz, 2H, $CH_2$Ph), 6.89-7.31 (m, 11H, ArH, 2x*p*-Tol) and 7.71 (d, *J*=8.6 Hz, 2Hx*p*-Tol); $\delta_C$ 21.6 ($CH_3$Ar), 34.5 (Ar$CH_2$CHS), 56.3, 56.8, 57.9 (3x$CH_2N$), 58.2 (CHS), 126.9, 127.0, 127.8, 128.2, 128.7, 128.8, 129.7, 129.8, 130.1, 134.2, 137.3, 137.9, 138.8 and 144.7 (ArC); *m/z* 390 ($M^+$, 2%), 301 (13), 300 (65), 236 (35), 234 (13), 144 (25), 117 (20), 115 (21), 92 (11), 91 (100) and 65 (17); Found: C, 73.69; H, 6.48; N, 3.54; S, 8.15. Calcd. for $C_{24}H_{25}NO_2S$: C, 73.63; H, 6.44; N, 3.58 and S, 8.19%.

**2-Benzyl-7,8-dimethoxy-2,3,4,5-tetrahydro-1*H*-benzo[c]azepin-4-yl 4-Methylphenyl Sulfone (13ae):** ν (KBr) 1311, 1301, 1290 and 1145 cm$^{-1}$ ($SO_2$); $\delta_H$ 2.46 (s, 3H, $CH_3$Ar), 3.06-3.49 (m, 7H, Ar$CH_2CHSCH_2N$, Ar$CH_2N$), 3.77, 3.89 (2s, 6H, 2x$CH_3O$), 3.61, 3.97 (2d, *J*=15.0 Hz, 2H, $NCH_2$Ph), 6.38, 6.78 (2s, 2H, ArH), 7.06-7.33 (m, 7H, PhH, 2x*p*-Tol) and 7.71 (d, *J*=8.2 Hz, 2Hx*p*-Tol); $\delta_C$ 21.6 ($CH_3$Ar), 33.8 (Ar$CH_2$CHS), 55.8, 55.9 (2x$CH_3O$), 56.0, 57.1, 57.2, 58.1 (3x$CH_2N$, CHS), 113.4, 113.8, 127.1, 128.1, 128.7, 129.2, 129.8, 130.7, 134.1, 137.8, 144.7, 147.1 and 147.7 (ArC); *m/z* 373 ($M^+$-PhH, <1%), 358 (14), 202 (17), 92 (10), 91 (100), 85 (20), 71 (23), 57 (34), 55 (12), 43 (26) and 41 (14). Found: C, 69.20; H, 6.43; N, 3.12; S, 7.07. Calcd. for $C_{26}H_{29}NO_4S$: C, 69.15; H, 6.47; N, 3.10 and S, 7.10%.

***N*-Benzyl-5,6-dimethoxy-2-tosyl-2,3-dihydro-1*H*-2-indenylmethanamine (21ae):** $R_f$ 0.66 (ether); mp 119-120°C (hexane/ether); ν (KBr) 3448, 3349 (NH), 1319, 1298, 1288 and 1139 cm$^{-1}$ ($SO_2$); $\delta_H$ 2.10 (br s, 1H, NH), 2.44 (s, 3H, $CH_3$Ar), 2.85, 3.61 (2s, 4H, 2x$CH_2N$), 3.08, 3.59 (2d, *J*=16.5 Hz, 4H, 2xAr$CH_2$CS), 3.78 (s, 6H, 2x$CH_3O$), 6.60 (s, 2H, ArH), 7.18-7.28 (m, 7H, PhH, 2x*p*-Tol) and 7.61 (d, *J*=8.2 Hz, 2Hx*p*-Tol); $\delta_C$ 21.1 ($CH_3$Ar), 37.8 (2xAr$CH_2$CS), 51.9, 53.4 (2x$CH_2N$), 55.6 (2x$CH_3O$), 72.6 (CS), 107.4, 126.5, 127.7, 128.0, 129.1, 129.2, 130.7, 132.9, 139.6, 144.3 and 148.2 (ArC); *m/z* 360 ($M^+$-Bz, <1%), 190 (13), 189 (100) and 91 (27); Found: C, 69.16; H, 6.46; N, 3.08; S, 7.11. Calcd. for $C_{26}H_{29}NO_4S$: C, 69.15; H, 6.47; N, 3.10 and S, 7.10%.

***cis*-*N*-Benzyl-4-tosyl-2-vinylpyrrolidine (13af):** ν 3083, 3062, 940 (C=C), 1314, 1302, 1290 and 1147 cm$^{-1}$ ($SO_2$); $\delta_H$ 2.08 (ddd, *J*=13.5, 9.5, 7.3 Hz, 1HxCS$CH_2$CH), 2.27 (ddd, *J*=13.5, 9.5, 6.4 Hz, 1HxCS$CH_2$CH), 2.41 (dd, *J*=11.3, 9.4 Hz, 1HxN$CH_2$), 2.45 (s, 3H, $CH_3$Ar), 2.89 (m, 1H, CHN), 2.99, 3.91 (2d, *J*=13.4 Hz, 2H, $CH_2$Ph), 3.33 (dd, *J*=11.3, 2.7 Hz, 1HxN$CH_2$), 3.57-3.67 (m, 1H, CHS), 5.10 (d, *J*=10.1 Hz, 1Hx$CH_2$=CH), 5.19 (d, *J*=17.0 Hz, 1Hx$CH_2$=CH), 5.52-5.64 (m, 1H, $CH$=$CH_2$), 7.12-7.33 (m, 7H, PhH, 2x*p*-Tol) and 7.69 (d, *J*=8.2 Hz, 2Hx*p*-Tol); $\delta_C$ 21.6 ($CH_3$Ar), 33.4 ($CH_2$CHS), 52.9, 56.6 (2x$CH_2N$), 61.7 (CHS), 67.7 (CHN), 118.3, 138.7 (CH=$CH_2$), 126.9, 128.1, 128.5, 129.0, 129.6, 134.7, 138.2 and 144.5 (ArC); *m/z* 341 ($M^+$, <1%), 250 (13), 185 (39), 158 (14), 94 (65), 92 (10), 91 (100) and 65 (17).

***N*-Benzyl-2-*tert*-butylpyrrole (13ag):** ν 3096, 3071 and 3027 cm$^{-1}$ (C=C); $\delta_H$ 1.32 [s, 9H, $(CH_3)_3C$], 5.30 (s, 2H, $CH_2N$), 5.99 (dd, *J*=3.7, 2.0 Hz, 1H, Bu$^t$C=C*H*), 6.10 (dd, *J*=3.7, 3.1 Hz, 1H, NCHC*H*), 6.49 (dd, *J*=3.1, 2.0 Hz, 1H, NCH), 7.23-7.33 (m, 5H, PhH); $\delta_C$ 30.9 [$(CH_3)_3C$], 31.9 [$C(CH_3)_3$], 51.7 ($CH_2N$), 104.9, 106.8, 123.1, 126.2, 127.1, 128.5, 139.4 and 141.7 (ArC); *m/z* 214

($M^+$+1, 4%), 213 ($M^+$, 26), 198 (59), 92 (18), 91 (100) and 65 (23).

**1-Benzyl-3-tosyl-4-phenyl-2,5-dihydro-1*H*-pyrrole (13ah):** $\nu$ 1299, 1288 and 1146 cm$^{-1}$ ($SO_2$); $\delta_H$ 2.44 (s, 3H, $C\mathit{H}_3Ar$), 3.36, 3.51, 4.66 (3s, 6H, 3x$CH_2N$), 7.09-7.35 (m, 12H, 2x*p*-Tol, PhH) and 7.93 (d, *J*=8.2 Hz, 2Hx*p*-Tol); $\delta_C$ 21.6 ($\mathit{C}H_3Ar$), 48.1, 53.0, 63.2 (3x$CH_2N$), 126.8, 127.4, 127.5, 127.9, 128.2, 128.5, 129.9, 138.3, 138.8, 139.6, 140.0, 144.5 and 154.7 (ArC and C=C); *m/z* 311 ($M^+$-PhH, <1%), 220 (16), 197 (11), 116 (10), 115 (19), 106 (32), 92 (11), 91 (100) and 65 (15).

**Synthesis of 7,8-Dimethoxy-2,3,4,5-tetrahydro-1*H*-benzo[c]azepine (24):** Compound **13ae** (30 mg, 0.067 mmol) was reduced with sodium amalgam as described for the reduction of aminoalcohols **12** (see above) and purified by flash chromatography (hexane/EtOAc) to afford pure compounds (>95% CG) **22** (11 mg, 55%) and **23** (9 mg, 45%). Then, in order to obtain the benzoazepine derivative **24**, to a stirred suspension of compound **22** (10 mg, 0.034 mmol) and an equal weight of 10% Pd-C in dry methanol (2 ml), anhydrous ammonium formate (20 mg, 1.2 mmol) was added in a single portion under argon. The resulting reaction mixture was stirred under reflux for 6 min (the reaction was monitored by TLC). Then, the catalyst was removed by filtration through a celite pad, which was then washed with 10 ml of methanol. The combined organic filtrate, on evaporation under reduced pressure (15 Torr), were extracted with EtOAc (3x10 ml) and water. The organic layer was dried ($Na_2SO_4$), concentrated in vacuo (15 Torr) and the residue was purified by flash chromatography (hexane/EtOAc) to yield compound **24** (7 mg, 80%). Physical, spectral and analytical data of the mentioned compounds follow:

**2-Benzyl-7,8-dimethoxy-2,3,4,5-tetrahydro-1*H*-benzo[c]azepine (22):** $R_f$ 0.45 (ether); $\nu$ 1264 cm$^{-1}$ (OMe); $\delta_H$ 1.75 (m, 2H, $NCH_2C\mathit{H}_2$), 2.86, 3.13 (2m, 4H, $C\mathit{H}_2CH_2C\mathit{H}_2N$), 3.54, 3.81 (2s, 4H, 2x$NC\mathit{H}_2Ar$), 3.78, 3.87 (2s, 6H, 2x$CH_3O$), 6.43, 6.70 (2s, 2H, ArH) and 7.30 (m, 5H, PhH); $\delta_C$ 25.2, 35.7 ($\mathit{C}H_2\mathit{C}H_2CH_2N$), 55.9, 56.0 (2x$CH_3O$), 57.4, 58.5, 59.0 (3x$CH_2N$), 112.8, 114.0, 126.9, 128.1, 129.1, 131.2, 135.3, 139.1, 146.3 and 147.3 (ArC); *m/z* 299 ($M^+$+2, <1%), 298 ($M^+$+1, 8), 297 ($M^+$, 41), 296 (20), 206 (12), 190 (20), 178 (46), 177 (16), 121 (13), 120 (97), 119 (15), 107 (10), 92 (13), 91 (100), 65 (16) and 44 (10).

***N*-Benzyl-2-allyl-4,5-dimethoxyphenylmethanamine (23):** $R_f$ 0.33 (ether); $\nu$ 3350 (NH), 3060, 910 (C=C) and 1265 cm$^{-1}$ (OMe); $\delta_H$ 1.66 (br s, 1H, NH), 3.35 (dd, *J*=6.1, 1.7 Hz 2H, $C\mathit{H}_2CH{=}CH_2$), 3.72, 3.82 (2s, 4H, 2x$CH_2N$), 3.86, 3.87 (2s, 6H, 2x$CH_3O$), 4.89-5.03 (m, 2H, $C\mathit{H}_2{=}CH$), 5.89-5.98 (m, 1H, $C\mathit{H}{=}CH_2$), 6.68, 6.90 (2s, 2H, ArH) and 7.26-7.35 (m, 5H, PhH); $\delta_C$ 36.5 ($\mathit{C}H_2CH{=}CH_2$), 50.2, 53.5 (2x$CH_2N$), 55.9, 56.0 (2x$CH_3O$), 115.3 ($\mathit{C}H_2{=}CH$), 112.8, 113.1, 126.9, 128.2, 128.3, 130.2, 137.7, 140.3, 147.2 and 147.9 (ArC, $CH{=}CH_2$); *m/z* 297 ($M^+$, 1%), 190 (100), 175 (38), 159 (26), 147 (14), 91 (55) and 65 (11).

**7,8-Dimethoxy-2,3,4,5-tetrahydro-1*H*-benzo[c]azepine (24):** $R_f$ 0.08 (MeOH); $\nu$ 3401 (NH), 2854 and 1277 cm$^{-1}$ (OMe); $\delta_H$ 1.79 (m, 2H, $ArCH_2C\mathit{H}_2CH_2$), 2.88 (m, 2H, $ArC\mathit{H}_2CH_2$), 3.20 (m, 2H, $CH_2C\mathit{H}_2N$), 3.50 (m, 1H, NH), 3.85-3.90 (m, 8H, 2x$CH_3O$, $ArC\mathit{H}_2N$), 6.68 and 6.70 (2s, 2H, ArH); $\delta_C$ 30.9 ($\mathit{C}H_2CH_2Ar$), 35.7 ($CH_2\mathit{C}H_2N$), 53.5, 54.7 (2x$CH_2N$), 56.0 (2x$CH_3O$), 112.6, 113.4, 135.2, 146.5 and 147.3 (ArC); *m/z* 209 ($M^+$+2, <1%), 208 ($M^+$+1, 9), 207 ($M^+$, 67), 206 (25), 190 (25), 179 (14), 178 (100), 177 (23), 164 (13), 147 (11), 146 (16), 107 (13), 103 (10), 91 (15), 77 (13), 65 (12), 51 (12) and 43 (12).

**Reaction of Anion 26 with Electrophiles. General Procedure.** To a solution of 1-benzyl-3-tosylpiperidine (**13aa**) (100 mg, 0.30 mmol) and DMPU (52 µl, 0.39 mmol) in THF (3 ml) cooled at -78°C, was added a 1.6 M solution of n-butyllithium (246 µl, 0.39 mmol) in hexane. After 10 min stirring at -78°C, the electrophile was added (0.36 mmol) and the reaction mixture was stirred during 1.5 h. Then the reaction was hydrolyzed with brine and extracted with EtOAc (3x10 ml). The organic layer was dried ($Na_2SO_4$), evaporated (15 Torr) and the residue was purified by flash chromatography (hexane/EtOAc) to afford compounds **27**. Yields and physical data are included in Table 4; spectral and analytical data follow:

***N*-Benzyl-3-deuterio-3-tosylpiperidine (27a)**: ν 1300 and 1150 cm$^{-1}$ ($SO_2$); $\delta_H$ 1.39-1.57 (m, 2H, 1xCSC*H*$_2$, 1xCSCH$_2$C*H*$_2$), 1.71-1.74 (m, 1HxCSCH$_2$C*H*$_2$), 1.84 (td, *J*=10.6, 2.7 Hz, 1H, CH$_2$C*H*$_2$N), 2.02 (br d, *J*=9.5 Hz, 1HxCSC*H*$_2$CH$_2$), 2.13 (d, *J*=10.9 Hz, 1HxCSCH$_2$N), 2.46 (s, 3H, C*H*$_3$Ar), 2.78 (br d, *J*=11.9 Hz, 1HxCH$_2$C*H*$_2$N), 3.17 (br d, *J*=10.9 Hz, 1HxCSCH$_2$N), 3.44, 3.56 (2d, *J*=13.1 Hz, 2H, C*H*$_2$Ph), 7.22-7.35 (m, 7H, PhH, 2x*p*-Tol) and 7.72 (d, *J*=7.9 Hz, 2Hx*p*-Tol); $\delta_C$ 21.6 (*C*H$_3$Ar), 23.8, 24.2 (CS*C*H$_2$*C*H$_2$), 52.2, 52.4, 63.0 (3xCH$_2$N), 61.6 (t, *J*=21.1 Hz, CSD), 127.1, 128.2, 128.8, 128.9, 129.7, 134.4, 137.6 and 144.6 (ArC); *m/z* 331 ($M^+$+1, <1%), 330 ($M^+$, <1%), 175 (15), 174 (62), 173 (13), 91 (100), 83 (10) and 65 (15).

***N*-Benzyl-3-isobutyl-3-tosylpiperidine (27b)**: ν 1311, 1298, 1285 and 1145 cm$^{-1}$ ($SO_2$); $\delta_H$ 1.00 [m, 6H, (C*H*$_3$)$_2$CH], 1.52-1.92 [m, 7H, C*H*$_2$CH, CS(CH$_2$)$_2$, 1xCH$_2$C*H*$_2$N], 2.31 (m, 1H, CH$_2$C*H*), 2.34 (d, *J*=11.1 Hz, 1HxNC*H*$_2$CS), 2.44 (s, 3H, C*H*$_3$Ar), 2.64-2.70 (m, 1HxCH$_2$C*H*$_2$N), 2.92 (d, *J*=11.1 Hz, 1HxNC*H*$_2$CS), 3.32, 3.53 (2d, *J*=13.1 Hz, 2H, C*H*$_2$Ph), 7.20-7.33 (m, 7H, PhH, 2x*p*-Tol) and 7.70 (d, *J*=8.2 Hz, 2Hx*p*-Tol); $\delta_C$ 21.6 (*C*H$_3$Ar), 21.7, 28.1 (CS*C*H$_2$*C*H$_2$), 23.7 (CH$_2$*C*H), 25.0, 25.2 [(*C*H$_3$)$_2$CH], 39.0 (*C*H$_2$CH), 52.4, 56.7, 63.0 (3xCH$_2$N), 66.7 (CS), 127.0, 128.2, 128.9, 129.3, 130.3, 133.4, 138.0 and 144.4 (ArC); *m/z* 385 ($M^+$, <1%), 230 (12), 229 (13), 186 (70), 92 (10), 91 (100) and 65 (11). Found: $M^+$ 385.20900. Calcd. for $C_{23}H_{31}NO_2S$, 385.20755.

**1-Benzyl-3-tosyl-3-piperidylmethyl(trimethyl)silane (27c)**: ν 1300, 1140 ($SO_2$), 1250, 850 and 750 cm$^{-1}$ (SiMe$_3$); $\delta_H$ 0.15 [s, 9H, (CH$_3$)$_3$Si], 1.32, 1.43 (2d, *J*=15.3 Hz, 2H, CH$_2$Si), 1.51-1.84 [m, 5H, (CH$_2$)$_2$CS, 1xCH$_2$C*H*$_2$N], 2.19, 2.82 (2d, *J*=11.0 Hz, 2H, CSCH$_2$N), 2.45 (s, 3H, C*H*$_3$Ar), 2.55 (m, 1HxCH$_2$C*H*$_2$N), 3.33, 3.49 (2d, *J*=13.1 Hz, 2H, C*H*$_2$Ph), 7.22-7.32 (m, 7H, PhH, 2x*p*-Tol) and 7.71 (d, *J*=8.2 Hz, 2Hx*p*-Tol); $\delta_C$ 1.0 [(CH$_3$)$_3$Si], 19.7 (CH$_2$Si), 21.6 (*C*H$_3$Ar), 21.6, 30.8 (CS*C*H$_2$*C*H$_2$), 52.7, 58.8, 63.1 (3xCH$_2$N), 66.5 (CS), 127.1, 128.2, 129.0, 129.2, 130.6, 133.3, 138.0 and 144.3 (ArC); *m/z* 415 ($M^+$, <1%), 260 (24), 259 (22), 186 (27), 120 (21), 91 (100) and 73 (32).

***tert*-Butyl 2-(1-Benzyl-3-tosyl-3-piperidyl)acetate (27d)**: ν 1725 (C=O), 1315, 1303, 1293 and 1144 cm$^{-1}$ ($SO_2$); $\delta_H$ 1.50 [s, 9H, (CH$_3$)$_3$C], 1.66-1.93 [m, 4H, 1xCH$_2$C*H*$_2$N, 1xCSC*H*$_2$CH$_2$, CSCH$_2$C*H*$_2$), 2.35-2.48 (m with s at 2.42, 4H, C*H*$_3$Ar, 1xCSC*H*$_2$CH$_2$), 2.40 (d, *J*=10.7 Hz, 1HxC*H*$_2$CO$_2$), 2.49 (d, *J*=15.5 Hz, 1HxNC*H*$_2$CS), 2.69 (br d, *J*=10.7 Hz, 1HxCH$_2$CO$_2$), 2.76 (br d, *J*=10.4 Hz, 1HxCH$_2$C*H*$_2$N), 3.11 (d, *J*=15.5 Hz, 1HxCSCH$_2$N), 3.40, 3.47 (2d, *J*=13.1 Hz, 2H, C*H*$_2$Ph), 7.19-7.32 (m, 7H, PhH, 2x*p*-Tol) and 7.79 (d, *J*=8.2 Hz, 2Hx*p*-Tol); $\delta_C$ 21.4, 25.5 [CS(*C*H$_2$)$_2$], 21.5 (*C*H$_3$Ar), 27.9 [(*C*H$_3$)$_3$C], 35.5 (*C*H$_2$C=O), 52.5, 56.8, 62.6 (3xCH$_2$N), 65.3 (CS), 80.0 (CO), 126.9, 128.0, 128.7, 129.2, 130.4, 131.9, 137.8, 144.7 (ArC) and 169.2 (C=O); *m/z* 386 ($M^+$-Bu$^t$, <1%), 232 (20), 186 (39), 92 (10), 91 (100), 65 (12), 57 (22) and 41 (14).

***erythro,threo*-1-Benzyl-3-tosyl-3-piperidylphenylmethanol (27e)**: ν 3500 (OH), 1310, 1299, 1286 and 1130 cm$^{-1}$ ($SO_2$); $\delta_H$ 0.83-2.34, 2.67-2.77, 3.26-3.61 [3m, 22H, 2xOH, 6xCH$_2$N, 2x(CH$_2$)$_2$CS], 2.40, 2.43 (2s, 6H, 2xC*H*$_3$Ar), 5.36, 5.67 (2s, 2H, 2xCHO), 7.21-7.37 and 7.50-7.71 (2m, 28H, ArH); $\delta_C$ 21.6, 21.8 (2x*C*H$_3$Ar), 21.6, 22.6, 24.7, 26.0 [2xCS(*C*H$_2$)$_2$], 52.1, 52.4, 56.6, 57.0, 63.0, 63.1 (6xCH$_2$N), 67.9, 69.4 (2xCS), 75.5 (2xCHO), 127.3, 127.5, 127.8, 127.9, 128.0, 128.3, 128.5, 128.6, 129.1, 129.2, 129.3, 129.4, 130.3, 133.4, 133.9, 136.6, 137.2, 139.6, 139.8 and 144.8 (ArC); *m/z* 328 ($M^+$-PhCHOH, 1%), 279 (21), 262 (16), 202 (10), 92 (11), 91 (100), 79 (12), 77 (11) and 65 (11).

***N*-Benzyl-3-tosyl-3-piperidylphenylmethanone (27f)**: ν 1674 (C=O), 1314, 1302, 1290 and 1144 cm$^{-1}$ ($SO_2$); $\delta_H$ 1.26, 1.50 [2m, 2H, CH$_2$C*H*$_2$CS), 1.87 (m, 2H, C*H*$_2$CH$_2$CS), 2.42-2.61 (m with s at 2.43, 5H, C*H*$_3$Ar, CH$_2$C*H*$_2$N), 2.74, 3.96 (2d, *J*=11.3 Hz, 2H, CSCH$_2$N), 3.19, 3.28 (2d, *J*=13.1 Hz, 2H, PhC*H*$_2$N), 6.77-6.80, 7.13-7.64 and 7.95-7.99 (3m, 14H, ArH); $\delta_C$ 21.7 (*C*H$_3$Ar), 22.3, 29.5 [CS(*C*H$_2$)$_2$], 51.8, 56.1, 63.0 (3xCH$_2$N), 72.3 (CS), 126.9, 127.9, 128.0, 128.1, 128.8, 129.3, 130.3, 131.3, 132.1, 137.4, 139.5, 145.4 (ArC) and 198.7 (C=O); *m/z* 278 ($M^+$-Ts, 50%), 105 (41), 92 (10), 91 (100), 77 (20) and 65 (17).

**Methyl 3-(1-Benzyl-3-tosyl-3-piperidyl)propenoate (27g)**: ν 1737 (C=O), 1310, 1299, 1286 and 1139 cm$^{-1}$ ($SO_2$); $\delta_H$ 1.59-1.86 (2m, 5H, 1x$CH_2CH_2N$, $(CH_2)_2CH_2N$), 2.14-2.30 (m, 2H, $CH_2CH_2CO_2$), 2.31 (d, *J*=11.0 Hz, 1Hx$CSCH_2N$), 2.44 (s, 3H, $CH_3Ar$), 2.56 (m, 2H, $CH_2CO_2$), 2.77 (br d, *J*=10.4 Hz, 1Hx$NCH_2CH_2$), 2.80 (br d, *J*=11.0 Hz, 1Hx$CSCH_2N$), 3.41, 3.47 (2d, *J*=13.4 Hz, 2H, $NCH_2Ph$), 3.69 (s, 3H, $CH_3O$), 7.23-7.35 (m, 7H, PhH, 2x*p*-Tol) and 7.69 (d, *J*=7.9 Hz, 2Hx*p*-Tol); $\delta_C$ 21.4, 24.8 27.1, 28.5 [$(CH_2)_2CH_2N$, $(CH_2)_2CO_2$], 21.6 ($CH_3Ar$), 51.6 ($CH_3O$), 52.8, 55.1, 63.0 (3x$CH_2N$), 64.3 (CS), 127.2, 128.2, 128.9, 129.5, 130.2, 132.2, 137.8, 144.8 (ArC) and 173.8 (C=O); *m/z* 384 ($M^+$-OMe, <1%), 260 (15), 259 (25), 186 (72), 92 (10), 91 (100) and 65 (10).

**Methyl (3*S**)-3-[(3*S**)-1-Benzyl-3-tosyl-3-piperidyl]butanoate (27h)**: ν (KBr) 1736 (C=O), 1307, 1287 and 1137 cm$^{-1}$ ($SO_2$); $\delta_H$ 1.15 (d, *J*=7.0 Hz, 3H, $CH_3CH$), 1.36 (td, *J*=12.8, 4.6 Hz, 1Hx$CSCH_2CH_2$), 1.53 (m, 1Hx$CSCH_2CH_2$), 1.72-1.80 (m, 2H, 1x$CSCH_2CH_2$, 1x$NCH_2CH_2$), 1.90 (d, *J*=11.6 Hz, 1Hx$CSCH_2N$), 2.22 (br d, *J*=10.4 Hz, 1Hx$CSCH_2CH_2$), 2.46 (s, 3H, $CH_3Ar$), 2.57-2.62 (m, 2H, $CH_2CO_2$), 2.77-2.82 (m, 1Hx$NCH_2CH_2$), 3.08 (br d, *J*=11.6 Hz, 1Hx$CSCH_2N$), 3.28, 3.54 (2d, *J*=13.1 Hz, 2H, $NCH_2Ph$), 3.33-3.42 (m, 1H, $CHCH_3$), 3.73 (s, 3H, $CH_3O$), 7.22-7.35 (m, 7H, PhH, 2x*p*-Tol) and 7.68 (d, *J*=8.2 Hz, 2Hx*p*-Tol); $\delta_C$ 14.3 ($CH_3CH$), 21.4, 28.3 [$(CH_2)_2CS$], 21.5 ($CH_3Ar$), 30.5 ($CHCH_3$), 36.4 ($CH_2CO_2$), 51.4 ($CH_3O$), 53.4, 54.9, 62.7 (3x$CH_2N$), 67.4 (CS), 127.2, 128.2, 128.8, 129.4, 130.2, 134.7, 138.2, 144.6 (ArC) and 173.9 (C=O); *m/z* 398 ($M^+$-OMe, <1%), 200 (55), 92 (13), 91 (100) and 65 (12); Found: C, 67.11; H, 7.26; N, 3.26; S, 7.46. Calcd. for $C_{24}H_{31}NO_4S$: C, 67.10; H, 7.27; N, 3.26 and S, 7.46%.

**Methyl (3*R**)-3-[(3*S**)-1-Benzyl-3-tosyl-3-piperidyl]butanoate (27h)**: ν 1736 (C=O), 1309, 1287 and 1139 cm$^{-1}$ ($SO_2$); $\delta_H$ 0.83-0.90 (m, 1Hx$CSCH_2CH_2$), 1.10 (d, *J*=7.0 Hz, 3H, $CH_3CH$), 1.31-1.50 (m, 2H, 1x$CSCH_2CH_2$, 1x$CSCH_2CH_2$), 1.65-1.82 (m, 1Hx$NCH_2CH_2$), 2.00 (d, *J*=11.3 Hz, 1Hx$NCH_2CS$), 2.10 (br d, *J*=13.7 Hz, 1Hx$CSCH_2CH_2$), 2.45 (s, 3H, $CH_3Ar$), 2.61-2.85 (m, 3H, $CH_2CO_2$, 1x$NCH_2CH_2$), 3.17-3.28 (m, 2H, 1x$CSCH_2N$, $CHCH_3$), 3.36, 3.47 (2d, *J*=13.0 Hz, 2H, $NCH_2Ph$), 3.70 (s, 3H, $CH_3O$), 7.21-7.34 (m, 7H, PhH, 2x*p*-Tol) and 7.71 (d, *J*=8.2 Hz, 2Hx*p*-Tol); $\delta_C$ 15.2 ($CH_3CH$), 21.3, 28.0 [$(CH_2)_2CS$], 21.5 ($CH_3Ar$), 31.3 ($CHCH_3$), 36.6 ($CH_2CO_2$), 51.5 ($CH_3O$), 53.0, 55.5, 63.0 (3x$CH_2N$), 67.6 (CS), 127.2, 128.2, 128.7, 129.4, 130.1, 134.6, 137.8, 144.6 (ArC) and 174.2 (C=O); *m/z* 398 ($M^+$-OMe, <1%), 200 (55), 92 (13), 91 (100) and 65 (12).

**Synthesis of *endo*- and *exo*-4-Methyl-5-tosyl-1-azabicyclo[3.3.1]nonan-2-one (29).** Compound **27h** as a mixture of diastereomers (75 mg, 0.17 mmol) was debenzylated as described for the reduction of compound **22** (see above) and purified by flash chromatography (hexane/EtOAc) to yield compounds **28** (39 mg, 65%) and ***endo*-29** (19 mg, 35%). Then, in order to obtain the *exo* isomer, to a solution of compound **28** (19 mg, 0.056 mmol) in dry THF (2 ml) cooled at -78°C, was added freshly prepared LDA (0.062 mmol) and the reaction mixture was stirred for 2 d at room temperature. Then, brine (3 ml) was added and the resulting mixture was extracted with EtOAc (2x5 ml), dried ($Na_2SO_4$) and evaporated (15 Torr) yielding crude product ***exo*-29** which was purified by flash chromatography (hexane/EtOAc) to afford 10 mg of pure product (60%). Physical, spectral and analytical data of the corresponding compounds follow:

**Methyl (3*S**)-3-[(3*S**)-3-Tosyl-3-piperidyl]butanoate (28)**: $R_f$ 0.20 (EtOAc); ν 3349 (NH), 1734 (C=O), 1298, 1285 and 1138 cm$^{-1}$ ($SO_2$); $\delta_H$ 1.09 (d, *J*=7.0 Hz, 3H, $CH_3CH$), 1.52-1.87, 2.07-2.12, 2.31-2.43, 2.52-2.64, 2.73-2.94, 3.07-3.23 [6m, 12H, $CSCH_2N$, $CHCH_2CO_2$, $CS(CH_2)_3N$, NH], 2.46 (s, 3H, $CH_3Ar$), 3.70 (s, 3H, $CH_3O$), 7.37 and 7.73 (2d, *J*=8.2 Hz, 4H, ArH); $\delta_C$ 15.0 ($CH_3CH$), 21.5 ($CH_3Ar$), 22.0, 27.3 [$(CH_2)_2CS$], 30.6 ($CHCH_3$), 36.5 ($CH_2CO_2$), 45.4, 48.7 (2x$CH_2N$), 51.7 ($CH_3O$), 65.5 (CS), 129.5, 130.1, 134.2, 144.7 (ArC) and 174.0 (C=O); *m/z* 324 ($M^+$-Me, <1%), 308 ($M^+$-OMe, <1), 184 (11), 152 (66), 124 (11), 110 (100), 91 (21), 84 (15), 82 (14), 69 (62), 67 (12), 65 (16), 57 (22), 56 (12), 55 (15), 44 (12), 43 (11), 42 (17) and 41 (26).

***endo*-4-Methyl-5-tosyl-1-azabicyclo[3.3.1]nonan-2-one (29):** $R_f$ 0.26 (ether); ν 1684 (C=O), 1300, 1289 and 1141 cm$^{-1}$ ($SO_2$); $\delta_H$ ($C_6D_6$) 0.55 (d, *J*=7.3 Hz, 3H, $C\mathit{H}_3CH$), 0.82-0.89 (m, 1Hx$NCH_2C\mathit{H}_2$), 1.41-1.47 (m, 2H, 1x$NCH_2C\mathit{H}_2$, 1x$CSC\mathit{H}_2CH_2$), 1.79 (d, *J*=14.7 Hz, 1Hx$CH_2CO$), 1.86 (s, 3H, $C\mathit{H}_3Ar$), 1.97 (m, 1Hx$CSC\mathit{H}_2CH_2$), 2.11 (m, 1Hx$NC\mathit{H}_2CH_2$), 2.31 (dd, *J*=14.7, 9.5 Hz, 1Hx$CH_2CO$), 3.02 (d, *J*=13.1 Hz, 1Hx$CSCH_2N$), 3.07 (m, 1H, $C\mathit{H}CH_3$), 3.49 (br d, *J*=13.1 Hz, 1Hx$CSCH_2N$), 4.04 (dd, *J*=11.6, 5.5 Hz, 1Hx$NC\mathit{H}_2CH_2$), 6.74 and 7.57 (2d, *J*=8.0 Hz, 4H, ArH); $\delta_C$ 16.4 ($\mathit{C}H_3CH$), 21.7 ($\mathit{C}H_3Ar$), 22.3, 24.9 [$(\mathit{C}H_2)_2CS$], 31.0 ($\mathit{C}HCH_3$), 40.5 ($\mathit{C}H_2CO_2$), 49.5, 51.7 (2x$CH_2N$), 66.0 (CS), 129.9, 130.0, 132.4, 145.4 (ArC) and 181.7 (C=O); *m/z* 152 ($M^+$-Ts, 100%), 149 (10), 94 (14), 91 (16), 85 (11), 84 (19), 83 (14), 71 (19), 70 (13), 69 (81), 67 (11), 65 (11), 57 (29), 56 (10), 55 (25), 43 (32) and 41 (32).

***exo*-4-Methyl-5-tosyl-1-azabicyclo[3.3.1]nonan-2-one (29):** $R_f$ 0.26 (ether); ν 1683 (C=O), 1300, 1288 and 1140 cm$^{-1}$ ($SO_2$); $\delta_H$ ($C_6D_6$) 0.32-0.42 (m, 1Hx$NCH_2C\mathit{H}_2$), 1.01-1.15 (m, 1Hx$NCH_2C\mathit{H}_2$), 1.28-1.37 (m, 1Hx$CSC\mathit{H}_2CH_2$), 1.56 (d, *J*=6.7 Hz, 3H, $C\mathit{H}_3CH$), 1.63-1.72 (m, 1Hx$CSC\mathit{H}_2CH_2$), 1.90-1.98 (m, 5H, $C\mathit{H}_3Ar$, 1x$NC\mathit{H}_2CH_2$, $C\mathit{H}CH_3$), 2.11 (dd, *J*=14.3, 11.0 Hz, 1Hx$CH_2CO$), 2.27 (dd, *J*=14.3, 5.0 Hz, 1Hx$CH_2CO$), 2.58 (d, *J*=13.4 Hz, 1Hx$CSCH_2N$), 3.46 (br d, *J*=13.4 Hz, 1Hx$CSCH_2N$), 3.90 (dt, *J*=13.4, 5.5 Hz, 1Hx$NC\mathit{H}_2CH_2$), 6.73 and 7.61 (2d, *J*=8.0 Hz, 4H, ArH); $\delta_C$ 17.8 ($\mathit{C}H_3CH$), 19.6, 31.2 [$(\mathit{C}H_2)_2CS$], 21.6 ($\mathit{C}H_3Ar$), 37.6 ($\mathit{C}HCH_3$), 42.8 ($\mathit{C}H_2CO_2$), 48.1, 49.7 (2x$CH_2N$), 65.3 (CS), 129.8, 130.2, 134.4, 145.3 (ArC) and 181.6 (C=O); *m/z* 152 ($M^+$-Ts, 100%), 149 (10), 94 (14), 91 (16), 85 (11), 84 (19), 83 (14), 71 (19), 70 (13), 69 (81), 67 (11), 65 (11), 57 (29), 56 (10), 55 (25), 43 (32) and 41 (32).

**Reaction of Methylenation of Sulfones 10b, 13aa and 13ad. General Procedure.** To a solution of (chloromethyl)magnesium chloride at -78°C in THF (2 mmol) [prepared from reaction of chloroiodomethane (2 mmol) and isopropylmagnesium chloride (2 mmol) at -78°C] was transferred with a cannula a solution of the corresponding lithiated sulfone (1 mmol) at -78°C, and the reaction mixture was allowed to warm to 0°C. Then the reaction was hydrolyzed with water and extracted with EtOAc (3x10 ml). The organic layer was dried ($Na_2SO_4$) and evaporated (15 Torr) to give the corresponding crude product which was then purified by column chromatography (hexane/EtOAc) to afford the pure compounds. Yields are included in the text, physical, spectral and analytical data follow:

***N*-Benzyl-1-phenyl-2-propen-1-amine (30):** $R_f$ 0.83 (hexane/EtOAc: 1/1); ν 3328 cm$^{-1}$ (NH); $\delta_H$ 1.45 (br s, 1H, NH), 3.73, 3.74 (2d, *J*=13.4 Hz, 2H, $C\mathit{H}_2Ph$), 4.23 (d, *J*=7.3 Hz, 1H, $C\mathit{H}Ph$), 5.12 (d, *J*=10.1 Hz, 1Hx$C=C\mathit{H}_2$), 5.23 (d, *J*=17.1 Hz, 1Hx$C=C\mathit{H}_2$), 5.89-6.01 (m, 1H, $\mathit{H}C=CH_2$) and 7.26-7.36 (m, 10H, ArH); $\delta_C$ 51.3 ($CH_2N$), 65.1 ($\mathit{C}HPh$), 115.0 ($HC=\mathit{C}H_2$), 126.9, 127.2, 127.3, 128.1, 128.4, 128.5, 140.4, 141.0 and 142.8 (ArC and $H\mathit{C}=CH_2$); *m/z* 223 ($M^+$, 20%), 222 (43), 197 (13), 196 (78), 146 (43), 133 (14), 132 (93), 118 (17), 117 (58), 115 (50), 106 (31), 105 (18), 104 (21), 92 (34), 91 (100), 89 (11), 77 (23), 65 (41), 63 (11), 54 (11), 51 (27) and 44 (10). Found: $M^+$-1 222.12798. Calcd. for $C_{16}H_{16}N$, 222.12828.

***N*-Benzyl-3-methylenepiperidine (31aa):** $R_f$ 0.66 (ether); ν 3064, 1658 and 894 cm$^{-1}$ (C=C); $\delta_H$ 1.63-1.70 (m, 2H, $=CC\mathit{H}_2CH_2$), 2.16, 2.50 (2m, 4H, $CH_2CH_2N$), 2.94 (s, 2H, $=CCH_2N$), 3.55 (s, 2H, $C\mathit{H}_2Ph$), 4.73 (br s, 2H, $CH_2=C$) and 7.25-7.33 (m, 5H, ArH); $\delta_C$ 26.2, 32.7 ($C=C\mathit{C}H_2\mathit{C}H_2$), 58.7, 60.3, 63.0 (3x$CH_2N$), 109.0 ($\mathit{C}H_2=C$), 126.9, 128.1, 129.2, 138.2 and 144.7 (ArC, $\mathit{C}=CH_2$); *m/z* 187 ($M^+$, 70%), 186 (48), 172 (37), 110 (27), 96 (44), 92 (22), 91 (100), 69 (17), 68 (23), 67 (12), 55 (12), 51 (11), 42 (35), 41 (69) and 40 (11); Found: $M^+$ 187.13570. Calcd. for $C_{13}H_{17}N$, 187.13610.

**2-Benzyl-4-methylene-2,3,4,5-tetrahydro-1*H*-benzo[c]azepine (31ad):** $R_f$ 0.65 (ether); ν

3063, 3026, 1648 and 906 cm$^{-1}$ (C=C); $\delta_H$ 3.31, 3.56, 4.07 (3s, 8H, 3xNCH$_2$, ArC$H_2$C=), 4.72, 4.99 (2br s, 2H, CH$_2$=C) and 6.93-7.29 (m, 9H, ArH); $\delta_C$ 44.4 ($C$H$_2$CCH$_2$N), 55.4, 58.7, 63.2 (3xCH$_2$N), 114.5 ($C$H$_2$=C), 126.0, 126.8, 127.3, 127.6, 128.1, 129.1, 130.3, 137.3, 139.2, 139.8 and 140.8 (ArC and $C$=CH$_2$); *m/z* 250 ($M^+$+1, 28%), 249 ($M^+$, 100), 248 (31), 234 (10), 172 (15), 159 (18), 158 (88), 144 (17), 143 (17), 141 (12), 131 (23), 130 (23), 129 (71), 128 (51), 127 (18), 118 (15), 117 (12), 116 (11), 115 (24), 104 (14), 103 (10), 92 (22), 91 (83), 89 (10), 77 (13), 65 (36), 63 (10), 51 (12), 42 (39) and 41 (12); Found: $M^+$ 249.15182. Calcd. for $C_{18}H_{19}N$, 249.15175.

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