Cleavage of sulfonamides with phenyldimethylsilyllithium

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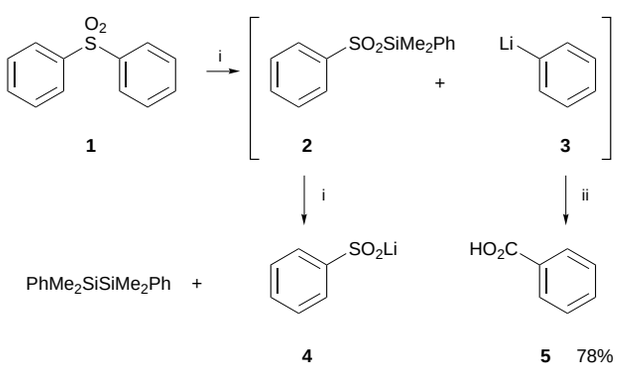
The toluene-*p*-sulfonamides of secondary amines and indoles are cleaved by treatment with phenyldimethylsilyllithium to give the secondary amines. Aziridine toluene-*p*-sulfonamides, however, are opened by attack of the silyllithium reagent on carbon to give β-silylethyl sulfonamides. The aziridine toluene-*p*-sulfonamide 22 derived from norbornene is different in giving the 2-[dimethyl(phenyl)silyl]-4-methylbenzenesulfonamide 23 of *exo*-norbornylamine. The aziridine toluene-*p*-sulfonamides 26, 28 and 30, derived from methyl cinnamate, methyl acrylate and cinnamyl acetate, are also anomalous, giving 3-[*N*-(*p*-tolylsulfonyl)amino]-3-phenylpropionic acid 27, {3-[*N*-(*p*-tolylsulfonyl)amino]propionyl}-dimethyl(phenyl)silane 29 and *trans*-cinnamyl alcohol 31, respectively, each derived by opening of the aziridine ring followed by loss of the silyl group.

Introduction

We have been studying some of the uses of Gilman's phenyldimethylsilyllithium reagent[1] as a reducing agent and find[2] unsurprisingly[3] that it reduces azobenzene to hydrazobenzene, and azoxybenzene to a mixture of azobenzene and hydrazobenzene. In the hope that it might also reduce sulfones, we treated[4] diphenyl sulfone **1** with this reagent and obtained in the organic layers from the work-up only the usual hydrolysis products from the silicon reagent, and no organic products derived from the diphenyl sulfone. We reasoned that the silyllithium reagent had attacked the sulfur to give the silyl sulfinate ester **2**, displacing phenyllithium **3** (Scheme 1). The former can



Scheme 1 *Reagents and conditions:* i, 2 equiv. $PhMe_2SiLi$, THF, 0 °C, 3–6 h; ii, CO_2

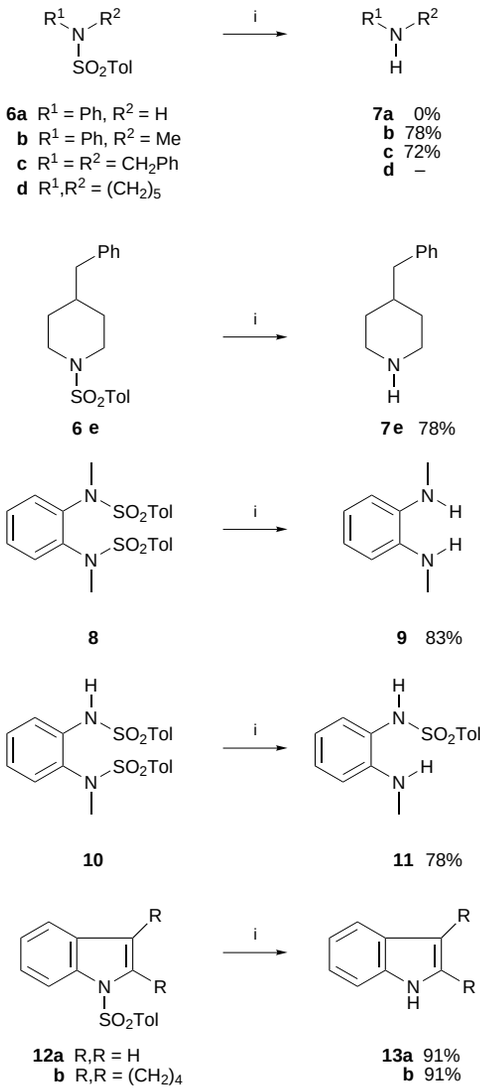
be expected[5] to react with more of the silyllithium reagent to give the lithium salt **4**, which will remain in the aqueous layer, and the latter will be protonated to give benzene, which would evaporate off. When we repeated this reaction, but treated the reaction mixture with carbon dioxide before working it up, we obtained benzoic acid **5** in good yield, showing that phenyllithium had indeed been displaced from the sulfur. There is some analogy for such a process in the cleavage of a strained sulfone with methyllithium.[6]

These observations suggested that sulfonamides might also be cleaved by this reagent, since a lithium amide ought to be a better leaving group than phenyllithium. It is usual to claim that sulfonamides are difficult to cleave, which they are hydrolytically,[7] but actually there is already quite a large list of reagents that have been used for this purpose.[8] The problem is that they all have incompatibilities with one functional group or another, and our reagent, if it works at all, will have its own limitations, since it is a powerful nucleophile reacting with a wide range of electrophiles. Since it might also have some advantages, we have studied the reaction, and report here that the sulfonamides of secondary amines are easily cleaved by the phenyldimethylsilyllithium reagent.

Results and discussion

We treated the toluene-*p*-sulfonamides **6**, **8** and **10** with the silyllithium reagent, typically in 2–4-fold excess in THF at 0 °C over 3–6 hours, and obtained the secondary amines **7b**–**e**, **9** and **11**, but not the primary amine **7a** (Scheme 2). Similarly, the *N*-sulfonylindoles **12** gave the indoles **13**. Significantly, the bis-sulfonamide **10** was cleaved only at the secondary amine site, to give the sulfonamide **11**. In this case, and in the case of the secondary amide **6a**, the silyllithium reagent must have acted first as a base to remove the sulfonamide proton, making this functional group resistant to cleavage. Of all the reagents known for cleaving sulfonamides,[7,8] the silyllithium reagent may be the only one able to discriminate between primary and secondary sulfonamides. In all these reactions we found that two or more molar equivalents of silyllithium reagent are necessary, because the by-product from the cleavage, which is probably phenyldimethylsilyl sulfinate **2**, reacts rapidly with the second equivalent of the silyllithium reagent, just as silyl chlorides and bromides do,[5] to give tetramethyl(diphenyl)disilane. In some preliminary experiments, we also carried out the reaction using toluene as the solvent in addition to the THF in which the silyllithium reagent had been made. The yields of the amides **9** and **11** were actually a little better, 89 and 90%, respectively, in the mixed solvent.

These substrates gave uneventful results, but we feared that aziridine sulfonamides, although much used in synthesis, were quite likely to react by ring-opening by attack at carbon rather than cleavage by attack at sulfur (or oxygen). We find that they are indeed opened by attack at carbon in almost every case, as shown by the aziridine sulfonamides **14**, **16**, **18** and **20**, which gave the β-silyl sulfonamides **15**, **17**, **19** and **21** (Scheme 3) at −78 °C, in contrast to the earlier reactions that needed several hours at 0 °C. The reaction is stereospecific, as shown by the diastereoisomeric pair of sulfonamides **14** and **16** giving the diastereoisomeric products **15** and **17**, presumed to have taken place with inversion of configuration. We hoped that the cyclohexene-derived sulfonamide **20** might have been less susceptible to opening, but it gave a single product **21** with no trace of the aziridine, which we had prepared separately, in the basic products. The yields of these reactions were optimised only for

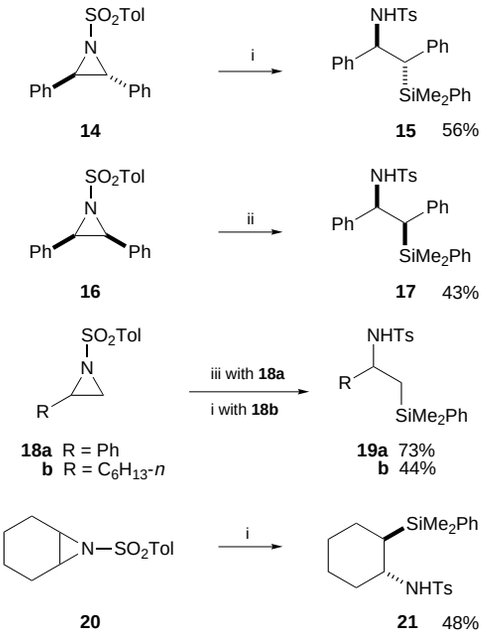


Scheme 2 *Reagents and conditions:* i, 2–4 equiv. $PhMe_2SiLi$, THF, 0 °C, 3–6 h

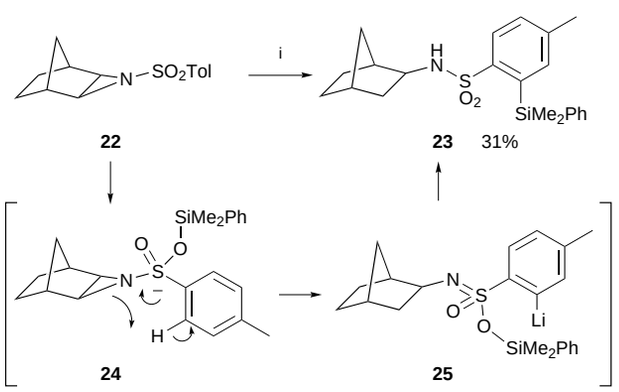
the ziridine **18a**, which gave the best yield of the sulfonamide **19a** (73%) when we used toluene as a solvent. It seems likely that the other reactions would be improved by this modification.

The norbornene-derived aziridine **22** was anomalous, presumably because the S_N2-like transition structure had been made unfavourable enough for something else to happen. The only identifiable product proved to be the sulfonamide **23**, which we suggest had been formed by attack of the silyl group on sulfur (or oxygen), opening the aziridine ring in the unnatural sense, concurrently with, or followed by, proton transfer **24** (arrows), and intramolecular silyl transfer in the aryllithium intermediate **25** (Scheme 4). The removal of protons *ortho* to a sulfonamide group has precedent.[9] The structure of the product **23** was evident from the ^{13}C and ^{1}H NMR spectra, and we confirmed it by removing the silyl group with fluoride ion to give the known *exo*-norbornyl toluene-*p*-sulfonamide.

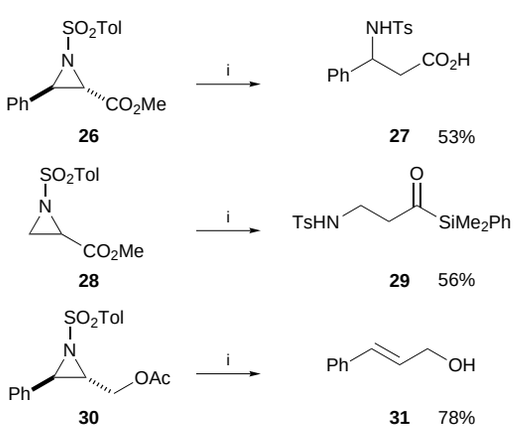
A few other aziridine sulfonamides also gave anomalous products (Scheme 5). The cinnamate-derived aziridine **26** gave ring-opening, but with loss of the silyl group, to give the acid **27**, presumably because the silyl group was initially α to an ester carbonyl group. The ester hydrolysis was probably an artefact of the work-up, for we isolated mixtures of acids and esters in other runs of this type of reaction. Evidently attack on the aziridine carbon takes place at a comparable rate or is actually faster than attack at the ester carbonyl group. Similarly, the



Scheme 3 *Reagents and conditions:* i, 3 equiv. $PhMe_2SiLi$, THF, 0 °C, 5 h; ii, 3 equiv. $PhMe_2SiLi$, THF, −78 °C, 6 h; iii, 3 equiv. $PhMe_2SiLi$, toluene, 0 °C, 6 h



Scheme 4 *Reagents and conditions:* i, 3 equiv. $PhMe_2SiLi$, THF, 0 °C, 6 h

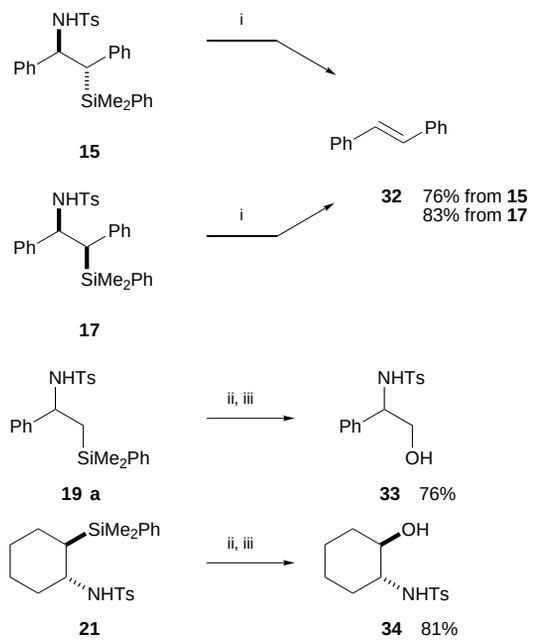


Scheme 5 *Reagents and conditions:* i, 3 equiv. $PhMe_2SiLi$, THF, 0 °C, 4–6 h

aziridine sulfonamide **28** derived from acrylate gave the sulfonamide **29** that is also an acyl silane, presumably by a similar pathway, but completed or preceded by the silyllithium reagent attacking the ester group.[10] The aziridine sulfonamide **30** derived from cinnamyl acetate was more surprising, giving cinnamyl alcohol **31**. We suggest that this is formed by silyllithium

attack opening the aziridine ring at either carbon, but more probably at the benzylic carbon, followed by intramolecular acyl transfer from oxygen to nitrogen, and then oxyanion-assisted elimination of the silyl group and the acylated sulfonamide group, a type of reaction related to one known[11] to be stereoselective for the formation of a *trans* double bond.

We used the pair of silyl sulfonamides **15** and **17** to check whether there might be a nitrogen equivalent of the Peterson elimination, and to check whether it might be stereospecific. The elimination took place on treating the sulfonamides with potassium hydride in THF at reflux, and proved to be merely stereoselective, with both diastereoisomers giving only *trans*-stilbene **32** (Scheme 6). The elimination is notably slow com-



Scheme 6 *Reagents and conditions:* i, KH, THF, reflux, 8 h; ii, TBAF, THF, reflux, 1 h; iii, H_2O_2, KF, $NaHCO_3$, THF, MeOH, reflux, 2 h

pared with normal Peterson eliminations, in spite of the benzylic nature of the silyl group. Although we only checked this point with the two silanes where benzylic stabilisation of an anionic intermediate might well lead to loss of stereospecificity, the slowness of the reaction does not bode well for the efficiency of this reaction in those cases which might stand a better chance of being stereospecific. We also used the products **19a** and **21** (from the opening of the sulfonylaziridines **18a** and **20**) to confirm that our silyl-to-hydroxy conversion[12] would give the alcohols **33** and **34**, effectively the products of opening the aziridine with hydroxide ion. We found that removal of the phenyl group from the silicon atom was easily achieved using fluoride ion, possibly with participation by the sulfonamide group, since this is not normally possible with phenyldimethylsilyl groups. This route, allowing the oxidation step to be carried out using Tamao's conditions,[13] was actually better in these cases than trying to carry out both steps using our mercuric acetate-based method. The two-step procedure gave yields of 76 and 81%, whereas mercuric acetate and peracetic acid gave yields of 35 and 48% in unoptimised attempts at the one-step procedure.

In conclusion, the phenyldimethylsilyllithium reagent is able to cleave the toluenesulfonamides of secondary amides but not primary amides. Aziridine sulfonamides, however, undergo opening by attack at carbon, giving products which can undergo an aza-Peterson reaction that is stereoselective but not stereospecific. A few anomalous reactions take place with aziridine sulfonamides that are resistant to opening or have additional functionality to divert the first-formed product.

Experimental

See the previous paper for general experimental details. Light petroleum refers to the fraction boiling between 40–60 °C and ether refers to diethyl ether.

Reaction of dimethyl(phenyl)silyllithium with azobenzene and with azoxybenzene †

Dimethyl(phenyl)silyllithium in THF (1.2 mol dm^{-3}, 6.6 cm^3, 6.5 mmol) and azobenzene (1 g, 5.5 mmol) were kept for 2 h at −78 °C under argon. The mixture was quenched with saturated ammonium chloride solution (50 cm^3) and extracted with ether (2 × 60 cm^3). The combined organic layers were washed with brine (50 cm^3), dried ($MgSO_4$) and the solvent removed under reduced pressure. The residue was flash chromatographed (SiO_2, CH_2Cl_2–light petroleum, 1:5) to give hydrazobenzene (0.43 g, 42%) mp 121–124 °C (from MeOH) and azobenzene (0.34 g, 34%) mp 70–71 °C (from light petroleum), identical (mp and TLC) with authentic samples. Similarly, the silyllithium reagent (1.0 mol dm^{-3}, 13 cm^3, 13 mmol) and azoxybenzene (1 g, 5.05 mmol) gave under the same conditions hydrazobenzene (0.51 g, 55%) mp 120–124 °C (from MeOH), azobenzene (0.21 g, 51%) mp 65–68 °C (from light petroleum) and azoxybenzene (0.20 g, 20%) mp 34–37 °C (from EtOH), identical (mp and TLC) with authentic samples.

Reaction of dimethyl(phenyl)silyllithium with diphenyl sulfone ‡

Dimethyl(phenyl)silyllithium in THF (1.04 mol dm^{-3}, 11.5 cm^3, 12 mmol) and diphenyl sulfone (1.08 g, 5 mmol) were kept in THF (5 cm^3) for 2 h at −78 °C under argon. Carbon dioxide was bubbled through the mixture for 30 min and the mixture allowed to warm to room temperature. Sodium hydrogen carbonate solution (saturated, 50 cm^3) was added, followed by sodium hydroxide solution (20 cm^3) and the mixture extracted with ether (2 × 50 cm^3). The aqueous layer was acidified with aqueous hydrochloric acid (3 mol dm^{-3}) and extracted with dichloromethane (2 × 50 cm^3). The combined organic layers were washed with brine (30 cm^3), dried ($MgSO_4$) and the solvent removed under reduced pressure. The residue was recrystallised to give benzoic acid (0.47 g, 78%) mp 120–121 °C (from H_2O), identical (mp and IR) with an authentic sample. A comparable reaction with di-*n*-decyl sulfone gave recovered starting material (69%).

Preparation of the sulfonamides

Typically, the amine (50 mmol) was shaken vigorously with toluene-*p*-sulfonyl chloride (75 mmol) in sodium hydroxide solution (10%, 150 cm^3) for 1–2 h. The solid products were separated and recrystallised from ethanol. The following new sulfonamides were prepared by this method.

4-Benzyl-1-(*p*-tolylsulfonyl)piperidine 6e. Prisms, mp 99–100 °C (from EtOH); δ_H(250 MHz; $CDCl_3$) 7.58 (2 H, d, *J* 9, ArH *o* to SO_2), 7.27–7.07 (5 H, m, Ph), 7.06 (2 H, d, *J* 9, ArH *o* to Me), 3.74 (2 H, dd, *J* 13 and 3, CH_AH_BN), 2.49 (2 H, d, *J* 6, CH_2Ph), 2.41 (3 H, s, Ar*Me*), 2.15 (2 H, ddd, *J* 13, 12 and 3, CH_AH_BN), 1.65 (2 H, m, CH_AH_BCHBn) and 1.51–1.20 (3 H, m, CH_AH_BCHBn and CH); *m*/*z* (EI) 329 (51%, M^+), 223 (25), 174 (100) and 91 (95) (Found: M^+, 329.1448. $C_{19}H_{23}NO_2S$ requires *M*, 329.1449).

1,2,3,4-Tetrahydro-9-(*p*-tolylsulfonyl)-9*H*-carbazole 12b. Prisms, mp 93–96 °C (from light petroleum); δ_H(250 MHz; $CDCl_3$) 8.14 (1 H, dd, *J* 8 and 2, ArH), 7.60 (2 H, d, *J* 9, ArH *o* to SO_2), 7.37–7.15 (5 H, m, ArH remainder), 3.01–2.96 (2 H, m, $ArCH_2$), 2.60–2.55 (2 H, m, $ArCH_2$), 2.32 (3 H, s, Ar*Me*) and 1.91–1.72 (4 H, m, CH_2CH_2); *m*/*z* (EI) 325 (78%, M^+), 170 (100), 169 (52), 168 (35) and 91 (22) (Found: M^+, 325.1133. $C_{19}H_{19}NO_2S$ requires *M*, 325.1136).

† Experiments carried out by Sarah Horswell.
‡ Experiments carried out by Michael D. Woodrow.

The known sulfonamides **8** and **10** were prepared by the method of Stetter.[14]

***N*,*N*′-Dimethyl-*N*,*N*′-bis(*p*-tolylsulfonyl)benzene-1,2-diamine 8.** Prisms, mp 177–178 °C (from EtOH) (lit.,[14] 175–176 °C); δ_H(250 MHz; $CDCl_3$) 7.71 (4 H, d, *J* 9, Ar*H o* to SO_2), 7.33 (4 H, d, *J* 9, Ar*H o* to Me), 7.24 (2 H, m, ArH), 6.88 (2 H, m, ArH), 3.20 (6 H, s, NMe) and 2.45 (6 H, Ar*Me*).

***N*-Methyl-*N*,*N*′-bis(*p*-tolylsulfonyl)benzene-1,2-diamine 10.** Needles, mp 217–219 °C (from MeOH) (lit.,[14] 139 °C); δ_H(250 MHz; $CDCl_3$) 7.77 (2 H, d, *J* 9, ArH *o* to SO_2), 7.63 (2 H, d, *J* 9, ArH *o* to Me), 7.14–7.12 (4 H, m, ArH), 6.86 (2 H, m, ArH), 6.46 (2 H, m, ArH), 3.46 (1 H, s, NH, exchanges with D_2O), 2.82 (3 H, s, NMe), 2.82 (3 H, s, ArMe) and 2.39 (3 H, s, ArMe); δ_C(250 MHz; $CDCl_3$) 148.2, 142.9, 141.8, 139.8, 136.5, 132.6, 129.5, 129.0, 127.8, 127.1, 120.9, 117.5, 38.0, 21.5 and 21.3.

Reaction of dimethyl(phenyl)silyllithium with toluene-*p*-sulfonamides

Typically, dimethyl(phenyl)silyllithium (4 mmol) and the sulfonamide (2 mmol) were kept in dry THF (15 cm^3) for 3–6 h at 0 °C under argon. The mixture was quenched with saturated ammonium chloride solution (5 cm^3) and saturated sodium chloride solution (15 cm^3) and the aqueous layer washed with ether (20 cm^3). The combined organic layers were washed with aqueous hydrochloric acid (6 mol dm^{-3}, 50 cm^3). The aqueous layer was extracted with ether (3 × 20 cm^3), made basic to pH 9–10 with sodium hydroxide solution (10 mol dm^{-3}) and extracted again with ether (4 × 75 cm^3). The combined organic layers from the second extraction were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was flash chromatographed (SiO_2, EtOAc–hexane, 30 : 70) to give the amine. The following amines, identical (TLC, ^{1}H NMR and, where appropriate, mp) with the authentic samples from which the sulfonamides had been made,[15] were prepared by this method:

N-Methylaniline **7b** (78%, 4 h), dibenzylamine **7c** (72%, 3 h), piperidine **7d** (too volatile for a yield to be calculated, 4 h), 4-benzylpiperidine **7e** (78%, 4 h) and the following amines.

1,2-Bis(methylamino)benzene 9.[14] (83%, 4 h; 89% when toluene was used in place of the THF); R_f (EtOAc–hexane, 30 : 70) 0.24; ν_{max}($CHCl_3$)/cm^{-1} 3356 (NH), 3049 (CH), 2807 (NMe), 1601 (Ar), 828 (*p*-substituted Ar) and 738 (*o*-substituted Ar); δ_H(400 MHz; $CDCl_3$) 6.85 (2 H, m, Ar*H m* to N), 6.70 (2 H, m, ArH *o* to N), 3.00 (2 H, s, NH, exchanges with D_2O) and 2.85 (6 H, s, NMe); δ_C($CDCl_3$) 138.4, 119.1, 110.6 and 31.1.

***N*-Methyl-*N*′-(*p*-tolylsulfonyl)benzene-1,2-diamine 11.** Needles, mp 122–123 °C (from MeOH) (78%, 6 h; 90% when toluene was used in place of the THF); R_f (EtOAc–hexane, 30 : 70) 0.15; ν_{max}($CHCl_3$)/cm^{-1} 3498 (NHMe), 3263 (NHTs), 1605 (Ar), 1326 (SO_2N), 1154 (SO_2N), 1037 (S=O), 815 (*p*-substituted Ar) and 738 (*o*-substituted Ar); δ_H(250 MHz; $CDCl_3$) 7.63 (2 H, d, *J* 8.3, ArH *o* to SO_2), 7.23 (2 H, d, *J* 8.0, ArH *o* to Me), 7.15 (1 H, m, ArH), 6.65 (1 H, m, ArH), 6.45 (2 H, m, ArH), 6.00 (1 H, br s, NH, exchanges with D_2O), 4.65 (1 H, br s, NH, exchanges with D_2O), 2.78 (3 H, s, NMe) and 2.41 (3 H, s, ArMe); *m*/*z* (EI) 276 (53%, M^+), 121 (100) and 94 (26) (Found: M^+, 276.0930. $C_{14}H_{16}N_2O_2S$ requires *M*, 276.0932).

The following indoles were prepared similarly, but without the extraction into acid; indole **13a** (91%, 3 mol equiv. of silyllithium reagent, 6 h) and tetrahydrocarbazole **13b** (91%, 3 mol equiv. of silyllithium reagent, 3 h).

Preparation of aziridine toluene-*p*-sulfonamides

Typically, following Evans,[16] the alkene (26.75 mmol) and *N*-(*p*-tolylsulfonyl)imino(phenyl)iodinane (2.0 g, 5.35 mmol) were added with stirring to a solution of copper(II) trifluoromethanesulfonate (0.275 mmol) in dry acetonitrile (10 cm^3) (**16**, **18b**, **20**, **22**, **26**, **28** and **30**) or in dichloromethane (10 cm^3) (**14** and **18a**) under argon, and the mixture stirred for 2 h. After all the *N*-(*p*-tolylsulfonyl)imino(phenyl)iodinane had dissolved, the mixture was filtered through a plug of silica gel eluting with ethyl acetate (150 cm^3). The solvent was removed under reduced pressure, and the residue was flash chromatographed (SiO_2, EtOAc–hexane, 20 : 80). The following aziridines were prepared by this method. Yields are based on the iodinane.

***trans*-*N*-(*p*-Tolylsulfonyl)-2,3-diphenylaziridine 14.** Prisms, mp 136–138 °C (from EtOH) (lit.,[17] 138–139 °C) (56%); R_f (EtOAc–hexane, 20 : 80) 0.20; ν_{max}(Nujol)/cm^{-1} 3046 (CH), 1603 (Ar), 1361 (SO_2N), 1157 (SO_2N), 1027 (S=), 894 (aziridine), 745 (aziridine) and 698 (aziridine); δ_H(250 MHz; $CDCl_3$) 7.60 (2 H, d, *J* 8.2, ArH *o* to SO_2), 7.00–7.45 (10 H, m, ArH), 7.18 (2 H, d, *J* 8.2, ArH *o* to Me), 4.28 (2 H, s, C*H*N) and 2.38 (3 H, s, Ar*Me*); δ_C($CDCl_3$) 143.9, 137.0, 133.0, 129.4, 128.7, 128.5, 128.3, 127.5, 50.4 and 21.6.

***cis*-*N*-(*p*-Tolylsulfonyl)-2,3-diphenylaziridine 16.** Prisms, mp 153–154 °C (from EtOH) (lit.,[16] 155–156 °C) (81%); R_f (EtOAc–hexane, 20 : 80) 0.20; ν_{max}(Nujol)/cm^{-1} 3043 (CH), 1599 (Ph), 1361 (SO_2N), 1154 (SO_2N), 1031 (S=O), 898 (aziridine), 805 (aziridine) and 698 (aziridine); δ_H(400 MHz; $CDCl_3$) 7.94 (2 H, d, *J* 8.3, ArH *o* to SO_2), 7.35 (2 H, d, *J* 8.0, ArH *o* to Me), 7.14–7.02 (10 H, m, ArH), 4.21 (2 H, s, CHN) and 2.44 (3 H, s, Ar*Me*); δ_C(100 MHz; $CDCl_3$) 144.8, 134.9, 132.1, 129.8, 128.8, 128.1, 127.9, 127.7, 47.5 and 21.7.

***N*-(*p*-Tolylsulfonyl)-2-phenylaziridine 18a.** Prisms, mp 87–88 °C (from EtOH) (lit.,[16] 88–89 °C) (85%); R_f (EtOAc–hexane, 33 : 67) 0.59; ν_{max}(Nujol)/cm^{-1} 3018 (CH), 1596 (Ph), 1330 (SO_2N), 1160 (SO_2N), 1078 (S=O), 916 (aziridine) and 780 (aziridine); δ_H(400 MHz; $CDCl_3$) 7.85 (2 H, d, *J* 8.3, ArH *o* to SO_2), 7.32 (2 H, d, *J* 8.2, ArH *o* to Me), 7.30–7.20 (5 H, m, ArH), 3.77 (1 H, dd, *J* 4.5 and 7.2, C*H*Ph), 2.96 (1 H, d, *J* 7.2, NCH_AH_B), 2.43 (3 H, s, Ar*Me*) and 2.37 (1 H, d, *J* 4.5, NCH_AH_B); δ_C(100 MHz; $CDCl_3$) 144.7, 135.1, 135.0, 129.7, 128.5, 128.3, 127.9, 126.6, 41.1, 35.9 and 21.7.

***N*-(*p*-Tolylsulfonyl)-2-*n*-hexylaziridine 18b.**[18] Prisms, mp 45–47 °C (from MeOH) (67%); R_f (EtOAc–hexane, 20 : 80) 0.39; ν_{max}(Nujol)/cm^{-1} 3030 (CH), 1325 (SO_2N), 1182 (SO_2N), 1082 (S=O), 931 (aziridine), 816 (aziridine) and 695 (aziridine); δ_H(400 MHz; $CDCl_3$) 7.80 (2 H, d, *J* 8.3, ArH *o* to SO_2), 7.30 (2 H, d, *J* 8.0, ArH *o* to Me), 2.68 (1 H, dddd, *J* 4.6, 4.8, 7.0 and 7.4, $C_6H_{13}CHN$), 2.61 (1 H, d, *J* 7.0, NCH_AH_B), 2.42 (3 H, s, Ar*Me*), 2.05 (1 H, d, *J* 4.6, NCH_AH_B), 1.60–1.50 (1 H, m, CH), 1.35–1.10 (9 H, m, CH_2s) and 0.85 (3 H, t, *J* 7.0, Me); δ_C($CDCl_3$) 144.4, 135.2, 129.6, 128.0, 40.5, 33.8, 31.6, 31.3, 28.7, 26.7, 22.4, 21.6 and 14.1; *m*/*z* (EI) 281 (1.1%, M^+), 184 (19, $TsNHCH_2$), 172 (15, $TsNH_3$), 155 (45, Ts), 126 (100, M − Ts), 91 (85, C_7H_7) (Found: M^+, 281.1450. $C_{15}H_{23}NO_2S$ requires *M*, 281.1449).

***N*-(*p*-Tolylsulfonyl)-7-azabicyclo[4.1.0]heptane 20.** Prisms, mp 54–55 °C (from MeOH) (lit.,[16] 55–56 °C) (68%); R_f (EtOAc–hexane, 20 : 80) 0.33; ν_{max}(Nujol)/cm^{-1} 3058 (CH), 1594 (Ar), 1355 (SO_2N), 1120 (SO_2N), 1090 (S=O), 998 (aziridine), 918 (aziridine) and 815 (aziridine); δ_H(400 MHz; $CDCl_3$) 7.80 (2 H, d, *J* 8.3, ArH *o* to SO_2), 7.30 (2 H, d, *J* 8.1, ArH *o* to Me), 2.98 (2 H, t, *J* 1.4, CHN), 2.43 (3 H, s, Ar*Me*), 1.77 (4 H, m, cyclohexyl-CH), 1.45–1.35 (2 H, m, cyclohexyl-CH) and 1.25–1.15 (2 H, m, cyclohexyl-CH).

***exo*-*N*-(*p*-Tolylsulfonyl)-3-azatricyclo[3.2.1.0^{2,4}]octane 22.** Prisms, mp 122–123 °C (from EtOH) (lit.,[16] 123–124 °C) (63%); R_f (EtOAc–hexane, 20 : 80) 0.21; ν_{max}(Nujol)/cm^{-1} 3017 (CH), 1310 (SO_2N), 1138 (SO_2N), 1082 (S=O), 895 (aziridine), 775 (aziridine) and 680 (aziridine); δ_H(250 MHz; $CDCl_3$) 7.80 (2 H, d, *J* 8.3, ArH *o* to SO_2), 7.34 (2 H, d, *J* 8.0, ArH *o* to Me), 2.91 (2 H, s, H-2 and H-3), 2.43 (5 H, s, Ar*Me*, H-1 and H-4), 1.50–1.40 (3 H, m, *syn*-H-7, H-5, H-6), 1.28–1.18 (2 H, m, H-5 and H-6) and 0.75 (1 H, d, *J* 10.1, *anti*-H-7); δ_C($CDCl_3$) 144.1, 135.9, 129.5, 127.6, 42.0, 35.8, 28.3, 25.6 and 21.6.

***trans*-*N*-(*p*-Tolylsulfonyl)-2-methoxycarbonyl-3-phenylaziridine 26.** Prisms, mp 42–43 °C (from EtOH) (lit.,[16] 44.2–44.6 °C) (73%); R_f (EtOAc–hexane, 20 : 80) 0.21; ν_{max}(Nujol)/cm^{-1} 3098

(CH), 1749 (CO), 1597 (Ar), 1315 (SO_2N), 1298 (C–O), 1163 (SO_2N), 1095 (S=O), 910 (aziridine) and 704 (aziridine); δ_H(400 MHz; $CDCl_3$) 7.83 (2 H, d, *J* 8.3, ArH *o* to SO_2), 7.30–7.20 (7 H, m, ArH *o* to Me and Ph), 4.43 (1 H, d, *J* 4.0, C*H*CO_2Me), 3.85 (3 H, s, OMe), 3.52 (1 H, d, *J* 4.0, PhC*H*N) and 2.41 (3 H, s, Ar*Me*).

***N*-(*p*-Tolylsulfonyl)-2-(methoxycarbonyl)aziridine 28.**[16] An oil (42%); R_f (EtOAc–hexane, 20:80) 0.27; ν_{max}(film)/cm^{-1} 3047 (CH), 1747 (CO), 1597 (Ar), 1395 (C–O), 1331 (SO_2N), 1232 (C–O), 1163 (SO_2N), 1094 (S=O), 908 (aziridine), 708 (aziridine) and 691 (aziridine); δ_H(400 MHz; $CDCl_3$) 7.84 (2 H, d, *J* 8.3, ArH *o* to SO_2), 7.35 (2 H, d, *J* 8.1, ArH *o* to Me), 3.73 (3 H, s, OMe), 3.34 (1 H, dd, *J* 4.0 and 7.1, C*H*CO), 2.75 (1 H, d, *J* 7.1, *cis*-C*H*N), 2.55 (1 H, d, *J* 4.0, *trans*-C*H*N) and 2.44 (3 H, s, Ar*Me*).

***trans*-*N*-(*p*-Tolylsulfonyl)-2-acetoxymethyl-3-phenylaziridine 30.** Prisms, mp 106–108 °C (from EtOH) (49%); R_f (EtOAc–hexane, 20:80) 0.25; ν_{max}(Nujol)/cm^{-1} 1746 (C=O), 1594 (Ar), 1376 (C–O), 1306 (SO_2N), 1228 (C–O), 1166 (SO_2N), 1087 (S=O), 900 (aziridine), 758 (Ar), 710 (aziridine) and 695 (Ar); δ_H(400 MHz; $CDCl_3$) 7.80 (2 H, d, *J* 8.3, ArH *o* to SO_2), 7.30–7.15 (7 H, m, ArH *o* to Me and other ArH), 4.75 (1 H, dd, *J* 6.0 and 12.2, CH_AH_BOAc), 4.65 (1 H, dd, *J* 6.0 and 12.2, CH_AH_B-OAc), 3.95 (1 H, d, *J* 4.2, PhC*H*N), 3.15 (1 H, dt, *J* 4.2 and 6.0, NC*H*CH_2OAc), 2.41 (3 H, s, Ar*Me*) and 2.06 (3 H, s, O_2C*Me*); δ_C($CDCl_3$) 170.5, 144.4, 136.9, 134.1, 129.6, 128.6, 128.5, 127.6, 126.8, 61.4, 48.9, 46.9, 21.6 and 20.7; *m*/*z* (EI) 345 (0.1%, M^+), 302 (0.2, M − Ac), 272 (1.5, M − CH_2OAc), 190 (95, M − Ts), 148 (100, M − Ts − Ac), 91 (70, C_7H_7) (Found: M^+ − Ac, 302.0846. $C_{18}H_{19}NO_4S - C_2H_3O$ requires *M* − Ac, 302.085).

Reaction of the dimethyl(phenyl)silyllithium with *p*-tolylsulfonylaziridines

Typically, dimethyl(phenyl)silyllithium (5.3 cm^3, 4.5 mmol) and the sulfonylaziridine (1.4 mmol) in dry THF (10 cm^3) were kept under argon at −78 or at 0 °C for 5–6 h. The mixture was quenched with saturated ammonium chloride solution (8 cm^3) and saturated sodium chloride solution (2 cm^3) and extracted with ether (3 × 20 cm^3). The combined organic layers were dried ($MgSO_4$), the solvent was removed under reduced pressure, and the residue was flash chromatographed (SiO_2, EtOAc–hexane, 20:80). The following products were prepared by this method.

(1*RS*,2*SR*)-2-Dimethyl(phenyl)silyl-1,2-diphenyl-*N*-(*p*-tolylsulfonyl)ethylamine 15. Prisms, mp 147–148 °C (from MeOH) (0 °C, 5 h, 56%; −78 °C, 6 h, 48%); R_f (EtOAc–hexane, 20:80) 0.21; ν_{max}(Nujol)/cm^{-1} 3273 (NH), 3066 (CH), 1598 (Ar), 1327 (SO_2N), 1155 (SO_2N), 1109 ($SiMe_2Ph$), 1036 (S=O), 836 (*p*-substituted Ar) and 700 (Ar); δ_H(400 MHz; $CDCl_3$) 7.30–6.70 (17 H, m, ArH *o* to SO_2 and other Ph), 6.95 (2 H, d, *J* 8.0, ArH *o* to Me), 4.70 (1 H, dd, *J* 3.4 and 11.2, PhC*H*N), 4.55 (1 H, d, *J* 3.4, NH, exchanges with D_2O), 2.60 (1 H, d, *J* 10.9, C*H*Si), 2.30 (3 H, s, Ar*Me*), −0.14 (3 H, s, Si$Me_A$$Me_B$) and −0.17 (3 H, s, $SiMe_A$$Me_B$); δ_C($CDCl_3$) 142.5, 139.7, 138.5, 137.2, 136.5, 134.0, 128.9, 128.8, 128.4, 128.1, 127.9, 127.6, 127.3, 126.9, 126.7, 126.5, 59.5, 45.2, 21.4, −3.6 and −3.7; *m*/*z* (EI) 485 (0.1%, M^+), 260 (80, $PhCH_2NTs$), 180 (100, PhCH=CHPh), 155 (15, Ts), 135 (32, $SiMe_2Ph$), 104 (8, PhCHN) and 91 (38, C_7H_7) (Found: C, 71.8; H, 6.55; N, 2.8. $C_{29}H_{31}NO_2SSi$ requires C, 71.7; H, 6.45; N, 2.9%).

(1*RS*,2*RS*)-2-Dimethyl(phenyl)silyl-1,2-diphenyl-*N*-(*p*-tolylsulfonyl)ethylamine 17. Prisms, mp 151–153 °C (from MeOH) (0 °C, 5 h, 38%; −78 °C, 5 h, 43%); R_f (EtOAc–hexane, 20:80) 0.21; ν_{max}(Nujol)/cm^{-1} 3267 (NH), 3064 (CH), 1598 (Ph), 1302 (SO_2N), 1154 (SO_2N), 1110 ($SiMe_2Ph$), 1035 (S=O), 835 (*p*-substituted Ar) and 699 (Ar); δ_H(400 MHz; $CDCl_3$) 7.62–6.70 (15 H, m, Ph), 7.17 (2 H, d, *J* 8.3, ArH *o* to SO_2), 6.60 (2 H, d, *J* 8.0, ArH *o* to Me), 4.85 (1 H, dd, *J* 9.2 and 10.6, PhC*H*N), 4.55 (1 H, d, *J* 9.2, NH), 2.60 (1 H, d, *J* 10.7, C*H*Si), 2.23 (3 H, s, Ar*Me*), 0.55 (3 H, s, Si$Me_A$$Me_B$) and 0.05 (3 H, s, $SiMe_A$$Me_B$); δ_C($CDCl_3$) 142.5, 140.6, 139.4, 138.2, 137.6, 134.4, 129.4, 129.3, 128.9, 128.2, 128.1, 127.7, 126.9, 126.7, 126.5, 125.5, 60.8, 45.9, 21.3, −1.9 and −5.0; *m*/*z* (EI) 485 (0.1%, M^+), 315 (1.5, M − TsNH), 260 (50, $PhCH_2NTs$), 180 (100, PhCH=CHPh), 155 (10, Ts), 135 (35, $SiMe_2Ph$), 104 (5, PhCHN) and 91 (40, C_7H_7) (Found: C, 71.8; H, 6.35; N, 2.9. $C_{29}H_{31}NO_2SSi$ requires C, 71.7; H, 6.45; N, 2.9%).

2-Dimethyl(phenyl)silyl-1-phenyl-*N*-(*p*-tolylsulfonyl)ethylamine 19a. Prisms, mp 93–94 °C (from MeOH) (0 °C, 5 h, 53%; −78 °C, 5 h, 31%; −78 °C, 2 h, 0 °C, 4 h, 42%; 0 °C, 4 h, with sonication, 65%; −78 °C, 5 h, in toluene, 61%; 0 °C, 6 h, in toluene, 73%); R_f (EtOAc–hexane, 20:80) 0.20; ν_{max}(Nujol)/cm^{-1} 3227 (NH), 1598 (Ar), 1324 (SO_2N), 1155 (SO_2N), 1113 ($SiMe_2Ph$), 1030 (S=O), 838 (*p*-substituted Ar) and 698 (Ar); δ_H(400 MHz; $CDCl_3$) 7.40 (2 H, *J* 8.3, ArH *o* to SO_2), 7.35–6.90 (12 H, m, ArH *o* to Me and other ArH), 4.70 (1 H, d, *J* 6.4, NH), 4.37 (1 H, dt, *J* 6.3 and 9.8, C*H*NH), 2.34 (3 H, s, Ar*Me*), 1.45 (1 H, dd, *J* 6.0 and 14.4, CH_AH_BSi), 1.35 (1 H, dd, *J* 9.8 and 14.4, CH_AH_BSi), 0.02 (3 H, s, Si$Me_A$$Me_B$) and 0.00 (3 H, s, $SiMe_A$$Me_B$); δ_C($CDCl_3$) 142.8, 141.8, 137.9, 137.6, 133.6, 129.2, 128.8, 128.4, 127.8, 127.5, 127.1, 126.6, 56.2, 26.4, 21.4, −2.5 and −3.4; *m*/*z* (EI) 409 (0.8%, M^+), 408 (50, M − H), 394 (39, M − Me), 332 (20, M − Ph), 290 (85, M − PhC_2H_3NH), 260 (65, $PhCH_2NTs$), 155 (30, Ts), 135 (100, $SiMe_2Ph$), 119 (15, PhC_2H_3NH), 104 (55, PhCH=CH_2) and 91 (90, C_7H_7) (Found: C, 67.0; H, 6.75; N, 3.3. $C_{23}H_{27}NO_2SSi$ requires C, 67.2; H, 6.65; N, 3.4%).

1-Dimethyl(phenyl)silyl-*N*-(*p*-tolylsulfonyl)octan-2-ylamine 19b. Prisms, mp 64–66 °C (from MeOH) (0 °C, 5 h, 44%); R_f (EtOAc–hexane, 20:80) 0.30; ν_{max}(Nujol)/cm^{-1} 3267 (NH), 1598 (Ph), 1326 (SO_2N), 1154 (SO_2N), 1139 ($SiMe_2Ph$), 1035 (S=O), 835 (*p*-substituted Ar) and 699 (Ph); δ_H(400 MHz; $CDCl_3$) 7.65 (2 H, d, *J* 8.3, ArH *o* to SO_2), 7.45–7.30 (5 H, m, ArH), 7.23 ((2 H, d, *J* 8.0, ArH *o* to Me), 4.20 (1 H, d, *J* 8.4, NH), 3.35 (1 H, dtt, *J* 1.5, 6.4, 8.0, C*H*NH), 2.41 (3 H, s, Ar*Me*), 1.40–0.90 (12 H, m, alkyl-CH_2 and CH_2Si), 0.82 (3 H, t, *J* 6.9, CH*Me*), 0.25 (3 H, s, Si$Me_A$$Me_B$) and 0.23 (3 H, s, $SiMe_A$$Me_B$); δ_C($CDCl_3$) 143.1, 138.4, 133.5, 133.1, 129.5, 129.2, 127.9, 127.1, 51.9, 37.2, 31.6, 28.8, 24.8, 24.1, 22.5, 21.5, 14.0, −2.3 and −2.4; *m*/*z* (EI) 417 (0.2%, M^+), 402 (11, M−Me), 332 (95, M−*n*-hexane), 268 (10, $TsNHC_7H_{14}$) 155 (15, Ts), 135 (100, $SiMe_2Ph$) and 91 (40, C_7H_7) (Found: C, 65.9; H, 8.55; N, 3.0. $C_{23}H_{35}NO_2SSi$ requires C, 66.0; H, 8.45; N, 3.15%).

***trans*-2-Dimethyl(phenyl)silyl-*N*-(*p*-tolylsulfonyl)cyclohexylamine 21.** Prisms, mp 153–155 °C (from MeOH) (0 °C, 6 h, 48%); R_f (EtOAc–hexane, 20:80) 0.29; ν_{max}(Nujol)/cm^{-1} 3253 (NH), 3064 (CH), 1597 (Ar), 1322 (SO_2N), 1158 (SO_2N), 1111 ($SiMe_2Ph$), 1062 (S=O), 842 (*p*-substituted Ar) and 701 (Ar); δ_H(400 MHz; $CDCl_3$) 7.65 (2 H, d, *J* 8.3, ArH *o* to SO_2), 7.45–7.30 (5 H, m, Ar), 7.23 (2 H, d, *J* 8.0, ArH *o* to Me), 4.10 (1 H, d, *J* 8.4, NH), 3.25 (1 H, ddd, *J* 3.7, 8.4 and 11.2, C*H*NH), 2.43 (3 H, s, Ar*Me*), 1.75–1.60 (2 H, m, cyclohexyl CH_2), 1.60–1.40 (2 H, m, cyclohexyl CH_2), 1.25–0.95 (4 H, m, cyclohexyl CH_2), 0.83 (1 H, dt, *J* 3.5 and 11.4, C*H*Si), 0.30 (3 H, s, Si$Me_A$$Me_B$) and 0.25 (3 H, s, $SiMe_A$$Me_B$); δ_C($CDCl_3$) 143.0, 139.2, 138.7, 133.9, 129.6, 129.0, 127.9, 126.9, 55.0, 35.7, 32.6, 27.0, 26.3, 24.7, 21.5, −3.6 and −3.9; *m*/*z* (EI) 387 (0.5%, M^+), 372 (10, M − Me), 197 (30, $TsNHC_2H_3$), 135 (100, $SiMe_2Ph$) and 91 (20, C_7H_7) (Found: C, 65.9; H, 7.85; N, 3.7. $C_{21}H_{28}NO_2SSi$ requires C, 65.8; H, 7.80; N, 3.6%).

***exo*-*N*-{2-[Dimethyl(phenyl)silyl]-4-methylphenylsulfonyl}-bicyclo[2.2.1]heptan-2-ylamine 23.** Prisms, mp 148–149 °C (from MeOH) (0 °C, 6 h, 31%; 0 °C, 4 h with sonication, 29%); R_f (EtOAc–hexane, 20:80) 0.16; ν_{max}($CHCl_3$)/cm^{-1} 3325 (NH), 3023 (CH), 1600 (Ar), 1335 (SO_2N), 1163 (SO_2N), 1110 ($SiMe_2Ph$), 1047 (S=O) and 812 (trisubstituted Ar); δ_H(500 MHz; $CDCl_3$) 7.85 (1 H, d, *J* 8.0, ArH *o* to SO_2), 7.66 (1 H, d, *J* 0.8, ArH *o* to Me and Si), 7.62 (2 H, m, Ph*H*), 7.40–7.35 (3 H, m, Ph*H*), 7.32 (1 H, dd, *J* 0.8 and 8.0, ArH *o* to Me and *p* to Si),

2.8 (1 H, dt, *J* 3.6 and 6.8, C*H*NH), 2.66 (1 H, d, *J* 6.6, NH, exchanges with D_2O), 2.45 (3 H, s, Ar*Me*), 2.0 (1 H, s, H-1), 1.79 (1 H, s, H-4), 1.35–1.25 (3 H, m, norbornyl-H), 0.95–0.80 (4 H, m, norbornyl-H), 0.67 (3 H, s, $SiMe_AMe_B$) and 0.65 (3 H, s, $SiMe_AMe_B$) and 0.61 (1 H, m, H-7); $\delta_C(CDCl_3)$ 143.2(+), 141.6(+), 138.6(+), 138.2(−), 136.6(+), 134.9(−), 130.1(−), 129.4(−), 129.3(−), 128.0(−), 56.3(−), 42.2(−), 40.3(+), 35.4(−), 34.9(+), 28.0(+), 26.4(+), 21.6(−), 0.1(−) and 0.4(−); *m*/*z* (EI) 399 (0.1%, M^+), 384 (100, M − Me), 322 (30, M − Ph), 290 (80, $TsSiMe_2Ph$), 228 (30, M − Me − Ts), 135 (30, $PhMe_2Si$) and 91 (10, C_7H_7) (Found: C, 65.1; H, 7.30; N, 3.1%; M^+ − Me, 384.1456. $C_{22}H_{29}NO_2SSi$ requires C, 65.1; H, 7.30; N, 3.3%; *M* − Me, 384.1453).

3-[*N*-(*p*-Tolylsulfonyl)amino]-3-phenylpropionic acid 27.[19] An oil (0 °C, 4 h, 53%); R_f (EtOAc–hexane, 40:60) 0.11; $\nu_{max}(CHCl_3)/cm^{-1}$ 3361 (OH), 3275 (NH), 3066 (CH), 1683 (C=O), 1598 (Ar), 1328 (SO_2N), 1217 (C–O), 1160 (SO_2N), 1093 (S=O), 813 (*p*-substituted Ar) and 733 (Ar); δ_H(250 MHz; $CDCl_3$) 11.2 (1 H, s, OH, exchanges with D_2O), 7.80 (2 H, d, *J* 8.3, ArH *o* to SO_2), 7.60 (2 H, d, *J* 8.0, ArH *o* to Me), 7.55–7.10 (5 H, m, ArH), 5.87 (1 H, d, *J* 7.1, NH, exchanges with D_2O), 4.85 (1 H, dt, *J* 6.3 and 6.6, CHN), 3.55 (1 H, dd, *J* 5.7 and 17.3, CH_AH_BCO), 3.45 (1 H, dd, *J* 6.4 and 17.3, CH_AH_BCO) and 2.33 (3 H, s, Ar*Me*); $\delta_C(CDCl_3)$ 197.7, 143.2, 139.9, 137.3, 129.6, 128.8, 128.1, 127.3, 126.8, 54.4, 44.9 and 21.5; *m*/*z* (EI) 319 (0.1%, M^+), 260 (15, $PhCH_2NHTs$), 241 (5, $TsNC_2H_3CO_2H$), 224 (32, $TsNC_2H_3CO$), 155 (35, Ts), 105 (PhCHNH) and 91 (100, C_7H_7).

Dimethyl(phenyl){3-[*N*-(*p*-tolysulfonyl)amino]propionyl}-silane 29. A yellow oil (−78 °C, 2 h, 0 °C, 4 h, 56%); R_f (EtOAc–hexane, 20:80) 0.22; ν_{max}(film)/cm^{-1} 3288 (NH), 3069 (CH), 1639 (C=O), 1598 (Ar), 1329 (SO_2N), 1252 (C–O), 1161 (SO_2N), 1112 ($SiMe_2Ph$), 1093 (S=O), 815 (*p*-substituted Ar) and 703 (Ar); δ_H(250 MHz; $CDCl_3$) 7.70 (2 H, d, *J* 8.3, ArH *o* to SO_2), 7.60–7.20 (7 H, m, ArH *o* to Me and other ArH), 5.05 (1 H, t, *J* 6.4, NH), 3.05 (2 H, dt, *J* 6.4 and 5.5, $NHCH_2$), 2.77 (2 H, t, *J* 5.5, CH_2CO), 2.41 (3 H, s, Ar*Me*) and 0.45 (6 H, s, $SiMe_2$); δ_C(100 MHz; $CDCl_3$) 208.5, 143.4, 137.0, 133.9, 133.1, 130.2, 129.7, 128.6, 127.1, 47.6, 37.2, 21.5 and −5.1; *m*/*z* (CI) 362 (22%, M^+ + 1), 345 (20, M − Me − H), 284 (100, M − Ph), 226 (42, $TsNHC_2H_4CO$), 195 (90, $TsNC_2H_2$), 155 (20, Ts), 135 (70, $PhMe_2Si$) and 91 (60, C_7H_7) (Found: M^+ + 1, 362.1237. $C_{18}H_{23}NO_3SSi$ requires *M* + 1, 362.1246).

***trans*-3-Phenylprop-2-en-1-ol 31.** Prisms, mp 30–32 °C (lit.,[20] 33–35 °C) (0 °C, 5 h, 78%); R_f (EtOAc–hexane, 30:70) 0.15; $\nu_{max}(CHCl_3)/cm^{-1}$ 3372 (OH), 3016 (CH), 1599 (Ph), 916 (Ph) and 695 (Ph); δ_H(400 MHz; $CDCl_3$) 7.60–7.00 (5 H, m, ArH), 6.60 (1 H, d, *J* 15.9, PhC*H*=CH), 6.35 (1 H, dt, *J* 5.7 and 15.9, PhCH=C*H*), 4.20 (2 H, dd, *J* 1.5 and 5.7, CH_2OH) and 1.75 (1 H, s, OH); *m*/*z* (EI) 134 (70%, MM^+), 117 (100, M − OH), 105 (40, PhC_2H_4), 91 (75, C_7H_7) and 78 (80, Ph).

***trans*-Stilbene 32**

Potassium hydride [50% slurry in oil, 0.1 g, washed with light petroleum (3 × 5 cm^3) and dried under reduced pressure, 1.25 mmol] and (1*RS*,2*SR*)- or (1*RS*,2*RS*)-2-dimethyl(phenyl)silyl-1,2-diphenyl-*N*-(*p*-tolylsulfonyl)ethylamine **15** or **17** (150 mg, 0.29 mmol) were refluxed in dry THF (4 cm^3) for 8 h. The reaction was quenched with cold aqueous ammonium chloride (5 cm^3 of a 10% solution) and ether (5 cm^3). The ether layer was separated, dried ($MgSO_4$) and concentrated under reduced pressure. The residue was flash chromatographed (SiO_2, EtOAc–hexane, 20:80) to give the alkene. Prisms, mp 121–122 °C (from $CHCl_3$–light petroleum 50:50) (lit.,[21] 123–124 °C) (76% from **15**; 83% from **17**); R_f (EtOAc–hexane, 20:80) 0.68; ν_{max}(Nujol)/cm^{-1} 3032 (CH), 3018 (CH), 1598 (Ph), 961 (Ph), 763 (monosubstituted Ph) and 691 (monosubstituted Ph); δ_H(250 MHz; $CDCl_3$) 7.60–7.20 (10 H, m, Ph), 7.11 (2 H, s, C*H*=C*H*); $\delta_C(CDCl_3)$ 133.0, 128.7, 127.7 and 126.5; identical with an authentic sample.

Silyl-to-hydroxy conversions

Typically, tetrabutylammonium fluoride in THF (1 mol dm^{-3}, 1.07 cm^3, 1.07 mmol) and the silane (0.24 mmol) were refluxed in dry tetrahydrofuran (2 cm^3) for 1 h. Potassium fluoride (43 mg, 0.73 mmol), sodium hydrogen carbonate (25 mg, 0.24 mmol), dry methanol (2 cm^3) and hydrogen peroxide (0.25 ml, 2.44 mmol of a 30% w/v solution) were added, and the mixture was refluxed for 2 h. The mixture was diluted with aqueous sodium hydrogen carbonate (10 cm^3) and extracted with ether (3 × 10 cm^3). The combined organic layers were dried ($MgSO_4$), and evaporated under reduced pressure, and the residue flash chromatographed (SiO_2, hexane–diethyl ether, 50:50) to give the alcohol. The following alcohols were prepared by this method.

2-Phenyl-2-[*N*-(*p*-tolysulfonyl)amino]ethanol 33.[22] As an oil (76%); R_f (hexane–diethyl ether, 50:50) 0.15; ν_{max}(Nujol)/cm^{-1} 3371 (OH), 3154 (NH), 3068 (CH), 3029 (CH), 1599 (Ph), 1336 (SO_2N), 1251 (C–O), 1161 (SO_2N), 1093 (=O) and 814 (*p*-substituted Ar); δ_H(250 MHz; $CDCl_3$) 7.60 (2 H, d, *J* 8.3, ArH *o* to SO_2), 7.40–7.00 (7 H, m, ArH *o* to Me and other ArH), 5.20 (1 H, d, *J* 6.8, NH), 4.60 (1 H, dt, *J* 7.0 and 12.1, C*H*NH), 4.20 (1 H, dd, *J* 11.6 and 14.3, CH_AH_B), 4.10 (1 H, dd, *J* 7.1 and 14.4, CH_AH_B), 2.38 (3 H, s, Ar*Me*) and 1.60 (1 H, s, OH).

***trans*-2-[*N*-(*p*-Tolysulfonyl)amino]cyclohexanol 34.**[23] (81%); R_f (hexane–Et_2O, 50:50) 0.15; ν_{max}(Nujol)/cm^{-1} 3465 (OH), 3253 (NH), 3018 (CH), 1598 (Ar), 1335 (SO_2N), 1158 (SO_2N), 1035 (S=O) and 817 (*p*-substituted Ar); δ_H(250 MHz; $CDCl_3$) 7.80 (2 H, d, *J* 8.3, ArH *o* to SO_2), 7.30 (2 H, d, *J* 8.1, ArH *o* to Me), 4.92 (1 H, s, NH), 3.28 (1 H, dt, *J* 4.6 and 9.7, C*H*NH), 2.82 (1 H, m, C*H*OH), 2.42 (3 H, s, Ar*Me*), 2.0 (1 H, s, OH), 1.80–1.50 (2 H, m, cyclohexyl-CH) and 1.40–0.80 (6 H, m, cyclohexyl-CH); $\delta_C(CDCl_3)$ 143.6, 137.4, 129.8, 127.2, 73.4, 55.0, 33.4, 31.9, 24.7, 23.8 and 21.6.

***exo*-*N*-(*p*-Tolysulfonyl)bicyclo[2.2.1]heptan-2-ylamine**

Tetrabutylammonium fluoride in tetrahydrofuran (1 mol dm^{-3}, 0.25 cm^3, 0.25 mmol) and *exo*-*N*-{2-[dimethyl(phenyl)silyl]-4-methylphenylsulfonyl}bicyclo[2.2.1]heptan-2-ylamine **23** (20 mg, 0.05 mmol) were kept in dry tetrahydrofuran (2 cm^3) under argon at room temperature for 24 h. Saturated ammonium chloride solution (2 cm^3) was added and the mixture extracted with ether (3 × 10 cm^3). The extract was dried ($MgSO_4$), concentrated under reduced pressure and the residue chromatographed (SiO_2, EtOAc–hexane, 20:80) to give the sulfonamide[24] (11.5 mg, 86%), mp 129–130 °C (from $CHCl_3$–light petroleum, 50:50); R_f (EtOAc–hexane, 20:80) 0.23; ν_{max}(Nujol)/cm^{-1} 3267 (NH), 1597 (Ar), 1322 (SO_2N), 1158 (SO_2N), 1090 (S=O) and 811 (*p*-substituted Ar); δ_H(400 MHz; $CDCl_3$) 7.75 (2 H, d, *J* 8.3, ArH *o* to SO_2), 7.30 (2 H, d, *J* 8.0, ArH *o* to Me), 4.72 (1 H, d, *J* 7.2, NH, exchanges with D_2O), 3.10 (1 H, dt, *J* 7.5 and 3.4, C*H*NH), 2.42 (3 H, s, Ar*Me*), 2.15 (1 H, d, *J* 4.1, H-1), 2.05 (1 H, d, *J* 3.5, H-4), 1.55 (1 H, ddd, *J* 2.3, 8.0 and 10.0, norbornyl-H), 1.45–1.25 (3 H, m, norbornyl-H) and 1.20–0.95 (4 H, m, norbornyl-H); $\delta_C(CDCl_3)$ 143.2, 138.0, 129.7, 127.1, 56.7, 42.5, 40.8, 35.6, 35.2, 28.0, 26.3 and 21.5. Identical (mp, IR, ^1H NMR and ^{13}C NMR) with a sample prepared (93%) by tosylation of commercially available *exo*-2-norbornylamine.

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