# Convenient syntheses of chiral 3-substituted 2-ethynylaziridines

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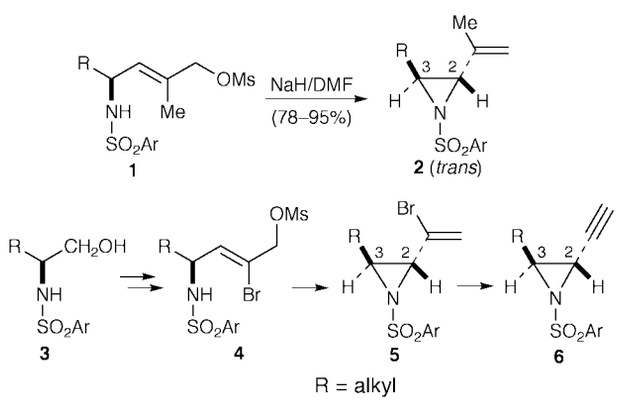
Two convenient methods for the synthesis of chiral 2-ethynylaziridines from natural α-amino acids are described. Sodium hydride-promoted aziridination of mesylates of 4-arylsulfonylamino-2-bromoalk-2-en-1-ols yields *trans*-2-(1-bromovinyl)aziridines in a highly stereoselective manner, and subsequent dehydrobromination of the aziridines by potassium *tert*-butoxide gives separable stereoisomeric mixtures of *trans*- and *cis*-2-ethynylaziridines in enantiomerically pure forms (>98% ee). Simple synthesis of 2-ethynylaziridines with high optical purities (91–98% ee) from chiral amino alcohols bearing an ethynyl group under Mitsunobu conditions is also presented.

Activated aziridines constitute an interesting class of compounds because of their high electrophilicity enabling them to undergo ring-opening reactions with a wide variety of nucleophiles in a stereoselective manner.[1,2] Particularly, activated or unactivated aziridines bearing an alkenyl group on one of the aziridine-ring carbon atoms have proven to be extremely valuable intermediates. Alkenylaziridines function as useful substrates for such carbon–carbon bond-forming reactions as the organocopper-mediated $S_N2'$ reaction,[3] aza-2,3-Wittig rearrangement,[4] palladium(0)-catalyzed carbonylation,[5] and thermal pyrrolysis.[6] These reactions provide efficient synthetic routes to (*E*)-alkene dipeptide isosteres,[3a–d] allylamines,[3e,f] indolizidine alkaloids,[4b,c] β-lactams,[5] and pyrrolizidine alkaloids.[6] However, relatively little investigation has been undertaken on the synthesis and reactivity of 2-ethynylaziridines, although these compounds could serve as potentially useful building blocks for the stereoselective synthesis of allenes or alkynes bearing an amino group. Recently, Dai and co-workers have reported the synthesis of racemic 2-ethynylaziridines by the reaction of *N*-tosylimines with sulfonium ylide.[7a] They also reported an asymmetric version of this reaction in moderate to good enantioselectivities (14–85% ee) by use of D-(+)-camphor-derived sulfonium ylide.[7b,c]

As part of an ongoing program aimed at the stereoselective synthesis and reaction of chiral amino allenes,[8,9] we required a reliable and efficient method for synthesizing 2-ethynylaziridines with high optical purity.[10]

Based on our recent successful results on the efficient and stereoselective synthesis of *trans*-2-alkenylaziridines of the type **2** from mesylates of *N*-protected (*E*)-4-amino-2-alkylalk-2-en-1-ols like **1** by treatment with sodium hydride in DMF,[11] it was our expectation to be able to synthesize 2-alkynylaziridines **6** *via* intermediates **4** and **5** in a stereoselective manner starting from readily available *N*-protected amino alcohols **3** as shown in Scheme 1. In principle, reaction of the bromo mesylate **4** with bases such as sodium hydride and potassium hydride could afford *trans*-2-(1-bromoethenyl)aziridine **5** predominantly or exclusively. Subsequent dehydrobromination of **5** with such bases as potassium *tert*-butoxide would produce the target alkynylaziridine **6**. In this paper we detail a synthetic method for the preparation of enantiopure 2-alkynylaziridines based on the above-described chemistry.[10] In addition, a simple and convenient synthesis of 2-ethynylaziridines from *N*-protected 4-aminoalk-1-yn-3-ols following the Mitsunobu procedure is also presented.




**Scheme 1**

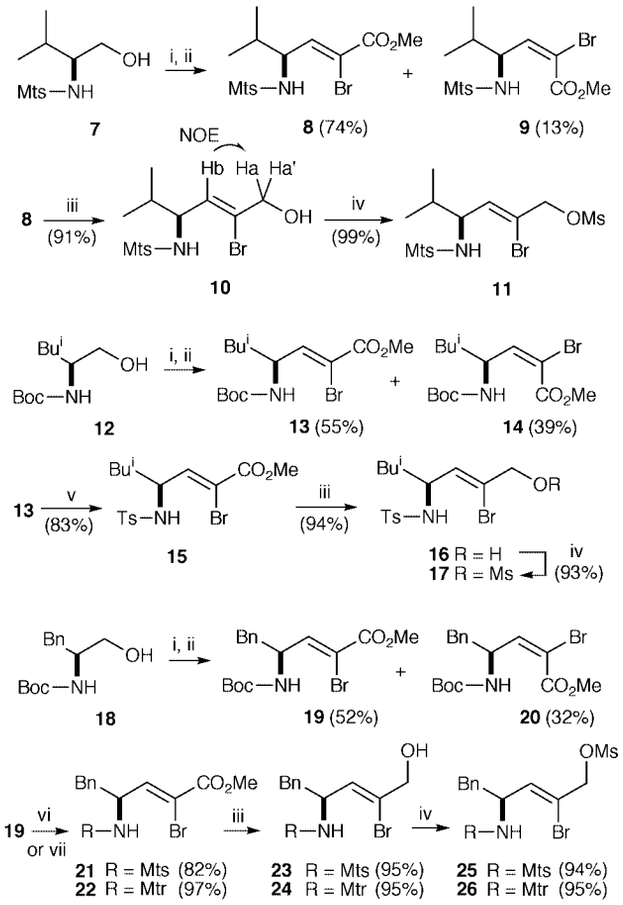
## Results and discussion

### 1. Synthesis of the mesylates of brominated allylic alcohols

For the synthesis of alkynylaziridines, an efficient preparative method for allylic mesylates bearing a bromo group on the double bond is required as synthetic intermediates. As shown in Scheme 2, the requisite chiral mesylates (**11**, **17**, **25**, and **26**) of the corresponding *N*-arylsulfonylamino alcohols (**10**, **16**, **23**, and **24**) were prepared in acceptable yields starting from the *N*-protected amino alcohols (**7**, **12**, and **18**) which were readily available from natural (*S*)-α-amino acids.[12]

Typically, (*S*)-*N*-arylsulfonyl valinol **7** was treated successively with oxalyl chloride–DMSO–*N,N*-diisopropylethylamine and the bromo-ylide $[Ph_3P{=}C(Br)CO_2Me]$[13] to afford a 74:13 mixture of the (*Z*)- and (*E*)-enoates **8** and **9** in 87% combined yield which were separated by flash chromatography. Reduction of the (*Z*)-enoate **8** with DIBAL-H yielded the allylic alcohol **10**, which can be readily converted into the mesylate **11** following the standard procedure. In a similar manner, the allylic mesylates **17** and (**25** and **26**) were readily prepared from the corresponding *N*-protected amino alcohols **12** and **18**.

Configurational assignments of the double bond geometry in α,β-unsaturated esters of type **8** and **9** were rather difficult. However, it turned out that the determination of configurations can be readily done by the use of allylic alcohols or their mesylates. For example, irradiation of the signals of the vinylic proton at $\delta$ 5.91 (Hb in structure **10**) led to a 1.6% NOE enhancement of the signals of one of the methylene protons at $\delta$ 4.21 (Ha in structure **10**). In contrast, no NOE enhancement



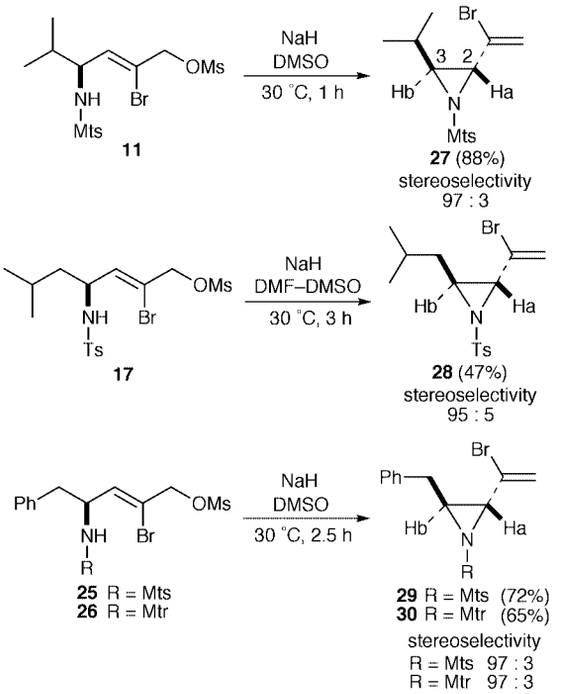
**Scheme 2** *Reagents*: i, $(COCl)_2$–DMSO–(*i*-Pr)$_2$NEt; ii, $Ph_3P{=}C(Br)$-$CO_2Me$; iii, DIBAL; iv, $MeSO_2Cl$–$Et_3N$; v, TFA, then TsCl–$Et_3N$; vi, TFA, then MtsCl–$Et_3N$; vii, TFA, then MtrCl–$Et_3N$. *Abbreviations*: Mts = 2,4,6-trimethylbenzenesulfonyl; Mtr = 4-methoxy-2,3,6-trimethylbenzenesulfonyl; Ts = *p*-tolylsulfonyl.

between the vinylic proton and one of the methylene protons was observed in the (*E*)-isomeric alcohol of **10**. By using similar $^1$H NMR analyses, configurational assignments for other allylic alcohols **16**, **23**, and **24** as well as the mesylates **17**, **25**, and **26** were unambiguously made.

It should be noted that the reaction of some aldehydes bearing an *N*-arylsulfonylamino group with the bromo-ylide [$Ph_3P{=}C(Br)CO_2Me$] gave poorer results. For example, reaction of (*S*)-*N*-(2,4,6-trimethylphenylsulfonyl)phenylalaninal with the bromo-ylide gave a 97 : 3 inseparable mixture of (*Z*)- and (*E*)-enoate in only 28% combined yield. On the other hand, treatment of (*S*)-*N*-Boc-leucinal and (*S*)-*N*-Boc-phenylalaninal with the same bromo-ylide gave the corresponding bromo esters (**13** and **14**) and (**19** and **20**) in high combined yields.

## 2. Aziridination reaction of the *N*-protected amino allylic mesylates with sodium hydride

Based on the previous synthetic studies of alkenylaziridines from the corresponding allylic mesylates,[11] we anticipated that 3-alkyl-2-(1-bromovinyl)aziridines of the type **27** could easily be prepared from the corresponding allylic mesylates of the type **11** (Scheme 3). However, this was not to be the case. The reaction could not be completed even after prolonged reaction time (20 h). After considerable experimentation, we found that improved yields in the aziridine ring-forming reaction could be obtained by the use of sodium hydride in DMSO or mixed solvents containing DMSO. As illustrated in Scheme 3, except for the bromo aziridine **28**, other aziridines (**27**, **29**, and **30**) were obtained from the corresponding allylic mesylates (**11**, **25**, and **26**) in both acceptable yields and high diastereoselectivities. Typically, the treatment of **11** with sodium hydride (1.2 equiv.) in DMSO at 30 °C gave a mixture of the bromo aziridine **27** and its *cis*-isomer. Analysis by HPLC or $^1$H NMR indicated a 97 : 3 ratio of diastereomers in favor of *trans*-isomer **27** as expected.[11b]



**Scheme 3**

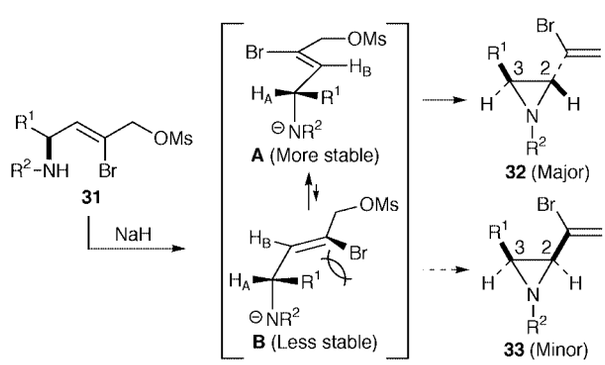


**Fig. 1**

The stereostructure of the major aziridines (**27**–**30**) was proved to be *trans* by $^1$H NMR analysis. We have previously reported that *trans*-2-(alk-1-enyl)aziridines show smaller $J_{Hab}$ values ($J$ = *ca.* 4.0 Hz) than those of the *cis*-isomers ($J$ = *ca.* 7.0 Hz).[11,12] The aziridines (**27**–**30**) show $J_{Hab}$ values of 3.8–4.3 Hz, which indicate the configuration of these compounds is *trans*.

It should be clearly noted that, in all cases examined, separation of *trans*-2-ethynylaziridines (**27**–**30**) from the corresponding *cis*-isomers was quite difficult. Only two *trans*-aziridines **28** and **29** could be isolated in a pure state by repeated flash chromatographic separation.

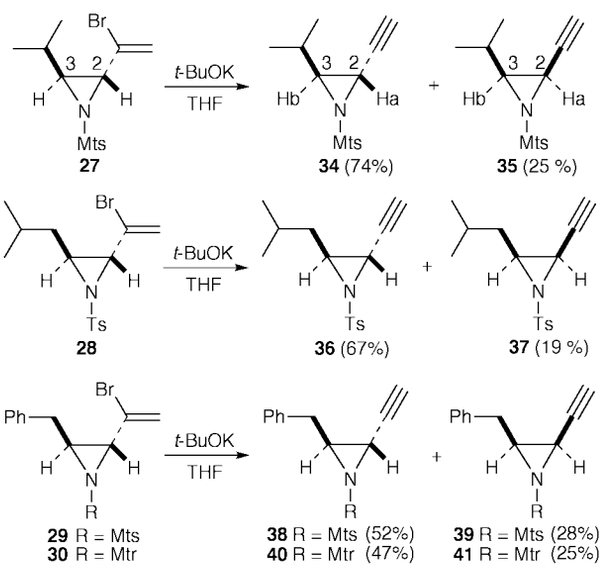
The predominant formation of *trans*-bromo aziridines (**27**–**30**) could be rationalized considering the 1,3-allylic strain of two aza-anionic intermediates **A** and **B** (Fig. 1). Although the ground state and the reactive conformer are not necessarily the same, the ground state conformations of various olefinic molecules containing the alkene moiety play an important role in the stereochemical outcome of π-facial selectivity.[14] If the reaction conformers are as depicted in **A** and **B**, the higher diastereoselectivity is readily understood. Examination of the non-bonded interactions in the conformers **A** and **B** reveals that in conformer **B**, which could lead to the *cis*-isomer **33** *via* the $S_N2'$ pathway, a substantial non-bonded interaction does exist to

destabilize this conformer. Thus, an aziridine ring-forming reaction would proceed preferentially from the more abundant conformer **A** to yield *trans*-aziridines **32** predominantly.

### 3. Dehydrobromination reaction of *trans*-2-(1-bromovinyl)-aziridines with potassium *tert*-butoxide

Having synthesized the four bromo aziridines (**27**–**30**), we next investigated the dehydrobromination reaction for the synthesis of 2-ethynylaziridines.

Exposure of pure bromo aziridine **29** to *t*-BuOK in THF unexpectedly gave a separable 65 : 35 mixture of *trans*- and *cis*-ethynylaziridines **38** and **39** in 80% combined yield. Consequently, without separating the mixtures of bromo aziridines, all the *trans*- and *cis*-mixtures (*trans* : *cis* = 95–97 : 5–3) were dehydrobrominated to yield the corresponding ethynylaziridines (*trans* : *cis* = 65–77 : 35–23) in good to excellent yields. The results are listed in Scheme 4. It should be clearly noted




**Scheme 4**

that, among various reaction conditions, only *t*-BuOK in THF gave satisfactory results. In addition, separation of the four stereoisomeric pairs of the 2-ethynylaziridines (**34** and **35**), (**36** and **37**), (**38** and **39**), and (**40** and **41**) was accomplished quite easily by flash chromatography.

As will be discussed later in more detail, *cis*- and *trans*-configurations of 2-ethynylaziridines were readily determined by $^1$H NMR analysis (*cis*: $J_{Hab}$ = 6.2–7.0 Hz; *trans*: $J_{Hab}$ = 3.2–4.2 Hz).

The formation of *cis*-2-alkynylaziridines as minor products from the corresponding *trans*-2-(1-bromovinyl)aziridines could be rationalized in the following way. Firstly, treatment of the ethynylaziridine **34** with *t*-BuOK under otherwise identical reaction conditions to those of dehydrobromination (−78→ 0 °C, 30 min) resulted in complete recovery of unchanged starting material. Secondly, treatment of **27** with *t*-BuOK in THF containing 5 equiv. of *t*-BuOD gave a mixture of *trans*- and *cis*-2-ethynylaziridines as expected. Although no evidence was obtained of the incorporation of deuterium in the C-2 position of *trans*-2-ethynylaziridine **34**, it is found that *ca*. 10% of deuterium was incorporated at the C-2 position of *cis*-2-ethynylaziridine **35**.

Although the details of the dehydrobromination reactions have still not been elucidated, we are working under the assumption that both paths B and C are involved as depicted in Fig. 2. If deprotonation of bromo aziridine **27** by *t*-BuOK occurs at the vinylic position (path C), it will produce only the *trans*-ethynylaziridine **34** and if it proceeds only by path B, it

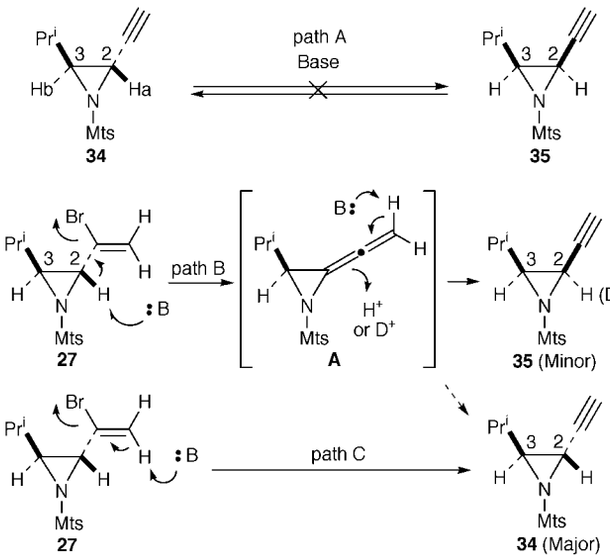



**Fig. 2**

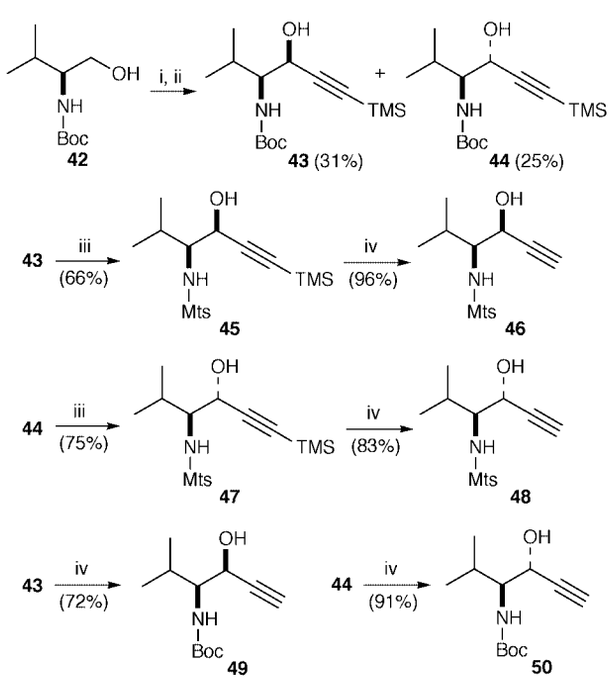
will generate either only *trans*-**34** or *cis*-**35** or a mixture of both *via* an allenic intermediate **A**. Considering the fact that the *trans*-isomer **34** was isolated as the major product, we propose that the reaction of the bromo aziridine **27** proceeds *via* two competitive paths B and C to yield *trans*- and *cis*-ethynylaziridines **34** and **35**.

Enantiopurities of all the ethynylaziridines (**34**–**41**) have been determined by HPLC with a chiral stationary phase (CHIRALCEL OD and/or OJ column; hexane : propan-2-ol = 98.5–93 : 1.5–7). It was shown that all compounds were found to be essentially enantiopure (ee >98%).[15]

### 4. Synthesis of 2-ethynylaziridines under Mitsunobu conditions

We next investigated the simple synthesis of 2-ethynylaziridines from amino alcohols bearing an ethynyl group under Mitsunobu conditions.

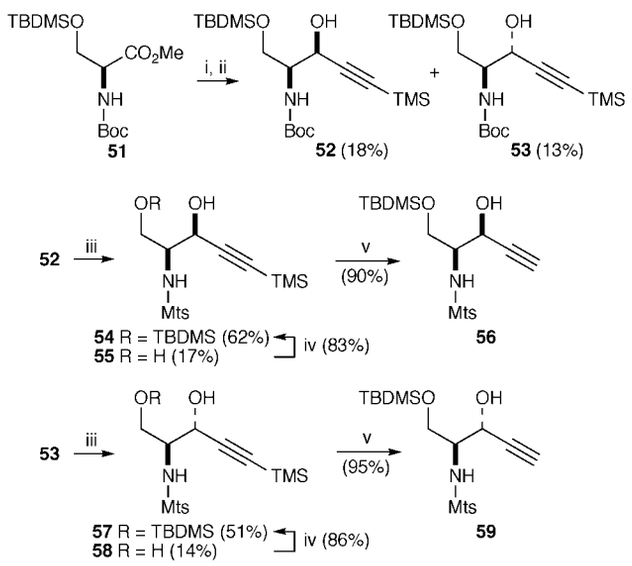
The requisite amino alcohols (**43**, **44**, **46**, **48**, **49**, and **50**) were synthesized by a sequence of reactions as shown in Scheme 5. Typically, (*S*)-*N*-Boc-valinal derived from (*S*)-*N*-Boc-valinol




**Scheme 5** *Reagents*: i, $(COCl)_2$–DMSO–$(i\text{-Pr})_2$NEt; ii, *n*-BuLi–trimethylsilylacetylene; iii, TFA, then MtsCl–$Et_3N$; iv, TBAF.

**42**[3f] was treated with trimethylsilylacetylide to give a separable stereoisomeric mixture of amino alcohols **43** and **44** in low yields. For reasons unknown, however, the yields of products were not improved. The *N*-Boc protecting group in **43** and **44** can be readily replaced by the *N*-(2,4,6-trimethylphenylsulfonyl) (Mts) group by treatment with trifluoroacetic acid (TFA) followed by MtsCl and $Et_3N$ to yield the corresponding products **45** and **47** in good yields. Exposure of **43**, **44**, **45**, and **47** to tetrabutylammonium fluoride ($Bu_4NF$) in THF afforded the desilylation products **49**, **50**, **46**, and **48**, respectively, in good to high yields (see the Experimental section).

As shown in Scheme 6, the *N*-Mts amino alcohols (**54**, **56**, **57**,

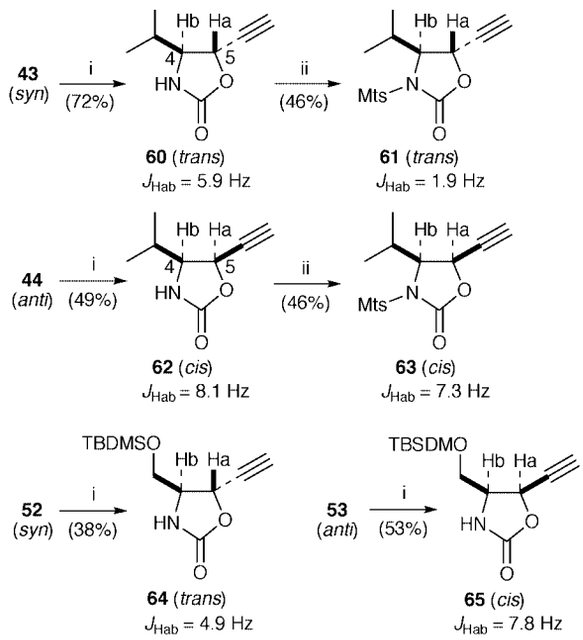



**Scheme 6** *Reagents*: i, DIBAL; ii, *n*-BuLi–trimethylsilylacetylene; iii, TFA, then MtsCl–$Et_3N$; iv, TBDMSCl–imidazole; v, NaOMe(cat)–MeOH. *Abbreviations*: TBDMS = *tert*-butyldimethylsilyl.

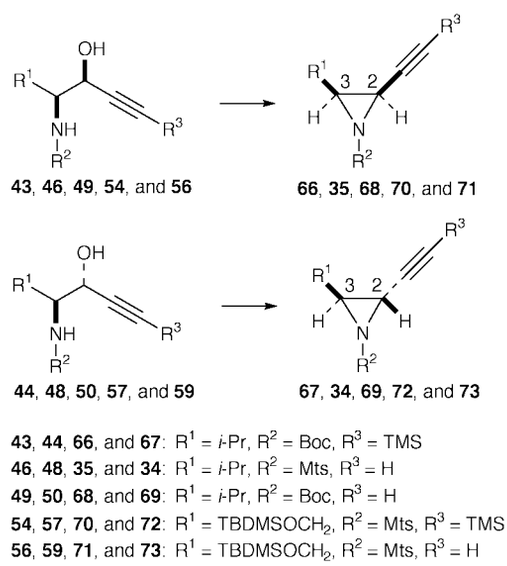
and **59**) were prepared from (*S*)-*N*-Boc-serine derivative **51**[16] by a sequence of reactions. Thus, reduction of **51** with DIBAL-H followed by treatment with lithium trimethylsilylacetylide yielded a separable mixture of *syn*- and *anti*-alcohols **52** and **53**. Not unexpectedly, deprotection of the *N*-Boc group in **52** with TFA followed by treatment with MtsCl–$Et_3N$ gave a 62 : 17 mixture of two products **54** and **55**. The latter compound **55** could be readily converted into the former **54** by following the standard silylation procedure. Finally, the alcohol **56** can be obtained in high yield from **54** by selective removal of the trimethylsilyl group by exposure to a catalytic amount of sodium methoxide in MeOH. In a similar manner, the requisite ethynyl amino alcohols **57** and **59** were prepared from the *anti*-amino alcohol **53**.

Stereostructural assignments for the synthesized diastereomeric amino alcohols (**43** and **44**) and (**52** and **53**) were readily made by transformation into three sets of two stereoisomeric oxazolidinone derivatives (**60** and **62**), (**61** and **63**), (**64** and **65**). As can be seen from Scheme 7, the *trans*-oxazolidinones (**60**, **61**, and **64**) show $J_{Hab}$ values ($J$ = 1.9–5.9 Hz) smaller than the $J_{Hab}$ values ($J$ = 7.3–8.1 Hz) of the corresponding *cis*-isomers (**62**, **63**, and **65**). The data are in good agreement with $^1$H NMR data for related oxazolidinones.[12,16]

Next, we investigated aziridination reactions of ethynyl amino alcohols under Mitsunobu conditions. The results are summarized in Scheme 8 and Table 1. Typically, treatment of **43** with triphenylphosphine and diethyl azodicarboxylate in THF at 25 °C for 0.5 h yielded the *cis*-2-ethynylaziridine **66** in 96% yield (entry 1, Table 1). In all cases, the ethynyl amino alcohols were effectively cyclized into the corresponding ethynylaziridines in good to excellent yields. However, aziridination reaction of *N*-Boc amino alcohols (**43**, **44**, **49**, and **50**: entries 1, 2, 5,




**Scheme 7** *Reagents*: i, NaH; ii, NaH–MtsCl.




**Scheme 8**

and 6 in Table 1) proceeded more slowly at 0 °C than that of the *N*-Mts derivatives (**46**, **48**, **54**, **56**, **57**, and **59**; 0 °C; entries 3, 4, and 7–10 in Table 1). Notably, the cyclization reaction of the *anti*-amino alcohols **44** and **50** required 2 h at 25 °C to give the expected *trans*-aziridines **70** and **71** in rather low yields (73 and 64% respectively; entries 2 and 6).

Although the compounds **34**, **35**, **46**, and **48** synthesized from (*S*)-valinol derivative **42** were essentially enantiomerically pure (>98% ee), the compounds such as **56**, **57**, **59**, **72**, and **73** prepared from methyl (*S*)-serinate derivative **51** were not optically pure (91–97% ee).

Table 2 lists spin–spin coupling constants for $J_{Hab}$ of the *cis*- and *trans*-3-alkyl-2-ethynylaziridines. As can be seen from Table 2, the *cis*-aziridines show $J_{Hab}$ values ($J$ = 6.2–7.0 Hz: entries 1–10, Table 2) larger than the $J_{Hab}$ values ($J$ = 3.2–4.3 Hz: entries 11–18, Table 2) of the *trans*-isomers. The data for 2-ethynylaziridines are in good agreement with $^1$H NMR data for 2-ethenylaziridines.[12]

## 5. Cross-coupling reaction at the terminal position of the ethynyl group of 2-ethynylaziridines with some electrophiles

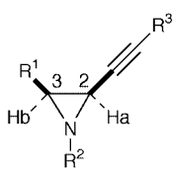
Finally, substitution reaction of the ethynylaziridines **34** and **35**

**Table 1** Synthesis of 2-ethynylaziridines from amino alcohols under Mitsunobu conditions[a]

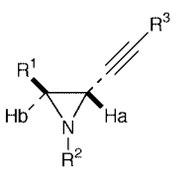
| Entry | Substrate | $R^1$ | $R^2$ | $R^3$ | *T*/°C | *t*/h | Product | *cis*/*trans* | Yield[b](%) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | **43** | *i*-Pr | Boc | TMS | 25 | 0.5 | **66** | *cis* | 96 |
| 2 | **44** | *i*-Pr | Boc | TMS | 25 | 2.0 | **67** | *trans* | 73 |
| 3 | **46** | *i*-Pr | Mts | H | 0 | 0.5 | **35** | *cis* | 97 |
| 4 | **48** | *i*-Pr | Mts | H | 0 | 0.5 | **34** | *trans* | 98 |
| 5 | **49** | *i*-Pr | Boc | H | 25 | 0.5 | **68** | *cis* | 87 |
| 6 | **50** | *i*-Pr | Boc | H | 25 | 2.0 | **69** | *trans* | 64 |
| 7 | **54** | $TBDMSOCH_2$ | Mts | TMS | 0 | 0.5 | **70** | *cis* | 94 |
| 8 | **56** | $TBDMSOCH_2$ | Mts | H | 0 | 0.5 | **71** | *cis* | 96 |
| 9 | **57** | $TBDMSOCH_2$ | Mts | TMS | 0 | 0.5 | **72** | *trans* | 99 |
| 10 | **59** | $TBDMSOCH_2$ | Mts | H | 0 | 0.5 | **73** | *trans* | 95 |

[a] All reactions were carried out in THF using diethyl azodicarboxylate (1.2–2.0 equiv.) and triphenylphosphine (1.2–2.0 equiv.). [b] Isolated yields.

**Table 2** Spin–spin coupling constants for $J_{Hab}$ of the *cis*- and *trans*-2-ethynylaziridines in $CDCl_3$[a]



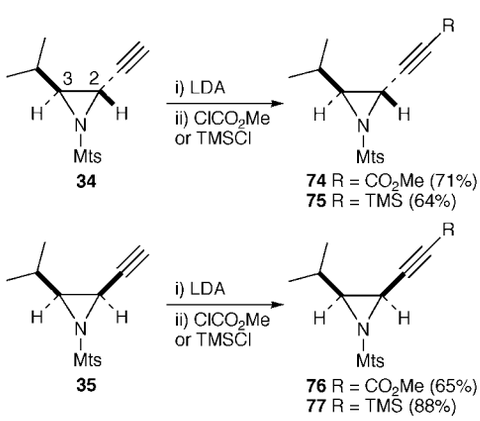

**A** (*cis*)




**B** (*trans*)

| Entry | Compound | $R^1$ | $R^2$ | $R^3$ | *cis*/*trans* | $J_{Hab}$ |
|---|---|---|---|---|---|---|
| 1 | **35** | *i*-Pr | Mts | H | *cis* | 6.8 |
| 2 | **37** | *i*-Bu | Ts | H | *cis* | 7.0 |
| 3 | **39** | Bn | Mts | H | *cis* | 6.8 |
| 4 | **41** | Bn | Mtr | H | *cis* | 6.8 |
| 5 | **66** | *i*-Pr | Boc | TMS | *cis* | 6.2 |
| 6 | **68** | *i*-Pr | Boc | H | *cis* | 6.5 |
| 7 | **70** | $TBDMSOCH_2$ | Mts | TMS | *cis* | 6.8 |
| 8 | **71** | $TBDMSOCH_2$ | Mts | H | *cis* | 7.0 |
| 9 | **76** | *i*-Pr | Mts | $CO_2Me$ | *cis* | 7.0 |
| 10 | **77** | *i*-Pr | Mts | TMS | *cis* | 6.8 |
| 11 | **34** | *i*-Pr | Mts | H | *trans* | 4.2 |
| 12 | **36** | *i*-Bu | Ts | H | *trans* | 3.8 |
| 13 | **38** | Bn | Mts | H | *trans* | 3.8 |
| 14 | **40** | Bn | Mtr | H | *trans* | 4.1 |
| 15 | **67** | *i*-Pr | Boc | TMS | *trans* | 3.2 |
| 16 | **69** | *i*-Pr | Boc | H | *trans* | 3.2 |
| 17 | **72** | $TBDMSOCH_2$ | Mts | TMS | *trans* | 4.3 |
| 18 | **73** | $TBDMSOCH_2$ | Mts | H | *trans* | 4.3 |
| 19 | **74** | *i*-Pr | Mts | $CO_2Me$ | *trans* | [b] |
| 20 | **75** | *i*-Pr | Mts | TMS | *trans* | [b] |

[a] All $^1H$ NMR spectra were recorded in $CDCl_3$ at 300 K. For designations of Ha and Hb, see structures A and B. [b] *J* values were unreadable because of an overlap of the two signals, Ha and Hb.




**Scheme 9**

at the acetylene terminus was briefly investigated (Scheme 9). Treatment of **34** with LDA at −78 °C for 1 h followed by addition of methyl chloroformate or chlorotrimethylsilane gave **74** or **75** in good yields. Similarly, *cis*-2-ethynylaziridine **35** was converted into the terminally-substituted ethynylaziridines **76** and **77**. From the above experimentation, it is apparent that lithium aziridinylacetylides are stable at −78 °C for at least a short period of time and they are reactive to undergo nucleophilic attack to methyl chloroformate or chlorotrimethylsilane at −78 °C.

In summary, we have developed two procedures for the preparation of *cis*- and *trans*-2-ethynylaziridines from natural α-amino acids. Exposure of brominated allylic mesylates to NaH in DMSO gives *trans*-2-(1-bromovinyl)aziridines stereoselectively in good yield, which could be easily transformed into separable mixtures of *cis*- and *trans*-2-ethynylaziridines (>98% ee) by treatment with *t*-BuOK in THF. Alternatively, cyclization of amino alcohols bearing an ethynyl group under Mitsunobu conditions also gives 2-ethynylaziridines efficiently (91–98% ee). The synthesized compounds could serve as useful synthetic intermediates to chiral allenes and acetylenes bearing an amino group, and we are now undertaking synthetic studies involving this class of compounds.

## Experimental

### General methods

The instrumentation has been described previously.[16] All reactions were carried out under a positive pressure of argon. All glassware and syringes were dried in an electric oven at 100 °C prior to use. All melting points are uncorrected. $^1$H NMR spectra were recorded using a JEOL EX-270 (270 MHz) or Bruker AC-300 (300 MHz) spectrometer in $CDCl_3$. Chemical shifts are reported in parts per million downfield from internal $Me_4Si$. *J* Values are given in Hz. For flash chromatography, silica gel 60 H (silica gel for thin-layer chromatography, Merck) or silica gel 60 (finer than 230 mesh, Merck) was employed. For the determination of optical purity, Chiralcel OD and OJ (DAICEL, 4.6 × 260 mm) was used. For reversed-phase HPLC, μ-Bondasphere–C-18 (3.9 × 150 mm, Waters) was employed (28 °C).

### General procedure for the preparation of *E*/*Z* pairs of methyl 4-amino-2-bromo-2-enoates (8 and 9), (13 and 14), and (19, and 20) from amino alcohols (7, 12, and 18). Methyl (4*S*,2*Z*)-2-bromo-5-methyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]hex-2-enoate 8 and its (4*S*,2*E*) isomer 9

To a stirred solution of oxalyl chloride (2.6 cm$^3$, 27.2 mmol) in a mixed solvent of $CHCl_3$ (25 cm$^3$) and *n*-hexane (20 cm$^3$) at −78 °C under argon was added dropwise a solution of DMSO (10.6 cm$^3$, 150 mmol) in $CHCl_3$ (15 cm$^3$). After 30 min, a solution of the alcohol **7** (8.56 g, 30 mmol) in $CHCl_3$ (15 cm$^3$) was added to the above reagent at −78 °C, and the mixture was stirred for 1 h. Diisopropylethylamine (36.6 cm$^3$, 210 mmol) was added to the above solution at −78 °C and the mixture was stirred for 30 min with warming to 0 °C. Saturated aqueous citric acid (40 cm$^3$) was added to the mixture and the whole was extracted with $Et_2O$. The extract was washed successively with water, 5% $NaHCO_3$, and water, and dried over $MgSO_4$. Usual workup gave a crude aldehyde, which was dissolved in $CHCl_3$ (40 cm$^3$). Bromo ylide [$Ph_3P$=C(Br)$CO_2Me$; 12.4 g, 30 mmol] was added to the above solution at 0 °C, and the mixture was stirred for 15 h at this temperature. Concentration under reduced pressure gave an oily residue, which was flash chromatographed over silica gel. Elution with *n*-hexane–EtOAc (4 : 1) gave **9** (1.59 g, 12.7%) and further elution yielded **8** (9.3 g, 74% yield). Compound **8**: 98% ee (*S*) by HPLC [Daicel Chiralcel OD, *n*-hexane : propan-2-ol = 95 : 5 (0.5 cm$^3$ min$^{-1}$), (*R*)-isomer 28.9 min, (*S*)-isomer 36.7 min]; colourless crystals, mp 112 °C (from $Et_2O$) (Found: C, 48.8; H, 5.8; N, 3.4. $C_{17}H_{24}BrNO_4S$ requires C, 48.8; H, 5.8; N, 3.35%); $[a]_D^{20}$ +20.9 (*c* 1.15 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.91 (3 H, d, *J* 6.8, CMe), 0.95 (3 H, d, *J* 7.0, CMe), 1.84–1.97 (1 H, m, 5-H), 2.27 (3 H, s, CMe), 2.63 (6 H, s, 2 × CMe), 3.75 (3 H, s, OMe), 4.02 (1 H, ddd, *J* 9.2, 8.6 and 5.9, 4-H), 4.81 (1 H, d, *J* 8.6, NH), 6.83 (1 H, d, *J* 9.2, 3-H), 6.91 (2 H, s, Ph). Compound **9**: 98% ee (*S*) by HPLC [Daicel Chiralcel OD, *n*-hexane : propan-2-ol = 97 : 3 (0.5 cm$^3$ min$^{-1}$), (*R*)-isomer 39.4 min, (*S*)-isomer 41.8 min]; colourless crystals, mp 135 °C (from $Et_2O$) (Found: C, 48.75; H, 5.75; N, 3.4. $C_{17}H_{24}BrNO_4S$ requires C, 48.8; H, 5.8; N, 3.35%); $[a]_D^{20}$ −60.1 (*c* 1.53 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.90 (3 H, d, *J* 7.0, CMe), 0.94 (3 H, d, *J* 7.0, CMe), 1.75–1.88 (1 H, m, 5-H), 2.30 (3 H, s, CMe), 2.59 (6 H, s, 2 × CMe), 3.74 (3 H, s, OMe), 4.50 (1 H, ddd, *J* 10.0, 8.9 and 5.9, 4-H), 4.73 (1 H, d, *J* 8.9, NH), 6.22 (1 H, d, *J* 10.0, 3-H), 6.93 (2 H, s, Ph).

### General procedure for the preparation of allylic alcohols (10, 16, 23, and 24). (4*S*,2*Z*)-2-Bromo-5-methyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]hex-2-en-1-ol 10

DIBAL-H (1.0 M solution in toluene; 209 cm$^3$, 209 mmol) was added dropwise to a stirred solution of the enoate **8** (25 g, 59.8 mmol) in a mixed solvent of toluene (150 cm$^3$) and $CHCl_3$ (60 cm$^3$) at −78 °C under argon. After stirring for 3 h with warming to −20 °C, a saturated $NH_4Cl$ solution (30 cm$^3$) was added with vigorous stirring. The mixture was made acidic with saturated citric acid and extracted with EtOAc. The extract was washed successively with water and $NaHCO_3$, and dried over $MgSO_4$. The usual workup followed by recrystallization from *n*-hexane–EtOAc (1 : 1) gave the title compound **10** (21.9 g, 94% yield) as colourless crystals, mp 104 °C (Found: C, 49.1; H, 6.3; N, 3.5. $C_{16}H_{24}BrNO_3S$ requires C, 49.2; H, 6.2; N, 3.6%); $[a]_D^{19}$ +44.6 (*c* 0.866 in $CHCl_3$); $\delta_H$ (300 MHz, $CDCl_3$; 258 K) 0.76 (3 H, d, *J* 6.8, CMe), 0.81 (3 H, d, *J* 6.8, CMe), 1.65–1.76 (1 H, m, 5-H), 2.33 (3 H, s, CMe), 2.68 (6 H, s, 2 × CMe), 3.31–3.38 (1 H, m, OH), 3.95 (1 H, ddd, *J* 9.0, 8.3 and 5.8, 4-H), 4.08 (1 H, dd, *J* 14.4 and 6.9, 1-C*H*H), 4.21 (1 H, dd, *J* 14.4 and 6.5, 1-CH*H*), 5.78 (1 H, d, *J* 8.3, NH), 5.91 (1 H, *J* 9.0, 3-H), 6.99 (2 H, s, Ph).

### General procedure for the preparation of allylic methanesulfonates (11, 17, 25, and 26). (4*S*,2*Z*)-2-Bromo-*O*-methylsulfonyl-5-methyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]hex-2-en-1-ol 11

To a stirred mixture of the alcohol **10** (3.12 g, 8 mmol) and $Et_3N$ (5.53 cm$^3$, 40 mmol) in THF (15 cm$^3$) was added dropwise methanesulfonyl chloride (2.17 cm$^3$, 28 mmol) at −78 °C. The mixture was stirred for 1 h with warming to 0 °C. Saturated aqueous $NaHCO_3$ (5 cm$^3$) was added with vigorous stirring. The whole was extracted with EtOAc and the extract was washed successively with 5% citric acid, water, 5% $NaHCO_3$, and water, and dried over $MgSO_4$. Usual workup followed by flash chromatography over silica gel with *n*-hexane–EtOAc (1 : 1) gave the title compound **11** (3.71 g, 99% yield) as colourless crystals, mp 86 °C (from $Et_2O$) (Found: C, 43.4; H, 5.5; N, 3.0. $C_{17}H_{26}BrNO_5S_2$ requires C, 43.6; H, 5.6; N, 3.0%); $[a]_D^{18}$ +30.2 (*c* 1.32 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.88 (3 H, d, *J* 6.8, CMe), 0.92 (3 H, d, *J* 7.0, CMe), 1.78–1.90 (1 H, m, 5-H), 2.31 (3 H, s, CMe), 2.64 (6 H, s, 2 × CMe), 3.04 (3 H, s, $SO_2Me$), 3.94 (1 H, ddd, *J* 8.9, 8.6 and 6.2, 4-H), 4.52–4.62 (2 H, m, 1-$CH_2$), 4.76 (1 H, d, *J* 6.2, NH), 5.86 (1 H, d, *J* 8.9, 3-H), 6.95 (2 H, s, Ph).

### Methyl (4*S*,2*Z*)-2-bromo-4-[*N*-(*tert*-butoxycarbonyl)amino]-6-methylhept-2-enoate 13 and its (4*S*,2*E*) isomer 14

By a procedure identical with that described for the preparation of the enoates **8** and **9** from **7**, the alcohol **12** (13.7 g, 63 mmol) was converted into the title compound **13** (12.2 g, 55% yield) and **14** (8.49 g, 39% yield). Compound **13**: colourless crystals, mp 71 °C (from *n*-hexane) (Found: C, 47.9; H, 7.1; N, 3.9. $C_{14}H_{24}BrNO_4$ requires C, 48.0; H, 6.9; N, 4.0%); $[a]_D^{28}$ +43.3 (*c* 1.08 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.96 (3 H, d, *J* 6.8, CMe), 0.98 (3 H, d, *J* 6.5, CMe), 1.30–1.45 (2 H, m, 5-$CH_2$), 1.44 (9 H, s, $CMe_3$), 1.61–1.74 (1 H, m, 6-H), 3.83 (3 H, s, OMe), 4.50–4.65 (2 H, m, 4-H and NH), 7.13 (1 H, d, *J* 6.6, 3-H). Compound **14**: colourless crystals, mp 91 °C (from *n*-hexane) (Found: C, 47.9; H, 6.7; N, 3.9. $C_{14}H_{24}BrNO_4$ requires C, 48.0; H, 6.9; N, 4.0%); $[a]_D^{28}$ −3.0 (*c* 1.37 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.93 (3 H, d, *J* 6.8, CMe), 0.97 (3 H, d, *J* 6.8, CMe), 1.35–1.50 (2 H, m, 5-$CH_2$), 1.43 (9 H, s, $CMe_3$), 1.60–1.75 (1 H, m, 6-H), 3.84 (3 H, s, OMe), 4.56 (1 H, br s, NH), 4.88–5.02 (1 H, m, 4-H), 6.50 (1 H, d, *J* 8.9, 3-H).

### General procedure for the preparation of *N*-arenesulfonamide (15, 21, 22, 45, 47, 54, 57) from the corresponding *N*-Boc derivatives. Methyl (4*S*,2*Z*)-2-bromo-6-methyl-4-[*N*-(4-methylphenylsulfonyl)amino]hept-2-enoate 15

Trifluoroacetic acid (20 cm$^3$) was added to a stirred solution of the enoate **13** (6.75 g, 19 mmol) in $CHCl_3$ (20 cm$^3$) at 0 °C, and the mixture was stirred for 1 h at this temperature. The mixture was concentrated to an oil under reduced pressure, which was made alkaline with 28% $NH_4OH$ at 0 °C and extracted with

$CHCl_3$. The extract was washed with water, and dried over $MgSO_4$. Usual workup gave an oily residue. To a stirred mixture of the oil and $Et_3N$ (5 $cm^3$, 36 mmol) in $CHCl_3$ (100 $cm^3$) was added toluene-*p*-sulfonyl chloride (4.3 g, 24.7 mmol) at 0 °C, and the mixture was stirred for 1 h at this temperature, followed by quenching with aqueous 5% $NaHCO_3$ (20 $cm^3$). The mixture was made acidic with saturated aqueous citric acid, and the whole was extracted with $Et_2O$. The extract was washed successively with water, aqueous 5% $NaHCO_3$, and water, and dried over $MgSO_4$. Usual workup followed by recrystallization from *n*-hexane–$Et_2O$ (4:1) gave the title compound **15** (6.49 g, 83% yield). 98% ee (*S*) by HPLC [Daicel Chiralcel OD, *n*-hexane : propan-2-ol = 95 : 5 (0.5 $cm^3$ $min^{-1}$), (*S*)-isomer 37.9 min]; colourless needles, mp 115 °C [from *n*-hexane–$Et_2O$ (4:1)] (Found: C, 47.6; H, 5.5; N, 3.4. $C_{16}H_{22}BrNO_4S$ requires C, 47.5; H, 5.5; N, 3.5%); $[a]_D^{30}$ −42.7 (*c* 1.19 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.80 (3 H, d, *J* 6.2, CMe), 0.89 (3 H, d, *J* 6.5, CMe), 1.27 (1 H, ddd, *J* 13.8, 8.6 and 5.1, 5-C*H*H), 1.45 (1 H, ddd, *J* 13.8, 9.5 and 5.4, 5-CH*H*), 1.55–1.72 (1 H, m, 6-H), 2.41 (3 H, s, CMe), 3.75 (3 H, s, OMe), 4.19–4.31 (1 H, m, 4-H), 4.91 (1 H, d, *J* 7.6, NH), 6.86 (1 H, d, *J* 8.6, 3-H), 7.26–7.29 (2 H, m, Ph), 7.74–7.77 (2 H, m, Ph).

### (4*S*,2*Z*)-2-Bromo-6-methyl-4-[*N*-(4-methylphenylsulfonyl)-amino]hept-2-en-1-ol 16

By a procedure identical with that described for the preparation of the alcohol **10** from **8**, the enoate **15** (6.48 g, 16 mmol) was converted into the title compound **16** (5.67 g, 94% yield) as colourless crystals, mp 119 °C (from $Et_2O$) (Found: C, 48.2; H, 5.8; N, 3.6. $C_{15}H_{22}BrNO_3S$ requires C, 47.9; H, 5.9; N, 3.7%); $[a]_D^{30}$ +11.6 (*c* 1.46 in $CHCl_3$); $\delta_H$ (300 MHz, $CDCl_3$) 0.78 (3 H, d, *J* 6.5, CMe), 0.86 (3 H, d, *J* 6.6, CMe), 1.26 (1 H, ddd, *J* 13.9, 8.0 and 6.2, 5-C*H*H), 1.41 (1 H, ddd, *J* 13.9, 8.5 and 6.0, 5-CH*H*), 1.52–1.65 (1 H, m, 6-H), 2.08 (1 H, br s, OH), 2.43 (3 H, s, CMe), 3.99 (1 H, dd, *J* 14.4 and 1.1, 1-C*H*H), 4.03 (1 H, dd, *J* 14.4 and 1.1, 1-CH*H*), 4.13–4.24 (1 H, m, 4-H), 4.89 (1 H, d, *J* 7.4, NH), 5.74 (1 H, ddd, *J* 8.6, 1.1 and 1.1, 3-H), 7.28–7.32 (2 H, m, Ph), 7.75–7.80 (2 H, m, Ph).

### (4*S*,2*Z*)-2-Bromo-*O*-methylsulfonyl-6-methyl-4-[*N*-(4-methyl-phenylsulfonyl)amino]hept-2-en-1-ol 17

By a procedure identical with that described for the preparation of the mesylate **11** from **10**, the alcohol **16** (5.67 g, 15.1 mmol) was converted into the title compound **17** (6.37 g, 93% yield) as colourless needles, mp 139 °C [from $CHCl_3$–$Et_2O$ (1:9)] (Found: C, 42.3; H, 5.3; N, 3.0. $C_{16}H_{24}BrNO_5S_2$ requires C, 42.3; H, 5.3; N, 3.1%); $[a]_D^{30}$ +13.4 (*c* 0.984 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.76 (3 H, d, *J* 6.2, CMe), 0.86 (3 H, d, *J* 6.5, CMe), 1.24 (1 H, ddd, *J* 14.0, 8.4 and 5.7, 5-C*H*H), 1.41 (1 H, ddd, *J* 14.0, 8.9 and 5.4, 5-CH*H*), 1.51–1.66 (1 H, m, 6-H), 2.44 (3 H, s, CMe), 3.05 (3 H, s, $SO_2Me$), 4.10–4.22 (1 H, m, 4-H), 4.610 (1 H, d, *J* 13.2, 1-C*H*H), 4.614 (1 H, d, *J* 13.2, 1-CH*H*), 4.97 (1 H, d, *J* 7.3, NH), 5.92 (1 H, d, *J* 8.6, 3-H), 7.29–7.33 (2 H, m, Ph), 7.74–7.78 (2 H, m, Ph).

### 2-[*N*-(*tert*-Butoxycarbonyl)amino]-3-phenylpropan-1-ol 18

To a stirred solution of (*S*)-phenylalaninol[17] (14 g, 92.6 mmol) and $Et_3N$ (25.6 $cm^3$, 185 mmol) in DMF (60 $cm^3$) was added $Boc_2O$ (20.2 g, 92.6 mmol) at 0 °C, and the mixture was stirred for 1 h at this temperature. Water (40 $cm^3$) was added to the mixture and the whole was extracted with $Et_2O$, and the extract was washed successively with 5% citric acid, water, 5% $NaHCO_3$, and water, and dried over $MgSO_4$. Usual workup followed by recrystallization from *n*-hexane–EtOAc (4:1) gave the title compound **18** (20.2 g, 87% yield) as colourless needles, mp 92 °C [from *n*-hexane–EtOAc (4:1)] (Found: C, 66.95; H, 8.65; N, 5.9. $C_{14}H_{21}NO_3$ requires C, 66.9; H, 8.4; N, 5.6%); $[a]_D^{31}$ −24.2 (*c* 0.756 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 1.41 (9 H, s, $CMe_3$), 2.65 (1 H, br s, OH), 2.82–2.85 (2 H, m, 3-$CH_2$), 3.54 (1 H, dd, *J* 10.8 and 5.4, 1-C*H*H), 3.65 (1 H, dd, *J* 10.8 and 3.8, 1-CH*H*), 3.80–3.93 (1 H, m, 2-H), 4.82 (1 H, br s, NH), 7.19–7.33 (5 H, m, Ph).

### Methyl (4*S*,2*Z*)-2-bromo-4-[*N*-(*tert*-butoxycarbonyl)amino]-5-phenylpent-2-enoate 19 and its (4*S*,2*E*) isomer 20

By a procedure identical with that described for the preparation of the enoates **8** and **9** from **7**, the alcohol **18** (28.4 g, 113 mmol) was converted into the title compound **19** (23.6 g, 54% yield) and **20** (14.2 g, 33% yield). Compound **19**: colourless needles, mp 133–135 °C [from *n*-hexane–EtOAc (5:1)] (Found: C, 53.0; H, 5.7; N, 3.6. $C_{17}H_{22}BrNO_4$ requires C, 53.1; H, 5.8; N, 3.6%); $[a]_D^{28}$ +56.3 (*c* 0.742 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 1.39 (9 H, s, $CMe_3$), 2.80–2.95 (1 H, m, 5-C*H*H), 2.96 (1 H, dd, *J* 13.8 and 4.9, 5-CH*H*), 3.83 (3 H, s, OMe), 4.60–4.79 (2 H, m, 4-H and NH), 7.18–7.36 (6 H, m, Ph and 3-H). Compound **20**: colourless needles, mp 124 °C [from *n*-hexane–EtOAc (5:1)] (Found: C, 53.0; H, 5.6; N, 3.65. $C_{17}H_{22}BrNO_4$ requires C, 53.1; H, 5.8; N, 3.6); $[a]_D^{28}$ +34.2 (*c* 1.30 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 1.38 (9 H, s, $CMe_3$), 2.81–2.96 (1 H, m, 5-C*H*H), 2.97 (1 H, dd, *J* 13.2 and 5.1, 5-CH*H*), 3.82 (3 H, s, OMe), 4.62 (1 H, br s, NH), 5.07–5.18 (1 H, m, 4-H), 6.62 (1 H, d, *J* 8.9, 3-H), 7.20–7.36 (5 H, m, Ph).

### Methyl (4*S*,2*Z*)-2-bromo-5-phenyl-4-[*N*-(2,4,6-trimethyl-phenylsulfonyl)amino]pent-2-enoate 21

By a procedure similar to that described for the preparation of **15** from **13**, the enoate **19** (10.0 g, 26 mmol) was converted into the title compound **21** (10.0 g, 82% yield). 98% ee (*S*) by HPLC [Daicel Chiralcel OD, *n*-hexane : propan-2-ol = 95 : 5 (0.5 $cm^3$ $min^{-1}$), (*S*)-isomer 59.4 min]; colourless needles, mp 109 °C [from *n*-hexane–$Et_2O$–$CHCl_3$ (3:1:1)] (Found: C, 53.95; H, 5.3; N, 2.9. $C_{21}H_{24}BrNO_4S$ requires C, 54.1; H, 5.2; N, 3.0%); $[a]_D^{28}$ −2.13 (*c* 0.937 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 2.28 (3 H, s, CMe), 2.34 (6 H, s, 2 × CMe), 2.68 (1 H, dd, *J* 13.8 and 9.2, 5-C*H*H), 2.96 (1 H, dd, *J* 13.8 and 4.6, 5-CH*H*), 3.80 (3 H, s, OMe), 4.17–4.27 (1 H, m, 4-H), 4.68–4.74 (1 H, m, NH), 6.84 (2 H, s, Ph), 7.02–7.06 (2 H, m, Ph), 7.17 (1 H, d, *J* 7.8, 3-H), 7.20–7.29 (3 H, m, Ph).

### Methyl (4*S*,2*Z*)-2-bromo-4-[*N*-(4-methoxy-2,3,6-trimethyl-phenylsulfonyl)amino]-5-phenylpent-2-enoate 22

By a procedure similar to that described for the preparation of **15** from **13**, the enoate **19** (14 g, 36.4 mmol) was converted into the title compound **22** (17.5 g, 97% yield) as colourless crystals, mp 142 °C [from *n*-hexane–EtOAc (5:2)] (Found: C, 53.05; H, 5.2; N, 2.5. $C_{22}H_{26}BrNO_5S$ requires C, 53.2; H, 5.3; N, 2.8%); $[a]_D^{28}$ +4.43 (*c* 1.31 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 2.02 (3 H, s, CMe), 2.09 (3 H, s, CMe), 2.53 (3 H, s, CMe), 2.67 (1 H, dd, *J* 13.8 and 9.2, 5-C*H*H), 2.95 (1 H, dd, *J* 13.8 and 4.3, 5-CH*H*), 3.79 (3 H, s, OMe), 3.85 (3 H, s, OMe), 4.19 (1 H, dddd, *J* 9.2, 8.4, 4.9 and 4.3, 4-H), 4.67 (1 H, d, *J* 4.9, NH), 6.52 (1 H, s, Ph), 7.03–7.08 (2 H, m, Ph), 7.11 (1 H, d, *J* 8.4, 3-H), 7.20–7.27 (3 H, m, Ph).

### (4*S*,2*Z*)-2-Bromo-5-phenyl-4-[*N*-(2,4,6-trimethylphenyl-sulfonyl)amino]pent-2-en-1-ol 23

By a procedure identical with that described for the preparation of the alcohol **10** from **8**, the enoate **21** (9.95 g, 21.3 mmol) was converted into the title compound **23** (8.85 g, 95% yield) as colourless crystals, mp 142 °C [from $CHCl_3$–$Et_2O$ (1:2)] (Found: C, 54.8; H, 5.6; N, 3.1. $C_{20}H_{24}BrNO_3S$ requires C, 54.8; H, 5.5; N, 3.2%); $[a]_D^{28}$ +24.6 (*c* 0.926 in $CHCl_3$); $\delta_H$ (300 MHz, $CDCl_3$) 2.04 (1 H, dd, *J* 7.0 and 6.9, OH), 2.29 (3 H, s, CMe), 2.39 (6 H, s, 2 × CMe), 2.67 (1 H, dd, *J* 13.9 and 8.8, 5-C*H*H), 2.92 (1 H, dd, *J* 13.9 and 5.0, 5-CH*H*), 4.03–4.16 (2 H, m, 1-$CH_2$), 4.24 (1 H, dddd, *J* 8.8, 8.1, 5.3 and 5.0, 4-H), 4.69 (1 H,

d, *J* 5.3, NH), 5.91 (1 H, ddd, *J* 8.1, 1.3 and 1.3, 3-H), 6.85–6.87 (2 H, m, Ph), 7.04–7.07 (2 H, m, Ph), 7.21–7.25 (3 H, m, Ph).

**(4*S*,2*Z*)-2-Bromo-4-[*N*-(4-methoxy-2,3,6-trimethylphenylsulfonyl)amino]-5-phenylpent-2-en-1-ol 24**

By a procedure identical with that described for the preparation of the alcohol **10** from **8**, the enoate **22** (17.4 g, 35 mmol) was converted into the title compound **24** (15.5 g, 95% yield) as colourless crystals, mp 126 °C (from $Et_2O$) (Found: C, 53.8; H, 5.6; N, 2.7. $C_{21}H_{26}BrNO_4S$ requires C, 53.85; H, 5.6; N, 3.0%); $[a]_D^{29}$ +31.5 (*c* 1.06 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 2.04 (3 H, s, CMe), 2.09 (3 H, s, CMe), 2.31–2.42 (1 H, m, OH), 2.55 (3 H, s, CMe), 2.64 (1 H, dd, *J* 13.8 and 9.2, 5-C*H*H), 2.90 (1 H, dd, *J* 13.8 and 4.6, 5-CH*H*), 3.86 (3 H, s, OMe), 4.05–4.20 (3 H, m, 1-$CH_2$ and 4-H), 4.71 (1 H, d, *J* 4.9, NH), 6.01 (1 H, d, *J* 8.4, 3-H), 6.53 (1 H, s, Ph), 7.01–7.06 (2 H, m, Ph), 7.17–7.25 (3 H, m, Ph).

**(4*S*,2*Z*)-2-Bromo-*O*-methylsulfonyl-5-phenyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]pent-2-en-1-ol 25**

By a procedure identical with that described for the preparation of the mesylate **11** from **10**, the alcohol **23** (701 mg, 1.6 mmol) was converted into the title compound **25** (776 mg, 94% yield) as colourless crystals, mp 106 °C [from $CHCl_3$–$Et_2O$ (1:2)] (Found: C, 48.8; H, 5.05; N, 2.7. $C_{21}H_{26}BrNO_5S_2$ requires C, 48.8; H, 5.1; N, 2.7%); $[a]_D^{30}$ +8.26 (*c* 1.03 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 2.30 (3 H, s, CMe), 2.35 (6 H, s, 2 × CMe), 2.68 (1 H, dd, *J* 13.8 and 8.9, 5-C*H*H), 2.92 (1 H, dd, *J* 13.8 and 4.9, 5-CH*H*), 3.04 (3 H, s, $SO_2Me$), 4.17 (1 H, dddd, *J* 8.9, 7.8, 5.1 and 4.9, 4-H), 4.64 (1 H, d, *J* 5.1, NH), 4.68–4.76 (2 H, m, 1-$CH_2$), 6.14 (1 H, d, *J* 7.8, 3-H), 6.86 (2 H, s, Ph), 7.02–7.06 (2 H, m, Ph), 7.20–7.28 (3 H, m, Ph).

**(4*S*,2*Z*)-2-Bromo-*O*-methylsulfonyl-4-[*N*-(4-methoxy-2,3,6-trimethylphenylsulfonyl)amino]-5-phenylpent-2-en-1-ol 26**

By a procedure identical with that described for the preparation of the mesylate **11** from **10**, the alcohol **24** (15.4 g, 32.9 mmol) was converted into the title compound **26** (17.0 g, 95% yield) as colourless crystals, mp 101–103 °C (from $Et_2O$) (Found: C, 48.05; H, 5.2; N, 2.4. $C_{22}H_{28}BrNO_6S_2$ requires C, 48.35; H, 5.2; N, 2.6%); $[a]_D^{28}$ +13.2 (*c* 1.59 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 2.03 (3 H, s, CMe), 2.07 (3 H, s, CMe), 2.53 (3 H, s, CMe), 2.66 (1 H, dd, *J* 13.8 and 9.2, 5-C*H*H), 2.91 (1 H, dd, *J* 13.8 and 4.9, 5-CH*H*), 3.05 (3 H, s, $SO_2Me$), 3.86 (3 H, s, OMe), 4.12 (1 H, dddd, *J* 9.2, 8.1, 4.9 and 4.6, 4-H), 4.64 (1 H, d, *J* 4.6, NH), 4.72–4.75 (2 H, m, 1-$CH_2$), 6.18 (1 H, d, *J* 8.1, 3-H), 6.54 (1 H, s, Ph), 7.01–7.06 (2 H, m, Ph), 7.19–7.29 (3 H, m, Ph).

**General procedure for aziridination of allylic mesylates (11, 17, 25 and 26) by exposure to sodium hydride in DMSO. (2*S*,3*S*)-2-(1-Bromovinyl)-3-isopropyl-*N*-(2,4,6-trimethylphenylsulfonyl)-aziridine 27 from the mesylate 11**

To a stirred suspension of NaH (328 mg, 8.2 mmol) in DMSO (14 $cm^3$) under argon was added a solution of the allylic mesylate **11** (3.2 g, 6.83 mmol) in DMSO (6 $cm^3$) at room temperature. After 1 h, the mixture was poured into ice–water saturated with $NH_4Cl$ (20 $cm^3$). The whole was extracted with $Et_2O$ and the extract was washed with water, and dried over $MgSO_4$. Usual workup followed by flash chromatography over silica gel with *n*-hexane–EtOAc (12:1) gave a 97:3 mixture (2.23 g, 88% combined yield) of the title compound **27** and (2*R*,3*S*) isomer. Compound **27** [as a mixture containing 3% of (2*R*,3*S*) isomer]: colourless oil [Found (FAB): $(M + H)^+$, 372.0630. $C_{16}H_{23}BrNO_2S$ requires *M* + H, 372.0633]; $[a]_D^{27}$ −5.50 (*c* 0.945 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 1.10 (3 H, d, *J* 6.8, CMe), 1.21 (3 H, d, *J* 6.8, CMe), 2.19–2.30 (1 H, m, $Me_2CH$), 2.30 (3 H, s, CMe), 2.57 (1 H, dd, *J* 9.5 and 4.3, 3-H), 2.71 (6 H, s, 2 × CMe), 3.39 (1 H, d, *J* 4.3, 2-H), 5.42 (1 H, d, *J* 1.9, C=C*H*H), 5.57 (1 H, dd, *J* 1.9 and 1.1, C=CH*H*), 6.94 (2 H, s, Ph); *m*/*z* (FAB) 374 ($MH^+$, $^{81}Br$), 372 ($MH^+$, $^{79}Br$), 318, 316, 190, 188, 183, 167, 119 (base peak), 91 and 55.

**(2*S*,3*S*)-2-(1-Bromovinyl)-3-(2-methylpropyl)-*N*-(4-methylphenylsulfonyl)aziridine 28**

By a procedure identical with that described for the preparation of the aziridine **27** from **11**, the mesylate **17** (2.9 g, 6.39 mmol) was converted into a 95:5 mixture (1.08 g, 47% combined yield) of the title compound **28** and its (2*R*,3*S*) isomer, by treatment with NaH in DMF–DMSO (3:1) at room temperature for 3 h. The major isomer **28** was isolated by repeated flash chromatography over silica gel with *n*-hexane–EtOAc (10:1). Compound **28**: colourless oil [Found (FAB): $(M + H)^+$, 358.0469. $C_{15}H_{21}BrNO_2S$ requires *M* + H; 358.0477]; $[a]_D^{30}$ +30.6 (*c* 1.40 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 1.02 (3 H, d, *J* 6.2, CMe), 1.03 (3 H, d, *J* 6.2, CMe), 1.73–1.93 (2 H, m, $Me_2CH$ and $Me_2CHCHH$), 2.21–2.29 (1 H, m, $Me_2CHCHH$), 2.44 (3 H, s, CMe), 2.82 (1 H, ddd, *J* 9.7, 4.3 and 3.8, 3-H), 3.42 (1 H, d, *J* 4.3, 2-H), 5.47 (1 H, d, *J* 1.9, C=C*H*H), 5.67 (1 H, dd, *J* 1.9 and 0.8, C=CH*H*), 7.30–7.34 (2 H, m, Ph), 7.83–7.86 (2 H, m, Ph); *m*/*z* (FAB) 360 ($MH^+$, $^{81}Br$), 358 ($MH^+$, $^{79}Br$), 204, 202, 155 (base peak), 139, 107 and 91.

**(2*S*,3*S*)-3-Benzyl-2-(1-bromovinyl)-*N*-(2,4,6-trimethylphenylsulfonyl)aziridine 29**

By a procedure identical with that described for the preparation of the aziridine **27** from **11**, the mesylate **25** (670 mg, 1.3 mmol) was converted into a 97:3 mixture (393 mg, 72% combined yield) of the title compound **29** and (2*R*,3*S*) isomer, by treatment with NaH in DMSO at 30 °C for 2.5 h. The major isomer **29** was isolated by repeated flash chromatography over silica gel with *n*-hexane–EtOAc (20:1). Compound **29**: colourless oil [Found (FAB): $(M + H)^+$, 420.0615. $C_{20}H_{23}BrNO_2S$ requires *M* + H, 420.0633]; $[a]_D^{31}$ +43.7 (*c* 0.856 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 2.31 (3 H, s, CMe), 2.72 (6 H, s, 2 × CMe), 2.99 (1 H, ddd, *J* 9.7, 4.1 and 3.8, 3-H), 3.29 (1 H, dd, *J* 14.6 and 9.7, PhC*H*H), 3.54 (1 H, dd, *J* 14.6 and 4.1, PhCH*H*), 3.64 (1 H, d, *J* 3.8, 2-H), 5.43 (1 H, d, *J* 2.2, C=C*H*H), 5.62 (1 H, dd, *J* 2.2 and 1.1, C=CH*H*), 6.96 (2 H, s, Ph), 7.22–7.36 (5 H, m, Ph); *m*/*z* (FAB) 422 ($MH^+$, $^{81}Br$), 420 ($MH^+$, $^{79}Br$), 238, 236, 183, 156, 119 (base peak) and 91.

**(2*S*,3*S*)-3-Benzyl-2-(1-bromovinyl)-*N*-(4-methoxy-2,3,6-trimethylphenylsulfonyl)aziridine 30**

By a procedure identical with that described for the preparation of the aziridine **27** from **11**, the mesylate **26** (16.4 g, 30 mmol) was converted into a 97:3 mixture (8.84 g, 65% combined yield) of the title compound **30** and its (2*R*,3*S*) isomer, by treatment with NaH in DMSO at 30 °C for 2.5 h. Compound **30** [as a mixture containing 3% of (2*R*,3*S*) isomer]: colourless oil [Found (FAB): $(M + H)^+$, 450.0714. $C_{21}H_{25}BrNO_3S$ requires *M* + H, 450.0739]; $[a]_D^{31}$ +33.7 (*c* 0.985 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 2.16 (3 H, s, CMe), 2.706 (3 H, s, CMe), 2.711 (3 H, s, CMe), 2.98 (1 H, ddd, *J* 10.0, 4.1 and 3.8, 3-H), 3.30 (1 H, dd, *J* 14.6 and 10.0, PhC*H*H), 3.52 (1 H, dd, *J* 14.6 and 4.1, PhCH*H*), 3.64 (1 H, d, *J* 3.8, 2-H), 3.86 (3 H, s, OMe), 5.44 (1 H, d, *J* 1.9, C=C*H*H), 5.66 (1 H, dd, *J* 1.9 and 1.1, C=CH*H*), 6.57 (1 H, s, Ph), 7.22–7.35 (5 H, m, Ph); *m*/*z* (FAB) 452 ($MH^+$, $^{81}Br$), 450 ($MH^+$, $^{79}Br$), 238, 236, 213, 197, 150, 149 (base peak), 119 and 91.

**General procedure for the dehydrobromination of 2-(1-bromovinyl)aziridines (27, 28, 29, and 30) by exposure to *t*-BuOK in THF. (2*S*,3*S*)-2-Ethynyl-3-isopropyl-*N*-(2,4,6-trimethylphenylsulfonyl)aziridine 34 and its (2*R*,3*S*) isomer 35 from 27**

To a stirred solution of *t*-BuOK (1.5 g, 13.4 mmol) in THF (15 $cm^3$) under argon was added a solution of the aziridine **27** (2.5

g, 6.71 mmol) in THF (10 cm³) at −78 °C. The mixture was stirred for 30 min with warming to 0 °C and the mixture was made acidic with saturated citric acid. Concentration under reduced pressure gave a residual oil, which was extracted with $Et_2O$. The extract was washed with water, and dried over $MgSO_4$. Usual workup followed by flash chromatography over silica gel with *n*-hexane–EtOAc (10:1) gave, in order of elution, ethynylaziridine **35** (0.496 g, 25% yield) and **34** (1.44 g, 74% yield). Compound **34**: 98% ee (2*S*,3*S*) by HPLC [Daicel Chiralcel OD, *n*-hexane:propan-2-ol = 98.5:1.5 (0.5 cm³ min⁻¹), (2*S*,3*S*)-isomer 25.9 min, (2*R*,3*R*)-isomer 28.7 min]; colourless crystals, mp 73 °C [from *n*-hexane–$Et_2O$ (10:1)] (Found: C, 65.7; H, 7.2; N, 4.6. $C_{16}H_{21}NO_2S$ requires C, 65.95; H, 7.3; N, 4.8%); $[\alpha]_D^{18}$ −20.5 (*c* 0.440 in $CHCl_3$); $\delta_H$ (300 MHz, $CDCl_3$) 0.71 (3 H, d, *J* 6.7, CMe), 0.90 (3 H, d, *J* 6.8, CMe), 1.42–1.54 (1 H, m, $Me_2CH$), 2.30 (3 H, s, CMe), 2.48 (1 H, d, *J* 2.0, C≡CH), 2.72 (6 H, s, 2 × CMe), 2.96 (1 H, dd, *J* 7.0 and 4.2, 3-H), 2.99 (1 H, dd, *J* 4.2 and 2.0, 2-H), 6.94–6.96 (2 H, m, Ph). Compound **35**: 98% ee (2*R*,3*S*) by HPLC [Daicel Chiralcel OJ, *n*-hexane:propan-2-ol = 98.5:1.5 (0.5 cm³ min⁻¹), (2*R*,3*S*)-isomer 15.8 min, (2*S*,3*R*)-isomer 17.7 min]; colourless crystals, mp 70 °C [from *n*-hexane–$Et_2O$ (5:1)] (Found: C, 65.85; H, 7.3; N, 4.7. $C_{16}H_{21}NO_2S$ requires C, 65.95; H, 7.3; N, 4.8%); $[\alpha]_D^{24}$ −61.6 (*c* 0.941 in $CHCl_3$); $\delta_H$ (300 MHz, $CDCl_3$) 0.84 (3 H, d, *J* 6.7, CMe), 1.00 (3 H, d, *J* 6.4, CMe), 1.55–1.68 (1 H, m, $Me_2CH$), 2.16 (1 H, d, *J* 1.9, C≡CH), 2.31 (3 H, s, CMe), 2.55 (1 H, dd, *J* 9.7 and 6.8, 3-H), 2.70 (6 H, s, 2 × CMe), 3.36 (1 H, dd, *J* 6.8 and 1.9, 2-H), 6.95–6.98 (2 H, m, Ph).

### (2*S*,3*S*)-2-Ethynyl-*N*-(4-methylphenylsulfonyl)-3-(2-methylpropyl)aziridine 36 and its (2*R*,3*S*) isomer 37

By a procedure identical with that described for the preparation of the 2-ethynylaziridines **34** and **35** from **27**, the 2-(1-bromovinyl)aziridine **28** (900 mg, 2.51 mmol) was converted into the ethynylaziridines **36** (465 mg, 67% yield) and **37** (135 mg, 19% yield), by treatment with *t*-BuOK in THF at −78→−20 °C for 1 h. Compound **36**: 98% ee (2*S*,3*S*) by HPLC [Daicel Chiralcel OD, *n*-hexane:propan-2-ol = 98.5:1.5 (0.5 cm³ min⁻¹), (2*S*,3*S*)-isomer 38.2 min]; colourless oil [Found (FAB): $(M + H)^+$, 278.1211. $C_{15}H_{20}NO_2S$ requires *M* + H, 278.1215]; $[\alpha]_D^{30}$ +38.9 (*c* 0.812 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.90 (3 H, d, *J* 6.8, CMe), 0.94 (3 H, d, *J* 6.2, CMe), 1.34–1.45 (1 H, m, $Me_2CHCHH$), 1.52–1.71 (2 H, m, $Me_2CHCHH$ and $Me_2CH$), 2.45 (4 H, m, CMe and C≡CH), 2.97 (1 H, dd, *J* 3.8 and 1.9, 2-H), 3.09 (1 H, ddd, *J* 6.8, 6.8 and 3.8, 3-H), 7.32–7.35 (2 H, m, Ph), 7.86–7.89 (2 H, m, Ph); *m*/*z* (FAB) 278 ($MH^+$, base peak). Compound **37**: 98% ee (2*R*,3*S*) by HPLC [Daicel Chiralcel OJ, *n*-hexane:propan-2-ol = 93:7 (0.5 cm³ min⁻¹), (2*R*,3*S*)-isomer 20.9 min]; colourless oil [Found (FAB): $(M + H)^+$, 278.1223. $C_{15}H_{20}NO_2S$ *M* + H, 278.1215]; $[\alpha]_D^{30}$ −88.2 (*c* 0.839 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.920 (3 H, d, *J* 6.8, CMe), 0.923 (3 H, d, *J* 6.5, CMe), 1.48–1.54 (2 H, m, $Me_2CHCH_2$), 1.61–1.76 (1 H, m, $Me_2CH$), 2.20 (1 H, d, *J* 1.9, C≡CH), 2.45 (3 H, s, CMe), 2.95 (1 H, ddd, *J* 7.0, 6.5 and 6.5, 3-H), 3.32 (1 H, dd, *J* 7.0 and 1.9, 2-H), 7.33–7.37 (2 H, m, Ph), 7.82–7.86 (2 H, m, Ph); *m*/*z* (FAB) 278 ($MH^+$, base peak).

### (2*S*,3*S*)-3-Benzyl-2-ethynyl-*N*-(2,4,6-trimethylphenylsulfonyl)aziridine 38 and its (2*R*,3*S*) isomer 39

By a procedure identical with that described for the preparation of the 2-ethynylaziridines **34** and **35** from **27**, the 2-(1-bromovinyl)aziridine **29** (1.33 g, 3.16 mmol) was converted into the 2-ethynylaziridines **38** (558 mg, 52% yield) and **39** (302 mg, 28% yield), by treatment with *t*-BuOK in THF at −78→−20 °C for 1 h. Compound **38**: 98% ee (2*S*,3*S*) by HPLC [Daicel Chiralcel OD, *n*-hexane:propan-2-ol = 96:4 (0.5 cm³ min⁻¹), (2*S*,3*S*)-isomer 35.3 min]; colourless needles, mp 104 °C [from *n*-hexane–$Et_2O$ (1:1)] (Found: C, 70.85; H, 6.3; N, 3.8. $C_{20}H_{21}NO_2S$ requires C, 70.8; H, 6.2; N, 4.1%); $[\alpha]_D^{29}$ +9.76 (*c* 1.23 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 2.31 (3 H, s, CMe), 2.49 (1 H, d, *J* 2.2, C≡CH), 2.55 (6 H, s, 2 × CMe), 2.59 (1 H, dd, *J* 14.0 and 7.3, PhC*H*H), 3.01 (1 H, dd, *J* 14.0 and 4.3, PhCH*H*), 3.07 (1 H, dd, *J* 3.8 and 2.2, 2-H), 3.33 (1 H, ddd, *J* 7.3, 4.3 and 3.8, 3-H), 6.86 (2 H, s, Ph), 6.87–6.92 (2 H, m, Ph), 7.02–7.16 (3 H, m, Ph). Compound **39**: 98% ee (2*R*,3*S*) by HPLC [Daicel Chiralcel OJ, *n*-hexane:propan-2-ol = 97:3 (0.5 cm³ min⁻¹), (2*R*,3*S*)-isomer 61.8 min]; colourless prisms, mp 100 °C [from *n*-hexane–$Et_2O$ (1:1)] (Found: C, 70.5; H, 6.4; N, 3.9. $C_{20}H_{21}NO_2S$ requires C, 70.8; H, 6.2; N, 4.1%); $[\alpha]_D^{28}$ −61.9 (*c* 1.65 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 2.297 (1 H, d, *J* 2.2, C≡CH), 2.304 (3 H, s, CMe), 2.58 (6 H, s, 2 × CMe), 2.81 (1 H, dd, *J* 14.6 and 7.0, PhC*H*H), 2.96 (1 H, dd, *J* 14.6 and 5.7, PhCH*H*), 3.07 (1 H, ddd, *J* 7.0, 6.8 and 5.7, 3-H), 3.44 (1 H, dd, *J* 6.8 and 2.2, 2-H), 6.88 (2 H, s, Ph), 7.04–7.16 (5 H, m, Ph).

### (2*S*,3*S*)-3-Benzyl-2-ethynyl-*N*-(4-methoxy-2,3,6-trimethylphenylsulfonyl)aziridine 40 and its (2*R*,3*S*) isomer 41

By a procedure identical with that described for the preparation of the 2-ethynylaziridines **34** and **35** from **27**, the 2-(1-bromovinyl)aziridine **30** (7.5 g, 16.7 mmol) was converted into the 2-ethynylaziridine **40** (2.88 g, 47% yield) and **41** (1.55 g, 25% yield), by treatment with *t*-BuOK in THF at −78→−20 °C for 1 h. Compound **40**: 98% ee (2*S*,3*S*) by HPLC [Daicel Chiralcel OD, *n*-hexane:propan-2-ol = 97:3 (0.5 cm³ min⁻¹), (2*S*,3*S*)-isomer 46.9 min]; colourless oil [Found (FAB): $(M + H)^+$, 370.1482. $C_{21}H_{24}NO_3S$ requires *M* + H, 370.1477]; $[\alpha]_D^{28}$ +3.59 (*c* 0.781 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 2.12 (3 H, s, CMe), 2.48 (1 H, d, *J* 2.2, C≡CH), 2.53 (3 H, s, CMe), 2.54 (3 H, s, CMe), 2.58 (1 H, dd, *J* 14.6 and 7.6, PhC*H*H), 3.01 (1 H, dd, *J* 14.6 and 5.1, PhCH*H*), 3.06 (1 H, dd, *J* 4.1 and 2.2, 2-H), 3.32 (1 H, ddd, *J* 7.6, 5.1 and 4.1, 3-H), 3.86 (3 H, s, OMe), 6.46 (1 H, s, Ph), 6.88–6.92 (2 H, m, Ph), 7.01–7.13 (3 H, m, Ph); *m*/*z* (FAB) 370 ($MH^+$), 213, 197, 156 (base peak), 150, 149, 119 and 91. Compound **41**: 98% ee (2*R*,3*S*) by HPLC [Daicel Chiralcel OJ, *n*-hexane:propan-2-ol = 93:7 (0.5 cm³ min⁻¹), (2*R*,3*S*)-isomer 44.3 min]; colourless needles mp 90 °C [from *n*-hexane–$Et_2O$ (2:1)] (Found: C, 68.2; H, 6.3; N, 3.7. $C_{21}H_{23}NO_3S$ requires C, 68.3; H, 6.3; N, 3.8%); $[\alpha]_D^{28}$ −56.3 (*c* 1.13 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 2.11 (3 H, s, CMe), 2.29 (1 H, d, *J* 1.9, C≡CH), 2.55 (3 H, s, CMe), 2.57 (3 H, s, CMe), 2.79 (1 H, dd, *J* 14.3 and 7.6, PhC*H*H), 2.96 (1 H, dd, *J* 14.3 and 5.4, PhCH*H*), 3.04 (1 H, ddd, *J* 7.6, 6.8 and 5.4, 3-H), 3.44 (1 H, dd, *J* 6.8 and 1.9, 2-H), 3.86 (3 H, s, OMe), 6.47 (1 H, s, Ph), 7.02–7.12 (5 H, m, Ph).

### (3*S*,4*S*)-4-[*N*-(*tert*-Butoxycarbonyl)amino]-5-methyl-1-trimethylsilylhex-1-yn-3-ol 43 and its (3*R*,4*S*)-isomer 44

To a stirred solution of oxalyl chloride (15.4 cm³, 148 mmol) in a mixed solvent of $CHCl_3$ (70 cm³) and *n*-hexane (50 cm³) at −78 °C under argon was added dropwise a solution of DMSO (40 cm³, 493 mmol) in $CHCl_3$ (15 cm³). After 45 min, a solution of the alcohol **42** (20 g, 98.5 mmol) in $CHCl_3$ (50 cm³) was added to the above reagent at −78 °C, and the mixture was stirred for 1 h at this temperature. Diisopropylethylamine (120 cm³, 690 mmol) was added to the above solution at −78 °C and the mixture was stirred for 30 min with warming to 0 °C. The mixture was made acidic with saturated aqueous citric acid, and the whole was extracted with $Et_2O$. The extract was washed successively with water, 5% $NaHCO_3$, and water, and dried over $MgSO_4$. Usual workup gave a crude aldehyde. To a stirred solution of trimethylsilylacetylene (34.8 cm³, 246 mmol) in dry THF (50 cm³) under argon was added *n*-BuLi (1.52 M in *n*-hexane; 162 cm³, 246 mmol) at 0 °C, and the mixture was stirred for 20 min at this temperature. The crude aldehyde in dry THF (50 cm³) was added to the above reagent at −78 °C, and the mixture was stirred for 2 h at this temperature, followed by quenching with saturated aqueous $NH_4Cl$ (20 cm³). The whole was extracted with $Et_2O$, and the extract was washed

successively with 5% aqueous citric acid, water, 5% aqueous $NaHCO_3$, and water, and dried over $MgSO_4$. Usual workup followed by flash chromatography over silica gel with *n*-hexane–EtOAc (8:1) gave, in order of elution, the title compound **43** (9.15 g, 31% yield) and **44** (7.23 g, 25% yield). Compound **43**: colourless crystals, mp 72–73 °C (from *n*-hexane) (Found: C, 59.9; H, 10.0; N, 4.8. $C_{15}H_{29}NO_3Si$ requires C, 60.2; H, 9.8; N, 4.7%); $[\alpha]_D^{24}$ +1.90 (*c* 1.16 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.16 (9 H, s, $SiMe_3$), 0.93 (3 H, d, *J* 7.0, CMe), 0.98 (3 H, d, *J* 6.5, CMe), 1.46 (9 H, s, $CMe_3$), 2.00–2.12 (1 H, m, 5-H), 2.84 (1 H, d, *J* 5.7, OH), 3.44 (1 H, ddd, *J* 9.5, 7.0 and 5.7, 4-H), 4.43 (1 H, dd, *J* 5.7 and 5.7, 3-H), 4.81 (1 H, d, *J* 9.5, NH). Compound **44**: colourless oil [Found (FAB): $(M + H)^+$, 300.1999. $C_{15}H_{30}NO_3Si$ requires *M* + H, 300.1995]; $[\alpha]_D^{24}$ −99.7 (*c* 0.662 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.18 (9 H, s, $SiMe_3$), 0.98 (6 H, d, *J* 7.0, $CMe_2$), 1.47 (9 H, s, $CMe_3$), 1.72–1.85 (1 H, m, 5-H), 3.20 (1 H, d, *J* 7.3, OH), 3.53–3.61 (1 H, m, 4-H), 4.52 (1 H, dd, *J* 7.3 and 3.2, 3-H), 4.66 (1 H, d, *J* 9.7, NH); *m*/*z* (FAB) 300 ($MH^+$), 244 (base peak), 226, 116, 73, 72, and 57.

### (3*S*,4*S*)-5-Methyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]-1-trimethylsilylhex-1-yn-3-ol 45

By a procedure similar to that described for the preparation of **21** from **19**, **43** (2.1 g, 7.0 mmol) was converted into the title compound **45** (1.76 g, 66% yield) as colourless needles, mp 107 °C [from *n*-hexane–$Et_2O$ (2:1)] (Found: C, 60.0; H, 8.0; N, 3.7. $C_{19}H_{31}NO_3SSi$ requires C, 59.8; H, 8.2; N, 3.7%); $[\alpha]_D^{20}$ −62.8 (*c* 1.38 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.15 (9 H, s, $SiMe_3$), 0.69 (3 H, d, *J* 6.8, CMe), 0.85 (3 H, d, *J* 7.0, CMe), 2.05–2.17 (1 H, m, 5-H), 2.30 (3 H, s, CMe), 2.61 (1 H, d, *J* 5.4, OH), 2.67 (6 H, s, 2 × CMe), 3.20 (1 H, ddd, *J* 10.0, 6.8 and 3.8, 4-H), 4.29 (1 H, dd, *J* 6.8 and 5.4, 3-H), 4.86 (1 H, d, *J* 10.0, NH), 6.95 (2 H, s, Ph).

### (3*S*,4*S*)-5-Methyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]-hex-1-yn-3-ol 46

To a stirred solution of **45** (1.55 g, 4.06 mmol) in THF (15 $cm^3$) was added dropwise tetrabutylammonium fluoride (1.0 M in THF; 4.06 $cm^3$, 4.06 mmol) at 0 °C, and the mixture was stirred for 15 min at this temperature. The mixture was made acidic with saturated aqueous citric acid, followed by concentration under reduced pressure to give a residual oil, which was extracted with $Et_2O$. The extract was washed with water, and dried over $MgSO_4$. Concentration under reduced pressure gave a crystalline mass, which was recrystallized from *n*-hexane–$Et_2O$ (2:1) to give the title compound **46** (1.21 g, 96% yield) as colourless needles, 98% ee (3*S*,4*S*) by HPLC [Daicel Chiralcel OD, *n*-hexane:propan-2-ol = 96:4 (0.5 $cm^3$ $min^{-1}$), (3*S*,4*S*)-isomer 42.3 min]; mp 138 °C [from *n*-hexane–$Et_2O$ (2:1)] (Found: C, 62.0; H, 7.4; N, 4.5. $C_{16}H_{23}NO_3S$ requires C, 62.1; H, 7.5; N, 4.5%); $[\alpha]_D^{25}$ −32.4 (*c* 0.978 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.72 (3 H, d, *J* 7.0, CMe), 0.88 (3 H, d, *J* 6.8, CMe), 2.01–2.14 (1 H, m, 5-H), 2.27 (1 H, d, *J* 1.9, 1-H), 2.29 (3 H, s, CMe), 2.62–2.66 (1 H, m, OH), 2.66 (6 H, s, 2 × CMe), 3.23 (1 H, ddd, *J* 9.5, 5.4 and 5.4, 4-H), 4.37 (1 H, ddd, *J* 5.4, 5.4 and 1.9, 3-H), 4.95 (1 H, d, *J* 9.5, NH), 6.94 (2 H, s, Ph).

### (3*R*,4*S*)-5-Methyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]-1-trimethylsilylhex-1-yn-3-ol 47

By a procedure identical with that described for the preparation of **21** from **19**, **44** (2.10 g, 7.0 mmol) was converted into the title compound **47** (2.00 g, 75% yield). 98% ee (3*R*,4*S*) by HPLC [Daicel Chiralcel OD, *n*-hexane:propan-2-ol = 98:2 (0.5 $cm^3$ $min^{-1}$), (3*R*,4*S*)-isomer 22.4 min]; colourless oil [Found (FAB): $(M + H)^+$, 382.1877. $C_{19}H_{32}NO_3SSi$ requires *M* + H, 382.1872]; $[\alpha]_D^{23}$ −81.2 (*c* 1.30 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.19 (9 H, s, $SiMe_3$), 0.86 (3 H, d, *J* 6.5, CMe), 0.91 (3 H, d, *J* 7.0, CMe), 1.69–1.82 (1 H, m, 5-H), 2.30 (3 H, s, CMe), 2.45 (1 H, d, *J* 9.5, OH), 2.68 (6 H, s, 2 × CMe), 3.17 (1 H, ddd, *J* 10.0, 7.0 and 2.4, 4-H), 4.40 (1 H, dd, *J* 9.5 and 2.4, 3-H), 4.92 (1 H, d, *J* 10.0, NH), 6.97 (2 H, s, Ph); *m*/*z* (FAB) 382 ($MH^+$), 364, 254, 183, 167, 119 (base peak), 73 and 72.

### (3*R*,4*S*)-5-Methyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]-hex-1-yn-3-ol 48

By a procedure identical with that described for the preparation of **46** from **45**, **47** (1.8 g, 4.72 mmol) was converted into the title compound **48** (1.21 g, 83% yield) as colourless crystals, 98% ee (3*R*,4*S*) by HPLC [Daicel Chiralcel OD, *n*-hexane:propan-2-ol = 98:4 (0.5 $cm^3$ $min^{-1}$), (3*R*,4*S*)-isomer 34.2 min]; mp 122 °C [from *n*-hexane–$Et_2O$ (2:1)] (Found: C, 62.0; H, 7.55; N, 4.5. $C_{16}H_{23}NO_3S$ requires C, 62.1; H, 7.5; N, 4.5%); $[\alpha]_D^{23}$ −55.6 (*c* 0.774 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.846 (3 H, d, *J* 7.0, CMe), 0.853 (3 H, d, *J* 6.8, CMe), 1.72–1.85 (1 H, m, 5-H), 2.30 (3 H, s, CMe), 2.55 (1 H, d, *J* 1.9, 1-H), 2.67 (6 H, s, 2 × CMe), 2.88 (1 H, d, *J* 9.7, OH), 3.15 (1 H, ddd, *J* 10.3, 7.6 and 3.0, 4-H), 4.45 (1 H, ddd, *J* 9.7, 3.0 and 1.9, 3-H), 4.95 (1 H, d, *J* 10.3, NH), 6.97 (2 H, s, Ph).

### (3*S*,4*S*)-4-[*N*-(*tert*-Butoxycarbonyl)amino]-5-methylhex-1-yn-3-ol 49

By a procedure identical with that described for the preparation of **46** from **45**, **43** (3.0 g, 7.96 mmol) was converted into the title compound **49** (1.66 g, 72% yield) as colourless needles, mp 42–43 °C [from *n*-hexane–$Et_2O$ (3:1)] (Found: C, 63.3; H, 9.25; N, 6.2. $C_{12}H_{21}NO_3$ requires C, 63.4; H, 9.3; N, 6.2%); $[\alpha]_D^{21}$ −8.75 (*c* 0.869 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.94 (3 H, d, *J* 6.5, CMe), 0.99 (3 H, d, *J* 7.0, CMe), 1.46 (9 H, s, $CMe_3$), 2.05–2.18 (1 H, m, 5-H), 2.47 (1 H, d, *J* 1.4, 1-H), 3.06 (1 H, d, *J* 5.4, OH), 3.42–3.51 (1 H, m, 4-H), 4.42–4.48 (1 H, m, 3-H), 4.83 (1 H, d, *J* 9.2, NH).

### (3*R*,4*S*)-4-[*N*-(*tert*-Butoxycarbonyl)amino]-5-methylhex-1-yn-3-ol 50

By a procedure identical with that described for the preparation of **46** from **45**, **44** (1.5 g, 5.0 mmol) was converted into the title compound **50** (1.03 g, 91% yield) as colourless needles, mp 81 °C [from *n*-hexane–$Et_2O$ (3:1)] (Found: C, 63.2; H, 9.3; N, 5.9. $C_{12}H_{21}NO_3$ requires C, 63.4; H, 9.3; N, 6.2%); $[\alpha]_D^{29}$ −84.3 (*c* 1.01 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.97–1.01 (6 H, m, 2 × CMe), 1.46 (9 H, s, $CMe_3$), 1.72–1.86 (1 H, m, 5-H), 2.46 (1 H, d, *J* 2.2, 1-H), 3.30 (1 H, d, *J* 7.6, OH), 3.59 (1 H, ddd, *J* 9.2, 8.9 and 3.5, 4-H), 4.53–4.58 (1 H, m, 3-H), 4.70 (1 H, d, *J* 8.9, NH).

### (3*S*,4*S*)-4-[*N*-(*tert*-Butoxycarbonyl)amino]-5-(*tert*-butyldimethylsiloxy)-1-trimethylsilylpent-1-yn-3-ol 52 and its (3*R*,4*S*)-isomer 53

To a stirred solution of the ester **51** (32 g, 96 mmol) in toluene (200 $cm^3$) was added dropwise DIBAL-H (1.0 M in toluene; 192 $cm^3$, 192 mmol) over 30 min at −78 °C under argon, and the mixture was stirred for 1 h at this temperature. Saturated aqueous citric acid (100 $cm^3$) was added to the mixture, and the whole was extracted with $Et_2O$. The extract was washed with water and brine, and dried over $MgSO_4$. Concentration under reduced pressure gave a crude aldehyde. To a stirred solution of trimethylsilylacetylene (34.0 $cm^3$, 240 mmol) in dry THF (100 $cm^3$) under argon was added *n*-BuLi (1.53 M in *n*-hexane; 157 $cm^3$, 240 mmol) at 0 °C, and the mixture was stirred for 30 min at this temperature. The crude aldehyde in dry THF (50 $cm^3$) was added to the above reagent at −78 °C, and the mixture was stirred for 1 h at this temperature, followed by quenching with saturated aqueous $NH_4Cl$ (20 $cm^3$). The whole was extracted with $Et_2O$, and the extract was washed successively with saturated aqueous citric acid, water, saturated aqueous $NaHCO_3$, and water, and dried over $MgSO_4$. Usual workup followed by

flash chromatography over silica gel with *n*-hexane–$Et_2O$ (10:3) gave, in order of elution, the title compound **52** (6.86 g, 18% yield), and **53** (5.03 g, 13% yield). Compound **52**: colourless oil [Found (FAB): $(M + H)^+$, 402.2505. $C_{19}H_{40}NO_4Si_2$ requires $M$ + H, 402.2496]; $[\alpha]_D^{22}$ +2.23 (*c* 1.35 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.09 (6 H, s, $SiMe_2$), 0.17 (9 H, s, $SiMe_3$), 0.90 (9 H, s, $CMe_3$), 1.46 (9 H, s, $CMe_3$), 3.44 (1 H, d, *J* 5.4, OH), 3.74–3.90 (3 H, m, 5-$CH_2$ and 4-H), 4.54 (1 H, dd, *J* 5.4 and 5.1, 3-H), 4.97–5.06 (1 H, m, NH); *m*/*z* (FAB) 402 ($MH^+$), 346, 303, 302 (base peak), 288, 218, 174, 89, 75, 73 and 57. Compound **53**: colourless oil [Found (FAB): $(M + H)^+$, 402.2490. $C_{19}H_{40}NO_4Si_2$ requires $M$ + H, 402.2496]; $[\alpha]_D^{22}$ +3.11 (*c* 0.996 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.09 (3 H, s, SiMe), 0.11 (3 H, s, SiMe), 0.18 (9 H, s, $SiMe_3$), 0.91 (9 H, s, $CMe_3$), 1.46 (9 H, s, $CMe_3$), 3.65 (1 H, d, *J* 9.5, OH), 3.74–3.81 (2 H, m, 4-H and 5-C*H*H), 4.19–4.27 (1 H, m, 5-CH*H*), 4.50 (1 H, dd, *J* 9.5 and 4.1, 3-H), 5.24 (1 H, d, *J* 7.6, NH); *m*/*z* (FAB) 402 ($MH^+$), 346, 303, 302 (base peak), 288, 218, 174, 89, 75, 73 and 57.

### (3*S*,4*S*)-5-(*tert*-Butyldimethylsiloxy)-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]-1-trimethylsilylpent-1-yn-3-ol 54 and (2*S*,3*S*)-2-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]-5-trimethylsilylpent-4-yne-1,3-diol 55

By a procedure similar to that described for the preparation of **21** from **19**, **52** (3.01 g, 7.5 mmol) was converted into the title compound **54** (2.26 g, 62% yield) and **55** (471 mg, 17% yield). Compound **54**: colourless crystals, mp 84 °C (from *n*-hexane) [Found (FAB): $(M + H)^+$, 484.2366. $C_{23}H_{42}NO_4SSi_2$ requires $M$ + H, 484.2373]; $[\alpha]_D^{23}$ −11.2 (*c* 0.845 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.04 (6 H, s, $SiMe_2$), 0.15 (9 H, s, $SiMe_3$), 0.87 (9 H, s, $CMe_3$), 2.30 (3 H, s, CMe), 2.66 (6 H, s, 2 × CMe), 3.26 (1 H, d, *J* 5.1, OH), 3.26–3.35 (1 H, m, 4-H), 3.53 (1 H, dd, *J* 10.3 and 5.7, 5-C*H*H), 3.85 (1 H, dd, *J* 10.3 and 3.0, 5-CH*H*), 4.36 (1 H, dd, *J* 6.2 and 5.1, 3-H), 5.17 (1 H, d, *J* 9.2, NH), 6.96 (2 H, s, Ph); *m*/*z* (FAB) 484 ($MH^+$), 468, 426, 356, 173, 119, 89, 75 and 73 (base peak). Compound **55**: colourless crystals, mp 95 °C [from *n*-hexane–$Et_2O$ (2:1)] (Found: C, 55.2; H, 7.5; N, 3.7. $C_{17}H_{27}NO_4SSi$ requires C, 55.25; H, 7.4; N, 3.8%); $[\alpha]_D^{23}$ −16.1 (*c* 0.843 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.15 (9 H, s, $SiMe_3$), 2.27 (1 H, dd, *J* 5.4 and 5.4, 1-OH), 2.30 (3 H, s, CMe), 2.67 (6 H, s, 2 × CMe), 2.72 (1 H, d, *J* 4.1, 3-OH), 3.24–3.33 (1 H, m, 2-H), 3.72 (1 H, ddd, *J* 11.9, 6.5 and 5.4, 1-C*H*H), 3.86 (1 H, ddd, *J* 11.9, 5.4 and 3.5, 1-CH*H*), 4.48 (1 H, dd, *J* 4.9 and 4.1, 3-H), 5.30 (1 H, d, *J* 7.6, NH), 6.97 (2 H, s, Ph).

### (3*S*,4*S*)-5-(*tert*-Butyldimethylsiloxy)-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]-1-trimethylsilylpent-1-yn-3-ol 54 from 55

To a stirred solution of **55** (450 mg, 1.21 mmol) in a mixed solvent of $CHCl_3$ (3 $cm^3$) and DMF (3 $cm^3$) were added imidazole (98.6 mg, 1.45 mmol) and *tert*-butyldimethylsilyl chloride (219 mg, 1.45 mmol) at 0 °C, and the mixture was stirred for 2 h at this temperature. Saturated aqueous $NaHCO_3$ (2 $cm^3$) was added to the mixture, and the whole was extracted with $Et_2O$. The extract was washed successively with saturated aqueous citric acid, water, saturated aqueous $NaHCO_3$, and water, and dried over $MgSO_4$. Usual workup followed by flash chromatography over silica gel with *n*-hexane–EtOAc (6:1) gave the title compound **54** (490 mg, 83% yield) as colourless crystals from *n*-hexane.

### (3*S*,4*S*)-5-(*tert*-Butyldimethylsiloxy)-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]pent-1-yn-3-ol 56

To a stirred solution of **54** (2.64 g, 5.45 mmol) in MeOH (15 $cm^3$) was added dropwise NaOMe (1.0 M solution in MeOH; 0.545 $cm^3$, 0.545 mmol) at 0 °C, and the mixture was stirred for 4.5 h at room temperature. Concentration under reduced pressure gave a crystalline mass, which was filtered though a short pad of $SiO_2$ with *n*-hexane–$CHCl_3$ (1:1). Recrystallization from *n*-hexane–$Et_2O$ (1:1) gave the title compound **56** (2.03 g, 90% yield) as colourless crystals, 97% ee (3*S*,4*S*) by HPLC [Daicel Chiralcel OD, *n*-hexane:propan-2-ol = 95:5 (0.5 $cm^3$ $min^{-1}$), (3*R*,4*R*)-isomer 18.3 min, (3*S*,4*S*)-isomer 19.9 min]; mp 117 °C [*n*-hexane–$Et_2O$ (1:1)] (Found: C, 58.1; H, 8.2; N, 3.4. $C_{20}H_{33}NO_4SSi$ requires C, 58.4; H, 8.1; N, 3.4%); $[\alpha]_D^{24}$ +21.7 (*c* 0.813 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.04 (6 H, s, $SiMe_2$), 0.87 (9 H, s, $CMe_3$), 2.30 (3 H, s, CMe), 2.33 (1 H, d, *J* 1.9, C≡CH), 2.66 (6 H, s, 2 × CMe), 3.23 (1 H, d, *J* 5.1, OH), 3.29–3.38 (1 H, m, 4-H), 3.59 (1 H, dd, *J* 10.3 and 5.9, 5-C*H*H), 3.83 (1 H, dd, *J* 10.3 and 3.0, 5-CH*H*), 4.43 (1 H, ddd, *J* 5.1, 5.1 and 1.9, 3-H), 5.21 (1 H, d, *J* 9.5, NH), 6.96 (2 H, s, Ph).

### (3*R*,4*S*)-5-(*tert*-Butyldimethylsiloxy)-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]-1-trimethylsilylpent-1-yn-3-ol 57 and (2*S*,3*R*)-2-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]-5-trimethylsilylpent-4-yne-1,3-diol 58

By a procedure identical with that described for the preparation of **21** from **19**, **53** (2.41 g, 6 mmol) was converted into the title compound **57** (1.49 g, 51% yield) and **58** (315 mg, 14% yield). Compound **57**: 92% ee (3*R*,4*S*) by HPLC [Daicel Chiralcel OD, *n*-hexane:propan-2-ol = 98:2 (0.5 $cm^3$ $min^{-1}$), (3*S*,4*R*)-isomer 15.6 min, (3*R*,4*S*)-isomer 17.1 min]; colourless oil [Found (FAB): $(M + H)^+$, 484.2376. $C_{23}H_{42}NO_4SSi_2$ requires $M$ + H, 484.2373]; $[\alpha]_D^{26}$ +4.40 (*c* 0.955 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.02 (3 H, s, SiMe), 0.04 (3 H, s, SiMe), 0.16 (9 H, s, $SiMe_3$), 0.87 (9 H, s, $CMe_3$), 2.30 (3 H, s, CMe), 2.66 (6 H, s, 2 × CMe), 3.15 (1 H, d, *J* 9.5, OH), 3.32–3.39 (1 H, m, 4-H), 3.60 (1 H, dd, *J* 10.3 and 4.3, 5-C*H*H), 4.08 (1 H, dd, *J* 10.3 and 3.2, 5-CH*H*), 4.36 (1 H, dd, *J* 9.5 and 3.2, 3-H), 5.35 (1 H, d, *J* 9.2, NH), 6.96 (2 H, s, Ph); *m*/*z* (FAB) 484 ($MH^+$), 468, 426, 356, 283, 183, 173, 119, 89 and 73 (base peak). Compound **58**: colourless crystals, mp 95 °C [from *n*-hexane–$Et_2O$ (2:1)] (Found: C, 55.0; H, 7.2; N, 3.9. $C_{17}H_{27}NO_4SSi$ requires C, 55.25; H, 7.4; N, 3.8%); $[\alpha]_D^{26}$ −16.0 (*c* 0.562 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.17 (9 H, s, $SiMe_3$), 2.25 (1 H, dd, *J* 8.4 and 4.3, 1-OH), 2.31 (3 H, s, CMe), 2.67 (6 H, s, 2 × CMe), 2.77 (1 H, d, *J* 7.3, 3-OH), 3.29–3.36 (1 H, m, 2-H), 3.58 (1 H, ddd, *J* 11.3, 8.4 and 4.6, 1-C*H*H), 4.02 (1 H, ddd, *J* 11.3, 4.3 and 4.1, 1-CH*H*), 4.47 (1 H, dd, *J* 7.3 and 3.2, 3-H), 5.53 (1 H, d, *J* 8.6, NH), 6.97 (2 H, s, Ph).

### (3*R*,4*S*)-5-(*tert*-Butyldimethylsiloxy)-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]pent-1-yn-3-ol 59

By a procedure identical with that described for the preparation of **56** from **54**, **57** (1.64 g, 3.39 mmol) was converted into the title compound **59** (1.32 g, 95% yield). 92% ee (3*R*,4*S*) by HPLC [Daicel Chiralcel OD, *n*-hexane:propan-2-ol = 95:5 (0.5 $cm^3$ $min^{-1}$), (3*S*,4*R*)-isomer 18.6 min, (3*R*,4*S*)-isomer 20.5 min]; colourless oil [Found (FAB): $(M + H)^+$, 412.1975. $C_{20}H_{34}NO_4SSi$ requires $M$ + H, 412.1978]; $[\alpha]_D^{26}$ +13.3 (*c* 0.813 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.02 (3 H, s, SiMe), 0.03 (3 H, s, SiMe), 0.86 (9 H, s, $CMe_3$), 2.30 (3 H, s, CMe), 2.50 (1 H, d, *J* 1.9, 1-H), 2.66 (6 H, s, 2 × CMe), 3.25 (1 H, d, *J* 9.5, OH), 3.31–3.39 (1 H, m, 4-H), 3.61 (1 H, dd, *J* 10.3 and 4.6, 5-C*H*H), 4.04 (1 H, dd, *J* 10.3 and 3.2, 5-CH*H*), 4.37 (1 H, ddd, *J* 9.5, 3.2 and 1.9, 3-H), 5.35 (1 H, d, *J* 9.2, NH), 6.96 (2 H, s, Ph); *m*/*z* (FAB) 412 ($MH^+$, base peak), 354, 280, 173, 167, 119, 89 and 73.

### General procedure for the preparation of 1,3-oxazolidin-2-ones (60, 62, 64, and 65)

**(4*S*,5*S*)-5-Ethynyl-4-isopropyl-1,3-oxazolidin-2-one 60.** To a stirred suspension of NaH (9.6 mg, 0.4 mmol) in DMF (2 $cm^3$) under argon was added **43** (60 mg, 0.2 mmol) in a mixed solvent of dry THF (1 $cm^3$) and DMF (1 $cm^3$) at 0 °C, and the mixture was stirred for 1 h. Saturated aqueous $NH_4Cl$ (3 $cm^3$) was added to the mixture at −78 °C, and the whole was extracted with $Et_2O$. The extract was washed with water, and dried over

$MgSO_4$. Usual workup followed by flash chromatography over silica gel with *n*-hexane–EtOAc (3:1) gave the title compound **60** (22 mg, 72% yield) as a colourless oil [Found (FAB): $(M + H)^+$, 154.0872. $C_8H_{12}NO_2$ requires $M + H$, 154.0868]; $[a]_D^{24}$ −48.2 (*c* 1.29 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.97 (3 H, d, *J* 6.8, CMe), 0.98 (3 H, d, *J* 6.5, CMe), 1.70–1.87 (1 H, m, $Me_2CH$), 2.69 (1 H, d, *J* 2.4, C≡CH), 3.60–3.66 (1 H, m, 4-H), 4.83 (1 H, dd, *J* 5.9 and 2.4, 5-H), 7.17 (1 H, br s, NH); *m*/*z* (FAB) 154 ($MH^+$, base peak), 137, 95, 81, 69, 57, 55 and 43.

**(4*S*,5*S*)-5-Ethynyl-4-isopropyl-*N*-(2,4,6-trimethylphenylsulfonyl)-1,3-oxazolidin-2-one 61.** To a stirred suspension of NaH (1.9 mg, 0.078 mmol) in DMF (0.2 $cm^3$) were added 1,3-oxazolidin-2-one **60** (10 mg, 0.065 mmol) in THF (0.1 $cm^3$) and 2,4,6-trimethylphenylsulfonyl chloride (16 mg, 0.072 mmol) in THF (0.1 $cm^3$) at 0 °C under argon. The mixture was stirred for 1 h at this temperature. Saturated aqueous $NH_4Cl$ (1 $cm^3$) was added to the mixture, and the whole was extracted with $Et_2O$. The extract was washed with water, and dried over $MgSO_4$. Usual workup followed by flash chromatography over silica gel with *n*-hexane–EtOAc (10:1) gave the title compound **61** (10 mg, 46% yield) as colourless crystals, mp 156–158 °C [from *n*-hexane–$Et_2O$ (3:1)] [Found (FAB): $(M + H)^+$, 336.1273. $C_{17}H_{22}NO_4S$ requires $M + H$, 336.1269]; $[a]_D^{25}$ +208 (*c* 0.488 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 1.06 (6 H, d, *J* 7.0, 2 × CMe), 2.32 (3 H, s, CMe), 2.55–2.67 (1 H, m, $Me_2CH$), 2.69 (1 H, d, *J* 2.4, C≡CH), 2.72 (6 H, s, 2 × CMe), 4.47 (1 H, dd, *J* 3.0 and 1.9, 4-H), 4.90 (1 H, dd, *J* 2.4 and 1.9, 5-H), 6.99 (2 H, s, Ph); *m*/*z* (FAB) 336 ($MH^+$, base peak), 183, 137 and 119.

**(4*S*,5*R*)-5-Ethynyl-4-isopropyl-1,3-oxazolidin-2-one 62.** By a procedure identical with that described for the preparation of the 1,3-oxazolidin-2-one **60** from **43**, the alcohol **44** (60 mg, 0.2 mmol) was converted into the title compound **62** (15 mg, 49% yield) as a colourless oil [Found (FAB): $(M + H)^+$, 154.0862. $C_8H_{12}NO_2$ requires $M + H$, 154.0868]; $[a]_D^{24}$ +41.2 (*c* 1.19 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.97 (3 H, d, *J* 6.8, CMe), 1.05 (3 H, d, *J* 6.5, CMe), 2.07–2.20 (1 H, m, $Me_2CH$), 2.70 (1 H, d, *J* 2.2, C≡CH), 3.62 (1 H, dd, *J* 8.1 and 7.8, 4-H), 5.25 (1 H, dd, *J* 8.1 and 2.2, 5-H), 6.82–6.95 (1 H, m, NH); *m*/*z* (FAB) 154 ($MH^+$, base peak), 137, 136, 110, 107, 77 and 43.

**(4*S*,5*R*)-5-Ethynyl-4-isopropyl-*N*-(2,4,6-trimethylphenylsulfonyl)-1,3-oxazolidin-2-one 63.** By a procedure identical with that described for the preparation of **61** from **60**, **62** (10 mg, 0.065 mmol) was converted into the title compound **63** (19 mg, 87% yield) as colourless crystals, mp 189–191 °C [from $Et_2O$–$CHCl_3$ (5:1)] [Found (FAB): $(M + H)^+$, 336.1263. $C_{17}H_{22}NO_4S$ requires $M + H$, 336.1269]; $[a]_D^{23}$ +170 (*c* 0.637 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 1.22 (3 H, d, *J* 6.5, CMe), 1.30 (3 H, d, *J* 7.3, CMe), 2.30 (3 H, s, CMe), 2.48–2.62 (1 H, m, $Me_2CH$), 2.65 (6 H, s, 2 × CMe), 2.85 (1 H, d, *J* 2.2, C≡CH), 4.49 (1 H, dd, *J* 7.3 and 2.4, 4-H), 5.24 (1 H, dd, *J* 7.3 and 2.2, 5-H), 6.98 (2 H, s, Ph); *m*/*z* (FAB) 336 ($MH^+$, base peak), 183, 137 and 119.

**(4*S*,5*S*)-4-[(*tert*-Butyldimethylsiloxy)methyl]-5-ethynyl-1,3-oxazolidin-2-one 64.** By a procedure identical with that described for the preparation of the 1,3-oxazolidin-2-one **60** from **43**, the alcohol **52** (127 mg, 0.316 mmol) was converted into the title compound **64** (31 mg, 38% yield) as a colourless oil [Found (FAB): $(M + H)^+$, 256.1364. $C_{12}H_{22}NO_3Si$ requires $M + H$, 256.1369]; $[a]_D^{23}$ −65.7 (*c* 0.280 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.07 (6 H, s, $SiMe_2$), 0.90 (9 H, s, $CMe_3$), 2.67 (1 H, d, *J* 1.9, C≡CH), 3.60–3.72 (2 H, m, $OCH_2$), 3.93 (1 H, ddd, *J* 5.1, 5.1 and 4.9, 4-H), 5.00 (1 H, dd, *J* 4.9 and 1.9, 5-H), 6.53 (1 H, br s, NH); *m*/*z* (FAB) 256 ($MH^+$, base peak), 240, 198, 168, 147, 137, 115, 89, 75, 73 and 59.

**(4*S*,5*R*)-4-[(*tert*-Butyldimethylsiloxy)methyl]-5-ethynyl-1,3-oxazolidin-2-one 65.** By a procedure identical with that described for the preparation of the 1,3-oxazolidin-2-one **60** from **43**, the alcohol **53** (201 mg, 0.5 mmol) was converted into the title compound **65** (68 mg, 53% yield) as a colourless oil [Found (FAB): $(M + H)^+$, 256.1374. $C_{12}H_{22}NO_3Si$ requires $M + H$, 256.1369]; $[a]_D^{23}$ −34.4 (*c* 0.194 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.08 (3 H, s, SiMe), 0.09 (3 H, s, SiMe), 0.90 (9 H, s, $CMe_3$), 2.69 (1 H, d, *J* 2.2, C≡CH), 3.79 (1 H, dd, *J* 10.3 and 7.8, OC*H*H), 3.83 (1 H, dd, *J* 10.3 and 4.9, OCH*H*), 3.96 (1 H, ddd, *J* 7.8, 7.8 and 4.9, 4-H), 5.30 (1 H, dd, *J* 7.8 and 2.2, 5-H), 5.76–5.87 (1 H, m, NH); *m*/*z* (FAB) 256 ($MH^+$, base peak), 240, 198, 168, 154, 137, 115, 105, 89, 75, 73 and 59.

### General procedure for the aziridination of ethynyl amino alcohols (43, 44, 46, 48, 49, 50, 54, 56, 57, and 59) under Mitsunobu conditions (Table 1)

**(2*R*,3*S*)-*N*-(*tert*-Butoxycarbonyl)-3-isopropyl-2-(2-trimethylsilylethynyl)aziridine 66 from 43 (Table 1, entry 1).** To a stirred solution of the amino alcohol **43** (300 mg, 1 mmol) and triphenylphosphine (393 mg, 1.5 mmol) in dry THF was added dropwise a solution of diethyl azodicarboxylate (40% in toluene; 0.601 $cm^3$, 1.5 mmol) at 0 °C and the mixture was stirred for 30 min at room temperature. Concentration under reduced pressure followed by flash chromatography over silica gel with *n*-hexane–EtOAc (20:1) gave the title compound **66** (269 mg, 96% yield) as a colourless oil [Found (FAB): $(M + H)^+$, 282.1887. $C_{15}H_{28}NO_2Si$ requires $M + H$, 282.1889]; $[a]_D^{28}$ −128 (*c* 1.03 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.16 (9 H, s, $SiMe_3$), 1.01 (3 H, d, *J* 7.0, CMe), 1.16 (3 H, d, *J* 6.5, CMe), 1.44 (9 H, s, $CMe_3$), 1.50–1.68 (1 H, m, $Me_2CH$), 2.14 (1 H, dd, *J* 9.2 and 6.2, 3-H), 2.98 (1 H, d, *J* 6.2, 2-H); *m*/*z* (FAB), 282 ($MH^+$), 281, 226 (base peak), 181, 73 and 57.

**(2*S*,3*S*)-*N*-(*tert*-Butoxycarbonyl)-3-isopropyl-2-(2-trimethylsilylethynyl)aziridine 67 (Table 1, entry 2).** A colourless oil [Found (FAB): $(M + H)^+$, 282.1894. $C_{15}H_{28}NO_2Si$ requires $M + H$, 282.1889]; $[a]_D^{27}$ +25.4 (*c* 0.906 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.16 (9 H, s, $SiMe_3$), 1.01 (3 H, d, *J* 7.0, CMe), 1.02 (3 H, d, *J* 6.5, CMe), 1.37–1.49 (1 H, m, $Me_2CH$), 1.50 (9 H, s, $CMe_3$), 2.43 (1 H, dd, *J* 7.3 and 3.2, 3-H), 2.73 (1 H, d, *J* 3.2, 2-H); *m*/*z* (FAB) 282 ($MH^+$), 281, 226 (base peak), 181, 73 and 57.

**(2*R*,3*S*)-*N*-(*tert*-Butoxycarbonyl)-2-ethynyl-3-isopropylaziridine 68 (Table 1, entry 5).** A colourless oil [Found (CI): $(M + H)^+$, 210.1499. $C_{12}H_{20}NO_2$ requires $M + H$, 210.1494]; $[a]_D^{28}$ −106 (*c* 1.18 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 1.02 (3 H, d, *J* 6.5, CMe), 1.16 (3 H, d, *J* 6.5, CMe), 1.45 (9 H, s, $CMe_3$), 1.51–1.68 (1 H, m, $Me_2CH$), 2.15 (1 H, dd, *J* 9.5 and 6.5, 3-H), 2.16 (1 H, d, *J* 1.9, C≡CH), 2.98 (1 H, dd, *J* 6.5 and 1.9, 2-H); *m*/*z* (CI) 210 ($MH^+$), 194, 182, 155, 154 (base peak), 110, 98.

**(2*S*,3*S*)-*N*-(*tert*-Butoxycarbonyl)-2-ethynyl-3-isopropylaziridine 69 (Table 1, entry 6).** A colourless oil [Found (CI): 210.1493. $C_{12}H_{20}NO_2$ requires $M + H$, 210.1494]; $[a]_D^{28}$ −106 (*c* 1.18 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 1.00 (3 H, d, *J* 7.0, CMe), 1.04 (3 H, d, *J* 6.8, CMe), 1.36–1.53 (1 H, m, $Me_2CH$), 1.49 (9 H, s, $CMe_3$), 2.24 (1 H, d, *J* 1.9, C≡CH), 2.44 (1 H, dd, *J* 7.6 and 3.2, 3-H), 2.71 (1 H, dd, *J* 3.2 and 1.9, 2-H); *m*/*z* (CI) 210 ($MH^+$), 194, 182, 155, 154 (base peak), 110.

**(2*R*,3*R*)-3-[(*tert*-Butyldimethylsiloxy)methyl]-*N*-(2,4,6-trimethylphenylsulfonyl)-2-(2-trimethylsilylethynyl)aziridine 70 (Table 1, entry 7).** A colourless oil [Found (FAB): $(M + H)^+$, 466.2259. $C_{23}H_{40}NO_3SSi_2$ requires $M + H$, 466.2267]; $[a]_D^{27}$ −38.6 (*c* 0.273 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) −0.05 (3 H, s, SiMe), −0.02 (3 H, s, SiMe), 0.15 (9 H, s, $SiMe_3$), 0.81 (9 H, s, $CMe_3$), 2.30 (3 H, s, CMe), 2.69 (6 H, s, 2 × CMe), 3.04 (1 H, ddd, *J* 6.8, 5.9 and 5.4, 2-H), 3.43 (1 H, d, *J* 6.8, 3-H), 3.66 (1 H, dd, *J* 11.3 and 5.9, OC*H*H), 3.75 (1 H, dd, *J* 11.3 and 5.4,

OCH*H*), 6.96 (2 H, s, Ph); *m*/*z* (FAB) 466 ($MH^+$), 408, 378, 229, 119, 89 and 73 (base peak).

**(2*R*,3*R*)-3-[(*tert*-Butyldimethylsiloxy)methyl]-2-ethynyl-*N*-(2,4,6-trimethylphenylsulfonyl)aziridine 71 (Table 1, entry 8).** A colourless oil [Found (FAB): $(M + H)^+$, 394.1870. $C_{20}H_{32}NO_3SSi$ requires *M* + H, 394.1872]; $[\alpha]_D^{27}$ −39.7 (*c* 1.21 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) −0.06 (3 H, s, SiMe), −0.02 (3 H, s, SiMe), 0.80 (9 H, s, $CMe_3$), 2.19 (1 H, d, *J* 1.9, C≡CH), 2.30 (3 H, s, CMe), 2.69 (6 H, s, 2 × CMe), 3.07 (1 H, ddd, *J* 7.0, 5.9 and 5.4, 2-H), 3.40 (1 H, dd, *J* 7.0 and 1.9, 3-H), 3.68 (1 H, dd, *J* 11.3 and 5.9, OC*H*H), 3.77 (1 H, dd, *J* 11.3 and 5.4, OCH*H*), 6.96 (2 H, s, Ph); *m*/*z* (FAB) 394 ($MH^+$), 337, 336, 306, 183, 167, 119 (base peak), 89 and 73.

**(2*R*,3*S*)-3-[(*tert*-Butyldimethylsiloxy)methyl]-*N*-(2,4,6-trimethylphenylsulfonyl)-2-(2-trimethylsilylethynyl)aziridine 72 (Table 1, entry 9).** 91% ee (2*R*,3*S*) by HPLC [Daicel Chiralcel OD, *n*-hexane : propan-2-ol = 99 : 1 (0.5 $cm^3$ $min^{-1}$), (2*R*,3*S*)-isomer 9.3 min, (2*S*,3*R*)-isomer 10.2 min]; colourless oil [Found (FAB): $(M + H)^+$, 466.2277. $C_{23}H_{40}NO_3SSi_2$ requires *M* + H, 466.2267]; $[\alpha]_D^{29}$ +35.1 (*c* 0.462 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) −0.09 (3 H, s, SiMe), −0.08 (3 H, s, SiMe), 0.17 (9 H, s, $SiMe_3$), 0.80 (9 H, s, $CMe_3$), 2.30 (3 H, s, CMe), 2.71 (6 H, s, 2 × CMe), 3.18 (1 H, d, *J* 4.3, 3-H), 3.32 (1 H, ddd, *J* 4.3, 4.3 and 3.8, 2-H), 3.69 (1 H, dd, *J* 11.6 and 4.3, OC*H*H), 3.76 (1 H, dd, *J* 11.6 and 3.8, OCH*H*), 6.93 (2 H, s, Ph); *m*/*z* (FAB) 466 ($MH^+$), 408, 378, 229, 119, 89 and 73 (base peak).

**(2*R*,3*S*)-3-[(*tert*-Butyldimethylsiloxy)methyl]-2-ethynyl-*N*-(2,4,6-trimethylphenylsulfonyl)aziridine 73 (Table 1, entry 10).** 94% ee (2*R*,3*S*) by HPLC [Daicel Chiralcel OD, *n*-hexane : propan-2-ol = 98 : 2 (0.5 $cm^3$ $min^{-1}$), (2*R*,3*S*)-isomer 15.7 min, (2*S*,3*R*)-isomer 17.9 min]; colourless crystals, mp 90 °C (from *n*-hexane) [Found (FAB): $(M + H)^+$, 394.1880. $C_{20}H_{32}NO_3SSi$ requires *M* + H, 394.1872]; $[\alpha]_D^{27}$ +5.94 (*c* 0.886 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) −0.12 (3 H, s, SiMe), −0.10 (3 H, s, SiMe), 0.78 (9 H, s, $CMe_3$), 2.30 (3 H, s, CMe), 2.47 (1 H, d, *J* 2.4, C≡CH), 2.71 (6 H, s, 2 × CMe), 3.17 (1 H, dd, *J* 4.3 and 2.4, 3-H), 3.33 (1 H, ddd, *J* 4.9, 4.3 and 3.5, 2-H), 3.64 (1 H, dd, *J* 11.6 and 4.9, OC*H*H), 3.73 (1 H, dd, *J* 11.6 and 3.5, OCH*H*), 6.95 (2 H, s, Ph); *m*/*z* (FAB) 394 ($MH^+$), 336, 306, 210, 167, 157, 119, 89 and 73 (base peak).

**(2*S*,3*S*)-3-Isopropyl-2-[2-(methoxycarbonyl)ethynyl]-*N*-(2,4,6-trimethylphenylsulfonyl)aziridine 74**

To a stirred solution of the aziridine **34** (291 mg, 1 mmol) in dry THF (2 $cm^3$) was added dropwise LDA (0.5 M in *n*-hexane–THF (1 : 2) 2.4 $cm^3$, 1.2 mmol) at −78 °C under argon. After stirring for 1 h at this temperature, methyl chloroformate (0.0852 $cm^3$, 1.2 mmol) was added at −78 °C. The mixture was stirred for 30 min at this temperature, followed by quenching with saturated aqueous $NH_4Cl$ (2 $cm^3$). The whole was extracted with $Et_2O$ and the extract was washed with water and dried over $MgSO_4$. Usual workup followed by flash chromatography over silica gel with *n*-hexane–EtOAc (5 : 1) gave the title compound **74** (249 mg, 71% yield) as colourless crystals, mp 75 °C [from *n*-hexane–$Et_2O$ (5 : 1)] (Found: C, 61.6; H, 6.5; N, 3.9. $C_{18}H_{23}NO_4S$ requires C, 61.9; H, 6.6; N, 4.0%]; $[\alpha]_D^{24}$ +51.1 (*c* 0.951 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.77 (3 H, d, *J* 6.5, CMe), 0.92 (3 H, d, *J* 7.0, CMe), 1.48–1.61 (1 H, m, $Me_2CH$), 2.31 (3 H, s, CMe), 2.72 (6 H, s, 2 × CMe), 3.02–3.07 (2 H, m, 2-H and 3-H), 3.78 (3 H, s, OMe), 6.96 (2 H, s, Ph).

**(2*S*,3*S*)-3-Isopropyl-*N*-(2,4,6-trimethylphenylsulfonyl)-2-(2-trimethylsilylethynyl)aziridine 75**

By a procedure similar to that described for the preparation of **74** from **34**, the aziridine **34** (437 mg, 1.5 mmol) was converted into the title compound **75** (347 mg, 64% yield) as a colourless oil [Found (FAB): $(M + H)^+$, 364.1761. $C_{19}H_{30}NO_2SSi$ requires *M* + H, 364.1766]; $[\alpha]_D^{19}$ +47.4 (*c* 1.01 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.18 (9 H, s, $SiMe_3$), 0.76 (3 H, d, *J* 6.8, CMe), 0.93 (3 H, d, *J* 7.0, CMe), 1.44–1.58 (1 H, m, $Me_2CH$), 2.30 (3 H, s, CMe), 2.72 (6 H, s, 2 × CMe), 2.95–3.00 (2 H, m, 2-H and 3-H), 6.94 (2 H, s, Ph); *m*/*z* (FAB) 364 ($MH^+$, base peak), 348, 229, 181, 180, 167, 119 and 73.

**(2*R*,3*S*)-3-Isopropyl-2-[2-(methoxycarbonyl)ethynyl]-*N*-(2,4,6-trimethylphenylsulfonyl)aziridine 76**

By a procedure identical with that described for the preparation of **74** from **34**, the aziridine **35** (204 mg, 0.7 mmol) was converted into the title compound **76** (158 mg, 65% yield) as a colourless oil [Found (FAB): $(M + H)^+$, 350.1433. $C_{18}H_{24}NO_4S$ requires *M* + H, 350.1426]; $[\alpha]_D^{22}$ −82.6 (*c* 0.860 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.85 (3 H, d, *J* 6.5, CMe), 1.01 (3 H, d, *J* 7.0, CMe), 1.50–1.68 (1 H, m, $Me_2CH$), 2.32 (3 H, s, CMe), 2.64 (1 H, dd, *J* 9.7 and 7.0, 3-H), 2.69 (6 H, s, 2 × CMe), 3.43 (1 H, d, *J* 7.0, 2-H), 3.76 (3 H, s, OMe), 6.98 (2 H, s, Ph); *m*/*z* (FAB) 350 ($MH^+$, base peak), 294, 183, 166, 137, 119, 91, 77 and 55.

**(2*R*,3*S*)-3-Isopropyl-*N*-(2,4,6-trimethylphenylsulfonyl)-2-(2-trimethylsilylethynyl)aziridine 77**

By a procedure similar to that described for the preparation of **74** from **34**, the aziridine **35** (117 mg, 0.40 mmol) was converted into the title compound **77** (128 mg, 88% yield) as a colourless oil [Found (FAB): $(M + H)^+$, 364.1772. $C_{19}H_{30}NO_2SSi$ requires *M* + H, 364.1766]; $[\alpha]_D^{26}$ −62.4 (*c* 0.857 in $CHCl_3$); $\delta_H$ (270 MHz, $CDCl_3$) 0.14 (9 H, s, $SiMe_3$), 0.81 (3 H, d, *J* 6.5, CMe), 0.98 (3 H, d, *J* 6.8, CMe), 1.50–1.67 (1 H, m, $Me_2CH$), 2.31 (3 H, s, CMe), 2.52 (1 H, dd, *J* 9.7 and 7.0, 3-H), 2.70 (6 H, s, 2 × CMe), 3.38 (1 H, d, *J* 7.0, 2-H), 6.96 (2 H, s, Ph); *m*/*z* (FAB) 364 ($MH^+$, base peak), 362, 348, 271, 229, 181, 180, 167, 119 and 73.

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