A 2,3-*cis*-selective synthesis of aziridines bearing a vinyl group from allyl methyl carbonates and allyl mesylates

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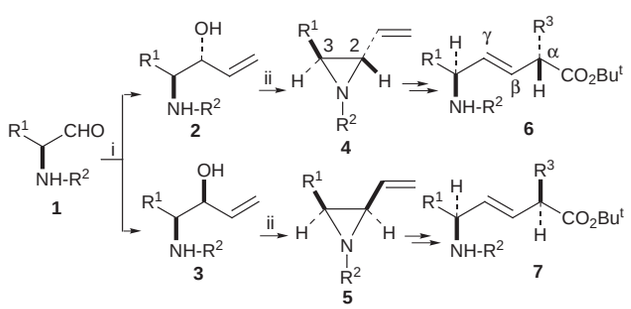
A convenient method for the synthesis of synthetically useful chiral 2-vinylaziridines from natural α-amino acids is described. Satisfactory 2,3-*cis*-selectivities are obtained by exposure of methyl carbonates of various allylic alcohols bearing an *N*-protected amino group to a catalytic amount of tetrakis(triphenylphosphine)palladium(0), $Pd(PPh_3)_4$, in aprotic solvents such as THF. Base-promoted aziridination of mesylates of various *N*-protected amino allylic alcohols followed by $Pd(PPh_3)_4$ catalyzed isomerization for the 2,3-*cis*-selective synthesis of vinylaziridines is also presented.

The *N*-activated or *N*-unactivated aziridines bearing an alkenyl group on one of the aziridine-ring carbon atoms have proven to be extremely valuable intermediates in synthetic chemistry today. Due to their very high reactivity and ability to function as carbon electrophiles, vinylaziridines and their analogues have been used as intermediates for the synthesis of azinomycin,[1] β-lactams,[2] (*R*)-(−)-dysidazirine,[3] azacycles such as 2,6-disubstituted tetrahydropyridines,[4] indolizidine alkaloids,[5] pyrrolizidine alkaloids,[6] allyl imines,[7] allyl amines,[8] sphingosines,[9] 3,7-disubstituted tetrahydroazepinone[10] and alkene dipeptide isosteres.[11]

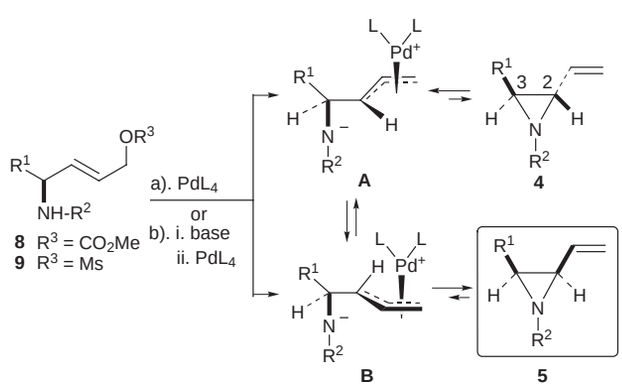
One of the simplest methods for the synthesis of dipeptide isosteres such as **6** and **7** *via* vinylaziridines of type **4** and **5** involves the use of *anti*- and *syn*-amino alcohols **2** and **3** which, in turn, could be synthesized from chiral amino aldehydes **1** by treatment with vinylic organometallic reagents (Scheme 1).



Scheme 1 *Reagents*: i, vinyl-M (M = Li, Mg, *etc.*); ii, PPh_3–$(NCO_2Et)_2$. R^1 = alkyl, aryl; R^2 = Boc, Ts, *etc.*; R^3 = alkyl.

However, when a chiral *N*-protected amino aldehyde **1** is reacted with excess vinylmagnesium bromide, vinyllithium, or vinylzinc halide a mixture of diastereomers **2** and **3** is always obtained in only moderate yields, even after extended periods, presumably due to enolization of the amino aldehydes to form the corresponding magnesio enolates.[12,13] In addition, the diastereomeric mixture of amino alcohols **2** and **3** derived from *N*-protected amino aldehydes such as (*S*)-alaninal and (*S*)-leucinal can be separated only with difficulty by repeated flash chromatography.[12,14] Moreover, the ratio of **2** and **3** is unpredictably highly dependent on the structure of the amino aldehyde, the reagent, the nature of the *N*-protective group,[12] the use of additives like boron trifluoride,[15] zinc chloride,[15] cerium trichloride[16] and diethylaluminum chloride,[15] and the solvent of the reaction.[12] It has been reported that the stereochemistry at the α-carbon in isosteres **6** and **7** is one of the essential factors for biological activity.[17] We also recently reported that some peptides containing a dipeptide isostere **7** are more potent than peptides containing a dipeptide isostere **6**.[18] In our continuing synthetic study of biologically active polypeptides containing an (*E*)-alkene dipeptide isostere, we were in need of a stereoselective synthetic route to 2,3-*cis*-aziridines **5**, which can be used to generate (*E*)-alkene dipeptide isosteres **7** with the desired stereochemistry at the α-position.

Since the discovery of the palladium-catalyzed reactions of allylic carbonates by Tsuji and co-workers,[19,20] the method has become an important tool for synthetic chemists today. As shown in Scheme 2, we anticipated that, by employing



Scheme 2 R^1 = alkyl, aryl, *etc.*; R^2 = Boc, Ts, *etc.*; L = PPh_3.

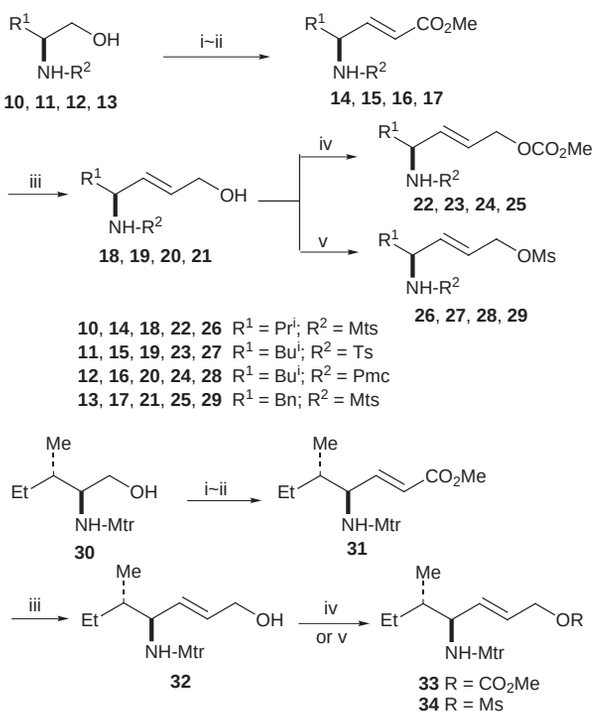
recent advances in palladium-catalyzed reactions of alkenylaziridines,[2,21,22] the palladium(0)-catalyzed reaction of readily available methyl carbonates **8** of amino allyl alcohols would aid in producing the desired, thermodynamically more stable 2,3-*cis*-isomers **5** predominantly *via* π-allyl palladium complexes **A** and **B**. Until now, a palladium(0)-catalyzed reaction of methyl allylic carbonates **8** for constructing synthetically important vinylaziridines has no precedent as far as we are aware. Detailed here is a new straightforward method for the synthesis of 2,3-disubstituted vinylaziridines **5** in a 2,3-*cis*-stereoselective manner from methyl carbonates **8** and methanesulfonates (mesylates) **9** of *N*-protected amino allylic alcohols.

Results and discussion

Synthesis of the methyl carbonates and mesylates of *N*-arylsulfonyl allylic alcohols

For the present study, it seemed that *N*-protection by the introduction of a strong electron-withdrawing group on the nitrogen atom was desirable. The choice of arylsulfonyl [*e.g.*, 2,4,6-trimethylphenylsulfonyl (Mts), 2,2,5,7,8-pentamethylchroman-6-ylsulfonyl (Pmc),[23] and 4-methoxy-2,3,6-trimethylphenylsulfonyl (Mtr)[24]] as both activating and protecting groups was based primarily on their ease of deprotection.

As shown in Scheme 3, the requisite chiral methyl allylic

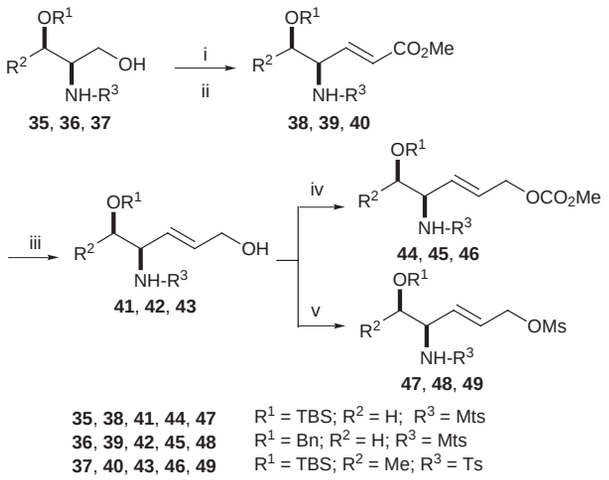


Scheme 3 *Abbreviations*: Mts = 2,4,6-trimethylphenylsulfonyl; Ts = *p*-tolylsulfonyl; Pmc = 2,2,5,7,8-pentamethylchroman-6-ylsulfonyl; Mtr = 4-methoxy-2,3,6-trimethylphenylsulfonyl. *Reagents*: i, $(COCl)_2$–DMSO–(*i*-Pr)$_2$NEt; ii, $Ph_3P{=}CHCO_2Me$; iii, DIBAL; iv, $ClCO_2Me$–pyridine; v, $MeSO_2Cl$–Et_3N.

carbonates (**22**–**25** and **33**) and the mesylates (**26**–**29** and **34**) of *N*-arylsulfonyl amino alcohols were prepared in acceptable yields starting from the *N*-arylsulfonyl amino alcohols (**10**–**13** and **30**) which, in turn, could be prepared from (*S*)-valinol,[25] (*S*)-leucinol,[26] (*S*)-phenylalaninol[25] and (*S*)-isoleucinol.[25] Typically, the known *N*-protected (*S*)-valinol **10**[21c] was treated successively with oxalyl chloride–DMSO–*N,N*-diisopropylethylamine and [(methoxycarbonyl)methylene]triphenylphosphorane to afford the (*E*)-enoate **14** which, on reduction with DIBAL, yielded the allylic alcohol **18**. Conversion of the alcohol **18** into both the carbonate **22** or the mesylate **26** was accomplished following standard procedures (see the Experimental section). The other chiral methyl allylic carbonates (**23**–**25** and **33**) and mesylates (**27**–**29** and **34**) listed in Scheme 3 were prepared from the corresponding *N*-protected amino alcohols (**11**–**13** and **30**) by a sequence of reactions similar to that described for the synthesis of the carbonate **22** and the mesylate **26** (see Experimental section).

In a similar manner, the *N*-protected amino alcohols **35**–**37**, readily available from methyl (*S*)-serinate hydrochloride,[12] *O*-benzyl-*N*-*tert*-butoxycarbonyl-(*S*)-serine,[27] and (*S*)-threonine, were converted into the corresponding methyl allylic carbonates **44**–**46** and the allylic mesylates **47**–**49** *via* the sequence of reactions shown in Scheme 4.

Finally, (*E*)-geometrical assignments for the α,β-enoates (**14**–



Scheme 4 *Reagents*: i, $(COCl)_2$–DMSO–(*i*-Pr)$_2$NEt; ii, $Ph_3P{=}CHCO_2Me$; iii, DIBAL; iv, $ClCO_2Me$–pyridine; v, $MeSO_2Cl$–Et_3N.

17, **31** and **38**–**40**), the methyl carbonates (**22**–**25**, **33** and **44**–**46**), and the mesylates (**26**–**29**, **34** and **47**–**49**) presented in Schemes 3 and 4 were ascertained from the coupling constant (*ca.* 15.5 Hz) of the two olefinic protons by ^{1}H NMR spectral analysis. In addition, optical purities of all α,β-unsaturated esters (**14**–**17**, **31** and **38**–**40**) as well as allylic alcohols (**18**–**21**, **32** and **41**–**43**) have been determined by HPLC with a chiral stationary phase (CHIRALCEL OD column; hexane–propan-2-ol = 97–85 : 3–15). Except for compounds **39** (ee 88%) and **42** (ee 88%) bearing a benzyloxy group, all other compounds were found to be essentially optically pure (ee >98%). Data for the optical purities of these compounds are listed in Table 1.

Palladium(0)-catalyzed aziridination reactions of methyl carbonates of *N*-arylsulfonyl amino alcohols

Having synthesized substrates for the possible palladium(0)-catalyzed aziridination reactions of methyl carbonates of *N*-arylsulfonyl amino alcohols, the reaction of *N*-protected methyl carbonates **52** and **53**, which in turn were readily prepared from the known corresponding allylic alcohols **50** and **51**,[21c] with $Pd(PPh_3)_4$ was briefly investigated (Scheme 5). As expected, when either the carbonate **52** or the isomeric carbonate **53** was treated with 5 mol% of $Pd(PPh_3)_4$ in THF at 60 °C for 20 min, a separable 94 : 6 ~ 95 : 5 mixture of 2,3-*cis*-3-isopropyl-2-vinylaziridine **54** and its 2,3-*trans*-isomer **55** was obtained in good yields *via* a decarboxylative ring closure.

Flash chromatographic separation of the mixture of **54** and **55** led to the isolation of the desired 2,3-*cis*-aziridine **54** in 85% yield from the carbonate **52**. The undesired 2,3-*trans*-aziridine **55** could be recycled for the palladium(0)-catalyzed isomerization reaction with a catalytic amount of $Pd(PPh_3)_4$. The 2,3-*cis*- and 2,3-*trans*-stereochemistries were readily established from ^{1}H NMR analysis. The 2,3-*cis*-aziridine **54** has a $J_{H_{2,3}}$ value (7.0 Hz) larger than the $J_{H_{2,3}}$ value (4.2 Hz) of the 2,3-*trans*-isomer. The data are in good agreement with ^{1}H NMR data for related compounds.[21b,c,28]

In a similar manner, palladium(0)-catalyzed reactions of carbonates (**22**–**25** and **33**) gave rise to the corresponding 2,3-*cis*-vinylaziridines (**54**, **56**, **58**, **60** and **62**) preferentially (Scheme 5 and Table 2). The stereoselection of the reaction of the carbonates was at least 94 : 6 favouring the thermodynamically more stable 2,3-*cis* cyclization products in good agreement with the *ab initio* calculations reported previously.[21b,c]

It should be clearly noted that the attempted palladium(0)-catalyzed reactions of carbonates such as **52** at 0 °C resulted in complete recovery of the unchanged starting substrates. The failed aziridination reaction of the carbonate **52** at 0 °C must be due to sluggishness in the formation of π-allyl intermediates.

Table 1 Synthesis of allylic methyl carbonates (**22**–**25**, **33** and **44**–**46**) and allylic mesylates (**26**–**29**, **34** and **47**–**49**)

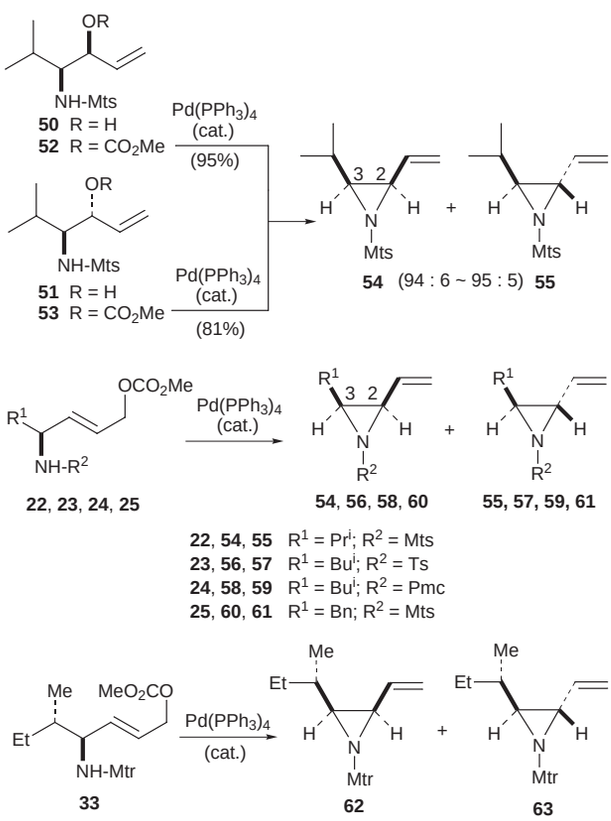
Entry	Amino alcohol	α,β-Enoate			Allylic alcohol			Carbonate		Mesylate	
		Product	Yield (%)[a]	% ee[b]	Product	Yield (%)[c]	% ee[b]	Product	Yield (%)[d]	Product	Yield (%)[d]
1	**10**	**14**	78	>98	**18**	86	>98	**22**	97	**26**	98
2	**11**	**15**	75	>98	**19**	87	>98	**23**	97	**27**	99
3	**12**	**16**	88	>98	**20**	52	>98	**24**	93	**28**	84
4	**13**	**17**	63	>98	**21**	86	>98	**25**	99	**29**	79
5	**30**	**31**	96	>98	**32**	88	>98	**33**	88	**34**	90
6	**35**	**38**	77	>98	**41**	79	>98	**44**	90	**47**	88
7	**36**	**39**	59	88	**42**	93	88	**45**	98	**48**	96
8	**37**	**40**	85	>98	**43**	90	>98	**46**	95	**49**	99

[a] Isolated yields based on amino alcohol. [b] Determined by chiral HPLC on a CHIRALCEL OD column (DAICEL; *n*-hexane–propan-2-ol = 97–83 : 3–15). [c] Isolated yields based on α,β-enoate. [d] Isolated yields based on allylic alcohol.

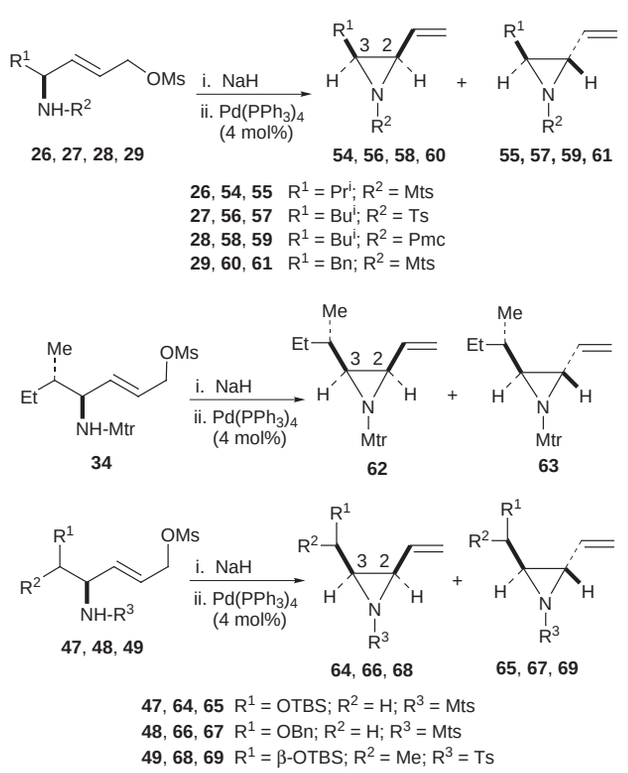
Table 2 $Pd(PPh_3)_4$ Catalyzed aziridination of allylic methyl carbonates **22**–**25** and **33**[a]

Entry	Substrate	$Pd(PPh_3)_4$ (mol%)	*T*/°C	*t*/min	*cis* : *trans*[b]	Yield (%)[c]
1	**22**	5	60	20	**54**:**55** = 94 : 6	72
2	**23**	4	65	10	**56**:**57** = 94 : 6	66
3	**24**	4	20	360	**58**:**59** = 97 : 3	59
4	**25**	4	65	5	**60**:**61** = 95 : 5	50
5	**33**	2	60	5	**62**:**63** = 98 : 2	85

[a] All reactions were carried out in THF. [b] Ratios were determined by reverse-phase HPLC ($MeOH : H_2O$ = 85–70 : 15–30 except for entry 2, $MeCN : H_2O$ = 1 : 1). [c] Combined isolated yields.



Scheme 5



Scheme 6

This was demonstrated by exposing an equimolar mixture of **52** and **55** to 5 mol% of $Pd(PPh_3)_4$ in THF at 0 °C for 1 h. Whereas the carbonate **52** was completely recovered unchanged, a 95 : 5 equilibrium mixture of 2,3-*cis*- and *trans*-aziridines **54** and **55** was obtained. Thus, the *N*-activated vinylaziridine **55** forms π-allyl intermediates more easily than the carbonate **52**.

It was assumed that the carbonates **44**–**46** bearing a benzyloxy or a *tert*-butyldimethylsilyl group (Scheme 4) under similar conditions would provide vinylaziridines. However, this was not to be the case since all attempts to cyclize the carbonates to vinylaziridines in the presence of $Pd(PPh_3)_4$ gave an inseparable mixture of products. The difficulty was overcome by treatment of the mesylates with sodium hydride followed by $Pd(PPh_3)_4$ as described below.

Aziridination reaction of the *N*-protected amino allylic mesylates with sodium hydride followed by equilibrated reaction with a catalytic amount of palladium(0)-catalyst

As shown in Scheme 6 and Table 3, following the Ohfune pro-

Table 3 Base-promoted aziridination of allylic mesylates **26**–**29**, **34** and **47**–**49** followed by equilibrated reaction with a catalytic amount of $Pd(PPh_3)_4$

			Aziridination reaction[a]		Pd(0)-Catalyzed equilibrated reaction[b]		
Entry	Substrate	*t*/h	*cis*:*trans*[c]	Yield (%)[d]	*t*/h	*cis*:*trans*[c]	Yield (%)[e]
1	**26**	0.5	**54**:**55** = 26:74	66	24	**54**:**55** = 96:4	99
2	**27**	1	**56**:**57** = 45:55	61	18	**56**:**57** = 96:4	97
3	**28**	0.5	**58**:**59** = 48:52	88	18	**58**:**59** = 97:3	95
4	**29**	0.5	**60**:**61** = 43:57	70	3	**60**:**61** = 95:5	82
5	**34**	0.5	**62**:**63** = 22:78	86	18	**62**:**63** = 98:2	95
6	**47**	4	**64**:**65** = 51:49	62	2	**64**:**65** = 92:8	90
7	**48**	3	**66**:**67** = 51:49	67	0.4	**66**:**67** = 94:6	77
8	**49**	2	**68**:**69** = 8:92	58	18	**68**:**69** = 92:8	92

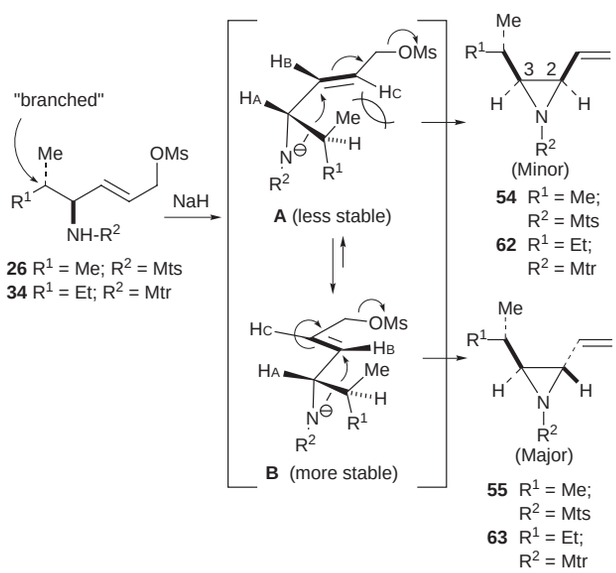
[a] All the aziridination reactions were carried out in DMF by treatment with NaH (1.5 equiv) at 0 °C except for entry 8 (25 °C). [b] The equilibrated reactions were carried out in THF at 0 °C using $Pd(PPh_3)_4$ (4 mol%). [c] Ratios were determined by reversed-phase HPLC ($MeOH:H_2O$ = 85–70:15–30 except for entry 2, $MeCN:H_2O$ = 1:1). [d] Combined isolated yields based on the corresponding allylic mesylates. [e] Combined isolated yields based on the base-promoted aziridination products.

cedure,[2a] the allylic mesylates (**26**–**29** and **34**) were treated with NaH in DMF at 0 °C to produce a mixture of the corresponding 2,3-*cis*-vinylaziridines (**54**, **56**, **58**, **60** and **62**) and their 2,3-*trans*-isomers (**55**, **57**, **59**, **61** and **63**) in variable ratios in moderate to high yields. Since the desired 2,3-*cis*-isomers were obtained as the minor products in all cases examined by base-promoted reactions, the mixtures of 2,3-*cis*- and 2,3-*trans*-isomers were treated with 5 mol% of $Pd(PPh_3)_4$ to yield the desired 2,3-*cis*-vinylaziridines as the major products.[21b,c]

Typically, a 26:74 mixture of 2,3-*cis*- and 2,3-*trans*-2-vinylaziridines **54** and **55** obtained by exposure of the mesylate **26** to sodium hydride was treated with 4 mol% of $Pd(PPh_3)_4$ in THF to yield a separable equilibrated 96:4 mixture of **54** and **55** in 99% combined yield in favour of the 2,3-*cis*-isomer **54**. Following this two-step procedure, the desired 2,3-*cis*-aziridines (**56**, **58**, **60** and **62**) were obtained predominantly starting from the corresponding mesylates (**27**–**29** and **34**) in satisfactory yields (Scheme 6 and Table 3).

As stated before, although the carbonates **44**–**46** bearing a *tert*-butyldimethylsiloxy or benzyloxy functionality could not be transformed into the corresponding vinylaziridines by treatment with a catalytic amount of $Pd(PPh_3)_4$, treatment of the mesylates **47**–**49** with sodium hydride followed by exposure to a catalytic amount of $Pd(PPh_3)_4$ gave the corresponding 2,3-*cis*-vinylaziridines (**64**, **66** and **68**) as the major products in synthetically acceptable yields (Scheme 6 and entries 6–8 in Table 3). Optical purities of all 2-vinylaziridines synthesized have been determined by HPLC with a chiral stationary phase (Chiralcel OD column; hexane:propan-2-ol = 99.5–99.0:0.5–1.0). Except for aziridines **66** (ee 88%) and **67** (ee 88%) bearing a benzyloxy group, all other 2-vinylaziridines were found to be essentially optically pure (ee >98%).

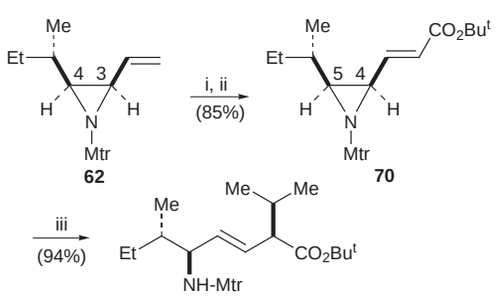
It should be clearly noted that treatment of the allylic mesylates **26** and **34** bearing a branched alkyl group with sodium hydride gave preferentially the corresponding 2,3-*trans*-aziridines **55** and **63** (Scheme 7, entries 1 and 5 in Table 3). Although the ground state and the reactive conformer 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.[29] The predominant formation of the 2,3-*trans*-isomers **55** and **63** from the corresponding mesylates **26** and **34** may be rationalized by assuming the preferred conformation **B** as shown in Scheme 7. The 2,3-*cis*- and the 2,3-*trans*-ratios of the S_N2' products may reflect the transition state energy difference related to the HA/HB staggered **B** and HA/HB eclipsed conformers **A**. In conformation **B**, the allylic 1,3-strain may be minimized. On the other hand, conformer **A**, which could lead to the 2,3-*cis*-isomer **54** *via* the S_N2' pathway, should be disfavoured by steric crowding between the isopropyl or the *sec*-butyl group and the HC hydrogen. Consequently, the reactions



Scheme 7

of the mesylates **26** and **34** with a branched alkyl group with sodium hydride yield the corresponding 2,3-*trans*-vinylaziridines **55** and **63** as the major products most probably *via* the conformer of type **B** (Scheme 7).

Finally, the synthesized 2,3-*cis*-vinylaziridines could be used for the synthesis of (*E*)-alkene isosteres (Scheme 8). For



Scheme 8 *Reagents*: i, O_3; ii, $(EtO)_2P(O)CH_2CO_2Bu^t$–$(i\text{-}Pr)_2NEt$–LiCl; iii, *i*-PrCu(CN)MgCl.

example, ozonolysis of vinylaziridine **62** followed by exposure to a mixture of *tert*-butyl diethylphosphonoacetate, lithium chloride and diisopropylethylamine gave the enoate **70** in 85% yield which, on reaction with $Pr^iCu(CN)MgCl$, gave the (*E*)-alkene isostere **71** in 94% yield as a single stereoisomer.

In summary, we have developed a reliable procedure for the

preparation of the synthetically useful 2,3-*cis*-vinylaziridines from natural α-amino acids. Satisfactory 2,3-*cis*-selectivities are obtained by exposure of methyl carbonates of various allylic alcohols bearing an *N*-protected amino group to a catalytic amount of $Pd(PPh_3)_4$ in aprotic solvents such as THF. Sodium hydride-promoted aziridination of various mesylates of *N*-protected amino allylic alcohols followed by $Pd(PPh_3)_4$-catalyzed isomerization for the 2,3-*cis*-selective synthesis of vinylaziridines is also presented. The described methodology involving palladium(0)-catalyzed 2,3-*cis*-selective aziridination has advantages over other methods in terms of mildness, selectivity and convenience.

Experimental

General methods

The instrumentation has already been described.[12b,c] 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 (Daicel, 4.6 × 260 mm) was used. For reversed-phase HPLC, μ-Bondasphere-C-18 (3.9 × 150 mm, Waters) was employed (28 °C).

(*S*)-*N*-(*p*-Tolylsulfonyl)leucinol 11

To a stirred mixture of (*S*)-leucinol (2.5 g, 21.3 mmol), Et_3N (5 cm^3, 36 mmol), THF (5 cm^3) and DMF (20 cm^3) was added toluene-*p*-sulfonyl chloride (4.87 g, 25.6 mmol) at 0 °C and the mixture was stirred for 6 h with warming to room temperature followed by quenching with 5 cm^3 of 5% aqueous $NaHCO_3$. The whole was extracted with a mixed solvent of Et_2O–EtOAc (3 : 1). The extract was washed successively with 5% aqueous citric acid, water, 5% aqueous $NaHCO_3$, and water, and dried over $MgSO_4$. Usual work-up gave the title compound **11** (4.68 g, 81%) as colourless crystals, mp 102 °C [from *n*-hexane–$CHCl_3$ (4 : 1)] (Found: C, 57.3; H, 7.55; N, 4.9. $C_{13}H_{21}NO_3S$ requires C, 57.5; H, 7.8; N, 5.2%); $[\alpha]_D^{19}$ −25.2 (*c* 1.03 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.64 (3 H, d, *J* 6.2, CMe), 0.78 (3 H, d, *J* 6.5, CMe), 1.16–1.33 (2 H, m, 3-CH_2), 1.36–1.54 (1 H, m, 4-H), 2.12–2.19 (1 H, m, OH), 2.43 (3 H, s, CMe), 3.24–3.36 (1 H, m, 2-H), 3.46 (1 H, ddd, *J* 11.3, 4.9 and 4.9, 1-C*H*H), 3.57 (1 H, ddd, *J* 11.3, 7.0 and 3.8, 1-CH*H*), 4.76 (1 H, d, *J* 7.6, NH), 7.30–7.33 (2 H, m, Ph), 7.70–7.80 (2 H, m, Ph).

(*S*)-*N*-(2,2,5,7,8-Pentamethylchroman-6-ylsulfonyl)leucinol 12

To a stirred mixture of (*S*)-leucinol (2.34 g, 20 mmol), Et_3N (5.56 cm^3, 40 mmol), THF (10 cm^3) and EtOAc (50 cm^3) was added 2,2,5,7,8-pentamethylchroman-6-ylsulfonyl chloride (6.2 g, 20 mmol) at 0 °C and the mixture was stirred at this temperature for 20 h followed by quenching with 5% aqueous $NaHCO_3$ (10 cm^3). The whole was extracted with Et_2O–EtOAc (1 : 1) and the extract was washed successively with 5% aqueous citric acid, brine, 5% aqueous $NaHCO_3$, and brine, and dried over $MgSO_4$. Usual work-up followed by flash chromatography over silica gel with *n*-hexane–EtOAc (2 : 3) gave the title compound **12** (5.02 g, 66%) as colourless crystals, mp 118 °C [from *n*-hexane–Et_2O (1 : 1)] (Found: C, 62.6; H, 8.6; N, 3.6. $C_{20}H_{33}NO_4S$ requires C, 62.6; H, 8.7; N, 3.65%); $[\alpha]_D^{19}$ −14.6 (*c* 0.997 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.68 (3 H, d, *J* 6.8, CMe), 0.76 (3 H, d, *J* 6.5, CMe), 1.19–1.29 (2 H, m, 3-CH_2), 1.32 (6 H, s, 2 × CMe), 1.40–1.53 (1 H, m, 4-H), 1.83 (2 H, t, *J* 7.0, 3′-CH_2), 2.09–2.12 (1 H, m, OH), 2.13 (3 H, s, CMe), 2.57 (3 H, s, CMe), 2.58 (3 H, s, CMe), 2.64 (1 H, t, *J* 7.0, 4′-CH_2), 3.25–3.35 (1 H, m, 2-H), 3.40–3.48 (1 H, m, 3-C*H*H), 3.57–3.65 (1 H, m, 3-CH*H*), 4.59 (1 H, d, *J* 8.1, NH).

(*S*)-*N*-(2,4,6-Trimethylphenylsulfonyl)phenylalaninol 13

To a stirred solution of (*S*)-phenylalaninol (6.05 g, 40 mmol) and Et_3N (8.3 cm^3, 60 mmol) in a mixed solvent of DMF (10 cm^3) and $CHCl_3$ (20 cm^3) was added mesitylenesulfonyl chloride (10.5 g, 48 mmol) in $CHCl_3$ (10 cm^3) at 0 °C and the mixture was stirred at this temperature for 48 h followed by quenching with 5% aqueous $NaHCO_3$ (10 cm^3). The whole was extracted with Et_2O and the extract was washed successively with 5% aqueous citric acid, H_2O, 5% aqueous $NaHCO_3$, and H_2O, and dried over $MgSO_4$. Usual work-up followed by flash chromatography over silica gel with *n*-hexane–EtOAc (2 : 1) gave the title compound **13** (12.3 g, 92%) as a colourless oil [Found (FAB): $(M + H)^+$, 334.1470. $C_{18}H_{24}NO_3S$ requires *M* + H, 334.1477]; $[\alpha]_D^{27}$ −29.4 (*c* 1.19 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 1.90 (1 H, br s, OH), 2.29 (3 H, s, CMe), 2.51 (6 H, s, 2 × CMe), 2.72 (1 H, dd, *J* 13.8 and 7.0, 3-C*H*H), 2.79 (1 H, dd, *J* 13.8 and 6.8, 3-CH*H*), 3.36–3.47 (1 H, m, 2-H), 3.52 (1 H, dd, *J* 11.1 and 4.3, 1-C*H*H), 3.65 (1 H, dd, *J* 11.1 and 4.1, 1-CH*H*), 4.91 (1 H, d, *J* 7.0, NH), 6.88 (2 H, s, Ph), 6.94–7.00 (2 H, m, Ph), 7.14–7.20 (3 H, m, Ph); *m*/*z* (FAB-LRMS) 334 (MH^+, base peak), 302, 242, 183, 152, 134, 119, 91, 60.

General procedure for preparation of γ-*N*-arylsulfonylamino-α,β-unsaturated esters 14–17, 31 and 38–40: methyl (4*S*,2*E*)-5-methyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]hex-2-enoate 14

To a stirred solution of oxalyl chloride (2.5 cm^3, 26 mmol) in a mixed solvent of $CHCl_3$ (30 cm^3) and *n*-hexane (30 cm^3) at −78 °C under argon was added dropwise a solution of DMSO (5.67 cm^3, 80 mmol) in $CHCl_3$ (10 cm^3). After 30 min, a solution of (*S*)-*N*-(2,4,6-trimethylphenylsulfonyl)valinol **10**[21c] (5.7 g, 20 mmol) in $CHCl_3$ (10 cm^3) was added to the above reagent at −78 °C, and the mixture was stirred for 30 min. Diisopropylethylamine (20.9 cm^3, 120 mmol) was added to the above solution at −78 °C and the mixture was stirred for 30 min with warming to 0 °C. A saturated NH_4Cl (10 cm^3) solution was added to the mixture and the whole was extracted with Et_2O. The extract was washed successively with 5% aqueous citric acid and water, and dried over $MgSO_4$. The extract was concentrated under reduced pressure to an oil, which was dissolved in $CHCl_3$ (50 cm^3). (Methoxycarbonylmethylene)triphenylphosphorane (6.68 g, 20 mmol) was added to the above solution at 0 °C, and the mixture was stirred for 1 h with warming to room temperature. Concentration under reduced pressure gave an oily residue, which was flash chromatographed on silica gel with *n*-hexane–EtOAc (3 : 1) to give the title compound **14** (5.3 g, 78%) as colourless needles, 98% ee (*S*) by HPLC [Daicel Chiralcel OD, *n*-hexane–propan-2-ol = 95 : 5 (0.5 cm^3 min^{-1}), (*S*)-isomer 34.7 min, (*R*)-isomer 29.9 min], mp 97 °C (from Et_2O) (Found: C, 59.9; H, 7.4; N, 4.0. $C_{17}H_{25}NO_4S$ requires C, 60.15; H, 7.4; N, 4.1%); $[\alpha]_D^{20}$ −60.9 (*c* 0.70 in $CHCl_3$); δ_H(270 MHz; $CDCl_3$) 0.82 (3 H, d, *J* 6.8, CMe), 0.90 (3H, d, *J* 6.5, CMe), 1.72–1.89 (1 H, m, 5-H), 2.28 (3 H, s, CMe), 2.62 (6 H, s, 2 × CMe), 3.64–3.68 (1 H, m, 4-H), 3.66 (3 H, s, OMe), 4.72 (1 H, d, *J* 8.6, NH), 5.61 (1 H, dd, *J* 15.4 and 1.1, 2-H), 6.54 (1 H, dd, *J* 15.4 and 7.3, 3-H), 6.92 (2 H, s, Ph).

Methyl (4*S*,2*E*)-6-methyl-4-[*N*-(*p*-tolylsulfonyl)amino]hept-2-enoate 15. By a procedure identical with that described for the preparation of the enoate **14** from **10**, the alcohol **11** (4.68 g, 17.3 mmol) was converted into the title compound **15** (4.21 g, 75%), mp 76 °C [colourless crystals from *n*-hexane–Et_2O (1 : 1)] (Found: C, 58.9; H, 7.2; N, 4.1. $C_{16}H_{23}NO_4S$ requires C, 59.05; H, 7.1; N, 4.3%); $[\alpha]_D^{20}$ −51.3 (*c* 0.834 in $CHCl_3$); δ_H(270 MHz,

$CDCl_3$) 0.78 (3 H, d, *J* 6.5, CMe), 0.83 (3 H, d, *J* 6.5, CMe), 1.30–1.36 (2 H, m, 5-CH_2), 1.53–1.62 (1 H, m, 6-H), 2.41 (3 H, s, CMe), 3.68 (3 H, s, OMe), 3.90–4.01 (1 H, m, 4-H), 4.78 (1 H, d, *J* 7.8, NH), 5.73 (1 H, dd, *J* 15.4 and 1.4, 2-H), 6.56 (1 H, dd, *J* 15.4 and 6.8, 3-H), 7.26–7.30 (2 H, m, Ph), 7.69–7.74 (2 H, m, Ph).

Methyl (4*S*,2*E*)-6-methyl-4-[*N*-(2,2,5,7,8-pentamethylchroman-6-ylsulfonyl)amino]hept-2-enoate 16. By a procedure identical with that described for the preparation of the enoate **14** from **10**, the alcohol **12** (4.78 g, 12.5 mmol) was converted into the title compound **16** (4.77 g, 88%) as a colourless oil [Found (FAB): $(M + H)^+$, 438.2290. $C_{23}H_{36}NO_5S$ requires *M* + H, 438.2314]; $[\alpha]_D^{21}$ −28.2 (*c* 1.64 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.81 (3 H, d, *J* 5.9, CMe), 0.83 (3 H, d, *J* 6.8, CMe), 1.24–1.46 (2 H, m, 5-CH_2), 1.31 (6 H, s, 2 × CMe), 1.52–1.67 (1 H, m, 6-H), 1.82 (2 H, t, *J* 7.0, 3′-CH_2), 2.10 (3 H, s, CMe), 2.52 (3 H, s, CMe), 2.54 (3 H, s, CMe), 2.63 (2 H, t, *J* 7.0, 4′-CH_2), 3.64 (3 H, s, OMe), 3.84–3.95 (1 H, m, 4-H), 4.44 (1 H, d, *J* 7.8, NH), 5.59 (1 H, dd, *J* 15.7 and 1.1, 2-H), 6.43 (1 H, dd, *J* 15.7 and 7.8, 3-H); *m*/*z* (FAB-LRMS) 438 (MH^+), 437, 267 (base peak), 219, 203, 170, 147.

Methyl (4*S*,2*E*)-5-phenyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]pent-2-enoate 17 and its (4*S*,2*Z*)-isomer. By a procedure identical with that described for the preparation of the enoate **14** from **10**, the alcohol **13** (4.0 g, 12.0 mmol) was converted into the title compound **17** (2.92 g, 63%) and its (*Z*)-isomer (190 mg, 4%). Compound **17**: mp 132 °C [colourless crystals from *n*-hexane–Et_2O (1 : 3)] (Found: C, 65.0; H, 6.5; N, 3.4. $C_{21}H_{25}NO_4S$ requires C, 65.1; H, 6.5; N, 3.6%); $[\alpha]_D^{27}$ −60.9 (*c* 1.14 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 2.28 (3 H, s, CMe), 2.46 (6 H, s, 2 × CMe), 2.79 (1 H, dd, *J* 13.8 and 7.3, 5-C*H*H), 2.86 (1 H, dd, *J* 13.8 and 6.2, 5-CH*H*), 3.68 (3 H, s, OMe), 4.03–4.14 (1 H, m, 4-H), 4.60 (1 H, d, *J* 7.0, NH), 5.77 (1 H, dd, *J* 15.9 and 1.4, 2-H), 6.71 (1 H, dd, *J* 15.9 and 6.2, 3-H), 6.87 (2 H, s, Ph), 6.98–7.05 (2 H, m, Ph), 7.20–7.28 (3 H, m, Ph). (*Z*)-Isomer of **17**: mp 154 °C [colourless crystals from *n*-hexane–$CHCl_3$ (5 : 1)] (Found: C, 64.85; H, 6.5; N, 3.6. $C_{21}H_{25}NO_4S$ requires C, 65.1; H, 6.5; N, 3.6%); $[\alpha]_D^{27}$ −42.7 (*c* 0.942 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 2.26 (6 H, s, 2 × CMe), 2.28 (3 H, s, CMe), 2.60 (1 H, dd, *J* 14.0 and 9.7, 5-C*H*H), 2.98 (1 H, dd, *J* 14.0 and 4.3, 5-CH*H*), 3.70 (3 H, s, OMe), 4.74 (1 H, d, *J* 4.6, NH), 4.87–4.97 (1 H, m, 4-H), 5.79 (1 H, dd, *J* 11.3 and 1.4, 2-H), 6.29 (1 H, dd, *J* 11.3 and 8.1, 3-H), 6.81 (2 H, s, Ph), 7.01–7.07 (2 H, m, Ph), 7.16–7.23 (3 H, m, Ph).

General procedure for preparation of allylic alcohols 18–21 and 32 and 41–43: (4*S*,2*E*)-5-methyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]hex-2-en-1-ol 18

DIBAL (1.0 mol dm^{-3} solution in toluene; 76.1 cm^3, 76.1 mmol) was added dropwise to a stirred solution of the enoate **14** (5.2 g, 34.6 mmol) in a mixed solvent of toluene (80 cm^3) and $CHCl_3$ (30 cm^3) at −78 °C under argon. After 1 h, a saturated NH_4Cl solution (30 cm^3) was added with vigorous stirring. The mixture was made acidic with saturated aqueous citric acid and extracted with EtOAc. The extract was washed with water and dried over $MgSO_4$. The usual work-up followed by recrystallization from Et_2O gave the title compound **18** (4.11 g, 86%) as colourless crystals, 98% ee (*S*) by HPLC [Daicel Chiralcel OD, *n*-hexane–propan-2-ol = 95 : 5 (0.5 cm^3 min^{-1}), (*S*)-isomer 46.4 min, (*R*)-isomer 42.0 min]; mp 122 °C (Found: C, 61.6; H, 8.15; N, 4.3. $C_{16}H_{25}NO_3S$ requires C, 61.7; H, 8.1; N, 4.5); $[\alpha]_D^{20}$ −22.8 (*c* 2.60 in $CHCl_3$); δ_H(270 MHz; $CDCl_3$) 0.80 (3 H, d, *J* 6.8, CMe), 0.87 (3 H, d, *J* 6.5, CMe), 1.35 (1 H, dd, *J* 5.1 and 5.1, OH), 1.62–1.80 (1 H, m, 5-H), 2.30 (3 H, s, CMe), 2.63 (6 H, s, 2 × CMe), 3.54 (1 H, ddd, *J* 7.8, 7.6 and 4.6, 4-H), 3.85 (1 H, d, *J* 5.1, 1-C*H*H), 3.87 (1 H, d, *J* 5.1, 1-CH*H*), 4.84 (1 H, d, *J* 7.8, NH), 5.32 (1 H, dddd, *J* 15.4, 7.8, 1.4 and 1.4, 3-H), 5.48 (1 H, dddd, *J* 15.4, 4.6, 4.6 and 0.7, 2-H), 6.94 (2 H, s).

(4*S*,2*E*)-6-Methyl-4-[*N*-(*p*-tolylsulfonyl)amino]hept-2-en-1-ol 19. By a procedure identical with that described for the preparation of the alcohol **18** from **14**, the enoate **15** (4.4 g, 13.5 mmol) was converted into the title compound **19** (3.5 g, 87%), mp 104 °C [colourless crystals from $CHCl_3$–Et_2O (1 : 2)] (Found: C, 60.4; H, 7.9; N, 4.8. $C_{15}H_{23}NO_3S$ requires C, 60.6; H, 7.8; N, 4.7%); $[\alpha]_D^{20}$ −20.4 (*c* 2.45 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.76 (3 H, d, *J* 6.5, CMe), 0.80 (3 H, d, *J* 6.5, CMe), 1.25 (1 H, dd, *J* 13.5 and 7.3, 5-C*H*H), 1.33 (1 H, dd, *J* 13.5 and 7.6, 5-CH*H*), 1.48–1.67 (1 H, m, 6-H), 1.85 (1 H, t, *J* 5.9, OH), 2.42 (3 H, s, CMe), 3.77 (1 H, dddd, *J* 7.8, 7.6, 7.3 and 7.3, 4-H), 3.89–3.93 (2 H, m, 1-CH_2), 5.12 (1 H, d, *J* 7.8, NH), 5.37 (1 H, ddd, *J* 15.7, 7.3 and 1.4, 3-H), 5.55 (1 H, ddd, *J* 15.7, 5.1 and 5.1, 2-H), 7.27–7.30 (2 H, m, Ph), 7.73–7.76 (2 H, m, Ph).

(4*S*,2*E*)-6-Methyl-4-[*N*-(2,2,5,7,8-pentamethylchroman-6-ylsulfonyl)amino]hept-2-en-1-ol 20. By a procedure similar to that described for the preparation of the alcohol **18** from **14**, the enoate **16** (4.59 g, 10.5 mmol) was converted into the title compound **20** (2.31 g, 52%), mp 113 °C [colourless crystals from *n*-hexane–Et_2O (1 : 1)] (Found: C, 64.3; H, 8.6; N, 3.3. $C_{22}H_{35}NO_4S$ requires C, 64.5; H, 8.6; N, 3.4%); $[\alpha]_D^{19}$ −8.61 (*c* 1.05 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.80 (3 H, d, *J* 6.8, CMe), 0.81 (3 H, d, *J* 6.5, CMe), 1.05–1.15 (1 H, m, OH), 1.18–1.31 (1 H, m, 5-C*H*H), 1.32 (6 H, s, 2 × CMe), 1.32–1.41 (1 H, m, 5-CH*H*), 1.49–1.63 (1 H, m, 6-H), 1.83 (2 H, t, *J* 6.8, 3′-CH_2), 2.13 (3 H, s, CMe), 2.54 (3 H, s, CMe), 2.55 (3 H, s, CMe), 2.65 (2 H, t, *J* 6.8, 4′-CH_2), 3.74–3.87 (3 H, m, 4-H and 1-CH_2), 4.42–4.46 (1 H, m, NH), 5.26 (1 H, dddd, *J* 15.7, 7.6, 1.1 and 1.1, 3-H), 5.52 (1 H, dddd, *J* 15.7, 5.4, 5.4 and 0.5, 2-H).

(4*S*,2*E*)-5-Phenyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]pent-2-en-1-ol 21. By a procedure identical with that described for the preparation of the alcohol **18** from **14**, the enoate **17** (2.7 g, 6.97 mmol) was converted into the title compound **21** (2.16 g, 86%), mp 99–100 °C [colourless needles from *n*-hexane–Et_2O (2 : 1)] (Found: C, 66.6; H, 6.95; N, 3.6. $C_{20}H_{25}NO_3S$ requires C, 66.8; H, 7.0; N, 3.9%); $[\alpha]_D^{19}$ −27.5 (*c* 0.75 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 1.27 (1 H, br s, OH), 2.29 (3 H, s, CMe), 2.48 (6 H, s, 2 × CMe), 2.75 (1 H, dd, *J* 13.5 and 7.6, 5-C*H*H), 2.81 (1 H, dd, *J* 13.5 and 6.8, 5-CH*H*), 3.88–3.95 (2 H, m, 1-CH_2), 3.92–4.02 (1 H, m, 4-H), 4.62–4.65 (1 H, m, NH), 5.46 (1 H, dd, *J* 15.7 and 7.0, 3-H), 5.58 (1 H, ddd, *J* 15.7, 4.9 and 4.9, 2-H), 6.88 (2 H, s, Ph), 7.02–7.05 (2 H, m, Ph), 7.17–7.29 (3 H, m, Ph).

General procedure for preparation of methyl carbonates 22–25, 33 and 44–46: (4*S*,2*E*)-*O*-methoxycarbonyl-5-methyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]hex-2-en-1-ol 22

To a stirred mixture of the alcohol **18** (2.06 g, 6.62 mmol), pyridine (5 cm^3) and $CHCl_3$ (3 cm^3) at −78 °C was added dropwise methyl chloroformate (1.03 cm^3, 13.2 mmol), and the mixture was stirred with warming to 0 °C. After 1 h, 5% $NaHCO_3$ (10 cm^3) was added to the mixture with vigorous stirring. The whole was extracted with a mixed solvent of Et_2O–EtOAc (3 : 1), and the extract was washed successively with 5% aqueous citric acid, H_2O, 5% aqueous $NaHCO_3$, and H_2O, and dried over $MgSO_4$. Usual work-up followed by flash chromatography over silica gel with *n*-hexane–EtOAc (3 : 1) gave the title compound **22** (2.37 g, 97%) as a colourless oil [Found (FAB): $(M + H)^+$, 370.1672. $C_{18}H_{28}NO_5S$ requires *M* + H, 370.1688]; $[\alpha]_D^{20}$ −10.4 (*c* 2.72 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.81 (3 H, d, *J* 7.0, CMe), 0.88 (3 H, d, *J* 6.5, CMe), 1.68–1.80 (1 H, m, 5-H), 2.29 (3 H, s, CMe), 2.61 (6 H, s, 2 × CMe), 3.49–3.57 (1 H, m, 4-H), 3.77 (3 H, s, OMe), 4.28–4.34 (2 H, m, 1-CH_2), 4.63 (1 H, d, *J* 7.8, NH), 5.35 (1 H, dd, *J* 15.7 and 4.9, C*H*=CH), 5.39 (1 H, dd, *J* 15.7 and 6.2, CH=C*H*), 6.92 (2 H, s, Ph); *m*/*z* (FAB-LRMS) 370 (MH^+), 368, 326, 294, 183, 171, 119 (base peak), 95.

(4*S*,2*E*)-*O*-Methoxycarbonyl-6-methyl-4-[*N*-(*p*-tolylsulfonyl)-amino]hept-2-en-1-ol 23. By a procedure identical with that described for the preparation of the carbonate **22** from **18**, the alcohol **19** (1.55 g, 5.2 mmol) was converted into the title compound **23** (1.80 g, 97%), mp 45 °C [colourless crystals from *n*-hexane–Et_2O (4:1)] (Found: C, 57.2; H, 7.0; N, 3.7. $C_{17}H_{25}NO_5S$ requires C, 57.4; H, 7.1; N, 3.9%); $[\alpha]_D^{20}$ −5.4 (*c* 2.07 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.79 (3 H, d, *J* 7.0, CMe), 0.82 (3 H, d, *J* 7.3, CMe), 1.26 (1 H, ddd, *J* 13.5, 7.0 and 7.0, 5-C*H*H), 1.34 (1 H, ddd, *J* 13.5, 7.0 and 7.0, 5-CH*H*), 1.53–1.68 (1 H, m, 6-H), 2.42 (3 H, s, CMe), 3.77 (3 H, s, OMe), 3.82 (1 H, dddd, *J* 7.8, 7.0, 7.0 and 6.2, 4-H), 4.34–4.41 (2 H, m, 1-CH_2), 4.81 (1 H, dd, *J* 7.8 and 4.3, NH), 5.42 (1 H, dd, *J* 15.9 and 6.2, 3-H), 5.48 (1 H, ddd, *J* 15.9, 5.4 and 5.4, 2-H), 7.26–7.29 (2 H, m, Ph), 7.71–7.74 (2 H, m, Ph).

(4*S*,2*E*)-*O*-Methoxycarbonyl-6-methyl-4-[*N*-(2,2,5,7,8-penta-methylchroman-6-ylsulfonyl)amino]hept-2-en-1-ol 24. By a procedure identical with that described for the preparation of the carbonate **22** from **18**, the alcohol **20** (2.11 g, 5 mmol) was converted into the title compound **24** (2.23 mg, 93%), mp 54 °C [colourless crystals from *n*-hexane–Et_2O (2:1)] (Found: C, 61.5; H, 8.0; N, 2.9. $C_{24}H_{37}NO_6S$ requires C, 61.6; H, 8.0; N, 3.0%); $[\alpha]_D^{18}$ −10.3 (*c* 1.00 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.79 (3 H, d, *J* 6.5, CMe), 0.81 (3 H, d, *J* 6.2, CMe), 1.26 (1 H, dd, *J* 13.5 and 7.3, 5-C*H*H), 1.32 (6 H, s, 2 × CMe), 1.36 (1 H, dd, *J* 13.5 and 7.3, 5-CH*H*), 1.49–1.62 (1 H, m, 6-H), 1.83 (2 H, t, *J* 6.8, 3′-CH_2), 2.12 (3 H, s, CMe), 2.52 (3 H, s, CMe), 2.54 (3 H, s, CMe), 2.65 (2 H, t, *J* 6.8, 4′-CH_2), 3.73–3.84 (1 H, m, 4-H), 3.77 (3 H, s, OMe), 4.25–4.37 (3 H, m, NH and 1-CH_2), 5.38 (1 H, dd, *J* 15.9 and 6.2, 3-H), 5.45 (1 H, ddd, *J* 15.9, 5.4 and 5.4, 2-H).

(4*S*,2*E*)-*O*-Methoxycarbonyl-5-phenyl-4-[*N*-(2,4,6-trimethyl-phenylsulfonyl)amino]pent-2-en-1-ol 25. By a procedure identical with that described for the preparation of the carbonate **22** from **18**, the alcohol **21** (290 mg, 0.81 mmol) was converted into the title compound **25** (335 mg, 99%) as a colourless oil [Found (FAB): $(M + H)^+$, 418.1683. $C_{22}H_{28}NO_5S$ requires *M* + H, 418.1688]; $[\alpha]_D^{22}$ −20.9 (*c* 0.766 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 2.28 (3 H, s, CMe), 2.47 (6 H, s, 2 × CMe), 2.76 (1 H, dd, *J* 13.8 and 7.3, 5-C*H*H), 2.81 (1 H, dd, *J* 13.8 and 6.2, 5-CH*H*), 3.78 (3 H, s, OMe), 3.91–4.00 (1 H, m, 4-H), 4.38 (1 H, d, *J* 14.3, 1-C*H*H), 4.40 (1 H, d, *J* 14.3, 1-CH*H*), 4.50 (1 H, d, *J* 6.2, NH), 5.51 (1 H, ddd, *J* 15.4, 4.9 and 4.9, 2-H), 5.53 (1 H, dd, *J* 15.4 and 5.7, 3-H), 6.87 (2 H, s, Ph), 7.01–7.07 (2 H, m, Ph), 7.17–7.28 (3 H, m, Ph); *m*/*z* (FAB-LRMS) 418 (MH^+), 342, 326, 219, 183, 143, 119 (base peak), 91.

General procedure for preparation of allylic methanesulfonates 26–29, 34 and 47–49: (4*S*,2*E*)-1-methylsulfonyloxy-5-methyl-4-[(2,4,6-trimethylphenylsulfonyl)amino]hex-2-ene 26

To a stirred mixture of the alcohol **18** (100 mg, 0.334 mmol), Et_3N (0.46 cm^3, 3.34 mmol), and THF (5 cm^3) was added dropwise methanesulfonyl chloride (0.13 cm^3, 1.67 mmol) at 0 °C. The stirring was continued for 0.5 h at 0 °C followed by quenching with 1 cm^3 of saturated aqueous $NaHCO_3$ with vigorous stirring. 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 work-up followed by flash chromatography over silica gel with *n*-hexane–EtOAc (2:1) gave the title compound **26** (127 mg, 98%), mp 56 °C [colourless crystals from *n*-hexane–Et_2O (1:10)] (Found: C, 52.45; H, 7.15; N, 3.4. $C_{17}H_{27}NO_5S_2$ requires C, 52.4; H, 7.0; N, 3.6%); $[\alpha]_D^{31}$ −31.4 (*c* 0.63 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.80 (3 H, d, *J* 6.8, CMe), 0.86 (3 H, d, *J* 7.0, CMe), 1.68–1.80 (1 H, m, 5-H), 2.30 (3 H, s, CMe), 2.62 (6 H, s, 2 × CMe), 2.98 (3 H, s, SO_2Me), 3.57 (1 H, ddd, *J* 7.8, 6.5 and 5.7, 4-H), 4.45–4.47 (2 H, m, 1-CH_2), 4.59 (1 H, d, *J* 7.8, NH), 5.49 (1 H, ddd, *J* 15.7, 5.7 and 5.7, 2-H), 5.55 (1 H, dd, *J* 15.7 and 6.5, 3-H), 6.94 (2 H, s).

(4*S*,2*E*)-*O*-Methylsulfonyloxy-6-methyl-4-[*N*-(*p*-tolylsulf-onyl)amino]hept-2-en-1-ol 27. By a procedure similar to that described for the preparation of the mesylate **26** from **18**, the alcohol **19** (100 mg, 0.336 mmol) was converted into the title compound **27** (125 mg, 99%) as a colourless oil [Found (FAB): $(M + H)^+$, 376.1236. $C_{16}H_{26}NO_5S_2$ requires *M* + H, 376.1252]; $[\alpha]_D^{28}$ −24.7 (*c* 0.825 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.76 (3 H, d, *J* 6.5, CMe), 0.82 (3 H, d, *J* 6.5, CMe), 1.23–1.35 (2 H, m, 5-CH_2), 1.55–1.65 (1 H, m, 6-H), 2.43 (3 H, s, CMe), 2.99 (3 H, s, SO_2Me), 3.80–3.90 (1 H, m, 4-H), 4.31 (1 H, d, *J* 7.8, NH), 4.52–4.54 (2 H, m, 1-CH_2), 5.52–5.60 (1 H, m, 2-H), 5.62 (1 H, dd, *J* 15.4 and 5.1, 3-H), 7.28–7.32 (2 H, m, Ph), 7.68–7.74 (2 H, m, Ph); *m*/*z* (FAB-LRMS) 376 (MH^+), 374, 280 (base peak), 240, 155, 139, 109, 91.

(4*S*,2*E*)-*O*-Methylsulfonyl-6-methyl-4-[*N*-(2,2,5,7,8-penta-methylchroman-6-ylsulfonyl)amino]hept-2-en-1-ol 28. By a procedure similar to that described for the preparation of the mesylate **26** from **18**, the alcohol **20** (90 mg, 0.22 mmol) was converted into the title compound **28** (90 mg, 84%) as a colourless oil [Found (FAB): $(M + H)^+$, 487.2070. $C_{23}H_{37}NO_6S_2$ requires *M* + H, 487.2062]; $[\alpha]_D^{24}$ −25.0 (*c* 1.17 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.76 (3 H, d, *J* 6.2, CMe), 0.81 (3 H, d, *J* 6.8, CMe), 1.18–1.43 (2 H, m, 5-CH_2), 1.32 (6 H, s, 2 × CMe), 1.47–1.61 (1 H, m, 6-H), 1.84 (2 H, t, *J* 7.0, 3′-CH_2), 2.13 (3 H, s, CMe), 2.53 (3 H, s, CMe), 2.54 (3 H, s, CMe), 2.65 (2 H, t, *J* 7.0, 4′-CH_2), 2.98 (3 H, s, SO_2Me), 3.75–3.87 (1 H, m, 4-H), 4.41 (1 H, d, *J* 7.6, NH), 4.43–4.53 (2 H, m, 1-CH_2), 5.55 (1 H, dd, *J* 15.6 and 2.1, 3-H), 5.57 (1 H, m, 2-H); *m*/*z* (FAB-LRMS) 487 (MH^+), 392, 267, 251, 203 (base peak), 202, 147, 109.

(4*S*,2*E*)-*O*-Methylsulfonyl-5-phenyl-4-[*N*-(2,4,6-trimethyl-phenylsulfonyl)amino]pent-2-en-1-ol 29. By a procedure similar to that described for the preparation of the mesylate **26** from **18**, the alcohol **21** (100 mg, 0.278 mmol) was converted into the title compound **29** (96 mg, 79%), mp 99–100 °C [colourless crystals from $CHCl_3$–Et_2O (1:10)] (Found: C, 57.4; H, 6.2; N, 3.3. $C_{21}H_{27}NO_5S_2$ requires C, 57.6; H, 6.2; N, 3.2%); $[\alpha]_D^{32}$ −34.2 (*c* 1.38 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 2.29 (3 H, s, CMe), 2.46 (6 H, s, 2 × CMe), 2.74 (1 H, dd, *J* 13.8 and 7.6, 5-C*H*H), 2.81 (1 H, dd, *J* 13.8 and 6.2, 5-CH*H*), 2.93 (3 H, s, SO_2Me), 3.92–4.02 (1 H, m, 4-H), 4.51–4.54 (2 H, m, 1-CH_2), 4.59 (1 H, d, *J* 6.5, NH), 5.61 (1 H, ddd, *J* 15.4, 5.1 and 5.1, 2-H), 5.70 (1 H, dd, *J* 15.4 and 6.2, 3-H), 6.88 (2 H, s, Ph), 6.97–7.03 (2 H, m, Ph), 7.19–7.24 (3 H, m, Ph).

(2*S*,3*S*)-2-[*N*-(4-Methoxy-2,3,6-trimethylphenylsulfonyl)-amino]-4-methylpentan-1-ol 30. To a stirred solution of (*S*)-isoleucinol (10 g, 85.3 mmol) in a mixed solvent of $CHCl_3$ (20 cm^3) and DMF (10 cm^3) were added Et_3N (24.8 cm^3, 179 mmol) and 4-methoxy-2,3,6-trimethylphenylsulfonyl chloride (22.3 g, 89.6 mmol) at 0 °C, and the mixture was stirred for 6 h at this temperature followed by quenching with 5 cm^3 of 5% aqueous $NaHCO_3$. The whole was extracted with Et_2O–EtOAc (1:1), and the extract was washed successively with 5% aqueous citric acid, water, 5% aqueous $NaHCO_3$, and water, and dried over $MgSO_4$. Concentration under reduced pressure gave an oily residue, which was filtered through a short pad of silica gel. The filtrate was concentrated under reduced pressure to leave a crystalline mass. Recrystallization from *n*-hexane–EtOAc (3:2) gave the title compound **30** (22.5 g, 80%) as colourless crystals. mp 63 °C (Found: C, 58.4; H, 8.2; N, 4.3. $C_{16}H_{27}NO_4S$ requires C, 58.3; H, 8.3; N, 4.25%); $[\alpha]_D^{25}$ −17.1 (*c* 1.51 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.76 (3 H, t, *J* 7.8, CMe), 0.77 (3 H, d, *J* 7.3, CMe), 0.95–1.11 (1 H, m, 4-C*H*H), 1.31–1.57 (2 H, m, 4-CH*H* and 3-H), 2.15 (3 H, s, CMe), 2.17 (1 H, m, OH), 2.61 (3 H, s, CMe), 2.68 (3 H, s, CMe), 3.10 (1 H, dddd, *J* 8.6, 5.4, 5.4 and

5.4, 2-H), 3.57 (1 H, d, *J* 5.4, 1-C*H*H), 3.59 (1 H, d, *J* 5.4, 1-CH*H*), 3.85 (3 H, s, OMe), 4.89–5.01 (1 H, m, NH), 6.58 (1 H, s, Ph).

Methyl (4*S*,5*S*,2*E*)-4-[*N*-(4-methoxy-2,3,6-trimethylphenylsulfonyl)amino]-5-methylhept-2-enoate 31. By a procedure identical with that described for the preparation of the enoate **14** from **10**, the alcohol **30** (4.5 g, 13.7 mmol) was converted into the title compound **31** (5.04 g, 96%) as a colourless oil [Found (FAB): $(M + H)^+$, 384.1841. $C_{19}H_{30}NO_5S$ requires *M* + H, 384.1845]; $[\alpha]_D^{23}$ −31.9 (*c* 1.13 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.80 (3 H, d, *J* 6.8, CMe), 0.85 (3 H, t, *J* 7.3, CMe), 1.02–1.26 (1 H, m, 6-C*H*H), 1.35–1.62 (2 H, m, 6-CH*H* and 5-H), 2.11 (3 H, s, CMe), 2.56 (3 H, s, CMe), 2.65 (3 H, s, CMe), 3.64 (3 H, s, OMe), 3.72 (1 H, ddd, *J* 8.1, 7.8 and 5.4, 4-H), 3.84 (3 H, s, OMe), 4.65 (1 H, d, *J* 8.1, NH), 5.53 (1 H, dd, *J* 15.7 and 1.1, 2-H), 6.47 (1 H, dd, *J* 15.7 and 7.8, 3-H), 6.55 (1 H, s, Ph); *m*/*z* (FAB-LRMS) 384 (MH^+), 382, 326, 213 (base peak), 197, 155, 149, 119, 91.

(4*S*,5*S*,2*E*)-4-[*N*-(4-Methoxy-2,3,6-trimethylphenylsulfonyl)amino]-5-methylhept-2-en-1-ol 32. By a procedure identical with that described for the preparation of the alcohol **18** from **14**, the enoate **31** (5.2 g, 13.6 mmol) was converted into the title compound **32** (4.25 g, 88%) as a colourless oil [Found (FAB): $(M + H)^+$, 356.1900. $C_{18}H_{30}NO_4S$ requires *M* + H, 356.1895]; $[\alpha]_D^{25}$ −7.26 (*c* 1.02 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.78 (3 H, d, *J* 6.5, CMe), 0.83 (3 H, t, *J* 7.0, CMe), 0.99–1.15 (1 H, m, 6-C*H*H), 1.21–1.54 (2 H, m, 6-CH*H* and 5-H), 2.15 (3 H, s, CMe), 2.58 (3 H, s, CMe), 2.66 (3 H, s, CMe), 3.65 (1 H, ddd, *J* 7.8, 7.3 and 6.2, 4-H), 3.85 (3 H, s, OMe), 3.86 (1 H, d, *J* 5.4, 1-C*H*H), 3.88 (1 H, d, *J* 5.4, 1-CH*H*), 4.70 (1 H, d, *J* 7.3, NH), 5.31 (1 H, dd, *J* 15.4 and 7.8, 3-H), 5.49 (1 H, ddd, *J* 15.4, 5.4 and 5.4, 2-H), 6.56 (1 H, s, Ph); *m*/*z* (FAB-LRMS) 356 (MH^+), 354, 338, 298, 230, 213 (base peak), 197, 165, 149, 119, 109, 91, 86.

(4*S*,5*S*,2*E*)-*O*-Methoxycarbonyl-4-[*N*-(4-methoxy-2,3,6-trimethylphenylsulfonyl)amino]-5-methylhept-2-en-1-ol 33. By a procedure identical with that described for the preparation of the carbonate **22** from **18**, the alcohol **32** (2.0 g, 5.63 mmol) was converted into the title compound **33** (2.05 g, 88%) as a colourless oil [Found (FAB): $(M + H)^+$, 414.1945. $C_{20}H_{32}NO_6S$ requires *M* + H, 414.1950]; $[\alpha]_D^{18}$ 0 ± 1 (*c* 1.12 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.79 (3 H, d, *J* 6.5, CMe), 0.84 (3 H, t, *J* 7.3, CMe), 0.99–1.16 (1 H, m, 6-C*H*H), 1.31–1.57 (2 H, m, 6-CH*H* and 5-H), 2.14 (3 H, s, CMe), 2.56 (3 H, s, CMe), 2.64 (3 H, s, CMe), 3.58–3.70 (1 H, m, 4-H), 3.77 (3 H, s, OMe), 3.85 (3 H, s, OMe), 4.30 (1 H, dd, *J* 14.3 and 1.1, 1-C*H*H), 4.32 (1 H, dd, *J* 14.3 and 1.6, 1-CH*H*), 4.49 (1 H, d, *J* 7.6, NH), 5.36 (1 H, dd, *J* 15.1 and 1.6, 3-H), 5.37–5.44 (1 H, m, 2-H), 6.55 (1 H, s, Ph); *m*/*z* (FAB-LRMS) 414 (MH^+), 412, 356, 338, 213 (base peak), 197, 149, 109.

(4*S*,5*S*,2*E*)-*O*-Methylsulfonyl-4-[*N*-(4-methoxy-2,3,6-trimethylphenylsulfonyl)amino]-5-methylhept-2-en-1-ol 34. By a procedure similar to that described for the preparation of the mesylate **26** from **18**, the alcohol **32** (711 mg, 2.0 mmol) was converted into the title compound **34** (780 mg, 90%) as a colourless oil [Found (FAB): $(M + H)^+$, 434.1659. $C_{19}H_{32}NO_6S_2$ requires *M* + H, 434.1671]; $[\alpha]_D^{24}$ −17.5 (*c* 0.902 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.78 (3 H, d, *J* 6.5, CMe), 0.83 (3 H, t, *J* 7.3, CMe), 0.99–1.15 (1 H, m, 6-C*H*H), 1.30–1.53 (2 H, m, 6-CH*H* and 5-H), 2.15 (3 H, s, CMe), 2.57 (3 H, s, CMe), 2.64 (3 H, s, CMe), 2.97 (3 H, s, SO_2Me), 3.64–3.71 (1 H, m, 4-H), 3.86 (3 H, s, OMe), 4.43–4.51 (2 H, m, 1-CH_2), 4.54 (1 H, d, *J* 7.8, NH), 5.50 (1 H, dd, *J* 15.7 and 5.4, 3-H), 5.53 (1 H, m, 2-H), 6.57 (1 H, s, Ph); *m*/*z* (FAB-LRMS) 434 (MH^+), 376, 338, 213 (base peak), 197, 149, 134, 109.

(2*R*)-1-*tert*-Butyldimethylsiloxy-2-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]propan-3-ol 35. By a procedure identical with that described for the preparation of the alcohol **18** from **14**, methyl (*S*)-*O*-*tert*-butyldimethylsilyl-*N*-(2,4,6-trimethylphenylsulfonyl)serinate (8.3 g, 20.0 mmol) was converted into the title compound **35** (4.87 g, 63%), mp 87 °C (colourless crystals from *n*-hexane) (Found: C, 55.8; H, 8.6; N, 3.4. $C_{18}H_{33}NO_4SSi$ requires C, 55.8; H, 8.6; N, 3.6%); $[\alpha]_D^{26}$ +16.3 (*c* 0.808 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.02 (6 H, s, 2 × SiMe), 0.86 (9 H, s, CMe_3), 2.27 (1 H, m, OH), 2.30 (3 H, s, CMe), 2.65 (6 H, s, 2 × CMe), 3.16–3.25 (1 H, m, 2-H), 3.48–3.57 (2 H, m, 1-C*H*H and 3-C*H*H), 3.63–3.72 (2 H, m, 1-CH*H* and 3-CH*H*), 5.29 (1 H, d, *J* 7.8, NH), 6.96 (2 H, s, Ph).

(2*R*)-1-Benzyloxy-2-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]propan-3-ol 36. By a procedure identical with that described for the preparation of the alcohol **18** from **14**, methyl (*S*)-*O*-benzyl-*N*-(2,4,6-trimethylphenylsulfonyl)serinate (5.7 g, 14.6 mmol) was converted into the title compound **36** (4.17 g, 79%) as a colourless oil [Found (FAB): $(M + H)^+$, 364.1586. $C_{19}H_{26}NO_4S$ requires *M* + H, 364.1582]; $[\alpha]_D^{27}$ +22.6 (*c* 1.37 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 2.20–2.27 (1 H, m, OH), 2.30 (3 H, s, CMe), 2.62 (6 H, s, 2 × CMe), 3.34 (1 H, m, 2-H), 3.39 (1 H, dd, *J* 9.2 and 4.3, 1-C*H*H), 3.53 (1 H, dd, *J* 9.2 and 4.1, 1-CH*H*), 3.53–3.59 (1 H, m, 3-C*H*H), 3.69 (1 H, ddd, *J* 11.6, 4.3 and 4.3, 3-CH*H*), 4.38 (2 H, m, PhCH_2), 5.31 (1 H, d, *J* 7.8, NH), 6.93 (2 H, s, Ph), 7.19–7.38 (5 H, m, Ph); *m*/*z* (FAB-LRMS) 364 (MH^+), 362, 256, 242, 182, 167, 150, 119, 91 (base peak), 74, 60.

(2*R*,3*R*)-3-*tert*-Butyldimethylsiloxy-2-[*N*-(*p*-tolylsulfonyl)amino]butan-1-ol 37. By a procedure identical with that described for the preparation of the alcohol **18** from **14**, methyl (2*S*,3*R*)-*O*-*tert*-butyldimethylsilyl-*N*-(*p*-tolylsulfonyl)threoninate (6.40 g, 15.9 mmol) was converted into the title compound **37** (4.55 g, 76%) as a colourless oil [Found (FAB): $(M + H)^+$, 374.1823. $C_{17}H_{32}NO_4SSi$ requires *M* + H, 374.1821]; $[\alpha]_D^{25}$ −10.9 (*c* 1.32 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.04 (6 H, s, $SiMe_2$), 0.86 (9 H, s, CMe_3), 0.92 (3 H, d, *J* 6.2, CMe), 2.19 (1 H, dd, *J* 7.6 and 4.3, OH), 2.42 (3 H, s, CMe), 3.11 (1 H, dddd, *J* 7.8, 6.5, 5.7 and 2.2, 2-H), 3.50 (1 H, ddd, *J* 10.8, 7.6 and 6.5, 1-C*H*H), 3.60 (1 H, ddd, *J* 10.8, 5.7 and 4.3, 1-CH*H*), 4.00 (1 H, qd, *J* 6.2 and 2.2, 3-H), 5.02 (1 H, d, *J* 7.8, NH), 7.28–7.32 (2 H, m, Ph), 7.75–7.80 (2 H, m, Ph); *m*/*z* (FAB-LRMS) 374 (MH^+, base peak), 316, 242, 220, 198, 155, 139, 91, 73.

Methyl (4*R*,2*E*)-5-*tert*-butyldimethylsiloxy-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]pent-2-enoate 38 and its (4*R*,2*Z*) isomer. By a procedure identical with that described for the preparation of the enoate **14** from **10**, the alcohol **35** (4.6 g, 11.9 mmol) was converted into the title compound **38** (4.02 g, 77%) and its (*Z*)-isomer (301 mg, 6%). Compound **38**: a colourless oil [Found (FAB): $(M + H)^+$, 442.2079. $C_{21}H_{36}NO_5SSi$ requires *M* + H, 442.2083]; $[\alpha]_D^{27}$ −47.4 (*c* 1.19 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.02 (6 H, s, 2 × SiMe), 0.86 (9 H, s, CMe_3), 2.29 (3 H, s, CMe), 2.61 (6 H, s, 2 × CMe), 3.50–3.61 (2 H, m, 5-CH_2), 3.68 (3 H, s, OMe), 3.83–3.92 (1 H, m, 4-H), 5.19 (1 H, d, *J* 6.5, NH), 5.85 (1 H, d, *J* 15.4, 2-H), 6.65 (1 H, dd, *J* 15.4 and 6.5, 3-H), 6.94 (2 H, s, Ph); *m*/*z* (FAB-LRMS) 442 (MH^+), 426, 384 (base peak), 256, 243, 183, 167, 119, 89, 73. (*Z*)-Isomer of **38**: mp 44 °C (colourless crystals from *n*-hexane) (Found: C, 56.8; H, 8.0; N, 2.9. $C_{21}H_{35}NO_5SSi$ requires C, 57.1; H, 8.0; N, 3.2%); $[\alpha]_D^{24}$ −23.9 (*c* 0.977 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.05 (6 H, s, 2 × SiMe), 0.86 (9 H, s, CMe_3), 2.29 (3 H, s, CMe), 2.59 (6 H, s, 2 × CMe), 3.51 (1 H, dd, *J* 9.7 and 5.7, 5-C*H*H), 3.65 (3 H, s, OMe), 3.66 (1 H, dd, *J* 9.7 and 4.1, 5-CH*H*), 4.79–4.89 (1 H, m, 4-H), 5.43 (1 H, d, *J* 5.4, NH), 5.72 (1 H, d, *J* 11.9, 2-H), 6.12 (1 H, dd, *J* 11.9 and 8.4, 3-H), 6.93 (2 H, s, Ph).

Methyl (4*R*,2*E*)-5-benzyloxy-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]pent-2-enoate 39 and its (4*R*,2*Z*) isomer. By a procedure identical with that described for the preparation of the enoate **14** from **10**, the alcohol **36** (4.0 g, 11.0 mmol) was converted into the title compound **39** (2.7 g, 59%) and its (*Z*)-isomer (320 mg, 7%). Compound **39**: a colourless oil [Found (FAB): $(M + H)^+$, 418.1684. $C_{22}H_{28}NO_5S$ requires *M* + H, 418.1688]; $[\alpha]_D^{25}$ −35.5 (*c* 1.41 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 2.29 (3 H, s, CMe), 2.58 (6 H, s, 2 × CMe), 3.37–3.46 (2 H, m, 5-CH_2), 3.69 (3 H, s, OMe), 3.95–4.05 (1 H, m, 4-H), 4.41 (1 H, d, *J* 12.2, PhC*H*H), 4.42 (1 H, d, *J* 12.2, PhCH*H*), 5.20 (1 H, d, *J* 6.8, NH), 5.88 (1 H, dd, *J* 15.7 and 1.4, 2-H), 6.68 (1 H, dd, *J* 15.7 and 6.5, 3-H), 6.91 (2 H, s, Ph), 7.20–7.38 (5 H, m, Ph); *m*/*z* (FAB-LRMS) 418 (MH^+), 416, 386, 310, 296, 290, 234, 209, 183, 167, 128, 119, 91 (base peak), 77. (*Z*)-Isomer of **39**: a colourless oil [Found (FAB): $(M + H)^+$, 418.1692. $C_{22}H_{28}NO_5S$ requires *M* + H, 418.1688]; $[\alpha]_D^{25}$ −14.6 (*c* 0.632 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 2.29 (3 H, s, CMe), 2.55 (6 H, s, 2 × CMe), 3.44 (1 H, dd, *J* 9.7 and 6.5, 5-C*H*H), 3.52 (1 H, dd, *J* 9.7 and 4.1, 5-CH*H*), 3.65 (3 H, s, OMe), 4.37 (1 H, d, *J* 12.2, PhC*H*H), 4.38 (1 H, d, *J* 12.2, PhCH*H*), 4.99–5.09 (1 H, m, 4-H), 5.43 (1 H, d, *J* 5.1, NH), 5.73 (1 H, dd, *J* 11.3 and 1.6, 2-H), 6.16 (1 H, dd, *J* 11.3 and 8.4, 3-H), 6.90 (2 H, s, Ph), 7.20–7.37 (5 H, m, Ph); *m*/*z* (FAB-LRMS) 418 (MH^+), 296, 234, 212, 183, 167, 119, 91 (base peak).

Methyl (4*R*,5*R*,2*E*)-5-*tert*-butyldimethylsiloxy-4-[*N*-(*p*-tolylsulfonyl)amino]hex-2-enoate 40. By a procedure identical with that described for the preparation of the enoate **14** from **10**, the alcohol **37** (4.34 g, 11.6 mmol) was converted into the title compound **40** (4.23 g, 85%). mp 63 °C (colourless needles from *n*-hexane) [Found (FAB): $(M + H)^+$, 428.1918. $C_{20}H_{34}NO_5SSi$ requires *M* + H, 428.1927]; $[\alpha]_D^{30}$ −47.4 (*c* 1.00 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) −0.02 (3 H, s, SiMe), 0.02 (3 H, s, SiMe), 0.84 (9 H, s, CMe_3), 1.08 (3 H, d, *J* 5.9, CMe), 2.41 (3 H, s, CMe), 3.68 (3 H, s, OMe), 3.78–3.89 (2 H, m, 4-H and 5-H), 4.99 (1 H, d, *J* 7.8, NH), 5.76 (1 H, d, *J* 15.9, 2-H), 6.67 (1 H, dd, *J* 15.9 and 5.9, 3-H), 7.26–7.30 (2 H, m, Ph), 7.69–7.73 (2 H, m, Ph); *m*/*z* (FAB-LRMS) 428 (MH^+), 412, 370, 296, 257, 228, 214, 159, 155, 91, 73 (base peak).

(4*R*,2*E*)-5-*tert*-Butyldimethylsiloxy-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]pent-2-en-1-ol 41. By a procedure identical with that described for the preparation of the alcohol **18** from **14**, the enoate **38** (3.9 g, 8.83 mmol) was converted into the title compound **41** (2.88 g, 79%) as a colourless oil [Found (FAB): $(M + H)^+$, 414.2138. $C_{20}H_{36}NO_4SSi$ requires *M* + H, 414.2134]; $[\alpha]_D^{24}$ −26.6 (*c* 1.53 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.029 (3 H, s, SiMe), 0.032 (3 H, s, SiMe), 0.87 (9 H, s, CMe_3), 1.11 (1 H, m, OH), 2.30 (3 H, s, CMe), 2.62 (6 H, s, 2 × CMe), 3.47 (1 H, dd, *J* 10.0 and 5.4, 5-C*H*H), 3.57 (1 H, dd, *J* 10.0 and 4.3, 5-CH*H*), 3.70–3.78 (1 H, m, 4-H), 3.89–3.92 (2 H, m, 1-CH_2), 5.18 (1 H, d, *J* 5.4, NH), 5.39 (1 H, dddd, *J* 15.7, 7.8, 1.6 and 1.6, 3-H), 5.65 (1 H, dddd, *J* 15.7, 5.1, 5.1 and 0.8, 2-H), 6.94 (2 H, s, Ph); *m*/*z* (FAB-LRMS) 414 (MH^+), 396, 356, 314, 298, 256, 215, 197, 167, 119, 89, 73 (base peak), 59.

(4*R*,2*E*)-5-Benzyloxy-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]pent-2-en-1-ol 42. By a procedure identical with that described for the preparation of the alcohol **18** from **14**, the enoate **39** (2.6 g, 6.23 mmol) was converted into the title compound **42** (2.26 g, 93%) as a colourless oil [Found (FAB): $(M + H)^+$, 390.1747. $C_{21}H_{28}NO_4S$ requires *M* + H, 390.1739]; $[\alpha]_D^{26}$ −23.2 (*c* 0.896 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 1.25 (1 H, dd, *J* 5.9 and 5.9, OH), 2.29 (3 H, s, CMe), 2.59 (6 H, s, 2 × CMe), 3.37 (1 H, dd, *J* 9.2 and 5.7, 5-C*H*H), 3.40 (1 H, dd, *J* 9.2 and 4.9, 5-CH*H*), 3.85–3.93 (3 H, m, 4-H and 1-CH_2), 4.42 (1 H, d, *J* 11.9, PhC*H*H), 4.43 (1 H, d, *J* 11.9, PhCH*H*), 5.19 (1 H, d, *J* 5.9, NH), 5.44 (1 H, dddd, *J* 15.9, 7.6, 1.4 and 1.4, 3-H), 5.67 (1 H, dddd, *J* 15.9, 5.4, 5.4 and 1.1, 2-H), 6.92 (2 H, s, Ph), 7.22–7.38 (5 H, m, Ph); *m*/*z* (FAB-LRMS) 390 (MH^+), 372, 290, 268, 200, 183, 167, 119, 91 (base peak).

(4*R*,5*R*,2*E*)-5-*tert*-Butyldimethylsiloxy-4-[*N*-(*p*-tolylsulfonyl)amino]hex-2-en-1-ol 43. By a procedure identical with that described for the preparation of the alcohol **18** from **14**, the enoate **40** (3.93 g, 9.19 mmol) was converted into the title compound **43** (3.32 g, 90%), mp 79 °C [colourless crystals from *n*-hexane–Et_2O (4:1)] (Found: C, 56.8; H, 8.6; N, 3.2. $C_{19}H_{33}NO_4SSi$ requires C, 57.1; H, 8.3; N, 3.5%); $[\alpha]_D^{31}$ −26.4 (*c* 1.39 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.01 (3 H, s, SiMe), 0.02 (3 H, s, SiMe), 0.86 (9 H, s, CMe_3), 1.07 (3 H, d, *J* 5.9, CMe), 1.26 (1 H, dd, *J* 5.9 and 5.9, OH), 2.41 (3 H, s, CMe), 3.56–3.64 (1 H, m, 5-H), 3.73–3.81 (1 H, m, 4-H), 3.92 (1 H, d, *J* 5.1, 1-C*H*H), 3.94 (1 H, d, *J* 5.1, 1-CH*H*), 4.95 (1 H, d, *J* 7.3, NH), 5.43 (1 H, dd, *J* 15.4 and 6.5, 3-H), 5.58 (1 H, ddd, *J* 15.4, 5.1 and 5.1, 2-H), 7.26–7.30 (2 H, m, Ph), 7.69–7.73 (2 H, m, Ph).

(4*R*,2*E*)-5-*tert*-Butyldimethylsiloxy-*O*-methoxycarbonyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]pent-2-en-1-ol 44. By a procedure identical with that described for the preparation of the carbonate **22** from **18**, the alcohol **41** (1.5 g, 3.63 mmol) was converted into the title compound **44** (1.54 g, 90%), mp 57 °C [colourless shiny needles from *n*-hexane–Et_2O (4:1)] [Found (FAB): $(M + H)^+$, 472.2186. $C_{22}H_{38}NO_6SSi$ requires *M* + H, 472.2189]; $[\alpha]_D^{27}$ −22.8 (*c* 0.996 in $CHCl_3$); δ_H(300 MHz, $CDCl_3$) 0.019 (3 H, s, SiMe), 0.020 (3 H, s, SiMe), 0.86 (9 H, s, CMe_3), 2.29 (3 H, s, CMe), 2.61 (6 H, s, 2 × CMe), 3.48 (1 H, dd, *J* 9.9 and 5.4, 5-C*H*H), 3.54 (1 H, dd, *J* 9.9 and 4.1, 5-CH*H*), 3.70–3.76 (1 H, m, 4-H), 3.77 (3 H, s, OMe), 4.38–4.41 (2 H, m, 1-CH_2), 5.12 (1 H, d, *J* 5.9, NH), 5.51 (1 H, dd, *J* 15.6 and 6.8, 3-H), 5.61 (1 H, ddd, *J* 15.6, 5.9 and 5.9, 2-H), 6.93 (2 H, s, Ph); *m*/*z* (FAB-LRMS) 472 (MH^+), 414, 396, 366, 326, 298, 256, 213, 197, 167, 119, 73 (base peak).

(4*R*,2*E*)-5-Benzyloxy-*O*-methoxycarbonyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]pent-2-en-1-ol 45. By a procedure identical with that described for the preparation of the carbonate **22** from **18**, the alcohol **42** (1.0 g, 2.57 mmol) was converted into the title compound **45** (1.13 g, 98%) as a colourless oil [Found (FAB): $(M + H)^+$, 448.1801. $C_{23}H_{30}NO_6S$ requires *M* + H, 448.1794]; $[\alpha]_D^{25}$ −18.4 (*c* 0.706 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 2.29 (3 H, s, CMe), 2.58 (6 H, s, 2 × CMe), 3.33–3.43 (2 H, m, 5-CH_2), 3.77 (3 H, s, OMe), 3.85–3.93 (1 H, m, 4-H), 4.37–4.47 (4 H, m, 1-CH_2 and PhCH_2), 5.13 (1 H, d, *J* 5.9, NH), 5.55 (1 H, dd, *J* 15.7 and 5.9, 3-H), 5.62 (1 H, ddd, *J* 15.7, 5.1 and 5.1, 2-H), 6.91 (2 H, s, Ph), 7.22–7.38 (5 H, m, Ph); *m*/*z* (FAB-LRMS) 448 (MH^+), 446, 372, 342, 326, 264, 183, 159, 119, 91 (base peak).

(4*R*,5*R*,2*E*)-5-*tert*-Butyldimethylsiloxy-*O*-methoxycarbonyl-4-[*N*-(*p*-tolylsulfonyl)amino]hex-2-en-1-ol 46. By a procedure identical with that described for the preparation of the carbonate **22** from **18**, the alcohol **43** (1.72 g, 4.30 mmol) was converted into the title compound **46** (1.87 g, 95%) as a colourless oil [Found (FAB): $(M + H)^+$, 458.2039. $C_{21}H_{36}NO_6SSi$ requires *M* + H, 458.2032]; $[\alpha]_D^{32}$ −15.1 (*c* 1.39 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) −0.01 (3 H, s, SiMe), 0.02 (3 H, s, SiMe), 0.85 (9 H, s, CMe_3), 1.08 (3 H, d, *J* 5.9, CMe), 2.41 (3 H, s, CMe), 3.63–3.70 (1 H, m, 5-H), 3.76–3.82 (1 H, m, 4-H), 3.77 (3 H, s, OMe), 4.40 (2 H, m, 1-CH_2), 4.89 (1 H, d, *J* 7.8, NH), 5.51 (1 H, dd, *J* 15.7 and 3.8, 3-H), 5.52 (1 H, d, *J* 15.7, 2-H), 7.25–7.28 (2 H, m, Ph), 7.68–7.72 (2 H, m, Ph); *m*/*z* (FAB-LRMS) 458 (MH^+), 400, 382, 338, 228, 159 (base), 155, 115, 73.

(4*R*,2*E*)-5-*tert*-Butyldimethylsiloxy-*O*-methylsulfonyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]pent-2-en-1-ol 47. By a procedure similar to that described for the preparation of the mesylate **26** from **18**, the alcohol **41** (300 mg, 0.725 mmol) was converted into the title compound **47** (314 mg, 88%) as colour-

less crystals, mp 57–59 °C [from *n*-hexane–Et_2O (1:1)] [Found (FAB): $(M + H)^+$, 492.1917. $C_{21}H_{38}NO_6S_2$ requires *M* + H, 492.1910]; $[\alpha]_D^{26}$ −29.8 (*c* 1.33 in $CHCl_3$); δ_H(270 MHz in $CDCl_3$) 0.02 (6 H, s, $SiMe_2$), 0.86 (9 H, s, CMe_3), 2.30 (3 H, s, CMe), 2.61 (6 H, s, 2 × CMe), 2.98 (3 H, s, SO_2Me), 3.48 (1 H, dd, *J* 9.7 and 5.1, 5-C*H*H), 3.52 (1 H, dd, *J* 9.7 and 4.3, 5-CH*H*), 3.72–3.77 (1 H, m, 4-H), 4.52-4.54 (2 H, m, 1-CH_2), 5.17 (1 H, d, *J* 5.9, NH), 5.61–5.67 (1 H, m, C*H*=CH), 5.69 (1 H, dd, *J* 15.7 and 5.4, CH=C*H*), 6.95 (2 H, s, Ph); *m*/*z* (FAB-LRMS) 492 (MH^+), 490, 434, 396, 366, 256, 153, 119, 73 (base peak).

(4*R*,2*E*)-5-Benzyloxy-*O*-methylsulfonyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]pent-2-en-1-ol 48. By a procedure similar to that described for the preparation of the mesylate **26** from **18**, the alcohol **42** (100 mg, 0.257 mmol) was converted into the title compound **48** (115 mg, 96%) as a colourless oil [Found (FAB): $(M + H)^+$, 468.1518. $C_{22}H_{30}NO_6S_2$ requires *M* + H, 468.1514]; $[\alpha]_D^{26}$ −20.7 (*c* 1.09 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 2.30 (3 H, s, CMe), 2.58 (6 H, s, 2 × CMe), 2.95 (3 H, s, SO_2Me), 3.33–3.42 (2 H, m, 5-CH_2), 3.85–3.95 (1 H, m, 4-H), 4.40 (1 H, d, *J* 11.9, PhC*H*H), 4.42 (1 H, d, *J* 11.9, PhCH*H*), 4.47–4.60 (2 H, m, 1-CH_2), 5.17 (1 H, d, *J* 6.5, NH), 5.64–5.72 (1 H, m, 2-H), 5.72 (1 H, dd, *J* 15.4 and 4.9, 3-H), 6.92 (2 H, s, Ph), 7.20–7.37 (5 H, m, Ph); *m*/*z* (FAB-LRMS) 468 (MH^+), 372, 342, 282, 183, 159, 119, 91 (base peak).

(4*R*,5*R*,2*E*)-5-*tert*-Butyldimethylsiloxy-*O*-methylsulfonyl-4-[*N*-(*p*-tolylsulfonyl)amino]hex-2-en-1-ol 49. By a procedure similar to that described for the preparation of the mesylate **26** from alcohol **18**, the alcohol **43** (100 mg, 0.25 mmol) was converted into the title compound **49** (119 mg, 99%) as a colourless oil [Found (FAB): $(M + H)^+$, 478.1745. $C_{20}H_{36}NO_6S_2Si$ requires *M* + H, 478.1753]; $[\alpha]_D^{27}$ −24.5 (*c* 1.24 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) −0.01 (3 H, s, SiMe), 0.02 (3 H, s, SiMe), 0.85 (9 H, s, CMe_3), 1.03 (3 H, d, *J* 6.2, CMe), 2.42 (3 H, s, CMe), 2.98 (3 H, s, SO_2Me), 3.63–3.69 (1 H, m, 4-H), 3.79 (1 H, qd, *J* 6.2 and 3.0, 5-H), 4.54–4.58 (2 H, m, 1-CH_2), 4.93 (1 H, d, *J* 7.6, NH), 5.58–5.66 (1 H, m, C*H*=CH), 5.67 (1 H, dd, *J* 15.7 and 5.4, CH=C*H*), 7.27–7.31 (2 H, m, Ph), 7.69–7.73 (2 H, m, Ph); *m*/*z* (FAB-LRMS) 478 (MH^+), 420, 382, 338, 228, 159, 115, 73 (base peak), 59.

(3*S*,4*S*)-*O*-Methoxycarbonyl-5-methyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]hex-1-en-3-ol 52. By a procedure identical with that described for the preparation of the carbonate **22** from **18**, the known alcohol **50**[21c] (218 mg, 0.7 mmol) was converted into the title compound **52** (232 mg, 90%) as colourless prisms, mp 72 °C [from *n*-hexane–Et_2O (2:1)] (Found: C, 58.2; H, 7.4; N, 3.9. $C_{18}H_{27}NO_5S$ requires C, 58.5; H, 7.4; N, 3.8%); $[\alpha]_D^{20}$ −29.6 (*c* 1.03 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.88 (3 H, d, *J* 6.8, CMe), 0.89 (3 H, d, *J* 6.2, CMe), 1.75–1.92 (1 H, m, 5-H), 2.29 (3 H, s, CMe), 2.62 (6 H, s, 2 × CMe), 3.33 (1 H, ddd, *J* 9.5, 6.2 and 3.8, 4-H), 3.71 (3 H, s, OMe), 4.75 (1 H, d, *J* 9.5, NH), 5.01 (1 H, ddd, *J* 10.3, 0.8 and 0.8, 1-C*H*H), 5.15 (1 H, dd, *J* 7.0 and 3.8, 3-H), 5.20 (1 H, ddd, *J* 17.1, 1.4 and 1.4, 1-CH*H*), 5.48 (1 H, ddd, *J* 17.1, 10.3 and 7.0, 2-H), 6.92 (2 H, s, Ph).

(3*R*,4*S*)-*O*-Methoxycarbonyl-5-methyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]hex-1-en-3-ol 53. By a procedure identical with that described for the preparation of the carbonate **22** from **18**, the known alcohol **51**[21c] (80 mg, 0.257 mmol) was converted into the title compound **53** (85 mg, 89%) as colourless crystals, mp 91 °C [from *n*-hexane–Et_2O (4:1)] (Found: C, 58.3; H, 7.3; N, 3.7. $C_{18}H_{27}NO_5S$ requires C, 58.5; H, 7.4; N, 3.8%); $[\alpha]_D^{20}$ +11.4 (*c* 0.70 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.86 (3 H, d, *J* 7.0, CMe), 0.91 (3 H, d, *J* 6.8, CMe), 1.75–1.92 (1 H, m, 5-H), 2.29 (3 H, s, CMe), 2.62 (6 H, s, 2 × CMe), 3.39 (1 H, ddd, *J* 9.7, 4.9 and 4.6, 4-H), 3.69 (3 H, s, OMe), 4.65 (1 H, d, *J* 9.7, NH), 5.02 (1 H, dddd, *J* 5.9, 4.6, 1.1 and 1.1, 3-H), 5.23 (1 H, ddd, *J* 10.6, 1.1 and 1.1, 1-C*H*H), 5.26 (1 H, ddd, *J* 17.3, 1.4 and 1.4, 1-CH*H*), 5.67 (1 H, ddd, *J* 17.3, 10.6 and 5.9, 2-H), 6.93 (2 H, s, Ph).

General procedure for aziridination reaction of acyclic allylic carbonates 22–25 and 33 with tetrakis(triphenylphosphine)-palladium(0): synthesis of (2*R*,3*S*)-3-isopropyl-*N*-(2,4,6-trimethylphenylsulfonyl)-2-vinylaziridine 54 and its (2*S*,3*S*)-isomer 55 from the carbonate 22

A stirred mixture of the allylic carbonate **22** (369 mg, 1 mmol) and $Pd(PPh_3)_4$ (57.7 mg, 0.05 mmol, 5 mol%) in dry THF (3 cm^3) was heated at 60 °C for 20 min. The mixture was concentrated under reduced pressure to leave an oil, which was flash chromatographed on a short silica gel column with *n*-hexane–EtOAc (10:1) to give a 94:6 mixture of the title compounds **54** and **55** (210 mg, 72% combined yield). The mixture was flash chromatographed over silica gel. Elution with *n*-hexane–EtOAc (12:1) gave **54** (197 mg, 68%) and further elution yielded **55** (13 mg, 4%). Compound **54**: 98% ee (2*R*,3*S*) by HPLC [Daicel Chiralcel OD, *n*-hexane–propan-2-ol = 99.5:0.5 (0.5 cm^3 min^{-1}), (2*R*,3*S*)-isomer 24.7 min, (2*S*,3*R*)-isomer 22.1 min]; colourless prisms, mp 46 °C (from cold *n*-hexane) (Found: C, 65.4; H, 8.0; N, 4.7. $C_{16}H_{23}NO_2S$ requires C, 65.5; H, 7.9; N, 4.8%); $[\alpha]_D^{20}$ −11.0 (*c* 1.20 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.78 (3 H, d, *J* 6.8, CMe), 0.88 (3 H, d, *J* 7.0, CMe), 1.34–1.53 (1 H, m, Me_2CH), 2.30 (3 H, s, CMe), 2.56 (1 H, dd, *J* 10.3 and 7.6, 3-H), 2.70 (6 H, s, 2 × CMe), 3.41 (1 H, dd, *J* 7.6 and 6.8, 2-H), 5.27 (1 H, dd, *J* 10.3 and 1.1, C=C*H*H), 5.41 (1 H, dd, *J* 17.1 and 1.1, C=CH*H*), 5.64 (1 H, ddd, *J* 17.1, 10.3 and 6.8, C*H*=CH_2), 6.95 (2 H, s, Ph). Compound **55**: 98% ee (2*S*,3*S*) by HPLC [Daicel Chiralcel OD, *n*-hexane–propan-2-ol = 99.5:0.5 (0.5 cm^3 min^{-1}), (2*S*,3*S*)-isomer 27.5 min, (2*R*,3*R*)-isomer 24.4 min]; colourless prisms, mp 67 °C (from *n*-hexane) (Found: C, 65.3; H, 8.0; N, 4.55. $C_{16}H_{23}NO_2S$ requires C, 65.5; H, 7.9; N, 4.8%); $[\alpha]_D^{20}$ −88.9 (*c* 1.90 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.70 (3 H, d, *J* 6.5, CMe), 0.87 (3 H, d, *J* 7.0, CMe), 1.42–1.57 (1 H, m, Me_2CH), 2.29 (3 H, s, CMe), 2.70 (6 H, 2 × CMe), 2.80 (1 H, dd, *J* 7.3 and 4.3, 3-H), 3.11 (1 H, dd, *J* 9.5 and 4.3, 2-H), 5.35 (1 H, dd, *J* 10.3 and 1.4, C=C*H*H), 5.50 (1 H, dd, *J* 17.3 and 1.4, C=CH*H*), 6.17 (1 H, ddd, *J* 17.3, 10.3 and 9.5, C*H*=CH_2), 6.93 (2 H, s, Ph).

General procedure for base-promoted aziridination of allylic mesylates 26–29, 34 and 47–49: aziridination of the mesylate 26 by exposure to sodium hydride in DMF. Synthesis of 3-isopropyl-2-vinyl-*N*-(2,4,6-trimethylphenylsulfonyl)aziridines 54 and 55

To a stirred suspension of NaH (7.2 mg, 0.3 mmol) in DMF (0.6 cm^3) under argon was added a solution of the allylic mesylate **26** (78 mg, 0.2 mmol) in DMF (0.4 cm^3) at 0 °C. After 0.5 h, 0.5 cm^3 of a saturated NH_4Cl solution was added to the mixture. The whole was extracted with Et_2O and the extract was washed with water, and dried over $MgSO_4$. Usual work-up followed by flash chromatography over a short silica gel column with *n*-hexane–EtOAc (12:1) gave a 26:74 mixture of the aziridines **54** and **55** (39 mg, 66% combined yield). The mixture was flash chromatographed over silica gel. Elution with *n*-hexane–EtOAc (12:1) gave **54** (10.1 mg, 17%) and further elution yielded **55** (29 mg, 49%).

Synthesis of (2*R*,3*S*)-*N*-(*p*-tolylsulfonyl)-3-(2-methylpropyl)-2-vinylaziridine 56 and its (2*S*,3*S*)-isomer 57 from the carbonate 23

By a procedure similar to that described for the aziridination of **22**, the allylic carbonate **23** (50 mg, 0.141 mmol) was converted into a 94:6 mixture of the title compounds **56** and **57** (26 mg, 66% combined yield) by treatment with 4 mol% of $Pd(PPh_3)_4$ in THF at 65 °C for 10 min followed by flash chromatography on a short silica gel column with *n*-hexane–EtOAc (4:1). The mix-

ture was flash chromatographed over silica gel. Elution with *n*-hexane–EtOAc (8:1) gave **56** (24.4 mg, 62%) and further elution yielded **57** (1.6 mg, 4%). Compound **56**: 98% ee (2*R*,3*S*) by HPLC [Daicel Chiralcel OD, *n*-hexane–propan-2-ol = 99.4:0.6 (0.5 cm^3 min^{-1}), (2*R*,3*S*)-isomer 30.6 min]; a colourless oil [Found (FAB): $(M + H)^+$, 280.1376. $C_{15}H_{22}NO_2S$ requires *M* + H, 280.1371]; $[\alpha]_D^{25}$ −6.08 (*c* 0.987 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.88 (3 H, d, *J* 6.5, CMe), 0.89 (3 H, d, *J* 6.8, CMe), 1.30 (1 H, ddd, *J* 14.0, 7.8 and 6.2, C*H*H), 1.39 (1 H, ddd, *J* 14.0, 7.0 and 5.7, CH*H*), 1.53–1.68 (1 H, m, Me_2CH), 2.44 (3 H, s, CMe), 2.97 (1 H, ddd, *J* 7.8, 7.3 and 7.0, 3-H), 3.33 (1 H, dd, *J* 7.3 and 7.3, 2-H), 5.26 (1 H, ddd, *J* 10.3, 1.1 and 1.1, C=C*H*H), 5.38 (1 H, ddd, *J* 17.3, 1.1 and 1.1, C=CH*H*), 5.59 (1 H, ddd, *J* 17.3, 10.3 and 7.3, C*H*=CH_2), 7.31–7.34 (2 H, m, Ph), 7.80–7.84 (2 H, m, Ph); *m*/*z* (FAB-LRMS) 280 (MH^+, base peak), 155, 139, 124, 91, 82, 68. Compound **57**: 98% ee (2*S*,3*S*) by HPLC [Daicel Chiralcel OD, *n*-hexane–propan-2-ol = 99.4:0.6 (0.5 cm^3 min^{-1}), (2*S*,3*S*)-isomer 41.1 min]; colourless crystals, mp 59 °C (from *n*-hexane) [Found (FAB): $(M + H)^+$, 280.1368. $C_{15}H_{22}NO_2S$ requires *M* + H, 280.1371]; $[\alpha]_D^{25}$ −69.8 (*c* 0.106 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.88 (3 H, d, *J* 6.2, CMe), 0.90 (3 H, d, *J* 6.2, CMe), 1.36–1.41 (1 H, m, C*H*H), 1.58–1.68 (2 H, m, CH*H* and Me_2CH), 2.43 (3 H, s, CMe), 2.92–2.98 (1 H, m, 3-H), 3.08 (1 H, dd, *J* 8.9 and 4.3, 2-H), 5.34 (1 H, d, *J* 10.3, C=C*H*H), 5.47 (1 H, d, *J* 16.7, C=CH*H*), 6.02 (1 H, ddd, *J* 16.7, 10.3 and 8.9, C*H*=CH_2), 7.29–7.32 (2 H, m, Ph), 7.81–7.84 (2 H, m, Ph); *m*/*z* (FAB-LRMS) 280 (MH^+, base peak), 155, 139, 124, 91, 82, 55.

Synthesis of (2*R*,3*S*)-3-(2-methylpropyl)-*N*-(2,2,5,7,8-pentamethylchroman-6-ylsulfonyl)-2-vinylaziridine 58 and its (2*S*,3*S*)-isomer 59 from the carbonate 24

By a procedure similar to that described for the aziridination of **22**, the allylic carbonate **24** (480 mg, 1.03 mmol) was converted into a 97:3 mixture of the title compounds **58** and **59** (238 mg, 59% combined yield) by treatment with 4 mol% of $Pd(PPh_3)_4$ in THF at 20 °C for 6 h followed by flash chromatography over a short silica gel column with *n*-hexane–EtOAc (8:1). The mixture was flash chromatographed over silica gel. Elution with *n*-hexane–EtOAc (12:1) gave **58** (231 mg, 57%) and further elution yielded **59** (7 mg, 2%). Compound **58**: 98% ee (2*R*,3*S*) by HPLC [Daicel Chiralcel OD, *n*-hexane–propan-2-ol = 99.5:0.5 (0.5 cm^3 min^{-1}), (2*R*,3*S*)-isomer 26.3 min]; a colourless oil [Found (FAB): $(M + H)^+$, 392.2252. $C_{22}H_{34}NO_3S$ requires *M* + H, 392.2259]; $[\alpha]_D^{16}$ +4.65 (*c* 1.00 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.83 (3 H, d, *J* 6.6, CMe), 0.87 (3 H, d, *J* 6.6, CMe), 1.18–1.44 (2 H, m, Me_2CHCH_2), 1.31 (6 H, s, 2 × CMe), 1.53–1.59 (1 H, m, Me_2CH), 1.83 (2 H, t, *J* 6.8, 3′-CH_2), 2.12 (3 H, s, CMe), 2.59 (3 H, s, CMe), 2.61 (3 H, s, CMe), 2.65 (2 H, t, *J* 6.8, 4′-CH_2), 2.92–3.00 (1 H, m, 3-H), 3.38 (1 H, dd, *J* 6.8 and 6.8, 2-H), 5.26 (1 H, dd, *J* 10.3 and 0.7, C=C*H*H), 5.37 (1 H, dd, *J* 17.1 and 0.7, C=CH*H*), 5.63 (1 H, ddd, *J* 17.1, 10.3 and 6.8, C*H*=CH_2); *m*/*z* (FAB-LRMS) 392 (MH^+), 267 (base peak), 251, 219, 203, 187, 147, 124. Compound **59**: 98% ee (2*S*,3*S*) by HPLC [Daicel Chiralcel OD, *n*-hexane–propan-2-ol = 99.5:0.5 (0.5 cm^3 min^{-1}), (2*S*,3*S*)-isomer 30.8 min]; a colourless oil [Found (FAB): $(M + H)^+$, 329.2260. $C_{22}H_{34}NO_3S$ requires *M* + H, 392.2259]; $[\alpha]_D^{25}$ −54.7 (*c* 0.42 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.87 (3 H, d, *J* 6.2, CMe), 0.88 (3 H, d, *J* 6.5, CMe), 1.31 (3 H, s, CMe), 1.32 (3 H, s, CMe), 1.34–1.44 (1 H, m, Me_2CHCHH), 1.52–1.75 (2 H, m, Me_2CHCHH and Me_2CH), 1.82 (2 H, t, *J* 7.0, 3′-CH_2), 2.12 (3 H, s, CMe), 2.58 (3 H, s, CMe), 2.60 (3 H, s, CMe), 2.64 (2 H, t, *J* 7.0, 4′-CH_2), 2.93 (1 H, ddd, *J* 7.6, 5.1 and 4.1, 3-H), 3.09 (1 H, dd, *J* 9.2 and 4.1, 2-H), 5.28 (1 H, dd, *J* 10.3 and 1.4, C=C*H*H), 5.44 (1 H, dd, *J* 17.0 and 1.1, C=CH*H*), 6.01 (1 H, ddd, *J* 17.0, 10.3 and 9.2, C*H*=CH_2); *m*/*z* (FAB-LRMS) 392 (MH^+), 267, 251, 219, 203, 187, 147, 124 (base peak).

Synthesis of (2*R*,3*S*)-3-benzyl-*N*-(2,4,6-trimethylphenylsulfonyl)-2-vinylaziridine 60 and its (2*S*,3*S*)-isomer 61 from the carbonate 25

By a procedure similar to that described for the aziridination of **22**, the allylic carbonate **25** (160 mg, 0.383 mmol) was converted into a 95:5 mixture of the title compounds **60** and **61** (65 mg, 50% combined yield) by treatment with 4 mol% of $Pd(PPh_3)_4$ in THF at 65 °C for 5 min followed by flash chromatography over a short silica gel column with *n*-hexane–EtOAc (5:1). The mixture was flash chromatographed over silica gel. Elution with *n*-hexane–EtOAc (10:1) gave **60** (62 mg, 48%) and further elution yielded **61** (3 mg, 2%). Compound **60**: 98% ee (2*R*,3*S*) by HPLC [Daicel Chiralcel OD, *n*-hexane–propan-2-ol = 99.2:0.8 (0.5 cm^3 min^{-1}), (2*R*,3*S*)-isomer 39.2 min]; colourless needles, mp 71 °C [from *n*-hexane–Et_2O (3:1)] (Found: C, 70.15; H, 6.8; N, 4.15. $C_{20}H_{23}NO_2S$ requires C, 70.35; H, 6.8; N, 4.1%); $[\alpha]_D^{24}$ −24.8 (*c* 0.935 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 2.30 (3 H, s, CMe), 2.58 (6 H, s, 2 × CMe), 2.66 (1 H, dd, *J* 14.6 and 7.6, PhC*H*H), 2.74 (1 H, dd, *J* 14.6 and 5.7, PhCH*H*), 3.10 (1 H, ddd, *J* 7.6, 6.8 and 5.7, 3-H), 3.48 (1 H, dd, *J* 6.8 and 6.8, 2-H), 5.38 (1 H, d, *J* 10.5, C=C*H*H), 5.50 (1 H, d, *J* 17.3, C=CH*H*), 5.78 (1 H, ddd, *J* 17.3, 10.5 and 6.8, C*H*=CH_2), 6.85 (2 H, s, Ph), 6.95–7.00 (2 H, m, Ph), 7.05–7.11 (3 H, m, Ph). Compound **61**: colourless needles, mp 105–106 °C [from *n*-hexane–Et_2O (3:1)] [Found (FAB): $(M + H)^+$, 342.1520. $C_{20}H_{24}NO_2S$ requires *M* + H, 342.1528]; $[\alpha]_D^{25}$ −35.5 (*c* 0.077, $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 2.30 (3 H, s, CMe), 2.54 (6 H, s, 2 × CMe), 2.66 (1 H, dd, *J* 14.0 and 6.8, PhC*H*H), 3.00 (1 H, dd, *J* 14.0 and 4.9, PhCH*H*), 3.16 (1 H, ddd, *J* 6.8, 4.9 and 3.8, 3-H), 3.21 (1 H, dd, *J* 8.9 and 3.8, 2-H), 5.36 (1 H, dd, *J* 10.0 and 1.1, C=C*H*H), 5.52 (1 H, dd, *J* 17.3 and 1.1, C=CH*H*), 6.08 (1 H, ddd, *J* 17.3, 10.0 and 8.9, C*H*=CH_2), 6.85 (2 H, s, Ph), 6.89–6.93 (2 H, m, Ph), 7.02–7.15 (3 H, m, Ph); *m*/*z* (FAB-LRMS) 342 (MH^+), 183, 158, 143, 119 (base peak), 91.

Synthesis of (3*R*,4*S*,5*S*)-5-methyl-3,4-epimino-*N*-(4-methoxy-2,3,6-trimethylphenylsulfonyl)hept-1-ene 62 and its (3*S*,4*S*,5*S*)-isomer 63 from the carbonate 33

By a procedure similar to that described for the aziridination of **22**, the allylic carbonate **33** (980 mg, 2.37 mmol) was converted into a 98:2 mixture of the title compounds **62** and **63** (680 mg, 85% combined yield) by treatment of **33** with 2 mol% $Pd(PPh_3)_4$ in THF at 60 °C for 5 min followed by chromatography over a short silica gel column with *n*-hexane–EtOAc (15:1). The mixture was flash chromatographed over silica gel. Elution with *n*-hexane–EtOAc (30:1) gave **62** (666 mg, 83%) and further elution yielded **63** (14 mg, 2%). Compound **62**: 98% ee (3*R*,4*S*,5*S*) by HPLC [Daicel Chiralcel OD, *n*-hexane–propan-2-ol = 99.4:0.6 (0.5 cm^3 min^{-1}), (3*R*,4*S*,5*S*)-isomer 43.0 min]; a colourless oil [Found (FAB): $(M + H)^+$, 338.1798. $C_{18}H_{28}NO_3S$ requires *M* + H, 338.1789]; $[\alpha]_D^{26}$ +0.83 (*c* 0.803 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.79 (t, *J* 7.6, CMe), 0.85 (d, *J* 7.0, CMe), 1.04–1.45 (3 H, m, 5-H and 6-CH_2), 2.15 (3 H, s, CMe), 2.63–2.68 (1 H, m, 4-H), 2.68 (3 H, s, CMe), 2.69 (3 H, s, CMe), 3.35 (1 H, dd, *J* 7.0 and 7.0, 3-H), 3.85 (3 H, s, OMe), 5.26 (1 H, d, *J* 10.0, 1-C*H*H), 5.38 (1 H, d, *J* 17.0, 1-CH*H*), 5.64 (1 H, ddd, *J* 17.0, 10.0 and 7.0, 2-H), 6.56 (1 H, s, Ph); *m*/*z* (FAB-LRMS) 338, (MH^+), 336, 213, 197, 165, 149, 124 (base peak), 119, 69, 41. Compound **63**: 98% ee (3*S*,4*S*,5*S*) by HPLC [Daicel Chiralcel OD, *n*-hexane–propan-2-ol = 99.4:0.6 (0.5 cm^3 min^{-1}), (3*R*,4*S*,5*S*)-isomer 47.6 min]; colourless prisms, mp 72 °C (from *n*-hexane) (Found: C, 64.1; H, 8.1; N, 4.0. $C_{18}H_{27}NO_3S$ requires C, 64.1; H, 8.1; N, 4.15%); $[\alpha]_D^{26}$ −50.7 (*c* 0.856 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.75 (3 H, t, *J* 7.3, CMe), 0.86 (3 H, d, *J* 6.8, CMe), 0.97–1.14 (1 H, m, 6-C*H*H), 1.19–1.38 (2 H, m, 5-H and 6-CH*H*), 2.15 (3 H, s, CMe), 2.68 (6 H, s, 2 × CMe), 2.87 (1 H, dd, *J* 7.3 and 4.3, 4-H), 3.07 (1 H, dd, *J* 9.5 and 4.3, 3-H), 3.85 (3 H, s, OMe), 5.32 (1 H, d, *J* 10.3,

1-C*H*H), 5.47 (1 H, d, *J* 17.3, 1-CH*H*), 6.18 (1 H, ddd, *J* 17.3, 10.3 and 9.5, 2-H), 6.55 (1 H, s, Ph).

Synthesis of (2*R*,3*R*)-2-*tert*-butyldimethylsiloxymethyl-*N*-(2,4,6-trimethylphenylsulfonyl)-3-vinylaziridine 64 and its (2*R*,3*S*)-isomer 65 from the mesylate 47

By a procedure identical with that described for the aziridination of **26**, the allylic mesylate **47** (98.3 mg, 0.2 mmol) was converted into a mixture of 2,3-*cis*- and 2,3-*trans*-aziridines **64** and **65** (**64**:**65** = 51:49) by treatment with NaH in DMF. The mixture was flash chromatographed over silica gel. Elution with *n*-hexane–$CHCl_3$–EtOAc (20:5:1) gave **65** (24 mg, 30%) and further elution yielded **64** (25 mg, 32%). Compound **64**: 98% ee (2*R*,3*R*) by HPLC [Daicel Chiralcel OD, *n*-hexane–propan-2-ol = 99.5:0.5 (0.5 cm^3 min^{-1}), (2*R*,3*R*)-isomer 19.4 min]; a colourless oil [Found (FAB): $(M + H)^+$, 396.2024. $C_{20}H_{34}NO_3SSi$ requires *M* + H, 396.2028]; $[\alpha]_D^{29}$ −0.74 (*c* 1.44 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) −0.09 (3 H, s, SiMe), −0.06 (3 H, s, SiMe), 0.79 (9 H, s, CMe_3), 2.29 (3 H, s, CMe), 2.69 (6 H, s, 2 × CMe), 3.07 (1 H, ddd, *J* 7.3, 5.9 and 5.9, 3-H), 3.44 (1 H, dd, *J* 7.3 and 6.8, 2-H), 3.58 (1 H, dd, *J* 11.6 and 5.9, OC*H*H), 3.61 (1 H, dd, *J* 11.6 and 5.9, OCH*H*), 5.28 (1 H, ddd, *J* 10.3, 1.1 and 0.5, C=C*H*H), 5.41 (1 H, ddd, *J* 17.0, 2.2 and 1.1, C=CH*H*), 5.66 (1 H, ddd, *J* 17.0, 10.3 and 6.8, C*H*=CH_2), 6.94 (2 H, s, Ph); *m*/*z* (FAB-LRMS) 396 (MH^+), 366, 338, 308, 241, 212, 177, 154, 119, 73 (base peak). Compound **65**: 98% ee (2*R*,3*S*) by HPLC [Daicel Chiralcel OD, *n*-hexane–propan-2-ol = 99.5:0.5 (0.5 cm^3 min^{-1}), (2*R*,3*S*)-isomer 26.3 min]; a colourless oil [Found (FAB): $(M + H)^+$, 396.2037. $C_{20}H_{34}NO_3SSi$ requires *M* + H, 396.2028]; $[\alpha]_D^{29}$ −38.7 (*c* 2.35, $CHCl_3$); δ_H(270 MHz, $CDCl_3$) −0.13 (3 H, s, SiMe), −0.10 (3 H, s, SiMe), 0.78 (9 H, s, CMe_3), 2.28 (3 H, s, CMe), 2.69 (6 H, s, 2 × CMe), 3.18 (1 H, ddd, *J* 5.4, 4.3 and 4.1, 3-H), 3.22 (1 H, dd, *J* 9.2 and 4.3, 2-H), 3.60 (1 H, dd, *J* 11.6 and 5.4, OC*H*H), 3.75 (1 H, dd, *J* 11.6 and 4.1, OCH*H*), 5.36 (1 H, dd, *J* 10.3 and 0.8, C=C*H*H), 5.51 (1 H, dd, *J* 16.7 and 0.8, C=CH*H*), 6.12 (1 H, ddd, *J* 16.7, 10.3 and 9.2, C*H*=CH_2), 6.92 (2 H, s, Ph); *m*/*z* (FAB-LRMS) 396 (MH^+), 366, 338, 308, 241, 212, 177, 154, 119, 73 (base peak).

General procedure for palladium-catalyzed equilibrated reaction of mixtures of 2,3-*cis*- and 2,3-*trans*-aziridines 54, 56, 58, 60, 62, 64, 66, 68 and 55, 57, 59, 61, 63, 65, 67, 69: equilibrated reaction of a mixture of (2*R*,3*R*)-2-*tert*-butyldimethylsiloxymethyl-*N*-(2,4,6-trimethylphenylsulfonyl)-3-vinylaziridine 64 and its (2*R*,3*S*)-isomer 65

A 51:49 mixture of 2,3-*cis*- and 2,3-*trans*-aziridines **64** and **65** (68 mg, 0.172 mmol) and $Pd(PPh_3)_4$ (7.9 mg, 0.0069 mmol, 4 mol%) in dry THF (3 cm^3) was stirred at 0 °C for 2 h. The mixture was concentrated under reduced pressure to leave an oil, which was flash chromatographed over silica gel with *n*-hexane–EtOAc (12:1) to give the title compounds **64** (57 mg, 83%) and **65** (4.3 mg, 7%).

Synthesis of (2*R*,3*R*)-2-benzyloxymethyl-*N*-(2,4,6-trimethylphenylsulfonyl)-3-vinylaziridine 66 and its (2*R*,3*S*)-isomer 67 from the mesylate 48

By a procedure identical with that described for the aziridination of **26**, the allylic mesylate **48** (234 mg, 0.5 mmol) was converted into a 51:49 mixture of the title compounds **66** and **67** (125 mg, 67% combined yield) by treatment with NaH followed by flash chromatography over a short silica gel column with *n*-hexane–EtOAc (8:1). The mixture was flash chromatographed over silica gel. Elution with *n*-hexane–$CHCl_3$–EtOAc (20:5:1) gave **67** (61 mg, 33%) and further elution yielded **66** (64 mg, 34%). Compound **66**: 98% ee (2*R*,3*R*) by HPLC [Daicel Chiralcel OD, *n*-hexane–propan-2-ol = 99.0:1.0 (0.5 cm^3 min^{-1}), (2*R*,3*R*)-isomer 54.0 min]; a colourless oil [Found (FAB): $(M + H)^+$, 372.1632. $C_{21}H_{26}NO_3S$ requires *M* + H, 372.1633]; $[\alpha]_D^{31}$ −0.86 (*c* 0.463 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 2.28 (3 H, s, CMe), 2.70 (6 H, s, 2 × CMe), 3.18 (1 H, ddd, *J* 7.3, 6.5 and 5.9, 3-H), 3.45 (1 H, dd, *J* 7.3 and 6.5, 2-H), 3.47 (1 H, dd, *J* 11.1 and 6.5, BnOC*H*H), 3.54 (1 H, dd, *J* 11.1 and 5.9, BnOCH*H*), 4.38 (1 H, d, *J* 11.9, PhC*H*H), 4.39 (1 H, d, *J* 11.9, PhCH*H*), 5.27 (1 H, ddd, *J* 10.3, 1.6 and 0.5, C=C*H*H), 5.40 (1 H, ddd, *J* 17.3, 1.6 and 0.8, C=CH*H*), 5.69 (1 H, ddd, *J* 17.3, 10.3 and 6.5, C*H*=CH_2), 6.94 (2 H, s, Ph), 7.14-7.34 (5 H, m, Ph); *m*/*z* (FAB-LRMS) 372 (MH^+), 342, 188, 183, 159, 119, 91 (base peak). Compound **67**: 98% ee (2*R*,3*S*) by HPLC [Daicel Chiralcel OD, *n*-hexane–propan-2-ol = 99.0:1.0 (0.5 cm^3 min^{-1}), (2*R*,3*S*)-isomer 48.5 min]; colourless prisms. mp 64 °C [from *n*-hexane–Et_2O (4:1)] [Found (FAB): $(M + H)^+$, 372.1637. $C_{21}H_{26}NO_3S$ requires *M* + H, 372.1633]; $[\alpha]_D^{31}$ −39.2 (*c* 1.31 in $CHCl_3$); δ_H(300 MHz, $CDCl_3$) 2.28 (3 H, s, CMe), 2.69 (6 H, s, 2 × CMe), 3.22 (1 H, dd, *J* 8.8 and 4.2, 2-H), 3.24 (1 H, ddd, *J* 5.1, 4.3 and 4.2, 3-H), 3.51 (1 H, dd, *J* 11.1 and 5.1, BnOC*H*H), 3.68 (1 H, dd, *J* 11.1 and 4.3, BnOCH*H*), 4.35 (1 H, d, *J* 12.1, PhC*H*H), 4.38 (1 H, d, *J* 12.1, PhCH*H*), 5.36 (1 H, dd, *J* 10.2 and 1.0, C=C*H*H), 5.49 (1 H, dd, *J* 17.1 and 1.1, C=CH*H*), 6.07 (1 H, ddd, *J* 17.1, 10.2 and 8.8, C*H*=CH_2), 6.93 (2 H, s, Ph), 7.10–7.13 (2 H, m, Ph), 7.24–7.30 (3 H, m, Ph); *m*/*z* (FAB-LRMS) 372 (MH^+), 280, 243, 188, 183, 159, 119, 105, 91 (base peak), 73.

Synthesis of (3*R*,4*R*,5*R*)-5-*tert*-butyldimethylsiloxy)-3,4-epimino-*N*-(*p*-tolylsulfonyl)hex-1-ene 68 and its (3*S*,4*R*,5*R*)-isomer 69 from the mesylate 49

By a procedure similar to that described for the aziridination of **26**, the allylic mesylate **49** (191 mg, 0.4 mmol) was converted into a mixture of 2,3-*cis*- and 2,3-*trans*-aziridines **68** and **69** (**68**:**69** = 8:92) by treatment with NaH in DMF. The mixture was flash chromatographed over silica gel. Elution with *n*-hexane–$CHCl_3$–EtOAc (20:5:1) gave **69** (81 mg, 53%) and further elution yielded **68** (7 mg, 5%). Compound **68**: 98% ee (3*R*,4*R*,5*R*) by HPLC [Daicel Chiralcel OD, *n*-hexane–propan-2-ol = 99.4:0.6 (0.5 cm^3 min^{-1}), (3*R*,4*R*,5*R*)-isomer 26.3 min]; a colourless oil [Found (FAB): $(M + H)^+$, 382.1877. $C_{19}H_{32}NO_3SSi$ requires *M* + H, 382.1872]; $[\alpha]_D^{32}$ +0.78 (*c* 2.04 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) −0.16 (3 H, s, SiMe), −0.04 (3 H, s, SiMe), 0.78 (9 H, s, CMe_3), 1.13 (3 H, d, *J* 6.2, CMe), 2.43 (3 H, s, CMe), 2.93 (1 H, dd, *J* 8.6 and 7.3, 4-H), 3.36 (1 H, dd, *J* 7.3 and 7.3, 3-H), 3.52 (1 H, dq, *J* 8.6 and 6.2, 5-H), 5.29 (1 H, ddd, *J* 10.0, 1.9 and 0.8, 1-C*H*H), 5.44 (1 H, dd, *J* 17.1 and 1.6, 1-CH*H*), 5.57 (1 H, ddd, *J* 17.3, 10.0 and 7.3, 2-H), 7.30–7.33 (2 H, m, Ph), 7.80–7.85 (2 H, m, Ph); *m*/*z* (FAB-LRMS) 382 (MH^+), 366, 338, 324, 280 (base peak), 226, 213, 159, 139, 115, 73. Compound **69**: 98% ee (3*S*,4*R*,5*R*) by HPLC [Daicel Chiralcel OD, *n*-hexane–propan-2-ol = 99.4:0.6 (0.5 cm^3 min^{-1}), (3*S*,4*R*,5*R*)-isomer 38.2 min]; a colourless oil [Found (FAB): $(M + H)^+$, 382.1866. $C_{19}H_{32}NO_3SSi$ requires *M* + H, 382.1872]; $[\alpha]_D^{31}$ −31.2 (*c* 0.746 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) −0.15 (3 H, s, SiMe), −0.06 (3 H, s, SiMe), 0.80 (9 H, s, CMe_3), 1.13 (3 H, d, *J* 6.5, CMe), 2.43 (3 H, s, CMe), 3.12 (1 H, dd, *J* 5.1 and 4.3, 4-H), 3.19 (1 H, dd, *J* 9.5 and 4.3, 3-H), 3.72 (1 H, qd, *J* 6.5 and 5.1, 5-H), 5.42 (1 H, dd, *J* 10.0 and 0.8, 1-C*H*H), 5.51 (1 H, dd, *J* 16.7 and 1.1, 1-CH*H*), 6.21 (1 H, ddd, *J* 16.7, 10.0 and 9.5, 2-H), 7.28–7.31 (2 H, m, Ph), 7.82–7.85 (2 H, m, Ph); *m*/*z* (FAB-LRMS) 382 (MH^+), 338, 324, 280 (base peak), 226, 213, 159, 139, 115, 73.

tert-Butyl (4*R*,5*S*,6*S*,2*E*)-6-methyl-4,5-epimino-*N*-(4-methoxy-2,3,6-trimethylphenylsulfonyl)oct-2-enoate 70

Ozone was bubbled through a solution of the vinylaziridine **62** (300 mg, 0.889 mmol) in a mixed solvent of $CHCl_3$ (5 cm^3) and *n*-hexane (3 cm^3) at −78 °C for 40 min. Zn powder (0.25 g) was added to the mixture at −78 °C, and the mixture was stirred for 1 h with warming to 0 °C. The inorganic precipitates were

removed by filtration through a short pad of SiO_2 with Et_2O. The filtrate was concentrated under reduced pressure to give a crude aldehyde as an oil. To a stirred suspension of LiCl (75 mg, 1.78 mmol) in MeCN (3 cm^3) under argon at room temperature were added *tert*-butyl diethylphosphonoacetate (0.45 g, 1.78 mmol) and *N*,*N*-diisopropylethylamine (0.31 cm^3, 1.78 mmol), and the mixture was cooled to 0 °C. To the above reagent, the crude aldehyde in MeCN (3 cm^3) was added at 0 °C and the mixture was stirred for 1 h with warming to room temperature. The mixture was made acidic with saturated aqueous citric acid followed by concentration under reduced pressure to yield an oily residue. The residue was dissolved in Et_2O and the solution was washed successively with H_2O, 5% aqueous $NaHCO_3$, and H_2O, and dried over $MgSO_4$. Usual work-up followed by flash chromatography over silica gel with *n*-hexane–EtOAc (6:1) gave the title compound **70** (330 mg, 85% yield) as colourless crystals, mp 83–85 °C (from *n*-hexane) (Found: C, 63.0; H, 8.1; N, 3.0. $C_{23}H_{35}NO_5S$ requires C, 63.1; H, 8.1; N, 3.2%); $[a]_D^{26}$ −48.6 (*c* 0.951 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.78 (3 H, t, *J* 7.3, CMe), 0.85 (3 H, d, *J* 6.5, CMe), 1.04–1.40 (3 H, m, 6-H and 7-CH_2), 1.48 (9 H, s, CMe_3), 2.16 (3 H, s, CMe), 2.67 (3 H, s, CMe), 2.69 (3 H, s, CMe), 2.74 (1 H, dd, *J* 9.7 and 7.8, 5-H), 3.41 (1 H, dd, *J* 7.8 and 6.8, 4-H), 3.86 (3 H, s, OMe), 6.01 (1 H, d, *J* 15.6, 2-H), 6.57 (1 H, s, Ph), 6.59 (1 H, dd, *J* 15.6 and 6.8, 3-H).

tert-Butyl (2*R*,5*S*,6*S*,3*E*)-2-isopropyl-6-methyl-5-[*N*-(4-methoxy-2,3,6-trimethylphenylsulfonyl)amino]oct-3-enoate 71

To a stirred solution of CuCN (108 mg, 1.2 mmol) and LiCl (102 mg, 2.4 mmol) in dry THF (2 cm^3) under argon was added by syringe isopropylmagnesium chloride (1.3 mol dm^{-3} solution in THF; 0.93 cm^3, 1.2 mmol) at −78 °C, and the mixture was allowed to warm to 0 °C and stirred at this temperature for 5 min. The enoate **70** (132 mg, 0.3 mmol) in dry THF (2 cm^3) was added dropwise to the above reagent at −78 °C, and the mixture was stirred for 30 min followed by quenching with a 1:1 solution (8 cm^3) of saturated NH_4Cl–28% NH_4OH. The whole was extracted with Et_2O and the extract was washed with H_2O, and dried over $MgSO_4$. Usual work-up followed by flash chromatography over silica gel with *n*-hexane–EtOAc (5:1) gave the title compound **71** (136 mg, 94% yield) as a colourless oil [Found (FAB): $(M + H)^+$, 482.2932. $C_{26}H_{44}NO_5S$ requires *M* + H, 482.2940]; $[a]_D^{24}$ −50.4 (*c* 0.164 in $CHCl_3$); δ_H(270 MHz, $CDCl_3$) 0.69 (3 H, d, *J* 6.5, CMe), 0.79 (3 H, d, *J* 6.8, CMe), 0.817 (3 H, d, *J* 6.2, CMe), 0.822 (3 H, t, *J* 7.3, CMe), 0.98–1.14 (1 H, m, CH), 1.25–1.44 (1 H, m, CH), 1.40 (9 H, s, CMe_3), 1.46–1.63 (1 H, m, CH), 1.72–1.85 (1 H, m, CH), 2.13 (3 H, s, CMe), 2.40 (1 H, dd, *J* 8.1 and 8.1, 2-H), 2.57 (3 H, s, CMe), 2.67 (3 H, s, CMe), 3.62 (1 H, ddd, *J* 7.6, 7.3 and 5.4, 5-H), 3.84 (3 H, s, OMe), 4.46 (1 H, d, *J* 7.6, NH), 5.26 (1 H, dd, *J* 15.1 and 7.3, 4-H), 5.31 (1 H, dd, *J* 15.1 and 8.1, 3-H), 6.55 (1 H, s, Ph); *m/z* (FAB-LRMS) 482 (MH^+), 480, 424, 380, 368, 298, 268, 230, 213 (base peak), 197, 149, 119, 95, 57, 41.

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