Stereodivergent Synthesis of Chiral 2-Alkenylaziridines: Palladium(0)-Catalyzed 2,3-*cis*-Selective Aziridination and Base-Mediated 2,3-*trans*-Selective Aziridination

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Whereas treatment of the allylic mesylates of *N*-protected 2-alkyl-4-amino-(*E*)-2-alken-1-ols with sodium hydride in DMF yields exclusively the corresponding thermodynamically less stable 2,3-*trans*-2-alkenyl-3-alkylaziridines, exposure of the methyl carbonates of *N*-protected 2-alkyl-4-amino-(*E*)-2-alken-1-ols to a catalytic amount of $Pd(PPh_3)_4$ in THF or 1,4-dioxane affords predominantly the corresponding thermodynamically more stable 2,3-*cis*-2-alkenyl-3-alkylaziridines. The kinetically favored *trans*-selective aziridination would be attributed to the allylic 1,3-strain in aza-anionic intermediates. The conformational analysis of the sterically highly congested 2-alkenylaziridines thus obtained is also presented.

Key words aziridine; palladium; cyclization; stereoselectivity; stereodivergent synthesis

Chiral *N*-activated aziridines are widely used as building blocks for the asymmetric synthesis of biologically and synthetically important compounds.[2—8)] Particularly, aziridines bearing an alkenyl[9—14)] or ethynyl group[15—18)] on one of the aziridine-ring carbon atoms have proven to be extremely useful intermediates for asymmetric preparation of such compounds as alkaloids,[9,10)] β-lactams,[11—13)] vinylglycines,[14)] amino allenes,[15,16)] amino alcohols,[17,18)] and (*E*)-alkene dipeptide isosteres.[19—22)] Although some stereoselective syntheses of enantiomerically pure 2-alkenylaziridines have been reported, most of the reported methods consist of two processes, formation of the aziridine ring and construction of the olefinic moiety, *via* several steps.

In connection with our program directed toward synthesis of (*E*)-alkene dipeptide isosteres,[19—21)] we required an efficient stereoselective synthetic method of chiral 2-alkenylaziridines. Recently, we reported a palladium(0)-catalyzed aziridination of allylic carbonates **1a** preferentially affording thermodynamically more stable 2,3-*cis*-2-vinylaziridines **2** over the corresponding *trans* isomers **3** in good selectivities (**2**:**3**=94:6—98:2, Eq. 1).[23)] In these reaction conditions, the palladium catalyst not only converts the carbonates **1a** into the aziridines **2** and **3** but also equilibrates the isomeric mixtures of **2** and **3** *via* π-allylpalladium(II) intermediates **A**.[20,21)] In contrast, base-mediated intramolecular amination of mesylates **1b** with NaH in DMF produces mixtures of **2** and **3** in variable ratios (2,3-*cis*:*trans*=8:92—51:49) depending on the steric bulkiness of the alkyl substituent R^1 (Eq. 2).[23—25)] Interestingly, while (*Z*)-allylic carbonates **4a** provide 2,3-*cis*-2-vinylaziridines **2** stereoselectively (**2**:**3**=94:6—97:3) under the palladium(0)-catalyzed cyclization conditions (Eq. 3), sodium hydride-mediated cyclization of (*Z*)-allylic mesylates **4b** affords 3-pyrrolines **5** as the sole isolable product (Eq. 4).[26)] Our present research is focused on how the substituent on the double bond changes the stereoselectivities of the aziridine formation. We expected that the introduction of the substituent on the double bond would improve the *trans*-selectivity in the base-mediated aziridination by increasing the unfavorable steric interaction in the anionic intermediates leading to the *cis*-aziridines. Detailed here is a highly stereodivergent synthesis of 2,3-*cis*-2-alkenylaziridines **7** (Eq. 5) and 2,3-*trans*-isomers **8** (Eq. 6), by the palladium-catalyzed decarboxylative ring closure of carbonates **6a** and the base-mediated aziridination of mesylates **6b**, respectively, from single allylic alcohols having an alkyl group (R^3) on the double bond.[27)]

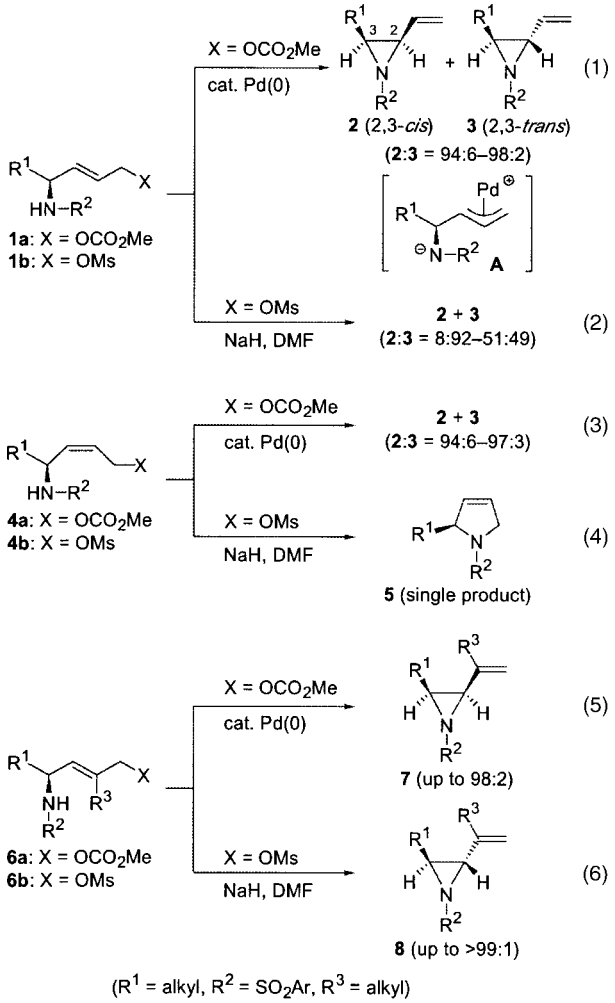

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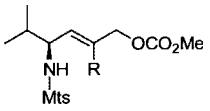
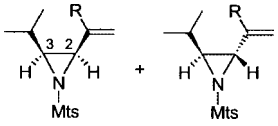
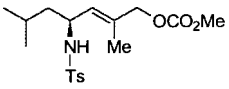
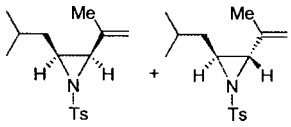
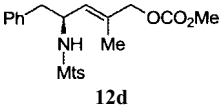
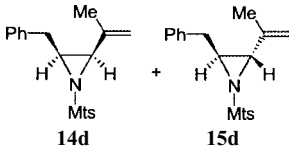
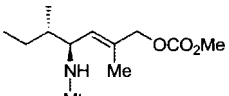
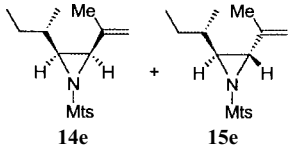
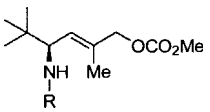
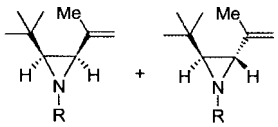
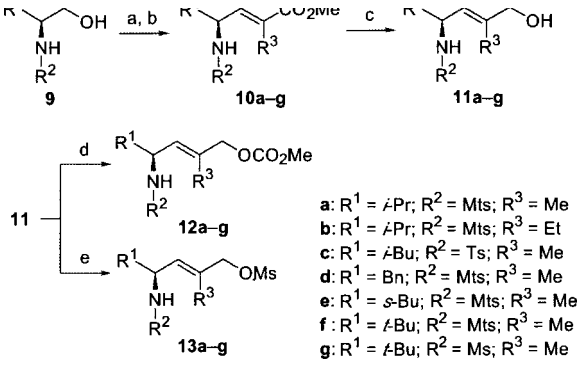
Table 1. $Pd(PPh_3)_4$-Catalyzed 2,3-*cis*-Selective Aziridination of Allylic Methyl Carbonates[a)]

Entry	Substrate	Solvent	$Pd(PPh_3)_4$ (mol%)	Temp. (°C)	Time (min)	Products	Ratio[b)] (**14** : **15**)	Yield[c)]
								
1	**12a** (R=Me)	THF	6	65	240	**14a** (R=Me) **15a** (R=Me)	98 : 2	85%
2	**12b** (R=Et)	Dioxane	10	101	15	**14b** (R=Et) **15b** (R=Et)	99 : 1	87%
3	 **12c**	Dioxane	4	101	15	 **14c** **15c**	98 : 2	69%
4	 **12d**	Dioxane	20	95	30	 **14d** **15d**	98 : 2	49%
5	 **12e**	Dioxane	20	101	30	 **14e** **15e**	97 : 3	68%
								
6	**12f** (R=Mts)	Dioxane	20	101	120	**14f** (R=Mts) **15f** (R=Mts)	87 : 13	68%
7	**12g** (R=Ms)	Dioxane	20	101	150	**14g** (R=Ms) **15g** (R=Ms)	91 : 9	64%

a) All reactions were carried out in dry THF or 1,4-dioxane (*ca.* 0.1 M solution) using a catalytic amount of $Pd(PPh_3)_4$. *b*) Product ratios were determined by HPLC. *c*) Combined isolated yields.



10a: 87%, **11a**: 95%, **12a**: 94%, **13a**: 98%
10b: 97%, **11b**: 97%, **12b**: 99%, **13b**: 89%
10c: 63%, **11c**: 80%, **12c**: 97%, **13c**: 86%
10d: 74%, **11d**: 99%, **12d**: 87%, **13d**: 83%
10e: 67%, **11e**: 82%, **12e**: 99%, **13e**: 99%
10f : 91%, **11f** : 88%, **12f** : 89%, **13f** : 72%
10g: 96%,[f] **11g**: 72%, **12g**: 94%, **13g**: 69%

Reagents: (a) $(COCl)_2$, DMSO, $(i\text{-}Pr)_2NEt$; (b) $Ph_3P{=}C(R^3)CO_2Me$; (c) DIBAL-H; (d) $ClCO_2Me$, pyridine; (e) MsCl, Et_3N; (f) **10g** was prepared from the corresponding *N*-Boc derivative.
Abbreviation: Mts = 2,4,6-trimethylphenylsulfonyl.

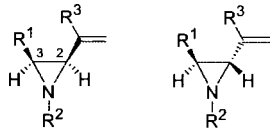
Chart 1. Synthesis of Allyl Carbonates **12** and Mesylates **13** Bearing an Alkyl (R^3) Group

Results and Discussion

Synthesis of the Methyl Carbonates and Mesylates of Allylic Alcohols Bearing an *N*-(Arylsulfonyl)amino Group

As shown in Chart 1, the requisite chiral methyl allylic carbonates **12a**—**g** and the mesylates **13a**—**g** of *N*-(arylsulfonyl)amino alcohols were prepared in good to high yields starting from the *N*-arylsulfonyl amino alcohols **9** which, in turn, could be prepared from (*S*)-valinol, (*S*)-leucinol, (*S*)-phenylalaninol, (*S*)-isoleucinol and (*S*)-*tert*-leucinol.[28)] Typically, Swern oxidation of *N*-protected (*S*)-valinol by successive treatment with oxalyl chloride, DMSO, and *N*,*N*-diisopropylethylamine, and olefination of the resulting aldehyde with a phosphonium ylide $[Ph_3P{=}C(Me)CO_2Me]$ afforded (*E*)-enoate **10a** in 87% yield, which was treated with DIBAL-H to give allylic alcohol **11a** in 95% yield. Conversion of the alcohol **11a** into both carbonate **12a** and mesylate **13a** was accomplished in high yields (94%, 98%, respectively) following standard procedures (see Experimental). The other chiral methyl allylic carbonates **12b**—**g** and mesylates **13b**—**g** listed in Chart 1 were prepared by a sequence of reactions similar to that described for the synthesis of the carbonate **12a** and the mesylate **13a** (see Experimental). Exceptionally, enoate **10g** was synthesized from *N*-Boc derivative of **10g**, which was readily prepared from *N*-Boc *tert*-leucinol, by

Table 2. Spin–Spin Coupling Constant for $J_{H_{2,3}}$ of the Highly Congested 2,3-*cis*- and 2,3-*trans*-2-Alkenylaziridines **14** and **15** in $CDCl_3$



14 **15**

Entry	Aziridine	Stereochemistry	$J_{H_{2,3}}$
1	**14a**	2,3-*cis*	7.3 Hz
2	**14b**	2,3-*cis*	7.3 Hz
3	**14c**	2,3-*cis*	7.6 Hz
4	**14d**	2,3-*cis*	7.3 Hz
5	**14e**	2,3-*cis*	7.3 Hz
6	**14f**	2,3-*cis*	7.6 Hz
7	**14g**	2,3-*cis*	7.8 Hz
8	**15a**	2,3-*trans*	4.3 Hz
9	**15b**	2,3-*trans*	4.6 Hz
10	**15c**	2,3-*trans*	4.3 Hz
11	**15d**	2,3-*trans*	4.0 Hz
12	**15e**	2,3-*trans*	4.6 Hz
13	**15f**	2,3-*trans*	5.1 Hz
14	**15g**	2,3-*trans*	5.1 Hz

treatment with TFA followed by MtsCl/Et_3N in 96% yield. Yields of each reaction are summarized in Chart 1.

Palladium(0)-Catalyzed 2,3-*cis*-Selective Aziridination Reaction of Allylic Carbonates Having synthesized the substrates for the palladium(0)-catalyzed aziridination reaction of allylic carbonates **12**, the aziridination reaction was then investigated (Table 1). As expected, when the carbonate **12a** having a methyl group on the double bond was treated with 6 mol% of $Pd(PPh_3)_4$ in THF at 65 °C for 4 h (entry 1), a separable 98 : 2 mixture of 3-isopropyl-2-vinylaziridine was obtained in 85% yield. The mixture was separated by recrystallization followed by flash column chromatography, and we confirmed that the major product was 2,3-*cis*-2-alkenylaziridine **14a** and the minor product was its 2,3-*trans* isomer **15a**. As shown in Table 1, methyl carbonates **12c**—**e** also gave the corresponding 2,3-*cis*-aziridines **14c**—**e** in extremely high diastereoselectivities by treatment with a catalytic amount of $Pd(PPh_3)_4$ under equilibrated conditions (entries 3—5).[20,21] Interestingly, the methyl carbonates **12f** and **12g** having a *tert*-butyl group also gave the corresponding sterically highly congested 2,3-*cis*-aziridines **14f** and **14g** as the major products. Apparently, the relatively low 2,3-*cis* selectivities (87 : 13—91 : 9) would be attributed to the unfavorable steric interaction between the *tert*-butyl group and the alkenyl group.

In some cases (entries 1, 2, 4, 5), pure 2,3-*cis*-2-alkenylaziridines **14** can be obtained by purification of the reaction mixture by a short column chromatography over silica gel followed by recrystallization of the resulting isomeric mixtures. The 2,3-*cis*- and 2,3-*trans*-stereochemistries were readily established from ^{1}H-NMR analyses. As shown in Table 2, the 2,3-*cis*-aziridines **14a**—**g** show the $J_{H_{2,3}}$ value (J=7.3—7.8 Hz, entries 1—7) larger than that of the corresponding 2,3-*trans*-isomers **15a**—**g** (J=4.0—5.1 Hz, entries 8—14). The data are in good agreement with ^{1}H-NMR data for related compounds.[20,21]

Sodium Hydride-Mediated 2,3-*trans*-Selective Aziridination Reaction of Allylic Mesylates Our previous results have shown that mesylates **1b** (Eq. 2) bearing a branched alkyl group (R^1) such as an isopropyl group afforded 2,3-*trans*-2-vinylaziridines in moderate to good stereoselectivities (2,3-*trans* : *cis*=74 : 26—92 : 8), while mesylates **1b** with a smaller R^1 group such as an isobutyl or a benzyloxymethyl group gave almost 1 : 1 mixtures of 2,3-*trans*- and 2,3-*cis*-2-vinylaziridines (2,3-*trans* : *cis*=49 : 51—57 : 43).[23] We next investigated the reaction of mesylates **13** and found that the effect of the alkyl group on the double bond on the stereoselectivity was more significant than we expected. The results are summarized in Table 3. Exposure of the mesylates **13a** to sodium hydride in DMF at 0 °C for 30 min gave exclusively the corresponding 2,3-*trans*-aziridines **15a** in 78% yields (entry 1). Similarly, 2,3-*trans*-aziridines **15b**—**g** were obtained in high isolated yields (82—95%) as a single isomer by the reaction of the mesylates **13b**—**g** with sodium hydride in DMF (entries 2—7). Irrespective of the structure of the starting mesylates, the diastereoselection of the products **15** is over 99% judging from reverse-phase HPLC.

Table 3. Sodium Hydride-Mediated 2,3-*trans*-Selective Aziridination of Allylic Mesylates[a]

Entry	Substrate	Product (Ratio[b])	Yield[c]
1	**13a** (R=Me)	**15a** (R=Me; >99 : 1)	78%
2	**13b** (R=Et)	**15b** (R=Et; >99 : 1)	95%
3	**13c**	**15c** (>99 : 1)	82%
4	**13d**	**15d** (>99 : 1)	86%
5	**13e**	**15e** (>99 : 1)	95%
6	**13f** (R=Mts)	**15f** (R=Mts; >99 : 1)	93%
7	**13g** (R=Ms)	**15g** (R=Ms; >99 : 1)	92%

a) All reactions were carried out in DMF (*ca.* 0.1 M solution) using 1.5 eq of NaH. *b*) Product ratios were determined by HPLC. *c*) Isolated yields.

It should be noted that the *N*-activated[29] 2,3-*trans*-2-vinylaziridines are thermodynamically less stable than the corresponding 2,3-*cis* isomers.[20,21,23,30] The results of the palladium(0)-catalyzed cyclization (Table 1) clearly show that this

thermodynamic preference for *cis*-aziridines is also applicable to the sterically congested 2-alkenylaziridines **14** and **15**. Actually, as shown in Chart 2, 2,3-*trans*-aziridine **15a**, obtained by exposure of the mesylate **13a** to sodium hydride, was stirred with 4 mol% of $Pd(PPh_3)_4$ for 12 h at 0 °C to yield a 98 : 2 equilibrated mixture of 2,3-*cis*-**14a** and 2,3-*trans*-**15a** in 96% combined isolated yield. This equilibrated reaction indicates that **14a** is estimated to be *ca.* 2.0 kcal/mol more stable than **15a**.

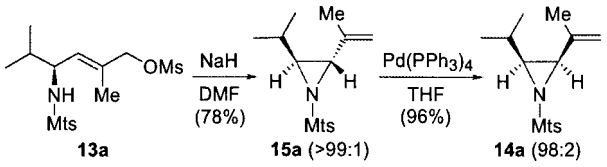


Chart 2. Palladium(0)-Catalyzed Equilibration Reaction of 2,3-*trans*-2-Alkenylaziridines **15a**

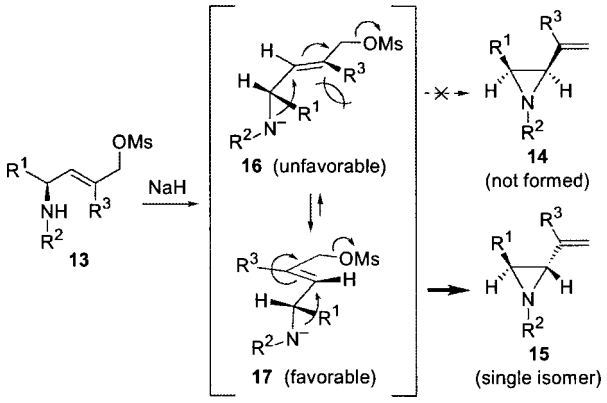


Chart 3. Formation of the 2,3-*trans*-2-Alkenylaziridines **15** from the Mesylates **13**

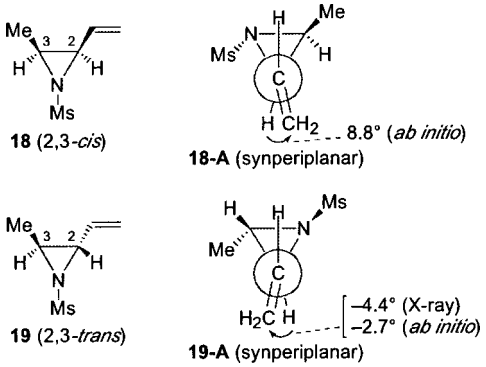


Fig. 1. Stable Conformations of 2,3-*cis*- and 2,3-*trans*-3-Methyl-*N*-mesyl-2-vinylaziridine **18** and **19**

These results show that sodium hydride-mediated aziridination of the allylic mesylates **13** exclusively yields thermodynamically less stable 2,3-*trans*-2-alkenylaziridines **15**. The exclusive formation of 2,3-*trans*-aziridine **15** from the mesylate **13** may be rationalized by assuming two aza-anionic intermediates **16** and **17** (Chart 3). Conformer **16**, which would lead to 2,3-*cis*-aziridine **14** with 2,3-stereochemistry opposite to what was observed experimentally, may be highly destabilized in comparison with **17** owing to unfavorable interactions (allylic 1,3-strain) between the R^1 and R^3 groups. In conformer **17**, the allylic 1,3-strain may be minimized.[31] Accordingly, treatment of the mesylate **13** with sodium hydride yields exclusively the 2,3-*trans*-aziridine **15** most probably *via* the conformer **17**.

Conformation of the Highly Congested 2-Alkenylaziridines In vinylcyclopropane, it has been well documented that the stable conformation has the vinyl group synperiplanar to the cyclopropyl hydrogen on the adjacent carbon atom.[32—36] Similarly, in simple non-congested 2,3-*cis*- and 2,3-*trans*-*N*-mesyl-2-vinyl-3-methylaziridines **18** and **19** (Fig. 1), the C(2)–H bond of the aziridine ring was predicted by *ab initio* calculations to be near-eclipsed with the vinyl group (**18-A** and **19-A**, respectively). In fact, solid conformation of 2,3-*trans*-*N*-mesyl-3-methyl-2-vinylaziridine has the $C{=}CH_2$ group rotated only less than 5° away from perfect eclipsing (synperiplanar arrangement).[20]

In sharp contrast to the vinylaziridine **18**, the hydrogen atom at the C-2 position of the sterically more congested aziridine **14f** and the CH_2 group of the alkenyl are shown to be anticlinal from both X-ray analysis and NOE investigations as shown in **14f-B** in Fig. 2.[37] The synplanar arrangement **14f-A** would be highly destabilized in comparison with conformer **14f-B** owing to unfavorable interactions between the bulky *tert*-butyl group and the methyl group. Similarly, the preferred conformation **15f-B** of 2,3-*trans*-aziridine **15f** can be deduced from X-ray and NOE analyses (Fig. 2). From these observations, both the congested 2,3-*cis*- and 2,3-*trans*-2-alkenylaziridines decrease the steric hindrance by changing

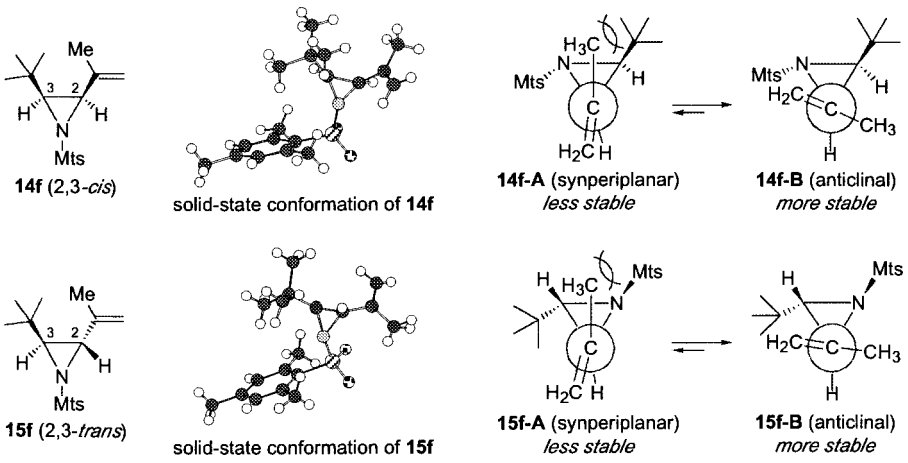


Fig. 2. Solid-State Conformation of the Highly Congested 2-Alkenylaziridines

their conformation from the generally-observed synperiplanar arrangement to the anticlinal one.

In summary, whereas treatment of the allylic mesylates of *N*-protected 2-alkyl-4-amino-(*E*)-2-alken-1-ols with sodium hydride in DMF yields exclusively the corresponding 2,3-*trans*-2-alkenyl-3-alkylaziridines, exposure of the methyl carbonates of the same alcohols to a catalytic amount of $Pd(PPh_3)_4$ in THF or 1,4-dioxane affords predominantly the corresponding 2,3-*cis*-2-alkenyl-3-alkylaziridines. The exclusive formation of 2,3-*trans*-aziridines from the mesylates may be rationalized by assuming the 1,3-allylic strain in the aza-anionic intermediates. It is interesting that the introduction of an alkyl group on the double bond of the vinylaziridines improves the thermodynamic preference for the 2,3-*cis*-2-vinylaziridines over their 2,3-*trans* isomers to up to 99 : 1, although the alkyl group apparently makes the *cis*-isomers more congested as well as the corresponding *trans*-isomers. The present aziridination reactions provide a powerful methodology for the synthesis of either of the two diastereomers of 2-alkenylaziridines from single intermediates.

Experimental

General Methods Melting points are uncorrected. Chemical shifts are reported in parts per million downfield from internal Me_4Si (s=singlet, d=doublet, dd=double doublet, ddd=doublet of double doublet, t=triplet, q=quartet, m=multiplet). Optical rotations were measured in $CHCl_3$. 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. The known compounds (*S*)-*N*-(2,4,6-trimethylphenylsulfonyl)valinol **9a**,[23] (*S*)-*N*-(4-methylphenylsulfonyl)leucinol **9c**,[23] (*S*)-*N*-(2,4,6-trimethylphenylsulfonyl)phenylalaninol **9d**,[23] (2*S*,3*S*)-isoleucinol,[28] and (*S*)-*tert*-leucinol[28] were synthesized according to the literature.

General Procedure for the Synthesis of 2-Alkyl-2-enoates (10). Synthesis of Methyl (4*S*,2*E*)-2,5-Dimethyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]hex-2-enoate (10a) To a stirred solution of oxalyl chloride (2.6 ml, 27.2 mmol) in CH_2Cl_2 (40 ml) at −78 °C under argon was added dropwise a solution of DMSO (6.4 ml, 90.5 mmol) in $CHCl_3$ (5 ml). After 30 min, a solution of (*S*)-*N*-(2,4,6-trimethylphenylsulfonyl)valinol **9a**[23] (5.16 g, 18.1 mmol) in $CHCl_3$ (7 ml) was added to the above reagent at −78 °C, and the mixture was stirred for 30 min. Diisopropylethylamine (22 ml, 127 mmol) was added to the above solution at −78 °C and the mixture was stirred for 30 min. Saturated citric acid (10 ml) was added to the mixture and the whole was extracted with Et_2O. The extract was washed successively with water, saturated $NaHCO_3$, and water, and dried over $MgSO_4$. The filterate was concentrated under reduced pressure to give a residual oil, which was dessolved in $CHCl_3$ (25 ml). A phosphonium ylide [Ph_3P=C(Me)CO_2Me] (15.7 g, 45.3 mmol) was added to the above solution at 0 °C, and the mixture was stirred for 18 h at this temperature. Concentration under reduced pressure gave an oily residue, which was flash chromatographed over silica gel with *n*-hexane–EtOAc (2 : 1) to give **10a** (5.56 g, 87% yield) as colorless crystals from *n*-hexane–EtOAc (2 : 1): mp 109—111 °C; $[\alpha]_D^{25}$ −27.2° (*c*=0.619, $CHCl_3$); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.86 (d, *J*=6.8 Hz, 3H), 0.92 (d, *J*=6.8 Hz, 3H), 1.59 (d, *J*=1.5 Hz, 3H), 1.72—1.84 (m, 1H), 2.26 (s, 3H), 2.60 (s, 6H), 3.64 (s, 3H), 3.83 (ddd, *J*=10.1, 7.9, 6.2 Hz, 1H), 4.68 (d, *J*=7.9 Hz, 1H), 6.22 (dq, *J*=10.1, 1.5 Hz, 1H), 6.89 (s, 2H). *Anal.* Calcd for $C_{18}H_{27}NO_4S$: C, 61.16; H, 7.70; N, 3.96. Found: C, 61.13; H, 7.69; N, 3.92.

Methyl (4*S*,2*E*)-2-Ethyl-5-methyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]hex-2-enoate (10b) According to the general procedure for the preparation of the enoate **10** except that Ph_3P=C(Et)CO_2Me was used as a phosphonium ylide, (*S*)-*N*-(2,4,6-trimethylphenylsulfonyl)valinol **9a**[23] (2.5 g, 8.76 mmol) was converted into **10b** (3.12 g, 97% yield): colorless oil; $[\alpha]_D^{22}$ −6.0° (*c*=0.910, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.86 (dd, *J*=7.5, 7.5 Hz, 3H), 0.88 (d, *J*=6.8 Hz, 3H), 0.92 (d, *J*=6.8 Hz, 3H), 1.71—1.83 (m, 1H), 2.04 (dq, *J*=17.3, 7.5 Hz, 1H), 2.08 (dq, *J*=17.3, 7.5 Hz, 1H), 2.26 (s, 3H), 2.60 (s, 6H), 3.65 (s, 3H), 3.88 (ddd, *J*=10.2, 7.9, 5.8 Hz, 1H), 4.61 (d, *J*=7.9 Hz, 1H), 6.19 (d, *J*=10.2 Hz, 1H), 6.89 (s, 2H); MS (FAB) *m*/*z* 368 (MH^+), 366, 324, 322, 254, 198, 169, 167, 137, 119 (base peak), 109, 91; HR-MS (FAB) calcd for $C_{19}H_{30}NO_4S$ (MH^+) 368.1895; found: 368.1892.

Methyl (4*S*,2*E*)-2,6-Dimethyl-4-[*N*-(4-methylphenylsulfonyl)amino]hept-2-enoate (10c) (*S*)-*N*-(4-Methylphenylsulfonyl)leucinol **9c**[23] (4.07 g, 15 mmol) was converted into **10c** (3.18 g, 63% yield): colorless needles from *n*-hexane–Et_2O (3 : 1); mp 72—74 °C; $[\alpha]_D^{27}$ +5.0° (*c*=1.06, $CHCl_3$); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.84 (d, *J*=6.5 Hz, 3H), 0.85 (d, *J*=6.5 Hz, 3H), 1.22 (ddd, *J*=13.9, 6.9, 6.9 Hz, 1H), 1.44 (ddd, *J*=13.9, 7.8, 6.7 Hz, 1H), 1.52—1.65 (m, 1H), 1.72 (d, *J*=1.5 Hz, 3H), 2.39 (s, 3H), 3.64 (s, 3H), 4.08—4.20 (m, 1H), 4.66 (d, *J*=7.7 Hz, 1H), 6.17 (dq, *J*=9.7, 1.5 Hz, 1H), 7.22—7.26 (m, 2H), 7.67—7.71 (m, 2H). *Anal.* Calcd for $C_{17}H_{25}NO_4S$: C, 60.15; H, 7.42; N, 4.13. Found: C, 60.02; H, 7.47; N, 4.15.

Methyl (4*S*,2*E*)-2-Methyl-5-phenyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]pent-2-enoate (10d) (*S*)-*N*-(2,4,6-Trimethylphenylsulfonyl)phenylalaninol **9d**[23] (4.0 g, 12.0 mmol) was converted into **10d** (3.56 g, 74% yield): colorless needles from *n*-hexane–Et_2O (2 : 1); mp 118—120 °C; $[\alpha]_D^{30}$ −7.1° (*c*=0.505, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.48 (d, *J*=1.4 Hz, 3H), 2.27 (s, 3H), 2.47 (s, 6H), 2.76 (dd, *J*=13.5, 7.0 Hz, 1H), 2.83 (dd, *J*=13.5, 6.8 Hz, 1H), 3.65 (s, 3H), 4.20 (dddd, *J*=9.5, 7.0, 6.8, 5.9 Hz, 1H), 4.67 (d, *J*=5.9 Hz, 1H), 6.34 (dq, *J*=9.5, 1.4 Hz, 1H), 6.87 (s, 2H), 7.00—7.09 (m, 2H), 7.20—7.29 (m, 3H). *Anal.* Calcd for $C_{22}H_{27}NO_4S$: C, 65.81; H, 6.78; N, 3.49. Found: C, 65.66; H, 6.88; N, 3.34.

Methyl (4*S*,5*S*,2*E*)-2,5-Dimethyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]hept-2-enoate (10e) To a stirred solution of (2*S*,3*S*)-isoleucinol[28] (10 g, 85.3 mmol) and Et_3N (24.8 ml, 179 mmol) in a mixed solvent of DMF (10 ml) and $CHCl_3$ (20 ml) was added MtsCl (19.6 g, 89.6 mmol) in $CHCl_3$ (15 ml) at 0 °C, and the mixture was stirred at this tempetature for 4 h followed by quenching with saturated $NaHCO_3$ (2 ml). The whole was extracted with a mixed solvent of Et_2O–EtOAc (3 : 1), and the extract was washed successively with saturated citric acid, water, saturated $NaHCO_3$, and water, and dried over $MgSO_4$. Usual workup followed by recrystallization from *n*-hexane–Et_2O (3 : 1) gave (2*S*,3*S*)-*N*-(2,4,6-trimethylphenylsulfonyl)isoleucinol **9e** (22.0 g, 86% yield): colorless crystals from *n*-hexane–Et_2O (3 : 1); mp 61 °C; $[\alpha]_D^{28}$ −18.7° (*c*=1.39, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.75 (t, *J*=7.0 Hz, 3H), 0.76 (d, *J*=7.0 Hz, 3H), 0.94—1.10 (m, 1H), 1.31—1.56 (m, 2H), 2.05—2.16 (m, 1H), 2.30 (s, 3H), 2.66 (s, 6H), 3.04—3.14 (m, 1H), 3.50—3.64 (m, 2H), 4.98—5.07 (m, 1H), 6.96 (s, 2H). *Anal.* Calcd for $C_{15}H_{25}NO_3S$: C, 60.17; H, 8.42; N, 4.68. Found: C, 60.23; H, 8.58; N, 4.54.

According to the general procedure for preparation of the enoate **10**, the alcohol **9e** (4.0 g, 13.4 mmol) was converted into **10e** (3.28 g, 67% yield): colorless oil; $[\alpha]_D^{30}$ −16.1° (*c*=0.884, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.84 (d, *J*=7.0 Hz, 3H), 0.87 (t, *J*=7.0 Hz, 3H), 1.00—1.18 (m, 1H), 1.39—1.64 (m, 2H), 1.58 (d, *J*=1.6 Hz, 3H), 2.27 (s, 3H), 2.60 (s, 6H), 3.64 (s, 3H), 3.93 (ddd, *J*=9.5, 7.8, 5.1 Hz, 1H), 4.66 (d, *J*=7.8 Hz, 1H), 6.23 (dq, *J*=9.5, 1.6 Hz, 1H), 6.89 (s, 2H); MS (FAB) *m*/*z* 368 (MH^+), 366, 336, 310, 268, 198, 169, 137, 119 (base peak), 109; HR-MS (FAB) calcd for $C_{19}H_{30}NO_4S$ (MH^+) 368.1895; found: 368.1903.

Methyl (4*R*,2*E*)-2,5,5-Trimethyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]hex-2-enoate (10f) To a stirred solution of (*S*)-*tert*-leucinol[28] (3.4 g, 29 mmol) and Et_3N (6.0 ml, 44 mmol) in a mixed solvent of DMF (5 ml) and $CHCl_3$ (10 ml) was added MtsCl (7.0 g, 32 mmol) in $CHCl_3$ (5 ml) at 0 °C, and the mixture was stirred at this tempetature for 16 h followed by quenching with saturated $NaHCO_3$ (2 ml). The whole was extracted with a mixed solvent of Et_2O–EtOAc (3 : 1) and the extract was washed successively with saturated citric acid, water, saturated $NaHCO_3$, and water, and dried over $MgSO_4$. Usual workup followed by recrystallization from *n*-hexane–EtOAc (2 : 1) gave (*S*)-*N*-(2,4,6-trimethylphenylsulfonyl)-*tert*-leucinol **9f** (8.18 g, 94% yield): colorless crystals; mp 140 °C; $[\alpha]_D^{26}$ −49.0° (*c*=1.65, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.80 (s, 9H), 2.17—2.27 (m, 1H), 2.30 (s, 3H), 2.67 (s, 6H), 2.96 (ddd, *J*=9.7, 5.9, 4.0 Hz, 1H), 3.61 (ddd, *J*=11.1, 5.9, 4.0 Hz, 1H), 3.69 (ddd, *J*=11.1, 7.0, 4.0 Hz, 1H), 4.91—5.03 (m, 1H), 6.95 (s, 2H). *Anal.* Calcd for $C_{15}H_{25}NO_3S$: C, 60.17; H, 8.42; N, 4.68. Found: C, 59.93; H, 8.62; N, 4.66.

According to the general procedure for preparation of the enoate **10**, the alcohol **9f** (4.0 g, 13.4 mmol) was converted into **10f** (4.48 g, 91% yield): colorless crystals from *n*-hexane–Et_2O (3 : 1); mp 81 °C; $[\alpha]_D^{29}$ −22.3° (*c*=1.39, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.90 (s, 9H), 1.52 (d, *J*=1.4 Hz, 3H), 2.26 (s, 3H), 2.60 (s, 6H), 3.63 (s, 3H), 3.71 (dd, *J*=10.5, 9.5 Hz, 1H), 4.66—4.75 (m, 1H), 6.24 (dq, *J*=10.5, 1.4 Hz, 1H), 6.87 (s, 2H). *Anal.* Calcd for $C_{19}H_{29}NO_4S$: C, 62.10; H, 7.95; N, 3.81. Found: C, 61.92; H, 7.85; N, 3.82.

Methyl (4*R*,2*E*)-2,5,5-Trimethyl-4-[*N*-(methylsulfonyl)amino]hex-2-enoate (10g) To a stirred solution of (*S*)-*tert*-leucinol[28] (3.3 g, 28.2 mmol) and Et_3N (8.19 ml, 59.2 mmol) in a mixed solvent of DMF (10 ml) and $CHCl_3$ (10 ml) was added Boc_2O (6.46 g, 29.6 mmol) at 0 °C. After 10 h, sat-

urated $NaHCO_3$ (5 ml) was added to the mixture and the whole was extracted with a mixed solvent of Et_2O–EtOAc (1 : 1). The extract was washed successively with saturated citric acid, water, saturated $NaHCO_3$, and water, and dried over $MgSO_4$. Usual workup followed by recrystallization from *n*-hexane–EtOAc (1 : 1) gave (*S*)-*N*-(*tert*-butoxycarbonyl)-*tert*-leucinol (4.87 g, 80% yield): colorless prisms; mp 101 °C; $[\alpha]_D^{19}$ −6.3° (*c*=0.896, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.94 (s, 9H), 1.46 (s, 9H), 2.15—2.25 (m, 1H), 3.44—3.54 (m, 2H), 3.79—3.90 (m, 1H), 4.57—4.68 (m, 1H). *Anal.* Calcd for $C_{11}H_{23}NO_3$: C, 60.80; H, 10.67; N, 6.45. Found: C, 60.71; H, 10.90; N, 6.29.

According to the general procedure for the preparation of the enoate **10**, (*S*)-*N*-(*tert*-butoxycarbonyl)-*tert*-leucinol (4.78 g, 22 mmol) was converted into methyl (4*R*,2*E*)-4-[*N*-(*tert*-butoxycarbonyl)amino]-2,5,5-trimethylhex-2-enoate (6.00 g, 96% yield): colorless oil; $[\alpha]_D^{14}$ −1.0° (*c*=0.834, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.92 (s, 9H), 1.43 (s, 9H), 1.94 (s, 3H), 3.75 (s, 3H), 4.26 (dd, *J*=10.0, 8.1 Hz, 1H), 4.55 (d, *J*=8.1 Hz, 1H), 6.56 (dd, *J*=10.0, 1.1 Hz, 1H); MS (FAB) *m*/*z* 286 (MH^+), 230, 228, 186, 172, 154 (base peak), 128, 57; HR-MS (FAB) calcd for $C_{15}H_{28}NO_4$ (MH^+) 286.2018; found: 286.2026.

Trifluoroacetic acid (15 ml) was added to this enoate (2.85 g, 10 mmol) at 0 °C, and the mixture was stirred for 30 min with warming to room temperature. The mixture was concentrated under reduced pressure to an oily residue, which was made alkaline with 28% NH_4OH and extracted with $CHCl_3$. The extract was washed with brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to leave an oil. The oil was dissovled in $CHCl_3$ (15 ml) and Et_3N (6.92 ml, 50 mmol), and MsCl (1.95 ml, 20 mmol) was added dropwise to the stirred mixture at −78 °C. The mixture was stirred for 30 min with warming to 0 °C followed by quenching with saturated $NaHCO_3$ (2 ml). The whole was extracted with EtOAc and the extract was washed successively with saturated citric acid, water, saturated $NaHCO_3$, and water, and dried over $MgSO_4$. Usual workup followed by flash chromatography over silica gel with *n*-hexane–EtOAc (2 : 1) gave **10g** (2.54 g, 96% yield): colorless oil; $[\alpha]_D^{19}$ +44.7° (*c*=1.03, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.97 (s, 9H), 1.96 (d, *J*=1.6 Hz, 1H), 2.86 (s, 3H), 3.78 (s, 3H), 3.99 (dd, *J*=10.5, 9.2 Hz, 1H), 4.68 (d, *J*=9.2 Hz, 1H), 6.61 (dq, *J*=10.5, 1.6 Hz, 1H); MS (FAB) *m*/*z* 264 (MH^+, base peak), 232, 206, 184, 169, 154, 137, 128, 109, 98, 96, 57; HR-MS (FAB) calcd for $C_{11}H_{22}NO_4S$ (MH^+) 264.1269; found: 264.1273.

General Procedure for the Synthesis of Allylic Alcohols (11). Synthesis of (4*S*,2*E*)-2,5-Dimethyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]hex-2-en-1-ol (11a) from 10a DIBAL-H (1.0 M solution in toluene; 49.5 ml, 49.5 mmol) was added dropwise to a stirred solution of the enoate **10a** (5.0 g, 14.1 mmol) in a mixed solvent of toluene (15 ml) and $CHCl_3$ (15 ml) at −78 °C under argon. After 1 h, saturated NH_4Cl (4 ml) was added with vigorous stirring. The mixture was made acidic with saturated citric acid and extracted with EtOAc. The extract was washed with water and dried over $MgSO_4$. The usual workup followed by recrystallization from *n*-hexane–$CHCl_3$ gave **11a** (4.35 g, 95% yield) as colorless needles: mp 129—131 °C; $[\alpha]_D^{21}$ +28.5° (*c*=0.555, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.84 (d, *J*=6.8 Hz, 3H), 0.86—0.89 (m, 1H), 0.90 (d, *J*=6.8 Hz, 3H), 1.43 (d, *J*=1.4 Hz, 3H), 1.66—1.79 (m, 1H), 2.30 (s, 3H), 2.62 (s, 6H), 3.66 (dd, *J*=13.8, 5.7 Hz, 1H), 3.71 (dd, *J*=13.8, 5.7 Hz, 1H), 3.84 (ddd, *J*=9.7, 7.3, 5.9 Hz, 1H), 4.57 (d, *J*=7.3 Hz, 1H), 4.94 (dq, *J*=9.7, 1.4 Hz, 1H), 6.93 (s, 2H). *Anal.* Calcd for $C_{17}H_{27}NO_3S$: C, 62.74; H, 8.36; N, 4.30. Found: C, 62.66; H, 8.37; N, 4.28.

(4*S*,2*E*)-2-Ethyl-5-methyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]-hex-2-en-1-ol (11b) The enoate **10b** (3.0 g, 8.16 mmol) was converted into **11b** (2.70 g, 97% yield): colorless needles from *n*-hexane–Et_2O (1 : 2); mp 96 °C; $[\alpha]_D^{22}$ +50.1° (*c*=0.891, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.85 (d, *J*=7.3 Hz, 3H), 0.87 (t, *J*=7.6 Hz, 3H), 0.89 (d, *J*=6.5 Hz, 3H), 1.67—1.84 (m, 2H), 1.98—2.12 (m, 1H), 2.29 (s, 3H), 2.62 (s, 6H), 3.71—3.83 (m, 2H), 3.89 (ddd, *J*=10.0, 7.0, 5.4 Hz, 1H), 4.64 (d, *J*=7.0 Hz, 1H), 4.97 (d, *J*=10.0 Hz, 1H), 6.93 (s, 2H). *Anal.* Calcd for $C_{18}H_{29}NO_3S$: C, 63.68; H, 8.61; N, 4.13. Found: C, 63.52; H, 8.42; N, 4.09.

(4*S*,2*E*)-2,6-Dimethyl-4-[*N*-(4-methylphenylsulfonyl)amino]hept-2-en-1-ol (11c) The enoate **10c** (3.0 g, 8.84 mmol) was converted into **11c** (2.20 g, 80% yield): colorless needles from *n*-hexane–Et_2O (1 : 4); mp 91 °C; $[\alpha]_D^{24}$ +28.8° (*c*=1.01, $CHCl_3$); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.830 (d, *J*=6.6 Hz, 3H), 0.833 (d, *J*=6.6 Hz, 3H), 1.21 (ddd, *J*=13.5, 7.2, 7.2 Hz, 1H), 1.22 (dd, *J*=6.4, 6.4 Hz, 1H), 1.40 (ddd, *J*=13.5 7.2, 7.2 Hz, 1H), 1.51 (d, *J*=1.3 Hz, 3H), 1.52—1.63 (m, 1H), 2.42 (s, 3H), 3.67—3.80 (m, 2H), 4.08 (dddd, *J*=9.5, 7.2, 7.2, 7.2 Hz, 1H), 4.62 (d, *J*=7.2 Hz, 1H), 4.97 (dq, *J*=9.5, 1.3 Hz, 1H), 7.25—7.29 (m, 2H), 7.69—7.74 (m, 2H). *Anal.* Calcd for $C_{16}H_{25}NO_3S$: C, 61.71; H, 8.09; N, 4.50. Found: C, 61.65; H, 8.26; N, 4.43.

(4*S*,2*E*)-2-Methyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]-5-phenylpent-2-en-1-ol (11d) The enoate **10d** (3.4 g, 8.47 mmol) was converted into **11d** (3.14 g, 99% yield): colorless oil; $[\alpha]_D^{29}$ +10.2° (*c*=0.492, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.12—1.17 (m, 1H), 1.29 (d, *J*=1.1 Hz, 3H), 2.29 (s, 3H), 2.50 (s, 6H), 2.72 (dd, *J*=13.5, 7.0 Hz, 1H), 2.79 (dd, *J*=13.5, 6.5 Hz, 1H), 3.64—3.78 (m, 2H), 4.20 (dddd, *J*=9.2, 7.0, 6.5, 5.4 Hz, 1H), 4.63 (d, *J*=5.4 Hz, 1H), 5.04 (dq, *J*=9.2, 1.1 Hz, 1H), 6.90 (s, 2H), 7.04—7.10 (m, 2H), 7.17—7.28 (m, 3H); MS (FAB) *m*/*z* 374 (MH^+), 356, 282, 200, 183, 157, 119 (base peak), 91; HR-MS (FAB) calcd for $C_{21}H_{28}NO_3S$ (MH^+) 374.1790; found: 374.1798.

(4*S*,5*S*,2*E*)-2,5-Dimethyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]-hept-2-en-1-ol (11e) The enoate **10e** (3.0 g, 8.16 mmol) was converted into **11e** (2.27 g, 82% yield): colorless crystals from *n*-hexane–Et_2O (2 : 1); mp 75 °C; $[\alpha]_D^{28}$ +28.3° (*c*=1.38, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.82 (d, *J*=7.0 Hz, 3H), 0.86 (t, *J*=7.0 Hz, 3H), 0.98—1.20 (m, 1H), 0.99 (dd, *J*=6.5, 6.5 Hz, 1H), 1.36—1.55 (m, 2H), 1.42 (d, *J*=1.4 Hz, 3H), 2.30 (s, 3H), 2.62 (s, 6H), 3.66 (dd, *J*=13.8, 6.5 Hz, 1H), 3.73 (dd, *J*=13.8, 6.5 Hz, 1H), 3.95 (ddd, *J*=9.7, 7.0, 5.7 Hz, 1H), 4.62 (d, *J*=7.0 Hz, 1H), 4.97 (dq, *J*=9.7, 1.4 Hz, 1H), 6.93 (s, 2H). *Anal.* Calcd for $C_{18}H_{29}NO_3S$: C, 63.68; H, 8.61; N, 4.13. Found: C, 63.62; H, 8.76; N, 4.04.

(4*R*,2*E*)-2,5,5-Trimethyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]-hex-2-en-1-ol (11f) The enoate **10f** (4.36 g, 11.9 mmol) was converted into **11f** (3.55 g, 88% yield): colorless crystals from *n*-hexane–$CHCl_3$ (4 : 1); mp 138 °C; $[\alpha]_D^{28}$ +39.6° (*c*=1.12, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.86 (s, 9H), 1.08—1.26 (br s, 1H), 1.40 (d, *J*=1.4 Hz, 3H), 2.29 (s, 3H), 2.62 (s, 6H), 3.64 (dd, *J*=13.2, 6.8 Hz, 1H), 3.68—3.72 (m, 1H), 3.72 (dd, *J*=13.2, 6.5 Hz, 1H), 4.76—4.87 (m, 1H), 5.02 (dq, *J*=10.0, 1.4 Hz, 1H), 6.92 (s, 2H). *Anal.* Calcd for $C_{18}H_{29}NO_3S$: C, 63.68; H, 8.61; N, 4.13. Found: C, 63.38; H, 8.56; N, 4.10.

(4*R*,2*E*)-2,5,5-Trimethyl-4-[*N*-(methylsulfonyl)amino]hex-2-en-1-ol (11g) The enoate **10g** (2.45 g, 9.30 mmol) was converted into **11g** (1.57 g, 72% yield): colorless crystals from Et_2O; mp 66 °C; $[\alpha]_D^{16}$ +60.2° (*c*=1.35, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.94 (s, 9H), 1.74 (d, *J*=1.4 Hz, 3H), 2.14 (br s, 1H), 2.88 (s, 3H), 3.89 (dd, *J*=10.5, 10.3 Hz, 1H), 4.00—4.10 (m, 2H), 4.67 (d, *J*=10.3 Hz, 1H), 5.41 (dq, *J*=10.5, 1.4 Hz, 1H). *Anal.* Calcd for $C_{10}H_{21}NO_3S$: C, 51.04; H, 8.99; N, 5.95. Found: C, 50.75; H, 8.92; N, 6.00.

General Procedure for the Synthesis of Methyl Carbonates (12). Synthesis of (4*S*,2*E*)-*O*-Methoxycarbonyl-2,5-dimethyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]hex-2-en-1-ol (12a) from 11a To a stirred mixture of the alcohol **11a** (2.2 g, 6.76 mmol) and pyridine (5.45 ml) in a mixed solvent of $CHCl_3$ (10 ml) and THF (10 ml) at −78 °C was added dropwise methyl chloroformate (0.89 ml, 11.5 mmol), and the mixture was stirred with warming to 0 °C. After 1 h, saturated $NaHCO_3$ (2 ml) was added to the mixture with vigorous stirring. The whole was extracted with a mixed solvent of Et_2O–EtOAc (1 : 1), and the extract was washed successively with saturated citric acid, water, saturated $NaHCO_3$, and water, and dried over $MgSO_4$. Usual workup followed by flash chromatography over silica gel with *n*-hexane–EtOAc (3 : 1) gave **12a** (2.43 g, 94% yield) as colorless prisms from *n*-hexane–EtOAc (5 : 1): mp 96—98 °C; $[\alpha]_D^{24}$ +13.9° (*c*=1.23, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.84 (d, *J*=7.0 Hz, 3H), 0.90 (d, *J*=7.0 Hz, 3H), 1.38 (s, 3H), 1.67—1.79 (m, 1H), 2.29 (s, 3H), 2.60 (s, 6H), 3.72—3.81 (m, 1H), 3.78 (s, 3H), 4.188 (dd, *J*=13.5 Hz, 1H), 4.192 (dd, *J*=13.5 Hz, 1H), 4.47 (d, *J*=7.6 Hz, 1H), 5.03 (m, 1H), 6.91 (s, 2H). *Anal.* Calcd for $C_{19}H_{29}NO_5S$: C, 59.51; H, 7.62; N, 3.65. Found: C, 59.57; H, 7.70; N, 3.74.

(4*S*,2*E*)-2-Ethyl-*O*-methoxycarbonyl-5-methyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]hex-2-en-1-ol (12b) The alcohol **11b** (735 mg, 2.0 mmol) was converted into **12b** (794 mg, 99% yield): colorless prisms from *n*-hexane–Et_2O (2 : 1); mp 50 °C; $[\alpha]_D^{20}$ +20.5° (*c*=0.945, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.84 (t, *J*=7.6 Hz, 3H), 0.85 (d, *J*=7.0 Hz, 3H), 0.88 (d, *J*=7.0 Hz, 3H), 1.65—1.79 (m, 2H), 1.88—2.05 (m, 1H), 2.28 (s, 3H), 2.60 (s, 6H), 3.78 (s, 3H), 3.82 (ddd, *J*=9.7, 7.6, 5.9 Hz, 1H), 4.27 (dd, *J*=12.4, 1.1 Hz, 1H), 4.32 (dd, *J*=12.4, 1.4 Hz, 1H), 4.49 (d, *J*=7.6 Hz, 1H), 5.07 (d, *J*=9.7 Hz, 1H), 6.90 (s, 2H). *Anal.* Calcd for $C_{20}H_{31}NO_5S$: C, 60.43; H, 7.86; N, 3.52. Found: C, 60.31; H, 7.79; N, 3.45.

(4*S*,2*E*)-*O*-Methoxycarbonyl-2,6-dimethyl-4-[*N*-(4-methylphenylsulfonyl)amino]hept-2-en-1-ol (12c) The alcohol **11c** (623 mg, 2.0 mmol) was converted into **12c** (713 mg, 97% yield): colorless needles from *n*-hexane–Et_2O (3 : 1); mp 76 °C; $[\alpha]_D^{28}$ +44.3° (*c*=0.716, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.84 (d, *J*=6.5 Hz, 3H), 0.84 (d, *J*=6.5 Hz, 3H), 1.21 (ddd, *J*=13.8, 6.8, 6.8 Hz, 1H), 1.40 (ddd, *J*=13.8, 7.3, 7.3 Hz, 1H), 1.50—1.64 (m, 1H), 1.52 (s, 3H), 2.41 (s, 3H), 3.78 (s, 3H), 4.09 (dddd, *J*=9.5,

7.5, 7.3, 6.8 Hz, 1H), 4.20—4.25 (m, 2H), 4.45 (d, J=7.5 Hz, 1H), 5.00 (d, J=9.5 Hz, 1H), 7.23—7.26 (m, 2H), 7.67—7.70 (m, 2H). *Anal.* Calcd for $C_{18}H_{27}NO_5S$: C, 58.51; H, 7.37; N, 3.79. Found: C, 58.52; H, 7.42; N, 3.73.

(4*S*,2*E*)-*O*-Methoxycarbonyl-2-methyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]-5-phenylpent-2-en-1-ol (12d) The alcohol **11d** (500 mg, 1.34 mmol) was converted into **12d** (501 mg, 87% yield): colorless crystals from *n*-hexane–Et_2O (1 : 1); mp 98 °C; $[\alpha]_D^{28}$ +10.2° (c=1.10, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.25 (d, J=1.4 Hz, 3H), 2.28 (s, 3H), 2.50 (s, 6H), 2.72 (dd, J=13.2, 7.3 Hz, 1H), 2.81 (dd, J=13.2, 6.2 Hz, 1H), 3.78 (s, 3H), 4.14 (dddd, J=9.2, 7.3, 6.2, 5.7 Hz, 1H), 4.22 (m, 2H), 4.52 (d, J=5.7 Hz, 1H), 5.12 (dq, J=9.2, 1.4 Hz, 1H), 6.88 (s, 2H), 7.03—7.10 (m, 2H), 7.17—7.28 (m, 3H). *Anal.* Calcd for $C_{23}H_{29}NO_5S$: C, 64.01; H, 6.77; N, 3.25. Found: C, 63.73; H, 6.80; N, 3.23.

(4*S*,5*S*,2*E*)-*O*-Methoxycarbonyl-2,5-dimethyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]hept-2-en-1-ol (12e) The alcohol **11e** (679 mg, 2.0 mmol) was converted into **12e** (790 mg, 99% yield): colorless oil; $[\alpha]_D^{29}$ +15.9° (c=0.796, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.81 (d, J=7.0 Hz, 3H), 0.86 (t, J=7.0 Hz, 3H), 0.97—1.15 (m, 1H), 1.35—1.56 (m, 2H), 1.37 (d, J=1.4 Hz, 3H), 2.29 (s, 3H), 2.60 (s, 6H), 3.78 (s, 3H), 3.87 (ddd, J=9.7, 7.3, 5.7 Hz, 1H), 4.14—4.24 (m, 2H), 4.49 (d, J=7.3 Hz, 1H), 5.05 (dq, J=9.7, 1.4 Hz, 1H), 6.91 (s, 2H); MS (FAB) m/z 396 (M−H), 338, 278, 264, 183, 153, 151, 75 (base peak), 64; HR-MS (FAB) calcd for $C_{20}H_{30}NO_5S$ (M−H) 396.1844; found: 396.1852.

(4*R*,2*E*)-*O*-Methoxycarbonyl-2,5,5-trimethyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]hex-2-en-1-ol (12f) The alcohol **11f** (976 mg, 2.87 mmol) was converted into **12f** (1.02 g, 89% yield): colorless needles from *n*-hexane–Et_2O (3 : 1); mp 122—124 °C; $[\alpha]_D^{27}$ +22.3° (c=1.12, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.88 (s, 9H), 1.31 (d, J=1.4 Hz, 3H), 2.28 (s, 3H), 2.59 (s, 6H), 3.63 (dd, J=10.0, 8.9 Hz, 1H), 3.78 (s, 3H), 4.13 (d, J=13.0 Hz, 1H), 4.14 (d, J=13.0 Hz, 1H), 4.49 (d, J=8.9 Hz, 1H), 5.04 (dq, J=10.0, 1.4 Hz, 1H), 6.89 (s, 2H). *Anal.* Calcd for $C_{20}H_{31}NO_5S$: C, 60.43; H, 7.86; N, 3.52. Found: C, 60.15; H, 7.75; N, 3.53.

(4*R*,2*E*)-*O*-Methoxycarbonyl-2,5,5-trimethyl-4-[*N*-(methylsulfonyl)-amino]hex-2-en-1-ol (12g) The alcohol **11g** (706 mg, 3.0 mmol) was converted into **12g** (823 mg, 94% yield): colorless oil; $[\alpha]_D^{19}$ +46.5° (c=0.891, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.94 (s, 9H), 1.79 (d, J=1.4 Hz, 3H), 2.86 (s, 3H), 3.79 (s, 3H), 3.91 (dd, J=10.5, 9.5 Hz, 1H), 4.47 (d, J=9.5 Hz, 1H), 4.56 (d, J=12.4 Hz, 1H), 4.57 (d, J=12.4 Hz, 1H), 5.42 (dq, J=10.5, 1.4 Hz, 1H); MS (FAB) m/z 294 (MH^+), 292, 236, 218 (base peak), 199, 162, 148, 123, 82, 57; HR-MS (FAB) calcd for $C_{12}H_{24}NO_5S$ (MH^+) 294.1375; found: 294.1365.

General Procedure for the Synthesis of Methanesulfonates (13). Synthesis of (4*S*,2*E*)-2,5-Dimethyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]-*O*-methylsulfonylhex-2-en-1-ol (13a) from 11a To a stirred mixture of the alcohol **11a** (500 mg, 1.54 mmol) and Et_3N (2.13 ml, 1.54 mmol) in THF (10 ml) was added dropwise MsCl (0.60 ml, 7.7 mmol) at 0 °C. The stirring was continued for 0.5 h at 0 °C followed by quenching with saturated $NaHCO_3$ (1 ml) with vigorous stirring. The whole was extracted with Et_2O and the extract was washed successively with saturated citric acid, water, saturated $NaHCO_3$, and water, and dried over $MgSO_4$. Usual workup followed by flash chromatography over silica gel with *n*-hexane–EtOAc (3 : 2) gave **13a** (605 mg, 98% yield) as a colorless oil: $[\alpha]_D^{30}$ −4.5° (c=0.927, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.84 (d, J=6.8 Hz, 3H), 0.89 (d, J=6.8 Hz, 3H), 1.50 (d, J=1.4 Hz, 3H), 1.66—1.79 (m, 1H), 2.30 (s, 3H), 2.60 (s, 6H), 2.97 (s, 3H), 3.78 (ddd, J=10.0, 7.3, 6.2 Hz, 1H), 4.30 (m, 2H), 4.57 (d, J=7.3 Hz, 1H), 5.18 (dq, J=10.0, 1.4 Hz, 1H), 6.93 (s, 2H); MS (FAB) m/z 404 (MH^+), 402, 360, 308, 252, 220, 183, 167, 124, 119 (base peak), 82; HR-MS (FAB) calcd for $C_{18}H_{30}NO_5S_2$ (MH^+) 404.1565; found: 404.1554.

(4*S*,2*E*)-2-Ethyl-5-methyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]-*O*-methylsulfonylhex-2-en-1-ol (13b) The alcohol **11b** (735 mg, 2.0 mmol) was converted into **13b** (746 mg, 89% yield): colorless prisms from *n*-hexane–Et_2O (1 : 2); mp 59—61 °C; $[\alpha]_D^{23}$ −3.9° (c=0.712, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.84 (d, J=7.0 Hz, 3H), 0.88 (d, J=7.0 Hz, 3H), 0.91 (dd, J=7.6, 7.6 Hz, 3H), 1.66—1.78 (m, 1H), 1.87 (dq, J=14.3, 7.6 Hz, 1H), 2.06 (dq, J=14.3, 7.6 Hz, 1H), 2.29 (s, 3H), 2.61 (s, 6H), 2.98 (s, 3H), 3.84 (ddd, J=10.0, 7.0, 5.7 Hz, 1H), 4.40 (dd, J=11.6, 1.1 Hz, 1H), 4.42 (dd, J=11.6, 1.1 Hz, 1H), 4.56 (d, J=7.0 Hz, 1H), 5.22 (d, J=10.0 Hz, 1H), 6.93 (s, 2H). *Anal.* Calcd for $C_{19}H_{31}NO_5S_2$: C, 54.65; H, 7.48; N, 3.35. Found: C, 54.45; H, 7.31; N, 3.34.

(4*S*,2*E*)-2,6-Dimethyl-4-[*N*-(4-methylphenylsulfonyl)amino]-*O*-methylsulfonylhept-2-en-1-ol (13c) The alcohol **11c** (623 mg, 2.0 mmol) was converted into **13c** (669 mg, 86% yield): colorless oil; $[\alpha]_D^{25}$ +6.7° (c=1.26, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.81 (d, J=6.8 Hz, 3H), 0.83 (d, J=6.5 Hz, 3H), 1.21 (ddd, J=13.8, 6.8, 6.8 Hz, 1H), 1.38 (ddd, J=13.8, 7.6, 7.6 Hz, 1H), 1.49—1.59 (m, 1H), 1.62 (d, J=1.4 Hz, 3H), 2.43 (s, 3H), 2.97 (s, 3H), 4.08 (dddd, J=9.7, 7.6, 7.3, 6.8 Hz, 1H), 4.30—4.38 (m, 2H), 4.45—4.58 (m, 1H), 5.17 (dq, J=9.7, 1.4 Hz, 1H), 7.26—7.30 (m, 2H), 7.68—7.71 (m, 2H); MS (FAB) m/z 390 (MH^+), 388, 332, 294 (base peak), 240, 184, 155, 123, 91, 82; HR-MS (FAB) calcd for $C_{17}H_{28}NO_5S_2$ (MH^+) 390.1409; found: 390.1397.

(4*S*,2*E*)-2-Methyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]-*O*-methylsulfonyl-5-phenylpent-2-en-1-ol (13d) The alcohol **11d** (500 mg, 1.34 mmol) was converted into **13d** (502 mg, 83% yield): colorless needles from Et_2O; mp 86 °C; $[\alpha]_D^{29}$ −6.7° (c=1.05, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.37 (m, 3H), 2.29 (s, 3H), 2.48 (s, 6H), 2.72 (dd, J=13.5, 7.3 Hz, 1H), 2.80 (dd, J=13.5, 6.8 Hz, 1H), 2.91 (s, 3H), 4.08—4.20 (m, 1H), 4.34 (m, 2H), 4.56—4.63 (m, 1H), 5.29 (dq, J=9.2, 1.4 Hz, 1H), 6.90 (s, 2H), 7.02—7.10 (m, 2H), 7.18—7.28 (m, 3H). *Anal.* Calcd for $C_{22}H_{29}NO_5S_2$: C, 58.51; H, 6.47; N, 3.10. Found: C, 58.24; H, 6.44; N, 3.05.

(4*S*,5*S*,2*E*)-2,5-Dimethyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]-*O*-methylsulfonylhept-2-en-1-ol (13e) The alcohol **11e** (680 mg, 2.0 mmol) was converted into **13e** (834 mg, 99% yield): colorless crystals from *n*-hexane–Et_2O (1 : 1); mp 80 °C; $[\alpha]_D^{27}$ −0.9° (c=0.920, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.82 (d, J=6.5 Hz, 3H), 0.85 (t, J=7.0 Hz, 3H), 0.99—1.15 (m, 1H), 1.34—1.58 (m, 2H), 1.48 (d, J=1.4 Hz, 3H), 2.30 (s, 3H), 2.61 (s, 6H), 2.97 (s, 3H), 3.88 (ddd, J=9.7, 7.6, 5.4 Hz, 1H), 4.30 (m, 2H), 4.60 (d, J=7.6 Hz, 1H), 5.19 (dq, J=9.7, 1.4 Hz, 1H), 6.93 (s, 2H). *Anal.* Calcd for $C_{19}H_{31}NO_5S_2$: C, 54.65; H, 7.48; N, 3.35. Found: C, 54.50; H, 7.43; N, 3.36.

(4*R*,2*E*)-2,5,5-trimethyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]-*O*-methylsulfonylhex-2-en-1-ol (13f) The alcohol **11f** (651 mg, 1.92 mmol) was converted into **13f** (580 mg, 72% yield): colorless needles from *n*-hexane–EtOAc (3 : 1); mp 147—149 °C; $[\alpha]_D^{26}$ −1.1° (c=1.46, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.87 (s, 9H), 1.45 (d, J=1.4 Hz, 3H), 2.30 (s, 3H), 2.60 (s, 6H), 2.97 (s, 3H), 3.66 (dd, J=10.3, 8.6 Hz, 1H), 4.25 (d, J=12.1 Hz, 1H), 4.26 (d, J=12.1 Hz, 1H), 4.55 (d, J=8.6 Hz, 1H), 5.18 (dq, J=10.3, 1.4 Hz, 1H), 6.92 (s, 2H). *Anal.* Calcd for $C_{19}H_{31}NO_5S_2$: C, 54.65; H, 7.48; N, 3.35. Found: C, 54.67; H, 7.70; N, 3.32.

(4*R*,2*E*)-2,5,5-Trimethyl-*O*-methylsulfonyl-4-[*N*-(methylsulfonyl)-amino]hex-2-en-1-ol (13g) The alcohol **11g** (471 mg, 2.0 mmol) was converted into **13g** (430 mg, 69% yield): colorless needles from $CHCl_3$–Et_2O (2 : 3); mp 116 °C; $[\alpha]_D^{17}$ +36.9° (c=0.943, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.95 (s, 9H), 1.84 (d, J=1.4 Hz, 3H), 2.89 (s, 3H), 3.04 (s, 3H), 3.91 (ddd, J=10.3, 9.5, 0.8 Hz, 1H), 4.54 (br s, 1H), 4.63 (d, J=11.9 Hz, 1H), 4.67 (d, J=11.9 Hz, 1H), 5.54 (dq, J=10.3, 1.4 Hz, 1H). *Anal.* Calcd for $C_{11}H_{23}NO_5S_2$: C, 42.15; H, 7.40; N, 4.47. Found: C, 42.37; H, 7.38; N, 4.58.

General Procedure for the Aziridination Reaction of the Allylic Cabonates (12) with Palladium(0). Synthesis of (2*R*,3*S*)-3-Isopropyl-*N*-(2,4,6-trimethylphenylsulfonyl)-2-(1-methylvinyl)aziridine (14a) and Its (2*S*,3*S*)-Isomer (15a) from 12a (Table 1, Entry 1) A stirred mixture of the carbonate **12a** (300 mg, 0.782 mmol) and $Pd(PPh_3)_4$ (54 mg, 0.047 mmol, 6 mol%) in dry THF (5 ml) was heated at 65 °C for 4 h. The mixture was concentrated under reduced pressure to leave an oil, which was flash chromatographed over silica gel with *n*-hexane–EtOAc (10 : 1) to give a 98 : 2 mixture of **14a** and **15a** (204 mg, 85% combined yield). The mixture was flash chromatographed over silica gel. Elution with *n*-hexane–EtOAc (20 : 1) gave **14a** (200 mg) and further elution yielded **15a** (4 mg).

Compound **14a**: Colorless needles from *n*-hexane; mp 83—85 °C; $[\alpha]_D^{28}$ −88.2° (c=0.550, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.75 (d, J=6.8 Hz, 3H), 0.88 (d, J=6.8 Hz, 3H), 1.32—1.46 (m, 1H), 1.76 (s, 3H), 2.30 (s, 3H), 2.57 (dd, J=9.7, 7.3 Hz, 1H), 2.72 (s, 6H), 3.32 (d, J=7.3 Hz, 1H), 4.93 (m, 2H), 6.95 (s, 2H). *Anal.* Calcd for $C_{17}H_{25}NO_2S$: C, 66.41; H, 8.20; N, 4.56. Found: C, 66.30; H, 8.11; N, 4.60.

Compound **15a**: Colorless oil; $[\alpha]_D^{29}$ −18.9° (c=0.264, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.03 (d, J=6.8 Hz, 3H), 1.15 (d, J=6.8 Hz, 3H), 1.57 (s, 3H), 2.11—2.24 (m, 1H), 2.29 (s, 3H), 2.55 (dd, J=9.2, 4.5 Hz, 1H), 2.70 (s, 6H), 3.20 (d, J=4.5 Hz, 1H), 4.84—4.89 (m, 2H), 6.92 (s, 2H); MS (FAB) m/z 308 (MH^+), 252, 183, 167, 124, 119 (base peak), 91, 77, 55, 41, 39; HR-MS (FAB) calcd for $C_{17}H_{26}NO_2S$ (MH^+) 308.1684; found: 308.1686.

(2*R*,3*S*)-3-(1-Ethylvinyl)-2-isopropyl-*N*-(2,4,6-trimethylphenylsulfonyl)aziridine (14b) and Its (2*S*,3*S*)-Isomer (15b) (Table 1, Entry 2) The carbonate **12b** (398 mg, 1.0 mmol) was converted into a 99 : 1 mixture of **14b** and **15b** (280 mg, 87% combined yield) by treatment with $Pd(PPh_3)_4$ (10 mol%) in dioxane under reflux for 15 min. The mixture was flash chromatographed over silica gel. Elution with *n*-hexane–EtOAc (20 : 1) gave **14b**

(277 mg) and further elution yielded **15b** (3 mg).

Compound **14b**: Colorless crystals from *n*-hexane; mp 47 °C; $[\alpha]_D^{16}$ −88.4° (c=0.770, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.73 (d, J=6.5 Hz, 3H), 0.86 (d, J=7.0 Hz, 3H), 1.05 (t, J=7.3 Hz, 3H), 1.30—1.44 (m, 1H), 2.06 (q, J=7.3 Hz, 2H), 2.30 (s, 3H), 2.56 (dd, J=9.5, 7.0 Hz, 1H), 2.72 (s, 6H), 3.37 (d, J=7.0 Hz, 1H), 4.91 (m, 1H), 4.95 (m, 1H), 6.95 (s, 2H). *Anal.* Calcd for $C_{18}H_{27}NO_2S$: C, 67.25; H, 8.47; N, 4.36. Found: C, 67.20; H, 8.41; N, 4.30.

Compound **15b**: Colorless prisms from *n*-hexane; mp 60 °C; $[\alpha]_D^{23}$ −19.6° (c=0.939, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.04 (t, J=7.6 Hz, 3H), 1.14 (d, J=6.8 Hz, 3H), 1.25 (d, J=6.5 Hz, 3H), 2.01 (q, J=7.6 Hz, 2H), 2.21—2.35 (m, 1H), 2.39 (s, 3H), 2.62 (dd, J=9.7, 4.3 Hz, 1H), 2.80 (s, 6H), 3.31 (d, J=4.3 Hz, 1H), 4.88—4.90 (m, 1H), 4.94—4.96 (m, 1H), 7.02 (s, 2H); MS (FAB) m/z 322 (MH^+), 320, 266, 183, 138 (base peak), 119, 96; HR-MS (FAB) calcd for $C_{18}H_{28}NO_2S$ (MH^+) 322.1841; found: 322.1837.

(2*R*,3*S*)-3-Isobutyl-*N*-(4-methylphenylsulfonyl)-2-(1-methylvinyl)aziridine (14c) and Its (2*S*,3*S*)-Isomer (15c) (Table 1, Entry 3) The carbonate **12c** (100 mg, 0.271 mmol) was converted into a 98 : 2 mixture of **14c** and **15c** (55 mg, 69% combined yield) by treatment with $Pd(PPh_3)_4$ (20 mol%) in dioxane under reflux for 15 min. The mixture was flash chromatographed over silica gel. Elution with *n*-hexane–EtOAc (20 : 1) gave **14c** (54 mg) and further elution yielded **15c** (1 mg).

Compound **14c**: Colorless oil; $[\alpha]_D^{23}$ −48.6° (c=1.12, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.88 (d, J=7.0 Hz, 3H), 0.89 (d, J=6.5 Hz, 3H), 1.17—1.33 (m, 2H), 1.52—1.68 (m, 1H), 1.69 (m, 3H), 2.44 (s, 3H), 2.97 (ddd, J=7.6, 7.3, 7.3 Hz, 1H), 3.22 (d, J=7.6 Hz, 1H), 4.87 (m, 1H), 4.91 (m, 1H), 7.30—7.33 (m, 2H), 7.82—7.86 (m, 2H); MS (FAB) m/z 294 (MH^+), 278, 238, 221, 155, 138 (base peak), 123, 91, 73; HR-MS (FAB) calcd for $C_{16}H_{24}NO_2S$ (MH^+) 294.1528; found: 294.1532.

Compound **15c**: Colorless oil; $[\alpha]_D^{31}$ −15.0° (c=0.846, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.98 (d, J=6.2 Hz, 3H), 1.00 (d, J=6.5 Hz, 3H), 1.53 (m, 3H), 1.69—1.89 (m, 2H), 2.18—2.31 (m, 1H), 2.42 (s, 3H), 2.75 (ddd, J=9.2, 4.3, 4.3 Hz, 1H), 3.26 (d, J=4.3 Hz, 1H), 4.87—4.89 (m, 1H), 4.94—4.96 (m, 1H), 7.28—7.31 (m, 2H), 7.78—7.84 (m, 2H); MS (FAB) m/z 294 (MH^+), 292, 278, 238, 184, 155, 138 (base peak), 123, 91, 82, 55; HR-MS (FAB) calcd for $C_{16}H_{24}NO_2S$ (MH^+) 294.1528; found: 294.1533.

(2*R*,3*S*)-3-Benzyl-*N*-(2,4,6-trimethylphenylsulfonyl)-2-(1-methylvinyl)-aziridine (14d) and Its (2*S*,3*S*)-Isomer (15d) (Table 1, Entry 4) The carbonate **12d** (30 mg, 0.0695 mmol) was converted into a 98 : 2 mixture of **14d** and **15d** (12 mg, 49% combined yield) by treatment with $Pd(PPh_3)_4$ (20 mol%) in dioxane at 95 °C for 30 min. The mixture was flash chromatographed over silica gel. Elution with *n*-hexane–EtOAc (20 : 1) gave **14d** (12 mg) and further elution yielded **15d** (0.2 mg).

Compound **14d**: Colorless crystals from *n*-hexane; mp 77 °C; $[\alpha]_D^{31}$ −95.2° (c=0.540, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.78 (m, 3H), 2.29 (s, 3H), 2.57 (dd, J=14.6, 7.8 Hz, 1H), 2.59 (s, 6H), 2.69 (dd, J=14.6, 5.4 Hz, 1H), 3.10 (ddd, J=7.8, 7.3, 5.4 Hz, 1H), 3.39 (d, J=7.3 Hz, 1H), 5.05 (m, 1H), 5.11 (m, 1H), 6.84 (s, 2H), 6.93—6.99 (m, 2H), 7.02—7.12 (m, 3H). *Anal.* Calcd for $C_{21}H_{25}NO_2S$: C, 70.95; H, 7.09; N, 3.94. Found: C, 71.07; H, 7.18; N, 3.87.

Compound **15d**: Colorless needles from *n*-hexane; mp 72—74 °C; $[\alpha]_D^{28}$ +38.1° (c=0.467, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.47 (m, 3H), 2.30 (s, 3H), 2.71 (s, 6H), 2.90 (ddd, J=10.0, 4.0, 4.0 Hz, 1H), 3.26 (dd, J=14.0, 10.0 Hz, 1H), 3.47 (d, J=4.0 Hz, 1H), 3.51 (dd, J=14.0, 4.0 Hz, 1H), 4.82 (m, 1H), 4.89 (m, 1H), 6.94 (s, 2H), 7.20—7.34 (m, 5H). *Anal.* Calcd for $C_{21}H_{25}NO_2S$: C, 70.95; H, 7.09; N, 3.94. Found: C, 70.67; H, 7.14; N, 3.91.

(3*R*,4*S*,5*S*)-3,4-Epimino-2,5-dimethyl-*N*-(2,4,6-trimethylphenylsulfonyl)hept-1-ene (14e) and Its (3*S*,4*S*,5*S*)-Isomer (15e) (Table 1, Entry 5) The carbonate **12e** (200 mg, 0.503 mmol) was converted into a 97 : 3 mixture of **14e** and **15e** (110 mg, 68% combined yield) by treatment with $Pd(PPh_3)_4$ (20 mol%) in dioxane under reflux for 30 min. The mixture was flash chromatographed over silica gel. Elution with *n*-hexane–EtOAc (20 : 1) gave **14e** (107 mg) and further elution yielded **15e** (3 mg).

Compound **14e**: Colorless crystals from cold *n*-hexane; mp 49 °C; $[\alpha]_D^{25}$ −73.1° (c=0.446, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.75 (t, J=7.0 Hz, 3H), 0.85 (d, J=6.8 Hz, 3H), 0.98—1.39 (m, 3H), 1.75 (m, 3H), 2.30 (s, 3H), 2.67 (dd, J=9.5, 7.3 Hz, 1H), 2.72 (s, 6H), 3.27 (d, J=7.3 Hz, 1H), 4.91 (m, 2H), 6.95 (s, 2H). *Anal.* Calcd for $C_{18}H_{27}NO_2S$: C, 67.25; H, 8.47; N, 4.36. Found: C, 67.16; H, 8.49; N, 4.35.

Compound **15e**: Colorless oil; $[\alpha]_D^{29}$ −36.5° (c=0.895, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.92 (t, J=7.3 Hz, 3H), 1.00 (d, J=7.0 Hz, 3H), 1.20—1.37 (m, 1H), 1.58 (m, 3H), 1.75—2.05 (m, 2H), 2.29 (s, 3H), 2.62 (dd, J=9.5, 4.6 Hz, 1H), 2.70 (s, 6H), 3.19 (d, J=4.6 Hz, 1H), 4.84 (m, 1H), 4.88 (m, 1H), 6.92 (s, 2H); MS (FAB) m/z 322 (MH^+), 320, 266, 252, 183, 167, 138 (base peak), 119, 82, 57; HR-MS (FAB) calcd for $C_{18}H_{28}NO_2S$ (MH^+) 322.1841; found: 322.1835.

(2*R*,3*S*)-3-(*tert*-Butyl)-*N*-(2,4,6-trimethylphenylsulfonyl)-2-(1-methylvinyl)aziridine (14f) and Its (2*S*,3*S*)-Isomer (15f) (Table 1, Entry 6) The carbonate **12f** (300 mg, 0.755 mmol) was converted into a 87 : 13 mixture of **14f** and **15f** (166 mg, 68% combined yield) by treatment with $Pd(PPh_3)_4$ (20 mol%) in dioxane under reflux for 2 h. The mixture was flash chromatographed over silica gel. Elution with *n*-hexane–EtOAc (20 : 1) gave **14f** (144 mg) and further elution yielded **15f** (22 mg).

Compound **14f**: Colorless needles from *n*-hexane; mp 83 °C; $[\alpha]_D^{30}$ −29.7° (c=1.01, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.83 (s, 9H), 1.76 (m, 3H), 2.31 (s, 3H), 2.59 (d, J=7.6 Hz, 1H), 2.75 (s, 6H), 3.24 (m, 1H), 4.85—4.88 (m, 1H), 4.96—4.98 (m, 1H), 6.96 (s, 2H). *Anal.* Calcd for $C_{18}H_{27}NO_2S$: C, 67.25; H, 8.47; N, 4.36. Found: C, 66.96; H, 8.44; N, 4.40.

Compound **15f**: Colorless oil; $[\alpha]_D^{26}$ −58.1° (c=0.248, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.72 (s, 9H), 2.04 (m, 3H), 2.29 (s, 3H), 2.71 (s, 6H), 3.07 (d, J=5.1 Hz, 1H), 3.14 (d, J=5.1 Hz, 1H), 5.18—5.21 (m, 2H), 6.92 (s, 2H); MS (FAB) m/z 322 (MH^+), 266, 252, 183, 167, 138 (base peak), 119, 82, 57; HR-MS (FAB) calcd for $C_{18}H_{28}NO_2S$ (MH^+) 322.1841; found: 322.1837.

(2*R*,3*S*)-3-(*tert*-Butyl)-2-(1-methylvinyl)-*N*-(methylsulfonyl)aziridine (14g) and Its (2*S*,3*S*)-Isomer (15g) (Table 1, Entry 7) The carbonate **12g** (147 mg, 0.5 mmol) was converted into a 91 : 9 mixture of **14g** and **15g** (70 mg, 64% combined yield) by treatment with $Pd(PPh_3)_4$ (20 mol%) in dioxane under reflux for 2.5 h. The mixture was flash chromatographed over silica gel. Elution with *n*-hexane–EtOAc (7 : 1) gave **14g** (64 mg) and further elution yielded **15g** (6 mg).

Compound **14g**: Colorless oil; $[\alpha]_D^{16}$ −120° (c=0.284, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.00 (s, 9H), 1.85—1.87 (m, 3H), 2.67 (d, J=7.8 Hz, 1H), 3.09 (s, 3H), 3.11—3.16 (m, 1H), 4.98—5.01 (m, 1H), 5.17—5.19 (m, 1H); MS (FAB) m/z 218 (MH^+), 162, 138, 97, 95, 83, 81, 71, 69, 67, 57 (base peak), 55, 43, 41; HR-MS (FAB) calcd for $C_{10}H_{20}NO_2S$ (MH^+) 218.1215; found: 218.1222.

Compound **15g**: Colorless oil; $[\alpha]_D^{13}$ +13.8° (c=0.781, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.98 (s, 9H), 1.99 (s, 3H), 3.06 (s, 3H), 3.08 (d, J=5.1 Hz, 1H), 3.16 (d, J=5.1 Hz, 1H), 5.21—5.23 (m, 2H); MS (FAB) m/z 218 (MH^+, base peak), 162, 148, 139, 138, 137, 123, 95, 83, 69, 57, 55, 43; HR-MS (FAB) calcd for $C_{10}H_{20}NO_2S$ (MH^+) 218.1215; found: 218.1206.

General Procedure for the Base-Promoted Aziridination of Allylic Mesylates (13). Aziridination of the Mesylate (13a) by Exposure to Sodium Hydride in DMF (Table 3, Entry 1) To a stirred suspension of NaH (27 mg, 1.11 mmol) in DMF (2 ml) under argon was added a solution of the mesylate **13a** (300 mg, 0.743 mmol) in DMF (2 ml) at 0 °C. After 0.5 h, saturated NH_4Cl (0.5 ml) 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 workup followed by flash chromatography over silica gel with *n*-hexane–EtOAc (10 : 1) gave **15a** (179 mg, 78% yield). The corresponding (2*R*,3*S*)-isomer **14a** could not be detected by ^{1}H-NMR and reverse phase HPLC.

Palladium(0)-Catalyzed Equilibrated Reaction of 2,3-*trans*-Aziridines (15a) The 2,3-*trans*-aziridine **15a** (54 mg, 0.176 mmol) and $Pd(PPh_3)_4$ (8.1 mg, 0.0070 mmol, 4 mol%) in dry THF (1 ml) was stirred at 0 °C for 12 h. The mixture was concentrated under reduced pressure to leave an oil, which was flash chromatographed over silica gel with *n*-hexane–EtOAc (10 : 1) to give **14a** (51 mg) and **15a** (1 mg) in 96% combined yield.

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