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Palladium-Catalyzed Reductive Ring Opening with Formic Acid of Aziridines Bearing an α,β-Unsaturated Ester Group

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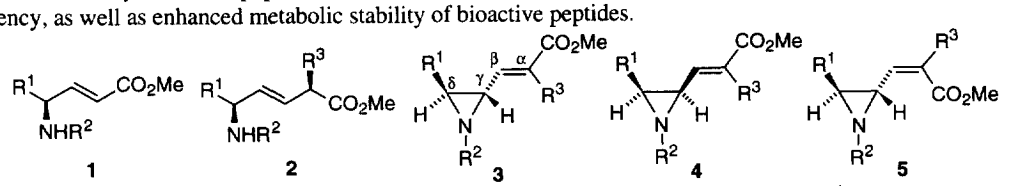
Abstract: The palladium-catalyzed reduction of various *N*-arenesulfonylaziridines bearing α,β-unsaturated ester groups with formic acid and the stereochemistry of the reaction products have been investigated in detail. In all cases examined, (*Z*)-α,β-enoates, (*E*)-α,β-enoates, and (*E*)-β,γ-enoates bearing amino functionality at the δ-position were obtained. The formation of these three reduction products was taken as an indication that palladium-catalyzed isomerization occurs prior to the reduction step. © 1997 Elsevier Science Ltd.

Peptide isosteres are important replacements in many biologically active natural peptides, and are currently of considerable interest.[1] Among the isosteres, α,β-unsaturated esters of type **1** (Scheme 1) involving amino functionality are indispensable constituents or building blocks in an increasing number of natural and synthetic compounds.[2] The use of such analogues and β,γ-unsaturated esters of type **2**[3] for the synthesis of conformationally restricted peptidomimetics is one important use which can lead to improve a selectivity and potency, as well as enhanced metabolic stability of bioactive peptides.



Scheme 1

Among functionalized aziridines, aziridines bearing various α,β-unsaturated ester groups at one of the aziridine carbon atoms have been successfully used by Hudlicky,[4] Pearson,[5] and others,[6] in the synthesis of natural products such as pyrrolizidine alkaloids and antibiotics. Additionally, such aziridines have emerged as valuable starting materials for the synthesis of (*E*)-alkene isosteres **2** via an organocopper-mediated S_N2' reaction.[7] More recently, two of the current authors (Satake and Shimizu) have communicated palladium-catalyzed reductions of γ,δ-epimino-α,β-enoates using formic acid.[8] With a few exceptions, this latter study was concentrated on reductive ring-openings of γ,δ-*trans*-(*E*)-enaotes of type **3**, bearing phenyl groups at the δ-position. We became interested in the question of how the stereochemistry of the reactants influenced stereochemistry of palladium-catalyzed reduction products. Such reactions may provide a good testing ground to examine subtle effects of reactant stereochemistries as well as the nature of substituent(s) on the aziridine ring

since the product mixture will be a finger print of the structure of the reaction intermediates. Accordingly, we detail here the palladium-catalyzed reduction of *N*-sulfonyl-γ,δ-epimino-α,β-enaotes, **4** and **5**, with formic acid.

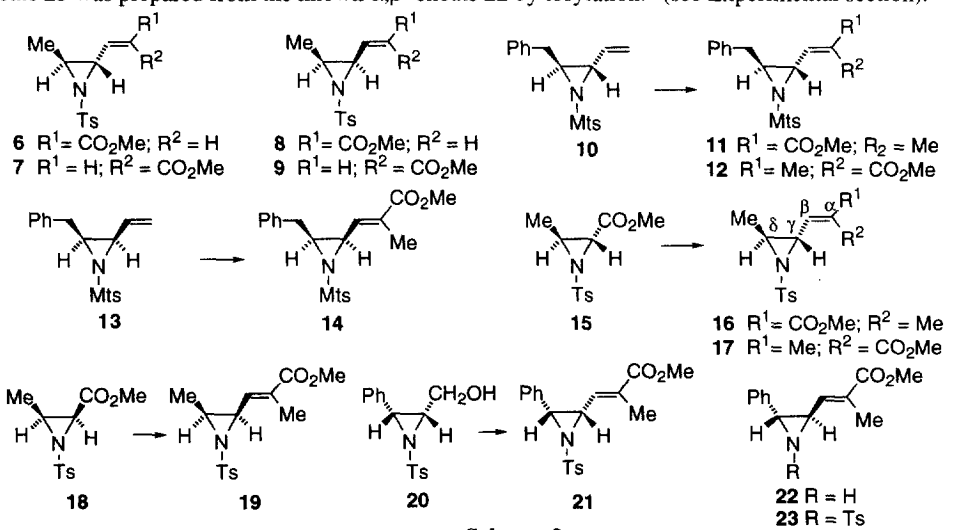
Results and Discussion

It is well documented that the reactivity of NH-aziridines toward nucleophiles is relatively low; hence, "activation" [9] by the introduction of an electron-withdrawing protecting group on the nitrogen atom of the aziridine is required. Arenesulfonyl groups such as *p*-toluenesulfonyl (tosyl; Ts) or 2-mesitylenesulfonyl (Mts) group serve as the most effective activating protecting groups. In addition, these *N*-arenesulfonyl groups can withstand a wide range of chemical manipulations and yet be removed by using Baldwin's protocol.[10]

The palladium-catalyzed regio- and stereoselective reduction of various types of vinyl oxiranes and γ,δ-epoxy-α,β-enoates with formic acid has recently been developed.[11] This method has been used in the synthesis of various natural and synthetic compounds.[12,13] Although the regio- and stereoselectivity of the palladium-catalyzed reduction of γ,δ-epimino-α,β-enoates with formic acid is expected to be controlled by a delicate balance of steric as well as electronic factors of substrates and reaction intermediates, it was our expectation to be able to synthesize isosteres by employing palladium-catalyzed reductions.

1. Synthesis of requisite substrates for palladium-catalyzed reduction with formic acid

We prepared requisite *N*-tosyl-γ,δ-epimino-α,β-enoates (**6**-**9**) according to a previous procedure.[7a,c] As shown in Scheme 2, The (*E*)- and (*Z*)-enoates (**11** and **12**) and the (*E*)-enoate **14** were prepared from the known vinyl aziridines **10**[14] and **13**,[14] respectively, by successive treatment with ozone and (α-carbomethoxyethylidene)triphenylphosphorane. The (*E*)- and (*Z*)-enoates (**16** and **17**) and the (*E*)-enoate **19** were readily prepared from the known methyl (2*R*,3*S*)-3-methyl-1-tosylaziridine-2-carboxylate **15**,[15] and its (2*S*,3*S*)-isomer **18**,[16] respectively. Typically, the aziridine **15** was treated successively with diisobutylaluminum hydride and (α-carbomethoxyethylidene)triphenylphosphorane in a one-pot reaction to give a separable 95:5 mixture of (*E*)- and (*Z*)-α,β-enoates **16** and **17** in 79% combined yield. The (*E*)-enoate **21** possessing a phenyl group on the aziridine-ring was prepared from the known aziridinemethanol **20**[15] by Swern oxidation followed by treatment with (α-carbomethoxyethylidene)triphenylphosphorane. Finally, the isomeric (*E*)-enoate **23** was prepared from the known α,β- enoate **22** by tosylation.[8] (see Experimental section).



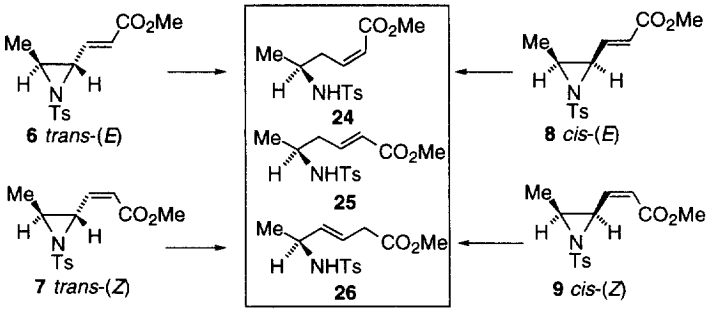
Scheme 2

The *E*-configuration of the substrates **11**, **14**, **16**, **19**, **21**, and **23** could easily be determined by NOE measurements. For example, the *E*-configuration of **11** was established unequivocally from the NOE (ca. 12% enhancement) of the hydrogen at the γ-position at δ 3.37 on irradiation of the methyl hydrogens at the α-position at δ 1.92. In a similar manner, *Z*-configuration of the substrate **12** was established by NOE enhancement of the vinylic hydrogen at the β-position upon irradiation of the methyl hydrogens at the α-position. The same *Z*-

configuration was assumed for the enoate **17** from NOE spectral analysis. In addition, the γ,δ-*trans*-aziridines **11**, **12**, **16**, **17**, and **23** showed $JH_{\gamma\delta}$ values (J = 4.1- 4.7 Hz) smaller than the $JH_{\gamma\delta}$ values (J = 7.2 - 7.5 Hz) of the γ,δ-*cis*-isomers **14**, **19**, and **21**. The data are in agreement with ^{1}H NMR data for related compounds.[15a,16a]

2. Palladium-catalyzed reduction of γ,δ-epimino-α,β-enoates with formic acid.

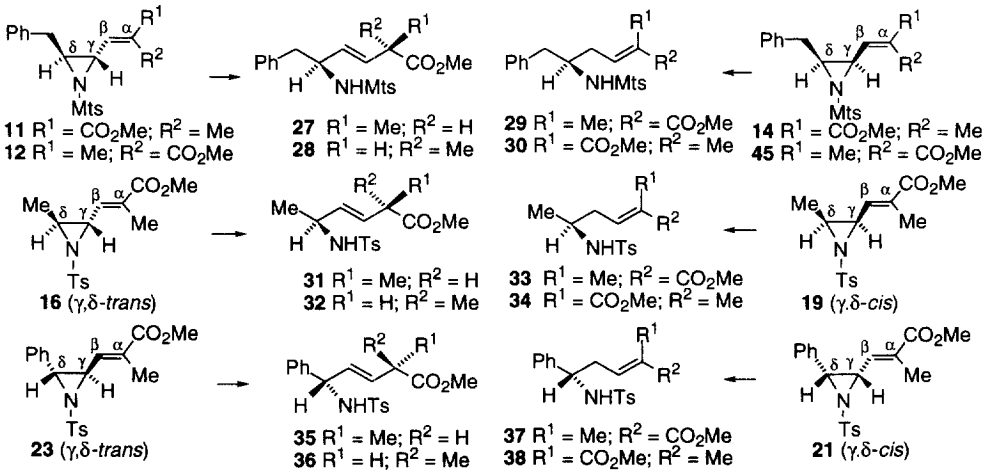
Using four stereoisomeric γ,δ-epimino-α,β-enoates **6**, **7**, **8**, and **9** as representative reactants, reactions with formic acid in the presence of palladium-catalyst were examined. Initially we attempted the reduction with formic acid-Et_3N in the presence of maleic anhydride (20 mol%) and a catalytic amount η^3-allylpalladium chloride dimer (5 mol%) in THF or MeCN. The reduction was very slow and did not proceed to completion at 25 °C. When treated in DMSO under the same reaction conditions, the enoate **6** was converted to reduction products **24**, **25**, and **26** (**24**:**25**:**26** = 6:81:13) in 96% combined yield. Similar results were obtained by palladium-catalyzed reduction of **7**, **8**, or **9** with formic acid. It was found that the (*E*)-α,β-unsaturated ester **25** was obtained as a major product (Scheme 3).



24 : **25** : **26** = 4~6 : 78~81 : 10~13

Reaction conditions: η^3-allylpalladium chloride dimer (5 mol%); maleic anhydride (20 mol%); formic acid (5 equiv.); Et_3N (2 equiv.), DMSO (0.9 mL)

Scheme 3



Scheme 4

Palladium-catalyzed reductions of γ,δ-epimino-α,β-enaotes **11**, **12**, **14**, **16**, **19**, **21**, **23**, and **45** bearing methyl groups at the α-position were also examined using η^3-allylpalladium chloride dimer, tetrakis(triphenylphosphine)palladium (0), or tris(dibenzylideneacetone)dipalladium(0) in various solvents under similar conditions described above. In all cases, (*E*)-β,γ-enoate(s) and (*E*)-and (*Z*)-α,β-enoates were obtained. In

each of the reductions, it was necessary to monitor reaction progress carefully by TLC and/or HPLC, in order to verify when complete consumption of the substrate was being approached, so as to minimize double bond reduction of the product(s). Results were summarized in Scheme 4 and Table 1.

The stereochemical assignments for (*E*)-β,γ-enoates **27** and **28** were based on comparison of their specific rotations as well as NMR data with those of authentic samples independently synthesized. The structures and the stereochemistries of other (*E*)-β,γ-enoates **31**, **32**, **35**, and **36** were confirmed by comparison of their spectral data with those of authentic samples.[7a,c] Likewise, the structures of all (*E*)- and (*Z*)-α,β-enoates (**29**, **33**, **37**) and (**30**, **34**, **38**) were ascertained by their NMR spectral data.

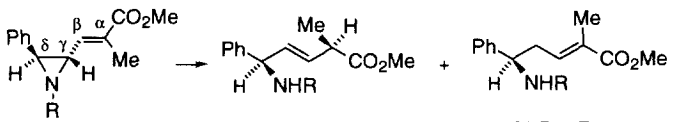
Table 1. Palladium-catalyzed Reduction of α-Alkyl-γ,δ-epimino-α,β-enoates with Formic Acid[a]

entry	substrate	solvent	catalyst[b] (additive[c])	react. time	combined yield (%)	reduction products (*E*-β,γ-enoate) : *E*-α,β-enoate : *Z*-α,β-enoate
1	**11**	THF	A (M, 4)	3.5 h	< 1	(**27** : **28**) : **29** : **30** = (0 : 0) : < 1 : 0
2	**11**	THF	A (-)	3.5 h	< 1	(**27** : **28**) : **29** : **30** = (0 : 0) : < 1 : 0
3	**11**	MeCN	A (M, 4)	3.5 h	< 1	(**27** : **28**) : **29** : **30** = (0 : 0) : < 1 : 0
4	**11**	MeCN	A (-)	3.5 h	< 2	(**27** : **28**) : **29** : **30** = (0 : 0) : < 1 : < 1
5	**11**	DMF	A (M, 4)	0.3 h	79	(**27** : **28**) : **29** : **30** = (8 : 0) : 80 : 12
6	**11**	DMF	C (-)	0.5 h	84	(**27** : **28**) : **29** : **30** = (10 : 0) : 75 : 15
7	**11**	DMF	C (T, 1)	0.5 h	67	(**27** : **28**) : **29** : **30** = (7 : 0) : 72 : 21
8	**12**	DMF	A (M, 4)	0.5 h	73	(**27** : **28**) : **29** : **30** = (0 : 13) : 48 : 39
9	**16**	DMF	C (-)	0.5 h	70	(**31** : **32**) : **33** : **34** = (9 : 0) : 79 : 12
10	**23**	DMF	C (-)	1.0 h	89	(**35** : **36**) : **37** : **38** = (20 : 0) : 64 : 16
11	**14**	DMF	A (M, 4)	1.0 h	84	(**27** : **28**) : **29** : **30** = (< 1 : 7) : 86 : 6
12	**14**	DMF	C (-)	1.5 h	87	(**27** : **28**) : **29** : **30** = (< 1 : 4) : 90 : 6
13	**19**	DMF	A (M, 4)	0.5 h	77	(**31** : **32**) : **33** : **34** = (2 : 5) : 86 : 7
14	**21**	DMF	C (-)	1.0 h	75	(**35** : **36**) : **37** : **38** = (2 : 25) : 64 : 9
15	**11**	DMSO	B (-)	1.5 h	75	(**27** : **28**) : **29** : **30** = (5 : 0) : 78 : 17
16	**11**	DMSO	C (T, 1)	0.5 h	67	(**27** : **28**) : **29** : **30** = (7 : 0) : 78 : 15
17	**14**	DMSO	B (-)	2.5 h	70	(**27** : **28**) : **29** : **30** = (< 1 : 5) : 80 : 15
18	**14**	DMSO	C (T, 1)	1.0 h	72	(**27** : **28**) : **29** : **30** = (2 : 9) : 75 : 14
19	**11**	DMSO	A (M, 4)	1.0 h	91	(**27** : **28**) : **29** : **30** = (56 : 0) : 33 : 11
20	**11**	DMSO	A (D, 4)	1.0 h	82	(**27** : **28**) : **29** : **30** = (52 : 0) : 35 : 13
21	**11**	DMSO	C (-)	0.5 h	82	(**27** : **28**) : **29** : **30** = (54 : 0) : 33 : 13
22	**16**	DMSO	A (M, 4)	0.5 h	82	(**31** : **32**) : **33** : **34** = (45 : 0) : 43 : 12
23	**12**	DMSO	A (M, 4)	0.5 h	75	(**27** : **28**) : **29** : **30** = (0 : 37) : 51 : 12
24	**14**	DMSO	A (M, 4)	2.0 h	93	(**27** : **28**) : **29** : **30** = (4 : 41) : 48 : 7
25	**14**	DMSO	A (D, 4)	2.5 h	87	(**27** : **28**) : **29** : **30** = (5 : 48) : 40 : 7
26	**14**	DMSO	C (-)	1.0 h	87	(**27** : **28**) : **29** : **30** = (5 : 49) : 37 : 9
27	**19**	DMSO	A (M, 4)	0.5 h	80	(**31** : **32**) : **33** : **34** = (11 : 34) : 44 : 11
28	**21**	DMSO	A (M, 4)	1.5 h	87	(**35** : **36**) : **37** : **38** = (2 : 71) : 20 : 7
29	**21**	DMSO	C (-)	1.0 h	70	(**35** : **36**) : **37** : **38** = (16 : 47) : 30 : 7
30	**23**	DMSO	A (M, 4)	0.6 h	81	(**35** : **36**) : **37** : **38** = (71 : 0) : 22 : 7
31	**23**	DMSO	C (-)	0.5 h	81	(**35** : **36**) : **37** : **38** = (65 : 0) : 29 : 6
32	**45**	DMSO	A (M, 4)	2.0 h	75	(**27** : **28**) : **29** : **30** = (35 : 4) : 41 : 20

a). All reactions were carried out at 20-25 °C as a ca. 0.05 molar solution using palladium catalyst (5 mol%), Et_3N (2 equiv.), formic acid (5 equiv.). *b*). A = η^3-allylpalladium chloride dimer; B = tetrakis(triphenylphosphine)palladium(0); C = tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct. *c*). M = maleic anhydride (equiv./Pd); T = triphenylphosphine (equiv./Pd); D = dimethyl acetylenedicarboxylate (equiv./Pd).

Although the proportion of product ratios from the palladium-catalyzed reduction of *N*-arenesulfonyl- γ,δ-epimino-α,β-enoates with formic acid would be expected to be controlled by many factors, the following trends could be seen from Table 1:

1) THF or MeCN was not a solvent of choice, as only low conversion of the substrate **11** into reduction product(s) was realized at around 25 °C (entries 1-4; Table 1). It is clear from Table 1 that the combined isolated yields of the reduction products were satisfactory when DMSO or DMF was used as solvent (entries 5-32).
2) In DMF, the major reduction products were (*E*)-α,β-enoates (**29**, **33**, and **37**) regardless of the types of the palladium catalysts used (entries 5-14).
3) In DMSO, the selection of palladium catalyst is an important factor.
   a) Reduction with $Pd_2(dba)_3{\cdot}CHCl_3$ in the presence of catalytic Ph_3P or with $Pd(PPh_3)_4$ yielded the α,β-enoates as the major products (entries 15-18).
   b) Reductions using of η^3-allylpalladium chloride dimer in the presence of maleic anhydride or dimethyl acetylenedicarboxylate as an additive gave an approximately equal amount of a mixture of α,β-enoates and β,γ-enoates (entries 19, 20, 22-25, and 27). This trend could also be seen by employing $Pd_2(dba)_3{\cdot}CHCl_3$ as a catalyst (entries 21 and 26).
   c) In DMSO, whereas reduction of α-unsubstituted reactants such as **6**-**9** afforded preferentially α,β-enoate **25**, reduction of α-methyl substituted reactants such as **16** or **19** gave a considerable amount of the α-methyl-β,γ-enoate **31** or **32**. (Scheme 3 and entries 22 and 27, Table 1).
4) The stereochemistry at the α-position of the (*E*)-β,γ-enoates obtained by reduction was found to be sensitive to the γ,δ-*cis* or γ,δ-*trans* stereochemistry of reactants. Whereas α-methyl-β,γ-enoates **27**, **28**, **31**, and **35** were obtained from corresponding γ,δ-*trans*-substrates **11**, **12**, **16** and **23** [entries (5-7, 15, 16, 19-21), (8, 23), (9, 22), and (10, 30, 31)], a mixture of α-methyl-β,γ-enoates (**27**, **28**), (**31**, **32**), and (**35**, **36**) were obtained from γ,δ-*cis*-reactants **14**, **19**, **21**, and **45** [entries (11, 12, 17, 18, 24-26), (13, 27), (14, 28, 29), and 32].
5) In DMSO, reduction of the substrates **21** and **23** bearing a phenyl group at the δ-position yielded the (*E*)-alkene isostere(s) **35** and/or **36** as the major products (entries 28-31).[12]



39 R = Ts
42 R = Boc

40 R = Ts
43 R = Boc

41 R = Ts
44 R = Boc

Scheme 5

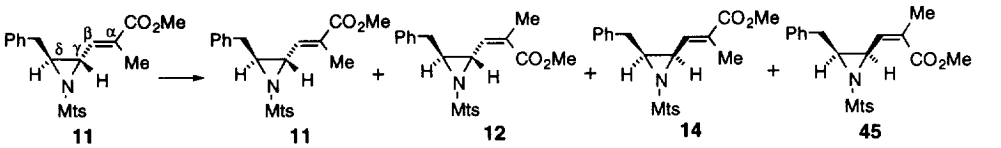
Table 2. Reductive Ring-opening Reaction with Some Reducing Agents

entry	substrate	reducing agent	products	combined yield	β,γ-enoate : α,β-enoate
1	**39**	HCO_2H-Et_3N	**40** + **41**	81%	65 : 35
2	**39**	HCO_2H	**40** + **41**	86%	43 : 57
3	**39**	HCO_2K	**40** + **41**	71%	< 1 : 99
4	**42**	HCO_2K	**43** + **44**	82%	71 : 29

The regioselectivity of the reduction may be also dependent on the nature of the substituents at the C-2 and C-3 positions, the *N*-protecting or activating group, and reducing agents. In the case of the *N*-Ts aziridine **39**, reduction with formic acid in the absence of Et3N increased the relative ratio of the α,β-enoate **41** (compare entries 1 and 2, Table 2). It should be clearly noted that the reduction of the aziridine **39** bearing a Ts group on the nitrogen atom with potassium formate yields only the α,β-enoate **41**. On the other hand, the reduction of the enoate **42** bearing a Boc group on the nitrogen atom under the same reaction condition gave the β,γ-enoate **43** as the major product along with the α,β-enoate **44** (entries 3 and 4, Table 2). Thus, the *N*-activating group plays an important role for the reduction reaction. After all, the regioselectivity of the reduction would be controlled by many factors such as added reagent systems and the structure of substrates.

Recently, we reported that palladium(0)-catalyzed isomerization reactions of various 4,5-epimino-2-enoates afforded mixtures of four possible stereoisomers *via* η^3-allyl intermediates.[17] The formation of a mixture of

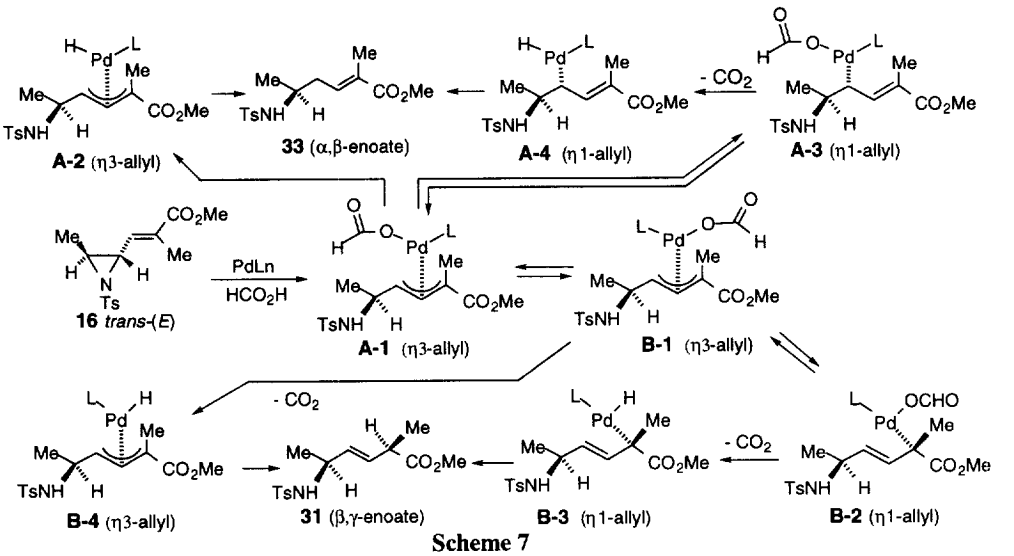
products in the present study suggests that palladium-catalyzed isomerization[18] is occuring prior to reduction in all the reactions examined. In actuality, the aziridine **11** afford four isomerization products **11**, **12**, **14** and **45** in 84% combined yield upon exposure to $Pd(PPh_3)_4$ (5 mol%) in DMSO at 25 °C for 1 h (Scheme 6).



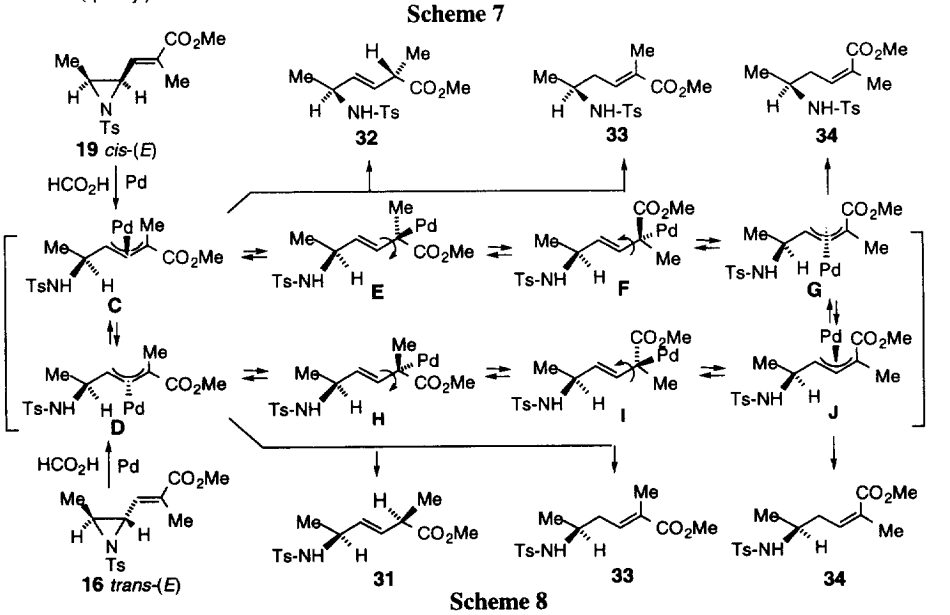
11 : **12** : **14** : **45** = 24 : < 0.1 : 24 : 52

Isomerization reaction of aziridine enoate **11** with $Pd(PPh_3)_4$ (5 mol%) in DMSO at 25 °C for 1 h.

Scheme 6



Scheme 7



Scheme 8

A plausible mechanistic pathway for the regioselectivity of the hydrogen transfer to the α- or γ-position as well as stereoselectivity (stereochemistry at the α-position and *E*- or *Z*-configuration) of the palladium(0)-catalyzed reduction could be drawn as shown in Schemes 7 and 8.

As can be seen from Scheme 7, whereas a η^3-allyl intermediate **A-1** and a η^1-allyl intermediate **A-3**, originated from the substrate **16**, would produce α,β-enoate **33** via palladium hydride intermediates **A-2** and/or **A-4** by a hydrogen transfer to the γ-position, a η^3-allyl intermediate **B-1** and/or a η^1-allyl intermediate **B-2** would provide the β,γ-enoate **31** via intermediates **B-3** and/or **B-4** in the same manner as described above.

Space restriction does not permit detailed discussion on a plausible mechanistic pathway for the palladium(0)-catalyzed reduction of **16** and **19** in terms of stereoselectivity (stereochemistry at the α-position and *E*- or *Z*-configuration). However, it is apparent that all the reduction products would be originated from various interconvertible η^3-allyl and η^1-allyl intermediates[18] as shown in Scheme 8.

In summary, although selectivities are not quantitative, we have shown that palladium-catalyzed reductions of γ,δ-epimino-α,β-enoates with formic acid yield (*E*)-β,γ-enoates, (*E*)-α,β-enoates, and (*Z*)-α,β-enoates. The ratios of reduction products depend upon many factors such as reaction solvents, catalysts employed, nature of substituent(s) at the δ-position, and the γ,δ-*cis*- or *trans*-stereochemistries of the substrates.

Experimental Section

General Methods. All reactions were carried out under a positive pressure of argon, and glassware and syringes were dried in an electric oven at 100 °C prior to use. Melting points are uncorrected. Nominal (LR-MS) and exact mass (HR-MS) spectra were recorded on a JEOL JMS-01SG-2 or JMS-HX/HX 110A mass spectrometer. ^{1}H NMR spectra (270 or 300 MHz) were recorded in $CDCl_3$ unless otherwise specified. 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, m = multiplet). Optical rotations were measured in $CHCl_3$ with a JASCO DIP-360 digital polarimeter. 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 HPLC, Cosmosil-5SL (10 x 250 mm, Nacalai Tesque) or μ-bondasphere-C18 (3.9 x 150mm, Merck) was employed.

Methyl (4*S*,5*S*,2*E*)-4,5-Imino-*N*-(4-methylphenyl)sulfonyl-2-hexenoate 6. Colorless crystals from Et_2O. mp 84 °C; $[a]^{20}_D$ + 28.4 (c = 1.07, $CHCl_3$); ν_{max}/cm^{-1} 1720 (CO), 1655 and 1603 (C=C); ^{1}H NMR (200 MHz; $CDCl_3$) δ 1.54 (d, *J* = 5.9 Hz, 3 H), 2.44 (s, 3 H), 3.01 (ddd, *J* = 11.5, 5.6, 4.1 Hz, 1 H), 3.21 (dd, *J* = 8.8, 4.1, 1 H), 3.73 (s, 3 H), 6.08 (d, *J* = 15.6 Hz, 1 H), 6.87 (dd, *J* = 15.6, 8.8 Hz, 1 H), , 7.30-7.34 (m, 2 H), 7.79-7.84 (m, 2 H). Anal. Calcd. for $C_{14}H_{17}NO_4S$: C, 56.93; H, 5.80; N, 4.74. Found: C, 56.76 ; H, 5.78 ; N, 4.74 .

Methyl (4*S*,5*S*,2*Z*)-4,5-Imino-*N*-(4-methylphenyl)sulfonyl-2-hexenoate 7. Colorless crystals from hexane:Et_2O (1:2). mp 51 °C; $[\alpha]^{20}_D$ - 181 (c = 1.13, $CHCl_3$); ν_{max}/cm^{-1} 1720 (CO), 1645 and 1601 (C=C); ^{1}H NMR (200 MHz; $CDCl_3$) δ 1.50 (d, *J* = 5.6 Hz, 3 H), 2.44 (s, 3 H), 3.01 (ddd, *J* = 11.5, 5.9, 4.2 Hz, 1 H), 3.75 (s, 3 H), 4.42 (dd, *J* = 9.3, 4.2 Hz, 1 H), 6.01 (d, *J* = 11.5 Hz, 1 H), 6.23 (dd, *J* = 11.5, 9.3 Hz, 1 H), 7.30-7.34 (m, 2 H), 7.80-7.84 (m, 2 H); LRMS (EI) *m/z*, 295 (M^+), 280, 264, 198, 155, 140 (base peak), 112, 108, 99 and 91; HRMS (EI), *m/z*, calcd. for $C_{14}H_{17}O_4NS$ (M^+) 295.0878. Found: 295.0887).

Methyl (4*R*,5*S*,2*E*)-4,5-Imino-*N*-(4-methylphenyl)sulfonyl-2-hexenoate 8. Colorless crystals from hexane:Et_2O (1:3); mp 92-93 °C $[\alpha]^{32}_D$ - 89 (c = 0.73, $CHCl_3$); ν_{max}/cm^{-1} 1710 (CO) and 1653 (C=C); ^{1}H NMR (200 MHz; $CDCl_3$) δ 1.21 (d, *J* = 5.9 Hz, 3 H), 2.45 (s, 3 H), 3.14 (m, 1 H), 3.40 (ddd, *J* = 7.6, 6.6, 1.0 Hz, 1 H), 3.72 (s, 3 H), 6.07 (dd, *J* = 15.6 Hz, 1.0 Hz, 1 H), 6.66 (dd, *J* = 15.6, 6.6 Hz, 1 H), 7.31-7.37 (m, 2 H), 7.78-7.84 (m, 2 H). Anal. Calcd. for $C_{14}H_{17}NO_4S$: C, 56.93; H, 5.80; N, 4.74. Found: C, 56.83 ; H, 5.84 ; N, 4.55 .

Methyl (4*R*,5*S*,2*Z*)-4,5-Imino-*N*-(4-methylphenyl)sulfonyl-2-hexenoate 9. Colorless crystals from hexane:Et_2O:CH_2Cl_2 (4:4:1); mp 75-77 °C; $[\alpha]^{27}_D$ + 10.1 (c = 0.92, $CHCl_3$); ν_{max}/cm^{-1} 1720 (CO) and

1644 (C=C); ^{1}H NMR (200 MHz; $CDCl_3$) δ 1.22 (d, J = 5.9 Hz, 3 H), 2.44 (s, 3 H), 3.15 (m, 1 H), 3.76 (s, 3 H), 4.36 (d, J = 7.6, 0.7 Hz, 1 H), 5.88 (dd, J = 11.7, 7.6 Hz, 1 H), 6.01 (dd, J = 11.7, 0.7 Hz, 1 H), 7.31-7.35 (m, 2 H), 7.80-7.84 (m, 2 H). Anal. Calcd. for $C_{14}H_{17}NO_4S$: C, 56.93; H, 5.80; N, 4.74. Found: C, 56.92; H, 5.81; N, 4.54.

Methyl (4*S*,5*S*,2*E*)-4,5-Epimino-2-methyl-*N*-[(2,4,6-trimethylphenyl)sulfonyl]-6-phenylhex-2-enoate (11) and Its (4*S*,5*S*,2*Z*)-Isomer (12). Ozone was bubbled through a solution of the vinylaziridine **10** (2.7 g, 7.9 mmol) in a mixed solvent of $CHCl_3$ (15 mL) and *n*-hexane (15 mL) until blue color persisted. Powdered zinc (1 g, 15.2 mmol) was added to the mixture and the mixture was allowed to warm to 0 °C with stirring. (Methoxycarbonylethylidene)triphenylphosphorane (7.16 g, 20.5 mmol) was added to the mixture at 0 °C and the mixture was stirred for 1 hr with warming to room temperature. The mixture was filtered, followed by concentration under reduced pressure to leave an oil, which was flash chromatographed on a silica gel column. Elution with *n*-hexane-EtOAc (10:1) gave **12** (135 mg, 4.1% yield), and further elution gave **11** (2.90 g, 88.7% yield). **11**: colorless needles from *n*-hexane-$CHCl_3$ (6:1); mp 147-150 °C; $[\alpha]^{36}_D$ - 21.5 (c = 0.91, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.92 (d, J = 1.4 Hz, 3 H), 2.30 (s, 3 H), 2.56 (s, 6 H), 2.84 (dd, J = 14.3, 6.6 Hz, 1 H), 3.03 (dd, J = 14.3, 5.6 Hz, 1 H), 3.24 (ddd, J = 6.6, 5.6, 4.1 Hz, 1 H), 3.37 (dd, J = 9.6, 4.1 Hz, 1 H), 3.73 (s, 3 H), 6.79 (dq, J = 9.6, 1.4 Hz, 1 H), 6.87 (s, 2 H), 6.95-6.99 (m, 2 H), 7.08-7.18 (m, 3 H). LRMS (FAB) m/z, 414 (MH^+), 382, 230, 199, 183, 167, 119 (base peak), 104, 91. HRMS (FAB) m/z, calcd. for $C_{23}H_{28}NO_4S$ (MH^+) 414.1739; found: 414.1736. **12**: colorless oil; $[\alpha]^{27}_D$ - 35.2 (c = 0.84, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.95 (d, J = 1.5 Hz, 3 H), 2.30 (s, 3 H), 2.53 (s, 6 H), 2.69 (dd, J = 14.1, 7.1 Hz, 1 H), 3.04 (dd, J = 14.1, 5.1 Hz, 1 H), 3.14 (ddd, J = 7.1, 5.1, 4.1 Hz, 1 H), 3.76 (s, 3 H), 4.28 (dd, J = 9.4, 4.1 Hz, 1 H), 6.19 (dq, J = 9.4, 1.5 Hz, 1 H), 6.85 (broad s, 2 H), 6.92-6.95 (m, 2 H), 7.03-7.14 (m, 3 H). LRMS (FAB) m/z, 414 (MH^+), 302, 230, 183, 170, 119 (base peak), 91. HRMS (FAB) m/z, calcd. for $C_{23}H_{28}NO_4S$ (MH^+) 414.1739; found: 414.1733.

Methyl (4*R*,5*S*,2*E*)-4,5-Epimino-2-methyl-*N*-[(2,4,6-trimethylphenyl)sulfonyl]-6-phenylhex-2-enoate (14). By a procedure identical with that described for the preparation of the enoates **11** and **12** from **10**, 2.2 g (6.45 mmol) of the vinylaziridine **13** was converted into 2.38 g (89% yield) of the title compound **14** as colorless needles from *n*-hexane-EtOAc (3:1); mp 123-125 °C; $[\alpha]^{36}_D$ - 26.7 (c = 0.82, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.98 (d, J = 1.4 Hz, 3 H), 2.30 (s, 3 H), 2.56 (s, 6 H), 2.66 (dd, J = 14.5, 8.1 Hz, 1 H), 2.80 (dd, J = 14.5, 5.2 Hz, 1 H), 3.19 (ddd, J = 8.1, 7.5, 5.2 Hz, 1 H), 3.64 (dd, J = 8.2, 7.5 Hz, 1 H), 3.77 (s, 3 H), 6.57 (dq, J = 8.2, 1.4 Hz, 1 H), 6.85 (broad s, 2 H), 6.93-6.97 (m, 2 H), 7.04-7.14 (m, 3 H). LRMS (FAB) m/z, 414 (MH^+), 382, 230, 199, 183, 170, 119 (base peak), 104, 91. HRMS (FAB) m/z, calcd. for $C_{23}H_{28}NO_4S$ (MH^+) 414.1739; found: 414.1747.

Methyl (4*S*,5*S*,2*E*)-4,5-Epimino-2-methyl-*N*-[(4-methylphenyl)sulfonyl]hex-2-enoate (16) and Its (4*S*,5*S*,2*Z*)-Isomer (17). To a stirred solution of the ester **15** (1.00 g, 3.71 mmol) in toluene (8 mL), DIBAL (1.5 M solution in toluene; 2.96 mL, 4.45 mmol) was added dropwise at -78 °C under argon. The mixture was stirred at this temperature for 1 h and a saturated NH_4Cl (2 mL) was added dropwise with vigorous stirring. To the above stirred solution was added (methoxycarbonylethylidene)triphenylphosphorane (2.59 g, 7.42 mmol) at -78 °C, and stirring was continued for 1.5 h with warming to room temperature. To the above solution was added 5% citric acid (2 mL) and the mixture was extracted with Et_2O. The extract was washed succesively with water, 5% $NaHCO_3$, and water, and dried over $MgSO_4$. Usual workup followed by flash chromatography over silica gel with *n*-hexane-EtOAc (3:1) gave **17** (25 mg, 2% yield). Further elution gave **16** (886 mg, 77% yield). **16**: colorless crystals from *n*-hexane-Et_2O (2:1); mp 63-64 °C; $[\alpha]^{27}_D$ - 72.1 (c = 1.35, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.53 (d, J = 5.8 Hz, 3 H), 1.94 (d, J = 1.5 Hz, 3 H), 2.43 (s, 3 H), 3.03 (qd, J = 5.8, 4.3 Hz, 1 H), 3.32 (dd, J = 9.4, 4.3 Hz, 1 H), 3.74 (s, 3 H), 6.58 (dq, J = 9.4, 1.5 Hz, 1 H), 7.31 (m, 2 H), 7.80 (m, 2 H). Anal. Calcd. for $C_{15}H_{19}NO_4S$: C, 58.23; H, 6.19; N, 4.53. Found: C, 58.10; H, 6.17; N, 4.54. **17**: colorless oil; $[\alpha]^{26}_D$ - 97.9 (c = 0.57, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.51 (d, J = 5.7 Hz, 3 H), 1.90 (d, J = 1.6 Hz, 3 H), 2.40 (s, 3 H), 2.92 (dq, J = 5.7, 4.6 Hz, 1 H), 4.10 (dd, J = 8.9, 4.6 Hz, 1 H), 5.91 (dd, J = 8.9, 1.6 Hz, 1 H), 7.23-7.32 (m, 2 H), 7.81 (m, 2 H). LRMS (FAB) m/z, 310 (MH^+), 296, 199 (base peak), 155, 139, 91, 73. HRMS (FAB) m/z, calcd. for $C_{20}H_{24}NO_4S$ (MH^+) 310.1113; found: 310.1129.

Methyl (4*R*,5*S*,2*E*)-4,5-Epimino-2-methyl-*N*-[(4-methylphenyl)sulfonyl]hex-2-enoate (19). By use of a procedure identical with that described for the preparation of **16** and **17** from **15**, the ester **18** (1.35 g, 5 mmol) was converted into 0.76 g (49% yield) of the title compound **19**. **19**: colorless needles from *n*-hexane-Et_2O (2:1); mp 96-97 °C; $[\alpha]^{20}_D$ - 22.4 (*c* = 1.07, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.24 (d, *J* = 5.9 Hz, 3 H), 1.94 (dd, *J* = 1.5, 0.4 Hz, 3 H), 2.45 (s, 3 H), 3.13 (m, 1 H), 3.49 (dd, *J* = 8.2, 7.8 Hz, 1 H), 3.73 (s, 3 H), 6.38 (dq, *J* = 8.2, 1.5 Hz, 1 H), 7.32-7.35 (m, 2 H), 7.79-7.84 (m, 2 H). Anal. Calcd. for $C_{15}H_{19}NO_4S$: C, 58.23; H, 6.19; N, 4.53. Found: C, 58.06; H, 6.15; N, 4.24.

Methyl (4*S*,5*R*,2*E*)-4,5-Epimino-2-methyl-*N*-[(4-methylphenyl)sulfonyl]-5-phenylpent-2-enoate (21). To a stirred solution of oxalyl chloride (0.72 mL, 7.5 mmol) in a mixed solvent of $CHCl_3$ (4 mL) and *n*-hexane (6 mL) at -78 °C under argon was added dropwise a solution of DMSO (1.77 mL, 25 mmol) in $CHCl_3$ (5 mL). After 30 min, a solution of the aziridine **20** (1.52 g, 5 mmol) in $CHCl_3$ (5 mL) was added to the above reagent at -78 °C, and the mixture was stirred for 30 min. Diisopropylethylamine (6.1 mL, 35 mmol) was added to the above solution at -78 °C and the mixture was stirred for 30 min. (Methoxycarbonylethylidene)triphenylphosphorane (3.83 g, 11 mmol) was added to the mixture at -78 °C, and the mixture was stirred for 1 h with warming to 0 °C. Water (5 mL) was added to the mixture and the whole was extracted with Et_2O-EtOAc (1:2). The extract was washed successively with 5% citric acid, water, 5% $NaHCO_3$, and water, and dried over $MgSO_4$. Usual workup followed by flash chromatography over silica gel with *n*-hexane-EtOAc (3:1) gave a crystalline mass. Recrystallization from *n*-hexane-$CHCl_3$ (4:1) gave 1.58 g (85% yield) of the title compound **21** as colorless crystals; mp 143-145 °C; $[\alpha]^{22}_D$ - 40.7 (*c* = 1.17, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.93 (d, *J* = 1.4 Hz, 3 H), 2.44 (s, 3 H), 3.61 (s, 3 H), 3.79 (dd, *J* = 8.4, 7.2 Hz, 1 H), 4.17 (d, *J* = 7.2 Hz, 1 H), 6.12 (dq, *J* = 8.4, 1.4 Hz, 1 H), 7.19-7.35 (m, 7 H), 7.86-7.91 (m, 2 H). Anal. Calcd. for $C_{20}H_{21}NO_4S$: C, 64.67; H, 5.70; N, 3.77. Found: C, 64.40; H, 5.71; N, 3.98.

Synthetic intermediates methyl (4*R*,5*S*,2*E*)-4-Azido-5-hydroxy-2-methyl-5-phenylpent-2-enoate and methyl (4*S*,5*R*,2*E*)-5-Azido-4-hydroxy-2-methyl-5-phenylpent-2-enoate were synthesized starting from (2*S*,3*S*)-2,3-epoxy-3-phenylpropan-1-ol in a sequence of reactions described below.

i). Methyl (4*S*,5*S*,2*E*)-4,5-Epoxy-2-methyl-5-phenylpent-2-enoate. By a procedure similar to that described for the preparation of the enoate **21** from **20**, (2*S*,3*S*)-2,3-epoxy-3-phenylpropan-1-ol (5.0 g, 33 mmol) (Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765) was converted into 4.8 g (66% yield) of methyl (4*S*,5*S*,2*E*)-4,5-epoxy-2-methyl-5-phenylpent-2-enoate as a colorless oil. $[\alpha]^{20}_D$ - 198 (*c* = 1.29, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.99 (d, *J* = 1.4 Hz, 3 H), 3.59 (dd, *J* = 8.7, 1.9 Hz, 1 H), 3.77 (s, 3 H), 3.89 (d, *J* = 1.9 Hz, 1 H), 6.45 (dq, *J* = 8.7, 1.4 Hz, 1 H), 7.27-7.41 (m, 5 H). LRMS (FAB) *m/z*, 219 (MH^+), 202, 187, 159, 112 (base peak), 105, 91. HRMS (FAB) *m/z*, calcd. for $C_{13}H_{15}O_3$ (MH^+) 219.1021; found: 219.1019.

ii). Methyl (4*R*,5*S*,2*E*)-4-Azido-5-hydroxy-2-methyl-5-phenylpent-2-enoate and Methyl (4*S*,5*R*,2*E*)-5-Azido-4-hydroxy-2-methyl-5-phenylpent-2-enoate. Sodium azide (6.5 g, 100 mmol) and ammonium chloride (2.12 g, 40 mmol) were added to a stirred solution of the above epoxy enoate (4.36 g, 20 mmol) in a mixed solvent of ethylene glycol monoethyl ether (25 mL) and H_2O (4 mL), and the mixture was heated at 80 °C for 3 h under stirring. Concentration under reduced pressure gave a semisolid, which was extracted with Et_2O-EtOAc (2:1). The extract was washed successively with 5% citric acid, water, 5% $NaHCO_3$, and water, and dried over $MgSO_4$. Concentration under reduced pressure gave an oily residue, which was flash chromatographed on silica gel with *n*-hexane-EtOAc (3:1) to give 3.49 g (67% yield) of methyl (4*R*,5*S*,2*E*)-4-azido-5-hydroxy-2-methyl-5-phenylpent-2-enoate, and further elution gave methyl (4*S*,5*R*,2*E*)-5-azido-4-hydroxy-2-methyl-5-phenylpent-2-enoate (1.05 g, 20% yield). Methyl (4*R*,5*S*,2*E*)-4-azido-5-hydroxy-2-methyl-5-phenylpent-2-enoate: colorless oil; $[\alpha]^{20}_D$ + 133 (*c* = 0.84, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 1.70 (d, *J* = 1.9 Hz, 3 H), 2.40 (d, *J* = 3.2, 1 H), 3.74 (s, 3 H), 4.41 (dd, *J* = 9.5, 4.9 Hz, 1 H), 4.85 (dd, *J* = 4.9, 3.2 Hz, 1 H), 6.74 (dq, *J* = 9.5, 1.9 Hz, 1 H), 7.27-7.40 (m, 5 H). LRMS (FAB) *m/z*, 262 (MH^+), 250, 234, 219, 202, 187, 161, 137, 129 (base peak), 105, 91. HRMS (FAB) *m/z*, calcd. for $C_{13}H_{16}O_3$ (MH^+) 262.1192; found: 262.1188. Methyl (4*S*,5*R*,2*E*)-5-azido-4-hydroxy-2-methyl-5-phenylpent-2-enoate: colorless crystals from *n*-hexane-Et_2O (3:2); mp 47-48 °C; $[\alpha]^{19}_D$ - 62.0 (*c* = 0.70, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 1.65

(d, J = 1.4 Hz, 3 H), 2.07 (d, J = 5.4 Hz, 1 H), 3.75 (s, 3 H), 4.59 (ddd, J = 8.6, 5.4, 5.4 Hz, 1 H), 4.72 (d, J = 5.4 Hz, 1 H), 6.64 (dq, J = 8.6, 1.4 Hz, 1 H), 7.31-7.46 (m, 5 H). LRMS (CI) *m/z*, 262 (MH^+), 230, 219 (base peak), 189, 187, 129, 106. HRMS (CI) *m/z*, calcd. for $C_{13}H_{16}O_3$ (MH^+) 262.1192; found: 262.1200.

Methyl (4*R*,5*R*,2*E*)-4,5-Epimino-2-methyl-5-phenylpent-2-enoate (22). Triphenylphosphine (220 mg, 0.84 mmol) was added to a stirred solution of methyl (4*R*,5*S*,2*E*)-4-azido-5-hydroxy-2-methyl-5-phenylpent-2-enoate (200 mg, 0.77 mmol) in toluene (4 mL) and the mixture was heated at 60 °C for 1 h under stirring. Concentration under reduced pressure gave a semisolid, which was purified by flash chromatography over silica gel with *n*-hexane-EtOAc (3:2) to give a crystalline mass. Recrystallization from *n*-hexane-Et_2O (2:1) gave 126 mg (75.8%) of the title compound **22** as colorless crystals. mp 61 °C; $[\alpha]^{20}_D$ + 299 (*c* = 0.77, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 1.25 (broad s, 1 H), 1.98 (d, J = 1.4 Hz, 1 H), 2.65 (broad s, 1 H), 3.16 (broad s, 1 H), 3.76 (s, 3 H), 6.25 (broad s, 1 H), 7.30-7.37 (m, 5 H). Anal. Calcd. for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.79; H, 6.99; N, 6.43. By a procedure identical with that described for the preparation of **22** from methyl (4*R*,5*S*,2*E*)-4-azido-5-hydroxy-2-methyl-5-phenylpent-2-enoate, methyl (4*S*,5*R*,2*E*)-5-azido-4-hydroxy-2-methyl-5-phenylpent-2-enoate (200 mg, 0.77 mmol) was converted into the title compound **22** (52 mg, 31% yield) as colorless crystals from *n*-hexane-Et_2O (2:1).

Methyl (4*R*,5*R*,2*E*)-4,5-Epimino-2-methyl-*N*-[(4-methylphenyl)sulfonyl]-5-phenylpent-2-enoate (23). To a stirred solution of **22** (1.5 g, 6.9 mmol) in $CHCl_3$ (20 mL) were added Et_3N (4.77 mL, 34.5 mmol) and *p*-toluenesulfonyl chloride (2.63 g, 13.8 mmol) at 0 °C and the mixture was stirred for 9 hr with warming to room temperature. To the above mixture was added 5% $NaHCO_3$ (2 mL) with vigorous stirring, and the whole was extracted with Et_2O. The extract was washed successively with 5% citric acid, water, 5% $NaHCO_3$, and water, and dried over $MgSO_4$. Usual workup followed by flash chromatography over silica gel with *n*-hexane-EtOAc (4:1) gave a crystalline residue, which was recrystallized from *n*-hexane-Et_2O (2:3) to give the title compound **23** (2.54 g, 99% yield) as colorless crystals; mp 105 °C; $[\alpha]^{20}_D$ + 58.8 (*c* = 1.44, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 1.94 (d, J = 1.4 Hz, 3 H), 2.41 (s, 3 H), 3,46 (dd, J = 10.0, 4.1 Hz, 1 H), 3.80 (s, 3 H), 4.13 (d, J = 4.1 Hz, 1 H), 7.11 (dq, J = 10.0, 1.4 Hz, 1 H), 7.18-7.32 (m, 7 H), 7.81-7.85 (m, 2 H). LRMS (FAB) *m/z*, 372 (MH^+), 340, 216 (base peak), 185, 184, 156, 155, 139, 91. HRMS (FAB) *m/z*, calcd. for $C_{20}H_{22}NO_4$ (MH^+) 372.1270; found: 372.1272.

General Procedure for Palladium-catalyzed Reduction of the Enoates (6), (7), (8), and (9). To a stirred mixture of η^3-allylpalladium chloride dimer (9.16 mg, 5 mol %) and maleic anhydride (10 mg, 20 mol %) in DMSO (0.5 mL) at 0 °C under argon was added a mixture of HCO_2H (0.094 mL, 5 equiv.) and Et_3N (0.139 mL, 2 equiv.) in DMSO (0.5 mL). To a stirred above mixture was added a solution of the enoate **6** (147 mg, 0.5 mmol) in DMSO (1 mL), and then the mixture was allowed to warm to 25 °C. After 1 h, water (5 mL) was added to the mixture with stirring. The mixture was extracted with Et_2O-EtOAc (1:1) and the extract was washed successively with 5% citric acid, water, 5% $NaHCO_3$, and water and then dried over $MgSO_4$. Concentration under reduced pressure gave a mixture of products, which was separated by flash chromatography over silica gel eluting with *n*-hexane-EtOAc (4:1), yielding, in order of elution, the (*Z*)-α,β-enoate **24**, the (*E*)-α,β-enoate **25**, and the (*E*)-β,γ-enoate **26**. **24**: 8.5 mg (5.8% yield); colorless oil. $[\alpha]^{20}_D$ - 53.9 (*c* 1.35, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 1.12 (d, J = 6.6 Hz, 3 H), 2.42 (s, 3 H), 2.50-2.64 (m, 1 H), 2.79 (dddd, J = 14.8, 8.6, 8.6, 1.3 Hz, 1 H), 3.46 (m, 1 H), 3.72 (s, 3 H), 4.99 (d, J = 7.3 Hz, 1 H), 5.76 (ddd, J = 11.6, 1.3, 1.3 Hz, 1 H), 6.06 (ddd, J = 11.6, 7.3, 7.3 Hz, 1 H), 7.20-7.30 (m, 2 H), 7.70-7.75 (m, 2 H). Anal. Calcd. for $C_{14}H_{19}NO_4S$: C, 56.55; H, 6.44; N, 4.71. Found: C, 56.32; H, 6.51; N, 4.60. **25**: 115 mg (77.8% yield). Colorless crystals from Et_2O, mp 106 °C, $[\alpha]^{20}_D$ - 59.3 (*c* 0.677, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 1.08 (d, J = 6.6 Hz, 3 H), 2.28 (m, 2 H), 2.43 (s, 3 H), 3.48 (m, 1 H), 3.72 (s, 3 H), 4.51 (d, J = 7.8 Hz, 1 H), 5.78 (d, J = 15.5 Hz, 1 H), 6.74 (ddd, J = 15.5, 7.6, 7.6 Hz, 1 H), 7.26-7.35 (m, 2 H), 7.72-7.80 (m, 2 H). Anal. Calcd. for $C_{14}H_{19}NO_4S$: C, 56.55; H, 6.44; N, 4.71. Found: C, 56.41; H, 6.37; N, 4.76. **26**: 18.5 mg (12.5% yield). A colorless oil. $[\alpha]^{20}_D$ - 36.3 (*c* 0.935, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 1.17 (d, J = 6.6 Hz, 3 H), 2.42 (s, 3 H), 2.90-2.93 (m, 2 H), 3.66 (s, 3 H), 3.89 (m, 1 H), 4.77 (d, J = 7.6 Hz, 1 H), 5.36 (dddd, J = 15.5, 6.3, 1.3, 1.3 Hz, 1 H), 5.58 (dddd, J = 15.5, 6.6, 6.6, 1.3 Hz, 1 H),

7.27-7.30 (m, 2 H), 7.72-7.77 (m, 2 H). LR-MS (FAB) *m/z*, 298 (MH^+), 266 (base peak), 198, 155, 127, 91. HR-MS (FAB) *m/z*, calcd. for $C_{14}H_{20}NO_4S$ (MH^+), 298.1113; found: 298.1109.

Methyl (2*R*,5*S*,3*E*)-2-Methyl-5-[(2,4,6-trimethylphenyl)sulfonylamino]-6-phenylhex-3-enoate (27), Methyl (5*R*,2*E*)-2-Methyl-5-[(2,4,6-trimethylphenyl)sulfonylamino]-6-phenylhex-2-enoate (29) and Methyl (5*R*,2*Z*)-2-Methyl-5-[(2,4,6-trimethylphenyl)-sulfonylamino]-6-phenylhex-2-enoate (30) (entry 19, Table 1). To a stirred solution of $(C_3H_5PdCl)_2$ (4.4 mg, 0.012 mmol, 5 mol%) and maleic anhydride (4.7 mg, 0.048 mmol, 20 mol%) in DMSO (1 mL) under argon was added a mixture of formic acid (0.046 mL, 1.2 mol, 5 equiv.) and Et_3N (0.067 mL, 0.48 mmol, 2 equiv.) in DMSO (2 mL) at room temperature. The α,β-enoate **11** (100 mg, 0.242 mmol) in DMSO (2 mL) was added to the above reagent at room temperature and the mixture was stirred for 1 hr followed by quenching with saturated $NaHCO_3$ (4 mL). The whole was extracted with EtOAc-Et_2O (3:2). The extract was washed successively with 5% citric acid, water, 5% $NaHCO_3$, and water and dried over $MgSO_4$. Usual workup gave a mixture of products. The mixture was separated by flash chromatography over silica gel with *n*-hexane-EtOAc (3:1), yielding, in order of elution, **30** (10 mg, 9.9% yield), **29** (30.2 mg, 30% yield), and **27** (50.8 mg, 51% yield). **27**: colorless crystals from *n*-hexane-Et_2O (2:1); mp 70-71 °C; $[\alpha]^{27}_D$ - 40.7 (*c* = 1.08, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 1.05 (d, *J* = 7.3 Hz, 3 H), 2.28 (s, 3 H), 2.48 (s, 6 H), 2.79 (m, 2 H), 2.92 (dq, *J* = 7.3, 7.3 Hz, 1 H), 3.62 (s, 3 H), 3.91 (m, 1 H), 4.47 (d, *J* = 5.9 Hz, 1 H), 5.29 (dd, *J* = 15.7, 7.3 Hz, 1 H), 5.42 (dd, *J* = 15.7, 7.3 Hz, 1 H), 6.87 (broad s, 2 H), 7.02-7.08 (m, 2 H), 7.17-7.27 (m, 3 H). Anal. Calcd. for $C_{23}H_{29}NO_4S$: C, 66.48; H, 7.03; N, 3.37. Found: C, 66.24; H, 6.93; N, 3.26. **29**: colorless crystals from *n*-hexane-EtOAc (3:1); mp 141-142 °C; $[\alpha]^{27}_D$ - 41.8 (*c* = 0.68, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.72 (m, 3 H), 2.29 (s, 3 H), 2.36 (m, 2 H), 2.50 (s, 6 H), 2.74 (dd, *J* = 13.8, 6.9 Hz, 1 H), 2.79 (dd, *J* = 13.8, 6.6 Hz, 1 H), 3.51 (m, 1 H), 3.72 (s, 3 H), 4.46 (d, *J* = 7.5 Hz, 1 H), 6.60 (m, 1 H), 6.86 (broad s, 2 H), 6.98-7.01 (m, 2 H), 7.17-7.22 (m, 3 H). LRMS (FAB) *m/z*, 416 (MH^+), 384, 302 (base peak), 183, 119, 91. HRMS (FAB) *m/z*, calcd. for $C_{23}H_{30}NO_4S$ (MH^+) 416.1895; found: 416.1888. **30**: colorless crystals from *n*-hexane-Et_2O (2:1); mp 107-108 °C; $[\alpha]^{23}_D$ - 33.0 (c = 0.77, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.74 (m, 3 H), 2.28 (s, 3 H), 2.53-2.62 (m, 2 H), 2.58 (s, 6 H), 2.68 (dd, *J* = 13.5, 8.2 Hz, 1 H), 2.92 (dd, *J* = 13.5, 5.0 Hz, 1 H), 3.48 (m, 1 H), 3.69 (s, 3 H), 5.21 (d, *J* = 6.9 Hz, 1 H), 5.54 (m, 1 H), 6.90 (broad s, 2 H), 7.05-7.08 (m, 2 H), 7.14-7.25 (m, 3 H). LRMS (FAB) *m/z*, 416 (MH^+), 384, 302, 183, 147, 119 (base peak), 91, 73. HRMS (FAB) *m/z*, calcd. for $C_{23}H_{30}NO_4S$ (MH^+) 416.1895; found: 416.1895.

Methyl (2*S*,5*S*,3*E*)-2-Methyl-5-[(2,4,6-trimethylphenyl)sulfonylamino]-6-phenylhex-3-enoate (28) (entry 24, Table 1). By a procedure identical with that described for the reduction of **11**, the aziridine **14** was reduced to a chromatographically separable 4:41:48:7 mixture of four products **27**, **28**, **29**, and **30** in 93% combined yield. The ratio of products was analyzed by reverse phase HPLC and ^1H-NMR (600 MHz). **28**: colorless oil; $[\alpha]^{23}_D$ - 3.70 (*c* = 0.90, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 1.02 (d, *J* = 7.3 Hz, 3 H), 2.28 (s, 3 H), 2.49 (s, 6 H), 2.78 (m, 2 H), 2.91 (dq, *J* = 7.3, 7.3 Hz, 1 H), 3.64 (s, 3 H), 3.93 (m, 1 H), 4.48 (d, *J* = 5.9 Hz, 1 H), 5.27 (dd, *J* = 15.4, 7.3 Hz, 1 H), 5.46 (dd, *J* = 15.4, 7.3 Hz, 1 H), 6.87 (broad s, 2 H), 7.02-7.05 (m, 2 H), 7.17-7.26 (m, 3 H). LRMS (FAB) *m/z*, 416 (MH^+), 414, 324, 217, 183, 157, 119 (base peak), 91. HRMS (FAB) *m/z*, calcd. for $C_{23}H_{30}NO_4S$ (MH^+) 416.1895; found: 416.1893.

Methyl (2*R*,5*S*,3*E*)-2-Methyl-5-[(4-methylphenyl)sulfonylamino]hex-3-enoate (31), Methyl (5*S*,2*E*)-2-Methyl-5-[(4-methylphenyl)sulfonylamino]hex-2-enoate (33), and Methyl (5*S*,2*Z*)-2-Methyl-5-[(4-methylphenyl)sulfonylamino]hex-2-enoate (34) (entry 22, Table 1). By a procedure identical with that discribed for the reduction of **11**, the aziridine **16** was reduced to a separable 45:43:12 mixture of **31**, **33**, and **34** in 82% combined yield. The mixture was separated by flash chromatography over silica gel with *n*-hexane-EtOAc (2:1), yielding, in order of elution, **34**, **33**, and **31**. **31** : 36.8% yield; colorless oil; $[\alpha]^{27}_D$ - 49.8 (*c* = 0.88, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 1.11 (d, *J* = 6.8 Hz, 3 H), 1.17 (d, *J* = 6.5 Hz, 3 H), 2.42 (s, 3 H), 2.99 (m, 1 H), 3.65 (s, 3 H), 3.90 (m, 1 H), 4.54 (d, *J* = 7.6 Hz, 1 H), 5.32 (ddd, *J* = 15.4, 6.2, 1.1 Hz, 1 H), 5.53 (ddd, *J* = 15.4, 7.3, 1.1 Hz, 1 H), 7.28 (m, 2 H), 7.74 (m, 2 H). LRMS (FAB) *m/z*, 312 (MH^+), 252, 156, 141 (base peak), 109, 91, 73. HRMS (FAB) *m/z*, calcd. for $C_{15}H_{22}NO_4S$ (MH^+) 312.1269; found: 312.1258. **33**: 35.2% yield; colorless crystals from *n*-hexane-Et_2O (2:1); mp 56-58 °C;

$[\alpha]^{27}_D$ - 56.7 (*c* = 1.10, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 1.09 (d, *J* = 6.8 Hz, 3 H), 1.76 (d, *J* = 1.4 Hz, 3 H), 2.30 (m, 2 H), 2.43 (s, 3 H), 3.46 (m, 1 H), 3.72 (s, 3 H), 4.52 (d, *J* = 8.1 Hz, 1 H), 6.58 (m, 1 H), 7.30 (m, 2 H), 7.75 (m, 2 H). Anal. Calcd. for $C_{15}H_{21}NO_4S$: C, 57.86; H, 6.80; N, 4.50. Found: C, 57.75; H, 6.78; N, 4.43. **34** : 9.5% yield; colorless oil; $[\alpha]^{26}_D$ - 98.7 (*c* = 0.31, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 1.16 (d, *J* = 6.5 Hz, 3 H), 1.75 (d, *J* = 1.4 Hz, 3 H), 2.26-2.37 (m, 1 H), 2.42 (s, 3 H), 2.50-2.62 (m, 1 H), 3.37 (m, 1 H), 3.74 (s, 3 H), 5.28 (d, *J* = 6.5 Hz, 1 H), 5.61 (m, 1 H), 7.28 (m, 2 H), 7.72 (m, 2 H). LRMS (FAB) *m/z*, 312 (MH^+), 281, 280 (base peak), 198, 155, 141, 91, 73. HRMS (FAB) *m/z*, calcd. for $C_{15}H_{22}NO_4S$ (MH^+) 312.1269; found: 312.1273.

Methyl (2*S*,5*S*,3*E*)-2-Methyl-5-[(4-methylphenyl)sulfonylamino]hex-3-enoate (32) (entry 27, Table 1). By a procedure identical with that described for the reduction of **16**, the aziridine **19** was reduced to a chromatographically separable 11:34:44:11 mixture of four products **31**, **32**, **33** and **34** in 80% combined yield. The ratio of products was analyzed by reverse phase HPLC and ^1H-NMR (600 MHz). Compound **32** was colorless crystals; mp 66 °C [from hexane:Et_2O (5:1)]; $[\alpha]^{20}_D$ - 22.2 (*c* 1.24, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 1.11 (d, *J* = 7.0 Hz, 3 H), 1.17 (d, *J* = 6.5 Hz, 3 H), 2.42 (s, 3 H), 2.99 (dq, *J* = 7.0, 7.0 Hz, 1 H), 3.66 (s, 3 H), 3.92 (m, 1 H), 4.37 (d, *J* = 7.8 Hz, 1 H), 5.33 (ddd, *J* = 15.9, 6.2, 1.2 Hz, 1 H), 5.55 (ddd, *J* = 15.9, 7.0, 1.2 Hz, 1 H), 7.26-7.30 (m, 2 H), 7.72-7.76 (m, 2 H). Anal. Calcd. for $C_{15}H_{21}NO_4S$: C, 57.86; H, 6.80; N, 4.50. found: C, 57.76; H, 6.98; N, 4.28.

Methyl (2*S*,5*S*,3*E*)-2-Methyl-5-[(4-methylphenyl)sulfonylamino]-5-phenylpent-3-enoate (35), Methyl (5*S*,2*E*)-2-Methyl-5-[(4-methylphenyl)sulfonylamino]-5-phenylpent-2-enoate (37), and Methyl (5*S*,2*Z*)-2-Methyl-5-[(4-methylphenyl)sulfonylamino]-5-phenylpent-2-enoate (38) (entry 30, Table 1). By a procedure identical with that described for the reduction of **11**, the aziridine **23** was reduced to a chromatographically separable 71:22:7 mixture of three products **35**, **37**, and **38** in 81% combined yield. The mixture was separated by flash chromatography over silica gel with *n*-hexane-EtOAc (5:1), yielding, in order of elution, **38** (5% yield), **35** (58% yield), and **37** (18% yield). **35**: colorless crystals from *n*-hexane-Et_2O (1:2); mp 82 °C; $[\alpha]^{17}_D$ + 10.6 (*c* 1.10, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 1.13 (d, *J* = 7.0 Hz, 3 H), 2.39 (s, 3 H), 3.04 (dq, *J* = 7.0, 7.0 Hz, 1 H), 3.64 (s, 3 H), 4.90 (m, 2 H), 5.55 (dd, *J* = 15.4, 5.4 Hz, 1 H), 5.61 (dd, *J* = 15.4, 7.0 Hz, 1 H), 7.10-7.26 (m, 7 H), 7.61-7.64 (m, 2 H). Anal. Calcd. for $C_{20}H_{23}NO_4S$: C, 64.32; H, 6.21; N, 3.75. Found: C, 64.35; H, 6.31; N, 3.64. **37**: colorless crystals from *n*-hexane-Et_2O (1:1); mp 94-95 °C; $[\alpha]^{20}_D$ - 7.72 (*c* = 0.82, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 1.70 (d, *J* = 0.5 Hz, 3 H), 2.37 (s, 3 H), 2.61 (dd, *J* = 15.4, 7.6 Hz, 1 H), 2.68 (dd, *J* = 15.4, 7.6 Hz, 1 H), 3.68 (s, 3 H), 4.40 (dd, *J* = 14.3, 7.6 Hz, 1 H), 5.07 (m, 1 H), 6.52 (m, 1 H), 7.03-7.08 (m, 2 H), 7.14-7.20 (m, 5 H), 7.56-7.60 (m, 2 H). Anal. Calcd. for $C_{20}H_{23}NO_4S$: C, 64.32; H, 6.21; N, 3.75. Found: C, 64.24; H, 6.25; N, 3.64. **38**: colorless oil; $[\alpha]^{20}_D$ - 42.2 (*c* = 0.25, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.81 (d, *J* = 0.7 Hz, 3 H), 2.36 (s, 3 H), 2.51 (m, 1 H), 2.90 (m, 1 H), 3.77 (s, 3 H), 4.41 (m, 1 H), 5.70 (m, 1 H), 5.96 (d, *J* = 6.1 Hz, 1 H), 7.11-7.23 (m, 7 H), 7.52-7.55 (m, 2 H). LRMS (FAB) *m/z*, 374 (MH^+), 342, 260, 203 (base peak), 171, 155, 143, 106, 91. HRMS (FAB) *m/z*, calcd. for $C_{20}H_{24}NO_4S$ (MH^+) 374.1427; found: 374.1422.

Methyl (2*R*,5*S*,3*E*)-2-Methyl-5-[(4-methylphenyl)sulfonylamino]-5-phenylpent-3-enoate (36) (entry 28, Table 1). By a procedure identical with that described for the reduction of **23**, the aziridine **21** was reduced to a chromatographically separable 2:71:20:7 mixture of four products **35**, **36**, **37**, and **38** in 87% combined yield. The major reduction product **36** was readily isolated by silica gel flash chromatography with *n*-hexane-EtOAc (5:1). Data for **36**: colorless crystals from *n*-hexane-Et_2O (1:3); mp 70 °C; $[\alpha]^{20}_D$ - 32.8 (*c* = 0.97, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 1.12 (d, *J* = 7.0 Hz, 3 H), 2.39 (s, 3 H), 3.05 (dq, *J* = 7.0, 6.8 Hz, 1 H), 3.66 (s, 3 H), 4.89 (m, 2 H), 5.55 (dd, *J* = 15.7, 5.4 Hz, 1 H), 5.62 (dd, *J* = 15.7, 7.0 Hz, 1 H), 7.09-7.25 (m, 7 H), 7.61-7.64 (m, 2 H). LRMS (FAB) *m/z*, 374 (MH^+), 372, 314, 286, 260, 203, 171, 143 (base), 91. HRMS (FAB) *m/z*, calcd. for $C_{20}H_{24}NO_4S$ (MH^+) 374.1427; found: 374.1421.

Methyl (2*E*)-4,5-Epimino-2-methyl-*N*-[(4-methylphenyl)sulfonyl]-5-phenylpent-2-enoate (39). Colorless crystals; mp 105 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 1.94 (d, *J* = 1.4 Hz, 3 H), 2.41 (s, 3 H), 3.46 (dd, *J* = 10.0, 4.1 Hz, 1 H), 3.80 (s, 3 H), 4.13 (d, *J* = 4.1 Hz, 1 H), 7.11 (dq, *J* = 10.0, 1.4 Hz, 1 H),

7.18-7.32 (m, 7 H), 7.81-7.85 (m, 2 H). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 12.7, 21.6, 49.1, 49.6, 52.2, 126.3, 127.6, 128.7, 129.6, 132.5, 134.5, 134.7, 136.5, 144.4, 167.3. LRMS (FAB) *m/z*, 372 (MH^+), 340, 216 (base peak), 185, 184, 156, 155, 139, 91. HRMS (FAB) *m/z*, calcd. for $C_{20}H_{22}NO_4$ (MH^+) 372.1270; found: 372.1272.

Methyl (3*E*)-2-Methyl-5-[(4-methylphenyl)sulfonylamino]-5-phenylpent-3-enoate (40). Colorless crystals from *n*-hexane-Et_2O (1:2); mp 82 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 1.13 (d, *J* = 7.0, 3 H), 2.39 (s, 3 H), 3.04 (dq, *J* = 7.0, 7.0 Hz, 1 H), 3.64 (s, 3 H), 4.90 (m, 2 H), 5.55 (dd, *J* = 15.4, 5.4 Hz, 1 H), 5.61 (dd, *J* = 15.4, 7.0 Hz, 1 H), 7.10-7.26 (m, 7 H), 7.61-7.64 (m, 2 H). Anal. Calcd. for $C_{20}H_{23}NO_4S$: C, 64.32; H, 6.21; N, 3.75. Found: C, 64.35; H, 6.31; N, 3.64.

Methyl (2*E*)-2-Methyl-5-[(4-methylphenyl)sulfonylamino]-5-phenylpent-2-enoate (41). Colorless crystals from *n*-hexane-Et_2O (1:1); mp 94-95 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 1.70 (d, *J* = 0.5 Hz, 3 H), 2.37 (s, 3 H), 2.61 (dd, *J* = 15.4, 7.6 Hz, 1 H), 2.68 (dd, *J* = 15.4, 7.6 Hz, 1 H), 3.68 (s, 3 H), 4.40 (dd, *J* = 14.3, 7.6 Hz, 1 H), 5.07 (m, 1 H), 6.52 (m, 1 H), 7.03-7.08 (m, 2 H), 7.14-7.20 (m, 5 H), 7.56-7.60 (m, 2 H). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 12.6, 21.5, 36.5, 51.8, 57.2, 126.4, 127.1, 128.6, 128.7, 129.4, 136.0, 139.8, 143.3. Anal. Calcd. for $C_{20}H_{23}NO_4S$: C, 64.32; H, 6.21; N, 3.75. Found: C, 64.24; H, 6.25; N, 3.64.

Methyl (4*S*,5*S*,2*E*)-4,5-Epimino-2-methyl-*N*-[(*tert*-butyloxy)carbonyl]-5-phenylpent-2-enoate (42). ^1H NMR (270 MHz, $CDCl_3$) δ 1.43 (s, 9 H), 2.00 (d, *J* = 1.6 Hz, 3 H), 3.26 (dd, *J* = 9.8, 2.7 Hz, 1 H), 3.58 (d, *J* = 2.7 Hz, 1 H), 3.76 (s, 3 H), 6.28 (dq, *J* = 9.8, 1.6 Hz, 1 H), 7.24-7.40 (m, 5 H). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 12.8, 27.7, 45.3, 46.5, 52.0, 82.0, 126.3, 128.0, 128.5, 132.5, 135.9, 159.6, 167.4. HRMS (FAB) *m/z*, calcd. for $C_{18}H_{24}NO_4$ (MH^+) 318.1705; found: 318.1732.

Methyl (2*R*,5*R*,3*E*)-5-Amino-*N*-[(*tert*-butyloxy)carbonyl]-2-methyl-5-phenylpent-3-enoate (43). ^1H NMR (400 MHz, $CDCl_3$) δ 1.28 (d, *J* = 7.0 Hz, 3 H), 1.43 (s, 9 H), 3.19 (dq, *J* = 7.0, 7.0 Hz, 1 H), 3.68 (s, 3 H), 5.72 (dd, *J* = 15.8, 4.5 Hz, 1 H), 5.75 (dd, *J* = 15.8, 7.0 Hz, 1 H), 7.24-7.37 (m, 5 H). ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 17.2, 28.4, 42.3, 51.8, 56.1, 79.7, 126.8, 127.4, 128.6, 130.3, 131.5, 141.3, 154.8, 174.6. HRMS (FAB) *m/z*, calcd. for $C_{18}H_{26}NO_4$ (MH^+) 320.1862; found: 320.1894.

Methyl (2*E*)-5-Amino-*N*-[(*tert*-butyloxy)carbonyl]-2-methyl-5-phenylpent-2-enoate (44). ^1H NMR (270 MHz, $CDCl_3$) δ 1.41 (s, 9 H), 1.78 (d, *J* = 1.3 Hz, 3 H), 2.59-2.75 (m, 2 H), 3.70 (s, 3 H), 4.65-4.93 (broad, 2 H), 6.69 (tq, *J* = 7.2, 1.3 Hz, 1 H), 7.22-7.38 (m, 5 H). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 12.6, 28.3, 35.9, 51.8, 54.1, 80.0, 126.2, 127.5, 128.7, 130.1, 137.1, 155.1, 168.2. HRMS (FAB) *m/z*, calcd. for $C_{18}H_{26}NO_4$ (MH^+) 320.1862; found: 320.1886.

Methyl (4*R*,5*S*,2*Z*)-4,5-Epimino-2-methyl-*N*-[(2,4,6-trimethylphenyl)sulfonyl]-6-phenylhex-2-enoate (45) isolated from a mixture obtained by reaction of (11) with $(Ph_3P)_4Pd$. Colorless oil; $[\alpha]^{19}_D$ - 58.1 (c = 0.50, $CHCl_3$); ^1H-NMR (300 MHz, $CDCl_3$): δ 1.97 (dd, *J* = 1.4, 0.8 Hz. 3 H), 2.30 (s, 3 H), 2.56 (s, 6 H), 2.57 (dd, *J* = 14.6, 8.4 Hz, 1 H), 2.77 (dd, *J* = 14.6, 4.9 Hz, 1 H), 3.18 (ddd, *J* = 8.4, 7.5, 4.9 Hz, 1 H), 3.76 (s, 3 H), 4.26 (ddq, *J* = 7.5, 7.5, 0.8 Hz, 1 H), 5.84 (dq, *J* = 7.5, 1.4 Hz, 1 H), 6.84 (broad s, 2 H), 6.91-6.95 (m, 2 H), 7.02-7.14 (m, 3 H). LRMS (FAB) *m/z*, 414 (MH^+), 302 (base), 230, 183, 149, 119, 91, 73. HRMS (FAB) *m/z*, calcd. for $C_{23}H_{28}NO_4S$ (MH^+) 414.1739; found: 414.1744.

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