

Silver(I)-Catalyzed Aminocyclization of 2,3-Butadienyl and 3,4-Pentadienyl Carbamates: An Efficient and Stereoselective Synthesis of 4-Vinyl-2-oxazolidinones and 4-Vinyltetrahydro-2*H*-1,3-oxazin-2-ones

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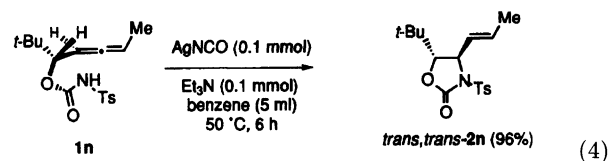
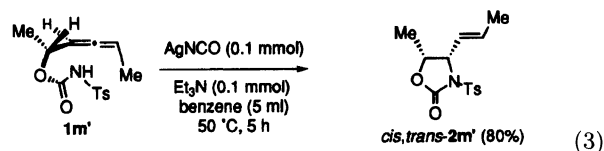
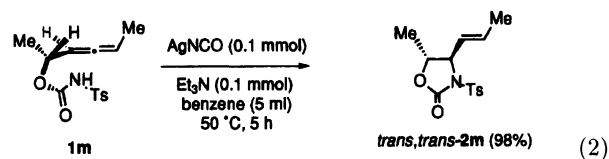
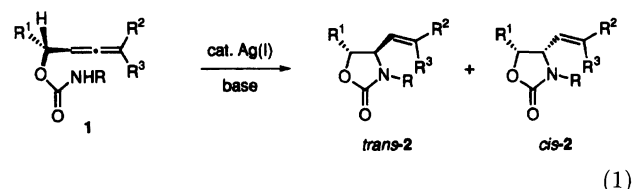
Silver(I) salts in combination with an appropriate base (mostly triethylamine) catalyzed the aminocyclization of *N*-substituted 2,3-butadienyl carbamates **1** (benzene, 50 °C) to provide 4-vinyl-2-oxazolidinones **2** in good yields. The stereoselectivity (*trans*-**2**/*cis*-**2**) ranged from 1.4 for C₅-Me to >30 for C₅-phenyl, isopropenyl, and *t*-butyl derivatives. 3,4-Pentadienyl tosylcarbamates **3**, the one-carbon higher homologues of **1**, underwent a similar cyclization to give 4-vinyltetrahydro-2*H*-1,3-oxazin-2-one **4** in synthetically useful yields and in higher *trans* selectivities than **1**.

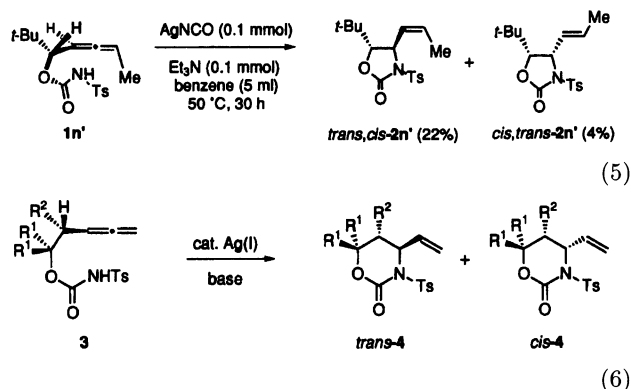
The introduction of an amino group at an unsymmetrical allylic position in a regio- and stereoselective manner is a synthetic challenge¹⁾ and of great importance in view of the increasing interest in the wide biological activities of amino sugars²⁾ and amino acids,³⁾ both natural and unnatural. For our on-going project⁴⁾ aimed to clarify the stereoelectronic effect that an allylic amino group exerts on the diastereoselectivity in the addition reactions of electrophiles (e.g., I⁺ and Pd²⁺) to the double bond, we required a series of derivatives of allylic amino alcohols (2-amino-3-buten-1-ols and 3-amino-4-penten-1-ols) with sterically defined structures. The former amino alcohols may be prepared by a few methods based on either Pd(0) catalysis⁵⁾ or Claisen-type rearrangement.⁶⁾ Recently, we developed a convenient method for the preparation of the latter amino alcohols.⁷⁾ All these methods rely on the substitution of a nitrogen atom for one of the hydroxyl groups of an unsaturated diol derivative.

As another and more versatile approach to these two types of alcohols, the cyclization reaction of 2,3-butadienyl **1** and 3,4-pentadienyl carbamates **3** may be utilized, provided that these carbamates serve as nitrogen nucleophiles and react selectively at the C₂ and C₃ allenic terminal carbons, respectively. Indeed, carbamate serves as an ambident (O and N nucleophile⁸⁾ and heteroatoms (e.g., N,⁹⁾ O,¹⁰⁾ S,¹¹⁾ and Sn¹²⁾ have been known to react with allenes in most cases at the allenic terminal carbons. However, in a few cases the reaction takes place at the central carbons.^{9d,10a,10g,11)}

Here we report that silver(I) salts (e.g., silver isocyanate and trifluoromethanesulfonate) in combination

with an appropriate base nicely catalyze the aminocyclization of **1** and **3** and provide 4-vinyl-2-oxazolidinones **2** (Eq. 1) and 4-vinyltetrahydro-2*H*-1,3-oxazin-2-ones **4** (Eq. 6), respectively. Yields are good to moderate, irrespective of a wide variety of substitution patterns (R¹–R³).





The stereoselectivity for the cyclization of **1** depends on the combination of the R^1 – R^3 substituents. When R^2 and R^3 are the same (H or Me), *trans*-**2** is obtained selectively (Eq. 1). When these groups are different, the stereoselectivity becomes rather complicated, providing either *trans*-**2** exclusively (Eqs. 2 and 4), *cis*-**2** exclusively (Eq. 3), or a mixture of *trans*-**2** and *cis*-**2** nonselectively (Eq. 5). This variability depends on the steric bulk of the R^1 substituents. Generally, the *trans* selectivity for the cyclization of **3** is higher than that of **1** (Eq. 6).

The scope of these cyclization reactions (Eqs. 1 and 6) and the origin of these stereoselectivities are discussed in detail. Besides being expedient as probes for our other investigations,⁴⁾ products **2** and **4**, the protected forms of allylic amino alcohols, may be important as key synthetic intermediates for many nitrogen-containing natural and unnatural products. This is a full account of our previous report.¹³⁾

Results and Discussion

Friesen et al. have shown that 2,3-butadienyl carbamates **1** (R =tosyl or trichloroacetyl) undergo an electrophile-induced cyclization in the presence of iodine to provide either 4-(1-iodovinyl)-2-oxazolidinones (aminocyclization)^{8b,c)} or 1-(1-iodovinyl)ethylene carbonimides (oxycyclization).^{8a)} Inspired by this, we examined a transition-metal-catalyzed cyclization of **1** (Eq. 1) and **3** (Eq. 6) in expectation of their selective aminocyclization, since this process might open a versatile, convenient entry to a variety of both types of allylic amino alcohols, 2-amino-3-buten-1-ols and 3-amino-4-penten-1-ols. Furthermore, by virtue of the cyclization forming five- and six-membered cyclic carbamates, high stereoselectivity was expected.

Ag(I)-Catalyzed Aminocyclization of *N*-Substituted 2,3-Butadienyl Carbamates: Synthesis of 4-Vinyl-2-oxazolidinones **2.** After examining many combinations of transition metals and *N*-substituents of **1**, we have found that *N*-sulfonyl derivatives of **1** are the most reactive, versatile substrates. Furthermore, silver isocyanate (0.1 equiv) in combination with an appropriate base (0.1 equiv) nicely catalyzes the selective cyclization of **1** (R =Ts, Eq. 1 and Table 1) at the nitrogen atom.

Some transition metals, such as Cu(I),^{9f)} Ag(I),^{9i,j,10c,d,g,h)} Pd(0),^{9b,c,10b,12)} Pd(II),^{9a,e,g,h,10e)} and Hg(II),^{10e,g)} have proven to effectively catalyze or promote the addition reaction of hetero-atoms to an allenic double bond. For the cyclization of **1** (R =Ts), however, copper(I) chloride was completely ineffective (Run 9, Table 1). Palladium(II) salts could be applied with marginal success. For example, the reaction of **1a** with either PdCl₂(PhCN)₂ or Pd(OAc)₂ (0.1 equiv) in the presence of triethylamine (0.1 equiv) in tetrahydrofuran (THF) caused a smooth decomposition of **1a** at room temperature and provided **2a** in less than 25% yield as a mixture of at least four or five kinds of unidentified products (TLC analysis). For silver(I) salts, we examined two kinds of salts, silver(I) isocyanate (AgNCO) and silver(I) trifluoromethanesulfonate (AgOTf). AgOTf is completely soluble in both THF and benzene, while a large portion of AgNCO apparently remains undissolved in these solvents under these reaction conditions. Both silver salts, however, turned out to promote the cyclization of most carbamates **1** (R =Ts) with similar efficiency. For the cyclization of unreactive substrates, e.g., **1f** and **1o**, AgNCO was marginally superior to AgOTf (Runs 12 and 13, Runs 24 and 25 in Table 1; also, see Runs 4 and 5 in Table 2, *vide infra*).

For successful cyclization, both the silver salt and some bases are indispensable. In the absence of either of these, no cyclization takes place (Runs 6–9, Table 1) and the starting material is recovered quantitatively.

The reaction seems to be quite general and accommodates a variety of combinations of R^1 – R^3 substituents (Table 1). Although all the reactions were performed with racemic substrates, only single stereoisomers were shown for simplicity. Those carbamates of tertiary alcohols (**1g**) and secondary alcohols with vinylic and phenyl substituents as the R^1 group (**1h–k** and **1p**) were unstable¹⁴⁾ and decomposed during storage at room temperature and could not be purified by means of column chromatography over silica gel. However, their triethylamine salts turned out to be rather stable and withstood storage at room temperature. Accordingly, the cyclization reactions of these carbamates were undertaken as their triethylamine salts without purification (footnote c, Table 1). For these cases, the yields listed in Table 1 are meant to refer to the overall isolated yields based on the starting alcohols (see Experimental Section).

Generally, the cyclization of terminally symmetrically-substituted carbamates **1** ($R^2=R^3$ =H, Runs 1–18 and $R^2=R^3$ =Me, Runs 24–26, Table 1) provided *trans*-**2** preferentially over *cis*-**2**. Especially, the *trans*-**2**/*cis*-**2** ratios increased gradually with an increase in the steric bulk of the R^1 substituents, ranging from *trans*-**2**/*cis*-**2**=1.4 for R^1 =Me to >30 for R^1 =*t*-Bu, isopropenyl, and phenyl. This selectivity may be rationalized by inspection of transition states **I** and **II**, the presumed

Table 1. Ag(I)-Catalyzed Cyclization of 2,3-Butadienyl Tosylcarbamate **1**^{a)}

Run	Carbamate 1			Base	Metal catalyst	Solvent	Conditions		% Isolated yield of 2 (% conv.)	<i>trans</i> - 2 : <i>cis</i> - 2
	R ¹	R ²	R ³				Temp/°C	Time/h		
1	1a :	H	H	H	Et ₃ N	AgNCO	Benzene	50, 6	2a : 78 (100)	
2	1a :	H	H	H	Sparteine ^{b)}	AgNCO	Benzene	50, 19	2a : 62 (80)	
3	1b :	Me	H	H	Et ₃ N	AgNCO	Benzene	50, 4	2b : 95 (100)	1.4 : 1
4	1c :	Et	H	H	Et ₃ N	AgOTf	Benzene	50, 6	2c : 74 (100)	1.5 : 1
5	1c :	Et	H	H	Et ₃ N	AgOTf	THF	Refl., 23	2c : 75 (100)	1.5 : 1
6	1d :	<i>n</i> -Pr	H	H	Et ₃ N	None	THF	Refl. 40	2d : 0 (0)	
7	1d :	<i>n</i> -Pr	H	H	<i>t</i> -BuOK	None	THF	Refl., 24	2d : 0 (0)	
8	1d :	<i>n</i> -Pr	H	H	None	AgNCO	Benzene	50, 23	2d : 0 (0)	
9	1d :	<i>n</i> -Pr	H	H	Et ₃ N	CuCl	THF	Refl., 19	2d : Trace	
10	1d :	<i>n</i> -Pr	H	H	Et ₃ N	AgNCO	Benzene	50, 23	2d : 73 (100)	1.8 : 1
11	1e :	<i>i</i> -Pr	H	H	Et ₃ N	AgOTf	Benzene	50, 43	2e : 74 (100)	7.1 : 1
12	1f :	<i>t</i> -Bu	H	H	Et ₃ N	AgOTf	Benzene	50, 21	2f : 53 (86)	>30 : 1
13	1f :	<i>t</i> -Bu	H	H	Et ₃ N	AgNCO	Benzene	50, 17	2f : 63 (100)	>30 : 1
14	1g : ^{c)}	Me ₂ ^{d)}	H	H	Et ₃ N	AgNCO	Benzene	50, 21	2g : 79 (100)	
15	1h : ^{c)}	CH ₂ =CH	H	H	Et ₃ N	AgNCO	Benzene	50, 28	2h : 76 (100)	1.8 : 1
16	1i : ^{c)}	MeCH=CH	H	H	Et ₃ N	AgNCO	Benzene	50, 28	2i : 79 (100)	2.1 : 1
17	1j : ^{c)}	CH ₂ =CMe	H	H	Et ₃ N	AgNCO	Benzene	50, 20	2j : 60 (100)	>30 : 1
18	1k : ^{c)}	Ph	H	H	Et ₃ N	AgNCO	Benzene	50, 24	2k : 83 (100)	>30 : 1
19	1l :	H	Me	H	Et ₃ N	AgNCO	Benzene	50, 28	2l : 79 (100)	
20	1m :	Me	Me	H	Et ₃ N	AgNCO	Benzene	50, 5 ^{e,g)}	2m : 98 (100)	>30 : 1
21	1m' :	Me	H	Me	Et ₃ N	AgNCO	Benzene	50, 5 ^{e,h)}	2m' : 80 (100)	1 : >30
22	1n :	<i>t</i> -Bu	Me	H	Et ₃ N	AgNCO	Benzene	50, 6 ^{f,i)}	2n : 96 (100)	>30 : 1
23	1n' :	<i>t</i> -Bu	H	Me	Et ₃ N	AgNCO	Benzene	50, 30 ^{j)}	2n' : 26 (100)	5.5 : 1
24	1o :	Et	Me	Me	Et ₃ N	AgNCO	Benzene	50, 32	2o : 57 (82)	4.9 : 1
25	1o :	Et	Me	Me	Et ₃ N	AgOTf	Benzene	50, 54	2o : 50 (83)	4.9 : 1
26	1p : ^{c)}	CH ₂ =CH	Me	Me	Et ₃ N	AgNCO	Benzene	50, 13	2p : 81 (100)	3.5 : 1

a) Reaction was undertaken using **1** (1.0 mmol) and a given base (0.1 mmol) and silver salt (0.1 mmol), if any, in a dry solvent (5 ml) under nitrogen. b) Optically active sparteine (0.2 mmol), obtained from (–)-sparteine sulfate pentahydrate (Aldrich), was used. c) This carbamate was unstable and its triethylamine salt was used for the reaction. d) The substrate (**1g**) is 1,1-dimethyl-2,3-butadienyl tosylcarbamate. e) A diastereomeric mixture of **1m** and **1m'** (1.5 : 1) was used. f) A diastereomeric mixture of **1n** and **1n'** (1.3 : 1) was used. Under the conditions, only **1n** underwent cyclization and **1n'** was recovered. g) For the structures of **1m** and **2m**, see Eq. 2. h) For the structures of **1m'** and **2m'**, see Eq. 3. i) For the structures of **1n** and **2n**, see Eq. 4. j) For the structures of **1n'** and **2n'**, see Eq. 5.

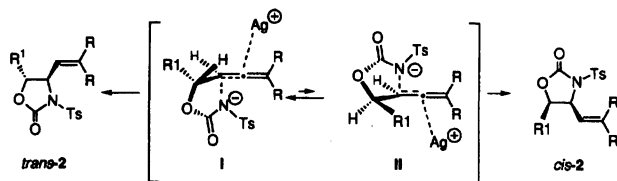
Table 2. Ag(I)-Catalyzed Cyclization of 2,3-Butadienyl Carbamates **1** (R²=R³=H) with Various *N*-Substituents^{a)}

Run	Carbamate 1		Base	Metal catalyst	Conditions		% Isolated yield of 2 (% conv.)	<i>trans</i> - 2 : <i>cis</i> - 2
	R	R ¹			Temp/°C	Time/h		
1	1a :	Ts	Et	Et ₃ N	AgOTf	50, 6	2a : 74 (100)	1.5 : 1
2	1q :	Tf ^{b)}	Et	Et ₃ N	AgNCO	50, 17	2q : 77 (100)	11.3 : 1
3	1r :	MeCO	Et	Et ₃ N	AgNCO	50, 24	2r : 0 (60)	
4	1r :	MeCO	Et	<i>t</i> -BuOK	AgOTf	50, 23	2r : 0 (49)	
5	1r :	MeCO	Et	<i>t</i> -BuOK	AgNCO	Refl., 49	2r : 34 (100)	3.8 : 1
6	1s : ^{c)}	PhCO	CH ₂ =CH	<i>t</i> -BuOK ^{d)}	AgNCO	50, 23	2s : 39 (100)	1.5 : 1
7	1t :	Ph	Et	<i>t</i> -BuOK	AgNCO	50, 23	2t : 0 (0)	
8	1u :	PhCH ₂	Et	<i>t</i> -BuOK	AgNCO	50, 20	2u : 0 (0)	

a) The reaction was undertaken using **1** (1.0 mmol), a base (0.1 mmol), and silver salt (0.1 mmol) in dry benzene (5 ml) under nitrogen. b) Tf is meant to refer to trifluoromethanesulfonyl group. c) Crude **1s** was used, since **1s** was unstable and could not be purified by column chromatography over silica gel (see Experimental Section). d) *t*-BuOK (1.0 mmol) was used.

pathway for the formation of *trans*-**2** and *cis*-**2**, respectively (Scheme 1). The A^(1,3)-strain¹⁵⁾ between *N*-sulfonyl and C₄-R (C₄ means the carbon in the 4-position) is of the same magnitude in these two transition states, while transition state **II** apparently is disfavored owing

to a gauche repulsion between R¹ and the allenic central carbon C₂. The higher *trans* selectivities of **1o** and **1p**, as compared with those of **1c** and **1h**, respectively, may be attributed to this gauche repulsion, increased by the substitution of methyl groups at the terminal carbon



Scheme 1. Ag^+ -catalyzed *trans* selective cyclization of terminally symmetrically substituted 2,3-butadienyl tosylcarbamates.

(C_4).

The stereoselectivity of the cyclization of terminally unsymmetrically-substituted carbamates **1** merits consideration in detail (Runs 19–23, Table 1 and Scheme 2). The cyclization of **11** provided the product with a *trans*-1-propenyl group as the C_4 substituent, 4-(*trans*-1-propenyl)-2-oxazolidinone (**21**), as a single stereoisomer (Run 19, Table 1). This result suggests that transition state **IV** ($\text{R}=\text{H}$) is strongly disfavored over **III** ($\text{R}=\text{H}$) owing to the $\text{A}^{(1,3)}$ -strain in the former.

Both components (**1m** and **1m'**) of an inseparable mixture (1.5:1) underwent cyclization with similar ease under usual conditions by heating at 50 °C for 5 h and provided *trans,trans*-**2m** and *cis,trans*-**2m'**, respectively, in a ratio of 1.8:1 in a 91% combined isolated yield (Runs 20 and 21, Table 1, and Eqs. 2 and 3). An interesting feature of these results is that of four possible stereoisomers (Scheme 2, $\text{R}=\text{Me}$), only two were formed. Especially rewarding was the selective formation of *cis,trans*-**2m'**, the product with the *cis*-4,5-di-

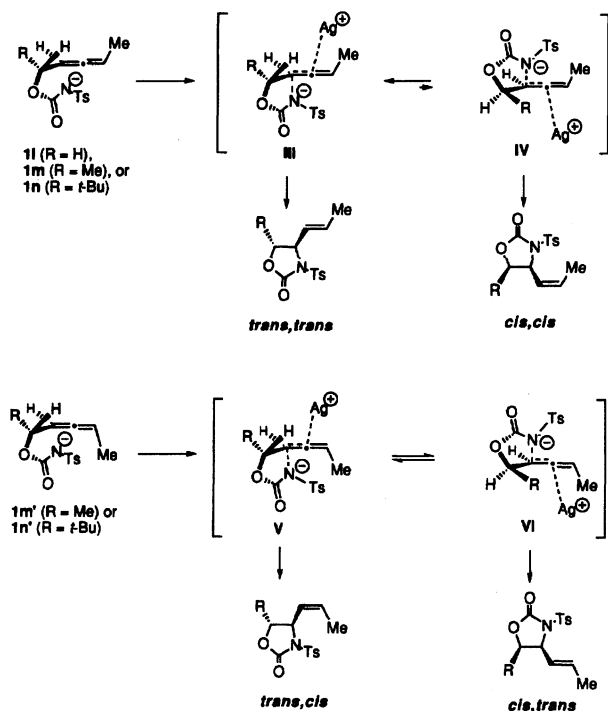
substituted 2-oxazolidinone structure, from **1m'** (Eq. 3 and Scheme 2). This result supports our proposal that the $\text{A}^{(1,3)}$ -strain between *N*-sulfonyl and the C_4 -Me in **V** (working to provide the *trans*- C_4 -olefins) outweighs the *gauche* repulsion between the C_1 -Me and the allenic central C_3 carbon in **VI** (working to yield *trans*- C_4 , C_5 -disubstituted 2-oxazolidinones), and the cyclization of **1m'** selectively proceeds via **VI** to provide the product with *trans*-olefin as the C_4 -substituent and the *cis*-4,5-disubstituted 2-oxazolidinone ring.

The remarkably higher *trans*-selective cyclization of **1m** (*trans,trans*-**2m**/*cis,cis*-**2m** => 30), as compared with that of **1b** (*trans*-**2b**/*cis*-**2b** = 1.4), may be accounted for in a similar way. Transition state **IV** ($\text{R}=\text{Me}$), providing *cis,cis*-**2m**, is plagued with both *gauche* repulsion around C_1 - C_2 and $\text{A}^{(1,3)}$ -strain between *N*-sulfonyl and C_4 -Me, while transition state **II** ($\text{R}^1=\text{Me}$, $\text{R}=\text{H}$), furnishing *cis*-**2b**, only suffers from *gauche* repulsion. The corresponding transition states **III** ($\text{R}=\text{Me}$), providing *trans,trans*-**2m**, and **I** ($\text{R}^1=\text{Me}$, $\text{R}=\text{H}$), giving *trans*-**2b**, are completely free from these repulsions.

In order to see the relative magnitude of importance between the $\text{A}^{(1,3)}$ -strain and the *gauche* repulsion, we examined, as an extreme, the cyclization of C_1 -*t*-Bu derivatives (**1n** and **1n'**). As expected, only the **1n** isomer of the inseparable mixture of **1n** and **1n'** (1.3:1) underwent complete cyclization with ease within 6 h at 50 °C to provide *trans,trans*-**2n** exclusively and in a high yield, probably via transition state **III** ($\text{R}=\text{t-Bu}$), free from both repulsions (Eq. 4). On the other hand, under the above conditions, the **1n'** isomer remained unchanged and was recovered in a quantitative yield. After prolonged heating at 50 °C, **1n'** was transformed to a mixture of *trans,cis*-**2n'** (22%) and *cis,cis*-**2n'** (4%), albeit in low isolated yields (Eq. 5). The diminished reactivity and the low yield as well as the product distribution suggest both transition states **V** and **VI** ($\text{R}=\text{t-Bu}$) are very high in energy and, in this particular case, the steric bulk of *t*-Bu is such that transition state **VI**, suffering from a *gauche* repulsion, is strongly disfavored.

Unfortunately, optically active sparteine, used as a base in place of triethylamine, did not exhibit any optical induction of the cyclization of **1a** (Run 2, Table 1). In the ^1H NMR spectra of product **2a**, measured in the presence of a chiral shift reagent [$\text{Eu}(\text{hfc})_3$, 400 MHz], all the olefinic, C_4 -H, and C_5 -H protons appeared in pairs of almost equal intensity.

The ease of cyclization of **1** depends highly on the electronic nature of the *N*-substituents (Table 2). While the structurally-related *N*-aralkyl 4,5-hexadienylamines^{9b,9g-i)} and *N*-aralkyl propargyl carbamates¹⁶⁾ undergo a ready cyclization to provide 2-vinylpyrrolidines (Ag^+ and Pd^{2+} catalysis) and 4-methylene-2-oxazolidinones (a base catalysis), respectively, *N*-phenyl (**1t**) and *N*-benzyl 2,3-butadienyl carbamates



Scheme 2. Ag^+ -catalyzed cyclization of diastereomeric 2,3-pentadienyl tosylcarbamates (**11**, **1m**, **1m'**, **1n**, and **1n'**).

(**1u**) were resistant toward cyclization and were recovered quantitatively by exposure to either *t*-BuOK (0.1 equiv) in THF at 50 °C or *t*-BuOK (0.1 equiv)–AgNCO (0.1 equiv) in benzene at 50 °C (Runs 7 and 8, Table 2).

The *N*-acyl derivatives (**1r** and **1s**), on the other hand, underwent cyclization to provide the expected products **2r** and **2s**, respectively, though in only moderate yields by the use of a specific combination of the catalysts, AgNCO (0.1 equiv) and *t*-BuOK (0.1 equiv, Runs 5 and 6, Table 2). Surprisingly, the use of either triethylamine in place of *t*-BuOK (Run 3) or AgOTf in place of AgNCO (Run 4) only caused decomposition of the substrates and no cyclization products were detected at all. Since *t*-BuOK and triethylamine are basic enough to generate the conjugate bases of *N*-acyl carbamates,^{17,18)} the contrasting results observed for these bases were quite unexpected.

Besides *p*-toluenesulfonyl, a trifluoromethanesulfonyl group may be utilized with similar efficiency (Run 2, Table 2). Notably, with this substituent, a remarkably high stereoselectivity was observed (cf., Runs 1 and 2, Table 2). The reason for this is not clear at present.

Ag(I)-Catalyzed Aminocyclization of 3,4-Pentadienyl Tosylcarbamates 3: Preparation of 4-Vinyltetrahydro-2H-1,3-oxazin-2-ones 4. Table 3 summarizes the results for cyclization of 3,4-pentadienyl tosylcarbamates **3** under the conditions established for the cyclization of **1** (0.1 equiv of AgNCO and 0.1 equiv of Et₃N in benzene). Since we had already established another convenient and versatile route to **4**,⁷⁾ only a typical and limited number of substrates have been examined in order to clarify the synthetic scope and stereoselectivity of the present approach.

By comparison of the reaction times in Tables 1 and 3, it is apparent that **3** reacts somewhat reluctantly relative to **1**. However, the reaction seems to be general, as judged from the satisfactory yields for most R¹ and R² derivatives. As being general for reactions that pass through a six-membered cyclic transition state, as compared with those that proceed via the corresponding five-membered cyclic transition state, the substituent R²=Me of **3** displays much higher influence on the stereoselectivity providing *trans*-**4** in higher selectivity than the R¹=Me of **1** does. Moreover, the *trans* selectivity of the present reaction is much higher than that of the reaction reported recently from our laboratories.⁷⁾

Structure Determination of 2 and 4. The occurrence of the present silver(I)-catalyzed cyclization of **1** and **3** at the nitrogen atom, and not at the oxygen atom, is evident from the spectral data of **2** and **4**. The ν_{CO} absorptions of **2** and **4** generally appear in the regions of about 1790–1810 and 1720–1730 cm⁻¹, respectively, in their infrared spectra. The corresponding cyclic carbonimidates may display ν_{CN} absorptions at lower wavenumbers (e.g., about 1650 cm⁻¹ for ethylene iminocarbonates).¹⁹⁾

In the ¹³C NMR spectrum of **2a**, the higher-field res-

onance of the vinyl-substituted C₄ carbon (δ =59.5) as compared with the unsubstituted C₅ carbon (δ =68.1) clearly indicates that a C₄–N bond, rather than a C₄–O bond, is formed by the cyclization. The appearance of resonances of both the vinylic protons at C₄ and C₅ as well as the C₄–H and C₅–H protons in pairs in the ¹H NMR spectra of 4,5-divinyl-substituted 2-oxazolidinones (both for *cis*- and *trans*-**2h**) further supports the assigned structure. If these were 4,5-divinyl-1,3-dioxolan-2-imines, owing to their symmetry, both the vinyl protons and the C₄–H and C₅–H ring protons might appear as single resonances.

The stereochemistry of *trans*-**2** and *cis*-**2** was determined unequivocally on the basis of their vicinal coupling constants, ³J_{H₄H₅} (Table 4), and the nuclear Overhauser effects in their ¹H NMR spectra as well as the steric compression effects (γ -effects) in their ¹³C NMR spectra.²⁰⁾

As is apparent from Table 4, the *trans* isomers of **2** generally show coupling constants between C₄H and C₅H in a region within 3.6–4.8 ppm, while the *cis* counterparts are within 6.2–8.4 ppm.^{20b)}

Figure 1 summarizes the selected NOE and ¹³C NMR data relevant for the determination of the stereochemistry using *cis*–*trans* pairs of **2d** and **2m** as representatives. For example, irradiation at the C₅–H proton of *cis*-**2d** caused a 10.4% increment in the area intensity of the C₄–H proton, while no increase in the area intensity was detected for the vinylic C₁–H proton. Irradiation at the C₅–H proton of *trans*-**2d**, on the other hand, displayed a greater increase in the area intensity of the vinylic C₁–H proton than that of the C₄–H proton. The structure of *cis*-**2d** was further supported by the higher field resonances of the propyl C₁ and vinyl C₁ carbons as compared with those of the corresponding carbons of *trans*-**2d**. The *trans*-1-propenyl structure of *cis,trans*-**2m'** and *trans,trans*-**2m** is apparent from the coupling constants between the olefinic protons (³J_{H₁H₂}=15 Hz) and the *cis*-1-propenyl configuration of *trans,cis*-**2n'** (Eq. 5) from the coupling constant, ³J_{H₁H₂}=10 Hz.

The stereochemical assignment of **2d** was confirmed further by the Pd(0)-catalyzed *cis*–*trans* isomerization that might proceed via σ – π interconversion of an allyl-palladium intermediate, formed by oxidative addition of Pd(0) to the C₄–N bond.⁷⁾ The ratio of *trans*-**2d**/*cis*-**2d** changed from 1.8:1 to 3.0:1, in favor of the thermodynamically more stable *trans* isomer, by refluxing the mixture in benzene in the presence of Pd(PPh₃)₄ (0.1 equiv) for 23 h with a quantitative recovery of the mixture of **2d**.

Scheme 3 demonstrates the chemical confirmation of the structure of *trans*-**2p**, which relies on a smooth isomerization of *cis*-2-(2-methyl-1-propenyl)-3-vinylaziridine (*cis*-**6**) to 4,5-dihydro-4,4-dimethyl-1H-azepine (**7**).²¹⁾ Hydrolysis of a mixture of *trans*- and *cis*-**2p** (3.5:1) with 0.5 M NaOH in ethanol/H₂O (3:1 vol.) at reflux for 6 h provided a mixture of *syn*- and *anti*-

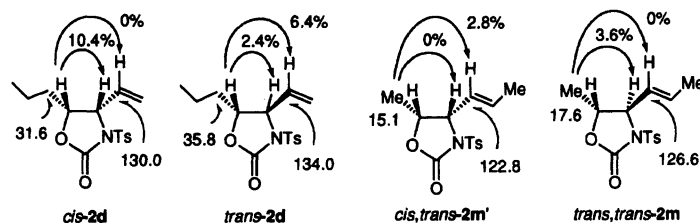
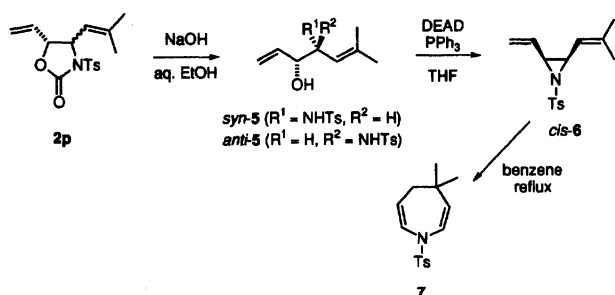
Table 3. Ag(I)-Catalyzed Cyclization of 3,4-Pentadienyl Tosylcarbamate **3**^{a)}

Run	Carbamate 3		Reaction conditions	% Isolated yield of 4 (% conv.)	<i>trans</i> - 4 : <i>cis</i> - 4	
	R ¹	R ²				
	Temp/°C, Time/h					
1	3a :	H	H	50, 28	4a : 41 (100)	10.9: 1
2	3b :	H	Me	50, 43	4b : 72 (100)	
3	3c :	Me	H	50, 40	4c : 70 (100)	
4	3d :	Me	Me	50, 28; Refl., 40	4d : 68 (100)	7.1: 1

a) Reaction conditions: **1** (1.0 mmol), triethylamine (0.1 mmol), and AgNCO (0.1 mmol) in dry benzene (5 ml) under nitrogen.

Table 4. Vicinal Coupling Constants, ³J_{H4H5} (Hz), of Products **2** and **4**

Compound	J _{trans}	J _{cis}	Compound	J _{trans}	J _{cis}
2a	4.0	8.4	<i>trans,trans</i> - 2m	4.4	
<i>trans</i> - 2b	4.8		<i>cis,trans</i> - 2m'		7.0
<i>cis</i> - 2b		7.0	<i>trans,trans</i> - 2n	4.0	
<i>trans</i> - 2c	4.4		<i>trans,cis</i> - 2n'	4.0	
<i>cis</i> - 2c		7.0	<i>cis,trans</i> - 2n'		6.2
<i>trans</i> - 2d	4.4		<i>trans</i> - 2o	4.4	
<i>cis</i> - 2d		7.0	<i>cis</i> - 2o		7.0
<i>trans</i> - 2e	3.8		<i>trans</i> - 2p	4.0	
<i>trans</i> - 2f	3.7		<i>cis</i> - 2p		7.0
<i>trans</i> - 2h	4.4		<i>trans</i> - 2q	4.4	
<i>cis</i> - 2h		7.3	<i>trans</i> - 2r	4.0	
<i>trans</i> - 2i	4.8				
<i>cis</i> - 2i		7.3	<i>trans</i> - 4b	0.0	
<i>trans</i> - 2j	4.2		4c	8.4	7.0
<i>trans</i> - 2k	4.8		<i>trans</i> - 4d	10.3	
2l	3.6	8.4	<i>cis</i> - 4d		5.5

Fig. 1. Selected NOE (%) and ¹³C NMR (δ in ppm) data for structure determination of *cis*- and *trans*-**2**.

Scheme 3.

5 (7.7:1) in a 65% isolated yield. The major isomer, *syn*-**5**, was purified by a single recrystallization from hexane–dichloromethane and was subjected to the Mitsunobu reaction (diethyl azodicarboxylate and triphenylphosphine, 1 equiv each, in dry THF at room

temperature, accompanying an inversion of the configuration at the carbon bearing the hydroxyl group) to give *cis*-**6** in a 60% isolated yield. The aziridine *cis*-**6** was rather stable at room temperature²¹⁾ and did not accompany the isomerization to **7** during the above transformation and purification over silica gel; however it underwent a Cope rearrangement under reflux in benzene for 6 h to give **7** in a 60% isolated yield.

4-Vinyltetrahydro-2*H*-1,3-oxazin-2-one and its C₅-methyl derivatives (**4a** and **4b**) showed identical melting points and spectral data (¹H NMR and IR) superimposable in all respects with those of the authentic samples.⁷⁾ It is known that the C₄-substituents in the *N*-tosyltetrahydro-2*H*-1,3-oxazin-2-one ring system, in general, preferentially take quasi-axial orientation in a chair conformation in order to avoid A^(1,2)-strain against the *N*-tosyl group.²²⁾ Indeed, the unusually

small coupling constant ($^3J=0.0$ Hz, Table 4) observed for *trans*-**4b** may be ascribed to the quasi-diaxial orientation of the C₄-vinyl and C₅-methyl substituents.⁷⁾ On the other hand, the C₄-vinyl and C₅-methyl groups of *trans*-**4d** seem to be oriented quasi-diequatorially as judged from a large $^3J_{\text{H}_4\text{H}_5}=10.3$ Hz. This is probably because the diaxial repulsion between the C₄-vinyl and C₆-methyl groups in the quasi-diaxial conformation outweighs the A^(1,2)-repulsion between the C₄-vinyl and *N*-tosyl groups in a quasi-diequatorial conformation.

These arguments are firmly supported by the X-ray structure analysis of *trans*-**4d** (Fig. 2). The observed $^3J_{\text{H}_4\text{H}_5}$ value for *trans*-**4d** (in solution) is qualitatively in good accord with the one ($^3J_{\text{H}_4\text{H}_5}=14.3$ Hz) calculated from the Karplus equation using the dihedral angle determined by X-ray analysis (H₄-C₄-C₅-H₅=161°). The quasi-diequatorial conformation of the C₄-vinyl and C₅-methyl groups is also apparent from the dihedral angle, C₁(vinyl)-C₄-C₅-C(methyl)=-79.1°. Another interesting feature, revealed by the X-ray structure analysis, is the distortion of the S-N-C₄ plane from coplanarity with the O-C(=O) plane, which might relieve the A^(1,2)-strain between the *N*-sulfonyl and the C₄-vinyl group, forced to orient in a quasi-equatorial position, at the expense of the bonding energy of the partially double bonded C(=O)-N linkage. The S-N-C=O dihedral angle was determined to be as large as 25.2°.

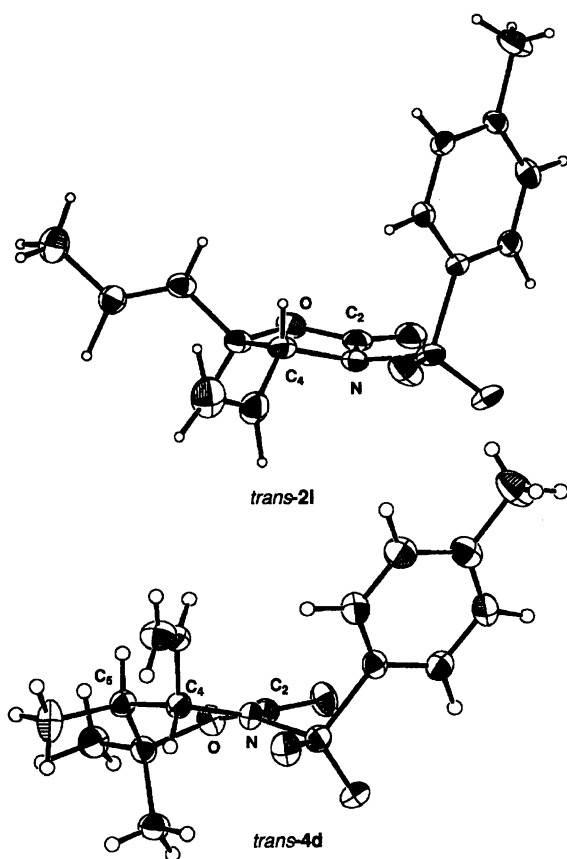
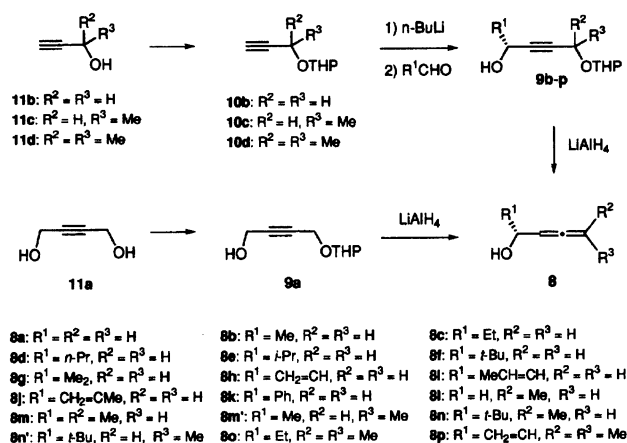


Fig. 2. X-Ray structures of *trans*-**2i** and *trans*-**4d**.

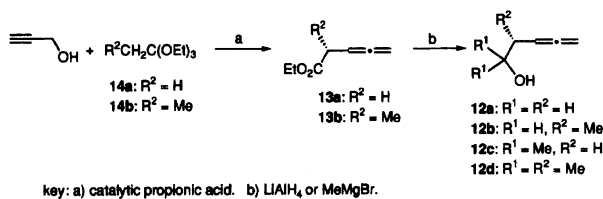
In Fig. 2 is also shown the X-ray structure of *trans*-**2i**. Interestingly, the nitrogen atom is not planar (sp²), but takes a shallow pyramidal structure as apparently seen from a downward shift 0.24 Å from the SC₂C₄ plane (the nitrogen of *trans*-**4d** being almost planar and locating 0.02 Å upward from the SC₂C₄ plane). As a consequence, the dihedral angle S-N-C=O is as large as 21.1°. This deformation from N(sp²) might be ascribed to the A^(1,2)-strain between the C₄-vinyl and *N*-sulfonyl groups and also to the rigidity of the cyclopentane envelop conformation that makes rotation around the C₂-N bond unfavorable.

Preparation of 2,3-Butadienyl Alcohols 8 and 3,4-Pentadienyl Alcohols 12. Precursors of Carbamates **1** and **3**. A variety of 2,3-butadienyl alcohols **8a-p** (18 kinds) were prepared in a straightforward manner according to the procedures shown in Scheme 4. All the starting propargyl alcohols **11a-d** are commercially available. The parent alcohol **8a** was prepared in a 60% isolated yield by the reduction of **9a** with lithium aluminum hydride (LiAlH₄).²³⁾ The R²=R³=H derivatives **8b-k** were prepared by the reaction of the lithium acetylide of **10b**, generated by treatment with butyllithium, with an appropriate aldehyde and ketone, followed by reduction with LiAlH₄ of the thus prepared **9b-k**. The R²=Me, R³=H (and R²=H, R³=Me) derivative (**8l** and diastereomeric mixtures of **1m** and **1n**) and the R²=R³=Me derivatives (**8o,p**) were synthesized in a similar way from **10c** and **10d**, respectively. In most cases, the yields of the alkylation step (from **10** to **9**) were around 70–85%. The yields for the reduction step (from **9** to **8**) were around 60–90%, except for the reduction of **9l-n** (35–45%).

3,4-Pentadienyl alcohols **12** were obtained according to Scheme 5. A slight modification of the literature procedure (Claisen rearrangement)²⁴⁾ furnished **13a,b** in better yields (see Experimental Section). Our procedure has the following merits: 1) this requires only 1.1 equiv of triethyl orthoacetate (**14a**) or orthopropi-



Scheme 4. Preparative scheme of 2,3-butadien-1-ol and its derivatives **8**.



Scheme 5. Preparative scheme of 3,4-pentadien-1-ol and its derivatives **12**.

onate (**14b**), as opposed to the 4—7 equiv stated in the literature and 2) provides the rearrangement products **13a,b** in much better yields (69—73%) than the literature procedure (**13a** in a 34% yield).

Ethyl 3,4-pentadienoate (**13a**) was converted either to **12a** by reduction with LiAlH_4 (75%) or to **12b** by reaction with 2.5 equiv of methylmagnesium iodide (78%). 3,4-Pentadienyl alcohols **12c** (75%) and **12d** (86%) were prepared in similar ways.

In conclusion, the utility of the present Ag(I)-catalyzed aminocyclization of **1** and **3** may be augmented by the high-yield formation of **2** and **4** in a synthetically useful level of stereoselectivity and by the ready availability of **1** and **3** and their precursor alcohols with a wide range of substitution patterns in a straightforward manner as well as by the ease with which the reaction can be performed. The products **2** and **4** are the protected forms of sterically defined allylic amino alcohols (2-amino-3-buten-1-ols and 3-amino-4-penten-1-ols, respectively) and may find applications in many fields. One example is demonstrated in Scheme 3.

Experimental

Melting points were determined with a Yanagimoto micro melting point apparatus and were not corrected. Unless otherwise specified, short-path (bulb-to-bulb) distillations were carried out in a Kugelrohr apparatus. In these cases, boiling points are meant to refer to the oven temperature. Microanalyses were performed by the Microanalysis Center of Nagasaki University. Analyses agreed with the calculated values within $\pm 0.3\%$. High-resolution mass spectra were measured with a JEOL JMS-DX303. Infrared spectra were measured with a JASCO A-100 infrared spectrophotometer. Proton magnetic resonance spectra were determined either at 60 MHz on a JEOL JNM-PMX60 or at 400 MHz on a JEOL-GX400 instrument with tetramethylsilane as an internal standard. ^{13}C NMR spectra were determined at 100 MHz on a JEOL-GX400 instrument with tetramethylsilane as an internal standard. Chemical shift values were given in ppm downfield from an internal standard.

Solvents and Reagents. Tetrahydrofuran and diethyl ether were dried and distilled from benzophenone and sodium immediately prior to use under nitrogen atmosphere. Benzene and triethylamine were distilled over calcium hydride. 3,4-Dihydro-2*H*-pyran, propargyl alcohol, 1-butyne-3-ol, 2-methyl-3-butyne-2-ol, 2-butyne-1,4-diol, and triethyl orthoacetate were purchased and used without further purification. *p*-Toluenesulfonyl isocyanate and phenyl isocyanate were purchased and distilled prior to use. Trifluoromethanesulfonyl isocyanate was prepared from chlorosulfonyl iso-

cyanate and trifluoromethanesulfonamide.²⁵⁾ Silver isocyanate was prepared according to the literature.²⁶⁾ Lithium aluminum hydride, copper(I) chloride, and silver trifluoromethanesulfonate (reagent grade) were used without further purification.

General Procedure for the Preparation of THP-Protected Propargyl Alcohols 10b—d. Into a mixture of an appropriate propargylic alcohol **11b**, **11c**, or **11d** (50 mmol) and a catalytic amount of *p*-toluenesulfonic acid (0.2 g, 1 mmol) in dry THF (30 ml) was added 3,4-dihydro-2*H*-pyran (4.6 ml, 50 mmol) in one portion at 0 °C. The reaction mixture was stirred under nitrogen at room temperature for 2 h. After neutralization with sat. NaHCO_3 , the mixture was extracted with ether (3×20 ml). The combined organic extracts were dried (magnesium sulfate), filtered, evaporated, and distilled by means of a Kugelrohr apparatus to give **10b**, **10c**, or **10d**.

3-(Tetrahydro-2-pyranyloxy)-1-propyne (10b): Bp 80 °C/25 mmHg (1 mmHg=133.322 Pa); 70% yield; IR (neat film) 3280 (s), 2940 (s), 2120 (w), 1210(m), 1120 (s), and 1040 cm^{-1} ; ^1H NMR (CCl_4 , 60 MHz) δ =1.33—1.86 (m, 6 H), 2.28 (t, J =2.0 Hz, 1 H), 3.25—3.90 (m, 2 H), 4.15 (d, J =2.0 Hz, 2 H), and 4.75 (m, 1 H).

3-Methyl-3-(tetrahydro-2-pyranyloxy)-1-propyne (10c): Bp 100 °C (20 mmHg); 80%; IR (neat film) 3280 (s), 2940 (s), 2120 (w), 1210 (m), 1120 (s), and 1030 cm^{-1} ; ^1H NMR (CCl_4 , 60 MHz) δ =1.46 (d, J =6.4 Hz, 3 H), 1.52—1.76 (m, 6 H), 1.90 (t, J =2.0 Hz, 1 H), 2.90—3.68 (m, 2 H), 4.12 (dq, J =2.0 and 6.4 Hz, 2 H), and 4.56 (m, 1 H).

3,3-Dimethyl-3-(tetrahydro-2-pyranyloxy)-1-propyne (10d): Bp 110 °C (10 mmHg); 61%; IR (neat film) 3280 (s), 2940 (s), 2120 (w), 1440 (s), 1380 (s), 1125 (s), and 1025 cm^{-1} ; ^1H NMR (CCl_4 , 60 MHz) δ =1.46 (s, 6 H), 1.54—1.93 (m, 6 H), 2.28 (s, 1 H), 3.20—4.18 (m, 2 H), and 5.07 (m, 1 H).

4-(Tetrahydro-2-pyranyloxy)-2-butyne-1-ol (9a): To a mixture of 2-butyne-1,4-diol (8.6 g, 100 mmol) and *p*-toluenesulfonic acid (1.9 g, 10 mmol) in THF (50 ml) was added 3,4-dihydro-2*H*-pyran (9.1 ml, 100 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 2 h. After addition of triethylamine (5 ml), and removal of the solvent by a rotary evaporator, the residue was washed with sat. NaHCO_3 and extracted with ethyl acetate (3×30 ml). The combined extracts were dried (magnesium sulfate), filtered, evaporated, and distilled by means of a Kugelrohr apparatus (140 °C/1 mmHg) to give **9a** in a 34% yield. IR (neat film) 3400 (s), 2940 (s), 1140 (s), and 1030 (s) cm^{-1} ; ^1H NMR (CCl_4 , 60 MHz) δ =1.30—1.85 (m, 6 H), 3.40—3.92 (m, 2 H), 3.45 (br s, 1 H), 4.15 (br s, 4 H), and 4.80 (m, 1 H).

General Procedure for the Preparation of 4-(Tetrahydro-2-pyranyloxy)-2-butyne-1-ol Derivatives 9b—p. A 200 ml two-necked round-bottom flask, containing a magnetic stirring bar, capped with a septum cap and equipped with a dropping funnel, was purged with nitrogen. Dry THF (50 ml) and an appropriate 3-(tetrahydro-2-pyranyloxy)-1-propyne derivative, **10b**, **10c**, or **10d** (50 mmol), were introduced via syringes through the septum cap. A solution of *n*-BuLi (1.6 M in hexane, 31 ml, 50 mmol) (1 M=1 mol dm^{-3}) was introduced via the dropping funnel at −78 °C and the reaction mixture was stirred for 2 h at the same temperature. An appropriate aldehyde or ketone (50

mmol) was added at -78°C and the mixture was stirred at the same temperature for 2 h. After allowing the solution to warm to room temperature, sat. NH_4Cl (15 ml) was added and the mixture was extracted with ether (3×20 ml). The combined extracts were dried (magnesium sulfate), filtered, and evaporated. The residue was distilled by means of a Kugelrohr apparatus to afford 4-(tetrahydro-2-pyranyloxy)-2-butyne-1-ol derivatives **9b—p**.

1-Methyl-4-(tetrahydro-2-pyranyloxy)-2-butyne-1-ol (9b): Bp 150°C (0.5 mmHg); 64% yield; IR (neat film) 3400 (s), 2940 (s), and 1025 (s) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) $\delta=1.40$ (d, $J=6.4$ Hz, 3 H) 1.42—1.90 (m, 6 H), 3.68 (br s, 1 H), 3.40—3.85 (m, 2 H), 4.15 (d, $J=2.0$ Hz, 2 H), 4.50 (dq, $J=2.0$ and 6.4 Hz, 1 H), and 4.80 (m, 1 H).

1-Ethyl-4-(tetrahydro-2-pyranyloxy)-2-butyne-1-ol (9c): Bp 105°C (0.2 mmHg); 68%; IR (neat film) 3300 (s), 2950 (s), and 1030 (s) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) $\delta=1.00$ (t, $J=6.4$ Hz, 3 H) 1.15—2.00 (m, 8 H), 2.30 (br s, 1 H), 3.30—3.90 (m, 3 H), 4.25 (br s, 2 H), and 4.75 (m, 1 H).

1-Propyl-4-(tetrahydro-2-pyranyloxy)-2-butyne-1-ol (9d): Bp 110°C (0.5 mmHg); 70%; IR (neat film) 3360 (s), 2950 (s), 1120 (s), and 1030 (s) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) $\delta=1.00$ (t, $J=6.4$ Hz, 3 H) 1.35—1.96 (m, 10 H), 3.50—3.75 (m, 3 H), 4.20 (br s, 2 H), and 4.80 (m, 1 H).

1-Isopropyl-4-(tetrahydro-2-pyranyloxy)-2-butyne-1-ol (9e): Bp 135°C (0.5 mmHg); 74%; IR (neat film) 3420 (s), 2960 (s), and 1030 (s) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) $\delta=0.95$ (d, $J=6.4$ Hz, 6 H) 1.18—1.90 (m, 7 H), 3.22—3.80 (m, 3 H), 4.15 (br s, 2 H), and 4.74 (m, 1 H).

1-*t*-Butyl-4-(tetrahydro-2-pyranyloxy)-2-butyne-1-ol (9f): Bp 150°C (0.5 mmHg); 76%; IR (neat film) 3430 (m), 2960 (s), and 1030 (s) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) $\delta=0.96$ (s, 9 H) 1.30—1.80 (m, 6 H), 2.66 (br s, 1 H), 3.60—3.83 (m, 2 H), 3.94 (t, $J=1.6$ Hz, 1 H), 4.25 (d, $J=1.6$ Hz, 1 H), and 4.80 (m, 1 H).

1,1-Dimethyl-4-(tetrahydro-2-pyranyloxy)-2-butyne-1-ol (9g): Bp 130°C (1 mmHg); 75%; IR (neat film) 3450 (s), 2950 (s), 1365 (s), 1125 (s), and 1022 (s) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) $\delta=1.45$ (s, 6 H), 1.58—1.80 (m, 6 H), 2.50 (br s, 1 H), 3.27—3.73 (m, 2 H), 4.16 (s, 2 H), and 5.75 (m, 1 H).

1-Vinyl-4-(tetrahydro-2-pyranyloxy)-2-butyne-1-ol (9h): Bp 120°C (0.3 mmHg); 67%; IR (neat film) 3390 (s), 2940 (s), 1120 (s), and 1030 (s) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) $\delta=1.30$ —1.83 (m, 6 H), 2.50 (br s, 1 H), 3.33—4.10 (m, 2 H), 4.30 (br s, 2 H), 4.68—5.00 (m, 2 H), 5.18 (br d, $J=9.0$ Hz, 1 H), 5.40 (br d, $J=16.0$ Hz, 1 H), and 5.96 (br dd, $J=9.0$ and 16.0 Hz, 1 H).

1-(*trans*-1-Propenyl)-4-(tetrahydro-2-pyranyloxy)-2-butyne-1-ol (9i): Bp 150°C (2 mmHg); 88%; IR (neat film) 3400 (s), 2950 (s), 1450 (m), 1120 (s), 1030 (s), and 980 (s) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) $\delta=1.25$ —1.84 (m, 8 H), 2.48 (br s, 1 H), 3.20—3.37 (m, 2 H), 4.10 (br s, 2 H), 4.43—4.83 (m, 2 H), and 5.40—6.02 (m, 2 H).

1-Isopropenyl-4-(tetrahydro-2-pyranyloxy)-2-butyne-1-ol (9j): Bp 160°C (0.1 mmHg); 78%; IR (neat film) 3400 (s), 2950 (s), 1450 (m), 1130 (s), and 1028 (s) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) $\delta=1.30$ —1.75 (m, 6 H), 1.80 (s, 3 H), 3.10 (br s, 1 H), 3.38—4.00 (m, 2 H), 4.18 (d, $J=2.0$ Hz, 2 H), 4.68 (m, 1 H), 4.80 (br s, 2 H), and 5.08

(t, $J=2.0$ Hz, 1 H).

1-Phenyl-4-(tetrahydro-2-pyranyloxy)-2-butyne-1-ol (9k): Bp 155°C (0.1 mmHg); 87%; IR (neat film) 3400 (s), 2950 (s), 1460 (m), 1140 (s), 1030 (s), and 700 (m) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) $\delta=1.30$ —1.88 (m, 6 H), 3.20 (br s, 1 H), 3.35—3.90 (m, 2 H), 4.20 (d, $J=2.0$ Hz, 2 H), 4.85 (m, 1 H), 5.36 (t, $J=2.0$ Hz, 1 H), and 7.05—7.60 (m, 5 H).

4-Methyl-4-(tetrahydro-2-pyranyloxy)-2-butyne-1-ol (9l): Bp 130°C (0.5 mmHg); 72%; IR (neat film) 3400 (s), 2950 (s), 1450 (m), 1125 (s), and 1026 (s) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) $\delta=1.42$ (d, $J=6.4$ Hz, 3 H), 1.50—1.80 (m, 6 H), 2.88 (br s, 1 H), 3.22—3.90 (m, 2 H), 4.30 (d, $J=2.0$ Hz, 2 H), 4.48 (tq, $J=2.0$ and 6.4 Hz, 1 H), and 4.90 (m, 1 H).

1,4-Dimethyl-4-(tetrahydro-2-pyranyloxy)-2-butyne-1-ol (9m): Bp 110°C (0.5 mmHg); 40%; IR (neat film) 3400 (s), 2940 (s), 1340 (m), 1130 (s), and 1025 (s) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) $\delta=1.13$ —1.90 (m, 12 H), 3.00 (br s, 1 H), 3.36—3.95 (m, 2 H), 4.22—4.70 (m, 2 H), and 4.93 (m, 1 H).

1-*t*-Butyl-4-methyl-4-(tetrahydro-2-pyranyloxy)-2-butyne-1-ol (9n): Bp 150°C (1.0 mmHg); 86%; IR (neat film) 3450 (m), 2960 (s), and 1020 (s) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) $\delta=0.98$ (s, 9 H), 1.42 (d, $J=6.4$ Hz, 3 H), 1.50—1.80 (m, 6 H), 1.83 (br s, 1 H), 3.40—3.80 (m, 2 H), 3.94 (br s, 1 H), 4.46 (br q, $J=6.4$ Hz, 1 H), and 4.88 (m, 1 H).

1-Ethyl-4,4-dimethyl-4-(tetrahydro-2-pyranyloxy)-2-butyne-1-ol (9o): Bp 140°C (0.5 mmHg); 79%; IR (neat film) 3400 (s), 2940 (s), 1250 (m), and 1020 (s) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) $\delta=1.02$ (t, $J=6.4$ Hz, 3 H), 1.45 (s, 3 H), 1.50 (s, 3 H), 1.20—1.95 (m, 8 H), 3.00 (br s, 1 H), 3.40—4.40 (m, 3 H), and 5.10 (m, 1 H).

1-Vinyl-4,4-dimethyl-4-(tetrahydro-2-pyranyloxy)-2-butyne-1-ol (9p): Bp 150°C (1.5 mmHg); 80%; IR (neat film) 3400 (s), 2950 (s), 1250 (s), 1130 (s), and 1025 (s) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) $\delta=1.43$ (s, 3 H), 1.50 (s, 3 H), 1.53—1.78 (m, 6 H), 2.90 (br s, 1 H), 3.25—4.08 (m, 2 H), 4.72 (m, 1 H), 5.06 (m, 1 H), 5.13 (br d, $J=9.8$ Hz, 1 H), 5.30 (br d, $J=17.0$ Hz, 1 H), and 5.90 (br dd, $J=9.8$ and 17.0 Hz, 1 H).

General Procedure for the Preparation of 2,3-Butadienyl Alcohols **8a—p.**²³⁾ A 200 ml two-necked round-bottom flask, containing a stirring bar, fitted with a dropping funnel and a reflux condenser, was purged with nitrogen. Dry ether (50 ml) was introduced via a syringe and lithium aluminum hydride (1.26 g, 33 mmol) was added under cooling with an ice bath. An appropriate derivative of 4-(tetrahydro-2-pyranyloxy)-2-butyne-1-ols **9a—p** (30 mmol) dissolved in dry ether (20 ml) was added over a period of 45 min via a dropping funnel at 0°C . The mixture was refluxed for 4 h and then the excess lithium aluminum hydride was decomposed by adding aqueous THF (3 ml, THF: water=3:1 v/v) dropwise until the gray slurry turned into white granules. After decantation, the residual solid was washed with ether (3×20 ml). The combined extracts were dried (magnesium sulfate) and filtered. The solvent was distilled off under atmospheric pressure and the residue was distilled by means of a Kugelrohr apparatus.

2,3-Butadien-1-ol (8a): Bp 90°C (80 mmHg); 60% yield; IR (neat film) 3350 (s), 2940 (m), 1960 (s), 1020 (s),

and 850 (m) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) δ =2.55 (br s, 1 H), 4.08 (dt, J =6.0, 3.0 Hz, 2 H), 4.78 (dt, J =6.0 and 3.0 Hz, 2 H), and 5.22 (quint., J =6.0 Hz, 1 H).

1-Methyl-2,3-butadien-1-ol (8b): Bp 90 °C (20 mmHg); 61%; IR (neat film) 3340 (s), 1955 (s), 1080 (m), and 850 (m) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) δ =1.30 (d, J =6.0 Hz, 3 H), 2.26 (br s, 1 H), 4.35 (br dq, J =5.8 and 6.0 Hz, 1 H), 4.86 (br d, J =6.4 Hz, 2 H), and 5.28 (dt, J =5.8 and 6.4 Hz, 1 H).

1-Ethyl-2,3-butadien-1-ol (8c): Bp 100 °C (20 mmHg); 70%; IR (neat film) 3325 (s), 2950 (s), 1960 (s), and 850 (s) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) δ =0.94 (t, J =6.8 Hz, 3 H), 1.52 (br q, J =6.8 Hz, 2 H), 2.90 (br s, 1 H), 4.10 (m, 1 H), 4.72 (br d, J =6.2 Hz, 2 H), and 5.20 (br t, J =6.2 Hz, 1 H).

1-Propyl-2,3-butadien-1-ol (8d): Bp 90 °C (5 mmHg); 60%; IR (neat film) 3340 (s), 2940 (s), 1950 (s), 1020 (m), and 845 (m) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) δ =0.70–1.70 (m, 7 H), 3.52 (br, 1 H), 4.00 (m, 1 H), 4.74 (br d, J =6.0 Hz, 2 H), and 5.35 (br t, J =6.0 Hz, 1 H).

1-Isopropyl-2,3-butadien-1-ol (8e): Bp 100 °C (30 mmHg); 58%; IR (neat film) 3360 (s), 2960 (s), 1960 (s), 1030 (m), and 840 (s) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) δ =0.94 (d, J =6.0 Hz, 6 H), 1.64 (dq, J =7.0 and 6.0 Hz, 1 H), 1.95 (br s, 1 H), 3.95 (br dd, J =7.0 and 7.6 Hz, 1 H), 4.83 (br d, J =5.8 Hz, 2 H), and 5.28 (dt, J =7.6 and 5.8 Hz, 1 H).

1-*t*-Butyl-2,3-butadien-1-ol (8f): Bp 75 °C (40 mmHg); 62%; IR (neat film) 3400 (s), 2960 (s), 1960 (s), 1050 (m), and 840 (m) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) δ =0.90 (s, 9 H), 1.40 (br s, 1 H), 3.70 (dt, J =6.8 and 2.4 Hz, 1 H), 4.77 (dd, J =2.4 and 6.4 Hz, 2 H), and 5.18 (dt, J =6.8 and 6.4 Hz, 1 H).

1,1-Dimethyl-2,3-butadien-1-ol (8g): Bp 100 °C (25 mmHg); 40%; IR (neat film) 3360 (s), 2970 (s), 1955 (s), 1150 (s), and 845 (m) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) δ =1.28 (s, 6 H), 2.60 (br s, 1 H), 4.80 (d, J =6.4 Hz, 2 H), and 5.30 (br t, J =6.4 Hz, 1 H).

1-Vinyl-2,3-butadien-1-ol (8h): Bp 60 °C (20 mmHg); 49%; IR (neat film) 3320 (s), 1960 (s), 1125 (m), 1020 (s), and 850 (s) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) δ =2.38 (br s, 1 H), 4.55 (m, 1 H), 4.70–5.00 (m, 3 H), 5.10 (br d, J =10.0 Hz, 1 H), 5.20 (br d, J =16.0 Hz, 1 H), and 5.80 (br dd, J =10.0 and 16.0 Hz, 1 H).

1-(*trans*-1-Propenyl)-2,3-butadien-1-ol (8i): Bp 100 °C (15 mmHg); 69%; IR (neat film) 3350 (s), 1955 (s), 1075 (m), 960 (s), and 840 (m) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) δ =1.72 (br d, J =5.0 Hz, 3 H), 2.18 (br s, 1 H), 4.50 (m, 1 H), 4.76 (br d, J =6.0 Hz, 2 H), 5.08 (br t, J =6.0 Hz, 1 H), and 5.30–5.72 (m, 2 H).

1-Isopropenyl-2,3-butadien-1-ol (8j): Bp 120 °C (30 mmHg); 75%; IR (neat film) 3350 (s), 1968 (s), 1075 (s), 1016 (s), 900 (s), and 848 (s) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) δ =1.70 (s, 3 H), 2.20 (br s, 1 H), 4.50 (m, 1 H), and 4.65–5.28 (m, 5 H).

1-Phenyl-2,3-butadien-1-ol (8k): Bp 90 °C (1 mmHg); 60%; IR (neat film) 3350 (s), 1960 (s), 1450 (s), 1025 (s), 850 (s), and 700 (s) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) δ =2.20 (br s, 1 H), 4.85 (dd, J =1.8 and 5.6 Hz, 2 H), 5.30 (dt, J =3.4 and 1.8 Hz, 1 H), 5.45 (dt, J =3.4 and 5.6 Hz, 1 H), and 7.12–7.58 (m, 5 H).

2,3-Pentadien-1-ol (8l): Bp 110 °C (25 mmHg); 34%;

IR (neat film) 3325 (s), 1965 (m), 1420 (m), 1018 (s), and 875 (m) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) δ =1.70 (dd, J =2.0 and 4.0 Hz, 3 H), 2.83 (br s, 1 H), 4.08 (br, 2 H), and 4.90–5.50 (m, 2 H).

1-Methyl-2,3-pentadien-1-ol (8m): Bp 120 °C (50 mmHg); 33%; IR (neat film) 3350 (s), 2960 (s), 1965 (m), 1075 (s), and 870 (m) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) δ =1.26 (d, J =6.4 Hz, 3 H), 1.70 (m, 3 H), 3.20 (br s, 1 H), 4.26 (br q, J =6.4 Hz, 1 H), and 4.95–5.35 (m, 2 H).

1-*t*-Butyl-2,3-pentadien-1-ol (8n): Bp 110 °C (20 mmHg); 46%; IR (neat film) 3360 (s), 2970 (m), 1960 (m), 1070 (m), and 840 (m) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) δ =0.90 (s, 9 H), 1.65 (m, 3 H), 1.78 (br s, 1 H), 3.70 (m, 1 H), and 4.96–5.30 (m, 3 H).

1-Ethyl-4-methyl-2,3-pentadien-1-ol (8o): Bp 80 °C (25 mmHg); 80%; IR (neat film) 3350 (s), 2950 (m), 1975 (w), 1450 (m), 1010 (m), and 970 (m) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) δ =0.92 (t, J =6.4 Hz, 3 H), 1.50 (dt, J =6.0 and 6.4 Hz, 2 H), 1.73 (d, J =3.0 Hz, 6 H), 2.08 (br s, 1 H), 3.93 (q, J =6.0 Hz, 1 H), and 5.00 (dq, J =6.0 and 3.0 Hz, 1 H).

1-Vinyl-4-methyl-2,3-pentadien-1-ol (8p): Bp 130 °C (25 mmHg); 96%; IR (neat film) 3380 (s), 1970 (w), 1200 (s), 1108 (m), 990 (m), and 924 (m) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) δ =1.70 (d, J =2.0 Hz, 6 H), 1.80 (br s, 1 H), 4.53 (br t, J =5.0 Hz, 1 H), 5.03 (dq, J =5.0 and 2.0 Hz, 1 H), 5.18 (br d, J =16.4 Hz, 1 H), 5.30 (br d, J =10.0 Hz, 1 H), and 5.92 (ddd, J =5.0, 10.0, and 16.4 Hz, 1 H).

General Procedure for the Preparation of Ethyl 3,4-Pentadienoates 12a,b.²⁴⁾ Into a 200 ml two-necked round-bottom flask, containing a magnetic stirring bar, equipped with a Vigreux column (8×150 mm) distillation apparatus, were added propargyl alcohol (9.0 ml, 155 mmol) and either triethyl orthoacetate (**14a**, 60.0 ml, 327 mmol) or triethyl orthopropionate (**14b**, 65.8 ml, 327 mmol) via syringes through a septum cap. The mixture was heated to 100 °C under nitrogen and then propionic acid (0.2 ml, 2.7 mmol) was added. The mixture was stirred vigorously at 150–160 °C (oil bath temperature) over a period of ca. 2 h, during which the temperature was controlled carefully to maintain continuous distillation of ethanol (75–82 °C). After the distillation of ethanol had subsided, another aliquot of propargyl alcohol (9.0 ml, 155 mmol) was added carefully and the mixture was heated at the same temperature for an additional 1 h to draw off ethanol. Then, two or three portions of propionic acid (0.2 ml) were added into the mixture at 30 min intervals until no more ethanol distilled off. After allowing the mixture to cool to room temperature, 2 M HCl (10 ml) was added and the resultant mixture was extracted with ether (3×20 ml). The combined extracts were washed with sat. NaHCO_3 (30 ml), dried (magnesium sulfate), and filtered. Volatile organics were distilled off under atmospheric pressure and the residue was distilled by means of a Kugelrohr apparatus under reduced pressure.

Ethyl 3,4-Pentadienoate (13a): Bp 65 °C (21 mmHg); 70% yield; IR (neat film) 2989 (m), 1956 (m), 1739 (s), 1370 (m), 1300 (m), 1251 (s), 1161 (s), 1034 (s), and 850 (s) cm^{-1} ; $^1\text{H NMR}$ (CCl_4 , 60 MHz) δ =1.25 (t, J =7.4 Hz, 3 H), 3.03 (br d, J =7.0 Hz, 2 H), 4.12 (q, J =7.4 Hz, 2 H), 4.72 (br d, J =7.0 Hz, 2 H), and 5.20 (quint., J =7.0 Hz, 1 H).

Ethyl 2-Methyl-3,4-pentadienoate (13b): Bp 85

$^{\circ}\text{C}$ (43 mmHg); 70%; IR (neat film) 2980 (s), 1958 (s), 1735 (s), 1453 (m), 1250 (s), 1180 (s), 1080 (s), and 850 (s) cm^{-1} ; ^1H NMR (CCl_4 , 60 MHz) δ =1.20 (d, J =6.2 Hz, 3 H), 1.23 (t, J =8.0 Hz, 3 H), 3.00 (dtq, J =6.4, 3.2, and 6.2 Hz, 1 H), 4.08 (q, J =8.0 Hz, 2 H), 4.74 (dd, J =7.2 and 3.2 Hz, 2 H), and 5.27 (dt, J =6.4 and 7.2 Hz, 1 H).

General Procedure for the Preparation of 3,4-Pentadienyl Alcohols 12a—d: a) **Reduction with LiAlH_4 .** A 200 ml two-necked round-bottom flask, containing a stirring bar, fitted with a dropping funnel and a reflux condenser, was purged with nitrogen. Dry THF (30 ml) was added via a syringe and then lithium aluminum hydride (1.40 g, 37 mmol) was added under cooling in an ice bath. An appropriate ethyl 3,4-pentadienoate **13a** or **13b** (50 mmol) dissolved in dry THF (20 ml) was added via a dropping funnel at 0°C . The mixture was then stirred at room temperature for 1 h. The excess lithium aluminum hydride was destroyed by adding aqueous THF (THF:water=3:1 v/v) at 0°C until the gray slurry turned into white granules. After decantation, the residual solid was washed with ether (2×20 ml). The combined extracts were dried (magnesium sulfate), filtered, and concentrated by distillation under atmospheric pressure, and the residue was distilled by means of a Kugelrohr apparatus under reduced pressure to give either **12a** or **12b**.

b) **Grignard Reaction.** Into a nitrogen-purged 200 ml two-necked round-bottom flask, containing a magnetic stirring bar and magnesium turnings (3.04 g, 125 mmol), equipped with a dropping funnel and a reflux condenser, were added successively dry ether (50 ml) and freshly distilled methyl iodide (8.6 ml, 138 mmol) over a period of 1 h at room temperature. The mixture was stirred for an additional 2 h at the same temperature. After allowing the mixture to cool to 0°C , either **13a** or **13b** (50 mmol) dissolved in dry ether (15 ml) was added through the dropping funnel over a period of 1 h and the mixture was refluxed for 2 h. Under cooling in an ice bath, sat. NH_4Cl (100 ml) was added slowly and the resultant mixture was extracted with ether (3×20 ml). The combined extracts were dried (magnesium sulfate), filtered, and concentrated by distillation under atmospheric pressure. The residue was distilled under reduced pressure by means of a Kugelrohr apparatus to give **12c** or **12d**.

3,4-Pentadien-1-ol (12a): Bp 80°C (58 mmHg); 86%; IR (neat film) 3330 (s), 1955 (s), 1430 (m), 1048 (s), and 842 (s) cm^{-1} ; ^1H NMR (CCl_4 , 60 MHz) δ =1.73 (br s, 1 H), 2.34 (br dt, J =6.4 and 6.2 Hz, 2 H), 3.60 (t, J =6.2 Hz, 2 H), 4.70 (br d, J =6.0 Hz, 2 H), and 5.06 (tt, J =6.0 and 6.4 Hz, 1 H).

2-Methyl-3,4-pentadien-1-ol (12b): Bp 95°C (26 mmHg); 75%; IR (neat film) 3325 (s), 2960 (s), 1952 (s), 1453 (m), 1031 (s), and 840 (s) cm^{-1} ; ^1H NMR (CCl_4 , 60 MHz) δ =1.02 (d, J =6.4 Hz, 3 H), 2.30 (dtq, J =8.0, 6.8, and 6.4 Hz, 1 H), 3.31 (br s, 1 H), 3.43 (d, J =6.8 Hz, 2 H), 4.68 (dd, J =3.0 and 6.0 Hz, 2 H), and 5.10 (dt, J =8.0 and 6.0 Hz, 1 H).

1,1-Dimethyl-3,4-pentadien-2-ol (12c): Bp 80°C (21 mmHg); 78%; IR (neat film) 3356 (s), 2964 (s), 1959 (s), 1468 (m), 1365 (m), 1144 (s), and 839 (s) cm^{-1} ; ^1H NMR (CCl_4 , 60 MHz) δ =1.25 (s, 6 H), 1.77 (br s, 1 H), 2.18 (dt, J =8.0 and 2.2 Hz, 2 H), 4.73 (dt, J =5.8 and 2.2 Hz, 2 H), and 5.15 (tt, J =5.8 and 8.0 Hz, 1 H).

1,1,2-Trimethyl-3,4-pentadien-1-ol (12d): Bp 90°C (24 mmHg), 86%; IR (neat film) 3391 (s), 2983 (s), 1961 (s), 1461 (m), 1371 (s), 1151 (s), 1131 (s), 943 (s), and 834 (s) cm^{-1} ; ^1H NMR (CCl_4 , 60 MHz) δ =1.04 (d, J =7.0 Hz, 3 H), 1.20 (s, 6 H), 1.65 (br s, 1 H), 2.23 (dtq, J =5.4, 2.4, and 7.0 Hz, 1 H), 4.68 (dd, J =2.4 and 6.2 Hz, 2 H), and 5.16 (dt, J =5.4 and 6.2 Hz, 1 H).

General Procedure for the Preparation of 2,3-Butadienyl and 3,4-Pentadienyl Tosylcarbamates (1 and 3, R=Ts). To a solution of an allenyl alcohol **8** or **12** (10 mmol) and triethylamine (1.4 ml, 10 mmol) in dry ether (20 ml) was added *p*-toluenesulfonyl isocyanate (2.0 g, 10 mmol) via a syringe at 0°C under nitrogen. The reaction mixture was stirred at room temperature for 2 h. The mixture was then washed with water (2×20 ml) and the combined aqueous extracts were acidified with 2 M HCl (5 ml) and extracted with ethyl acetate (2×20 ml). The organic extracts were dried (magnesium sulfate), filtered, evaporated, and subjected to column chromatography over silica gel (eluent; hexane:ethyl acetate=4:1) to give **1** or **3** in 80–90% yields. Compounds **1g–k** and **1p** were unstable and were isolated as triethylamine salts by evaporating water from the above aqueous extracts and were used for the aminocyclization without purification. Trifluoromethanesulfonyl carbamate **1q** was prepared in a similar way using trifluoromethanesulfonyl isocyanate²⁵ in place of *p*-toluenesulfonyl isocyanate.

2,3-Butadienyl Tosylcarbamate (1a): IR (neat film) 3250 (s), 1960 (m), 1750 (s), 1600 (m), 1450 (s), 1350 (s), 1220 (s), 1160 (s), 1090 (s), 850 (s), and 650 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 60 MHz) δ =2.40 (s, 3 H), 4.60 (br d, J =7.0 Hz, 2 H), 4.86 (br d, J =6.0 Hz, 2 H), 5.08 (tt, J =6.0 and 7.0 Hz, 1 H), 7.26 (d, J =8.2 Hz, 2 H), and 7.90 (d, J =8.2 Hz, 2 H).

1-Methyl-2,3-butadienyl Tosylcarbamate (1b): IR (neat film) 3250 (s), 1960 (s), 1750 (s), 1600 (m), 1440 (s), 1350 (s), 1220 (s), 1160 (s), 858 (m), 820 (m), 760 (s), and 650 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 60 MHz) δ =1.30 (d, J =6.0 Hz, 3 H), 2.45 (s, 3 H), 4.70–4.93 (m, 2 H), 5.02–5.40 (m, 2 H), 7.31 (d, J =8.4 Hz, 2 H), 7.73 (br s, 1 H), and 7.90 (d, J =8.4 Hz, 2 H).

1-Ethyl-2,3-butadienyl Tosylcarbamate (1c): IR (neat film) 3250 (s), 2950 (m), 1955 (m), 1740 (s), 1600 (m), 1450 (s), 1350 (s), 1220 (s), 1160 (s), 850 (m), and 760 (m) cm^{-1} ; ^1H NMR (CDCl_3 , 60 MHz) δ =0.80 (t, J =7.0 Hz, 3 H), 1.60 (br q, J =7.0 Hz, 2 H), 2.40 (s, 3 H), 4.65–5.10 (m, 4 H), 7.25 (d, J =8.0 Hz, 2 H), and 7.90 (d, J =8.0 Hz, 2 H).

1-Propyl-2,3-butadienyl Tosylcarbamate (1d): IR (neat film) 3240 (m), 2940 (m), 1950 (w), 1730 (s), 1590 (m), 1440 (m), 1340 (m), 1160 (s), 840 (m), and 650 (m) cm^{-1} ; ^1H NMR (CDCl_3 , 60 MHz) δ =0.94 (t, J =6.4 Hz, 3 H), 1.23–1.80 (m, 4 H), 2.40 (s, 3 H), 4.73–5.30 (m, 4 H), 7.30 (d, J =8.0 Hz, 2 H), and 7.85 (d, J =8.0 Hz, 2 H).

1-Isopropyl-2,3-butadienyl Tosylcarbamate (1e): IR (neat film) 3250 (s), 2970 (m), 1960 (w), 1750 (s), 1610 (m), 1450 (s), 1360 (s), 1230 (s), 1170 (s), 860 (s), and 660 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 60 MHz) δ =0.90 (d, J =6.4 Hz, 6 H), 1.80 (m, 1 H), 2.45 (s, 3 H), 4.55–5.00 (m, 4 H), 7.32 (d, J =8.0 Hz, 2 H), and 7.90 (d, J =8.0 Hz, 2 H).

1-*t*-Butyl-2,3-butadienyl Tosylcarbamate (1f): IR (neat film) 3250 (s), 2960 (s), 1960 (m), 1750 (s), 1600 (m), 1450 (s), 1360 (s), 1170 (s), 1100 (s), 870 (m), and 650 (m)

cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 60 MHz) δ =0.90 (s, 9 H), 2.45 (s, 3 H), 4.60–5.10 (m, 4 H), 7.25 (d, J =8.0 Hz, 2 H), and 7.95 (d, J =8.0 Hz, 2 H).

2,3-Pentadienyl Tosylcarbamate (1l): IR (neat film) 3260 (s), 2950 (w), 1960 (m), 1740 (s), 1600 (m), 1450 (s), 1350 (s), 1220 (s), 1160 (s), 850 (m), and 650 (m) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 60 MHz) δ =1.61 (dd, J =4.0 and 6.4 Hz, 3 H), 2.44 (s, 3 H), 4.28 (m, 2 H), 4.88–5.42 (m, 2 H), 7.35 (d, J =8.1 Hz, 2 H), 7.94 (d, J =8.1 Hz, 2 H), and 8.00 (br s, 1 H).

1-Methyl-2,3-pentadienyl Tosylcarbamate (1m): IR (neat film) 3300 (m), 2960 (w), 1960 (w), 1740 (s), 1600 (m), 1450 (m), 1350 (m), 1220 (m), 1160 (m), and 650 (m) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ =1.27 (d, J =6.2 Hz, 3 H, minor isomer), 1.28 (d, J =6.2 Hz, 3 H, major isomer), 1.60 (d, J =7.0 Hz, 3 H, major isomer), 1.61 (d, J =7.0 Hz, 3 H, minor isomer), 2.44 (s, 3 H), 5.12 (br q, J =6.2 Hz, 1 H), 5.16–5.27 (m, 2 H), 7.34 (d, J =8.4 Hz, 2 H), 7.50 (br s, 1 H), and 7.90 (d, J =8.4 Hz, 2 H).

1-*t*-Butyl-2,3-pentadienyl Tosylcarbamate (1n): IR (neat film) 3240 (s), 2850 (s), 1970 (w), 1740 (s), 1600 (m), 1440 (s), 1350 (s), 1170 (m), 1090 (s), 860 (s), and 650 (m) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ =0.85 (s, 9 H, minor isomer), 0.86 (s, 9 H, major isomer), 1.51 (dd, J =4.0 and 6.8 Hz, 3 H, major isomer), 1.53 (dd, J =4.0 and 6.8 Hz, 3 H, minor isomer), 2.44 (s, 3 H), 4.81 (br d, J =7.3 Hz, 1 H, minor isomer), 4.83 (br d, J =7.3 Hz, 1 H, major isomer), 4.92 (m, 1 H), 5.00 (br q, J =6.8 Hz, 1 H, minor isomer), 5.11 (br q, J =6.8 Hz, 1 H, major isomer), 7.33 (d, J =8.0 Hz, 2 H), and 7.92 (d, J =8.0 Hz, 2 H).

1-Ethyl-4-methyl-2,3-pentadienyl Tosylcarbamate (1o): IR (neat film) 3200 (s), 2950 (m), 1730 (s), 1600 (w), 1450 (s), 1370 (s), 1240 (s), 1170 (s), 910 (s), 870 (s), and 650 (m) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 60 MHz) δ =0.85 (t, J =7.0 Hz, 3 H), 1.40 (br q, J =7.0 Hz, 2 H), 1.65 (s, 3 H), 1.70 (s, 3 H), 2.40 (s, 3 H), 4.60–5.00 (m, 2 H), 7.20 (d, J =8.0 Hz, 2 H), 7.50 (br s, 1 H), and 7.95 (d, J =8.0 Hz, 2 H).

1-Ethyl-2,3-butadienyl Trifluoromethanesulfonylcarbamate (1q): IR (neat film) 3200 (m), 1958 (m), 1750 (s), 1460 (s), 1400 (s), 1215 (s), 1142 (s), 1050 (m), and 860 (s) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 60 MHz) δ =0.95 (t, J =7.0 Hz, 3 H), 1.68 (br q, J =7.0 Hz, 2 H), 4.68–5.05 (m, 2 H), and 5.05–5.40 (m, 2 H).

3,4-Pentadienyl Tosylcarbamate (3a): IR (neat film) 3250 (m), 1960 (m), 1750 (s), 1600 (w), 1450 (s), 1350 (s), 1240 (s), 1160 (s), and 860 (m) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 60 MHz) δ =2.30 (dt, J =3.8 and 6.4 Hz, 2 H), 2.40 (s, 3 H), 4.15 (t, J =6.4 Hz, 2 H), 4.55–5.20 (m, 3 H), 7.30 (d, J =8.0 Hz, 2 H), and 7.95 (d, J =8.0 Hz, 2 H).

2-Methyl-3,4-pentadienyl Tosylcarbamate (3b): IR (neat film) 3217 (s), 1945 (m), 1742 (s), 1587 (m), 1437 (s), 1339 (s), 1213 (s), 1152 (s), 1081 (s), 947 (m), 849 (s), 750 (m), and 688 (m) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 60 MHz) δ =1.02 (d, J =7.0 Hz, 3 H), 2.43 (s, 3 H), 2.50 (br tq, J =6.4 and 7.0 Hz, 1 H), 3.97 (d, J =6.4 Hz, 2 H), 4.60 (br d, J =6.0 Hz, 2 H), 4.90 (br t, J =6.0 Hz, 1 H), 7.28 (d, J =8.4 Hz, 2 H), 7.88 (d, J =8.4 Hz, 2 H), and 7.84 (br s, 1 H).

1,1-Dimethyl-3,4-pentadienyl Tosylcarbamate (3c): IR (neat film) 3246 (s), 1956 (m), 1746 (s), 1601 (m), 1436 (s), 1348 (s), 1214 (s), 1167 (s), 1056 (s), 914 (s), 836 (s), and 737 (s) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 60 MHz) δ =1.38

(s, 6 H), 2.31 (dt, J =8.0 and 2.2 Hz, 2 H), 2.43 (s, 3 H), 4.60 (dt, J =5.8 and 2.2 Hz, 2 H), 5.88 (tt, J =5.8 and 8.0 Hz, 1 H), 7.26 (d, J =8.2 Hz, 2 H), 7.35 (br s, 1 H), and 7.84 (d, J =8.2 Hz, 2 H).

1,1,2-Trimethyl-3,4-pentadienyl Tosylcarbamate (3d): IR (neat film) 3250 (s), 2992 (s), 1957 (m), 1745 (s), 1600 (m), 1438 (s), 1350 (s), 1230 (s), 1169 (s), 1130 (s), 1091 (s), 818 (s), 734 (s), and 659 (s) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 60 MHz) δ =0.92 (d, J =7.0 Hz, 3 H), 1.38 (s, 6 H), 2.43 (s, 3 H), 3.73 (dq, J =7.6 and 7.0 Hz, 1 H), 4.68 (br d, J =6.0 Hz, 2 H), 4.92 (dt, J =7.6 and 6.0 Hz, 1 H), 7.33 (d, J =8.2 Hz, 2 H), 7.62 (br s, 1 H), and 7.90 (d, J =8.2 Hz, 2 H).

1-Ethyl-2,3-butadienyl Phenylcarbamate (1t): To a solution of 1-ethyl-2,3-butadien-1-ol **8c** (196.3 mg, 2 mmol) and triethylamine (280 μl , 2 mmol) in ether (20 ml) was added phenyl isocyanate (238.2 mg, 2 mmol) via a syringe at 0 °C under nitrogen. The reaction mixture was stirred at room temperature for 6 h. After the addition of 2 M HCl (10 ml), the reaction mixture was extracted with ethyl acetate (2 $\times$ 20 ml). The combined organic extracts were washed with sat. NaCl (20 ml), dried (magnesium sulfate), filtered, and concentrated. The residue was purified by means of column chromatography over silica gel (eluent; benzene) to give **1t** in an 80% yield. IR (neat film) 3360 (s), 2970 (m), 1960 (m), 1710 (s), 1610 (s), 1540 (s), 1440 (s), 1230 (s), 1045 (s), 850 (m), 750 (m), and 690 (s) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 60 MHz) δ =0.98 (t, J =6.4 Hz, 3 H), 1.78 (br q, J =6.4 Hz, 2 H), 4.70–5.50 (m, 4 H), 6.78 (br s, 1 H), and 6.90–7.58 (m, 5 H).

General Procedure for the Preparation of *N*-Acetyl (1r), *N*-Benzoyl (1s), and *N*-Benzyl Derivatives (1u) of 2,3-Butadienyl Carbamates. A 200 ml two-necked round-bottom flask, containing a magnetic stirring bar and silver isocyanate (2.25 g, 15 mmol), was fitted with a dropping funnel and a reflux condenser equipped at the top with a three-way stopcock connected with a balloon filled with nitrogen. The apparatus was purged with nitrogen. Dry ether (40 ml) and acetyl chloride (1.1 ml, 15 mmol), or benzoyl chloride (1.7 ml, 15 mmol), or benzyl bromide (1.8 ml, 15 mmol) were introduced into the flask via syringes. The heterogeneous mixture was stirred and refluxed for 2 h. After allowing the mixture to cool to room temperature, a solution of an appropriate derivative of 2,3-butadienyl alcohol (15 mmol) and triethylamine (2 ml, 15 mmol) in ether (20 ml) was added over a 30 min period via the dropping funnel. The reaction mixture was stirred for 3 h at ambient temperature and then filtered with suction through a celite pad on a glass filter. The filter cake was washed with ethyl acetate (2 $\times$ 20 ml) and the filtrates were concentrated on a rotary evaporator. The residue was subjected to column chromatography over silica gel (eluent; benzene). 1-Vinyl-2,3-butadienyl benzoylcarbamate (**1s**) was unstable and decomposed during purification by column chromatography, hence, it was prepared prior to use and applied for the aminocyclization reaction without purification (Run 6, Table 2).

1-Ethyl-2,3-butadienyl Acetylcarbamate (1r): 38%; IR (neat film) 3300 (s), 2950 (s), 1960 (s), 1770 (s), 1710 (s), 1510 (s), 1210 (s), 1080 (m), and 850 (m) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 60 MHz) δ =0.95 (t, J =6.4 Hz, 3 H), 1.70 (br q, J =6.4 Hz, 2 H), 2.45 (s, 3 H), 4.75–5.35 (m, 4 H),

and 7.55 (br s, 1 H).

1-Ethyl-2,3-butadienyl Benzylcarbamate (1u): 23%; IR (neat film) 3350 (s), 2950 (s), 1960 (s), 1710 (s), 1520 (s), 1460 (s), 1250 (s), 1140 (m), 850 (m), and 700 (m) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 60 MHz) δ =0.95 (t, J =7.0 Hz, 3 H), 1.70 (br q, J =7.0 Hz, 2 H), 4.40 (d, J =6.0 Hz, 2 H), 4.75–5.40 (m, 4 H), and 7.35 (s, 5 H).

General Procedure for the Ag(I)-Catalyzed Aminocyclization of Allenyl Carbamates 1 and 3 (Run 1 in Table 1 as a typical example): A 25 ml two-necked round-bottom flask, containing a magnetic stirring bar, **1a** (267.2 mg, 1 mmol), and AgNCO (15.0 mg, 0.1 mmol), was fitted with a septum cap and a reflux condenser equipped at the top with a three-way stopcock connected with a nitrogen balloon. The apparatus was purged with nitrogen by pumping and filling several times via the three-way stopcock. Dry benzene (6 ml) and triethylamine (14 μl , 0.1 mmol) were added via syringes. The reaction mixture was stirred at 50 $^\circ\text{C}$ for 6 h. The reaction was monitored with thin-layer chromatography (Merck Kiesel-gel 60F₂₅₄, R_f (**1a**)=0.45, R_f (**2a**)=0.67, hexane–ethyl acetate, 1/1 vol.). After addition of sat. NaHCO_3 (20 ml), the reaction mixture was extracted with ethyl acetate (2 $\times$ 20 ml). The combined extracts were dried (magnesium sulfate), filtered, and concentrated. The residue was purified by means of column chromatography over silica gel (eluent; benzene) to give *N-p*-toluenesulfonyl-4-vinyl-2-oxazolidinone (**2a**) as a solid in a 78% yield.

***N-p*-Toluenesulfonyl-4-vinyl-2-oxazolidinone (2a):** Mp 80.5–81.9 $^\circ\text{C}$ (benzene–hexane); IR (KBr disk) 2980 (w), 1790 (s), 1600 (m), 1380 (s), 1180 (s), 920 (m), 820 (m), 740 (w), and 660 (m) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ =2.45 (s, 3 H), 4.04 (dd, J =4.0 and 8.8 Hz, 1 H), 4.49 (dd, J =8.4 and 8.8 Hz, 1 H), 4.90 (dt, J =4.0 and 8.4 Hz, 1 H), 5.38 (d, J =9.9 Hz, 1 H), 5.47 (d, J =17.2 Hz, 1 H), 5.82 (ddd, J =8.4, 9.9, and 17.2 Hz, 1 H), 7.34 (d, J =8.4 Hz, 2 H), and 7.92 (d, J =8.4 Hz, 2 H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ =21.7, 59.5, 68.1, 120.7, 128.7, 129.6, 133.7, 135.1, 145.6, and 151.8. Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{NO}_4\text{S}$: C, 53.9; H, 4.90; N, 5.24; S, 12.00%. Found: C, 53.77; H, 4.89; N, 5.26; S, 11.89%.

***N-p*-Toluenesulfonyl-5-methyl-4-vinyl-2-oxazolidinone (2b):**

***trans*-Isomer:** Mp 91.0–91.2 $^\circ\text{C}$ (benzene–hexane); IR (KBr disk) 2985 (w), 1790 (s), 1600 (m), 1370 (s), 1180 (s), 910 (m), 740 (m), and 650 (m) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ =1.41 (d, J =6.6 Hz, 3 H), 2.44 (s, 3 H), 4.26 (dq, J =4.8 and 6.6 Hz, 1 H), 4.37 (dd, J =4.8 and 8.4 Hz, 1 H), 5.38 (d, J =10.3 Hz, 1 H), 5.45 (d, J =16.9 Hz, 1 H), 5.81 (ddd, J =8.4, 10.3, and 16.9 Hz, 1 H), 7.32 (d, J =8.4 Hz, 2 H), and 7.95 (d, J =8.4 Hz, 2 H).

***cis*-Isomer:** $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ =1.27 (d, J =6.2 Hz, 3 H), 2.44 (s, 3 H), 4.80 (dq, J =7.0 and 6.2 Hz, 1 H), 4.84 (dd, J =7.0 and 8.4 Hz, 1 H), 5.43 (d, J =9.9 Hz, 1 H), 5.47 (d, J =16.9 Hz, 1 H), 5.62 (ddd, J =8.4, 9.9, and 16.9 Hz, 1 H), 7.35 (d, J =8.4 Hz, 2 H), and 7.97 (d, J =8.4 Hz, 2 H). Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_4\text{S}$: C, 55.50; H, 5.37; N, 4.98; S, 11.40%. Found: C, 55.76; H, 5.32; N, 4.92; S, 11.48%.

***N-p*-Toluenesulfonyl-5-ethyl-4-vinyl-2-oxazolidinone (2c):**

***trans*-Isomer:** Mp 55.5–57.0 $^\circ\text{C}$ (benzene–hexane); IR (KBr disk) 2950 (m), 1790 (s), 1600 (w), 1370 (s), 1180

(s), 920 (m), 760 (m), and 650 (m) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ =0.97 (t, J =7.3 Hz, 3 H), 1.52 (br dq, J =5.9 and 7.3 Hz, 2 H), 2.44 (s, 3 H), 4.09 (br dt, J =4.4 and 5.9 Hz, 1 H), 4.48 (dd, J =4.4 and 8.4 Hz, 1 H), 5.37 (d, J =9.9 Hz, 1 H), 5.45 (d, J =17.2 Hz, 1 H), 5.80 (ddd, J =8.4, 9.9, and 17.2 Hz, 1 H), 7.31 (d, J =8.4 Hz, 2 H), and 7.91 (d, J =8.4 Hz, 2 H).

***cis*-Isomer:** $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ =0.96 (t, J =7.3 Hz, 3 H), 1.72 (br dq, J =5.9 and 7.3 Hz, 2 H), 2.43 (s, 3 H), 4.51 (br dt, J =7.0 and 5.9 Hz, 1 H), 4.86 (dd, J =7.0 and 8.8 Hz, 1 H), 5.43 (d, J =9.9 Hz, 1 H), 5.47 (br d, J =16.9 Hz, 1 H), 5.59 (ddd, J =8.8, 9.9, and 16.9 Hz, 1 H), 7.30 (d, J =8.4 Hz, 2 H), and 7.92 (d, J =8.4 Hz, 2 H). Anal. Calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_4\text{S}$: C, 56.93; H, 5.80; N, 4.74; S, 10.89%. Found: C, 56.96; H, 5.67; N, 4.73; S, 10.82%.

***N-p*-Toluenesulfonyl-5-propyl-4-vinyl-2-oxazolidinone (2d):**

***trans*-Isomer:** Mp 131.5–133.0 $^\circ\text{C}$ (benzene–hexane); IR (KBr disk) 2940 (m), 1780 (s), 1595 (m), 1360 (m), 1170 (m), 810 (m), and 650 (m) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ =0.94 (t, J =7.3 Hz, 3 H), 1.42 (tq, J =5.9 and 7.3 Hz, 2 H), 1.65 (m, 2 H), 2.45 (s, 3 H), 4.14 (br d, J =4.4 Hz, 1 H), 4.45 (dd, J =4.4 and 8.1 Hz, 1 H), 5.37 (d, J =10.3 Hz, 1 H), 5.44 (d, J =16.9 Hz, 1 H), 5.80 (ddd, J =8.1, 10.3, and 16.9 Hz, 1 H), 7.33 (d, J =8.2 Hz, 2 H), and 7.93 (d, J =8.2 Hz, 2 H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ =13.6, 17.7, 21.7, 35.8, 64.7, 80.1, 120.4, 128.6, 129.7, 134.1, 135.2, 145.5, and 151.5.

***cis*-Isomer:** $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ =0.92 (t, J =7.3 Hz, 3 H), 1.43 (m, 2 H), 1.66 (m, 2 H), 2.43 (s, 3 H), 4.59 (br d, J =7.0 Hz, 1 H), 4.83 (dd, J =7.0 and 9.0 Hz, 1 H), 5.42 (d, J =10.2 Hz, 1 H), 5.45 (d, J =17.2 Hz, 1 H), 5.61 (ddd, J =9.0, 10.2, and 17.2 Hz, 1 H), 7.31 (d, J =8.1 Hz, 2 H), and 7.91 (d, J =8.1 Hz, 2 H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ =13.6, 18.6, 21.7, 31.6, 63.7, 79.1, 122.5, 128.9, 129.5, 130.0, 135.4, 145.4, and 151.6. Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_4\text{S}$: C, 58.23; H, 6.19; N, 4.53; S, 10.36%. Found: C, 58.21; H, 6.19; N, 4.56; S, 10.28%.

***trans-N-p*-Toluenesulfonyl-5-isopropyl-4-vinyl-2-oxazolidinone (2e):** Mp 84.5–85.2 $^\circ\text{C}$ (benzene–hexane); IR (KBr disk) 2970 (m), 1790 (s), 1600 (w), 1370 (s), 1180 (s), 910 (m), 730 (s), and 650 (m) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ =0.95 (d, J =6.6 Hz, 3 H), 0.96 (d, J =6.6 Hz, 3 H), 1.91 (dq, J =6.4 and 6.6 Hz, 1 H), 2.45 (s, 3 H), 3.93 (dd, J =3.8 and 6.4 Hz, 1 H), 4.61 (dd, J =3.8 and 8.1 Hz, 1 H), 5.36 (d, J =10.3 Hz, 1 H), 5.45 (d, J =16.9 Hz, 1 H), 5.78 (ddd, J =8.1, 10.3, and 16.9 Hz, 1 H), 7.33 (d, J =8.2 Hz, 2 H), and 7.91 (d, J =8.2 Hz, 2 H). Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_4\text{S}$: C, 58.23; H, 6.19; N, 4.53; S, 10.36%. Found: C, 58.29; H, 6.10; N, 4.57; S, 10.27%.

***trans-N-p*-Toluenesulfonyl-5-*t*-butyl-4-vinyl-2-oxazolidinone (2f):** Mp 98.4–99.0 $^\circ\text{C}$ (benzene–hexane); IR (KBr disk) 2960 (m), 1790 (s), 1580 (m), 1370 (s), 1220 (s), 1140 (s), 860 (m), and 710 (m) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ =0.92 (s, 9 H), 2.44 (s, 3 H), 3.85 (d, J =3.7 Hz, 1 H), 4.69 (dd, J =3.7 and 6.4 Hz, 1 H), 5.36 (d, J =10.3 Hz, 1 H), 5.45 (d, J =16.9 Hz, 1 H), 5.79 (ddd, J =6.4, 10.3, and 16.9 Hz, 1 H), 7.32 (d, J =8.4 Hz, 2 H), and 7.92 (d, J =8.4 Hz, 2 H). Anal. Calcd for $\text{C}_{16}\text{H}_{21}\text{NO}_4\text{S}$: C, 59.42; H, 6.54; N, 4.33; S, 9.92%. Found: C, 59.41; H, 6.45; N, 4.37; S, 9.84%.

***N-p*-Toluenesulfonyl-5,5-dimethyl-4-vinyl-2-ox-**

azolidinone (2g): Mp 121.2–122.0 °C (benzene–hexane); IR (KBr disk) 1780 (s), 1600 (w), 1370 (s), 1318 (s), 1180 (s), 1128 (s), 930 (m), 808 (m), and 678 (m) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ =1.29 (s, 3 H), 1.47 (s, 3 H), 2.45 (s, 3 H), 4.44 (d, J =8.0 Hz, 1 H), 5.41 (d, J =10.3 Hz, 1 H), 5.42 (d, J =16.9 Hz, 1 H), 5.69 (ddd, J =8.0, 10.3, and 16.9 Hz, 1 H), 7.33 (d, J =8.2 Hz, 2 H), and 7.92 (d, J =8.2 Hz, 2 H). Anal. Calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_4\text{S}$: C, 56.93; H, 5.80; N, 4.74; S, 10.86%. Found: C, 56.87; H, 5.75; N, 4.70; S, 10.92%.

***N-p*-Toluenesulfonyl-4,5-divinyl-2-oxazolidinone (2h):**

***trans*-Isomer:** Mp 156.5–158.0 °C (benzene–hexane); IR (KBr disk) 1780 (s), 1598 (m), 1360 (s), 1174 (s), 935 (m), 818 (m), 750 (m), and 650 (m) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ =2.45 (s, 3 H), 4.53 (dd, J =4.4 and 8.1 Hz, 1 H), 4.54 (dd, J =4.4 and 6.2 Hz, 1 H), 5.36 (d, J =10.3 Hz, 1 H), 5.39 (d, J =17.1 Hz, 1 H), 5.41 (d, J =10.3 Hz, 1 H), 5.46 (d, J =17.1 Hz, 1 H), 5.84 (ddd, J =6.2, 10.3, and 17.1 Hz, 1 H), 5.86 (ddd, J =8.1, 10.3, and 17.1 Hz, 1 H), 7.33 (d, J =8.4 Hz, 2 H), and 7.91 (d, J =8.4 Hz, 2 H).

***cis*-Isomer:** ^1H NMR (CDCl_3 , 400 MHz) δ =2.44 (s, 3 H), 4.93 (dd, J =7.3 and 8.8 Hz, 1 H), 5.08 (dd, J =6.6 and 7.3 Hz, 1 H), 5.39 (br d, J =17.0 Hz, 1 H), 5.41 (br d, J =10.4 Hz, 1 H), 5.44 (br d, J =10.4 Hz, 1 H), 5.45 (br d, J =17.0 Hz, 1 H), 5.57 (ddd, J =8.8, 10.4, and 17.0 Hz, 1 H), 5.66 (ddd, J =6.6, 10.4, and 17.0 Hz, 1 H), 7.34 (d, J =8.4 Hz, 2 H), and 7.94 (d, J =8.4 Hz, 2 H). Anal. Calcd for $\text{C}_{14}\text{H}_{15}\text{NO}_4\text{S}$: C, 57.32; H, 5.15; N, 4.77; S, 10.93%. Found: C, 57.13; H, 5.07; N, 4.69; S, 10.77%.

***N-p*-Toluenesulfonyl-5-(*trans*-1-propenyl)-4-vinyl-2-oxazolidinone (2i):**

***trans*-Isomer:** Mp 183.5–184.4 °C (benzene–hexane); IR (KBr disk) 1780 (s), 1670 (m), 1600 (m), 1360 (s), 1180 (s), 1090 (s), 940 (s), 820 (s), and 650 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ =1.74 (dd, J =1.5 and 6.6 Hz, 3 H), 2.45 (s, 3 H), 4.47 (dd, J =4.8 and 7.0 Hz, 1 H), 4.50 (dd, J =4.8 and 7.0 Hz, 1 H), 5.38 (d, J =10.3 Hz, 1 H), 5.42 (d, J =16.9 Hz, 1 H), 5.47 (ddq, J =7.0, 16.0, and 1.5 Hz, 1 H), 5.81 (ddq, J =7.0, 10.3, and 16.9 Hz, 1 H), 5.85 (dq, J =16.0 and 6.6 Hz, 1 H), 7.35 (d, J =8.4 Hz, 2 H), and 7.91 (d, J =8.4 Hz, 2 H).

***cis*-Isomer:** ^1H NMR (CDCl_3 , 400 MHz) δ =1.74 (dd, J =1.1 and 6.6 Hz, 3 H), 2.44 (s, 3 H), 4.85 (dd, J =7.3 and 8.8 Hz, 1 H), 5.02 (dd, J =7.3 and 8.4 Hz, 1 H), 5.34 (ddq, J =8.4, 15.4, and 1.1 Hz, 1 H), 5.41 (dd, J =0.7 and 9.9 Hz, 1 H), 5.42 (dd, J =0.7 and 16.9 Hz, 1 H), 5.60 (ddd, J =8.8, 9.9, and 16.9 Hz, 1 H), 5.90 (dq, J =15.4 and 6.6 Hz, 1 H), 7.32 (d, J =8.3 Hz, 2 H), and 7.92 (d, J =8.3 Hz, 2 H). Anal. Calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_4\text{S}$: C, 58.61; H, 5.57; N, 4.56; S, 10.43%. Found: C, 58.46; H, 5.47; N, 4.48; S, 10.60%.

***trans-N-p*-Toluenesulfonyl-5-isopropenyl-4-vinyl-2-oxazolidinone (2j):** Mp 92.0–93.4 °C (benzene–hexane); IR (KBr disk) 1780 (s), 1600 (m), 1375 (s), 1290 (s), 1180 (s), 1065 (s), 818 (m), and 650 (m) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ =1.72 (s, 3 H), 2.44 (s, 3 H), 4.51 (d, J =4.2 Hz, 1 H), 4.57 (dd, J =4.2 and 8.2 Hz, 1 H), 5.00 (br s, 1 H), 5.02 (br s, 1 H), 5.40 (d, J =10.3 Hz, 1 H), 5.48 (d, J =17.1 Hz, 1 H), 5.86 (ddd, J =8.2, 10.3, and 17.1 Hz, 1 H), 7.32 (d, J =8.4 Hz, 2 H), and 7.92 (d, J =8.4 Hz, 2 H). Anal. Calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_4\text{S}$: C, 58.62; H, 5.57; N, 4.56; S, 10.43%. Found: C, 58.60; H, 5.47; N, 4.54; S, 10.35%.

***trans-N-p*-Toluenesulfonyl-5-phenyl-4-vinyl-2-ox-**

azolidinone (2k): Mp 94.5–96.0 °C (benzene–hexane); IR (KBr disk) 3050 (w), 1790 (s), 1600 (m), 1380 (s), 1180 (s), 910 (m), 730 (m), and 650 (m) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ =2.46 (s, 3 H), 4.69 (dd, J =4.8 and 8.4 Hz, 1 H), 5.10 (d, J =4.8 Hz, 1 H), 5.43 (d, J =16.9 Hz, 1 H), 5.45 (d, J =10.3 Hz, 1 H), 5.95 (ddd, J =8.4, 10.3, and 16.9 Hz, 1 H), 7.33 (d, J =8.4 Hz, 2 H), 7.37 (m, 5 H), and 7.90 (d, J =8.4 Hz, 2 H). Anal. Calcd for $\text{C}_{18}\text{H}_{17}\text{NO}_4\text{S}$: C, 62.96; H, 4.99; N, 4.08; S, 9.34%. Found: C, 62.93; H, 5.00; N, 4.10; S, 9.58%.

***N-p*-Toluenesulfonyl-4-(*trans*-1-propenyl)-2-ox-**

azolidinone (2l): Mp 138.0–140.6 °C (benzene–hexane); IR (KBr disk) 2980 (w), 1790 (s), 1600 (m), 1380 (s), 1180 (s), 910 (m), 820 (m), and 650 (m) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ =1.74 (dd, J =1.5 and 6.6 Hz, 3 H), 2.44 (s, 3 H), 4.01 (dd, J =3.6 and 8.8 Hz, 1 H), 4.46 (dd, J =8.4 and 8.8 Hz, 1 H), 4.88 (dt, J =3.6 and 8.4 Hz, 1 H), 5.38 (ddq, J =8.4, 14.7, and 1.5 Hz, 1 H), 5.92 (dq, J =14.7 and 6.6 Hz, 1 H), 7.32 (d, J =8.3 Hz, 2 H), and 7.89 (d, J =8.3 Hz, 2 H). Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_4\text{S}$: C, 55.50; H, 5.37; N, 4.98; S, 11.40%. Found: C, 55.49; H, 5.30; N, 4.99; S, 11.49%.

***trans-N-p*-Toluenesulfonyl-5-methyl-4-(*trans*-1-**

propenyl)-2-oxazolidinone (*trans,trans*-2m): Mp 93.4–95.2 °C (benzene–hexane); IR (KBr disk) 2960 (w), 1790 (s), 1590 (m), 1360 (m), 1170 (m), 810 (m), and 650 (m) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ =1.39 (d, J =6.2 Hz, 3 H), 1.75 (dd, J =1.8 and 6.6 Hz, 3 H), 2.44 (s, 3 H), 4.24 (dq, J =4.4 and 6.2 Hz, 1 H), 4.36 (dd, J =4.4 and 8.8 Hz, 1 H), 5.35 (ddq, J =8.8, 15.0, and 1.8 Hz, 1 H), 5.90 (dq, J =15.0 and 6.6 Hz, 1 H), 7.33 (d, J =8.2 Hz, 2 H), and 7.89 (d, J =8.2 Hz, 2 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ =17.6, 19.3, 21.6, 66.0, 76.8, 126.6, 128.6, 129.6, 132.7, 135.4, 145.4, and 151.4.

***cis-N-p*-Toluenesulfonyl-5-methyl-4-(*trans*-1-pro-**

penyl)-2-oxazolidinone (*cis,trans*-2m'): ^1H NMR (CDCl_3 , 400 MHz) δ =1.23 (d, J =6.2 Hz, 3 H), 1.74 (dd, J =1.8 and 6.6 Hz, 3 H), 2.43 (s, 3 H), 4.75 (dq, J =7.0 and 6.2 Hz, 1 H), 4.79 (dd, J =7.0 and 9.2 Hz, 1 H), 5.16 (ddq, J =9.2, 15.2, and 1.8 Hz, 1 H), 5.90 (dq, J =15.2 and 6.6 Hz, 1 H), 7.31 (d, J =8.2 Hz, 2 H), and 7.89 (d, J =8.2 Hz, 2 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ =15.1, 19.3, 21.6, 63.9, 75.5, 122.8, 128.8, 129.4, 134.3, 135.6, 145.3, and 151.6. Anal. Calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_4\text{S}$: C, 56.93; H, 5.80; N, 4.74; S, 10.86%. Found: C, 56.83; H, 5.77; N, 4.69; S, 10.80%.

***trans-N-p*-Toluenesulfonyl-5-*t*-butyl-4-(*trans*-1-**

propenyl)-2-oxazolidinone (*trans,trans*-2n): Mp 140.4–142.8 °C (benzene–hexane); IR (KBr disk) 2860 (m), 1790 (s), 1570 (m), 1370 (s), 1220 (s), 1140 (m), 850 (m), and 700 (m) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ =0.92 (s, 9 H), 1.74 (dd, J =1.5 and 6.6 Hz, 3 H), 2.44 (s, 3 H), 3.80 (d, J =4.0 Hz, 1H), 4.65 (dd, J =4.0 and 8.8 Hz, 1H), 5.36 (ddq, J =8.8, 15.0, and 1.5 Hz, 1 H), 5.89 (dq, J =15.0 and 6.6 Hz, 1 H), 7.32 (d, J =8.4 Hz, 2 H), and 7.88 (d, J =8.4 Hz, 2 H).

***trans-N-p*-Toluenesulfonyl-5-*t*-butyl-4-(*cis*-1-pro-**

penyl)-2-oxazolidinone (*trans,cis*-2n'): ^1H NMR (CDCl_3 , 400 MHz) δ =0.94 (s, 9 H), 1.85 (dd, J =1.5 and 7.3 Hz, 3 H), 2.44 (s, 3 H), 3.77 (d, J =4.0 Hz, 1 H), 5.04 (dd, J =4.0 and 10.3 Hz, 1 H), 5.35 (ddq, J =10.3, 10.9, and 1.5 Hz, 1 H), 5.78 (dq, J =10.9 and 7.3 Hz, 1 H), 7.34 (d, J =8.4 Hz, 2 H), and 7.90 (d, J =8.4 Hz, 2 H).

***cis-N-p*-Toluenesulfonyl-5-*t*-butyl-4-(*trans*-1-pro-**

penyl)-2-oxazolidinone (*cis*, *trans*-2n'): $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ =0.97 (s, 9 H), 1.71 (dd, J =1.8 and 6.6 Hz, 3 H), 2.44 (s, 3 H), 4.26 (d, J =6.2 Hz, 1 H), 4.86 (dd, J =6.2 and 10.3 Hz, 1 H), 5.18 (ddq, J =10.3, 15.4, and 1.8 Hz, 1 H), 5.90 (dq, J =15.4 and 6.6 Hz, 1 H), 7.31 (d, J =8.4 Hz, 2 H), and 7.89 (d, J =8.4 Hz, 2 H). Anal. Calcd for $\text{C}_{17}\text{H}_{23}\text{NO}_4\text{S}$: C, 60.51; H, 6.87; N, 4.15; S, 9.50%. Found: C, 60.25; H, 6.28; N, 4.12; S, 9.46%.

***N*-*p*-Toluenesulfonyl-5-ethyl-4-(2-methyl-1-propenyl)-2-oxazolidinone (2o):**

***trans*-Isomer:** Mp 118.9–119.8 °C (benzene–hexane); IR (KBr disk) 2950 (w), 1790 (s), 1580 (m), 1365 (s), 1215 (s), 1140 (m), 855 (m), and 650 (m) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ =0.97 (t, J =7.3 Hz, 3 H), 1.72 (br dq, J =5.9 and 7.3 Hz, 2 H), 1.76 (br s, 3 H), 1.83 (br s, 3 H), 2.44 (s, 3 H), 4.09 (br dt, J =4.4 and 5.9 Hz, 1 H), 4.76 (dd, J =4.4 and 10.1 Hz, 1 H), 5.03 (br d, J =10.1 Hz, 1 H), 7.31 (d, J =8.4 Hz, 2 H), and 7.91 (d, J =8.4 Hz, 2 H).

***cis*-Isomer:** $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ =0.96 (t, J =7.3 Hz, 3 H), 1.43 (br dq, J =5.9 and 7.3 Hz, 2 H), 1.76 (br s, 3 H), 1.83 (br s, 3 H), 2.43 (s, 3 H), 4.51 (br dt, J =7.0 and 5.9 Hz, 1 H), 4.84 (br d, J =11.0 Hz, 1 H), 5.13 (dd, J =7.0 and 11.0, 1 H), 7.30 (d, J =8.4 Hz, 2 H), and 7.92 (d, J =8.4 Hz, 2 H). Anal. Calcd for $\text{C}_{16}\text{H}_{21}\text{NO}_4\text{S}$: C, 59.42; H, 6.55; N, 4.30; S, 9.92%. Found: C, 59.34; H, 6.48; N, 4.32; S, 9.89%.

***N*-*p*-Toluenesulfonyl-4-(2-methyl-2-propenyl)-5-vinyl-2-oxazolidinone (2p):**

***trans*-Isomer:** Mp 108.0–109.0 °C (benzene–hexane); IR (KBr disk) 1775 (s), 1600 (m), 1375 (s), 1280 (m), 1190 (s), 1100 (s), 945 (s), 818 (s), 758 (s), and 650 (m) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ =1.77 (br s, 3 H), 1.82 (br s, 3 H), 2.44 (s, 3 H), 4.48 (br dd, J =4.0 and 6.4 Hz, 1 H), 4.83 (dd, J =4.0 and 9.6 Hz, 1 H), 5.07 (br d, J =9.6 Hz, 1 H), 5.36 (br d, J =10.4 Hz, 1 H), 5.41 (br d, J =17.0 Hz, 1 H), 5.87 (ddd, J =6.4, 10.4, and 17.0 Hz, 1 H), 7.34 (d, J =8.4 Hz, 2 H), and 7.82 (d, J =8.4 Hz, 2 H).

***cis*-Isomer:** $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ =1.72 (br s, 3 H), 1.77 (br s, 3 H), 2.43 (s, 3 H), 4.83 (dd, J =7.0 and 10.6 Hz, 1 H), 5.03 (dd, J =7.0 and 7.0 Hz, 1 H), 5.20 (br d, J =10.6 Hz, 1 H), 5.33 (br d, J =10.4 Hz, 1 H), 5.43 (br d, J =17.0 Hz, 1 H), 5.64 (ddd, J =7.0, 10.4, and 17.0 Hz, 1 H), 7.31 (d, J =8.4 Hz, 2 H), and 7.82 (d, J =8.4 Hz, 2 H). Anal. Calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_4\text{S}$: C, 59.79; H, 5.96; N, 4.36; S, 9.98%. Found: C, 59.74; H, 5.87; N 4.27; S, 10.00%.

***trans*-*N*-Trifluoromethanesulfonyl-5-ethyl-4-vinyl-2-oxazolidinone (2q):** Oil; IR (neat film) 1816 (s), 1418 (s), 1365 (s), 1210 (s), 1050 (s), and 750 (m) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ =1.08 (t, J =7.5 Hz, 3 H), 1.82 (dq, J =6.6 and 7.5 Hz, 2 H), 4.28 (dt, J =4.4 and 6.6 Hz, 1 H), 4.49 (dd, J =4.4 and 8.8 Hz, 1 H), 5.47 (d, J =10.6 Hz, 1 H), 5.49 (d, J =17.2 Hz, 1 H), and 5.89 (ddd, J =8.8, 10.6, and 17.2 Hz, 1 H). High-resolution MS, Calcd for $\text{C}_8\text{H}_{10}\text{NF}_3\text{O}_4\text{S}$: 273.0830. Found: m/z (rel intensity) 273.0278 (M, 2), 202 (2), 141 (2), 140 (19), and 69 (100).

***trans*-*N*-Acetyl-5-ethyl-4-vinyl-2-oxazolidinone (2r):** Oil; IR (neat film) 1790 (s), 1710 (s), 1650 (m), 1220 (m), and 760 (m) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ =1.03 (t, J =7.3 Hz, 3 H), 1.76 (dq, J =6.9 and 7.3 Hz, 2 H), 2.53 (s, 3 H), 4.10 (dt, J =4.0 and 6.9 Hz, 1 H), 4.52 (dd, J =4.0 and 7.0 Hz, 1 H), 5.32 (dd, J =1.5 and 17.1 Hz, 1 H), 5.34 (dd, J =1.5 and 10.1 Hz, 1 H), and 5.82 (ddd,

J =7.0, 10.1, and 17.1 Hz, 1 H). High-resolution MS, Calcd for $\text{C}_9\text{H}_{13}\text{NO}_3$: M, 183.0895. Found: m/z (rel intensity) 183.0895 (M, 44), 141 (16), 113 (9), and 43 (100).

***N*-Benzoyl-4,5-divinyl-2-oxazolidinone (2s):** As a mixture of *cis*-2s: *trans*-2s=1:1.5; oil; IR (neat film) 1785 (s), 1700 (s), 1600 (m), 1300 (s), 1215 (s), 1124 (s), 940 (s), 760 (m), and 700 (s) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ =4.72 (br dd, J =7.0 and 7.3 Hz, 1 H, major isomer), 4.79 (br dd, J =7.0 and 7.3 Hz, 1 H, major isomer), 5.10–5.20 (m, 2 H, minor isomer), 5.40–5.60 (m, 4 H), 5.70–6.00 (m, 2 H), and 7.38–7.80 (m, 5 H). High-resolution MS, Calcd for $\text{C}_{14}\text{H}_{13}\text{NO}_3$: M, 243.0895. Found: m/z (rel intensity) 243.0916 (M, 33), 106 (6), 105 (100), and 77 (23).

***N*-*p*-Toluenesulfonyl-4-vinyltetrahydro-2H-1,3-oxazin-2-one (4a):** Mp 122.0–123.0 °C (dichloromethane–hexane); IR (KBr disk) 1730 (s), 1600 (w), 1415 (m), 1350 (s), 1280 (s), 1170 (s), 1160 (s), 1090 (m), 950 (m), 810 (m), and 675 (s) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ =1.80–2.28 (m, 2 H), 2.42 (s, 3 H), 4.15–4.44 (m, 2 H), 5.11–5.50 (m, 3 H), 5.89 (ddd, J =5.1, 10.5, and 16.1 Hz, 1 H), 7.30 (d, J =8.3 Hz, 2 H), and 7.92 (d, J =8.3 Hz, 2 H). Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_4\text{S}$: C, 55.50; H, 5.37; N, 4.98; S, 11.40%. Found: C, 55.39; H, 5.24; N, 5.00; S, 11.33%.

***trans*-*N*-*p*-Toluenesulfonyl-4-vinyl-5-methyltetrahydro-2H-1,3-oxazin-2-one (4b):** Mp 144.0–145.0 °C (dichloromethane–hexane); IR (KBr disk) 1720 (s), 1600 (m), 1400 (m), 1345 (m), 1255 (m), 1158 (s), 1080 (m), 910 (m), 808 (m), 745 (m), and 676 (m) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ =1.15 (d, J =7.3 Hz, 3 H), 2.12 (br dq, J =3.0 and 7.3 Hz, 1 H), 2.43 (s, 3 H), 3.98 (br d, J =11.3 Hz, 1 H), 4.37 (dd, J =3.0 and 11.3 Hz, 1 H), 4.85 (m, 1 H), 5.39 (br d, J =17.0 Hz, 1 H), 5.42 (br d, J =10.3 Hz 1 H), 5.85 (ddd, J =5.0, 10.3, and 17.0 Hz, 1 H), 7.31 (d, J =8.2 Hz, 2 H), and 7.92 (d, J =8.2 Hz, 2 H). Anal. Calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_4\text{S}$: C, 56.93; H, 5.80; N, 4.74; S, 10.86%. Found: C, 56.86; H, 5.67; N, 4.73; S, 10.97%.

***N*-*p*-Toluenesulfonyl-4-vinyl-6,6-dimethyltetrahydro-2H-1,3-oxazin-2-one (4c):** Mp 128.0–130.0 °C (dichloromethane–hexane); IR (KBr disk) 1720 (s), 1600 (m), 1355 (s), 1280 (s), 1175 (s), 1090 (s), 980 (s), 815 (m), and 650 (s) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ =1.40 (s, 3 H), 1.45 (s, 3 H), 1.94 (dd, J =8.4 and 14.3 Hz, 1 H), 2.17 (dd, J =7.0 and 14.3 Hz 1 H), 2.42 (s, 3 H), 4.97 (dt, J =8.4 and 7.0 Hz, 1 H), 5.27 (d, J =10.3 Hz, 1 H), 5.37 (d, J =17.2 Hz, 1 H), 5.74 (ddd, J =7.0, 10.3, and 17.2 Hz, 1 H), 7.30 (d, J =8.4 Hz, 2 H), and 7.95 (d, J =8.4 Hz, 2 H). Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_4\text{S}$: C, 58.23; H, 6.19; N, 4.53; S, 10.37%. Found: C, 58.13; H, 6.04; N, 4.54; S, 10.43%.

***N*-*p*-Toluenesulfonyl-4-vinyl-5,6,6-trimethyltetrahydro-2H-1,3-oxazin-2-one (4d):**

***trans*-Isomer:** Mp 149.0–149.5 °C (dichloromethane–hexane); IR (KBr disk) 1736 (s), 1600 (w), 1358 (s), 1280 (s), 1178 (s), 1090 (s), 1005 (m), 930 (s), 808 (m), and 678 (m) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ =1.02 (d, J =7.0 Hz, 3 H), 1.36 (s, 3 H), 1.39 (s, 3 H), 1.75 (dq, J =10.3 and 7.0 Hz, 1 H), 2.42 (s, 3 H), 4.30 (dd, J =7.7 and 10.3 Hz, 1 H), 5.37 (dd, J =1.7 and 9.5 Hz, 1 H), 5.43 (dd, J =1.7 and 16.9 Hz, 1 H), 5.51 (ddd, J =7.7, 9.5, and 16.9 Hz, 1 H), 7.29 (d, J =8.2 Hz, 2 H), and 7.97 (d, J =8.2 Hz, 2 H).

***cis*-Isomer:** $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ =1.10 (d, J =7.0 Hz, 3 H), 1.29 (s, 3 H), 1.39 (s, 3 H), 2.35 (dq, J =5.5 and 7.0 Hz, 1 H), 2.42 (s, 3 H), 4.92 (dd, J =5.5 and 7.3 Hz, 1

H), 5.32 (br d, $J=10.6$ Hz, 1 H), 5.39 (br d, $J=17.2$ Hz, 1 H), 5.81 (ddd, $J=7.3$, 10.6, and 17.2 Hz, 1 H), 7.29 (d, $J=8.2$ Hz, 2 H), and 7.90 (d, $J=8.2$ Hz, 2 H). Anal. Calcd for $C_{16}H_{21}NO_4S$: C, 59.42; H, 6.54; N, 4.33; S, 9.91%. Found: C, 59.31; H, 6.45; N, 4.25; S, 9.65%.

***syn*-4-*p*-Toluenesulfonylamino-6-methyl-1,5-heptadien-3-ol (*syn*-5):** A solution of **2p** (5.5 g, 17 mmol, *trans*-5: *cis*-5=3.5:1) in EtOH (30 ml) and 2 M NaOH (10 ml) was refluxed for 6 h. After allowing the mixture to cool to room temperature, 2 M HCl (10 ml) was added and the mixture was extracted with ethyl acetate (3×20 ml). The combined extracts were dried (magnesium sulfate), filtered, and evaporated. The residue was purified by means of column chromatography over silica gel (eluent; hexane:ethyl acetate=2:1) to give a mixture of *syn*-5 and *anti*-5 in a ratio of 7.7:1 in a 65% yield. Single recrystallization of the mixture from dichloromethane–hexane provided pure *syn*-5. Mp 111.0–113.0 °C (dichloromethane–hexane); IR (KBr disk) 3490 (s), 3245 (s), 1600 (w), 1420 (w), 1300 (w), 1144 (s) 902 (m) and 660 (s) cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz) δ =1.39 (br s, 3 H), 1.48 (br s, 3 H), 2.29 (d, $J=4.8$ Hz, 1 H), 2.41 (s, 3 H), 3.91 (ddd, $J=7.0$, 9.7, and 10.5 Hz, 1 H), 4.02 (ddd, $J=4.8$, 5.9, and 10.5 Hz, 1 H), 4.78 (br d, $J=9.7$ Hz, 1 H), 5.00 (d, $J=7.0$ Hz, 1 H), 5.18 (br d, $J=10.6$ Hz, 1 H), 5.36 (br d, $J=16.5$ Hz, 1 H), 5.78 (ddd, $J=5.9$, 10.6, and 16.5 Hz, 1 H), 7.25 (d, $J=8.4$ Hz, 2 H), and 7.70 (d, $J=8.4$ Hz, 2 H). Anal. Calcd for $C_{15}H_{21}NO_3S$: C, 60.99; H, 7.17; N, 4.74; S, 10.86%. Found: C, 60.77; H, 7.02; N, 4.79; S, 10.68%.

***cis*-*N*-*p*-Toluenesulfonyl-2-(1-isobutenyl)-3-vinylaziridine (*cis*-6):** To a solution of *syn*-5 (295.4 mg, 1.0 mmol) and triphenylphosphine (262.3 mg, 1.0 mmol) in dry THF (15 ml) was added diethyl azodicarboxylate (174.2 mg, 1.0 mmol) dissolved in THF (5 ml) at room temperature under N_2 . After allowing the reaction mixture to stir for 12 h at room temperature, the solvent was evaporated and the residue was subjected to column chromatography over silica gel (eluent; hexane:ethyl acetate=8:1) to give *cis*-6 in a 60% yield. R_f =0.78 (Merck Kiesel-gel 60F₂₅₄, hexane:ethyl acetate=1:1); oil; IR (neat film) 2930 (m), 1600 (m), 1440 (m), 1328 (s), 1160 (s), 1094 (s), 928 (s), 840 (m), and 680 (s) cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz) δ =1.72 (br s, 3 H), 1.74 (br s, 3 H), 2.43 (s, 3 H), 3.44 (dd, $J=7.1$ and 7.5 Hz, 1 H), 3.64 (dd, $J=7.5$ and 8.2 Hz, 1 H), 4.93 (br d, $J=8.2$ Hz, 1 H), 5.28 (br d, $J=10.6$ Hz, 1 H), 5.40 (br d, $J=17.4$ Hz, 1 H), 5.60 (ddd, $J=7.1$, 10.6, and 17.4 Hz, 1 H), 7.31 (d, $J=8.4$ Hz, 2 H), and 7.82 (d, $J=8.4$ Hz, 2 H). Anal. Calcd for $C_{15}H_{19}NO_2S$: C, 64.95; H, 6.90; N, 5.05; S, 11.56%. Found: C, 64.74; H, 6.88; N, 5.03; S, 11.71%.

***N*-*p*-Toluenesulfonyl-4,5-dihydro-4,4-dimethyl-1*H*-azepine (7):** A solution of *cis*-6 (167.3 mg, 0.6 mmol) in benzene (3 ml) was refluxed under N_2 for 6 h. The solvent was then evaporated and the residue was subjected to column chromatography over silica gel (eluent; hexane:ethyl acetate=8:1) to give **7** in a 60% yield. R_f =0.84 (Merck Kiesel gel 60F₂₅₄, hexane:ethyl acetate=1:1); oil; IR (neat film) 2960 (m), 1650 (m), 1600 (m), 1352 (s), 1166 (s), 1088 (s), 1020 (m), 806 (m), and 665 (s) cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz) δ =0.87 (s, 6 H), 1.87 (d, $J=6.6$ Hz, 2 H), 2.35 (s, 3 H), 4.80 (d, $J=10.3$ Hz, 1 H), 5.08 (dt, $J=9.2$ and 6.6 Hz, 1 H), 6.32 (br d, $J=10.3$ Hz, 1 H), 6.48 (br d, $J=9.2$ Hz, 1 H), 7.23 (d, $J=8.4$ Hz, 2 H), and 7.62 (d, $J=8.4$ Hz, 2 H).

High-resolution MS, Calcd for $C_{15}H_{19}NO_2S$: M, 277.1136. Found: m/z (rel intensity) 277.1141 (M, 53), 262 (15), 122 (100), and 91 (8).

Crystallography. The structure of *trans*-**2i** was solved by direct methods (SAPI91) and refined by full-matrix least-squares methods. All non-hydrogen atoms were defined anisotropically whereas some hydrogen atoms were defined isotropically. The parameters of the other hydrogen atoms were fixed during the refinement. The structure of *trans*-**4d** was solved by direct methods (MITHRIL84) and refined by full-matrix least-squares methods. All non-hydrogen atoms were defined anisotropically whereas all hydrogen atoms were defined isotropically.

Crystal Data for *trans*-2i: $C_{15}H_{17}O_4NS$, monoclinic, $C2/c$, $a=21.933(2)$, $b=12.4194(9)$, $c=16.083(1)$ Å, $\beta=133.251(3)^\circ$, $V=3191.0(4)$ Å³, $Z=8$, $D_{cal}=1.279$ g cm⁻³, $\lambda(Cu K\alpha)=1.54178$ Å (graphite monochromated), Rigaku AFC-7S diffractometer, 2492 unique reflections ($4^\circ \leq 2\theta \leq 120.1^\circ$) on a colorless crystal (0.40×0.20×0.45 mm), 1740 [$I_o \geq 3\sigma(I_o)$] used, 239 parameters, $R=0.062$, $R_w=0.044$.

Crystal Data for *trans*-4d: $C_{16}H_{21}O_4NS$, monoclinic, $P2_1/n$, $a=6.957(2)$, $b=19.250(1)$, $c=12.189(1)$ Å, $\beta=94.46(1)^\circ$, $V=1627.3(5)$ Å³, $Z=4$, $D_{cal}=1.320$ g cm⁻³, $\lambda(Mo K\alpha)=0.71069$ Å (graphite monochromated), Rigaku AFC-7S diffractometer, 3841 unique reflections ($4^\circ \leq 2\theta \leq 55^\circ$) on a colorless crystal (0.2×0.2×0.4 mm), 1902 [$I_o \geq 3\sigma(I_o)$] used, 284 parameters, $R=0.045$, $R_w=0.030$.

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References

- 1) a) B. M. Trost and R. C. Bunt, *J. Am. Chem. Soc.*, **116**, 4089 (1994); b) Y. Ichikawa, M. Yamazaki, and M. Isobe, *J. Chem. Soc., Perkin Trans. 1*, **1993**, 2429; c) J. Gonzalez, M. Sabat, and W. D. Harman, *J. Am. Chem. Soc.*, **115**, 8857 (1993); d) P. Magnus, P. Rigollier, J. Lacour, and H. Tobler, *J. Am. Chem. Soc.*, **115**, 12629 (1993); e) H. Hirai, T. Terada, Y. Amemiya, and T. Momose, *Tetrahedron Lett.*, **33**, 7893 (1992); f) J. K. Whitesell and H. K. Yaser, *J. Am. Chem. Soc.*, **113**, 3526 (1991); g) R. E. Dolle, K. I. Osifo, and C.-S. Li, *Tetrahedron Lett.*, **32**, 5029 (1991); h) R. C. Larock, N. G. Berrios-Penã, and C. A. Fried, *J. Org. Chem.*, **56**, 2615 (1991); i) M. Jensen and T. Livinghouse, *J. Am. Chem. Soc.*, **111**, 4495 (1989); j) S. L. Buchwald, B. T. Watson, M. W. Wannamaker, and J. C. Dewan, *J. Am. Chem. Soc.*, **111**, 4486 (1989).
- 2) a) S. B. King and B. Ganem, *J. Am. Chem. Soc.*, **116**, 562 (1994); b) B. M. Trost and D. L. Vranken, *J. Am. Chem. Soc.*, **115**, 444 (1993); c) F. M. Houser and S. R. Ellenberger, *Chem. Rev.*, **86**, 35 (1986).
- 3) a) J. A. Marshall and A. W. Garafalo, *J. Org. Chem.*, **58**, 3675 (1993); b) R. Jumnah, J. M. A. Williams, and A. C. Williams, *Tetrahedron Lett.*, **34**, 6619 (1993); c) H. Iida, K. Kasahara, and C. Kibayashi, *J. Am. Chem. Soc.*, **108**, 4647 (1986).

- 4) Y. Tamaru, H. Harayama, and T. Bando, *J. Chem. Soc., Chem. Commun.*, **1993**, 1601.
- 5) a) K. Tadano, K. Takao, Y. Nigawara, E. Nishino, I. Takagi, K. Maeda, and S. Ogawa, *Synlett*, **1993**, 565; b) B. M. Trost, D. L. Vranken, and C. Bingel, *J. Am. Chem. Soc.*, **114**, 9327 (1992); c) B. M. Trost and D. L. Vranken, *Angew. Chem., Int. Ed. Engl.*, **31**, 228 (1992); d) R. C. Bernotas and R. V. Cube, *Tetrahedron Lett.*, **32**, 161 (1991); e) Y. Hirai, M. Chintani, T. Yamazaki, and T. Momose, *Chem. Lett.*, **1989**, 1449; f) T. Hayashi, A. Yamamoto, and Y. Ito, *Tetrahedron Lett.*, **29**, 99 (1988); g) B. M. Trost and A. R. Sudhakar, *J. Am. Chem. Soc.*, **110**, 7933 (1988).
- 6) a) S.-E. Yoo, S.-H. Lee, K.-Y. Yi, and N. Jeong, *Tetrahedron Lett.*, **31**, 6877 (1990); b) D. M. Vyas, Y. Chiang, and T. W. Doyle, *J. Org. Chem.*, **49**, 2037 (1984).
- 7) T. Bando, H. Harayama, Y. Fukuzawa, M. Shiro, K. Fugami, S. Tanaka, and Y. Tamaru, *J. Org. Chem.*, **59**, 1465 (1994).
- 8) a) R. W. Friesen and A. Giroux, *Tetrahedron Lett.*, **34**, 1867 (1993); b) R. W. Friesen and A. E. Kolaczewska, *J. Org. Chem.*, **56**, 4888 (1991); c) R. W. Friesen, *Tetrahedron Lett.*, **31**, 4249 (1990). See, also Ref. 19.
- 9) a) M. Kimura, N. Saeki, S. Uchida, H. Harayama, S. Tanaka, K. Fugami, and Y. Tamaru, *Tetrahedron Lett.*, **34**, 7611 (1993); b) I. W. Davies, D. I. C. Scopers, and T. Gallagher, *Synlett*, **1993**, 85; c) R. W. Shaw, D. Lathbury, and T. Gallagher, *Synlett*, **1993**, 710; d) M. Gray, P. J. Parsons, and A. P. Neary, *Synlett*, **1993**, 281; e) M. Kimura, K. Fugami, S. Tanaka, and Y. Tamaru, *J. Org. Chem.*, **57**, 6377 (1992); f) A. M. Caporusso, R. Geri, C. Polizzi, and L. Lardicci, *Tetrahedron Lett.*, **32**, 7471 (1991); g) D. N. A. Fox, D. Lathbury, M. F. Mahon, and K. C. Molloy, *J. Am. Chem. Soc.*, **113**, 2652 (1991); h) D. Lathbury, P. Vernon, and T. Gallagher, *Tetrahedron Lett.*, **27**, 6009 (1986); i) S. Arseniyadis and J. Gore, *Tetrahedron Lett.*, **24**, 3997 (1983); j) A. Claesson, C. Sohlberg, and K. Luthman, *Acta Chem. Scand., Ser. B*, **B33**, 309 (1979).
- 10) a) M. Gray, P. J. Parsons, and A. P. Neary, *Synlett*, **1992**, 597; b) R. D. Walkup, L. Guan, M. D. Mosher, S. W. Kim, and Y. S. Kim, *Synlett*, **1993**, 88; c) E. J. Corey and G. B. Jones, *Tetrahedron Lett.*, **32**, 5713 (1991); d) J. A. Marshall and X. Wang, *J. Org. Chem.*, **56**, 960 (1991); e) R. D. Walkup and G. Park, *Tetrahedron Lett.*, **28**, 1023 (1987); f) T. Delair and A. Doutheau, *Tetrahedron Lett.*, **27**, 2859 (1986); g) J. J. Chilot, A. Doutheau, J. Gore, and A. Saroli, *Tetrahedron Lett.*, **27**, 849 (1986); h) P. Audin, A. Doutheau, and J. Gore, *Tetrahedron Lett.*, **23**, 4337 (1982).
- 11) H. Tanaka, Y. Kameyama, A. Kosaka, T. Yamauchi, and S. Torii, *Tetrahedron Lett.*, **32**, 7445 (1991).
- 12) K. Koerber, J. Gore, and J.-M. Vatele, *Tetrahedron Lett.*, **32**, 1187 (1991).
- 13) M. Kimura, K. Fugami, S. Tanaka, and Y. Tamaru, *Tetrahedron Lett.*, **32**, 6359 (1991).
- 14) R. W. Friesen, A. E. Kolaczewska, and N. Khazanovich, *Tetrahedron Lett.*, **33**, 6715 (1992).
- 15) a) R. W. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **31**, 1124 (1992); b) F. Johnson, *Chem. Rev.*, **68**, 375 (1968).
- 16) a) Y. Tamaru, M. Kimura, S. Tanaka, S. Kure, and Z. Yoshida, *Bull. Chem. Soc. Jpn.*, **67**, 2838 (1994); b) M. Kimura, S. Kure, Z. Yoshida, S. Tanaka, K. Fugami, and Y. Tamaru, *Tetrahedron Lett.*, **31**, 4887 (1990); c) N. Shachat and J. J. Bagnell, Jr., *J. Org. Chem.*, **28**, 991 (1963).
- 17) Approximate pK_a value of sulfonylcarbamate is 4,¹⁸⁾ alkylcarbamate 11, Et_3NH^+ 11, and t -BuOH 18. The pK_a of acylcarbamate is not known, but should be in between those of sulfonyl- and alkylcarbamates.
- 18) L. D. Tayler, R. J. MacDonald, and E. L. Rubin, *J. Polym. Sci., Part A-1*, **9**, 3059 (1971).
- 19) Palladium(II)-catalyzed carbonylation of a mixture of **1n** and **1n'** in methanol provides a mixture of aminocyclization products (*trans*-*N*-tosyl-5-*t*-butyl-4-[(*E*)-1-methoxycarbonyl-1-propenyl]-2-oxazolidinone and *trans*-*N*-tosyl-5-*t*-butyl-4-[(*Z*)-1-methoxycarbonyl-1-propenyl]-2-oxazolidinone, $\nu_{CO}=1790\text{ cm}^{-1}$) and oxycyclization products (*trans*-4-*t*-butyl-5-[(*E*)-1-methoxycarbonyl-1-propenyl]-1,3-dioxolan-2-imine and *trans*-4-*t*-butyl-5-[(*Z*)-1-methoxycarbonyl-1-propenyl]-1,3-dioxolan-2-imine, $\nu_{CN}=1650\text{--}1655\text{ cm}^{-1}$): Y. Tamaru, S. Uchida, and M. Kimura, unpublished results.
- 20) a) E. Breitmaier, "Structure Elucidation by NMR in Organic Chemistry," Wiley, New York (1993); b) A. Gaudemer, in "Stereochemistry," ed by H. B. Kagan, Georg Thieme Verlag, Stuttgart (1979).
- 21) a) J. C. Pommelet and J. Chuche, *Can. J. Chem.*, **54**, 1571 (1976); b) J. C. Pommelet and J. Chuche, *Tetrahedron Lett.*, **1974**, 3897; c) E. L. Stogryn and S. J. Brois, *J. Am. Chem. Soc.*, **89**, 605 (1967).
- 22) a) P. G. M. Wuts and Y.-W. Jung, *J. Org. Chem.*, **56**, 365 (1991); b) I. G. Pojarlieff, M. J. Lyapova, and B. J. Kurtev, *J. Chem. Res., Synop.*, **1980**, 231.
- 23) J. S. Cowie, P. D. Landor, and S. R. Landor, *J. Chem. Soc., Perkin Trans. 1*, **1973**, 720.
- 24) J. K. Crandall and G. L. Tindell, *J. Chem. Soc., Chem. Commun.*, **1970**, 1411.
- 25) R. Appel and M. Montenarh, *Chem. Ber.*, **107**, 706 (1974).
- 26) R. G. Neville, J. J. McGee, C. Wright, and E. L. Mutter, *Inorg. Synth.*, **VIII**, 23.