Palladium-Catalyzed Stereoselective Allylaminocyclization and 1,3-Butadien-2-ylaminocyclization of Allenyl Tosylcarbamates

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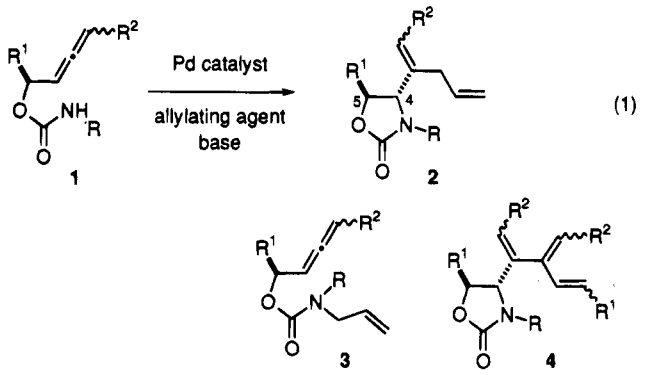
Palladium [$PdCl_2(PhCN)_2$ or $Pd_2(dba)_3{\cdot}CHCl_3$ (dba = dibenzylideneacetone)], in the presence of a base (Et_3N or K_2CO_3) in THF at room temperature, catalyzes an allylaminocyclization of 2,3-butadienyl tosylcarbamates **1** with allylic chlorides to selectively provide *trans*-4,5-disubstituted 2-oxazolidinones **2** in good yields. Under similar conditions, $Pd(PPh_3)_4$ catalyzes an N-allylation of **1** to give **3**. A limited number of 3,4-pentadienyl tosylcarbamates **5** undergo the allylaminocyclization to provide tetrahydro-1,3-oxazin-2-ones **6**. In the absence of an allylic chloride, $Pd(PPh_3)_4$ and $PdCl_2(PhCN)_2$ catalyze a formal dimerization of **1** to provide C_4-triene-substituted 2-oxazolidinones **4** in moderate to good yields.

Introduction

The utility of (π-allyl)palladium complexes as synthetic intermediates is primarily due to their ease of generation by a variety methods and their accommodation of a wide range of reaction partners (soft and hard carbanions, heteroatom nucleophiles, organotins, carbon monoxide, etc.) to create C–C and carbon–heteroatom bonds in a stereochemically predictable way.[1] (π-Allyl)palladium complexes, however, are generally unreactive toward simple olefins and enter into reactions only with highly polarized or polarizable (e.g. enamines, vinyl ethers, 1,3-dienes,[2] etc.) and strained double bonds (e.g. norbornene).[3] Intramolecular versions of the reaction of (π-allyl)palladium complexes with double bonds work well in some cases.[4]

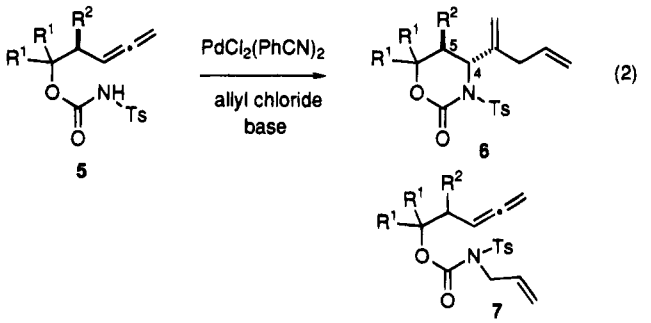
We report here that (π-allyl)palladium complexes, generated in situ from allylic chlorides and a catalytic amount of palladium, react selectively with 2,3-butadienyl carbamates **1** at the allenic C_2–C_3 double bond to provide 4-(1-allylvinyl)-2-oxazolidinones **2** in high yields, rather than at the carbamate nitrogen atom to provide **3** (eq 1).[5] In the absence of an allylic chloride, the outcome changes dramatically, and the substrates **1** react to form 4-[1-(1,3-butadien-2-yl)vinyl]-2-oxazolidinones **4** in moderate to good yields (eq 1).



(1)

These allylaminocyclizations (providing **2**) and dienylaminocyclizations (providing **4**) are stereoselective with respect to the C_4 and C_5 substituents of the oxazolidinone ring and in most cases provide the *trans* isomers with excellent selectivity.

3,4-Pentadienyl carbamates **5**, on the other hand, are prone to undergo N-allylation to provide **7** selectively, under conditions optimized for the allylaminocyclization of **1** (eq 2). The allylaminocyclization of **5** to provide **6** is



(2)

only successful for some limited combinations of R^1 and R^2 under some specified conditions.

In view of the increasing interest in amino sugars[6] and rare amino acids,[7] much effort has been devoted to developing efficient stereoselective methods for the synthesis of allylic amines.[8,9] In this context, the present reaction, which can provide **2**, **4**, and **6**, the protected forms of dienyl and trienyl allylic aminoalcohols of defined stereochemistry, might find wide application in synthesis.

[⊗] Abstract published in *Advance ACS Abstracts*, May 15, 1995.

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Table 1. Palladium-Catalyzed Allylaminocyclization of 2,3-Butadienyl Tosylcarbamates 1 (R = Ts)[a]

run	tosylcarbamate 1	R^1	R^2	allylating agent (equiv)[b]	catalyst (equiv)[c]	base	reaction time (h)	product (yield, %)[d]
1	**1a**	H	H	AC (20)	BZ (0.1)	Et_3N	19	**2a** (53)[e]
2	**1a**	H	H	AC (2)	BZ (0.1)	Et_3N	24	**2a** (32)
3	**1b**	H	Me	AC (20)	BZ (0.1)	Et_3N	15	**2b** (63)[f]
4	**1c**	Me	H	AC (20)	BZ (0.1)	Et_3N	17	**2c** (65)
5	**1d**[g]	Me	Me	AC (20)	BZ (0.1)	K_2CO_3	23	**2d** (79)[h]
6	**1e**	Et	H	AC (20)	BZ (0.1)	Et_3N	12	**2e** (58)
7	**1e**	Et	H	AC (20)	$PdCl_2$ (0.1)	K_2CO_3	15[i]	**2e** (67)
8	**1e**	Et	H	AA (20)	BZ (0.1)	Et_3N	18	**4e** (57)[j]
9	**1f**	*n*-Pr	H	AC (20)	BZ (0.1)	Et_3N	19	**2f** (80)
10	**1f**	*n*-Pr	H	AB (20)	BZ (0.1)	Et_3N	16	**2f** (45)
11	**1g**	*i*-Pr	H	AC (20)	BZ (0.1)	Et_3N	19	**2g** (80)
12	**1h**	*t*-Bu	H	AC (20)	BZ (0.1)	Et_3N	21	**2h** (74)
13	**1h**	*t*-Bu	H	AC (20)	DBA (0.05)	Et_3N	13	**2h** (60)
14	**1h**	*t*-Bu	H	AC (20)	TET (0.05)	Et_3N	17	**3h** (89)
15	**1h**	*t*-Bu	H	AC (20)	$Pd(OAc)_2$ (0.05)	Et_3N	17	**2h** (21), **3h** (45)
16	**1h**	*t*-Bu	H	AMC (10)	BZ (0.05)	Et_3N	24	**2h** (51)
17	**1i**	Ph	H	AC (20)	BZ (0.1)	Et_3N	10	**2i** (24)
18	**1j**[k]	Me_2	H	AC (20)	BZ (0.1)	Et_3N	17	**2j** (0)[l]

[a] Reaction conditions: **1**, 1 mmol; allylating agent, indicated amount; palladium catalyst, indicated amount; base, 1 mmol in dry THF (3 mL) at room temperature under nitrogen. [b] AC = allyl chloride, AA = allyl acetate, AB = allyl bromide, AMC = allyl methyl carbonate. [c] BZ = $PdCl_2(PhCN)_2$, DBA = $Pd_2(dba)_3{\cdot}CHCl_3$ (dba = dibenzylideneacetone), TET = $Pd(PPh_3)_4$. [d] Isolated yield for spectroscopically homogeneous product. [e] In addition to **2a**, *N*-tosyl-4-vinyl-2-oxazolidinone in 8% yield. [f] A mixture of (*E*)- and (*Z*)-**2b** (2.3:1) with respect to R^2 = Me substituent. [g] **1d** as a diastereomeric mixture (1.4:1). [h] **2d** as a diastereomeric mixture (1:2:11:14). [i] Acetonitrile (3 mL) as a solvent, in place of THF. [j] **4e** (57%) in the absence of allyl acetate. [k] **1j** as 1,1-dimethyl-2,3-butadienyl tosylcarbamate. [l] *N*-Tosyl-5,5-dimethyl-4-vinyl-2-oxazolidinone in 50% yield.

Results and Discussion

Palladium-Catalyzed Allylaminocyclization of 2,3-Butadienyl Carbamates 1. We recently reported that silver(1+) salts catalyze the cyclization of **1** and provide 4-vinyl-2-oxazolidinones in good yields.[10,11] Unfortunately, this reaction showed only moderate stereoselectivity with respect to the C_4 and C_5 substituents on the oxazolidinone ring. We also reported that palladium(2+) salts nicely catalyze an aminocarbonylation of **1**. In this reaction, *trans*-4-[(1-alkoxycarbonyl)vinyl]-2-oxazolidinones were obtained with excellent stereoselectivity.[12]

In this paper, we disclose that (π-allyl)palladium complexes bring about a similar aminocyclization for a variety of substrates **1**, providing 2-oxazolidinone rings, accompanied by an allylation at the allenic central carbon to provide the allylaminocyclization products **2** in good yields and with excellent *trans* stereoselectivity as shown in Table 1. The reaction proceeds smoothly at room temperature when a tetrahydrofuran solution of **1**, a large excess (20 equiv) of an allylic chloride, bromide, or carbonate, and a catalytic amount of an appropriate palladium species are mixed in the presence of 1 equiv of a base under nitrogen. The use of 1 equiv of an organic or inorganic base is essential to promote the reaction. In the absence of a base, no reaction is discernible. All of the experiments indicated in Table 1 were undertaken with racemic **1**. For simplicity, only one enantiomer is indicated.

$PdCl_2(PhCN)_2$ (BZ) was most often utilized as the palladium catalyst. $Pd_2(dba)_3{\cdot}CHCl_3$ (DBA, dba = dibenzylideneacetone, run 13) and $PdCl_2$ (run 7) may be used with similar efficiency. $Pd(OAc)_2$ was marginally effective. With this catalyst, the reaction is contaminated with a significant amount of the N-allylation product **3h** (run 15). $Pd(PPh_3)_4$ (TET) and $PdCl_2/4PPh_3$, on the other hand, only catalyze the N-allylation to provide **3** in good yields (e.g. run 14). Deletion of TET from the reaction mixture of run 14 (room temperature, 19 h) resulted in the formation of **3h** in 9% isolated yield, suggesting that a (π-allyl)palladium complex in the presence of triphenylphosphine serves as a more effective N-allylation agent than allyl chloride alone.

Of the allylating agents studied, allyl chloride (AC) was most effective. Allyl bromide (AB, run 10) and allyl methyl carbonate (AMC, run 16) might be utilized. However, allyl acetate (AA, run 8) turned out to be unsuitable; with this reagent, no allylaminocyclization product **2e** was formed at all, and instead, **4e**, a self-condensation product of **1e**, was formed in 57% yield (run 8, Table 1).

1-Phenyl- and 1,1-dimethyl-2,3-butadienyl carbamates (**1i** and **1j**, respectively) were unstable[13] and were isolated and subjected to the reactions as their triethylamine salts. The yields of **2** from these substrates were unacceptably low, presumably due to the instability of **1i** (run 17) and to the high propensity for **1j** to undergo aminocyclization to 5,5-dimethyl-4-vinyl-2-oxazolidinone, which was isolated in 50% yield (footnote l, run 18, Table 1).

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(11) For transition metal-catalyzed cyclization of allenic amines and alcohols, see: (a) Audin, P.; Doutheau, A.; Gore, J. *Tetrahedron Lett.* **1982**, *23*, 4337. (b) Arseniyadis, S.; Gore, J. *Ibid.* **1983**, *24*, 3997. (c) Lathbury, D.; Vernon, P.; Gallagher, T. *Ibid.* **1986**, *27*, 6009. (d) Walkup, R. D.; Park, G. *Ibid.* **1987**, *28*, 1023. (e) Fox, D. N. A.; Lathbury, D.; Mahon, M. F.; Molloy, K. C.; Gallagher, T. *J. Am. Chem. Soc.* **1991**, *113*, 2652. (f) Davies, I. W.; Scopers, D. I. C.; Gallagher, T. *Synlett* **1993**, 85. (g) Walkup, R. D.; Guan, L.; Mosher, M. D.; Kim, S. W.; Kim, Y. S. *Ibid.* **1993**, 88. (h) Shaw, R. W.; Lathbury, D.; Gallagher, T. *Ibid.* **1993**, 710.

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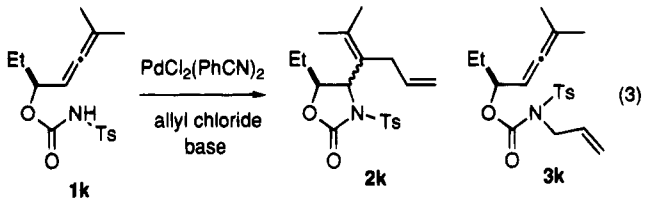
Table 2. Palladium-Catalyzed Allylaminocyclization of 4,4-Dimethyl-2,3-butadienyl Tosylcarbamate 1k[a]

run	base	pK_a[b]	solvent	reaction conditions	% isolated yield 2k[c]	% isolated yield 3k
1	Et_3N	10.92	THF	rt, 15 h	0	79
2	Et_3N	10.92	THF	rt, 12 h[d]	45	18
3	morpholine	8.49	THF	50 °C, 12 h	no reaction	
4	K_2CO_3	6.35	MeCN	rt, 15 h	21	57
5	K_2CO_3	6.35	THF	rt, 26 h	25	35
6	K_2CO_3	6.35	benzene	40 °C, 24 h	51	31
7	Cs_2CO_3	6.35	THF	rt, 12 h	0	66
8	pyridine	5.42	THF	50 °C, 4 h	no reaction	
9	NaOAc	4.56	AcOH	40 °C, 24 h	54	0
10	NaO_2CCH_2Cl	2.68	MeOH	rt, 13 h	75	0

[a] Reaction conditions: **1k**, (1 mmol; allyl chloride, 20 mmol; $PdCl_2(PhCN)_2$, 0.1 mmol; base, 1 mmol in a given dry solvent (6 mL) under nitrogen. [b] pK_a value of conjugate acid in water. pK_a of **1k**, being estimated to be ca. 4.0 (in water): Taylor, L. D.; MacDonard, R. J.; Rubin, E. L. *J. Polym. Sci., Polym. Chem. Ed.* **1971**, *9*, 3059. [c] **2k** as a mixture of *trans*:*cis* = 1.5:1. [d] Slow addition of a solution of Et_3N (1 equiv) in THF (10 mL) via a syringe pump over a period of 6 h.

Interestingly, **1k**, having dimethyl substitution at the terminal olefinic carbon, underwent N-allylation to provide **3k** exclusively, under the optimized conditions for the formation of **2** (eq 3, run 1, Table 2). Interestingly,

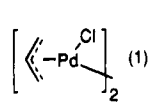
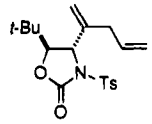
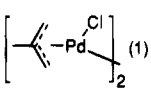
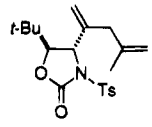
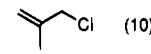
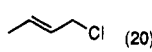
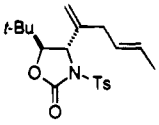
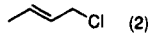
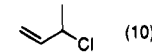
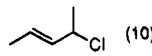
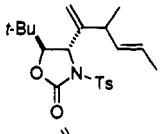
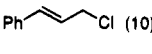
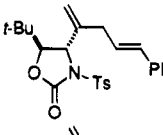
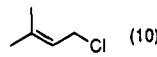
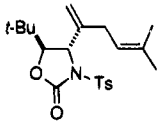


however, a slow addition of 1 equiv of triethylamine over a period of 6 h caused a dramatic change in the product distribution from this reaction and furnished the allylaminocyclization product **2k** as the major product in 45% yield together with **3k** in 18% yield (run 2, Table 2). The results obtained from experiments using K_2CO_3 in several solvents (runs 4–6, Table 2) seem to indicate that the lower the solubility of K_2CO_3 in a given solvent, the higher the proportion of the product **2k** formed. Indeed, Cs_2CO_3, being completely soluble in tetrahydrofuran under the conditions, gave rise to the N-allylation product exclusively (run 7, Table 2).

All of these observations suggest that the formation of **2k** is favored when the reactions are performed with low concentrations of a base and hence with low concentrations of the conjugate base of the carbamate **1k**. Accordingly, in order to keep the concentration of the carbamate anion low, we examined several bases having basicities comparable to or lower than that of **1k**, and we found that sodium acetate in acetic acid (run 9, Table 2) and sodium monochloroacetate in methanol (run 10, Table 2) worked well. Morpholine (run 3, Table 2) and pyridine (run 8, Table 2) completely inhibited the reaction. These amine bases, being less basic and less sterically demanding than triethylamine, might have served as a catalyst poison.

Next, we examined the allylaminocyclization of the substrate **1h** with a variety of allylating agents (Table 3). Chloro-(π-allyl)palladium(2+) dimers (runs 1 and 2, Table 3) were reluctant to undergo the allylaminocyclization and provided **2h** and **2l**, respectively, in low yields. These results were unexpected since we had anticipated that (π-allyl)palladium complexes were necessary intermediates for the allylaminocyclization discussed above (Tables 1 and 2). Instead, these reactions provided **4h**, a self-condensation product of **1h**, as the major product.

Table 3. Palladium-Catalyzed Allylaminocyclization of 1h with Various Allylating Agents[a]

run	allylating agent (equiv)	reaction time (h)	product % isolated yield
1	 (1)	42	 **2h**: 17, **4h**: 50[b]
2	 (1)	40	 **2l**: 5, **4h**: 31[b]
3	 (10)	23	**2l**: 46
4	 (20)	8	 **2m**: 76
5	 (2)	8	**2m**: 65
6	 (10)	15	**2m**: 78
7	 (10)	15	 **2n**: 33
8	 (10)	11	 **2o**: 60
9	 (10)	8	 **2p**: 51

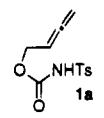
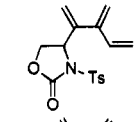
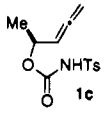
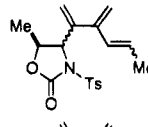
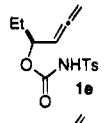
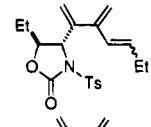
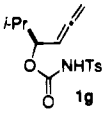
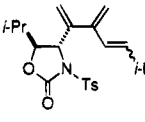
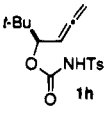
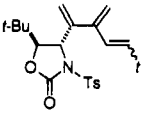
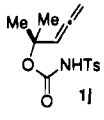
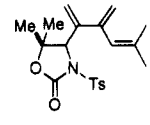
[a] Reaction conditions: **1h**, 1 mmol; allylating agent, indicated amount; $PdCl_2(PhCN)_2$, 0.1 mmol; triethylamine, 1 mmol in dry THF (3 mL) at room temperature. [b] For the structure of **4h**, runs 5 and 6, Table 4.

Other allylic chlorides functioned nicely as allylating agents in the presence of a catalytic amount of BZ and furnished the corresponding allylaminocyclization products **2** in moderate to good yields (runs 3–9, Table 3). In these reactions, the amount of allylating agent used may be reduced without serious deterioration of the yield (2–10 equiv, as opposed to 20 equiv for the cases listed in Table 1).

In all cases, the products were obtained as single diastereomers, being *trans* with respect to the C_4–C_5 substituents on the oxazolidinone ring and also being *trans* with respect to the allylic groups transferred from the allylating agents. All of the unsymmetrical allylating agents studied uniformly reacted at the allylic termini bearing the smallest number of substituents.

The palladium-mediated allylaminocyclization reaction depends markedly on the N-substituent of the carbamate **1**. As exemplified in Tables 1–3, the reaction was successful for tosylcarbamates. However, neither *N*-(benzyloxycarbonyl)- nor *N*-phenylcarbamate derivatives of **1e** underwent the expected cyclization under the usual (room temperature) or forcing conditions [50 °C, allyl chloride (20 equiv), BZ (0.1 equiv), triethylamine (1 equiv) in THF]. Neither potassium *tert*-butoxide (room temperature) nor *n*-butyllithium (−78 °C to room temperature), in place of triethylamine, effected the cyclization.

Table 4. Palladium-Catalyzed Dienylaminocyclization of 2,3-Butadienyl Tosylcarbamates 1[a]

run	carbamate 1	base	reaction time (h)	product % isolated yield (isomer ratio)[b]
1	 1a	Et_3N	16	 4a: 22
2	 1c	Et_3N	6	 4c: 75 (2.3:1.9:1.7:1)
3	 1e	Et_3N	6	 4e: 69[c] (3.1:1)
4	 1g	Et_3N	24	 4g: 80 (7.5:1)
5	 1h	none	16	 4h: 77
6		Et_3N	12	4h: 92
7		NaH	12	4h: 0 (2.2:1)
8	 1j	Et_3N	12	 4j: 76

[a] Reaction conditions: **1**, 1 mmol; $Pd(PPh_3)_4$, 0.1 mmol; base, 1 mmol in dry THF (3 mL) at room temperature under nitrogen. [b] Determined by ^1H NMR (400 MHz). [c] **4e** in 57% yield by the use of $PdCl_2(PhCN)_2$ (room temperature, 18 h), in place of $Pd(PPh_3)_4$.

In these attempts, the starting materials were recovered quantitatively.

Palladium-Catalyzed 1,3-Butadien-2-ylaminocyclization of 2,3-Butadienyl Tosylcarbamates 1. In the experiments using unreactive allylating agents (run 8, Table 1; runs 1 and 2, Table 3), we observed that **1** underwent a self-condensation reaction to provide **4** in modest yields. Exactly the same results as those indicated in run 8 of Table 1 were obtained when the reaction was undertaken in the absence of allyl acetate, providing **4e** in 57% yield (footnote *j*, Table 1).

From these observations, we envisioned that **1** first underwent an oxidative addition of the Pd(0) species to the C_1-O bond to generate carbon dioxide, tosylamide, and a 1,3-butadien-2-ylpalladium(2+) species,[14] which further reacted with another molecule of **1** and finally provided **4**. Accordingly, we tested various Pd(0) species as catalysts for this reaction and found that TET was more efficient than BZ (run 3 and footnote *c*, Table 4).

As is apparent from Table 4, the reaction is general for a variety of substrates **1**. It appears that the derivatives of **1** bearing the sterically bulkier substituents over C_1 provide **4** in better yields. In these reactions, the stereoselectivity is not as high as that observed for the allylaminocyclization reactions. For example, **1c** provided **4c** as a chromatographically inseparable mixture of the four possible diastereomers (run 2, Table 4), as opposed to forming *trans*-**2c** as a single isomer, in the allylaminocyclization reaction (run 4, Table 1). The other derivatives **4e–h** were formed with better selectivity, providing mixtures of only two stereoisomers (runs 3–6, Table 4). These isomers were tentatively assigned as the olefinic stereoisomers, all being *trans* with respect to the C_4-C_5 stereochemistry, primarily judging from the vicinal C_4H-C_5H coupling constants observed in their 400 MHz ^1H NMR spectra (see the Experimental Section, Table 6).

Interestingly, the present dienylaminocyclization did not necessarily require a base (run 5, Table 4). A stronger base, NaH, on the other hand, completely inhibited the reaction, and no expected product was obtained at all (run 7).

The observed reactivity and stereoselectivity are in marked contrast to those observed for the allylaminocyclization, suggesting that these two aminocyclization reactions, though constructing the same oxazolidinone skeleton, follow completely different reaction mechanisms.

Palladium-Catalyzed Allylaminocyclization of 3,4-Pentadienyl Tosylcarbamates 5. It has been pointed out that reactions that are successful for the formation of five-membered nitrogen heterocycles cannot always be applied to the synthesis of the six-membered ring analogs.[15] This seems to be the case for the reactions of 3,4-pentadienyl tosylcarbamates **5** (eq 2).

As summarized in Table 5, the carbamates **5a–d** selectively underwent N-allylation to provide **7a–d**, respectively, under the usual conditions successfully applied for the allylaminocyclization of **1** (e.g. runs 1, 3, and 4, Table 5). Only 1,1-dimethyl-3,4-pentadienyl derivatives (**5c,d**) provided the expected cyclization products, tetrahydro-1,3-oxazin-2-ones **6** (runs 5 and 6, Table 5), under the conditions modified for the allylaminocyclization of **1k** (Table 2). Under such conditions, however, the parent carbamate **5a** was immune to both allylaminocyclization and N-allylation and was recovered quantitatively (run 2, Table 5). The 1,1-dimethyl group of **5c,d** may promote the allylaminocyclization by conformationally buttressing both of the reaction centers (olefinic C_3 and carbamate nitrogen), enabling them to get close to each other. **6d** was obtained as a single diastereomer, whose stereochemistry was determined to be *trans* (see the Experimental Section, Table 6).

Mechanistic Considerations. The reaction pathway for the aminocyclization providing **2**, **4**, and **6** (eqs 1–3) is more complicated than it first appears. In Scheme 1 are illustrated three pathways that merit consideration, using **1h** and crotyl chloride as representative reactants.

Pathway a starts with the coordination of crotylpalladium(2+) to the C_2-C_3 double bond of **1h**, which might promote the nucleophilic addition of the carbamate nitrogen to the double bond to give vinyl(crotyl)palladium(2+) intermediate **I**.[16] Reductive elimination of Pd(0) would convert **I** to **2m**. Pathway b involves a (π-allyl)palladium intermediate **II** that is generated by the addition of crotylpalladium(2+) to the allenic C_2-C_3

(14) For the related oxidative addition of allylic carbamates and isoureas to Pd(0), see: (a) Minami, I.; Ohashi, Y.; Shimizu, I.; Tsuji, J. *Tetrahedron Lett.* **1985**, *26*, 2449. (b) Inoue, Y.; Toyofuku, M.; Taguchi, M.; Okada, S.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 885.

(15) Tamaru, Y.; Kimura, M.; Tanaka, S.; Kure, S.; Yoshida, Z. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 2838.

(16) A similar mechanism was proposed for a Pd(0)-catalyzed allyloxycyclization across acetylenic triple bonds, lithium alkynoate with allylic acetates[16a] and allyl alkynoates:[16b] (a) Yanagihara, N.; Lambert, C.; Iritani, K.; Utimoto, K.; Nozaki, H. *J. Am. Chem. Soc.* **1986**, *108*, 2753. (b) Tsuda, T.; Ohashi, Y.; Nagahama, N.; Sumiya, R.; Saegusa, T. *J. Org. Chem.* **1988**, *53*, 2650. See also: (c) Arcadi, A.; Burini, A.; Cacchi, S.; Delmastro, M.; Marinelli, F.; Pietroni, B. R. *J. Org. Chem.* **1992**, *57*, 976. For aryloxycyclization of hexa-4,5-dien-1-ols, see ref 11g.

Table 5. Palladium-Catalyzed Allylaminocyclization of 3,4-Pentadienyl Tosylcarbamates 5[a]

run	carbamate 5	R^1	R^2	base	solvent	reaction conditions	% yield 6	% yield 7
1	**5a**	H	H	Et_3N	THF	rt, 44 h	0	67 (**7a**)
2	**5a**	H	H	$ClCH_2CO_2Na$	MeOH	50 °C, 24 h	0	0
3	**5b**	H	Me	Et_3N	THF	rt, 22 h	0	64 (**7b**)
4	**5c**	Me	H	Et_3N	THF	50 °C, 20 h	0	78 (**7c**)
5	**5c**	Me	H	$ClCH_2CO_2Na$	MeOH	50 °C, 25 h	52 (**6c**)	0
6	**5d**	Me	Me	AcONa	MeOH	50 °C, 43 h	44 (**6d**)	25 (**7d**)

[a] Reaction conditions: **5**, 1 mmol; allyl chloride, 20 mmol; $PdCl_2(PhCN)_2$, 0.1 mmol; base, 1 mmol in a given dry solvent (6 mL) under nitrogen.

Table 6. Vicinal Coupling Constants, $^3J_{H4H5}$ (Hz), of Products 2, 4, and 6[a]

compound	J_{trans}	J_{cis}	compound	J_{trans}	J_{cis}
2a	3.4	8.7	*trans*-**2m**	2.9	
(*E*)-**2b**	3.3	8.8	*trans*-**2n**	2.2	
(*Z*)-**2b**	3.3	8.8	*trans*-**2o**	2.6	
trans-**2c**	3.3		*trans*-**2p**	2.8	
trans-**2e**	3.3		**4a**	2.6	8.6
trans-**2f**	3.3		*trans,trans*-**4e**	3.0	
trans-**2g**	2.9		*trans,trans*-**4g**	2.6	
trans-**2h**	2.9		*trans,trans*-**4h**	2.4	
trans-**2i**	3.3		*trans,cis*-**4h**	3.1	
trans-**2k**	3.8		**6c**	9.2	7.7
cis-**2k**		5.7	*trans*-**6d**	10.1	
trans-**2l**	2.6				

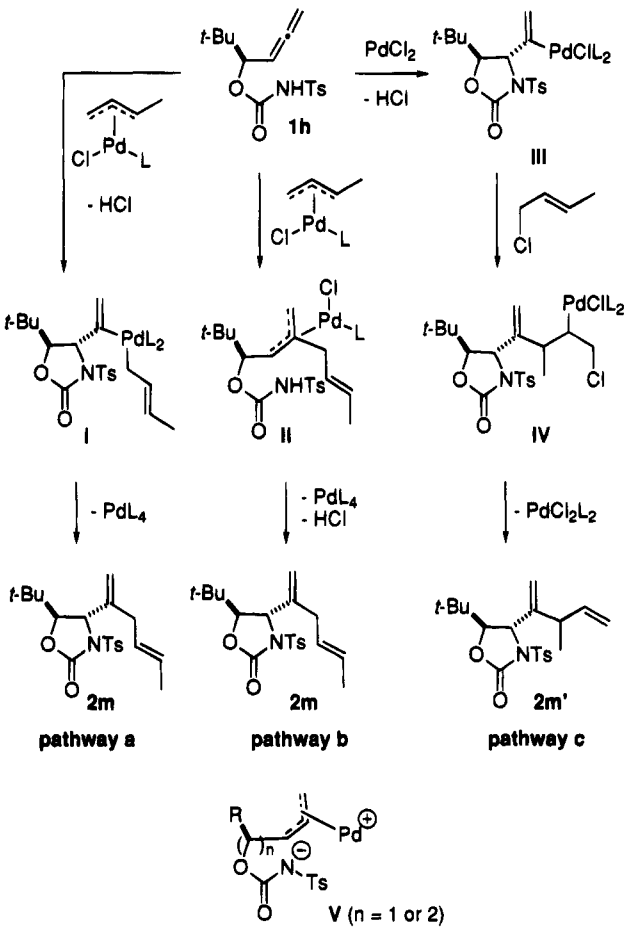
[a] Determined by 400 MHz ^1H NMR.

bond.[3c,17] Intramolecular nucleophilic substitution with the carbamate anion furnishes **2m** and Pd(0). Pathway c is initiated by the coordination of $PdCl_2$ to the C_2-C_3 double bond of **1h**, which promotes cycloamination to generate a vinylpalladium(2+) chloride intermediate **III**, which adds to the double bond of crotyl chloride in such a way as to give a β-chloroethylpalladium(2+) chloride intermediate **IV**.[18] Dechloropalladation from **IV** provides **2m′** and $PdCl_2$.

Of these possibilities, pathway c may be safely excluded because it predicts the wrong regiochemistry in the product, providing **2m′** as opposed to **2m**. This pathway would be acceptable if crotyl chloride isomerized to α-methallyl chloride under the reaction conditions and **III** reacted selectively with α-methallyl chloride. However, no such isomerization was detected at all throughout the reaction by monitoring the mixture by GLC (gas–liquid chromatography).

The dependence of the product selectivity (**2k** vs **3k**, Table 2) on the concentration of carbamate anion, providing **2k** in higher proportion with the lower concentrations of carbamate anion, may be rationalized by supposing that a (π-allyl)palladium complex is a common intermediate with which the allene C_2-C_3 double bond and carbamate anion react competitively. Thus, in the case of **1k**, the terminal dimethyl group sterically hinders an approach of the (π-allyl)palladium complex to the allene C_2-C_3 double bond, and therefore, the (π-allyl)palladium complex may only be able to react with the carbamate moiety to selectively provide **3k**; in this case, the addition of (π-allyl)palladium complex to the C_2-C_3 double bond may become probable only when the N-allylation is retarded by making the concentration of the carbamate

Scheme 1. Reaction Pathways for the Pd-Catalyzed Allylaminocyclizationof 1h with Crotyl Chloride



anion very low. On the other hand, the C_2-C_3 double bonds of **1a–i**, judging from the selective formation of **2a–i**, seem to be much more reactive toward (π-allyl)palladium than carbamate, although under the conditions, the carbamate moiety must be fully ionized.

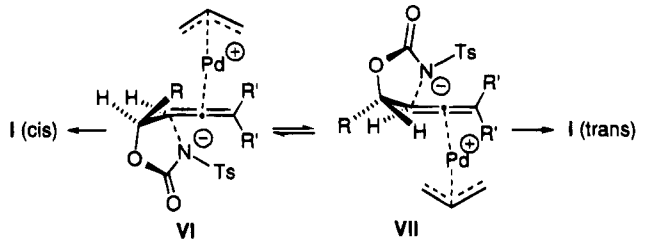
Between pathways a and b, the former is preferred, since the following arguments suggest that the latter is much less likely. (a) An intermediate **V** ($n = 1$, Scheme 1), of a structure similar to **II**, was proposed by Trost for the palladium-catalyzed transformation of vinyl epoxides into 4-vinyl-2-oxazolidinones.[19] In those reactions, the C_4-C_5 *trans* selectivity is not as high as observed in our cases. (b) 3,4-Pentadienyl carbamates **5** are very reluctant to undergo the allylaminocyclization (eq 2, Table 5). If the present allylaminocyclization follows pathway b, there is no rationalization for this reluctance; the (π-allyl)palladium should add to the C_3-C_4 double bond of

(17) For the generation of (π-allyl)palladium via an addition of C(sp²)–Pd to allenic double bonds, see: (a) Shimizu, I.; Tsuji, J. *Chem. Lett.* **1984**, 233. (b) Koerber, K.; Gore, J.; Vatele, J.-M. *Tetrahedron Lett.* **1991**, *32*, 1187. (c) Ganthier, V.; Cazes, B.; Gore, J. *Ibid.* **1991**, *32*, 915. (d) Larock, R. C.; Berrios-Pena, N. G.; Fried, C. A. *J. Org. Chem.* **1991**, *56*, 2615. See also ref 11f.

(18) (a) Iritani, K.; Yanagihara, N.; Utimoto, K. *J. Org. Chem.* **1986**, *51*, 5499. (b) Fukuda, Y.; Shiragami, H.; Utimoto, K.; Nozaki, H. *Ibid.* **1991**, *56*, 5816.

(19) (a) Trost, B. M.; Sudhakar, A. R. *J. Am. Chem. Soc.* **1987**, *109*, 3792. (b) Trost, B. M.; Sudhakar, A. R. *Ibid.* **1988**, *110*, 7933.

Scheme 2. Transition States for Allylaminocyclization



5 and provide a 4-allyl-substituted derivative of **V** (n = 2, Scheme 1) as easily as **II** is formed from **1h**. We previously proposed an intermediate **V** (n = 2) for the palladium-catalyzed transformation of cyclic carbonates of 1-vinylpropane-1,3-diols into 4-vinyltetrahydro-1,3-oxazin-2-ones.[20] This transformation, providing six-membered nitrogen heterocycles, proceeded smoothly at room temperature.

Pathway a seems to be further supported by the contrasting reactivity between **1** and **5** since, in this pathway, the cyclization step is rate-determining. The disinclination of **5** toward cyclization to form six-membered rings may be attributed to the larger losses of entropy of activation, as compared with the cyclization of **1** to provide a five-membered intermediate like **I**.

Pathways a and b seem to be flawed by the slow reaction and the low yield of **2**, observed for the reactions of **1h** with stoichiometric amounts of chloro-(π-allyl)-palladium(2+) dimers (runs 1 and 2, Table 3). However, the slow reaction and the side reaction, furnishing **4**, might be attributed to subtle differences in either the ligands on palladium or the forms in which the palladium species exist in solution.

The dienylaminopalladation providing **4**, on the other hand, seems to follow pathway b; i.e. 1,3-butadien-2-ylpalladium(2+) intermediate may add to the C_2-C_3 double bond of **1** in such a way as to generate a (π-allyl)-palladium intermediate like **II**, which undergoes cyclization to provide **4** with moderate *trans* selectivity.[19] Inhibition of the reaction by NaH (run 7, Table 4) might be attributed to a reluctant oxidative addition of the C_1-carbamate anion bond to Pd(0) and hence a reluctant generation of the 1,3-butadien-2-ylpalladium(2+) intermediate.

The interpretation of the excellent *trans* selectivity of **2** seems to be straightforward according to pathway a. Of the two transition states indicated in Scheme 2, **VII** (R′ = H) is apparently favored over **VI** (R′ = H) since **VI** (R′ = H) suffers from a gauche repulsion between R and the allenic central carbon, the latter being coordinated by (π-allyl)palladium complexes and hence being sterically demanding. The exceptionally low stereoselectivity of **2k** (footnote *c*, Table 2) may be attributed to the severe repulsive interactions of R′ (= Me) groups against *N*-Ts and (π-allyl)palladium, being present in both **VI** and **VII** (R′ = Me), which diminish the preference of **VII** over **VI** (R′ = Me).

Conclusions

2,3-Butadienyl tosylcarbamates (**1**, R = Ts) display a versatile reactivity, the nitrogen atom serving either as an intramolecular nucleophile toward the C_2 carbon of the C_2-C_3 double bond activated by the coordination of (π-allyl)palladium(2+) to provide 2-oxazolidinones **2** or as an intermolecular nucleophile toward (π-allyl)palladium(2+) to give **3**. Under appropriate conditions, the carbamate moiety of **1** also serves as a leaving group by the reaction with Pd(0) and provides 1,3-butadien-2-ylpalladium(2+), an intermediate for a self-condensation of **1** to provide 2-oxazolidinone **4**. These reactions, providing either **2**, **3**, or **4**, can be controlled by an appropriate selection of the reaction conditions. Products **2** are obtained with excellent *trans* selectivity and in good yields by using $PdCl_2(PhCN)_2$ or $Pd_2(dba)_3{\cdot}CHCl_3$ as a catalyst in the presence of Et_3N or K_2CO_3 and 2−20 equiv of allylic chlorides, and products **3** are obtained under similar conditions, using $Pd(PPh_3)_4$ or $PdCl_2/4PPh_3$ as a catalyst. The products **4** are obtained by simply mixing **1**, Et_3N, and a catalytic amount of $Pd(PPh_3)_4$ at room temperature in THF. The allylaminocyclization of **5** to provide **6** is successful only for some derivatives having appropriate combinations of R^1 and R^2 substituents.

The products **2**, **4**, and **6** are the protected forms of dienyl and trienyl allylic amino alcohols of defined stereochemistry and might be utilized effectively as intermediates for the synthesis of amino sugars, rare amino acids, and related compounds of physiological interest.

Experimental Section

Melting points are not corrected. Unless otherwise specified, short-path (bulb-to-bulb) distillations were carried out in a Kugelrohr apparatus. In these cases, boiling points refer to the oven temperature. Microanalyses were performed by the Microanalysis Center of Nagasaki University. Analysis agreed with the calculated values within ±0.3%. Proton magnetic resonance spectra were determined either at 60 or 400 MHz with TMS as an internal standard. Chemical shift values were given in ppm downfield from TMS. R_f values were measured with Merck Kieselgel $60F_{254}$.

Solvents and Reagents. THF and ether were dried and distilled from benzophenone sodium ketyl immediately before use under nitrogen. Benzene, triethylamine, and pyridine were distilled over CaH_2. Methanol was dried and distilled from Mg and I_2 under nitrogen. $PdCl_2$, $Pd(OAc)_2$, K_2CO_3, $ClCH_2CO_2Na$, AcONa, and Cs_2CO_3 were purchased and used without purification. $PdCl_2(PhCN)_2$, $Pd_2(dba)_3{\cdot}CHCl_3$, and $Pd(PPh_3)_4$ were prepared from $PdCl_2$ according to the literature.[21] Allyl chloride, allyl bromide, cinnamyl chloride, crotyl chloride, α-methallyl chloride, and prenyl chloride were purchased and distilled prior to use. 2-Chloro-3-pentene[22] and allyl methyl carbonate[23] were prepared according to the literature. 2,3-Butadienyl tosylcarbamates **1a−k** and 3,4-pentadienyl tosylcarbamates **5a−d** were prepared according to the method reported previously from the authors' laboratories.[10b]

General Procedure for the Allylaminocyclization of 2,3-Butadienyl Carbamates 1. Case 1 (run 1 in Table 1). A two-necked round-bottomed flask, containing a magnetic stirring bar, **1a** (267.2 mg, 1 mmol), and $PdCl_2(PhCN)_2$ (38.4 mg, 0.1 mmol), was fitted with a serum cap and a reflux condenser equipped with a three-way stopcock connected to a nitrogen balloon. The apparatus was purged with nitrogen several times via the three-way stopcock. Dry THF (3 mL), triethylamine (140 μL, 1 mmol), and allyl chloride (1.6 mL, 20 mmol) were added in this order in one portion via syringes. The reaction mixture was stirred at rt for 19 h. The reaction was monitored by TLC (R_f(**1a**) = 0.38, R_f(**2a**) = 0.51, hexane−ethyl acetate, 2/1 v/v). After the addition of saturated $NaHCO_3$ (20 mL), the reaction mixture was extracted with ethyl acetate (2 × 20 mL). The combined extracts were dried ($MgSO_4$), filtered, and concentrated. The residue was purified by column

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chromatography over silica gel (eluent, hexane–ethyl acetate, 9:1, v/v) to give **2a** in 53% yield.

Case 2 (run 2, Table 2). Into a stirred mixture of **1k** (323 mg, 1 mmol), $PdCl_2(PhCN)_2$ (38.4 mg, 0.1 mmol), and allyl chloride (1.6 mL, 20 mmol) in dry THF (3 mL), prepared via the same procedure as case 1, was added triethylamine (140 μL, 1 mmol) dissolved in dry THF (10 mL) over a period of 6 h at rt with a syringe pump. The mixture was stirred for an additional 6 h at rt, worked up, and purified in the same way as in case 1 to provide **2k** (45%, R_f = 0.59) and **3k** (18%, R_f = 0.69, hexane–ethyl acetate, 2:1, v/v).

***N*-*p*-Toluenesulfonyl-4-(1-allylvinyl)-2-oxazolidinone (2a):** oil; IR (neat film) 1790 (s), 1370 (s), 910 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.45 (s, 3 H), 2.50 (dd, *J* = 7.0, 16.5 Hz, 1 H), 2.67 (dd, *J* = 7.0, 16.5 Hz, 1 H), 4.09 (dd, *J* = 3.4, 8.7 Hz, 1 H), 4.46 (t, *J* = 8.7 Hz, 1 H), 4.96 (dd, *J* = 3.4, 8.7 Hz, 1 H), 5.00 (br d, *J* = 17.0 Hz, 1 H), 5.08 (s, 1 H), 5.10 (br d, *J* = 10.3 Hz, 1 H), 5.17 (s, 1 H), 5.66 (ddt, *J* = 10.3, 17.0, 7.0 Hz, 1 H), 7.34 (d, *J* = 8.2 Hz, 2 H), 7.93 (d, *J* = 8.2 Hz, 2 H); HRMS calcd for $C_{15}H_{17}NO_4S$ 307.0879, found *m*/*z* (relative intensity) 307.0879 (M, 19), 243 (17), 152 (100), 138 (18), 122 (13), 108 (19), 91 (74).

***N*-*p*-Toluenesulfonyl-4-(1-allyl)-1-propenyl-2-oxazolidinone (2b):** a mixture of (*E*)- and (*Z*)-**2b** in a ratio of 2.3:1; oil; IR (neat film) 1790 (s), 1375 (s), 1180 (s), 655 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, (*E*)-**2b**) δ 1.64 (d, *J* = 7.0 Hz, 3 H), 2.43 (dd, *J* = 6.7, 16.1 Hz, 1 H), 2.45 (s, 3 H), 2.63 (dd, *J* = 5.5, 16.1 Hz, 1 H), 4.12 (dd, *J* = 3.3, 8.8 Hz, 1 H), 4.37 (t, *J* = 8.8 Hz, 1 H), 4.87 (dd, *J* = 3.3, 8.8 Hz, 1 H), 4.98 (br dd, *J* = 1.5, 10.3 Hz, 1 H), 5.01 (br dd, *J* = 1.5, 16.9 Hz, 1 H), 5.62 (dddd, *J* = 5.5, 6.7, 10.3, 16.9 Hz, 1 H), 5.71 (q, *J* = 7.0 Hz, 1 H), 7.33 (d, *J* = 8.4 Hz, 2 H), 7.88 (d, *J* = 8.4 Hz, 2 H); ^1H NMR ($CDCl_3$, 400 MHz, (*Z*)-**2b**) δ 1.81 (d, *J* = 6.8 Hz, 3 H), 2.28 (br dd, *J* = 6.7, 16.1 Hz, 1 H), 2.45 (s, 3 H), 2.52 (br dd, *J* = 5.5, 16.1 Hz, 1 H), 4.08 (dd, *J* = 3.3, 8.8 Hz, 1 H), 4.46 (t, *J* = 8.8 Hz, 1 H), 5.45 (dd, *J* = 3.3, 8.8 Hz, 1 H), 4.98–5.70 (m, 4 H), 7.33 (d, *J* = 8.4 Hz, 2 H), 7.88 (d, *J* = 8.4 Hz, 2 H); HRMS calcd for $C_{16}H_{19}NO_4S$ 321.1035, found *m*/*z* (relative intensity) 321.1037 (M, 18), 257 (18), 166 (51), 122 (45), 91 (100).

***trans*-*N*-*p*-Toluenesulfonyl-5-methyl-4-(1-allylvinyl)-2-oxazolidinone (*trans*-2c):** oil; IR (neat film) 1785 (s), 1370 (s), 1170 (s), 950 (s), 740 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.39 (d, *J* = 6.2 Hz, 3 H), 2.45 (s, 3 H), 2.60 (dd, *J* = 7.0, 16.5 Hz, 1 H), 2.69 (dd, *J* = 7.0, 16.5 Hz, 1 H), 4.33 (dq, *J* = 3.3, 6.2 Hz, 1 H), 4.45 (d, *J* = 3.3 Hz, 1 H), 5.03 (br dd, *J* = 2.9, 17.2 Hz, 1 H), 5.07 (br s, 1 H), 5.11 (br dd, *J* = 2.9, 10.3 Hz, 1 H), 5.15 (s, 1 H), 5.69 (ddt, *J* = 10.3, 17.2, 7.2 Hz, 1 H), 7.34 (d, *J* = 8.4 Hz, 2 H), 7.93 (d, *J* = 8.4 Hz, 2 H); HRMS calcd for $C_{16}H_{19}NO_4S$ 321.1035, found *m*/*z* (relative intensity) 321.1038 (M, 28), 257 (34), 166 (100), 139 (5), 123 (23), 91 (88).

***N*-*p*-Toluenesulfonyl-5-methyl-4-(1-allyl)-1-propenyl-2-oxazolidinone (2d):** a mixture of diastereomers in a ratio of 14:11:2:1; oil; IR (neat film) 1780 (s), 1370 (s), 1170 (s), 650 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, the former two isomers, assigned) δ 1.23 (d, *J* = 6.2 Hz, Me for the major isomer), 1.35 (d, *J* = 6.6 Hz, Me for the minor isomer), 1.56 (d, *J* = 7.0 Hz, Me for the minor isomer), 1.66 (d, *J* = 7.0 Hz, Me for the major isomer), 2.44 (s, Me for the minor isomer), 2.45 (s, Me for the major isomer), 2.47–2.56 (m, 1 H, one of the CH_2 groups for both isomers), 2.71 (dd, *J* = 5.5, 16.1 Hz, one of the CH_2 groups for the major isomer), 2.87 (br dd, *J* = ca. 5.1, 16.0 Hz, one of the CH_2 groups for the minor isomer), 4.33–4.40 (m, CHO and CHN for the major isomer), 4.75 (quint, *J* = 6.7 Hz, CHO for the minor isomer), 4.82 (d, *J* = 6.7 Hz, CHN for the minor isomer), 4.91–5.13 (m, CH_2= for both isomers), 5.26 (br q, *J* = ca. 7 Hz, =C*H*Me for the minor isomer), 5.60–5.72 (m, =C*H*Me for the major isomer and =C*H*CH_2 for both isomers), 7.30–7.35 (m, 2 H), 7.87–7.90 (m, 2 H); HRMS calcd for $C_{17}H_{21}NO_4S$ 335.1191, found *m*/*z* (relative intensity) 335.1194 (M, 100), 271 (8), 180 (35), 136 (13), 100 (8), 91 (54).

***trans*-*N*-*p*-Toluenesulfonyl-5-ethyl-4-(1-allylvinyl)-2-oxazolidinone (*trans*-2e):** oil; IR (neat film) 1780 (s), 1370 (s), 1170 (s), 730 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.95 (t, *J* = 7.3 Hz, 3 H), 1.69 (m, 2 H), 2.45 (s, 3 H), 2.56 (dd, *J* = 7.0, 16.5 Hz, 1 H), 2.68 (dd, *J* = 7.0, 16.5 Hz, 1 H), 4.13 (dt, *J* = 3.3, 6.2 Hz, 1 H), 4.53 (d, *J* = 3.3 Hz, 1 H), 5.03 (br d, *J* = 17.2 Hz, 1 H), 5.06 (br s, 1 H), 5.11 (br d, *J* = 10.2 Hz, 1 H), 5.15 (s, 1 H), 5.69 (ddt, *J* = 10.2, 17.2, 7.0 Hz, 1 H), 7.34 (d, *J* = 8.1 Hz, 2 H), 7.92 (d, *J* = 8.1 Hz, 2 H); HRMS calcd for $C_{17}H_{21}NO_4S$ 335.1191, found *m*/*z* (relative intensity) 335.1196 (M, 48), 265 (18), 180 (93), 166 (18), 122 (36), 91 (100).

***trans*-*N*-*p*-Toluenesulfonyl-5-*n*-propyl-4-(1-allylvinyl)-2-oxazolidinone (*trans*-2f):** oil; IR (neat film) 1780 (s), 1360 (s), 1170 (s), 910 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.93 (t, *J* = 7.3 Hz, 3 H), 1.43 (tq, *J* = 5.9, 7.3 Hz, 2 H), 1.51–1.70 (m, 2 H), 2.45 (s, 3 H), 2.55 (dd, *J* = 6.8, 16.5 Hz, 1 H), 2.67 (dd, *J* = 6.8, 16.5 Hz, 1 H), 4.17 (br d, *J* = 3.3 Hz, 1 H), 4.51 (d, *J* = 3.3 Hz, 1 H), 5.02 (br dd, *J* = 1.5, 16.8 Hz, 1 H), 5.06 (br s, 1 H), 5.11 (br d, *J* = 10.3 Hz, 1 H), 5.15 (s, 1 H), 5.69 (ddt, *J* = 10.3, 16.8, 6.8 Hz, 1 H), 7.35 (d, *J* = 8.4 Hz, 2 H), 7.92 (d, *J* = 8.4 Hz, 2 H); HRMS calcd for $C_{18}H_{23}NO_4S$ 349.1348, found *m*/*z* (relative intensity) 349.1350 (M, 46), 285 (32), 247 (16), 194 (100), 149 (5), 91 (71).

***trans*-*N*-*p*-Toluenesulfonyl-5-isopropyl-4-(1-allylvinyl)-2-oxazolidinone (*trans*-2g):** oil; IR (neat film) 2960 (m), 1780 (s), 1600 (m), 1370 (s), 1170 (s), 910 (s), 760 (m) ; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.93 (d, *J* = 6.8 Hz, 3 H), 0.95 (d, *J* = 6.8 Hz, 3 H), 1.88 (br dq, *J* = 5.9, 6.8 Hz, 1 H), 2.44 (s, 3 H), 2.52 (dd, *J* = 6.9, 16.7 Hz, 1 H), 2.65 (dd, *J* = 6.9, 16.7 Hz, 1 H), 3.95 (dd, *J* = 2.9, 5.9 Hz, 1 H), 4.65 (d, *J* = 2.9 Hz, 1 H), 4.99 (br d, *J* = 16.9 Hz, 1 H), 5.05 (br s, 1 H), 5.10 (br d, *J* = 10.3 Hz, 1 H), 5.16 (s, 1 H), 5.68 (ddt, *J* = 10.3, 16.9, 6.9 Hz, 1 H), 7.33 (d, *J* = 8.2 Hz, 2 H), 7.92 (d, *J* = 8.2 Hz, 2 H); HRMS calcd for $C_{18}H_{23}NO_4S$ 349.1348, found *m*/*z* (relative intensity) 349.1366 (M, 53), 194 (100), 180 (17), 122 (33), 91 (97), 79 (20).

***trans*-*N*-*p*-Toluenesulfonyl-5-*tert*-butyl-4-(1-allylvinyl)-2-oxazolidinone (*trans*-2h):** oil; IR (neat film) 1790 (s), 1370 (s), 1180 (s), 930 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.92 (s, 9 H), 2.45 (s, 3 H), 2.50 (dd, *J* = 7.0, 16.7 Hz, 1 H), 2.63 (dd, *J* = 7.0, 16.7 Hz, 1 H), 3.82 (d, *J* = 2.9 Hz, 1 H), 4.73 (d, *J* = 2.9 Hz, 1 H), 5.01 (br d, *J* = 17.2 Hz, 1 H), 5.05 (br s, 1 H), 5.12 (br d, *J* = 10.3 Hz, 1 H), 5.16 (s, 1 H), 5.67 (ddt, *J* = 10.3, 17.2, 7.0 Hz, 1 H), 7.33 (d, *J* = 8.2 Hz, 2 H), 7.93 (d, *J* = 8.2 Hz, 2 H); HRMS calcd for $C_{19}H_{25}NO_4S$ 363.1505, found *m*/*z* (relative intensity) 363.1496 (M, 76), 208 (50), 91 (100).

***trans*-*N*-*p*-Toluenesulfonyl-5-phenyl-4-(1-allylvinyl)-2-oxazolidinone (*trans*-2i):** oil; IR (neat film) 1780 (s), 1598 (m), 1368 (s), 1170 (s), 1130 (s), 1088 (m), 918 (m), 805 (m), 650 (m); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.47 (s, 3 H), 2.73 (dd, *J* = 6.8, 16.5 Hz, 1 H), 2.82 (dd, *J* = 6.8, 16.5 Hz, 1 H), 4.74 (d, *J* = 3.3 Hz, 1 H), 5.08 (br d, *J* = 17.0 Hz, 1 H), 5.14 (br d, *J* = 10.3 Hz, 1 H), 5.15 (s, 1 H), 5.16 (d, *J* = 3.3 Hz, 1 H), 5.21 (s, 1 H), 5.78 (ddt, *J* = 10.3, 17.0, 6.8 Hz, 1 H), 7.14–7.40 (m, 5 H), 7.33 (d, *J* = 8.4 Hz, 2 H), 7.88 (d, *J* = 8.4 Hz, 2 H); HRMS calcd for $C_{21}H_{21}NO_4S$ 383.1192, found *m*/*z* (relative intensity) 383.1192 (M, 27), 229 (3), 228 (57), 184 (26), 170 (15), 123 (21), 122 (100), 91 (45).

***N*-*p*-Toluenesulfonyl-5-ethyl-4-(1-allyl-2,2-dimethylvinyl)-2-oxazolidinone (2k):** a mixture of *trans*-**2k** and *cis*-**2k** in a ratio of 1.5:1; oil; IR (neat film) 2960 (m), 1790 (s), 1600 (w), 1370 (s), 1180 (s), 760 (w), 650 (m); ^1H NMR ($CDCl_3$, 400 MHz, *trans*-**2k**) δ 0.95 (t, *J* = 7.4 Hz, 3 H), 1.63–1.76 (m, 2 H), 1.72 (s, 3 H), 1.91 (s, 3 H), 2.28 (m, 1 H), 2.44 (m, 1 H), 2.45 (s, 3 H), 4.20 (dt, *J* = 3.8, 5.9 Hz, 1 H), 4.91 (br d, *J* = 17.0 Hz, 1 H), 4.93 (br d, *J* = 10.1 Hz, 1 H), 5.06 (d, *J* = 3.8 Hz, 1 H), 5.64 (br dd, *J* = 10.1, 17.0 Hz, 1 H), 7.33 (d, *J* = 8.4 Hz, 2 H), 7.84 (d, *J* = 8.4 Hz, 2 H); ^1H NMR ($CDCl_3$, 400 MHz, *cis*-**2k**) δ 0.93 (t, *J* = 7.4 Hz, 3 H), 1.35–1.50 (m, 2 H), 1.75 (s, 3 H), 1.88 (s, 3 H), 2.20–2.52 (m, 2 H), 2.45 (s, 3 H), 4.48 (br d, *J* = 5.7 Hz, 1 H), 4.83 (br d, *J* = 10.1 Hz, 1 H), 4.84 (br d, *J* = 17.0 Hz, 1 H), 5.46 (d, *J* = 5.7 Hz, 1 H), 5.48 (br dd, *J* = 10.1, 17.0 Hz, 1 H), 7.33 (d, *J* = 8.4 Hz, 2 H), 7.88 (d, *J* = 8.4 Hz, 2 H); HRMS calcd for $C_{19}H_{25}NO_4S$ 363.1505, found *m*/*z* (relative intensity) 363.1513 (M, 100), 290 (12), 168 (8), 209 (7), 208 (57), 91 (41).

***trans*-*N*-*p*-Toluenesulfonyl-5-*tert*-butyl-4-[1-(2-methylallyl)vinyl]-2-oxazolidinone (*trans*-2l):** oil; IR (neat film) 1790 (s), 1370 (s), 1170 (s), 810 (m), 660 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.91 (s, 9 H), 1.71 (s, 3 H), 2.44 (s, 3 H), 2.61 (br s, 2 H), 3.81 (d, *J* = 2.6 Hz, 1 H), 4.70 (d, *J* = 2.6 Hz, 1 H), 4.77 (br s, 1 H), 4.91 (br s, 1 H), 5.04 (br s, 1 H), 5.16 (s, 1 H), 7.33 (d, *J* = 8.2 Hz, 2 H), 7.94 (d, *J* = 8.2 Hz, 2 H); HRMS calcd for $C_{20}H_{27}NO_4S$ 377.1661, found *m*/*z* (relative intensity) 377.1681 (M, 32), 222 (100), 166 (20), 91 (46).

***trans*-N-*p*-Toluenesulfonyl-5-*tert*-butyl-4-(1-*trans*-crotylvinyl)-2-oxazolidinone (*trans,trans*-2m):** oil; IR (neat film) 1790 (s), 1375 (s), 1180 (s), 815 (m), 650 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.92 (s, 9 H), 1.66 (dd, J = 1.5, 6.4 Hz, 3 H), 2.44 (s, 3 H), 2.45 (dd, J = 6.6, 16.9 Hz, 1 H), 2.59 (dd, J = 6.6, 16.9 Hz, 1 H), 3.81 (d, J = 2.9 Hz, 1 H), 4.71 (d, J = 2.9 Hz, 1 H), 5.02 (s, 1 H), 5.12 (s, 1 H), 5.27 (dtq, J = 15.0, 6.6, 1.5 Hz, 1 H), 5.40 (dq, J = 15.0, 6.4 Hz, 1 H), 7.32 (d, J = 8.2 Hz, 2 H), 7.92 (d, J = 8.2 Hz, 2 H); HRMS calcd for $C_{20}H_{27}NO_4S$ 377.1661, found m/z (relative intensity) 377.1656 (M, 100), 293 (12), 222 (27), 166 (28), 91 (29).

***trans*-N-*p*-Toluenesulfonyl-5-*tert*-butyl-4-[1-(*trans*-1,3-dimethylallyl)vinyl]-2-oxazolidinone (*trans,trans*-2n):** oil; IR (neat film) 2950 (m), 1785 (s), 1370 (s), 1170 (s), 810 (m), 665 (m); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.90 (s, 9 H), 1.20 (d, J = 7.0 Hz, 3 H), 1.59 (br d, J = 6.0 Hz, 3 H), 2.43 (s, 3 H), 2.79 (quint, J = 7.0 Hz, 1 H), 3.85 (d, J = 2.2 Hz, 1 H), 4.66 (d, J = 2.2 Hz, 1 H), 5.00 (br s, 1 H), 5.04 (br s, 1 H), 5.21 (br dd, J = 7.0, 15.2 Hz, 1 H), 5.48 (br dq, J = 15.2, 6.0 Hz, 1 H), 7.31 (d, J = 8.2 Hz, 2 H), 7.91 (d, J = 8.2 Hz, 2 H); HRMS calcd for $C_{21}H_{29}NO_4S$ 391.1818, found m/z (relative intensity) 391.1823 (M, 100), 377 (19), 296 (14), 240 (13), 236 (87), 180 (38), 166-(22), 91 (51).

***trans*-N-*p*-Toluenesulfonyl-5-*tert*-butyl-4-[1-(*trans*-3-phenylallyl)vinyl-2-oxazolidinone (*trans,trans*-2o):** mp 159.0–160.5 °C (benzene–hexane); IR (KBr disk) 1780 (s), 1380 (s), 1175 (s), 750 (m), 660 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.93 (s, 9 H), 2.44 (s, 3 H), 2.67 (dd, J = 7.0, 16.9 Hz, 1 H), 2.81 (dd, J = 7.0, 16.9 Hz, 1 H), 3.87 (d, J = 2.6 Hz, 1 H), 4.76 (d, J = 2.6 Hz, 1 H), 5.10 (s, 1 H), 5.20 (s, 1 H), 6.04 (dt, J = 15.8, 7.0 Hz, 1 H), 6.32 (d, J = 15.8 Hz, 1 H), 7.29 (m, 5 H), 7.34 (d, J = 8.1 Hz, 2 H), 7.95 (d, J = 8.1 Hz, 2 H). Anal. Calcd for $C_{25}H_{29}NO_4S$: C, 68.32; H, 6.65; N, 3.19; S, 7.29. Found: C, 68.15; H, 6.58; N, 3.29; S, 7.22.

***trans*-N-*p*-Toluenesulfonyl-5-*tert*-butyl-4-[1-(3,3-dimethylallyl)vinyl]-2-oxazolidinone (*trans*-2p):** oil; IR (neat film) 1790 (s), 1375 (s), 1175 (s), 650 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.92 (s, 9 H), 1.51 (s, 3 H), 1.71 (s, 3 H), 2.44 (s, 3 H), 2.49 (dd, J = 7.3, 17.2 Hz, 1 H), 2.60 (dd, J = 7.3, 17.2 Hz, 1 H), 3.82 (d, J = 2.8 Hz, 1 H), 4.70 (d, J = 2.8 Hz, 1 H), 5.00 (br s, 1 H), 5.02 (br t, J = 7.3 Hz, 1 H), 5.09 (s, 1 H), 7.33 (d, J = 8.4 Hz, 2 H), 7.93 (d, J = 8.4 Hz, 2 H); HRMS calcd for $C_{21}H_{29}NO_4S$ 391.1818, found m/z (relative intensity) 391.1818 (M, 100), 290 (24), 237 (9), 236 (24), 91 (63).

***tert*-Butyl-2,3-butadienyl *N*-allyl-*N*-tosylcarbamate (3h):** oil; IR (neat film) 1955 (m), 1735 (s), 1370 (s), 1175 (s), 930 (m), 650 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 0.90 (s, 9 H), 2.43 (s, 3 H), 4.30–5.05 (m, 6 H), 5.10–5.55 (m, 2 H), 5.60–6.30 (m, 1 H), 7,28 (d, J = 8.4 Hz, 2 H), 7.87 (d, J = 8.4 Hz, 2 H); HRMS calcd for $C_{19}H_{25}NO_4S$ 363.1505, found m/z (relative intensity) 363.1507 (M, 4), 307 (18), 239 (5), 238 (39), 91 (100).

1-Ethyl-4-methyl-2,3-pentadienyl *N*-allyl-*N*-tosylcarbamate (3k): oil; IR (neat film) 2960 (m), 1970 (w), 1730 (s), 1600 (m), 1440 (m), 1364 (s), 1265 (s), 1178 (s), 1090 (s), 920 (m), 818 (w), 744 (m), 660 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.82 (t, J = 7.3 Hz, 3 H), 1.58 (br q, J = 7.3 Hz, 2 H), 1.59 (br d, J = 2.9 Hz, 3 H), 1.61 (br d, J = 2.9 Hz, 3 H), 2.43 (s, 3 H), 4.47 (br d, J = 5.5 Hz, 2 H), 4.48 (br hept, J = 2.9 Hz, 1 H), 4.99 (br d, J = 6.0 Hz, 1 H), 5.25 (br d, J = 10.3 Hz, 1 H), 5.31 (br d, J = 17.2 Hz, 1 H), 5.93 (ddt, J = 10.3, 17.2, 5.5 Hz, 1 H), 7.30 (d, J = 8.4 Hz, 2 H), 7.83 (d, J = 8.4 Hz, 2 H); HRMS calcd for $C_{19}H_{25}NO_4S$ 363.1505, found m/z (relative intensity) 363.1505 (M, 21), 211 (6), 155 (100), 139 (8), 125 (21).

General Procedure for the 1,3-Dien-2-ylaminocyclization of 2,3-Butadienyl Tosylcarbamates 1 (run 1, Table 4 as a typical example). A two-necked round-bottomed flask, containing a magnetic stirring bar, **1a** (267.3 mg, 1.0 mmol), and $Pd(PPh_3)_4$ (115.6 mg, 0.1 mmol), was fitted with a serum cap and a reflux condenser equipped with a three-way stopcock connected to a nitrogen balloon. The apparatus was purged with nitrogen several times via the three-way stopcock. Dry THF (3 mL) and triethylamine (140 μL, 1.0 mmol) were introduced via syringes. The reaction mixture was stirred at rt for 16 h. After the addition of saturated $NaHCO_3$ (20 mL), the reaction mixture was extracted with ethyl acetate (2 × 20 mL). The combined extracts were dried ($MgSO_4$), filtered, and concentrated. The residue was purified by column chromatography over silica gel (eluent, hexane–ethyl acetate, 9:1) to give **4a** in 22% yield.

***N*-*p*-Toluenesulfonyl-4-[1-(1,3-butadien-2-yl)vinyl]-2-oxazolidinone (4a)** oil; IR (neat film) 1790 (s), 1600 (m), 1380 (s), 1180 (s), 1100 (m), 920 (m), 820 (m), 740 (m), 660 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.46 (s, 3 H), 4.04 (dd, J = 2.6, 8.6 Hz, 1 H), 4.37 (t, J = 8.6 Hz, 1 H), 5.01 (br s, 1 H), 5.14 (dd, J = 2.6, 8.6 Hz, 1 H), 5.24 (s, 1 H), 5.25 (s, 1 H), 5.26 (d, J = 10.3 Hz, 1 H), 5.27 (s, 1 H), 5.47 (d, J = 17.2 Hz, 1 H), 6.40 (dd, J = 10.3, 17.2 Hz, 1 H), 7.34 (d, J = 8.2 Hz, 2 H), 7.97 (d, J = 8.2 Hz, 2 H); HRMS calcd for $C_{16}H_{17}NO_4S$ 319.0879, found m/z (relative intensity) 319.0876 (M, 25), 267 (8), 224 (10), 223 (100), 171 (6), 149 (4).

***N*-*p*-Toluenesulfonyl-5-methyl-4-[1-(1,3-pentadien-2-yl)vinyl]-2-oxazolidinone (4c):** a mixture of four diastereomers in a ratio of 1:1.7:1.9:2.3; oil; IR (neat film) 1790 (s), 1600 (m), 1370 (s), 1175 (s), 910 (s), 730 (s); ^{1}H NMR ($CDCl_3$, 400 MHz, a mixture of four isomers, not resolved well) δ 1.23, 1.25, 1.30, 1.39 (d, J = 6.2 Hz, Me of each diastereomer); HRMS calcd for $C_{18}H_{21}NO_4S$ 347.1191, found m/z (relative intensity) 347.1191 (M, 4), 192 (35), 148 (37), 107 (18), 91 (100).

***trans*-N-*p*-Toluenesulfonyl-5-ethyl-4-[1-(1,3-hexadien-2-yl)vinyl]-2-oxazolidinone (*trans*-4e):** a mixture of *trans*- and *cis*-1,3-hexadien-2-yl derivatives in a ratio of 3.1:1; oil; IR (neat film) 2940 (m), 1780 (s), 1600 (m), 1460 (m), 1362 (s), 1170 (s), 810 (m), 660 (s); ^{1}H NMR ($CDCl_3$, 400 MHz, *trans,trans*-**4e**) δ 0.88 (t, J = 7.0 Hz, 3 H), 1.06 (t, J = 7.0 Hz, 3 H), 1.48–1.76 (m, 2 H), 2.10–2.22 (m, 2 H), 2.42 (s, 3 H), 4.08 (dt, J = 3.0, 6.4 Hz, 1 H), 4.72 (d, J = 3.0 Hz, 1 H), 4.93 (br s, 1 H), 5.12 (br s, 1 H), 5.20 (br s, 2 H), 6.00 (dt, J = 16.0, 6.0 Hz, 1 H), 6.07 (d, J = 16.0 Hz, 1 H), 7.36 (d, J = 8.2 Hz, 2 H), 7.96 (d, J = 8.2 Hz, 2 H); ^{1}H NMR ($CDCl_3$, 400 MHz, *trans,cis*-**4e**) 0.96 (t, J = 7.0 Hz, 3 H), 1.00 (t, J = 7.0 Hz, 3 H), 1.48–1.76 (m, 4 H), 2.42 (s, 3 H), 4.12 (ddd, J = 3.0, 5.0, 6.4 Hz, 1 H), 4.87 (d, J = 3.0 Hz, 1 H), 5.09 (br s, 1 H), 5.11 (br s, 1 H), 5.20 (br s, 1 H), 5.33 (br s, 1 H), 5.64 (dt, J = 11.2, 7.0 Hz, 1 H), 5.85 (br d, J = 11.2 Hz, 1 H), 7.48 (d, J = 8.2 Hz, 2 H), 7.67 (d, J = 8.2 Hz, 2 H); HRMS calcd for $C_{20}H_{25}NO_4S$ 375.1505, found m/z (relative intensity) 375.1505 (M, 9), 268 (4), 220 (100), 219 (53), 155 (38), 107 (33), 91 (51).

***trans*-N-*p*-Toluenesulfonyl-5-isopropyl-4-[1-(5-methyl-1,3-hexadien-2-yl)vinyl]-2-oxazolidinone (*trans*-4g):** a mixture of *trans*- and *cis*-5-methyl-1,3-hexadien-2-yl isomers in a ratio of 7.5:1; oil; IR (neat film) 2965 (m), 1790 (s), 1600 (m), 1375 (s), 1175 (s), 660 (s); ^{1}H NMR ($CDCl_3$, 400 MHz, *trans,trans*-**4g**) δ 0.83 (d, J = 6.6 Hz, 3 H), 0.84 (d, J = 6.6 Hz, 3 H), 1.05 (d, J = 6.6 Hz, 3 H), 1.06 (d, J = 6.6 Hz, 3 H), 1.73 (m, 1 H), 2.41 (m, 1 H), 2.45 (s, 3 H), 3.98 (dd, J = 2.6, 6.6 Hz, 1 H), 4.79 (d, J = 2.6 Hz, 1 H), 4.93 (br s, 1 H), 5.10 (br s, 1 H), 5.17 (br s, 1 H), 5.18 (br s, 1 H), 5.98 (d, J = 15.0 Hz, 1 H), 5.98 (dd, J = 6.6, 15.0 Hz, 1 H), 7.36 (d, J = 8.4 Hz, 2 H), 7.96 (d, J = 8.4 Hz, 2 H); HRMS calcd for $C_{22}H_{29}NO_4S$ 403.1818, found m/z (relative intensity) 403.1818 (M, 55), 282 (100), 121 (50), 92 (45).

***trans*-N-*p*-Toluenesulfonyl-5-*tert*-butyl-4-[1-(5,5-dimethyl-1,3-hexadien-2-yl)vinyl]-2-oxazolidinone (*trans*-4h):** a mixture of *trans*- and *cis*-5,5-dimethyl-1,3-hexadien-2-yl isomers in a ratio of 2.2:1; oil; IR (neat film) 1790 (s), 1370 (s), 1170 (s), 650 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, *trans,trans*-**4h**) δ 0.80 (s, 9 H), 1.09 (s, 9 H), 2.44 (s, 3 H), 3.79 (d, J = 2.4 Hz, 1 H), 4.83 (d, J = 2.4 Hz, 1 H), 4.95 (d, J = 1.6 Hz, 1 H), 5.10 (d, J = 1.6 Hz, 1 H), 5.17 (s, 2 H), 5.97 (d, J = 16.3 Hz, 1 H), 6.06 (d, J = 16.3 Hz, 1 H), 7.35 (d, J = 8.1 Hz, 2 H), 7.96 (d, J = 8.1 Hz, 2 H); ^{1}H NMR ($CDCl_3$, 400 MHz, *trans,cis*-**4h**) δ 0.94 (s, 9 H), 1.08 (s, 9 H), 2.43 (s, 3 H), 3.89 (d, J = 3.1 Hz, 1 H), 5.04 (d, J = 3.1 Hz, 1 H), 5.13 (s, 1 H), 5.15 (s, 1 H), 5.29 (s, 1 H), 5.39 (s, 1 H), 5.51 (d, J = 12.6 Hz, 1 H), 5.65 (d, J = 12.6 Hz, 1 H), 7.29 (d, J = 8.1 Hz, 2 H), 7.88 (d, J = 8.1 Hz, 2 H); HRMS calcd for $C_{24}H_{33}NO_4S$ 431.2131, found m/z (relative intensity) 431.2134 (M, 14), 375 (9), 277 (25), 276 (100), 240 (5), 220 (12), 91 (36).

***N*-*p*-Toluenesulfonyl-5,5-dimethyl-4-[1-(4-methylpenta-1,3-dien-2-yl)vinyl]-2-oxazolidinone (4j):** mp 154.0–154.8 °C (dichloromethane–hexane); IR (KBr disk) 1775 (s), 1600 (m), 1365 (s), 1260 (s), 1168 (s), 910 (m), 750 (s), 660 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.28 (s, 3 H), 1.49 (s, 3 H), 1.74 (br s, 3 H), 1.84 (br s, 3 H), 2.45 (s, 3 H), 4.89 (br s, 1 H), 5.00 (br

s, 1 H), 5.06 (br s, 1 H), 5.26 (br s, 1 H), 5.40 (br s, 1 H), 5.72 (br s, 1 H), 7.32 (d, J = 8.2 Hz, 2 H), 7.93 (d, J = 8.2 Hz, 2 H). Anal. Calcd for $C_{20}H_{25}NO_4S$: C, 63.98; H, 6.71; N, 3.73; S, 8.54. Found: C, 63.99; H, 6.66; N, 3.76; S, 8.61.

General Procedure for the Allylaminocyclization of 3,4-Pentadienyl Tosylcarbamates 5. The procedure is the same as that described for the allylaminocyclization of **1** (case 1).

***N*-*p*-Toluenesulfonyl-6,6-dimethyl-4-(1-allylvinyl)-tetrahydro-1,3-oxazin-2-one (6c):** mp 81.0–82.0 °C (dichloromethane–hexane); IR (KBr disk) 1725 (s), 1600 (w), 1360 (s), 1264 (m), 1180 (s), 1088 (s), 918 (m), 730 (m), 660 (m); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.38 (s, 3 H), 1.42 (s, 3 H), 1.99 (dd, J = 9.2, 14.3 Hz, 1 H), 2.18 (dd, J = 7.7, 14.3 Hz, 1 H), 2.42 (s, 3 H), 2.65 (dd, J = 7.0, 16.3 Hz, 1 H), 2.77 (dd, J = 7.0, 16.3 Hz, 1 H), 4.93 (dd, J = 7.7, 9.2 Hz, 1 H), 5.01 (br s, 1 H), 5.02 (br d, J = 9.9 Hz, 1 H), 5.08 (br s, 1 H), 5.12 (br d, J = 16.9 Hz, 1 H), 5.73 (ddt, J = 9.9, 16.9, 7.0 Hz, 1 H), 7.29 (d, J = 8.4 Hz, 2 H), 7.94 (d, J = 8.4 Hz, 2 H). Anal. Calcd for $C_{18}H_{23}NO_4S$: C, 61.87; H, 6.63; N, 4.01; S, 9.18. Found: C, 61.67; H, 6.54; N, 4.02; S, 9.29.

***trans*-*N*-*p*-Toluenesulfonyl-5,6,6-trimethyl-4-(1-allylvinyl)tetrahydro-1,3-oxazin-2-one (*trans*-6d):** mp 124.0–125.0 °C (dichloromethane–hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.02 (d, J = 6.8 Hz, 3 H), 1.38 (s, 3 H), 1.42 (s, 3 H), 1.95 (dq, J = 10.1, 6.8 Hz, 1 H), 2.20 (br dd, J = 7.0, 17.0 Hz, 1 H), 2.43 (s, 3 H), 2.50 (br dd, J = 7.0, 17.0 Hz, 1 H), 4.45 (d, J = 10.1 Hz, 1 H), 4.85 (br d, J = 17.2 Hz, 1 H), 5.00 (br d, J = 10.0 Hz, 1 H), 5.09 (br s, 1 H), 5.26 (br s, 1 H), 5.51 (ddt, J = 10.0, 17.2, 7.0 Hz, 1 H), 7.28 (d, J = 8.4 Hz, 2 H), 7.97 (d, J = 8.4 Hz, 2 H). Anal. Calcd for $C_{18}H_{23}NO_4S$: C, 61.87; H, 6.63; N, 4.01; S, 9.18. Found: C, 61.67; H, 6.54; N, 4.02; S, 9.29.

3,4-Pentadienyl *N*-allyl-*N*-tosylcarbamate (7a): oil; IR (neat film) 1958 (m), 1730 (s), 1600 (m), 1360 (s), 1240 (s), 1170 (s), 1090 (s), 760 (s), 650 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 1.98–2.40 (m, 2 H), 2.44 (s, 3 H), 4.10 (t, J = 7.0 Hz, 2 H), 4.40 (br d, J = 5.0 Hz, 2 H), 4.50–5.02 (m, 3 H), 5.18 (br d, J = 12.0 Hz, 1 H), 5.25 (br d, J = 17.0 Hz, 1 H), 5.90 (ddt, J = 12.0, 17.0, 5.0 Hz, 1 H), 7.30 (d, J = 8.2 Hz, 2 H), 7.82 (d, J = 8.2 Hz, 2 H); HRMS calcd for $C_{16}H_{19}NO_4S$ 321.1035, found m/z (relative intensity) 321.1039 (M, 10), 156 (7), 238 (7), 156 (10), 155 (100), 92 (61).

2-Methyl-3,4-pentadienyl *N*-Allyl-*N*-tosylcarbamate (7b): oil; IR (neat film) 2960 (m), 1950 (m), 1730 (s), 1600 (m), 1350 (s), 1240 (s), 1160 (s), 1078 (m), 750 (m), 660 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.97 (d, J = 6.6 Hz, 3 H), 2.43 (s, 3 H), 2.44 (m, 1 H), 3.94 (dd, J = 6.8, 10.4 Hz, 1 H), 4.01 (dd, J = 6.8, 10.4 Hz, 1 H), 4.47 (br d, J = 5.9 Hz, 2 H), 4.70 (dd, J = 2.9, 6.6 Hz, 2 H), 5.00 (q, J = 6.6 Hz, 1 H), 5.25 (br d, J = 10.3 Hz, 1 H), 5.34 (br d, J = 17.2 Hz, 1 H), 5.97 (ddt, J = 10.3, 17.2, 5.9 Hz, 1 H), 7.30 (d, J = 8.4 Hz, 2 H), 7.84 (d, J = 8.4 Hz, 2 H); HRMS calcd for $C_{17}H_{21}NO_4S$ 335.1191, found m/z (relative intensity) 335.1193 (M, 24), 256 (22), 238 (9), 156 (9), 155 (100), 92 (4), 91 (32).

1,1-Dimethyl-3,4-pentadienyl *N*-allyl-*N*-tosylcarbamate (7c): oil; IR (neat film) 2975 (m), 1952 (m), 1730 (s), 1600 (m), 1430 (m), 1360 (s), 1176 (s), 1090 (s), 810 (m), 722 (m), 660 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.35 (s, 6 H), 2.35 (dt, J = 8.1, 2.6 Hz, 2 H), 2.43 (s, 3 H), 4.44 (br d, J = 5.6 Hz, 2 H), 4.58 (dt, J = 6.6, 2.6 Hz, 2 H), 4.78 (br tt, J = 6.6, 8.1 Hz, 1 H), 5.26 (br d, J = 10.3 Hz, 1 H), 5.33 (br d, J = 17.2 Hz, 1 H), 5.93 (ddt, J = 10.3, 17.2, 5.6 Hz, 1 H), 7.30 (d, J = 8.1 Hz, 2 H), 7.79 (d, J = 8.1 Hz, 2 H); HRMS calcd for $C_{18}H_{23}NO_4S$ 349.1348, found m/z (relative intensity) 349.1349 (M, 2), 255 (4), 238 (9), 155 (100).

1,1,2-Trimethyl-3,4-pentadienyl *N*-allyl-*N*-tosylcarbamate (7d): oil; IR (neat film) 3000 (m), 1965 (m), 1740 (s), 1600 (m), 1378 (s), 1285 (m), 1182 (s), 1100 (m), 945 (m), 820 (m), 668 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.87 (d, J = 7.0 Hz, 3 H), 1.32 (s, 3 H), 1.34 (s, 3 H), 2.43 (s, 3 H), 2.75 (br q, J = 7.0 Hz, 1 H), 4.46 (br d, J = 5.5 Hz, 2 H), 4.65 (dd, J = 2.7, 6.8 Hz, 2 H), 4.89 (q, J = 6.8 Hz, 1 H), 5.25 (br d, J = 10.2 Hz, 1 H), 5.33 (br d, J = 17.2 Hz, 1 H), 5.97 (ddt, J = 10.2, 17.2, 5.5 Hz, 1 H), 7.29 (d, J = 8.1 Hz, 2 H), 7.80 (d, J = 8.1 Hz, 2 H). Anal. Calcd for $C_{19}H_{25}NO_4S$: C, 62.78; H, 6.93; N, 3.85; S, 8.82. Found: C, 62.69; H, 6.85; N, 3.79; S, 8.88.

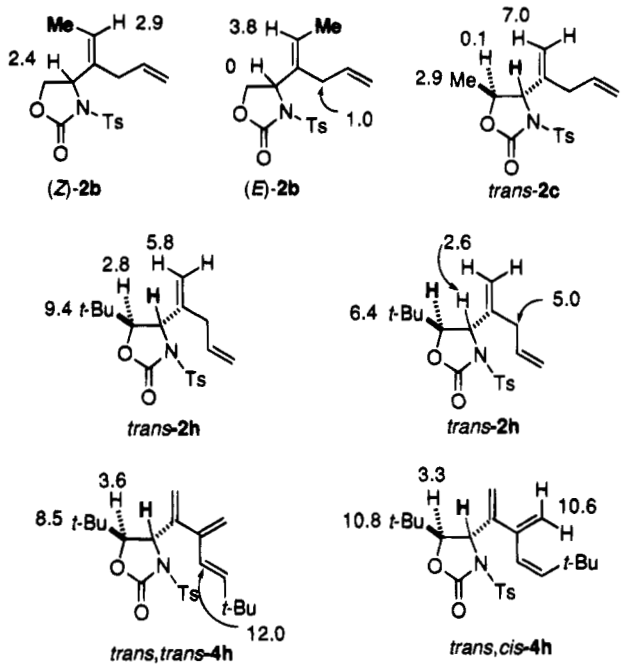

Figure 1. NOE (in %) observed by irradiation at the protons indicated in boldface.

Structure Determination. The stereochemistries of products **2**, **4**, and **6** were determined on the basis of nuclear Overhauser effects[24] and vicinal coupling constants $^3J_{H_4H_5}$ in their 400 MHz ^{1}H NMR spectra[25] (Figure 1 and Table 6).

As is apparent from Table 6, generally the *trans* isomers of **2** and **4** show smaller vicinal coupling constants (2.2–3.8 Hz) than do the *cis* counterparts (around 8.8 Hz).[25] The exceptionally small coupling constant observed for *cis*-**2k** might be attributed to distortion of the oxazolidinone ring caused by the steric repulsion between the C_4–C_5 substituents.

In Figure 1 are listed the selected data of nuclear Overhauser effects obtained by irradiation at the protons indicated in boldface. Olefinic stereoisomers of **2b** were assigned on the basis of contrasting NOE's observed by irradiation at the individual methyl protons (Figure 1). The structure of *trans*-**2c** was determined on the basis of the increment in the area intensities of the C_5-methyl and one of the vinyl protons by irradiation at the C_4-methyne proton. The structure of *trans*-**2h** was deduced from a pronounced increase in the area intensity of methylene protons flanked with double bonds by irradiation at the C_5-methyne proton. The stereochemical assignment around double bonds of *trans,trans*-**4h** and *trans,cis*-**4h** was based on their characteristic vicinal coupling constants (16.1 and 12.8 Hz, respectively) between the terminal olefinic protons.

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Supplementary Material Available: ^{1}H NMR spectra (400 MHz) of **2g**, **2i**, **2k**, **2n**, **3k**, **4a**, **4c**, **4e**, **4g**, **7a** (60 MHz), and **7b,c** (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information. The ^{1}H NMR spectra (400 MHz) of **2a–f**, **2h**, **2l,m**, **2o,p**, **3h**, and **4h** were recorded in the microfilm version of the journal of ref 5.

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