Regio- and Stereoselective Synthesis of 1,3-Hydroxyl Amines via Palladium-Catalyzed Carbonate–Carbamate Transformation with Unique Stereoselectivity: Synthesis of 3-Amino-4-penten-1-ols

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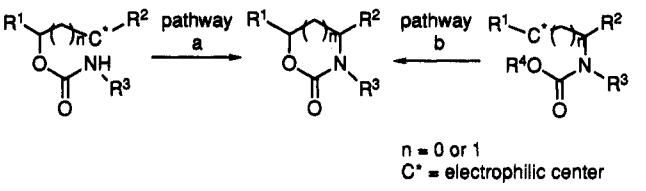
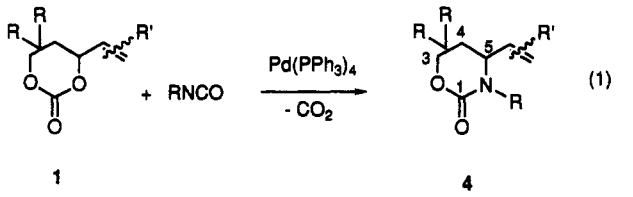
The transformation of cyclic carbonates **1** to cyclic carbamates **4** is achieved in the presence of aryl or sulfonyl isocyanate by the catalysis of Pd(0) in high yield and with high structural flexibility. The reaction shows unique stereoselectivity: 3,4-disubstituted carbonates **2**, irrespective of the composition of their stereoisomers, provide *trans*-**5** exclusively or predominantly over *cis*-**5**. Mixtures of *cis*- and *trans*-3,5-disubstituted carbonates **3** furnish either *cis*-**6** or *trans*-**6** in high selectivity depending on the reaction conditions (kinetic or thermodynamic control, respectively). ^{1}H NMR and X-ray structure analyses of **5** and **6** indicate that the stereochemical outcome is governed by an $A^{1,2}$-strain between *N*-sulfonyl and C_5-vinyl substituents.

Recently, 1,2- and 1,3-amino hydroxyl systems have received much attention from synthetic chemists owing to their presence in a variety of physiologically important natural products, such as amino sugars[1] and unusual amino acids.[2] For the preparation of the amino hydroxyl systems, the methodology based on an intramolecular nucleophilic addition of urethanes (carbamates) either at the nitrogen atom (pathway a) or at the oxygen atom (pathway b) have been widely examined (Scheme 1), probably owing to ready accessibility, generally high crystallinity, ease of hydrolysis to hydroxyl amines of carbamate functionality, and above all, the expected high 1,2- and 1,3-relative asymmetric induction between R^1 and R^2 substituents. Of the two pathways, pathway b has been developed for cases of both $n = 0$[3] and 1;[2a] however, pathway a has been confined to the case of $n = 0$.[4] This is presumably owing to the poor nucleophilic reactivity of the nitrogen atom for the six-membered cyclization ($n = 1$).

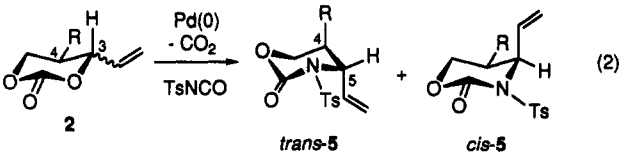
Scheme 1

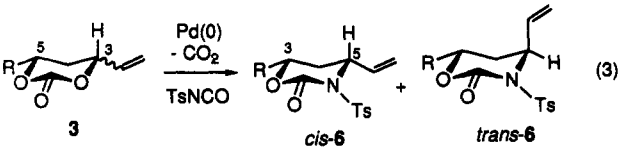


Here, we report a convenient and useful synthesis of 1,3-amino hydroxyl system based on the palladium catalyzed carbonate–carbamate transformation (eq 1).[5] This is, to the best of our knowledge, the first example that



realizes the cyclization according to the mode of pathway a, $n = 1$ (Scheme 1). The reaction is quite general for six-membered carbonates **1** with a variety of substituents on both the ring carbons and the olefinic carbons (eq 1) and provides six-membered carbamates **4** in good to excellent yields. The reaction shows unique stereoselectivities as depicted in eqs 2 and 3: 3,4-Disubstituted





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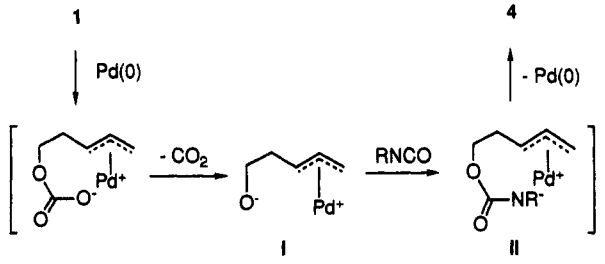
0022-3263/94/1959-1465$04.50/0

Scheme 2. Plausible Reaction Pathway for Pd(0)-Catalyzed Transformation of Cyclic Carbonate 1 to Cyclic Carbamate 4



carbonates **2**, irrespective of the composition of their stereoisomers, predominantly provide *trans*-4,5-disubstituted carbamates, *trans*-**5**, exclusively or predominantly over *cis*-**5**. Similarly, mixtures of *cis*- and *trans*-3,5-disubstituted carbonates **3**, independent of their stereochemistries, furnish *cis*-3,5-disubstituted carbamates, *cis*-**6**, in high selectivity (kinetic control). Under thermodynamic control, on the other hand, *cis*-**6** isomerizes via inversion of configuration at the C_5 carbon to give *trans*-**6** selectively.

A variety of the structurally defined 3-amino-4-penten-1-ols, available by the hydrolysis of **4**–**6**, may be utilized not only as a key synthetic intermediate of many natural products but also as a probe to examine the stereoelectronic effects of the allylic amino group on the diastereoselective addition of electrophiles (e.g., I_2, Pd^{2+}) to the double bond.[6]

Results and Discussion

Recently, we have demonstrated that, under 1 atm of carbon monoxide, cyclic 3-vinyl carbonates **1** undergo a smooth decarboxylation and carbonylation in the presence of a Pd(0) catalyst and furnish 2-vinyl-γ-butyrolactones in good yields.[7] In this reaction, an alkoxy-π-allylpalladium species **I** was proposed as an intermediate (Scheme 2). The similar intermediate, but with one less carbon in the chain, has been generated by the reaction of vinyl epoxides with a Pd(0) complex and utilized for many useful transformations, involving the reaction with isocyanates to provide 4-vinyloxazolidin-2-ones (pathway a, n = 0, Scheme 1).[4a,b,k,l] Encouraged by this, we examined the similar reaction of the intermediate **I** with isocyanates,[6] not only because the expected product **4** seemed to be useful as a synthetic intermediate of many natural and unnatural products, but also because the cyclization forming six-membered carbamates at the nitrogen atom via the pathway a (n = 1, Scheme 1) had never been explored. Furthermore, it seemed to us to be of great value to clarify the level of the relative asymmetric induction between R^1 and R^2 accompanied with this new type of reaction and also to develop a method convenient for the preparation of allylic amines in high regio- and stereoselectivity.[8]

We sometimes meet difficulties in attempts to extend the reaction, successful in forming five-membered nitrogen heterocycles, to the synthesis of six-membered nitrogen heterocycles, especially according to pathway a in Scheme 1.[4j,9] Fortunately, the carbonate **1**–carbamate **4** transformation (eq 1) proceeds smoothly at room temperature to 60 °C in the presence of 1.2 equiv of isocyanate and 0.03 equiv of tetrakis(triphenylphosphine)palladium. Results examined for 18 kinds of carbonates[7] are summarized in Table 1. As is apparent from Table 1, the reaction is quite general for carbonates with a wide structural variety. Substituents on any of the carbons of **1**, except for C_3, are tolerated. Carbonate **1g**, possessing a tertiary reaction center, failed to give the corresponding carbamate and decomposed (run 15).

A variety of aryl isocyanates with electron-donating and electron-attracting substituents, as well as sulfonyl isocyanates, react equally well (runs 1–6, Table 1). Benzyl isocyanate, however, failed to participate, and an intractable mixture of products resulted (run 13), presumably because of the slower trapping of **I** with this isocyanate than the unimolecular decomposition of **I** and/or the poor nucleophilicity of *N*-benzyl carbamate anion toward π-allylpalladium in an intermediate **II** (Scheme 2).

Reactions of 3,4-disubstituted carbonates **2** (eq 2) are summarized in runs 16–23 in Table 1. Interestingly, carbonates **2a–d**, irrespective of the composition of their stereoisomers (*trans*:*cis* = 1:0.7–1.5), provide *trans* carbamates either selectively (**5a,b**) or exclusively (**5c,d**). To prove unambiguously that the stereochemistry of the process is independent of the stereochemistry of the starting material, we demonstrated that the pure *trans*-**2d** and the pure *cis*-**2d** both gave the same product *trans*-**5d**.

The stereochemical outcome observed for runs 16–20 may be rationalized according to the mechanism depicted in Scheme 3, which involves a faster interconversion of the two diastereomeric π-allylpalladiums **III** and **VI** through σ-allylpalladium intermediates **IV** and **V** than the cyclization to form **5**. A transition state leading from **III** to *cis*-**5** is unfavorable owing to a gauche interaction between C_1 and C_4 in a chair cyclohexane template. Accordingly, the cyclization predominantly proceeds via **VI** to give *trans*-**5**.

In sharp contrast, the reactions of *trans*-**2f** and *cis*-**2f** (runs 22 and 23) proceed with complete retention of configuration at the C_3 carbon of these carbonates and provide *trans*-**5f** and *cis*-**5f**, respectively. In these reactions, the inversion at the C_3 carbon through σ-allylpalladium intermediates, as discussed above, accompanies the isomerization at the C_5 carbon (Scheme 4). The thus formed π-allylpalladium intermediates with *Z* geometry (**VIII** and **X**) are apparently less favored in the equilibriums with **VII** and **IX**, respectively, and may not participate in the cyclization reaction.

Similarly, mixtures of *cis*- and *trans*-3,5-disubstituted carbonates **3** (eq 3, runs 25, 27, and 28), irrespective of their stereochemistries, furnish *cis*-**6** in high selectivity. To our surprise, the ratio of *cis*-**6a** to *trans*-**6a** changed dramatically in favor of *trans*-**6a** (run 26) during prolonged reaction at room temperature. After 2 h at 25 °C, no trace of *cis*-**6a** was detected on the crude product by ^1H NMR spectroscopy. The similar change in the product ratios

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Table 1. Pd(0)-Catalyzed Regio- and Stereoselective Transformation of Carbonates 1–3 to Carbamates 4–6

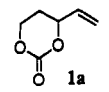
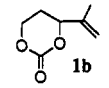
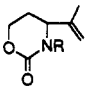
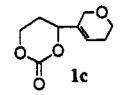
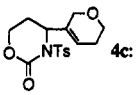
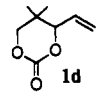
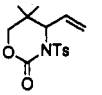
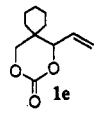
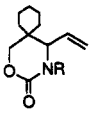
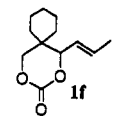
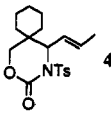
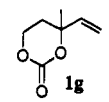
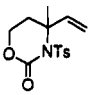
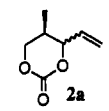
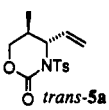
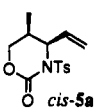
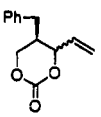
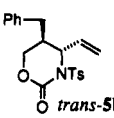
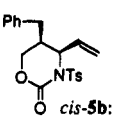
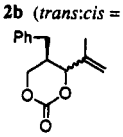
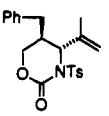
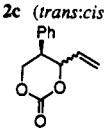
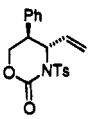
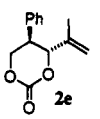
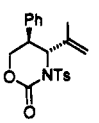
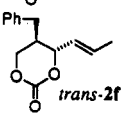
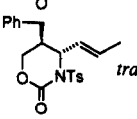
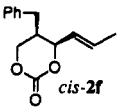
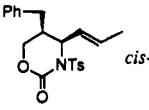
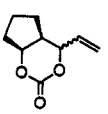
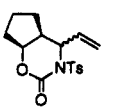
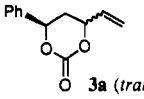
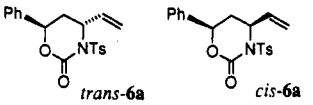
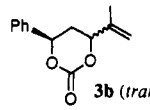
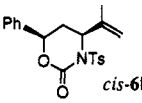
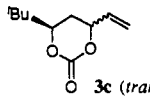
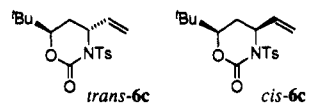
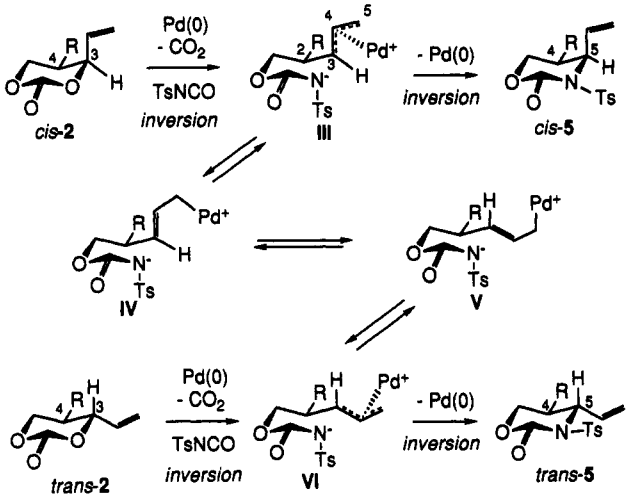
run	carbonates 1–3	condns[a]	carbamates 4–6: % isolated yield
1	 **1a**	dioxane, rt, 11 h	**4a** (R = *p*-toluenesulfonyl): 80%[b]
2		THF, rt, 12 h	**4a** (R = 2,4,6-trimethylphenyl): 63%
3		THF, rt, 9 h	**4a** (R = *p*-methylphenyl): 65%
4		dioxane, rt, 8 h	**4a** (R = *p*-chlorophenyl): 84%
5		THF, rt, 8 h	**4a** (R = *p*-(ethoxycarbonyl)phenyl): 80%
6		THF, rt, 9 h	**4a** (R = *p*-nitrophenyl): 87%
7			
8	 **1b**	dioxane, 60 °C, 19 h	 **4b** (R = *p*-toluenesulfonyl): 74%
		dioxane, 60 °C, 23 h	**4b** (R = phenyl): 70%
9	 **1c**	dioxane, 60 °C, 2 h	 **4c**: 98%
10	 **1d**	dioxane, 60 °C, 5 h	 **4d**: 88%
11			
12	 **1e**	dioxane, 60 °C, 2 h	 **4e** (R = *p*-toluenesulfonyl): 98%
13		dioxane, 60 °C, 11 h	**4e** (R = phenyl): 90%
		dioxane, 60 °C, 10 h	**4e** (R = benzyl): 0%
14	 **1f**	dioxane, 60 °C, 10 h	 **4f**: 51%
15	 **1g**	dioxane, 60 °C, 3 h	 **4g**: 0%
	 **2a** (*trans*:*cis* = 1:1.5)		 *trans*-**5a**  *cis*-**5a**
16		dioxane, 25 °C, 40 min	*trans*-**5a**:*cis*-**5a** = 88:12, 80%
17		dioxane, 60 °C, 24 h	*trans*-**5a**:*cis*-**5a** = 77:23, 84%
18	 **2b** (*trans*:*cis* = 1:1.5)	dioxane, 60 °C, 1 h	 *trans*-**5b**: 57%  *cis*-**5b**: 23%
19	 **2c** (*trans*:*cis* = 1:1)	dioxane, 60 °C, 2 h	 *trans*-**5c**: 91%
20	 **2d** (*trans*:*cis* = 1: 0.7)	dioxane, rt , 2 h	 *trans*-**5d**: 66%
21	 **2e**	dioxane, 60 °C, 1 h	 *trans*-**5e**: 61%
22	 *trans*-**2f**	dioxane, 60 °C, 3 h	 *trans*-**5f**: 95%
23	 *cis*-**2f**	dioxane, 60 °C, 3 h	 *cis*-**5f**: 69%
24	 **2g** (*trans*:*cis* = 1:1.3)	dioxane, 60 °C, 2 h	 **5g**: 56%[c]

Table 1. (Continued)

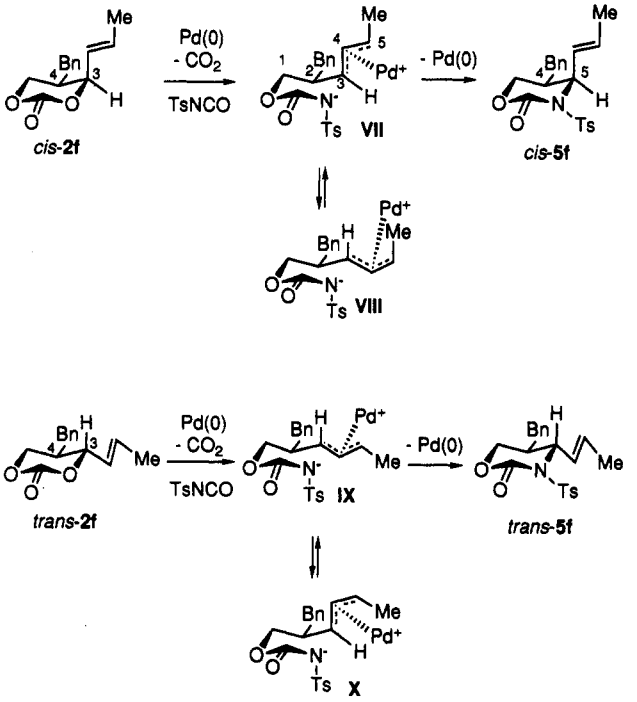
run	carbonates 1–3	condns[a]	carbamates 4–6: % isolated yield
	 3a (*trans*:*cis* = 1:0.8)		 *trans*-6a *cis*-6a
25		THF, 15 °C, 20 min	*trans*-6a:*cis*-6a = 15:85,[d] 88%
26		THF, 25 °C, 2 h	*trans*-6a:*cis*-6a = >95: <5, 90%
27	 3b (*trans*:*cis* = 1:0.8)	dioxane, 60 °C, 1.5 h	 *cis*-6b: 84%
	 3c (*trans*:*cis* = 1:1)		 *trans*-6c *cis*-6c
28		THF, 25 °C, 15 min	*trans*-6c:*cis*-6c = 10:90, 90%
29		THF, 60 °C, 8 h	*trans*-6c:*cis*-6c = 86:14, 98%

[a] Carbonate (1 mmol), $Pd(PPh_3)_4$ (0.02–0.03 mmol), isocyanate (1.2 mmol) in a given dry solvent (5 mmol) under argon. [b] **4a**, isolated in 91% yield with 1.5 equiv of toluenesulfonyl isocyanate. [c] Stereochemistry not determined. [d] Approximate ratio (^1H NMR) owing to a facile isomerization (see text).

Scheme 3. Stereoselective Conversion of a Mixture of 4-Substituted *cis*- and *trans*-3-Vinyl-2,6-dioxacyclohexan-1-ones (*cis*- and *trans*-2) to 4-Substituted *trans*-5-Vinyl-6-aza-2-oxacyclohexan-1-ones (*trans*-5)



Scheme 4. Stereoselective Conversion of *cis*- and *trans*-4-Benzyl-3-((*E*)-1′-propenyl)-2,6-dioxacyclohexan-1-ones (*cis*- and *trans*-2f) to *cis*- and *trans*-4-Benzyl-5-((*E*)-1′-propenyl)-6-aza-2-oxacyclohexan-1-ones (*cis*- and *trans*-5f), Respectively



was observed for the pair of *cis*-**6c** and *trans*-**6c**, though in this case in a much slower process (runs 28 and 29).

Judging from the yields, apparently *trans*-**6a** and *trans*-**6c** must be formed at the expense of their *cis* counterparts. Indeed, when the purified *cis*-**6c** was heated at 60 °C for 4 h in the presence of 1.2 equiv of tosyl isocyanate and 0.1 equiv of tetrakis(triphenylphosphine)palladium in dioxane, a mixture of *trans*-**6c** and *cis*-**6c** in a ratio of 6:4 was isolated in 95% yield. Under the similar or even more forcing conditions, however, *cis*-**6b** did not isomerize to any detectable extent and was recovered quantitatively (90% yield at 90 °C for 4 h in dioxane; 88% yield at 150 °C for 5 h in *N*,*N*-dimethylacetamide).

The isomerization may involve S_N2 attack of a Pd(0) catalyst on the allylic C–N bond of **6**, an interconversion of the thus formed diastereomeric π-allylpalladium complexes via a similar process shown in Scheme 3 and a cyclization to regenerate **6** with different diastereomeric compositions.

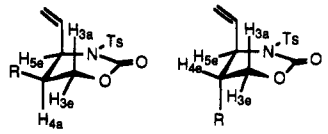
Although it is difficult to offer an explanation for the tremendous difference in the rates of the *cis*–*trans* isomerization observed for **6a–c** at present, this phenomenon is beneficial from a synthetic point of view. Starting from stereochemical mixtures of carbonates **3**, both the *cis*- and *trans*-**6** isomers can be separately prepared only changing the reaction conditions: *cis*-**6** under kinetic control and *trans*-**6** under thermodynamic control.

Structure Determination of 4,5-Disubstituted Six-Membered Carbamates 5 and 3,5-Disubstituted Six-Membered Carbamates 6. Generally, the structure of vicinally disubstituted cyclohexane derivatives, especially when both stereoisomers are available, may be readily determined from their ^1H NMR coupling constants of the protons on the carbons bearing these substituents: typically, ^3J = 1–3 Hz for *cis* isomers and ^3J = 8–10 Hz for *trans* isomers. None of the *cis*–*trans* pairs of **5**, however, showed such diagnostic coupling patterns (Table 2), and no conclusive information about their structure was obtained by NMR analysis. The small coupling constants, J_{H4H5} = 0–4 Hz, suggest that *trans*-**5** takes a pseudodiaxial

Table 2. ^3J and ^5J for *cis*- and *trans*-5 (in Hz, $CDCl_3$)[a]

compd	$J_{H3a-H4a}$	$J_{H3e-H4a}$	$J_{H3a-H4e}$	$J_{H3e-H4e}$	$J_{H4a-H5e}$	$J_{H4e-H5e}$	$J_{H3e-H5e}$
cis-**5a**	11.0	4.8			4.4		0
trans-**5a**			3.0 (−50°)	3.0 (75°)		ca. 0 (−77°)	1.5
cis-**5b**	*b*	*b*			*b*		0
trans-**5b**			3.2	2.0		ca. 1	2.0
trans-**5c**			3.2	2.7		ca. 1	1.7
trans-**5d**			4.0	2.6		3.3	1.5
cis-**5f**	*b*	*b*			2.9		0
trans-**5f**			3.4	2.7		ca. 1	2.0

[a] Dihedral angles, determined by X-ray crystal structure analysis, in parentheses. [b] H_{3a}, H_{3e}, and H_{4a}: not well resolved.



cis-5 *trans*-5

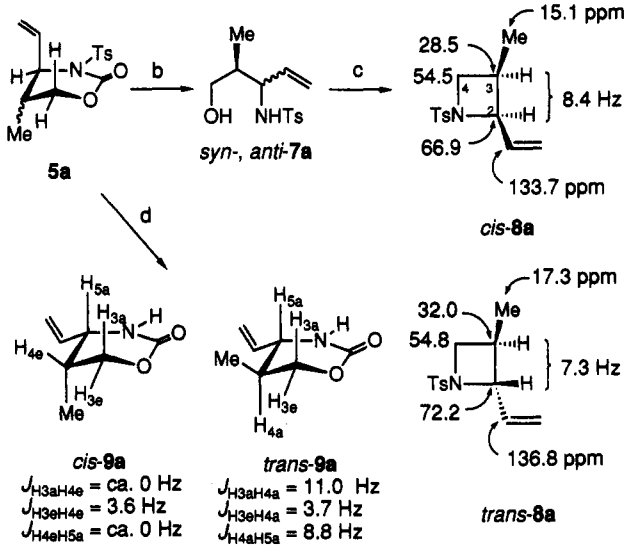
conformation. The assignment of diaxial conformation for *trans*-5 may not be as unreasonable as it appears if the following destabilization interactions related to their diaxial and diequatorial conformations are taken into consideration. For instance, in a diequatorial conformation of *trans*-**5a**, the C_5-vinyl group experiences an (approximate) eclipsing repulsion with the sulfonyl group residing on the sp^2-N plane ($A^{1,2}$-strain)[10] together with a gauche repulsion with the C_4-methyl group. In a diaxial conformation, on the other hand, the C_4 methyl group is exposed to gauche interactions with sterically small N and O_2 atoms and the C_5-vinyl group with sterically small C_1-(=O) and C_3-methylene groups. Apparently, the destabilization interactions associated with the diequatorial conformer[11] outweigh those related to the diaxial conformer.

The destabilization associated with *trans*-**5a** may diminish the relative thermodynamic stability between *cis*-**5a** and *trans*-**5a**. Indeed, this is supported by the slight, but significant, change of the ratio of *trans*-**5a** to *cis*-**5a** in favor of *cis*-**5a** under thermodynamic control (run 17, Table 1).

To unambiguously establish the stereochemistry of **5**, the isomers were converted to *N*-tosylazetidines **8** and carbamates **9**. Typical procedures and the selected NMR data for *cis*- and *trans*-**8a** and **9a** are summarized in Scheme 5.[12] Since the separation of *cis*- and *trans*- **5a** was rather laborious (*vide infra*), the transformations to *N*-tosylazetidines **8a** and carbamates **9a** were undertaken using a mixture of stereoisomers (*cis*-**5a**:*trans*-**5a** = 1:1.5). The yields for both transformations were quantitative and **8a** and **9a** were obtained as mixtures of stereoisomers in almost the same ratios to that of **5a**. The authentic samples of *cis*-**8a** and *trans*-**9a** were prepared according to the similar procedures from the pure *cis*-**5a** and the pure *trans*-**5a**, respectively, which were obtained as follows.

cis- and *trans*-**5a** were not separable by means of chromatography, and hence, the *trans* isomer was purified by repeated recrystallization of the mixture from hot benzene, albeit in low recovery. The pure *cis* isomer, on

Scheme 5. Transformations Aimed for the Structure Determination of 5a[a]



[a] For the similar transformations of **5b**, **5e**, and **5f**, see Experimental Section. [b] 1 N KOH (6 equiv), EtOH reflux for 2 h, quantitative. [c] PPh_3 (1.2 equiv), diethyl azodicarboxylate (1.2 equiv), THF at 0 °C for 2 h, then at rt for 5 h, 90–95%. [d] Naphthalene (7 equiv), Na (6 equiv), THF at −78 °C for 10 min, then at 0 °C for 10 min, 90–95%.

the other hand, could be obtained as its hydrolysis derivative, *syn*-**7a** (Scheme 5), a remainder of the reaction of *syn* and *anti* mixture of **7a** with I_2 and $NaHCO_3$, 2 equiv each, in ether–H_2O at 0 °C for 10 h. In this reaction, only *anti*-**7a** was consumed to provide iodoetherification products: *cis*,*cis*- and *trans*,*cis*-*N*-tosyl-3-amino-2-(iodomethyl)-4-methyltetrahydrofurans.[6]

The ^{13}C NMR of the mixture of *cis*- and *trans*-**8a** (1:1.5) showed the resonances of C_2, C_3, C_4, C_3-*Me*, and C_2-*C*H=CH_2 in pairs and, as expected from the steric compression effect,[13] the major peaks of the pairs appeared at the lower fields by ca. 1–5 ppm relative to the corresponding minor peaks. The ^{13}C NMR of the minor isomer was completely superimposable to that of the authentic sample independently prepared from the pure *cis*-**5a**.

With removal of the *N*-tosyl group by a reductive desulfonylation, *trans*-**5a** underwent a dramatic conformational change from pseudodiaxial to pseudodiequato-

(10) (a) Johnson, F. *Chem. Rev.* **1968**, *68*, 375–413. (b) Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1124–1134.

(11) (a) Pojarlieff, I. G.; Lyapova, M. J.; Kurtev, B. J. *J. Chem. Res., Synop.* **1980**, 231. (b) Wuts, P. G. M.; Jung, Y.-W. *J. Org. Chem.* **1991**, *56*, 365–372.

(12) Similar transformation was performed for **5b**, **5e**, and **5f**. *cis*- and *trans*-**7b** were also independently converted to acetals (*cis*- and *trans*-*N*-(*p*-toluenesulfonyl)-5-benzyl-4-vinyl-3-aza-1-oxacyclohexanes, *cis*- and *trans*-**10b**). Unfortunately, however, no conclusive information about their stereochemistries could be deduced from their ^1H NMR spectra. See Experimental Section.

(13) Gaudemer, A. In *Stereochemistry*; Kagan, H. B., Ed.; Georg Thieme Verlag: Stuttgart, 1977.

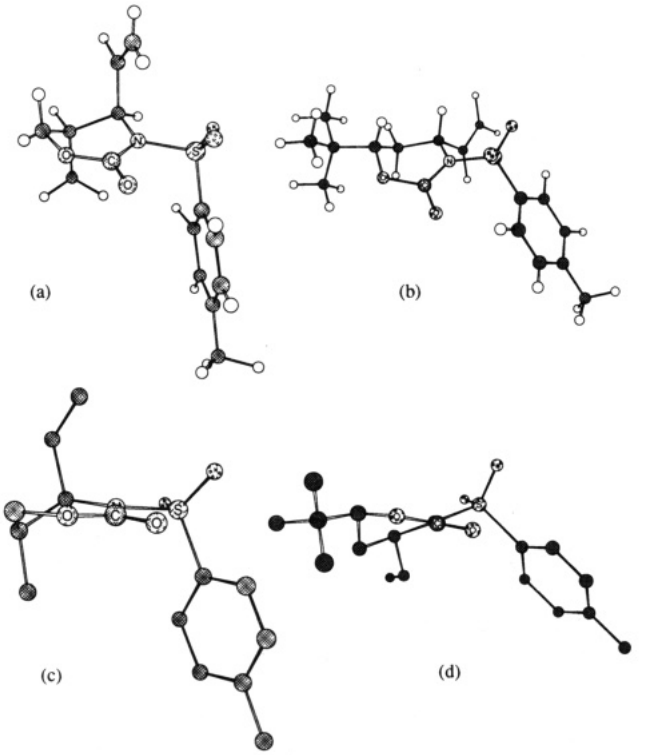


Figure 1. X-ray structure of *trans*-**5a** and *cis*-**6c**. (a) A view showing the quasidiaxial conformation of *trans*-**5a**. (b) A view showing the quasidiequatorial conformation of *cis*-**6c**. (c) A view showing a normal dihedral angle of S—N—C=O = 1.3° of *trans*-**5a**. (d) A view showing an unusual dihedral angle of S—N—C=O = 23.6° of *cis*-**6c**. All hydrogens are omitted in c and d for clarity.

rial. The large coupling constants of *trans*-**9a**, J_{H3aH4a} = 11.0 Hz and J_{H4aH5a} = 8.8 Hz, establish its pseudodiequatorial conformation (Scheme 5). A similar conformational change was observed for the transformation of *cis*-**5a** to *cis*-**9a**: from C_4-Me(eq)-C_5-vinyl(ax) of *cis*-**5a** to C_4-Me-(ax)-C_5-vinyl(eq) of *cis*-**9a**.

The X-ray crystal structure of *trans*-**5a** is shown in Figure 1 (a and c). In accord with the conclusion drawn from ^{1}H NMR analysis (in a solution state), *trans*-**5a** favors a pseudodiaxial conformation in a solid state. However, *trans*-**5a** seems to take slightly different conformations in these two states as judged from the small irregular deviation of the ^3J values ($J_{H3a-H4e}$= 4.1 Hz, $J_{H3e-H4e}$= 0.7 Hz, $J_{H4e-H5e}$= 0.5 Hz), obtained from Karplus equation using the dihedral angles determined by X-ray analysis, from the ones observed in ^{1}H NMR (Table 2) .

Generally, the other *cis* isomers of **5**, except for *cis*-**5a**, showed H_{3a}, H_{3e}, and H_{4a} protons nonresolved owing to overlap of absorptions with one another and with other protons (Table 2). The *trans* isomers, on the other hand, showed well-resolved signals for these protons, and their structure was determined on the basis of the close resemblance of ^3J values to those of *trans*-**5a**. The long-range coupling (^5J) between H_{3e} and H_{5e}, characteristically observed only for the *trans* isomers, further supports the structure assignment. The *E* structure of the C_5-propenyl substituent of *cis*- and *trans*-**5f** follows from the coupling constants of the olefinic protons (J = ca. 15 Hz) and the absorptions at 960–970 cm^{-1} in their IR spectra.

The X-ray structures of *trans*-**5a** and *cis*-**6c**, shown in Figure 1, indicate that there are, at least, two modes of deformation with which the $A^{1,2}$-strain between the C_5-substituents and N_{sp^2}-sulfonyl group can be effectively relieved. One is to place the C_5-substituents in an axial position, as typically seen in the structure of **5a**. In this case, the S—N—C=O dihedral angle is very close to zero, because the partial double bond nature of the N—C(=O) linkage is retained. The other mode is, as observed for **6c**, to distort the S—N—C_5 plane from the coplanality with the O_2—C(=O) plane at the expense of the bonding energy of the C(=O)—N linkage. The S—N—C=O dihedral angle in this case becomes as large as 23.6°.

It is apparent that *cis*-**6c** takes very similar conformations both in a solution state and in a solid state, as judged from the good correlation of the vicinal coupling constants between the observed ones (Table 3) and the ones ($J_{H3a-H4a}$ = 16.0 Hz, $J_{H3a-H4e}$ = 3.1 Hz, $J_{H4a-H5a}$ = 12.2 Hz, $J_{H4e-H5a}$ = 11.8 Hz) calculated from the Karplus equation using the dihedral angles determined by X-ray structure analysis. The small coupling constants between H_4 protons and H_5 proton of *trans*-**6a** and *trans*-**6c** clearly indicate that the C_5-vinyl groups are oriented axial (Table 3) as in those cases of **5**.

Experimental Section

Melting points were determined in capillary tubes with a Büchi 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 refer to the oven temperature. Microanalyses were performed by the Microanalysis Center of either Kyoto University or Nagasaki University. Analyses agreed with the calculated values within ±0.3%. Infrared spectra were measured with a Hitachi Model EPI-G3 grating spectrophotometer. Proton magnetic resonance spectra were determined either at 60 MHz on a JEOL JNM-PMX60, at 90 MHz on a JEOL FX90Q, or at 400 MHz on a JEOL-GX400 instrument with tetramethylsilane as an internal standard. Carbon-13 NMR spectra were determined at 22.4 MHz on a JEOL FX90Q instrument with chloroform-*d* (76.92 ppm) as an internal standard. Chemical shift values were given in ppm downfield from an internal standard. Mass spectra were measured either on a Hitachi Model RMU6C or on a JEOL D-300 instrument (high-resolution mass spectrophotometer). R_f values were determined over Merck Kieselgel 60F_{254}.

Dioxane was dried and distilled from sodium under argon. Tetrahydrofuran (THF) was dried over sodium–benzophenone. *p*-Toluenesulfonyl, phenyl, and *p*-chlorophenyl isocyanates were purchased from Aldrich. Other aryl isocyanates were prepared as follows: A solution of an aniline derivative (30 mmol) in 30 mL of ethyl acetate was slowly added to a solution of trichloromethyl chloroformate (30 mmol, a gift from Hodogaya Chemical Co.) in 50 mL of ethyl acetate at room temperature. The mixture was stirred at 40–50 °C for 1 h and then at 80 °C for 2 h. The majority of the solvent was distilled off under atmospheric pressure. Isocyanates were isolated by means of Kugelrohr distillation under reduced pressure and used without further purification. *p*-Nitrophenyl isocyanate was recrystallized from ethyl acetate–carbon tetrachloride prior to distillation. 4-Pentene-1,3-diols and their cyclic carbonates **1–3** were prepared according to the method reported previously from our laboratories.[7]

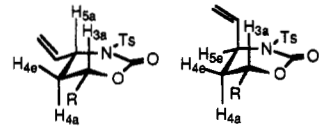
General Procedure for the Reaction of 4-Pentene-1,3-diol Carbonates 1–3 with Isocyanates. Into a flask containing Pd(PPh_3)$_4$ (0.02–0.03 mmol) equipped with a rubber balloon filled with argon were successively added a solution of a carbonate (1 mmol) in a dry solvent (5 mL, Table 1) and an isocyanate (1.2 mmol) via syringes. Then, the solution was stirred at the temperature for the period of time indicated in Table 1. Then the solvent was evaporated, and the residue was directly subjected to column chromatography over silica gel (benzene–ethyl acetate gradient). One typical example is as follows.

Preparation of *N*-(*p*-Toluenesulfonyl)-4,4-pentamethylene-5-vinyl-6-aza-2-oxacyclohexan-1-one (4e, R = Ts). Into a flask containing Pd(PPh_3)$_4$ (33.6 mg, 0.029 mmol) equipped with a rubber balloon filled with argon were added successively a solution of 4,4-pentamethylene-3-vinyl-2,6-dioxacyclohexan-1-one (**1e**) (190.4 mg, 0.97 mmol) in dry dioxane (5 mL) and *p*-toluenesulfonyl isocyanate (0.177 mL, 1.16 mmol) via syringes.

Table 3. ^3J for *cis*- and *trans*-6 (in Hz, $CDCl_3$)[a]

compd	$J_{H3a-H4a}$	$J_{H3a-H4e}$	$J_{H4a-H5a}$	$J_{H4e-H5a}$	$J_{H4a-H5e}$	$J_{H4e-H5e}$
cis-6a	11.1	2.3	9.6	7.9		
trans-6a[b]	12.3	3.1			5.3	2.7
cis-6b	11.7	2.4	9.8	9.0		
cis-6c	11.6 (177°)	1.8 (−64°)	10.3 (151°)	7.8 (31°)		
trans-6c[b]	12.3	3.1			5.1	2.8

[a] Dihedral angles, determined by X-ray crystal structure analysis, in parentheses. [b] Determined in C_6D_6.



cis-6 *trans*-6

The solution was heated at 60 °C for 2 h, and then the solvent was evaporated under reduced pressure. The residue was directly chromatographed over silica gel (benzene–ethyl acetate gradient). The reaction was analyzed by silica gel TLC [carbonate **1e**, R_f = 0.61; carbamate **4e**, R_f = 0.73 (benzene:ethyl acetate = 4:1)]: yield 98%; mp 157.5–159.0 °C (benzene–hexane); IR (KBr disk) 2940 (s), 1720 (s), 1640 (w), 1350 (s), 1205 (s), 1085 (m), 750 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07–1.89 (m, 10 H), 2.42 (s, 3 H), 4.00 (pseudo s, 2 H), 4.95 (d, J = 6.1 Hz, 1 H), 5.28–5.57 (m, 2 H), 5.89 (ddd, J = 6.1, 10.7, 18.8 Hz, 1 H), 7.29 (d, J = 8.0 Hz, 2 H), 7.89 (d, J = 8.0 Hz, 2 H); MS m/z (relative intensity) 285 (15), 190 (15), 155 (Ts, 21), 145 (60), 91 (51), 72 (100). Anal. Calcd for $C_{18}H_{23}NO_4S$: C, 61,87; H, 6.63; N, 4.01; S, 9.18. Found: C, 61.77; H, 6.88; N, 3.96; S, 9.01.

***N*-(*p*-Toluenesulfonyl)-5-vinyl-6-aza-2-oxacyclohexan-1-one (4a, R = Ts):** mp 116.0–117.0 °C (benzene–hexane); IR (KBr disk) 2940 (w), 1730 (s), 1650 (w), 1415 (m), 1350 (s), 1280 (s), 1170 (s), 1160 (s), 1090 (m), 950 (m), 810 (m), 675 (s) cm^{-1}; ^1H NMR ($CDCl_3$) 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, 16.1 Hz, 1 H), 7.30 (d, J = 8.3 Hz, 2 H), 7.92 (d, J = 8.3 Hz, 2 H). Anal. Calcd for $C_{13}H_{15}NO_4S$: C, 55.50; H, 5.37; N, 4.98; S, 11.40. Found: C, 55.77; H, 5.37; N, 5.01; S, 11.25.

***N*-(2,4,6-Trimethylphenyl)-5-vinyl-6-aza-2-oxacyclohexan-1-one (4a, R = 2,4,6-trimethylphenyl):** mp 131.0–131.5 °C; IR (KBr disk) 2900 (m), 1690 (s), 1610 (w), 1480 (m), 1410 (s), 1280 (s), 1200 (m), 1170 (m), 1000 (m) 850 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.75–2.40 (m, 2 H), 2.16 (s, 9 H), 3.80–4.55 (m, 3 H), 4.65–5.10 (m, 2 H), 5.80 (ddd, J = 8.0, 10.0, 16.4 Hz, 1 H), 6.78 (s, 2 H). Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.37; H, 7.76, N, 5.73.

***N*-(*p*-Methylphenyl)-5-vinyl-6-aza-2-oxacyclohexan-1-one (4a, R = *p*-methylphenyl):** mp 77.5–79.0 °C (benzene–hexane); IR (KBr disk) 2920 (w), 1690 (s), 1520 (m), 1420 (m), 1180 (m), 1100 (w), 1000 (w), 930 (w), 820 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.57–2.55 (m, 2 H), 2.25 (s, 3 H), 4.05–4.50 (m, 3 H), 4.80–5.25 (m, 2 H), 5.73 (ddd, J = 6.0, 8.8, 17.6 Hz, 1 H), 7.08 (s, 4 H). Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.82; H, 6.91, N, 6.47.

***N*-(*p*-Chlorophenyl)-5-vinyl-6-aza-2-oxacyclohexan-1-one (4a, R = *p*-chlorophenyl):** mp 75.5–77.0 °C (benzene–hexane); IR (KBr disk) 2950 (w), 1700 (s), 1480 (m), 1420 (m), 1300 (m), 1160 (m), 1080 (m), 990 (m), 920 (w), 820 (m), 740 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.75–2.70 (m, 2 H), 4.25–4.70 (m, 3 H), 4.85–5.30 (m, 2 H), 5.70 (m, 1 H), 7.25 (br s, 4 H). Anal. Calcd for $C_{12}H_{12}NO_2Cl$: C, 60.64; H, 5.09; N, 5.89. Found: C, 60.50; H, 5.05; N, 6.07.

***N*-[*p*-(Ethoxycarbonyl)phenyl]-5-vinyl-6-aza-2-oxacyclohexan-1-one (4a, R = *p*-(ethoxycarbonyl)phenyl):** mp 77.5–78.5 °C (benzene–hexane); IR (KBr disk) 3000 (m), 1710 (s) 1690 (s), 1600 (m), 1270 (s), 1170 (m), 1100 (m), 1010 (m), 930 (m), 850 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.36 (t, J = 7.0 Hz, 3 H), 1.70–2.70 (m, 2 H), 4.35 (q, J = 7.0 Hz, 2 H), 4.10–4.70 (m, 3 H), 4.90–5.30 (m, 2 H), 5.75 (m, 1 H), 7.37 (d, J = 8.5 Hz, 2 H), 8,00 (d, J = 8.5 Hz, 2 H). Anal. Calcd for $C_{15}H_{17}NO_4$: C, 65,44; H, 6.22; N, 5.09. Found: C, 65.46; H, 6.16; N, 5.35.

***N*-(*p*-Nitrophenyl)-5-vinyl-6-aza-2-oxacyclohexan-1-one (4a, R = *p*-nitrophenyl):** mp 125.5–127.0 °C (benzene); IR (KBr disk) 3350 (m), 1730 (s), 1600 (m), 1570 (m), 1500 (m), 1320 (s), 1250 (m), 1180 (m), 1100 (m), 990 (w), 840 (m), 750 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.80–2.80 (m, 2 H), 4.20–4.80 (m, 3 H), 5.00–5.45 (m, 2 H), 5.80 (m, 1 H), 7.50 (d, J = 9.0 Hz, 2 H), 8.20 (d, J = 9.0 Hz, 2 H). Anal. Calcd for $C_{12}H_{12}N_2O_4$: C, 58.06; H, 4.87; N, 11.28. Found: C, 58.32; H, 4.86; N, 11.43.

***N*-(*p*-Toluenesulfonyl)-5-isopropenyl-6-aza-2-oxacyclohexan-1-one (4b, R = *p*-toluenesulfonyl):** mp 129.0–130.0 °C (benzene); IR (KBr disk) 2970 (m), 1720 (s), 1705 (s), 1410 (s), 1350 (s), 1300 (s), 1270 (s), 1240 (s), 1170 (s), 1150 (s), 1080 (s), 815 (s), 745 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.81 (s, 3 H), 1.99–2.27 (m, 2 H), 2.43 (s, 3 H), 4.18–4.38 (m, 2 H), 4.91 (br s, 1 H), 5.04 (m, 1 H), 5.16 (br s, 1 H), 7.29 (d, J = 8.3 Hz, 2 H), 7.92 (d, J = 8.3 Hz, 2 H). Anal. Calcd for $C_{14}H_{17}NO_4S$: C, 56.93; H, 5.80; N, 4.74; S, 10.86. Found: C, 56.74; H, 5.69; N, 4.68; S, 10.87.

***N*-Phenyl-5-isopropenyl-6-aza-2-oxacyclohexan-1-one (4b, R = Ph):** mp 115.5–116.5 °C (benzene–hexane); IR (KBr disk) 2980 (m), 1680 (s), 1595 (m), 1490 (s), 1420 (s), 1310 (s), 1280 (s), 1230 (s), 1160 (m), 1100 (s), 890 (s), 775 (s), 745 (s), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.69 (s, 3 H), 1.86–2.55 (m, 2 H), 4.43 (dd, J = 4.2, 9.3 Hz, 3 H), 5.08 (br s, 2 H), 7.31 (br s, 5 H). Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 72.11; H, 6.95; N, 6.29.

***N*-(*p*-Toluenesulfonyl)-5-(5′-oxa-1′-cyclohexenyl)-6-aza-2-oxacyclohexan-1-one (4c):** oil; IR (neat film) 2930 (m), 1730 (s), 1355 (s), 1160 (m), 870 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.71–2.33 (m, 4 H), 2.43 (s, 3 H), 3.63–3.88 (m, 2 H), 3.99–4.11 (m, 4 H), 4.95 (m, 1 H), 5.67 (m, 1 H), 7.29 (d, J = 8.3 Hz, 2 H), 7.90 (d, J = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.2, 24.4, 26.1, 55.9, 63.7, 64.4, 65.0, 122.2, 128.8, 129.1, 134.7, 144.7, 148.3; HRMS calcd for $C_{16}H_{19}NO_5S$ 337.0984, found m/z (relative intensity) 337.0988 (M, 1), 273 (10), 182 (100).

***N*-(*p*-Toluenesulfonyl)-4,4-dimethyl-5-vinyl-6-aza-2-oxacyclohexan-1-one (4d):** mp 115.5–116.0 °C (benzene–hexane); IR (KBr disk) 2970 (m), 1720 (s), 1595 (m), 1480 (m), 1345 (s), 1170 (s), 1085 (m), 935 (m), 815 (s), 750 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.01 (s, 3 H), 1.19 (s, 3 H), 2.42 (s, 3 H), 3.76 (dd, J = 2.0, 11.0 Hz, 1 H), 4.09 (d, J = 11.0 Hz, 1 H), 4.67 (dd, J = 2.0, 6.1 Hz, 1 H), 5.39 (dd, J = 1.2, 16.6 Hz, 1 H), 5.46 (dd, J = 1.2, 10.0 Hz, 1 H), 5.91 (ddd, J = 6.1, 10.0, 16.6 Hz, 1 H), 7.29 (d, J = 8.3 Hz, 2 H), 7.90 (d, J = 8.3 Hz, 2 H). Correct elemental analysis was obtained as the hydrolysis product, *N*-(*p*-toluenesulfonyl)-3-amino-2,2-dimethyl-4-penten-1-ol: mp 105.0–106.0 °C (benzene–hexane); IR (KBr disk) 3470 (s), 3180 (s), 2960 (s), 1600 (m), 1470 (s), 1325 (s), 1300 (s), 1150 (s), 1095 (s), 1055 (s), 1030 (s), 1015 (s), 925 (s), 810 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.73 (s, 3 H), 0.94 (s, 3 H), 2.41 (s, 3 H), 2.55 (dd, J = 5.6, 7.3 Hz, 1 H), 3.19 (dd, J = 7.3, 11.5 Hz, 1 H), 3.58–3.88 (m, 2 H), 4.71 (dd, J = 1.2, 16.6 Hz, 1 H), 4.87 (dd, J = 1.2, 10.0 Hz, 1 H), 5.10 (d, J = 9.3 Hz, 1 H), 5.57 (ddd, J = 7.3, 10.0, 16.6 Hz, 1 H), 7.25 (d, J = 8.3 Hz, 2 H), 7.72 (d, J = 8.3 Hz, 2 H). Anal. Calcd for $C_{14}H_{21}NO_3S$: C, 59.34; H, 7.47; N, 4.94; S, 11.31. Found: C, 59.11, H, 7.37; N, 4.90; S, 11.22.

***N*-Phenyl-4,4-pentamethylene-5-vinyl-6-aza-2-oxacyclohexan-1-one (4e, R = Ph):** oil; IR (neat film) 2950 (s), 1710 (s), 1425 (s), 1175 (s), 765 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20–1.98 (m, 10 H), 3.97 (d, J = 7.3 Hz, 1 H), 3.97 (dd, J = 1.7, 11.0 Hz, 1 H), 4.22 (d, J = 11.0 Hz, 1 H), 5.01–5.38 (m, 2 H), 5.84 (ddd, J = 7.3, 10.3, 17.6 Hz, 1 H), 7.09–7.48 (m, 5 H); MS m/z (relative intensity) 271 (M, 15), 212 (15), 131 (100), 93 (98), 77 (45). Anal. Calcd for $C_{17}H_{21}NO_2$: C, 75.25; H, 7.80; N, 5.16. Found: C, 75.22; H, 8.03; N, 5.25.

***N*-(*p*-Toluenesulfonyl)-4,4-pentamethylene-5-[(1′*E*)-propenyl]-6-aza-2-oxacyclohexan-1-one (4f):** mp 190.0–191.0 °C (benzene–hexane); IR (KBr disk) 2925 (s), 1710 (s), 1475 (m), 1400 (s), 1350 (s), 1200 (s), 1165 (s), 1145 (s), 1180 (s), 970 (m), 880 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.15–1.69 (m, 10 H), 1.77 (d, J = 6.1 Hz, 3 H), 2.41 (s, 3 H), 4.00 (s, 2 H), 4.87 (d, J = 7.3 Hz, 1 H), 5.40 (ddd, J = 1.2, 7.3, 14.9 Hz, 1 H), 5.86 (dq, J = 14.9, 6.1 Hz, 1 H), 7.27 (d, J = 8.3 Hz, 2 H), 7.86 (d, J = 8.3 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, 6.96; N, 3.72; S, 8.70.

***cis*-*N*-(*p*-Toluenesulfonyl)-4-methyl-5-vinyl-6-aza-2-oxacyclohexan-1-one (*cis*-5a):** a mixture of *cis*-5a:*trans*-5a = 1:1.5; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.99 (d, J = 6.7 Hz, 3 H), 2.27 (m, 1 H), 2.42 (s, 3 H), 3.96 (t, J = 11.0 Hz, 1 H), 4.13 (dd, J = 4.8, 11.0 Hz, 1 H), 5.02 (m, 1 H, coalescing to d, J = 4.4 Hz, by irradiation at 5.80), 5.40 (d, J = 16.9 Hz, 1 H), 5.50 (d, J = 10.3 Hz, 1 H), 5.80 (ddd, J = 5.5, 10.3, 16.9 Hz, 1 H), 7.29 (d, J = 8.1 Hz, 2 H), 7.89 (d, J = 8.1 Hz, 2 H).

***trans*-*N*-(*p*-Toluenesulfonyl)-4-methyl-5-vinyl-6-aza-2-oxacyclohexan-1-one (*trans*-5a).** This compound was obtained by recrystallization from a mixture of *cis*- and *trans*-5a: mp 147.0–148.0 °C (benzene); IR (KBr disk) 2950 (m), 2900 (m), 2855 (m), 1725 (s), 1640 (w), 1425 (m), 1320 (s), 1150 (s), 1090 (m), 800 (m), 700 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.16 (d, J = 7.3 Hz, 3 H), 2.12 (m, 1 H), 2.43 (s, 3 H), 3.97 (ddd, J = 1.5, 3.0, 11.0 Hz, 1 H), 4.37 (dd, J = 3.0, 11.0 Hz, 1 H), 4.85 (m, 1 H), 5.39 (dd, J = 1.5, 17.0 Hz, 1 H), 5.42 (dd, J = 1.5, 10.3 Hz, 1 H), 5.85 (ddd, J = 4.0, 10.3, 17.0 Hz, 1 H), 7.30 (d, J = 8.1 Hz, 2 H), 7.89 (d, J = 8.1 Hz, 2 H). Anal. Calcd for $C_{14}H_{17}NO_4S$: C, 56.93; H, 5.80; N, 4.74; S, 10.86. Found: C, 56.88; H, 5.76; N, 4.81; O, 21.67; S, 10.88.

***cis*-*N*-(*p*-Toluenesulfonyl)-4-benzyl-5-vinyl-6-aza-2-oxacyclohexan-1-one (*cis*-5b):** R_f = 0.48 (benzene:ethyl acetate = 16:1); mp 147.5–150.0 °C (benzene–hexane); IR (KBr disk) 2930 (m), 1730 (s), 1640 (w), 1415 (s), 1345 (s), 1210 (s), 1090 (s), 965 (m), 670 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.41 (s, 3 H), 2.51–2.95 (m, 3 H), 3.90–4.29 (m, 2 H), 5.05 (dd, J = 2.2, 6.3 Hz, 1 H), 5.28–5.65 (m, 2 H), 5.90 (ddd, J = 6.3, 10.3, 16.4 Hz, 1 H), 7.07–7.48 (m, 7 H), 7.86 (d, J = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.4, 33.9, 38.7, 59.6, 68.7, 118.,4, 121.5, 128.5, 129.0, 129.4, 131.2, 136.8, 144.7. Anal. Calcd for $C_{20}H_{21}NO_4S$: C, 64.67; H, 5.70; N, 3.77; S, 8.63. Found: C, 64.95; H, 5.74; N, 3.74; S, 8.48.

***trans*-*N*-(*p*-Toluenesulfonyl)-4-benzyl-5-vinyl-6-aza-2-oxacyclohexan-1-one (*trans*-5b):** R_f = 0.52 (benzene:ethyl acetate = 16:1); semisolid; IR neat film) 2930 (m), 1725 (s), 1645 (w), 1410 (m), 1355 (s), 1175 (s), 1090 (m), 750 (m), 700 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.15 (m, 1 H), 2.42 (s, 3 H), 2.50–3.01 (m, 2 H), 3.99 (DT, J = 11.2, 2.0 Hz, 1 H, coalescing to dd, J = 2.0, 11.2 Hz, by irradiation at 2.15; coalescing to dd, J = 11.2, 2.0 Hz, by irradiation at 4.99), 4.30 (dt, J = 11.2, 3.2 Hz, 1 H), 4.99 (br s, 1 H), 5.19–5.62 (m, 2 H), 5.88 (ddd, J = 4.9, 10.5, 16.6 Hz, 1 H), 7.06–7.49 (m, 7 H), 7.93 (d, J = 8.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.2, 35.3, 38.0, 60.5, 66.9, 117.9, 126.7, 127.5, 128.8, 129.2, 135.9, 137.2, 144.6.

***trans*-*N*-(*p*-Toluenesulfonyl)-4-benzyl-5-isopropenyl-6-aza-2-oxacyclohexan-1-one (*trans*-5c):** mp 76.5–78.0 °C (benzene–hexane); IR (KBr disk) 1720 (s), 1355 (s), 1180 (s), 1090 (m), 815 (m), 750 (s), 705 (s), 680 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.73 (s, 3 H), 2.22 (m, 1 H), 2.43 (s, 3 H), 2.54–3.01 (m, 2 H), 3.98 (ddd, J = 1.7, 2.7, 11.2 Hz, 1 H, coalescing to dd, J = 1.7, 11.2 Hz, by irradiation at 2.22), 4.29 (dd, J = 3.2, 11.2 Hz, 1 H), 4.75 (br s, 1 H), 4.89–5.19 (m, 2 H), 7.09–7.38 (m, 7 H), 7.93 (d, J = 8.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.2, 21.3, 35.7, 35.9, 63.6, 66.7, 114.0, 126.8, 128.6, 128.8, 129.5, 135.3, 37.3, 142.6, 144.7, 148.3. Anal. Calcd for $C_{21}H_{23}NO_4S$: C, 65.43; H, 6.01, N, 3.63; S, 8.31. Found: C, 65.27; H, 6.14; N, 3.63; S, 8.02.

***trans*-*N*-(*p*-Toluenesulfonyl)-4-phenyl-5-vinyl-6-aza-2-oxacyclohexan-1-one (*trans*-5d):** mp 200.0–200.5 °C (benzene); IR (KBr disk) 1720 (s), 1415 (s), 1350 (s), 1280 (s), 1270 (s), 1190 (s), 1090 (s), 700 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.36 (s, 3 H), 3.30 (pseudo q, J = 3.3 Hz, coalescing to br t, J = 3.1 Hz by irradiation at 5.30, 1 H), 4.60 (ddd, J = 1.5, 2.6, 11.4 Hz, 1 H), 4.65 (dd, J = 4.0, 11.4 Hz, 1 H), 5.30 (m, 1 H), 5.50 (dd, J = 1.8, 10.6 Hz, 1 H), 5.54 (dd, J = 1.8, 16.9 Hz, 1 H), 6.07 (ddd, J = 4.5, 10.6, 16.9 Hz, 1 H), 7.04 (d, J = 8.4 Hz, 2 H), 7.16–7.42 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 21.5, 41.7, 63.9, 67.9, 119.1, 127.3, 128.1, 128.9, 129.4, 135.2, 135.6, 137.9, 144.5. Anal. Calcd for $C_{19}H_{19}NO_4S$: C, 63.85; H, 5.36; N, 3.92; S, 8.97. Found: C, 63.66; H, 5.31; N, 3.97; S, 9.02.

***trans*-*N*-(*p*-Toluenesulfonyl)-4-phenyl-5-isopropenyl-6-aza-2-oxacyclohexan-1-one (*trans*-5e):** mp 148–149 °C (benzene–hexane); IR (KBr disk) 2980 (m), 1725 (s), 1655 (w), 1350 (s), 1290 (s), 1180 (s), 700 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.88 (s, 3 H), 2.37 (s, 3 H), 3.32 (pseudo q, J = 3.9 Hz, 2 H), 4.54 (pseudo d, J = 3.9 Hz, 2 H), 5.01–5.24 (m, 3 H), 7.07 (d, J = 8.3 Hz, 2 H), 7.19–7.49 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 19.1, 21.3, 40.2, 67.0, 47.6, 114.8, 127.1, 127.6, 128.7, 128.8, 129.1, 135.2, 137.9, 142.0, 144.3. Anal. Calcd for $C_{20}H_{21}NO_4S$: C, 64.67; H, 5.70; N, 3.77; S, 8.63. Found: C, 64.72; H, 5.65; N, 3.75; S, 8.53.

***cis*-*N*-(*p*-Toluenesulfonyl)-4-benzyl-5-[(1′*E*)-propenyl]-6-aza-2-oxacyclohexan-1-one (*cis*-5f):** mp 145.5–146.0 °C (benzene–hexane); IR (KBr disk) 2990 (m), 1730 (s), 1670 (m), 1415 (m), 1350 (s), 1170 (s), 1090 (s), 1050 (s), 975 (m), 705 (m), 680 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.83 (dd, J = 1.2, 6.2 Hz, 3 H), 2.41 (s, 3 H), 2.48–2.85 (m, 3 H), 3.89–4.31 (m, 2 H), 4.98 (dd, J = 2.9, 7.3 Hz, 1 H), 5.42 (qdd, J = 1.2, 7.3, 15.0 Hz, 1 H), 5.86 (dq, J = 15.0, 6.2 Hz, 1 H), 7.05–7.49 (m, 7 H), 7.85 (d, J = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.4, 21.2, 33.7, 39.4, 59.1, 68.6, 123.8, 126.7, 128.6, 128.7, 129.0, 133.0, 136.9, 144.4, 147.8. Anal. Calcd for $C_{21}H_{23}NO_4S$: C, 65.43; H, 6.01; N, 3.63; S, 8.32. Found: C, 65.61; H, 6.01; N, 3.62; S, 8.46.

***trans*-*N*-(*p*-Toluenesulfonyl)-4-benzyl-5-[(1′*E*)-propenyl]-6-aza-2-oxacyclohexan-1-one (*trans*-5f):** mp 73.5–75.0 °C (benzene–hexane); IR (KBr disk) 2930 (m), 1735 (s), 1400 (m), 1360 (s), 1175 (s), 1160 (m), 980 (m), 700 (m), 665 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.73 (d, J = 5.9 Hz, 3 H), 2.13 (m, 1 H), 2.43 (s, 3 H), 2.54–3.02 (m, 2 H), 3.99 (pseudo dt, J = 11.5, 2.0 Hz, 1 H, coalescing to dd, J = 2.7, 11.5 Hz, by irradiation at 4.89), 4.30 (dd, J = 3.4, 11.5 Hz, 1 H, coalescing to d, J = 11.5 Hz, by irradiation at 2.13), 4.89 (br s, 1 H, coalescing to br d, J = 5.6 Hz, by irradiation at 2.13; coalescing to br s, by irradiation at 5.43), 5.43 (ddd, J = 0.7, 5.6, 15.5 Hz, 1 H), 5.75 (dq, J = 15.5, 5.9 Hz, 1 H), 7.06–7.44 (m, 7 H), 7.91 (d, J = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.1, 21.2, 35.4, 38.7, 60.2, 67.0, 126.6, 128.0, 128.5, 128.8, 129.2, 129.7, 137.3, 144.5.

***N*-(*p*-Toluenesulfonyl)-5-vinyl-4-aza-2-oxabicyclo[4.3.0]-nona-3-one (5g):** mp 129.5–131.0 °C (benzene–hexane); IR (KBr disk) 2980 (s), 1720 (s), 1600 (m), 1350 (s), 1200 (s), 1095 (m), 970 (m), 825 (m), 765 (m), 680 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.41–2.65 (m, 7 H), 2.43 (s, 3 H), 4.82 (br, 1 H, C_1H, coalescing to d, J = 4.9 Hz, by irradiation at 1.95), 5.08 (dd, J = 1.7, 5.6 Hz, 1 H, C_5H, coalescing to d, J = 1.7 Hz, by irradiation at 5.90), 5.17–5.43 (m, 2 H), 5.90 (ddd, J = 5.6, 9.8, 17.1 Hz, 1 H), 7.29 (d, J = 8.3 Hz, 2 H), 7.92 (d, J = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.2, 22.2, 27.0, 33.6, 42.3, 58.8, 82.7, 117.1, 128.8, 129.1, 135.8, 144.5. Anal. Calcd for $C_{16}H_{19}NO_4S$: C, 59.79; H, 5.96; N, 4.36; S, 9.98. Found: C, 59.77; H, 5.96; N, 4.23; S, 9.92.

***cis*-*N*-(*p*-Toluenesulfonyl)-3-phenyl-5-vinyl-6-aza-2-oxacyclohexan-1-one (*cis*-6a):** R_f = 0.7 (benzene:ethyl acetate = 16:1); mp 138.0–139.0 °C (benzene–hexane); IR 1720 (s), 1595 (m), 1355 (s), 1250 (s), 1175 (s), 1130 (m), 1090 (m), 940 (m), 810 (m), 750 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.07 (ddd, J = 9.6, 11.1, 14.3 Hz, 1 H), 2.44 (s, 3 H), 2.56 (ddd, J = 2.3, 7.9, 14.3 Hz, 1 H), 5.07 (br q, J = 8.5 Hz, 1 H), 5.24 (d, J = 10.0 Hz, 1 H), 5.28 (dd, J = 2.3, 11.1 Hz, 1 H), 5.40 (d, J = 17.0 Hz, 1 H), 5.59 (ddd, J = 8.1, 10.0, 17.0 Hz, 1 H), 7.3–7.4 (m, 7 H), 8.01 (d, J = 8.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.4, 38.3, 58.4, 77.5, 118.1, 125.8, 128.7, 129.1, 129.6, 137.0, 144.7.

***trans*-*N*-(*p*-Toluenesulfonyl)-3-phenyl-5-vinyl-6-aza-2-oxacyclohexan-1-one (*trans*-6a):** R_f = 0.6 (benzene:ethyl acetate = 16:1); mp 181.0–182.0 °C (benzene–hexane); IR (KBr disk) 2930 (w), 1720 (s), 1650 (w), 1390 (m), 1360 (s), 1210 (s), 1170 (s), 750 (s), 660 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.26 (m, 2 H), 2.44 (s, 3 H), 5.29 (br s, 1 H), 5.39 (pseudo t, J = 7.5 Hz, 1 H), 5.46 (d, J = 17.6 Hz, 1 H), 5.51 (d, J = 10.6 Hz, 1 H), 6.02 (ddd, J = 4.8, 10.6, 17.6 Hz, 1 H), 7.25–7.39 (m, 7 H), 7.95 (d, J = 8.1 Hz, 2 H); ^{1}H NMR (C_6D_6, 400 MHz) δ 1.46 (pseudo dt, J = 14.3, 2.7 Hz, 1 H), 1.65 (ddd, J = 5.3, 12.3, 14.3 Hz, 1 H), 1.95 (s, 3 H), 4.99 (dd, J = 3.1, 12.3 Hz, 1 H), 5.11 (m, 1 H), 5.16 (d, J = 10.4 Hz, 1 H), 5.35 (d, J = 17.0 Hz, 1 H), 5.49 (ddd, J = 4.9, 10.4, 17.0 Hz, 1 H), 6.89 (d, J = 8.3 Hz, 2 H), 6.91–6.96 (m, 2 H), 7.09–7.14 (m, 3 H), 8.28 (d, J = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.4, 35.2, 56.1, 76.7, 118.6, 125.6, 128.6, 129.1, 129.3, 135.5, 137.7, 144.8. Anal. Calcd for $C_{19}H_{19}NO_4S$: C, 63.85; H, 5.36; N, 3.92; S, 8.97. Found: C, 64.15; H, 5.39; N, 3.91; S, 8.97.

***cis*-N-(*p*-Toluenesulfonyl)-3-phenyl-5-isopropenyl-6-aza-2-oxacyclohexan-1-one (*cis*-6b):** mp 159.5–160.5 °C (benzene); IR (KBr disk) 1710 (s), 1350 (s), 1275 (s), 1165 (s), 1140 (s), 1090 (m), 945 (m), 900 (m), 820 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.43 (s, 3 H), 2.06 (ddd, J = 9.8, 11.7, 14.4 Hz, 1 H), 2.43 (s, 3 H), 2.57 (ddd, J = 2.4, 9.0, 14.4 Hz 1 H), 4.93 (m, 1 H), 5.09 (m, 1 H), 5.12 (dd, J = 9.0, 9.8 Hz, 1 H), 5.27 (dd, J = 2.4, 11.7 Hz, 1 H), 7.29 (d, J = 8.3 Hz, 2 H), 7.35 (s, 5 H), 8.03 (d, J = 8.3 Hz, 2 H). Irradiation of C_4H proton (*trans* to phenyl) increased area intensities of C_3H, C_4H (*cis* to phenyl), and C_5H by 10.0, 29.6, and 18.3%, respectively, while irradiation of C_4H proton (*cis* to phenyl) increased area intensities of C_3H, C_4H (*trans* to phenyl), and C_5H by 3.5, 24.6, and 0%, respectively: ^{13}C NMR ($CDCl_3$) δ 16.5, 21.7, 37.2, 61.4, 77.6, 115.7, 126.0, 128.8, 128.9, 129.1, 129.7, 135.3, 136.7, 142.5, 145.1, 150.9. Anal. Calcd for $C_{20}H_{21}NO_4S$: C, 64.67; H, 5.70; N, 3.77; S, 8.63. Found: C, 64.63; H, 5.67; N, 3.84; S, 8.63.

***cis*-N-(*p*-Toluenesulfonyl)-3-*tert*-butyl-5-vinyl-6-aza-2-oxacyclohexan-1-one (*cis*-6c):** R_f = 0.66 (benzene:ethyl acetate = 16:1); mp 119.5–120.0 °C (benzene–hexane), 130.0–131.0 °C (CH_2Cl_2–hexane); IR (KBr disk) 2970 (m), 1735 (s), 1360 (s), 1250 (m), 1170 (s), 945 (m), 660 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.96 (s, 9 H), 1.64 (ddd, J = 10.3, 11.6, 14.0 Hz, 1 H), 2.27 (ddd, J = 1.8, 7.8, 14.0 Hz, 1 H), 2.42 (s, 3 H), 3.89 (dd, J = 1.8, 11.6 Hz, 1 H), 4.86 (ddd, J = 7.8, 8.3, 10.3 Hz, 1 H), 5.23 (d, J = 10.0, 1 H), 5.37 (d, J = 18.1 Hz, 1 H), 5.53 (ddd, J = 8.3, 10.0, 18.1 Hz, 1 H), 7.28 (d, J = 8.7 Hz, 2 H), 7.99 (d, J = 8.7 Hz, 2 H). Irradiation of C_3H proton increased area intensities of C_4H (*trans* to *tert*-butyl), C_4H (*cis* to *tert*-butyl), C_5H, and vinylic $C_{1'}H$ by 2.3, 1.5, 5.0, and 0%, respectively.

***trans*-N-(*p*-Toluenesulfonyl)-3-*tert*-butyl-5-vinyl-6-aza-2-oxacyclohexan-1-one (*trans*-6c):** R_f = 0.53 (benzene:ethyl acetate = 16:1); mp 127.0–128.0 °C (benzene–hexane); IR (KBr disk) 2980 (m), 2960 (m), 1715 (s), 1640 (w), 1390 (m), 1350 (s) 1170 (s), 1090 (m), 750 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.91 (s, 9 H), 1.90–2.01 (m, 2 H), 2.42 (s, 3 H), 4.02 (dd, J = 4.2, 10.7 Hz, 1 H), 5.22 (m, 1 H), 5.34 (dd, J = 1.7, 17.1 Hz, 1 H), 5.40 (dd, J = 1.3, 10.5 Hz, 1 H), 5.88 (ddd, J = 4.9, 10.5, 17.1 Hz, 1 H), 7.30 (d, J = 8.5 Hz, 2 H), 7.93 (d, J = 8.5 Hz, 2 H); irradiation of C_3H proton increased area intensities of C_4H and vinylic $C_{1'}H$ by 0.4 and 5.8%, respectively: ^1H NMR (C_6D_6, 400 MHz) δ 0.63 (s, 9 H), 1.21 (pseudo dt, J = 13.9, 2.8 Hz, 1 H), 1.35 (ddd, J = 5.1, 12.3, 13.9 Hz, 1 H), 3.71 (dd, J = 3.1, 12.3 Hz, 1 H, coalescing to dd, J = 2.4, 13.9 Hz, by irradiation at 3.71), 5.06 (d, J = 10.5 Hz, 1 H), 5.09 (m, 1 H), 5.24 (dd, J = 0.7, 17.2 Hz, 1 H), 5.43 (ddd, J = 5.1, 10.5, 17.2 Hz, 1 H), 6.80 (d, J = 8.4 Hz, 2 H), 8.19 (d, J = 8.4 Hz, 2 H). Anal. Calcd for $C_{17}H_{23}NO_4S$: C, 60.51, H, 6.87; N, 4.15; S, 9.50. Found: C, 60.76; H, 6.80; N, 3.90; S, 9.20.

General Procedure for the Preparation of *N*-(*p*-Toluenesulfonyl)-3-amino-4-penten-1-ol (7): Hydrolysis of *N*-(*p*-Toluenesulfonyl)-5-vinyl-6-aza-2-oxacyclohexan-1-one (5). A solution of a carbamate 5 (0.5 mmol) in EtOH (3 mL) and 1 N KOH (3 mL) was refluxed for 2 h. To the resultant solution was added 2 N HCl (1.8 mL), and the solution was extracted with ethyl acetate (4 × 10 mL). Drying over magnesium sulfate and evaporation of the solvent followed by purification by means of either chromatography over silica gel or recrystallization provided 7 in quantitative yield (85–95%).

***syn*-N-(*p*-Toluenesulfonyl)-3-amino-2-methyl-4-penten-1-ol (*syn*-7a):** a mixture of *syn*-7a:*anti*-7a = 1:1.5; IR (neat) 3500 (m), 3275 (s), 1600 (m), 1320 (s), 1150 (s), 1090 (s), 1030 (s), 920 (s), 810 (s), 700 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.71 (d, J = 7.6 Hz, 3 H), 1.87–1.98 (m, 1 H), 2.41 (s, 3 H), 3.66–3.49 (m, 2 H), 4.09–4.15 (m, 1 H), 4.85 (d, J = 17.5 Hz, 1 H), 4.94 (d, J = 10.6 Hz, 1 H), 5.56 (ddd, J = 5.5, 10.6, 17.5 Hz, 1 H), 7.28 (d, J = 9.0 Hz, 2 H), 7.74 (d, J = 9.0 Hz, 2 H). Correct elemental analysis was obtained as 8a.

***anti*-N-(*p*-Toluenesulfonyl)-3-amino-2-methyl-4-penten-1-ol (*anti*-7a):** ^1H NMR ($CDCl_3$, 400MHz) δ 0.89 (d, J = 7.1 Hz, 3 H), 1.68–1.71 (m, 1 H), 2.41 (s, 3 H), 3.33–3.97 (m, 3 H), 4.89 (dd, J = 1.2, 17.6 Hz, 1 H), 4.95 (dd, J = 1.2, 9.3 Hz, 1 H), 5.46 (d, J = 5.9 Hz, 1 H), 5.50–5.60 (m, 1 H), 7.26 (d, J = 8.3 Hz, 2 H), 7.74 (d, J = 8.3 Hz, 2 H). Correct elemental analysis was obtained as 8a.

***syn*-N-(*p*-Toluenesulfonyl)-3-amino-2-benzyl-4-penten-1-ol (*syn*-7b):** semisolid; IR (neat film) 3500 (br, s), 3280 (m) 2930 (m), 1635 (w), 1450 (s), 1320 (s), 1160 (s), 1090 (m), 920 (m), 810 (m) cm^{-1}; ^1H NMR ($CDCl_3$, D_2O added) δ 1.90–2.70 (m, 3 H), 2.41 (s, 3 H), 3.29–3.80 (m, 2 H), 4.04 (dd, J = 2.7, 5.3 Hz, 1 H), 4.87–5.16 (m, 2 H), 5.70 (ddd, J = 5.3, 8.8, 17.1 Hz, 1 H), 6.92–7.37 (m, 7 H), 7.67 (d, J = 8.3 Hz, 2 H). Correct HRMS was obtained as *cis*-10b.

***anti*-N-(*p*-Toluenesulfonyl)-3-amino-2-benzyl-4-penten-1-ol (*anti*-7b):** semisolid; IR (neat film) 3150 (br s), 3280 (br s), 2930 (m), 1640 (m), 1450 (m), 1325 (s), 1155 (s), 1030 (m), 930 (m), 810 (s) cm^{-1}; ^1H NMR ($CDCl_3$, D_2O added) δ 1.60–1.98 (m, 1 H), 2.38 (s, 3 H), 2.44–2.88 (m, 2 H, benzyl protons), 3.39 (dd, J = 4.4, 11.2 Hz, 1 H), 3.78 (dd, J = 2.9, 11.2 Hz, 1 H), 3.94 (t, J = 6.8 Hz, 1 H, coalescing to d, J = 6.8 Hz, by irradiation at 5.63), 4.74–5.06 (m, 2 H), 5.63 (ddd, J = 6.8, 11.2, 17.8 Hz, 1 H), 6.89–7.38 (m, 7 H), 7.74 (d, J = 8.3 Hz, 2 H). Correct HRMS was obtained as *trans*-10b.

***anti*-N-(*p*-Toluenesulfonyl)-3-amino-4-methyl-2-phenyl-4-penten-1-ol (*trans*-7e):** mp 174.0–175.0 °C (benzene–hexane); IR (KBr disk) 3460 (br s), 2930 (m), 1650 (s), 1455 (m), 1330 (s), 1150 (s), 1095 (m), 1075 (m), 900 (m), 810 (m), 700 (s), 670 (s) cm^{-1}; ^1H NMR ($CDCl_3$, D_2O added) δ 2.84 (pseudo quintet, J = 5.1 Hz, 1 H), 3.77–4.22 (m, 3 H), 4.44 (br s, 2 H), 7.00–7.38 (m, 7 H), 7.72 (d, J = 8.3 Hz, 2 H). Correct elemental analysis was obtained as *trans*-8e.

***(E)-syn*-N-(*p*-Toluenesulfonyl)-3-amino-2-benzyl-4-hexen-1-ol (*syn*-7f):** oil; IR (neat film) 3500 (br, s), 3270 (br, s), 2940 (m), 1670 (w), 1600 (m), 1460 (m), 1325 (s), 1160 (s) 1030 (m), 970 (m), 820 (m), 700 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.48 (d, J = 4.9 Hz, 3 H), 1.73–2.69 (m, 3 H), 2.39 (s, 3 H), 3.37–3.71 (m, 2 H), 3.93 (m, 1 H), 5.01–5.62 (m, 2 H), 5.75 (d, J = 8.8 Hz, 1 H, NH), 6.89–7.36 (m, 7 H), 7.65 (d, J = 8.0 Hz, 2 H). Correct elemental analysis was obtained as *cis*-8f.

***(E)-anti*-N-(*p*-Toluenesulfonyl)-3-amino-2-benzyl-4-hexen-1-ol (*anti*-7f):** semisolid; IR (KBr disk) 3580 (s), 3320 (s), 2970 (m), 1670 (w), 1600 (m), 1420 (m), 1335 (s), 1160 (s), 1135 (m), 970 (m), 815 (s), 750 (m), 700 (m), 670 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.42 (d, J = 4.6 Hz, 3 H), 1.58–1.95 (m, 1 H), 2.15 (br s, 1 H, OH), 2.40 (s, 3 H), 2.46–2.79 (m, 2 H, benzyl protons), 3.40 (dd, J = 4.2, 11.7 Hz, 1 H), 3.69–3.97 (m, 2 H), 4.94–5.99 (m, 3 H, olefinic protons and NH), 7.00–7.37 (m, 7 H), 7.72 (d, J = 8.3 Hz, 2 H). Correct HRMS was obtained as *trans*-8f.

General Procedure for the Synthesis of *N*-(*p*-Toluenesulfonyl)-2-vinylazetidine (8) by the Mitsunobu Method. To a solution of *N*-(*p*-toluenesulfonyl)-3-amino-4-penten-1-ol (7) (0.30 mmol) and triphenylphosphine (0.36 mmol) in dry THF (3 mL) was added diethyl azodicarboxylate (0.36 mmol) at 0 °C. The solution was then allowed to warm to room temperature and stirred for several hours. Then 2 N HCl (0.5 mL) was added, and the mixture was extracted with ethyl acetate (4 × 10 mL). After the mixture was dried over magnesium sulfate, the solvent was evaporated to afford crude azetidine 8, which was purified by flash column chromatography over silica gel (benzene–ethyl acetate gradient).

***N*-(*p*-Toluenesulfonyl)-3-methyl-2-vinylazetidine (8a):** oil; a mixture of *cis*-8a:*trans*-8a = 1:1.5, obtained from a mixture of *syn*- and *anti*-7a of the same ratio; IR (neat film) 2965 (m), 1600 (m), 1500 (m), 1460 (m), 1350 (s), 1170 (s), 935 (m), 820 (m), 710 (s), 670 (s) cm^{-1}. *cis*-8a: ^1H NMR ($CDCl_3$, 400 MHz) δ 1.11 (d, J = 7.3 Hz, 3 H), 2.38 (m, 1 H), 2.45 (s, 3 H), 3.28 (dd, J = 3.7, 7.7 Hz, 1 H), 3.72 (t, J = 7.7 Hz, 1 H), 4.33 (dd, J = 7.3, 8.4 Hz, 1 H), 5.27 (d, J = 10.6 Hz, 1 H), 5.35 (d, J = 17.2 Hz, 1 H), 5.85 (ddd, J = 8.4, 10.6, 17.2 Hz, 1 H), 7.35 (d, J = 8.4 Hz, 2 H), 7.71 (d, J = 8.4 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 15.1, 21.6, 28.5, 54.5, 66.9, 118.9, 133.7. *trans*-8a: ^1H NMR ($CDCl_3$, 400 MHz) δ 0.90 (d, J = 6.6 Hz, 3 H), 2.38 (m, 1 H), 2.45 (s, 3 H), 3.18 (t, J = 7.7 Hz, 1 H), 3.78 (dd, J = 7.3, 7.7 Hz, 1 H), 3.81 (t, J = 7.3 Hz, 1 H), 5.15 (d, J = 10.6 Hz, 1 H), 5.26 (d, J = 17.2 Hz, 1 H), 5.93 (ddd, J = 7.3, 10.6, 17.2 Hz, 1 H), 7.35 (d, J = 8.4 Hz, 2 H), 7.71 (d, J = 8.4 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.3, 21.6, 32.0, 54.8, 72.2, 117.2, 136.8. Anal. Calcd for $C_{13}H_{17}NO_2S$: C, 62.12; H, 6.82; N, 5.57; S, 12.76. Found: C, 61.98; H, 6.83; N, 5.59; S, 12.84.

***trans*-N-(*p*-Toluenesulfonyl)-2-isopropenyl-3-phenylazetidine (*trans*-8e):** mp 88.0–89.0 °C (benzene–hexane); IR (KBr disk) 2980 (m), 2930 (m), 1655 (m), 1455 (m), 1350 (s), 1165 (s), 1090 (m), 1070 (m), 825 (m), 755 (s), 700 (s), 670 (s) cm^{-1}; ^1H NMR (C_6D_6, 400 MHz) δ 1.77 (t, J = 1.0 Hz, 3 H), 1.99 (s, 3 H), 3.23 (pseudo q, J = 8.1 Hz, 1 H), 3.81 (t, J = 8.0 Hz, 1 H), 3.86 (pseudo t, J = 8.0 Hz, 1 H), 4.51 (dd, J = 7.7 Hz, 1 H), 4.94 (br

s, 1 H), 5.25 (br s, 1 H), 7.86–6.88 (m, 2 H), 6.87 (d, J = 8.3 Hz, 2 H), 7.01–7.05 (m, 3 H), 7.89 (d, J = 8.3 Hz, 2 H). Irradiation at olefinic methyl protons caused increase in the area intensities of C_3H, C_2H, and vinylic H (*cis* to the methyl). Anal. Calcd for $C_{19}H_{21}NO_2S$: C, 69.69; H, 6.46; N, 4.28; S, 9.79. Found: C, 69.85; H, 6.42; N, 4.22, S, 9.93.

***cis*-*N*-(*p*-Toluenesulfonyl)-3-benzyl-2-[(1′*E*)-propenyl]-azetidine (*cis*-8f):** mp 77.5–79.0 °C (benzene); IR (KBr disk) 2980 (m), 1670 (m), 1605 (m), 1345 (s), 1160 (s), 965 (m), 830 (m), 675 (s) cm^{-1}; ^{1}H NMR (C_6D_6, 400 MHz) δ 1.68 (pseudo dq, J = 6.6, 0.7 Hz, 3 H), 2.03 (s, 3 H), 2.12 (m, 1 H), 2.64–2.67 (m, 2 H), 3.42 (dd, J = 3.9, 8.0 Hz, 1 H), 3.47 (pseudo t, J = 8.1 Hz, 1 H), 4.38 (pseudo t, J = 7.9 Hz, 1 H), 5.63 (pseudo ddq, J = 7.3, 15.3, 1.7 Hz, 1 H), 5.90 (ddq, J = 1.1, 15.3, 6.6 Hz, 1 H), 6.84–6.87 (m, 2 H), 6.94 (d, J = 8.4 Hz, 2 H), 7.11–7.21 (m, 3 H), 7.89 (d, J = 8.4 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.4, 21.2, 35.1, 35.5, 52.3, 66.4, 126.1, 126.8, 128.2, 128.3, 129.3, 130.4, 139.1, 143.4. Irradiation at olefinic C_1′H caused increase in the area intensity of benzylic protons. Anal. Calcd for $C_{20}H_{23}NO_2S$: C, 70.35; H, 6.79; N, 4.10; S, 9.39. Found: C; 70.45; H, 6.88; N, 4.14; S, 9.27.

***trans*-*N*-(*p*-Toluenesulfonyl)-3-benzyl-2-[(1′*E*)-propenyl]-azetidine (*trans*-8f):** oil; IR (neat film) 2930 (m), 1670 (w), 1345 (s), 1170 (s), 965 (m), 670 (s) cm^{-1}; ^{1}H NMR (C_6D_6, 400 MHz) δ 1.57 (dd, J = 1.0, 5.4 Hz, 3 H), 2.01 (s, 3 H), 2.02–2.40 (m, 3 H), 3.43 (pseudo t, J = 7.6 Hz, 1 H), 3.62 (pseudo t, J = 7.5 Hz, 1 H), 4.20 (pseudo t, J = 6.5 Hz, 1 H), 5.56–5.73 (m, 2 H), 6.77–6.81 (m, 2 H), 6.92 (d, J = 8.2 Hz, 2 H), 7.07–7.19 (m, 3 H), 7.90 (d, J = 8.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.2, 21.2, 38.0, 38.4, 52.7, 69.9, 126.2, 128.8, 128.3, 129.2, 130 0, 143.4; irradiation at olefinic C_1′H caused increase in the area intensity of C_3H; HRMS calcd for $C_{20}H_{23}NO_2S$ 341.1449, found m/z (relative intensity) 341.1451 (M, 10), 327 (24), 326 (100), 184 (40), 158 (93), 155 (60).

General Procedure for Reductive Removal of Tosyl Group of *N*-(*p*-Toluenesulfonyl)-5-vinyl-6-aza-2-oxacyclohexan-1-one (5) by Sodium/Naphthalene. A suspension of sodium (3 mmol) in dry THF (5 mL) containing naphthalene (3.5 mmol) was stirred at room temperature for 1 h under argon, during which time a green solution formed. To this was added carbamate 5 (0.5 mmol) in dry THF (ca. 2 mL) at −78 °C via a syringe. After being stirred for about 10 min at −78 °C, the mixture was allowed to warm to 0 °C (within about 10 min) and stirred for 10 min. To this solution was carefully added 2-propanol until the green color of the solution turned colorless. After neutralization with dilute HCl, the mixture was extracted with ethyl acetate (4 × 10 mL). Drying over magnesium sulfate and evaporation of the solvent, followed by purification by means of either chromatography over silica gel or recrystallization, provided 5-vinyl-6-aza-2-oxacyclohexan-1-one (9) in quantitative yield (90–95%).

***cis*-4-Methyl-5-vinyl-6-aza-2-oxacyclohexan-1-one (*cis*-9a):** a mixture of *cis*-9a:*trans*-9a = 1:1.5; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.96 (dd, J = 1.1, 7.3 Hz, 3 H), 2.34 (m, 1 H), 3.96 (t, J = 11.0 Hz, 1 H), 4.04 (dd, J = 3.3, 8.0 Hz, 1 H), 4.13 (dd, J = 3.6, 11.0 Hz, 1H), 5.30–5.36 (m, 2 H), 5.80 (ddd, J = 8.0, 10.3, 17.3 Hz, 1 H), 6.3 (br s, 1 H).

***trans*-4-Methyl-5-vinyl-6-aza-2-oxacyclohexan-1-one (*trans*-9a):** oil; IR (neat film) 3250 (m), 3120 (m), 1700 (s), 1480 (m), 1430 (m), 1280 (m), 1125 (m), 925 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.00 (d, J = 6.6 Hz, 3 H), 1.87 (m, 1 H), 3.54 (t, J = 8.8 Hz, 1 H, coalescing to d, J = 8.8 Hz, by irradiation at 5.69), 3.91 (t, J = 11.0 Hz, 1 H), 4.21 (dd, J = 3.7, 11.0 Hz, 1 H), 5.29 (d, J = 10.3 Hz, 1 H), 5.30 (d, J = 17.3 Hz, 1 H), 5.69 (ddd, J = 8.8, 10.3, 17.3 Hz, 1 H), 6.2 (br s, 1 H). Anal. Calcd for $C_7H_{11}NO_2$: C, 59.56; H, 7.85; N, 9.92. Found: C, 59.33; H, 8.01; N, 9.78.

***cis*-4-Benzyl-5-vinyl-6-aza-2-oxacyclohexan-1-one (*cis*-9b):** mp 135.5–137.0 °C (benzene–hexane); IR (KBr disk) 3250 (m), 3120 (m), 2930 (m), 1700 (s), 1645 (w), 1475 (m), 1430 (m), 1090 (m), 930 (m), 770 (s), 700 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.48 (m, 1 H), 2.53 (m, 1 H of benzyl protons), 2.67 (dd, J = 5.4, 13.0 Hz, 1 H of benzyl protons), 4.02–4.10 (m, 3 H), 5.35 (d, J = 17.1 Hz, 1 H), 5.41 (d, J = 10.5 Hz, 1 H), 5.82 (br s, 1 H, NH), 5.91 (ddd, J = 6.1, 10.5, 17.1 Hz, 1 H), 7.17–7.19 (m, 2 H), 7.22–7.34 (m, 3 H).

***trans*-4-Benzyl-5-vinyl-6-aza-2-oxacyclohexan-1-one (*trans*-9b):** mp 133.0–134.0 °C (benzene–hexane); IR (KBr disk) 3250 (m), 3130 (m), 1705 (s), 1645 (w), 1315 (s), 930 (m), 710 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.03 (m, 1 H), 2.56 (dd, J = 9.5, 13.9 Hz, 1 H of benzyl protons), 2.92 (dd, J = 5.6, 13.9 Hz, 1 H of benzyl protons), 3.76 (pseudo t, J = 6.1 Hz, 1 H, C_5H), 3.96 (dd, J = 7.3, 11.1 Hz, 1 H, C_3H), 4.17 (dd, J = 3.3, 11.1 Hz, 1 H, C_3H), 5.34 (d, J = 10.1 Hz, 1 H), 5.35 (d, J = 16.9 Hz, 1 H), 5.47 (br s, 1 H, NH), 5.78 (ddd, J = 6.6, 10.1, 16.9 Hz, 1 H), 7.15–7.17 (m, 2 H), 7.23–7.36 (m, 3 H). Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.81; H, 6.99; N, 6.42.

General Procedure for Acetalization of *N*-(*p*-Toluenesulfonyl)-3-amino-4-penten-1-ol (7) with 1,3,5-Trioxane. A solution of *N*-(*p*-toluenesulfonyl)-3-amino-4-penten-1-ol (7) (0.4 mmol) and 1,3,5-trioxane (2 mmol) in dichloromethane (5 mL) was stirred in the presence of a catalytic amount of concd H_2SO_4 for 2 h at room temperature. Addition of aqueous $NaHCO_3$, extraction with ethyl acetate (4 × 10 mL), and drying over magnesium sulfate followed by evaporation of the solvent afforded a crude acetal 10, which was purified by either flash column chromatography over silica gel (benzene–ethyl acetate gradient) or recrystallization.

***cis*-*N*-(*p*-Toluenesulfonyl)-5-benzyl-4-vinyl-3-aza-1-oxacyclohexane (*cis*-10b):** oil; IR (neat film) 2930 (m), 2860 (m), 1640 (w), 1345 (s), 1160 (s), 1050 (s), 970 (m), 930 (m), 815 (m), 665 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.84 (m, 1 H), 2.05–2.70 (m, 2 H), 2.45 (s, 3 H), 3.19–3.72 (m, 2 H), 4.31 (pseudo t, J = 5.6 Hz, 1 H, coalescing to d, J = 4.9 Hz, by irradiation at 6.01), 4.63 (d, J = 11.5 Hz, 1 H), 5.15–5.48 (m, 2 H), 5.42 (d, J = 11.5 Hz, 1 H), 6.01 (ddd, J = 5.6, 8.5, 17.8 Hz, 1 H), 6.79–7.39 (m, 7 H), 7.72 (d, J = 8.3 Hz, 2 H); HRMS calcd for $C_{20}H_{23}NO_3S$ 357.1398, found m/z (relative intensity) 357.1403 (M, 8), 293 (4), 210 (51), 202 (60), 155 (31), 118 (100).

***trans*-*N*-(*p*-Toluenesulfonyl)-5-benzyl-4-vinyl-3-aza-1-oxacyclohexane (*trans*-10b):** oil; IR (neat film) 2930 (m), 2870 (m), 1645 (w), 1345 (s), 1150 (s), 1045 (s), 965 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.80 (m, 1 H), 2.40 (s, 3 H), 2.43–2.71 (m, 2 H), 3.38–3.76 (m, 2 H, coalescing to a pair of d, 3.48, J = 12.0 Hz, and 3.61, J = 12.0 Hz, by irradiation at 2.80), 4.44 (br s, 1 H, coalescing to s, by irradiation at 5.81), 4.63 (d, J = 10.5 Hz, 1 H), 5.03–5.32 (m, 2 H), 5.33 (d, J = 10.5 Hz, 1 H), 5.81 (ddd, J = 4.2, 10.5, 16.8 Hz, 1 H), 6.96–7.38 (m, 7 H), 7.44 (d, J = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.2, 36.6, 39.3, 57.6, 65.7, 74.1, 117.4, 126.0, 127.0, 128.2, 128.9, 129.4, 135.0, 139.3, 143.1; HRMS calcd for $C_{20}H_{23}NO_3S$ 357.1398, found m/z (relative intensity) 357.1394 (M, 9), 293 (4), 210 (50), 202 (75), 155 (41), 118 (100).

Crystallography. Both structures were solved by direct methods. There are two molecules of *cis*-6c in the asymmetric unit. The structure of *trans*-5a was refined by block-diagonal least-squares methods whereas those of the two molecules of *cis*-6c were refined by full-matrix least-squares methods. In both structures the non-hydrogen atoms were defined anisotropically. Positions for all hydrogen atoms bonded to carbon atoms were calculated on the basis of stereochemical considerations and refined with isotropic thermal parameters identical to the *Beq* (equivalent isotropic temperature factor) of the carbon atoms on which the hydrogens are attached.[14]

Crystal data for *trans*-5a: $C_{14}H_{17}NO_4S$, monoclinic, $P2_1$, a = 8.473(3) Å, b = 11.280(1) Å, c = 7.880(1) Å, β = 97.30(2)°, V = 747.0(3) Å^3, Z = 2, D_{calcd} = 1.31 g/cm^3, λ (Cu Kα) = 1.541 78 Å (Ni-filtered), Rigaku AFC-5R diffractometer, 1340 reflections ($5° \le 2\theta \le 130°$) on a colorless crystal of 0.3 × 0.3 × 0.1 mm, 1311 [$|F_o| \ge 3.0\sigma|F_o|$] used, R = 0.061, R_w = 0.083.

Crystal data for *cis*-6c: $C_{17}H_{23}NO_4S$, monoclinic, $P2_1/a$, a = 13.5848(8) Å, b = 13.6898(8) Å, c = 20.251(2) Å, β = 105.843(7)°, V = 3623.0(5) Å^3, Z = 8, D_{calcd} = 1.24 g/cm^3, λ (Cu Kα) = 1.541 78 Å (graphite monochromated), Rigaku AFC-4 diffractometer, 5854 reflections ($5° \le 2\theta \le 126°$) on a colorless crystal of 0.3 × 0.3 × 0.4 mm, 4795 [$|F_o| \ge 3.0\sigma|F_o|$] used, 554 parameters, R = 0.060, R_w = 0.077.

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(14) The author has deposited atomic coordinates for 5a and 6c with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.