Convenient Synthesis of 4-Methylene-2-oxazolidinones and 4-Methylenetetrahydro-1,3-oxazin-2-ones via Transition-Metal Catalyzed Intramolecular Addition of Nitrogen Atom to Acetylenic Triple Bond

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2-Propynyl tosylcarbamates **1** undergo cyclization smoothly by the catalysis of CuCl/Et_3N or AgNCO/Et_3N to furnish 4-methylene-2-oxazolidinones **2** in good yields. The similar cyclization of the *N*-acyl derivatives of **1** (PhCO, MeCO, EtOCO, etc.) is catalyzed effectively by AgNCO/*t*-BuOK. These reactions accommodate a variety of substituents at C_1 and C_3 of 2-propyn-1-ol and provide (*Z*)-**2** as single stereoisomers. The scope of the cyclization of 3-butynyl carbamates is rather limited, and in general only *N*-tosyl derivatives of terminally unsubstituted 3-butyn-1-ols undergo cyclization to give 4-methylenetetrahydro-1,3-oxazin-2-ones in synthetically useful yields by the catalysis of AgNCO/Et_3N or AgNCO/*t*-BuOK.

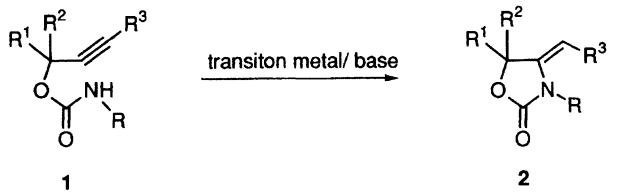
Addition of heteroatom nucleophiles, especially oxygen and nitrogen nucleophiles, to acetylenic triple bond is a transformation of great synthetical value.[1] Through this reaction the electrophilic nature of the triple bond can be altered to the nucleophilic one of the double bonds of vinyl ethers and enamines. Accordingly, many studies have been focused on this subject in pursuit of the milder reaction conditions, the higher regio- and stereoselectivities, and the better yields. The oxygen atoms of alcohols (phenols),[2] carboxylic acids,[3] carbonic acids,[4] and carbamic acids[5] have proven to undergo such addition reactions, in most cases, by the catalysis of transition metals. The examples with nitrogen nucleophiles, on the other hand, are scarce.[6]

2-Oxazolidinones constitute an important class of heterocycles that are widely used in the industrial,[7] pharmaceutical,[8] and agricultural fields[9] as well as in organic synthesis. Among them, 4-alkylidene-2-oxazolidinones **2** are of special interest as synthetic intermediates, since they are functioned with enamine and allylic alcohol moieties. *N*-Alkyl- and *N*-aryl-4-alkylidene-2-oxazolidinones **2** can be obtained via base-catalyzed addition reactions of the nitrogen atom to 2-propynyl aralkylcarbamates to their triple bonds.[10] The similar cyclization has been achieved starting from 2-propyn-1-ols and alkyl- and arylamines under high pressures of carbon dioxide and at high temperatures in the presence of copper salts or phosphines as catalysts.[11] *N*-Tosyl and *N*-acyl derivatives of 4-alkylidene-2-oxazolidinones **2**, on the other hand, have not been prepared according to this type of addition reaction.

Here we would like to report that the nitrogen atoms of *N*-tosyl and *N*-acyl derivatives of 2-propynyl carbamates **1** undergo an intramolecular addition reaction to the triple bonds and provide 4-methylene-2-oxazolidinones **2** (Eq. 1) in good yields by the catalysis of transition metal salts (CuCl or AgNCO) in the presence of small amounts of appropriate bases. We also demonstrates here that the one-carbon higher homologues of **1**, 3-butynyl tosylcarbamates **3**, undergo the similar cyclization to give 4-methylenetetrahydro-1,3-oxazin-2-ones **4** (Eq. 3), though the synthetic utility of this cyclization being diminished somewhat owing to the limited tolerance toward to variety of the kinds of R^2 substituents in **3**. This is a full account of our previous work.[12] The similar transformation of **1** to **2** (R=Ts) was reported by Murai et at.[13]

Results and Discussion

The cyclization reaction of 2-propynyl carbamate **1a** with a variety of *N*-substituents, widely differing in their electronic nature, was examined, using the combinations of bases and metal salts (Cu^+, Ag^+, Pd^{2+}, Zn^{2+}, Ru^0), some of which had proven to promote the addition of heteroatoms to triple bond effectively (Table 1). The reaction feature largely changes and seems to depend on the extent of the electron-withdrawing ability of the *N*-substituents and hence the nucleophilicity of the nitrogen atoms. They may be classified grossly into the following three categories: *N*-sulfonyl (Runs 1—6), *N*-acyl (Runs 7—14), and *N*-alkyl and -aryl groups (Runs 15—19).



1 **2**

(1)

The *N*-sulfonyl derivative of **1a** undergoes cyclization smoothly at room temperature in the presence of catalytic amounts of CuCl and triethylamine, and provides **2a** (R=tosyl) in a quantitative yield (Run 1, Table 1). Both the copper(I) salt and the base are indispensable. In the absence of either of them, no cyclization took place (Runs 2 and 3) and the starting

Table 1. Transition-Metal Catalyzed Aminocyclization of 2-Propynyl Carbamates **1a** (R^1=R^2=R^3=H) with Various *N*-Substituents[a)]

Run	Carbamate **1a**:R	Metal cat./base	Solvent	Reaction conditions[b)]	Isolated of **2a**/%
1	Ts	CuCl/Et_3N	THF	r.t. 24 h	94
2	Ts	None/Et_3N	THF	r.t. 45 h	0
3	Ts	CuCl/None	THF	r.t. 36 h	0
4	Ts	$ZnCl_2$/Et_3N	THF	r.t. 24 h	69
5	Ts	$PdCl_2$/Et_3N	THF	r.t. 24 h	46
6	Ts	Ru(COD)(COT)/Et_3N	THF	r.t. 24 h	54
7	PhCO	CuCl/Et_3N	THF	refl. 20 h	0
8	PhCO	CuCl/*t*-BuOK	THF	r.t. 24 h	32
9	PhCO	AgNCO/*t*-BuOK	THF	r.t. 20 h	88[c)]
10	CH_3CO	CuCl/*t*-BuOK	THF	r.t. 48 h then refl. 9 h	77
11	CH_3CO	AgNCO/*t*-BuOK	Benzene	r.t. 20 h then refl. 2 h	89
12	CH_3CO	None/*t*-BuOK	THF	r.t. 24 h then refl. 3 h	0
13	*trans*-MeCH=CHCO	AgNCO/*t*-BuOK	Benzene	r.t. 30 h	81
14	EtOCO	AgNCO/*t*-BuOK	Benzene	refl. 12 h	54
15	Ph	CuCl/*t*-BuOK	THF	r.t. 24 h then refl. 20 h	95
16	Ph	None/*t*-BuOK	THF	r.t. 24 h	91
17	*p*-$MeOC_6H_4CH_2$	None/*t*-BuOK	THF	r.t. 20 h	99
18	CH_2=$CHCH_2$	CuCl/*t*-BuOK	THF	r.t. 24 h then refl. 18 h	86
19	CH_2=$CHCH_2$	None/*t*-BuOK	THF	r.t. 20 h	93

a) Reaction was undertaken using **1** (1.0 mmol), a base (0.1 mmol), and a transition-metal catalyst (0.1 mmol) in a given dry solvent (5 ml) under N_2. b) Reaction time is meant to refer to an approximate time required for completion of reaction. c) **2a** (R=PhCO) was obtained in 71% isolated yield, when undertaken in benzene, in place of in THF, at room temperature for 24 h.

material was recovered quantitatively. Other metals, such as $ZnCl_2$, $PdCl_2$ and Ru(COD)(COT) [COD=cyclooctadiene, COT=cyclooctatriene], were less effective and provided **2a** (R=Ts) in modest yields (Runs 4—6).

For the cyclization of the *N*-acyl derivatives, including benzoyl, acetyl, *trans*-crotonoyl, ethoxycarbonyl, the above CuCl and triethylamine catalytic system was completely ineffective and the expected cyclization product, e.g., **2a** (R=PhCO, Run 7), was not formed at all. The use of stronger bases, such as *t*-BuOK, in combination with CuCl improved the reaction considerably (Runs 8 and 10). Much more satisfactory results were obtained by the use of AgNCO as a catalyst in place of CuCl (Runs 9 and 11), though most portion of AgNCO apparently remains undissolved in the reaction mixture.

Making sharp contrast to the cyclization of *N*-tosyl and *N*-acyl derivatives (e.g., Runs 2 and 12), the cyclization of *N*-alkyl and -aryl derivatives of **1a** proceeds smoothly only in the presence of a catalytic amount of *t*-BuOK.[10)] The reaction, irrespective of a wide range differences in basicity of aralkylamines, attains completion at room temperature within 24 h. In these reactions copper(I) salt, being indispensable for the cyclization of *N*-tosyl and *N*-acyl derivatives of **1a**, seems to retard the reaction (Runs 15 vs. 16 and 18 vs. 19).

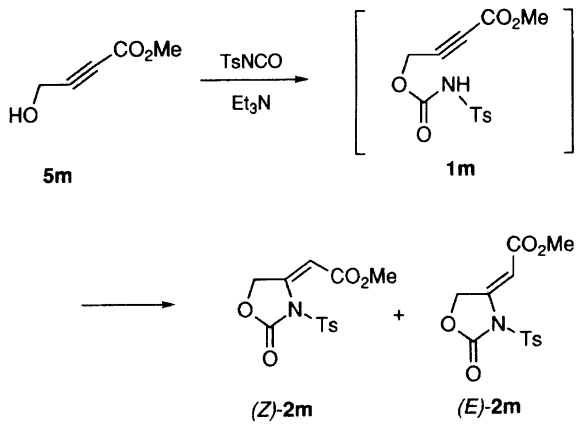
All these results indicate that for the cyclization of **1a** (R=aralkyl, acyl, and sulfonyl) to proceed in a reasonable rate and to provide **2a** in satisfactory yields, the acidic NH protons of carbamates must be dissociated to their amide anions in sufficient concentrations by bases with appropriate basicity.[14)] Triethylamine suffices for the deprotonation of tosyl carbamates, while *N*-aralkyl and *N*-acylcarbamates require *t*-BuOK. The nucleophilicity of the amide anions of *N*-aralkyl derivatives is such that they are able to undergo an intramolecular addition reaction to triple bond without catalysis of any transition metals, while the amide anions of *N*-acyl and *N*-sulfonyl derivatives are less nucleophilic and their addition is only promoted by the catalysis of appropriate transition metals (e.g., Ag^+ and Cu^+).

In Table 2 are summarized the results for the cyclization of substituted derivatives of 2-propyn-1-ol at C_1- (Runs 2—11), C_3 (Runs, 12—16), and at the both carbons (Runs 17 and 18), examined under the conditions optimized in Table 1. The results in Runs 3—7 clearly indicate that the individual conditions optimized for a variety of *N*-substituents can be applied well to these C_1-substituted derivatives. Moreover, as apparent by comparison of Run 1 with Runs 2,3,9, and 10, the reactivity increases with an increase in the number of the C_1-substituents. In these cases, the C_1-substituents may serve as a buttress to render both reaction centers, nitrogen nucleophile and C_2 acetylenic carbon, close together. The reaction of **1g** (Run 11) is one exception to this generalization. The reason for the diminished reactivity and the low yield formation of the product is not clear at present.

1-Vinyl substituted derivative **1d** was unstable[15)] and decomposed during storage at room temperature and could not be purified by means of column chromatography over silica gel. However, the triethylamine salt

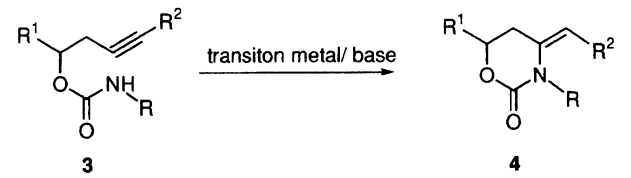
turned out to be rather stable and withstands storage at room temperature. The reaction in Run 8, Table 2 was performed in one flask without isolation of **1d** just by mixing 4-penten-1-yn-3-ol, *N*-tosyl isocyanate, and triethylamine (each equimolar amount) at room temperature, followed by addition of CuCl (0.1 molar amount). The yield is based on the starting alcohol.

The cyclization of the C_3-substituted derivatives of 2-propynyl-1-ol, especially **1i** and **1j**, is somewhat reluctant and provides products in low yields under the catalytic system, CuCl–Et_3N (Runs 13 and 15). These reactions, however, can be nicely promoted by the catalysis of AgNCO–Et_3N (Runs 14 and 16). These cyclization reactions are highly stereoselective and the (*Z*)-isomers of **2h**—**l** were obtained as single stereoisomers (Runs 12—18, Table 2).



(2)

3-Methoxycarbonyl-2-propynyl carbamate (**1m**), formed from 3-methoxycarbonyl-2-propyn-1-ol (**5m**), *p*-toluenesulfonyl isocyanate, and triethylamine (each equimolar amount) at room temperature, was very reactive and spontaneously underwent a cyclization (Eq. 2). This cyclization, however, was not stereoselective and provided a mixture of (*Z*)- and (*E*)-**2m** in a ratio of 4:3 in 65% combined isolated yield, suggesting that the reactions shown in Eqs. 1 and 2 are mechanistically different.



(3)

Next, we examined the aminocyclization of 3-butynyl carbamate **3** (Eq. 3). The results are summarized in Table 3. As shown in Run 2 in this Table 3, the standard conditions (CuCl–Et_3N in THF) optimized for the cyclization of *N*-tosyl derivatives of **1**, could not be applied successfully to the cyclization of the *N*-tosyl derivatives of **3**, under which the reaction was very slow and the isolated yields of the expected 4-methylenetetrahydro-1,3-oxazin-2-one **4b** (R=Ts) was unacceptably low. Instead, the conditions optimized for the cyclization of *N*-acyl derivatives of **1**, i.e., and AgNCO–*t*-BuOK system, turned out to be very effective, especially when undertaken in benzene as a solvent (Run 4, Table 3). Interestingly, the same reaction when undertaken in THF, however, was very slow and the yield was very low (Run 3, Table 3). A ruthenium complex, Ru(COD)(COT), having been pointed out as an effective catalyst for the addition reaction of the oxygen atom of carbamates to triple bonds,[5c] was totally ineffective for the addition reaction of the nitrogen atom of carbamates **3** to the triple bonds (Run 5, Table 3).

Unfortunately, the synthetic scope of the present cyclization seems to be rather limited. Despite our extensive efforts, we have been unable to find out any satisfactory conditions, which promote the cyclization of terminally substituted carbamate **3c**. The best result ever obtained was shown in Run 6, Table 3.

In order to overcome this difficulty, terminally trimethylsilyl substituted derivative **3d** was examined, since many precedents indicate that trimethylsilyl group activates acetylenic triple bonds toward nucleophilic addition reactions[16] and also the trimethylsilyl group in the expected product **4d** may be transformed to many other functional groups of interest.[17] In fact, the results were quite unexpected (Run 7, Table 3). The reaction rate and the isolated yield were comparable to those with the terminally methyl substituted derivative, **3c**. Moreover the product was not **4d** but its desilylated derivative, 6-methyl-4-methylenetetrahydro-1,3-oxazine-2-one (**4b**). No loss of trimethylsilyl group in the recovered material **3d** (80% conversion, an independent control experiment) suggests that the desilylated product **4b** was formed via a protio-desilylation[17] of the primary cyclization product, **4d**, and not via the desilylation of **3d**, followed by the cyclization of the product **3b**.

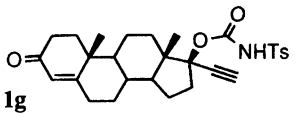
As another trial to facilitate the cyclization of terminally substituted **3**, we examined **3e**, having the acetylenic bond activated with electron-attracting carbonyl group (Runs 8 and 9, Table 3). The reaction, however, was very reluctant and required the higher temperatures and prolonged reaction times. With AgNCO–*t*-BuOK was obtained the expected product **4e** in 53% yield together with methyl 3-(tosylamino)-2,4-hexadienoate, a product formed probably via an extrusion of carbon dioxide from **4e** (Run 9, Table 3). Only the latter was obtained by the use of triethylamine as a base (Run 8, Table 3). The product **4e** was stereochemically homogenous and the structure was determined to be (*Z*) on the basis of NOE experiments (vide infra).

The low reactivity and high stereoselectivity observed for the cyclization of **3e** make interesting contrast to those observed for **1m** (Eq. 2), where the cyclization proceeds spontaneously at room temperature in the absence of transition-metal catalysts and provides an (*E*)-

Table 2. Transition-Metal Catalyzed Aminocyclization of Substituted 2-Propynyl Carbamates **1**[a)]

Run	Carbamate **1**				Metal cat./base	Reaction	Isolated
	R^1	R^2	R^3	R		time/h	yield of **2** /%
1 **1a**:	H	H	H	Ts	CuCl/Et_3N	4	**2a** (R=Ts): 91
2 **1b**:	Me	H	H	Ts	CuCl/Et_3N	2	**2b** (R=Ts): 94
3 **1c**:	Et	H	H	Ts	CuCl/Et_3N	2	**2c** (R=Ts): 95
4 **1c**:	Et	H	H	COPh	AgNCO/*t*-BuOK[b)]	3	**2c** (R=COPh): 90
5 **1c**:	Et	H	H	COPh	CuCl/*t*-BuOK[c)]	1	**2c** (R=COPh): 61
6 **1c**:	Et	H	H	Ph	None/*t*-BuOK	1	**2c** (R=Ph): 83
7 **1c**:	Et	H	H	Me	None/*t*-BuOK	1	**2c** (R=Me): 80
8 **1d**:[d)]	CH_2=CH	H	H	Ts	CuCl/None	10	**2d** (R=Ts): 90
9 **1e**:	Me	Me	H	Ts	CuCl/Et_3N	2	**2e** (R=Ts): 94
10 **1f**:	$(CH_2)_5$		H	Ts	CuCl/Et_3N	1	**2f** (R=Ts): 96
11 **1g**:	See footenote e)				CuCl/Et_3N	4	**2g** (R=Ts): 68
12 **1h**:	H	H	Me	Ts	CuCl/Et_3N	21	**2h** (R=Ts): 91
13 **1i**:	H	H	CMe=CH_2	Ts	CuCl/Et_3N	30	**2i** (R=Ts): 30
14 **1i**:	H	H	CMe=CH_2	Ts	AgNCO/Et_3N	10	**2i** (R=Ts): 66
15 **1j**:	H	H	CH_2OTHP	Ts	CuCl/Et_3N	20	**2j** (R=Ts): 22
16 **1j**:	H	H	CH_2OTHP	Ts	AgNCO/Et_3N	20	**2j** (R=Ts): 66
17 **1k**:	Me	H	Me	Ts	CuCl/Et_3N	7	**2k** (R=Ts): 78
18 **1l**:	Me	Me	Me	Ts	CuCl/Et_3N	2	**2l** (R=Ts): 54

a) Unless otherwise specified, reaction was undertaken under the following condition: **1** (1.0 mmol), a transition metal (0.1 mmol), and a base (0.1 mmol) in dry THF (5 ml) at the refluxing temperature under nitrogen atmosphere. b) Benzene (5 ml) was used instead of THF. c) CuCl (0.2 mmol) was used. d) **1d** was unstable and its triethylamine salt was used for the reaction. e)

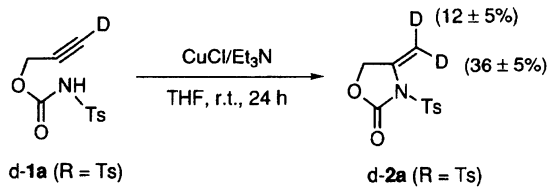


1g

and (*Z*)-mixture of products non-stereoselectively.

In sharp contrast to the ready cyclization of 2-propynyl aralkylcarbamates **1** (Runs 15—19, Table 1 and Runs 6 and 7, Table 2), 3-butynyl aralkylcarbamates **3** were totally unreactive under any conditions ever examined and recovered quantitatively (Runs 10 and 11, Table 3).

The Cu^+- and Ag^+-catalyzed cyclization reactions shown in Eqs. 1 and 3 display very high stereoselectivity and (*Z*)-**2g**—**l** (Runs 12—18, Table 2) and (*Z*)-**4c,e** (Runs 6 and 9, Table 3) are obtained as single stereoisomers. The uniform (*Z*)-selectivity might be rationalized as a consequence of *trans*-aminometallation (metal=Cu^+ or Ag^+) across the triple bond, followed by a protonolysis of the thus formed vinylic metal intermediate with retention of configuration.



d-**1a** (R = Ts) d-**2a** (R = Ts) (4)

In order to clarify the stereochemical course for the cyclization of terminal acetylenic substrates, monodeuteriated d-**1a** (R=Ts, 100% deuteriated based on ^{1}H NMR analysis) was subjected to the cyclization under usual conditions (Eq. 4). The results, obtained from the ^{1}H NMR analysis (400 MHz) of the isolated product, are rather complicated. First, considerable amounts of deuterium (ca. 50%) are lost. Second, deuterium distributes not only at the (*Z*)-, but also at the (*E*)-positions of the product. Furthermore, the staring **1a**, only 50% deuteriated, was recovered for the control experiment stopped at ca. 20% conversion. Such a facile loss of deuterium from the starting material might be rationalized supposing intermediacy of copper(I) acetylide, which mediates deuterium exchange between acetylenic CH and tosylcarbamate NH and/or surroundings. Water as a contaminant in the reaction medium might be most likely as one of proton sources. It is apparently impractical, however, to ascribe the whole part of the "extra" proton (50%) introduced into the product to water, since, according to calculations based on statistic distribution, the "extra" proton corresponds to the amount of water as much as ca. 1 equiv to d-**1a**. The experiment was undertaken in THF carefully dried and distilled from sodium-benzophenone under nitrogen. Accordingly, some other mechanisms must be operating that supplies, at least, some part of the "extra" hydrogen from surroundings. Although the reaction is apparently complicated owing to the H–D exchange reaction, the cyclization of terminal acetylenic substrates may proceed via the similar process to the one of the internal acetlyenic substrates, discussed above. Some deuterium, transferred to tosylamide and surroundings, may be retrieved as the (*E*)-deuterium of d-**2a** via

Table 3. Transition-Metal Catalyzed Aminocyclization of 3-Butynyl Carbamate **3**[a)]

Run	Carbamate **3**			Metal cat./base	Solvent	Reaction condition	Isolated yield of **4**[b)]/%		
	R^1	R^2	R						
1 **3a**	H	H	Ts	$AgNCO/Et_3N$	Benzene	refl. 4 h	**4a**:	75	(100)
2 **3b**	Me	H	Ts	$CuCl/Et_3N$	THF	refl. 45 h	**4b**:	16	(92)
3 **3b**	Me	H	Ts	AgNCO/*t*-BuOK	THF	refl. 24 h	**4b**:	23	(100)
4 **3b**	Me	H	Ts	AgNCO/*t*-BuOK	Benzene	refl. 4 h	**4b**:	86	(100)
5 **3b**	Me	H	Ts	$Ru(COD)(COT)/Et_3N$	Benzene	refl. 24 h	**4b**:	15	(100)
6 **3c**	Me	Me	Ts	AgNCO/*t*-BuOK	Benzene	refl. 6 h	**4c**:	15	(73)
7 **3d**	Me	Me_3Si	Ts	AgNCO/*t*-BuOK	Benzene	refl. 12 h	**4b**:	39	(100)
8 **3e**	Me	CO_2Me	Ts	$AgNCO/Et_3N$	Benzene	refl. 46 h	**4e**:	0	(100)[c)]
9 **3e**	Me	CO_2Me	Ts	AgNCO/*t*-BuOK	Benzene	refl. 21 h	**4e**:	53	(100)[d)]
10 **3b**	Me	H	Ph	AgNCO/*t*-BuOK	Benzene	refl. 17 h	**4b**:	0	(0)
11 **3b**	Me	H	$CH_2=CHCH_2$	None/*t*-BuOK	THF	r.t. 28 h	**4b**:	0	(0)

a) Reaction was undertaken using **3** (1.0 mmol), a base (0.1 mmol), and a transition metal (0.1 mmol) in a given dry solvent (5 ml) under N_2. b) Yields are based on conversions, shown in pathenthesis. c) Methyl 3-tosylamino-2,4-hexadienoate was obtained in 28% yield. d) In addition to **4e**, methyl 3-tosylamino-2,4-hexadienoate was obtained in 9% yield.

protonolysis of vinylcopper(I) intermediate formed by *trans*-aminocupriation.

The stereochemistry of products was determined on the basis of nuclear Overhauser effects.[18)] Some representative results are summarized in Fig. 1. One of the

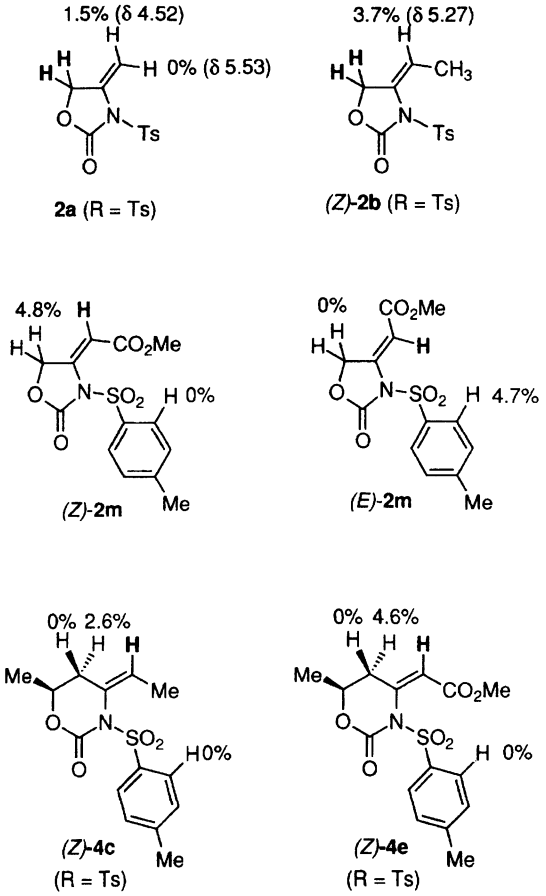


Fig. 1. Selected data for the nuclear overhauser effects observed by the irradiation at the proton(s) indicated in bald face.

olefinic protons of **2a** (R=Ts) resonates (δ=5.53) characteristically at the lower filed than the other proton (δ=4.52). Irradiation at the *ortho*-protons of the tosyl phenyl ring causes an increment of the area intensity of the former, and irradiation at the C_5 methylene protons an increase in the area intensity of the latter, indicating that the phenyl ring and the olefinic proton resonating at the lower field locate in sterically close proximity each other. The (*Z*)-structure of **2b** was deduced from the chemical shift of the olefinic proton (δ=5.27) and an increase in the area intensity of the same proton by the irradiation at the C_5 methylene protons. The stereochemistry of the other products was determined unequivocally in similar sequence.

In summary, cyclization of 2-propynyl tosylcarbamates **1** (R=Ts) proceeds smoothly by the catalysis of $CuCl/Et_3N$ or $AgNCO/Et_3N$ to furnish 4-methylene-2-oxazolidinones **2** (R=Ts) in good yields. The similar cyclization of the *N*-acyl derivatives of **1** (R=PhCO, MeCO, EtOCO, etc.) is catalyzed most effectively by AgNCO/*t*-BuOK. These reactions accommodate a variety of substituents at C_1 and C_3 of 2-propyn-1-ol and provide (*Z*)-**2** as single stereoisomers. The scope of the cyclization of 3-butynyl carbamates **3** is rather limited, and in general only *N*-tosyl derivatives of terminally unsubstituted 3-butyn-1-ols undergo cyclization to give 4-methylenetetrahydro-1,3-oxazin-2-ones **4** in synthetically useful yields by the catalysis of $AgNCO/Et_3N$ or AgNCO/*t*-BuOK.

The products obtained here are densely functionalized molecules with stereochemically defined enamine and protected allylic and homoallylic alcohol moieties as well as a variety of substituents, useful for the further transformations. The enamine moiety, for example, may serves as an active component to undergo intramolecular enamine–enone Michael addition reaction (e.g., **2a**, R=crotonoyl), intramolecular Friedel–Crafts reaction (e.g., **2a**, R=$CH_2C_6H_4$-*p*-OMe), and

aza-Claisene rearrangement (e.g., **2a**, R=allyl). An interesting use of **2a** (R=Ts) as a precursor of the so-called aza-trimethylenemethane–palladium complexes has been demonstrated recently by Murai et at.[19] Extensive studies in these lines are in progress in our laboratories.

Experimental

Melting points were determined with Yanaco micro melting point apparatus and were not corrected. Unless otherwise specified, short-path (bulb-to-bulb) distillations were carried out in a Kugelrohr apparatus. In these cases, boiling points are meant to refer to the oven temperatures. Microanalysis were performed by the Microanalysis Centers of Nagasaki University and Kyoto University. Analysis agreed with the calculated values within ±0.3%. High-resolution mass spectra were measured with JEOL JMS-DX303. Infrared spectra were measured with a JASCO A-100 infrared spectrophotometer. Proton magnetic resonance spectra were determined either at 60 MHz on a JEOL JNM-PMX60, at 90 MHz on a JEOL 90Q, or at 400 MHz on a JEOL-GX400 instrument with tetramethylsilane as an internal standard. Chemical shift values were given in ppm downfiled from an internal standard.

Solvent and Reagents. Tetrahydrofuran and diethyl ether were dried and distilled from benzophenone and sodium immediately prior to use under nitrogen atmosphere. Benzene and triethylamine were distilled over calcium hydride. The following acetylenic alcohols (**5** and **6**) were purchased and used without further purification: propargyl alcohol (**5a**), 1-butyn-3-ol (**5b**), 1-pentyn-3-ol (**5c**), 2-methyl-3-butyn-2-ol (**5e**), 1-ethynyl-1-cyclohexanol (**5f**), ethisterone (**5g**), 2-butyn-1-ol (**5h**), 3-butyn-1-ol (**6a**), 4-pentyn-2-ol (**6b**), 4-hexyn-2-ol (**6c**). 4-Methyl-4-penten-2-yn-1-ol (**5i**) was prepared according to the literature procedure.[20] 3-Pentyn-2-ol (**5k**) and 2-methyl-3-pentyn-2-ol (**5l**) were prepared in quantitative yields by the reaction of 1-propynylmagnesium bromide, prepared by the reaction of ethylmagnesium bromide and propyne, with acetaldehyde and acetone, respectively, in THF. *p*-Toluenesulfonyl isocyanate, phenyl isocyanate, and allyl isocyanate were purchased and distilled prior to use. Copper(II) chloride, zinc chloride, and palladium(II) chloride (reagent grade) were used without further purification. Ru(COD)(COT) was prepared from $RuCl_3(H_2O)_n$ (n=1—3) and 1,5-cyclooctadiene with zinc dust in MeOH.[21] Silver isocyanate was prepared according to the literature.[22]

Preparation of Acetylenic Alcohols 5 and 6. 1-Penten-4-yl-3-ol (5d): Into a 100 ml two-necked round bottomed flask, equipped with a dropping funnel, was added ethynylmagnesium bromide (0.5 M in THF, 40 ml, 20 mmol, Aldrich, 1 M=1 mol dm^{-3}) via a syringe under nitrogen. At −78 °C, acrylaldehyde (1.4 ml, 22 mmol, freshly distilled from $CaCl_2$), was added slowly via a dropping funnel and the reaction mixture was stirred for 2 h, and then the temperature was allowed to rise to room temperature. After addition of sat. NH_4Cl (30 ml), the mixture was extracted with ether (3×20 ml). The combined extracts were dried (magnesium sulfate), filtered, evaporated, and distilled by means of Kugelrohr (70 °C/20 mmHg, 1 mmHg=133.322 Pa) to give **5d** in 43% yield: IR (neat film) 3330 (s), 3275 (s), 2100 (w), 1645 (w), 1400 (m), 1118 (m), 1015 (s), cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ=2.30 (d, J=2.0 Hz, 1-H), 2.94 (br s, 1-H), 4.75 (br dd, J=2.0, 4.4 Hz, 1-H), 5.10 (br d, J=9.8 Hz, 1-H), 5.33 (br d, J=16.0 Hz, 1-H), 5.89 (ddd, J=4.4, 9.8, 16.0 Hz, 1-H).

4-(Tetrahydro-2-pyranyloxy)-2-butyn-1-ol (5j): To a mixture of 2-butyn-1,4-diol (3.44 g, 40 mmol) and *p*-toluenesulfonic acid (0.76 g, 4 mmol) in THF (30 ml) was added 3,4-dihydro-2-*H*-pyran (3.36 g, 40 mmol) at room temperature over 10 min period. The mixture was stirred for 2 h. After addition of triethylamine (5 ml), removal of the solvent by rotary evaporator, the residue was diluted with sat. $NaHCO_3$ and extracted with ethyl acetate (3×30 ml). The combined extracts were dried (magnesium sulfate), filtered, evaporated, and purified by means of column chromatography over silica gel (eluent; hexane : ethyl acetate=4 : 1) to give **5j** in 38% yield. IR (neat film) 3400 (s), 2940 (s), 1140 (m), 1030 (s) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ=1.30—1.85 (m, 6-H), 3.40—3.92 (m, 2-H), 3.45 (br s, 1-H), 4.15 (br s, 4-H), 4.80 (m, 1-H).

Methyl 4-Hydroxy-2-butynoate (5m): (1) Into a mixture of propargyl alcohol (3 ml, 51 mmol) and a catalytic amount of *p*-toluenesulfonic acid (0.19 g, 1 mmol) in THF (30 ml) was added 3,4-dihydro-2*H*-pyran (4.6 ml, 50 mmol) in one portion at 0 °C. The reaction mixture was stirred under nitrogen at room temperature for 2 h. After neutralization with sat. $NaHCO_3$, the mixture was extracted with ether (3×20 ml). The combined organic extracts were dried (magnesium sulfate), filtered, evaporated, and distilled by means of Kugelrohr (80 °C/25 mmHg) to give 3-(tetrahydro-2-pyranyloxy)-1-propyne in 70% yield; IR (neat film) 3280 (m), 2940 (s), 2120 (w), 1210 (m), 1130 (s), 1040 (s), 910 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ=1.33—1.86 (m, 6-H), 2.28 (t, J=2.0 Hz, 1-H), 3.25—3.90 (m, 2-H), 4.15 (d, J=2.0 Hz, 2-H), 4.75 (m, 1-H).

(2) To a solution of *n*-BuLi (1.6 M in hexane, 14 ml, 22 mmol) in dry THF (30 ml) was added a solution of 3-(tetrahydro-2-pyranyloxy)-1-propyne (3.0 g, 20 mmol) dissolved in THF (10 ml) at −78 °C and the mixture was stirred for 1 h. Methyl chloroformate (1.6 ml, 20 mmol) was added to the mixture at −78 °C and was stirred for 2 h at the same temperature and then at room temperature for an additional 2 h. After addition of 2 M HCl (15 ml) at 0 °C and evaporation of the solvents with rotary evaporator, the aqueous residue was extracted with ether (3×20 ml). The ethereal extracts were dried (magnesium sulfate), filtered, concentrated, and distilled by means of Kugelrohr (70 °C/0.5 mmHg) to afford methyl 4-(tetrahydro-2-pyranyloxy)-2-butynoate in 62% yield: IR (neat film) 2940 (m), 2240 (w), 1720 (s), 1250 (s), 1120 (m), 1030 (s) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ=1.33—1.92 (m, 6-H), 3.20—3.85 (m, 2-H), 3.78 (s, 3-H), 4.32 (s, 2-H), 4.80 (m, 1-H).

(3) In a flask were placed methyl 4-(tetrahydro-2-pyranyloxy)-2-butynoate (1.14 g, 5.75 mmol), *p*-toluenesulfonic acid (0.11 g, 0.6 mmol), and methanol (10 ml). The mixture was stirred at room temperature for 2 h. After neutralization with sat. $NaHCO_3$, the mixture was extracted with dichloromethane (3×15 ml). The combined organic extracts were dried (magnesium sulfate), filtered, concentrated, and purified by Kugelrohr distillation (100 °C/15 mmHg) to give **5m** in 86 % yield; IR (neat film) 3300 (s), 2220 (m), 1710 (s), 1430 (m), 1250 (s), 1020 (m) cm^{-1}; ^1H NMR (CCl_4, 60

MHz) δ=3.20 (t, J=6.0 Hz, 1-H), 3.75 (s, 3-H), 4.40 (d, J=6.0 Hz, 2-H).

5-Trimethylsilyl-4-pentyn-2-ol (6d): To a 200 ml round-bottomed flask, containing *n*-BuLi (1.6 M in hexane, 19 ml, 30 mmol) and dry THF (20 ml), was added 4-pentyn-2-ol (**6b**, 1.4 ml, 15 mmol) via a syringe at −78 °C under nitrogen. After stirring for 1 h, trimethylchlorosilane (3.2 g, 30 mmol) was introduced via a syringe at −78 °C. The mixture was stirred at room temperature for 2 h and then poured into cold 2 M HCl (20 ml). After evaporation of the solvents under a reduced pressure, the residue was extracted with ether (3×20 ml). The extracts were dried (magnesium sulfate), filtered, concentrated, and distilled by means of Kugelrohr (100 °C/10 mmHg) to afford **6d** in 48% yield. IR (neat film) 3345 (s), 2180 (s), 1250 (s), 1025 (s), 840 (s), 750 (s) cm^{-1}; ^{1}H NMR (CCl_4, 60 MHz) δ=0.14 (s, 9-H), 1.25 (d, J=6.2 Hz, 3-H),1.95 (br s, 1-H), 2.40 (d, J=5.8 Hz, 2-H), 3.65 (br dd, J=5.8, 6.2 Hz, 1-H).

Methyl 5-Hydroxy-2-hexynoate (6e): **6e** was prepared from 4-pentyn-2-ol according to the similar procedures to those for the synthesis of **5m**. bp 130 °C/4 mmHg; IR (neat film) 3380 (s), 2225 (s), 1710 (s), 1250 (s) 1070 (s) cm^{-1}; ^{1}H NMR (CCl_4, 60 MHz) δ=1.24 (d, J=5.8 Hz, 3-H), 2.42 (d, J=6.2 Hz, 2-H), 2.95 (br s, 1-H), 3.63 (s, 3-H), 3.95 (br tq, J=6.2 5.8 Hz, 1-H).

2-Propyn-3-*d*-1-ol: To a solution of *n*-BuLi (1.6 M in hexane, 13 ml, 21 mmol) in dry THF (20 ml) was added a THF (5 ml) solution of 3-(tetrahydro-2-pyranyloxy)-1-propyne (3.0 g, 21 mmol), prepared as before, at −78 °C and the mixture was stirred for 2 h. D_2O (5 ml) was added to this mixture at 0 °C and was stirred at room temperature for 2 h. The separated organic portion was dried (magnesium sulfate), filtered, evaporated, and distilled by means of Kugelrohr (90 °C/20 mmHg) to give 3-(tetrahydro-2-pyranyloxy)-1-propyne-1-*d* in 79% yield. In a flask were placed 1-tetrahydropyranyloxy-3-d_1-2-propyne (2.0 g, 14 mmol), *p*-toluenesulfonic acid (0.2 g, 1.1 mmol), and methanol (10 ml). The mixture was stirred at room temperature for 2 h. After neutralization with sat. $NaHCO_3$, the mixture was extracted with dichloromethane (3×20 ml). The combined extracts were dried (magnesium sulfate), filtered, and distilled under an atmospheric pressure. The residue was purified by means of Kugelrohr distillation (80 °C/70 mmHg) to give 2-propyn-3-*d*-1-ol in 70% yield: IR (neat film) 3370 (s), 2602 (m), 1992 (m), 1045 (s) cm^{-1}; ^{1}H NMR (CCl_4, 60 MHz) δ=2.30 (br s, 1-H), 4.29 (s, 2-H).

General Procedure for the Preparation of 2-Propynyl and 3-Butynyl Tosylcarbamates and Phenylcarbamates (**1** and **3**, R=Ts and Ph). To a solution of an acetylenic alcohol (**5** or **6**, 20 mmol) and triethylamine (2.8 ml, 20 mmol) in ether (20 ml) was added *p*-toluenesulfonyl isocyanate or phenyl isocyanate (3.0 ml, 20 mmol) via a syringe at 0 °C under nitrogen and the mixture was stirred at room temperature for 2 h. For the isolation of *N*-tosylcarbamates, the mixture was washed with water (2×20 ml). The combined aqueous extracts were acidified with 2 M HCL (15 ml) and extracted with ethyl acetate (3×30 ml). For the isolation of *N*-phenylcarbamates, the mixture was washed with 2 M HCl (15 ml) and extracted with ethyl acetate (2×20 ml). The organic extracts were dried (magnesium sulfate), filtered, evaporated, and subjected to column chromatography over silica gel (eluent; hexane : ethyl acetate=ca. 4 : 1 vol) to give **1** or **3** (R=Ts or phenyl) in 80—90 % yield. **1d** (R=Ts) was unstable and isolated as the triethylamine salt by evaporation of water from the aqueous extracts.

2-Propynyl Tosylcarbamate (**1a**, R=Ts): IR (KBr disk) 3250 (s), 2150 (w), 1740 (s), 1600 (m), 1450 (s), 1350 (s), 1220 (s), 1160 (s), 1085 (s), 980 (s), 820 (s), 650 (m) cm^{-1} ^{1}H NMR ($CDCl_3$, 60 MHz) δ=2.45 (s, 3-H), 2.46 (t, J=2.8 Hz, 1-H), 4.67 (d, J=2.8 Hz, 2-H), 7.20 (s, 1-H), 7.35 (d, J=8.2 Hz, 2-H), 7.95 (d, J=8.2 Hz, 2-H).

2-Propynyl Phenylcarbamate (**1a**, R=Ph): IR (neat film) 3250 (s), 2135 (m), 1715 (s), 1640 (m), 1600 (s), 1540 (s), 1440 (s), 1320 (m), 1220 (s), 1060 (s), 850 (m), 750 (m) cm^{-1} ^{1}H NMR ($CDCl_3$, 60 MHz) δ=2.50 (t, J=2.4 Hz, 1-H), 4.73 (d, J=2.4 Hz, 2-H), 6.62 (s, 1-H), 7.33 (m, 5-H).

1-Methyl-2-propynyl Tosylcarbamate (**1b**, R=Ts): IR (neat film) 3270 (s), 2130 (w), 1740 (s), 1600 (m), 1440 (s), 1350 (s), 1220 (s), 1160 (s), 1080 (s), 1020 (s), 810 (s), 660 (s) cm^{-1} ^{1}H NMR ($CDCl_3$, 60 MHz) δ=1.47 (d, J=6.6 Hz, 3-H), 2.45 (s, 3-H), 2.46 (d, J=2.2 Hz, 1-H), 5.32 (dq, J=2.2, 6.6 Hz, 1-H), 7.35 (d, J=8.2 Hz, 2-H), 7.35 (br s, 1-H), 7.93 (d, J=8.2 Hz, 2-H).

1-Ethyl-2-propynyl Tosylcarbamate (**1c**, R=Ts): IR (neat film) 3260 (s), 2120 (w), 1740 (s), 1590 (m), 1440 (s), 1350 (s), 1220 (s), 1160 (s), 1090 (s), 890 (m), 810 (m), 660 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz) δ=1.95 (t, J=7.0 Hz, 3-H), 1.76 (dq, J=6.0, 7.0 Hz, 2-H), 2.35 (d, J=2.0 Hz, 1-H), 2.40 (s, 3-H), 5.13 (dt, J=2.0, 6.0 Hz, 1-H), 7.20 (d, J=8.2 Hz, 2-H), 7.84 (d, J=8.2 Hz, 2-H).

1,1-Dimethyl-2-propynyl Tosylcarbamate (**1e**, R=Ts): IR (KBr disk) 3250 (s), 2120 (w), 1750 (s), 1600 (m), 1440 (s), 1350 (s), 1230 (s), 1160 (s), 1090 (s), 990 (m), 810 (m), 660 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz) δ=1.63 (s, 6-H), 2.44 (s, 3-H), 2.50 (s, 1-H), 7.33 (d, J=8.2 Hz, 2-H), 7.93 (d, J=8.2 Hz, 2-H).

1-Ethynylcyclohexyl Tosylcarbamate (**1f**, R=Ts): IR (KBr disk) 3230 (s), 2120 (w), 1740 (s), 1600 (m), 1430 (s), 1340 (s), 1230 (s), 1160 (s), 1140 (s), 1090 (s), 1020 (m), 880 (m), 810 (s), 710 (s), 650 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ=1.20—2.20 (m, 10-H), 2.44 (s, 3-H), 2.55 (s, 1-H), 7.33 (d, J=8.3 Hz, 2-H), 7.40 (br s, 1-H), 7.93 (d, J=8.3 Hz, 2-H).

17-*O*-Tosylcarboamoylethisterone (**1g**, R=Ts): IR (KBr disk) 3250 (m), 2100 (w), 1750 (s), 1600 (s), 1450 (s), 1350 (s), 1220 (s), 1160 (s), 1090 (s), 960 (m), 890 (s), 820 (m), 660 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ=0.79—2.62 (m, 10-H), 0.85 (s, 3-H), 1.19 (s, 3-H), 2.44 (s, 3-H), 2.56 (s, 1-H), 5.73 (s, 1-H), 7.32 (d, J=8.3 Hz, 2-H), 7.49 (d, J=8.3 Hz, 2-H).

2-Butynyl Tosylcarbamate (**1h**, R=Ts): IR (neat film) 3280 (s), 2240 (w), 1730 (s), 1600 (m), 1440 (s), 1340 (s), 1220 (s), 1160 (s), 1090 (m), 840 (s), 650 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz) δ=1.81 (t, J=2.2 Hz, 3-H), 2.44 (s, 3-H), 4.63 (q, J=2.2 Hz, 2-H), 7.33 (d, J=8.2 Hz, 2-H), 7.94 (d, J=8.2 Hz, 2-H).

4-Methyl-4-pentene-2-ynyl Tosylcarbamate (**1i**, R=Ts): IR (neat film) 3240 (s), 2240 (w), 1750 (s), 1590 (m), 1440 (s), 1340 (s), 1290 (s), 1160 (s), 1080 (s), 860 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz) δ=1.84 (br d, J=1.2 Hz, 3-H), 2.44 (s, 3-H), 4.79 (s, 2-H), 5.28 (q, J=1.2 Hz, 2-H), 7.33 (d, J=8.2 Hz, 2-H), 7.95 (d, J=8.2 Hz, 2-H).

4-(Tetrahydro-2-pyranyloxy)-2-butynyl Tosylcar-

bamate (**1j**, R=Ts): IR (neat film) 3210 (s), 2240 (w), 1740 (s), 1590 (m), 1440 (s), 1340 (s), 1150 (s), 850 (s), 650 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ=1.40—1.83 (m, 6-H), 2.36 (s, 3-H), 3.35—3.98 (m, 2-H), 4.21 (br s, 2-H), 4.53—4.98 (m, 3-H), 7.26 (d, J=8.0 Hz, 2-H), 7.91 (d, J=8.0 Hz, 2-H).

1-Methyl-2-butynyl Tosylcarbamate (**1k**, R=Ts): IR (neat film) 3230 (m), 2250 (w), 1740 (s), 1600 (m), 1440 (s), 1350 (s), 1220 (s), 1160 (s), 1090 (s) 1050 (s), 980 (m), 910 (m), 820 (s), 770 (m), 660 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ=1.41 (d, J=6.8 Hz, 3-H), 1.79 (d, J=2.2 Hz, 3-H), 2.44 (s, 3-H), 5.29 (qq, J=2.2, 6.8 Hz, 1-H), 7.34 (d, J=8.5 Hz, 2-H), 7.95 (d, J=8.5 Hz, 2-H).

1,1-Dimethyl-2-butynyl Tosylcarbamate (**1l**, R=Ts): IR (KBr disk) 3260 (s), 2240 (w), 1750 (s), 1590 (m), 1430 (s), 1330 (s), 1230 (s), 1160 (s), 1120 (s), 1090 (s), 910 (s), 810 (s), 770 (s), 650 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ=1.58 (s, 6-H), 1.77 (s, 3-H), 2.45 (s, 3-H), 7.32 (d, J=8.3 Hz, 2-H), 7.92 (d, J=8.3 Hz, 2-H).

3-Butynyl Tosylcarbamate (**3a**, R=Ts): IR (neat film) 3280 (s), 2120 (w), 1750 (s), 1600 (m), 1450 (s), 1350 (s), 1230 (s), 1160 (s), 1090 (s), 1020 (m), 650 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ=1.90 (t, J=2.4 Hz, 1-H), 2.40 (s, 3-H), 2.44 (dt, J=2.4, 6.5 Hz, 2-H), 4.15 (t, J=6.5 Hz, 2-H), 7.25 (d, J=8.4 Hz, 2-H), 7.90 (d, J=8.4 Hz, 2-H).

1-Methyl-3-butynyl Phenylcarbamate (**3a**, R=Ph): IR (neat film) 3280 (s), 2300 (w), 1700 (s), 1600 (s), 1530 (s), 1440 (s), 1310 (s), 1060 (s), 890 (m), 650 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ=1.40 (d, J=6.0 Hz, 3-H), 2.05 (t, J=2.0 Hz, 1-H), 2.50 (dd, J=2.0, 6.0 Hz, 2-H), 5.00 (br d, J=6.0 Hz, 1-H), 6.70 (br s, 1-H), 7.30 (m, 5-H).

1-Methyl-3-butynyl Tosylcarbamate (**3b**, R=Ts): IR (neat film) 3280 (s), 2120 (m), 1750 (s), 1600 (m), 1450 (s), 1340 (s), 1230 (s), 1160 (s), 1090 (s), 760 (m), 650 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ=1.30 (d, J=6.4 Hz, 3-H), 1.95 (t, J=2.4 Hz, 1-H), 2.40 (br d, J=2.4 Hz, 2-H), 2.45 (s, 3-H), 4.90 (br q, J=6.4 Hz, 1-H), 7.30 (d, J=8.4 Hz, 2-H), 7.90 (d, J=8.4 Hz, 2-H).

1-Methyl-3-pentynyl Tosylcarbamate (**3c**, R=Ts): IR (neat film) 3250 (s), 2245 (w), 1730 (s), 1590 (m), 1370 (s), 1340 (s), 1300 (s), 1160 (s), 850 (m), 650 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ=1.22 (d, J=6.0 Hz, 3-H), 1.68 (t, J=2.0 Hz, 3-H), 2.33 (dq, J=5.8, 2.0 Hz, 2-H), 2.40 (s, 3-H), 4.82 (tq, J=5.8, 6.0 Hz, 1-H), 7.28 (d, J=8.4 Hz, 2-H), 7.48 (br s, 1-H), 7.93 (d, J=8.4 Hz, 2-H).

1-Methyl-4-trimethylsilyl-3-butynyl Tosylcarbamate (**3d**, R=Ts): IR (neat film) 3250 (s), 2180 (w), 1750 (s), 1605 (m), 1450 (m), 1350 (m), 1170 (s), 840 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ=0.12 (s, 9-H), 1.28 (d, J=6.4 Hz, 3-H), 2.38 (d, J=5.8 Hz, 2-H), 2.39 (s, 3-H), 4.83 (tq, J=5.8, 6.4 Hz, 1-H), 7.28 (d, J=8.2 Hz, 2-H), 7.92 (d, J=8.2 Hz, 2-H).

1-Methyl-4-methoxycarbonyl-3-butynyl Tosylcarbamate (3e): IR (neat film) 3260 (m), 2250 (m), 1720 (s), 1600 (m), 1450 (s), 1350 (s), 1270 (s), 1170 (s), 1095 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ=1.30 (d, J=6.4 Hz, 3-H), 2.43 (s, 3-H), 2.58 (d, J=5.8 Hz, 2-H), 3.78 (s, 3-H), 4.95 (tq, J=5.8, 6.4 Hz, 1-H), 7.30 (d, J=8.2 Hz, 2-H), 7.88 (br s, 1-H), 7.90 (d, J=8.2 Hz, 2-H).

General Procedure for the Preparation of 2-Propynyl Acylcarbamates (**1a**, R=benzoyl, acetyl, crotonoyl, ethoxycarbonyl). A 100 ml two necked round-bottomed flask, containing silver isocyanate (2.25 g, 15 mmol), was purged with nitrogen. Into this were added ether (40 ml) and an acid chloride (1.75 ml, 17 mmol) and the heterogeneous mixture was refluxed for 4 h. A solution of 2-propyn-1-ol (0.85 ml, 15 ml) and triethylamine (2 ml, 15 mmol) in ether (20 ml) was added via a dropping funnel over 20 min period at room temperature and stirred at the same temperature for additional 4 h. Filtration with suction through celite pad on a glass filter, washing with ether (2×20 ml), evaporation of the solvent, followed by column chromatography on silica gel (eluent; benzene) gave the titled compound in 40—50% yield.

2-Propynyl Benzoylcarbamate (**1a**, R=PhCO): IR (neat film) 3280 (s), 2135 (m), 1770 (s), 1690 (m), 1600 (m), 1520 (s), 1500 (s), 1290 (m), 1200 (s), 1040 (m), 1020 (m), 995 (m), 770 (m), 690 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ=2.50 (t, J=2.4 Hz, 1-H), 4.76 (d, J=2.4 Hz, 2-H), 7.58 (m, 5-H), 8.43 (br s, 1-H).

2-Propynyl Acetylcarbamate (**1a**, R=CH_3CO): IR (neat film) 3250 (s), 2120 (w), 1750 (s), 1700 (s), 1670 (m), 1490 (m), 1370 (m), 1190 (s), 1070 (m), 940 (m), 800 (m), 740 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ=2.40 (s, 3-H), 2.50 (t, J=2.4 Hz, 1-H), 4.75 (d, J=2.4 Hz, 2-H).

2-Propynyl Crotonoylcarbamate (**1a**, R=*trans*-MeCH=CHCO): IR (neat film) 3260 (s), 2350 (w), 1770 (s), 1680 (s), 1650 (m), 1530 (s), 1410 (m), 1220 (m), 1190 (m), 1050 (m), 990 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ=1.90 (d, J=6.0 Hz, 3-H), 2.50 (t, J=2.4 Hz, 1-H), 4.70 (d, J=2.4 Hz, 2-H), 7.12 (dq, J=13.0, 6.0 Hz, 1-H), 7.20 (d, J=13.0 Hz, 1-H), 7.70 (br, 1-H).

2-Propynyl Ethoxycarbonylcarbamate (**1a**, R=EtOCO): IR (neat film) 3270 (s), 2120 (w), 1780 (s), 1730 (s), 1520 (s), 1300 (m), 1190 (s), 1100 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ=1.33 (t, J=6.8 Hz, 3-H), 2.58 (t, J=2.4 Hz, 1-H), 4.30 (q, J=6.8 Hz, 2-H), 4.80 (d, J=2.4 Hz, 2-H), 7.50 (br s, 1-H).

2-Propynyl *p*-Methyoxybenzylcarbamate (**1a**, R=*p*-$MeOC_6H_4CH_2$): A 200 ml two-necked round bottomed flask, fitted with a dropping funnel and a refluxing condenser, at the top of which was connected with a nitrogen balloon, was purged with nitrogen. Into this, dry dioxane (30 ml) and trichloromethyl chloroformate (phosgene dimer) (2.5 ml, 20 mmol) were placed. *p*-Methoxybenzylamine (2.74 g, 20 mmol) dissolved in dry dioxane (20 ml) was added over 30 min period via a dropping funnel at room temperature and the reaction mixture was stirred at 50 °C for 2 h and then refluxed for 4 h. The solvent was distilled off under atmospheric pressure under nitrogen. Into this was added a mixture of 2-propyn-1-ol (1.12 g, 20 mmol) and triethylamine (4.05 g, 40 mmol) via the dropping funnel at 0 °C. After stirring for 2 h at an ambient temperature, the reaction mixture was diluted with water (30 ml) and extracted with ethyl acetate (2×50 ml). The combined extracts were dried (magnesium sulfate), filtered, condensed, and subjected to column chromatography over silica gel (eluent; benzene–ethyl acetate) to give **1a** (R=*p*-$MeOC_6H_4CH_2$) in 42% yield: IR (neat film) 3320 (s), 2135 (w), 1700 (s), 1620 (m), 1590 (m), 1520 (s), 1440 (m), 1310 (m), 1250 (s), 1040 (s), 840 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ=2.46 (t, J=2.4 Hz, 1-H), 3.78 (s, 3-H), 4.30 (d, J=6.0 Hz, 2-H), 4.70 (d, J=2.4 Hz, 2-H), 6.85 (d, J=8.4 Hz, 2-H), 7.20 (d, J=8.4 Hz, 2-H), 7.30 (br s, 1-H).

General Procedure for the Preparation of 2-Propynyl and 3-Butynyl Allylcarbamates (**1a** and **3a**, R=$CH_2CH{=}CH_2$). To a solution of an alkynyl alcohol **5** or **6** (30 mmol) and allyl isocyanate (2.65 ml, 30 mmol) in ether (20 ml) was added boron trifluoride-diethyl ether[23] (3.7 ml, 30 mmol) via a syringe at room temperature over 20 min period. After stirring for 3 h at the same temperature and dilution with ether (100 ml), the mixture was washed with sat. $NaHCO_3$ (30 ml), dried (magnesium sulfate), filtered, and evaporated. The residue was purified by means of Kugelrohr distillation (ca. 110 °C/1 mmHg) to give the titled compound in quantitative yield.

2-Propynyl Allylcarbamate (**1a**, R=$CH_2CH{=}CH_2$): IR (neat film) 3320 (s), 2130 (m), 1720 (s), 1530 (s), 1410 (s), 1250 (s), 920 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ=2.48 (t, J=2.6 Hz, 1-H), 3.83 (br d, J=5.7 Hz, 2-H), 4.69 (d, J=2.6 Hz, 2-H), 4.98 (br s, 1-H), 5.14 (br dd, J=1.5, 10.3 Hz, 1-H), 5.21 (br dd, J=1.5, 17.2 Hz, 1-H), 5.85 (ddt, J=10.3, 17.2, 5.7 Hz, 1-H).

1- Methyl- 3- butynyl Allylcarbamate (**3b**, R=$CH_2CH{=}CH_2$): IR (neat film) 3300 (s), 2120 (w), 1700 (s), 1650 (s), 1560 (s), 1250 (s), 1140 (m) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ=1.30 (d, J=6.4 Hz, 3-H), 1.90 (t, J=2.0 Hz, 1-H), 2.28 (dd, J=2.0, 6.0 Hz, 1-H), 3.68—3.90 (m, 2-H), 4.83 (tq, J=6.0, 6.4 Hz, 1-H), 4.94 (br dd, J=1.8, 9.0 Hz, 1-H), 5.04 (br dd, J=1.8, 16.2 Hz, 1-H), 5.76 (br dd, J=9.0, 16.2 Hz, 1-H), 6.08 (br s, 1-H).

General Procedure for the Intramolecular Aminocyclization of Alkynyl Carbamates 1 and 3 (Run 1 in Table 1 as a typical example). A 25 ml two necked round-bottomed flask, containing a magnetic stirring bar, **1a** (R=Ts, 253.3 mg, 1 mmol), and CuCl (10 mg, 0.1 mmol), was fitted with a serum cap and a reflux condenser equipped at the top with a three-way stopcock connected with a nitrogen balloon. The apparatus was purged with nitrogen by pumping and filling several times via the three-way stopcock. Dry THF (5 ml) and triethylamine (14 μl, 0.1 mmol) were added via syringes. The mixture was stirred at room temperature for 24 h. After addition of sat. $NaHCO_3$ (20 ml), the reaction mixture was extracted with ethyl acetate (2×20 ml). The combined organic extracts were dried (magnesium sulfate), filtered, and concentrated. The residue was purified by means of column chromatography over silica gel (eluent; benzene) to give **2a** (R=Ts) in 94% yield, mp 145.0—145.5 °C (benzene–hexane); IR (KBr disk) 1800 (s), 1670 (s), 1600 (m), 1380 (s), 1290 (s), 1160 (s), 1085 (s), 820 (m), 680 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ=2.45 (s, 3-H), 4.52 (q, J=2.4 Hz, 1-H), 4.78 (t, J=2.4 Hz, 2-H), 5.53 (q, J=2.4 Hz, 1-H), 7.38 (d, J=8.4 Hz, 2-H), 7.96 (d, J=8.4 Hz, 2-H). Anal. Calcd for $C_{11}H_{11}NO_4S$: C, 52.16; H, 4.38; N, 5.53; S, 12.66%. Found: C, 51.90; H, 4.41; N, 5.58; S, 12.41%.

3- Benzoyl- 4- Methylene- 2- oxazolidinone (**2a**, R=PhCO): Mp 85.8—86.5 °C (hexane–benzene); IR (KBr disk) 1800 (s), 1710 (s), 1610 (m), 1370 (s), 1280 (s), 1200 (s), 1035 (m), 710 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ=4.65 (br d, J=2.4 Hz, 1-H), 4.90 (t, J=2.4 Hz, 2-H), 5.50 (br d, J=2.4 Hz, 1-H), 7.70 (m, 5-H). Anal. Found: C, 65.00; H, 4.55; N, 6.83%. Calcd for $C_{11}H_9NO_3$: C, 65.02; H, 4.46; N, 6.89%.

3- Acetyl- 4- methylene- 2- oxazolidinone (**2a**, R=MeCO): Mp 64.2—65.5 °C (hexane–benzene); IR (KBr disk) 1790 (s), 1710 (s), 1660 (s), 1370 (s), 1200 (s), 1110 (s), 1050 (s), 950 (m), 730 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ=3.55 (s, 3-H), 4.60 (dt, J=2.0, 1.6 Hz, 1-H), 4.80 (dd, J=1.6, 2.4 Hz, 2-H), 5.85 (dt, J=2.0, 2.4 Hz, 1-H). Anal. Found: C, 51.00; H, 4.96; N, 9.85%. Calcd for $C_6H_7NO_3$: C, 51.06; H, 5.00; N, 9.93%.

3- Crotonoyl- 4- methylene- 2- oxazolidinone (**2a**, R=*trans*-MeCH=CHCO): Mp 85.5—86.0 °C (hexane–benzene); IR (KBr disk) 1770 (s), 1690 (s), 1650 (m), 1630 (m), 1360 (m), 1220 (m), 1160 (m), 1100 (m), 1020 (m), 950 (m), 860 (m), 740 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ=1.98 (d, J=5.9 Hz, 3-H), 4.67 (dt, J=1.8, 2.2 Hz, 1-H), 4.87 (dd, J=2.2, 2.6 Hz, 2-H), 5.92 (dt, J=1.8, 2.6 Hz, 1-H), 7.15 (dq, J=13.9, 5.9 Hz, 1-H), 7.21 (d, J=13.9 Hz, 1-H). Anal. Found: C, 57.44; H, 5.42; N, 8.38%. Calcd for $C_8H_9NO_3$: C, 57.48; H, 5.43; N, 8.38%.

Ethyl 4-Methylene-2-oxooxazolidine-3-carboxylate (**2a**, R=EtOCO): IR (neat film) 1800 (s), 1740 (s), 1670 (m), 1370 (s), 1260 (s), 1190 (s), 1030 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ=1.40 (t, J=8.0 Hz, 3-H), 4.40 (q, J=8.0 Hz, 2-H), 4.50 (dt, J=2.4, 2.6 Hz, 1-H), 4.85 (t, J=2.6 Hz, 2-H), 5.68 (dt, J=2.4, 2.6 Hz, 1-H). High-resolution MS, Calcd for $C_7H_9NO_4$: M, 171.0532. Found m/z (rel intensity) 171.0531 (M, 40), 99 (100).

4- Methylene- 3- phenyl- 2- oxazolidinone (**2a**, R=Ph): Mp 99.8—101.0 °C (benzene); IR (KBr disk) 1780 (s), 1690 (s), 1600 (m), 1510 (m), 1420 (m), 1350 (m), 1250 (s), 1210 (s), 1070 (s), 760 (s), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ=4.10 (dd, J=1.0, 2.9 Hz, 1-H), 4.25 (dd, J=1.0, 2.2 Hz, 1-H), 5.10 (dd, J=2.2, 2.9 Hz, 2-H), 7.40 (m, 5-H). Anal. Found: C, 68.57; H, 5.23; N, 7.90%. Calcd for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00%.

3- *p*-Methoxybenzyl- 4- methylene- 2- oxazolidinone (**2a**, R=*p*-$MeOC_6H_4CH_2$): Mp 112.3—113.2 °C (benzene); IR (KBr disk) 1760 (s), 1610 (m), 1510 (s), 1410 (m), 1350 (m), 1250 (s), 1170 (m), 1020 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ=3.80 (s, 3-H), 4.10 (dt, J=1.8, 2.0 Hz, 1-H), 4.18 (dt, J=1.8, 2.0 Hz, 1-H), 4.60 (s, 2-H), 4.85 (t, J=2.0 Hz, 2-H), 6.85 (d, J=8.4 Hz, 2-H), 7.20 (d, J=8.4 Hz, 2-H). Anal. Found: C, 65.48; H, 5.95; N, 6.48%. Calcd for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39%.

3- Allyl- 4- methylene- 2- oxazolidinone (**2a**, R=$CH_2CH{=}CH_2$): IR (neat film) 1730 (s), 1680 (s), 1630 (m), 1380 (s), 1360 (s), 1280 (m), 1170 (m), 1040 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ=4.09 (br d, J=5.5 Hz, 2-H), 4.12 (br t, J=2.5 Hz, 1-H), 4.21 (br t, J=2.5 Hz, 1-H), 4.89 (t, J=2.5 Hz, 2-H), 5.24 (br d, J=10.6 Hz, 1-H), 5.26 (br d, J=17.2 Hz, 1-H) 5.78 (ddt, J=10.6, 17.2, 5.5 Hz, 1-H). Anal. Found: C, 60.33; H, 6.61; N, 10.16%. Calcd for $C_7H_9NO_2$: C, 60.42; H, 6.52; N, 10.17%.

5- Methyl- 4- methylene- 3- tosyl- 2- oxazolidinone (**2b**, R=Ts): IR (neat film) 1795 (s), 1675 (s), 1600 (m), 1380 (s), 1285 (m), 1170 (s), 1090 (s), 750 (m), 660 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ=1.46 (d, J=6.2 Hz, 3-H), 2.46 (s, 3-H), 4.47 (dd, J=1.8, 2.9 Hz, 1-H), 5.00 (tq, J=1.8, 6.2 Hz, 1-H), 5.53 (dd, J=1.8, 2.9 Hz, 1-H), 7.39 (d, J=8.4 Hz, 2-H), 7.96 (d, J=8.4 Hz, 2-H). Anal. Found: C, 53.77; H, 4.79; N, 5.20; S, 11.83%. Calcd for $C_{12}H_{13}NO_4S$: C, 53.92; H, 4.90; N, 5.24; S, 12.00%.

5-Ethyl-4-methylene-3-tosyl-2-oxazolidinone (**2c**, R=Ts): IR (neat film) 1800 (s), 1660 (s), 1600 (m), 1370 (s), 1340 (s), 1280 (s), 1090 (s), 860 (m), 760 (m), 700 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ=0.90 (t, J=7.0 Hz, 3-

H), 1.70 (br d, J=7.0 Hz, 2-H), 2.30 (s, 3-H), 4.40 (br d, J=2.4 Hz, 1-H), 4.82 (m, 1-H), 5.50 (br d, J=2.4 Hz, 1-H), 7.26 (d, J=8.4 Hz, 2-H), 7.89 (d, J=8.4 Hz, 2-H). Anal. Found: C, 55.52; H, 5.30; N, 4.80; S, 11.24%. Calcd for $C_{13}H_{15}NO_4S$: C, 55.50; H, 5.37; N, 4.98; S, 11.40%.

3-Benzoyl-5-ethyl-4-methylene-2-oxazolidinone (**2c**, R=PhCO): IR (KBr disk) 1780 (s), 1690 (s), 1350 (s), 1320 (s), 1270 (m), 1190 (s), 1100 (s), 980 (m), 910 (m), 860 (m), 750 (m), 650 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ=1.10 (t, J=7.3 Hz, 3-H), 2.00 (m, 2-H), 4.62 (t, J=2.0 Hz, 1-H), 5.08 (m, 1-H), 5.61 (dd, J=2.0, 2.2 Hz, 1-H), 7.32—7.76 (m, 5-H). High-resolution MS, Calcd for $C_{13}H_{13}NO_3$: M, 231.0896. Found: m/z (rel intensity) 231.0911 (8.9), 106 (51), 105 (100), 78 (15), 77 (100), 51 (55).

5-Ethyl-4-methylene-3-phenyl-2-oxazolidinone (**2c**, R=Ph): Mp 95.5—96.0 °C; IR (KBr disk) 1760 (s), 1650 (s), 1600 (m), 1490 (s), 1400 (s), 1330 (m), 1280 (m), 1260 (m), 1210 (s), 1090 (s), 980 (m), 840 (m), 750 (m), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ=1.10 (t, J=7.3 Hz, 3-H), 1.62—2.21 (m, 2-H), 4.07 (t, J=2.4 Hz, 1-H), 4.21 (dd, J=2.4, 2.7 Hz, 1-H), 5.14 (m, 1-H), 7.23—7.60 (m, 5-H). Anal. Found: C, 70.96; H, 6.44; N, 6.93%. Calcd for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45; N, 6.89%.

5-Ethyl-3-methyl-4-methylene-2-oxazolidinone (**2c**, R=Me): IR (neat film) 1770 (s), 1670 (s), 1440 (s), 1390 (s), 1130 (s), 1000 (s), 950 (m), 810 (m), 750 (m), 690 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ=1.00 (t, J=7.3 Hz, 3-H), 1.55—2.06 (m, 2-H), 2.98 (s, 3-H), 4.02 (dd, J=2.0, 2.7 Hz, 1-H), 4.12 (dd, J=2.4, 2.7 Hz, 1-H), 4.96 (m, 1-H). High-resolution MS, Calcd for $C_7H_{11}NO_2$: M, 141.0789. Found: m/z (rel intensity) 141.0777 (38), 139 (13), 126 (19), 113 (100).

4-Methylene-3-tosyl-5-vinyl-2-oxazolidinone (**2d**, R=Ts): IR (neat film) 1795 (s), 1670 (s), 1600 (m), 1375 (s), 1275 (s), 1175 (s), 1080 (s), 750 (m), 670 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ=2.46 (s, 3-H), 4.49 (br d, J=2.6 Hz, 1-H), 5.24 (br d, J=7.1 Hz, 1-H), 5.42 (br d, J=10.3 Hz, 1-H), 5.43 (br d, J=17.2 Hz, 1-H), 5.58 (br d, J=2.6 Hz, 1-H), 5.73 (ddd, J=7.1, 10.3, 17.2 Hz, 1-H), 7.37 (d, J=8.4 Hz, 2-H), 7.95 (d, J=8.4 Hz, 2-H). High-resolution MS, Calcd for $C_{13}H_{13}NO_4S$: M, 279.0565. Found: m/z (rel intensity) 279.0560 (M, 53), 124 (24), 91 (100).

5,5-Dimethyl-4-methylene-3-tosyl-2-oxazolidinone (**2e**, R=Ts): Mp 90.4—90.8 °C (hexane–dichloromethane); IR (KBr disk) 1790 (s), 1708 (m), 1600 (m), 1375 (s), 1260 (s), 1180 (s), 1050 (s), 818 (m), 755 (s), 675 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ=1.45 (s, 6-H), 2.45 (s, 3-H), 4.45 (d, J=2.9 Hz, 1-H), 5.50 (d, J=2.9 Hz, 1-H), 7.30 (d, J=8.4 Hz, 2-H), 7.90 (d, J=8.4 Hz, 2-H). Anal. Calcd for $C_{13}H_{15}NO_4S$: C, 53.92; H, 4.90; N, 5.24; S, 12.00%. Found: C, 53.95; H, 4.83; N, 5.33; S, 12.08%.

4-Methylene-3-tosyl-1-oxa-3-azaspiro[4.5]decan-2-one (**2f**, R=Ts): Mp 89.5—90.0 °C ; IR (KBr disk) 1780 (s), 1680 (s), 1370 (s), 1300 (s), 1260 (s), 1180 (s), 1100 (s), 810 (m), 700 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ=1.10 (m, 10-H), 2.45 (s, 3-H), 4.41 (d, J=2.9 Hz, 1-H), 5.50 (d, J=2.9 Hz, 1-H), 7.33 (d, J=8.3 Hz, 2-H), 7.93 (d, J=8.3 Hz, 2-H). Anal. Found: C, 59.76; H, 5.84; N, 4.35; S, 10.03%. Calcd for $C_{16}H_{19}NO_4S$: C, 59.79; H, 5.96; N, 4.36; S, 9.98%.

4-Methylene-2-oxazolidinone Derivative of Ethisterone (**2g**, R=Ts, for the structure, see Table 2): Mp 178.5—179.0 °C; IR (KBr disk) 1780 (s), 1660 (s), 1370 (m), 1270 (s), 1180 (s), 1080 (m), 1010 (m), 860 (m), 810 (m), 750 (m), 670(m) cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ=0.94 (s, 3-H), 1.07 (s, 3-H), 0.99—2.39 (m, 19-H), 2.45 (s, 3-H), 4.49 (d, J=3.2 Hz, 1-H), 5.58 (d, J=3.2 Hz, 1-H), 5.72 (s, 1-H), 7.35 (d, J=8.3 Hz, 2-H), 7.96 (d, J=8.3 Hz, 2-H). Anal. Found: C, 68.55; H, 6.99; N, 2.88; S, 6.51%. Calcd for $C_{29}H_{35}NO_5S$: C, 68.34; H, 6.92; N, 2.75; S, 6.29%.

4-Ethylidene-3-tosyl-2-oxazolidinone (**2h**, R=Ts): Mp 81.0—82.5 °C (benzene–hexane); IR (KBr disk) 1790 (s), 1710 (m), 1600 (m), 1370 (s), 1230 (m), 1190 (m), 1170 (s), 1150 (m), 1100 (m), 1060 (m), 810 (m), 760(m), 720 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ=1.87 (dt, J=7.3, 1.8 Hz, 3-H), 2.84 (s, 3-H), 4.67 (dq, J=1.5, 1.8 Hz, 2-H), 5.27 (tq, J=1.5, 7.3 Hz, 1-H), 7.36 (d, J=8.4 Hz, 2-H), 7.96 (d, J=8.4 Hz, 2-H). Anal. Found: C, 53.92; H, 4.87; N, 5.22; S, 12.09%. Calcd for $C_{12}H_{13}NO_4S$: C, 53.92; H, 4.90; N, 5.24; S, 12.00%.

4-(2-Methyl-2-propenylidene)-2-oxazolidinone (**2i**, R=Ts): Mp 113.0—114.0 °C (benzene–hexane); IR (KBr disk) 1790 (s), 1670 (m), 1380 (s), 1210 (s), 1180 (m), 1140 (s), 1090 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ=1.99 (s, 3-H), 2.44 (s, 3-H), 4.70 (d, J=1.8 Hz, 2-H), 4.85 (br s, 1-H), 4.98 (br s, 1-H), 5.67 (br t, J=1.8 Hz, 1-H), 7.32 (d, J=8.4 Hz, 2-H), 7.91 (d, J=8.4 Hz, 2-H). Anal. Found: C, 57.06; H, 5.07; N, 4.62; S, 11.11%. Calcd for $C_{14}H_{15}NO_4S$: C, 57.32; H, 5.15; N, 4.77; S, 10.93%.

4-[2-(Tetrahydro-2-pyranyloxy)ethylidene]-3-tosyl-2-oxazolidinone (**2j**, R=Ts): Mp 116.0—117.0 °C (benzene–hexane); IR (KBr disk) 1805 (s), 1708 (m), 1600 (m), 1375 (s), 1155 (s), 1032 (s), 810 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ=1.45—1.89 (m, 6-H), 2.45 (s, 3-H), 3.50 (m, 1-H), 3.83 (m, 1-H), 4.33 (ddt, J=6.2, 14.1, 1.8 Hz, 1-H), 4.54 (ddt, J=5.5, 14.1, 1.8 Hz, 1-H), 4.64 (m, 1-H), 4.71 (br t, J=1.8 Hz, 2-H), 5.32 (ddt, J=5.5, 6.2, 1.8 Hz, 1-H), 7.36 (d, J=8.2 Hz, 2-H), 7.94 (d, J=8.2 Hz, 2-H). Anal. Found: C, 55.65; H, 5.67; N, 3.80; S, 8.74%. Calcd for $C_{17}H_{21}NO_6S$: C, 55.57; H, 5.67; N, 3.81; S, 8.73%.

(*Z*)-4-Ethylidene-3-tosyl-5-methyl-2-oxazolidinone (**2k**, R=Ts): IR (neat film) 1790 (s), 1600 (m), 1370 (s), 1220 (s), 1170 (s), 1090 (s), 810 (m), 760 (m), 650 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ=1.40 (d, J=6.4 Hz, 3-H), 1.87 (dd, J=1.7, 7.1 Hz, 3-H), 2.45 (s, 3-H), 4.90 (dqq, J=1.7, 1.7, 6.4 Hz, 1-H), 5.21 (dq, J=1.7, 7.1 Hz, 1-H), 7.35 (d, J=8.3 Hz, 2-H), 7.96 (d, J=8.3 Hz, 2-H). High-resolution MS, Cacld for $C_{13}H_{15}NO_4S$: M, 281.0721. Found: m/z (rel intensity) 281.0716 (20), 155 (74), 109 (94), 91 (100).

(*Z*)-4-Ethylidene-5,5-dimethyl-3-tosyl-2-oxazolidinone (**2l**, R=Ts): Mp 111.3—111.9 °C; IR (KBr disk) 1770 (s), 1350 (s), 1250 (s), 1160 (s), 1090 (s), 820 (m), 660 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ=1.47 (s, 6-H), 1.83 (d, J=7.1 Hz, 3-H), 2.45 (s, 3-H), 5.18 (q, J=7.1 Hz, 1-H), 7.35 (d, J=8.3 Hz, 2-H), 7.95 (d, J=8.3 Hz, 2-H). Anal. Found: C, 56.76; H, 5.76; N, 4.97; S, 11.06%. Calcd for $C_{14}H_{17}NO_4S$: C, 56.93; H, 5.80; N, 4.74; S, 10.86%.

Methyl (*Z*)-2-Oxo-3-tosyloxazolidin-4-ylideneacetate ((*Z*)-2m): Mp 148.5—149.4 °C (benzene–hexane); IR (KBr disk) 1800 (s), 1720 (s), 1680 (m), 1370 (s), 1240 (s), 1170 (s), 1080 (m), 810 (m), 650 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ=2.46 (s, 3-H), 3.92 (s, 3-H), 4.86 (d, J=2.6 Hz, 2-H), 5.46 (d, J=2.6 Hz, 1-H), 7.38 (d, J=8.2 Hz, 2-H), 8.03 (d, J=8.2 Hz, 2-H). Anal. Found: C, 50.15; H, 4.23; N, 4.50; S, 10.27%. Calcd for $C_{13}H_{13}NO_6S$: C, 50.15;

H, 4.21; N, 4.50; S, 10.30%.

Methyl (*E*)-2-Oxo-3-tosyloxazolidin-4-ylideneacetate ((*E*)-2m): Mp 133.6—134.5 °C (benzene–hexane); IR (KBr disk) 1810 (s), 1710 (s), 1660 (s), 1370 (s), 1200 (s), 1170 (s), 1070 (m), 910 (w), 650 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ=2.47 (s, 3-H), 3.75 (s, 3-H), 5.30 (d, J=2.6 Hz, 2-H), 6.48 (t, J=2.6 Hz, 1-H), 7.39 (d, J=8.2 Hz, 2-H), 7.98 (d, J=8.2 Hz, 2-H). Anal. Found: C, 50.10; H, 4.22; N, 4.49; S, 10.24%. Calcd for $C_{13}H_{13}NO_6S$: C, 50.15; H, 4.21; N, 4.50; S, 10.30%.

4-Methylene-3-tosyltetrahydro-1,3-oxazin-2-one (**4a**, R=Ts): Mp 122.0—123.0 °C; (benzene–hexane); IR (KBr disk) 1740 (s), 1660 (m), 1600 (m), 1400 (m), 1360 (m), 1280 (s), 1170 (s), 1120 (m), 1090 (m), 810 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ=2.44 (s, 3-H), 2.64 (br d, J=5.9 Hz, 2-H), 4.31 (t, J=5.9 Hz, 2-H), 5.02 (br d, J=1.5 Hz, 1-H), 5.40 (d, J=1.5 Hz, 1-H), 7.34 (d, J=8.2 Hz, 2-H), 7.94 (d, J=8.2 Hz, 2-H). Anal. Found: C, 53.80; H, 4.81; N, 5.30; S, 12.09%. Calcd for $C_{12}H_{13}NO_4S$: C, 53.92; H, 4.90; N, 5.24; S, 12.00%.

6-Methyl-4-methylene-3-tosyltetrahydro-1,3-oxazine-2-one (**4b**, R=Ts): Mp 119.2—120.5 °C; (benzene–hexane); IR (KBr disk) 1750 (s), 1660 (m), 1350 (s), 1270 (s), 1230 (s), 1190 (s), 1170 (s), 670 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ=1.35 (d, J=6.4 Hz, 3-H), 2.30 (dd, J=8.8, 14.4 Hz, 1-H), 2.40 (s, 3-H), 2.65 (dd, J=4.2, 14.4 Hz, 1-H), 4.45 (ddq, J=4.2, 8.8, 6.4 Hz, 1-H), 4.90 (br s, 1-H), 5.30 (br s, 1-H), 7.30 (d, J=8.2 Hz, 2-H), 7.92 (d, J=8.2 Hz, 2-H). Anal. Found: C, 55.57; H, 5.42; N, 4.83; S, 11.26%. Calcd for $C_{13}H_{15}NO_4S$: C, 55.50; H, 5.37; N, 4.98; S, 11.40%.

(*Z*)-4-Ethylidene-6-methyl-3-tosyltetrahydro-1,3-oxazin-2-one (**4c**, R=Ts): Mp 186.5—187.3 °C; (benzene–hexane); IR (KBr disk) 1740 (s), 1690 (m), 1600 (w), 1370 (s), 1240 (m), 1180 (s), 1090 (m), 670 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ=1.29 (d, J=6.2 Hz, 3-H), 1.90 (d, J=6.9 Hz, 3-H), 2.18 (dd, J=8.2, 13.4 Hz, 1-H), 2.43 (s, 3-H), 2.61 (dd, J=4.9, 13.4 Hz, 1-H), 4.47 (ddq, J=4.9, 8.2, 6.2 Hz, 1-H), 5.63 (q, J=6.9 Hz, 1-H), 7.31 (d, J=8.2 Hz, 2-H), 7.90 (d, J=8.2 Hz, 2-H). Anal. Found: C, 56.78; H, 5.73; N, 4.73; S, 10.59%. Calcd for $C_{14}H_{17}NO_4S$: C, 56.93; H, 5.80; N, 4.74; S, 10.86%.

Methyl (*Z*)-6-Methyl-2-oxo-3-tosyltetrahydro-1,3-oxazine-4-ylideneacetate (4e): Mp 143.5—145.0 °C; (hexane–dichloromethane); IR (KBr disk) 1730 (s), 1675 (m), 1600 (m), 1375 (s), 1175 (s), 1085 (s), 650 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ=1.35 (d, J=7.2 Hz, 3-H), 2.66 (dd, J=8.4, 13.1 Hz, 1-H), 2.43 (s, 3-H), 2.64 (dd, J=4.2, 13.1 Hz, 1-H), 3.83 (s, 3-H), 4.54 (ddq, J=4.2, 8.4, 7.2 Hz, 1-H), 5.78 (s, 1-H), 7.27 (d, J=8.4 Hz, 2-H), 7.86 (d, J=8.4 Hz, 2-H). Anal. Found: C, 53.08; H, 4.96; N, 3.99; S, 9.33%. Calcd for $C_{15}H_{17}NO_6S$: C, 53.09; H, 5.05; N, 4.13; S, 9.45%.

Methyl 3-(Tosylamino)-2,4-hexadienoate: IR (neat film) 3150 (w), 1680 (s), 1620 (s), 1450 (s), 1250 (s), 1165 (s), 1090 (m), 705 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ=1.72 (d, J=6.0 Hz, 3-H), 2.33 (s, 3-H), 3.62 (s, 3-H), 5.06 (s, 1-H), 5.95 (dq, J=15.0, 6.0 Hz, 1-H), 6.40 (d, J=15.0 Hz, 1-H), 7.30 (d, J=8.4 Hz, 2-H), 7.67 (d, J=8.4 Hz, 2-H), 10.68 (br s, 1-H). High-resolution MS, Calcd for $C_{14}H_{17}NO_4S$: M, 295.0878. Found: m/z (rel intensity) 295.0880 (M^+, 75), 264 (13), 231 (26), 199 (9), 172 (23), 140 (18), 92 (100).

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