# Preparation, Structure, and Unique Thermal [2 + 2], [4 + 2], and [3 + 2] Cycloaddition Reactions of 4-Vinylideneoxazolidin-2-one

**Yoshikazu Horino,[a] Masanari Kimura,[a] Shuji Tanaka,[a] Toshiya Okajima,[b] and Yoshinao Tamaru*[a]**

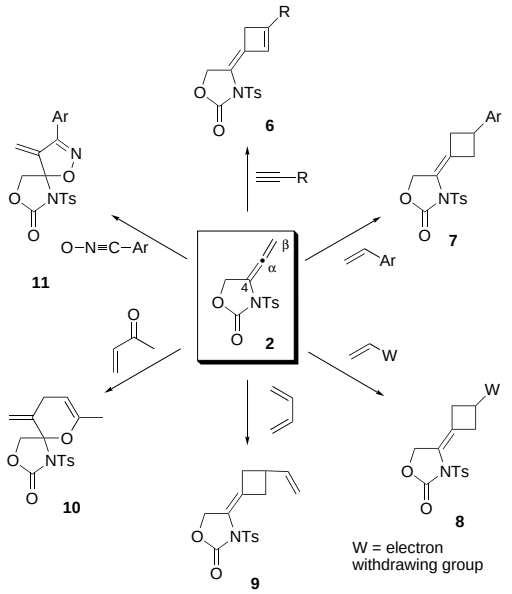
**Abstract:** The terminal allene $C_\alpha$=$C_\beta$ bonds of 4-vinylidene-2-oxazolidinone (**2**) readily undergo [2 + 2] cycloaddition with a wide variety of terminal alkynes, alkenes, and 1,3-dienes irrespective of their electronic nature under strictly thermal activation conditions (70–100 °C) and provide 3-substituted (*Z*)-methylenecyclobutenes **6**, 3-substituted methylenecyclobutanes **7** and **8**, and 3-vinylmethylenecyclobutanes **9**, respectively, in good to excellent yields. Alkenes react with **2** with complete retention of configuration. The [2 + 2] cycloaddition is concluded to proceed via a concerted $[(\pi_{2s} + \pi_{2s})_{allene} + \pi_{2s}]$ Hückel transition state on the basis of experimental evidences and quantum mechanical methods. Some highly polarized enones and nitrile oxide, on the other hand, react with **2** selectively at the internal $C_4$=$C_\alpha$ double bonds and give spiro compounds **10** and **11**, respectively. The bent allene bonds (173–176°) and the unique reactivity associated with **2** are attributed to a low-lying LUMO ($C_\alpha$=$C_\beta$) that is substantiated by a through-space $\sigma^*(N\text{-}SO_2) - \pi^*(C_\alpha{=}C_\beta)$ orbital interaction.

**Keywords:** alkenes · alkynes · allenes · cycloaddition · dienes

## Introduction

Owing to their inherent strain, allenes have been recognized as an active and excellent reaction partner for many types of cycloaddition reactions. Especially, [2 + 2] cycloaddition of allenes with alkenes has been of special interest because of the synthetic importance of the reaction, providing methylenecyclobutane units of structural interest.

The Woodward–Hoffmann rule and the Fukui frontier orbital theory predict that [2 + 2] cycloaddition is photochemically allowed, but thermally forbidden. In accord, photochemical reactions of allenes proceed smoothly and provide products with expected regio- and stereochemistry in good yields and have been utilized for the syntheses of natural and unnatural products of structural complexity.[1] On the other hand, thermal [2 + 2] cycloaddition of allenes requires high temperatures (> 200 °C) and/or long reaction times. This process has suffered from low regio- and stereoselectivity, and in general, low yields of the methylenecyclobutane products.[2] Therefore, as an alternative, a variety of methods relying on activation of allenes (e.g., allene carboxylic esters and heteroatom substituted allenes) with Lewis acids[3] or transition metals[4, 5] and also relying on an intramolecular version that facilitates the reaction by virtue of entropic factors,[6] have been developed. From a practical point of view aimed at




Scheme 1. Regio- and stereoselective, [2 + 2], [4 + 2] and [3 + 2] cycloaddition of **2**.

[a] Prof. Y. Tamaru, Dr. Y. Horino, Dr. M. Kimura, Dr. S. Tanaka
Department of Applied Chemistry
Faculty of Engineering, Nagasaki University
1-14 Bunkyo-Machi, Nagasaki 852-8521 (Japan)
Fax: (+81) 95-847-9008
E-mail: tamaru@net.nagasaki-u.ac.jp

[b] Dr. T. Okajima
Department of Chemistry
Faculty of Culture and Education, Saga University
Honjo, Saga 840-8502 (Japan)

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

 **DOI: 10.1002/chem.200304586**  

the construction of the cyclobutane ring, ketene is the reagent of choice since, owing to its polarized structure, ketene is much more reactive than allene and readily reacts with many types of double bonds (C=C, C=N, etc.) to form for example cyclobutanones, $\beta$-lactams.[7]

In 1968, two contradicting reports appeared, one supporting the concertedness of [2+2] cycloaddition of allene and alkene and the other not; Okamura et al.[8d] reported the concertedness of the reactions of dimethyl maleate and fumarate with 1,1-dimethylallene, which proceeded in a stereospecific manner. On the other hand, Dolbier et al.[9e] claimed that the [2+2] cycloaddition of [$D_2$]allene and acrylonitrile proceeded via stepwise processes (radical addition–cyclization) on the basis of secondary deuterium kinetic isotope effects.

In 1979, Pasto proposed an attractive idea that [2+2] cycloaddition might proceed concertedly by virtue of a contribution of the cumulated orthogonal π-bond of allene via a $[(\pi_{2s}+\pi_{2s})_{allene}+\pi_{2s,\,alkene}]$ process (see Figure 6).[10e] In fact, however, despite extensive studies by himself[10] and others,[2, 9, 11] the vast majority of results that have been accumulated to date seems to point to a stepwise biradical mechanism. Concertedness has been claimed sporadically in a few reports with some limited number of examples.[8]

In this article, we would like to disclose for the first time that the allene moiety of 4-vinylidene-2-oxazolidinones **2** is surely able to undergo [2+2] cycloaddition via a concerted mechanism under mild, strictly thermal reaction conditions; **2** reacts at the terminal $C_\alpha$=$C_\beta$ bond with alkynes and alkenes of a widely varying structural and electronic nature and gives rise to methylenecyclobutenes **6** and methylenecyclobutanes **7**–**9**, respectively, in good to excellent yields by heating at 70–100 °C(Scheme 1).[12]

With terminal alkynes and alkenes, the reactions are highly regio- and stereoselective, delivering their unsaturated bonds syn to the N-substituents of **2** and placing the substituents of alkynes and alkenes at the 3-position of methylenecyclobutenes and methylenecyclobutanes, respectively. Importantly, alkenes react with **2** with complete retention of configuration of their double bond geometries.

Furthermore, the internal $C_4$=$C_\alpha$ double bond of **2** participates in [4+2] and [3+2] cycloaddition reactions toward highly polarized enones and nitrile oxide and provides **10** and **11**, respectively. Some enones provide **8** exclusively, while some other enones furnish **10** selectively along with **8** as the minor products. The mechanistic detail for the selective formation of **6**–**11** is discussed on the basis of quantum mechanical methods (RHF/3-21G* level).

The 4-vinylidene-2-oxazolidinones **2** are characteristic in the bent structure of the allene bonds, where the $C_\beta$ carbons bend away from the *N*-sulfonyl group in the plane defined by N-$C_4$-$C_5$, and the bond angles $\angle C_4$-$C_\alpha$-$C_\beta$ significantly deviate from linearity, from 172.5–176.0°.[13]

The allene $\pi^*(C_\alpha$=$C_\beta)$ orbital may lie low in energy owing to a through-space $\sigma^*(N-SO_2)-\pi^*(C_\alpha$=$C_\beta)$ orbital interaction, which brings about the allene bent bond (an attractive $n_O(_{=SO})-\pi^*(C_\alpha$=$C_\beta)$ charge transfer type interaction) as well as the unique reactivity of **2**.

**Abstract in Japanese:**

アレンオキサゾリジノン **2** のアレン結合は折れ曲がっている(173~176°)。これはσ*$_{N-SO2}$–π*$_{Cα=Cβ}$ through-space 相互作用によるもので、その結果 $C_\alpha$=$C_\beta$ の LUMO のエネルギー準位は低く、そのため末端 $C_\alpha$=$C_\beta$は各種アルキン、アルケン、ジエンと容易に[2+2]環化付加し、それぞれ(*Z*)-**6**, **7**(**8**), **9** を位置および立体選択的に与える(反応温度: 70~100 ℃)。実験および理論計算から、この[2+2]環化付加は熱的に許容で、協奏的に進むとの結論を得た［ヒュッケル環状 6π系:($\pi$2s + $\pi$2s)$_{allene}$ + $\pi$2s］。極性の高いエノンやニトリルオキシドは **2** の内部 $C_4$=$C_\alpha$で反応し、それぞれスピロ化合物 **10** と **11** を与える。

## Results and Discussion

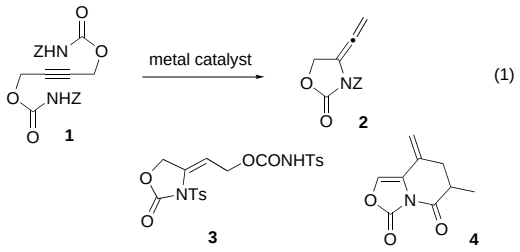
**Preparation of 4-vinylidene-2-oxazolidinones 2**: Bis-*N*-sulfonyl (**1a**–**c**), bis-*N*-acyl (**1d**,**e**), and bis-*N*-phenyl (**1f**) biscarbamates of but-2-yn-1,4-diol were prepared quantitatively by treatment of the corresponding isocyanate (2.2 equiv) and the diol in the presence of triethylamine (2.2 equiv) in THF at 0 °C → room temperature. Other bis-*N*-tosyl biscarbamates involving unsymmetrical ones (**1g**–**r**) were also obtained in a similar way using the corresponding but-2-yn-1,4-diols in quantitative yield. These biscarbamates, except **1e**, **p**, and **r**, form a nice crystalline solid (or powder) and withstand storage for months in a refrigerator. Biscarbamates **1e**, **p**, and **r** each appear as a heavy oil; purification by means of column chromatography over silica gel and/or crystallization from reaction mixtures all resulted in significant loss owing to decomposition. Accordingly, these biscarbamates were prepared prior to use and used without purification.

We planned preparation of **2** in expectation that the $Cu^I$·$Et_3N$ catalytic system, developed by the authors for the cyclization of propargyl carbamate to 4-methylene-2-oxazolidinone,[14] might promote cyclization at the N atom of one of the two carbamates of **1** in conjunction with elimination of the other carbamate in an $S_N2'$ fashion. However, the expected reaction did not take place; instead, only the cyclization product **3** was produced in modest yield (run 6, Table 1).

Next, we examined palladium complexes as a catalyst bearing in mind that oxidative addition of one of the two carbamate moieties to the $Pd^0$ species followed by extrusion of *p*-toluenesulfonamide and carbon dioxide might form a propargylpalladium **I** or an allenylpalladium intermediate **II**, which would be reactive enough to undergo an intramolecular displacement of Pd by the N anion of the other remaining carbamate via either $S_N2'$ or reductive elimination, respectively (Scheme 2).[12a] As was expected, all the palladium(**0**) species examined turned out to serve as a catalyst for the transformation of **1** to **2**, though the efficiency largely depended on the kind of palladium species (runs 3–5). The phosphine-free $[Pd_2(dba)_3]$·$CHCl_3$·$Et_3N$ system was the combination of choice, judging from the reaction temperature and the yield of **2**.

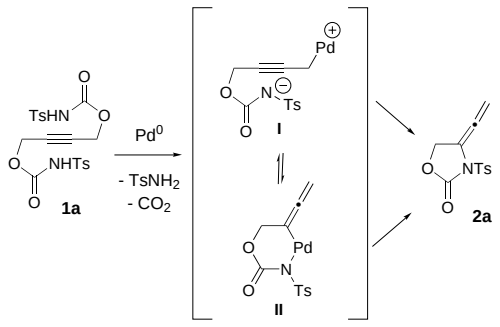
Remarkably, lowering the catalyst loading to 0.5 mol% showed a significant increase in the yields (cf. runs 1 and 3, Table 1). It should be noted that the use of a catalytic amount

Table 1. Transition-metal catalyzed preparation of 4-vinylidene-2-oxazolidin-2-ones **2**.[a]




| Run | **1** | (*Z*) | Metal (equiv) | Base (equiv) | *T*/*t* [b] | Product | Yield [%] [c] |
|---|---|---|---|---|---|---|---|
| 1 | **1a** | *p*-Ts | $[Pd_2(dba)_3]\cdot CHCl_3$ (0.005) | $Et_3N$ (0.1) | 25/7 | **2a** | 73 |
| 2 | **1a** | *p*-Ts | $[Pd_2(dba)_3]\cdot CHCl_3$ (0.005) | none | 65/3 | **2a** | 0 |
| 3 | **1a** | *p*-Ts | $[Pd_2(dba)_3]\cdot CHCl_3$ (0.1) | $Et_3N$ (0.1) | 25/2 | **2a** | 44 |
| 4 | **1a** | *p*-Ts | $[Pd(PPh_3)_4]$ (0.1) | $Et_3N$ (0.1) | 65/4 | **2a** | 45 |
| 5 | **1a** | *p*-Ts | $[Pd(OAc)_2]$ (0.1) | $Et_3N$ (0.1) | 25/4 | **2a** | 3 |
| 6 | **1a** | *p*-Ts | CuCl (0.1) | $Et_3N$ (0.1) | 50/5 | **3** | 54 |
| 7 | **1b** | *o*-Ts | $[Pd_2(dba)_3]\cdot CHCl_3$ (0.005) | $Et_3N$ (0.1) | 25/12 | **2b** | 53 |
| 8 | **1c** | Ms | $[Pd_2(dba)_3]\cdot CHCl_3$ (0.005) | $Et_3N$ (0.1) | 25/12 | **2c** | 54 |
| 9 | **1d** | Bz | $[Pd_2(dba)_3]\cdot CHCl_3$ (0.005) | $Et_3N$ (0.1) | 25/10 | **2d** | 66 |
| 10 | **1e** | $\alpha$-Met[d] | $[Pd_2(dba)_3]\cdot CHCl_3$ (0.005) | $Et_3N$ (0.1) | 25/47 | **2e**<br>**4** | 14[e]<br>15 |
| 11 | **1e** | $\alpha$-Met[d] | $[Pd_2(dba)_3]\cdot CHCl_3$ (0.005) | $Et_3N$ (0.1) | 50/7 | **4** | 33[e] |
| 12 | **1f** | Ph | $[Pd_2(dba)_3]\cdot CHCl_3$ (0.005) | $Et_3N$ (0.1) | 50/55 | no rx[f] | |
| 13 | **1f** | Ph | $[Pd_2(dba)_3]\cdot CHCl_3$ (0.005) | *t*BuOK (0.1) | 50/55 | dec.[g] | |

[a] Reaction conditions: **1** (1 mmol), transition-metal complex and base (amount given) in dry THF (5 mL) under $N_2$. [b] Temperature in °C and reaction time in h. [c] Isolated yield for spectroscopically homogeneous product. [d] $\alpha$-Met = $\alpha$-methylacryloyl. [e] Overall yield based on but-2-yn-1,4-diol. [f] Recovery of **1e**. [g] Decomposition of **1f**.




Scheme 2. Palladium-catalyzed cyclization of biscarbamate **1**.

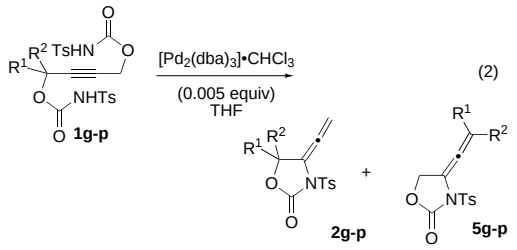
of $Et_3N$ is essential to promote the reaction. In the absence of $Et_3N$, no trace amount of **2a** was formed even under harsh conditions; instead, **1a** decomposed completely to give an intractable mixture of products (run 2). Hereafter, we uniformly applied the conditions established in run 1 of Table 1 to the elimination–cyclization reaction of the other biscarbamates **1**.

Results for the elimination–cyclization reaction of biscarbamates with various *N*-substituents, **1b–f**, are summarized in Table 1. Bis-*N*-*o*-tosyl (**1b**), bis-*N*-methanesulfonyl (**1c**), and bis-*N*-benzoyl biscarbamates (**1d**) reacted with similar ease, and the reaction was completed within 12 h at room temperature. Bis-*N*-$\alpha$-methacryloyl biscarbamate (**1e**) was rather reluctant and required over 2 d for completion of the reaction (run 10). The expected product **2e** was isolated in low yield (14%). In addition to **2e**, **4** (15%) was obtained in a comparable amount. At an elevated temperature, only **4** was produced in 33% yield (run 11). These results suggest that **2e** is a primary product and is labile under the conditions, undergoing subsequent reactions, that is 1) aza-Claisen rearrangement, 2) imine–enamine isomerization, and 3) cyclization and/or 1) intramolecular Michael addition of the enamine moiety to enone and 2) hydrogen shift, to finally provide **4**. Bis-*N*-phenyl biscarbamate (**1f**) was completely unreactive and was recovered even by heating at 50 °C over 2 d (run 12). In the presence of a stronger base, it decomposed (run 13). These results clearly indicate that the ease of the conversion of 1 to 2 depends on the acidity of carbamates.

Among **2a–d**, the allene carbamates **2a** and **b** form a nice stable crystalline solid, while **2c** and **d** are a heavy oil and partially decompose during purification by flash column chromatography over silica gel and also during storage in a refrigerator. Accordingly, **2c** and **d** were prepared and used promptly after purification by chromatography over silica gel with a short column.

Table 2 summarizes the results for the cyclization of bis-*N*-tosyl biscarbamates of 1-substituted but-2-yn-1,4-diols (**1g–p**). In these reactions, two regioisomers of products **2** and **5** are

Table 2. Preparation of 5-substituted 4-vinylideneoxazolidine-2-ones **2g–p**.[a]



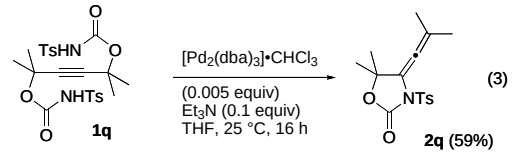

| Run | **1** | $R^1$ | $R^2$ | *T* [°C]/*t* [h] | % yield | **2**:**5**[b] |
|---|---|---|---|---|---|---|
| 1 | **1g** | Me | H | 25/6 | 47 | 2.1:1 |
| 2 | **1h** | Et | H | 25/56 | 47 | 1.7:1 |
| 3 | **1i** | *i*Pr | H | 50/24 | 45 | 2.5:1 |
| 4 | **1j** | *c*Hex | H | 60/20 | 40 | 2.5:1 |
| 5 | **1k** | Ph | H | 25/11 | 58 | 2.1:1 |
| 6 | **1l** | *t*Bu | H | 40/25 | 58 | 2.1:1 |
| 7 | **1m** | Me | Me | 25/13 | 70 | 30:1 |
| 8 | **1n** | $(CH_2)_4$ | | 25/4 | 56 | 20:1 |
| 9 | **1o** | $(CH_2)_5$ | | 25/6 | 56 | 21:1 |
| 10 | **1p** | 2-adamantyl | | 60/23 | 20[c] | **2p** only |

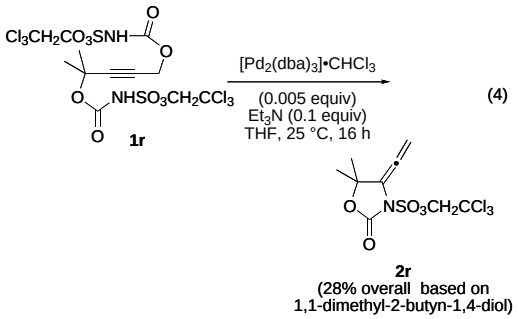
[a] Reaction conditions: **1** (1 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (0.005 mmol), $Et_3N$ (0.1 mmol) in dry THF (5 mL) under $N_2$. For runs 7 and 8, the palladium catalyst in 0.02 mmol. [b] Non-separable mixture by means of column chromatography over silica gel, the ratio being determined on the basis of $^1H$ NMR (400 MHz). [c] Overall yield based on but-2-yn-1,4-diol.

conceivable, depending on which one of the two carbamates serves as a nitrogen nucleophile and the other as a leaving group. Surprisingly, the regioselectivity of the cyclization of 1-monosubstituted biscarbamates **1g–l** was almost independent of the steric bulk and the electronic nature of the substituents, and mixtures of **2** and **5** were obtained in a ratio of about 2:1. On the other hand, 1,1-geminally disubstituted biscarbamates **1m–p** underwent cyclization to provide **2** almost exclusively. The regioselectivity may be attributed to steric hindrance of oxidative addition of the $C_1$–O bond to $Pd^0$ as well as to the Breseley–Ingold–Thorpe effects[15] (buttressing effects) of the $C_1$ substituents that make the nitrogen atom of $C_1$ carbamate and the $C_2$ carbon come close to each other.

Equations (3) and (4) demonstrate that the present Pd-catalyzed cyclization is applicable not only to highly substituted biscarbamates, but also to biscarbamates with a variety of electron-withdrawing substituents on the nitrogen atom. The products **2q** and **2r** form a nice crystalline solid. It should




be noted that **2r** was obtained in 28% overall yield based on 1,1-dimethylbut-2-yn-1,4-diol in three-step assembly-line operations without purification of the intermediates: moisture and thermal-sensitive 2,2,2-trichloroethoxysulfonyl isocyanate[16] and biscarbamate **1r** with a propensity to readily undergo polymerization.

**Structure of 4-vinylidene-2-oxazolidinones 2 characterized by the bent allene bond**: Figures 1 and 2 list the Chem 3D presentation of the structure of allene carbamates **2** of interest, determined by single-crystal X-ray diffraction methods. The dihedral angles, bond angles and lengths of interest for all **2** determined by X-ray analyses are compiled in Table 3.[17, 18] The X-ray crystallographic analyses have revealed that all of the oxazolidinones **2** possess common but unique structural features.

First, the 2-oxazolidinone ring of **2** is almost planar, except that of **2p** (Figure 2). For this particular compound, the deformation of the oxazolidinone ring may be caused by steric

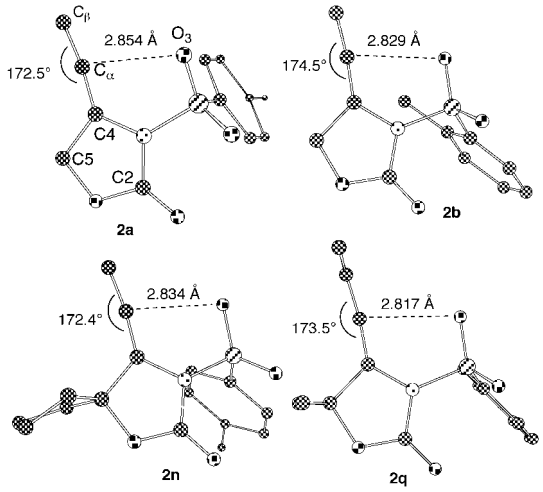



Figure 1. Chem 3D drawing of X-ray structure of 4-vinylidene-2-oxazolidinones **2**, placing $C_4$-$C_\alpha$–$C_\beta$ atoms in an *xy* plane. One of the sulfonyl oxygens points to $C_\alpha$ and forms a loose planar five-membered ring. For clarity, all hydrogens are omitted.

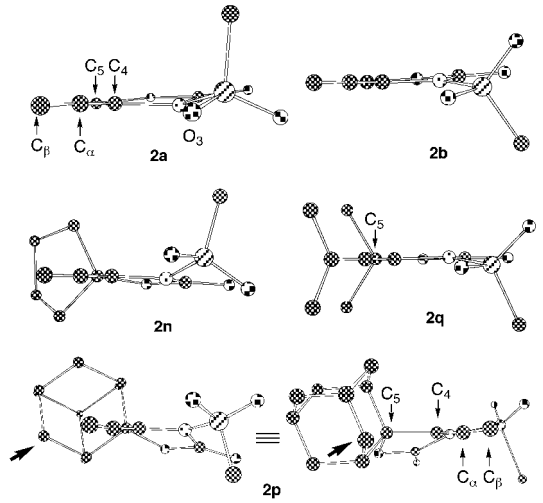



Figure 2. Chem 3D Drawing of X-ray structure of 4-vinylidene-2-oxazolidinones **2**, placing $C_5$-$C_4$-$C_\alpha$ atoms in an *xz* plane. Except the one of **2p**, all $C_\beta$ reside in the $C_5$-$C_4$-$C_\alpha$ plane. For clarity, all hydrogens are omitted, and tolyl is replaced by Me.

repulsion between one of the adamantyl methylene groups (indicated by an arrow) and the allene $C_\beta$. In fact, as is seen by a close examination of Figure 2, the $C_4$=$C_\alpha$=$C_\beta$ allene bond of **2p** deviates from linearity and the $C_\beta$ carbon is located out of the $C_4$-$C_5$-$C_\alpha$ plane, though the $C_\beta$ carbons of the other **2** compounds all reside on the plane. Second, either one of the two oxygen atoms ($O_3$) of the sulfonyl group points to the allene central carbon, $C_\alpha$, and seems to form a loose, planar five-membered ring composed of $C_\alpha$, $C_4$, N, S, and $O_3$, as if there exists an attractive interaction between them (Figure 1). The $O_3$–$C_\alpha$ distances are in the range of 2.82–2.87 Å and are shorter than the sum of van der Waals radii of O (1.75 Å) and C (1.70 Å).[19] This feature may be inherent in allene carbamates **2**, and may not be due to crystal packing effects since, as is seen in Figure 1, the *p*-tolyl and *o*-tolyl groups take a variety of conformations in the crystals. Furthermore, this arrangement seems to be a general feature of all **2** and not

affected by the space requirements of the $C_5$ and/or $C_\beta$ substituents. Finally, and most importantly, the $C_4{=}C_\alpha{=}C_\beta$ allene bonds significantly deviate from linearity away from the sulfonyl groups, forming the bond angles between 173–176° (Figure 1 and Table 3), where the $C_\beta$ carbons reside almost in the plane defined by N-$C_4$-$C_\alpha$ (cf., dihedral angles, ∠N-$C_4$-$C_\alpha$-$C_\beta$ and ∠$C_5$-$C_4$-$C_\alpha$-$C_\beta$ Table 3) even for the molecules that possess sterically bulky substituents at the $C_5$ position (e.g., **2n**, **2q**).

This is, to the best of our knowledge, the first example which demonstrates that the allene bond deviates from linearity in the absence of any steric factors (e.g., ring strain, torsional strain and/or packing effects).[13, 20]

In order to address the reason why **2** take such an unfavorable configuration and conformation on steric grounds, we examined the quantum mechanical calculations. The RHF/3-21G* optimized parameters for the atomic angles for the allene bond of 4-vinylidene-2-oxazolidinones with H, Me, $SO_2$Me, $SO_2$-*o*-Tol, and $SO_2$-*p*-Tol substituents on the nitrogen atom are listed in Table 4, together with the angles determined by X-ray studies (in parentheses). The results indicate that a clear-cut discrepancy does exist in the optimized bond angles between *N*-H, -Me derivatives and *N*-sulfonyl derivatives; the *N*-H and *N*-Me derivatives are the most stable with an almost linear allene bond, irrespective of the $C_5$ substituents while, in good accord with the experimental results, *N*-sulfonyl derivatives take uniformly a bent allene bond. The amount of the bending angle determined by calculation is about 5°.

The population analysis based on the Merz–Kollman scheme (MSK) in shown in Figure 3; the values were evaluated at Becke3LYP/6-31+G*//RHF/3-21G*) for the simplest allene carbamate **2c**. For the most stable parallel conformer a) the oxygen atom, pointing to $C_\alpha$, carries a considerable amount of negative charge (−0.45), which is

Table 4. Allene bond angles [°] of 4-vinylidene-2-oxazolidinones calculated at RHF/3-21G(*). Values in parentheses were determined by X-ray crystallographic analyses.

| | | N–H | N–Me | N–$SO_2$Me | N-$SO_2$-*o*-Tol | N-$SO_2$-*p*-Tol |
|---|---|---|---|---|---|---|
| C5 | H,H | 178.9 | 178.5 | 174.8 | 174.0 (174.5) | 175.0 (172.5) |
| $C_5$ | H,Me | – | – | – | – | 174.9 (175.3) |
| $C_5$ | Me,Me | 178.8 | 178.4 | 174.9 | – | 175.2 (176.0) |
| $C_5$ | $(CH_2)_4$ | 179.0 | 178.5 | 174.9 | – | 175.0 (172.4) |

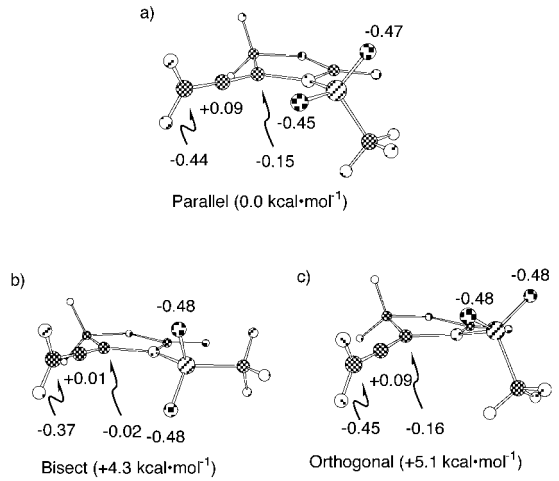
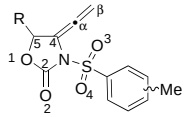



Figure 3. Population analyses of **2c** based on MSK scheme.

Table 3. Selected bond and dihedral angles [°] and bond lengths [Å] of 4-vinylidene-2-oxazolidinones **2**.



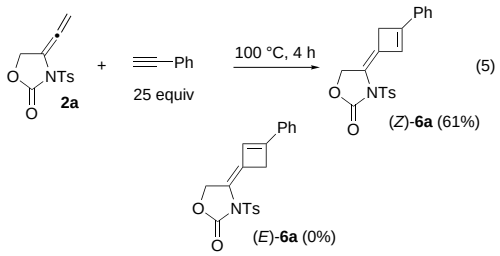

| | **2a** | **2b** | **2g** | **2k** | **2m** | **2n** | **2p** | **2q** |
|---|---|---|---|---|---|---|---|---|
| | | | | angles | | | | |
| $C_4$-$C_\alpha$-$C_\beta$ | 172.5 | 174.5 | 175.3 | 173.6 | 176.0 | 172.4 | 175.0 | 173.5 |
| N-$C_4$-$C_\alpha$ | 128.7 | 129.2 | 129.5 | 130.4 | 129.5 | 129.5 | 125.8 | 129.8 |
| $C_5$-$C_4$-$C_\alpha$ | 126.8 | 127.0 | 125.9 | 126.3 | 126.2 | 126.0 | 130.4 | 125.6 |
| N-$C_4$-$C_5$ | 104.5 | 103.8 | 104.5 | 103.3 | 104.3 | 104.5 | 103.7 | 104.5 |
| $C_2$-N-$C_4$ | 109.0 | 110.5 | 109.0 | 112.2 | 110.0 | 111.0 | 109.8 | 111.0 |
| $C_2$-N-S | 122.0 | 121.5 | 123.0 | 120.5 | 122.3 | 119.7 | 122.0 | 121.0 |
| S-N-$C_4$ | 125.0 | 127.8 | 124.7 | 127.3 | 125.4 | 125.3 | 127.5 | 126.9 |
| $O_3$-S-N-$C_4$ | 31.0 | 2.9 | 31.8 | 6.7 | 25.2 | 20.4 | −16.6 | −6.8 |
| S-N-$C_4$-$C_\alpha$ | −14.2 | 10.2 | −15.0 | 13.9 | −0.5 | −28.3 | −16.0 | 11.9 |
| N-$C_4$-$C_\alpha$-$C_\beta$ | −163.0 | −176.9 | −147.5 | 164.5 | 166.3 | 174.6 | 81.5 | 180.0 |
| $C_5$-$C_4$-$C_\alpha$-$C_\beta$ | 15.3 | 5.7 | 28.5 | 14.6 | −12.6 | −8.8 | −102.8 | 2.0 |
| | | | | bond lengths | | | | |
| $O_1$–$C_2$ | 1.334 | 1.338 | 1.318 | 1.479 | 1.337 | 1.338 | 1.341 | 1.333 |
| $C_2$–N | 1.398 | 1.394 | 1.413 | 1.396 | 1.400 | 1.396 | 1.398 | 1.391 |
| N–$C_4$ | 1.434 | 1.435 | 1.429 | 1.406 | 1.432 | 1.437 | 1.433 | 1.431 |
| $C_4$–$C_5$ | 1.487 | 1.500 | 1.496 | 1.497 | 1.520 | 1.523 | 1.521 | 1.519 |
| $C_5$–$O_1$ | 1.435 | 1.431 | 1.431 | 1.402 | 1.466 | 1.470 | 1.486 | 1.462 |
| $C_4$–$C_\alpha$ | 1.296 | 1.295 | 1.291 | 1.276 | 1.298 | 1.286 | 1.300 | 1.294 |
| $C_\alpha$–$C_\beta$ | 1.283 | 1.297 | 1.292 | 1.285 | 1.293 | 1.290 | 1.293 | 1.302 |
| $C_2$–$O_2$ | 1.195 | 1.192 | 1.191 | 1.193 | 1.193 | 1.202 | 1.194 | 1.195 |
| N–S | 1.683 | 1.673 | 1.687 | 1.711 | 1.680 | 1.686 | 1.681 | 1.678 |
| $C_\alpha \cdots O_3$ | 2.854 | 2.829 | 2.837 | 2.852 | 2.845 | 2.834 | 2.867 | 2.817 |

apparently less than that of the other oxygen atom (−0.47). The bisect b) and orthogonal c) conformers are higher in energy by 4.3 and 5.1 kcal mol$^{-1}$, respectively, as compared with the parallel conformer a). From the results of the calculations we conclude that the stability of the bent bond structure of allenes **2** of the parallel conformer a) is brought about by a charge transfer type interaction between the oxygen of the parallel S=O bond and the $C_\alpha$=$C_\beta$ double bond, that is, an $n_O - \pi^*(C_\alpha{=}C_\beta)$ interaction. This n−π* interaction may be substantiated by the low-lying LUMO ($C_\alpha$=$C_\beta$), which might be caused by $\pi^*(C_\alpha{=}C_\beta) - \sigma^*(N\text{-}SO_2)$ interaction. These orbitals are aligned parallel in close proximity to each other and might be able to interact through space effectively.

**Concerted thermal [2 + 2] cycloaddition of 2 at the terminal $C_\alpha$=$C_\beta$ bonds with alkynes, alkenes, and dienes**: When **2a** was heated in an excess amount of phenylacetylene at 100 °C for 4 h, a spot of **2a** ($R_f$ = 0.45, hexane/AcOEt 2:1 *v*/*v*) disappeared completely and a new spot ($R_f$ = 0.55) appeared on the TLC [Eq. (5)]. The $^1$H NMR spectrum of the crude reaction mixture measured after removal of excess phenylacetylene under reduced pressure revealed that product **6a** was composed of a single isomer, which decomposed gradually in an NMR tube upon standing for several hours at room temperature. Crystallization from dichloromethane/hexane provided **6a** as a fine colorless solid, which also partially decomposed and the color turned brown even in a refrigerator within a few days.

Of the two conceivable stereoisomers, we first expected the structure of **6a** to be (*E*)-**6a**, simply because of the easier access of acetylene to **2a** from the less crowded side of the allene bond, being distal from the *N*-sulfonyl group. Surprisingly, however, NOE experiments of the product indicated




(5)

that **6a** should in fact be (*Z*)-**6a** (Figure 4). The reproducibility of the experiment was confirmed by three individual runs. Each time, the absence of (*E*)-**6a** was confirmed by close scrutiny of the $^1$H NMR spectra (400 MHz).

In order to confirm this unexpected high stereoselectivity, we next examined ethyl propiolate as an alkyne of different electronic nature under similar reaction conditions (run 1, Table 5). To our pleasant surprise, the reaction proceeded much smoother and was completed within 4 h at 80 °C, giving rise to (*Z*)-**6b** as a single isomer. The methylenecyclobutene product (*Z*)-**6b** (m.p. 66.0–66.5 °C from $CH_2Cl_2$/hexane) again turned out to be rather unstable especially in a solution under air; the color gradually turned brown or black-brown.[21]

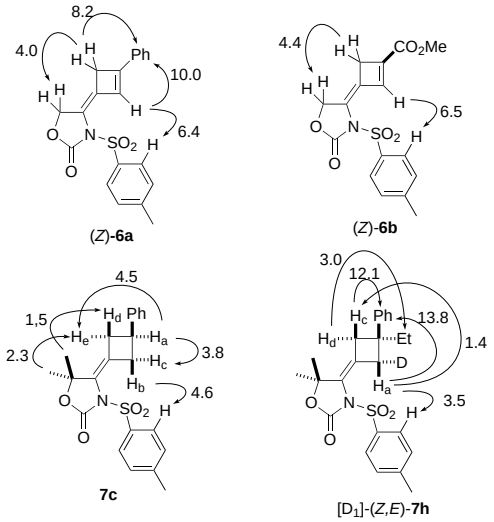
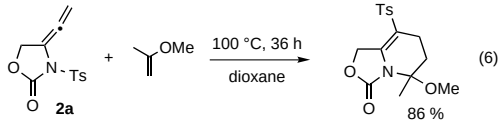



Figure 4. NOE increment (%) determined by $^1$H NMR (400 MHz).

Encouraged with the unique and unprecedented reactivity of the allene bond of **2** toward alkynes, we next examined extensively the reaction with alkenes of a wide structural and electronic variety. The results are summarized in Table 5. In general, alkenes bearing conjugated π-systems (e.g., styrenes and dienes) and electron-withdrawing groups showed parallel results. The results for the reactions with dienes are summarized separately in Table 6.

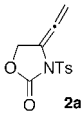
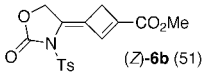
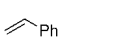
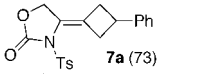
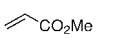
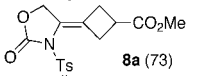
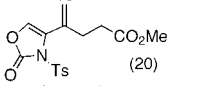
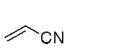
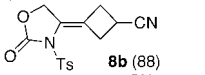
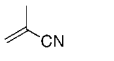
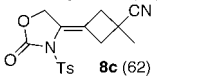
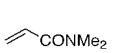
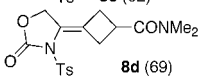
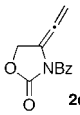
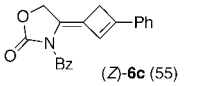
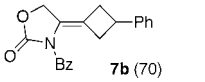
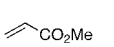
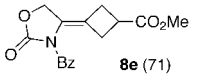
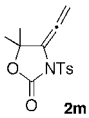
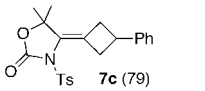
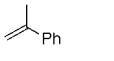
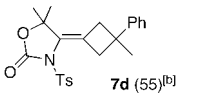
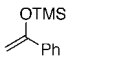
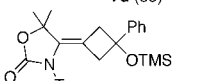
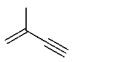
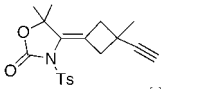
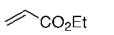
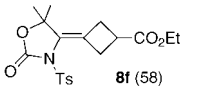
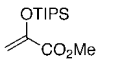
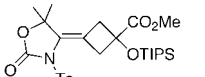
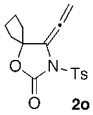
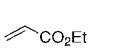
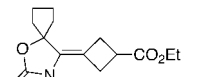
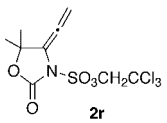
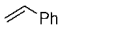
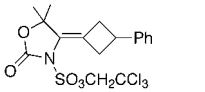
Alkenes bearing electron-donating substituents (e.g., enol ethers,[22] allylsilanes)[23] displayed a completely different reactivity [Eq. (6)]. They induced 1,3-sulfonyl migration and provided tetrahydropyridines formed by a formal [4 + 2] cycloaddition reaction. This type of reactivity of **2** is general toward a variety of other nucleophiles, encompassing alcohols, silanes (ΣSiH), indoles; the results will be reported elsewhere in due course. Simple alkenes, such as 1-decene and 3-phenyl-1-propene, were unreactive and **2** were recovered in almost all cases.




(6)

In contrast to the instability of methylenecyclobutenes **6**, methylenecyclobutanes, **7** and **8**, were stable and could be readily purified by means of column chromatography over silica gel and/or, in some instances, direct crystallization from the reaction mixtures. As might be apparent from Table 5, no discernible differences in reactivity among **2** were observed, although they differed in the N-substituents and the $C_5$ substituents. Adamantane derivative **2p** was one exception, which was totally unreactive and was recovered quantitatively by exposure to styrene and acrylonitrile under usual and even somewhat harsh conditions (100 °C for 10 h). The adamantyl group may sterically protect the allene bond from an attack of these alkenes.

Table 5. Thermal [2+2] cycloaddition of **2** with alkynes and alkenes.[a]

| Run | Allene **2** | Alkene or alkyne | $T$ [°C]/ $t$ [h] | Product (% isolated yield) |
|---|---|---|---|---|
| 1 |  **2a** |  | 80/4 |  (*Z*)-**6b** (51) |
| 2 | **2a** |  | 100/22 |  **7a** (73) |
| 3 | **2a** |  | 80/22 |  **8a** (73) |
| | | | |  (20) |
| 4 | **2a** |  | 80/17 |  **8b** (88) |
| 5 | **2a** |  | 80/10 |  **8c** (62) |
| 6 | **2a** |  | 80/22 |  **8d** (69) |
| 7 |  **2d** |  | 80/23 |  (*Z*)-**6c** (55) |
| 8 | **2d** |  | 80/46 |  **7b** (70) |
| 9 | **2d** |  | 80/22 |  **8e** (71) |
| 10 |  **2m** |  | 100/5 |  **7c** (79) |
| 11 | **2m** |  | 80/48 |  **7d** (55)[b] |
| 12 | **2m** |  | 80/48 |  **7e** (55)[b] |
| 13 | **2m** |  | 80/120 |  **7f** (55)[c] |
| 14 | **2m** |  | 80/17 |  **8f** (58) |
| 15 | **2m** |  | 100/8 |  **8g** (98)[d] |
| 16 |  **2o** |  | 80/13 |  **8h** (55) |
| 17 |  **2r** |  | 80/10 |  **7g** (88)[d] |

[a] Unless otherwise specified, **2** (0.5 mmol) and alkyne or alkene (4.0 mL, 30–60 mmol) were heated under $N_2$. [b] **2** (0.5 mmol) and alkene (5.0 mmol) were heated under $N_2$. [c] **2** (0.5 mmol) and alkene (10.0 mmol) in dioxane (1.0 mL) were heated in a sealed tube under $N_2$. [d] **2** (0.5 mmol) and an alkene (10.0 mmol) were heated under $N_2$.

Among the data in Table 5, the selective reaction of 2-methylbut-1-en-3-yne at the double bond, giving rise to **7f** (run 13) and a quantitative formation of **8g** by the reaction with methyl $\alpha$-siloxyacrylate are especially impressive (run 15). These results along with the reaction with $\alpha$-(trimethylsiloxy)styrene (run 12) demonstrate that the present [2+2] cycloaddition is highly tolerant of a wide range of alkenes with different electronic nature; this is in sharp contrast to the reaction pattern displayed by simple electron-rich alkenes [Eq. (6)].

Interestingly, however, the reaction is tolerant only of terminal alkenes and alkynes. Internal alkenes, such as methyl $\beta$-methylacrylate, $\beta$-methylacrylonitrile, $\beta$-phenylacrylonitrile, 2-cyclohexenone, dimethylmaleate, and internal alkynes, such as dimethyl acetylenedicarboxylate and diphenylacetylene, were all unreactive and resulted in a recovery (or slight decomposition) of **2** under usual reaction conditions. All attempts employing higher temperature and longer reaction time (e.g., 120 °C for 1 d) resulted only in the decomposition of **2**.

The decisively low reactivity of internal alkenes might be rationalized by assuming that the alkenes would react with **2** in similar way to alkynes and the allylic methylenes of the cyclobutane ring *syn* to *N*-Ts might be delivered from the alkene terminal carbons. The methylene groups of **7** and **8** *syn* to *N*-Ts suffer from allylic strain against the *N*-Ts group. Therefore, there is not enough room to accommodate substituents on the methylene carbon.

In fact, this proved to be the case. In order to clarify the stereochemical course of the [2+2] cycloaddition reaction, commercial [$D_8$]styrene was used as a probe [Eq. (7) and (8)]. The 400 MHz $^1$H NMR spectrum of the cyclobutane part of the product [$D_8$]-**7c** (b) is shown in Figure 5 along with that of **7c** (a) for comparison. Fortunately, all the methylene protons and the methyne proton of **7c** appeared separately and could be assigned unequivocally as indicated in Figure 5a on the basis of NOE experiments (Figure 4).

Comparison of Figure 5a and b clearly indicates that [$D_8$]-**7c** is composed of a single stereoisomer and possesses a (*Z*)-structure, since the methylene protons *syn* to the tosyl group, $H_b$ and $H_c$, of **7c** disappear completely and the methylene protons *anti* to the tosyl group, $H_d$ and $H_e$, remain and appear as a pair of doublets. The absence of a pair of doublets ascribable to $H_b$ and $H_c$ of the other stereoisomer, (*E*)-[$D_8$]-**7c**, indicates that the degree of stereoselectivity is more than 97% (a limit of $^1$H NMR detection). The reaction of **2a** with [$D_8$]styrene showed completely parallel results [Eq. (7)], though the $^1$H NMR spectra of **7a** and (*Z*)-[$D_8$]-**7a** appeared not as simple as those of **7c** and [$D_8$]-**7c** owing to a long-range coupling with the $C_5$ methylene protons.[21]

Parallel results were obtained for the reactions of **2a** with [$D_5$]-$\alpha$-methylacrylonitrile [97% atom D, Eq. (9)] and **2m** with $\beta,\beta$-dideuterio-$\alpha$-(trimethylsiloxy)styrene [96% atom D, Eq. (10)], where [$D_5$]-(*Z*)-**8c** and [$D_2$]-(*Z*)-**7e**, respectively, were produced exclusively.[21] The results given in Equations (7)–(10) clearly indicate that the allylic methylene groups of methylenecyclobutanes *syn* to the *N*-Ts group originate from the terminal $sp^2$ carbons of alkenes, irrespective of the stereoelectronic nature of the substituents.

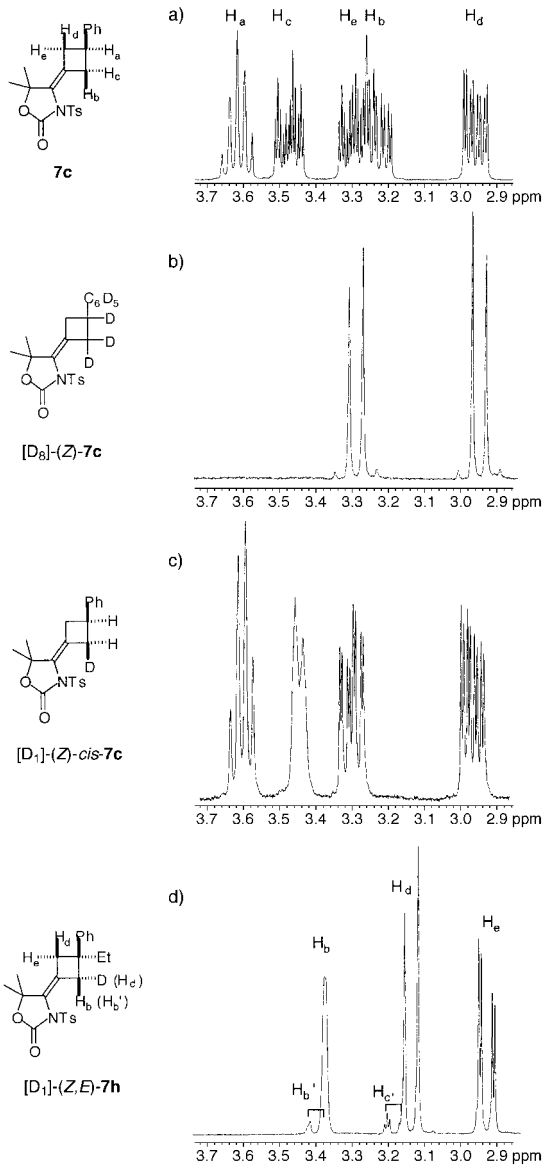
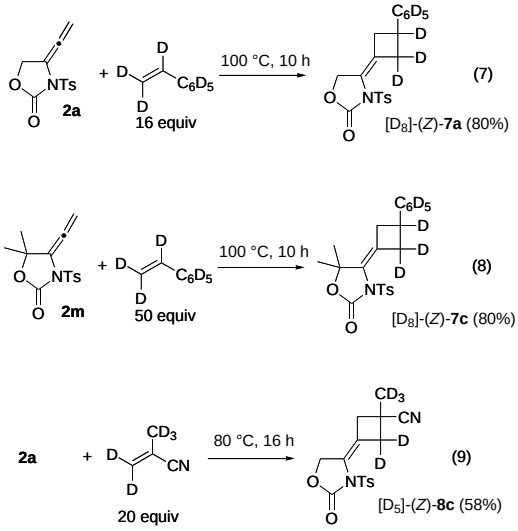
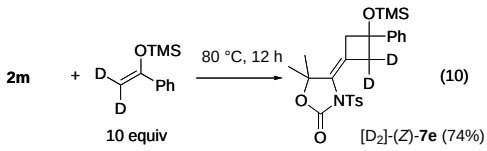
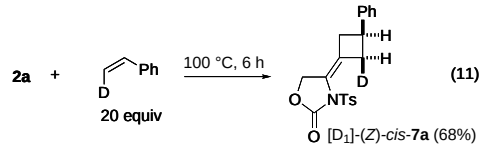


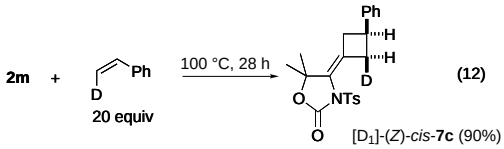

Figure 5. $^1$H NMR spectra (400 MHz) of the cyclobutane moieties of **7c** (a), (*Z*)-[$D_8$]-**7c** (b), (*Z*)-*cis*-[$D_1$]-**7c** (c), and (*Z*,*E*)-[$D_1$]-**7h** (d). In (d), the small peaks, $H_b'$ and $H_c'$, are due to [$D_0$]-$\alpha$-ethylstyrene.



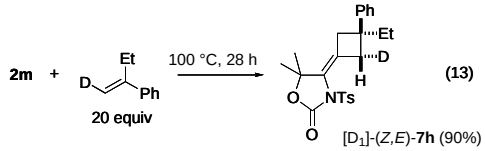




In order to shed more light on the stereochemical course, we next examined the reaction of **2a** and **2m** with *cis*-$\beta$-monodeuteriostyrene (96% atom D) [Eq. (11) and (12)], and we were gratified to find that these reactions proceeded with complete retention of configuration of the double bond (Figure 5c).[24] Disappearance of the resonance of $H_b$, no change in the coupling pattern of $H_d$, coalescing of the resonance of $H_e$ from a ddt to a ddd, and a change in the absorption of $H_c$ from a ddt to a broad doublet, all combine to indicate the substitution of D for $H_b$.




Furthermore, stereochemically defined trisubstituted alkene, (*E*)-$\alpha$-ethyl-$\beta$-monodeuteriostyrene [90% atom D, Eq. (13)], was subjected to the reaction. Figure 5d and the

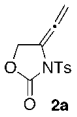
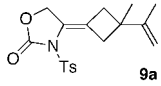
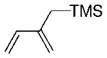
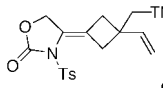
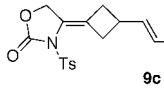
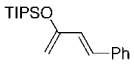
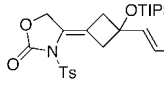
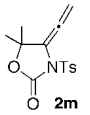
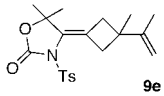
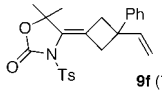
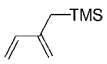
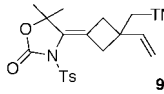
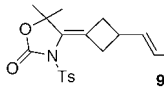
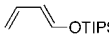
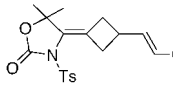
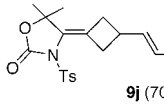
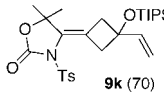
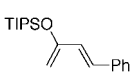
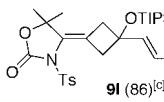
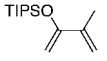
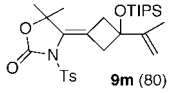
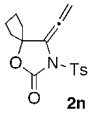
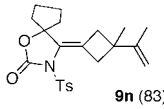



NOE data in Figure 4 clearly indicate that the reaction proceeds stereoselectively and the selectivity is more than 97% (a limit of $^1$H NMR detection).[24] The product (*Z*,*E*)-[$D_1$]-**7h** is *Z* with respect to the exocyclic double bond and *E* with respect to the substituents of the cyclobutane ring. The spectrum is contaminated by small peaks $H_b'$ (br d) and $H_c'$ (dt), which are apparently attributed to the product formed by the reaction with non-deuterated $\alpha$-ethylstyrene (10%) present in the starting material as a contaminant.

Allenes are good reaction partners in the Diels–Alder reaction and serve as reactive dienophiles.[25, 26] The internal allene double bonds of vinylallenes form a 4π-system in conjunction with the vinyl groups and, in turn, they serve as reactive dienes toward a variety of dienophiles.[26a, 27] In sharp contrast, the allene of **2** displayed no dienophilic reactivity toward a variety of dienes, but instead, selectively underwent [2+2] cycloaddition to provide 3-vinyl-1-methylenecyclobu-

tanes **9** in good to excellent yields (Table 6).[6, 28] Furthermore, in general, the [2+2] cycloaddition of **2** with dienes proceeded much easier than that with alkenes and alkynes. This may be apparent by comparing the reaction conditions shown in Tables 5 and 6; for the reaction with dienes, in most cases, 10 equivalents or less of dienes (runs 4 and 12) were used. In addition, the reactions proceeded smoothly even as a diluted solution in dioxane. Dioxane was used uniformly as a solvent in order to avoid the loss of dienes by evaporation.

Table 6. Thermal [2+2] cycloaddition of **2** with 1,3-dienes.[a]

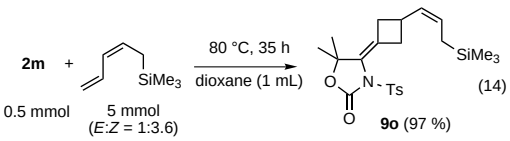
| Run | Allene | 1,3-Diene | $T$ [°C]/ $t$ [h] | Product (% isolated product) |
|---|---|---|---|---|
| 1 |  **2a** |  | 70/44 |  **9a** (75)[b] |
| 2 | **2a** |  | 80/36 |  **9b** (80) |
| 3 | **2a** |  | 80/9 |  **9c** (30) |
| 4 | **2a** |  | 80/22 |  **9d** (73)[c] |
| 5 |  **2m** |  | 70/91 |  **9e** (68) |
| 6 | **2m** |  | 80/10 |  **9f** (70) |
| 7 | **2m** |  | 80/42 |  **9g** (90) |
| 8 | **2m** |  | 80/22 |  **9h** (65) |
| 9 | **2m** |  | 80/22 |  **9i** (86) |
| 10 | **2m** |  | 80/29 |  **9j** (70) |
| 11 | **2m** |  | 80/42 |  **9k** (70) |
| 12 | **2m** |  | 80/22 |  **9l** (86)[c] |
| 13 | **2m** |  | 100/37 |  **9m** (80) |
| 14 |  **2n** |  | 80/45 |  **9n** (83) |

[a] Unless otherwise specified, **2** (0.5 mmol) and diene (5.0 mmol) in dioxane (0.5 mL) were heated under $N_2$. [b] **2** (0.5 mmol) and diene (20 mmol) in dioxane (1.5 mL) were heated under $N_2$. [c] **2** (0.5 mmol) and a diene (2.0 mmol) in dioxane (0.5 mL) were heated under $N_2$.

The exclusive [2+2] preference over [4+2] cycloaddition associated with **2** is quite remarkable taking into consideration the fact that [2+2] cycloaddition of allenes and dienes has been reported sporadically only for a limited number of intramolecular reactions, where allenes and dienes are designed deliberately to undergo [4+2] cycloaddition under great difficulty.[29]

A general trend has been observed for the regioselectivity of dienes; one of the two double bonds undergoes reaction selectively; 1) 1-substituted dienes react at the distal nonsubstituted 3,4-double bonds (e.g., runs 3 and 9, Table 6), 2) 2-substituted dienes react selectively at the 1,2-double bonds irrespective of the electronic nature of the substituents (e.g., runs 2, 6, and 11), and 3) unsymmetrically 2,3-disubstituted dienes react selectively at the double bonds with higher electron density (run 13). For example, although both the methyl and triisopropylsilyloxy groups of 2-methyl-3-triisopropylsiloxy-1,3-butadiene are electron-donating, the latter is by far more powerful in the ability; hence, this diene reacted exclusively at the $C_3$–$C_4$ double bond and provided **9m** as a single product (run 13).

It should be noted that dienes bearing siloxy substituents either at the 1- or at the 2-position (runs 4, 9, and 13), like $\alpha$-siloxystyrene [run 12, Table 5 and Eq. (10)], all undergo [2+2] cycloaddition, which is in contrast to the reaction behavior that simple vinyl ethers display [Eq. (6)].[22] The geometry of dienes was retained completely in the products, that is, *trans* dienes provided 3-(*trans*-1-alkenyl)methylenecyclobutanes (e.g., runs 3, 4, and 8–10) and *cis*-dienes 3-(*cis*-1-alkenyl)methylenecyclobutanes exclusively [Eq. (14)]. A mixture of *cis*- and *trans*-5-trimethylsilyl-1,3-pentadiene (*E*:*Z* 1.0:3.6) provided **9o** as a single isomer in excellent yield. Interestingly, the reaction with a *trans*-enriched mixture (*E*:*Z* 4:1, obtained by isomerization of the *cis*-rich mixture by catalytic amounts of phenylmercaptane/azobisisobutyronitrile (AIBN), benzene reflux) was very slow and provided **9o** in 45% isolated yield with recovery of **2m** in 30% yield under the same reaction conditions as Equation (14) (96 h). These results indicate that only *cis*-5-trimethylsilyl-1,3-pentadiene participates in these reactions and provide **9o** with retention of configuration of the double bond.




As was observed for internal alkynes and alkenes and in good accord with 1), described above, internal dienes, such as 1,3-cyclohexadiene and 1,3-cyclopentadiene, were also unreactive and no expected products were obtained at all.

The mechanistic details associated with the thermal [2+2] cycloaddition (either concerted or stepwise) constitute a topic of much study and debate. Most studies, evidenced by the

regio- and stereochemical outcomes[6, 9–11, 26, 27] and H/D isotope effects,[9e] seem to strongly favor a stepwise biradical mechanism. In sharp contrast to this, all experimental results obtained for the [2+2] addition of **2** with a wide variety of alkynes, alkenes and 1,3-dienes presented here seem to point to a concerted mechanism involving a six-electron Hückel $[(\pi_{2s}+\pi_{2s})_{allene}+\pi_{2s}]$ transition state, proposed by Pasto[10e] and predicted by Fukui et al. based on the frontier orbital theory (Figure 6).[30]

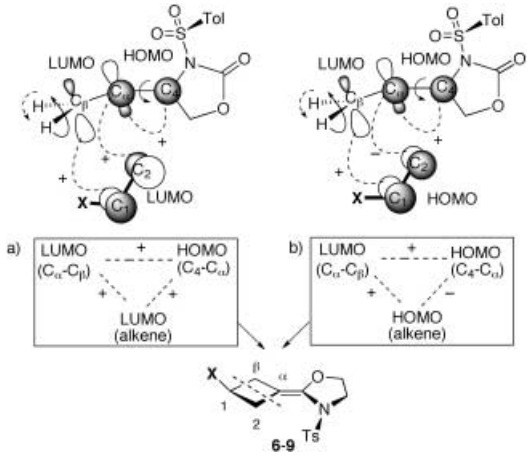



Figure 6. Possible explanation for a thermal, concerted [2+2] cycloaddition based on "the orbital interaction in three-systems".[30] a) Reactions for electron-deficient alkenes and alkynes. b) Reactions for electron-rich and conjugated alkenes and alkynes.

The unique reactivity associated with **2** might be primarily attributed to a strong $\sigma^*(N-SO_2)-\pi^*(C_\alpha{=}C_\beta)$ interaction of **2a**, **m**, **o**, **r** (or $\sigma^*(N-CO)-\pi^*(C_\alpha{=}C_\beta)$ interaction for **2d**), which causes 1) the lowering of the $\pi^*(C_\alpha{=}C_\beta)$ energy level (and hence, lowering of the activation energy for the [2+2] addition) and 2) the rehybridization of the $\pi^*(C_\alpha{=}C_\beta)$ orbitals ($sp^3$-like, and hence, better overlap between the p orbitals of alkene $C_1$ and allene $C_\beta$ in the opposite face to *N*-Ts). As is illustrated in Figure 6a for electron-deficient alkynes and alkenes and in Figure 6b for electron-rich and conjugated alkynes and alkenes, the three-system interaction,[30] with a coaxial overlap of the p orbitals of $C_\alpha$ and $C_2$ and a perpendicular overlap of the p orbitals of $C_\beta$ and $C_1$, necessitates a 90° counter-clockwise rotation of the oxazolidinone ring (i.e., a rotation of the *N*-Ts group toward $C_2$) to furnish (*Z*)-**6**–**9**.

The mechanism proposed here was supported by the RHF/3-21G* concerted transition-state structures and the geometrical transformation along the intrinsic reaction coordinate for the reaction of **2a** ($SO_2Me$ in place of $SO_2Tol$) with acrylonitrile (Figure 7a) and methyl $\alpha$-methylvinyl ketone (Figure 7b). An alternative coaxial approach of the p orbitals of C$\beta$ and $C_1$, accompanied with perpendicular interaction between the p orbitals of $C_\alpha$ and $C_2$, could hardly be reconciled with the reactivity observed for **2m** and **2n**, since the bulky $C_5$ substituents of these allenes would render this mode of approach sterically unfavorable.

The transition-state structures a) and b) in Figure 7 are apparently asynchronous and similar to the one located by

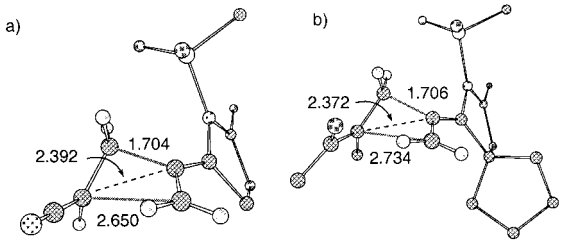



Figure 7. RHF/3-21G* transition structures leading to **8b** (a) and **8k** (b) with $SO_2Me$ in place of $SO_2$-*p*-Tol. For clarity, all hydrogens except the hydrogens on the reaction centers were omitted. For further discussion of the TS structure b) leading **8k**, see next Section.

quantum mechanical methods for the concerted [2+2] cycloaddition of ketene and ethylene;[7l] the single bonds between the $C_\alpha$ and the alkene $C_2$ are almost fully formed (1.70–1.71 Å). The other incipient carbon–carbon bonds, between $C_\beta$ and the alkene $C_1$, are much longer (2.65–2.73 Å). The $C_1$ carbons are in fact much closer to the $C_\alpha$ in the transition states (2.37–2.39 Å) than to the $C_\beta$ to which they will be bonded in the products.

**Concerted thermal [4+2] and [3+2] cycloadditions of 2 at the internal double bonds with enones and nitrile oxides**: In contrast to the fact that electron-deficient alkenes, such as acrylonitrile, acrylamide, and ethyl acrylate, selectively underwent [2+2] cycloaddition toward **2** at the terminal $C_\alpha{=}C_\beta$ bonds (Table 5), a similarly electron-deficient ketone, methyl vinyl ketone, displayed completely different reactivity; this ketone selectively reacted with **2n** at the internal $C_4{=}C_\alpha$ bond, giving rise to a spiro compound, **10a**, as the major product along with a [2+2] cycloaddition product **8i** as the minor product (run 1, Table 7). Other enones that display this inverse electron demand [4+2] cycloaddition reactivity[31] are summarized in Table 7.[32]

The common structural feature of electron-deficient alkenes that show [4+2] reactivity is that they are all $\alpha,\beta$-unsaturated aldehydes and ketones. Judging from the reaction conditions (temperature, time, and equivalency of enones relative to **2**), the enones are more reactive than the electron-deficient alkenes listed in Table 5. The ratio of **10** to **8** largely depends on the kind of enones, ranging from 80:18 (% isolated yield, run 1) for methyl vinyl ketone to 11:83 (run 4) for $\alpha$-methylacrolein.

Before discussing the product ratios in detail, it should be clarified whether the ratios are due to either kinetic or thermodynamic control, because the cyclobutane C–C bonds of **8i**–**l** and the dihydropyran C–O bonds of **10a**–**d** [indicated with a dotted line, Eq. (15)] are expected to undergo heterolytic cleavage, giving rise to zwitterionic intermediates III (a pair of +/−) characterized by the carbanions stabilized by aldehyde or ketone and the allylic

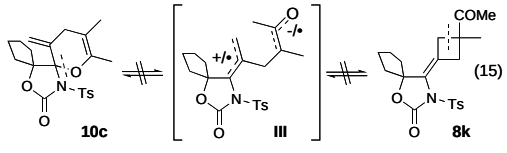
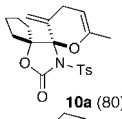
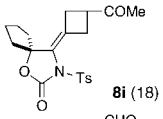
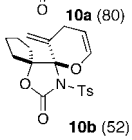
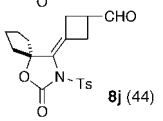
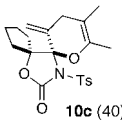
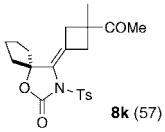
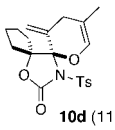
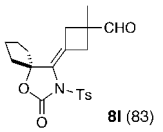


Table 7. Concomitant thermal [4 + 2] and [2 + 2] cycloaddition reaction of enones with **2n**.

| Run | Enone | $t$[a] [h] | Yield [%] of **10** and **8**[b] **10** | **8** | $E_{act}$[c] **10** | **8** |
|---|---|---|---|---|---|---|
| 1 |  | 2 |  **10a** (80) |  **8i** (18) | −3.0 | 3.4 |
| 2 |  | 6 |  **10b** (52) |  **8j** (44) | 0.0 | 0.0 |
| 3 |  | 14 |  **10c** (40) |  **8k** (57) | 9.3 | 7.3 |
| 4 |  | 10 |  **10d** (11) |  **8l** (83) | 12.7 | 2.7 |

[a] Allene **2n** and enone (20 equiv) were heated at 80 °C under $N_2$. [b] Yields refer to the isolated materials by means of column chromatography over silica gel. [c] Relative activation energies [kJ mol$^{-1}$] for TSs leading to **10** and **8** calculated at the Becke3LYP/6-31G* level based on the RHF/3-21G* optimized geometries (the reaction with acrolein as a standard).

carbocations stabilized by the nitrogen atom.[28a] These bonds are also subject to homolytic cleavage, giving rise to biradical intermediates III (a pair of ●/●). Accordingly, we examined a set of thermal isomerization experiments, that is, heating of pure, isolated **8k** and **10c** separately at 80 °C for 68 h using 20 equivalents of methyl $\alpha$-methylvinyl ketone as a solvent. The results were clear-cut and no isomerization between them took place at all, that is, **8k** and **10c** were recovered quantitatively, indicating that the product distributions listed in Table 7 are the ones controlled kinetically.

It is worth noting that the behavior of **2** is in sharp contrast to that of *N*-allenyl-2-oxazolidinones of close structural similarity, reported recently by Hsung et al.,[33] which exclusively undergo inverse electron demand [4 + 2] cycloaddition upon exposure to a variety of enones and enals, including methyl vinyl ketone and acrolein.

The product distribution in Table 7 may be rationalized qualitatively by supposing that the substituents $R^1$ and $R^2$ (Figure 8) that are capable of increasing a negative charge on the oxygen and a positive charge on the terminal $CH_2$, respectively, would promote [4 + 2] cycloaddition. For example, the methyl group of methyl vinyl ketone increases the electron density on the O atom and promotes the inverse electron demand hetero Diels–Alder reaction (run 1, Table 7), while the methyl group of $\alpha$-methacrolein decreases a positive charge on the terminal $CH_2$ and retards the hetero Diels–Alder reaction (run 4). Of the two methyl groups of methyl $\alpha$-methylvinyl ketone, the methyl group attached to C=O increases a negative charge on the O atom, while

Figure 8.

the methyl group at the $\alpha$-position of the vinyl group decreases a positive charge on the terminal $CH_2$ carbon. As a consequence, these two methyl groups offset their electronic effects, giving rise to a mixture of **10c** and **8k** in almost the same amounts (run 3).

In order to test the feasibility of this explanation, the reaction of run 3 was examined in polar solvents in expectation that in such solvents a transition state leading to **10c** involving such polarized enone as a reaction partner might be stabilized and **10c** would be formed in a higher proportion. However, on the contrary, **10c** was obtained in significantly lesser amounts in polar solvents: **10c** and **8k** in 9 and 78% yields in ethanol (61 h at reflux) and 23 and 70% yields in DMSO (38 h at 80 °C), respectively.

In order to rationalize these unexpected results, pathways leading to **8** and **10** were analyzed with quantum mechanical methods using GAUSSIAN 98 program[34] with density functional theory (DFT).[35] Relative activation energies ($E_{act}$), investigated at the Becke3LYP/6-31G* level based on the RHF/3-21G* optimized geometries, are tabulated in Table 7; the reaction with acrolein was set as a standard (run 2).

Figure 9 shows two pairs of TSs leading to **8j** (a) and **10b** (b) (reaction with acrolein) and **8k** (c) and **10c** (d) (reaction with methyl $\alpha$-methylvinyl ketone) that are located utilizing a gradient method without any geometrical constraint at the RHF/3-21G* basis set.

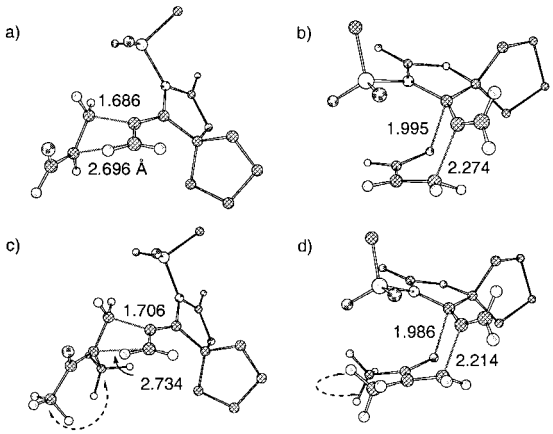


Figure 9. RHF/3-21G* transition structures leading to **8j** (a), **10b** (b), **8k** (c), and **10c** (d) with $SO_2Me$ in place of $SO_2$-*p*-Tol. For clarity, all hydrogens of **2n** except for the hydrogens on $C_\beta$ are omitted.

The activation energy for inverse electron demand [4 + 2] addition ($E_{act}$, [4 + 2]) changes as expected qualitatively (see above), and increases gradually in the order of run 1 to 4. On the other hand, the activation energy for [2 + 2] addition ($E_{act}$, [2 + 2]) scarcely depends on the electronic nature of enones; a part (3–4 kJ mol$^{-1}$) of the large $E_{act}$, [2 + 2] (as well as the $E_{act}$, [4 + 2] in run 3 may be attributed to steric repulsion between the eclipsed methyl groups indicated by double-headed curved arrow in Figure 9c and d.

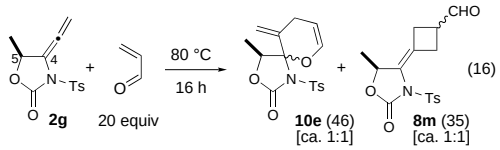
Interestingly, all TSs leading to **8i–l** turned out to possess s-*cis* conformation with respect to the enone double bond and carbonyl, although the corresponding s-*trans*-methyl vinyl ketone, acrolein, methyl $\alpha$-methylvinyl ketone, and $\alpha$-methylacrolein are more stable in energy by 0.7, 9.0, 4.0, and

13.7 kJ mol$^{-1}$, respectively. The unusual stabilization of s-*cis* conformers is probably attributed to (C=)O···H-C$_\beta$ type electrostatic attractive interaction [*d* C$_\beta$···O; 2.108 Å (**8i**), 2.008 Å (**8j**), 2.148 Å (**8k**), 2.162 Å (**8l**)].

A large amount of asynchronicity for [2+2] cycloaddition (Figures 7 and 9a, c), with the carbonyl (or cyano) group being exposed to the surroundings, is in good accord with a large solvent effect (see above). A small difference in the $E_{act}$, [2+2] is also in good accord with the fact that this process is tolerant to a wide range of alkenes and alkynes (see above).

Surprisingly, the inverse electron demand Diels–Alder reaction of **2g** and acrolein exhibited no facial stereoselectivity and furnished **10e** as a mixture of 1:1 diastereomers, although the event took place at the C$_4$ carbon next to a stereogenic center C$_5$ [Eq. (16)]. The non-stereoselective formation of **10** was also confirmed spectroscopically (400 MHz $^1$H NMR) for the other enones listed in Table 7.



(16)

This inconsistency was, however, resolved by inspections of the X-ray structure of **2g** (Figure 10); the TS structures are shown in Figure 9b and d. The C$_5$-methyl group of **2g** lies close to the oxazolidinone plane. Furthermore, enones approach the C$_4$=C$_\alpha$ π-bond with their two terminal p-orbitals not coaxially, but inclined a little away from C$_5$ (an endo-approach with respect to the enamide moiety of **2g**). Accordingly, in such a transition state, enones would react with **2g** without perceiving the C$_5$-Me group.

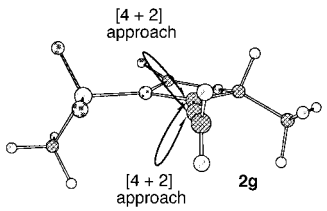
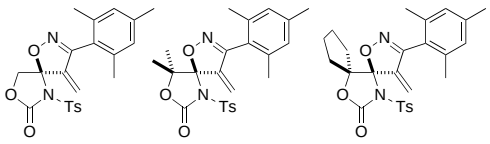



Figure 10. Chem 3D view of **2g** and top and bottom face approaches of enones. Double-headed arrows represent an approaching direction of enones (for clarity, *p*-tolyl is replaced by Me).

The results listed in Table 7 and Equation (16) suggest that the C$_4$=C$_\alpha$ double bonds of **2** possess an enamine-like reactivity. Accordingly, [3+2] cycloaddition of **2** with nitrile oxide was examined. Indeed, as was expected, **2a**,**m**,**o** all reacted smoothly with 2,4,6-trimethylbenzonitrile *N*-oxide[36] at the internal C$_4$=C$_\alpha$ bonds at room temperature and selectively provided diazadioxaspiro compounds **11a–c** in moderate yields (Figure 11).

## Conclusion

In this article, we have disclosed for the first time that the terminal allene C$_\alpha$=C$_\beta$ bonds of **2** showed a reaction profile as



**11a** (1 h, 50%) **11b** (6 h, 60%) **11c** (10 h, 66%)

Figure 11. [3+2] Cycloaddition of **2a**, **2m**, and **2o** with 2,4,6-trimethylbenzonitrile *N*-oxide. Reaction conditions: **2** (0.5 mmol) and nitrile oxide (1 mmol) in dry dioxane (1.5 mL) at 25 °C under N$_2$.

if they violated both the Woodward–Hoffmann rule and the Fukui frontier orbital theory, and readily underwent [2+2] cycloaddition with a wide variety of terminal alkynes, alkenes, and 1,3-dienes irrespective of their electronic nature under strictly thermal activation reaction conditions (70–100 °C) and provided 3-substituted (*Z*)-methylenecyclobutenes **6**, 3-substituted methylenecyclobutanes **7** and **8**, and 3-vinylmethylenecyclobutanes **9**, respectively, in good to excellent yields. Internal alkynes, alkenes, and 1,3-dienes were all unreactive. The [2+2] cycloaddition was concluded to proceed via a concerted [$(\pi_{2s}+\pi_{2s})_{allene}+\pi_{2s}$] Hückel transition state on the basis of stereochemical relationships between the starting alkynes/alkenes/1,3-dienes and the products as well as quantum mechanical methods. With some highly polarized alkenes (enones) and nitrile oxide, on the other hand, **2** reacted selectively at the internal C$_4$=C$_\alpha$ bond and underwent [4+2] and [3+2] cycloadditions to give spiro compounds **10** and **11**, respectively. The competition between [2+2] and [4+2] cycloadditions observed for some enones was rationalized on the basis of the relative activation energies of these two processes obtained by quantum mechanical calculations. The allene bonds of **2** significantly deviate from linearity (173–176°) owing to an attractive $n_O(=SO)-\pi^*(C_\alpha=C_\beta)$ charge transfer type interaction. The unique structure and reactivity associated with **2** may be primarily attributed to a low-lying LUMO (C$_\alpha$=C$_\beta$) that is substantiated by a through-space $\sigma^*(N-SO_2)-\pi^*(C_\alpha=C_\beta)$ orbital interaction.

## Experimental Section

Reactions employed oven-dried glassware unless otherwise noted. Thin-layer chromatography (TLC) employed glass 0.25 mm silica gel plates with UV indicator (Merck, silica gel 60F$_{254}$). Flash chromatography columns were packed with 230–400 mesh silica gel as a slurry in hexane. Gradient flash chromatography was conducted eluting with a continuous gradient from hexane to the indicated solvent. Melting points were determined on a Yanaco apparatus and are uncorrected. Boiling points refer to the Kugelrohr oven temperatures. Proton and carbon NMR data were obtained with a JEOL-GX400 with tetramethylsilane as an internal standard. Coupling patterns: q = quartet, quint = quintet. Chemical shift values were given in ppm downfield from the internal standard. Infrared spectra were recorded with a JASCO A-100 FT-IR spectrophotometer. High resolution mass spectra (HRMS) were measured with a JEOL JMS-DX303. Combustion analyses were performed by the Instrumental Analysis Center of Nagasaki University. Analysis agreed with the calculated values within ±0.4%.

**Solvents and reagents**: THF (tetrahydrofuran), Et$_2$O, and dioxane were distilled from sodium/benzophenone under N$_2$ prior to use. Triethylamine was distilled from CaH$_2$ under N$_2$. Alkenes, alkynes, enones were distilled prior to use in the presence of a small amount of *p*-methoxyphenol. 3,4-Dihydro-2*H*-pyran (Tokyo Chemical Industry) and but-2-yn-1,4-diol (Na-

calai Tesque) were purchased and used without further purification. *o*- and *p*-Toluenesulfonyl isocyanates, phenyl isocyanate (Aldrich), chlorosulfonyl isocyanate, and 2,2,2-trichloroethanol (Tokyo Chemical Industry) were purchased and distilled prior to use. Methanesulfonyl isocyanate[37] and benzoyl isocyanate[38] were prepared according to the literature procedure. $\alpha$-Methylacryloyl isocyanate was a gift from Nippon Paint Co. Chloroprene and 1-chloro-1,3-butadiene were gifts from Tosoh Corp. (*E*)-$\beta$-Monodeuterio-ethylstyrene (90% atom D),[39] (*Z*)-$\beta$-monodeuteriostyrene (96% atom D),[40] dienes (1-triisopropylsiloxy-1,3-diene,[41] 2-triisopropylsiloxy-1,3-diene,[41] 1-phenyl-3-triisopropylsiloxy-1,3-diene,[41] 2-methyl-3-triisopropylsiloxy-1,3-diene,[42] 2-trimethylsilylmethyl-1,3-diene,[43] 5-trimethylsilyl-1,3-pentadiene),[43] $[Pd_2(dba)_3]\cdot CHCl_3$[44] and $[Pd(PPh_3)_4]$[45] were prepared according to the literature procedure. All other organic and inorganic materials were used as received from commercial sources or purified by standard procedures.

**General procedure for the preparation of substituted but-2-yn-1,4-diols**: 1) 3,4-Dihydro-2*H*-pyran (4.6 mL, 50 mmol) was added in one portion at 0 °C to a mixture of propargyl alcohol (50 mmol) and a catalytic amount of *p*-toluenesulfonic acid (0.2 g, 1 mmol) in dry THF (30 mL). The mixture was allowed to warm to room temperature and stirred for 2 h. After neutralization with sat. $NaHCO_3$ and concentration, the reaction mixture was extracted with ethyl acetate ($2\times 20$ mL). The combined organic extracts were dried ($MgSO_4$), filtered, concentrated, and distilled by means of Kugelrohr to give 3-(tetrahydro-2-pyranoxy)-1-propyne (128 °C/55 mm Hg, 84%).

2) A 200 mL three-necked round bottomed flask, equipped with a septum, a reflux condenser at the top bearing $N_2$ balloon, and a dropping funnel, was purged with nitrogen. Dry THF (50 mL) and 3-(tetrahydro-2-pyranoxy)-1-propyne (7.0 g, 50 mmol) were introduced through a septum via syringe. The mixture was cooled in a dry ice/isopropanol bath (−78 °C). A solution of *n*BuLi (1.6 M in hexane, 32 mL, 50 mmol) was added slowly via the dropping funnel and the reaction mixture was stirred for 2 h at the same temperature. An appropriate aldehyde (50 mmol) or ketone (50 mmol) was added at −78 °C and the mixture was stirred for 1 h at the same temperature. After allowing to warm to ambient temperature, sat. $NH_4Cl$ (20 mL) was added and the mixture was extracted with ethyl acetate. The extract was washed with brine, dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was distilled under reduced pressure by means of Kugelrohr to afford 1-substituted 4-(tetrahydro-2-pyranoxy)but-2-yn-1-ol in quantitative yield.

3) In a 100 mL round bottomed flask, a mixture of 1-substituted 4-(tetrahydro-2-pyranoxy)but-2-yn-1-ol (30 mmol), methanol (30 mL), and *p*-toluenesulfonic acid (0.57 g, 3.0 mmol) was stirred for 2 h at ambient temperature. After addition of sat. $NaHCO_3$, the mixture was concentrated and the residue was partitioned into ethyl acetate and brine. The organic phase was dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was distilled under reduced pressure by means of Kugelrohr to afford 1-substituted but-2-yn-1,4-diols in reasonable yield (80–95%).

**General procedure for the preparation of but-2-yn-1,4-diol biscarbamates 1a–q**: Dry THF (50 mL), the but-2-yn-1,4-diol derivative (30 mmol), and triethylamine (10 mL, 66 mmol) were introduced via syringe to a 200 mL two-necked round bottomed flask, equipped with a septum and a nitrogen balloon. The mixture was cooled to 0 °C and then an appropriate isocyanate (66 mmol) was introduced dropwise. After completion of addition, the mixture was allowed to warm to ambient temperature and stirred for 2 h, during which a lot of white precipitate appeared. The mixture was diluted with THF (50 mL) washed with 2 N HCl and then brine. The THF layer was dried ($MgSO_4$), filtered, and concentrated in vacuo to give a white solid. The solid was crystallized from THF/AcOEt. Compound **1e** tends to polymerize during recrystallization; hence, **1e** was subjected to the transformation to **2e** without purification (runs 10 and 11, Table 1).

**1,1-Dimethylbut-2-yn-1,4-diol bis(*N*-2,2,2-trichloroethoxysulfonyl) carbamates (1r)**: 1) A solution of 2,2,2-trichloroethanol (2.8 mL, 30 mmol) in $Et_2O$ (30 mL) was added over 0.5 h at 0 °C under $N_2$ to a solution of chlorosulfonyl isocyanate (2.8 mL, 32 mmol) in dry $Et_2O$ (10 mL). The mixture was allowed to warm to room temperature and stirred for 2 h. The solvent was removed, and the residue was recrystallized from $Et_2O$ to give *N*-chlorosulfonyl 2,2,2-trichloroethyl carbamate as a white solid (7.99 g, 92%).

2) This solid was heated under reflux in toluene (20 mL) under $N_2$ for 6 h. 2,2,2-Trichloroethoxysulfonyl isocyanate was isolated as a colorless liquid (2.30 g, 34%), after removal of toluene and purification by means of Kugelrohr distillation under reduced pressure (100–120 °C/1.0 mm Hg).[49] The isocyanate was rather unstable and was used immediately after distillation.

3) 2,2,2-Trichloroethoxysulfonyl isocyanate (2.3 g, 9 mmol) was added at 0 °C under $N_2$ to a solution of 1,1-dimethylbut-2-yn-1,4-diol (0.47 g, 4.1 mmol) and triethyl amine (1.3 mL, 8.8 mmol) in THF (5 mL). The mixture was allowed to warm to room temperature and stirred for 0.5 h. Addition of 2 N HCl, extraction with ethyl acetate, washing the organic phase with water, followed by drying ($MgSO_4$) and concentration, gave an yellow oil (3.5 g, 140%). This crude material was subjected to the cyclization to give **2r** [Eq. (4)].

**Preparation of [$D_2$]-$\alpha$-trimethylsiloxystyrene**: A solution of acetophenone (60 mmol), NaOH (5 mmol) and $D_2O$ [99% D] (2 mol) was stirred at room temperature for 16 h under $N_2$. The reaction mixture was diluted with dry $Et_2O$ (20 mL) and separated. The organic layer was dried ($MgSO_4$), filtered, concentrated, and distilled by Kugelrohr (120 °C/50 mm Hg). [$D_3$]Acetophenone [96% atom D] was obtained in 93% yield. To a solution of LDA (48 mmol) in dry THF (30 mL) prepared at −78 °C, [$D_3$]acetophenone (48 mmol) was added dropwise over 30 min and stirred for an additional 30 min. TMSCl (79 mmol) was added slowly over 10 min at −78 °C, and the reaction mixture was allowed to warm to room temperature and stirring was continued for 30 min. After addition of dry hexane (20 mL) and filtration of white solid (LiCl), the solvents were distilled under ambient pressure and the residue was distilled by Kugelrohr (135 °C/30 mm Hg) to give [$D_2$]-$\alpha$-trimethylsiloxystyrene (96% atom D) in 62% yield.

**Preparation of [$D_5$]-$\alpha$-methacrylonitrile**: 30% $H_2SO_4$ (36 mL) was added dropwise at 0 °C over 1 h to a solution of [$D_6$]acetone (99.5% atom D, Aldrich) (136 mmol) and KCN (108 mmol) in water (30 mL). After stirring for 0.5 h at 0 °C, the reaction mixture was extracted with $Et_2O$ ($2\times 20$ mL), washed with sat. $NaHCO_3$, and dried ($MgSO_4$). $Et_2O$ was removed under reduced pressure and the residue was distilled by Kugelrohr (90–100 °C/10–15 mm Hg) to afford a [$D_6$]acetone cyanohydrin in 64% yield. To a mixture of a [$D_6$]acetone cyanohydrin (69 mmol) and dry pyridine (76 mmol) was added thionyl chloride (138 mmol) at 0 °C over 15 min, and the mixture was allowed to warm to ambient temperature and stirred for an additional 3 h. The mixture was poured into water (10 mL) at 0 °C and extracted with $Et_2O$ ($2\times 20$ mL). The combined extracts were washed with sat. $NaHCO_3$ and brine and dried ($MgSO_4$). After distillation of the solvents under ambient pressure, and the crude resulting product was distilled by Kugelrohr (100 °C/150 mm Hg) to provide [$D_5$]-$\alpha$-methacrylonitrile (97% atom D) in 20% yield.

**Preparation of 2-phenyl-1,3-butadiene**: 1) Acetophenone (5 mL, 40 mmol) dissolved in THF (15 mL) was added dropwise over 0.5 h at 0 °C to a solution of vinylmagnesium bromide (50 mL, 50 mmol, 1 M THF solution, Aldrich). The mixture was allowed to warm to room temperature and stirred for 0.5 h at the same temperature. The mixture was filtered through a glass filter. The filtrate was partitioned into 2 N HCl and $Et_2O$. The organic layer was washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The oily residue was purified by distillation (90 °C/1 mm Hg) to give 2-phenyl-3-buten-1-ol in 88% yield.

2) 2-Phenyl-3-buten-1-ol (2.4 g, 16 mmol), $NaHSO_4$ (0.01 g, 5 mol%), and hydroquinone (18 mg, 1 mol%) were heated at 120 °C under reduced pressure (30 mm Hg) in a Kugelrohr oven. Once dehydration started, the pressure was reduced (10 mm Hg) in order to remove the product as quickly as possible (0.9 g, 43%).

**Preparation of (*E*)-1-phenyl-1,3-butadiene**: 1) A solution of allyl bromide (19.4 mL, 225 mmol) in $Et_2O$ (150 mL) was added dropwise over 1 h at 0 °C to a stirred mixture of benzaldehyde (15.3 mL, 150 mmol) and Mg (10.9 mg, 450 mmol) in $Et_2O$ (20 mL). The mixture was allowed to warm to room temperature and stirred for 1 h. The mixture was filtered through a glass filter and the filtrate was washed with 2 N HCl. The organic layer was washed with brine, dried ($MgSO_4$), and concentrated. Distillation (100 °C/1 mm Hg) of the residue furnished 1-phenyl-3-buten-1-ol in 96% yield.

2) 1-Phenyl-3-buten-1-ol (6.22 g, 42 mmol), $NaHSO_4$ (0.29 g, 5 mol%), and hydroquinone (46 mg, 1 mol%) were heated at 120 °C under reduced pressure (30 mm Hg) in a Kugelrohr oven. Once dehydration started, the

pressure was reduced (10 mm Hg) in order to remove the product as quickly as possible (2.35 g, 43 %).

**General procedure for the preparation of 3-tosyl-4-vinylidene-2-oxazolidinones 2 and 5**: Compound **1** (0.5 mmol) and $[Pd_2(dba)_3]\cdot CHCl_3$ (2.5 mg, 2.5 μmol) were placed in a 25 mL two-necked round bottomed flask, one of the two necks being sealed with a septum and the other fitted with a reflux condenser at the top bearing a nitrogen balloon. The flask was purged with $N_2$, and THF (5 mL) and triethyl amine (7 μL, 50 μmol) were added through a septum. The mixture was stirred at the temperature and for the period of time indicated in Tables 1 and 2 and Equations (3) and (4). The reaction was monitored by TLC in hexane/EtOAc 2:1: $R_f$ (**1**) = 0.05, $R_f$ (**2a**) = $R_f$ (**2b**) = $R_f$ (**2c**) = $R_f$ (**2d**) = $R_f$ (**2e**) = 0.35; in hexane/EtOAc 1:1, $R_f$ (**1**) = 0.1, $R_f$ (**2g**) = $R_f$ (**5g**) = 0.6; $R_f$ (**2h**) = $R_f$ (**5h**) = 0.63; $R_f$ (**2i**) = $R_f$ (**5i**) = 0.63; $R_f$ (**2j**) = $R_f$ (**5j**) = 0.74; $R_f$ (**2k**) = $R_f$ (**5k**) = 0.74; $R_f$ (**2l**) = $R_f$ (**5l**) = 0.74; $R_f$ (**2m**) = $R_f$ (**5m**) = 0.74; $R_f$ (**2n**) = $R_f$ (**5n**) = 0.74; $R_f$ (**2o**) = $R_f$ (**5o**) = 0.74; $R_f$ (**2p**) = 0.77). The mixture was diluted with ethyl acetate and filtered through a Celite pad. The filtrate was concentrated in vacuo and the residue was purified by means of silica gel column chromatography over silica gel or in some cases, by crystallization. The yields refer to the averaged values of experiments undertaken at least two times.

**3-(*p*-Toluenesulfonyl)-4-vinylideneoxazolidin-2-one (2a)**: CCDC-181558; m.p. 101.2–103.0 °C (AcOEt/hexane); IR (KBr): $\nu$ = 1805 (s), 1385(s), 1370 (s), 1290 (s), 1230 (s), 1180 (s), 1160 (s), 1150 (s), 650 $cm^{-1}$ (s); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 2.46 (s, 3H), 4.86 (t, $J$ = 4.8 Hz, 2H), 5.71 (t, $J$ = 4.8 Hz, 2H), 7.36 (d, $J$ = 8.4 Hz, 2H), 7.93 (d, $J$ = 8.4 Hz, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 21.8, 63.9, 92.6, 103.8, 128.3, 129.9, 134.1, 146.1, 150.3, 192.0; elemental analysis calcd (%) for $C_{12}H_{11}NO_4S$: C 54.88, H 4.18, N 5.28, S 12.09; found: C 54.57, H 4.15, N 5.13, S 12.00.

**3-(*o*-Toluenesulfonyl)-4-vinylideneoxazolidin-2-one (2b)**: CCDC-181724; m.p. 84.0–84.5 °C (AcOEt/hexane); IR (KBr): $\nu$ = 1805 (s), 1385 (s), 1370 (s), 1290 (s), 1230 (s), 1180 (s), 1160 (s), 1150 (s), 650 $cm^{-1}$ (s); $^1H$ NMR (400 MHz, $CDCl_3$):$\delta$ = 2.68 (s, 3H), 4.80 (t, $J$ = 4.8 Hz, 2H), 5.65 (t, $J$ = 4.8 Hz, 2H), 7.27–7.58 (m, 3H), 8.03 (d, $J$ = 8.4 Hz, 1H); elemental analysis calcd (%) for $C_{12}H_{11}NO_4S$: C 54.88, H 4.18, N 5.28, S 12.09; found: C 54.47, H 4.14, N 5.15, S 12.41.

**3-Methanesulfonyl-4-vinylideneoxazolidin-2-one (2c)**: oil; IR (neat): $\nu$ = 1778 (s), 1664 (s), 1371 (s), 1151 (s), 999 (s), 771 $cm^{-1}$ (s); $^1H$ NMR (300 MHz, $C_6D_6$): $\delta$ = 2.46 (s, 3H), 3.70 (t, $J$ = 4.5 Hz, 2H), 5.06 (t, $J$ = 4.5 Hz, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 40.4, 63.8, 92.4, 102.9, 154.4, 191; MS $m/z$ (%): 189 (1) $[M]^+$, 163 (30), 116 (16), 97 (26), 83 (100), 79 (36); HRMS: $m/z$ (%): calcd for $C_6H_7NO_4S$: 189.0096; found: 189.0117 (72) $[M]^+$, 174 (44), 162 (100).[17]

**3-Benzoyl-4-vinylideneoxazolidin-2-one (2d)**: m.p. 103.6–104.5 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu$ = 1790 (s), 1690 (s), 1360 (s), 1300 (s), 1160 (s), 1060 $cm^{-1}$ (s); $^1H$ NMR (60 MHz, $CDCl_3$): $\delta$ = 5.01 (t, $J$ = 4.5 Hz, 2H), 5.60 (t, $J$ = 4.5 Hz, 2H), 7.27–7.95 (m, 5H); elemental analysis calcd (%) for $C_{12}H_9NO_3$: C 66.97, H 4.22, N 6.51; found: C 67.03, H 4.37, N 6.43.

**3-(α-Methylacryloyl)-4-vinylideneoxazolidin-2-one (2e)**: m.p. 126.3–126.7 °C ($Et_2O$/hexane); IR (KBr): $\nu$ = 1780 (s), 1690 (s), 1380 (s), 1310 (s), 1270 (s), 1170 (s), 1075 (s), 750 $cm^{-1}$ (m); $^1H$ NMR (400 MHz, [$D_6$]DMSO): $\delta$ = 1.92 (s, 3H), 5.04 (t, $J$ = 4.8 Hz, 2H), 5.47 (br s, 2H), 5.59 (t, $J$ = 4.8 Hz, 2H); elemental analysis calcd (%) for $C_9H_9NO_3$: C 60.33, H 5.06, N 7.82; found: C 60.08, H 4.98, N 7.65.

**5-Methyl-3-(*p*-toluenesulfonyl)-4-vinylideneoxazolidin-2-one (2g)**: CCDC-188289; m.p. 68.2–70.2 °C ($Et_2O$/hexane, contaminated by a trace amount of **5g**); IR (KBr): $\nu$ = 1780 (s), 1370 (s), 1170 $cm^{-1}$ (s); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.43 (d, $J$ = 6.6 Hz, 3H), 2.46 (s, 3H), 5.09 (tq, $J$ = 4.5, 6.2 Hz, 1H), 5.71 (dd, $J$ = 4.5, 10.6 Hz, 1H), 5.74 (dd, $J$ = 4.5, 10.6 Hz, 1H), 7.36 (d, $J$ = 8.1 Hz, 2H), 7.90 (d, $J$ = 8.1 Hz, 2H); elemental analysis calcd (%) for $C_{13}H_{13}NO_4S$: C 55.90, H 4.69, N 5.01, S 11.48; found: C 55.90, H 4.69, N 5.05, S 11.40.

**4-(2-Propenylidene)-3-(*p*-toluenesulfonyl)oxazolidin-2-one (5g)**: $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.90 (d, $J$ = 7.2 Hz, 3H), 2.46 (s, 3H), 4.76 (dd, $J$ = 4.0, 11.7 Hz, 1H), 4.80 (dd, $J$ = 4.5, 11.7 Hz, 1H), 6.07 (tq, $J$ = 4.0, 7.2 Hz, 1H), 7.36 (d, $J$ = 8.1 Hz, 2H), 7.90 (d, $J$ = 8.1 Hz, 2H).

**5-Ethyl-4-vinylidene-3-(*p*-toluenesulfonyl)oxazolidin-2-one (2h)**: Obtained as a mixture with **5h** in a ratio of 1.7:1: IR (neat): $\nu$ = 1790 (s), 1370 (s), 1340 (m), 1280 (m), 1250 (m), 1190 (s), 1150 (m), 1090 (m), 800 $cm^{-1}$ (m); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 0.90 (t, $J$ = 7.4 Hz, 3H), 1.67 (dquint, $J$ = 7.4, 14.6 Hz, 1H), 1.79 (ddq, $J$ = 4.4, 14.6, 7.4 Hz, 1H), 2.46 (s, 3H), 4.95 (dq, $J$ = 7.4, 4.4 Hz, 1H), 5.71 (d, $J$ = 4.4 Hz, 2H), 7.36 (d, $J$ = 8.3 Hz, 2H), 7.92 (d, $J$ = 8.3 Hz, 2H); elemental analysis calcd (%) for $C_{14}H_{15}NO_4S$: C 57.32, H 5.15, N 4.77, S 10.93; found: C 57.72, H 5.15, N 4.70, S 10.55.

**4-(2-Butenylidene)-3-(*p*-toluenesulfonyl)oxazolidin-2-one (5h)**: $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.07 (t, $J$ = 7.3 Hz, 3H), 2.20(ddq, $J$ = 6.1, 7.3, 13.4 Hz, 2H), 2.46 (s, 3H), 4.78 (dd, $J$ = 4.1, 11.7 Hz, 1H), 4.82 (dq, $J$ = 4.1, 11.7 Hz, 1H), 6.15 (tt, $J$ = 4.1, 6.1 Hz, 1H), 7.36 (d, $J$ = 8.3 Hz, 2H), 7.92 (d, $J$ = 8.3 Hz, 2H).

**5-Isopropyl-3-(*p*-toluenesulfonyl)-4-vinylideneoxazolidin-2-one (2i)**: Obtained as a mixture with **5i** in a ratio of 2.5:1: IR (neat): $\nu$ = 1790 (s), 1380 (m), 1170 (m); 1090 (m), 1050 (m), 1010 (m), 890 (m), 800 $cm^{-1}$ (m); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 0.81 (d, $J$ = 6.7 Hz, 3H), 0.97 (d, $J$ = 6.7 Hz, 3H), 1.92 (dhept, $J$ = 3.7, 6.7 Hz, 1H), 2.46 (s, 3H), 4.84 (q, $J$ = 3.7 Hz, 1H), 5.70 (d, $J$ = 3.7 Hz, 1H), 7.36 (d, $J$ = 8.4 Hz, 2H), 7.92 (d, $J$ = 8.4 Hz, 2H); HRMS: $m/z$ (%): calcd for $C_{15}H_{17}NO_4S$: 307.0878; found: 307.0873 (26) $[M]^+$, 198 (6), 152 (76), 139 (37), 91 (100).

**4-(2-Isopentenylidene)-3-*p*-toluenesulfonyloxazolidin-2-one (5i)**: $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.09 (d, $J$ = 6.8 Hz, 3H), 1.11 (d, $J$ = 6.8 Hz, 3H), 2.45 (s, 3H), 2.48 (dhept, $J$ = 4.4, 6.8 Hz, 1H), 4.80 (dd, $J$ = 4.4, 5.5 Hz, 1H), 4.83 (dd, $J$ = 4.4, 5.5 Hz, 1H), 6.08 (dt, $J$ = 4.4, 5.5 Hz, 1H), 7.36 (d, $J$ = 8.4 Hz, 2H), 7.91 (d, $J$ = 8.4 Hz, 2H).[17]

**5-Cyclohexyl-3-(*p*-toluenesulfonyl)-4-vinylideneoxazolidin-2-one (2j)**: Obtained as a mixture with **5j** in a ratio of 2.5:1: IR (neat): $\nu$ = 1790 (s), 1380 (s), 1290 (m), 1220 (m), 1170 (s); 1090 (m), 990 (m), 810 $cm^{-1}$ (m); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.09–1.30 (m, 11H), 2.38 (s, 3H), 4.78 (m, 1H), 5.70 (d, $J$ = 4.0 Hz, 2H), 7.36 (d, $J$ = 8.4 Hz, 2H), 7.92 (d, $J$ = 8.4 Hz, 2H); HRMS: $m/z$ (%): calcd for $C_{18}H_{21}NO_4S$: 347.1191; found: 347.1209 (17) $[M]^+$, 192 (100).[17]

**4-(2-Cyclopentylvinylidene)-3-*p*-toluenesulfonyloxazolidin-2-one (5j)**: $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.09–1.30 (m, 11H), 2.38 (s, 3H), 4.78 (m, 1H), 5.70 (d, $J$ = 4.0 Hz, 2H), 7.36 (d, $J$ = 8.4 Hz, 2H), 7.92 (d, $J$ = 8.4 Hz, 2H).

**5-Phenyl-3-*p*-toluenesulfonyl-4-vinylidene-2-oxazolidinone (2k)**: CCDC-181726, the sample was prepared by repeated recrystallization; m.p. 107.9–108.8 °C ($CH_2Cl_2$/hexane, contaminated by a trace amount of **5k**); IR (KBr): $\nu$ = 1790 (s), 1380 (s), 1330 (s), 1295 (s), 1230 (s), 1200 (s), 1190 (s), 1150 (s), 650 $cm^{-1}$ (s); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 2.46 (s, 3H), 5.56 (dd, $J$ = 4.0, 10.6 Hz, 1H), 5.67 (dd, $J$ = 4.0, 10.6 Hz, 1H), 5.88 (t, $J$ = 4.0 Hz, 1H), 7.19 (d, $J$ = 8.1 Hz, 2H), 7.93 (d, $J$ = 8.1 Hz, 2H); elemental analysis calcd (%) for $C_{18}H_{15}NO_4S$: C 63.33, H 4.43, N 4.10, S 9.39; found: C 63.26, H 4.45, N 4.16, S 9.40.

**4-(2-Phenylvinylidene)oxazolidin-2-one (5k)**: $^1H$ NMR 400 MHz, $CDCl_3$: $\delta$ = 2.42 (s, 3H), 4.80 (d, $J$ = 3.9 Hz, 2H), 6.98 (t, $J$ = 3.9 Hz, 1H), 7.24 (d, $J$ = 8.1 Hz, 2H), 7.89 (d, $J$ = 8.1 Hz, 2H).

**5-*tert*-Butyl-4-vinylidene-3-*p*-toluenesulfonyloxazolidin-2-one (2l)**: m.p. 69.1–71.2 °C ($CH_2Cl_2$/hexane, contaminated with a trace amount of **5l**); IR (KBr): $\nu$ = 1800 (s), 1380 (s), 1220 (s), 1190 (s), 1180 (s), 1150 (s), 1060 (w), 670 $cm^{-1}$ (s); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.13 (s, 9H), 2.46 (s, 3H), 4.60 (t, $J$ = 3.7 Hz, 1H), 5.68 (dd, $J$ = 1.5, 3.7 Hz, 1H), 5.71 (dd, $J$ = 1.5, 3.7 Hz, 1H), 7.36 (d, $J$ = 8.3 Hz, 2H), 7.92 (d, $J$ = 8.3 Hz, 2H); elemental analysis calcd (%) for $C_{16}H_{19}NO_4S$: C 59.79, H 5.96, N 4.36, S 9.98; found: C 59.53, H 5.90, N 4.28, S 9.66.

**4-(2-*tert*-Butylvinylidene)-3-*p*-toluenesulfonyloxazolidin-2-one (5l)**: $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 0.91 (s, 9H), 2.46 (s, 3H), 4.77 (dd, $J$ = 4.4, 11.4 Hz, 1H), 4.83 (dd, $J$ = 4.4, 11.4 Hz, 1H), 6.01 (t, $J$ = 4.4 Hz, 1H), 7.36 (d, $J$ = 8.3 Hz, 2H), 7.92 (d, $J$ = 8.3 Hz, 2H).

**5,5-Dimethyl-3-*p*-toluenesulfonyl-4-vinylideneoxazolidin-2-one (2m)**: CCDC-181555, the sample was prepared by repeated recrystallization; m.p. 93.4–94.6 °C ($CH_2Cl_2$/hexane, contaminated with a trace of **5m**); IR (KBr): $\nu$ = 1785 (s), 1380 (s), 1170 (s), 906 (s), 728 $cm^{-1}$ (s); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.43 (s, 6H), 2.43 (s, 3H), 5.76 (br s, 2H), 7.38 (d, $J$ = 8.4 Hz, 2H), 7.92 (d, $J$ = 8.4 Hz, 2H); elemental analysis calcd (%) for $C_{14}H_{15}NO_4S$: C 57.32, H 5.15, N 4.77, S 10.93; found: C 57.19, H 5.13, N 4.79, S 10.79.

**4-(2-Isobutenylidene)-3-*p*-toluenesulfonyloxazolidin-2-one (5m)**: $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.90 (s, 6H), 2.43 (s, 3H), 4.76 (br s, 2H), 7.38 (d, $J$ = 8.4 Hz, 2H), 7.88 (d, $J$ = 8.4 Hz, 2H).

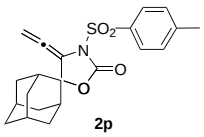
**3-*p*-Toluenesulfonyl-4-vinylidene-1-oxa-3-azaspiro[4.4]nonan-2-one (2n)**: CCDC-181553, the sample was prepared by repeated recrystallization; m.p. 105.5–106.5 °C ($CH_2Cl_2$/hexane, contaminated with a trace amount of **5n**); IR (KBr): $\nu$ = 1780 (s), 1370 (s), 1230 (s), 1160 (s), 1130 (m), 960 (s), 750 $cm^{-1}$ (m); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.66–1.88 (m, 6H), 1.98–2.12 (m, 2H), 2.46 (s, 3H), 5.72 (s, 2H), 7.36 (d, $J$ = 8.4 Hz, 2H), 7.93 (d, $J$ = 8.4 Hz, 2H); elemental analysis calcd (%) for $C_{17}H_{17}NO_4S$: C 60.17, H 5.37, N 4.39, S 10.04; found: C 59.94, H 5.28, N 4.26, S 10.03.

**4-Cyclopenthylidenemethylene-3-*p*-toluenesulfonyloxazolidin-2-one (5n)**: $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.66–1.88 (m, 6H), 1.98–2.12 (m, 2H), 2.46 (s, 3H), 4.75 (br s, 2H), 7.36 (d, $J$ = 8.4 Hz, 2H), 7.83 (d, $J$ = 8.4 Hz, 2H).

**3-*p*-Toluenesulfonyl-4-vinylidene-1-oxa-3-azaspiro[4.5]decan-2-one (2o)**: m.p. 93.0–94.2 °C ($Et_2O$/hexane, contaminated with a trace amount of **5o**); IR (KBr): $\nu$ = 1790 (s), 1380 (s), 1180 (s), 910 (m), 810 $cm^{-1}$ (m); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.46–1.85 (m, 10H), 2.46 (s, 3H), 5.71 (s, 2H), 7.38 (d, $J$ = 8.4 Hz, 2H), 7.92 (d, $J$ = 8.4 Hz, 2H); elemental analysis calcd (%) for $C_{17}H_{19}NO_4S$: C 61.24, H 5.74, N 4.20, S 9.62; found: C 61.38, H 5.69, N 4.25, S 9.72.

**4-Cyclohexylidenemethylene-3-*p*-toluenesulfonyloxazolidin-2-one (5o)**: $^1H$ NMR (400 MHz, $CDCl_3$):$\delta$ = 1.46–1.85 (m, 10H), 2.46 (s, 3H), 4.75 (s, 2H), 7.38 (d, $J$ = 8.5 Hz, 2H), 7.90 (d, $J$ = 8.5 Hz, 2H).

Compound **2p**: CCDC-181554; m.p. 110.5–110.9 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu$ = 1800 (s), 1610 (m), 1390 (s), 1280 (s), 1250 (s), 1190 (s), 1180 (s), 1110 (m), 1080 (m), 980 (m), 920 $cm^{-1}$ (m); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.51–1.63 (m, 3H), 1.64–1.73 (m, 3H), 1.76–1.87 (m, 2H), 1.99–2.05 (m, 2H), 2.11–2.20 (m, 4H), 2.46 (s, 3H), 5.76 (s, 2H), 7.35 (d, $J$ = 8.6 Hz, 2H), 7.92 (d, $J$ = 8.6 Hz, 2H); elemental analysis calcd (%) for $C_{21}H_{23}NO_4S$: C 65.43, H 6.01, N 3.63, S 8.32; found: C 65.11, H 5.97, N 3.46, S 8.60.



**2p**

**5,5-Dimethyl-4-(2-isobutenylidene)-3-*p*-toluenesulfonyloxazolidin-2-one (2q)**: CCDC-181559; m.p. 126.0–127.2 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu$ = 1785 (s), 1370 (s), 1280 (s), 1190 (s), 1180 (s), 1160 (s), 670 $cm^{-1}$ (s); $^1H$ NMR (60 MHz, $CDCl_3$): $\delta$ = 1.40 (s, 6H), 1.90 (s, 6H), 2.42 (s, 3H), 7.40 (d, $J$ = 8.0 Hz, 2H), 7.90 (d, $J$ = 8.0 Hz, 2H); 13C NMR (100 MHz, $CDCl_3$): $\delta$ = 21.7, 22.0, 27.1, 81.3, 110.4, 115.0, 128.0, 129.6, 134.7, 145.5, 149.7, 182.9; elemental analysis calcd (%) for $C_{16}H_{19}NO_4S$: C 59.79, H 5.96, N 4.36, S 9.56; found: C 59.62, H 5.94, N 4.26, S 9.62.

**3-(2,2,2-Trichloroethoxysulfonyl)-5,5-dimethyl-4-vinylideneoxazolidin-2-one (2r)**: m.p. 88.0–88.3 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu$ = 1810 (s), 1380 (s), 1310 (m), 1260 (s), 1200 (s), 1170 (m), 1080 (m), 1060 (s), 990 (s), 910 (m), 770 $cm^{-1}$ (s); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.60 (s, 6H), 4.99 (s, 2H), 5.76 (s, 2H); HRMS: $m/z$ (%): calcd for $C_9H_{10}NO_5SCl_3$: 348.9345; found: 348.9366 (21) $[M]^+$, 232 (7), 175 (100).[17]

**(*Z*)-*N*-*p*-Toluenesulfonyl 2-(2-oxo-3-*p*-toluenesulfonyloxazolidin-4-ylidene)ethyl carbamate (3)**: m.p. 52.0–53.0 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu$ = 1800 (s), 1750 (s), 1600 (w), 1450 (s), 1370 (s), 1090 $cm^{-1}$ (s); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 2.45 (s, 3H), 2.46 (s, 3H), 4.68 (d, $J$ = 1.4 Hz, 2H), 4.90 (d, $J$ = 6.1 Hz, 2H), 5.13 (tt, $J$ = 1.4, 6.1 Hz, 1H), 7.35 (d, $J$ = 8.2 Hz, 2H), 7.81 (br s, 1H), 7.89 (d, $J$ = 8.2 Hz, 2H), 7.93 (d, $J$ = 8.2 Hz, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 21.3, 21.4, 63.0, 68.8, 107.5, 126.1, 128.0, 128.2, 129.2, 129.3, 129.4, 129.7, 133.8, 134.9, 144.9, 146.1, 149.9, 152.2; elemental analysis calcd (%) for $C_{20}H_{20}N_2O_8S_2$: C 49.99, H 4.19, N 5.83, S 13.35; found: C 49.68, H 4.14, N 5.93, S 13.64.

**6-Methyl-8-methylene-tetrahydrooxazolo[3.4]-3,5-dione (4)**: m.p. 144.6–145.5 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu$ = 1805 (s), 1711 (s), 1362 (s), 1333 (s), 1267 (s), 1097 (m), 1072 (m), 885 $cm^{-1}$ (m); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.33 (d, $J$ = 7.0 Hz, 3H), 2.51 (dd, $J$ = 9.5, 14.3 Hz, 1H), 2.72 (dd, $J$ = 4.8, 14.3 Hz, 1H), 2.79 (ddq, $J$ = 4.8, 9.5, 7.0 Hz, 1H), 5.22 (s, 1H), 5.46 (s, 1H), 6.92 (s, 1H); elemental analysis calcd (%) for $C_9H_9NO_3$: C 60.33, H 5.06, N 7.82; found: C 60.15, H 4.99, N 7.72.

**General procedure for the thermal cycloaddition of 2 with alkynes, alkenes, enones, and nitrile oxides**: An appropriate combination of **2** and an alkyne, an alkene, an enone, or a nitrile oxide was heated in a thermostated oil bath under $N_2$. For the detail of the experimental conditions (*T*, solvent, *t*, etc.), see Tables 5–7, Figure 11 and relevant Equations.

**(*Z*)-4-(3-Phenyl-2-cyclobutenylidene)-3-*p*-toluenesulfonyloxazolidin-2-one [(*Z*)-6a]**: m.p. 153.9–154.1 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu$ = 1800 (s), 1380 (s), 1260 (s), 1108 (m), 750 (s), 650 $cm^{-1}$ (s); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 2.45 (s, 3H), 3.15 (s, 2H), 4.87 (s, 2H), 6.98 (s, 1H), 7.32–7.41 (m, 5H), 7.46 (d, $J$ = 8.3 Hz, 2H), 7.96 (d, $J$ = 8.3 Hz, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 21.7, 33.7, 66.5, 112.6, 116.9, 125.6, 126.9, 128.3, 128.7, 129.0, 129.9, 133.2, 134.7, 145.9, 147.6, 152.4; elemental analysis calcd (%) for $C_{20}H_{17}NO_4S$: C 64.74, H 4.73, N 4.01, S 8.64; found: C 64.76, H 4.72, N 3.77, S 8.57.

**(*Z*)-4-(3-Methoxycarbonyl-2-cyclobutenylidene)-3-*p*-toluenesulfonyloxazolidin-2-one [(*Z*)-6b]**: m.p. 66.0–66.5 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu$ = 1800 (s), 1680 (s), 1260 (s), 1120 (s), 1080 (s), 730 $cm^{-1}$ (m); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 2.45 (s, 3H), 3.06 (s, 2H), 3.81 (s, 3H), 4.87 (s, 2H), 7.37 (d, $J$ = 8.8 Hz, 2H), 7.91 (s, 1H), 7.93 (d, $J$ = 8.8 Hz, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 21.8, 33.9, 51.8, 66.2, 113.9, 119.2, 128.4, 130.0, 134.2, 137.9, 142.5, 146.4, 151.9, 163.0; HRMS: $m/z$ (%): calcd for $C_{16}H_{15}NO_6S - CO_2$: 305.0722; found: 305.0744 (55) $[M - CO_2]^+$, 91 (100).[17]

**(*Z*)-4-(3-Phenyl-2-cyclobutenylidene)-3-benzoyloxazolidin-2-one [(*Z*)-6c]**: m.p. 135.5–136.5 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu$ = 1790 (s), 1720 (s), 1690 (s), 1370 (s), 1170 $cm^{-1}$ (s); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 3.22 (s, 2H), 5.11 (s, 2H), 6.59 (s, 1H), 7.29–7.79 (m, 10H); HRMS: $m/z$ (%): calcd for $C_{20}H_{15}NO_3$: 317.1052; found: 317.1068 (31) $[M]^+$, 273 (2), 105 (100).[17]

**4-(3-Phenylcyclobutylidene)-3-*p*-toluenesulfonyloxazolidin-2-one (7a)**: oil; IR (neat): $\nu$ = 1795 (s), 1380 (s), 1245 (s), 1164 (s), 750 (s), 700 $cm^{-1}$ (s); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 2.45 (s, 3H), 2.76 (dm, $J$ = 15.0 Hz, 1H), 2.99 (dm, $J$ = 15.0 Hz, 1H), 3.24 (dm, $J$ = 16.2 Hz, 1H), 3.49 (dm, $J$ = 16.2 Hz, 1H), 3.65 (quint, $J$ = 8.2 Hz, 1H), 4.60 (dm, $J$ = 12.8 Hz, 1H), 4.70 (br d, $J$ = 12.8 Hz, 1H), 7.21–7.34 (m, 5H), 7.34 (d, $J$ = 8.2 Hz, 2H), 7.92 (d, $J$ = 8.2 Hz, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 21.7, 35.7, 36.4, 39.3, 66.3, 117.8, 119.4, 126.4, 126.5, 128.4, 128.6, 129.8, 135.1, 144.6, 145.7, 152.5; HRMS: $m/z$ (%): calcd for $C_{20}H_{19}NO_4S$: 369.1034; found: 369.1030 (81) $[M]^+$, 265 (42), 214(96), 131 (30), 104 (77), 91 (100), 77 (13); elemental analysis calcd (%) for $C_{20}H_{19}NO_4S$: C 65.02, H 5.18, N 3.79, S 8.68; found: C 65.19, H 5.25, N 3.64, S 8.53.

**(*Z*)-4-(2,2,3-Trideuterio-3-pentadeuteriophenylcyclobutylidene)-3-*p*-toluenesulfonyloxazolidin-2-one [*Z*-[D$_8$]-7a]**: $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 2.44 (s, 3H), 2.74 (br d, $J$ = 15.0 Hz, 1H), 2.98 (br d, $J$ = 15.0 Hz, 1H), 4.59 (dm, $J$ = 12.1 Hz, 1H), 4.69 (dm, $J$ = 12.1 Hz, 1H), 7.34 (d, $J$ = 8.1 Hz, 2H), 7.93 (d, $J$ = 8.1 Hz, 2H).[17]

**(*Z*)-4-(*cis*-2-Deuterio-3-phenylcyclobutylidene)-3-*p*-toluenesulfonyloxazolidin-2-one [(*Z*)-*cis*-[D$_1$]-7a]**: $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 2.44 (s, 3H), 2.75 (dm, $J$ = 15.0 Hz, 1H), 2.99 (dm, $J$ = 15.0 Hz, 1H), 3.47 (m, 1H), 3.66 (q, $J$ = 8.30 Hz, 1H), 4.59 (dm, $J$ = 11.7 Hz, 1H), 4.69 (dm, $J$ = 11.7 Hz, 1H), 7.21–7.35 (m, 7H), 7.93 (d, $J$ = 8.4 Hz, 2H).[17]

**3-Benzoyl-4-(3-phenylcyclobutylidene)oxazolidin-2-one (7b)**: m.p. 96.5–97.0 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu$ = 1800 (s), 1740 (m), 1690 (s), 1370 (s), 1170 $cm^{-1}$ (s); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 2.76–2.94 (m, 2H), 2.99–3.10 (m, 2H), 3.65 (quint, $J$ = 8.2 Hz, 1H), 4.82 (dquint, $J$ = 15.0, 2.7 Hz, 1H), 4.90 (dm, $J$ = 15.0 Hz, 1H), 7.16–7.34 (m, 4H), 7.42–7.48 (m, 2H), 7.54–7.61 (m, 2H), 7.75–7.81 (m, 2H); elemental analysis calcd (%) for $C_{20}H_{17}NO_3$: C 75.22, H 5.37, N 4.39; found: C 74.95, H 5.42, N 4.31.

**5,5-Dimethyl-4-(3-phenylcyclobutylidene)-3-*p*-toluenesulfonyloxazolidin-2-one (7c)**: CCDC-181551; m.p. 145.0–146.0 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu$ = 1800 (s), 1740 (m), 1370 (s), 1170 $cm^{-1}$ (m); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.45 (s, 3H), 1.56 (s, 3H), 2.43 (s, 3H), 2.95 (ddd, $J$ = 3.0, 7.5, 15.0 Hz, 1H), 3.22 (ddd, $J$ = 3.0, 7.5, 16.5 Hz, 1H), 3.29 (ddt, $J$ = 9.2, 15.0, 3.0 Hz, 1H), 3.47 (ddt, $J$ = 8.8, 16.5, 3.0 Hz, 1H), 3.62 (quint, $J$ = 8.3 Hz, 1H), 7.21–7.30 (m, 7H), 7.92 (d, $J$ = 8.4 Hz, 2H); elemental analysis calcd (%) for $C_{22}H_{23}NO_4S$: C 66.48, H 5.83, N 3.52, S 8.07; found: C 66.29, H 5.88, N 3.38, S 7.67.

**(*Z*)-5,5-Dimethyl-4-(2,2,3-trideuterio-3-pentadeuteriophenylcyclobutylidene)-3-*p*-toluenesulfonyloxazolidin-2-one [(*Z*)-[D$_8$]-7c]**: $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.56 (s, 3H), 1.57 (s, 3H), 2.45 (s, 3H), 2.95 (d,

$J = 15.4$ Hz, 1H), 3.29 (d, $J = 15.4$ Hz, 1H), 7.34 (d, $J = 7.3$ Hz, 2H), 7.94 (d, $J = 7.3$ Hz, 2H).[46]

**(*Z*)-5,5-Dimethyl-4-(*cis*-2-deuterio-3-phenylcyclobutylidene)-3-*p*-toluenesulfonyloxazolidin-2-one [(*Z*)-*cis*-[D$_1$]-7c]**: $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.45$ (s, 3H), 1.52 (s, 3H), 2.44 (s, 3H), 3.61 (q, $J = 8.7$ Hz, 1H), 2.94 (ddd, $J = 2.6$, 7.4, 15.2 Hz, 1H), 3.30 (ddd, $J = 2.6$, 8.7, 15.2 Hz, 1H), 3.45 (br q, $J = 9.2$ Hz, 1H), 7.14 – 7.29 (m, 5H), 7.34 (J = 8.4 Hz, 2H), 7.97 (J = 8.4 Hz, 2H).[46]

**5,5-Dimethyl-4-(3-methyl-3-phenylcyclobutylidene)-3-*p*-toluenesulfonyloxazolidin-2-one (7d)**: oil; IR (neat): $\nu = 1800$ (s), 1720 (s), 1600 (s), 1490 (m), 1440 (m), 1370 (s), 1260 (s), 1170 (s), 1100 (m), 1080 (m), 980 cm$^{-1}$ (m); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.38$ (s, 3H), 1.51 (s, 3H), 1.57 (s, 3H), 2.44 (s, 3H), 2.90 (dt, $J = 14.7$, 2.8 Hz, 1H), 3.14 (dt, $J = 14.7$, 2.8 Hz, 1H), 3.20 (dd, $J = 2.8$, 14.7 Hz, 1H), 3.46 (dd, $J = 2.8$, 14.7 Hz, 1H), 7.19 – 7.25 (m, 3H), 7.32 – 7.36 (m, 4H), 7.92 (d, $J = 8.4$ Hz, 2H); HRMS: *m*/*z* (%): calcd for $C_{23}H_{25}NO_4S$: 411.1504; found: 411.1541 (4) $[M]^+$, 256 (100).[17]

**5,5-Dimethyl-4-(3-trimethylsiloxy-3-phenylcyclobutylidene)-3-*p*-toluenesulfonyloxazolidin-2-one (7e)**: m.p. 71.0 – 72.0 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu = 1780$ (s), 1710 (m), 1380 (m), 1270 (m), 1180 (m), 1110 (m), 930 cm$^{-1}$ (m); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 0.06$ (s, 9H), 1.43 (s, 3H), 1.44 (s, 3H), 2.45 (s, 3H), 3.23 (dt, $J = 15.4$ 2.2 Hz, 1H), 3.28 (dd, $J = 2.2$, 15.4 Hz, 1H), 3.49 (dd, $J = 2.2$, 16.7 Hz, 1H), 3.64 (dt, $J = 16.7$, 2.2 Hz, 1H), 7.29 – 7.39 (m, 5H), 7.45 (d, $J = 8.1$ Hz, 2H), 7.92 (d, $J = 8.1$ Hz, 2H); HRMS: *m*/*z* (%): calcd for $C_{25}H_{31}NO_5SSi$: 485.1692; found: 485.1666 (19) $[M]^+$, 470(100); elemental analysis calcd (%) for $C_{25}H_{31}NO_5SSi$: C 61.83, H 6.43, N 2.88; found: C 61.85, H 6.44, N 2.81.[17]

**(*Z*)-5,5-Dimethyl-4-(3-trimethylsiloxy-3-phenyl-2,2-[D$_2$]cyclobutylidene)-3-*p*-toluenesulfonyloxazolidin-2-one (7e)**: see ref. [17].

**4-(3-Ethynyl-3-methylcyclobutylidene)-3-*p*-toluenesulfonyloxazolidin-2-one (7f)**: oil; IR (neat): $\nu = 1782$ (s), 1717 (m), 1600 (m), 1373 (s), 1263 (s), 1175 (m), 1090 (m), 1034 (m), 966 cm$^{-1}$ (s); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.45$ (s, 3H), 1.47 (s, 3H), 1.48 (s, 3H), 2.29 (s, 1H), 2.45 (s, 3H), 2.76 (ddd, $J = 1.8$, 2.9, 15.0 Hz, 1H), 3.02 (ddd, $J = 1.8$, 2.9, 16.3 Hz, 1H), 3.16 (dd, $J = 2.9$, 15.0 Hz, 1H), 3.36 (dd, $J = 2.9$, 16.3 Hz, 1H), 7.38 (d, $J = 8.4$ Hz, 2H), 7.92 (d, $J = 8.4$ Hz, 2H); HRMS: *m*/*z* (%): calcd for $C_{19}H_{21}NO_4S$: 359.1191; found: 359.1179 (17) $[M]^+$, 204 (100).[17]

**5,5-Dimethyl-4-(3-phenylcyclobutylidene)-3-(2,2,2-trichloroethoxysulfonyl)oxazolidin-2-one (7g)**: oil; IR (neat): $\nu = 1810$ (s), 1720 (m), 1390 (m), 1370 (m), 1270 (s), 1200 (s), 1170 (m), 1120 (m), 1090 (m), 1000 (s), 860 cm$^{-1}$ (s); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.51$ (s, 3H), 1.57 (s, 3H), 2.89 (ddd, $J = 2.9$, 7.5, 15.4 Hz, 1H), 3.14 (ddd, $J = 2.9$, 7.5, 16.7 Hz, 1H), 3.23 (ddt, $J = 9.2$, 15.4, 2.9 Hz, 1H), 3.43 (ddt, $J = 9.2$, 16.7, 2.9 Hz, 1H), 3.57 (br tt, $J = 7.5$, 9.2 Hz, 1H), 4.87 (d, $J = 11.4$ Hz, 1H), 4.90 (d, $J = 11.4$ Hz, 1H), 7.13 – 7.28 (m, 5H); HRMS: *m*/*z* (%): calcd for $C_{17}H_{18}NO_5SCl_3$: 452.9984; found 452.9971 (2) $[M]^+$, 418(2), 198 (100).[17]

**(*Z*,*E*)-5,5-Dimethyl-4-(2-[D$_1$]-3-ethyl-3-phenylcyclobutylidene)-3-*p*-toluenesulfonyloxazolidin-2-one [(*Z*,*E*)-[D$_1$]-7h]**: oil; $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 0.70$ (t, $J = 7.3$ Hz, 3H), 1.36 (s, 3H), 1.57 (s, 3H), 1.80 (q, $J = 7.3$ Hz, 2H), 2.44 (s, 3H), 2.93 (dd, $J = 2.9$, 15.0 Hz, 1H), 3.14 (d, $J = 15.0$ Hz, 1H), 3.38 (br s, 1H), 7.14 – 7.35 (m, 7H), 7.92 (d, $J = 8.4$ Hz, 2H).[46]

**4-(3-Methoxycarbonylcyclobutylidene)-3-*p*-toluenesulfonyloxazolidin-2-one (8a)**: CCDC-181560; m.p. 152.8 – 153.5 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu = 1800$ (s), 1790 (s), 1730 (s), 1370 (s), 1190 (s), 1160 cm$^{-1}$ (s); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 2.46$ (s, 3H), 2.77 (ddd, $J = 1.8$, 9.1, 15.8 Hz, 1H), 2.92 (dm, $J = 15.8$ Hz, 1H), 3.25 (tt, $J = 6.2$, 9.2 Hz, 1H), 3.32 – 3.37 (m, 2H), 3.74 (s, 3H), 4.59 (dm, $J = 11.7$ Hz, 1H), 4.64 (br d, $J = 11.7$ Hz, 1H), 7.36 (d, $J = 8.4$ Hz, 2H), 7.92 (d, $J = 8.4$ Hz, 2H); 13C NMR (100 MHz, $CDCl_3$): $\delta = 21.7$, 31.6, 33.9, 35.3, 52.0, 66.0, 115.5, 120.2, 128.4, 129.9, 134.9, 145.8, 152.3, 174.8; elemental analysis calcd (%) for $C_{16}H_{17}NO_6S$; C 54.69, H 4.88, N 3.99, S 9.13; found: C 54.57, H 4.82, N 4.03, S 9.00.

**4-[2-Oxo-3-*p*-toluenesulfonyl-2,3-dihydrooxazol-4-ylpent-4-enoic methyl ester**: The by-product appeared in run 3, Table 5): m.p. 114.0 – 114.5 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu = 1800$ (s), 1740 (s), 1270 (s), 1200 (m), 1180 cm$^{-1}$ (m); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 2.45$ (s, 3H), 2.50 (t, $J = 7.5$ Hz, 2H), 2.82 (t, $J = 7.5$ Hz, 2H), 3.68 (s, 3H), 5.28 (br s, 1H), 5.34 (br s, 1H), 6.59 (s, 1H), 7.36 (d, $J = 8.4$ Hz, 2H), 7.99 (d, $J = 8.4$ Hz, 2H); 13C NMR (100 MHz, $CDCl_3$): $\delta = 21.8$, 30.4, 32.7, 51.7, 120.2, 126.4, 128.4, 128.6, 130.0, 133.6, 135.6, 146.5, 151.1, 172.8; HRMS: *m*/*z* (%): calcd for $C_{16}H_{17}NO_6S$: 351.0777; found: 351.0787 (33) $[M]^+$, 320(10), 196 (70), 164 (100).[17]

**4-(3-Cyanocyclobutylidene)-3-*p*-toluenesulfonyloxazolidin-2-one (8b)**: m.p. 107.5 – 108.0 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu = 1800$ (s), 1770 (s), 1720 (s), 1370 (s), 1260 (s), 1180 (s), 1120 (s), 1050 (s), 650 cm$^{-1}$ (s); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 2.46$ (s, 3H), 2.94 – 3.05 (m, 2H), 3.25 (ddt, $J = 7.0$, 8.1, 9.2 Hz, 1H), 3.43 – 3.59 (m, 2H), 4.61 (m, 2H), 7.39 (d, $J = 8.6$ Hz, 2H), 7.89 (d, $J = 8.6$ Hz, 2H); HRMS: *m*/*z* (%): calcd for $C_{15}H_{14}N_2O_4S$: 318.0674; found: 318.0671 (27) $[M]^+$, 293 (15), 163 (14), 155 (100); elemental analysis calcd (%) for $C_{15}H_{14}N_2O_4S$: C 56.59, H 4.43, N 8.80, S 10.07; found: C 56.72, H 4.39, N 8.58, S 9.95.

**4-(3-Cyano-3-methylcyclobutylidene)-3-*p*-toluenesulfonyloxazolidin-2-one (8c)**: m.p. 149.8 – 150.8 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu = 1800$ (s), 1730 (s), 1370 (s), 1250 (s), 1170 (s), 1150 (s), 980 (s), 750 cm$^{-1}$ (s); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.61$ (s, 3H), 2.47 (s, 3H), 2.61 (dm, $J = 16.1$ Hz, 1H), 3.14 (dm, $J = 16.1$ Hz, 1H), 3.18 (dm, $J = 16.1$ Hz, 1H), 3.64 (dm, $J = 16.1$ Hz, 1H), 4.61 (br s, 2H), 7.38 (d, $J = 8.2$ Hz, 2H), 7.90 (d, $J = 8.2$ Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 21.8$, 25.1, 27.7, 40.5, 43.9, 65.9, 110.2, 122.6, 124.1, 128.5, 130.0, 134.5, 146.2, 151.9; elemental analysis calcd (%) for $C_{16}H_{16}N_2O_4S$: C 57.82, H 4.85, N 8.43, S 9.65; found: C 57.50, H 4.79, N 8.35, S 9.36.

**(*Z*)-4-(3-Cyano-3-[D$_3$]methyl-2,2-[D$_2$]cyclobutylidene)-3-*p*-toluenesulfonyloxazolidin-2-one [(*Z*)-[D$_5$]-8c]**: see ref. [17].

**4-[3-(*N*,*N*-Dimethylcarbamoyl)cyclobutylidene]-3-*p*-toluenesulfonyloxazolidin-2-one (8d)**: m.p. 158.1 – 158.9 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu = 1760$ (s), 1730 (s), 1680 (s), 1385 (s), 1260 (s), 1190 (s), 1170 (s), 1140 (s), 1120 (s), 1060 cm$^{-1}$ (s); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 2.45$ (s, 3H), 2.67 (m, 1H), 2.97 (s, 3H), 2.98 (s, 3H), 3.10 (dm, $J = 15.1$ Hz, 1H), 3.23 – 3.42 (m, 3H), 4.57 (dm, $J = 15.0$ Hz, 1H), 4.64 (br d, $J = 15.0$ Hz, 1H), 7.34 (d, $J = 8.2$ Hz, 2H), 7.90 (d, $J = 8.2$ Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 21.7$, 31.0, 33.1, 35.3, 35.6, 36.7, 66.2, 116.2, 119.8, 128.4, 130.0, 134.8, 145.8, 152.4, 173.0; HRMS: *m*/*z* (%): calcd for $C_{17}H_{20}N_2O_5S$: 364.1093; found: 364.1106 (5) $[M]^+$, 209 (100); elemental analysis calcd (%) for $C_{17}H_{20}N_2O_5S$: C 56.03, H 5.53, N 7.69, S 8.80; found: C 55.61, H 5.40, N 7.48, S 8.63.

**3-Benzoyl-4-(3-methoxycarbonylcyclobutylidene)oxazolidin-2-one (8e)**: oil; IR (neat): $\nu = 1800$ (s), 1750 (s), 1690 (s), 1370 (s), 1170 cm$^{-1}$ (s); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 2.86$ (m, 1 H), 2.94 – 2.97 (m, 3H), 3.24 (tt, $J = 7.6$, 8.1 Hz, 1H), 3.69 (s, 3H), 4.83 (quint, $J = 2.6$ Hz, 2H), 7.46 (t, $J = 8.1$ Hz, 2H), 7.59 (t, $J = 8.1$ Hz, 1H), 7.70 (d, $J = 8.1$ Hz, 2H); elemental analysis calcd (%) for $C_{16}H_{15}NO_5$: C 63.78, H 5.02, N 4.65; found: C 63.38, H 4.87, N 4.43.

**5,5-Dimethyl-4-(3-methoxycarbonylcyclobutylidene)-3-*p*-toluenesulfonyloxazolidin-2-one (8f)**: m.p. 71.0 – 72.0 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu = 1790$ (s), 1730 (m), 1370 (s), 1260 (s), 1170 (s), 1110 (s), 840 cm$^{-1}$ (w); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.29$ (t, $J = 7.2$ Hz, 3H), 1.44 (s, 3H), 1.51 (s, 3H), 2.45 (s, 3H), 3.02 – 3.08 (m, 1H), 3.14 (dd, $J = 2.3$, 6.3 Hz, 1H), 3.17 – 3.23 (m, 1H), 3.30 (ddd, $J = 2.3$, 6.3, 16.8 Hz, 1H), 3.37 (m, 1H), 4.18 (q, $J = 7.2$ Hz, 2H), 7.35 (d, $J = 8.4$ Hz, 2H), 7.92 (d, $J = 8.4$ Hz, 2H); elemental analysis calcd (%) for $C_{19}H_{23}NO_6S$: C 58.00, H 5.89, N 3.56, S 8.15; found: C 57.96, H 5.81, N 3.58, S 8.22.

**5,5-Dimethyl-4-(3-methoxycarbonyl-3-triisopropylsiloxycyclobutylidene)-3-*p*-toluenesulfonyloxazolidin-2-one (8g)**: m.p. 112.5 – 113.0 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu =$ 1790 (s), 1750 (s), 1720 (m), 1590 (w), 1460 (m), 1370 (s), 1270 (s), 1210 (m), 1190 (m), 1170 (m), 1120 (s), 990 cm$^{-1}$ (m); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.02 – 1.13$ (m, 21H), 1.41 (s, 3H), 1.50 (s, 3H), 2.45 (s, 3H), 2.96 (dd, $J = 3.1$, 15.4 Hz, 1H), 3.28 (dd, $J = 3.1$, 16.9 Hz, 1H), 3.47 (dt, $J = 15.4$ 3.1 Hz, 1H), 3.60 (dt, $J = 16.9$, 3.1 Hz, 1H), 3.76 (s, 3H), 7.35 (d, $J = 8.1$ Hz, 2H), 7.90 (d, $J = 8.1$ Hz, 2H); HRMS: *m*/*z* (%): calcd for $C_{27}H_{41}NO_7SSi$: 508.1825 $[M - i\mathrm{Pr}]^+$; found: 508.1820, 396 (100).

**3-(2-Oxo-3-*p*-toluenesulfonyl-1-oxa-3-azaspiro[4.4]non-4-ylidene)cyclobutanecarboxylic ethyl ester (8h)**: oil; IR (neat): $\nu = 1790$ (s), 1730 (s), 1370 (s), 1260 (s), 1170 (s), 1090 (s), 810 (m), 750 cm$^{-1}$ (m); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.28$ (t, $J = 7.1$ Hz, 3H), 1.70 – 2.10 (m, 8H), 2.45 (s, 3H), 3.02 (m, 1H), 3.14 (dm, $J = 13.0$ Hz, 1H), 3.18 (dm, $J = 16.8$ Hz, 1H), 3.32 (dm, $J = 16.8$ Hz, 1H), 3.39 (m, 1H), 4.18 (q, $J = 7.1$ Hz, 1H), 7.35 (d, $J = 8.4$ Hz,

2H), 7.89 (d, $J = 8.4$ Hz, 2H); HRMS: $m/z$ (%): calcd for $C_{21}H_{25}NO_6S$: 419.1402; found: 420.1476 (5) $[M]^+$, 374 (8), 264 (100).[17]

**4-(3-Acetylcyclobutylidene)-3-*p*-toluenesulfonyl-1-oxa-3-azaspiro[4.4]-nonan-2-one (8i)**: m.p. 83.0–84.0 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu = 1790$ (s), 1720 (s), 1380 (s), 1340 (m), 1270 (s), 1180 (s), 1130 (m), 1090 (m), 910 (m), 730 $cm^{-1}$ (s); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 1.65–2.08$ (m, 8H), 2.17 (s, 3H), 2.45 (s, 3H), 2.88 (m, 1H), 3.16 (ddd, $J = 2.8, 6.6, 15.7$ Hz, 1H), 3.22 (ddd, $J = 2.8, 6.6, 15.7$ Hz, 1H), 3.32 (m, 1H), 3.41 (m, 1H), 7.35 (d, $J = 8.4$ Hz, 2H), 7.88 (d, $J = 8.4$ Hz, 2H); HRMS: $m/z$ (%): calcd for $C_{20}H_{23}NO_5S$: 389.1297; found: 390.1289 (100) $[M]^+$.[17]

**3-(2-Oxo-3-*p*-toluenesulfonyl-1-oxa-3-aza-spiro[4.4]non-4-ylidene)cyclobutanecarbaldehyde (8j)**: m.p. 83.0–84.0 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu = 1790$ (s), 1720 (s), 1380 (s), 1270 (s), 1180 (s), 1120 (s), 1090 (s), 990 (m), 910 (m), 840 (m), 730 $cm^{-1}$ (s); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 1.71–2.08$ (m, 8H), 2.45 (s, 3H), 2.92–2.99 (m, 1H), 3.16 (ddd, $J = 2.5, 5.6, 15.7$ Hz, 1H), 3.23–3.30 (m, 1H), 3.31–3.41 (m, 2H), 7.35 (d, $J = 8.4$ Hz, 2H), 7.89 (d, $J = 8.4$ Hz, 2H), 9.81 (d, $J = 1.5$ Hz, 1H); HRMS: $m/z$ (%): calcd for $C_{19}H_{21}NO_5S$: 375.1140; found: 375.1122 (66) $[M]^+$, 331 (33), 220 (54), 176 (100).[17]

**4-(3-Acetyl-3-methylcyclobutylidene)-3-*p*-toluenesulfonyl-1-oxa-3-aza-spiro[4.4]nonan-2-one (8k)**: CCDC–179982; m.p. 136.0–136.9 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu = 1780$ (s), 1703 (s), 1383 (s), 1099 (s), 752 (s), 704 $cm^{-1}$ (m); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 1.45$ (s, 3H), 1.66–2.12 (m, 8H), 2.18 (s, 3H), 2.45 (s, 3H), 2.49 (ddd, $J = 1.8, 2.9, 15.4$ Hz, 1H), 2.98 (ddd, $J = 1.8, 2.9, 16.7$ Hz, 1H), 3.30 (dd, $J = 3.2, 15.4$ Hz, 1H), 3.37 (dd, $J = 3.2, 16.7$ Hz, 1H), 7.35 (d, $J = 8.2$ Hz, 2H), 7.88 (d, $J = 8.2$ Hz, 2H); HRMS: $m/z$ (%): calcd for $C_{21}H_{25}NO_5S$: 403.1453; found: 403.1430 (34) $[M]^+$, 91 (100).[17]

**1-Methyl-3-(2-oxo-3-*p*-toluenesulfonyl-1-oxa-3-azaspiro[4.4]non-4-ylidene)cyclobutanecarbaldehyde (8l)**: IR (neat): $\nu = 1790$ (s), 1720 (s), 1450 (m), 1370 (s), 1270 (s), 1170 (s), 1110 (m), 1090 (s), 990(m), 900 (s), 810 (m), 730 $cm^{-1}$ (s); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 1.40$ (s, 3H), 1.54–2.07 (m, 8H), 2.45 (s, 3H), 2.55 (dd, $J = 2.9, 15.4$ Hz, 1H), 2.94 (dd, $J = 2.9, 16.9$ Hz, 1H), 3.22 (dd, $J = 2.9, 15.4$ Hz, 1H), 3.37 (dd, $J = 2.9, 16.9$ Hz, 1H), 7.36 (d, $J = 8.4$ Hz, 2H), 7.88 (d, $J = 8.4$ Hz, 2H), 9.67 (s, 1H); HRMS: $m/z$ (%): calcd for $C_{20}H_{23}NO_5S$: 389.1297; found: 389.1258 (66) $[M]^+$, 70 (100).[17]

**3-(5-Methyl-2-oxo-3-*p*-toluenesulfonyloxazolidin-4-ylidene)cyclobutane-carbaldehyde (8m)**: ≈1:1 mixture of stereoisomers: IR (neat): $\nu = 1778$ (s), 1715 (s), 1339 (s), 758 $cm^{-1}$ (m); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta = 1.21$ (d, $J = 6.6$ Hz, 3H, one isomer), 1.29 (d, $J = 6.2$ Hz, 3H, the other isomer), 2.46 (s, 3H), 2.68 (ddm, $J = 8.6, 15.2$ Hz, 1H, one isomer), 2.90 (m, 1H), 3.03–3.11 (m, 1H, one isomer), 3.12–3.21 (m, 2H), 3.25–3.54 (m, 2H), 4.93 (m, 1H), 7.36 (d, $J = 8.2$ Hz, 2H), 7.89 (d, $J = 8.2$ Hz, 2H, one isomer), 7.90 (d, $J = 8.2$ Hz, 2H, the other isomer), 9.82 (d, $J = 1.5$ Hz, 1H, one isomer), 9.83 (d, $J = 1.5$ Hz, 1H, the other isomer); HRMS: $m/z$ (%): calcd for $C_{16}H_{17}NO_5S$: 335.0827; found: 335.0836 (52) $[M]^+$, 180 (100).[17]

**4-(3-Isopropenyl-3-methylcyclobutylidene)-3-*p*-toluenesulfonyloxazolidin-2-one (9a)**: oil; IR (neat): $\nu = 1800$ (s), 1780 (m), 1380 (s), 1260 (s), 1180 (m), 1160 $cm^{-1}$ (m); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 1.23$ (s, 3H), 1.66 (s, 3H), 2.16 (br d, $J = 14.7$ Hz, 1H), 2.37 (s, 3H), 2.69 (dd, $J = 2.2, 14.7$ Hz, 1H), 2.70 (dt, $J = 14.7, 2.2$ Hz, 1H), 3.10 (dm, $J = 14.7$ Hz, 1H), 4.48 (dm, $J = 13.2$ Hz, 1H), 4.58 (br d, $J = 13.2$ Hz, 1H), 4.65 (s, 1H), 4.72 (s, 1H), 7.28 (d, $J = 8.1$ Hz, 2H), 7.83 (d, $J = 8.1$ Hz, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta = 17.6, 20.6, 26.0, 38.8, 40.2, 41.8, 65.3, 107.6, 115.5, 119.2, 128.0, 128.7, 134.0, 144.6, 149.8, 151.6$; HRMS: $m/z$ (%): calcd for $C_{18}H_{21}NO_4S$: 347.1191; found 347.1193 (2) $[M]^+$, 193 (10), 192 (64), 132 (100).[17]

**3-*p*-Toluenesulfonyl-4-[3-(trimethylsilylmethyl)-3-vinylcyclobutylidene]oxazolidin-2-one (9b)**: oil; IR (neat): $\nu = 1789$ (s), 1732 (s), 1373 (s), 1250 (s), 1175 (s), 1080 (m), 1050 (m), 950 $cm^{-1}$ (s); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 0.01$ (s, 9H), 1.06 (d, $J = 14.5$ Hz, 1H), 1.10 (d, $J = 14.5$ Hz, 1H), 2.37 (dm, $J = 15.0$ Hz, 1H), 2.44 (s, 3H), 2.61 (dm, $J = 16.5$ Hz, 1H), 2.85 (dm, $J = 16.5$ Hz, 1H), 3.12 (dm, $J = 15.0$ Hz, 1H), 4.56–4.60 (m, 2H), 5.00 (dd, $J = 1.1, 17.2$ Hz, 1H), 5.02 (dd, $J = 1.1, 10.6$ Hz, 1H), 5.97 (dd, $J = 10.6, 17.2$ Hz, 1H), 7.34 (d, $J = 8.3$ Hz, 2H), 7.90 (d, $J = 8.3$ Hz, 2H); HRMS: $m/z$ (%): calcd for $C_{20}H_{27}NO_4SSi - Me$: 390.1195; found: 390.1203 (2) $[M - Me]^+$, 250 (42), 91 (39), 73 (100).[17]

**4-(3-*trans*-β-Styrylcyclobutylidene)-3-*p*-toluenesulfonyloxazolidin-2-one (9c)**: m.p. 59.0–59.5 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu = 1780$ (s), 1370 (s), 1260 (s), 1170 (s), 1110 (s), 1090 (s), 900 (s), 750 $cm^{-1}$ (m); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 2.45$ (s, 3H), 2.55 (m, 1H), 2.82 (m, 1H), 3.03 (dm, $J = 15.8$ Hz, 1H), 3.24 (m, 1H), 3.32 (m, 1H), 4.46–4.68 (m, 2H), 6.36 (dd, $J = 6.1, 15.8$ Hz, 1H), 6.42 (d, $J = 15.8$ Hz, 1H), 7.19–7.41 (m, 7H), 7.94 (d, $J = 8.4$ Hz, 2H); HRMS: $m/z$ (%): calcd for $C_{22}H_{21}NO_4S$: 395.1192; found: 395.1197 (11) $[M]^+$, 240 (40), 130 (100); elemental analysis calcd (%) for $C_{22}H_{21}NO_4S$: C 66.82, H 5.35, N 3.54, S 8.11; found: C 66.91, H 5.34, N 3.66, S 7.99.

**4-[3-*trans*-β-Styryl-3-(triisopropylsiloxy)cyclobutylidene]-3-*p*-toluenesulfonyloxazolidin-2-one (9d)**: m.p. 123.0–123.8 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu = 1790$ (s), 1725 (s), 1390 (m), 1365 (m), 1250 (m), 1190 (s), 1170 (m), 1135 (s), 1120 (s), 1090 (s), 990 (m), 960 (m), 875 $cm^{-1}$ (m); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 1.00–1.13$ (m, 21H), 2.44 (s, 3H), 2.81 (dm, $J = 15.6$ Hz, 1H), 2.90 (dm, $J = 15.6$ Hz, 1H), 3.32 (dm, $J = 16.9$ Hz, 1H), 3.44 (dm, $J = 16.9$ Hz, 1H), 4.59 (dm, $J = 11.9$ Hz, 1H), 4.66 (dm, $J = 11.9$ Hz, 1H), 6.41 (d, $J = 16.1$ Hz, 1H), 6.57 (d, $J = 16.1$ Hz, 1H), 7.31–7.38 (m, 5H), 7.34 (d, $J = 8.4$ Hz, 2H), 7.92 (d, $J = 8.4$ Hz, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta = 3.3, 14.8, 20.9, 40.0, 72.6, 76.3, 118.7, 125.4, 126.5, 126.9, 127.7, 127.9, 128.4, 129.5, 129.6, 134.9, 136.3, 140.9, 153.9$; HRMS: $m/z$ (%): calcd for $C_{31}H_{41}NO_5SSi$: 567.2474; found: 567.2473 (14) $[M]^+$, 523 (14), 103 (41), 91 (100).[17]

**5,5-Dimethyl-4-(3-isopropenyl-3-methylcyclobutylidene)-3-*p*-toluenesulfonyloxazolidin-2-one (9e)**: oil; IR (neat): $\nu = 1790$ (s), 1370 (s), 1270 (s), 1190 (s), 1170 (s), 1140 (m), 1090 (m), 990 $cm^{-1}$ (m); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 1.30$ (s, 3H), 1.39 (s, 3H), 1.53 (s, 3H), 1.73 (s, 3H), 2.44 (s, 3H), 2.55 (dt, $J = 14.6, 2.9$ Hz, 1H), 2.77 (dt, $J = 16.0, 2.9$ Hz, 1H), 2.93 (dd, $J = 2.9, 14.6$ Hz, 1H), 3.15 (dd, $J = 2.9, 16.0$ Hz, 1H), 4.71 (s, 1H), 4.79 (t, $J = 1.3$ Hz, 1H), 7.34 (d, $J = 8.4$ Hz, 2H), 7.91 (d, $J = 8.4$ Hz, 2H); HRMS: $m/z$ (%): calcd for $C_{20}H_{25}NO_4S$: 375.15050; found: 375.1512 (12) $[M]^+$, 220 (80), 206 (15), 176 (85), 160 (100); elemental analysis calcd (%) for $C_{20}H_{25}NO_4S$: C 63.98, H 6.71, N 3.73, S 8.54; found: C 63.63, H 7.06, N 3.36, S 8.33.

**5,5-Dimethyl-4-(3-phenyl-3-vinylcyclobutylidene)-3-*p*-toluenesulfonyloxazolidin-2-one (9f)**: m.p. 49.0–50.5 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu = 1780$ (s), 1370 (s), 1280 (s), 1260 (s), 1170 (s), 1115 (s), 900 $cm^{-1}$ (m); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 1.32$ (s, 3H), 1.35 (s, 3H), 2.45 (s, 3H), 2.69 (dd, $J = 6.6, 16.3$ Hz, 1H), 3.41 (dm, $J = 20.0$ Hz, 1H), 3.67 (dm, $J = 20.0$ Hz, 1H), 3.75 (dm, $J = 16.3$ Hz, 1H), 5.45 (dm, $J = 18.8$ Hz, 2H), 6.15 (m, 1H), 7.22–7.37 (m, 7H), 7.98 (d, $J = 8.4$ Hz, 2H); HRMS: $m/z$ (%): calcd for $C_{24}H_{25}NO_4S$: 423.15050; found: 423.1514 (6) $[M]^+$, 268 (66), 182 (14), 154 (11), 91 (100); elemental analysis calcd (%) for $C_{24}H_{25}NO_4S$: C 68.06, H 5.95, N 3.31, S 7.57; found: C 68.15, H 5.88, N 3.29, S 7.63.

**5,5-Dimethyl-3-*p*-toluenesulfonyl-4-(3-trimethylsilylmethyl-3-vinylcyclobutylidene)oxazolidin-2-one (9g)**: oil; IR (neat): $\nu = 1790$ (s), 1735 (m), 1360 (m), 1270 (m), 1190 (m), 1170 (m), 1120 (m), 1090 (m), 1035 (m), 910 (m), 850 $cm^{-1}$ (m); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 0.01$ (s, 9H), 1.05 (d, $J = 14.3$ Hz, 1H), 1.10 (d, $J = 14.3$ Hz, 1H), 1.45 (s, 3H), 1.46 (s, 3H), 2.44 (s, 3H), 2.63 (dm, $J = 15.4$ Hz, 1H), 2.83 (dm, $J = 16.9$ Hz, 1H), 2.87 (dm, $J = 15.4$ Hz, 1H), 3.07 (dm, $J = 16.9$ Hz, 1H), 5.02 (dd, $J = 0.7, 17.7$ Hz, 1H), 5.03 (dd, $J = 0.7, 10.2$ Hz, 1H), 5.96 (dd, $J = 10.2, 17.7$ Hz, 1H), 7.34 (d, $J = 8.1$ Hz, 2H), 7.94 (d, $J = 8.1$ Hz, 2H); HRMS: $m/z$ (%): calcd for $C_{22}H_{31}NO_4SSi$: 433.1743; found 433.1743 (6) $[M]^+$, 91 (41), 73 (100).[17]

**5,5-Dimethyl-4-(3-*trans*-β-styrylcyclobutylidene)-3-*p*-toluenesulfonyloxazolidin-2-one (9h)**: m.p. 160.5–161.0 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu = 1800$ (s), 1740 (m), 1380 (s), 1260 (s), 1180 (s), 1120 (s), 1090 (s), 980 $cm^{-1}$ (m); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 1.54$ (s, 3H), 1.55 (s, 3H), 2.45 (s, 3H), 2.78 (ddd, $J = 2.9, 6.4, 15.7$ Hz, 1H), 3.01 (ddd, $J = 2.9, 6.4, 15.7$ Hz, 1H), 3.12 (ddd, $J = 2.9, 6.4, 11.8$ Hz, 1H), 3.19 (m, 1H), 3.30 (ddt, $J = 2.9, 8.4, 15.7$ Hz, 1H), 6.35 (dd, $J = 6.4, 15.8$ Hz, 1H), 6.40 (d, $J = 15.8$ Hz, 1H), 7.20–7.39 (m, 7H), 7.94 (d, $J = 8.4$ Hz, 2H); HRMS: $m/z$ (%): calcd for $C_{24}H_{25}NO_4S$: 423.15050; found: 423.1514 (8) $[M]^+$, 270 (13), 267 (12), 210 (13), 91 (100); elemental analysis calcd (%) for $C_{24}H_{25}NO_4S$: C 68.06, H 5.95, N 3.31, S 7.57; found: C 67.63, H 5.94, N 3.09, S 7.19.

**5,5-Dimethyl-3-*p*-toluenesulfonyl-4-[3-(*trans*-2-triisopropylsiloxyvinyl)cyclobutylidene]oxazolidin-2-one (9i)**: m.p. 102.8–104.0 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu = 1790$ (s), 1660 (m), 1370 (m), 1270 (s), 1210 (m), 1170 (s), 1110 (m), 1080 (m), 910 $cm^{-1}$ (m); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 1.04–1.15$ (m, 21H), 1.42 (s, 3H), 1.50 (s, 3H), 2.44 (s, 3H), 2.59 (ddd, $J = 2.6, 6.8, 14.7$ Hz, 1H), 2.81 (ddd, $J = 2.6, 6.8, 15.4$ Hz, 1H), 2.90 (dtt, $J = 8.6, 6.8, 8.2$ Hz, 1H), 3.02 (ddt, $J = 8.2, 14.7, 2.6$ Hz, 1H), 3.21 (ddt, $J = 8.2, 15.4, 2.6$ Hz, 1H), 5.17 (dd, $J = 8.6, 12.1$ Hz, 1H), 6.37 (d, $J = 12.1$ Hz, 1H),

7.33 (d, $J = 8.1$ Hz, 2H), 7.92 (d, $J = 8.1$ Hz, 2H); HRMS: $m/z$ (%): calcd for $C_{27}H_{41}NO_5SSi - i$Pr: 476.1927; found: 476.1917 (4) $[M - i\mathrm{Pr}]^+$, 364 (100); elemental analysis calcd (%) for $C_{27}H_{41}NO_5SSi$: C 62.39, H 7.95, N 2.69; found: C 63.30, H 7.85, N 2.80.

**4-[3-(*trans*-2-Methoxyvinyl)cyclobutylidene]-5,5-dimethyl-3-(*p*-toluenesulfonyl)oxazolidin-2-one (9j)**: m.p. 87.7–88.3 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu = 1815$ (s), 1390 (s), 1275 (s), 1220 (m), 1205 (m), 1190 (s), 1155 (m), 990 (m), 760 cm$^{-1}$ (m); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.43$ (s, 3H), 1.51 (s, 3H), 2.45 (s, 3H), 2.61 (ddd, $J = 2.9$, 6.6, 15.0 Hz, 1H), 2.84 (ddd, $J = 2.9$, 6.6, 15.8 Hz, 1H), 2.93 (br tq, $J = 6.6$, 8.4 Hz, 1H), 3.04 (ddt, $J = 8.4$, 15.0, 2.9 Hz, 1H), 3.21 (ddt, $J = 8.4$, 15.8, 2.9 Hz, 1H), 3.53 (s, 3H), 4.89 (dd, $J = 8.4$, 12.5 Hz, 1H), 6.34 (d, $J = 12.5$ Hz, 1H), 7.34 (d, $J = 8.1$ Hz, 2H), 7.92 (d, $J = 8.1$ Hz, 2H); HRMS: $m/z$ (%): calcd for $C_{19}H_{23}NO_5S$: 377.1297; found: 377.1333 (1) $[M]^+$, 222 (100).[17]

**5,5-Dimethyl-3-*p*-toluenesulfonyl-4-[3-(triisopropylsiloxy)-3-vinylcyclobutylidene]oxazolidin-2-one (9k)**: m.p. 138.0–139.0 °C ($CH_2Cl_2$/hexane); IR (KBr):$\nu = 1780$ (s), 1370 (s), 1275 (s), 1120 cm$^{-1}$ (s); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.01$–1.10 (m, 21H), 1.40 (s, 3H), 1.50 (s, 3H), 2.44 (s, 3H), 2.98 (br d, $J = 15.0$ Hz, 1H), 3.02 (br d, $J = 15.0$ Hz, 1H), 3.20 (br d, $J = 17.0$ Hz, 1H), 3.29 (br d, $J = 17.0$ Hz, 1H), 5.06 (dd, $J = 1.1$, 10.6 Hz, 1H), 5.24(dd, $J = 1.1$, 17.4 Hz, 1H), 6.07 (dd, $J = 10.6$, 17.4 Hz, 1H), 7.34 (d, $J = 8.2$ Hz, 1H), 7.90 (d, $J = 8.2$ Hz, 1H); 13C NMR (100 MHz, $CDCl_3$): $\delta = 13.3$, 18.2, 21.7, 25.2, 26.0, 45.3, 47.5, 72.8, 84.2, 111.9, 114.7, 128.3, 129.7, 130.2, 135.4, 142.5, 145.5, 151.4; HRMS: $m/z$ (%): calcd for $C_{27}H_{41}NO_5SSi$: 519.2475; found 519.2417 (2) $[M]^+$, 364 (100); elemental analysis calcd (%) for $C_{27}H_{41}NO_5SSi$: C 62.39, H 7.95, N 2.69; found: C 62.14, H 7.85, N 2.70.

**5,5-Dimethyl-4-[3-*trans*-*β*-styryl-3-(triisopropylsiloxy)cyclobutylidene]-3-*p*-toluenesulfonyl-oxazolidin-2-one (9l)**: oil; IR (neat): $\nu = 1790$ (s), 1370 (m), 1260 (m), 1190 (m), 1170 (m), 1115 (m), 1085 (m), 1010 (m), 990 (s), 960 (m), 875 (m), 805 cm$^{-1}$ (m); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.08$ (s, 21H), 1.42 (s, 3H), 1.49 (s, 3H), 2.43 (s, 3H), 3.08 (br d, $J = 14.3$ Hz, 1H), 3.12 (br d, $J = 14.3$ Hz, 1H), 3.30 (br d, $J = 16.7$ Hz, 1H), 3.42 (br d, $J = 16.7$ Hz, 1H), 6.42 (d, $J = 15.9$ Hz, 1H), 6.61 (d, $J = 15.9$ Hz, 1H), 6.40–6.63 (m, 2H), 7.31–7.39 (m, 5H), 7.92 (d, $J = 8.4$ Hz, 1H); HRMS: $m/z$ (%): calcd for $C_{33}H_{45}NO_5SSi$: 595.2788; found: 595.2821 (2) $[M]^+$, 440 (100).

**4-[3-Isopropenyl3-(triisopropylsiloxy)cyclobutylidene]-5,5-dimethyl-3-*p*-toluenesulfonyloxazolidin-2-one (9m)**: m.p. 118.0–118.2 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu = 1782$ (s), 1369 (s), 1275 (s), 1120 cm$^{-1}$ (s); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.00$–1.09 (m, 21H), 1.40 (s, 3H), 1.47 (s, 3H), 1.81 (br s, 3H), 2.45 (s, 3H), 2.94 (dd, $J = 2.9$, 15.2 Hz, 1H), 3.07 (dt, $J = 15.2$, 2.9 Hz, 1H), 3.14 (dd, $J = 2.9$, 16.9 Hz, 1H), 3.44 (dt, $J = 16.9$. 2.9 Hz, 1H), 4.84 (t, $J = 1.5$ Hz, 1H), 4.96 (br s, 1H), 7.34 (d, $J = 8.1$ Hz, 2H), 7.90 (d, $J = 8.1$ Hz, 2H); HRMS: $m/z$ (%): calcd for $C_{28}H_{43}NO_5SSi$: 533.2631; found: 533.2594 (14) $[M]^+$, 91 (100); elemental analysis calcd (%) for $C_{28}H_{43}NO_5SSi$: C 63.00, H 8.12, N 2.62; found: C 62.65, H 8.06, N 2.75.

**4-(3-Isopropenyl-3-methylcyclobutylidene)-3-*p*-toluenesulfonyl-1-oxa-3-azaspiro[4.4]nonan-2-one (9n)**: m.p. 106.0–107.0 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu = 1790$ (s), 1370 (s), 1280 (m), 1170 (s), 1110 (w), 880 cm$^{-1}$ (w); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.30$ (s, 3H), 1.73 (br s, 3H), 1.59–2.18 (m, 8H), 2.44 (s, 3H), 2.52 (dt, $J = 14.5$, 3.0 Hz, 1H), 2.81 (dt, $J = 16.1$, 3.0 Hz, 1H), 2.91 (dd, $J = 3.0$, 14.5 Hz, 1H), 3.19 (dd, $J = 3.0$, 16.1 Hz, 1H), 4.71 (s, 1H), 4.79 (br s, 1H), 7.43 (d, $J = 8.2$ Hz, 2H), 7.88 (d, $J = 8.2$ Hz, 2H); HRMS: $m/z$ (%): calcd for $C_{22}H_{27}NO_4S$: 401.1661; found: 401.1661 (2) $[M]^+$, 357 (17), 246 (35), 202 (100); elemental analysis calcd (%) for $C_{22}H_{27}NO_4S$: C 65.81, H 6.78, N 3.49, S 7.99; found: C 65.91, H 6.69, N 3.40, S 8.11.

**5,5-Dimethyl-3-(*p*-toluenesulfonyl)-4-{3-[3-*trans*-(trimethylsilyl)propenyl]cyclobutylidene}oxazolidin-2-one (9o)**: m.p. 86.5–87.5 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu = 1790$(s), 1371 (s), 1177 (s), 858 cm$^{-1}$ (s); $^1$H NMR (400 MHz, $C_6D_6$): $\delta = 0.04$ (s, 9H), 1.08 (s, 3H), 1.14 (s, 3H), 1.46 (d, $J = 8.1$ Hz, 2H), 1.84 (s, 3H), 2.35 (ddd, $J = 2.9$, 7.0, 15.2 Hz, 1H), 2.71 (ddt, $J = 8.1$, 15.2, 2.9 Hz, 1H), 3.04 (ddd, $J = 2.9$, 7.0, 15.6 Hz, 1H), 3.12 (ttm, $J = 7.0$, 8.1 Hz, 1H), 3.45 (ddt, $J = 8.1$, 15.6, 2.9 Hz, 1H), 5.42 (dt, $J = 10.6$, 8.1 Hz, 1H), 5.48 (dd, $J = 8.1$, 10.6 Hz, 1H), 6.75 (d, $J = 8.2$ Hz, 2H), 8.11 (d, $J = 8.2$ Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 1.25$, 22.2, 24.3, 28.1, 28.6, 32.0, 39.8, 43.2, 87.1. 123.9, 128.9, 132.1, 132.7, 135.3, 139.6, 148.1, 154.7; HRMS: $m/z$ (%): calcd for $C_{22}H_{31}NO_4SSi$: 433.1743; found: 433.1744 (35) $[M]^+$, 91 (24), 73 (100); elemental analysis calcd (%) for $C_{22}H_{31}NO_4SSi$: C 60.93, H 7.21, N 3.23; found: C 60.90, H 7.11, N 3.20.

**8-Methyl-11-methylene-12-*p*-toluenesulfonyl-7,14-dioxa-12-azadispiro-[4.0.5.3]tetradec-8-en-13-one (10a)**: m.p. 192.0–193.0 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu = 1790$ (s), 1380 (m), 1260 (m), 1180 (s), 1140 (m), 1040 cm$^{-1}$ (m); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.26$–1.93 (m, 8H), 1.86 (br s, 3H), 2.44 (s, 3H), 2.79 (dquint, $J = 19.8$, 2.6 Hz, 1H), 2.99 (dd, $J = 5.0$, 19.8 Hz, 1H), 4.65 (d, $J = 5.0$ Hz, 1H), 5.44 (d, $J = 2.6$ Hz, 1H), 5.56 (d, $J = 2.6$ Hz, 1H), 7.31 (d, $J = 8.2$ Hz, 2H), 8.02 (d, $J = 8.2$ Hz, 2H); elemental analysis calcd (%) for $C_{20}H_{23}NO_5S$: C 61.68, H 5.95, N 3.60, S 8.23; found: C 61.37, H 5.86, N 3.46, S 8.02.

**11-Methylene-12-*p*-toluenesulfonyl-7,14-dioxa-12-aza-dispiro[4.0.5.3]tetradec-8-en-13-one (10b)**: m.p. 157.5–158.5 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu = 1790$ (s), 1680 (m), 1370 (s), 1340 (s), 1310 (m), 1270 (s), 1230 (s), 1180 (s), 1150 (m), 1090 (s), 1070 (s), 1040 (s), 980 (m), 910 cm$^{-1}$ (m); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.65$–1.94 (m, 8H), 2.44 (s, 3H), 2.82 (ddm, $J = 2.6$, 20.1 Hz, 1H), 3.03 (dd, $J = 6.0$, 20.1 Hz, 1H), 4.93 (dt, $J = 1.8$, 6.0 Hz, 1H), 5.48 (d, $J = 2.6$ Hz, 1H), 5.59 (d, $J = 2.6$ Hz, 1H), 6.47 (ddm, $J = 1.8$, 6.0 Hz, 1H), 7.32 (d, $J = 8.4$ Hz, 2H), 7.99 (d, $J = 8.4$ Hz, 2H); HRMS: $m/z$ (%): calcd for $C_{19}H_{21}NO_5S$: 375.1140; found 375.1160 (12) $[M]^+$, 221 (11), 176 (100).[17]

**8,9-Dimethyl-11-methylene-12-*p*-toluenesulfonyl-7,14-dioxa-12-azadispiro-[4.0.5.3]tetradec-8-en-13-one (10c)**: m.p. 212.0–212.3 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu = 1778$ (s), 1713 (m), 1377 (s), 1335 (m), 1232 (m), 1159 (s), 1124 (m), 1086 (m), 1061 cm$^{-1}$ (s); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.65$–1.91 (m, 8H), 1.65 (s, 3H), 1.84 (s, 3H), 2.44 (s, 3H), 2.77 (d, $J = 19.4$ Hz, 1H), 2.85 (d, $J = 19.4$ Hz, 1H), 5.40 (d, $J = 2.6$ Hz, 1H), 5.53 (d, $J = 2.6$ Hz, 1H), 7.31 (d, $J = 8.2$ Hz, 2H), 8.02 (d, $J = 8.2$ Hz, 2H); HRMS: $m/z$ (%): calcd for $C_{21}H_{25}NO_5S$: 403.1453; found: 403.1433 (20), 248 (100).[17]

**9-Methyl-11-methylene-12-*p*-toluenesulfonyl-7,14-dioxa-12-aza-dispiro-[4.0.5.3]tetradec-8-en-13-one (10d)**: m.p. 109.0–110.0 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu = 1790$ (s), 1700 (m), 1370 (s), 1330 (m), 1310 (m), 1260 (m), 1180 (s), 1150 (s), 1090 (m), 1040 (s), 940 cm$^{-1}$ (m); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.56$ (s, 3H), 1.61–1.90 (m, 8H), 2.44 (s, 3H), 2.78 (dm, $J = 20.5$ Hz, 1H), 2.88 (dm, $J = 20.5$ Hz, 1H), 5.46 (d, $J = 2.2$ Hz, 1H), 5.57 (d, $J = 2.2$ Hz, 1H), 6.27 (t, $J = 1.1$ Hz, 1H), 7.31 (d, $J = 8.4$ Hz, 2H), 7.98 (d, $J = 8.4$ Hz, 2H); HRMS: $m/z$ (%): calcd for $C_{20}H_{23}NO_5S$: 389.1297; found: 389.1293 (18) $[M]^+$, 234 (68), 190 (100).[17]

**4-Methyl-10-methylene-1-(*p*-toluenesulfonyl)-3,6-dioxa-1-azaspiro[4.5]-dec-7-en-2-one (10e)**: ≈1:1.2 mixture of stereoisomers): m.p. 113.0–114.5 °C; IR (KBr): $\nu = 1786$ (s), 1375 (s), 1177 (s), 762 (m), 704 cm$^{-1}$ (m); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.26$ (d, $J = 6.6$ Hz, 3H, major isomer), 1.35 (d, $J = 6.4$ Hz, 3H, minor isomer), 2.44 (s, 3H), 2.87 (dm, $J = 19.8$ Hz, 1H, minor isomer), 2.91 (dm, $J = 19.8$ Hz, 1H, major isomer), 3.07 (dm, $J = 19.8$ Hz, 1H, major isomer), 3.09 (dm, $J = 19.8$ Hz, 1H, minor isomer), 4.40 (q, $J = 6.4$ Hz, 1H, minor isomer), 4.52 (q, $J = 6.6$ Hz, 1H, major isomer), 4.96 (m, 1H), 5.40 (br s, 1H, minor isomer), 5.53 (m, 1H, major isomer), 5.58 (m, 1H), 6.41 (dm, $J = 5.7$ Hz, 1H, major isomer), 6.46 (dm, $J = 5.7$ Hz, 1H, minor isomer), 7.33 (d, $J = 8.2$ Hz, 2H), 7.98 (d, $J = 8.2$ Hz, 2H, minor isomer), 8.00 (d, $J = 8.2$ Hz, 2H, major isomer); HRMS: $m/z$ (%): calcd for $C_{16}H_{17}NO_5S$: 335.0827; found 335.0836 (17) $[M]^+$, 180 (52), 91 (100).[17]

**4-Methylene-6-*p*-toluenesulfonyl-3-(2,4,6-trimethylphenyl)-1,8-dioxa-2,6-diazaspiro[4.4]non-2-en-7-one (11a)**: m.p. 252.0–253.0 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu = 1790$ (s), 1660 (s), 1370 (m), 1250 (m), 1230 (m), 1050 (m), 850 cm$^{-1}$ (m); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 2.32$ (s, 3H), 2.39 (s, 6H), 2.43 (s, 3H), 4.35 (d, $J = 9.2$ Hz, 1H), 4.43 (d, $J = 9.2$ Hz, 1H), 5.28 (s, 1H), 6.94 (s, 1H), 6.69 (s, 2H), 7.30 (d, $J = 8.4$ Hz, 2H), 7.90 (d, $J = 8.4$ Hz, 2H); HRMS: $m/z$ (%): calcd for $C_{22}H_{22}N_2O_5S$: 426.1249; found: 426.1242 (6) $[M]^+$, 271 (100); elemental analysis calcd (%) for $C_{22}H_{22}N_2O_5S$: C 61.96, H 5.20, N 6.57, S 7.52; found: C 61.86, H 5.25, N 6.47, S 7.66.

**9,9-Dimethyl-4-methylene-6-*p*-toluenesulfonyl-3-(2,4,6-trimethylphenyl)-1,8-dioxa-2,6-diaza-spiro[4.4]non-2-en-7-one (11b)**: m.p. 199.0–200.0 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu = 1800$ (s), 1630 (m), 1380 (m), 1190 (m), 1180 (m), 1150 (m), 1140 (m), 1090 (m), 970 cm$^{-1}$ (m); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.48$ (s, 3H), 1.49 (s, 3H), 2.13 (s, 3H), 2.34 (s, 3H), 2.41 (s, 3H), 2.45 (s, 3H), 5.57 (d, $J = 1.5$ Hz, 1H), 5.78 (d, $J = 1.5$ Hz, 1H), 6.93 (s, 1H), 7.00 (s, 3H), 7.35 (d, $J = 8.6$ Hz, 2H), 8.05 (d, $J = 8.6$ Hz, 2H); elemental

analysis calcd (%) for $C_{24}H_{26}N_2O_5S$: C 63.42, H 5.77, N 6.16, S 7.05; found: C 63.28, H 5.80, N 6.06, S 6.81.

**4-Methylene-13-*p*-toluenesulfonyl-3-(2,4,6-trimethylphenyl)-1,11-dioxa-2,3-diazadispiro[4.0.4.3]tridec-2-en-12-one (11c)**: m.p. 190.5–191.0 °C ($CH_2Cl_2$/hexane); IR (KBr): $\nu = 1800$ (s), 1630 (m), 1440 (m), 1380 (m), 1190 (m), 1150 (m), 1090 (m), 970 $cm^{-1}$ (m); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 1.57$–1.94 (m, 8H), 2.10 (s, 3H), 2.34 (s, 3H), 2.41 (s, 3H), 2.45 (s, 3H), 5.59 (d, $J = 1.3$ Hz, 1H), 5.73 (d, $J = 1.3$ Hz, 1H), 6.93 (s, 1H), 7.00 (s, 1H), 7.35 (d, $J = 8.6$ Hz, 1H), 7.97 (d, $J = 8.6$ Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta = 19.6$, 20.1, 21.1, 21.8, 22.0, 22.8, 23.6, 33.3, 34.5, 51.1, 97.1, 101.3, 119.5, 122.8, 128.5, 129.1, 129.5, 129.8, 134.7, 136.8, 138.8, 139.8, 143.1, 145.8, 150.7, 159.8; elemental analysis calcd (%) for $C_{26}H_{28}N_2O_5S$: C 64.98, H 5.87, N 5.83, S 6.67; found: C 64.91, H 5.88, N 5.80, S 7.00.

## Acknowledgement

We thank Mr. Y. Ohhama (400 MHz $^1H$ NMR measurements, Nagasaki Univ.) and Dr. H. Kawano (X-ray structure analysis, NU). We also thank Dr. S. Kanemasa (Institute of Advanced Material Study, Kyushu University) for his helpful guidance for the treatment of nitrile oxides and Mr. Y. Wakamiya, Mr. K. Odaka, and Mr. M. Mori (NU) for their technical assistance. $\alpha$-Methylacryloyl isocyanate and chlorobutadienes were a gift from Nippon Paint Co. and Tosoh Corp., respectively. This research has been supported by the Ministry of Education, Science, Sports and Culture, Japanese Government, Grant-in-Aid for Scientific Research B.

[1] a) Photochemical [2+2] cycloaddition of allenes: J. D. Winkler, M. B. Rouse, M. F. Greaney, S. J. Harrion, T. T. Jeon, *J. Am. Chem. Soc.* **2002**, *124*, 9726–9728; b) T. Tsuno, K. Sugiyama, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 519–531; c) M. S. Shepard, E. M. Carreira, *J. Am. Chem. Soc.* **1997**, *119*, 2597–2605; d) E. M. Carreira, C. A. Hastings, M. S. Shepard, L. A. Yerkey, D. B. Millward, *J. Am. Chem. Soc.* **1994**, *116*, 6622–6630; e) Y. Tobe, D. Yamashita, T. Takahashi, M. Inata, J.-I. Sato, K. Kakiuchi, K. Kobiro, Y. Odaira, *J. Am. Chem. Soc.* **1990**, *112*, 775–779; f) P. Magnus, M. J. Slater, L. M. Principe, *J. Org. Chem.* **1989**, *54*, 5148–5153; g) C. Iwata, Y. Takemoto, M. Doi, T. Imanishi, *J. Org. Chem.* **1988**, *53*, 1623–1628; h) W. Stensen, J. S. Svendsen, O. Hofer, L. K. Sydnes, *Acta Chem. Scand.* **1988**, *B42*, 259–268.

[2] a) B. Bienfait, G. Coppe-Motte, R. Merenyi, H. G. Viehe, *Tetrahedron* **1991**, *47*, 8167–8176; b) L. Skattebøl, Y. Stenstrøm, *Tetrahedron Lett.* **1983**, *24*, 3021–3024; c) Z. Komiya, S. Nishida, *J. Org. Chem.* **1983**, *48*, 1500–1509; d) H. N. Cripps, J. K. Williams, W. H. Sharkey, *J. Am. Chem. Soc.* **1959**, *81*, 2723–2728.

[3] a) Lewis-acid catalyzed [2+2] cycloaddition: K. Hojo, C. Murakami, S. Nakamura, A. Hosomi, *Chem. Lett.* **1998**, 331–332; b) T. A. Engler, K. Agrios, J. P. Reddy, R. Iyengar, *Tetrahedron Lett.* **1996**, *37*, 327–330; c) K. Narasaka, Y. Hayashi, H. Shimadzu, S. Niihara, *J. Am. Chem. Soc.* **1992**, *114*, 8869–8885; d) Y. Hayashi, S. Hiihara, K. Narasaka, *Chem. Lett.* **1990**, 2091–2094; e) B. B. Snider, E. Ron, *J. Org. Chem.* **1986**, *51*, 3643–3652; f) H. M. R. Hoffmann, Z. M. Ismail, A. Weber, *Tetrahedron Lett.* **1981**, *22*, 1953–1956; g) B. B. Snider, D. K. Spindell, *J. Org. Chem.* **1980**, *45*, 5017–5020.

[4] Transition-metal catalyzed [2+2] cyclodimerization of allenes: a) S. Saito, K. Hirayama, C. Kabuto, Y. Yamamoto, *J. Am. Chem. Soc.* **2000**, *122*, 10776–10780; b) K. Lautens, W. Klute, W. Tam, *Chem. Rev.* **1996**, *96*, 49–92.

[5] Transition-metal catalyzed [2+2] cycloaddition of allenes and alkenes: M. Murakami, H. Amii, K. Itami, Y. Ito, *Angew. Chem.* **1995**, *107*, 1649–1650; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1476–1477.

[6] a) A. Padwa, M. Meske, S. S. Murphree, S. H. Watterson, Z. Ni, *J. Am. Chem. Soc.* **1995**, *117*, 7071–7080; b) A. Padwa, M. A. Filipkowski, M. Meske, S. H. Watterson, Z. Ni, *J. Am. Chem. Soc.* **1993**, *115*, 3776–3777.

[7] a) P. V. Bharatam, R. S. Kumar, M. P. Mahajan, *Org. Lett.* **2000**, *2*, 2725–2728; b) A. E. Taggi, A. M. Hafez, H. Wack, B. Young, W. J. Drury III, T. Lectka, *J. Am. Chem. Soc.* **2000**, *122*, 7831–7832; c) T. Sugimura, T. Tei, A. Mori, T. Okuyama, A. Tai, *J. Am. Chem. Soc.* **2000**, *122*, 2128–2129; d) T. Machiguchi, T. Hasegawa, A. Ishiwata, S. Terashima, S. Yamabe, T. Minato, *J. Am. Chem. Soc.* **1999**, *121*, 4771–4786; e) S. G. Nelson, T. J. Peelen, Z. Wan, *J. Am. Chem. Soc.* **1999**, *121*, 9742–9743; f) J. R. Cagnon, F. L. Bideau, J. Marchand-Brynaert, L. Ghosez, *Tetrahedron Lett.* **1997**, *38*, 2291–2294; g) J.-M. Pons, M. Oblin, A. Pommier, M. Rajzmann, D. Liotard, *J. Am. Chem. Soc.* **1997**, *119*, 3333–3338; h) A. B. Concepcion, K. Maruoka, H. Yamamoto, *Tetrahedron* **1995**, *51*, 4011–4020; i) A. Pommier, J.-M. Pons, P. J. Kocienski, *J. Org. Chem.* **1995**, *60*, 7334–7339; j) L. S. Hegedus, *Acc. Chem. Res.* **1995**, *28*, 299–305; k) J. A. Hyatt, P. W. Raynolds, *Org. React.* **1994**, *45*, 159–646; l) X. Wang, K. N. Houk, *J. Am. Chem. Soc.* **1990**, *112*, 1754–1756; m) H. R. Seikaly, T. T. Tidwell, *Tetrahedron* **1986**, *42*, 2587–2613; intramolecular version: n) K. L. McCaleb, R. L. Halcomb, *Org. Lett.* **2000**, *2*, 2631–2634; o) J.-M. Adam, L. Ghosez, K. N. Houk, *Angew. Chem.* **1999**, *111*, 2897–2899; *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 2728–2730; p) P.-J. Shim, H.-D. Kim, *Tetrahedron Lett.* **1998**, *39*, 9517–9520; q) L. A. Paquette, L.-Q. Sun, T. J. N. Watson, D. Friedrich, B. T. Freeman, *J. Am. Chem. Soc.* **1997**, *119*, 2767–2768; r) W. H. Moser, L. S. Hegedus, *J. Am. Chem. Soc.* **1996**, *118*, 7873–7880; s) B. B. Snider, *Chem. Rev.* **1988**, *88*, 793–811.

[8] a) R. L. Elliott, N. H. Nicholson, F. E. Peaker, A. K. Takle, C. M. Richardson, J. W. Tyler, J. White, M. J. Pearson, D. S. Eggleston, R. C. Haltiwanger, *J. Org. Chem.* **1997**, *62*, 4998–5016; b) R. Ruzziconi, Y. Maruse, M. Schlosser, *Tetrahedron* **1991**, *47*, 4603–4610; c) J. E. Baldwin, U. V. Roy, *J. Chem. Soc. Chem. Commun.* **1969**, 1225–1226; d) E. F. Kiefer, M. Okamura, *J. Am. Chem. Soc.* **1968**, *90*, 4187–4189.

[9] a) W. R. Jr. Dolbier, Cycloadditions of Allenes in *Advances in Detailed Reaction Mechanisms*, *Vol. 1*, JAI Press, **1991**, p. 127–179; b) W. R. Dolbier Jr., *Acc. Chem. Res.* **1991**, *24*, 63–69; c) W. R. Dolbier Jr., S. L. Weaver, *J. Org. Chem.* **1990**, *55*, 711–715; d) S.-H. Dai, W. R. Dolbier Jr., *J. Am. Chem. Soc.* **1972**, *94*, 3946–3952; e) W. R. Dolbier Jr., S.-H. Dai, *J. Am. Chem. Soc.* **1968**, *90*, 5028–5030.

[10] a) D. J. Pasto, D. Sugi, *J. Org. Chem.* **1992**, *57*, 12–17; b) D. J. Pasto, K. D. Sugi, *J. Org. Chem.* **1991**, *56*, 3795–3801; c) D. J. Pasto, K. D. Sugi, *J. Org. Chem.* **1991**, *56*, 6216–6224 and references therein; d) D. J. Pasto, *Tetrahedron* **1984**, *40*, 2805–2827; e) D. J. Pasto, *J. Am. Chem. Soc.* **1979**, *101*, 37–46.

[11] 2-Methylenecyclobutene formation via thermal radical cyclization of $\omega$-enyne-allene: a) C. Ikemoto, T. Kawano, I. Ueda, *Tetrahedron Lett.* **1998**, *39*, 5053–5056; b) M. Schmittel, S. Kiau, T. Siebert, M. Strittmatter, *Tetrahedron Lett.* **1996**, *37*, 7691–7694; c) J. G. Garcia, B. Ramos, L. M. Pratt, A. Rodriguez, *Tetrahedron Lett.* **1995**, *36*, 7391–7394; d) T. Gillmann, T. Hülsen, W. Massa, S. Wocadlo, *Synlett* **1995**, 1257–1259; e) K. Fujiwara, H. Sakai, M. Hirama, *J. Org. Chem.* **1991**, *56*, 1688–1689.

[12] Preliminary communications: a) M. Kimura, Y. Wakamiya, Y. Horino, Y. Tamaru, *Tetrahedron Lett.* **1997**, *38*, 3963–3966; b) M. Kimura, Y. Horino, Y. Wakamiya, T. Okajima, Y. Tamaru, *J. Am. Chem. Soc.* **1997**, *119*, 10869–10870.

[13] Allenes with bent bond of bond angles within 161–176° due to ring strain, torsional strain, and/or packing effects in the crystals: a) F. Hojo, K. Fujiki, W. Ando, *Organometallics* **1996**, *15*, 3606–3610; b) E. Weber, W. Seichter, B. Hess, G. Will, H.-J. Dasting, *J. Phys. Org. Chem.* **1995**, *8*, 94–96; c) J. Lin, Y. Pang, V. G. Young Jr., T. J. Barton, *J. Am. Chem. Soc.* **1993**, *115*, 3794–3795; d) T. Shimizu, F. Hojo, W. Ando, *J. Am. Chem. Soc.* **1993**, *115*, 3111–3115; e) A. N. Chekhov, V. K. Brel, E. V. Abramkin, N. S. Zefirov, *Dokl. Akad. Nauk.* **1992**, *326*, 295–299; f) R. P. Johnson, *Chem. Rev.* **1989**, *89*, 1111–1124; g) M. Traetteberg, P. Bakken, A. Almenningen, *J. Mol. Struct.* **1981**, *70*, 287–295; h) V. A. Gieren, C.Hahn, *Acta Crystallogr.* **1979**, *B35*, 1008–1010; allenes with bent bond due to coordination to transition-metals: i) H. Werner, R. W. Lass, O. Gevert, J. Wolf, *Organometallics* **1997**, *16*, 4077–4088; j) C. E. Kerr, B. E. Eaton, J. A. Kaduk, *Organometallics* **1995**, *14*, 269–273; allenes with bent bond stabilized by coordination to transition metals: k) J. Yin, K. A. Abboud, W. N. Jones, *J. Am. Chem. Soc.* **1993**, *115*, 3810–3811; l) K. A. Abboud, Z. Lu, W. M. Jones, *Acta Crystallogr.* **1992**, *C48*, 909–912; m) A. W. Cordes, S. Siegel, S.-T. Lin, M. C. Noble, S. Barsoum, J. Fairman, *Acta Crystallogr.* **1989**, *C45*, 1426–1428; cyclohepta-1,2,4,6-tetraene stabilized by incarceration: n) R. Warmuth, M. A. Marvel, *Chem. Eur. J.*

**2001**, *7*, 1209 – 1220; matrix-isolated cyclohepta-1,2,4,6-tetraene: o) S. Matzinger, T. Bally, *J. Phys. Chem. A* **2000**, *104*, 3544 – 3552.
[14] Y. Tamaru, M. Kimura, S. Tanaka, S. Kure, Z. Yoshida, *Bull. Chem. Soc. Jpn*. **1994**, *67*, 2838 – 2849.
[15] R. M. Beesley, C. K. Ingold, J. F. Thorpe, *J. Chem. Soc.* **1915**, 1080 – 1106.
[16] A. G. M. Barrett, M. J. Betts, A. Fenwick, *J. Org. Chem.* **1985**, *50*, 169 – 175.
[17] $^1$H NMR spectrum of this compound is compiled in the Supporting Information.
[18] CCDC-181558 (**2a**), -181724 (**2b**), -188289 (**2g**), -181726 (**2k**), -181555 (**2m**), -181553 (**2n**), -181554 (**2p**), -181559 (**2q**), -181551 (**7c**), -181560 (**8a**), -179982 (**8k**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; (fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).
[19] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441 – 451.
[20] Ketenes are such unstable molecules that a vast number of X-ray crystallographic analyses have been reported as their transition-metal complexes. X-ray structural analyses of ketenes without coordination of transition metals: a) L. Pandolfo, G. Paiaro, L. K. Dragani, C. Maccatom, R. Bertani, G. Facchin, L. Zanotto, P. Ganis, G. Valle, *Organometallics* **1996**, *15*, 3250 – 3252; b) N. S. Radu, M. P. Engeler, C. P. Gerlach, T. D. Tilley, *J. Am. Chem. Soc.* **1995**, *117*, 3621 – 3622; c) C. O. Kappe, R. A. Evans, C. H. L. Kennard, C. Wentrup, *J. Am. Chem. Soc.* **1991**, *113*, 4233 – 4237; d) J. J. Daly, *J. Chem. Soc. A* **1967**, 1913 – 1917.
[21] The NMR spectrum is given in the Supporting Information.
[22] Y. Horino, M. Kimura, Y. Wakamiya, T. Okajima, Y. Tamaru, *Angew. Chem.* **1999**, *111*, 123 – 126, *Angew. Chem. Int. Ed.* **1999**, *38*, 121 – 123
[23] Y. Horino, M. Kimura, M. Naito, S. Tanaka, Y. Tamaru, *Tetrahedron Lett.* **2000**, *41*, 3427 – 3431.
[24] Complete loss of stereochemical integrity of *cis*-$\beta$-monodeuteriostyrene for the [2 + 2] addition with cyclohexa-1,3-diene: a) M. Christl, M. Schreck, *Chem. Ber.* **1987**, *120*, 915 – 920; b) S. Harnos, S. Tivakornpannarai, E. E. Waali, *Tetrahedron Lett.* **1986**, *27*, 3701 – 3704.
[25] a) F. Scheufler, M. E. Maier, *Eur. J. Org. Chem.* **2000**, 3945 – 3948; b) M. Nendel, L. M. Tolbert, L. E. Herring, M. N. Islam, K. N. Houk, *J. Org. Chem.* **1999**, *64*, 976 – 983; c) H.-J. Wu, C.-H. Yen, C.-T. Chuang, *J. Org. Chem.* **1998**, *63*, 5064 – 5070; d) C. P. Raj, A. Dhas, C. Cherkinski, A. Gedanken, S. Breverman, *Tetrahedron Lett.* **1998**, *39*, 5413 – 5416; e) G. Himbert, H.-J. Schlindwein, *Liebigs Ann./Recueil* **1997**, *435* – 439; f) N. P. Pavri, M. L. Trudell, *Tetrahedron Lett.* **1997**, *38*, 7993 – 7996; g) M. Schmittel, C. Wöhrle, I. Bohn, *Chem. Eur. J.* **1996**, *2*, 1031 – 1040; h) S. Braverman, Z. Lior, *Tetrahedron Lett.* **1994**, *35*, 6725 – 6728; i) K. Kanematsu, I. Kinoyama, *J. Chem. Soc. Chem. Commun.* **1992**, 735 – 736; j) A. Padwa, W. H. Bullock, B. H. Norman, J. Perumattam, *J. Org. Chem.* **1991**, *56*, 4252 – 4259; k) F. Foriadu, A. Archavlis, G. Buono, *Tetrahedron Lett.* **1990**, *31*, 4859 – 4862; l) E. Block, D. Putman, *J. Am. Chem. Soc.* **1990**, *112*, 4072 – 4074; m) D. Spitzner, I. Klein, *Liebigs Ann. Chem.* **1990**, 63 – 68; n) T. Yasukouchi, K. Kanematsu, *Tetrahedron Lett.* **1989**, *30*, 6559 – 6562.
[26] Transition-metal catalyzed Diels – Alder reaction of allene/diene: a) M. Murakami, K. Itami, Y. Ito, *J. Am. Chem. Soc.* **1997**, *119*, 7163 – 7164; b) P. A. Wender, T. E. Jenkins, S. Suzuki, *J. Am. Chem. Soc.* **1995**, *117*, 1843 – 1844.
[27] C. Spino, C. Thibault, S. Gingras, *J. Org. Chem.* **1998**, *63*, 5283 – 5287; b) M. Murakami, M. Ubukata, K. Itami, Y. Ito, *Angew. Chem.* **1998**, *110*, 2362 – 2364; *Angew. Chem. Int. Ed.* **1998**, *37*, 2248 – 2250; ; c) H. J. Reich, E. K. Eisenhart, *J. Org. Chem.* **1984**, *49*, 5282 – 5283.
[28] Concomitant [2 + 2] and [4 + 2] addition reactions for the reaction of allenes and dienes: a) M. E. Jung, N. Nishimura, *J. Am. Chem. Soc.* **1999**, *121*, 3529 – 3530; b) J. R. Bull, N. S. Desmond-Smith, S. J. Heggie, R. Hunter, F.-C. Tien, *Synlett* **1998**, 900 – 902; c) M. E. Jung, J. A. Lowe III, M. A. Lyster, M. Node, R. W. Pfluger, R. W. Brown, *Tetrahedron* **1984**, *40*, 4751 – 4766; see also, ref. [6] and [8a,b].
[29] a) S.-K. Yeo, M. Shiro, K. Kanematsu, *J. Org. Chem.* **1994**, *59*, 1621 – 1632; b) K. Hayakawa, K. Aso, M. Shiro, K. Kanematsu, *J. Am. Chem. Soc.* **1989**, *111*, 5312 – 5320; c) M. Yoshida, Y. Hidaka, Y. Nawata, J. M. Rudzinski, E. Osawa, K. Kanematsu, *J. Am. Chem. Soc.* **1988**, *110*, 1232 – 1238.
[30] S. Inagaki, H. Fujimoto, K. Fukui, *J. Am. Chem. Soc.* **1976**, *98*, 4693 – 4701.
[31] G. J. Bodwell, J. Li, *Angew. Chem.* **2002**, *114*, 3395 – 3396; *Angew. Chem. Int. Ed.* **2002**, *41*, 3261 – 3262; b) M. Largeron, A. Neudorffer, M. Vuilhorgne, E. Blattes, M.-B. Fleury, *Angew. Chem.* **2002**, *114*, 852 – 855; *Angew. Chem. Int. Ed.* **2002**, *41*, 824 – 827; c) E. R. Bilbao, M. Alvarado, C. F. Masaguer, E. Ravina, *Tetrahedron Lett.* **2002**, *43*, 3551 – 3554; d) K. C. Nicolaou, K. Sugita, P. S. Baran, Y.-L. Zhong, *Angew. Chem.* **2001**, *113*, 213 – 216; *Angew. Chem. Int. Ed*. **2001**, *40*, 207 – 210; e) D. L. Boger, J. Hong, *J. Am. Chem. Soc.* **2001**, *123*, 8515 – 8519; f) R. Nomak, J. K. Snyder, *Tetrahedron Lett.* **2001**, *42*, 7929 – 7933; g) O. A. Attanasi, L. D. Crescentini, P. Fillippone, F. Fringuelli, M. Mantellini, O. Piermatti, F. Pizzo, *Helv. Chim. Acta* **2001**, *84*, 513 – 525; h) R. C. Boruah, S. Ahmed, U. Sharma, J. S. Sandhu, *J. Org. Chem.* **2000**, *65*, 922 – 925; i) L. Balazs, I. Kadas, L. Toke, *Tetrahedron Lett.* **2000**, *41*, 7583 – 7587; j) M.-F. Hsieh, P. D. Rao, C.-C. Liao, *Chem. Commun.* **1999**, 1441 – 1442; k) L. Lee, J. K. Snyder, *Adv. Cycloaddition*, **1999**, *6*, 119 – 171; l) C.-H. Chen, P. D. Rao, C.-C. Liao, *J. Am. Chem. Soc.* **1998**, *120*, 13254 – 13255.
[32] The other allenes **2a** and **2m** showed almost the same reactivity and selectivity as those of **2n**. For example, the reaction of **2a** and methyl vinyl ketone provided the corresponding **8** and **10** in 10 and 86% yield, respectively.[12a]
[33] a) L.-L. Wei, H. Xiong, C. J. Douglas, R. P. Hsung, *Tetrahedron Lett.* **1999**, *40*, 6903 – 6907; b) L.-L. Wei, R. P. Hsung, H. Xiong, J. A. Mulder, N. T. Nkansah, *Org. Lett.* **1999**, *1*, 2145 – 2148.
[34] Gaussian 98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.
[35] a) C.-H. Hu, D. P. Chong, in *Encyclopedia of Computational Chemistry*, (Ed.: P. von R. Schleyer), Wile, Chichester, **1998**, pp. 664 – 689; b) A. D. Becke, *Phys. Rev*. **1988**, *A38*, 3098 – 3100; c) C. Lee, W. Yang, R. G. Parr, *Phys. Rev.* **1988**, *B37*, 785 – 789; d) A. D. J. Becke, *Chem. Phys.* **1993**, *98*, 1372 – 1377; e) A. D. J. Becke, *Chem. Phys.* **1993**, *98*, 5648 – 5652.
[36] S. Kanemasa, K. Okuda, H. Yamamoto, S. Kaga, *Tetrahedron Lett.* **1997**, *38*, 4095 – 4098.
[37] R. Appel, M. Montenarh, *Chem. Ber.* **1974**, *107*, 706 – 709.
[38] a) A. G. M. Barrett, M. J. Betts, A. Fenwick, *J. Org. Chem.* **1985**, *50*, 169 – 175; b) A. Speziale, L. R. Smith, *J. Org. Chem.* **1962**, *27*, 3742 – 3743
[39] S. A. Rao, P. Knochel, *J. Am. Chem. Soc.* **1991**, *113*, 5735 – 5741.
[40] H. C. Brown, S. K. Gupta, *J. Am. Chem. Soc.* **1975**, *97*, 5249 – 5255.
[41] B. M. Trost, L. S. Chupak, T. Lübbers, *J. Org. Chem.* **1997**, *62*, 736 – 742.
[42] P. Cazeau, F. Duboudin, F. Moulines, O. Babot, J. Dunogues, *Tetrahedron* **1987**, *43*, 2089 – 2100.
[43] A. Hosomi, M. Saito, H. Sakurai, *Tetrahedron Lett.* **1979**, 429 – 432.
[44] T. Ukai, H. Kawazura, Y. Ishii, *J. Organomet. Chem.* **1974**, *65*, 253 – 266.
[45] D. R. Coulson, *Inorg. Synth.* **1972**, *13*, 121 – 124.
[46] The $^1$H NMR spectrum is shown in Figure 5 in the text.

Received: November 19, 2002 [F4586]