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Chameleon Reactivity of the Allene Bond of 4-Vinylidene-2-oxazolidinone: Novel Through-Space Conjugative Nucleophilic Addition of Electron-Rich Alkenes and Hetero-Nucleophiles

Masanari Kimura,[b] Yoshikazu Horino,[c] Masahiko Mori,[b] and Yoshinao Tamaru*[a]

Abstract: The Cα=Cβ double bond of allene carbamates **1** serves as an electron acceptor similar to the double bond of conjugated enones by means of a through-space interaction with the N–SO_2 bond; the carbamate double bond is thus subject to nucleophilic addition for a wide variety of nucleophiles, which proceeds under mild conditions by heating at 70–100 °C. Depending on the kind of nucleophiles, **1** displays three different reaction modes: 1) Typically enol ethers and allylsilanes promote 1,3-sulfonyl migration of **1** and undergo the inverse electron demand Diels–Alder reaction with the 1-aza-1,3-butadiene intermediates **II** thus formed to furnish bicyclic 2-alkoxy-5-sulfonyltetrahydropyridines **2** and 2-silylmethyl-5-sulfonyltetrahydropyridines **3**, respectively, with high regio- and stereoselectivity and retention of configuration of the double bonds of these electron-rich alkenes; 2) silanes (R_nSiH_{4-n}, $n=1$–3) and thiols deliver the hydride and the thiolate at the Cβ carbon and promote the 1,3-sulfonyl migration, followed by protonation of the thus-formed carbamate anion (*Z*)-**III** to provide, for example, (*Z*)-**4a** and (*Z*)-**4j**, respectively; 3) alcohols simply add to the Cα=Cβ double bond and provide (*E*)-**6**. Usually, the reaction with alcohols is accompanied by the second pathway, giving rise to, for example, (*Z*)-**4b** in addition to (*E*)-**6b**. Phenol engages in the third pathway and provides (*E*)-**6g** exclusively. Heteroaromatics, such as furans and benzofurans follow the first pathway, however, in a different regioselectivity from enol ethers and allylsilanes, delivering the oxygen atom at the 3-position of 5-sulfonyltetrahydropyridines (**2g** and **2h**). Indoles, on the other hand, show a dichotomy, equally enjoying the first and the third pathways and provide mixtures of (*E*)-**7** and (*E*)-**8**, respectively.

Keywords: allenes · Diels–Alder reactions · enols · indoles · sulfonamides

Introduction

We report that the allene bond of 4-vinylidene-2-oxazolidinones **1** significantly deviated from linearity (173–176°) and that the terminal allene Cα=Cβ bond reacted with a variety of terminal alkynes and alkenes under strictly thermal activation conditions (80–100 °C, Scheme 1) undergoing [2+2] cycloaddition though in potential violation of the Woodward–Hoffmann rule and the Fukui frontier orbital theory.[1a,b] Alkynes and alkenes provided 3-substituted (*Z*)-methylenecyclobutenes **A** and 3-substituted methylenecyclobutanes **B**, respectively, in good to excellent yields. The [2+2] cycloaddition was concluded to proceed via a concerted $[(\pi_{2s}+\pi_{2s})_{allene}+\pi_{2s}]$ Hückel transition state. Enones and nitrile oxides, on the other hand, reacted with **1** selectively at the internal allene C4=Cα double bond and underwent [4+2] and [3+2] cycloaddition reactions to give spiro compounds **C** and **D**, respectively.

In this article, we disclose that the allene carbamates **1** behave like a chameleon dramatically changing the reaction patterns depending on the reaction partners.[2] That is, in sharp contrast to the reactions with alkenes and alkynes mentioned above, the Cα=Cβ double bond of **1** behaves like an electron-deficient double bond of enones and is subject to nucleophilic addition at the Cβ carbon when exposed to a

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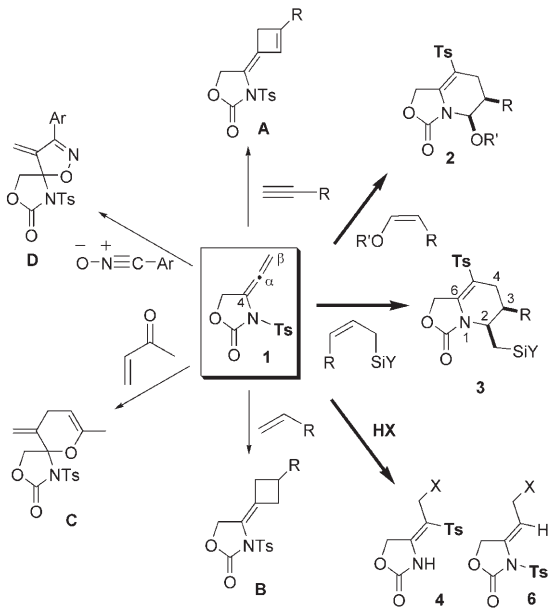


Scheme 1. Chameleon reactivity of the allene double bond of **1**, providing seven different products depending on reaction partners. For the reactions giving **A** ≈**D**, see ref. [1a,b]. R = CO_2Me, CN, phenyl, vinyl; X = OR″, SR″, H; Y = Me_3, Ph_3

variety of carbon nucleophiles (enol ethers, allylsilanes, furans, benzofurans, indoles) and hetero nucleophiles (alcohols, thiols, silanes R_nSiH_{4-n}, $n=1$–3).

Interestingly, these nucleophilic addition reactions are accompanied with an intramolecular migration of the sulfonyl group from N to Cα as can be seen explicitly, for example, for the conversion of **1** to **4** (Scheme 1). Ethers and sulfides **4**, with a Z structure with respect to the tetrasubstituted enamine double bonds, are produced stereoselectively in excellent yields for the reactions with alcohols and thiols, respectively. Silanes (R_nSiH_{4-n}, $n=1$–3) react in a way similar to alcohols and thiols, delivering a hydride in place of RO or RS.

The reactions with enol ethers and allylsilanes are also triggered by nucleophilic attack at the Cβ carbon accompanied by the 1,3-sulfonyl shift; however, the reaction feature has changed dramatically. In these reactions, bicyclic tetrahydropyridine derivatives **2** and **3** are formed in good to excellent yields, where the double bonds of enol ethers and allylsilanes are incorporated as the C2–C3 component of the tetrahydropyridine ring regio- and stereoselectively with retention of configuration at the double bond. The other tetrahydropyridine components (N, C4, C5, C6) originate from **1**.

The unique reactivity of **1** may be apparent by taking the following aspects into consideration: 1) Usually, allenes are susceptible to electrophilic addition[3] to both the central[4] and the terminal carbons.[5] In contrast, they are robust to nucleophilic attack. For example, addition of alcohols to allenes at the central sp carbon is an important industrial process to produce enol ethers. For this purpose, activation of an alcohol as the metal alkoxide in a vast excess amount of the alcohol as well as high temperatures (170–250 °C) are necessitated.[6] In sharp contrast to this, 1.5–2.0 equivalents of alcohols are sufficient to complete the addition to **1**. Furthermore, the reaction is completed at a temperature as low as 80 °C under neutral conditions even diluted with a solvent. 2) Nucleophilic addition ordinarily takes place at the central carbon of allenes,[7] while the reaction of **1** with alcohols and other nucleophiles takes place exclusively at the terminal allene carbon of **1**. It has been reported sporadically that allenyl amides,[8] allenyl alkoxides,[9] and allenyl thiolates[10] undergo *intramolecular* nucleophilic attack at the allene terminal carbons to furnish pyrrole, furan, and thiophene derivatives, respectively. To the best our knowledge, however, the reactions indicated in Scheme 1 with thick arrows are the first examples that nucleophilic addition even proceeds at the allene terminal carbons in an *intermolecular* fashion. 3) The sulfonamide bond is so strong that, in order to break the SO_2–N bond, generally either strong nucleophiles or strong reducing agents under harsh conditions are required.[11] In contrast, the Cα carbanion, generated by addition of electronically neutral carbo- and hetero-nucleophiles to the Cβ position of **1**, is capable of cleaving the sulfonamide bond. All these unique reactivity associated with **1** may be ascribed to a through-space interaction in a transition state between the π*(Cα=Cβ) and σ*(N-SO_2) orbitals, which makes the Cα=Cβ double bond as a good electrophile for a variety of nucleophiles.

Results and Discussion

Reaction of 1 with enol ethers derived from aldehydes, ketones, and esters: Table 1 summarizes the reactions of allene carbamates **1a** and **1b** with a wide range of enol ethers. The reaction was usually performed by stirring a mixture of **1** (0.5 mmol) and an excess amount of an enol ether in neat or as a solution in dioxane at 70–100 °C under nitrogen. Table 1 shows that a wide structural variety of enol ethers, encompassing those derived from aldehydes, ketones, and esters, provide 5-tosyltetrahydropyridines **2** in good to excellent yields.

The structure of **2** was elucidated by means of spectroscopic (FT-IR, ^1H and ^{13}C NMR) and analytical (HRMS, combustion) methods. In addition, in some cases, the structure was determined unequivocally by means of the single-crystal X-ray diffraction methods (see below).[12] The structure of **2** indicates that the reaction involves migration of the sulfonyl group from N to Cα as a key step.

Among the results in Table 1, run 7 is especially noteworthy. Despite its aromaticity, furan acts as a 4π component in the Diels–Alder reaction when exposed to electron-deficient alkenes[13] and allenes.[14,15] For the reaction with **1a**, however, furan behaved just like other enol ethers and served as a 2π component to give rise to **2g** in reasonable yield. Benzofuran displayed a reactivity similar to furan (run 8). It should be noted that furan and benzofuran furnish the positional isomers and introduce the oxygen atoms at the 3-position of the tetrahydropyridine ring (runs 7 and 8), although

Table 1. Thermal [4+2] cycloaddition of **2a**,**b** and enol ethers.[a]

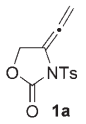
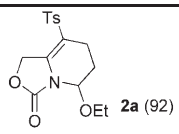
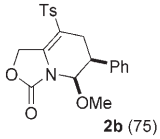
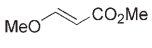
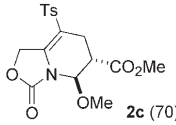
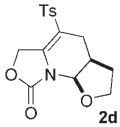
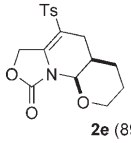
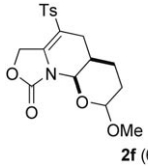
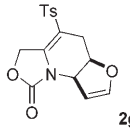
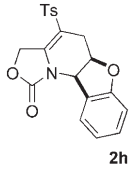
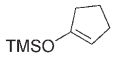
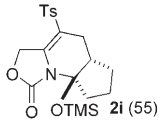
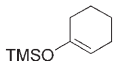
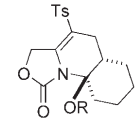
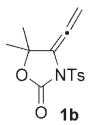
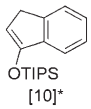
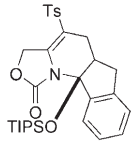
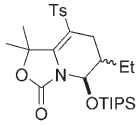
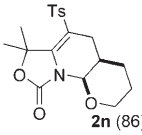
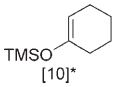
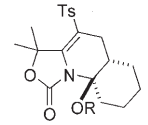
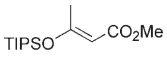
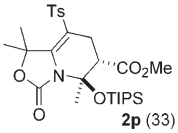
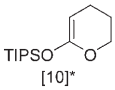
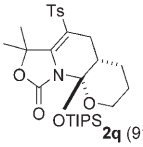
Run	Alene **1**	Vinyl ether [equiv]	T [°C]/t [h]	Product (% isolated yield)
1	 **1a**	 [100]*	100/8	 **2a** (92)
2	**1a**	 [20][b]	100/22	 **2b** (75)
3	**1a**	 [40]	70/23	 **2c** (70)
4	**1a**	 [80]*	100/24	 **2d** (75)
5	**1a**	 [20]*	80/12	 **2e** (89)
6	**1a**	 [40]	80/6	 **2f** (65)
7	**1a**	 [20]*	80/48	 **2g** (60)
8	**1q**	 [20]	100/23	 **2h** (41)
9	**1a**	 [10]*	80/48	 **2i** (55)
10	**1a**	 [10]*	80/24	 **2j** (R = TMS,59) + **2j'** (R = H, 29)
11	 **1b**	 [10]*	80/85	 **2k** (66)

Table 1. (Continued)

Run	Alene **1**	Vinyl ether [equiv]	T [°C]/t [h]	Product (% isolated yield)
12	**1b**	 [20][c]	80/33	 **2m** (90) *cis*/*trans* 4:1
13	**1b**	 [20]*	80/23	 **2n** (86)
14	**1b**	 [10]*	80/57	 **2o** (R = TMS, 70) + **2o'** (R = H, 25)
15	**1b**	 [10]*	100/26	 **2p** (33)
16	**1b**	 [10]*	80/12	 **2q** (91)

[a] A mixture of **1** (0.5 mmol), and an enol ether was heated at the temperature and for the period of time indicated under nitrogen. The reaction asterisked was undertaken as a dioxane solution (1 mL). [b] At start, *Z*/*E* 17:1; at end, *Z*/*E* 1.3:1.0. [c] At start, *Z*/*E* 10:1; at end, *Z*/*E* 2.2:1.0

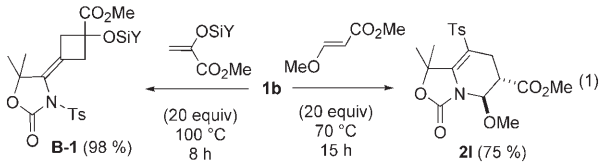
dihydrofuran and all other enol ethers provide tetrahydropyridines bearing the oxygen atoms at the 2-position.

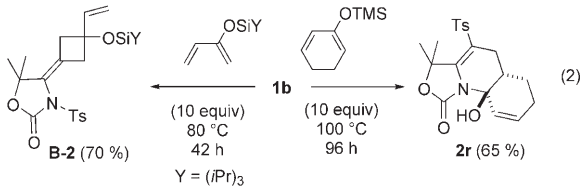
Enol ethers derived from ketones and esters create quaternary carbon centers at the 2-position of tetrahydropyridine ring (runs 9–11 and 14–16). The quaternary carbon centers are sterically congested and bear two or three electron-donating hetero atom substituents. Accordingly, these products were expected to be rather unstable and to decompose owing to heterolytic cleavage of these substituents. Contrary to our expectation, however, they turned out to be very stable. The high stability of **2j′**, **2o′**, and **2q** is remarkable; **2j′** and **2o′** exist as a hemiaminal and do not undergo ring opening to give a keto imine (or a keto enamine) form. The orthoester **2q** is stable and withstands purification by column chromatography over silica gel and recrystallization, and forms a nice crystalline solid suitable for X-ray crystallographic analysis.[12]

In the light of the fact that methyl acrylate and methyl α-methoxyacrylate selectively react with **1** to give [2+2] cycloaddition products [e.g. **B-1**, Eq. (1)],[1a,b] it is quite surprising that methyl *trans*-β-methoxyacrylate reacts with **1b** to provide a tetrahydropyridine product **2l** exclusively as a single diastereomer. A similar, but a more exciting result was observed for the reaction of **1b** and methyl (*E*)-3-silyloxy-2-butenoate (run 15), where **2p** was obtained exclusively with

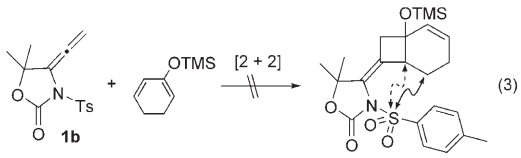
complete retention of configuration of the double bond of the trisubstituted enol ether.

Further contrasting results were observed for the reaction of dienyl ethers [Eq. (2)]. A wide variety of 1,3-dienes, including 1- and 2-siloxy-1,3-butadienes uniformly undergo [2+2] cycloaddition exclusively and provide 3-vinylmethylenecyclobutanes (e.g., **B-2**) in excellent yields.[1a,b] 2-Siloxy-1,3-cyclohexadiene, on the other hand, underwent formal [4+2] (four-component from **1b** and two from an enol ether) cycloaddition to give rise to a tricyclic compound **2r** in reasonable yield.



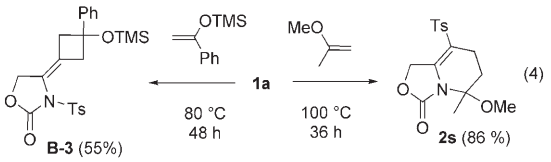


These contrasting results [Eqs. (1) and (2)] may be rationalized on the basis of steric repulsion in the imaginary [2+2] cycloaddition products with enol ethers bearing substituents on the β carbon, as is illustrated in Equation (3) using 2-siloxy-1,3-cyclohexadiene as an example. The allylic methylene group of cyclobutane *syn* to Ts is subject to an allylic strain against the Ts group (indicated with a dotted double-headed arrow); hence, there might be no room to accommodate substituents on the same carbon any more (indicated by a double-headed arrow).

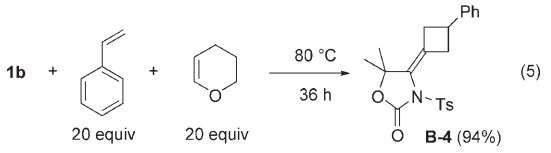


Equation (4) indicates that the [2+2] versus [4+2] selectivity depends on a subtle difference in the electronic nature of enol ethers; an enol ether bearing a phenyl group at the α-position behaves like styrene, providing [2+2] cycloaddition product **B-3** exclusively,[1a,b] while an enol ether bearing a methyl group in place of a phenyl group provides a [4+2] cycloaddition product **2s** exclusively.

In good agreement with this, the [2+2] cycloaddition with styrene proceeded much faster than the [4+2] cycloaddition with dihydropyran [Eq. (5)], where only [2+2] cycloaddition



product, **B-4**, was obtained exclusively in excellent yield. This suggests that a phenyl group is more influential than an alkoxy group to determine the course of reactions.



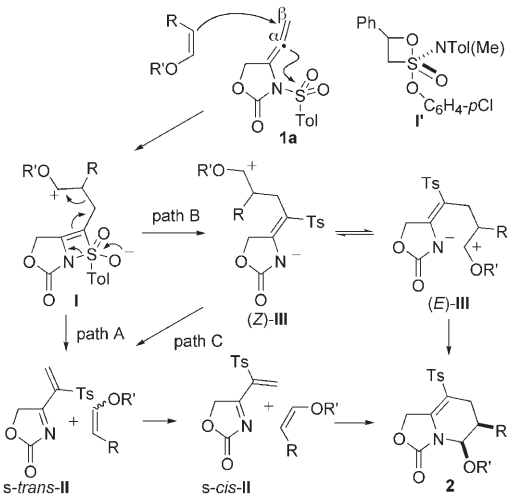
As for the reaction mechanism, two routes, pathways A and B giving rise to intermediates s-*trans*-**II** and (*Z*)-**III**, respectively, which pass through a sulfurane oxide **I** as a common intermediate, are conceivable as illustrated in Scheme 2 using **1a** and a (*Z*)-enol ether as the starting materials. The intermediacy of four-membered sulfurane oxide **I** that might be formed via intramolecular addition of Cα carbanion to S, the anion being generated by nucleophilic addition of vinyl ether upon Cβ, relies on a four-membered aminodioxysulfuran oxide **I′** of structural similarity, which is isolated as crystals.[16] The intermediate **I** would be unstable owing to greater ring strain and zwitterionic nature placing anionic charge on O, hence would react to give either s-*trans*-**II** (path A) or a zwitterionic intermediate (*Z*)-**III** (path B). The zwitterionic intermediate (*Z*)-**III** might either fragment to give a mixture of s-*trans*-**II** and an enol ether (path C) or isomerize to (*E*)-**III**, which is ready to cyclize to give **2** (path D).

During the isomerization of **1a** to **II** (path A and paths B–C), the enol ether might lose its geometrical integrity, that is, in these processes, the enol ether serves as a catalyst for the isomerization of **1a** to **II** at the expense of its geometrical purity.

The high stereoselectivity, giving rise to **2b**, **2c** **2l**, and **2p** with complete retention of configuration of the starting alkene geometries [runs 2, 3, and 15, Table 1 and Eq. (1)], may be rationalized by the route involving an intermediate **II**.

The 1-azabutadiene intermediate s-*cis*-**II** is nicely assembled as an enophile for the inverse electron demand Diels–Alder reaction,[17] possessing a highly polarized structure with a partial negative charge on N and a partial positive charge on the terminal carbon. The polar nature of **II** is enhanced by the CO on N and the Ts on the C_3 carbon of 1-aza-1,3-diene unit. Accordingly, it should react with enol ethers as soon as formed.[17j,k]

According to pathway D (Scheme 2), a faster rotation about the C–C single bond bearing R and OR′ as compared



Scheme 2. 1,3-Migration of toluenesulfonyl group promoted by a (*Z*)-vinyl ether via a four-membered sulfurane oxide **I** as a common intermediate: path A: N→C sulfonyl shift giving rise to an s-*trans*-1-aza-1,3-butadine **II** accompanying vinyl ether isomerization. Path B: N→C sulfonyl shift giving rise to a zwitterionic intermediate (*Z*)-**III**. Path C: elimination of a mixture of (*E*)- and (*Z*)-vinyl ether giving rise to s-*trans*-**II**.

with a rotation around the C4–Cα bond that has a higher bond order should result in a formation of stereoisomeric mixtures of **2**. Apparently this is not the case and the pathway D might be ruled out.

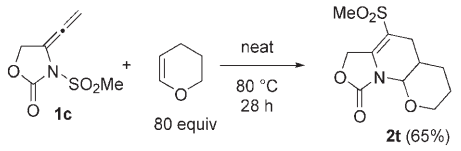
In accord with the proposed mechanism, enol ethers turned out to isomerize to a considerable extent; (*Z*)-β-methoxystyrene (*Z*/*E* 17:1, at start) was recovered as a mixture of 1.3:1.0 after completion of reaction (run 2, Table 1), and 1-siloxy-1-butene (*Z*/*E* 10:1, at start) as a mixture of 2.2:1.0 (run 12). It was established independently that these enol ethers were geometrically stable and, in the absence of **1**, no isomerization took place under the reaction conditions. Accordingly, the exclusive and selective formation of *cis*-**2b** (run 2) and *cis*-**2m** (run 12), respectively, might be attributed to an easier access of **II** to the (*Z*)-enol ethers than to the (*E*)-isomers just from steric reasons. (*E*)-β-Methoxy acrylate (run 3) and (*E*)-β-siloxy-2-butenoate (run 15) were recovered without any isomerization after the reaction with **1**.

As expected from a rate-determining formation of zwitterionic **I**, all the reactions examined in polar solvents showed reasonable reaction rates and yields: for example, **2e**; 95% at 80°C for 8 h in DMSO; 93% at 80°C for 8 h in acetonitrile, 89% at 80°C for 12 h in dioxane (run 5, Table 1), while 62% at 80°C for 20 h in benzene.

The catalytic role of enol ethers for the isomerization of **1** to **II** is reminiscent of the role that amines and phosphines play in the Baylis–Hillman reaction;[18] these Lewis bases promote a kind of aldol addition of unsaturated carbonyl compounds to aldehydes to provide the same unsaturated carbonyl compounds, the H on the Cα being replaced with 1-hydroxyalkyl groups. Accordingly, we examined a variety of Lewis bases in order to isolate or detect the intermediate **II**, or to accelerate the present [4+2] cycloaddition reaction. However, no positive results were obtained. For example, neither Et_3N (1 equiv) nor PPh_3 (1 equiv) had nothing to do with the reactions in the presence and absence of dihydropyran. Interestingly, DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) caused facile and complete decomposition of **1b** in the presence and absence of dihydropyran even at room temperature and provided an intractable black tarry mixture of products.

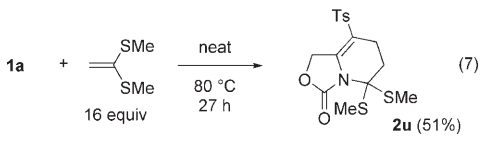
The generation of **2** indicates that a strong sulfonamide bond[11] of **1** is cleaved under such mild conditions as heating at 70–100°C with weak neutral nucleophiles. This may sound rather unreasonable, and alternative pathways, for example, a pathway that involves radical intermediates should be taken into consideration: 1) a single electron transfer from an enol ether to **1**; 2) a homolytic SO_2–N bond cleavage of the radical anion of **1** to give a carbamate anion and an SO_2Tol radical;[19] 3) recombination of the carbamate anion and the SO_2Tol radical at the Cα position; and 4) an inverse electron transfer from the radical anion $\mathbf{II}^{\bullet-}$ to the enol ether radical cation.

However, this is probably not the case. As shown in Equation (6), *N*-methanesulfonylallene carbamate **1c** behaves just like *N*-toluenesulfonylallene carbamates **1a** and **1b**, providing **2t** in reasonable yield. Provided that a radical species like methanesulfonyl radical were involved as an intermediate, **1c** should provide some desulfonylated products. The life-time of alkylsulfonyl radicals is much shorter than that of arylsulfonyl radicals. By virtue of the ready extrusion of SO_2, alkylsulfonyl radials, and never arylsulfonyl radicals, have been utilized as efficient alkyl radical carriers for a wide range of radical chain reactions of synthetic importance.[20]



The carbamates **1a**,**b** form stable crystalline solid, while the carbamate **1c** is a heavy oil and rather unstable decomposing gradually during storage in a refrigerator. Furthermore, **1c** was less reactive compared with **1a**,**b** and necessitated heating at 80°C using dihydropyran as a solvent (cf. runs 5 and 13, Table 1). The comparably low yield of **2t** may be ascribed to these factors.

Enol ethers with low electron density on the double bonds, such as [1,3]dioxol-2-one and vinyl acetate, as well as vinylamines and vinylamides, such as *N*-vinylimidazole and *N*-vinyl-γ-butyrolactam, were unreactive, and **1** was recovered. Ketene dithioacetal[21] turned out to be reactive enough and provided **2u** in moderate yield [Eq. (7)].



The tetrahydropyridine structure of **2** was determined unequivocally by the X-ray crystallographic analyses of **2a**, **2e**, **2i**, **2l**, **2o**, **2q**, and **2t**.[12] They showed standard values of coupling constants (^3J) of cyclohexenes with respect to the substitution patterns of the C2 and C3 positions. For example, the C3-H_{eq} of **2l** resonates at δ 2.99 ppm and splits into dt (J = 5.7 and 2.2 Hz), which are ascribed to the couplings with C4-H_{ax} and C4-H_{eq} and C2-H_{eq}, respectively. The substitution pattern of other **2** was determined on the same grounds. For example, the axial orientation of the CO_2Me group of **2p** was determined on the basis of the similarity of the coupling pattern of C3-H (dd, J=6.2, 1.8 Hz) to that of **2l**. The axial C2-OMe and the equatorial C3-Ph orientations of **2b** are also deduced on the basis of their coupling pattern: C2-H_{eq} (δ=5.15 ppm, d, J=2.3 Hz) and C3-H_{ax} (δ= 2.78 ppm, ddd, J=2,3, 4.1, 13.2 Hz).

The regioisomeric attachment of the oxygen atom on the tetrahydropyridine ring observed for **2g** and **2h** could be determined by comparing the ^{1}H and ^{13}C NMR chemical shifts at the C2 and C3 positions of relevant reference compounds. Typical examples are illustrated in Figure 1. NOE experiments also support the structure of **2h**.

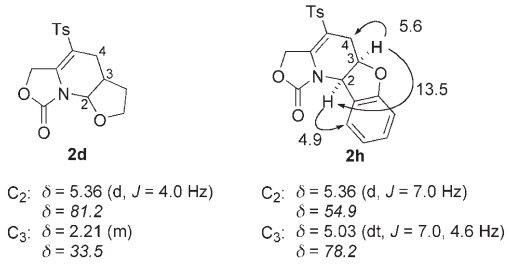


Figure 1. Chemical shifts of ^{1}H (400 MHz) and ^{13}C (100 MHz, in italic) NMR for **2d** and **2h** (δ in ppm). Relevant coupling constants and NOE increments (%) are also shown.

Figure 2 shows the Chem 3D presentation of the structures of **2** of interest determined by the single-crystal X-ray diffraction methods, along with the structures of the other products **3**, **4** and **6**,[12] which will be referred to later in this article.

The short C2–O bond lengths observed for **2a**, **2l** and **2q**, as compared with the standard C_{sp^3}–O_{sp^3} values, 1.42–1.45 Å, may suggest polarization of the N–C2 bond of the tetrahydropyridine ring in a way of $N^{\delta-}$–$C2^{\delta+}$, though apparent lengthening of the N–C2 bonds is not observed (Table 2). Similar shortening of the C2–O bond lengths was observed for **2e**, **2i**, **2o** and **2t**.[12] Another common structural feature of **2** is that the C2 substituents occupy a

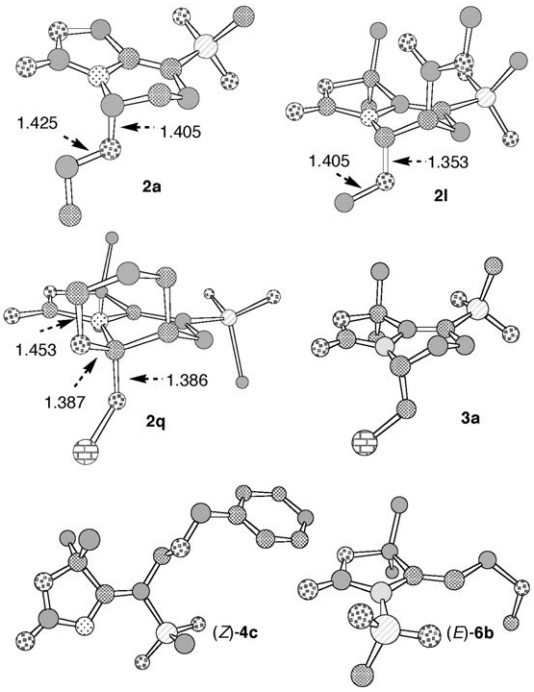
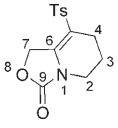


Figure 2. Chem3D X-ray structures for products **2**, **3**, **4**, and **6**. For clarity, all hydrogens, carbons of tolyl group (replaced for Me), and alkyl groups on Si are omitted. Ethereal C–O bond lengths are shown in Å.

quasi-axial position. This is apparently due to an allylic strain that quasi-equatorial substituents might experience against the oxazolidinone carbonyl oxygen. In those cases where C2 bears both O and C substituents, as in **2i**, **2o**, and **2p**, the oxygen substituents monopolize a quasi-axial position, suggesting that the electrostatic C9=O···O-C2 repulsion is decisively influential over the van der Waals repulsion between C9=O and alkyl-C2.

The essential bond lengths and dihedral angles of **2** of interest are summarized in Table 2, which indicate that, except **2q**, C5, C6, N, and C2 lie almost in a plane and C3 and C4 move either up and down (**2a**, **2e**, **2l**, **2o**, **2q**), or down and up (**2i**) to a similar extent to each other from the plane. The tricyclic compound **2q** is unique, in which the C2 bears two

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

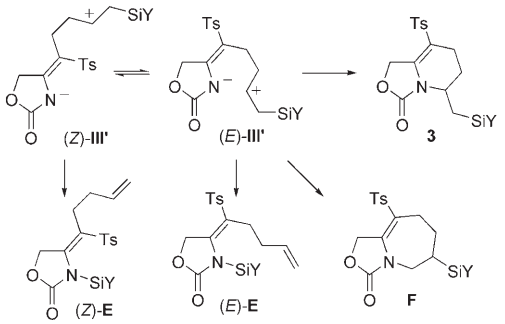


	2a	**2e**	**2i**	**2l**	**2o**	**2q**	**3a**	**3h**	(*Z*)-**4c**
d O8–C9	1.349	1.345	1.343	1.369	1.332	1.330	1.334	1.343	1.338
d C9=0	1.196	1.201	1.191	1.183	1.195	1.197	1.209	1.202	1.196
d C9–N	1.372	1.375	1.395	1.342	1.388	1.392	1.370	1.374	1.369
d N–C6	1.468	1.378	1.385	1.435	1.403	1.393	1.385	1.383	1.370
d N–C2	1.468	1.451	1.470	1.513	1.480	1.487	1.465	1.466	
d C5–C6	1.326	1.335	1.336	1.269	1.349	1.348	1.340	1.345	1.348
∢ C5-C6-N-C2	2.5	−0.5	1.6	1.0	−2.2	−14.3	−2.0	−2.9	
∢ C6-N-C2-C3	20.0	27.0	−23.6	30.0	34.4	42.5	32.5	31.6	
∢ N-C2-C3-C4	−53.8	−50.2	48.5	−59.4	−57.8	−57.9	−56.0	−55.5	

oxygen substituents and the tetrahydropyran oxygen atom is forced to locate in a quasi-equatorial position in a distance (2.788 Å) to the carbonyl oxygen, much shorter than the sum of the van der Waals radius of oxygen (1.75 Å) (Figure 2). This may correspond to an unusually large dihedral angle, C5-C6-N-C2 −14.3°.

Reaction of 1 with allylsilanes: Allylsilanes are a rather poor nucleophile as compared with enol ethers, yet they belong to a unique class of compounds in that the double bonds display versatile nucleophilic reactivities; they serve not only as an allylating agent toward carbonyl compounds, but also as a two- and three-carbon component for [2+2] and [2+3] cycloaddition reactions with compounds possessing highly polarized C=C double bonds.[22]

In order to shed more light on the mechanistic aspects of the unique 1,3-sulfonyl rearrangement (Scheme 2), we examined the reaction of allylsilanes as a probe in expectation that an intermediate (*Z*)-**III′** (corresponding to (*Z*)-**III** in Scheme 2) might possibly undergo either desilylation to provide (*Z*)-**E** or isomerization to (*E*)-**III′** to give (*E*)-**E** and/or **F** (via 1,2-silyl migration, Scheme 3).



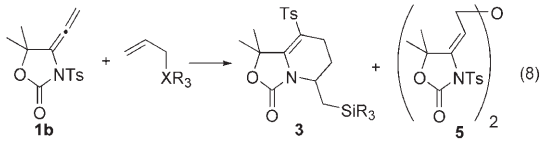
Scheme 3. Possible routes that an imaginary intermediate **III′** might undergo.

As seen in run 1 of Table 3, however, when **1b** and allyltrimethylsilane were heated in dry dioxane at 80 °C under N_2, no trace amounts of (*Z*)-**E**, (*E*)-**E**, and **F** were detected; instead, a formal [4+2] addition product **3a** was isolated in 56% yield [Eq. (8)]. Strangely, in addition to **3a**, a bis-allyl ether **5** was also isolated in a considerable amount (20%). The yield of **5** is calculated on the mole base of **5** and should be doubled to estimate the material balance of the reaction. This treatment indicates that the reaction is quantitative with respect to **1b**. The structures of **3a** and **5** were determined by the X-ray crystallographic analyses.[12] Chem 3D drawing of the structure of **3a** is shown in Figure 2.

The reaction was also examined in the presence of LiCl in order to stabilize the ionic intermediate **III′**, and at the same time, to help desilylation by an attack by the chloride ion on silicon; however, there were no appreciable changes in the presence and absence of LiCl.

At present, the mechanism for the generation of **5** is not clear. One suggested route is the reaction of **1b** with a trace amount of water, present as a contaminant in the reaction mixture; however, this seems to be improbable; the reaction was undertaken several times with great care under rigorously dry conditions, but the results were reproducible. Furthermore, an independent reaction undertaken in the presence of two equivalents of water added deliberately did not give **5** at all and **1b** was recovered cleanly.

Table 3. Thermal cycloaddition of allylsilanes and -stannanes toward **1b**.[a]

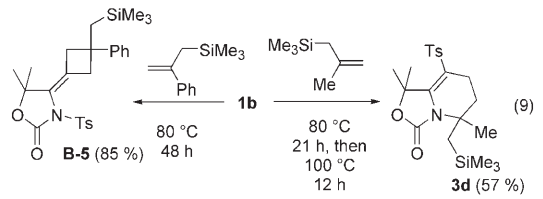


Run	Allyl-X	*T* [°C]/*t* [h]	Isolated yield [%]	
			3	**5**
1	X = $SiMe_3$	80/25	**3a**: 56	**5**: 20
2	X = Si(*i*-Pr)$_3$	80/12	**3b**: 48	**5**: 19
3	X = $SiPh_3$	80/10	**3c**: 40	**5**: 10
4	X = Si(OEt)$_3$	80/24	0[b]	0[b]
5	X = $SnMe_3$	80/98 then 100/21	0[b]	0[b]

[a] **1b** (0.5 mmol) and allyl-X (5 mmol) in dry dioxane (1 mL) under N_2. [b] Decomposition of **1b**. No detection of characteristic spots ascribable to **3** and **5**.

We next examined allylsilanes with higher migratory aptitude[22] (runs 2 and 3, Table 3) in an attempt to detect the type of product **F**; however, allyltriisopropyl- and allyltriphenylsilanes reacted in a way similar to allyltrimethylsilane. Allyltriethoxysilane caused decomposition of **1b** (run 4).

The reaction feature turned out to depend significantly on the substitution pattern of the allylic moiety of allylsilanes [Eq. (9)]. β-Methylallyl(trimethyl)silane reacted as usual to give a [4+2] product **3d**, though under rather harsh conditions, while β-phenylallyl(trimethyl)silane underwent [2+2] cycloaddition exclusively and provided **B-5** in excellent yield.[1a,b] These results well correspond to those described in Equation (4).



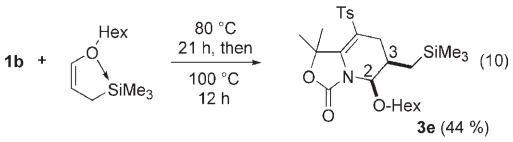
All these results clearly indicate that the conjugation of a phenyl and a vinyl group is decisively more influential than the allylic conjugation with silicone to determine the course of the reaction.

It may be worth noting that the relative reactivity order observed for [4+2] cycloaddition among allylsilanes [(*i*Pr)$_3$Si(allyl), Ph_3Si(allyl) > Me_3Si(allyl) > Me_3Si(β-methylallyl)], estimated roughly on the basis of the reaction

times and temperatures required for completion of reaction, seems to be reversely correlated to "the scales of nucleophilicity", proposed by Mayr et al. [Me_3Si(α-methylallyl) ≫ (iPr)$_3$Si(allyl), Me_3Si(allyl) > Ph_3Si(allyl)].[23]

In accord with this, allyltrimethylstannane, expected to be by far more reactive as a nucleophile than allylsilanes,[23] turned out to be reluctant to undergo cycloaddition to **1** (run 5, Table 3). Thus, **1b** was recovered almost quantitatively when heated with allyltrimethylstannane at 80 °C for 10–20 h. Prolonged heating at higher temperatures only resulted in the decomposition of **1b**.

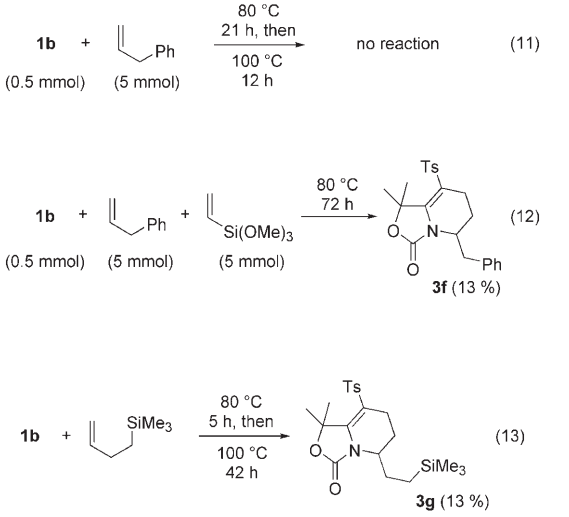
These results suggest that some factors other than nucleophilicity, such as Lewis acidity of silicone, might operate to promote the [4+2] cycloaddition. That is, the silicone of allylsilanes coordinates to the sulfonamide oxygen so as to facilitate the formation of **I**.



Bearing this in mind, we examined the reaction of (*Z*)-3-hexyloxyl-2-propenyl(trimethyl)silane and **1b** [Eq. (10)] in expectation that intramolecular coordination of the silicon to the ether oxygen might render an intermolecular coordination of the silicon to the sulfonamide oxygen of **1b** ineffective and hence retard the [4+2] cycloaddition. Indeed, almost no reaction proceeded when the mixture was heated under the usual conditions (80 °C, 21 h). For the reaction to proceed at a reasonable rate, heating at a higher temperature was required (100 °C, 12 h). Taking into consideration the fact that the enol ethers of a similar structural type (e.g., runs 11 and 12, Table 1) are reactive enough at 80 °C, the sluggish reaction of this enol ether may be attributed to intramolecular coordination of the oxygen to the silicone, which decreases the electron donation ability of the oxygen atom to the enol double bond.

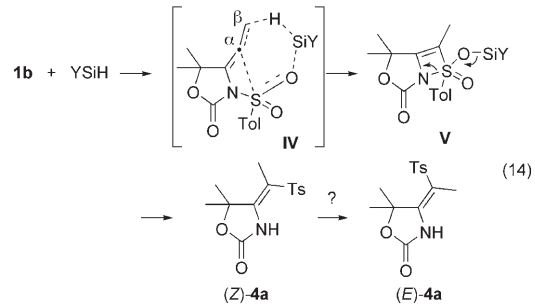
The reaction displayed interesting regio- and stereoselectivity; the product **3e** possesses an opposite regiochemistry to **3a**–**d**, locating the trimethylsilylmethyl group at the C3 position of the tetrahydropyridine ring. This result clearly indicates that (*Z*)-3-hexyloxyl-2-propenyl(trimethyl)silane displays the reactivity as an enol ether rather than an allylsilane. The reaction proceeded with complete retention of configuration as generally observed for enol ethers (Table 1). The structure of *cis*-**3e** was determined on the basis of NOE experiments: a large increment of the area intensity of C3H (9.0 %) and a small enhancement of the area intensity of one of the diastereotopic methylene protons of the trimethylsilylmethyl group (3.8 %) by the irradiation upon C2H.

Further supporting results that silane serves as a promoter for 1,3-sulfonyl shift were obtained in the following experiments [Eqs. (11–13)]. The reaction of **1b** and allylbenzene did not take place at all even by heating the mixture under harsh reaction conditions [Eq. (11)]. On the other hand, in the presence of trimethoxyvinylsilane, the [4+2] cycloaddition of **1b** and allylbenzene *did* proceed to give **3f**, albeit in low yield [Eq. (12)]. Homoallylsilanes might be regarded as a simple, non-activated alkene, since the orbital interaction between the π-bond and the C–Si bond is negligibly small.[24] However, homoallyltrimethylsilane *did* undergo cycloaddition and provided **3g**, though again albeit in low yield [Eq. (13)].



During examination of silicone compounds as a promoter of 1,3-sulfonyl shift, we found by chance that some silicone compounds possessing an Si–H bond promote a reductive 1,3-sulfonyl shift and deliver the hydrogens at the Cβ position of **1** to provide 2-oxazolidinones **4** in reasonable yields (Table 4). Among silanes, tris(trimethylsilyl)silane gave the cleanest results and provided (*Z*)-**4a** as a single product in

Table 4. Reductive 1,3-tosyl migration induced by silanes.[a]



Run	Silane	T [°C])/t [h]	Isolated yield [%]	
			(*Z*)-**4a**	(*E*)-**4a**
1	$(TMS)_3SiH$	80/33	70	0
2	$PhSiH_3$	80/23	60	4
3	Et_3SiH	80/60	26	31
4	Et_2SiH_2	50/118	40	0

[a] **1b** (0.5 mmol) and a silane (5 mmol) in dry dioxane (1 mL) under nitrogen.

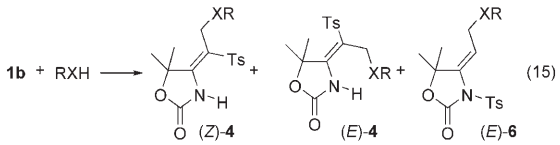
70% isolated yield just by heating a mixture of the silane (10 equiv) and **1b** in dry dioxane at 80°C for 33 h. With some other silanes, (*Z*)-**4a** was produced together with (*E*)-**4a** (runs 2 and 3).

Interestingly, despite the presence of acidic NH, these tetrasubstituted enamines, (*Z*)- and (*E*)-**4a**, did not isomerize to each other. Independent heating at 80°C for over 40 h of each of the isolated pure isomers (*E*)- and (*Z*)-**4a** in dioxane did not cause isomerization and each isomer was recovered quantitatively. The geometrical stability seems to be reflected in the bond lengths of C9–N, N–C6, and C5–C6, which are almost identical for **2**, **3**, and **4** (Table 2).

The geometric stability of **4** indicates that the *E* and *Z* isomers were produced either via different routes independently or more likely via an isomerization of (*Z*)-**4a** to (*E*)-**4a** promoted by some unknown catalysts that might be produced in the reaction mixture. The exclusive (runs 1 and 4) and the selective formation of (*Z*)-**4a** (run 2) suggests the reaction most probably proceeds via a bicyclic transition state **IV**. A sulfurane oxide intermediate **V** is electronically neutral, as opposed to the zwitterionic intermediate **I** (Scheme 2) and possesses a strong Si–O bond. Accordingly, **V** [Eq. (14)] is expected to be stable enough to be isolated. Despite our careful examination, however, no **V** was detected in the reaction mixture (crude ^{1}H NMR and TLC).

Reaction of 1 with hetero-nucleophiles: Encouraged by the smooth nucleophilic reductive 1,3-sulfonyl shift promoted by silanes, we examined hetero-nucleophiles as reaction partners. To our pleasant surprise, alcohols and thiols smoothly reacted with **1**, and the reactions completed even by exposure to a small excess amount of alcohols and thiols (1.5–2.0 equiv, as opposed to 10 equiv of silanes) under neutral conditions. The reaction feature, however, was somewhat different to the one observed for silanes; in addition to 1,3-sulfonyl migration products (*Z*)-**4**, were produced non-sulfonyl migration products (*E*)-**6** [Eq. (15)] in considerable amounts (Table 5).

Table 5. Addition of alcohols and thiols to the allene terminal double bond of **1b** with and without 1,3-tosyl migration.[a]



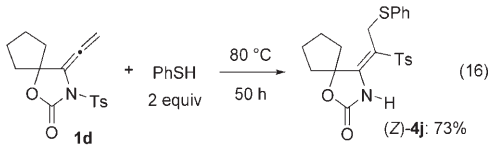
Run	Alcohol [equiv]	T [°C]/t [h]	Isolated yield [%] (*Z*)-**4**	(*E*)-**4**	(*E*)-**6**
1	MeOH (2)	80/22	**4b**: 47	0	**6b**: 35
2	$PhCH_2OH$ (2)	80/22	**4c**: 48	0	**6c**: 35
3	CH_2=$CMeCH_2OH$ (1.5)	80/22	**4d**: 11	0	**6d**: 61
4	*i*PrOH (2)	80/12	**4e**: 34	0	**6e**: 44
5	CH_2=$CHCHMeOH$ (1.5)	80/41	**4f**: 14	0	**6f**: 60
6	PhOH (3)	80/24	**4g**: 0	0	**6g**: 70
7	$C_{16}H_{33}SH$ (2)	80/21	**4h**: 5	31	**6h**: 0
8	PhSH (2)	80/42	**4i**: 72	12	**6i**: 15

[a] **1b** (0.5 mmol) and an alcohol or a thiol (indicated amount) in dry dioxane (1 mL) under N_2.

The ratio of **4** to **6** seems to depend on the steric bulk and the acidity of alcohols; roughly, the bulkier and the higher the acidity, the higher is the proportion of **6**. Phenol is one extreme that provides (*E*)-**6g** exclusively in good yield (run 6, Table 5).

Thiols, on the other hand, displayed a general trend to provide **4** either exclusively (run 7) or highly selectively (run 8). The product distribution slightly depends on the kind of **1**, and the reaction of **1d** and thiophenol provided (*Z*)-**4j** exclusively [Eq. (16)]. The relatively high proportion of **4** to **6** for the reactions with thiols as compared with alcohols may be attributed to the higher nucleophilicity of thiols. Reagents with poor nucleophilicity like alcohols may be unable to supply a sufficient anionic charge to the allene Cα carbon to displace the sulfonyl group and end up with providing (*E*)-**6** just via simple addition to the Cα=Cβ double bond.

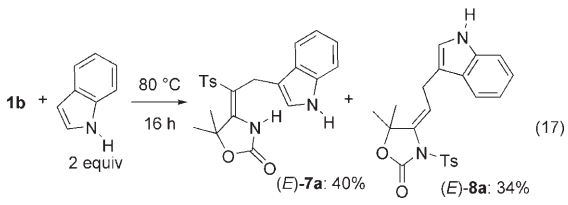
In these reactions, the products (*E*)-**4** were only produced in the reaction with thiols and it may be reasonable to attribute their formation to a thiyl radical-mediated isomerization of the primary products (*Z*)-**4**.[25]

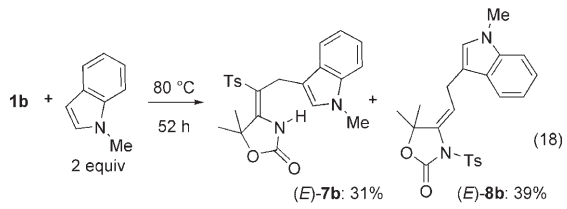


Surprisingly, in sharp contrast to alcohols and thiols, secondary amines, such as *N*-methylaniline and dipropylamine, were definitively unreactive under the usual conditions and the starting **1b** was recovered quantitatively. Among secondary amines examined, indole was one exception and served as a C-nucleophile rather than an N-nucleophile and provided a mixture of (*E*)-**7a** and (*E*)-**8a** in comparable amounts and in a reasonable combined isolated yield [Eq. (17)]. *N*-Methylindole displayed almost parallel results [Eq. (18)].

We also examined Meldrum's acid and diethyl malonate as a typical soft carbon nucleophile; however, all attempts either in the presence or absence of a base [Et_3N, NaH, potassium bis(trimethylsilyl)amide] were unsuccessful and resulted in the formation of intractable mixtures of products.

The electrophilic reactivity of the allene Cα=Cβ double bond of **1** is very specific to the kind of nucleophiles, and at present it is difficult to give a rationale for the distinct difference of reactivities that nucleophiles display; alcohols, thiols, and indoles are allowed to react with **1**, while amines



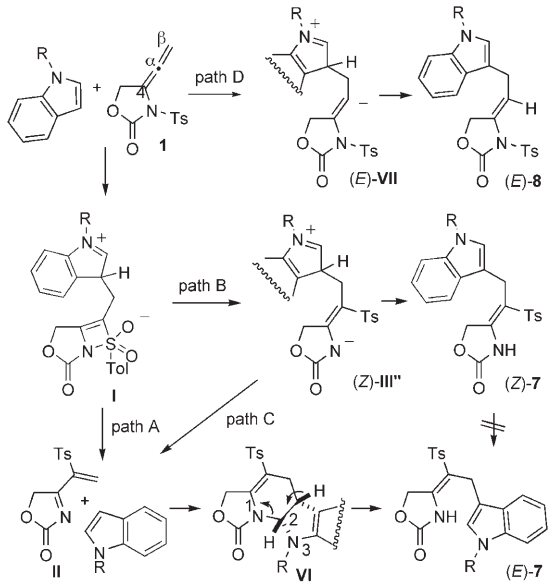


and soft carbon nucleophiles like malonates are not. However, for the reactions that show positive results [Table 5 and Eqs. (16–18)], the mechanism seems to be rationalized according to Scheme 2.

Alcohols and thiols are able to form such a stable and strong oxonium Cβ–O^+ bond (or neutral Cβ–O bond by deprotonation) and sulfonium Cβ–S^+ bond (or neutral Cβ–S bond by deprotonation), respectively, that pathway B might be favored over pathway A and the thus-formed zwitterionic intermediates (non-vinylogous analogue of (*Z*)-**III**) would immediately undergo proton exchange to give the final products **4**. Protonation at the Cα leads to (*E*)-**6**. The selective formation of (*Z*)-**4** and (*E*)-**6**, the structures of which have been determined firmly on the basis of NOE experiments, lends further support to the reaction mechanism passing through pathway B; through pathway A, that is, via the Michael addition of alcohols and thiols to a 1-aza-1,3-butadiene intermediate **II**, random mixtures of (*E*)- and (*Z*)-**4** should result.

The nucleophilic addition of indoles providing (*E*)-**8** [Eqs. (17 and 18)], in a sense, might be regarded as electrophilic aromatic substitution of **1**; that is, despite the fact that **1** is a neutral species, it is even capable of undergoing the Friedel–Crafts type electrophilic aromatic substitution in the absence of any Lewis acid catalysts (path D, Scheme 4). Electrophilic addition of **1** to indoles and aromatization by deprotonation would provide (*E*)-**8**.

The exclusive formation of (*E*)-**7** can hardly be explained according to pathway B followed by aromatization leading (*Z*)-**7**. Like **4**, the exocyclic enamide double bond of (*Z*)-**7** is expected to be geometrically stable and would not isomerize to (*E*)-**7**. Furthermore, there seems to be no such strong thermodynamic bias to cause complete isomerization from (*Z*)-**7** to (*E*)-**7**. Instead, pathway A or pathway C that follows pathway B seems to be more likely, where a tetracyclic intermediate **VI**, formed by the inverse electron demand Diels–Alder reaction of **II** and indole,[17n] would readily undergo dehydroamination to give rise to (*E*)-**7**. That is, a dichotomy exists for the reaction of **1** and indoles; one is electrophilic substitution (path D) and the other is a sequential 1,3-sulfonyl shift and the inverse electron demand Diels–Alder reaction (path A or paths B–C), followed by ring opening. Strain relief, significant N1–C2 bond weakening by electron-donation by N3, and, in particular, aromatization stabilization of indole[26] would contribute to a facile conversion of **VI** to (*E*)-**7**. The second and the third factors are crucial to rationalize the contrasting stability that the intermediate **VI** (R = H, Me) and a series of compounds **2**, especially **2q** (Table 1), display. The structure of **7** and **8** was determined unequivocally on the basis of NOE experiments (Figure 3).



Scheme 4. A plausible mechanism for the reaction of **1** and indoles (R = H or Me).

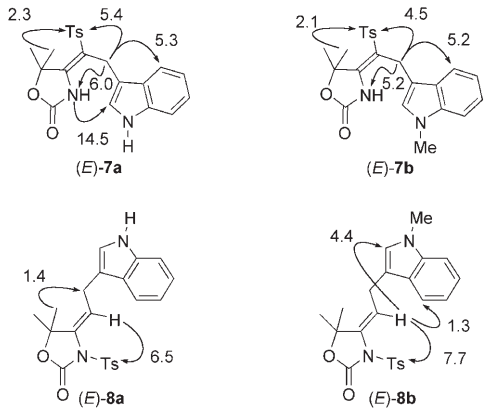


Figure 3. NOE increments (%) in area intensities for **1b**–indole adducts **7** and **8**.

It should be noted that indole and benzofuran undergo the inverse electron demand Diels–Alder reaction in an opposite direction, placing N and O at the C2 and C3 positions of tetrahydropyridine ring, respectively, which is in good accord with precedents.[17l,m,27]

The unique electrophilic reactivity associated with the allene Cα=Cβ bond of **1** is reminiscent of the reactivity of the double bond of unsaturated carbonyl compounds and suggests a strong through-space orbital interaction between the Cα=Cβ double bond and the N–SO_2 single bond (Figure 4).

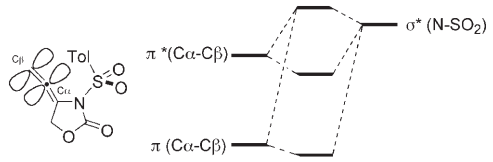


Figure 4. Through-space orbital interaction of the Cα=Cβ double bond and the N−SO_2 single bond of **1a**.

We envisage that a π*(Cα=Cβ)-σ*(N-SO_2) interaction makes the LUMO (Cα=Cβ) low in energy and the double bond an excellent electron acceptor. Furthermore, a π(Cα=Cβ)-σ*(N-SO_2) interaction weakens the N−SO_2 bond so that the novel 1,3-sulfonyl migration even proceeds by treatment with some weak nucleophiles.

Conclusion

The exocyclic allene Cα=Cβ bond of **1** serves as a potential electron acceptor and undergoes nucleophilic addition of a wide variety of nucleophiles, encompassing enol ethers, allylsilanes, hydrosilanes (R_nSiH_{4-n}, $n=1$–3), alcohols, thiols, and some aromatic compounds, such as furans, benzofurans, and indoles. The reaction proceeds readily just by heating a mixture of **1** and a nucleophile at about 70–100 °C.

The unique reaction behavior of the allene Cα=Cβ bond is primarily due to a through-space interaction of the Cα=Cβ π-orbital and the N−SO_2 σ-orbital, which renders the LUMO (Cα=Cβ) low in energy and electrophilic in nature. The interaction was evidenced by a 1,3-sulfonyl shift from N to Cα in the reactions with nucleophiles. The reactions of **1** and enol ethers derived from aldehydes, ketones and esters, all provided 2-alkoxy-5-sulfonyltetrahydropyridines **2** in good to excellent yields. Furans and benzofurans were exceptional and furnished 3-alkoxy-5-sulfonyltetrahydropyridines **2g**,**h**. Enol ethers, irrespective of their structure, were incorporated in the products with complete retention of configuration of the double bond. Based on these results, a mechanism relying on enol ether promoted isomerization of **1** to 1-azabutadienes **II**, followed by the inverse electron demand Diels–Alder reaction, was proposed (Scheme 2).

Allylsilanes reacted with **1** in a way similar to enol ethers and provided 2-silylmethyl-5-sulfonyltetrahydropyridines **3**. The interesting reaction feature of allylsilanes is that it is a Lewis acid-base promoted reaction, that is, the nucleophilicity of the double bond brought about by allylic conjugation with the C−Si bond is merely one of the factors for promoting [4+2] cycloaddition; silicone plays an important role as a Lewis acid; coordination of silicone to the sulfonyl oxygen facilitates the formation of four-membered sulfurane oxide **I**. This conclusion is based on many observations. For example, 1) silicone compounds promote the [4+2] cycloaddition of simple, non-functionalized alkenes, which are otherwise unreactive. 2) Allylstannanes are more nucleophilic than allylsilanes, yet they are absolutely reluctant to reaction with **1**. Hydrosilanes (R_4SiH_{4-n}, $n=1$–3) nicely promote 1,3-sulfonyl-migration, delivering a hydride at the Cβ position of **1**, and furnish 4-(1-sulfonylethylidene)oxazolidin-2-ones **4** exclusively. Alcohols react in a way similar to hydrosilanes, delivering alkoxy groups at the Cβ position (**4**, X = OR). However, in this case, simple addition to the Cα=Cβ bond concomitantly takes place to give **6** in comparable amounts. Phenol is one exception and provides **6** exclusively. Thiols, on the other hand, selectively provide the type of product **4**.

An interesting dichotomy exists for the reaction of indoles and **1**; indoles behave like enol ethers yielding **II** as an intermediate (Scheme 4) as well as like phenols giving rise to the addition products at the Cα=Cβ double bond of **1** without accompanying 1,3-sulfonyl shift.

Thus, allene carbamates **1** may be referred to as a chameleon compound that dramatically alters its reaction features, giving rise to **2**--**8** and also **A** ≈ **D**[1a,b] [Scheme 1 and Eqs. (17,18)].

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 60F254). 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 (see Supporting Information for ^{1}H NMR spectra for all previously unreported compounds.). 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: 1,4-Dioxane was dried and distilled from sodium prior to use under nitrogen atmosphere. Enol ethers[28] and allylsilanes[29] were prepared according to the literature.

General procedure for the reaction of 1 with nucleophiles (run 3, Table 1): A mixture of **1a** (0.5 mmol, $R_f=0.57$, hexane/ethyl acetate 2:1) and methyl β-methoxyacrylate (20 mmol, E/Z >99:1, Aldrich) was heated at 70 °C for 23 h under N_2. After completion of the reaction, the ester was removed in vacuo. The resultant sticky mixture was purified by column chromatography over silica gel (hexane/ethyl acetate 2:1) to give **2c** ($R_f=0.23$) as a white solid in 70% isolated yield.

5-Ethoxy-8-(*p*-toluenesulfonyl)-1,5,6,7-tetrahydro-oxazolo[3,4-*a*]pyridin-3-one (2a): CCDC-181727; m.p. 133.7–134.1 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.14$ (t, $J=7.0$ Hz, 3H), 1.44 (ddt, $J=2.3$, 13.6, 9.4 Hz, 1H), 2.12 (ddt, $J=2.3$, 13.6, 3.5 Hz, 1H), 2.21 (dd, $J=3.5$, 9.4 Hz, 2H), 2.44 (s, 3H), 3.65 (q, $J=7.0$ Hz, 2H), 5.24 (t, $J=2.3$ Hz, 1H), 7.34 (d, $J=7.7$ Hz, 2H), 7.72 ppm (d, $J=7.7$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=15.1$, 17.1, 21.6, 25.9, 65.0, 68.2, 77.5, 108.5, 127.2, 129.9, 137.5, 141.3, 144.5, 155.5 ppm; IR (KBr): $\tilde{\nu}$ = 1800 (vs), 1680 (vs), 1420 (s), 1380 (s), 1300 (s), 1160 (s), 1140 (s), 1080 (s), 1020 cm^{-1} (s); elemental analysis calcd (%) for $C_{16}H_{19}NO_5S$: C 56.92, H 5.68, N 4.15, S 9.48; found: C 56.54, H 5.56, N 4.31, S, 9.66.

***cis*-5-Methoxy-6-phenyl-8-(*p*-toluenesulfonyl)-1,5,6,7-tetrahydro-oxazolo-[3,4-a]pyridin-3-one (*cis*-2b)**: M.p. 238.0–238.5 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=2.44$ (s, 3H), 2.44 (ddm, $J=4.1$, 16.0 Hz, 1H), 2.72 (ddt, $J=13.2$, 16.0, 3.3 Hz, 1H), 2.84 (ddd, $J=2.3$, 4.1, 13.2 Hz, 1H), 3.31 (s, 3H), 5.15 (d, $J=2.3$ Hz, 1H), 5.56 (dm, $J=3.3$ Hz, 2H), 7.33–7.56 (m, 5H), 7.32 (d, $J=8.1$ Hz, 2H), 7.73 ppm (d, $J=8.1$ Hz, 2H);

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 23.2, 42.7, 58.0, 68.2, 82.6, 108.8, 127.3, 127.7, 128.3, 128.6, 130.1, 137.4, 137.8, 141.0, 144.6, 155.2 ppm; IR (KBr): $\tilde{\nu}$ = 1780 (s), 1670 (s), 1300 (s), 1240 (s), 1140 (s), 1130 (s), 1080 (s), 820 (s), 750 cm^{-1} (s); elemental analysis calcd (%) for $C_{21}H_{21}NO_5S$: C 63.14, H 5.30, N 5.30, S 8.03; found: C 63.24, H 5.56, N 5.31, S, 8.66.

***trans*-5-Methoxy-3-oxo-8-(*p*-toluenesulfonyl)-1,5,6,7-tetrahydro-oxazolo-[3,4-*a*]pyridine-6-carboxylic acid methyl ester (*trans*-2c)**: M.p. 142.5–143.5 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.45 (s, 3H), 2.58 (br d, J = 15.0 Hz, 1H), 2.68 (br d, J = 15.0 Hz, 1H), 3.07 (br s, 1H), 3.33 (s, 3H), 3.47 (s, 3H), 5.40 (s, 1H), 5.46 (d, J = 18.5 Hz, 1H), 5.51 (d, J = 18.5 Hz, 1H), 7.35 (d, J = 7.8 Hz, 2H), 7.71 ppm (d, J = 7.8 Hz, 2H); IR (KBr): $\tilde{\nu}$ = 1800 (s), 1720 (s), 1640 (s), 1600 (m), 1370 (s), 1310 (s), 1290 (s), 1220 (m), 1150 (s), 1120 (m), 1100 (s), 1080 cm^{-1} (s); elemental analysis calcd (%) for $C_{17}H_{19}NO_7S$: C 53.53, H 5.02, N 3.67, S 8.41; found: C 53.42, H 5.21, N 3.41, S 8.53.

5-(*p*-Toluenesulfonyl)-2,3,3a,4,6,8b-hexahydro-1,7-dioxa-8a-aza-*as*-inda-cen-8-one (2d): M.p. 223.2–224.0 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.82 (dddd, J = 2.9, 5.2, 7.3, 12.1 Hz, 1H), 1.93 (ddt, J = 8.8, 15.4, 2.9 Hz, 1H), 2.21 (m, 1H), 2.31 (m, 1H), 2.45 (s, 3H), 2.48 (ddm, J = 6.5, 15.8 Hz, 1H), 3.94 (dd, J = 6.5, 8.4 Hz, 1H), 3.97 (dd, J = 5.2, 8.4 Hz, 1H), 5.36 (d, J = 4.0 Hz, 1H), 5.45 (ddd, J = 1.8, 2.9, 16.9 Hz, 1H), 5.55 (ddd, J = 1.8, 2.9, 16.9 Hz, 1H), 7.35 (d, J = 8.1 Hz, 2H), 7.71 ppm (d, J = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 23.5, 29.6, 33.5, 64.7, 68.1, 81.2, 106.7, 127.2, 130.1, 137.4, 141.7, 144.7, 154.7 ppm; IR (KBr): $\tilde{\nu}$ = 1790 (s), 1670 (s), 1290 (m), 1240 (m), 1200 (m), 1150 (m), 1050 (m), 990 (m), 945 cm^{-1} (m); elemental analysis calcd (%) for $C_{16}H_{17}NO_5S$: C 57.29, H 5.12, N 4.18, S 9.54; found: C 57.18, H 5.03, N 4.11, S 9.68.

4-(*p*-Toluenesulfonyl)-3,5,5a,7,8,9a-hexahydro-6*H*-2,9-dioxa-9b-aza-cyclo-penta[*a*]naphthalen-1-one (2e): CCDC-181562; M.p. 199.5–200.0 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.37 (dd, J = 2.3, 13.4 Hz, 1H), 1.74 (m, 1H, coalescing to dq, J = 4.8, 13.4 Hz by irradiation at 3.98), 1.84–1.98 (m, 3H), 2.18 (dd, J = 4.0, 16.0 Hz, 1H), 2.40 (ddm, J = 12.1, 16.0 Hz, 1H), 2.45 (s, 3H), 3.65 (dt, J = 2.3, 12.1 Hz, 1H), 3.98 (dd, J = 4.8, 12.1 Hz, 1H), 5.06 (d, J = 1.1 Hz, 1H), 5.43 (ddd, J = 1.1, 3.1, 16.5 Hz, 1H), 5.50 (ddd, J = 1.1, 3.1, 16.5 Hz, 1H), 7.35 (d, J = 8.2 Hz, 2H), 7.71 ppm (d, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.1, 21.4, 21.6, 26.1, 30.6, 68.0, 68.2, 78.2, 107.3, 127.2, 130.0, 137.5, 141.3, 144.6, 154.2 ppm; IR (KBr): $\tilde{\nu}$ = 1790 (s), 1670 (s), 1410 (s), 1380 (m), 1360 (m), 1300 (m), 1240 (m), 1210 (m), 1050 cm^{-1} (m); HRMS: *m/z* (%): calcd for $C_{17}H_{19}O_5NS$: 349.4076, found: 349.09840 (22) $[M]^+$, 194 (100); elemental analysis calcd (%) for $C_{17}H_{19}NO_5S$: C 58.44, H 5.48, N 4.01, S 9.18; found: C 58.48, H 5.50, N 3.98, S 9.20.

8-Methoxy-4-(*p*-toluenesulfonyl)-3,5,5a,7,8,9a-hexahydro-6*H*-2,9-dioxa-9b-aza-cyclopenta[a]naphthalen-1-one (2f): M.p. 203.0–203.5 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.55 (dd, J = 4.8, 13.9 Hz, 1H), 1.61 (ddt, J = 4.8, 13.9, 2.4 Hz, 1H), 1.75 (ddt, J = 3.3, 4.8, 13.9 Hz, 1H), 1.87 (m, 1H), 2.15 (ddd, J = 1.5, 5.5, 15.8 Hz, 1H), 2.24 (tt, J = 4.8, 13.9 Hz, 1H), 2.38 (ddt, J = 15.8, 12.8, 3.3 Hz, 1H), 2.45 (s, 3H), 3.48 (s, 3H), 4.71 (br d, J = 3.3 Hz, 1H), 5.45 (ddd, J = 1.5, 3.3, 16.5 Hz, 1H), 5.51 (d, J = 2.2 Hz, 1H), 5.52 (ddd, J = 1.5, 3.3, 16.5 Hz, 1H), 7.34 (d, J = 8.1 Hz, 2H), 7.71 ppm (d, J = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.3, 21.0, 21.2, 21.6, 23.9, 29.7, 55.2, 65.9, 68.2, 70.9, 76.8, 77.1, 77.4, 99.8, 107.1, 127.2, 130.1, 137.5, 141.4, 144.6, 154.2 ppm; IR (KBr): $\tilde{\nu}$ = 1775 (s), 1660 (s), 1410 (s), 1375 (w), 1295 (w), 1190 (w), 1130 (w), 1070 (w), 1025 (w), 980 cm^{-1} (s); HRMS: *m/z* (%): calcd for $C_{18}H_{21}NO_6S$: 379.1090, found: 379.1069 (100) $[M]^+$; elemental analysis calcd (%) for $C_{18}H_{21}NO_6S$: C 56.98, H 5.58, N 3.69; found: C 56.59, H 5.52, N 3.55.

4-(*p*-Toluenesulfonyl)-3,5,5a,8a-tetrahydro-2,6-dioxa-8b-aza-*as*-indacen-1-one (2g): M.p. 186.2–187.0 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.45 (s, 3H), 2.56 (br ddd, J = 3.1, 5.1, 16.9 Hz, 1H), 2.79 (dd, J = 16.9, 1.3 Hz, 1H), 4.60 (dd, J = 2.6, 7.7 Hz, 1H), 4.90 (ddd, J = 2.6, 5.1, 7.7 Hz, 1H), 5.46 (dd, J = 3.1, 1.3 Hz, 2H), 5.57 (t, J = 2.6 Hz, 1H), 6.40 (d, J = 2.6 Hz, 1H), 7.35 (d, J = 8.4 Hz, 2H), 7.72 ppm (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 24.1, 55.4, 68.5, 77.6, 101.9, 102.7, 127.2, 130.0, 137.3, 144.0, 144.6, 150.1 ppm; IR (KBr): $\tilde{\nu}$ = 1780 (s), 1670 (s), 1360 (m), 1300 (m), 1260 (m), 1160 (m), 1140 (m), 1120 (m), 1020 (m), 800 cm^{-1} (m); HRMS: *m/z* (%): calcd for $C_{16}H_{15}NO_5S$: 333.0671, found: 333.0652 (100) $[M]^+$.

4-(*p*-Toluenesulfonyl)-3,5,5a,10b-tetrahydro-2,6-dioxa-10c-aza-cyclopen-ta[c]fluoren-1-one (2h): M.p. 56.0–57.2 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.46 (s, 3H), 2.65–2.76 (m, 2H), 5.06 (dt, J = 7.0, 4.6 Hz, 1H), 5.21 (d, J = 7.0 Hz, 1H), 5.38 (dm, J = 16.5 Hz, 1H), 5.53 (dm, J = 16.5 Hz, 1H), 6.77 (d, J = 8.2 Hz, 1H), 6.93 (br t, J = 8.2 Hz, 1H), 7.25 (br t, J = 8.2 Hz, 1H), 7.34 (d, J = 8.2 Hz, 2H), 7.69 (d, J = 8.2 Hz, 1H), 7.43 ppm (d, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 24.8, 54.9, 68.3, 78.2, 103.3, 110.8, 121.6, 125.4, 127.3, 128.0, 130.0, 131.2, 137.3, 143.7, 144.7, 155.0, 158.8; IR (KBr): $\tilde{\nu}$ = 2341 (m), 1778 (s), 1665 (s), 1076 (s), 818 (m), 675 cm^{-1} (s); HRMS: *m/z* (%): calcd for $C_{20}H_{17}NO_5S$: 383.0827, found: 383.0818 (100) $[M]^+$, 266 (10).

4-(*p*-Toluenesulfonyl)-8a-trimethylsiloxy-5,5a,6,7,8,8a-hexahydro-3*H*-2-oxa-8b-aza-*as*-indacen-1-one (2i): CCDC-181723; m.p. 162.0–162.1 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.01 (s, 9H), 0.86 (m, 1H), 1.29–1.55 (m, 2H), 1.55–1.78 (m, 2H), 2.04–2.28 (m, 3H), 2.34 (s, 3H), 3.19 (m, 1H), 5.29 (br d, J = 18.3 Hz, 1H), 5.33 (br d, J = 18.3 Hz, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.62 ppm (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 1.4, 19.0, 21.5, 21.6, 24.2, 33.4, 44.6, 66.7, 91.2, 106.1, 127.1, 129.9, 137.7, 142.1, 144.4, 154.0 ppm; IR (KBr): $\tilde{\nu}$ = 1786 (s), 1665 (s), 1597 (m), 1389 (s), 1344 (s), 1286 (s), 1250 (s), 1167 (s), 1080 (s), 833 (s), 762 cm^{-1} (m); HRMS: *m/z* (%): calcd for $C_{20}H_{27}NO_5SSi$: 421.1379, found: 421.1378 (100) $[M]^+$; elemental analysis calcd (%) for $C_{20}H_{27}NO_5SSi$: C 56.98, H 6.46, N 3.32, S 7.61; found: C 56.73, H 6.46, N 3.41, S 7.58.

4-(*p*-Toluenesulfonyl)-9a-trimethylsiloxy-3,5,5a,6,7,8,9,9a-octahydro-oxazolo[3,4-*a*]quinolin-1-one (2j, a mixture with **2j′** in a ratio of 3.5:1): m.p. 39.5–40.5 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.03 (s, 9H), 0.92 (m, 1H), 1.12–2.03 (m, 8H), 2.13 (br d, J = 14.5 Hz, 1H, minor), 2.44 (s, 3H), 2.53 (m, 1H), 3.22 (br d, J = 12.5 Hz, 1H, minor), 3.45 (d, J = 12.8 Hz, 1H), 5.31–5.48 (m, 2H), 7.34 (d, J = 7.7 Hz, 2H), 7.72 ppm (d, J = 7.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.6, 20.7, 22.7, 23.8, 24.0, 27.6, 33.9, 41.1, 65.7, 85.0, 106.9, 126.2, 129.0, 136.9, 140.9, 143.5, 153.2 ppm; IR (KBr): $\tilde{\nu}$ = 1790 (s), 1668 (s), 1381 (m), 1340 (m), 1250 (m), 1148 (m), 845 cm^{-1} (m); HRMS: *m/z* (%): calcd for $C_{21}H_{29}NO_5SSi$: 435.1536, found: 435.1516 (49) $[M]^+$, 280 (100).

9a-Hydroxy-4-(*p*-toluenesulfonyl)-3,5,5a,6,7,8,9,9a-octahydro-oxazolo[3,4-*a*]quinolin-1-one (2j′): M.p. 224.0–224.2 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ1.24- 1.78 (m, 8H), 1.97 (ddt, J = 15.4, 18.7, 3.3 Hz, 1H), 2.22 (dd, J = 4.2, 15.4 Hz, 1H), 2.44 (s, 3H), 3.01 (br s, 1H), 3.23 (br d, J = 12.8 Hz, 1H), 5.31 (dm, J = 14.7 Hz, 1H), 5.45 (dm, J = 14.7 Hz, 1H), 7.34 (d, J = 8.25 Hz, 2H), 7.72 ppm (d, J = 8.25 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 24.0, 24.3, 27.3, 32.8, 65.6, 84.5, 108.0, 129.1, 137.1, 141.6, 153.0 ppm; IR (KBr): $\tilde{\nu}$ = 3260 (m), 1790 (s), 1660 (s), 1600 (m), 1380 (m), 1320 (m), 1220 (m), 1150 (m), 1080 (w), 1030 cm^{-1} (w); elemental analysis calcd (%) for $C_{18}H_{21}NO_5S$: C 59.49, H 5.82, N 3.85, S 8.82; found: C 59.39, H 5.76, N 3.67, S 8.80.

3,3-Dimethyl-4-(*p*-toluenesulfonyl)-10b-triisopropylsiloxy-5,5a,6,10b-tetrahydro-3*H*-2-oxa-10c-aza-cyclopenta[*c*]fluoren-1-one (2k): M.p. 169.0–170.0 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.77–1.09 (m, 21H), 1.18–1.25 (m, 2H), 1.60–1.70 (m, 2H), 2.30 (m, 1H), 2.47 (s, 3H), 2.60 (m, 1H), 2.83 (m, 1H), 5.36 (ddd, J = 1.7, 3.3, 15.4 Hz, 1H), 7.16–7.27 (m, 4H), 7.36 (d, J = 8.1 Hz, 2H), 7.75 ppm (d, J = 8.1 Hz, 2H); IR (KBr): $\tilde{\nu}$ = 1810 (s), 1675 (s), 1380 (m), 1320 (m), 1260 (m), 1215 (m), 1160 (s), 1115 (m), 1080 (m), 1040 (w), 920 cm^{-1} (m); elemental analysis calcd (%) for $C_{31}H_{41}NO_5SSi$: C 65.57, H 7.28, N 2.47; found: C 65.35, H 7.27, N 2.43.

***trans*-5-Methoxy-1,1-dimethyl-3-oxo-8-(*p*-toluenesulfonyl)-1,5,6,7-tetrahy-dro-oxazolo[3,4-*a*]pyridine-6-carboxylic acid methyl ester (2l)**: CCDC-181552; m.p. 193.0–193.3 °C (CH_2Cl_2/hexane); ^{1}H (400 MHz, $CDCl_3$): δ = 1.94 (s, 3H), 1.99 (s, 3H), 2.45 (s, 3H), 2.52 (dd, J = 5.7, 16.5 Hz, 1H), 2.66 (ddd, J = 1.1, 2.2, 16.5 Hz, 1H), 2.99 (dt, J = 5.7, 2.2 Hz, 1H), 3.42 (s, 3H), 3.45 (s, 3H), 5.39 (dd, J = 1.1, 2.2 Hz, 1H), 7.35 (d, J = 8.4 Hz, 2H), 7.75 ppm (d, J = 8.4 Hz, 2H); IR (KBr): $\tilde{\nu}$ = 1800 (s), 1720 (s), 1640 (s), 1600 (m), 1370 (s), 1310 (s), 1290 (s), 1220 (m), 1150 (s), 1120 (m), 1100 (s), 1080 (s), 960 cm^{-1} (m); elemental analysis calcd (%) for $C_{19}H_{23}NO_7S$: C 55.73, H 5.66, N 3.42, S 7.83; found: C 55.42, H 5.61, N 3.31, S 7.43.

6-Ethyl-1,1-dimethyl-8-(*p*-toluenesulfonyl)-5-triisopropylsiloxy-1,5,6,7-tetrahydro-oxazolo[3,4-*a*]pyridin-3-one (*cis*-2m): M.p. 186.2–187.0 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91–0.99 (m, 21H), 1.05–1.14 (m, 3H), 1.32 (dq, J = 14.3, 7.4 Hz, 1H), 1.44 (m, 1H), 1.50 (dq, J = 14.3, 7.4 Hz, 1H), 1.87 (dd, J = 12.3, 15.9 Hz, 1H), 2.41 (dd, J = 4.8, 15.9 Hz, 1H), 5.53 (d, J = 1.5 Hz, 1H), 7.29 (d, J = 8.1 Hz, 2H), 7.71 ppm (d, J = 8.1 Hz, 2H); ***trans*-2m**: δ = 0.73 (t, J = 7.0 Hz, 3H), 0.91–0.99 (m, 21H), 1.05–1.14 (m, 3H), 1.26–1.55 (m, 3H), 1.87 (dd, J = 12.3, 15.9 Hz, 1H), 2.41 (dd, J = 4.8, 15.9 Hz, 1H), 5.37 (d, J = 1.8 Hz, 1H), 7.30 (d, J = 8.6 Hz, 2H), 7.73 ppm (d, J = 8.6 Hz, 2H); IR (KBr): $\tilde{\nu}$ = 1770 (s), 1630 (s), 1325 (m), 1305 (s), 1260 (m), 1220 (m), 1170 (m), 1140 (s), 1080 (s), 1055 (m), 995 (m), 960 (m), 940 (m), 870 (m), 840 (m), 800 cm^{-1} (m); HRMS: *m/z* (%): calcd for $C_{27}H_{43}NO_5SSi-i$Pr: 478.2083, found: 478.2074 (100) $[M-i\mathrm{Pr}]^+$; elemental analysis calcd (%) for $C_{27}H_{43}NO_5SSi$: C 62.15, H 8.31, N 2.68; found: C 62.08, H 8.20, N 2.70.

3,3-Dimethyl-4-(*p*-toluenesulfonyl)-3,5,5a,7,8,9a-hexahydro-6*H*-2,9-dioxa-9b-azacyclopenta[*a*]naphthalen-1-one (2n): M.p. 224.0–225.0 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.33 (dm, J = 13.4 Hz, 1H), 1.68 (ttm, J = 4.4, 13.4 Hz, 1H), 1.79–2.06 (m, 3H), 1.97 (s, 3H), 1.98 (s, 3H), 2.16 (ddm, J = 4.8, 15.8 Hz, 1H), 2.43 (dm, J = 15.8 Hz, 1H), 2.45 (s, 3H), 3.63 (dm, J = 12.1 Hz, 1H), 3.98 (dd, J = 4.8, 12.1 Hz, 1H), 5.07 (br s, 1H), 7.35 (d, J = 8.2 Hz, 2H), 7.73 ppm (d, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.0, 21.6, 23.5, 26.0, 26.3, 26.9, 30.1, 68.0, 78.2, 86.8, 107.8, 127.5, 130.0, 137.5, 144.3, 147.7, 152.9 ppm; IR (KBr): $\tilde{\nu}$ = 1786 (s), 1634 (s), 1333 (s), 1294 (s), 1267 (s), 1148 (s), 847 (m), 762 cm^{-1} (m); elemental analysis calcd (%) for $C_{19}H_{23}NO_5S$: C 60.46, H 6.14, N 3.71, S 8.50; found: C 59.96, H 6.07, N 3.71, S 8.62.

3,3-Dimethyl-4-(*p*-toluenesulfonyl)-9a-trimethylsiloxy-3,5,5a,6,7,8,9,9a-octahydrooxazolo[3,4-*a*]quinolin-1-one (2o): CCDC-181722; m.p. 117.0–118.0 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.05 (s, 9H), 1.06–1.45 (m, 5H), 1.53–1.78 (m, 3H), 1.93 (s, 3H), 1.95 (s, 3H), 1.96 (m, 1H), 2.41 (s, 3H), 2.48 (dd, J = 5.5, 15.9 Hz, 1H), 3.54 (br d, J = 15.9 Hz, 1H), 7.31 (d, J = 8.5 Hz, 2H), 7.70 ppm (d, J = 8.5 Hz, 2H); IR (KBr): $\tilde{\nu}$ = 1780 (s), 1640 (s), 1370 (m), 1350 (m), 1290 (s), 1250 (m), 1160 (s), 1130 (s), 1110 (s), 1070 (m), 950 cm^{-1} (m); elemental analysis calcd (%) for $C_{23}H_{33}NO_5SSi$: C 59.58, H 7.17, N 3.02; found: C 59.39, H 7.16, N 2.67.

9a-Hydroxy-3,3-dimethyl-4-(toluene-4-sulfonyl)-3,5,5a,6,7,8,9,9a-octahydro-oxazolo[3,4-*a*]quinolin-1-one (2o′): M.p. 217.5–218.0 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18–1.80 (m, 8H), 1.92 (s, 3H), 1.94 (m, 1H), 1.98 (s, 3H), 2.20–2.39 (m, 2H), 2.45 (s, 3H), 4.42 (br s, 1H), 7.34 (d, J = 7.0 Hz, 2H), 7.72 (d, J = 7.0 Hz, 2H); IR (KBr): $\tilde{\nu}$ = 3470 (m), 1760 (s), 1650 (s), 1370 (w), 1300 (m), 1150 (m), 1100 cm^{-1} (w); HRMS: *m/z* (%): calcd for $C_{20}H_{25}NO_5S$: 391.1453, found: 391.1470 (50) $[M]^+$, 236 (100); elemental analysis calcd (%) for $C_{20}H_{25}NO_5S$: C 61.36, H 6.44, N 3.58, S 8.19; found: C 60.39, H 6.77, N 3.67, S 8.48.

1,1,5-Trimethyl-3-oxo-8-(*p*-toluenesulfonyl)-5-triisopropylsilanyloxy-1,5,6,7-tetrahydro-oxazolo[3,4-*a*]pyridine-6-carboxylic acid methyl ester (2p): M.p. 132.0–132.2 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92–1.06 (m, 21H), 1.97 (s, 6H), 2.02 (s, 3H), 2.43 (s, 3H), 2.50 (dd, J = 1.8, 16.5 Hz, 1H), 2.64 (dd, J = 6.2, 16.5 Hz, 1H), 2.77 (dd, J = 1.8, 6.2 Hz, 1H), 3.49 (s, 3H), 7.32 (d, J = 7.8 Hz, 2H), 7.72 ppm (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.2, 18.1, 18.2, 21.5, 24.3, 25.0, 26.5, 26.9, 49.5, 51.8, 82.2, 84.3, 106.3, 127.7, 129.7, 137.7, 144.0, 150.1, 152.4, 170.1 ppm; IR (KBr): $\tilde{\nu}$ = 1782 (s), 1741 (s), 1618 (s), 1350 (m), 1332 (m), 1294 (s), 1144 (s), 962 (m), 760 cm^{-1} (m); HRMS: *m/z* (%): calcd for $C_{28}H_{43}NO_7SSi-i$Pr: 522.1982, found: 522.1985 (100) $[M-i\mathrm{Pr}]^+$.

3,3-Dimethyl-4-(*p*-toluenesulfonyl)-9a-triisopropylsiloxy-3,5,5a,7,8,9a-hexahydro-6*H*-2,9-dioxa-9b-aza-cyclopenta[*a*]naphthalen-1-one (2q): CCDC-181725; m.p. 110.5–110.9 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (d, J = 1.8 Hz, 9H), 0.97 (d, J = 1.8 Hz, 9H), 1.05–1.28 (m, 4H), 1.46 (m, 1H), 1.55 (m, 1H), 1.65 (m, 1H), 1.81 (m, 1H), 1.95 (s, 3H), 1.98 (s, 3H), 2.18 (dd, J = 1.8, 16.3 Hz, 1H), 2.43 (s, 3H), 2.53 (dd, J = 5.9, 16.3 Hz, 1H), 3.58 (dt, J = 2.6, 12.5 Hz, 1H), 3.99 (dd, J = 5.1, 12.5 Hz, 1H), 7.31 (d, J = 8.4 Hz, 2H), 7.71 ppm (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.3, 12.9, 18.1, 21.6, 24.4, 26.0, 26.6, 27.5, 29.2, 39.2, 65.6, 83.6, 102.8, 106.6, 127.5, 129.8, 138.0, 144.0, 150.0, 150.7 pppm; IR (KBr): $\tilde{\nu}$ = 1782 (s), 1626 (s), 1337 (m), 1317 (s), 883 (m), 756 cm^{-1} (m); HRMS: *m/z* (%): calcd for $C_{28}H_{43}NO_6SSi-i$Pr: 506.2033, found: 506.2030 (100) $[M-i\mathrm{Pr}]^+$.

9a-Hydroxy-3,3-dimethyl-4-(toluene-4-sulfonyl)-3,5,5a,6,7,9a-hexahydro-oxazolo[3,4-*a*]quinolin-1-one (2r): M.p. 61.0–62.0 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06 (s, 3H), 1.45 (s, 3H), 1.47 (m, 1H), 1.85 (m, 1H), 1.98 (m, 1H), 2.30–2.44 (m, 2H), 2.40 (s, 3H), 2.85 (dd, J = 2.8, 15.2 Hz, 1H), 2.94 (d, J = 15.2 Hz, 1H), 3.80 (br s, 1H), 5.80 (m, 1H), 5.82 (m, 1H), 7.31 (d, J = 8.3 Hz, 2H), 7.85 ppm (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.6, 21.7, 25.2, 26.6, 44.6, 53.7, 67.3, 85.2, 121.2, 128.9, 129.7, 129.8, 130.4, 130.8, 146.0, 152.3 ppm; IR (KBr): $\tilde{\nu}$ = 3400 (s), 1786 (s), 1281 (s), 1267 (s), 1177 (s), 1088 (m), 937 cm^{-1} (m); elemental analysis calcd (%) for $C_{20}H_{23}NO_5S$: C 61.68, H 5.95, N 3.60; O, 20.54, S 8.23; found: C 61.70, H 5.61, N 3.31, S 8.53.

5-Methoxy-5-methyl-8-(*p*-toluenesulfonyl)-1,5,6,7-tetrahydro-oxazolo[3,4-*a*]pyridin-3-one (2s): M.p. 133.0–133.1 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.57 (m, 1H), 1.88 (s, 3H), 2.02 (ddd, J = 2.6, 4.8, 13.6 Hz, 1H), 2.29 (m, 2H), 2.45 (s, 3H), 3.29 (s, 3H), 5.44 (ddd, J = 1.7, 3.3, 14.5 Hz, 1H), 5.45 (ddd, J = 1.7, 3.3, 14.5 Hz, 1H), 7.34 (d, J = 8.1 Hz, 2H), 7.72 ppm (d, J = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.4, 20.5, 21.6, 34.9, 51.1, 66.9, 85.2, 109.1, 127.2, 130.0, 137.7, 142.6, 144.5, 193.9 ppm; IR (KBr): $\tilde{\nu}$ = 1780 (s), 1670 (s), 1380 (s), 1300 (s), 1160 (s), 1140 (s), 1080 (s), 1020 (s), 760 cm^{-1} (m); HRMS: *m/z* (%): calcd for $C_{16}H_{19}NO_5S$: 337.0984, found: 337.0988 (100) $[M]^+$; elemental analysis calcd (%) for $C_{16}H_{19}NO_5S$: C 56.96, H 5.68, N 4.15, S 9.50; found: C 56.86, H 5.78, N 4.10, S 9.48.

4-Methanesulfonyl-3,5,5a,7,8,9a-hexahydro-6*H*-2,9-dioxa-9b-aza-cyclopenta[*a*]naphthalene-1-one (2t): CCDC-188831; m.p. 201.5–202.0 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.47 (dm, J = 15.8 Hz, 1H), 1.80–2.07 (m, 4H), 2.39 (tm, J = 15.4 Hz, 1H), 2.95 (s, 3H), 3.73 (dtm, J = 2.6, 11.5 Hz, 1H), 4.10 (ddm, J = 4.8, 11.5 Hz, 1H), 5.12 (br s, 1H), 5.30 (dm, J = 17.7 Hz, 1H), 5.35 ppm (dm, J = 17.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.2, 21.7, 26.2, 30.7, 42.2, 67.8, 68.4, 78.2, 106.1, 142.1, 154.1 pp,; IR (KBr): $\tilde{\nu}$ = 2862 (m), 1788 (s), 1665 (s), 1298 (s), 1020 (s), 783 cm^{-1} (m); HRMS: *m/z* (%): calcd for $C_{11}H_{13}NO_3S$: 273.0671, found: 273.0652 (95) $[M]^+$, 214 (100), 194 (28), 193 (73).

5,5-Bis-methylsulfanyl-8-(*p*-toluenesulfonyl)-1,5,6,7-tetrahydro-oxazolo-[3,4-*a*]pyridin-3-one (2u): M.p. 231.0–231.2 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.23 (br d, J = 6.4 Hz, 2H), 2.26 (s, 6H), 2.42 (tt, J = 2.4, 6.4 Hz, 2H), 2.46 (s, 3H), 5.43 (t, J = 2.4 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 7.72 ppm (d, J = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3, 20.3, 21.6, 34.6, 66.7, 72.8, 108.6, 127.1, 130.1, 137.4, 142.2, 144.7. 153.2 ppm; IR (KBr): $\tilde{\nu}$ = 1780 (s), 1660 (s), 1380 (s), 1300 (s), 1290 (s), 740 cm^{-1} (s); HRMS: *m/z* (%): calcd for $C_{16}H_{19}NO_4S_3$: 385.0476, found: 385.0477 (1) $[M]^+$, 338 (100).

6-Aza-5-(trimethylsilylmethyl)-9,9-dimethyl-2-(p-toluenesulfonyl)-8-oxabicyclo[4.3.0]non-1-en-7-one (3a): CCDC-139284; m.p. 173.0–173.5 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.05 (s, 9H), 0.69 (dd, J = 10.3, 14.5 Hz, 1H), 0.94 (dm, J = 14.5 Hz, 1H), 1.57 (dm, J = 13.6 Hz, 1H), 1.80 (dm, J = 13.6 Hz, 1H), 1.94 (s, 3H), 1.98 (s, 3H), 2.15 (dm, J = 16.7 Hz, 1H), 2.30 (dm, J = 16.7 Hz, 1H), 2.45 (s, 3H), 4.20 (br quint, J = 4.2 Hz, 1H), 7.34 (d, J = 8.2 Hz, 2H), 7.73 ppm (d, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −1.1, 19.8, 21.3, 21.6, 25.1, 26.3, 26.7, 47.3, 86.4, 106.1, 127.3, 129.8, 137.9, 144, 149.7, 153.4 ppm; IR (KBr): $\tilde{\nu}$ = 1770 (s), 1630 (s), 1390 (m), 1370 (m), 1320 (m), 1290 (s), 1240 (m), 1160 (m), 1140 (s), 1090 (m), 960 cm^{-1} (m); HRMS: *m/z* (%): calcd for $C_{20}H_{21}NO_4SSi$: 407.1587, found: 407.1595 (100) $[M]^+$; elemental analysis calcd (%) for $C_{20}H_{21}NO_4SSi$: C 58.93, H 7.17, N 3.44; found: C 58.47, H 7.03, N 3.42.

6-Aza-5-(triisopropylsilylmethyl)-9,9-dimethyl-2-(*p*-toluenesulfonyl)-8-oxabicyclo[4.3.0]non-1-en-7-one (3b): M.p. 177.0–177.5 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91–1.11 (m, 21H), 1.53 (d, J = 1.8 Hz, 2H), 1.56 (dm, J = 16.5 Hz, 1H), 1.85 (dm, J = 16.5 Hz, 1H), 1.96 (s, 3H), 1.97 (s, 3H), 2.22 (dm, J = 16.5 Hz, 1H), 2.33 (dm, J = 16.5 Hz, 1H), 2.43 (s, 3H), 4.34 (tm, J = 1.8 Hz, 1H), 7.32 (d, J = 8.4 Hz, 2H), 7.73 ppm (d, J = 8.4 Hz, 2H); IR (KBr): $\tilde{\nu}$ = 1800 (s), 1780 (s), 1680 (s), 1210 (s), 1150 (s), 1140 (s), 1090 (m), 1070 (w), 1060 (w), 960 cm^{-1}

(m); elemental analysis calcd (%) for $C_{26}H_{41}NO_4SSi$: C 63.50, H 8.40, N 2.85; found: C 63.20, H 8.72, N 2.92.

6-Aza-5-(triphenylsilylmethyl)-9,9-dimethyl-2-(*p*-toluenesulfonyl)-8-oxabicyclo[4.3.0]non-1-en-7-one (3c): M.p. 223.5–224.5 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.42–1.52 (m, 2H), 1.89 (dm, J = 16.9 Hz, 1H), 1.94 (s, 3H), 1.95 (s, 3H), 1.98 (dm, J = 16.9 Hz, 1H), 2.44 (s, 3H), 4.41 (dm, J = 12.1 Hz, 1H), 7.31–7.44 (m, 11H), 7.54 (dm, J = 8.4 Hz, 6H), 7.67 ppm (d, J = 8.4 Hz, 2H); IR (KBr): $\tilde{\nu}$ = 1769 (s), 1620 (s), 1427 (m), 1396 (m), 1366 (s), 1352 (m), 1292 (s), 1148 (s), 1111 (m), 729 cm^{-1} (s); HRMS: *m/z* (%): calcd for $C_{35}H_{35}O_4NSSi-Ph$: 516.1665, found: 516.1661 (100) $[M-Ph]^+$; elemental analysis calcd (%) for $C_{35}H_{35}O_4NSSi$: C 70.79, H 5.94, N 2.36; found: C 70.85, H 6.03, N 2.34.

6-Aza-5-methyl-5-(trimethylsilylmethyl)-9,9-dimethyl-2-(*p*-toluenesulfonyl)-8-oxabicyclo[4.3.0]non-1-en-7-one (3d): M.p. 164.5–165.1 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.03 (s, 9H), 1.36 (d, J = 14.7 Hz, 1H), 1.46 (d, J = 14.7 Hz, 1H), 1.49 (s, 3H), 1.59 (ddd, J = 5.1, 8.1, 13.9 Hz, 1H), 1.72 (ddd, J = 5.1, 7.3, 13.9 Hz, 1H), 1.94 (s, 6H), 2.16 (ddd, J = 5.1, 7.3, 16.5 Hz, 1H), 2.25 (ddd, J = 5.1, 8.4, 16.5 Hz, 1H), 2.45 (s, 3H), 7.34 (d, J = 8.2 Hz, 2H), 7.73 ppm (d, J = 8.2 Hz, 2H); IR (KBr): $\tilde{\nu}$ = 1774 (s), 1629 (s), 1375 (m), 1366 (m), 1335 (m), 1310 (s), 1304 (s), 1248 (m), 1213 (m), 1150 (m), 1143 (s), 1099 (m), 1078 (m), 1057 (m), 966 cm^{-1} (m); HRMS: *m/z* (%): calcd for $C_{21}H_{31}NO_4SSi$: 421.1743, found: 421.1738 (40) $[M]^+$, 406 (100).

5-Hexyloxy-1,1-dimethyl-8-(*p*-toluenesulfonyl)-6-trimethylsilylmethylhexahydro-oxazolo[3,4-*a*]pyridin-3-one (3e): M.p. 86.5–87.5 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = −0.06 (s, 9H), 0.60 (dd, J = 8.4, 15.0 Hz, 1H), 0.69 (dd, J = 6.2, 15.0 Hz, 1H), 0.89 (t, J = 7.0 Hz, 3H), 1.18–1.31 (m, 6H), 1.43–1.52 (m, 2H), 1.60 (m, 1H), 1.95 (s, 3H), 1.98 (m, 1H), 2.01 (s, 3H), 2.17 (dd, J = 5.0, 10.3 Hz, 1H), 2.44 (s, 3H), 3.50–3.60 (m, 2H), 4.96 (d, J = 2.6 Hz, 1H), 7.33 (d, J = 8.2 Hz, 2H), 7.71 ppm (d, J = 8.2 Hz, 2H); IR (KBr): $\tilde{\nu}$ = 1776 (s), 1634 (s), 1344 (m), 1300 (s), 1144 (s), 1113 (s), 841 cm^{-1} (m); HRMS: *m/z* (%): calcd for $C_{26}H_{41}NO_5SSi$: 507.2475, found: 504.2490 (100) $[M]^+$, 318 (87), 274 (58), 73 (29).

5-Benzyl-1,1-dimethyl-8-(*p*-toluenesulfonyl)-1,5,6,7-tetrahydrooxazolo-[3,4-*a*]pyridin-3-one (3f): M.p. 168.5–169.0 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.42 (tt, J = 4.9, 13.2 Hz, 1H), 1.80 (dm, J = 13.2 Hz, 1H), 1.99 (s, 3H), 2.00 (s, 3H), 2.16 (ddd, J = 4.8, 13.2, 16.9 Hz, 1H), 2.33 (br dd, J = 4.9, 16.9 Hz, 1H), 2.46 (s, 3H), 2.52 (dd, J = 9.9, 13.4 Hz, 1H), 2.94 (dd, J = 4.8, 13.4 Hz, 1H), 4.26 (dt, J = 9.9, 4.8 Hz, 1H), 7.13 (d, J = 7.0 Hz, 2H), 7.20–7.30 (m, 3H), 7.35 (d, J = 8.4 Hz, 2H), 7.73 ppm (d, J = 8.4 Hz, 2H); IR (KBr): $\tilde{\nu}$ = 1776 (s), 1632 (s), 1375 (s), 1292 (s), 1170 (m), 1142 (s), 1063 (m) cm^{-1}; HRMS: *m/z* (%): calcd for $C_{23}H_{25}NO_4S$: 411.1504, found: 411.1511 (100).

6-Aza-5-(trimethylsilylethyl)-9,9-dimethyl-2-(*p*-toluenesulfonyl)-8-oxabicylo[4.3.0]non-1-en-7-one (3g): M.p. 139.5–140.0 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = − 0.07 (s, 9H), 0.37 (dt, J = 4.8, 13.9 Hz, 1H), 0.45 (dt, J = 4.8, 13.9 Hz, 1H), 1.16 (ddt, J = 4.4, 8.8, 8.8 Hz, 1H), 1.44–1.53 (m, 2H), 1.96 (s, 3H), 1.99 (s, 3H), 1.92–2.04 (m, 2H), 2.32 (dm, J = 15.7 Hz, 1H), 2.44 (s, 3H), 3.96 (quint, J = 4.7 Hz, 1H), 7.33 (d, J = 8.2 Hz, 2H), 7.71 ppm (d, J = 8.2 Hz, 2H); IR (KBr): $\tilde{\nu}$ = 1765 (s), 1622 (s), 1334 (m), 1302 (s), 1292 (s), 1250 (m), 1207 (m), 1143 (s), 1110 (m), 964 cm^{-1} (m); HRMS: *m/z* (%): calcd for $C_{21}H_{31}NO_4SSi$: 421.1743, found: 421.1731 (100) $[M]^+$.

(*Z*)-5,5-Dimethyl-4-[1-(*p*-toluenesulfonyl)ethylidene]oxazolidin-2-one [(*Z*)-4a]: M.p. 188.2–189.1 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.63 (s, 6H), 1.84 (s, 3H), 2.46 (s, 3H), 7.35 (d, J = 8.2 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H), 9.51 ppm (br s, 1H); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 12.2, 21.6, 25.3, 85.2, 102.8, 127.3, 130.1, 136.9, 144.9, 149.6, 153.3 ppm; IR (KBr): $\tilde{\nu}$ = 3323 (m), 1805 (br s), 1653 (s), 1298 (s), 1277 (m), 1126 (m), 1078 (m), 820 (m), 658 cm^{-1} (m); HRMS: *m/z* (%): calcd for $C_{14}H_{17}NO_4S$: 295.0878, found: 295.0909 (100) $[M]^+$.

(*E*)-5,5-Dimethyl-4-[1-(*p*-toluenesulfonyl)-ethylidene]-oxazolidin-2-one [(*E*)-4a]: M.p. 202.0–202.5 °C (THF/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.53 (s, 3H), 2.01 (s, 6H), 2.44 (s, 3H), 7.33 (d, J = 8.6 Hz, 2H), 7.72 (d, J = 8.6 Hz, 2H), 7.94 ppm (br s, 1H); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 15.3, 21.6, 26.7, 89.25, 106.6, 127.6, 129.9, 137.6, 144.3, 150.2, 154.9 ppm; IR (KBr): $\tilde{\nu}$ = 3497 (w), 3192 (m), 3134 (m), 1771 (s), 1757 (s), 1636 (s), 1300 (s), 1288 (m), 1126 (m), 1078 (m), 810 (m), 658 cm^{-1} (m); HRMS: *m/z* (%): calcd for $C_{14}H_{17}NO_4S$: 295.0878, found: 295.0873 (100) $[M]^+$.

Ether connected at C-2′ of (*E*)-4-Ethylidene-5,5-dimethyl-3-(*p*-toluenesulfonyl)oxazolidin-2-one (5): CCDC-139285; m.p. 160.3–161.3 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.56 (s, 6H), 2.46 (s, 3H), 4.10 (d, J = 7.7 Hz, 2H), 6.23 (t, J = 7.7 Hz, 1H), 7.37 (d, J = 8.2 Hz, 2H), 7.94 ppm (J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.8, 27.2, 64.7, 82.7, 104.2, 128.2, 129.9, 134.5, 140.9, 146.2, 150.0 ppm; IR (KBr): $\tilde{\nu}$ = 1790 (s), 1690 (s), 1390 (m), 1340 (m), 1280 (m), 1180 (m), 1110 (m), 1090 (m), 810 (m), 750 cm^{-1} (m); elemental analysis calcd (%) for $C_{28}H_{32}N_2O_9S_2$: C 55.61, H 5.33, N 4.63, S 10.61; found: C 55.77, H 5.41, N 4.69, S 10.58.

(*Z*)-4-[2-Methoxy-1-(*p*-toluenesulfonyl)ethylidene]-5,5-dimethyloxazolidin-2-one [(*Z*)-4b]: M.p. 106.1–107.0 °C (hexane/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.67 (s, 6H), 2.44 (s, 3H), 3.17 (s, 2H), 4.11 (s, 2H), 7.33 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 9.50 ppm (br s, 1H); IR (KBr): $\tilde{\nu}$ = 3364 (m), 1782 (s), 1639 (s), 1302 (m), 1078 (m), 1007 (m), 899 (m), 816 cm^{-1} (m); HRMS: *m/z* (%): calcd for $C_{15}H_{19}NO_5S$: 325.0984, found: 325.0981 (72) $[M]^+$, 91 (100).

(*E*)-4-(2-Methoxyethylidene)-5,5-dimethyl-3-(*p*-toluenesulfonyl)oxazolidin-2-one [(*E*)-6b]: CCDC-181556; m.p. 102.3–103.1 °C (hexane/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.53 (s, 6H), 2.45 (s, 3H), 3.37 (s, 3H), 4.01 (d, J = 7.6 Hz, 2H), 6.22 (t, J = 7.6 Hz, 1H), 7.36 (d, J = 8.2 Hz, 2H), 7.94 ppm (d, J = 8.2 Hz, 2H); IR (KBr): $\tilde{\nu}$ = 1790 (s), 1682 (s), 1655 (w), 1381 (s), 1273 (s), 1084 (s), 1016 (w), 914 (w), 816 cm^{-1} (m); HRMS: *m/z* (%): calcd for $C_{15}H_{19}NO_5S$: 325.0984, found: 325.0989 (12) $[M]^+$, 91 (100).

(*Z*)-4-[2-Benzyloxy-1-(*p*-toluenesulfonyl)ethylidene]-5,5-dimethyloxazolidin-2-one [(*Z*)-4c]: CCDC-186252; m.p. 139.9–140.6 °C (hexane/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.61 (s, 6H), 2.41 (s, 3H), 4.17 (s, 2H), 4.35 (s, 2H), 7.07 (br d, J = 2.2 Hz, 1H), 7.09 (br d, J = 3.7 Hz, 1H), 7.27–7.30 (m, 5H), 7.73 (d, J = 8.4 Hz, 2H), 9.53 ppm (br s, 1H); IR (KBr): $\tilde{\nu}$ = 3317 (w), 1780 (s), 1626 (s), 1302 (m), 1148 (m), 1061 (m), 935 (w), 812 cm^{-1} (w); HRMS: *m/z* (%): calcd for $C_{21}H_{23}NO_5S$ - CH_2Ph: 310.0749, found: 310.0777 (9) $[M-CH_2Ph]^+$, 296 (14), 251 (66), 139 (46), 107 (32), 95 (57), 91 (100).

(*E*)-4-(2-Benzyloxyethylidene)-5,5-dimethyl-3-(*p*-toluenesulfonyl)oxazolidin-2-one [(*E*)-6c]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.46 (s, 6H), 2.45 (s, 3H), 4.07 (d, J = 7.7 Hz, 2H), 4.55 (s, 2H), 6.26 (t, J = 7.7 Hz, 1H), 7.30–7.39 (m, 7H), 7.94 ppm (d, J = 8.4, 2H); IR (neat): $\tilde{\nu}$ = 1790 (s), 1375 (m), 1273 (m), 1177 (s), 1088 (m), 1070 (m), 912 (w), 915 cm^{-1} (w).

(*Z*)-4-[2-Allyloxy-1-(*p*-toluenesulfonyl)ethylidene]-5,5-dimethyloxazolidin-2-one [(*Z*)-4d]: M.p. 129.5–130.5 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.58 (s, 3H), 1.68 (s, 6H), 2.43 (s, 3H), 3.72 (br s, 2H), 4.13 (s, 2H), 4.75 (br s, 1H), 4.82 (br s, 1H), 7.30 (d, J = 8.2 Hz, 2H), 7.77 (d, J = 8.2 Hz, 2H), 9.50 ppm (br s, 1H); IR (KBr): $\tilde{\nu}$ = 3306 (m), 1774 (s), 1734 (w), 1639 (s), 1308 (s), 1288 (s), 1146 (m), 1124 (m), 1082 (m), 1009 (m), 894 cm^{-1} (m); HRMS: *m/z* (%): calcd for $C_{18}H_{23}NO_5S$: 365.1297, found: 365.1320 (12) $[M]^+$, 310 (14), 294 (88), 210 (100).

(*E*)-5,5-Dimethyl-4-[2-(2-methylallyloxy)ethylidene]-3-(*p*-toluenesulfonyl)-oxazolidin-2-one [(*E*)-6d]: M.p. 76.5–78.0 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.52 (s, 6H), 1.76 (s, 3H), 2.45 (d, 3H), 3.91 (br s, 2H), 4.03 (d, J = 7.7 Hz, 2H), 4.94 (br s, 1H), 4.98 (br s, 1H), 6.23 (t, J = 7.7 Hz, 1H), 7.35 (d, J = 8.3 Hz, 2H), 7.93 ppm (d, J = 8.3 Hz, 2H); IR (KBr): $\tilde{\nu}$ = 1788 (s), 1684 (s), 1369 (s), 1275 (s), 1191 (m), 1178 (s), 1088 (s), 978 cm^{-1} (m); HRMS: *m/z* (%): calcd for $C_{18}H_{23}NO_5S$: 365.1297, found: 365.1294 (2) $[M]^+$, 310 (2), 294 (15), 210 (91), 91 (100).

(*Z*)-4-[2-Isopropoxy-1-(*p*-toluenesulfonyl)ethylidene]-5,5-dimethyl-oxazolidin-2-one [(*Z*)-4e]: M.p. 109.5–110.5 °C (hexane/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.98 (d, J = 6.1 Hz, 6H), 1.69 (s, 6H), 2.44 (s, 3H), 3.44 (hept, J = 6.1 Hz, 1H), 4.13 (s, 2H), 7.32 (d, J = 7.9 Hz, 2H), 7.77 (d, J = 7.9 Hz, 2H), 9.49 ppm (br s, 1H); IR (KBr): $\tilde{\nu}$ = 3350 (w), 1784 (s), 1636 (s), 1373 (m), 1302 (m), 1055 (m), 1018 (m), 897 (m), 818 cm^{-1} (m); HRMS: *m/z* (%): calcd for $C_{17}H_{23}NO_5S$: 353.1297, found: 353.1291 (69) $[M]^+$, 310 (100).

(*E*)-4-(2-Isopropoxyethylidene)-5,5-dimethyl-3-(*p*-toluenesulfonyl)oxazolidin-2-one [(*E*)-6e]: M.p. 70.9–71.9 °C (hexane/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.19 (d, J = 6.2 Hz, 6H), 1.54 (s, 6H), 2.45 (s, 3H), 3.64 (hept, J = 6.2 Hz, 1H), 4.03 (d, J = 7.7 Hz, 2H), 6.21 (t, J = 7.7 Hz, 1H), 7.36 ppm (d, J = 8.3 Hz, 2H), 7.94 (d, J = 8.3 Hz, 2H); IR (KBr): $\tilde{\nu}$ = 1782 (s), 1749 (m), 1682 (s), 1655 (w), 1379 (s), 1263 (s), 1086 (s), 1016 (w), 914 (m), 817 cm^{-1} (s); HRMS: *m/z* (%): calcd for $C_{17}H_{23}NO_5S$: 353.1297, found: 353.1314 (6) $[M]^+$, 139 (8), 91 (100).

(*Z*)-5,5-Dimethyl-4-[2-(1-methylallyloxy)-1-(*p*-toluenesulfonyl)ethylidene]oxazolidin-2-one [(*Z*)-4f]: M.p. 100.5–101.5 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.00 (d, J = 6.2 Hz, 1H), 1.66 (s, 3H), 1.67 (s, 3H), 2.44 (s, 3H), 3.67 (br quint, J = 6.2 Hz, 1H), 3.98 (d, J = 12.3 Hz, 1H), 4. 16 (d, J = 12.3 Hz, 1H), 5.11 (dm, J = 10.3 Hz, 1H), 5.13 (dm, J = 16.9 Hz, 1H), 5.52 (ddd, J = 6.2, 10.3, 12.3 Hz, 1H), 7.32 (d, J = 7.3 Hz, 2H), 7.77 (d, J = 7.3 Hz, 2H), 9.53 ppm (br s, 1H); IR (KBr): $\tilde{\nu}$ = 3321 (m), 1782 (s), 1634 (s), 1375 (m), 1300 (s), 1279 (s), 1150 (s), 1124 (m), 1076 (s), 1040 (m), 1011 (m), 950 cm^{-1} (w); HRMS: *m/z* (%): calcd for $C_{18}H_{23}NO_5S$: 365.1297, found: 365.1267 (26) $[M]^+$, 294 (57), 210 (100).

(*E*)-5,5-Dimethyl-4-[2-(1-methylallyloxy)ethylidene]-3-(*p*-toluenesulfonyl)-oxazolidin-2-one [(*E*)-6f]: M.p. 66.5–67.0 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27 (d, J = 6.6 Hz, 3H), 1.51 (s, 6H), 2.43 (s, 3H), 3.89 (br quint, J = 6.6 Hz, 3H), 3.91 (dd, J = 7.7, 11.7 Hz, 1H), 4.08 (dd, J = 7.7, 11.7 Hz, 1H), 5.18 (dm, J = 17.2 Hz, 1H), 5.22 (dm, J = 10.3 Hz, 1H), 5.73 (ddd, J = 6.6, 10.3, 17.2 Hz, 1H), 6.21 (t, J = 7.7 Hz, 1H), 7.35 (d, J = 8.6 Hz, 2H), 7.93 ppm (d, J = 8.6 Hz, 2H); IR (KBr): $\tilde{\nu}$ = 3321 (m), 1782 (s), 1634 (s), 1375 (m), 1300 (s), 1279 (s), 1192 (w), 1150 (s), 1124 (m), 1076 (s), 1040 (m), 1011 (m), 950 cm^{-1} (w); HRMS: *m/z* (%): calcd for $C_{18}H_{23}NO_5S$: 365.1297, found: 365.1295 (10) $[M]^+$, 91 (100).

(*E*)-4-(2-Phenoxyethylidene)-5,5-dimethyl-3-(*p*-toluenesulfonyl)-oxazolidin-2-one [(*E*)-6g]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.55 (s, 6H), 2.45 (s, 3H), 4.59 (d, J = 7.7 Hz, 2H), 6.40 (t, J = 7.7 Hz, 1H), 6.91 (dd, J = 1.1, 8.6 Hz, 2H), 7.00 (tt, J = 1.1, 7.3 Hz, 1H), 7.25–7.35 (m, 4H), 7.91 ppm (d, J = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.8, 27.1, 62.6, 82.9, 103.5, 115.0, 121.5, 128.2, 129.7, 129.9, 134.5, 141.6, 146.1, 150.1, 158.1 ppm; IR (neat): $\tilde{\nu}$ = 1790 (s), 1599 (s), 1177 (s), 1088 (s), 667 cm^{-1} (s); HRMS: *m/z* (%): calcd for $C_{20}H_{21}NO_5S$: 387.1140, found: 387.1137 (100) $[M]^+$, 294 (51).

5,5-Dimethyl-4-[2-hexadecylsulfanyl-1-(*p*-toluenesulfonyl)ethylidene]oxazolidin-2-one (4h): a mixture of two isomers in a ratio of 7:1 (*E*/*Z*); ^{1}H NMR (400 MHz, $CDCl_3$, major isomer): δ = 0.88 (t, J = 6.8 Hz, 3H), 1.26 (s, 24H), 1.40–1.50 (m, 4H), 2.00 (s, 6H), 2.37 (t, J = 7.5 Hz, 2H), 2.44 (s, 3H), 3.31 (s, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.73 (d, J = 8.1 Hz, 2H), 8.29 ppm (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, major isomer): δ = 14.4, 21.6, 22.7, 26.5, 28.8, 29.2, 29.4, 29.5, 29.7, 30.8, 32.0, 89.1, 106.8, 127.8, 129.9, 137.7, 144.5, 153.4, 154.2 ppm; IR (KBr): $\tilde{\nu}$ = 2853 (s), 1784 (s), 1628 (s), 1298 (s), 1080 (m), 656 cm^{-1} (m); HRMS: *m/z* (%): calcd for $C_{30}H_{49}NO_5S$: 551.3103, found: 551.3123 (100) $[M]^+$, 396 (16).

5,5-Dimethyl-4-[2-phenylsulfanyl-1-(*p*-toluenesulfonyl)ethylidene]oxazolidin-2-one (4i): a mixture of two isomers in a ratio of 6:1 (*Z*:*E*); ^{1}H NMR (400 MHz, $CDCl_3$, major isomer): δ = 1.69 (s, 6H), 2.45 (s, 3H), 3.85 (s, 2H), 7.20–7.30 (m, 5H), 7.33 (d, J = 8.3 Hz, 2H), 7.79 (d, J = 8.3 Hz, 2H), 9.59 ppm (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, major isomer): δ = 21.7, 26.4, 32.3, 85.9, 104.9, 127.2, 127.5, 129.2, 129.9, 130.3, 135.9, 138.1, 145.1, 152.8, 153.5 ppm; IR (KBr): $\tilde{\nu}$ = 1769 (s), 1300 (s), 1016 (s), 740 (s), 656 cm^{-1} (s); HRMS: *m/z* (%): calcd for $C_{20}H_{21}NO_4S_2$: 403.0912, found: 403.0889 (100) $[M]^+$.

(*E*)-4-(2-Phenylsulfanylethylidene)-5,5-dimethyl-3-(*p*-toluenesulfonyl)-oxazolidin-2-one [(*E*)-6i]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.40 (s, 6H), 2.46 (s, 3H), 3.57 (d, J = 8.4 Hz, 2H), 6.20 (t, J = 8.4 Hz, 1H), 7.26–7.32 (m, 3H), 7.34 (d, J = 8.3 Hz, 2H), 7.39–7.44 (m, 2H), 7.84 ppm (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.7, 27.0, 32.3, 82.5, 104.4, 127.3, 127.6, 128.1, 129.1, 129.9, 132.0, 134.6, 139.1, 146.0, 150.0, 154.6 ppm; IR (neat): $\tilde{\nu}$ = 1790 (s), 1271 (s), 1177 (s), 746 (s), 671 cm^{-1} (s); HRMS: *m/z* (%): calcd for $C_{20}H_{21}NO_4S_2$: 403.0912, found: 403.0883 (100) $[M]^+$.

4-[2-Phenylsulfanyl-1-(*p*-toluenesulfonyl)ethylidene]-1-oxa-3-aza-spiro-[4.4]nonan-2-one [(*Z*)-4j]: M.p. 174.5–175.5 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.66–1.71 (m, 2H), 1.85–1.89 (m, 2H), 2.13–2.19 (m, 2H), 2.25–2.32 (m, 2H), 2.46 (s, 3H), 3.75 (s, 2H), 7.21–7.30 (m, 5H), 7.34 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 8.4 Hz, 2H), 9.62 ppm (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.7, 25.3, 25.6, 32.5, 39.6, 40.3, 95.5, 104.6, 127.3, 127.7, 129.2, 129.9, 130.6, 136.0, 138.1, 145.1, 152.8, 153.1 ppm; IR (KBr): $\tilde{\nu}$ = 1784 (s), 1290 (s), 1130 (s), 741 (m), 654 cm^{-1} (m); HRMS: *m/z* (%): calcd for $C_{22}H_{23}NO_4S_2$: 429.1068, found: 429.1071 (6) $[M]^+$, 320 (100).

5,5-Dimethyl-4-[2-(1*H*-indol-3-yl)-1-(*p*-toluenesulfonyl)ethylidene]oxazolidin-2-one [(*E*)-7a]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.05 (s, 6H), 2.42 (s, 3H), 3.62 (br s, 2H), 6.78 (br s, 1H), 6.81 (br s, 1H), 7.12 (br t, J = 8.1 Hz, 1H), 7.22 (br t, J = 8.1 Hz, 1H), 7.30 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.1 Hz, 1H), 7.48 (d, J = 8.1 Hz, 1H), 7.78 (d, J = 8.2 Hz, 2H), 8.02 ppm (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 25.8, 26.7, 88.9, 109.5, 111.6, 118.2, 120.2, 121.8, 123.1, 126.4, 127.9, 130.0, 136.6, 137.7, 144.4, 152.2, 153.1, 193.9 ppm; IR (neat): $\tilde{\nu}$ = 1763 (s), 1632 (s), 1020 (s), 660 cm^{-1} (s); HRMS: *m/z* (%): calcd for $C_{22}H_{22}N_2O_4S$: 410.1300, found: 410.1315 (59) $[M]^+$, 254 (100), 225 (12), 210 (13), 209 (41).

5,5-Dimethyl-3-(*p*-toluenesulfonyl)-4-[2-(1*H*-indol-3-yl)-ethylidene]oxazolidin-2-one [(*E*)-8a]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.58 (s, 6H), 2.44 (s, 3H), 3.58 (br d, J = 8.1 Hz, 2H), 6.36 (t, J = 8.1 Hz, 1H), 6.97 (br s, 1H), 7.14 (br t, J = 8.1 Hz, 1H), 7.23 (br t, J = 8.1 Hz, 1H), 7.35 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.1 Hz, 1H), 7.55 (d, J = 8.1 Hz, 1H), 7.89 (d, J = 8.2 Hz, 2H), 8.06 ppm (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.8, 23.2, 26.9, 29.7, 82.9, 107.5, 111.4, 114.2, 119.6, 121.6, 122.4, 128.1, 129.9, 134.8, 136.5, 137.1, 145.8, 150.5, 193.3 ppm; IR (neat): $\tilde{\nu}$ = 1782 (s), 1086 (s), 739 cm^{-1} (m); HRMS: *m/z* (%): calcd for $C_{22}H_{22}N_2O_4S$: 410.1300, found: 410.1317 (100) $[M]^+$, 293 (7), 282 (11), 281 (28).

5,5-Dimethyl-4-[2-(1-methyl-1*H*-indol-3-yl)-1-(*p*-toluenesulfonyl)ethylidene]-oxazolidin-2-one [(*E*)-7b]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.16 (s, 6H), 2.43 (s, 3H), 3.59 (s, 2H), 3.69 (s, 3H), 6.62 (s, 1H), 6.81 (br s, 1H), 7.09 (m, 1H), 7.24 (m, 1H), 7.26 (m, 1H), 7.31 (d, J = 8.1 Hz, 2H), 7.45 (dt, J = 1.1, 8.1 Hz, 1H), 7.78 ppm (d, J = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 25.7, 26.7, 32.8, 88.8, 107.7, 109.2, 118.2, 119.7, 122.5, 126.5, 126.8, 127.2, 127.9, 129.9, 137.4, 137.8, 144.3, 152.1, 153.1 ppm; IR (neat): $\tilde{\nu}$ = 1784 (s), 1277 (s), 1090 (m), 743 cm^{-1} (m); HRMS: *m/z* (%): calcd for $C_{23}H_{24}N_2O_4S$: 424.1457, found: 424.1434 (100) $[M]^+$.

5,5-Dimethyl-3-(*p*-toluenesulfonyl)-4-[2-(1-methyl-1*H*-indol-3-yl)-ethylidene]oxazolidin-2-one [(*E*)-8b]: M.p. 136.5–137.0 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.58 (s, 6H), 2.45 (s, 3H), 3.57 (br d, J = 8.1 Hz, 2H), 3.77 (s, 3H), 6.33 (t, J = 8.1 Hz, 1H), 6.80 (s, 1H), 7.12 (dt, J = 1.1, 8.1 Hz, 1H), 7.26 (dt, J = 1.1, 8.1 Hz, 1H), 7.31 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.1 Hz, 1H), 7.53 (d, J = 8.1 Hz, 1H), 7.90 ppm (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.8, 23.1, 27.0, 32.7, 82.8, 107.5, 109.4, 112.6, 118.6, 119.0, 120.0, 126.4, 127.3, 128.1, 129.8, 134.9, 137.0, 137.3, 145.8, 150.4 ppm; IR (KBr): $\tilde{\nu}$ = 1786 (s), 1178 (s), 739 cm^{-1} (s); HRMS: *m/z* (%): calcd for $C_{23}H_{24}N_2O_4S$: 424.1457, found: 424.1454 (100) $[M]^+$.

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[1] a) Y. Horino, M. Kimura, S. Tanaka, T. Okajima, Y. Tamaru, *Chem. Eur. J.* **2003**, *9*, 2419–2438; b) M. Kimura, Y. Horino, Y. Wakamiya, T. Okajima, Y. Tamaru, *J. Am. Chem. Soc.* **1997**, *119*, 10869–10870.

For recent development in the intramolecular [2+2] cycloaddition of allenes and alkenes (or alkynes), see: c) H. Ohno, T. Mizutani, Y. Kadoh, K. Miyamura, T. Tanaka, *Angew. Chem.* **2005**, *117*, 5243–5245; *Angew. Chem. Int. Ed.* **2005**, *44*, 5113–5115; d) C. H. Oh, A. K. Gupta, D. I. Park, N. Kim, *Chem. Commun.* **2005**, 5670–5672; e) B. Alcaide, P. Almendros, C. Aragonicillo, *Org. Lett.* **2003**, *5*, 3795–3798.

[2] Preliminary communications: a) Y. Horino, M. Kimura, Y. Wakamiya, T. Okajima, Y. Tamaru, *Angew. Chem.* **1999**, *111*, 123–126; *Angew. Chem. Int. Ed.* **1999**, *38*, 121–123; b) Y. Horino, M. Kimura, M. Naito, S. Tanaka, Y. Tamaru, *Tetrahedron Lett.* **2000**, *41*, 3427–3431.

[3] W. Smadja, *Chem. Rev.* **1983**, *83*, 263–320.

[4] a) I. Kadota, L. M. Lutete, A. Shibuya, Y. Yamamoto, *Tetrahedron Lett.* **2001**, *42*, 6207–6210; b) R. Grigg, I. Köppen, M. Rasparini, V. Sridharan, *Chem. Commun.* **2001**, 964–965; c) A. V. Kel'in, A. W. Sromek, V. Gevorgyan, *J. Am. Chem. Soc.* **2001**, *123*, 2074–2075; d) S. Ma, S. Zhao, *J. Am. Chem. Soc.* **2001**, *123*, 5578–5579; e) B. M. Trost, A. B. Pinkerton, D. Kremzow, *J. Am. Chem. Soc.* **2000**, *122*, 12007–12008; f) C. Jonasson, A. Horvath, J.-E. Bäckwall, *J. Am. Chem. Soc.* **2000**, *122*, 9600–9609; g) S. Ma, S. Zhao, *Org. Lett.* **2000**, *2*, 2495–2497; h) S. Ma, L. Li, *Org. Lett.* **2000**, *2*, 941–944; i) B. M. Trost, A. B. Pinkerton, *J. Am. Chem. Soc.* **1999**, *121*, 4068–4069; j) S. Ma, Z. Shi, Z. Yu, *Tetrahedron Lett.* **1999**, *40*, 2393–2396; k) M. Anzai, A. Toda, H. Ohno, Y. Takemoto, N. Fujii, T. Ibuka, *Tetrahedron Lett.* **1999**, *40*, 7393–7397; l) V. M. Arredondo, S. Tian, F. E. McDonald, T. J. Marks, *J. Am. Chem. Soc.* **1999**, *121*, 3633–3639; m) F. P. J. T. Rutjes, K. C. M. F. Tjen, L. B. Wolf, W. F. J. Karstens, H. E. Schoemaker, H. Hiemstra, *Org. Lett.* **1999**, *1*, 717–720; n) R. C. Larock, Y. He, W. W. Leong, X. Han, M. D. Refvik, J. M. Zenner, *J. Org. Chem.* **1998**, *63*, 2154–2160; o) R. C. Larock, C. Tu, P. Pace, *J. Org. Chem.* **1998**, *63*, 6859–6866; p) M. Al-Masum, Y. Yamamoto, *J. Am. Chem. Soc.* **1998**, *120*, 3809–3810; q) B. M. Trost, P.-Y. Michellys, V. J. Gerusz, *Angew. Chem.* **1997**, *109*, 1837–1839; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1750–1753; r) J. A. Marshall, M. A. Wolf, E. M. Wallace, *J. Org. Chem.* **1997**, *62*, 367–371; s) Y. Tamaru, M. Kimura, *Synlett* **1997**, 749–757.

[5] a) J. S. Johnson, R. G. Bergman, *J. Am. Chem. Soc.* **2001**, *123*, 2923–2924; b) M. V. Chevliakov, J. Montgomery, *J. Am. Chem. Soc.* **1999**, *121*, 11139–11143; c) O. Kitagawa, T. Suzuki, H. Fujiwara, T. Taguchi, *Tetrahedron Lett.* **1999**, *40*, 2549–2552; d) B. W. G. van Henegouwen, R. M. Fieseler, F. P. J. T. Rutjes, H. Hiemstra, *Angew. Chem.* **1999**, *111*, 2351–2355; *Angew. Chem. Int. Ed.* **1999**, *38*, 2214–2217; e) W. F. J. Karstens, M. Stol, F. P. J. T. Rutjes, H. Hiemstra, *Synlett* **1998**, 1126–1128; f) A. Ogawa, A. Kudo, T. Hirao, *Tetrahedron Lett.* **1998**, *39*, 5213–5216; g) A. Stephen, K. Hashimi, *Angew. Chem.* **1995**, *107*, 1749–1751; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1581–1583.

[6] K. Breuer, J. H. Teles, D. Demuth, H. Hibst, A. Schäfer, S. Brode, H. Domgörgen, *Angew. Chem.* **1999**, *111*, 1497–1502; *Angew. Chem. Int. Ed.* **1999**, *38*, 1401–1405, and references therein.

[7] a) H. Hamaguchi, S. Kosaka, H. Ohno, T. Tanaka, *Angew. Chem.* **2005**, *117*, 1537–1541; *Angew. Chem. Int. Ed.* **2005**, *44*, 1513–1517; b) S. Ma, W. Gao, *Synlett* **2002**, 65–68; c) N. Waizumi, T. Itoh, T. Fukuyama, *Tetrahedron Lett.* **1998**, *39*, 6015–6018; d) Z. Xu, X. Lu, *J. Org. Chem.* **1998**, *63*, 5031–5041; e) S. Ma, Z. Shi, L. Li, *J. Org. Chem.* **1998**, *63*, 4522–4523; f) H. Urabe, T. Takeda, D. Hideura, F. Sato, *J. Am. Chem. Soc.* **1997**, *119*, 11295–11305; g) S. Yamanoi, T. Imai, T. Matsumoto, K. Suzuki, *Tetrahedron Lett.* **1997**, *38*, 3031–3034; h) G. Zhu, Z. Chen, Q. Jiang, D. Xiao, P. Cao, X. Zhang, *J. Am. Chem. Soc.* **1997**, *119*, 3836–3837; i) K. Banert, C. Toth, *Angew. Chem.* **1995**, *107*, 1776–1778; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1627–1629.

[8] a) Z. Zhang, C. Liu, R. E. Kinder, X. Han, H. Qian, R. A. Widenfoefer, *J. Am. Chem. Soc.* **2006**, *128*, 9066–9073; b) P. H. Lee, H. Kim, K. Lee, M. Kim, K. Noh, H. Kim, D. Seomoon, *Angew. Chem.* **2005**, *117*, 1874–1877; *Angew. Chem. Int. Ed.* **2005**, *44*, 1840–1843; c) V. Breuil-Desvergnes, P. Compain, J.-M. Vatele, J. Gore, *Tetrahedron Lett.* **1999**, *40*, 5009–5012; d) V. Breuil-Desvergnes, P. Compain, J.-M. Vatele, J. Gore, *Tetrahedron Lett.* **1999**, *40*, 8789–8792.

[9] a) S. Ma, Z. Zheng, X. Jiang, *Org. Lett.* **2007**, *9*, 529–532; b) B. Alcaide, P. Almendros, T. M. del Campo, *Angew. Chem.* **2006**, *118*, 4613–4616; *Angew. Chem. Int. Ed.* **2006**, *45*, 4501–4504; c) S. Ma, Z. Gu, *J. Am. Chem. Soc.* **2005**, *127*, 6182–6183; d) A. Al-Harrasi, H.-U. Reißig, *Angew. Chem.* **2005**, *117*, 6383–6387; Reißig, *Angew. Chem.* **2005**, *117*, 6383–6387; *Angew. Chem. Int. Ed.* **2005**, *44*, 6227–6231; e) M. Helms, W. Schade, R. Pulz, T. Watanabe, A. Al-Harrasi, L. Fisera, I. Hlobilová, G. Zahn, H.-U. Reißig, *Eur. J. Org. Chem.* **2005**, 1003–1019; f) S. W. Youn, Y. H. Kim, J.-W. Hwang, Y. Do, *Chem. Commun.* **2001**, 996–997.

[10] C.-F. Lee, L.-M. Yang, T.-Y. Hwu, A.-S. Feng, J.-C. Tseng, T.-Y. Luh, *J. Am. Chem. Soc.* **2000**, *122*, 4992–4993, and references therein.

[11] Cleavage of N–SO_2 bond by reduction: a) T. Hosaka, Y. Torisawa, M. Nakagawa, *Tetrahedron Lett.* **1997**, *38*, 3535–3538; b) D. J. Ramon, G. Guillena, D. Seebach, *Helv. Chim. Acta* **1996**, *79*, 875–894. By alkaline hydrolysis: c) Z. Xu, X. Lu, *Tetrahedron Lett.* **1997**, *38*, 3461–3464; d) S. B. Sobolov, J. Sun, B. A. Cooper, *Tetrahedron Lett.* **1998**, *39*, 5685–5688. By acid hydrolysis: e) W. J. Drury III, D. Ferraris, C. Cox, B. Young, T. Lectka, *J. Am. Chem. Soc.* **1998**, *120*, 11006–11007; f) G. Li, K. B. Sharpless, *Acta Chem. Scand.* **1996**, *50*, 649–651; g) J. M. Wood, P. S. Hinchliffe, S. Paul S. A. M. Davis, R. P. Austin, M. I. Page, *Chem. Commun.* **2002**, 772–773. Current devices for the N–SO_2 bond cleavage under mild conditions: h) G. M. Sammis, E. C. Flamme, H. Xie, D. M. Ho, E. J. Sorensen, *J. Am. Chem. Soc.* **2005**, *127*, 8612–86613; i) A. Yasuhara, T. Sakamoto, *Tetrahedron Lett.* **1998**, *39*, 595–596; j) A. Fürstner, H. Szillatt, B. Gabor, R. Mynott, *J. Am. Chem. Soc.* **1998**, *120*, 8305–8314; k) T. Fukuyama, M. Cheung, C.-K. Jow, Y. Hidai, T. Kan, *Tetrahedron Lett.* **1997**, *38*, 5831–5835; l) S. M. Weinreb, D. M. Demko, T. A. Lessen, *Tetrahedron Lett.* **1986**, *27*, 2099–2102.

[12] CCDC-181727 (**2a**), -181562 (**2e**), -181723 (**2i**), -181552 (**2l**), -181722 (**2o**), -181725 (**2q**), -188831 (**2t**), -139284 (**3a**), -139285 (**5**), -181556 (*E*-**6b**), -186252 (*Z*-**4c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[13] a) D. Graham, A, Enright, *Curr. Org. Synth.* **2006**, *3*, 9–17; b) M. Shoji, J. Yamaguchi, H. Kakeya, H. Osada, Y. Hayashi, *Angew. Chem.* **2002**, *114*, 3324–3326; *Angew. Chem. Int. Ed.* **2002**, *41*, 3192–3194; c) V. O. Rogatchov, H. Bernsmann, P. Schwab, R. Frohlich, B. Wibbeling, P. Metz, *Tetrahedron Lett.* **2002**, *43*, 4753–4756; d) A. Padwa, M. Dimitroff, B. Liu, *Org. Lett.* **2000**, *2*, 3233–3235; e) B. A. Keay, I. R. Hunt, *Adv. Cycloaddit.* **1999**, *6*, 173–210.

[14] a) F. Algi, R. Ozen, M. Balci, *Tetrahedron Lett.* **2002**, *43*, 3129–3131; b) M. Nendel, L. M. Tolbert, L. E. Herring, M. N. Islam, K. N. Houk, *J. Org. Chem.* **1999**, *64*, 976–983; c) I. Ikeda, A. Gondo, M. Shiro, K. Kanematsu, *Heterocycles* **1993**, *36*, 2669–2672; d) S. G. Cauwberghs, P. J. De Clercq, *Tetrahedron Lett.* **1988**, *29*, 6501–6504; e) P. Missiaen, P. J. De Clercq, *Bull. Soc. Chim. Belg.* **1987**, *96*, 105–113.

[15] Strained allenes: a) F. Algi, R. Ozen, M. Balci, *Tetrahedron Lett.* **2002**, *43*, 3129–3131; b) M. Nendel, L. M. Tolbert, L. E. Herring, M. N. Islam, K. N. Houk, *J. Org. Chem.* **1999**, *64*, 976–983.

[16] a) K. Okuma, Y. Tanaka, H. Ohta, *J. Am. Chem. Soc.* **1981**, *103*, 5976–5977. For five-membered sulfurane oxides, see: b) K. Ohkata, M. Ohnishi, K. Yoshinaga, K. Akiba, J. C. Rongione, J. C. Martin, *J. Am. Chem. Soc.* **1991**, *113*, 9270–9276; c) J. C. Rongione, J. C. Martin, *J. Am. Chem. Soc.* **1990**, *112*, 1637–1638.

[17] a) K. A. Jorgensen, *Asym. Synth*, **2007**, 191–195; b) K. A. Jorgensen, *Eur. J. Org. Chem.* **2004**, 2093–2102; c) L. F. Tietze, N. Rackelmann, *Pure Appl. Chem.* **2004**, *76*, 1967–1983; d) G. J. Bodwell, J. Li, *Angew. Chem.* **2002**, *114*, 3395–3396; *Angew. Chem. Int. Ed.* **2002**, *41*, 3261–3262; e) 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; f) E. R. Bilbao, M. Alvarado, C. F. Masaguer, E. Ravina, *Tetrahedron Lett.* **2002**, *43*, 3551–3554; g) 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; h) D. L. Boger, J. Hong, *J. Am. Chem. Soc.* **2001**, *123*, 8515–8519; i) R. Nomak, J. K. Snyder, *Tetrahedron Lett.* **2001**, *42*, 7929–7933; j) O. A. Attanasi, L. D. Crescentini, P. Fillippone, F. Fringuelli, F. Mantellini, O. Piermatti, M. Matteucco, F. Pizzo, *Helv. Chim. Acta* **2001**, *84*, 513–525; k) R. C. Boruah, S. Ahmed, U. Sharma, J. S. Sandhu, *J. Org. Chem.* **2000**, *65*, 922–925; l) L. Balazs, I. Kadas, L. Toke, *Tetrahedron Lett.* **2000**, *41*, 7583–7587; m) M.-F. Hsieh, P. D. Rao, C.-C. Liao, *Chem. Commun.* **1999**, 1441–1442; n) L. Lee, J. K. Snyder, *Adv. Cycloaddit.* **1999**, *6*, 119–171.

[18] a) S. M. Weinreb, R. K. Orr, *Synthesis* **2005**, 1205–1227; b) T. Kataoka, H. Kinoshita, *Eur. J. Org. Chem.* **2005**, 45–58; c) J. J. Li, *Name Reactions*, Springer, Berlin, **2002**.

[19] a) S. Caddick, D. Hamza, S. N. Wadman, *Tetrahedron Lett.* **1999**, *40*, 7285–7288; b) C. Wang, G. A. Russell, *J. Org. Chem.* **1999**, *64*, 2346–2352; c) D. C. Craig, G. L. Edwards, C. A. Muldoon, *Synlett* **1997**, 1441–1443; d) S. Caddick, C. L. Shering, S. N. Wadman, *Tetrahedron Lett.* **1997**, *38*, 6249–6250.

[20] a) C. Ollivier, P. Renaud, *J. Am. Chem. Soc.* **2001**, *123*, 4717–4727; b) Y.-L. Wu, C.-P. Chuang, P.-Y. Lin, *Tetrahedron* **2000**, *56*, 6209–6217; c) R. Nouguier, S. Gastaldi, D. Stien, M. Bertrand, P. Renaud, *Tetrahedron Lett.* **1999**, *40*, 3371–3374; d) B. Sire, S. Seguin, S. Z. Zard, *Angew. Chem.* **1998**, *110*, 3056–3058; *Angew. Chem. Int. Ed.* **1998**, *37*, 2864–2866; e) S. Kim, J.-Y. Yoon, *J. Am. Chem. Soc.* **1997**, *119*, 5982–5983; f) B. Quiclet-Sire, S. Z. Zard, *J. Am. Chem. Soc.* **1996**, *118*, 1209–1210.

[21] K. Narasaka, Y. Hayashi, H. Shimadzu, S. Niihata, *J. Am. Chem. Soc.* **1992**, *114*, 8869–8885.

[22] a) C. Rernandez-Rivas, M. Mendez, C. Nieto-Oberhuber, A. M. Eschavarren, *J. Org. Chem.* **2002**, *67*, 5197–5201; b) V. Nair, C. Rajesh, R. Dhanya, N. P. Rath, *Org. Lett.* **2002**, *4*, 953–955; c) S. Giese, L. Kastrup, D. Stiens, F. G. West, *Angew. Chem.* **2000**, *112*, 2046–2049; *Angew. Chem. Int. Ed.* **2000**, *39*, 1970–1973; d) H.-J. Knoelker, N. Foitzik, C. Gabler, R. Graf, *Synthesis* **1999**, 145–151, and references therein.

[23] H. Mayr, T. Bug, M. F. Gotta, N. Hering, B. Irrgang, B. Janker, B. Kempf, R. Loos, A. R. Ofial, G. Remennikov, H. Schimmel, *J. Am. Chem. Soc.* **2001**, *123*, 9500–9512.

[24] a) M. Sugawara, Y. Yoshida, *Bull. Chem. Soc. Jpn*, **2000**, *73*, 1253–1257; b) M. Sugawara, J. Yoshida, *Tetrahedron* **2000**, *56*, 4683–4689, and references therein. c) O. Andrey, C. Glanzmann, Y. Landais, L. Parra-Rapado, *Tetrahedron* **1997**, *53*, 2835–2854.

[25] D. M. Graham, R. L. Mieville, C. Sivertz, *Can. J. Chem.* **1964**, *42*, 2239–2249.

[26] Z. Zhou, R. G. Parr, *J. Am. Chem. Soc.* **1989**, *111*, 7371–7379.

[27] There has been reported one exception that shows that indole[17k] shows the same regioselectivity as that of furan and benzofuran toward inverse electron demand Diels–Alder reaction.

[28] P. Cazeau, F. Duboudin, F. Moulines, O. Babot, J. Dunogues, *Tetrahedron* **1987**, *43*, 2089–2100.

[29] A. Hosomi, M. Saito, H. Sakurai, *Tetrahedron Lett.* **1979**, *20*, 429–432.

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