A NEW SYNTHETIC ROUTE TO 1,3-OXAZOLIDINES *VIA* PALLADIUM-CATALYZED REGIOSELECTIVE [3 + 2] CYCLOADDITION OF VINYLIC OXIRANES WITH IMINES†

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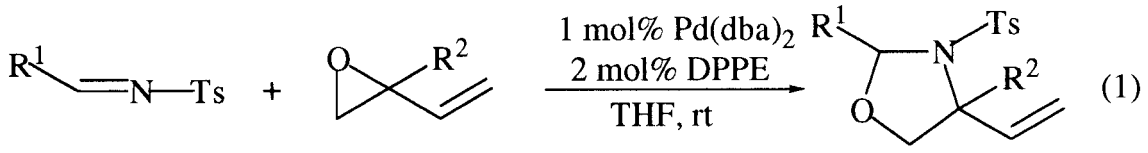
Abstract-*Palladium-catalyzed intermolecular reaction of imines (**1**) with vinylic oxiranes (**2**) gives the regioselective [3+2] cycloaddition products, 1,3-oxazolidine derivatives (**3**), in good to excellent yields. The present reaction permits the use of uncoventional starting materials (imines and vinylic oxiranes) for the synthesis of 1,3-oxazolidines (**3**).*

The palladium - catalyzed [3 + 2] cycloaddition reaction of vinylic oxiranes with heterocumulenes ($X^{\delta-}$ = $Y^{\delta+}$ = Z) has been considered to be a versatile tool for constructing certain heterocycles in organic synthesis.[1] For example, heterocumulenes such as isocyanate,[2] carbon dioxide,[3] and carbodiimide,[4] afford oxazolidin-2-one, cyclic carbonate, and oxazolidin-2-one derivatives, respectively, in good to high yields. Recently, we reported that the palladium-catalyzed regioselective [3 + 2] cycloaddition of vinylic oxiranes with certain activated olefins, $C^{\delta+}$ = $C^{\delta-}(EWG)_2$, in which EWG should be an electron-withdrawing group such as CN, SO_2R or Meldrum's acid, gave polysubstituted tetrahydrofuran derivatives in good yields.[5] It occurred to us that 1,3-oxazolidines would be obtained if imines are able to be used as a counterpart, instead of the activated C = C bond. The majority of approaches to prepare 1,3-oxazolidines reported up to date is the condensation of 1,2-amino alcohols with carbonyl compounds (or their corresponding acetals).[6-11] In those instances, the N and O atoms of the resulting 1,3-oxazolidine framework come from the 1,2-amino alcohol, and the carbon between the N and O atoms of the heterocycles comes from the carbonyl carbon of the counterpart. It was envisaged that the imine incorporated [3 + 2] cycloaddition would produce 1,3-oxazolidines *via* entirely different synthetic strategy in comparison with the well-known method. Here we describes that the palladium - catalyzed intermolecular reaction of imines (**1**) with vinylic oxiranes (**2**) gives the regioselective [3 + 2] cycloaddition products, 1,3-oxazolidine derivatives (**3**), in good to excellent yields (Eq 1).[12]

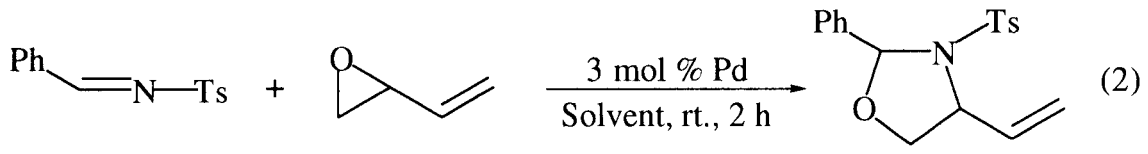
Results and Discussion



1 **2** **3**

Investigation on the Reaction Conditions

Initial studies focused on the development of optimal reaction conditions for this transformation (Eq 2 and Table 1). At the outset, the reaction of imine (**1a**) with vinyl oxirane (**2a**) in THF was investigated by using 3 mol % $Pd(PPh_3)_4$ at room temperature. After 2 h, the starting imine (**1a**) was consumed completely. As expected, ^1H NMR analysis of the reaction mixture revealed that the corresponding 1,3-oxazolidine (**3a**) was produced in essentially quantitative yield (entry 1). Polar and nonpolar solvents such as DMF, CH_3CN, toluene and CH_2Cl_2 gave the cycloaddition product (**3a**) in excellent yields, while the use of 1,4-dioxane as a solvent did not afford the cyclized product at all (entries 2 - 6). Although $Pd(PPh_3)_4$ or $Pd(dba)_2$-$4PPh_3$ was an effective catalyst, $Pd(dba)_2$-2dppe system was the most effective catalyst for the present transformation (entries 1, 8 and 9). Interestingly, even the use of 1 mol % of the catalyst afforded the desired product (**3a**) in 97 % yield (entry 10).



1a **2a** **3a**

Cycloaddition of Vinylic Oxiranes with Imines

Various kinds of imines (**1**) were treated with vinylic oxiranes (**2**) in the presence of 1 mol % $Pd(dba)_2$ and 2 mol % dppe in THF (0.1 M) at room temperature. The results are summarized in Table 2. The imines (**1a-b**) possessing a phenyl or a furyl substituent reacted effectively with vinyl oxirane (**2a**) to afford the 1,3-oxazolidines (**3a-b**), respectively, in excellent yields (entries 1 - 2). In addition, the aromatic imines (**1c-d**) containing electron-donating substituents at the para position were converted smoothly to the five-membered heterocycles (**3c-d**), respectively, in essentially quantitative yields (entries 3 - 4). Naphthyl imine (**1e**) gave **3e** in high yield (entry 5). Even the imines (**1f-g**), having sterically crowding substituents as the R^1 group, afforded **3f-g** in 82 % and 75 % yields, respectively (entries 6 - 7). Meanwhile, in order to understand the effect of a substituent of vinylic oxiranes, the reactions of a substituted vinylic oxirane (**2b**) with imines were examined. Although the reaction of **2b** was sluggish in comparison with that of **2a** (entries 8 - 9), the regioselective [3 + 2] cycloaddition products (**3h-i**) were obtained from **1a** and **1b** in 78 % and74 % yields, respectively. Diminished reaction rates and chemical yields in these cases are presumably attributed to the steric congestion of a π- allylpalladium intermediate (**5**) (*vide post*). In all the

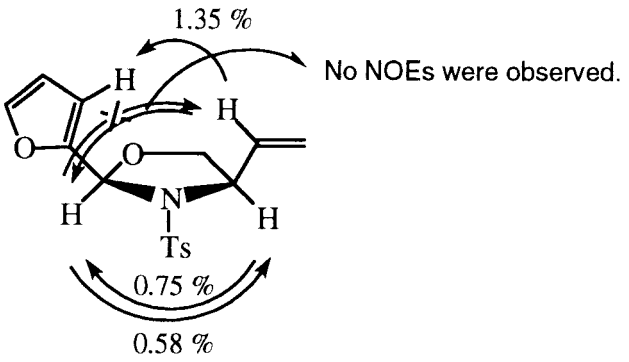
Table 1. Palladium - catalyzed regioselective [3 + 2] cycloaddition of 1a with 2a.[a]

entry	catalyst	solvent	yield of **3a** (%)[b]
1	$Pd(PPh_3)_4$	THF	> 99 (97)[c]
2	$Pd(PPh_3)_4$	DMF	> 99
3	$Pd(PPh_3)_4$	CH_3CN	89
4	$Pd(PPh_3)_4$	toluene	92
5	$Pd(PPh_3)_4$	CH_2Cl_2	> 99
6	$Pd(PPh_3)_4$	1,4-dioxane	N. R
7	$Pd(dba)_2$	THF	N. R
8	$Pd(dba)_2$-2dppe	THF	> 99
9	$Pd(dba)_2$-$4PPh_3$	THF	95
10[d]	$Pd(dba)_2$-2dppe	THF	> 99 (97)[c]

[a] All reactions (see the general procedure in the experimental section) were conducted at room temperature. [b] ^1H NMR yield using *p*-xylene as an internal standard. [c] Isolated yield based on **1a**. [d] The reactions were carried out in the presence of 1 mol % of catalyst.

above reactions, seven-membered heterocycles were not obtained.

Determination of Stereochemistry

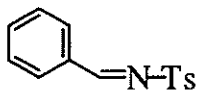
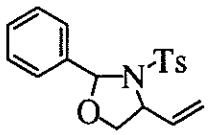
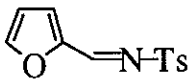
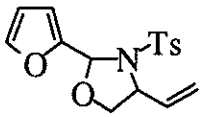
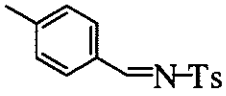
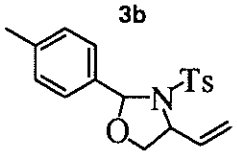
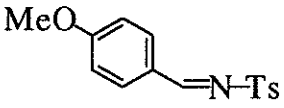
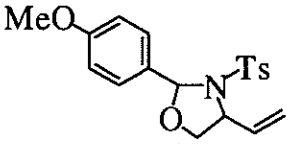
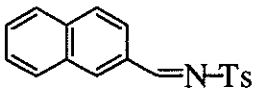
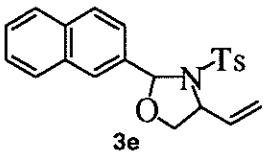
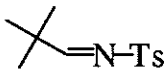
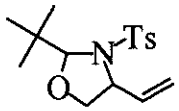
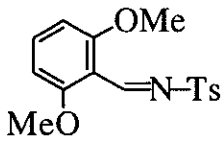
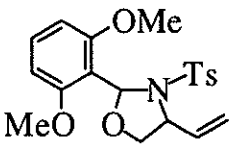
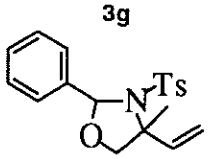
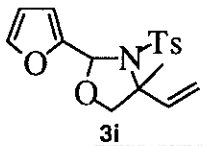


Major diastereoisomer of **3b** (*cis*)

The stereochemistries of the products (**3a**, **3b** and **3d**) were determined by NOE studies using 500 MHz ^1H NMR. For example, the NOE correlations of **3b** are shown below.

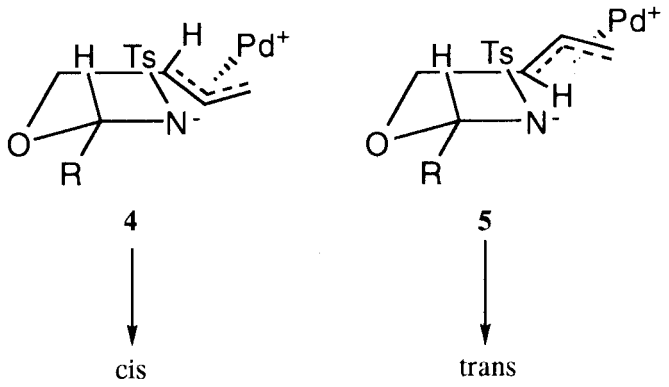
As depicted in **4** and **5**, the *cis* preference of the [3+2] cycloaddition reactions can be explained by the 1,2 - repulsion between R and tosyl, and/or tosyl and the allylic moiety of π-allylpalladium. Since a sterically bulky R group takes a pseudo-axial position of the cyclic transition states (see mechanistic part mentioned below) (**4** and **5**), Ts group is forced to take an up (or pseudo-axial) position. In the case of the transi-

Table 4.2. Palladium - catalyzed regioselective [3 + 2] cycloaddition of 1 with 2.[a]

Entry	Imine 1	Vinylic Oxirane 2	Time	Product 3	Yield[b] (%)
1	 1a	 2a	2 h	 3a	97 (73 : 27)[c,d]
2	 1b	2a	2 h	 3b	96 (88 : 12)[c,d]
3	 1c	2a	4 h	 3c	>99 (70 : 30)[c]
4	 1d	2a	3 h	 3d	>99 (60 : 40)[c,d]
5	 1e	2a	3 h	 3e	93 (62 : 38)[c]
6	 1f	2a	3 h	 3f	82 (55 : 45)[c]
7	 1g	2a	4 h	 3g	75 (90 : 10)[c]
8[e]	1a	 2b	1 d	 3h	78 (57 : 43)[c]
9[e]	1b	2b	1 d	 3i	74 (50 : 50)[c]

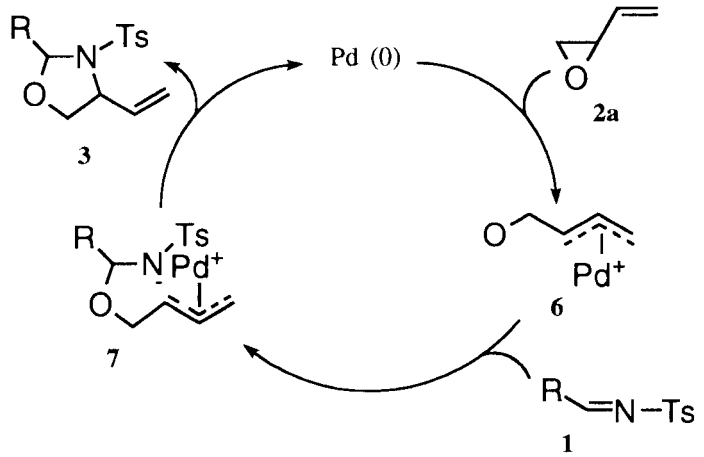
[a] All reactions were conducted in THF at room temperature. [b] Isolated yields based on 1. [c] Diastereomeric ratios were indicated in parentheses. [d] The configuration of the major isomer was *cis* (by means of 500 MHz NOE studies). In the other cases, the stereochemistries of the diastereoisomers were not determined. [e] 3 mol % of catalyst were used.

tion state (**5**) affording the *trans*-isomer, the 1,2-repulsion between tosyl and the allylic moiety of π-allylpalladium presumably destabilizes this transition state. However, in the case of the transition state (**4**) affording the *cis* - isomer, there is no 1,2 - repulsion between R and the allylic moiety of π-allylpalladium.



Mechanism

The following mechanistic rationale may account for the present palladium - catalyzed regioselective [3 + 2] cycloaddition. Initially, Pd(0) catalyst would add oxidatively to vinyloxirane (**2a**) to give a π-allylpalladium intermediate (**6**). The nucleophilic addition of the oxygen nucleophile of **6** to imines (**1**) would produce **7**. Then the resulting intermediate (**7**) would undergo the intramolecular nucleophilic attack on the inner π-allylic carbon atom to give the cyclized products (**3**), and Pd(0) species would be regenerated. A key step of the present [3 + 2] cycloaddition is the nucleophilic addition of the oxygen anion of **6**, which is generated by the reaction of vinylic oxiranes (**2**) with palladium, to imines (**1**). It is noteworthy that the regioselective [3 + 2] cycloaddition reported here is accomplished by using activated tosyl imines, whereas other imines having ordinary *N*-substitutons such as methyl, phenyl and phosphinoyl did not give the cycloaddition products at all.



Phosphine omitted for clarity

Summary

A novel and effective route to 1,3-oxazolidine derivatives (**3**) by the successive addition reactions of the O and N atoms of vinyloxiranes with imines was developed. The present palladium-catalyzed intermolecular regioselective [3 + 2] cycloaddition of imines (**1**) with vinylic oxiranes (**2**) is a new version of 1,3-dipolar cycloadditions affording the five-membered heterocycles and permits the use of unconventional

starting materials to produce 1,3-oxazolidines (**3**) with a high degree of efficiency and regioselectivity.

EXPERIMENTAL

All solvents were purified and dried before use according to the standard procedure. All reactions were conducted under an argon atmosphere in oven - dried glassware. 1,3-Butadiene monoxide (**2a**) and 2-methyl-2-vinyloxirane (**2b**) were purchased from Aldrich Chemical Co. The starting tosyl imines (**1**) were synthesized according to the reported procedures.[13] $Pd(PPh_3)_4$ was prepared according to the known method.[14]

Synthesis of tosyl imines

Verious tosyl imines (**1**) were synthesized by the condensation of *p*-toluenesulfonamide with the corresponding aldehydes. The synthesis of **1a** from the reaction of *p*-toluenesulfonamide with benzaldehyde is representative. A CH_2Cl_2 solution of $TiCl_4$ (1M, 6.3 mL, 6.3 mmol) in dry CH_2Cl_2 (10 mL) was added dropwise under nitrogen atmosphere to a stirred ice - cooled solution of benzaldehyde (1.218 mL, 12 mmol), *p*-toluenesulfonamide (1.95 g, 11.4 mmol) and anhydrous triethylamine (4.820 mL, 35 mmol) in dry CH_2Cl_2 (50 mL). After the addition was complete, the mixture was stirred for 30 min at 0^oC. The titanium dioxide was then removed by suction filtration through celite and washed with CH_2Cl_2 (20 mL). Rotary evaporation of the filtrate gave a solid mixture of the corresponding imine and triethylamine hydrochloride. Dry ether (75 mL) was added and the mixture was refluxed for 10 min. Insoluble triethylamine hydrochloride was removed by suction filtration and washed with dry ether. Concentration of the ether extracts, followed by silica gel column chromatography using hexane-ether (10:1) as an eluent, afforded phenyl *N*-tosyl imine (**1a**) (2.300 g, 78 %).

Phenyl *N*-tosyl imine (**1a**) White solid; ^1H NMR ($CDCl_3$) δ 9.03 (s, 1H), 7.87 (m, 4H), 7.64 - 7.30 (m, 5H), 2.44 (s, 3H) ; ^{13}C NMR ($CDCl_3$) δ 170. 122, 144.592, 135.026, 132.288, 131.259, 129.771, 129.096, 128.044, 21.614; MS (M^+) 259.

2-Furyl *N*-tosyl imine (**1b**) Yellow solid; ^1H NMR ($CDCl_3$) δ 9.08 (s, 1H), 7.86 (m, 2H), 7.74 (m, 1H), 7.34 (m, 3H), 6.64 (m, 1H), 2.42 (s, 3H) ; ^{13}C NMR ($CDCl_3$) δ 155.605, 149.716, 148.968, 144.502, 135.117, 129.713, 127.937, 126.325, 113.675, 21.540; MS (M^+) 249.

4-Methylphenyl *N*-tosyl imine (**1c**) White solid; ^1H NMR ($CDCl_3$) δ 8.96 (s, 1H), 7.82 (m, 4H), 7.31 (m, 4H), 2.43 (s, 6H) ; ^{13}C NMR ($CDCl_3$) δ 169.933, 146.360, 144.403, 131.391, 129.894, 129.828, 129.730, 127.986, 21.959, 21.605; MS (M^+) 273.

4-Methoxyphenyl *N*-tosyl imine (**1d**) White solid; ^1H NMR ($CDCl_3$) δ 8.94 (s, 1H), 7.87 (m,

4H), 7.31 (d, 2H, J = 8.1 Hz), 6.97 (d, 2H, J = 8.8 Hz), 3.88 (s, 3H), 2.43 (s, 3H) ; ^{13}C NMR ($CDCl_3$) δ 169.160, 165.236, 144.230, 135.750, 133.694, 129.689, 127.871, 125.198, 114.645, 55.648, 21.597; MS (M^+) 289.

2-Naphthyl *N*-tosyl imine (1e) White solid; ^{1}H NMR ($CDCl_3$) δ 9.17 (s, 1H), 8.33 (s, 1H), 8.05 - 7.87 (m, 6H), 7.66 - 7.55 (m, 2H), 7.28 (d, 2H, J = 25.9 Hz), 2.44 (s, 6H) ; ^{13}C NMR ($CDCl_3$) δ 169.974, 144.493, 136.458, 136.022, 135.249, 132.567, 130.050, 129.763, 129.434, 129.409, 129.105, 128.060, 127.994, 127.188, 124.046, 21.581; MS (M^+) 309.

***tert*-Butyl *N*-tosyl imine (1f)** White solid; ^{1}H NMR ($CDCl_3$) δ 8.44 (s, 1H), 7.80 (d, 2H, J = 8.3 Hz), 7.34 (d, 2H, J = 7.9 Hz), 2.44 (s, 3H), 1.14 (s, 9H) ; ^{13}C NMR ($CDCl_3$) δ 183.816, 144.518, 134.846, 129.738, 127.986, 37.833, 25.833, 21.622; MS (M^+) 240.

2,6-Dimethoxyphenyl *N*-tosyl imine (1g) White solid; ^{1}H NMR ($CDCl_3$) δ 9.56 (s, 1H), 7.89 (d, 2H, J = 8.5 Hz), 7.46 (t, 1H, J = 8.4 Hz), 7.31 (d, 2H, J = 8.1 Hz), 6.54 (d, 2H, J = 8.6 Hz), 3.82 (s, 6H), 2.42 (s, 6H) ; ^{13}C NMR ($CDCl_3$) δ 165.483, 162.522, 143.696, 136.737, 136.359, 129.508, 127.912, 110.278, 103.731, 56.175, 21.581; MS (M^+) 319.

General procedure

Palladium - catalyzed regioselective [3 + 2] cycloaddition of imine **(1a)** with vinyloxirane **(2a)** is representative. To a solution of $Pd(dba)_2$ (0.003 g, 1 mol %), DPPE (0.004 g, 2 mol %) and **1a** (0.129 g, 0.5 mmol) in THF (5.0 mL) was added vinyloxirane **(2a)** (0.046 mL, 0.6 mmol) under argon atmosphere. The reaction mixture was stirred at rt and the progress of reaction was monitored by TLC. When the starting substrate **(1a)** was consumed completely, the reaction mixture was filtered through a short celite column using ether as an eluent. After the usual workup, analytically pure product **(3a)** was isolated in 97 % yield (0.159 g) by column chromatography on silica gel using *n*-hexane - ethyl acetate (15 : 1) as eluent.

2-Phenyl-*N*-tosyl-4-vinyloxazolidine (3a)

Colorless oil: ^{1}H NMR δ 7.64 (d, 2H, J = 8.2 Hz, minor diastereoisomer), 7.46 (m, 2H, minor diastereoisomer), 7.29 - 7.16 (m, 7H, major diastereoisomer and m, 5H, minor diastereoisomer), 7.03 (d, 2H, J = 8.0 Hz, major diastereoisomer), 6.16 (s, 1H, minor diastereoisomer), 6.11 (s, 1H, major diastereoisomer), 5.84 - 5.73 (m, 1H, major diastereoisomer), 5.70 - 5.58 (m, 1H, minor diastereoisomer), 5.22 (m, 2H, major diastereoisomer), 5.09 (m, 2H, minor diastereoisomer), 4.33 (m, 1H, major diastereoisomer), 4.24 (m, 1H, minor diastereoisomer), 4.13 (dd, 1H, J = 8.6, 6.0 Hz, major diastereoisomer), 3.81 (dd, 1H, J = 8.8, 7.1 Hz, minor diastereoisomer), 3.68 (dd, 1H, J = 8.5, 4.7 Hz,

diastereoisomer), 2.29 (s, 3H, major diastereoisomer); ^{13}C NMR δ 144.099, 143.112, 138.053, 137.675, 137.543, 135.627, 134.599, 129.771, 129.055, 128.989, 128.693, 128.274, 128.068, 127.863, 127.616, 127.460, 126.933, 118.717, 118.272, 92.010, 91.920, 71.218, 70.379, 62.080, 61.644, 21.531, 21.408; IR (neat) 2875, 1597, 1352, 1165, 1107, 665 cm^{-1}; HRMS calcd $C_{18}H_{19}NO_3S$ 329.1086, found 329.1121; Anal. Calcd for $C_{18}H_{19}NO_3S$: C, 65.630; H, 5.814; N, 4.251. Found: C, 65.334; H, 5.967; N, 4.271.

2-(2-Furyl)-*N*-tosyl-4-vinyloxazolidine (3b)

Colorless oil: ^{1}H NMR δ 7.69 (d, 2H, *J* = 8.2 Hz, major diastereoisomer), 7.39 (m, 1H, major diastereoisomer), 7.36 (d, 2H, *J* = 8.4 Hz, minor diastereoisomer), 7.31 (m, 2H, major diastereoisomer), 7.14 (m, 2H, minor diastereoisomer), 6.49 (m, 1H, major diastereoisomer), 6.47 (m, 1H, minor diastereoisomer), 6.34 (dd, 1H, *J* = 3.3, 1.9 Hz, major diastereoisomer), 6.29 (dd, 1H, *J* = 3.3, 1.8 Hz, minor diastereoisomer), 5.94 (m, 1H, minor diastereoisomer), 5.92 - 5.80 (m, 1H, major diastereoisomer), 5.36 - 5.20 (m, 2H, major diastereoisomer), 5.25 - 5.22 (m, 2H, minor diastereoisomer), 4.35 (m, 1H, minor diastereoisomer), 4.23 (dd, 1H, *J* = 14.5, 7.1 Hz, major diastereoisomer), 3.98 (dd, 1H, *J* = 8.8, 7.0 Hz, major diastereoisomer), 3.85 (m, 1H, minor diastereoisomer), 3.75 (dd, 1H, *J* = 8.8, 7.1 Hz, major diastereoisomer), 2.43 (s, 3H, major diastereoisomer), 2.39 (s, 3H, minor diastereoisomer); ^{13}C NMR (major diastereoisomer) δ 150.826, 144.156, 143.391, 135.068, 129.779, 127.805, 118.782, 110.270, 110.146, 86.080, 70.716, 61.578, 21.564; IR (neat) 2926, for $C_{16}H_{17}NO_4S$: 1599, 1356, 1167, 1107, 665 cm^{-1}; HRMS calcd $C_{16}H_{17}NO_4S$ 319.0877, found 319.0880; Anal. Calcd for $C_{16}H_{17}NO_4S$: C, 60.171; H, 5.365; N, 4.386. Found: C, 60.318; H, 5.465; N, 4.393.

2-(4-Methylphenyl)-N-tosyl-4-vinyloxazolidine (3c)

White solid: ^{1}H NMR δ 7.72 (d, 2H, *J* = 8.2 Hz, major diastereoisomer), 7.43 - 7.06 (m, 6H, major diastereoisomer and m, 8H, minor diastereoisomer), 6.19 (s, 1H, major diastereoisomer), 6.14 (s, 1H, minor diastereoisomer), 5.85 (m, 1H, minor diastereoisomer), 5.72 (m, 1H, major diastereoisomer), 5.30 (m, 2H, major diastereoisomer), 5.19 (m, 2H, minor diastereoisomer), 4.40 (m, 1H, minor diastereoisomer), 4.27 (dd, 2H, *J* = 14.4, 7.1 Hz, major diastereoisomer), 4.20 (dd, 1H, *J* = 8.5, 5.9 Hz, minor diastereoisomer), 3.88 (dd, 1H, *J* = 8.8, 7.2 Hz, major diastereoisomer), 3.75 (dd, 1H, *J* = 8.6, 4.6 Hz, minor diastereoisomer), 2.43 (s, 3H, major diastereoisomer), 2.38 (s, 3H, minor diastereoisomer), 2.35 (s, 3H, major diastereoisomer), 2.34 (s, 3H, minor diastereoisomer); ^{13}C NMR (major diastereoisomer) δ 144.049, 138.547, 135.750, 135.109, 129.754, 128.981, 127.896, 127.550, 126.900, 118.231, 92.076 70.338, 61.661, 21.548, 21.153; IR (KBr) 2885, 1597, 1350, 1163, 1109, 669 cm^{-1}; HRMS calcd $C_{19}H_{21}NO_3S$ 343.1240, found 343.1228; Anal. Calcd for $C_{19}H_{21}NO_3S$: C, 66.447; H, 6.163; N, 4.078. Found: C, 66.540; H, 6.281; N, 4.053.

2-(4-Methoxyphenyl)-*N*-tosyl-4-vinyloxazolidine (3d)

White solid: ^{1}H NMR δ 7.69 (d, 2H, *J* = 8.2 Hz, major diastereoisomer), 7.44 (d, 2H, *J* = 8.8 Hz, major diastereoisomer), 7.34 (d, 2H, *J* = 8.2 Hz, minor diastereoisomer), 7.29 (d, 2H, *J* = 8.3 Hz, major diastereoisomer), 7.24 (d, 2H, *J* = 8.8 Hz, minor diastereoisomer), 7.11 (d, 2H, *J* = 8.2 Hz, minor

diastereoisomer), 6.16 (s, 1H, major diastereoisomer), 6.11 (s, 1H, minor diastereoisomer), 5.93 - 5.81 (m, 1H, minor diastereoisomer), 5.77 - 5.69 (m, 1H, major diastereoisomer), 5.30 (m, 2H, major diastereoisomer), 5.18 (m, 2H, minor diastereoisomer), 4.40 (m, 1H, minor diastereoisomer), 4.29 (dd, 1H, J = 13.0, 7.0 Hz, major diastereoisomer), 4.20 (dd, 1H, J = 8.6, 6.1 Hz, minor diastereoisomer), 3.86 (dd, 1H, J = 8.8, 7.2 Hz, major diastereoisomer), 3.80 (s, 3H, major diastereoisomer), 3.80 (s, 3H, minor diastereoisomer), 3.75 (dd, 1H, J = 8.6, 4.8 Hz, minor diastereoisomer), 3.65 (dd, 1H, J = 8.8, 5.9 Hz, major diastereoisomer), 2.43 (s, 3H, major diastereoisomer), 2.37 (s, 3H, minor diastereoisomer); ^{13}C NMR δ 160.219, 159.964, 143.992, 143.013, 137.691, 135.816, 134.903, 134.813, 130.100, 129.721, 129.039, 129.006, 128.356, 127.846, 127.451, 118.519, 118.174, 113.642, 113.403, 91.986, 91.673, 71.111, 70.346, 62.113, 61.578, 55.253, 21.523, 21.416; IR (KBr) 2870, 1614, 1516, 1346, 1165, 667 cm^{-1}; HRMS calcd $C_{19}H_{21}NO_4S$ 359.1190, found 359.1194; Anal. Calcd for $C_{19}H_4NO_4S$: C, 63.489; H, 5.889; N, 3.897; S, 8.921. Found: C, 63.474; H, 5.773; N, 3.883; S, 8.530.

2-(2-Naphthyl)-*N*-tosyl-4-vinyloxazolidine (3e)

White solid: ^{1}H NMR δ 8.30 - 7.24 (m, 11H, major diastereoisomer and m, 9H, minor diastereoisomer), 6.93 (d, 2H, J = 8.0 Hz, minor diastereoisomer), 6.40 (s, 1H, major diastereoisomer), 6.32 (s, 1H, minor diastereoisomer), 6.00 - 5.88 (m, 1H, minor diastereoisomer), 5.80 - 5.68 (m, 1H, major diastereoisomer), 5.33 (m, 2H, major diastereoisomer), 5.18 (m, 2H, minor diastereoisomer), 4.51 (m, 1H, minor diastereoisomer), 4.34 (dd, 1H, J = 13.6, 7.0 Hz, major diastereoisomer), 4.27 (dd, 1H, J = 8.5, 5.9 Hz, minor diastereoisomer), 3.94 (dd, 1H, J = 9.0, 7.1 Hz, major diastereoisomer), 3.81 (dd, 1H, J = 8.6, 4.8 Hz, major diastereoisomer), 3.66 (dd, 1H, J = 8.8, 6.3 Hz, major diastereoisomer), 2.40 (s, 3H, major diastereoisomer), 2.26 (s, 3H, minor diastereoisomer); ^{13}C NMR δ 144.197, 143.128, 135.660, 135.397, 134.706, 133.661, 133.464, 132.863, 132.641, 129.820, 128.957, 128.381, 128.348, 128.315, 127.978, 127.632, 127.534, 127.402, 126.563, 126.522, 126.473, 126.226, 126.168, 124.778, 124.326, 118.749, 118.462, 92.191, 92.019, 77.469, 77.041, 76.622, 71.407, 70.478, 62.335, 61.759, 21.564, 21.351; IR (KBr) 3059, 1342, 1165, 669 cm^{-1}; HRMS calcd $C_{22}H_{21}NO_3S$ 379.1241, found 379.1241; Anal. Calcd for $C_{22}H_{21}NO_3S$: C, 69.633; H, 5.578; N, 3.691; S, 8.450. Found; C, 69.505; H, 5.619; N, 3.808; S, 8.440.

2-*tert*-Butyl-*N*-tosyl-4-vinyloxazolidine (3f)

Colorless oil: ^{1}H NMR δ 7.76 (d, 4H, J = 8.0 Hz, major diastereoisomer), 7.34 (d, 2H, J = 7.9 Hz, minor diastereoisomer), 7.26 (d, 2H, J = 7.9 Hz, minor diastereoisomer), 6.10 - 5.98 (m, 1H, minor diastereoisomer), 5.95 - 5.84 (m, 1H, major diastereoisomer), 5.43 (s, 1H, minor diastereoisomer), 5.20 (m, 2H, major diastereoisomer), 5.09 (m, 2H, minor diastereoisomer), 4.99 (s, 1H, major diastereoisomer), 4.26 (m, 1H, major diastereoisomer), 4.12 (m, 1H, minor diastereoisomer), 3.90 (dd, 1H, J = 8.0, 6.0 Hz, minor diastereoisomer), 3.79 (dd, 1H, J = 8.6, 4.8 Hz, major diastereoisomer), 3.57 (dd, 1H, J = 8.6, 7.5 Hz, major diastereoisomer), 3.29 (dd, 1H, J = 10.4, 8.0 Hz, minor diastereoisomer), 2.44 (s, 3H, major diastereoisomer), 2.42 (s, 3H, minor diastereoisomer), 1.03 (s, 9H, minor diastereoisomer), 1.01 (s, 9H, major diastereoisomer); ^{13}C NMR δ 144.115, 143.735, 138.933, 136.227, 134.591, 129.795, 129.705, 129.417, 128.249, 127.970, 120.978, 117.771, 99.709, 98.878, 70.420, 70.132, 63.314, 61.998,

37.759, 36.920, 26.409, 25.784, 21.540, 21.515; IR (neat) 2959, 1354, 1167, 667 cm^{-1}; HRMS calcd $C_{17}H_{25}NO_3S$ (M^+ - Me) 294.1162, found 294.1161; Anal. Calcd for $C_{17}H_{25}NO_3S$: C, 62.107; H, 7.492; N, 4.527; S, 10.363. Found: C, 62.199; H, 7.100; N, 4.551; S, 10.120.

2-(2,4-Dimethoxyphenyl)-*N*-tosyl-4-vinyloxazolidine (3g)

White solid: ^1H NMR δ 7.72 (d, 1H, J = 8.2 Hz, minor diastereoisomer), 7.56 (d, 2H, J = 8.3 Hz, major diastereoisomer), 7.44 (t, 1H, J = 8.4 Hz, minor diastereoisomer), 7.27 (m, 2H, minor diastereoisomer), 7.25 - 7.18 (m, 3H, major diastereoisomer), 7.06 (d, 1H, J = 8.1 Hz, minor diastereoisomer), 6.85 (s, 1H, minor diastereoisomer), 6.57 (d, 1H, J = 8.4 Hz, minor diastereoisomer), 6.50 (d, 2H, J = 1.6 Hz, major diastereoisomer), 6.47 (s, 1H, major diastereoisomer), 6.37 (d, 1H, J = 8.4 Hz, minor diastereoisomer), 6.21 - 6.10 (m, 1H, major diastereoisomer), 6.08 - 5.98 (m, 1H, minor diastereoisomer), 5.38 - 5.21 (m, 2H, major diastereoisomer), 5.10 (m, 2H, minor diastereoisomer), 4.39 - 4.30 (m, 1H, major diastereoisomer and m, 1H, minor diastereoisomer), 4.04 (dd, 1H, J = 8.6, 3.9 Hz, major diastereoisomer), 3.88 (m, 1H, major diastereoisomer and m, 2H, minor diastereoisomer), 3.76 (s, 6H, major diastereoisomer), 3.56 (s, 6H, minor diastereoisomer), 2.39 (s, 3H, major diastereoisomer), 2.34 (s, 3H, minor diastereoisomer); ^{13}C NMR δ 189.442, 162.136, 159.257, 159.076, 143.375, 143.112, 137.395, 136.162, 135.931, 135.125, 134.385, 130.832, 130.577, 129.549, 129.047, 128.628, 127.797, 127.139, 117.804, 117.277, 116.858, 114.193, 112.836, 112.688, 104.216, 103.936, 103.780, 85.546, 84.764, 73.217, 72.024, 64.589, 62.302, 61.932, 57.523, 55.994, 55.582, 55.451, 21.416, 21.326; IR (KBr) 2953, 1595, 1477, 1356, 1256, 1113, 667 cm^{-1}; HRMS calcd $C_{20}H_{23}NO_5S$ 389.1295, found 389.1291.

2-Phenyl-*N*-tosyl-4-methyl-4-vinyloxazolidine (3h)

White solid: ^1H NMR δ 7.51 - 7.06 (m, 9H, major diastereoisomer and m, 9H, minor diastereoisomer), 6.23 (s, 1H, major diastereoisomer), 6.20 (s, 1H, minor diastereoisomer), 6.13 (dd, 1H, J = 18.6, 10.8 Hz, minor diastereoisomer), 5.95 (dd, 1H, J = 17.4, 10.8 Hz, major diastereoisomer), 5.33 (dd, 2H, J = 17.3, 4.2 Hz, major diastereoisomer), 5.20 (m, 2H, minor diastereoisomer), 3.94 (d, 1H, J = 8.6, 6.0 Hz, minor diastereoisomer), 3.78 (dd, 2H, J = 14.0, 8.6 Hz, major diastereoisomer), 3.71 (d, 1H, J = 8.6 Hz, minor diastereoisomer), 2.37 (s, 3H, major diastereoisomer), 2.34 (s, 3H, minor diastereoisomer), 1.72 (s, 3H, minor diastereoisomer), 1.71 (s, 3H, major diastereoisomer); ^{13}C NMR δ 143.120, 143.013, 139.912, 139.246, 138.481, 138.160, 138.061, 137.765, 128.998, 128.899, 128.833, 128.142, 128.076, 127.970, 127.830, 127.599, 127.509, 115.895, 115.254, 92.693, 92.586, 77.428, 77.329, 66.957, 66.497, 22.115, 21.877, 21.441, 21.408; IR (KBr) 2870, 1348, 1159, 671 cm^{-1}; HRMS calcd $C_{19}H_{21}NO_3S$ (M^+ - H) 342.1162. Found: 342.1159; Anal. Calcd for $C_{19}H_{21}NO_3S$: C, 66.447; H, 6.163; N, 4.078; S, 9.337. found C, 66.456; H, 6.163; N, 3.985;S, 9.120.

2-(2-Furyl)-*N*-tosyl-4-methyl-4-vinyloxazolidine (3i)

Colorless oil: ^1H NMR δ 7.48 (d, 2H, J = 8.2 Hz), 7.36 (d, 2H, J = 8.4 Hz), 7.24 (m, 2H), 7.13 (dd, 4H, J = 15.6, 8.0 Hz), 6.43 (d, 1H, J = 3.3 Hz), 6.38 (m, 1H), 6.28 (m, 2H), 6.25 (s, 1H), 6.21 (s, 1H), 6.05 - 5.91 (m, 2H), 5.41 - 5.17 (m, 4H), 4.08 (d, 1H), 3.99 (d, 1H, J = 8.6 Hz), 3.87 (d, 1H, J = 8.6 Hz), 3.75 (d, 1H, J = 8.4 Hz), 2.38 (s, 3H), 2.36 (s, 3H), 1.75 (s, 3H), 1.69 (s, 3H); ^{13}C NMR δ 151.238,

151.221, 143.087, 143.029, 142.922, 142.899, 139.715, 138.785, 138.325, 137.946, 129.063, 128.948, 127.632, 127.361, 116.998, 114.900, 110.730, 110.714, 110.187, 110.122, 85.472, 85.266, 78.184, 78.077, 66.398, 66.168, 22.124, 21.433, 21.416, 21.030; HRMS calcd $C_{17}H_{19}NO_4S$ 333.1033, found 333.1028; Anal. Calcd for $C_{19}H_{19}NO_4S$: C, 61.242; H, 5.744; N, 4.201. Found: C, 61.084; H, 5.815; N, 4.231.

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† Dedicated to Professor Teruaki Mukaiyama on the occasion of his 73rd birthday in recognition of his outstanding contributions to the areas of organic synthesis.

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