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Synthesis of Allylic Alcohols from Oxazolinyloxiranes

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Received July 24, 2002

Lithium diisopropylamide (LDA) (or *s*-BuLi/TMEDA) in diethyl ether promotes smooth ring opening of oxazolinyl alkyl oxiranes to give oxazolinyl allylic alcohols, which are masked Baylis−Hillman adducts, in good to excellent yields. An E_2−E_1cb-like syn-β-elimination is proposed to explain the easy base-promoted isomerization of the studied oxiranes.

Introduction

The Baylis−Hillman (BH) reaction, which combines the Michael addition of a tertiary amine, usually 1,4-diazabicyclo[2.2.2]octane (DABCO), and an aldehyde to an α,β-unsaturated carbonyl compound, is a useful method of preparation of allylic alcohols.[1] However, at least in the classical version, the BH reaction presents some drawbacks: (a) it is too slow; some reactions take days and even weeks to occur; (b) it works well only with particularly electrophilic α,β-unsaturated carbonyl compounds; (c) it does not take place when a ketone is used instead of an aldehyde; and (d) it works almost exclusively with β-unsubstituted α,β-unsaturated carbonyl compounds and cyclic enones. A number of physical and chemical methods have been developed to accelerate the notoriously slow BH reaction.[2] Lewis acids have also been used to this end, but extremely delicate experimental conditions must be used.[3] Alternative routes planned to make the BH reaction reasonably fast use the "MAC" procedure (Michael addition−aldol reaction−Cope elimination).[4] The base-promoted rearrangement of oxiranes, on the other hand, often provides a convenient method of preparation of allylic alcohols, which are useful intermediates in synthetic organic chemistry.[5] Asymmetric variants of this reaction have been the subject of recent investigations and have been used as the key step in the synthesis of numerous commercially and biologically important substances such as carbovir,[6] lasiol,[7] faranal,[8] leukotrienes,[9] and prostaglandin precursors.[10]

Results and Discussion

In this paper, we report a quite simple route to oxazolinyl allylic alcohols based on the isomerization reaction of oxazolinyl alkyl oxiranes. The leading idea was that lithiated 2-(1-chloroalkyl)oxazolines D[11] (Scheme 1) can be considered synthetic equivalents of the BH reagent (the electron-withdrawing oxazolinyl system is a well-known masked form of the carbonyl functionality),[12] and their reaction with carbonyl compounds leads to alkyl oxazolinyloxiranes that are the precursors of the BH reaction adducts A as shown in the following retrosynthetic approach (Scheme 1). According to such an approach, the BH reaction product A would be afforded upon deblocking of the oxazolinyl moiety of the allylic alcohol B, which in turn could derive from the isomerization of the oxazolinyloxirane C on its turn obtainable by the coupling reaction of a carbonyl compound with the oxazolinyl-α-chloroalkyl anion D, a Darzens-type reagent.[11]

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10.1021/jo026234d CCC: $22.00
Published on Web 10/31/2002

SCHEME 1

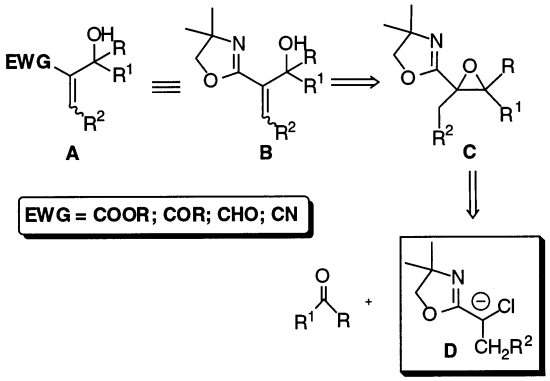
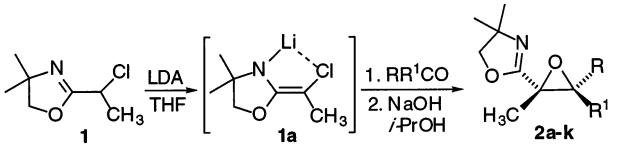


TABLE 1. Synthesis of Oxazolinyloxiranes 2a−k by Lithiation of 2-(1-Chloroethyl)-2-oxazoline 1

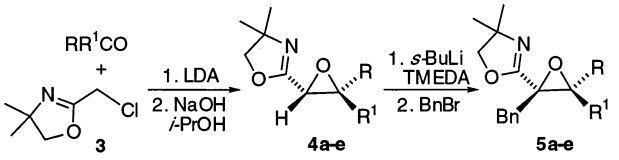


oxirane	R	R1	yield[a] (%)
2a	Ph	Ph	66[b]
2b		$-(CH_2)_5-$	76[b]
2c	Et	Et	80
2d	H	cyclohexyl	42[c]
2e	cyclohexyl	H	41[c]
2f	H	*i*-Pr	45[c]
2g	*i*-Pr	H	43[c]
2h	Me	Ph	39[c]
2i	Ph	Me	39[c]
2j	Me (*n*-Pr)	*n*-Pr (Me)	87[d]
2k	Me	Me	83[b]

[a] Isolated yields. [b] As reported in ref 11. [c] A 1:1 diastereomeric mixture of separable (silica gel, petroleum ether/AcOEt 6−7/4−3) diastereoisomers formed. [d] Combined isolated yield; an inseparable mixture of diastereomeric oxiranes **2j** (dr 1/1 by ^{1}H NMR) formed.

Oxiranes **2a**−**k**[13] were prepared by the Darzens reaction of α-lithiated 2-(1-chloroethyl)oxazoline[14] **1a** and the appropriate carbonyl compound (Table 1) according to a procedure recently reported from our laboratory,[11] while oxiranes **4a**−**e** (Table 2) were synthesized from 2-chloromethyl-2-oxazoline **3** by lithiation in the presence of the appropriate carbonyl compound by using the Barbier technique.[15] Compounds **5a**−**e** could be prepared from **4a**−**e** by a procedure based on lithiation of the oxazolinyloxirane and reaction with the appropriate electrophile (Table 2).[16]

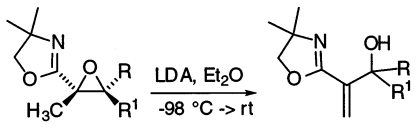
TABLE 2. Synthesis of Oxazolinyloxiranes 4a−e and 5a−e



oxirane	R	R1	yield[a] (%)
4a	Ph	Ph	78[b]
4b	Et	Et	86[c]
4c	Me	Me	84[b]
4d	H (*t*-Bu)	*t*-Bu (H)	64[d]
4e	H (cyclohexyl)	cyclohexyl (H)	62[d]
5a	Ph	Ph	70
5b	Et	Et	85
5c	Me	Me	85
5d	H (*t*-Bu)	*t*-Bu (H)	55[e]
5e	H (cyclohexyl)	cyclohexyl (H)	55[e]

[a] Isolated yields. [b] As preliminarly reported in ref 15a. [c] Optimized yield with respect to that preliminarly reported in ref 15b. [d] Overall isolated yield in both cis and trans isomers (42% cis and 22% trans for **4d**, 40% cis and 22% trans for **4e**); a 1.2/1 diastereomeric mixture separable by column chromatography (silica gel, petroleum ether/AcOEt 7−8/3−2) in favor of the trans isomer formed in the crude reaction mixture for both **4d** and **4e**. [e] Overall isolated yield in both (*R**,*R**) and (*R**,*S**) isomers not separable by column chromatography (*R**,*S**/*R**,*R** ratio = 5.7/1 for **5d**; *R**,*S**/*R**,*R** ratio = 2.3/1 for **5e**).

TABLE 3. Synthesis of Allylic Alcohols 6a−e



oxirane	R	R1	allylic alcohol **6** (yield, %)[a]
2a	Ph	Ph	**6a** (76)
2b		$-(CH_2)_5-$	**6b** (86)
2c	Et	Et	**6c** (78)
2d	H	cyclohexyl	**6d** (71)
2e	cyclohexyl	H	**6d** (70)
2f	H	*i*-Pr	**6e** (72)
2g	*i*-Pr	H	**6e** (71)

[a] Isolated yields.

Treatment of **2a** with lithium diisopropylamide (LDA) in Et_2O at −98 °C followed by warming to room temperature and quenching with aqueous NH_4Cl resulted in the formation of the allylic alcohol **6a** (Table 3). Comparable results were achieved when oxiranes **2b**−**g** were treated with LDA leading to allylic alcohols **6b**−**e** in a regioselective manner. The same allylic alcohol **6d** was obviously obtained from oxiranes **2d** and **2e** and the alcohol **6e** formed from oxiranes **2f** and **2g**.

Allylic alcohols **6a**−**e** are likely the result of a β-elimination reaction involving the methyl group and the oxygen of the oxirane ring, the α-elimination being impossible for the absence of oxirane ring hydrogens. The

(13) Oxiranes **2d**, **2f**, and (*R**,*S**)-**5d** were assigned the configuration on the basis of the very small long-range $^3J_{CH}$ coupling constant ($^3J_{CH2-H} \sim 0$ Hz) between the oxirane β-hydrogen and the carbon of the methylene group (or of the methyl group) of the substituent on the α-carbon, as reported: Kingsbury, C. A.; Durham, D. L.; Hutton, R. *J. Org. Chem.* **1978**, *43*, 4696−4700. The configuration to **2h**/**2i** and **5e** was assigned either by analogy to similar trisubstituted aryl methyl oxazolinyloxiranes as reported in ref 16 or by analogy to **5d**, respectively. The configuration to the inseparable diastereomers **2j** could not be assigned.

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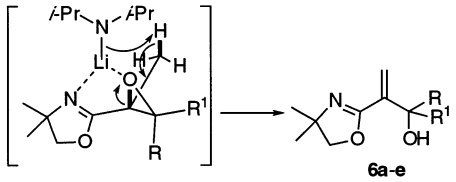
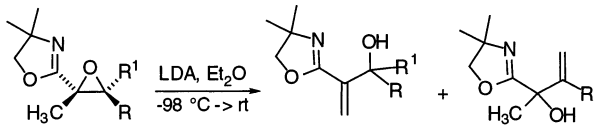
SCHEME 2



relief of the ring strain of the oxirane, which provides sufficient driving force to overcome the reluctance of the ether oxygen atom to act as a leaving group in the β-elimination reaction, and the strength of the base used (LDA) do not suffice to explain the ease with which the above isomerization takes place. Indeed, it has been reported[17a] that, even by using very strong bases, the β-elimination of epoxides not carrying electron-withdrawing groups capable of enhancing the acidity on the β-carbon takes hours or days to occur. In some cases, a cosolvent or a ligand is needed and superbases are used.[17b] We believe that the oxazoline system, jointly with the oxirane ring, plays a crucial role providing coordination to the lithium cation of LDA in a sort of complex such as the one shown below (Scheme 2), thus exalting the LDA basicity and driving the elimination reaction to occur. An E_2-E_1cb like mechanism with a syn stereochemical course could be invoked, as reported for other base-promoted isomerization reactions of alkyl oxiranes.[3d,17c,d]

It was proposed[18] that, especially in the presence of bad leaving groups and strong bases, as in our case, the syn elimination is favored by the cation coordination provided by the oxirane oxygen. The regioselectivity of the isomerization reaction of oxiranes **2b**−**g**, involving the methyl and not the other alkyl groups of the oxirane ring, can be explained with the Hofmann rule according to which the abstraction of protons from methyl proceeds faster than from methylene (or methynic) groups especially with a poor leaving group and a strong base. It is also worth noting that compounds **6a**−**e** resemble the BH adducts that would derive from the reaction involving ketones, which, as mentioned above, do not react in the classic BH reaction. The inspection of results listed in Table 3 allows us to say that the reaction tolerates several different substituents in the β position (with respect to the oxazolinyl ring). However, the presence of a β-methyl group, as in epoxides **2h**−**k** (Table 4), has been found to cause an alternative or competitive β-elimination reaction. When the epoxide (*R**,*R**)-**2i** was treated with LDA under the standard experimental conditions, a 1:1 mixture of allylic alcohols **6f** and **7a** (Table 4) formed in quite good yields. The approach of the base to the two methyl groups of oxirane **2i**, which are cis each other, seems to be equally feasible. In contrast, the reaction of the epoxide (*R**,*S**)-**2h** gave compound **7a** as the sole product. Such a regioselectivity could be accounted for by considering that in compound **2h** the β-methyl group, being cis with respect to the oxazolinyl group, can be more easily approached by the base (LDA) via a preliminary coordination of lithium of LDA by the aza group of the oxazoline system and the oxygen of the oxirane ring, thus promoting the syn β-elimination as visualized in Scheme 3.

TABLE 4. Competitive Elimination in β-Methyl-Substituted Oxazolinyloxiranes 2h−k

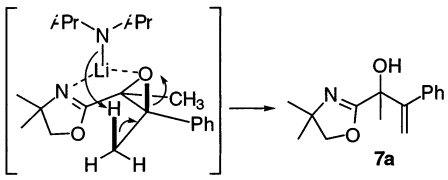


2h-k **6f-h** **7a-c**

oxirane	R	R[1]	LDA (equiv)	allylic alcohol **6** (yield, %)[a]	allylic alcohol **7** (yield, %)[a]
2h	Ph	Me	1.5		**7a** (89)
2i	Me	Ph	1.5	**6f** (42)	**7a** (42)
2j	*n*-Pr(Me)[b]	Me(*n*-Pr)[b]	1.5		**7b** (76)[c]
2j	*n*-Pr(Me)[b]	Me(*n*-Pr)[b]	2.5	**6g** (10)[d]	**7b** (68)[c]
2k	Me	Me	1.5		**7c** (81)
2k	Me	Me	2.5	**6h** (13)	**7c** (75)

[a] Isolated yields. [b] 1:1 mixture of (*R**,*R*)- and (*R**,*S**)-**2j**. [c] R = *n*-Pr. [d] This product could not be isolated as it tends to decompose with the time and during column chromatography.

SCHEME 3



As expected, lithiation of the trimethyl oxazolinyl oxirane **2k** afforded allylic alcohol **7c**; a small amount (13%) of allylic alcohol **6h** also formed when 2.5 equiv of LDA were used. Allylic alcohol **7b** formed in the reaction of a 1:1 mixture of *cis*- and *trans*-oxiranes **2j** with 1.5 equiv of LDA, whereas the use of 2.5 equiv produced also about 10% of the alcohol **6g**.

Treatment of benzyl oxazolinyloxiranes **5a**−**c** with LDA furnished good yields of allylic alcohols **8a**−**c** [19] as *Z* and *E* diastereomeric mixtures (Table 5). Of course, here, the eliminative ring fission of the oxirane system is facilitated by the enhancing acidity effect of the phenyl group attached to the exocyclic methylene group. Interestingly, *Z* isomers of allylic alcohols **8a** and **8b** formed exclusively when oxiranes **5a** and **5b** were reacted with *s*-BuLi/TMEDA, while oxirane **5c** afforded allylic alcohol **8c** with a good diastereoselectivity (*Z*/*E* ratio: 84/16).

The formation of allylic alcohols **8a**−**c** can be accounted for by assuming that treatment of oxiranes **5a**−**c** with the base (LDA or *s*-BuLi/TMEDA) promotes an eliminative oxirane ring fission involving the α-alkyl substituent. Here, an E_2-E_1cb-like mechanism, more shifted toward

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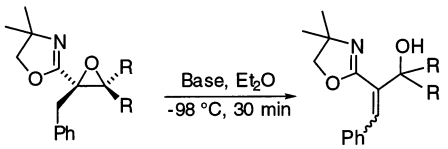
(19) Configuration to allylic alcohols **8a**−**e** could be assigned on the basis of the $^3J(CN,H)$ coupling constants between the iminic carbon and the olefinic proton. In the case of the *E* isomers (having a cis-type arrangement between the above groups) couplings have been found to be always smaller (7.5−8.5 Hz) than those of the *Z* ones (10.6−11.5 Hz) as reported for similar π-bonded systems: Kalinowski, H.-O.; Berger, S.; Braun, S. *Carbon-13 NMR Spectroscopy*; Wiley: New York, 1988; Chapter 4, pp 526−543.

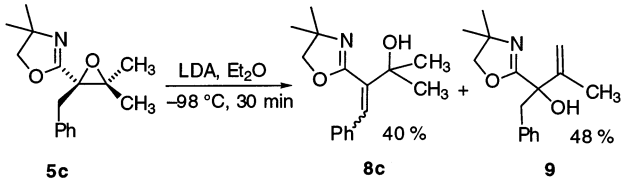
TABLE 5. Deprotonation of Oxazolinyloxiranes 5a−c



oxirane	R	base	allylic alcohol **8** (yield, %)[a]	*Z*/*E* ratio[b]
5a	Ph	LDA	**8a** (91)	64/36
5a	Ph	*s*-BuLi[c]	**8a** (80)	>99/1
5b	Et	LDA	**8b** (92)	77/23
5b	Et	*s*-BuLi[c]	**8b** (85)	>99/1
5c	Me	LDA	**8c** (40)[d]	50/50
5c	Me	*s*-BuLi[c]	**8c** (91)	84/16

[a] Combined isolated yields; isomers *Z* and *E* could be separated by column chromatography. [b] Diastereomeric ratio determined by ^{1}H NMR on the crude reaction mixture. [c] TMEDA was always employed in stoichiometric amount with respect to *s*-BuLi. [d] The major product of this reaction was allylic alcohol **9** as shown in Scheme 4.

SCHEME 4



the E_1cb mechanism for involving benzylic hydrogens, might be proposed as reported for ring opening reactions of other oxiranes.[3d] Coordination offered to the lithium base by the oxazolinyl group and the oxirane oxygen should facilitate the syn-β-elimination reaction. Two competitive syn-β-eliminations occur when a methyl group is present on the β-carbon atom (with respect to the oxazoline ring) of benzyl oxiranes. In the case of oxirane **5c** (Table 5 and Scheme 4), indeed, treatment with LDA affords the expected allylic alcohol **8c** (40%, *Z*/*E* ratio: 1/1) together with the isomeric allylic alcohol **9** (48%). This is probably the result of a balance between steric and electronic effects. The coordinative assistance of the oxazoline ring to the β-elimination involving the methyl group cis to it must also be taken into consideration. Concerning the isomerization reactions of **5a**−**c** promoted by LDA, an appreciable increase of the *Z*/*E* ratio was observed on going from **5c** to **5a** and **5b**; this could be tentatively explained with the different steric hindrance of the R groups.

The *Z*-stereoselectivity observed when *s*-BuLi was used as the base can be accounted for by considering the possible different aggregation state of *s*-BuLi in Et_2O with respect to LDA[20,21] and the reactive conformations

SCHEME 5

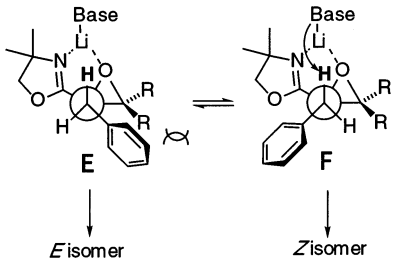


TABLE 6. Deprotonation of Oxazolinyloxiranes 5d,e

oxirane	R	R^1	base	allylic alcohol **8** (yield, %)[a]	*Z*/*E* ratio[b]
5d	*t*-Bu (H)[c]	(H) *t*-Bu[c]	LDA	**8d** (90)[d]	87/13
5d	*t*-Bu (H)[c]	(H) *t*-Bu[c]	*s*-BuLi	**8d** (90)[d]	87/13
5e	cyclohexyl (H)[e]	(H) cyclohexyl[e]	LDA	**8e** (89)[f]	85/15
5e	cyclohexyl (H)[e]	(H) cyclohexyl[e]	*s*-BuLi	**8e** (89)[f]	85/15

[a] Isolated yields. [b] Diastereomeric ratio determined by ^{1}H NMR on the crude reaction mixture. Isomers *Z* and *E* could be separated by column chromatography. [c] 85/15 mixture of (*R**,*S*)- and (*R**,*R**)-**5d**. [d] R = *t*-Bu. [e] 70/30 mixture of (*R**,*R*)- and (*R**,*S**)-**5e**. [f] R = cyclohexyl.

of the starting oxirane. There are two conformers **E** and **F** (Scheme 5) that permit the syn-β-elimination. Conformer **E**, which is of higher energy with respect to **F** for experiencing a higher steric compression that originates from the interaction of the R groups on the oxirane ring and the phenyl group, would lead to the *E* stereoisomer while conformer **F** would give the *Z* isomer. The role of the ligand TMEDA, which on the other hand exalts the basicity of *s*-BuLi, could be that of enlarging the energy difference between the transition states leading to the *Z* and *E* isomers.

When a diastereomeric mixture of oxirane **5d** (*R**,*S**/*R**,*R** ratio: 85/15)[22] was reacted with LDA (or *s*-BuLi/TMEDA) in Et_2O, a regioselective eliminative ring fission reaction involving the benzyl group occurred leading to a diastereomeric mixture (*Z*/*E* ratio: 87/13) of allylic alcohol **8d** (Table 6). It is useful to note that there is no change in stereoselection passing from LDA to *s*-BuLi/TMEDA. Such an absence of the base effect on the stereoselection could be accounted for by assuming that in the case of the reactions of **5d** the interactions between the phenyl and β-R groups are playing the major role. The *Z*/*E* ratio in the final product, which substantially parallels the diastereomeric ratio of the starting oxirane, seems to indicate a stereospecificity in the elimination reaction of the diastereomers of **5d**.

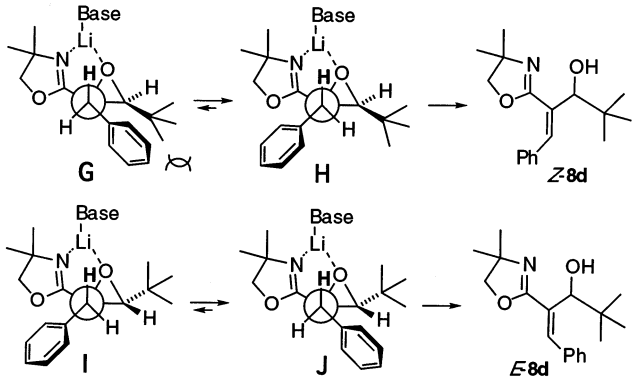
To go in more detail, we presume that base−epoxide complexes are involved in the β-elimination as in base-mediated isomerizations of other epoxides.[17a] Steric interactions between the phenyl and the β-substituents

(20) LDA is recognized to exist as a disolvated dimer in ethereal solvents (Sun, X.; Collum, D. B. *J. Am. Chem. Soc.* **2000**, *122*, 2452−2458), while *s*-BuLi complexed by TMEDA is usually monomeric going towards an endothermic disproportionation from a 1:1 complex to a 1:2 complex according to the temperature (Catala, J. M.; Clouet, G.; Brossas, J. *J. Organomet. Chem.* **1981**, *219*, 139−143).

(21) The possibility that the lower stereoselection of reactions promoted by LDA could be attributed to an isomerization reaction of *Z* isomers into *E* isomers promoted by the formed diisopropylamine can be ruled out. Indeed, *Z*-**8a**, *Z*-**8b**, and *Z*-**8d** do not isomerize to the corresponding *E* isomers when treated with diisopropylamine and *E*-**8d** does not isomerize to *Z*-**8d**.

(22) All efforts made in order to separate diastereomers **5d** and **5e** failed so far.

SCHEME 6



on the oxirane ring will dictate which conformers will be predominating. Accordingly, the complex derived from diastereomer (*R**,*S**)-**5d** (having the *t*-Bu and benzyl group cis with respect to the oxirane ring) and placing the phenyl group synclinal to the oxazoline ring (conformer **H**, Scheme 6), which experiences a lower steric compression with respect to conformer **G** (Scheme 6), would furnish *Z* allylic alcohol **8d**, while complex **J** (prevailing in the equilibrium with complex **I**), derived from diastereomer (*R**,*R**)-**5d**, would lead to the *E* allylic alcohol **8d**.

LDA- or *s*-BuLi-promoted isomerization of a diastereomeric mixture (*R**,*S**/*R**,*R** ratio: 70/30) of oxirane **5e** generated a diastereomeric mixture (*Z*/*E* ratio: 85/15) of allylic alcohol **8e**. This result could be accounted for by considering the steric interactions occurring between the phenyl and the cyclohexyl groups in the complexes preceding the formation of the final product. Considering the (*R**,*S**)-**5e**, this would react in a stereospecific manner passing through conformer **L** (Scheme 7) (preferred with respect to conformer **K**) to give the *Z* isomer, while the (*R**,*R**)-**5e** would produce a mixture of *Z*, which, therefore, adds to that obtained from the (*R**,*S**)-**5e**, and *E* allylic alcohol **8e**, going through base−oxirane complexes **M** and **N**, which should be of comparable energy.

In conclusion, we have developed a simple method of preparation of oxazolinyl allylic alcohols based on the base-promoted isomerization of alkyl epoxides. The obtained allylic alcohols seem to be promising in synthetic organic chemistry for the possible elaboration of their oxazoline system. The chiral version of the isomerization reaction of the above oxazolinyl alkyl oxiranes is under way in our lab and results will be reported in due course.

Experimental Section

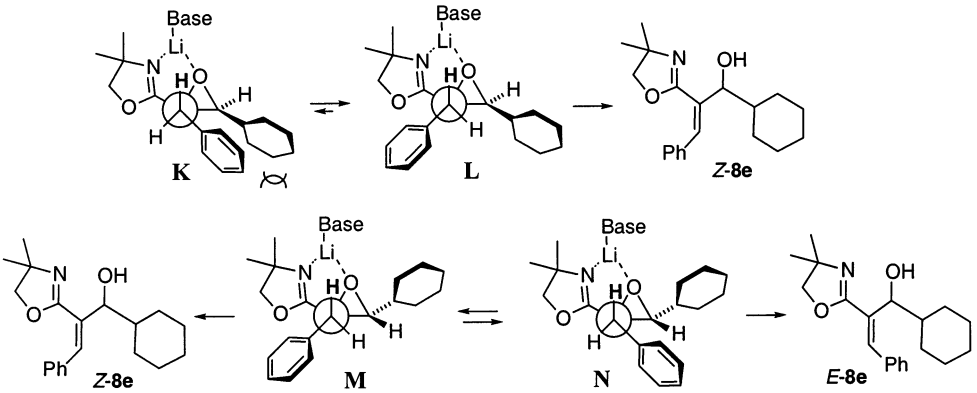
General Methods. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were freshly distilled under a nitrogen atmosphere over sodium/benzophenone ketyl. *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (TMEDA) was distilled over finely powdered calcium hydride. All other chemicals were of commercial grade and used without further purification. Petroleum ether refers to the 40−60 °C boiling fraction. Commercial solutions of *n*-BuLi (2.5 M solution in hexanes) and *s*-BuLi (1.3 M solution in cyclohexane) were titrated by using *N*-pivaloyl-*o*-toluidine prior to use.[23] For the ^{1}H and ^{13}C NMR spectra (^{1}H NMR 200, 300, 500 MHz; ^{13}C NMR 75.4, 125 MHz), $CDCl_3$ was used as the solvent. GC−MS spectrometry analyses were performed on a gas chromatograph HP 6890 (HP-5 MS capillary column, 30 m, 0.25 mm i.d. × 0.25 μm) equipped with a 5973 mass selective detector operating at 70 eV (EI). Melting points were uncorrected. TLC was performed on Merck silica gel plates with F-254 indicator; visualization was accomplished by UV light (254 nm) or by exposure to I_2 vapor. All reactions involving air-sensitive reagents were performed under nitrogen in oven-dried glassware using the syringe−septum cap technique. Spectroscopic data of oxazolinyloxiranes **2a**,[11] **2b**, [11] **2k**,[11] and **4a**[15c] have been reported.

3-Ethyl-2-(4,4-dimethyl-2-oxazolin-2-yl)-2,3-epoxypentane (2c): colorless oil; 80%; ^{1}H NMR (300 MHz) δ 0.89 (t, J = 7.5 Hz, 3 H), 0.93 (t, J = 7.5 Hz, 3 H), 1.20 (s, 3 H), 1.21 (s, 3 H), 1.47 (s, 3 H), 1.49−1.53 (m, 3 H), 1.64−1.66 (m, 1 H), 3.85 and 3.92 (2 × d, AB system, J = 8.2 Hz, 2 H); ^{13}C NMR (75.4 MHz) δ 8.6, 8.7, 16.7, 22.0, 22.9, 27.7, 27.8, 60.5, 67.0, 68.7, 78.7, 164.0; GC−MS (70 eV) *m*/*z* 196 (M^+-15, 2), 168 (10), 156 (15), 142 (19), 112 (100), 86 (21), 70 (46), 69 (37), 55 (19), 43 (29), 41 (17); FT-IR (film, cm^{-1}) 2964, 2877, 1671 (s, C=N), 1463, 1299, 1186, 1097, 961, 733, 547.

(1*R,2*S**)-1-Cyclohexyl-2-(4,4-dimethyl-2-oxazolin-2-yl)-1,2-epoxypropane (2d):** colorless oil; 42%; ^{1}H NMR (500 MHz) δ 1.12−1.24 (m, 6 H), 1.23 (s, 3 H), 1.24 (s, 3 H), 1.52 (s, 3 H), 1.58−1.71 (m, 4 H), 1.89−1.92 (m, 1 H), 2.94 (d, J = 9.0 Hz, 1 H), 3.91 (s, 2 H); ^{13}C NMR (125 MHz) δ 14.4, 25.2, 28.1, 28.5, 30.4, 37.1, 55.0, 66.4, 67.5, 79.3, 164.9; GC−MS (70 eV) *m*/*z* 237 (M^+, 4), 194 (20), 192 (38), 182 (21), 142 (26), 138 (36), 127 (25), 95 (100), 55 (26), 43 (54); FT-IR (film, cm^{-1}) 2927, 2852, 1670 (s, C=N), 1450, 1366, 1117, 1079, 974, 856. Anal. Calcd for $C_{14}H_{23}NO_2$: C, 70.85; H, 9.77; N, 5.90. Found: C, 71.15; H, 10.03; N, 5.69.

(1*R,2*R**)-1-Cyclohexyl-2-(4,4-dimethyl-2-oxazolin-2-yl)-1,2-epoxypropane (2e):** colorless oil; 41%; ^{1}H NMR (500 MHz) δ 1.05−1.29 (m, 6 H), 1.25 (s, 3 H), 1.27 (s, 3 H), 1.51 (s, 3 H),1.60−1.75 (m, 4 H), 1.89−1.93 (m, 1 H), 2.61 (d, J = 9.2 Hz, 1 H), 3.90 and 3.96 (2 × d, AB system, J = 8.2 Hz, 2 H); ^{13}C NMR (125 MHz) δ 20.5, 25.1, 25.5, 28.1, 28.2, 30.3, 37.1,

SCHEME 7



56.3, 67.5, 68.8, 79.4, 163.3; GC−MS (70 eV) *m/z* 237 (M^+, 4), 194 (28), 192 (41), 182 (21), 142 (31), 138 (34), 127 (25), 95 (100), 55 (31), 43 (57); FT-IR (film, cm^{-1}): 2927, 2853, 1656 (s, C=N), 1523, 1450, 1364, 1070, 974, 856. Anal. Calcd for $C_{14}H_{23}NO_2$: C, 70.85; H, 9.77; N, 5.90. Found: C, 70.90; H, 10.06; N, 5.73.

***(2R*,3S*)*-4-Methyl-2-(4,4-dimethyl-2-oxazolin-2-yl)-2,3-epoxypentane (2f):** colorless oil; 45%; ^1H NMR (300 MHz) δ 0.84 (d, J = 6.8 Hz, 3 H), 0.99 (d, J = 6.8 Hz, 3 H), 1.23 (s, 3 H), 1.25 (s, 3 H), 2.86 (d, J = 9.3 Hz, 1 H), 3.45−3.60 (m, 1 H), 3.88 (s, 2 H); ^{13}C NMR (125 MHz) δ 18.2, 20.0, 20.6, 27.7, 28.1, 28.2, 56.8, 67.5, 70.2, 79.3, 163.3; GC−MS (70 eV) *m/z* 197 (M^+, 4), 182 (7), 154 (43), 142 (38), 124 (15), 98 (49), 83 (13), 72 (40), 55 (46), 43 (100); FT-IR (film, cm^{-1}) 2964, 2877, 1660 (s, C=N), 1465, 1366, 1163, 1068, 864. Anal. Calcd for $C_{11}H_{19}NO_2$: C, 66.97; H, 9.71; N, 7.10. Found: C, 66.75; H, 9.53; N, 6.91.

(2R*,3R*)-4-Methyl-2-(4,4-dimethyl-2-oxazolin-2-yl)-2,3-epoxypentane (2g): colorless oil; 43%. ^1H NMR (300 MHz) δ 0.90 (d, J = 6.7 Hz, 3 H), 1.05 (d, J = 6.7 Hz, 3 H), 1.24 (s, 3 H), 1.25 (s, 3 H), 1.53 (s, 3 H), 2.58 (d, J = 9.4 Hz, 1 H), 3.45−3.60 (m, 1 H), 3.93 (s, 2 H); ^{13}C NMR (125 MHz) δ 18.1, 20.0, 27.6, 28.0, 60.5, 67.6, 70.1, 79.3, 164.8; GC-MS (70 eV) *m/z* 197 (M^+, 3), 182 (17), 154 (28), 142 (40), 126 (14), 98 (48), 83 (18), 72 (44), 55 (50), 43 (100); FT-IR (film, cm^{-1}) 2964, 2869, 1671 (s, C=N), 1522, 1463, 1191, 972, 547. Anal. Calcd for $C_{11}H_{19}NO_2$: C, 66.97; H, 9.71; N, 7.10. Found: C,66.70; H, 9.80; N, 7.00.

(2R*,3S*)-2-(4,4-Dimethyl-2-oxazolin-2-yl)-3-phenyl-2,3-epoxybutane (2h): colorless oil; 39%; ^1H NMR (200 MHz) δ 1.16 (s, 3 H), 1.29 (s, 3 H), 1.30 (s, 3 H), 1.62 (s, 3 H), 3.94 and 4.02 (2 × d, AB system, J = 8.1 Hz, 2 H), 7.22−7.31 (m, 5 H); ^{13}C NMR (125 MHz) δ 17.5, 20.6, 28.3, 61.7, 66.8, 67.7, 79.3, 126.1, 127.4, 128.0, 139.4, 163.9; GC-MS (70 eV) *m/z* 245 (M^+, 1), 228 (3), 202 (8), 146 (100), 120 (6), 103 (9), 77 (8), 43 (6); FT-IR (film, cm^{-1}): 3059, 2968, 2931, 1669 (s, C=N), 1450, 1091, 752, 700. Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.65; H, 7.92; N, 5.70.

(2R*,3R*)-2-(4,4-Dimethyl-2-oxazolin-2-yl)-3-phenyl-2,3-epoxybutane (2i): colorless oil; 39%; ^1H NMR (200 MHz) δ 0.74 (s, 3 H), 0.91 (s, 3 H), 1.66 (s, 3 H), 1.68 (s, 3 H), 3.42 and 3.56 (2 × d, AB system, J = 8.0 Hz, 2H), 7.16−7.36 (m, 5 H); ^{13}C NMR (125 MHz) δ 16.8, 20.2, 27.5, 27.6, 61.6, 66.1, 66.8, 78.9, 126.2, 127.1, 127.5, 139.6, 163.0; GC−MS (70 eV) *m/z* 245 (M^+, 1), 202 (13), 146 (100), 120 (9), 103 (14), 91 (4), 77 (12), 43 (10); FT-IR (film, cm^{-1}) 3058, 3029, 2969, 1658 (s, C=N), 1448, 1091, 764, 700, 566.

3-Methyl-2-(4,4-dimethyl-2-oxazolin-2-yl)-2,3-epoxyhexane (2j): inseparable mixture of two diastereoisomers, dr (2*R**,3*R**)/(2*R**,3*S**) 1/1; colorless oil; 87%; ^1H NMR (500 MHz) δ 0.80 (t, J = 6.5 Hz, 3 H), 0.87 (t, J = 6.6 Hz, 3 H), 1.19 (s, 6 H), 1.22 (s, 3 H), 1.26 (s, 3 H), 1.45 (s, 3 H), 1.46 (s, 3 H), 1.30−1.65 (m, 8 H), 3.85−3.93 (m, 4 H); ^{13}C NMR (125 MHz) δ 14.3, 14.4, 17.2, 17.6, 18.1, 18.8, 28.4, 28.5, 36.0, 36.9, 60.5, 60.7, 65.3, 65.5, 67.6, 67.7, 79.4, 79.5, 164.6; GC−MS (70 eV) *m/z* stereoisomer with a lower t_R 211 (M^+, 1), 168 (20), 156 (16), 142 (21), 127 (13), 112 (100), 86 (24), 70 (63), 69 (39), 55 (19), 43 (39); stereoisomer with a higher t_R 211 (M^+, 1), 168 (19), 156 (16), 142 (18), 127 (8), 112 (100), 86 (25), 70 (66), 69 (42), 55 (19), 43 (41); FT-IR (film, cm^{-1}) 2964, 2877, 1673 (s, C=N), 1464, 1382, 1097, 978, 539.

2-Ethyl-1-(4,4-dimethyl-2-oxazolin-2-yl)-1,2-epoxybutane (4b): colorless oil; 86%; ^1H NMR (300 MHz) δ 0.90 (t, J = 7.7 Hz, 3 H), 0.93 (t, J = 7.5 Hz, 3 H), 1.24 (s, 3 H), 1.25 (s, 3 H), 1.61−1.72 (m, 4 H), 3.36 (s, 1 H), 3.94 (s, 2 H); ^{13}C NMR (75.4 MHz) δ 8.5, 9.3, 22.8, 26.3, 28.2, 55.4, 66.8, 67.4, 79.3, 161.4; GC−MS (70 eV) *m/z* 197 (M^+, 1), 180 (9), 168 (13), 142 (100), 128 (28), 112 (74), 86 (46),70 (74), 55 (45), 41 (52); FT-IR (film, cm^{-1}) 2969, 2926, 2882, 1659 (s, C=N), 1462, 1365, 1104, 975, 921.

2-Methyl-1-(4,4-dimethyl-2-oxazolin-2-yl)-1,2-epoxypropane (4c): colorless oil; 84%; ^1H NMR (300 MHz) δ 1.30 (s, 6 H), 1.40 (s, 6 H), 3.35 (s, 1 H), 4.01 (s, 2 H); ^{13}C NMR (75.4 MHz) δ 18.0, 23.8, 28.0, 56.5, 59.2, 67.2, 79.0, 161.1; GC−MS (70 eV) *m/z* 169 (M^+, 1), 114 (56), 84 (100), 56 (45), 41 (66); FT-IR (film, cm^{-1}): 2971, 2920, 1653 (s, C=N), 1380, 1184, 976, 807.

3,3-Dimethyl-1-(4,4-dimethyl-2-oxazolin-2-yl)-1,2-epoxybutane (4d) *(1R*,2S*)*: colorless oil; 22%; ^1H NMR (300 MHz) δ 0.94 (s, 9 H), 1.28 (s, 3 H), 1.29 (s, 3 H), 3.03 (d, J = 2.2 Hz, 1 H), 3.41 (d, J = 2.2 Hz, 1 H), 3.97 (s, 2 H); ^{13}C NMR (75.4 MHz) δ 25.4, 28.1, 28.2, 30.8, 48.2, 65.5, 67.4, 79.3, 162.4; GC−MS (70 eV) *m/z* 182 (M^+ − 15, 12), 142 (28), 140 (100), 128 (21), 112 (44), 95 (21),70 (46), 55 (45), 41 (35); FT-IR (film, cm^{-1}) 2966, 2871, 1665 (s, C=N), 1482, 1464, 1365, 1302, 993, 896. **(1R*,2R*):** colorless oil; 42%; ^1H NMR (500 MHz) δ 0.97 (s, 9 H), 1.23 (s, 3 H), 1.27 (s, 3 H), 2.86 (d, J = 4.7 Hz, 1 H), 3.45 (d, J = 4.7 Hz, 1 H), 3.91 and 3.98 (2 × d, AB system, J = 8.2 Hz, 2 H); ^{13}C NMR (75.4 MHz) δ 26.4, 27.6, 28.1, 31.7, 50.8, 65.6, 67.5, 79.2, 160.5; GC−MS (70 eV) *m/z* 182 (6), 142 (21), 140 (49), 128 (20), 113 (100), 98 (47), 95 (23), 70 (53), 55 (60), 41 (40). FT-IR (film, cm^{-1}); 2966, 2871, 1679 (s, C=N), 1483, 1464, 1365, 1241, 1193, 981, 934, 838.

2-Cyclohexyl-1-(4,4-dimethyl-2-oxazolin-2-yl)-1,2-epoxyethane (4e) (1R*,2S*): colorless oil; 22%; ^1H NMR (300 MHz) δ 1.03−1.23 (m, 6 H), 1.24 (s, 3 H), 1.27 (s, 3 H), 1.56−1.82 (m, 4 H), 1.98−2.04 (m, 1 H), 3.02 (dd, J = 2.7, 6.4 Hz, 1 H), 3.36 (d, J = 2.7 Hz, 1 H), 3.92 (s, 2 H); ^{13}C NMR (75.4 MHz) δ 25.3, 25.4, 26.0, 28.1, 28.2, 28.6, 29.0, 39.3, 49.9, 62.2, 67.4, 79.2, 162.0; GC-MS (70 eV); *m/z* 223 (M^+, 1), 192 (10), 140 (13), 95 (100), 81 (23), 67 (23), 56 (35), 55 (52), 41 (90); FT-IR (film, cm^{-1}) 2964, 2922, 2853, 1664 (s, C=N), 1450, 1302, 1188, 993, 801. Anal. Calcd for $C_{13}H_{21}NO_2$: C, 69.92; H, 9.48; N, 6.27. Found: C, 69.72; H, 9.75; N, 6.15. **(1R*,2R*):** colorless oil; 40%; ^1H NMR (300 MHz) δ 1.03−1.22 (m, 5 H), 1.25 (s, 3 H), 1.27 (s, 3 H), 1.43−1.52 (m, 2 H), 1.62−1.78 (m, 3 H), 1.96−2.02 (m, 1 H), 2.85 (dd, J = 4.4 Hz, J = 8.9 Hz, 1 H), 3.53 (d, J = 4.4 Hz, 1 H), 3.96 (s, 2 H); ^{13}C NMR (75.4 MHz) δ = 25.1, 25.4, 26.0, 28.1, 28.2, 28.4, 30.5, 36.4, 50.0, 62.1, 67.4, 79.3, 161.1; GC−MS (70 eV) *m/z* 223 (M^+, 1), 206 (18), 113 (27), 95 (100), 67 (22), 56 (33), 55 (54), 41 (90); FT-IR (film, cm^{-1}) 2965, 2922, 2852, 1676, 1661 (s, C=N), 1450, 1161, 981, 870.

2-(4,4-Dimethyl-2-oxazolin-2-yl)-1,1,3-triphenyl-1,2-epoxybutane (5a): white solid; mp 135 °C (Et_2O); 70%; ^1H NMR (300 MHz) δ 0.76 (s, 3 H), 0.87 (s, 3 H), 2.52 (d, J = 14.6 Hz, 1 H), 3.38−3.55 (2 × d, AB system, J = 8.0 Hz, 2 H), 3.43 (d, J = 14.6 Hz, 1 H), 7.13−7.41 (m, 11 H), 7.56−7.65 (m, 4 H); ^{13}C NMR (75.4 MHz) δ 27.4, 27.5, 37.5, 66.7, 67.1, 70.3, 79.0, 126.5, 127.1, 127.2, 127.5, 127.7, 127.9, 128.1, 128.4, 129.4, 136.2, 137.8, 138.2, 161.2; GC−MS (70 eV) *m/z* 383 (M^+, 5), 292 (7), 209 (29), 208 (100), 165 (52), 105 (8), 91 (20), 77 (8); FT-IR (film cm^{-1}) 3058, 3029, 2967, 1656 (s, C=N), 1495, 1449, 1082, 750, 700. Anal. Calcd for $C_{26}H_{25}NO_2$: C, 81.43; H, 6.57; N, 3.65. Found: C, 81.61; H, 6.91; N, 3.63.

3-Ethyl-2-(4,4-dimethyl-2-oxazolin-2-yl)-1-phenyl-2,3-epoxypentane (5b): colorless oil; 85%; ^1H NMR (300 MHz) δ 0.95−1.00 (m, 6 H), 1.02−1.07 (m, 6 H), 1.53−1.61 (m, 2 H), 1.64−1.72 (m, 1 H), 1.75−1.79 (m, 1 H), 2.89 (d, J = 14.4 Hz, 1 H), 3.34 (d, J = 14.4 Hz, 1 H), 3.66 (s, 2 H), 7.11−7.29 (m, 5 H); ^{13}C NMR (75.4 MHz) δ 9.3, 9.6, 23.1, 24.1, 28.2, 37.3, 65.5, 67.6, 69.4, 79.1, 126.7, 128.3, 129.8, 136.8, 162.8; GC−MS (70 eV) *m/z* 287 (M^+, 1), 258 (53), 201 (43), 200 (54), 186 (17), 112 (89), 103 (14), 91 (100), 70 (30), 55 (14); FT-IR (film, cm^{-1}) 3064 3031, 2971, 2884, 1658 (s, C=N), 1497, 1462, 1191, 1078, 967, 756, 699. Anal. Calcd for $C_{18}H_{25}NO_2$: C, 75.22; H, 8.77; N, 4.87. Found: C, 75.11; H, 9.05; N, 4.98.

3-Methyl-2-(4,4-dimethyl-2-oxazolin-2-yl)-1-phenyl-2,3-epoxybutane (5c): colorless oil; 85%; ^1H NMR (300 MHz) δ 1.01 (s, 3 H), 1.07 (s, 3 H), 1.34 (s, 3 H), 1.50 (s, 3 H), 2.90 (d, J = 14.5 Hz, 1 H), 3.35 (d, J = 14.5 Hz, 1 H), 3.70 (s, 2 H), 7.15−7.30 (m, 5 H); ^{13}C NMR (75.4 MHz) δ 20.5, 21.4, 28.2, 28.3, 37.6, 62.7, 64.6, 67.6, 79.2, 126.8, 128.3, 129.8, 136.8,

(23) Suffert, J. *J. Org. Chem.* **1989**, *54*, 509−512.

162.7; GC−MS (70 eV) *m*/*z* 259 (M^+, 1), 244 (60), 200 (58), 186 (13), 172 (16), 119 (813), 91 (100), 84 (59), 41 (12); FT-IR (film, cm^{-1}) 3088, 3064, 3031, 2966, 2929, 1660 (s, C═N), 1497, 146, 1299, 1192, 1136, 1058, 967, 755, 700.

4,4-Dimethyl-2-(4,4-dimethyl-2-oxazolin-2-yl)-1-phenyl-2,3-epoxypentane (5d): inseparable mixture of two diastereoisomers, dr (2*R**,3*R**)/(2*R**,3*S**) = 85/15; colorless oil; 55%; ^{1}H NMR (500 MHz) δ 0.99 (s, 9 H, minor), 1.04 (s, 3 H, minor), 1.06 (s, 3 H, major), 1.09 (s, 3 H, major), 1.10 (s, 3 H, minor), 1.11 (s, 9 H, major), 2.77 (d, J = 14.4 Hz, 1 H, minor), 2.95 (s, 2 H, 1 H major + 1 H minor), 3.27−3.41 (2 × d, AB system, J = 15.3 Hz, 2 H, major), 3.37 (d, J = 14.4 Hz, 1 H, minor), 3.74 (s, 2 H, minor), 3.76 and 3.80 (2 × d, AB system, J = 8.3 Hz, 2 H, major), 7.18−7.34 (m, 10 H, 5 H major + 5 H minor); ^{13}C NMR (125 MHz) δ 26.4 (minor), 27.5 (minor), 27.7 (major), 31.8 (minor), 27.9 (major), 34.3 (major), 42.8 (minor), 59.8 (major), 60.4 (minor), 67.3 (major + minor), 70.1 (major), 70.7 (minor), 78.9 (minor), 79.1 (major), 126.3 (major), 126.7 (minor), 127.9 (major), 128.0 (minor), 129.3 (major), 129.6 (minor), 135.5 (minor), 136.9 (major), 161.3 (minor), 164.1 (major); GC−MS (70 eV) (major) *m*/*z* 287 (M^+, 1), 230 (100), 200 (20), 158 (25), 112 (6), 91 (18), 55 (9); GC−MS (70 eV) (minor); *m*/*z* 287 (M^+, 1), 230 (72), 200 (12), 158 (13), 119 (13), 91 (100), 55 (10); FT-IR (film, cm^{-1}) 3063, 3031, 2970, 2925, 2852, 1658 (s, C═N), 1452, 1365, 1193, 977, 732, 700.

1-Cyclohexyl-2-(4,4-dimethyl-2-oxazolin-2-yl)-3-phenyl-1,2-epoxypropane (5e): inseparable mixture of two diastereoisomers, dr (1*R**,2*S**)/(1*R**,2*R**) = 70/30; colorless oil; 55%; ^{1}H NMR (300 MHz) δ 1.08−1.28 (m, 24 H, 12 H major + 12 H minor), 1.56−1.82 (m, 8 H, 4 H major + 4 H minor), 1.93−2.02 (m, 2 H, 1 H major + 1 H minor), 2.66 (d, J = 8.8 Hz, 1 H, minor), 2.84 (d, J = 14.6 Hz, 1 H, minor), 2.94 (d, J = 9.1 Hz, 1 H, major), 2.99 (d, J = 14.9 Hz, 1 H, major), 3.36 (d, J = 14.9 Hz, 1 H, major), 3.42 (d, J = 14.6 Hz, 1 H, minor), 3.80 (s, 2 H, minor), 3.78 and 3.85 (2 × d, AB system, J = 8.2 Hz, 2 H, major), 7.14−7.33 (m, 10 H, 5 H major + 5 H minor); ^{13}C NMR (75.4 MHz) δ 25.1 (minor), 25.3 (major), 25.5 (minor), 26.0 (major), 27.9 (minor), 28.0 (major), 28.3 (minor), 28.6 (major), 30.2 (minor), 30.4 (major), 34.5 (major), 37.2 (major), 37.3 (minor), 40.1 (minor), 58.2 (major), 60.1 (minor), 66.7 (minor), 66.8 (major), 67.4 (major + minor), 79.0 (minor), 79.2 (major), 126.3 (major), 126.6 (minor), 128.0 (major), 128.1 (minor), 129.5 (major), 129.6 (minor), 135.7 (minor), 136.5 (major), 162.2 (minor), 163.8 (major); GC−MS (70 eV) (major) *m*/*z* 313 (M^+, 1), 296 (3), 230 (100), 200 (12), 158 (19), 91 (83), 55 (11); GC−MS (70 eV) (minor) *m*/*z* 313 (M^+, 1), 296 (3), 230 (100), 201 (10), 200 (16), 158 (21), 91 (61), 55 (9); FT-IR (film, cm^{-1}) 3063, 3031, 2970, 2925, 2852, 1658 (s, C═N), 1452, 1365, 1193, 977, 732, 700.

Typical Procedure. A solution of **2a** (1 mmol) and TMEDA (1.5 mmol) in 5 mL of Et_2O at −98 °C (with a methanol−liquid nitrogen bath) and under N_2 was reacted with *s*-BuLi (1.5 mmol), and the resulting orange mixture was stirred for 30 min at −98 °C. Alternatively, a solution of LDA (1.5 mmol from 1.5 mmol of *i*-Pr_2NEt and 1.5 mmol of *n*-BuLi) in 5 mL of Et_2O was treated under N_2 with a solution of **2a** (1 mmol in 2 mL of Et_2O) for 30 min at −98 °C. Then, the reaction mixture was warmed to room temperature, quenched with saturated aqueous NH_4Cl, poured into 20 mL of saturated brine, extracted with Et_2O (3 × 10 mL), dried (Na_2SO_4), and evaporated under reduced pressure. The crude mixture was flash chromatographed (silica gel; petroleum ether:AcOEt = 7−8:3−2) to give the allylic alcohols with the following data:

2-(4,4-Dimethyl-2-oxazolin-2-yl)-1,1-diphenyl-2-propen-1-ol (6a): colorless oil; 76%; ^{1}H NMR (300 MHz) δ 1.08 (s, 6 H), 3.90 (s, 2 H), 5.03 (d, J = 0.9 Hz, 1 H), 6.13 (d, J = 0.9 Hz, 1 H), 7.06 (br s, 1 H, exchanges with D_2O), 7.22−7.33 (m, 6 H), 7.37−7.45 (m, 4 H); ^{13}C NMR (125 MHz) δ 27.6, 67.6, 78.0, 81.2, 124.8, 127.0, 127.4, 127.6, 141.4, 144.9, 162.0; GC−MS (70 eV) *m*/*z* 307 (M^+, 49), 306 (100), 230 (12), 202 (16), 158 (12), 125 (22), 105 (44), 77 (26), 55 (6); FT-IR (film, cm^{-1}) 3313, 3060, 2969, 2929, 1655 (s, C═N), 1602, 1450, 1366, 1177, 1114, 970, 759, 702. Anal. Calcd for $C_{20}H_{21}NO_2$: C, 78.15; H, 6.89; N, 4.56. Found: C, 78.25; H, 7.19; N 4.56.

1-[1-(4,4-Dimethyl-2-oxazolin-2-yl)vinyl]cyclohexanol (6b): colorless oil; 86%; ^{1}H NMR (300 MHz) δ 1.27 (s, 6 H), 1.42−1.53 (m, 6 H), 1.64−1.93 (m, 4 H), 3.90 (s, 2 H), 5.53 (s, 1 H), 5.74 (br. s, 1 H, exchanges with D_2O), 5.86 (s, 1 H); ^{13}C NMR (75.4 MHz) δ 22.0, 26.1, 28.4, 37.0, 68.0, 72.1, 77.9, 119.6, 143.7, 161.8; GC−MS (70 eV) *m*/*z* 235 (M^+, 1), 206 (11), 195 (47), 194 (26), 181 (55), 180 (100), 168 (19), 166 (44), 152 (31), 139 (34), 126 (80), 55 (29), 41 (21); FT-IR (film, cm^{-1}) 3382, 2934, 2856, 1648 (s, C═N), 1599, 1364, 1191, 1121, 976, 935. Anal. Calcd for $C_{13}H_{21}NO_2$: C, 69.92; H, 9.48; N, 6.27. Found: C, 70.20; H, 9.80; N 5.95.

3-Ethyl-2-(4,4-dimethyl-2-oxazolin-2-yl)-1-penten-3-ol (6c): yellow oil; 78%; ^{1}H NMR (300 MHz) δ 0.84 (t, J = 7.41 Hz, 6 H), 1.29 (s, 6 H), 1.72 (q, J = 7.41 Hz, 4 H), 3.91 (s, 2 H), 5.43 (s, 1 H), 6.02 (s, 1 H), 6.20 (br. s, 1 H, exchanges with D_2O); ^{13}C NMR (75.4 MHz) δ 8.37, 8.49, 28.3, 28.5, 29.9, 32.1, 68.0, 71.5, 77.8, 121.7, 139.6, 162.1; GC−MS (70 eV) *m*/*z* 194 (M^+ − 17, 2), 183 (12), 182 (100), 154 (44), 110 (47), 73 (40), 57 (16), 55 (19); FT-IR (film, cm^{-1}) 3359, 2962, 2931, 1645 (s, C═N), 1599, 1463, 1365, 1261, 1099, 977. Anal. Calcd for $C_{12}H_{21}NO_2$: C, 68.21; H, 10.02; N, 6.63. Found: C, 68.58; H, 10.25; N 6.58.

1-Cyclohexyl-2-(4,4-dimethyl-2-oxazolin-2-yl)-2-propen-1-ol (6d): colorless oil; 71%; ^{1}H NMR (300 MHz) δ 0.81−1.41 (m, 6 H), 1.24 (s, 3 H), 1.27 (s,3 H), 1.46−1.88 (m, 4 H), 2.07−2.09 (m, 1 H), 3.85−3.91 (m, 3 H), 4.59 (br. s, 1 H, exchanges with D_2O), 5.40 (d, J = 1.2 Hz, 1 H), 5.84 (d, J = 1.2 Hz, 1 H); ^{13}C NMR (125 MHz) δ 26.0, 26.1, 26.4, 28.0, 28.2, 29.2, 29.9, 43.0, 67.6, 77.7, 79.3, 121.9, 137.0, 161.0; GC−MS (70 eV) *m*/*z* 219 (M^+ − 18, 16), 204 (6), 176 (5), 154 (100), 140 (15), 55 (20), 41 (10); FT-IR (film, cm^{-1}) 3385, 2961,2920, 2857, 1654 (s, C═N), 1602, 1451, 1367, 1120, 1034. Anal. Calcd for $C_{14}H_{23}NO_2$: C, 70.85; H, 9.77; N, 5.90. Found: C, 71.15; H, 10.02; N 5.90.

4-Methyl-2-(4,4-dimethyl-2-oxazolin-2-yl)-1-penten-3-ol (6e): colorless oil; 71%; ^{1}H NMR (300 MHz) δ 0.80 (d, J = 6.7 Hz, 3 H), 0.99 (d, J = 6.7 Hz, 3 H), 1.26 (s, 3 H), 1.29 (s, 3 H), 1.85−1.98 (m, 1 H), 3.84−3.95 (m, 3 H), 4.63 (br. s, exchanges with D_2O, 1 H), 5.46 (dd, ^2J = 1.4 Hz, ^4J = 0.9 Hz, 1 H), 5.87 (d, J = 1.4 Hz, 1 H); ^{13}C NMR (75.4 MHz) δ 18.9, 19.9, 28.3, 28.5, 33.7, 67.9, 68.1, 77.9, 80.3, 122.3, 137.5, 161.3; GC−MS (70 eV) *m*/*z* 197 (M^+, 1), 180 (10), 179 (12), 154 (100), 140 (7), 125 87), 83 (18), 73 (23), 55 (17), 41 (10); FT-IR (film cm^{-1}) 3398, 2969, 2930, 2873, 1653 (s, C═N), 1602, 1464, 1366, 1041, 972. Anal. Calcd for $C_{11}H_{19}NO_2$: C, 66.97; H, 9.71; N, 7.10. Found: C, 66.96, H, 9.80, N, 7.14.

3-(4,4-Dimethyl-2-oxazolin-2-yl)-2-phenyl-3-buten-2-ol (6f): colorless oil; 42%; ^{1}H NMR (300 MHz) δ 0.84 (s, 3 H), 1.19 (s, 3 H), 1.62 (s, 3 H), 3.77 (s, 2 H), 5.66 (br. s, 1 H, exchanges with D_2O), 5.98 (s, 1 H), 6.54 (s, 1 H), 7.10−7.30 (m, 3 H), 7.37−7.40 (m, 2 H); ^{13}C NMR (75.4 MHz) δ 28.0, 28.1, 29.1, 67.9, 75.9, 78.1, 121.0, 125.2, 126.7, 127.9, 141.7, 147.5, 161.7; GC−MS (70 eV) *m*/*z* 245 (M^+, 100), 244 (23), 230 (91), 202 (43), 168 (53), 158 (53), 154 (27), 130 (33), 125 (61), 105 (36), 77 (31), 55 (25), 43 (44); FT-IR (film, cm^{-1}) 3346, 3060, 2980, 2940, 1687 (s, C═N), 1658, 1603, 1365, 1131, 977, 934, 766, 703. Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.68; H, 8.02; N 5.70.

2-Methyl-3-(4,4-dimethyl-2-oxazolin-2-yl)-3-buten-2-ol (6h): colorless oil; 13%; ^{1}H NMR (500 MHz) δ 1.31 (s, 6 H), 1.45 (s, 6 H), 3.94 (s, 2 H), 5.60 (d, J = 0.7 Hz, 1 H), 5.85 (d, J = 0.7 Hz, 1 H), 6.03 (br s, 1 H, exchanges with D_2O); ^{13}C NMR (75.4 MHz) δ 27.7, 28.7, 67.3, 71.0, 77.3, 118.7, 142.4, 161.0; GC−MS (70 eV) *m*/*z* 168 (M^+ − 15, 100), 140 (34), 125 (14), 110 (10), 96 (23), 73 (39), 55 (17), 43 (14). 3385, 2960, 2925,2848, 1646 (s, C═N), 1601, 1459, 1257, 1094. Anal. Calcd for $C_{10}H_{17}NO_2$: C, 65.54; H, 9.35; N, 7.64. Found: C, 65.83; H, 9.63; N 7.44.

2-(4,4-Dimethyl-2-oxazolin-2-yl)-3-phenyl-3-buten-2-ol (7a): colorless oil; 89%; ^{1}H NMR (300 MHz) δ 1.10 (s, 3 H), 1.20 (s, 3 H), 1.65 (s, 3 H), 3.28 (br. s, 1 H, exchanges with

D_2O), 3.90 and 3.98 (2 × d, AB system, J = 8.1 Hz, 2 H), 5.23 (d, J = 0.7 hz, 1 H), 5.51 (d, J = 0.7 Hz, 1 H), 7.23−7.36 (m, 5 H); ^{13}C NMR (75.4 MHz) δ 25.5, 28.2, 28.3, 67.2, 73.2, 80.9, 115.6, 127.6, 127.9, 128.8, 140.2, 151.8, 168.9; GC−MS (70 eV) m/z 245 (M^+, 1), 229 (26), 228 (100), 200 (11), 157 (9), 91 (7), 77 (10), 43 (9); FT-IR (film, cm^{-1}) 3461, 3044, 2968, 2928, 1660 (s, C═N), 1490, 1460, 1366, 1283, 1097, 777, 702.

2-(4,4-Dimethyl-2-oxazolin-2-yl)-3-propyl-3-buten-2-ol (7b): colorless oil; 76%; ^{1}H NMR (300 MHz) δ 0.91 (t, J = 7.3 Hz, 3 H), 1.27 (s, 6 H), 1.42−1.52 (m, 2 H), 1.54 (s, 3 H), 1.99−2.08 (m, 2 H), 3.30 (br. s, 1 H, exchanges with D_2O), 3.99 and 4.02 (2 × d, AB system, J = 8.1 Hz, 2 H), 4.95 (d, J = 0.7 Hz, 1 H), 5.22 (d, J = 0.7 Hz, 1 H); ^{13}C NMR (125 MHz) δ 14.2, 21.7, 25.1, 28.3, 28.4, 33.0, 67.3, 73.5, 80.8, 110.2, 151.0, 169.2; GC−MS (70 eV) m/z 211 (M^+, 1), 194 (100), 166 (9), 143 (8), 69 (8), 55 (8), 43 (14); FT-IR (film, cm^{-1}) 3483, 2962, 2928, 2873, 1660 (s, C═N), 1464, 1366, 1284, 1137, 1099, 974, 905. Anal. Calcd for $C_{12}H_{21}NO_2$: C, 68.21; H, 10.02; N, 6.63. Found: C, 68.49; H, 10.29; N 6.58.

3-Methyl-2-(4,4-dimethyl-2-oxazolin-2-yl)-3-buten-2-ol (7c): colorless oil; 81%; ^{1}H NMR (500 MHz) δ 1.26 (s, 6 H), 1.52 (s, 3 H), 1.75−1.76 (m, 3 H), 3.35 (br. s, 1 H, exchanges with D_2O), 3.99 and 4.01 (2 × d, AB system, J = 8.3 Hz, 2H), 4.91−4.93 (m, 1 H), 5.10−5.11 (m, 1 H); ^{13}C NMR (75.4 MHz) δ 18.5, 24.4, 28.1, 67.0, 73.0, 80.6, 111.5, 146.7, 168.7; GC−MS (70 eV) m/z 166 (M^+ − 17, 100), 138 (20), 112 (9), 84 (10), 69 (19), 55 (11), 43 (19), 41 (15); FT-IR (film, cm^{-1}) 3387, 2971, 2927, 1657 (s, C═N), 1462, 1367, 1287, 1139, 1108, 973. Anal. Calcd for $C_{10}H_{17}NO_2$: C, 65.54; H, 9.35; N, 7.64. Found: C, 65.85; H, 9.68; N 7.60.

2-(4,4-Dimethyl-2-oxazolin-2-yl)-1,1,3-triphenyl-2-propen-1-ol (8a) (*Z*): white solid; mp 140−141 °C (Et_2O); 80%; ^{1}H NMR (300 MHz) δ 0.95 (s, 6 H), 3.62 (s, 2 H), 6.35 (s, 1 H), 6.89 (br. s, 1 H, exchanges with D_2O), 7.20−7.57 (m, 15 H); ^{13}C NMR (75.4 MHz) δ 27.5, 67.4, 78.6, 82.5, 127.4, 128.0, 128.1, 128.2, 128.5, 128.8, 134.8, 136.1, 137.5, 144.6, 163.5; GC−MS (70 eV) m/z 383 (M^+, 94), 382 (100), 366 (13), 364 (12), 306 (10), 278 (36), 234 (13), 201 (52), 200 (28), 186 (19), 156 (14), 105 (99), 77 (55); FT-IR (film, cm^{-1}) 3325, 3059, 2967, 2926, 1659 (s, C═N), 1609, 1449, 1387, 1201, 1022, 753, 700. Anal. Calcd for $C_{26}H_{25}NO_2$: C, 81.43; H, 6.57; N, 3.65. Found: C, 81.15; H, 6.81; N 3.70. **(*E*):** white solid; mp 140−142 °C; 32%; ^{1}H NMR (300 MHz) δ 1.00 (s, 3 H), 1.07 (s, 3 H) 3.63 and 3.67 (2 × d, AB system, J = 8.2 Hz, 2 H), 6.48 (s,1 H), 6.82 (br. s, 1 H, exchanges with D_2O), 7.11−7.41 (m, 10 H), 7.48−7.51 (m, 3 H), 7.60−7.63 (m, 2 H); ^{13}C NMR (75.4 MHz) δ 27.5, 27.6, 67.4, 78.5, 83.5, 124.2, 126.7, 127.7, 127.9, 128.2 128.6, 128.8, 129.2, 132.1, 135.8, 136.4, 141.8, 142.9, 143.4, 163.2; GC−MS (70 eV) m/z 366 (M^+ − 17, 1), 262 (28), 260 (32), 201 (16), 200 (48), 186 (70), 183 (27), 181 (16), 152 (12), 130 (22), 115 (23), 105 (100), 77 (48), 76 (16), 51 (16); FT-IR (film, cm^{-1}) 3280, 3059, 2965, 2926, 2855, 1656 (s, C═N), 1608, 1449, 1260, 1201, 1030, 754, 700. Anal. Calcd for $C_{26}H_{25}NO_2$: C, 81.43; H, 6.57; N, 3.65. Found: C, 81.76; H, 6.23; N 3.79.

3-Ethyl-2-(4,4-dimethyl-2-oxazolin-2-yl)-1-phenyl-1-penten-3-ol (8b) (*Z*): white solid; mp 120−121 °C (Et_2O); 85%; ^{1}H NMR (300 MHz) δ 0.96 (t, J = 7.4 Hz, 6 H), 1.27 (s, 6 H), 1.64−1.87 (m, 4 H), 3.57 (br s, 1 H, exchanges with D_2O), 3.82 (s, 2 H), 6.85 (s, 1 H), 7.20−7.32 (m, 5 H); ^{13}C NMR (75.4 MHz) δ 8.2, 28.1, 31.9, 67.8, 77.3, 78.6, 127.9, 128.2, 128.6, 133.3, 134.5, 136.6, 162.2; GC−MS (70 eV) m/z 287 (M^+, 29), 286 (100), 258 (46), 187 (11), 186 (67), 130 (30), 115 (7), 57 (8); FT-IR (film, cm^{-1}) 3415, 3024, 2969, 2927, 1664, 1622 (s, C═N), 1461, 1365, 968, 752, 697. Anal. Calcd for $C_{18}H_{25}NO_2$: C, 75.22; H, 8.77; N, 4.87. Found: C, 75.09; H, 9.09; N 4.87. **(*E*):** white solid; mp 121−123 °C; 21%; ^{1}H NMR (300 MHz) δ 0.86 (t, J = 7.3 Hz, 6 H), 1.34 (s, 6 H), 1.43−1.61 (m, 4 H), 3.95 (s, 2 H), 6.62 (br., 1 H, exchanges with D_2O), 7.16−7.34 (m, 5 H), 7.61 (s, 1 H); ^{13}C NMR (75.4 MHz) δ 8.5, 28.4, 34.3, 68.2, 77.7, 78.2, 127.3, 127.4, 128.1, 133.9, 136.7, 138.0, 163.7; GC−MS (70 eV) m/z 287 (M^+, 6), 286 (26), 258 (97), 230 (17), 187 (16), 186 (100), 130 (42), 115 (9), 57 (11); FT-IR (film, cm^{-1}) 3287, 3052, 2961, 2927, 1632 (s, C═N), 1608, 1462, 1368, 1292, 1017, 969, 755, 701. Anal. Calcd for $C_{18}H_{25}NO_2$: C, 75.22; H, 8.77; N, 4.87. Found: C, 74.95; H, 8.98; N 4.90.

2-Methyl-2-(4,4-dimethyl-2-oxazolin-2-yl)-4-phenyl-3-buten-2-ol (8c) (*Z*): colorless oil; 80%; ^{1}H NMR (300 MHz) δ 1.31 (s, 6 H), 1.49 (s, 6 H), 3.83 (s, 2 H), 4.51 (br. s, 1 H, exchanges with D_2O), 6.94 (s, 1 H), 7.24−7.30 (m, 5 H); ^{13}C NMR (125 MHz) δ 28.2, 28.9, 67.8, 72.3, 78.8, 128.1, 128.2, 128.6, 131.5, 136.3, 136.5, 162.5; GC−MS (70 eV) m/z 259 (M^+, 20), 258 (100), 244 (4), 186 (20), 172 (22), 130 (13), 43 (6); FT-IR (film, cm^{-1}) 3382, 3059, 3026, 2971, 2929, 1667 (s, C═N), 1627, 1462, 1365, 1180, 1021, 960, 753, 698. Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16; N, 5.40. Found: C, 74.36; H, 8.20; N 5.38. **(*E*):** colorless oil; 30%; ^{1}H NMR (300 MHz) δ 1.24 (s, 6 H), 1.27 (s, 6 H), 3.95 (s, 2 H), 6.69 (br. s, 1 H, exchanges with D_2O), 7.12−7.25 (m, 5 H), 7.54 (s, 1 H); ^{13}C NMR (125 MHz) δ 27.9, 28.2, 67.7, 72.2,?77.6, 127.1, 127.4, 127.9, 136.2, 136.3, 137.8 162.8; GC−MS (70 eV) m/z 259 (M^+, 21), 258 (77), 244 (90), 201 (23), 186 (25), 172 (100), 130 (37), 43 (14); FT-IR (film, cm^{-1}) 3358, 3059, 2970, 2929, 1666 (s, C═N), 1613, 1366, 1170, 735, 700 Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16; N, 5.40. Found: C, 74.32; H, 8.30; N 5.40.

4,4-Dimethyl-2-(4,4-dimethyl-2-oxazolin-2-yl)-1-phenyl-1-penten-3-ol (8d) (*Z*): white solid; mp 100−102 °C (Et_2O); 81%; ^{1}H NMR (300 MHz) δ 0.96 (s, 9 H), 1.27 (s, 3 H), 1.35 (s, 3 H), 3.77 and 3.82 (2 × d, AB system, J = 8.2 Hz, 2 H), 4.08 (s, 1 H), 4.80 (br. s, exchanges with D_2O, 1 H), 6.80 (s, 1 H), 7.24−7.33 (m, 5 H); ^{13}C NMR (75.4 MHz) δ 26.5, 27.8, 28.5, 36.9, 67.7, 78.7, 84.1, 128.1, 128.2, 128.5, 129.1, 136.2, 137.4, 162.5; GC−MS (70 eV) m/z 287 (M^+, 16), 286 (66), 231 (28), 230 (100), 158 (80), 140 (25), 130 (12), 103 (18), 77 (9); FT-IR (film cm^{-1}) 3307, 3061, 2964, 2930, 2871, 1661 (s, C═N), 1612, 1463, 1365, 1194, 969, 751, 699. Anal. Calcd for $C_{18}H_{25}NO_2$: C, 75.22; H, 8.77; N, 4.87. Found: C, 75.44; H, 9.03;N, 4.93. **(*E*):** white solid; mp 100−102 °C; 9%; ^{1}H NMR (500 MHz) δ 0.72 (s, 9 H), 1.27 (s, 3 H), 1.35 (s, 3 H), 3.91 and 3.97 (2 × d, AB system, J = 8.0 Hz, 2 H), 4.05 (s, 1 H), 4.90 (br s, exchanges with D_2O, 1 H), 7.22−7.32 (m, 5 H), 7.46 (s, 1 H); ^{13}C NMR (125 MHz) δ 26.7, 27.9, 28.0, 38.0, 68.0, 76.1, 77.6, 127.7, 128.7, 129.0, 136.2, 138.0, 162.8; GC−MS (70 eV) m/z 287 (M^+, 1), 231 (23), 230 (100), 159 (14), 158 (61), 140 (18), 103 (14), 77 (7); FT-IR (film cm^{-1}) 3344, 3028, 2964, 2930, 2871, 1642 (s, C═N), 1612, 1463, 1365, 1190, 1053, 756, 700. Anal. Calcd for $C_{18}H_{25}NO_2$: C, 75.22; H, 8.77; N, 4.87. Found: C, 75.50; H, 8.90; N, 4.90.

1-Cyclohexyl-3-(4,4-dimethyl-2-oxazolin-2-yl)-3-phenyl-2-propen-1-ol (8e) (*Z*): colorless oil; 80%; ^{1}H NMR (300 MHz) δ 0.85−1.22 (m, 5 H), 1.28 (s, 3 H), 1.33 (s, 3 H), 1.42−1.56 (m, 1 H), 1.59−1.82 (m, 4 H), 2.06−2.18 (m, 1 H), 3.82 and 3.87 (2 × d, AB system, J = 8.2 Hz, 2 H), 3.97 (d, J = 8.0 Hz, 1 H), 4.25 (br. s, exchanges with D_2O, 1 H), 6.78 (s, 1 H), 7.22−7.32 (m, 5 H); ^{13}C NMR (75.3 MHz) δ 26.1, 26.2, 26.4, 28.0, 28.1, 29.1, 29.8, 43.1, 67.2, 78.4, 81.0, 128.0, 128.6, 130.5, 135.6, 135.8, 161.9; GC−MS (70 eV) m/z 313 (M^+, 21), 312 (88), 230 (100), 158 (57), 140 (14), 103 (11), 55 (10); FT-IR (film cm^{-1}) 3254, 3022, 1667 (s, C═N), 1614, 1449, 1366, 1193, 752, 697. Anal. Calcd for $C_{20}H_{27}NO_2$: C, 76.64; H, 8.68; N, 4.47. Found: C, 77.00; H, 8.98; N, 4.49. **(*E*):** colorless oil; 9%; ^{1}H NMR (300 MHz) δ 0.85−1.22 (m, 5 H), 1.23 (s, 3 H), 1.25 (s, 3 H), 1.42−1.85 (m, 5 H), 2.04−2.16 (m, 1 H), 3.93 and 4.01 (2 × d, AB system, J = 8.2 Hz, 2 H), 4.43 (d, J = 8.0 Hz, 1 H), 4.75 (br. s, exchanges with D_2O, 1 H), 7.22−7.32 (m, 5 H), 7.41 (s, 1 H); ^{13}C NMR (75.4 MHz) δ 26.0, 26.2, 26.3, 28.0, 28.3, 29.6, 29.7, 43.8, 67.8, 73.6, 77.5, 127.9, 128.4, 129.0, 130.5, 130.7, 135.5, 136.7, 162.0; GC−MS (70 eV) m/z 313 (M^+, 2), 312 (8), 252 (17), 230 (100), 158 (38), 140 (10), 103 (8), 55 (10); FT-IR (film cm^{-1}) 3368, 3022, 2964, 2927, 2852, 1648 (s, C═N), 1610, 1450, 1365, 762, 701. Anal. Calcd for $C_{20}H_{27}NO_2$: C, 76.64; H, 8.68; N, 4.47. Found: C, 76.70; H, 8.87; N, 4.49.

3-Methyl-2-(4,4-dimethyl-2-oxazolin-2-yl)-1-phenyl-3-buten-2-ol (9): colorless oil; 48%; ^{1}H NMR (300 MHz) δ 0.92 (s, 3 H), 1.18 (s, 3 H), 1.86 (s, 3 H), 3.06 (d, J = 13.2 Hz, 1 H),

3.25 (d, J = 13.2 Hz, 1 H), 3.40 (br. s, 1 H, exchanges with D_2O), 3.96 and 4.01 (2 × d, AB system, J = 8.0 Hz, 2 H), 5.02 (s, 1 H), 5.22 (s, 1 H), 7.12−7.24 (m, 5 H); ^{13}C NMR (75.4 MHz) δ 19.0, 28.1, 31.0, 42.5, 66.6, 75.4, 80.8, 112.5, 126.5, 127.7, 130.6, 135.7, 145.7, 167.2; GC−MS (70 eV) m/z 259 (M^+, 1), 242 (3), 168 (100), 91 (24), 73 (20), 69 (37), 41 (15); FT-IR (film, cm^{-1}) 3473, 3088, 3063, 3031, 2970, 2924, 1669 (s, C═N), 1455, 1290, 1100, 735, 700. Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16; N, 5.40. Found: C, 74.44; H, 8.38; N 5.25.

Acknowledgment. This work was carried out under the framework of the National Project "Stereoselezione in Sintesi Organica. Metodologie ed Applicazioni" supported by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST, Rome), by the University of Bari and CNR (Rome) and by C.I.N.M.P.I.S. (Consorzio Interuniversitario Nazionale Metodologie e Processi Innovativi di Sintesi).

Supporting Information Available: ^{13}C NMR spectra for compounds **2c**,**i**,**j**, **4b**,**c**, (1*R**,2*S**)-**4d**, (1*R**,2*R**)-**4d**, (1*R**,2*R**)-**4e**, **5c**−**e**, and **7a**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO026234D