cooled to −15 °C. The reaction was stirred at −15 °C for 5 min and then at 0 °C for 15 min before water was added. After stirring for 24 h, the methylene chloride layer was separated and the aqueous layer extracted with two 50-mL portions of methylene chloride. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated to give 3.0 g (50%) of tetrakis(mesylate) **18** with the two-carbon side chain (cf. **11**) after recrystallization from hot benzene and several drops of methylene chloride, mp 149–150 °C. ^{1}H NMR ($CDCl_3$): δ 2.45 (s, 6 H, $ArOSO_2CH_3$), 3.0 (s, 6 H, SO_2CH_3), 3.16–3.32 (m, 2 H, diastereotopic –CH of $ArCH_2$), 3.32–3.48 (m, 2 H, diastereotopic –CH of $ArCH_2$), 4.56 (m, 4 H, OCH_2), 7.40 (m, 6 H, Ar H). Anal. Calcd for $C_{20}H_{26}O_{12}S_4$: C, 40.95; H, 4.47; S, 21.86. Found: C, 40.73; H, 4.35; S, 21.48.

3,3′-Bis(2-((methylsulfonyl)oxy)ethyl)-2,2′-bis(benzyloxy)biphenyl (23). The same procedure was used as for the preparation of **6** and yielded 6.35 g (86%) of bis(mesylate) **23** which was purified by flash chromatography using 2:3 ethyl acetate–hexanes: ^{1}H NMR ($CDCl_3$) δ 3.78 (s, 6 H, SO_2CH_3), 3.10 (t, 4 H, $ArCH_2$), 4.34 (t, 4 H, CH_2), 4.50 (s, 4 H, OCH_2Ar), 7.0–7.43 (m 16 H, Ar H). Anal. Calcd for $C_{32}H_{34}O_8S_2$: C, 62.93; H, 5.61; S, 10.50. Found: C, 62.56; H, 5.61; S, 10.61.

3,3′-Bis[2-(1-pyrazolyl)ethyl]-2,2′-biphenol (25). Sodium pyrazolate was generated by the addition of 0.58 g (8.5 mmol) of pyrazole in 10 mL of DMF to a slurry of 0.323 g (13.5 mmol) of NaH in 30 mL of DMF under dinitrogen. After 2 h, 2.6 g (4.3 mmol) of the bis(mesylate) **23** in 10 mL of DMF was added dropwise to the sodium pyrazolate solution. The reaction was stirred for 24 h, treated with 150 mL of water, and extracted with three 50-mL portions of toluene. The combined toluene layers were washed with water, dried over $MgSO_4$, filtered, and concentrated. After flash chromatography with 1:1 ethyl acetate–hexanes, 1.0 g (42%) of the protected product **24** was obtained as an oil. ^{1}H NMR ($CDCl_3$): δ 3.15 (t, 4 H, $ArCH_2$), 4.20 (t, 4 H, NCH_2), 4.40 (s, 4 H, OCH_2Ar), 6.75 (t, 2 H, Pz H), 6.95–7.30 (m, 18 H, Ar H, Pz H), 7.35 (d, 2 H, Pz H).

Hydrogenolysis was carried out by the same experimental procedure described for **9**. A tan solid was obtained which was soluble in hot ethanol. Attempts at recrystallization lead to decomposition and the solid **25** was purified by high-vacuum sublimation at 175 °C (3 × 10^{-2} torr); mp 168–169 °C. ^{1}H NMR ($CDCl_3$): δ 3.45 (t, 4 H, $ArCH_2$–), 4.47 (t, 4 H, NCH_2–), 6.23 (t, 2 H, Pz H), 6.93–7.19 (m, 6 H, Ar H), 7.32 (, 2 H, Pz H), 7.54 (d, 2 H, Pz H), 8.88 (s, 2 H, ArOH). Anal. Calcd for $C_{22}H_{22}N_4O_2$: C, 70.57; H, 5.92; N, 14.96. Found: C, 69.64; H, 5.32; N, 14.50. The compound is somewhat unstable and decomposes to unidentified products upon standing. This may account for the poor analytical results.

3,3′-Bis[2-(methylthio)ethyl]-2,2′-bis(benzyloxy)biphenyl (26). The same experimental procedure was followed as reported for the synthesis of **7**. Recrystallization from ethanol–pentane yielded 2.0 g (75%) of the thioether **26**, mp ~27 °C. ^{1}H NMR ($CDCl_3$): δ 2.0 (s, 6 H, SCH_3), 2.5–3.1 (m, 8 H, CH_2CH_2), 4.5 (s, 4 H, OCH_2Ar), 7.2 (m, 16 H, Ar H). Anal. Calcd for $C_{32}H_{34}O_2S_2$: C, 74.66; H, 6.66; S, 12.46. Found: C, 74.66; H, 7.30; S, 11.03. Compound **26** was difficult to purify because of its low melting point.

3,3′-Bis[2-(methylthio)ethyl]-2,2′-biphenol (27). Two milliliters of ethanethiol was added to 0.26 g (0.5 mmol) of thioether **26** followed by the dropwise addition of 2.0 mL of $BF_3{\cdot}OEt_2$. The reaction mixture was stirred for 24 h in a stoppered flask. Water was added and the mixture extracted with methylene chloride. The combined organic layers were washed with saturated aqueous NaCl, dried over $MgSO_4$, and concentrated. The resulting oil was purified by flash chromatography with 3:1 methylene chloride–hexanes. The oil from chromatography solidified and was crystallized from methanol–benzene, mp ~28 °C. ^{1}H NMR ($CDCl_3$): δ 2.16 (s, 6 H, SCH_3), 2.80 (t, 4 H, $ArCH_2$), 3.0 (t, 4 H, SCH_2), 5.56 (br s, 2 H, –OH), 6.88–7.30 (m, 6 H, Ar H). Anal. Calcd for $C_{18}H_{22}O_2S_2$: C, 64.64; H, 6.63; S, 19.17. Found: C, 64.80; H, 6.93; S, 18.7.

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Enantioselective Preparation of 3-Substituted-4-pentenoic Acids via the Claisen Rearrangement

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Asymmetric C–C bond formation via the diastereoselective aza-Claisen rearrangement of *N*-allylketene *N*,*O*-acetal **4** is described. The starting materials, allylic alkylating agent **1** and optically pure oxazoline **2**, are easily prepared and, in a one-pot procedure, generate rearranged oxazolines **5** in 52–94% diastereomeric excess. The overall chemical yields for **2** → **5** range from 51 to 78%. The aza-Claisen rearrangement (**4** → **5**) proceeds with excellent *N*,*O*-acetal face selectivity and with good to excellent chair selectivity. Hydrolysis of rearranged oxazoline **5** completes an enantioselective synthesis of 3-substituted pent-4-enoic acids.

Achieving absolute stereocontrol in the construction of acyclic systems is a particularly challenging goal in organic synthesis. While the Claisen rearrangement and its variants have been gainfully employed in addressing this challenge, all but a few of these Claisen protocols are self-immolative[1] at the original chiral center.[2] As one approach to nonimmolative asymmetric induction, we recently reported the diastereoselective chiron-mediated[3] aza-Claisen rearrangement of *N*-allylketene *N*,*O*-acetals.[4] The methodology developed in that work, which was based on the pioneering aza-Claisen work of Ireland and Willard,[5] provides a general, highly enantioselective preparation of 2-substituted-4-pentenoic acids by C(α) asymmetric in-

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[1] Mislow, K. "Introduction to Stereochemistry"; Benjamin: New York, **1965**; p. 131.

[2] For example, see: (a) Ziegler, F. E.; Thottathil, J. K. *Tetrahedron Lett.* **1982**, *23*, 3531. (b) Kurth, M. J.; Yu, C.-M. *Tetrahedron Lett.* **1984**, *25*, 5003. (c) Kurth, M. J.; Yu, C.-M. *J. Org. Chem.*, in press.

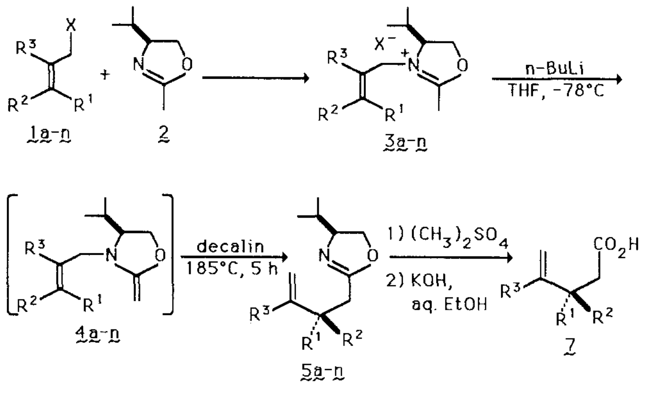
[3] Hanessian, S. In "Total Synthesis of Natural Products: The 'Chiron' Approach"; Baldwin, J. E., Ed.; Pergamon Press Ltd.: New York, **1983**; p. 21.

[4] Kurth, M. J.; Decker, O. H. W.; Hope, H.; Yanuck, M. D. *J. Am. Chem. Soc.* **1985**, *107*, 443.

[5] Ireland, R. E.; Willard, A. K. *J. Org. Chem.* **1974**, *39*, 421.

0022-3263/85/1950-5769$01.50/0

Scheme I. General Enantioselective Method



duction. We demonstrated that the excellent C(α) asymmetric induction observed in the rearrangement is a consequence of (i) nearly complete (*Z*)-*N*,*O*-acetal olefin selectivity, (ii) high *N*,*O*-acetal (C(α)-*re*/*si*) face selectivity, and (iii) nonepimerization under the conditions of the reaction.

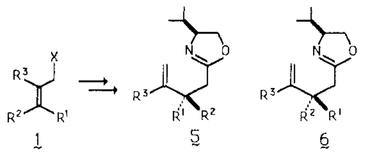
We now extend that methodology to include an enantioselective preparation of 3-substituted-4-pentenoic acids by C(β) asymmetric induction, as depicted in Scheme I. Inspection of **4** → **5**/**6** reveals three parameters which collectively determine rearrangement diastereoselectivity. They are (i) *E*/*Z* isomeric purity of the allyl olefin moiety, (ii) transition-state *N*,*O*-acetal face selectivity, and (iii) transition-state chair/boat conformation selectivity. Indeed, the latter parameter provides the most significant difference between C(α) and C(β) asymmetric induction: C(α) being independent of chair/boat selectivity. Herein we report our C(β) induction studies.

Results and Discussion

Preparation of *N*-Allyloxazolinium Salts 3. Enantiomerically pure oxazoline **2** was N-allylated with a variety of allylic bromide and sulfonate alkylating agents. The reactivity of allylic bromides in this reaction was found to depend upon their degree of C(3) olefin substitution. 3,3-Disubstituted bromides such as geranyl bromide (**1i**),[6] neryl bromide (**1j**),[6] and (2-methyl-1-cyclopentenyl)methyl bromide (**1n**) condensed with **2** to form oxazolinium salts in high yield when the neat reactants were stirred at room temperature overnight. In contrast, 3-monosubstituted allylic bromides such as (*E*)-1-bromo-4-methylpent-2-ene[7] react sluggishly, giving 45% reaction after 4 days at room temperature. Allyl bromide itself failed to react appreciably with **2**, even when stirred at elevated temperatures for several days.[8]

Fortunately, it was found that 3-monosubstituted mesylate and tosylate esters readily N-allylate oxazolines. Allylic tosylates were generally more convenient in this condensation since the corresponding mesylates often proved difficult to isolate. These tosylate esters are generally unstable and were therefore used without purification. While excess tosyl chloride interferes in the subsequent N-allylation step, excess allylic alcohol, even up to 1 full equiv, is not detrimental. The tosylate of allyl alcohol, which is easily prepared and distilled, readily N-allylates a variety of oxazolines.[4] In contrast, difficulties in isolating 3,3-disubstituted allylic mesylate and tosylate esters preclude their use in the formation of *N*-allyloxazolinium salts. Thus, judicious choice of allylating agent, bromide or sulfonate, provides access to oxazolinium salts covering the entire range of substitution at C(3) in the allylic moiety.

Table I. C(β) Diastereoselective Aza-Claisen Rearrangements



entry	X	R^1	R^2	R^3	**5**:**6**[a]	yield[b]
A	OTs	H	CH_3	H	81:19	76%
B	OTs	CH_3	H	H	87:13[c]	75%
C	OTs	H	CH_3	CH_3	85:15	57%
D	OTs	CH_3	H	CH_3	90:10[c]	61%
E	OTs	H	$CH(CH_3)_2$	H	76:24	71%
F	OTs	$CH(CH_3)_2$	H	H	89:11[c]	21%
G	OMs	H	CH_2OCH_2Ph	H	81:19	78%
H	OMs	CH_2OCH_2Ph	H	H	85:15[c]	32%
I	Br	CH_3	$CH_2CH_2CH{=}C(CH_3)_2$	H	87:13[c]	54%
J	Br	$CH_2CH_2CH{=}C(CH_3)_2$	CH_3	H	–:–	0%
K	OTs	H	$\vdash CH_2CH_2CH_2CH_2 \dashv$		90:10	53%
L	OTs	H	$\vdash C(CH_3)_2CH_2CH_2CH_2 \dashv$		93:7	57%
M	OTs	H	$\vdash CH_2CH_2CH_2C(CH_3)_2 \dashv$		97:3	51%
N	Br	CH_3	$\vdash CH_2CH_2CH_2 \dashv$		90:10	57%

[a] These diastereomer ratios were determined by high-pressure liquid chromatography on **5**/**6** and/or 360-MHz ^1H NMR on the *N*-methyloxazolinium salts of **5**/**6**. [b] Refers to the overall chromatographed yield of **5**/**6** from **1**. [c] Corrected by from 1 to 3% to reflect the isomeric purity of **1**. For uncorrected ratios, see Experimental Section. Note that the capitol letter designations A-N are equivalent to the a-n used in the text and in Scheme I.

***N*-Allylketene *N*,*O*-Acetals 4: Preparation and Rearrangement.** The *N*,*O*-acetal moiety of **4** was readily introduced by *n*-butyllithium neutralization of a THF solution of **3** at −78 °C. Since these hygroscopic oxazolinium salts were neutralized without purification, it was most convenient to add the indicator 1,10-phenanthroline and then add *n*-butyllithium to a rust-colored endpoint.[9] As was demonstrated in our C(α) study,[4] a slight excess of *n*-butyllithium is not detrimental. The subsequent rearrangement step was effected by heating a decalin solution of **4** to 185 °C for 5 h. Oxazolines **5** were thus obtained in 60–90% diastereomeric excess (de) and in 50–80% purified overall yield from **2** (see Table I).

Factors Determining Rearrangement Diastereoselectivity.[10] The diastereoselectivity of rearrangement **4** → **5**/**6** is contingent on the *E*/*Z* stereochemistry of the starting allyl moiety in **4**. Therefore, the possibility of *N*-alkylation with either the *E*- or *Z*-allylating agent and subsequent stereochemical stability of the allyl olefin in **3** → **5**/**6** were recognized as critical parameters in C(β) induction. A comparison of entries A and B in Table I illustrates, both (*E*)- and (*Z*)-crotyl tosylate are amenable to the N-allylation/rearrangement sequence depicted in Scheme I. ^1H NMR analyses of the oxazolinium salts derived from these two tosylates (**3a** and **3b**) indicate that, to the limits of detection, there is no olefin geometry crossover in either N-allylation. In each *E*/*Z* system studied, the thermodynamically less stable (*Z*)-allyl moiety resulted in a higher diastereoselectivity than the more stable *E* isomer (cf. entries A/B, C/D, E/F, and G/H in Table I). These observations imply that *E*/*Z* isomerization in **3** → **5**/**6** is insignificant.

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[6] (a) Grieco, P. A.; Masaki, Y. *J. Org. Chem.* **1974**, *39*, 2135. (b) Barnard, D.; Bateman, L. *J. Chem. Soc.* **1950**, 926.

[7] Raucher, S. *Tetrahedron Lett.* **1977**, 3909.

[8] (a) Ireland[5] and Maguet[8b] have reported similar difficulties in the attempted allylation of the dihydrooxazine nucleus. (b) Maguet, M.; Poirier, Y.; Guglielmetti, R. *Bull. Soc. Chim. Fr.* **1978**, 550.

[9] Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.

[10] For a discussion of the factors determining diastereoselectivity in sigmatropic rearrangements, see: Hill, R. K. In "Asymmetric Synthesis"; Morrison, J. D., Ed.; Academic Press: New York, **1984**; Vol. 3B, p 503.

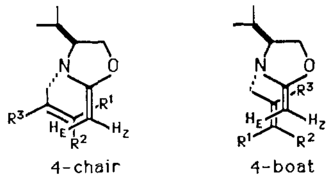


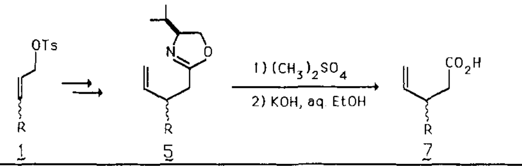
Figure 1. Transition states.

Our C(α) induction studies established that *N,O*-acetal face selectivity is a consequence of rapid nitrogen inversion prior to rearrangement with an anti relationship between the oxazoline C(4)-isopropyl and *N*-allyl substituents favored energetically over the corresponding syn conformation. In C(α) induction, a face selectivity of 97:3 was observed; *N,O*-acetal face selectivity in C(β) induction was expected to closely parallel this result. Although complete quantification of face selectivity in C(β) induction has not been realized, entry M in Table I is consistent with comparable *N,O*-acetal face selectivities in both C(α) and C(β) induction.

While chair/boat transition-state selectivity is of no consequence in C(α) induction, it is the critical parameter in C(β) induction. Indeed the varied diastereoselectivities observed in the present study reflect the impact of chair/boat transition-state selectivity on C(β) induction. The relative stabilities of the transition states in these competing reaction pathways can be deduced by comparing product diastereoselectivity with the steric requirements of substituents R^1, R^2, and R^3 (see Table I). As depicted in Figure 1, the substituents of the nascent C–C bond in transition-state 4-chair are approximately staggered while in transition state 4-boat they are approximately eclipsed. Comparison of entries A, E, and G (*E* olefins) or B, F, and H (*Z* olefins) in Table I indicates that varying the steric bulk of the C(3)-alkyl substituent in the allyl moiety results in no discernable trend. Even 3,3-disubstitution does not significantly improve rearrangement diastereoselectivity (entry 1). However, a consistent enrichment is noted when *E*/*Z* entries A/B, C/D, E/F, and G/H are considered. In each case, the (*Z*)-allyl moiety results in from 4 to 13% greater diastereoselectivity than the (*E*)-allyl moiety. This uptrend appears to be a consequence of a higher chair/boat selectivity for (*Z*)- than for (*E*)-*N*-allylketene *N,O*-acetals: $\Delta\Delta G^{\ddagger}$ (4-chair vs. 4-boat) in the (*Z*)-*N*-allylketene *N,O*-acetal is greater than $\Delta\Delta G^{\ddagger}$ (4-chair vs. 4-boat) in the (*E*)-*N*-allylketene *N,O*-acetal. Unfortunately this improved diastereoselectivity is offset by a corresponding decrease in chemical yield (cf. entries F, H, and J).

Substituent R^3 also influences the chair/boat selectivity of **4** → **5**/**6**. A contrast of acyclic entries A and C or B and D illustrates a 3–4% increase in de for $R^3 = CH_3$ over $R^3 = H$. Cyclohexene methanol derivatives depicted in entries K and M further demonstrate the effects of increasing the steric requirements of R^3. The relative importance of substituents R^2 and R^3 on product diastereoselectivity is clearly delineated in entries L and M. Indeed, we were gratified to find that the allylic substrate employed in entry M resulted in a product de equal to that obtained in our C(α) work (94% de).

Table II. Enantioselective Preparation of Pent-4-enoic Acids



entry	allyl tosylate geometry	R	observed $[\alpha]_D^{20}$	(R)-**7**:(S)-**7**	yield
A	(*E*)	CH_3	-13.0^a	81:19	87%
B	(*Z*)	CH_3	$+14.0^a$	14:86	81%
E	(*E*)	$CH(CH_3)_2$	$+5.0^b$	76:24	85%
F	(*Z*)	$CH(CH_3)_2$	-7.3^b	13:87	78%

[a] See reference 13. [b] See reference 14.

Enantioselective Preparation of Pent-4-enoic Acids. All of the oxazolines prepared in this C(β) study were derived from optically pure L-valinol.[11] Consequently, the diastereomer ratios indicated in Table I give the absolute *R*:*S* ratios for our aza-Claisen products. All that remained was to unambiguously establish the absolute sense of C(β) asymmetric induction. Precedent for rearrangement through a chair transition state[12] via the diastereoface opposite the C(4) isopropyl moiety[4] (Figure 1a) suggested that (*E*)-crotyl alcohol would give rise to (*R*)-3-methylpent-4-enoic[13] acid while (*Z*)-crotyl alcohol would generate (*S*)-3-methylpent-4-enoic acid.[13] As indicated in Table II (entries A and B), chiroptic measurements on these two acids corroborate this transition-state analysis. Likewise, the *E*- and *Z*-geometric isomers of 4-methylpent-2-en-1-ol (Table II, entries E and F) produced, respectively, the (*R*)- and (*S*)-antipodes of 3-(1-methylethyl)pent-4-enoic acid. These assignments were verified by esterification and correlation with the known (*R*)-(+)-ethyl ester.[14] While the oxazoline hydrolyses presented in Table II were effected by a two-step sequence, N-methylation followed by base catalyzed hydrolysis,[15] a simple acid catalyzed hydrolysis is equally effective and allows for recovery of the transient chiron.

Conclusions. We have confirmed the feasibility of C(β) asymmetric induction in the chiron-mediated aza-Claisen rearrangement of *N*-allylketene *N,O*-acetals. The method affords remote stereocontrol, is ammenable to both acyclic and cyclic allylic substrates, provides a versatile enantioselective preparation of C(3) chiral pent-4-enoic acids, and allows for recovery of the chiron. While moderate chair/boat selectivity is shown to be the de limiting transition-state parameter, judicious choice of the allylic substrate can effectively preclude the boat pathway. Studies designed to afford improved chair selectivity, particularly Lewis acid mediated variants, are currently underway.

Experimental Section

General. Elemental analyses were performed by the University of California, Berkeley, Analytical Laboratories. MPLC refers to chromatography done at 10–50 psi through EM Lobar columns packed with LiChroprep Si60 (40–63 μm) with *n*-hexane/EtOAc eluent and monitored by refractive-index detection. HPLC was

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[11] (a) L-Valinol is commercially available for Aldrich Chemical Co. (18670-8) or is easily prepared by borane–methyl sulfide reduction of L-valine.[11b] (b) Meyers, A. I.; Knaus, G.; Kamata, K.; Ford, M. E. *J. Am. Chem. Soc.* **1976**, *98*, 567.

[12] Reviews: (a) Murray, A. W. *Org. React. Mech.* **1980**, 517. (b) Bartlett, P. A. *Tetrahedron* **1980**, *36*, 1. (c) Bennett, G. B. *Synthesis* **1977**, 589. (d) Ziegler, F. E. *Acc. Chem. Res.* **1977**, *10*, 227. (e) Rhoads, S. J.; Raulins, N. R. *Org. React.* **1975**, *22*, 1.

[13] (a) Ireland, R. E.; McGarvey, G. J.; Anderson, R. C.; Badoud, R.; Fitzsimmons, B.; Thaisrivongs, S. *J. Am. Chem. Soc.* **1980**, *102*, 6178. (b) Personal communication with Professor G. McGarvey, University of Virginia.

[14] Irwin, A. J.; Jones, J. B. *J. Am. Chem. Soc.* **1977**, *99*, 556.

[15] Meyers, A. I.; Temple, D. L.; Nolen, R. L.; Mihelich, E. *J. Org. Chem.* **1974**, *39*, 2778.

run on a 5-μm silica column using 95:5 *n*-hexane/EtOAc as eluent at 2 mL/min and monitored by refractive index or ultraviolet (254 nm) detection.

General Procedure for the Preparation of Tosylate Esters 1a–1f and 1j–1l. *n*-Butyllithium (1.6 M in hexane) was added over 2 min to a −78 °C, 0.2 M solution of the appropriate allylic alcohol in tetrahydrofuran to a 1,10-phenanthroline end point. Tosyl chloride (1.0 equiv) was added in one portion, and the solution stirred for 24–48 h. Workup was accomplished by dilution of the −78 °C solution with 3 volumes of petroleum ether, washing the still cold solution with 50% saturated brine, followed by saturated brine, and then drying 15 min over anhydrous K_2CO_3. The solution was decanted and concentrated under reduced pressure. The residual oil was taken up in anhydrous Et_2O and the solution dried over a second portion of anhydrous K_2CO_3. Filtration and evaporation at 1 torr yielded the tosylate esters as light yellow to orange oils. **CAUTION**: These powerful alkylating agents must be presumed carcinogenic. Several are quite unstable, tending to solidify with decomposition, and should be concentrated only just before use. Upon admixture with oxazolines, these tosylates are stabilized, and excesses do not decompose during several days at room temperature.

(*E*)-2-Butenyl 4-methylbenzenesulfonate (**1a**) was prepared from commercial (*E*)-2-buten-1-ol purified by spinning band distillation, >99:1 *E*:*Z* by GLC: 11.89 g, 52.5 mmol, 99% yield; ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.67 (dd, J = 6.6, 1.5 Hz, 3 H), 2.46 (s, 3 H), 4.48 (d, J = 6.8 Hz, 2 H), 5.84 (qdd, J = 6.6, 6.6, 1.5 Hz, 1 H), 5.77 (dd, J = 6.8, 6.8 Hz, 1 H), 7.34 (d, J = 8.2 Hz, 2 H), 7.79 (d, J = 8.2 Hz, 2 H); IR (CCl_4) 3040, 2960, 2880, 1670, 1595, 1490, 1440, 1360, 1190, 920, 780, 665 cm^{-1}.

(*Z*)-2-Butenyl 4-methylbenzenesulfonate (**1b**) was prepared from (*Z*)-2-buten-1-ol 99:1 *Z*:*E* by GLC, obtained by reduction of 2-butyn-1-ol:[16] 14.80 g, 65.4 mmol, 97% yield; ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.60 (d, J = 7.1 Hz, 3 H), 2.45 (s, 3 H), 4.62 (d, J = 7.1 Hz, 2 H), 5.42–5.53 (m, 1 H), 5.69–5.81 (m, 1 H), 7.34 (d, J = 8.1 Hz, 2 H), 7.80 (d, J = 8.1 Hz, 2 H); IR (CCl_4) 3050, 2970, 2890, 1650, 1595, 1490, 1445, 1360, 1180, 1095, 930, 790, 700, 665 cm^{-1}.

(*E*)-2-Methyl-2-butenyl 4-methylbenzenesulfonate (**1c**) was prepared from (*E*)-2-methyl-2-buten-1-ol, >99:1 *E*:*Z* by HPLC, obtained by reduction of methyl tiglate:[17] 5.33 g, 22.2 mmol, 94% yield; ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.40–1.66 (m, 6 H), 2.42 (s, 3H), 4.40 (s, 2 H), 5.50 (q, J = 7 Hz, 1 H), 7.32 (d, J = 8 Hz, 2 H), 7.78 (d, J = 8 Hz, 2 H); IR (KBr, neat) 3060, 3000, 2970, 1650, 1600, 1595, 1450, 1370, 1180, 1100, 900, 710, 670 cm^{-1}.

(*Z*)-2-Methyl-2-butenyl 4-methylbenzenesulfonate (**1d**) was prepared from (*Z*)-2-methyl-2-buten-1-ol, 99:1 *Z*:*E* by HPLC, obtained by epoxidation/reduction of isoprene:[18] 5.41 g, 22.5 mmol, 96% yield; ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.29–1.78 (m, 6 H), 2.42 (s, 3 H), 4.55 (s, 2 H), 5.48 (q, J = 7 Hz, 1 H), 7.35 (d, J = 8 Hz, 2 H), 7.82 (d, J = 8 Hz, 2 H); IR (KBr, neat) 3050, 3000, 2950, 1650, 1595, 1495, 1450, 1355, 1175, 1095, 920, 850, 800, 670 cm^{-1}.

(*E*)-4-Methyl-2-pentenyl 4-methylbenzenesulfonate (**1e**) was prepared from (*E*)-4-methyl-2-penten-1-ol, >99:1 *E*:*Z* by HPLC, obtained by reduction of 4-methyl-2-pentyn-1-ol:[19] 3.18 g, 12.5 mmol, 92% yield; ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.98 (d, J = 7 Hz, 6 H), 1.75–2.30 (m, 1 H), 2.48 (s, 3 H), 4.54 (d, J = 6 Hz, 2 H), 5.03–5.97 (m, 2 H), 7.37 (d, J = 8 Hz, 2 H), 7.82 (d, J = 8 Hz, 2 H); IR (KBr, neat) 3050, 2960, 2872, 1669, 1599, 1496, 1466, 1360, 1180, 1097, 925, 816, 664, 555 cm^{-1}.

(*Z*)-4-Methyl-2-pentenyl 4-methylbenzenesulfonate (**1f**) was prepared from (*Z*)-4-methyl-2-penten-1-ol, 98:2 *Z*:*E* by HPLC, obtained by reduction of 4-methyl-2-pentyn-1-ol:[16] 3.39 g, 13.3 mmol, 89% yield; ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.91 (d, J = 7 Hz, 6 H), 2.35–2.80 (m, 1 H), 2.45 (s, 3 H), 4.61 (d, J = 6 Hz, 2 H), 5.09–5.84 (m, 2 H), 7.37 (d, J = 8 Hz, 2 H), 7.81 (d, J = 8 Hz, 2 H); IR (KBr, neat) 3040, 2960, 2870, 1659, 1599, 1496, 1467, 1365, 1177, 1098, 928, 844, 815, 667, 555 cm^{-1}.

1-Cyclohexenyl-1-methyl 4-methylbenzenesulfonate (**1k**) was prepared from 1-cyclohexene-1-methanol:[20] 4.50 g, 19.9 mmol, 92% yield; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.31–2.30 (m, 8 H), 2.42 (s, 3 H), 4.37 (s, 2 H), 5.69 (broad s, 1 H), 7.30 (d, J = 8 Hz, 2 H), 7.76 (d, J = 8Hz, 2 H); IR (KBr, neat) 2960, 2890, 1465, 1170, 660 cm^{-1}.

(3,3-Dimethyl-1-cyclohexen-1-yl)methyl 4-methylbenzenesulfonate (**1l**) was prepared from 3,3-dimethyl-1-cyclohexen-1-methanol:[21] 5.50 g, 18.8 mmol, 87% yield; ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.90 (s, 6 H), 1.10–2.10 (m, 6 H), 2.45 (s, 3 H), 4.41 (s, 2 H), 5.41 (s, 1 H), 7.38 (d, J = 8 Hz, 2 H), 7.82 (d, J = 8 Hz, 2 H); IR (KBr, neat) 2960, 2890, 1465, 1375, 1360, 1170, 660 cm^{-1}.

(6,6-Dimethyl-1-cyclohexen-1-yl)methanol. To a solution of 1-chloro-5,5-dimethyl-1-cyclohexene[22] (5.0 g, 34.6 mmol) in 70 mL of anhydrous Et_2O at 25 °C under N_2 was added finely cut lithium (0.72 g, 104 mmol). After stirring 48 h gaseous formaldehyde, from paraformaldehyde (3.11 g, 104 mmol), was introduced. After 24 h additional stirring, the solution was poured onto crushed ice. Workup, drying over Na_2SO_4, and distillation gave 6,6-dimethyl-1-cyclohexene-1-methanol as a colorless oil with a minty aroma: 2.58 g, 18.4 mmol, 53%); bp 80–81 °C (8 torr); ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.03 (s, 6 H), 1.20–1.80 (m, 5 H), 1.90–2.20 (m, 2 H), 4.11 (broad s, 2 H), 5.70 (t, J = 3 Hz, 1 H); IR (KBr, neat) 3350, 2960, 2890, 1460, 1380, 1360, 1010, 870, 705 cm^{-1}.

(6,6-Dimethyl-1-cyclohexen-1-yl)methyl 4-methylbenzenesulfonate (**1m**) was prepared from 6,6-dimethyl-1-cyclohexene-1-methanol: 3.45 g, 11.7 mmol, 82% yield; ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.99 (s, 6 H), 1.10–2.10 (m, 6 H), 2.43 (s, 3 H), 4.48 (s, 2 H), 5.68 (t, J = 2 Hz, 1 H), 7.35 (d, J = 8 Hz, 2 H), 7.81 (d, J = 8 Hz, 2 H); IR (KBr, neat) 2970, 2890, 1450, 1365, 1170, 880, 810, 660 cm^{-1}.

Preparation of Allylic Bromides. Geranyl bromide (**1i**), neryl bromide (**1j**), and (*E*)-1-bromo-4-methyl-2-pentene were prepared from the corresponding alcohols according to a procedure published for geranyl bromide[6] and here described for the preparation of **bromo(2-methyl-1-cyclopenten-1-yl)methane** (**1n**). 2-Methyl-1-cyclopentene-1-methanol[23] (7.2 g, 64 mmol), pyridine (11.20 g, 142 mmol), and lithium bromide (11.18 g, 129 mmol) were vigorously stirred under N_2 in 260 mL of dry Et_2O at −10 °C. Phosphorus tribromide (8.71 g, 32 mmol) was added over 20 min. After being stirred 2 h at 0 °C and 5 h at room temperature, the mixture was washed twice with 10% HCl, once with saturated aqueous $NaHCO_3$, and once with brine. Drying over $MgSO_4$, filtration, evaporation, and distillation gave **1m** as a colorless oil, which darkened rapidly on standing room temperature but could be stored several hours at −20 °C: 6.28 g, 36 mmol, 56%; bp 67–70 °C (18 torr); ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.70 (s, 3 H), 1.45–2.00 (m, 2 H), 2.19–2.62 (m, 4 H), 4.09 (s, 2 H); IR (KBr, neat) 2950, 2860, 1660, 1440, 1380, 1200, 600 cm^{-1}.

(*E*)-4-(Phenylmethoxy)-2-buten-1-ol. NaH (2.31 g as a 50% dispersion in mineral oil, 48 mmol) was washed 2× with cyclohexane and suspended in 100 mL of dry DMF. To the stirred suspension under N_2 at room temperature was added over 20 min (*E*)-2-butene-1,4-diol[19] (8.5 g, 96 mmol). After stirring for 2 h benzyl bromide (5.50 g, 32 mmol) was added and stirring continued 16 h. The mixture was cautiously poured into 300 g of crushed ice, and the solution was extracted with Et_2O (3 × 100 mL). The ethereal solutions were combined, washed with water (2×) and brine (1×), dried (Na_2SO_4), filtered, concentrated under reduced pressure, and distilled to give the ether as a colorless oil: 12.0 g, 67 mmol, 79%; bp 130–133 (0.05 torr); >99:1 *E*:*Z* by HPLC; ^{1}H NMR (60 MHz, $CDCl_3$) δ 2.05 (broad s, 1 H), 3.86–4.21 (m, 4 H), 4.49 (s, 2 H), 5.72–5.94 (m, 2 H), 7.31 (m, 5 H); IR (KBr, neat) 3400, 3050, 2890, 1660, 1495, 1450, 1360, 1210, 1080, 995, 745, 700 cm^{-1}; MS (EI), *m*/*e* (relative intensity) 178 (0.26, M^+), 177 (1.29), 160 (1.33), 150 (1.30), 107 (13), 91 (100), 77 (13), 65

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(9). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.14; H, 7.90.

(*E*)-4-(Phenylmethoxy)-2-butenyl Methanesulfonate (1g). (*E*)-4-(Phenylmethoxy)-2-buten-1-ol (2.70 g, 15.2 mmol) and triethylamine (2.63 g, 25.8 mmol) were dissolved in 76 mL of dry CH_2Cl_2 under dry N_2. After cooling to -10 °C, methanesulfonyl chloride (1.91 g, 16.7 mmol) was added over 10 min. After 20 min of stirring, the mixture was washed with cold water, ice cold 10% HCl (2×), saturated aqueous $NaHCO_3$, and brine. Drying over K_2CO_3, filtration, and concentration yielded **1g** as a viscous yellow oil: 3.61 g, 14.1 mmol, 93%; ^1H NMR (60 MHz, $CDCl_3$) δ 2.97 (s, 3 H), 3.94–4.10 (m, 2 H), 4.50 (s, 2 H), 4.69 (d, *J* = 4 Hz, 2 H), 5.80–6.07 (m, 2 H), 7.30 (m, 5 H); IR (KBr, neat) 3050, 2980, 2870, 1670, 1585, 1495, 1450, 1340, 1170, 1100, 1065, 940, 825, 740, 705 cm^{-1}.

(*Z*)-4-(Phenylmethoxy)-2-butenyl methanesulfonate (1h) was prepared from (*Z*)-4-(phenylmethoxy)-2-buten-1-ol[24] (3.00 g, 16.8 mmol) 97:3 *Z*:*E* by HPLC, triethylamine (2.92 g, 28.6 mmol), and methanesulfonyl chloride (2.12 g, 18.5 mmol) in the manner described for **1g**: light yellow oil; (3.59 g, 14.0 mmol, 83%); ^1H NMR ($CDCl_3$, 60 MHz) δ 2.87 (s, 3 H), 4.12 (d, *J* = 5 Hz, 2 H), 4.51 (s, 2 H), 4.82 (d, *J* = 6 Hz, 2 H), 5.51–6.20 (m, 2 H), 7.36 (m, 5 H); IR (KBr, neat) 3050, 2950, 2880, 1650, 1595, 1495, 1450, 1340, 1170, 1080, 975, 930, 830, 745, 705 cm^{-1}. Anal. Calcd for $C_{12}H_{16}O_4S$: C, 56.23; H, 6.29. Found: C, 56.31; H, 6.37.

4,5-Dihydro-2-methyl-4-(1-methylethyl)oxazole (2). Following Meyers' general procedure,[11b] L-2-amino-3-methyl-1-butanol (40.89 g, 382 mmol) and ethyl acetimidate hydrochloride (49.53 g, 401 mmol) were condensed by stirring 24 h in dry CH_2Cl_2 (400 mL). The mixture was next washed with saturated aqueous $NaHCO_3$ (100 mL) and brine (100 mL), then dried (K_2CO_3), and filtered. Fractional distillation (146–148°C/760 torr) gave **2**: 33.1 g, 260 mmol, 68.1%; ^1H NMR (90 MHz, $CDCl_3$) δ 0.89 (d, *J* = 7 Hz, 3 H), 0.97 (d, *J* = 7 Hz, 3 H), 1.68 (qqd, *J* = 7, 7, 7 Hz, 1 H), 1.97 (s, 3 H), 3.87 (dd, *J* = 8, 8 Hz, 1 H), 4.06 (ddd, *J* = 10, 8, 7 Hz, 1 H), 4.23 (dd, *J* = 10, 8 Hz, 1 H); IR (CCl_4) 2990, 2905, 1665, 1465, 1435, 1385, 1365, 1230, 1190, 985, 900 cm^{-1}; UV (MeOH) λ_{max} 215 nm; EI mass spectrum (relative intensity), *m/e* 127 (3, M^+), 84 (100), 83 (38), 56 (20); calcd for $C_7H_{13}NO$, 127.0998; found, 127.1001.

Procedure for Preparation of Oxazolinium Salts 3. Oxazoline **2** and 120 mol % of the appropriate bromide or sulfonate **1a–n** were stirred together in an oven-dried flask under nitrogen at room temperature until no further increase in viscosity was noted or the product crystallized. Trituration three times with ten volumes of dry Et_2O at 0 °C, and evaporation at 1 torr provided salts **3** as light yellow liquids or solids, which were used without further purification. For best results care must be taken that oxazoline **2** and alkylating agent **1** be as dry as possible.

(*S*)-(−)-(*E*)-3-(2-Butenyl)-4,5-dihydro-2-methyl-4-(1-methylethyl)oxazolium 4-Methylbenzenesulfonate (3a). The oxazoline and sulfonate were stirred 48 h and gave **3a** as a yellow oil: 18.28 g, 51.7 mmol, 99% yield; $[\alpha]^{25}$D −27.1° (*c* 10.8 $CHCl_3$); ^1H NMR (90 MHz, $CDCl_3$) δ 0.81 (d, *J* = 7 Hz, 3 H), 0.88 (d, *J* = 7 Hz, 3 H), 1.68 (d, *J* = 6 Hz, 3 H), 1.80–2.40 (m, 1 H), 2.31 (s, 3 H), 2.51 (s, N=CCH_3, 3 H), 4.18–4.78 (m, 4 H), 4.80–5.25 (m, NCH, 1 H), 5.31–6.10 (m, 2 H), 7.12 (d, *J* = 8 Hz, 2 H), 7.74 (d, *J* = 8 Hz, 2 H); IR ($CHCl_3$) 3440, 3010, 2485, 1650, 1490, 1445, 1395, 1378, 1225, 1180, 1120, 1032, 1010, 815, 670 cm^{-1}.

(*S*)-(−)-(*Z*)-3-(2-Butenyl)-4,5-dihydro-2-methyl-4-(1-methylethyl)oxazolium 4-Methylbenzenesulfonate (3b). The oxazoline and sulfonate were stirred 48 h and gave **3b** as a yellow oil: 19.09 g, 54.0 mmol, 98% yield; $[\alpha]^{25}_D$ −27.1° (*c* 9.18 $CHCl_3$); ^1H NMR (90 MHz, $CDCl_3$) δ 0.87 (d, *J* = 7 Hz, 3 H), 0.90 (d, *J* = 7 Hz, 3 H), 1.68 (d, *J* = 7 Hz, 3 H), 1.80–2.40 (m, 1 H), 2.31 (s, 3 H), 2.52 (s, N=CCH_3, 3 H), 4.25–4.78 (m, 4 H), 4.95–5.33 (m, NCH, 1 H), 5.34–6.07 (m, 2 H), 7.17 (d, *J* = 8 Hz, 2 H), 7.78 (d, *J* = 8 Hz, 2 H); IR ($CHCl_3$) 3430, 3010, 2490, 1650, 1490, 1445, 1395, 1378, 1235, 1180, 1120, 1035, 1010, 815, 675 cm^{-1}.

(*S*)-(*E*)-4,5-Dihydro-2-methyl-3-(2-methyl-2-butenyl)-4-(1-methylethyl)oxazolium 4-Methylbenzenesulfonate (3c). The oxazoline and sulfonate were stirred 48 h and gave **3c** as a yellow oil: 4.11 g, 11.2 mmol, 99% yield; ^1H NMR (60 MHz, $CDCl_3$) δ 0.69–1.04 (m, 6 H), 1.42–1.69 (m, 6 H), 1.80–2.40 (m, 1 H), 2.32 (s, 3 H), 2.44 (s) and 2.54 (s), (1:2.5 ratio, N=CCH_3, 3 H), 4.07–4.84 (m, 4 H), 4.86–5.25 (m, NCH, 1 H), 5.30–5.85 (m, 1 H), 7.08 (d, *J* = 8 Hz, 2 H), 7.70 (d, *J* = 8 Hz, 2 H); IR (KBr, neat) 3500, 3040, 2950, 1640, 1485, 1450, 1395, 1380, 1195, 1115, 1030, 1000, 920, 815, 670 cm^{-1}.

(*S*)-(*Z*)-4,5-Dihydro-2-methyl-3-(2-methyl-2-butenyl)-4-(1-methylethyl)oxazolium 4-Methylbenzenesulfonate (3d). The oxazoline and sulfonate were stirred 44 h and gave **3d** as a yellow oil: 4.24 g, 11.5 mmol, 98% yield; ^1H NMR (60 MHz, $CDCl_3$) δ 0.88 (d, *J* = 7 Hz, 3 H), 0.89 (d, *J* = 7 Hz, 3 H), 1.54–1.84 (m, 6 H), 1.85–2.50 (m, 1 H), 2.32 (s, 3 H), 2.46 (s) and 2.57 (s), (1:10 ratio, N=CCH_3, 3 H), 4.23–4.85 (m, 4 H), 4.89–5.23 (m, NCH, 1 H), 5.28–5.80 (m, 1 H), 7.08 (d, *J* = 8 Hz, 2 H), 7.70 (d, *J* = 8 Hz, 2 H); IR (KBr, neat) 3460, 3020, 2950, 1645, 1485, 1450, 1395, 1385, 1195, 1115, 1010, 905, 830, 670 cm^{-1}.

(*S*)-(*E*)-4,5-Dihydro-2-methyl-4-(1-methylethyl)-3-(4-methyl-2-pentenyl)oxazolium 4-Methylbenzenesulfonate (3e). The oxazoline and sulfonate were stirred 27 h and gave **3e** as a yellow oil: 3.36 g, 8.80 mmol, 84% yield; ^1H NMR (60 MHz, $CDCl_3$) δ 0.83–1.09 (m, 12 H), 1.86–2.55 (m, 2 H), 2.30 (s, 3 H), 2.46 (s) and 2.51 (s), (1:5 ratio, N=CCH_3, 3 H), 4.19–4.86 (m, 4 H), 4.90–5.31 (m, NCH, 1 H), 5.35–6.05 (m, 2 H), 7.11 (d, *J* = 8 Hz, 2 H), 7.74 (d, *J* = 8 Hz, 2 H); IR (KBr, neat) 3020, 2960, 2900, 2350, 1640, 1460, 1380, 1190, 1115, 1030, 1000, 930, 815, 670 cm^{-1}.

(*S*)-(*E*)-4,5-Dihydro-2-methyl-4-(1-methylethyl)-3-(4-methyl-2-pentenyl)oxazolium Bromide. The oxazoline and sulfonate were stirred 96 h and gave the product as a light yellow solid: 2.09 g, 7.20 mmol, 45% yield; ^1H NMR (90 MHz, $CDCl_3$) δ 0.86–1.11 (m, 12 H), 2.10–2.45 (m, 2 H), 2.63 (s) and 2.70 (s), (1:20 ratio, N=CCH_3, 3 H), 4.14–4.88 (m, 4 H), 4.93–5.36 (m, NCH, 1 H), 5.36–6.09 (m, 2 H); IR ($CHCl_3$) 3380, 2960, 2460, 1645, 1485, 1450, 1395, 1375, 1225, 980 cm^{-1}.

(*S*)-(*Z*)-4,5-Dihydro-2-methyl-4-(1-methylethyl)-3-(4-methyl-2-pentenyl)oxazolium 4-Methylbenzenesulfonate (3f). The oxazoline and sulfonate were stirred 34 h and gave **3f** as a yellow oil: 3.77 g, 9.89 mmol, 89% yield; ^1H NMR (60 MHz, $CDCl_3$) δ 0.80–1.12 (m, 12 H), 1.82–2.80 (m, 2 H), 2.31 (s, 3 H), 2.51 (s) and 2.56 (s), (1:2 ratio, N=CCH_3, 3 H), 4.15–4.87 (m, 4 H), 4.89–5.83 (m, 3 H), 7.13 (d, *J* = 8 Hz, 2 H), 7.74 (d, *J* = 8 Hz, 2 H); IR (KBr, neat) 3400, 2970, 2350, 1650, 1485, 1450, 1190, 1115, 1030, 1005, 715, 675 cm^{-1}.

(*S*)-(*E*)-4,5-Dihydro-2-methyl-4-(1-methylethyl)-3-(4-(phenylmethoxy)-2-butenyl)oxazolium Methanesulfonate (3g). The oxazoline and sulfonate were stirred 72 h and gave **3g** as a yellow oil: 3.70 g, 9.65 mmol, 86% yield; ^1H NMR (90 MHz, $CDCl_3$) δ 0.77 (d, *J* = 7 Hz, 3 H), 0.93 (d, *J* = 7 Hz, 3 H), 1.90–2.40 (m, 1 H), 2.57 (s, N=CCH_3, 3 H), 2.67 (s, 3 H), 4.03 (d, *J* = 3 Hz, 2 H), 4.28–4.84 (m, 4 H), 4.48 (s, 2 H), 4.98–5.36 (m, NCH, 1 H), 5.65–6.23 (m, 2 H), 7.17–7.40 (m, 5 H); IR (KBr, neat) 3500, 3020, 2970, 2880, 1650, 1485, 1450, 1365, 1200, 1035, 920, 820, 755, 700 cm^{-1}.

(*S*)-(*Z*)-4,5-Dihydro-2-methyl-4-(1-methylethyl)-3-(4-(phenylmethoxy)-2-butenyl)oxazolium Methanesulfonate (3h). The oxazoline and sulfonate were stirred 50 h and gave **3h** as a yellow oil: 3.87 g, 10.1 mmol, 95% yield; ^1H NMR (90 MHz, $CDCl_3$) δ 0.81 (d, *J* = 7 Hz, 3 H), 0.88 (d, *J* = 7 Hz, 3 H), 1.85–2.38 (m, 1 H), 2.65 (s, N=CCH_3, 3 H), 2.69 (s, 3 H), 4.13 (d, *J* = 5 Hz, 2 H), 4.22–4.83 (m, 4 H), 4.49 (s, 2 H), 4.96–5.37 (m, NCH, 1 H), 5.56–6.18 (m, 2 H), 7.18–7.43 (m, 5 H); IR (KBr, neat) 3490, 3040, 2970, 2890, 1650, 1480, 1450, 1200, 1040, 920, 830, 755, 700 cm^{-1}.

(*S*)-(*E*)-3-(3,7-Dimethyl-2,6-octadienyl)-4,5-dihydro-2-methyl-4-(1-methylethyl)oxazolium Bromide (3i). The oxazoline and bromide were stirred 20 h and gave **3i** as a yellow oil: 4.93 g, 14.3 mmol, 91% yield; ^1H NMR (90 MHz, $CDCl_3$) δ 0.97 (d, *J* = 7 Hz, 3 H), 0.99 (d, *J* = 7 Hz, 3 H), 1.60 (s, 3 H), 1.70 (s, 3 H), 1.77 (s, 3 H), 2.40–2.90 (m, 5 H), 2.68 (s) and 2.71 (s), (1:10 ratio, N=CCH_3, 3 H), 4.51 (d, *J* = 8 Hz, 2 H), 4.57–4.92 (m, 2 H), 4.92–5.50 (m, 3 H); IR ($CHCl_3$) 3400, 3060, 2950, 2400, 1650, 1485, 1450, 1395, 1380, 1230, 995, 915, 735, 660 cm^{-1}.

(*S*)-(*Z*)-3-(3,7-Dimethyl-2,6-octadienyl)-4,5-dihydro-2-methyl-4-(1-methylethyl)oxazolium Bromide (3j). The oxazoline and bromide were stirred 40 h and gave **3j** as a yellow oil: 5.39 g, 15.6 mmol, 79% yield; ^1H NMR (90 MHz, $CDCl_3$) δ 0.97 (d, *J* = 7 Hz, 3 H), 1.01 (d, *J* = 7 Hz, 3 H), 1.63 (s, 3 H), 1.70 (s, 3 H), 1.82 (s, 3 H), 1.80–2.40 (m, 5 H), 2.67 (s) and 2.71 (s), (1:3

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ratio, N=CCH$_3$, 3 H), 4.30–4.59 (m, 2 H), 4.60–4.90 (m, 2 H), 4.93–5.69 (m, 3 H); IR (CHCl$_3$) 3380, 3040, 2960, 2440, 1645, 1480, 1440, 1380, 1215, 995, 815, 745, 665 cm^{-1}.

(*S*)-3-(1-Cyclohexen-1-ylmethyl)-4,5-dihydro-2-methyl-4-(1-methylethyl)oxazolium 4-Methylbenzenesulfonate (3k). The oxazoline and sulfonate were stirred 48 h and gave **3k** as a yellow oil: 6.17 g, 15.5 mmol, 99% yield; ^{1}H NMR (90 MHz, CDCl$_3$) δ 0.85–1.12 (m, 6 H), 1.47–1.80 (m, 4 H), 1.80–2.30 (m, 5 H), 2.32 (s, 3 H), 2.53 (s) and 2.62 (s), (1:3 ratio, N=CCH$_3$, 3 H), 4.30 (broad s, 2 H), 4.40–4.75 (m, 2 H), 4.84–5.40 (m, NCH, 1 H), 5.68–5.94 (m, 1 H), 7.17 (d, J = 8 Hz, 2 H), 7.80 (d, J = 8 Hz, 2 H); IR (CHCl$_3$) 3400, 2970, 2450, 1640, 1480, 1445, 1230, 1165, 1115, 1010, 815, 670 cm^{-1}.

(*S*)-3-((3,3-Dimethyl-1-cyclohexen-1-yl)methyl)-4,5-dihydro-2-methyl-4-(1-methylethyl)oxazolium 4-Methylbenzenesulfonate (3l). The oxazoline and sulfonate were stirred 44 h and gave **3l** as a yellow oil: 5.40 g, 12.8 mmol, 92% yield; ^{1}H NMR (90 MHz, CDCl$_3$) δ 0.76–1.10 (m, 12 H), 1.21–2.08 (m, 6 H), 2.0–2.45 (m, 1 H), 2.31 (s, 3 H), 2.50 (s) and 2.58 (s), (1:10 ratio, N=CH$_3$, 3 H) 4.28 (s, 2 H), 4.40–4.77 (m, 2 H), 4.80–5.38 (m, NCH, 1 H), 5.50 (s, 1 H), 7.16 (d, J = 8 Hz, 2 H), 7.78 (d, J = 8 Hz, 2 H); IR (CHCl$_3$) 3430, 2990, 2440, 1640, 1485, 1450, 1230, 1170, 1120, 1035, 1010, 815, 670 cm^{-1}.

(*S*)-3-((6,6-Dimethyl-1-cyclohexen-1-yl)methyl)-4,5-dihydro-2-methyl-4-(1-methylethyl)oxazolium 4-Methylbenzenesulfonate (3m). The oxazoline and sulfonate were stirred 48 h, and gave **3m** as a yellow oil: 3.58 g, 8.49 mmol, 91% yield; ^{1}H NMR (90 MHz, CDCl$_3$) δ 0.78–1.13 (m, 12 H), 1.40–1.67 (m, 4 H), 1.85–2.40 (m, 3 H), 2.31 (s, 3 H), 2.57 (s, N=CH$_3$, 3 H), 4.06–5.00 (m, 4 H), 5.12–5.54 (m, 2 H), 7.17 (d, J = 8 Hz, 2 H), 7.78 (d, J = 8 Hz, 2 H); IR (CHCl$_3$) 3400, 2960, 2460, 1640, 1480, 1440, 1230, 1160, 1115, 1005, 810, 670 cm^{-1}.

(*S*)-4,5-Dihydro-2-methyl-3-((2-methyl-1-cyclopenten-1-yl)methyl)-4-(1-methylethyl)oxazolium Bromide (3n). The oxazoline and bromide were stirred 16 h and gave **1m** as a yellow oil: 4.26 g, 14.1 mmol, 81% yield; ^{1}H NMR (90 MHz, CDCl$_3$) δ 0.93 (d, J = 7 Hz, 3 H), 1.60–2.57 (m, 7 H), 1.80 (s, 3 H), 2.70 (s, N=CCH$_3$, 3 H), 4.50–4.84 (m, 2 H), 4.54 (s, 2 H), 5.12–5.47 (m, NCH, 1 H); IR (CHCl$_3$) 3400, 3030, 2950, 2410, 1640, 1475, 1440, 1205, 1020, 920, 805, 670 cm^{-1}.

(4*S*,2′*S*)-4,5-Dihydro-2-(2-methyl-3-butenyl)-4-(1-methylethyl)oxazole (5b and 6b). MPLC gave as a colorless oil an unresolved mixture of diastereomers which HPLC showed to be an 86:14 mixture of **5b** and **6b**: 6.28 g, 34.6 mmol, 75% yield; ^{1}H NMR (360 MHz, CDCl$_3$): only the three methyl resonances differed from those of **5a**; δ 0.88 (d, J = 6.7 Hz, 3 H), 0.95 (d, J = 6.9, 3 H), 1.06 (d, J = 6.7 Hz, 3 H); IR (CCl$_4$) and EI mass spectra were essentially superimposable.

(4*S*,2′*S*)-2-(2,3-Dimethyl-3-butenyl)-4,5-dihydro-4-(1-methylethyl)oxazole (5c and 6c). MPLC gave as a colorless oil an unresolved mixture of diastereomers which HPLC analysis showed to be an 85:15 mixture of **5c** and **6c**: 1.30 g, 6.65 mmol, 57% yield; ^{1}H NMR (90 MHz, CDCl$_3$) δ 0.85 (d, J = 7 Hz, 3 H), 0.97 (d, J = 7 Hz, 3 H), 1.07 (d, J = 7 Hz, 3 H), 1.70 (d, J = 2 Hz, 3 H), 1.95–2.85 (m, 3 H), 3.60–4.45 (m, 3 H), 4.68 (broad s, 2 H); IR (CCl$_4$) 3100, 2990, 2920, 1665, 1450, 1360, 1165, 990, 740 cm^{-1}; EI mass spectrum (relative intensity), *m/e* 195 (10, M+), 194(10), 180 (100), 152 (13), 138 (11), 127 (17), 109 (21), 95 (20), 84 (14), 69 (16). Anal. Calcd for C$_{12}$H$_{21}$NO: C, 73.80; H, 10.76; N, 7.17. Found: C, 73.89; H, 10.93; N, 7.20.

(4*S*,2′*R*)-2-(2,3-Dimethyl-3-butenyl)-4,5-dihydro-4-(1-methylethyl)oxazole (5d and 6d). MPLC gave as a colorless oil an unresolved mixture of diastereomers which HPLC analysis showed to be an 89:11 mixture of **5d** and **6d**: 1.37 g, 7.02 mmol, 61% yield; 90 MHz ^{1}H NMR, IR, and EI mass spectra were essentially superimposable on those of the 87:13 mixture of **5f** and **6f** described above. Anal. Calcd for C$_{12}$H$_{21}$NO: C, 73.80; H, 10.75; N, 7.17. Found: C, 73.77; H, 10.87; N, 7.41.

(4*S*,2′*R*)-4,5-Dihydro-4-(1-methylethyl)-2-(2-(1-methylethyl)-3-butenyl)oxazole (5e and 6e). MPLC gave as a colorless oil an unresolved mixture of diastereomers which HPLC analysis showed to be a 76:24 mixture of **5e** and **6e**: 1.30 g, 6.21 mmol, 71% yield; ^{1}H NMR (90 MHz, CDCl$_3$) δ 0.70–1.10 (m, 12 H), 1.15–2.05 (m, 2 H), 2.10–2.15 (m, 3 H), 3.55–4.40 (m, 3 H), 4.72–5.16 (m, 2 H), 5.31–5.92 (m, 1 H); IR (KBr, neat) 3100, 2090, 2900, 1670, 1640, 1470, 1445, 1385, 1365, 1240, 1175, 985, 910, 800, 740 cm^{-1}; EI mass spectrum (relative intensity), *m/e* 209 (1.1, M$^+$), 208 (1.5), 194 (18), 166 (100), 127 (20), 84 (13). Anal. Calcd for C$_{13}$H$_{23}$NO: C, 74.59; H, 11.08; N, 6.69. Found: C, 74.52; H, 10.95; N, 6.88.

(4*S*,2′*S*)-4,5-Dihydro-4-(1-methylethyl)-2-(2-(1-methylethyl)-3-butenyl)oxazole (5f and 6f). MPLC gave as a colorless oil an unresolved mixture of diastereomers which HPLC analysis showed to be an 87:13 mixture of **5f** and **6f**: 0.39 g, 1.84 mmol, 21% yield; 90 MHz ^{1}H NMR, IR, and EI mass spectra were essentially superimposable on those of the 76:24 mixture of **5e** and **6e** described above. Anal. Calcd for C$_{13}$H$_{23}$NO: C, 74.59; H, 11.08; N, 6.69. Found: C, 74.26; H, 11.00; N, 6.80.

(4*S*,2′*R*)-4,5-Dihydro-4-(1-methylethyl)-2-(2-(phenylmethoxy)-4-butenyl)oxazole (5g and 6g). MPLC gave as a colorless oil an unresolved mixture of diastereomers which HPLC showed to be an 82:18 mixture of **5g** and **6g**: 0.822 g, 2.86 mmol, 32% yield; ^{1}H NMR (500 MHz, CDCl$_3$), for **5g**: δ 0.85 (d, J = 6.8 Hz, 3 H), 0.93 (d, J = 6.8 Hz, 3 H), 1.66 (dqq, J = 6.8, 6.8, 6.8 Hz, 1 H), 2.33 (dd, J = 1.47, 8.5 Hz, 1 H), 2.55 (dd, J = 14.7, 6.1 Hz, 1 H), 2.84 (ddddd, J = 9.2, 8.9, 8.5, 7.8, 6.1 Hz, 1 H), 3.43 (dd, J = 9.2, 6.4 Hz, 1 H), 3.47 (dd, J = 8.9, 6.4 Hz, 1 H), 3.85 (ddd, J = 19.0, 8.9, 6.8 Hz, 1 H), 3.88 (dd, J = 19.0, 7.8 Hz, 1 H), 4.16 (dd, J = 8.9, 7.8 Hz, 1 H), 4.50 (d, J = 12.2 Hz, 1 H), 4.53 (d, J = 12.2 Hz, 1 H), 5.07 (d, J = 10.1 Hz, 1 H), 5.13 (d, J = 17.3 Hz, 1 H), 5.78 (ddd, J = 17.3, 10.1, 7.8 Hz, 1 H), 7.23–7.38 (m, 5 H); IR (KBr, neat) 3090, 3050, 2975, 2800, 1665, 1650, 1450, 1360, 1195, 1095, 1055, 985, 915, 735, 700 cm^{-1}; EI mass spectrum (relative intensity), *m/e* 287 (0.3, M$^+$), 196 (35), 166 (31), 127 (47), 91 (100), 84 (17). Anal. Calcd for C$_{18}$H$_{25}$NO$_2$: C, 75.23; H, 8.77; N, 4.87. Found: C, 75.43; H, 8.86; N, 4.98.

(4*S*,2′*S*)-4,5-Dihydro-4-(1-methylethyl)-2-(2-(phenylmethoxy)-4-butenyl)oxazole (5h and 6h). MPLC gave as a colorless oil an unresolved mixture of diastereomers which HPLC showed to be a 85:15 mixture of **5h** and **6h**: 1.16 g, 4.03 mmol, 54% yield; for **5h**, ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.85 (d, J = 6.7 Hz, 3 H), 0.93 (d, J = 6.7 Hz, 3 H), 1.69 (dqq, J = 6.7, 6.7, 6.7 Hz, 1 H), 2.36 (dd, J = 14.7, 8.3 Hz, 1 H), 2.53 (dd, J = 14.7, 6.3 Hz, 1 H), 2.83 (ddddd, J = 8.3, 7.9, 6.6, 6.3, 6.2 Hz, 1 H), 3.43 (dd, J = 9.1, 6.6 Hz, 1 H), 3.49 (dd, J = 9.1, 6.2 Hz, 1 H), 3.84 (ddd, J = 15.2, 7.9, 6.7 Hz, 1 H), 3.87 (dd, J = 15.2, 7.9 Hz, 1 H), 4.15 (dd, J = 8.0, 7.9 Hz, 1 H), 4.51 (s, 2 H), 5.08 (d, J = 10.2 Hz, 1 H), 5.13 (d, J = 17.5, 1 H), 5.78 (ddd, J = 17.5, 10.2, 7.9 Hz, 1 H), 7.23–7.38 (m, 5 H); IR (KBr, neat) 3090, 3050, 2980, 2900, 1665, 1640, 1450, 1360, 1285, 1190, 1100, 985, 915, 740, 700 cm^{-1}; EI mass spectrum (relative intensity), *m/e* 287 (0.4, M$^+$), 196 (41), 166 (31), 127 (46), 91 (100), 84 (13). Anal. Calcd for C$_{18}$H$_{25}$NO$_2$: C, 75.23; H, 8.77; N, 4.87. Found: C, 75.39; H, 8.75; N, 4.88.

(4*S*,2′*R*)-2-(2,6-Dimethyl-2-ethenyl-5-heptenyl)-4,5-dihydro-4-(1-methylethyl)oxazole (5i and 6i). MPLC gave as a colorless oil an unresolved mixture of diastereomers which HPLC analysis and 360 MHz ^{1}H NMR analysis of its dimethylsulfate adduct showed to be an 85:15 mixture of **5i** and **6i**: 2.88 g, 11.0 mmol, 78% yield; ^{1}H NMR (90 MHz, CDCl$_3$) δ 0.90 (d, J = 7 Hz, 3 H), 0.95 (d, J = 7 Hz, 3 H), 1.13 (s, 3 H), 1.27–2.20 (m, 5 H), 1.62 (s, 3 H), 1.70 (s, 3 H), 2.35 (s, 2 H), 3.60–4.44 (m, 3 H), 4.70–5.30 (m, 3 H), 5.88 (dd, J = 17, 11 Hz, 1 H); IR (KBr, neat) 3095, 2990, 2940, 1660, 1445, 1355, 1205, 985, 910, 825, 735 cm^{-1}; EI mass spectrum (relative intensity), *m/e* 263 (2.5, M$^+$), 248 (15), 220 (14), 194 (25), 181 (100), 180 (56), 166 (31), 138 (21), 127 (29), 84 (12), 69 (15). Anal. Calcd for C$_{17}$H$_{29}$NO: C, 77.51; H, 11.10; N, 5.32. Found: C, 77.53; H, 11.20; N, 5.42.

(4*S*,2′*R*)-4,5-Dihydro-2-((2-methylenecyclohex-1-yl)methyl)-4-(1-methylethyl)oxazole (5k and 6k). MPLC gave as a colorless oil an unresolved mixture of diastereomers which HPLC analysis and 360 MHz ^{1}H NMR analysis of its dimethyl sulfate adduct showed to be a 90:10 mixture of **5k** and **6k**: 1.36 g, 6.15 mmol, 53% yield; ^{1}H NMR (90 MHz, CDCl$_3$) δ 0.87 (d, J = 6 Hz, 3 H), 0.95 (d, J = 6 Hz, 3 H), 1.05–2.70 (m, 12 H), 3.75–4.40 (m, 3 H), 4.60 (broad s, 1 H), 4.68 (broad s, 1 H); IR (CCl$_4$) 3090, 2950, 2890, 1665, 1645, 1465, 1445, 1385, 1355, 1220, 1162, 980, 890 cm^{-1}; EI mass spectrum (relative intensity), *m/e* 221 (45, M$^+$), 220 (100), 219 (50), 206 (29), 192 (32), 178 (65), 127 (45), 95 (26), 94 (26), 84 (24). Anal. Calcd for C$_{14}$H$_{23}$NO: C, 75.97; H, 10.47; N, 6.33. Found: C, 75.74; H, 10.53; N, 6.22.

(4*S*,2′*R*)-2-((2,2-Dimethyl-6-methylenecyclohex-1-yl)methyl)-4,5-dihydro-4-(1-methylethyl)oxazole (5l and 6l).

MPLC gave as a colorless oil an unresolved mixture of diastereomers which HPLC analysis and 360 MHz ^{1}H NMR analysis[25] of its dimethyl sulfate adduct showed to be a 92:7 mixture of **5l** and **6l**: 1.30 g, 5.20 mmol, 51% yield; ^{1}H NMR (360 MHz, CDCl$_3$) δ 0.83 (s, 3 H), 0.84 (d, J = 6.9 Hz, 3 H), 0.92 (d, J = 6.8 Hz, 3 H), 0.97 (s, 3 H), 1.25–1.35 (m, 1 H), 1.41–1.49 (m, 1 H), 1.50–1.60 (m, 2 H), 1.71 (qqd, J = 6.9, 6.8, 6.8 Hz, 1 H), 1.99–2.08 (m, 1 H), 2.17–2.27 (m, 1 H), 2.33 (dd, J = 7.7, 7.7 Hz, CCCH, 1 H), 2.43–2.49 (m, CHCH$_2$C=N, 2 H), 3.84 (ddd, J = 15.3, 9.1, 6.8 Hz, NCH, 1 H), 3.88 (dd, J = 15.3, 7.7 Hz, 1 H), 4.13 (dd, J = 9.1, 7.7 Hz, 1 H), 4.61 (broad s, 1 H), 4.74 (broad s, 1 H); IR (KBr, neat) 3090, 2960, 1665, 1645, 1450, 1380, 1360, 1235, 1160, 980, 890, 730 cm^{-1}; EI mass spectrum, (relative intensity) 249 (42, M$^+$), 248 (93), 234 (43), 206 (17), 192 (100), 179 (28), 166 (14), 107 (15), 91 (14), 79 (16), 69 (12). Anal. Calcd for C$_{16}$H$_{27}$NO: C, 77.06; H, 10.91; N, 5.62. Found: C, 77.23; H, 10.89; N, 5.69.

(4*S*,2′*R*)-2-((3,3-Dimethyl-2-methylenecyclohex-1-yl)methyl)-4,5-dihydro-4-(1-methylethyl)oxazole (5m and 6m). MPLC gave as a colorless oil an unresolved mixture of diastereomers which 360 MHz ^{1}H NMR analysis of its dimethyl sulfate adduct showed to be a 97:3 mixture of **5m** and **6m**: 0.074 g, 0.30 mmol, 51% yield; ^{1}H NMR (90 MHz, CDCl$_3$) δ 0.87 (d, J = 7 Hz, 3 H), 0.96 (d, J = 7 Hz, 3 H), 1.09 (s, 6 H), 1.20–2.15 (m, 7 H), 2.15–2.88 (m, 3 H), 3.58–4.35 (m, 3 H), 4.60 (s, 1 H), 4.73 (s, 1 H); IR (CCl$_4$) 2960, 1665, 1630 (C=C), 1460, 1380, 1350, 1190, 980, 890 cm^{-1}; EI mass spectrum (relative intensity), *m/e* 249 (6,M$^+$), 248 (7), 234 (100), 206 (15), 127 (20), 107 (16), 91 (10), 84 (10), 81 (10), 79 (10). Anal. Calcd for C$_{16}$H$_{27}$NO: C, 77.06; H, 10.91; N, 5.62. Found: C, 76.93; H, 10.97; N, 5.81.

(4*S*,2′*R*)-4,5-Dihydro-4-(1-methylethyl)-2-((1-methyl-2-methylenecyclopent-1-yl)methyl)oxazole (5n and 6n). MPLC gave as a colorless oil an unresolved mixture of diastereomers which HPLC analysis and 360 MHz ^{1}H NMR analysis of its dimethyl sulfate adduct showed to be a 90:10 mixture of **5n** and **6n**: 1.78 g, 8.08 mmol, 57% yield; ^{1}H NMR (360 MHz, CDCl$_3$) δ 0.88 (d, J = 6.9 Hz, 3 H), 0.97 (d, J = 6.9 Hz, 3 H), 1.14 (s, 3 H), 1.48–1.70 (m, 3 H), 1.74 (dqq, J = 6.9, 6.9, 6.9 Hz, 1 H), 1.91 (ddd, J = 11.7, 7.7, 7.0 Hz, 1 H), 2.33 (d, J = 8.0 Hz, 1 H), 2.37 (d, J = 8.0 Hz, 1 H), 2.41 (dddd, J = 7.0, 7.0, 2.0, 2.0 Hz, 2 H), 3.88 (ddd, J = 15.0, 9.0, 6.9 Hz, 1 H), 3.91 (dd, J = 15.0, 7.2 Hz, 1 H), 4.19 (dd, J = 9.0, 7.2 Hz, 1 H), 4.75 (dd, J = 2.0, 2.0 Hz, 1 H), 4.87 (dd, J = 2.0, 2.0 Hz, 1 H); IR (CCl$_4$) 3090, 2980, 2830, 1660, 1460, 1355, 1205, 980, 885, 770 cm^{-1}; EI mass spectrum (relative intensity), *m/e* 221 (25), 220 (23), 206 (100), 178 (41), 127 (99), 95 (85), 84 (43), 79 (29), 67 (23). Anal. Calcd for C$_{14}$H$_{23}$NO: C, 75.97; H, 10.47; N, 6.33. Found: C, 76.20; H, 10.55; N, 6.29.

Procedure for the Preparation of 50:50 Mixtures of Diastereomeric Oxazolines 5i–n and 6i–n. The racemic ethyl pent-4-enoates were prepared by ortho-ester Claisen rearrangement of the appropriate allylic alcohol and triethyl orthoacetate. Distillative removal of excess orthoacetate gave the crude esters which were saponified in excess aqueous KOH/EtOH (2 h at 60 °C). After workup, the crude, dried (Na$_2$SO$_4$) acids were condensed with L-valinol as follows. The substituted pent-4-enoic acid (1.71 mmol) and L-valinol (2.20 mmol) were heated with 1.3 g of 4-Å molecular sieves in 5.0 mL of cyclohexane for 16 h at 180 °C in a resealable tube. Cooling, filtration, and rotary evaporation gave the crude oxazolines as yellow oils. MPLC chromatography gave the pure, unresolved 1:1 mixtures of diastereomers **5i–n** and **6i–n**. Proton NMR (90 MHz) and IR spectra were essentially identical with those of enriched samples prepared by the chiron-mediated Claisen rearrangement. At 360 MHz, differences in the ^{1}H NMR's of the diastereomers appeared, but baseline-resolved, quantifiable resonances were absent. However, the 360 MHz ^{1}H NMR's of n-methyloxazolinium salts were in every case quantifiably resolved (see Supplemental Material).

Hydrolysis of Rearranged Oxazolines to Enantiomerically Enriched Acids (7a,b,e,f). In a typical experiment an 81:19 mixture of diastereomeric oxazolines **5a** and **6a** (0.438 g, 2.24 mmol) was stirred with dimethyl sulfate (0.566 g, 4.49 mmol) for 1.5 h at 25 °C. To this was added EtOH (5.0 mL) and 6.0 M KOH (5.0 mL), and the mixture was refluxed 5 h. Upon cooling, the solution was diluted with 25 mL of H$_2$O, washed with Et$_2$O (2×), acidified with concentrated HCl, and extracted with Et$_2$O (3×). Washing with brine, then drying over MgSO$_4$, filtration, and rotary evaporation gave as a yellow oil, the known **(*R*)-(−)-3-methyl-4-pentenoic acid**,[13] (**7a**), 62% ee: 0.222 g, 1.95 mol, 87% yield. Analytical samples were prepared by GLC; $[\alpha]^{25}_{\mathrm{D}}$ −13.0° (c 1.82, CHCl$_3$).

Hydrolysis of an 86:14 mixture of **5b** and **6b** gave the known **(*S*)-(+)-3-methyl-4-pentenoic acid**,[13] (**7b**), 72% ee: 0.132 g, 1.16 mol, 81% yield; $[\alpha]^{25}_{\mathrm{D}}$ +14.0° (c 1.61, CHCl$_3$).

Hydrolysis of a 76:24 mixture of **5e** and **6e** gave **(*R*)-(+)-3-(1-methylethyl)-4-pentenoic acid** (**7e**), 52% ee; 0.225 g, 1.58 mmol, 85% yield; $[\alpha]^{25}_{\mathrm{D}}$ +5.4° (c 2.96, CHCl$_3$); ^{1}H NMR (90 MHz, CDCl$_3$) δ 0.92 (d, J = 7 Hz, 6 H), 1.46–1.90 (m, 1 H), 2.20–2.62 (m, 3 H), 4.90–5.19 (m, 2 H), 5.49–5.99 (m, 1 H), 10.6 (broad s, 1 H); IR (CCl$_4$) 2950, 1705, 1640, 1420, 1390, 1375, 1290, 1180, 990, 915, 745 cm^{-1}. Anal. Calcd for C$_8$H$_{14}$O$_2$: C, 67.57; H, 9.92. Found: C, 67.53; H, 10.08. Treatment of this acid with SOCl$_2$ (2 h, 60 °C), then with NaOEt/CH$_2$Cl$_2$ gave the known ester **(*R*)-(+)-ethyl 2-(1-methylethyl)-4-pentenoate**;[14] 52% ee: 0.159 g, 0.93 mmol, 76% yield, $[\alpha]^{25}_{\mathrm{D}}$ +7.9° (c 1.48, CHCl$_3$).

Hydrolysis of an 87:13 mixture of **5f** and **6f** gave **(*S*)-(−)-3-(1-methylethyl)-4-pentenoic acid** (**7f**), 74% ee: 0.063 g, 0.44 mmol, 78% yield; $[\alpha]^{25}_{\mathrm{D}}$ −5.5° (c 1.27, CHCl$_3$).

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Supplementary Material Available: Spectral data for the *N*-methyloxazolium salts derived from **5i**, **6i**, **5k**, **6k**, **5l**, **6l**, **5m**, **6m**, **5n**, and **6n** (4 pages). Ordering information is given on any current masthead page.

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(25) For spectral data, see supplementary material.