A Synthesis of Various Substituted Naphthalenones by Additions to Naphthyloxazolines

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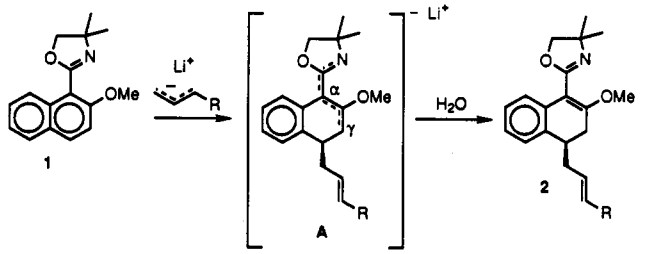
Received March 2, 1992

A series of synthetic manipulations on the naphthalene nucleus, containing a 1-(2-oxazolinyl) moiety, is described. Nucleophilic additions afford both regio- and stereoselective products in the 1- and 4-positions. The latter is oxidatively transformed in the 4-keto system 4 which can undergo various substitutions as well as carbonyl transpositions.

Studies from these laboratories as well as others[1] on oxazoline-mediated aromatic substitution have provided a number of useful synthetic transformations. Both achiral and chiral oxazolines have proved quite valuable in the synthesis of structurally interesting and biologically active natural products including podophyllotoxin[2] and schizandrin.[3]

Recently, it was disclosed[4] that the naphthalene 1 reacts readily with lithioallyl anions affording the adducts, 2.

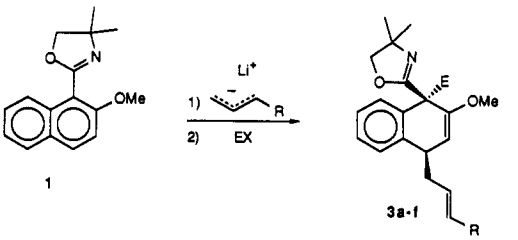


The unexpected addition leading to the 4-allyldihydronaphthalene prompted further study on the properties of the presumed intermediate azadienolate, **A**, and further transformations of the product, **2**. It may be assumed that the latter dihydronaphthalene arose from protonation at the γ-position or at the α-position in **A** with subsequent rearrangement to maintain conjugation in the product, **2**.

In an effort to evaluate the fate of the initially formed anion (**A**), electrophiles other than protons were examined which would, of course, negate any prototropic behavior. Thus, **A**, was treated with carbon electrophiles after the introduction of the allyllithio species. When methyl iodide was introduced into the solution containing **A**, a high yield of regio- and diastereomerically pure adduct, **3a**, was obtained. A series of other carbon electrophiles were also introduced into the intermediate **A** (Table I).

The favorable stereochemical outcome of the two newly introduced alkyl groups in **3** was initially unexpected in view of the seemingly remote placement of these groups. However, considering models of the two most reasonable conformers of the azadienolate **A**, there is a significant difference in the extent of non-bonding interactions between the 4-allyl group and the flanking peri-hydrogen (Figure 1, **B**). Thus, when the allyl moiety occupies a pseudoequatorial position, these nonbonding interactions ($A_{1,3}$-strain (**B**) are quite obvious.[5] On the other hand, if the 4-allyl position assumes a pseudoaxial orientation (**C**), then both nonbonded interactions mentioned above disappear. Instead, the axial group in the latter conformation (**C**) now severely blocks the top (β) face of the azadienolate allowing electrophilic entry only from the bottom (α) face. Based on these models (Chem 3D) which only provide a qualitative assessment of the nature of the anion **A** prior to its alkylation, one can present a reasonable argument that the major conformer present at the point of alkylation to **3** is that depicted by **C**. Single-crystal X-ray study of **3a** showed the anti-disposition of the C-1 methyl and the C-4 (trimethylsilyl)propenyl group.

Table I. Addition of Allyllithiums to 1 Followed by Electrophilic Trapping to Yield Adducts 3a–f



R in allyl	electrophile	% yield of **3a–f**
$SiMe_3$	MeI	**3a**, 95
$SiMe_3$	$I(CH_2)_4Cl$	**3b**, 96
$SiMe_3$	$Br(CH_2)_2CH{=}C(CH_3)_2$	**3c**, 92
$SiMe_3$	$Br(CH_2)_3CO_2Et$	**3d**, 52
$SiMe_3$	$I(CH_2)_3CO_2Et$	**3d**, 89
H	MeI	**3e**, 97
$SiPh_3$	MeI	**3f**, 97

From Table I, the efficiency of the tandem alkylation is clearly seen by the high, isolated yields of the diastereomerically pure adducts **3**. In one instance (**3d**), the yield of the pure material is only 52% when the 4-bromobutyrate ester was employed. This process was also accompanied by the unalkylated adduct **2** in 26% yield. However, when the 4-iodobutyrate was introduced into the lithio intermediate, the yield of product increased to 89%. The easier displacement of iodide by nucleophiles avoided the competitive α-proton abstraction observed with the bromo derivative.

The high degree of regioselectivity observed when the carbon electrophiles were introduced into **A** reflects chelation of the lithium ion to the adjacent methoxyl group and the oxazoline nitrogen that together serve to sequester the electrophile into a complex-induced proximity effect (CIPE).[6]

A rather interesting and significant event occurred during the course of preparing the dialkylated naphthalenes **3a–f**. Small traces of a new material were found when, for example, **3a** was allowed to stand in air.[7] This

(1) Reuman, M.; Meyers, A. I. *Tetrahedron* **1985**, *41*, 837–860 (review).
(2) Andrews, R. C.; Teague, S. J.; Meyers, A. I. *J. Am. Chem. Soc.* **1988**, *110*, 7854–7858.
(3) Warshawsky, A. M.; Meyers, A. I. *J. Am. Chem. Soc.* **1990**, *112*, 8090–8099.
(4) Gant, T. G.; Meyers, A. I. *J. Am. Chem. Soc.* **1992**, *114*, 1010–1015.
(5) The effects of allylic 1,3-strain have been reviewed: (a) Hoffmann, R. W. *Chem. Rev.* **1989**, *89*, 1841–1860. (b) Johnson, F. *Chem. Rev.* **1968**, *68*, 375–413.
(6) Meyers, A. I. *Acc. Chem. Res.* **1978**, *11*, 375–381. For more recent discussions see: Beak, P.; Meyers, A. I. *Acc. Chem. Res.* **1986**, *19*, 356. Also see: Arnett, E. M.; Nichols, M. A.; McPhail, A. T. *J. Am. Chem. Soc.* **1990**, *112*, 7059.
(7) Storage of **3a** "under argon" for approximately 2 months yielded 2.7% of **4a**. The remainder of the mass balance was **3a**.

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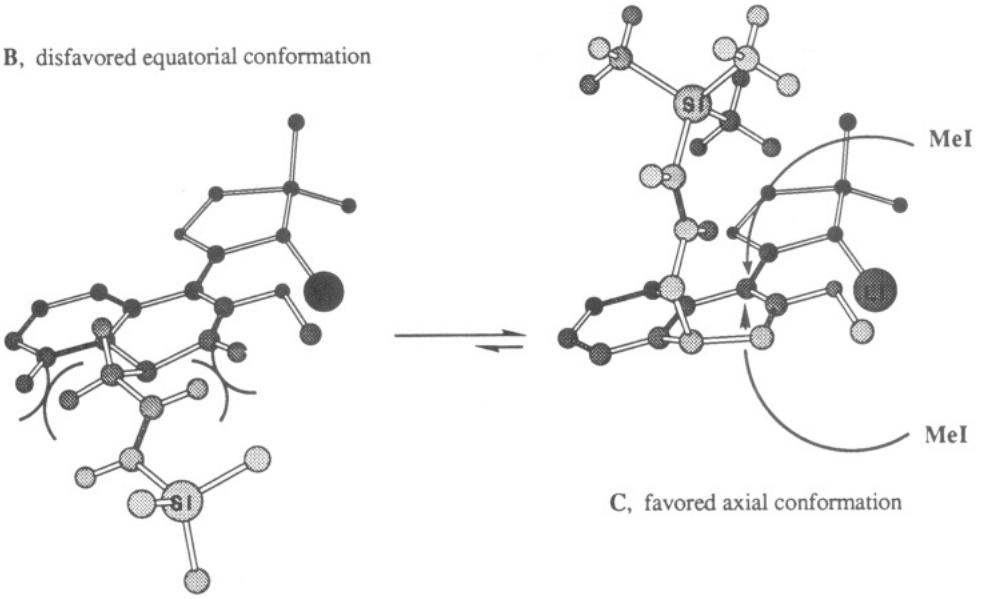
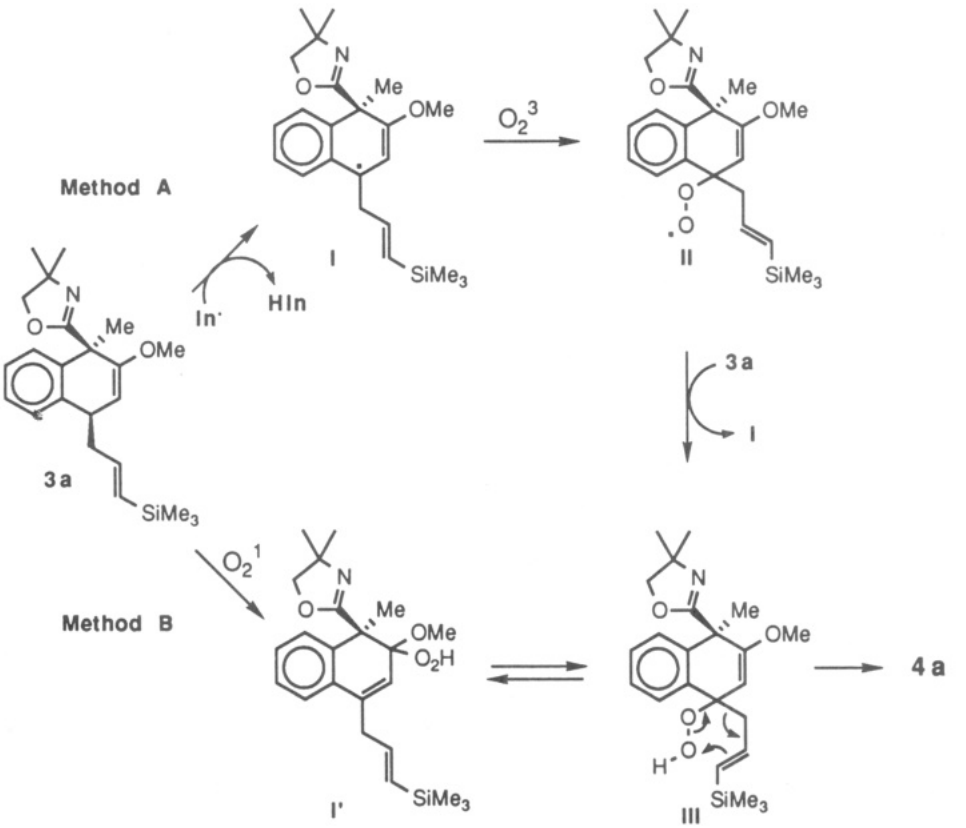
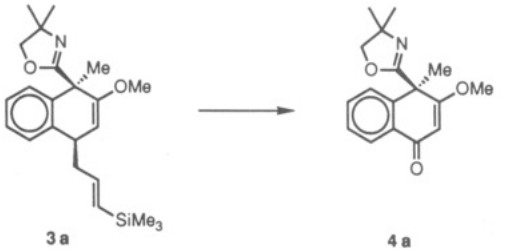


Figure 1.

Scheme I

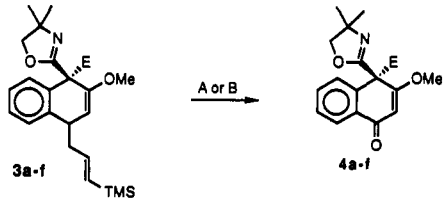


new substance was very polar and highly UV-active and was separated (TLC) and identified as the naphthalenone **4a**. Although numerous examples[8] of benzylic and allylic C–H bond cleavages to oxidized material have been reported, it was still unusual to see the process deliver only two clean compounds (**3a** and **4a**). Furthermore, after 3–6



(8) Numerous examples of benzylic and allylic oxidation exist wherein C–H bonds are oxidized. See, for example: (a) Schultz, A. G.; Taveras, A. G.; Harrington, R. E. *Tetrahedron Lett.* **1988**, *29*, 3907–3910. (b) Pearson, A. J.; Han, G. R. *J. Org. Chem.* **1985**, *50*, 2791–2792. (c) Knight, H. B.; Swern, D. *Organic Syntheses*; Rabjohn, N., Ed.; John Wiley and Sons: New York, 1963; Collect. Vol. IV, pp 895–897. Comparable systems allowing oxidative dealkylation to give the carbonyl compound are much less common. For comparison, see: (d) Kawase, M. *J. Chem. Soc., Chem. Commun.* **1990**, 1328–1329. (e) Siddall, J. B.; Baddeley, G. V.; Edwards, J. A. *Chem. Ind.* **1966**, 25. (f) Sprinzak, Y. *J. Am. Chem. Soc.* **1958**, *80*, 5449–5455.

Table II. Oxidation of Tandem-Addition Products (3a–f) via O_2[3] (Method A) and O_2[1] (Method B)



3[a]	method	E	% yield of 4
a	A	-Me	91 (94)[b]
	B		89
b	A	$-(CH_2)_4Cl$	71 (90)[b]
c	A	$-(CH_2)_2CH{=}C(CH_3)_2$	58 (94)[b]
d	B	$-(CH_2)_3CO_2Et$	85
e	B	-Me	73
f	B	-Me	81

[a] See Table I. [b] Based on recovered starting material.

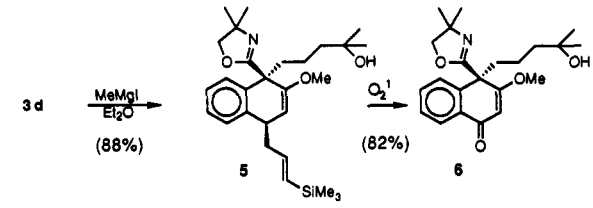
weeks' exposure to the atmosphere, the naphthalenone could be generated in yields as high as 91%.[9] In order to effect a decrease in the reaction time of this oxidative dealkylation, it was necessary to consider the site at which the reaction occurred by some radical initiator, **In**• (Scheme I, method A). The benzylic position, once converted to the radical **I** could, presumably, couple with triplet oxygen in a diffusion-controlled process producing **II**. The latter may propagate the process by transforming starting material **3a** to **I** and itself; now a hydroperoxide **III** can fragment to the observed naphthalenone, **4a**. The above speculative discussion may be responsible for the slow oxidative process observed. However, any effort to accelerate this autoxidation[10] would require generating radical intermediates in the presence of oxygen—a difficult and inefficient process.[11]

The most reasonable conditions under which one may expect acceleration of the oxidation should involve singlet oxygen.[12] Thus, treatment of **3a** with singlet oxygen (method B, Scheme I) was expected to generate **I'** via the well-known hetero-ene process.[13] Since allyl hydroperoxides are known[14] to undergo [2,3] shifts, the formation of **III** might be expected to occur as a part of the equilibrating system. This would be consistent with the key precursor to the final product (**4a**) as suggested above using atmospheric oxygen (method A). Furthermore, since the reaction leading to **4a** is almost certainly irreversible, the nature of the equilibration (**I'**, **III**) is of no consequence.

To test the singlet oxygen-mediated process leading to **4a**, a solution of the 4-allyldihydronaphthalene **3a** in toluene containing rose bengal as sensitizer was irradiated with a 450-W mercury lamp under a steady stream of oxygen. An 89% yield of **4a** was achieved after 12–15 h. Thus, the postulated sequence as written (Scheme I, method B) possessed some validity.

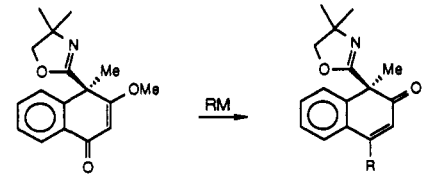
Utilizing both methods (A or B) to achieve oxidative cleavage of the various dihydronaphthalenes **3**, a series of naphthalenones were produced in good yields (Table II).

With these novel substituted naphthalenones in hand, a series of transformations were carried out to demonstrate their synthetic versatility. The addition of methylmagnesium iodide to **3d** (E = $(CH_2)_3CO_2Et$, R = Me_3Si) generated, after workup, the carbinol **5** in good yield (88%) without any effect upon the oxazoline moiety.[15] The oxidative cleavage of the TMS-propenyl group was smoothly accomplished using singlet oxygen and produced the corresponding naphthalenone **6** in 82% yield.



Another organometallic reaction which deserves mention is the 1,2-addition of various reagents to **4a** which furnished the transposed keto derivatives **7a–d** in 70–87% yields (Table III).[16] The use of Grignard or organolithium reagents served equally well in achieving this task. During these studies leading to **7**, it was noted that the virtually

Table III. Organometallic Additions to Enone 4a



RM	R	% yield of 7a–d
MeLi	Me	a, 85
PhLi	Ph	b, 71
allylMgBr	allyl	c, 74
i-PrMgBr	*i*-Pr	d, 87

Table IV. Effect of Solvent on Ratio of 1,2-Addition Product (7d) to 1,6-Addition Product (10)

solvent	% yield of 7d[a]	% yield of 10[a]
THF	57–65	30–39 (33)[b]
THF/TMEDA	66	26
dioxane	73	20
Et_2O	83	11
benzene	92 (87)[b]	0

[a] GLC yields. [b] The numbers in parentheses are the maximum isolated yields obtained for each product.

(9) Direct exposure to the atmosphere resulted in a conversion rate of 2–8% per day.

(10) For discussions of autoxidation, see: (a) Porter, N. A. *Acc. Chem. Res.* **1986**, *19*, 262–268. (b) Patai, S. *The Chemistry of Peroxides*; John Wiley and Sons: New York, 1983. (c) Voronenkov, V. V.; Vinogradov, A. N.; Belyaev, V. A. *Russ. Chem. Rev.* **1970**, *39*(11), 944–952. (d) Ingold, K. U. *Acc. Chem. Res.* **1969**, *2*, 1–9. (e) Mayo, F. R. *Acc. Chem. Res.* **1968**, *1*, 193–201. (f) Stewart, R. *Oxidation Mechanisms, Applications to Organic Chemistry*; W. A. Benjamin, Inc.: New York, 1964.

(11) The question of autoxidation acceleration has been addressed: (a) Larkin, D. R. *J. Org. Chem.* **1990**, *55*, 1563–1568 and references cited therein. (b) Niu, Q.; Mendenhall, G. D. *J. Am. Chem. Soc.* **1990**, *112*, 1656–1657 and references cited therein. (c) Boga, E.; Peintler, G.; Nagypal *J. Am. Chem. Soc.* **1990**, *112*, 151–153 and references cited therein. A number of these methods were tried without any observable rate increase. An extensive literature survey of these methods was not carried out due to the success of the triplet oxygen technique.

(12) For reviews of singlet oxygen chemistry, see: (a) Wasserman, H. H.; Ives, J. L. *Tetrahedron* **1981**, *37*, 1825–1852. (b) Frimer, A. A. *Chem. Rev.* **1979**, *79*, 359–385. (c) Denny, R. W.; Nickon, A. *Org. React.* **1973**, *20*, 133–336. (d) Kearns, D. R. *Chem. Rev.* **1971**, *71*, 395–427.

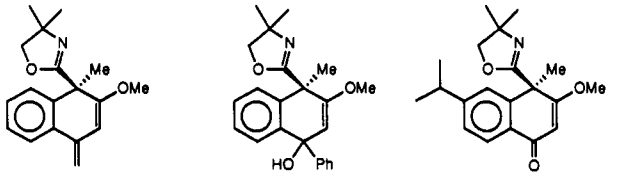
(13) Concerning the mechanism of the singlet oxygen ene reaction, see: (a) Yamaguchi, K.; Yabushita, S.; Fueno, T.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 5043–5046. (b) Harding, L. B.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1980**, *102*, 439–449.

(14) For a recent study on the equilibration of allyl hydroperoxides, see: Dang, H.-S.; Davies, A. G.; Davison, I. G. E.; Schiesser. C. H. *J. Org. Chem.* **1990**, *55*, 1432–1438.

(15) The oxazoline resistance to Grignard reagents has been well documented. See, for example: Greene, T. W. *Protective Groups in Organic Synthesis*; J. Wiley and Sons: New York, 1981; pp 315–318.

(16) For recent examples of additions of organometallics to β-alkoxy enones, see: (a) Zimmerman, H. E.; Solomon, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 6276–6289. (b) Curran, D. P.; Kuo, S.-C. *J. Am. Chem. Soc.* **1986**, *108*, 1106–1107.

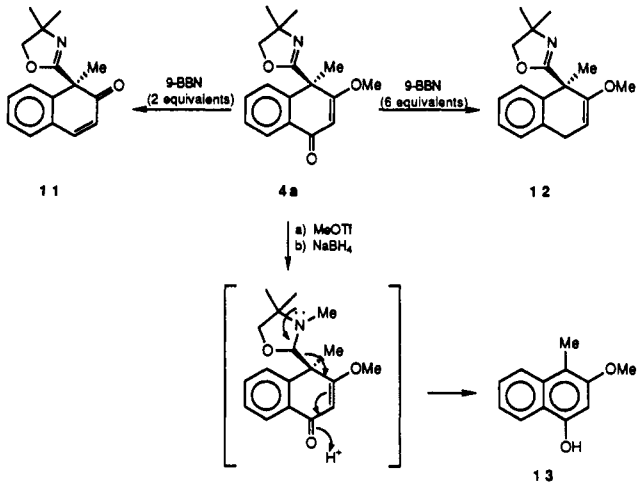
exclusive 1,2-additions also provided varying amounts of labile intermediates (e.g., **8**, **9**) which, as expected, were easily transformed into their corresponding products (**7a**, **7b**, respectively). When isopropylmagnesium bromide was employed, the presence of the alkylation product **10** was observed along with the major product, **7d**. The former undoubtedly arose from the rarely observed 1,6-addition.[17] In an effort to shed further light on the factors affecting this process, the isopropylmagnesium bromide was added in several different solvents varying in polarity (Table IV). It may be seen from the data that the ratio of 1,2 (**7d**) to 1,6 addition (**10**) roughly parallels the coordinating



8 **9** **10**

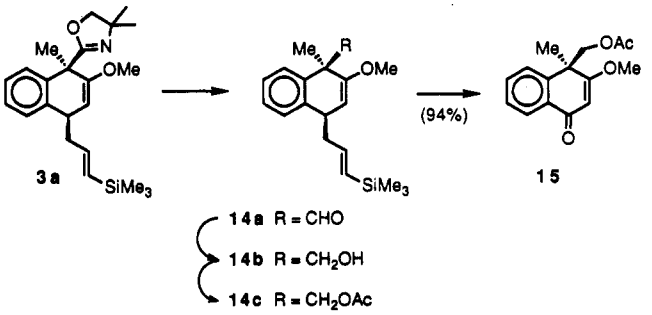
strength of the solvent and reaches a maximum of 33% yield of **10** in THF. In benzene, the total absence of **10** was noted and the 1,2-addition product was obtained in 87% yield. It should be noted that no change in 1,2- to 1,6-addition ratio was seen when the temperature of the additions was varied from −78 °C to reflux in THF.

Useful levels of selectivity were observed when the naphthalene **4a** was subjected to reduction by 9-BBN.[18] When 2.0 equiv of 9-BBN was employed, an 80% yield of the enone **11** was obtained along with a trace of the overreduced enol ether, **12**. When an excess of 9-BBN (6.0 equiv) was added to **4a**, the enol ether **12** was found to be the major product (74%). Again, it is interesting to note



11 **4a** **12** **13**

that the oxazoline moiety survived these conditions. Removal of the oxazoline moiety, a necessary transformation in most of these synthetic sequences so that more varied and useful functional groups could be introduced, was performed by previously described methods.[1] When **4a** was treated with methyl triflate (to alkylate the nitrogen), sodium borohydride (to reduce the iminium bond), and aqueous oxalic acid, it was surprising to find as the only product, the α-naphthol derivative, **13** in 60% yield. Presumably, the intermediate oxazolidine–naphthalenone is highly susceptible to proton-catalyzed aromatization with concurrent loss of the oxazoline group.[19] This highly undesirable reaction was circumvented by returning to the 4-allyl derivatives **3a**, devoid of the enone properties such as found in **4a**. By removal of the oxazoline in **3a**, utilizing the methyl triflate–$NaBH_4$–oxalic acid treatment, the aldehyde **14a** was obtained in over 80% yield. Reduction to the carbinol **14b** with $NaBH_4$ proceeded in 96% yield and acylation to the acetoxy derivative **14c** took place smoothly in quantitative yield. At this point the singlet oxygen process was brought into play (Table II, method B) and afforded the acetoxynaphthalenone **15** in 94% yield. Thus, oxazoline removal should not be a problem



when faced with related systems, so long as the naphthalenone moiety is absent at the stage of removal. Efforts toward several naturally occurring materials are underway.[20]

Experimental Section

General. All compounds were purified via silica gel chromatography yielding suitably pure materials as judged by the authors. In certain instances, NMR data have been included as supplementary material in lieu of combustion analyses. Melting points are uncorrected. ^1H NMR spectra were recorded at 300 MHz, and ^{13}C NMR spectra were recorded at 75.5 MHz (in $CDCl_3$). Carbon multiplicities were obtained from DEPT experiments, and chemical shifts are expressed as δ.

Tandem-Addition Products 3a–f. General Procedure. A stirred solution of allyltrimethylsilane[21] **3a–d**, allyltributyltin **3e**, or allyltriphenylsilane[22] **3f** (2.33 equiv) and TMEDA (2 equiv) in THF (5 mL/mmol 1) was cooled to −78 °C and treated with *s*-BuLi (**3a–d,f**) (2 equiv) or *n*-BuLi (**3e**) (2 equiv) dropwise over 10 min. Stirring was continued for 1 h at −78 °C and an additional 1 h at −40 °C. The mixture was recooled to −78 °C followed by addition of 2-methoxy-1-naphthyloxazoline, **1**, in THF (3 mL/mmol 1) was added dropwise over 5 min. The solution was allowed to warm to ambient temperature over 16 h, recooled to −78 °C and treated with electrophile (4 equiv) (see Table I) dropwise. The solution was then warmed to 0 °C over 5 h. Saturated aqueous NH_4Cl, ether, and water were added sequentially. The organic layer was dried ($MgSO_4$), filtered, and concentrated. Radial chromatography using hexanes/ethyl acetate (4:1) (**3a–c,f**) or (10:1) (**3d,e**) as eluent provided pure materials.

1-(5,5-Dimethyl-2-oxazolinyl)-2-methoxy-1-methyl-4-(1-(trimethylsilyl)-2-propenyl)-1,4-dihydronaphthalene (3a). Obtained as white crystals (1.098 g, 2.86 mmol, 95%): mp 67–67.5 °C; IR (KBr pellet) 2975, 2954, 1687, 1660, 1618, 1450, 1278, 1244,

(17) A similar 1,6-addition/hydride–elimination has been previously observed: Fuson, R. C.; Tull, R. *J. Am. Chem. Soc.* **1949**, *71*, 2543–2546.

(18) (a) Reduction of the enol ethers of β-diketones by LAH: Gannon, W. F.; House, H. O. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, pp 294–296. (b) 9-BBN has been employed in the reduction of enones to allylic alcohols: Krishnamurthy, S.; Brown, H. C. *J. Org. Chem.* **1977**, *42*, 1197–1201.

(19) Unpublished results.

(20) Representative examples of targeted natural products include: (a) Halenaquinone: Harada, N.; Sugioka, T.; Ando, Y.; Uda, H.; Kuriki, T. *J. Am. Chem. Soc.* **1988**, *110*, 8483–8487. (b) Nimbiol: *The Merck Index*, 11th *ed.* Budavri, S., Ed.; Merck and Co.: Rahway, NJ, 1989; p 1035 and references cited therein. (c) Salvinolone: Lin, L.-Z.; Blasko, G.; Cordell, G. A. *Phytochem.* **1989**, *28*(1), 177–181. For a recent example of a tetralin system that is particularly suited to this synthetic sequence, cf. Lejeune, J.; Lallemand, J. Y.; Prange, T.; Ricard, L. *Tetrahedron Lett.* **1991**, *32*, 2621–2624.

(21) Lithioallyltrimethylsilane prepared according to: Lau, P. W. K.; Chan, T. H. *Tetrahedron Lett.* **1978**, *27*, 2383–2386 and references cited therein.

(22) Allyltriphenylsilane has been previously prepared by an alternative procedure: Henry, M. C.; Noltes, J. G. *J. Am. Chem. Soc.* **1960**, *82*, 555–558.

1206, 1111, 866, 836 cm^{-1}; ^{1}H NMR 0.030 (s, 9 H), 1.27 (s, 3 H), 1.34 (s, 3 H), 1.69 (s, 3 H), 2.39–2.50 (m, 1 H), 2.65–2.74 (m, 1 H), 3.59 (s, 3 H), 3.61–3.68 (m, 1 H), 3.75 (A of AB, J = 8.0 Hz, 1 H), 3.84 (B of AB, J = 8.0 Hz, 1 H), 4.86 (d, J = 3.7 Hz, 1 H), 5.69 (dt, J = 18.5, 1.2 Hz, 1 H), 6.05 (ddd, J = 18.5, 7.2, 6.0, 1 H), 7.15–7.35 (m, 4 H); ^{13}C NMR -1.2, 27.6, 27.8, 28.1, 37.6, 44.0, 46.7, 54.6, 66.8, 79.3, 95.8, 126.3, 126.4, 126.6, 127.6, 132.5, 136.4, 138.4, 144.7, 154.5, 168.2. For complete X-ray data, see supplementary material. Anal. Calcd for $C_{23}H_{33}NO_2Si$: C, 72.01; H, 8.67; N, 3.65. Found: C, 72.10; H, 8.69; N, 3.62.

1-(5,5-Dimethyl-2-oxazolinyl)-1-(4-chlorobutyl)-2-methoxy-4-(1-(trimethylsilyl)-2-propenyl)-1,4-dihydronaphthalene (3b). Obtained as a clear colorless oil that solidified upon standing (442 mg, 0.96 mmol, 96%): IR (CCl_4) 2959, 1688, 1654, 1616, 1450, 1247, 1210, 1000 cm^{-1}; ^{1}H NMR 0.00 (s, 9 H), 0.54–0.70 (m, 1 H), 1.10–1.18 (m, 1 H), 1.23 (s, 3 H), 1.31 (s, 3 H), 1.50–1.67 (m, 2 H), 2.04 (dt, J = 4.6, 12.6 Hz, 1 H), 2.31–2.48 (m, 2 H), 2.61–2.72 (m, 1 H), 3.26–3.42 (m, 2 H), 3.56 (s, 3 H), 3.58–3.65 (m, 1 H), 3.70 (A of AB, J = 8.0 Hz, 1 H), 3.79 (B of AB, J = 8.0 Hz, 1 H), 4.97 (d, J = 3.7 Hz, 1 H), 5.67 (dt, J = 18.5, 1.2 Hz, 1 H), 6.03 (ddd, J = 5.9, 7.2, 18.5 Hz, 1 H), 7.11–7.30 (m, 4 H); ^{13}C NMR -1.2 (q), 21.0 (t), 27.8 (q), 28.1 (q), 32.4 (t), 36.7 (t), 37.6 (d), 44.8 (t), 46.8 (t), 47.8 (s), 54.5 (q), 66.8 (s), 79.0 (t), 98.2 (d), 125.6 (d), 126.5 (d), 126.6 (d), 127.6 (d), 132.5 (d), 136.0 (s), 137.8 (s), 144.7 (d), 151.5 (s), 168.2 (s).

1-(5,5-Dimethyl-2-oxazolinyl)-2-methoxy-1-(4-methyl-3-pentenyl)-4-(1-(trimethylsilyl)-2-propenyl)-1,4-dihydronaphthalene (3c). Obtained as a clear colorless oil that solidified upon standing (415 mg, 0.92 mmol, 92%): IR (neat) 2961, 1742, 1688, 1656, 1615, 1450, 1246, 1206, 999 cm^{-1}; ^{1}H NMR 0.01 (s, 9 H), 1.09–1.30 (m, 1 H), 1.23 (s-overlaps multiplet, 3 H), 1.30 (s, 6 H), 1.51 (s, 3 H), 1.51–1.68 (m, 1 H), 2.04 (dt, J = 4.8, 12.6 Hz, 1 H), 2.31–2.46 (m, 2 H), 2.67 (dt, J = 4.8, 13.7 Hz, 1 H), 3.56 (s, 3 H), 3.56–3.64 (m, 1 H), 3.70 (A of AB, J = 8.0 Hz, 1 H), 3.79 (B of AB, J = 8.0 Hz, 1 H), 4.92–4.98 (m, 2 H), 5.68 (d, J = 18.5 Hz, 1 H), 6.04 (dt, J = 18.5, 7.1 Hz, 1 H), 7.15–7.32 (m, 4 H); ^{13}C NMR -1.2 (q), 17.2 (q), 22.4 (t), 25.5 (q), 27.8 (q), 28.1 (q), 37.7 (d), 37.8 (t), 46.9 (t), 47.9 (s), 54.5 (q), 66.8 (s), 79.0 (t), 98.0 (d), 124.2 (d), 125.8 (d), 126.4 (d), 126.5 (d), 127.4 (d), 131.0 (s), 132.4 (d), 136.2 (s), 137.8 (s), 144.8 (d), 151.75 (s), 168.2 (s); MS m/z 483 (M$^+$). Anal. Calcd for $C_{28}H_{41}NO_2Si$: C, 74.45; H, 9.15; N, 3.10. Found: C, 74.46; H, 9.20; N, 3.11.

1-(5,5-Dimethyl-2-oxazolinyl)-1-(4-(ethoxycarbonyl)propyl)-2-methoxy-4-(1-(trimethylsilyl)-2-propenyl)-1,4-dihydronaphthalene (3d). Obtained as a clear colorless oil. **Method A.** Utilizing ethyl 4-iodobutyrate (0.92 mL, 6.00 mmol) as electrophile, a clear oil was obtained (431 mg, 0.89 mmol, 89%): IR (neat) 2960, 1736, 1689, 1655, 1616, 1248, 1208 cm^{-1}; ^{1}H NMR 0.00 (s, 9 H), 0.73–0.90 (m, 1 H), 1.15 (t, J = 7.1 Hz, 3 H), 1.20–1.35 (m, 7 H), 1.97–2.20 (m, 3 H), 2.31–2.46 (m, 2 H), 2.62–2.72 (m, 1 H), 3.56 (s, 3 H), 3.60–3.65 (m 1 H), 3.70 (A of AB, J = 8.0 Hz, 1 H), 3.79 (B of AB, J = 8.0 Hz, 1 H), 3.99 (q, J = 7.1 Hz, 2 H), 4.97 (d, J = 3.6 Hz, 1 H), 5.67 (d, J = 18.5 Hz, 1 H), 6.03 (dt, J = 18.5, 7.1 Hz, 1 H), 7.10–7.30 (m, 4 H); ^{13}C NMR -1.2 (q), 14.1 (q), 19.2 (t), 27.8 (q), 28.1 (q), 34.1 (t), 37.2 (t), 37.5 (d), 46.7 (t), 47.8 (s), 54.5 (q), 60.0 (t), 66.7 (s), 79.0 (t), 98.2 (d), 125.7 (d), 126.5 (d), 126.6 (d), 127.6 (d), 132.5 (d), 135.8 (s), 137.7 (s), 144.7 (d), 151.3 (s), 168.2 (s), 173.5 (s); MS m/z 483 (M$^+$), 370, 253, 115.

Method B. Utilizing ethyl 4-bromobutyrate (0.86 mL, 6.00 mmol) as electrophile, a clear oil with spectral characteristics as described above was obtained (252 mg, 0.52 mmol, 52%) along with protonated product **2** (95 mg, 0.26 mmol, 26%). The spectral characteristics of **2** have been previously described.[4]

1-(5,5-Dimethyl-2-oxazolinyl)-2-methoxy-1-methyl-4-(2-propenyl)-1,4-dihydronaphthalene (3e). Obtained as a clear oil (302 mg, 0.97 mmol, 97%): IR (neat) 2972, 2934, 1686, 1656, 1451, 1210, 911 cm^{-1}; ^{1}H NMR 1.26 (s, 3 H), 1.33 (s, 3 H), 1.69 (s, 3 H), 2.31–2.44 (m, 1 H), 2.60–2.71 (m, 1 H), 3.58–3.66 (m, 4 H), 3.76 (A of AB, J = 8.0 Hz, 1 H), 3.84 (B of AB, J = 8.0 Hz, 1 H), 4.90 (d, J = 3.7 Hz, 1 H), 5.02–5.11 (m, 2 H), 5.80–5.94 (m, 1 H), 7.17–7.36 (m, 4 H); ^{13}C NMR 27.4 (q), 27.8 (q), 28.1 (q), 37.7 (d), 43.7 (t), 44.0 (s), 54.6 (q), 66.8 (s), 79.2 (t), 95.6 (d), 116.4 (t), 126.3 (d), 126.4 (d), 126.6 (d), 127.5 (d), 136.3 (s), 136.6 (d), 138.3 (s), 154.6 (s), 168.1 (s); MS m/z 311 (M$^+$), 270, 238, 184.

Allyltriphenylsilane. A solution of triphenylpropargylsilane (5.97 g, 20.0 mmol) in benzene (35 mL) was added to a suspension of Lindlar's catalyst (Aldrich) (100 mg) and quinoline (0.5 mL) in hexane (15 mL). The resulting mixture was subjected to an atmosphere of H_2 at ambient temperature for 9 h (reaction progress was monitored by GC–MS). Filtration through Celite, concentration, and recrystallization (hexanes/ethyl acetate) followed by radial chromatographic purification of the mother liquor using hexanes/ethyl acetate (4:1) yielded 5.77 g (19.2 mmol, 96%) of a white crystalline material: mp 88–89 °C (lit.[22] mp 84–86 °C); ^{1}H NMR 2.40 (dt, J = 7.9, 1.0 Hz, 2 H), 4.87–4.99 (m, 2 H), 5.80–5.95 (m, 1 H), 7.33–7.44 (m, 9 H), 7.51–7.55 (m, 6 H); MS m/z 300 (M$^+$), 259, 181, 105.

1-(5,5-Dimethyl-2-oxazolinyl)-2-methoxy-1-methyl-4-(1-(triphenylsilyl)-2-propenyl)-1,4-dihydronaphthalene (3f). Obtained as a crystalline white foam (277 mg, 0.486 mmol, 97%): mp 61–63 °C; IR (CCl_4) 3070, 2966, 1656, 1428, 1112 cm^{-1}; ^{1}H NMR 1.17 (s, 3 H), 1.26 (s, 3 H), 1.68 (s, 3 H), 2.60–2.70 (m, 1 H), 2.83 (dt, J = 13.9, 4.3 Hz, 1 H), 3.32 (A of AB, J = 8.0 Hz, 1 H), 3.52 (B of AB, J = 8.0 Hz, 1 H), 3.54 (s, 3 H), 3.69–3.75 (m, 1 H), 4.87 (d, J = 3.5 Hz, 1 H), 6.16–6.34 (m, 2 H), 7.19–7.55 (m, 19 H); ^{13}C NMR 27.6, 27.8, 28.1, 37.5, 44.0, 46.4, 54.6, 54.6, 66.7, 79.0, 95.7, 126.2, 126.3, 126.4, 126.7, 127.5, 127.7, 127.8, 129.3, 129.5, 134.4, 134.9, 135.8, 135.9, 138.4, 150.6, 154.7, 168.1.

Naphthalenones 4a–d, 6. General Procedures. Method A. Into a flask was placed the tandem-addition product **3a–c** in Et_2O. This solution was allowed to concentrate to an oily residue, open to the atmosphere. The residue was redissolved every 1–4 days to allow GLC analysis. After 3–6 weeks, the residue was dissolved in CH_2Cl_2 for application onto a chromatotron plate. Radial chromatography using hexanes/ethyl acetate (4:1–2:1) yielded pure materials. (Reaction time was highly variable for all substrates depending on reaction container used. Specifically, a large flat surface area produced oxidized products faster owing to increased surface area).

Method B. A solution of tandem-addition product **3a,d–f** in toluene (1 mL/10 mg of **3**) was treated with Rose Bengal (1 mg/10 mg of **3**) and a gentle stream of oxygen (20-gauge needle bubbler) under irradiation by medium-pressure Hg lamp (450 W) for 15–24 h. To the reaction mixture was added ether and a small amount of triethylamine. Filtration through a small plug of Celite/silica gel, concentration, and radial chromatography using hexanes/ethyl acetate (4:1–2:1) (with ~1% triethylamine to hold the rose bengal to the base line) yielded pure materials.

4-(5,5-Dimethyl-2-oxazolinyl)-3-methoxy-4-methylnaphthal-2-en-1-one (4a) from 3a. Method A. Obtained as light yellow crystals (107 mg, 0.375 mmol, 91%) as well as starting material (5 mg, 0.013 mmol, 3%) (94% based on consumed starting material): mp 157–159 °C; IR (KBr pellet) 2969, 2942, 1650, 1622, 1600, 1574, 1460, 1374, 1354, 1237, 1219, 1141, 993, 974 cm^{-1}; ^{1}H NMR 1.30 (s, 3 H), 1.36 (s, 3 H), 1.82 (s, 3 H), 3.79 (A of AB, J = 8.1 Hz, 1 H), 3.85 (s, 3 H), 3.87 (B of AB, J = 8.1 Hz, 1 H), 7.42–7.59 (m, 3 H), 8.19 (dd, J = 1.3, 7.7 Hz, 1 H); ^{13}C NMR 27.3 (q), 27.8 (q), 28.0 (q), 45.7 (s), 56.3 (q), 67.2 (s), 79.7 (t), 102.0 (d), 125.5 (d), 126.5 (d), 127.6 (d), 129.9 (s), 132.6 (d), 142.6 (s), 165.4 (s), 175.4 (s), 185.0 (s); MS m/z 285 (M$^+$), 270, 240, 214, 187, 155, 127. Anal. Calcd for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.71; N, 4.91. Found: C, 71.43; H, 6.68; N, 4.96.

Method B. Obtained as light yellow crystals (401 mg, 1.41 mmol, 89%): spectral characteristics matched those listed above.

4-(4-Chlorobutyl)-4-(5,5-dimethyl-2-oxazolinyl)-3-methoxynaphthal-2-en-1-one (4b). Method A. Obtained as a white powder (105 mg, 0.29 mmol, 71%) in addition to starting material (40 mg, 0.087 mmol, 21%) (90% based on consumed starting material): mp 141–141.5 °C; IR (CCl_4) 2967, 1650, 1624, 1455, 1361, 1233, 1219, 1000 cm^{-1}; ^{1}H NMR 0.58–0.73 (m, 1 H), 1.00–1.15 (m, 1 H), 1.28 (s, 3 H), 1.35 (s, 3 H), 1.52–1.69 (m, 2 H), 2.32 (dt, J = 4.5, 13.0 Hz, 1 H), 2.54 (dt, J = 4.6, 12.9 Hz, 1 H), 3.28–3.42 (m, 2 H), 3.75 (A of AB, J = 8.0 Hz, 1 H), 3.84 (B of AB, J = 8.0 Hz, 1 H), 3.85 (s, 3 H), 5.98 (s, 1 H), 7.42–7.49 (m, 2 H), 7.55–7.60 (m, 1 H), 8.18–8.21 (m, 1 H); ^{13}C NMR 20.3 (t), 27.6 (q), 27.9 (q) 32.0 (t), 37.1 (t), 44.1 (t), 49.5 (s), 56.3 (q), 67.1 (s), 79.3 (t), 104.3 (d), 125.0 (d), 126.3 (d), 127.8 (d), 131.4 (s), 132.7 (d), 140.5 (s), 165.4 (s), 173.0 (s), 185.1 (s); MS m/z 361 (M$^+$), 346, 326, 296, 271, 199, 115. Anal. Calcd for $C_{20}H_{24}ClNO_3$: C, 66.38; H, 6.68; N, 3.87. Found: C, 66.45; H, 6.69; N, 3.90.

4-(5,5-Dimethyl-2-oxazolinyl)-3-methoxy-4-(4-methyl-3-pentenyl)naphthal-2-en-1-one (4c). Method A. Obtained as

a white powder (141 mg, 0.42 mmol, 58%) in addition to starting material (125 mg, 0.277 mmol, 38%) (94% based on consumed starting material): mp 105–107 °C; IR (CCl_4) 2968, 1650, 1625, 1455, 1363, 1224, 998 cm^{-1}; ^1H NMR 1.24–1.36 (complex, 10 H), 1.51–1.68 (complex, 4 H), 2.29–2.39 (m, 1 H), 2.49–2.59 (m, 1 H), 3.75 (A of AB, J = 8.0 Hz, 1 H), 3.84 (B of AB, J = 8.0 Hz, 1 H), 3.85 (s, 3 H), 4.84–4.94 (m, 1 H), 5.98 (s, 1 H), 7.28–7.60 (m, 3 H), 8.19 (dd, J = 1.2, 7.8 Hz, 1 H); ^{13}C NMR 17.2, 21.9, 25.4, 27.7, 28.0, 38.2, 49.6, 56.2, 67.1, 79.3, 104.2, 122.8, 125.2, 126.2, 127.7, 131.5, 132.2, 132.6, 140.8, 165.5, 173.3, 185.3.

4-(5,5-Dimethyl-2-oxazolinyl)-4-(4-(ethoxycarbonyl)-propyl)-3-methoxynaphthal-2-en-1-one (4d). Method B. Obtained as a clear colorless oil (171 mg, 0.444 mmol, 85%): IR (CCl_4) 2975, 1736, 1651, 1626, 1456, 1358, 1224, 999 cm^{-1}; ^1H NMR 0.67–0.85 (m, 1 H), 1.06 (t, J = 7.2 Hz, 3 H), 1.09–1.28 (m, 7 H), 2.04 (app. dt, J = 2.8, 7.4 Hz, 2 H), 2.24 (dt, J = 4.4, 13.1 Hz, 1 H), 2.44 (dt, J = 4.6, 12.9 Hz, 1 H), 3.64 (A of AB, J = 8.1 Hz, 1 H), 3.73 (B of AB, J = 8.1 Hz, 1 H), 3.75 (s, 3 H), 3.91 (q, J = 7.2 Hz, 2 H), 5.88 (s, 1 H), 7.31–7.50 (m, 3 H), 8.08 (dd, J = 1.3, 7.7 Hz, 1 H); ^{13}C NMR 13.9 (q), 18.4 (t), 27.5 (q), 27.8 (q), 33.4 (t), 37.2 (t), 49.3 (s), 56.2 (q), 60.0 (t), 66.9 (s), 79.1 (t), 104.1 (d), 125.0 (d), 126.1 (d), 127.6 (d), 131.2 (s), 132.6 (d), 140.2 (s), 165.2 (s), 172.5 (s), 172.8 (s), 184.9 (s); MS m/z 385 (M^+), 370, 354, 314, 271, 115.

4-(5,5-Dimethyl-2-oxazolinyl)-3-methoxy-4-methylnaphthal-2-en-1-one (4a) from 3e. Method B. Obtained as light orange crystals (204 mg, 0.71 mmol, 73%). Spectral characteristics matched those listed above.

4-(5,5-Dimethyl-2-oxazolinyl)-3-methoxy-4-methylnaphthal-2-en-1-one (4a) from 3f. Method B. Obtained as light orange crystals (293 mg, 1.03 mmol, 81%). Spectral characteristics matched those listed above.

4-(5,5-Dimethyl-2-oxazolinyl)-3-methoxy-4-(4-methyl-4-hydroxypentyl)naphthal-2-en-1-one (6). Method B. Obtained as white crystals (91 mg, 0.245 mmol, 82%): mp 135–136.5 °C; IR (CCl_4) 3371, 2970, 1656, 1649, 1627, 1357, 1229, 994 cm^{-1}; ^1H NMR 0.51–0.68 (m, 1 H), 0.85–1.07 (m, 7 H), 1.11–1.42 (m, 9 H), 2.28 (dt, J = 4.5, 13.2 Hz, 1 H), 2.49 (dt, J = 4.6, 12.3 Hz, 1 H), 3.72 (A of AB, J = 8.1 Hz, 1 H), 3.80 (B of AB, J = 8.1 Hz, 1 H), 3.81 (s, 3 H), 5.94 (s, 1 H), 7.38–7.56 (m, 3 H), 8.15 (dd, J = 1.2, 7.6 Hz, 1 H); ^{13}C NMR 17.9 (t), 27.6 (q), 27.9 (q), 28.8 (q), 29.1 (q), 38.6 (t), 43.1 (t), 49.7 (s), 56.2 (q), 67.0 (s), 70.4 (s), 79.2 (t), 104.0 (d), 125.1 (d), 126.2 (d), 127.6 (d), 131.2 (s), 132.6 (d), 140.7 (s), 165.5 (s), 173.4 (s), 185.2 (s); MS m/z 371 (M^+), 356, 340, 284, 271, 199. Anal. Calcd for $C_{22}H_{29}NO_4$: C, 71.13; H, 7.87; N, 3.77. Found: C, 71.06; H, 7.84; N, 3.74.

1-(5,5-Dimethyl-2-oxazolinyl)-2-methoxy-1-(4-methyl-4-hydroxypentyl)-4-(1-(trimethylsilyl)-2-propenyl)-1,4-dihydronaphthalene (5). To a stirred mixture of methylmagnesium iodide (0.90 mL of a 3.0 M solution in ether, 2.7 mmol) in ether (20 mL) was added a solution of ester (217 mg, 0.45 mmol) in ether (10 mL). After being heated at reflux 4 h, the mixture was quenched (H_2O, vigorous bubbling), extracted (ether), dried ($MgSO_4$), and purified via radial chromatography (2-mm plate) using hexanes/ethyl acetate (4:1–1:1) as eluent to afford a clear colorless oil (186 mg, 0.396 mmol, 88%): IR (CCl_4) 3395 (br), 2962, 1689, 1654, 1616, 1465, 1450, 1247, 1210, 1000 cm^{-1}; ^1H NMR 0.00 (s, 9 H), 0.51–0.69 (m, 1 H), 0.90–1.41 (m, 16 H), 1.93–2.10 (m, 1 H), 2.28–2.46 (m, 2 H), 2.60–2.73 (m, 1 H), 3.55 (s, 3 H), 3.56–3.63 (m, 1 H), 3.70 (A of AB, J = 7.9 Hz, 1 H), 3.78 (B of AB, J = 7.9 Hz, 1 H), 4.96 (d, J = 3.5 Hz, 1 H), 5.67 (d, J = 18.5 Hz, 1 H), 6.03 (dt, J = 18.5, 6.5 Hz, 1 H), 7.12–7.28 (m, 4 H); ^{13}C NMR −1.2 (q), 18.3 (t), 27.8 (q), 28.1 (q), 28.95 (q), 29.04 (q), 37.6 (d), 38.2 (t), 43.6 (t), 46.8 (t), 48.0 (s), 54.5 (q), 66.7 (s), 70.8 (s), 78.9 (t), 98.1 (d), 125.7 (d), 126.4 (d), 126.5 (d), 127.5 (d), 132.5 (d), 136.2 (s), 137.7 (s), 144.7 (d), 151.8 (s), 168.3 (s); MS m/z 469 (M^+), 454, 356, 324, 256, 184.

Addition of Organometallics to 4a Producing 7a–d, 8, 9, and 10. General Procedure. A solution of **3a** in THF (5–10 mL/mmol of **3a**) (*i*-PrMgBr reactions were run with various solvents and temperatures as given in Table IV) was cooled to −78 °C and treated with the appropriate organometallic reagent (1.1–1.2 equiv). The mixture was allowed to warm to ambient temperature and was then quenched (saturated aqueous NH_4Cl) and diluted (ether). Where appropriate, a minimal quantity of HCl (6 N) was added to assist hydrolysis of intermediates. The organic layer was then separated, dried ($MgSO_4$), concentrated, and purified via radial chromatography (2-mm plate) using hexanes/ethyl acetate (4:1) as eluent to yield pure materials.

1-(5,5-Dimethyl-2-oxazolinyl)-2-methoxy-1-methyl-4-methylidene-1,4-dihydronaphthalene (8). Obtained as a waxy solid: ^1H NMR 1.27 (s, 3 H), 1.32 (s, 3 H), 1.70 (s, 3 H), 3.70 (s, 3 H), 3.76 (A of AB, J = 8.0 Hz, 1 H), 3.84 (B of AB, J = 8.0 Hz, 1 H), 4.97 (s, 1 H), 5.52 (s, 1 H), 5.71 (s, 1 H), 7.19–7.39 (m, 3 H), 7.75–7.83 (m, 1 H).

1,4-Dimethyl-1-(5,5-dimethyl-2-oxazolinyl)naphthal-3-en-2-one (7a). Obtained as white crytals: mp 124–126 °C; IR (CCl_4) 2973, 1671, 1622, 1379, 1254, 973 cm^{-1}; ^1H NMR 1.32 (s, 3 H), 1.39 (s, 3 H), 1.69 (s, 3 H), 2.41 (d, J = 1.2 Hz, 3 H), 3.81 (A of AB, J = 8.0 Hz, 1 H), 3.90 (B of AB, J = 8.0 Hz, 1 H), 6.17 (d, J = 1.2 Hz, 1 H), 7.33–7.48 (m, 3 H), 7.56–7.63 (m, 1 H); ^{13}C NMR 20.6 (q), 27.4 (q), 27.9 (q), 28.0 (q), 52.9 (s), 66.9 (s), 79.5 (t), 124.1 (d), 125.8 (d), 126.5 (d), 127.6 (d), 129.8 (s), 130.2 (d), 142.4 (s), 153.0 (s), 165.5 (s), 197.6 (s). Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.61; H, 7.30; N, 4.98.

1-(5,5-Dimethyl-2-oxazolinyl)-4-hydroxy-2-methoxy-1-methyl-4-phenyl-1,4-dihydronaphthalene (9). Obtained as a clear, colorless oil: ^1H NMR 1.27 (s, 3 H), 1.31 (s, 3 H), 1.82 (s, 3 H), 3.12 (br s, 1 H), 3.60 (s, 3 H), 3.77 (A of AB, J = 8.0 Hz, 1 H), 3.85 (B of AB, J = 8.0 Hz, 1 H), 5.10 (s, 1 H), 7.20–7.45 (m, 9 H).

1-(5,5-Dimethyl-2-oxazolinyl)-1-methyl-4-phenylnaphthal-3-en-2-one (7b). Obtained as white crystals: mp 144–145 °C; IR (CCl_4) 2970, 1671, 1350, 1250, 974 cm^{-1}; ^1H NMR 1.36 (s, 3 H), 1.42 (s, 3 H), 1.80 (s, 3 H), 3.87 (A of AB, J = 8.0 Hz, 1 H), 3.95 (B of AB, J = 8.0 Hz, 1 H), 6.19 (s, 1 H), 7.21–7.53 (m, 9 H); ^{13}C NMR 27.7 (q), 27.9 (q), 27.9 (q), 53.2 (s), 66.9 (s), 79.5 (t), 123.8 (d), 126.7 (d), 127.2 (d), 128.2 (d), 128.4 (d), 128.8 (d), 128.9 (d), 129.0 (s), 130.1 (d), 137.4 (s), 142.8 (s), 156.5 (s), 165.3 (s), 197.7 (s). Anal. Calcd for $C_{22}H_{21}NO_2$: C, 79.73; H, 6.39; N, 4.23. Found: C, 79.67; H, 6.39; N, 4.24.

1-(5,5-Dimethyl-2-oxazolinyl)-1-methyl-4-(2-propenyl)-naphthal-3-en-2-one (7c). Obtained as a waxy solid: ^1H NMR 1.32 (s, 3 H), 1.39 (s, 3 H), 1.70 (s, 3 H), 3.50 (d, J = 6.4 Hz, 2 H), 3.82 (A of AB, J = 8.0 Hz, 1 H), 3.90 (B of AB, J = 8.0 Hz, 1 H), 5.21 (dd, J = 1.3, 7.8 Hz, 1 H), 5.25 (s, 1 H), 5.93–6.06 (m, 1 H), 6.18 (s, 1 H), 7.30–7.46 (m, 3 H), 7.63 (d, J = 7.4 Hz, 1 H); ^{13}C NMR 27.5 (q), 27.9 (q), 28.0 (q), 37.3 (t), 52.9 (s), 66.9 (s), 79.5 (t), 118.7 (t), 123.5 (d), 125.8 (d), 126.7 (d), 127.5 (d), 128.9 (s), 130.2 (d), 133.5 (d), 142.7 (s), 154.6 (s), 165.4 (s), 197.8 (s).

1-(5,5-Dimethyl-2-oxazolinyl)-4-isopropyl-1-methylnaphthal-3-en-2-one (7d). Obtained as white crystals: mp 85–87 °C; IR (CCl_4) 2969, 1670, 1616, 1283, 1256, 973 cm^{-1}; ^1H NMR 1.29–1.34 (complex, 9 H), 1.40 (s, 3 H), 1.69 (s, 3 H), 3.30 (heptet, J = 6.7 Hz, 1 H), 3.83 (A of AB, J = 8.0 Hz, 1 H), 3.91 (B of AB, J = 8.0 Hz, 1 H), 6.19 (s, 1 H), 7.35–7.42 (m, 3 H), 7.68–7.71 (m, 1 H); ^{13}C NMR 21.8 (q), 22.1 (q), 27.6 (q), 27.8 (q), 27.9 (q), 28.9 (d), 52.7 (s), 66.8 (s), 79.4 (t), 119.5 (d), 125.1 (d), 126.7 (d), 127.4 (d), 128.5 (s), 129.8 (d), 142.8 (s), 162.3 (s), 165.4 (s), 198.3 (s). Anal. Calcd for $C_{19}H_{23}NO_2$: C, 76.73; H, 7.79; N, 4.71. Found: C, 76.69; H, 7.81; N, 4.58.

4-(5,5-Dimethyl-2-oxazolinyl)-6-isopropyl-3-methoxy-4-methylnaphthal-2-en-1-one (10). Obtained as white crystals: mp 128–130 °C; IR (CCl_4) 2964, 1651, 1627, 1606, 1352, 1225 cm^{-1}; ^1H NMR 1.24 (s, 3 H), 1.27 (s, 3 H), 1.29 (s, 3 H), 1.38 (s, 3 H), 1.82 (s, 3 H), 2.96 (heptet, J = 6.9 Hz, 1 H), 3.79 (A of AB, J = 6.2 Hz, 1 H), 3.86 (B of AB, J = 6.2 Hz, 1 H), 3.84 (s, 3 H), 5.84 (s, 1 H), 7.30 (dd, J = 1.5, 8.2 Hz, 1 H), 7.37 (d, J = 1.5 Hz, 1 H), 8.10 (d, J = 8.2 Hz, 1 H); ^{13}C NMR 23.3 (q), 23.8 (q), 27.3 (q), 27.7 (q), 27.8 (q), 34.2 (d), 45.6 (s), 56.2 (q), 67.0 (s), 79.6 (t), 101.9 (d), 123.2 (d), 126.2 (d), 126.4 (d), 127.9 (s), 142.5 (s), 153.8 (s), 165.6 (s), 175.1 (s), 184.9 (s). Anal. Calcd for $C_{20}H_{25}NO_3$: C, 73.37; H, 7.70; N, 4.28. Found: C, 73.13; H, 7.74; N, 4.20.

Reduction of 4a with 9-BBN To Yield Transposed Naphthalenone (11) or, Alternatively, Methyl Enol Ether Protected Tetralone (12). General Procedure. To a solution of **3a** in THF (10 mL/mmol of **3a**) cooled to −78 °C was added 9-BBN (0.5 M solution in THF, 2 equiv for production of 11, 6 equiv for production of 12). The mixture was warmed to ambient temperature overnight, quenched with saturated aqueous NH_4Cl solution, and stirred for 3 h. Extraction (ether), drying ($MgSO_4$), and purification via radial chromatography (2-mm plate) using

hexanes/ethyl acetate (4:1) yielded pure material.

1-(5,5-Dimethyl-2-oxazolinyl)-2-methoxy-1-methylnaphthal-3-en-2-one (11). Obtained as a white crystalline material (143 mg, 0.56 mmol, 80%): mp 76–77.5 °C; IR (CCl_4) 2973, 1678, 1664, 1281, 1248, 974 cm^{-1}; ^1H NMR 1.32 (s, 3 H), 1.39 (s, 3 H), 1.70 (s, 3 H), 3.82 (A of AB, J = 8.0 Hz, 1 H), 3.90 (B of AB, J = 8.0 Hz, 1 H), 6.21 (d, J = 9.9 Hz, 1 H), 7.26–7.57 (m, 5 H); ^{13}C NMR 27.2 (q), 28.0 (q), 52.9 (s), 66.9 (s), 79.5 (t), 124.2 (d), 126.5 (d), 127.8 (d), 128.5 (s), 129.7 (d), 130.4 (d), 142.4 (s), 145.6 (d), 165.3 (s), 198.4 (s); MS m/z 255 (M^+), 227, 214, 159, 143, 128, 115. Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.04; H, 6.77; N, 5.46.

1-(5,5-Dimethyl-2-oxazolinyl)-2-methoxy-1-methyl-1,4-dihydronaphthalene (12). Obtained as a white crystalline material (201 mg, 0.74 mmol, 74%): mp 79–81 °C; IR (CCl_4) 2966, 1686, 1657, 1452, 1212, 1113, 1083 cm^{-1}; ^1H NMR 1.30 (s, 3 H), 1.34 (s, 3 H), 1.69 (s, 3 H), 3.56 (d, J = 3.7 Hz, 2 H), 3.61 (s, 3 H), 3.79 (A of AB, J = 8.0 Hz, 1 H), 3.86 (B of AB, J = 8.0 Hz, 1 H), 4.94 (t, J = 3.7 Hz, 1 H), 7.11–7.24 (m, 3 H), 7.25–7.33 (m, 1 H); ^{13}C NMR 27.1 (q), 27.8 (q), 28.0 (q), 28.6 (t), 44.2 (s), 54.6 (q), 66.9 (s), 79.4 (t), 91.1 (d), 126.0 (d), 126.3 (d), 126.4 (d), 128.1 (d), 132.5 (s), 138.2 (s), 155.2 (s), 168.0 (s); MS m/z 271 (M^+), 256, 240, 184, 172, 157, 115.

3-Methoxy-4-methyl-1-naphthol (13). A solution of **4a** (220 mg, 0.771 mmol) in CH_2Cl_2 (10 mL) at ambient temperature was treated with methyl trifluoromethanesulfonate (0.10 mL, 0.925 mmol). After the solution was stirred for 3 h, a solution of THF/MeOH (4/1 mL) was added followed by $NaBH_4$ (87.5 mg, 2.31 mmol). Stirring was continued 0.5 h followed by addition of water and ether. The ether layer was washed (H_2O), dried, concentrated, and purified via radial chromatography using hexanes/ethyl acetate (10:1) to yield a white solid (87 mg, 0.46 mmol, 60%): ^1H NMR 2.45 (s, 3 H), 3.79 (s, 3 H), 5.54 (v br s, 1 H), 6.62 (s, 1 H), 7.31–7.36 (m, 1 H), 7.46–7.51 (m, 1 H), 7.89 (d, J = 8.4 Hz, 1 H), 8.09 (d, J = 8.4 Hz, 1 H).

1-Formyl-2-methoxy-1-methyl-4-(1-(trimethylsilyl)-2-propenyl)-1,4-dihydronaphthalene (14a). A 0 °C solution of **3a** (1.84 g, 4.98 mmol) in CH_2Cl_2 (50 mL) was treated with MeOTf (0.676 mL, 5.976 mmol) and stirred for 8 h. To the methylated oxazoline salt was added THF/MeOH (12 mL/6 mL) and solid $NaBH_4$ (565 mg, 14.9 mmol). After the solution was stirred for an additional 8 h, excess reducing agent was quenched with water. Extraction with ether followed by drying of the organic layer ($MgSO_4$) and concentration gave crude methylated oxazolidine which was dissolved in THF/H_2O (100 mL/25 mL) and treated with oxalic acid dihydrate (3.14 g, 24.9 mmol). After being stirred for 2 d, the mixture was partitioned between water and ether. The organic layer was washed (H_2O), dried ($MgSO_4$), concentrated, and purified via radial chromatography using hexanes/ethyl acetate (10:1) as eluent to afford a clear, colorless oil (1.27 g, 4.05 mmol, 81%): IR (neat) 2954, 2834, 2700, 1731, 1682, 1210 cm^{-1}; ^1H NMR 0.01 (s, 9 H), 1.56 (s, 3 H), 2.32–2.48 (m, 1 H), 2.64–2.76 (m, 1 H), 3.59 (s, 3 H), 3.75–3.93 (m, 1 H), 5.02 (d, J = 3.9 Hz, 1 H), 5.64 (dt, J = 18.5, 1.1 Hz, 1 H), 5.91 (ddd, J = 18.5, 7.1, 6.4 Hz, 1 H), 7.08 (dd, J = 7.8, 1.4 Hz, 1 H), 7.20–7.38 (m, 3 H), 9.34 (s, 1 H); ^{13}C NMR −1.3 (q), 20.4 (q), 38.0 (d), 47.5 (t), 54.6 (q), 55.3 (s), 98.2 (d), 126.7 (d), 126.9 (s), 127.4 (d), 127.7 (d), 128.0 (d), 133.7 (s), 133.8 (d), 143.2 (d), 152.3 (s), 197.6 (d).

1-(Hydroxymethyl)-2-methoxy-1-methyl-4-(1-(trimethylsilyl)-2-propenyl)-1,4-dihydronaphthalene (14b). A solution of **14a** (268 mg, 0.852 mmol) in MeOH (15 mL) at ambient temperature was treated with $NaBH_4$ (115 mg, excess), stirred for 20 min, and quenched with water. The mixture was diluted with ether, washed (H_2O), dried ($MgSO_4$), concentrated, and purified via radial chromatography using hexanes/ethyl acetate (4:1) as eluent to afford a clear colorless oil (260 mg, 0.821 mmol, 96%): IR (CCl_4) 3561 (br), 3466 (br), 2954, 1682, 1615, 1209, 1036 cm^{-1}; ^1H NMR 0.05 (s, 9 H), 1.43 (s, 3 H), 1.66 (dd, J = 8.0, 5.2 Hz, 1 H), 2.31–2.44 (m, 1 H), 2.67–2.79 (m, 1 H), 3.61 (s, 3 H) superimposed on 3.60–3.74 (m, 2 H), 3.85 (dd, J = 10.5, 8.1 Hz, 1 H), 4.94 (d, J = 4.2 Hz, 1 H), 5.67 (d, J = 18.5 Hz, 1 H), 6.04 (ddd, J = 18.5, 7.2, 6.2 Hz, 1 H), 7.21–7.40 (m, 4 H); ^{13}C NMR −1.3 (q), 23.1 (q), 38.3 (d), 44.3 (s), 48.5 (t), 54.3 (q), 70.8 (t), 96.9 (d), 126.2 (d), 126.4 (d), 127.8 (d), 133.2 (d), 138.0 (s), 139.2 (s), 144.2 (d), 155.4 (s).

1-(Acetoxymethyl)-2-methoxy-1-methyl-4-(1-(trimethylsilyl)-2-propenyl)-1,4-dihydronaphthalene (14c). A solution of **14b** (246 mg, 0.777 mmol) in THF (10 mL) was treated successively with triethylamine (0.16 mL, 1.17 mmol), DMAP (19 mg, 0.16 mmol), and acetic anhydride (0.092 mL, 0.97 mmol). After being stirred at ambient temperature for 3 h, the mixture was partitioned between ether and water. The organic layer was washed (H_2O), dried ($MgSO_4$), concentrated, and purified via radial chromatography using hexanes/ethyl acetate (4:1) as eluent to afford a clear colorless oil (277 mg, 0.773 mmol, 99%): IR (neat) 2953, 1745, 1684, 1615, 1370, 1247, 1210, 1041 cm^{-1}; ^1H NMR 0.10 (s, 9 H), 1.45 (s, 3 H), 1.89 (s, 3 H), 2.18–2.31 (m, 1 H), 2.67–2.79 (m, 1 H), 3.57 (s, 3 H) superimposed on 3.52–3.67 (m, 1 H), 4.25 (A of AB, J = 10.5 Hz, 1 H), 4.35 (B of AB, J = 10.5 Hz, 1 H), 4.95 (d, J = 4.5 Hz, 1 H), 5.69 (d, J = 18.5 Hz, 1 H), 6.16 (ddd, J = 18.5, 7.7, 5.9 Hz, 1 H), 7.18–7.30 (m, 3 H), 7.32–7.41 (m, 1 H); ^{13}C NMR −1.2 (q), 20.9 (q), 23.5 (q), 38.5 (d), 42.0 (s), 49.4 (t), 54.3 (q), 70.4 (t), 96.8 (d), 126.0 (d), 126.1 (d), 126.2 (d), 127.8 (d), 132.6 (d), 138.1 (s), 138.9 (s), 145.0 (d), 154.3 (s), 170.5 (s).

4-(Acetoxymethyl)-3-methoxy-4-methylnaphthal-2-en-1-one (15). Method B. Obtained as white crystals (183 mg, 0.703 mmol, 94%): mp 137–138 °C; IR (KBr pellet) 2992, 1731, 1644, 1621, 1602, 1467, 1252 cm^{-1}; ^1H NMR 1.54 (s, 3 H), 1.75 (s, 3 H), 3.84 (s, 3 H), 4.48 (A of AB, J = 10.7 Hz, 1 H), 4.57 (B of AB, J = 10.7 Hz, 1 H), 5.89 (s, 1 H), 7.42 (t, J = 7.5 Hz, 1 H), 7.50 (d, J = 7.5 Hz, 1 H), 7.59 (dt, J = 1.3, 7.5 Hz, 1 H), 8.20 (dd, J = 1.2, 7.8 Hz); ^{13}C NMR 20.4 (q), 23.5 (q), 44.3 (s), 56.1 (q), 69.1 (t), 103.1 (d), 125.2 (d), 126.2 (d), 127.1 (d), 131.2 (s), 132.4 (d), 143.6 (s), 170.2 (s), 176.0 (s), 185.3 (s). Anal. Calcd for $C_{15}H_{16}O_4$: C, 69.22; H, 6.20. Found: C, 69.12; H, 6.22.

Acknowledgment. The authors are grateful to the National Institutes of Health for financial support of this program.

Supplementary Material Available: Proton and carbon magnetic resonance spectra of **3b–f**, **4c**, **4d**, **5**, **7c**, **8**, **9**, **12**, **13**, and **14a–c** and X-ray data (35 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.