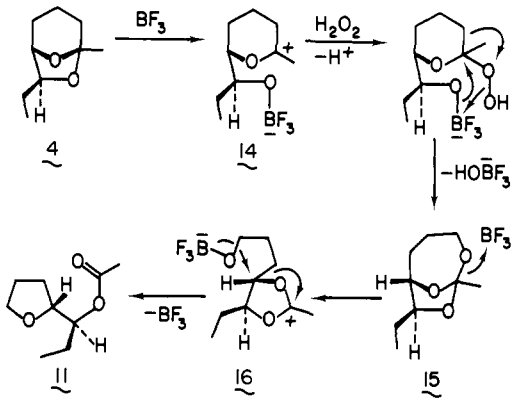
Scheme III



the formation of endoperoxide **6** to be favored over **7**. This stereochemical bias seems quite reasonable, since in both **6** and **10** the ethyl substituent is situated in the less hindered "equatorial" configuration, while in **7**, it is "axially" configured. If **6** is indeed the preferred isomer resulting from bicyclization, then concerted rearrangements of the endoperoxides **6** and **7** should lead to **4** and **5**, respectively, with **4** being the major isomer. However, since the rearrangements of the endoperoxides **6** and **7** could not be studied separately, one cannot be certain that some stereochemical scrambling does not take place as indicated by the dashed arrows in Scheme II. Nevertheless, these results not only confirm the previous observation of exclusive one-carbon rather than three-carbon bridge migration to oxygen[4,10] but also demonstrate the exclusive migration of the more highly substituted one-carbon bridge bond (I rather than II in **6** of Scheme II).

Finally, treatment of **8** with $H_2O_2 \cdot BF_3$ leads to the formation of two additional products which become the major reaction products at higher temperatures and prolonged reaction times (Scheme II). These products were shown to be the diastereomeric furanyl acetates **11** and **12** on the basis of their spectroscopic properties[11] and an independent synthesis of **11** (vide infra). Furthermore, treatment of pure **4** and **5** with $H_2O_2 \cdot BF_3$ under slightly more vigorous conditions then used in their formation led to the exclusive formation of **11** and **12**, respectively. The alcohol **13**[12] was prepared and correlated with the acetate **11** derived from **4** as shown in Scheme II. This correlation not only confirms the relative stereochemistries of **11** and **12** but also demonstrates that the oxidative cleavage of the bicyclic ketals to **11** and **12** occurs with inversion at one of the two ether carbon atoms of **4** and **5**.

A mechanism for this oxidative cleavage which is consistent with the aforementioned observations is outlined in Scheme III. In the very few instances where these normally robust bicyclic ketals are known to undergo acid-catalyzed cleavage,[13] the two-atom bridge undergoes cleavage at the ketal carbon. Thus, the carbocation **14** is probably the initial intermediate in this oxidative cleavage. Reaction of **14** with H_2O_2, followed by a ketal analogue of the Baeyer-Villiger rearrangement[14] might form the bicyclic ortho ester **15** or some closely allied species. Acid-catalyzed cleavage of **15** followed by collapse of the carbocation **16** with inversion during the formation of the new carbon-oxygen bond would afford the furanyl acetate **11**.

In summary, this work not only provides the first expression of this new strategy for the synthesis of bicyclic ketals but also further defines the stereoelectronic factors involved in this bicyclization approach to endoperoxides and their subsequent rearrangement to bicyclic ketals. In addition, a new and unexpected correlation has been observed between the ubiquitous, naturally occurring 6,8-dioxabicyclo[3.2.1]octane and 2-(1′-hydroxyalkyl)furanyl[15] structural units. Finally, the high degree of stereoselectivity available from acyclic precursors through these transformations should make them of considerable utility in the synthesis of polyether natural products.

Acknowledgment. We thank the National Science Foundation (CHE-8312691) for financial support and for funds (CHE-8102974 and PCM-8219912) used to help establish the NMR and mass spectrometry facilities used in this work.

Registry No. (±)-**4**, 60018-04-4; (±)-**5**, 62532-53-0; **8**, 110243-75-9; **10**, 110243-76-0; (±)-**11**, 110243-77-1; (±)-**12**, 110243-78-2; (±)-**13**, 110243-79-3; (*E*)-$CH_3CH_2CH{=}CH(CH_2)_3OH$, 24469-79-2.

Supplementary Material Available: Spectroscopic data are available for compounds **10-13** (1 page). Ordering information is given on any current masthead page.

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(11) All new compounds obtained in this work have spectroscopic properties in accord with the proposed structures. See Supplementary Material.
(12) The erythro alcohol **13** and its threo isomer have been synthesized previously (Lebouc, A. *Bull. Soc. Chem. Fr.* **1971**, 3037.), but without high field NMR data, it was impossible to correlate the data from these alcohols with that obtained from the alcohols derived from the brevicomin oxidation products **11** and **12**. See Supplementary Material.
(13) Colonge, J.; Buendia, J.; Guignard, H. *Bull. Soc. Chim. Fr.* **1969**, 956. Wakamatsu, T.; Nakamura, H.; Nishikimi, Y.; Yoshida, K.; Noda, T.; Taniguchi, M.; Ban, Y. *Tetrahedron Lett.* **1986**, *27*, 6071.
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Synthesis and Characterization of Symmetrical and Unsymmetrical Low-Valent Rhenium-Oxo Dimers, $Re_2O_2(RC{\equiv}CR)_4$

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The preference for terminal or bridging ligation of an oxo group is of fundamental importance to the chemistry of inorganic reagents (permanganate vs MnO_2),[2] catalysts (different crystal faces of MoO_3),[3] metalloenzymes (cytochrome P450 vs hemerythrin),[4] and materials (osmium tetroxide vs zirconia).[5] Terminal oxo ligands, with metal-oxygen multiple bonds, are normally favored only in high oxidation state species.[6] In the course of our studies of novel rhenium(III) oxo-acetylene compounds.[6,7] we have prepared two very different forms of rhenium-oxo dimers $Re_2O_2(RC{\equiv}CR)_4$. The symmetric form is a rhenium(II) dimer, the first example of an isolated terminal oxo complex with a metal formal oxidation state as low as +2 or with an electron count as high as d^5.[8] Remarkably this rhenium(II) terminal oxo complex is more stable than an asymmetric isomer with both bridging and terminal oxo groups.

(1) (a) University of Washington. (b) University of Delaware. (c) Danforth-Compton Fellow.
(2) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981.
(3) Farneth, W. E.; Staley, R. H.; Sleight, A. W. *J. Am. Chem. Soc.* **1986**, *108*, 2327-2332, and references therein.
(4) *Cytochrome P-450*; Sato, R., Omura, T., Eds.; Kodansha Ltd: Tokyo, 1987. *Cytochrome P-450: Structure, Mechanism, and Biochemistry*, Ortiz de Montellano, P., Ed.; Plenum Press: New York, 1986, especially J. T. Groves, Chapter 1. Stenkamp, R. E.; Sieker, L. C.; Jensen, L. H. *J. Am. Chem. Soc.* **1984**, *106*, 618-622, and references therein.
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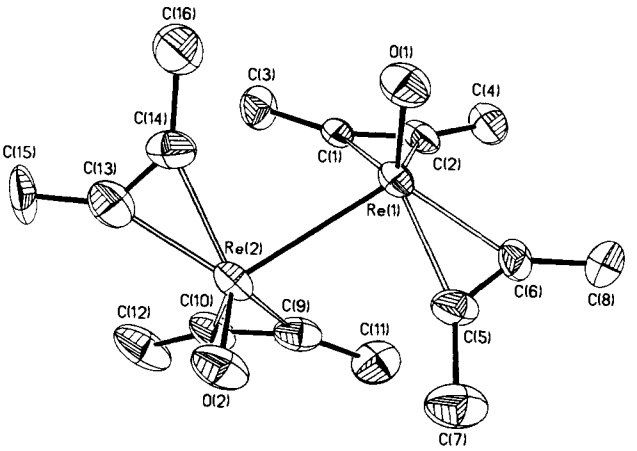
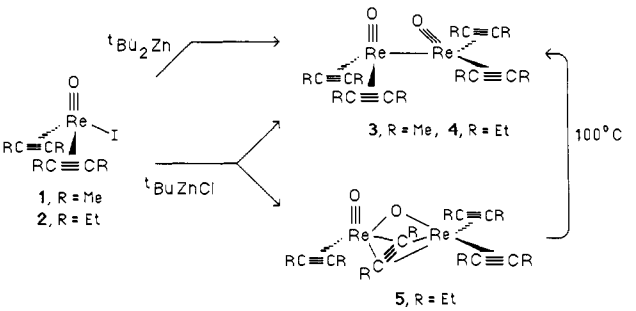


Figure 1. ORTEP drawing of $[Re(O)(MeC{\equiv}CMe)_2]_2$ (**3**) with 40% ellipsoids. Average bond lengths (Å) and angles (°) not mentioned in the text: Re–C, 2.06 (2); C≡C, 1.32 (3); O–Re–Re, 114.4 (6).

Scheme I



We have been examining the formation of oxo–alkyl complexes by the reaction of $Re(O)I(RC{\equiv}CR)_2$ (R = Me (**1**), Et (**2**))[6] with dialkyl zinc reagents.[9] While this reaction works well with Me_2Zn and Et_2Zn, the reaction of **1** with t-Bu_2Zn[10] does not produce a *tert*-butyl complex but results in reduction of the rhenium center with formation of an unusual rhenium–oxo dimer $[Re(O)(RC{\equiv}CR)_2]_2$ (R = Me (**3**), Et (**4**), Scheme I). Compounds **3** and **4** are isolated after chromatography in 85–95% yield as diamagnetic, air stable materials.

The NMR and IR spectra of **3** and **4** are similar to those of **1** and **2**, with ^{13}C resonances for the acetylenic carbons in the range 140–151 δ and IR absorptions at 934–955 cm^{-1} for terminal oxo groups.[11] However, there are four sets of acetylenic resonances in the NMR spectra of **3** and **4**, compared to only two sets for **1** and **2**. An X-ray crystal structure determination (Figure 1)[12] shows that **3** is composed of two rhenium(II)–terminal oxo fragments $Re(O)(MeC{\equiv}CMe)_2$, related by an approximate twofold axis perpendicular to an unsupported rhenium–rhenium bond. The bond lengths and angles within the $Re(O)(MeC{\equiv}CMe)_2$ units are similar to those in the structures of **1**[6] and $[Re(O)(MeC{\equiv}CMe)_2(L)]SbF_6$ (L = py, bipy):[7] each rhenium has a short multiple bond to oxygen (av 1.69 (1) Å), and the rhenium–acetylenic carbon distances vary from 2.019 (25) to 2.119 (17) Å. Since the $Re(O)(RC{\equiv}CR)_2$ group is a 17-electron fragment,[6] the dimers are best described as having a single rhenium–rhenium bond. The Re–Re distance of 2.686 (1) Å is at the short end of the reported range of single bond lengths[13] (cf. $Cp_2{}^*Re_2(CO)_4(\mu\text{-}O)$, 2.817 (1) Å[14]). The geometry about each rhenium can be described as tetrahedral with the acetylene midpoints occupying two vertices; the dimer is then an ethane-like molecule, in a staggered-gauche configuration with an O–Re–Re–O torsion angle of 74.2°. The NMR spectra of **3** and **4** indicate that there is restricted rotation about the rhenium–rhenium bond even at 90 °C, likely due to steric interactions among the acetylene substituents.

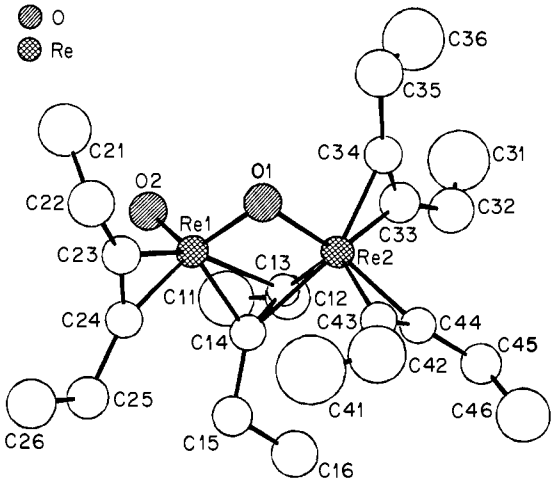


Figure 2. ORTEP drawing of $Re_2O_2(EtC{\equiv}CEt)_4$ (**5**) with 30% ellipsoids. Selected bond distances (Å) and angles (°) not mentioned in the text: Re(1)–C(13), 2.52 (3); Re(1)–C(14), 2.04 (3); Re(2)–C(13), 1.89 (2); Re(2)–C(14), 2.32 (3); C(13)–C(14), 1.34 (3); O(2)–Re(1)–Re(2), 117.4; Re(1)–O(1)–Re(2), 86.1 (7); C(12)–C(13)–C(14), 126 (3); C(13)–C(14)–C(15), 136 (3).

In contrast, the reaction of **2** with t-BuZnCl produces a bright yellow product **5** in addition to **4** (Scheme I). Separation of the roughly 1:1 mixture is accomplished by chromatography on silica gel (80% combined yield). Complex **5** is an isomer of **4** as indicated by analytical and spectral data[11] and an X-ray crystal structure (Figure 2).[15] The mechanism of formation of **4** and **5**, including the difference in reactivity between t-BuZnCl and $(t\text{-}Bu)_2Zn$, is currently under study.

Compound **5** is a dimer with a remarkably asymmetric solid-state structure: Re(1) is bound to a terminal oxo (Re(1)–O(2) 1.64 (2) Å) and an acetylene ligand while Re(2) binds two acetylenes. The rhenium–rhenium bond (2.677 (2) Å) is bridged unsymmetrically by both an oxo group (Re(1)–O(1) 1.84 (2), Re(2)–O(1) 2.08 (2) Å) and an unusual acetylene ligand, which is twisted roughly 34° away from an orientation perpendicular to the Re–Re axis.[16] The Re–C bonds for the bridging acetylene

(9) Valencia, E.; Mayer, J. M., manuscript in preparation.

(10) Prepared in situ from $ZnCl_2$ and t-BuLi (Alpha): Boersma, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, Vol. 2, p 824.

(11) Full spectroscopic and analytical data are given in the Supplementary Material. **3**: ^1H NMR ($CDCl_3$) 1.03, 2.80, 3.06, 3.16 (each 6 H, q, ^5J = 1 Hz, CH_3); IR 941 s, 951 s, ν(ReO). **4**: ^{13}C NMR (C_6D_6) 144.0, 147.2, 150.3, 150.8 (Et*C*≡*C*Et); IR 955 s, 934 w, ν(ReO). **5**: ^{13}C NMR (CD_2Cl_2, −40 °C) 196.5, 192.9, 180.8, 169.7, 168.6, 165.1, 153.5, 150.1 (Et*C*≡*C*Et); IR 928 s ν(ReO), 700 m.

(12) Crystal data for **3**: monoclinic, $P2_1/c$: a = 17.530 (4) Å, b = 7.264 (2) Å, c = 18.638 (5) Å, β = 131.72 (2)°, V = 1772 (1) Å^3, Z = 4, D_{calcd} = 2.327 g cm^{-3}, T = 293 K, μ(Mo Kα) = 144.4 cm^{-1}. Of 3501 data collected (Nicolet R3m, 2θ max = 50°) and empirically corrected for absorption, 3119 were independent (R_{int} = 2.50%) and 2044 were observed ($F_o \geq 4\sigma(F_o)$). The Re atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically; methyl group hydrogen atom locations were calculated, but their rotational orientation with regard to the ReC_2 planes is uncertain. At convergence, R_f = 4.47%, R_{wf} = 5.58%, GOF = 1.183, Δ/σ = 0.002, $\Delta(\rho)$ = 1.3 e/Å^3, and N_o/N_v = 10.7. A 5% occupied alternative site for Re(2) was refined as Re(2′); Re(2) and Re(2′) are similarly positioned relative to Re(1). At the 5% level, none of the light atoms bonded to it were found.

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(14) Herrmann, W. A.; Serrano, R.; Küsthardt, U.; Ziegler, M. L.; Guggolz, E.; Zahn, T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 515–517.

(15) Crystal data for **5**: monoclinic, $P2_1/c$; a = 9.424 (1) Å, b = 13.833 (1) Å, c = 20.067 (2) Å; β = 94.05 (1)°, V = 2609.4 (8) Å^3, Z = 4, D_{calcd} = 1.866 g cm^{-3}, T = 296 K, μ(Mo Kα) = 94.1 cm^{-1}. The 5112 reflections collected (Enraf-Nonius CAD4, 2$\theta \leq$ 50°) were empirically corrected for absorption and averaged over 2/m symmetry yielding 2483 reflections (R_{int} = 4.4%) of which 1426 had $I > 3\sigma(I)$. The Re atoms were derived from a Patterson map. Only the Re atoms were refined anisotropically; ethyl group hydrogen atoms were calculated. Final cycle: R_f = 5.4%, R_{wf} = 5.1%, GOF = 1.38, $\Delta(\rho)$ = 1.27 e/Å^3, and N_o/N_v = 11.6.

(16) The only other example of a twisted bridging acetylene ligand was recently reported: Ahmed, K. J.; Chisholm, M. H.; Folting, K.; Huffman, J. C. *Organometallics* **1986**, *5*, 2171–2181. Calhorda, M. J.; Hoffmann, R. *Organometallics* **1986**, *5*, 2181–2187.

vary from a typical double bond distance to longer than a normal single bond (1.89 (2) - 2.52 (3) Å). The structure and bonding in **5** are clearly quite unusual, but in one resonance form **5** can be viewed as containing a rhenium(III) center with a terminal oxo ligand, $Re(O)(\mu\text{-}O\text{-})(EtC{\equiv}CEt)_2$, similar to **2**, and a rhenium(I) center, $Re(\mu\text{-}O\text{-})(EtC{\equiv}CEt)_3$, related to $ReI(EtC{\equiv}CEt)_3$[17] and isoelectronic $W(CO)(PhC{\equiv}CPh)_3$.[18]

The ^1H and ^{13}C NMR spectra of **5** at -40 °C show eight nonequivalent ethyl groups and eight acetylenic carbon resonances,[11] but on warming four of the sets of ethyl groups coalesce to two sets; the nature of this fluxional process will be described in detail in a future publication. On heating to 100 °C, **5** stoichiometrically converts to **4** in 1 h (Scheme I). Our inability to observe a 2-butyne analogue of **5** starting from **1** may be due to its more facile conversion to **3**. The fact that the isomer with two terminal oxo groups bound to rhenium(II) centers (**4**) is thermodynamically more stable than the isomer with a bridging oxo ligand (**5**) indicates that rhenium-oxygen multiple bonding is favorable in this case despite the low formal oxidation state.

Acknowledgment. This work was supported by an M. J. Murdock Charitable Trust Grant of the Research Corporation, by the Chevron Research Co., by the National Science Foundation (CHE-8617965), and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We also acknowledge support of X-ray equipment from the National Science Foundation (CHE-8617023) and the Graduate School Research Fund of the Universtiy of Washington (PHS Grant RR-07096).

Supplementary Material Available: Listing of spectroscopic and analytical data for **3-5** and tables of atomic coordinates, bond distances and angles, anisotropic temperature factors, and hydrogen atom coordinates for **3** and **5** (12 pages); tables of observed and calculated structure factors for **3** and **5** (27 pages). Ordering information is given on any current masthead page.

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A Convergent Strategy for Synthesis of *Erythrina* Alkaloids

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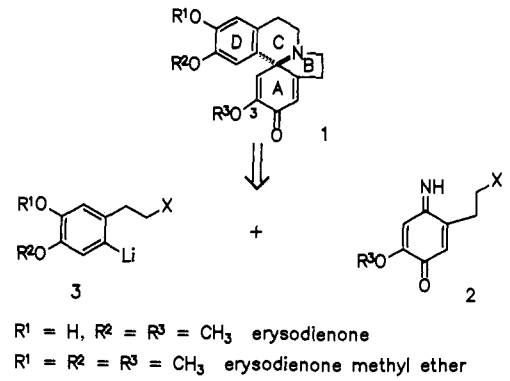
The synthesis of *Erythrina* alkaloids and homoerythrinans has been of interest for over 25 years,[1,2] and a variety of synthetic strategies have been employed in preparing the tetracyclic ring system of these compounds.[1,3] The addition of a functionalized organolithium reagent, e.g., **3**, to a quinone imine such as **2** would comprise a new, convergent strategy to the ring system of these biologically and synthetically interesting compounds (Scheme I). Quinone imide ketals are available in one step by anodic oxidation of the corresponding *p*-alkoxyanilides[4] and could serve as regiospecific equivalents of quinone imine such as **2**. Since the dienone moiety of the A ring has been converted to the various oxygenation patterns present in the naturally occurring compounds,[1,5] an intermediate such as **1** would be especially useful synthetically. We report herein the successful execution of the general strategy outlined in Scheme I to afford the methyl ether of erysodienone.

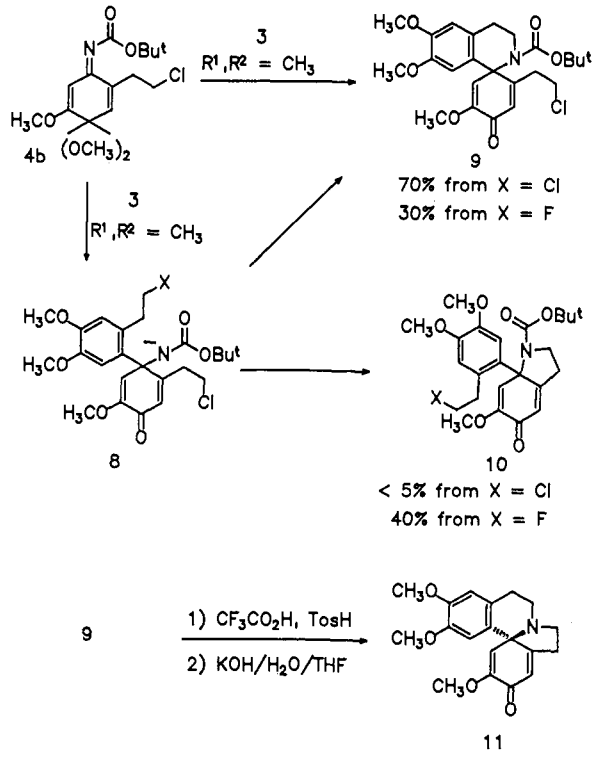
Since many *Erythrina* alkaloids possess a methoxyl group at C-3 and since this group would be expected to deactivate the imide linkage toward organolithium addition to the imide carbon, the viability of the strategy was examined by studying the reaction of aryllithium reagents with the quinone imides **4a** and **6**. The required compounds for this study were either commercially available or prepared via standard methods from commercially

Scheme I. Strategy for a Convergent Approach to the *Erythrina* Alkaloid Skeleton



$R^1 = H, R^2 = R^3 = CH_3$ erysodienone
$R^1 = R^2 = R^3 = CH_3$ erysodienone methyl ether

Scheme II. The Quinone Imide Ketal Route to *Erythrina* Alkaloids



(1) For reviews on *Erythrina* alkaloids, see: Chawla, A. S.; Jackson, A. H. *Nat. Prod. Rep.* **1986**, 556; **1984**, 371. Dyke, S. F.; Quessy, S. N. In *The Alkaloids: Chemistry and Physiology*; Manske, R. H. F., Rodrigo, R. G. A., Eds.; Academic: New York, 1981; Vol. XVIII, Chapter 1.
(2) For more recent synthetic studies and leading references dealing with *Erythrina* alkaloids, see: (a) Dagne, E.; Steglich, W. *Tetrahedron Lett.* **1983**, *24*, 5067. (b) Joyeau, R.; Dugenet, Y.; Wakselman, M. *J. Chem. Soc., Chem. Commun.* **1983**, 431. (c) Brumfield, M. A.; Mariano, P. S.; Yoon, U. C. *Tetrahedron Lett.* **1983**, *24*, 5567. (d) Tsuda, Y.; Hosoi, S.; Nakai, A.; Ohshima, T.; Sakai, Y.; Kiuchi, F. *J. Chem. Soc., Chem. Commun.* **1984**, 1216. (e) Ito, K.; Suzuki, F.; Haruna, M. *J. Chem. Soc., Chem. Commun.* **1978**, 733. (f) Tsuda, Y.; Murata, M. *Tetrahedron Lett.* **1986**, *27*, 3385. (g) Westling, M.; Smith, R.; Livinghouse, T. *J. Org. Chem.* **1986**, *51*, 1159. (h) Danishefsky, S. J.; Panek, J. S. *J. Am. Chem. Soc.* **1987**, *109*, 917. (i) Ahmed-Schofield, R.; Mariano, P. S. *J. Org. Chem.* **1987**, *52*, 1478.
(3) (a) Hill, R. K. *The Alkaloids*; Manske, R. H. F., Ed.; Academic: New York, 1967; Vol. IX, pp 483-515. (b) For general reviews of *Erythrina* alkaloid synthetic approaches, see: Manske, R. H. F. *Alkaloids*; Academic: New York, 1967; Vol. X, Chapter 12, p 483. Reference 3a, 1960, Vol. VII, Chapter 11, p 201. Reference 3a, 1960, Vol. II, Chapter 14, p 499.

(4) Chen, C-P.; Chou, C-T.; Swenton, J. S. *J. Am. Chem. Soc.* **1987**, *109*, 946.
(5) Mondon, A.; Ehrhardt, M. *Tetrahedron Lett.* **1966**, 2557.

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