Studies Directed toward the Total Synthesis of Cerorubenic Acid-III. 5. A Radical Cyclization Route Leading to the Methyl Ester of the Natural Isomer[1]

Leo A. Paquette* and Brian P. Dyck

Contribution from the Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210

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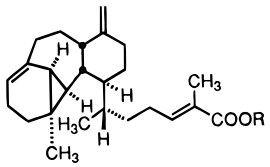
Abstract: The first total synthesis of cerorubenic acid-III methyl ester is detailed. Enantiopure **4**, obtained by anionic oxy-Cope rearrangement of **3**, was transformed via diol **11** into lactol **20**. Following proper establishment of both side chains as in **25**, a 6-exo radical cyclization was employed to set the configuration of the remaining stereogenic centers. This very useful process set the stage for construction of the pendant side chain. The complete route to **2** from 3-methylcyclohexenone required 30 steps (0.3% overall yield) confirmed the initial complex structural assignment and established the absolute configuration of the natural kairomone.

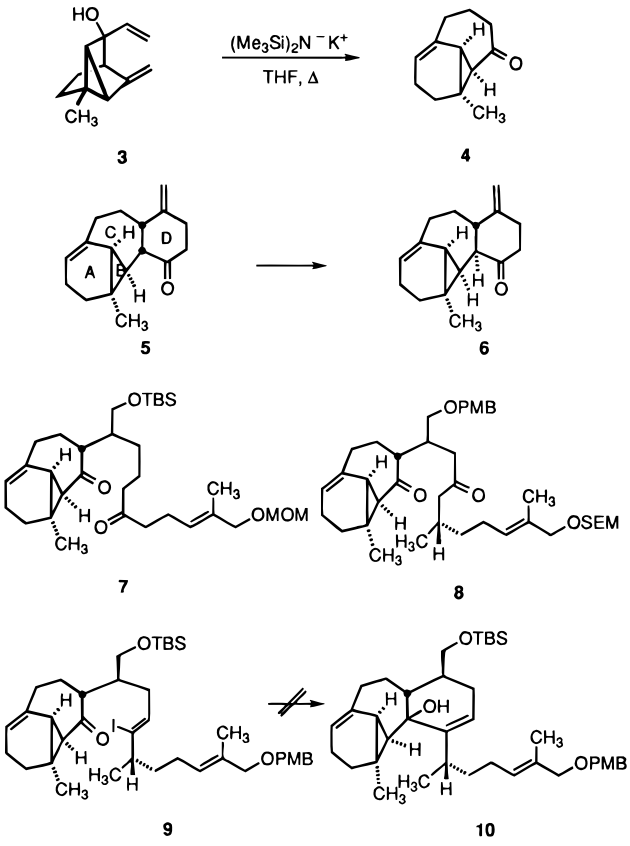
Cerorubenic acid-III (**1**), an architecturally unique sesterterpene first isolated in 1983 by Yoko Naya and his collaborators at the Suntory Institute for Bioorganic Research from secretions of the scale insect *Ceroplastes rubens* Maskell,[2] merits consideration as a synthetic target in that it qualifies as the most complex substance currently recognized to play an important role in insect communication.[3] Indeed, this novel tetracyclo[8.4.1.0.0]pentadecane system functions very effectively as a kairomone responsible for control of the ovipositional behavior and feeding traits of the encyrtid wasp *Anicetus beneficus*.[4] The structural assignment to **1** was based on detailed ^{1}H and ^{13}C NMR spectral analysis of its methyl ester **2**. Central to the molecular architectural features in these molecules are a vinylcyclopropane fragment whose double bond occupies a



1, R = H
2, R = CH_3

bridgehead site, an array of seven stereogenic centers all of which are contiguous, and a pendant side chain in which the only oxygenated functionality resides.

Despite the fact that **1** and **2** have been known for well over a decade, neither structure has yet been confirmed either by X-ray analysis or by total synthesis. Our early work in this area has documented the readiness with which carbinol **3** can be assembled and subjected to anionic oxy-Cope rearrangement[5] in a notably direct route to the entire ABC substructure.[6] The conciseness with which **4** can be produced and its ready acquisition in either antipodal form[1b] were regarded as particularly attractive. From the retrosynthetic perspective, modest functional group manipulation within **4** in various ways appeared



(1) (a) Part 4: Paquette, L. A.; Hormuth, S.; Lovely, C. J. *J. Org. Chem.* **1995**, *60*, 4813. (b) Part 3: Paquette, L. A.; Deaton, D. N.; Endo, Y.; Poupart, M.-A. *J. Org. Chem.* **1993**, *58*, 4262. (c) Part 2: Paquette, L. A.; Lassalle, G. Y.; Lovely, C. J. *J. Org. Chem.* **1993**, *58*, 4254. (d) Part 1: Paquette, L. A.; Poupart, M.-A. *J. Org. Chem.* **1993**, *58*, 4245.

(2) Tempesta, M. S.; Iwashita, T.; Miyamoto, F.; Yoshihara, K.; Naya, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 1182.

(3) (a) Noda, T.; Kitamura, A.; Takahashi, S.; Tagaki, K.; Kashio, T.; Tanaka, M. *Appl. Ent. Zool.* **1982**, *3*, 350. (b) Takahashi, S.; Takabayashi, J. *Appl. Ent. Zool.* **1984**, *19*, 1117; **1985**, *20*, 173.

(4) (a) Yasumatsu, K.; Tachikawa, T. *J. Fac. Agri., Kyushu University* **2949**, *9*, 99. (b) Ishii, T.; Yasumatsu, K. *Mushi* (Fukuoka) **1954**, *27*, 69. (c) Ohgushi, R. *Mem. Coll. Sci. University Kyoto* (*B*) **1956**, *23*, 55; **1058**, *25*, 31.

(5) Paquette, L. A. *Tetrahedron* **1997**, *53*, 13971.

(6) Poupart, M.-A.; Paquette, L. A. *Tetrahedron Lett.* **1988**, *29*, 269.

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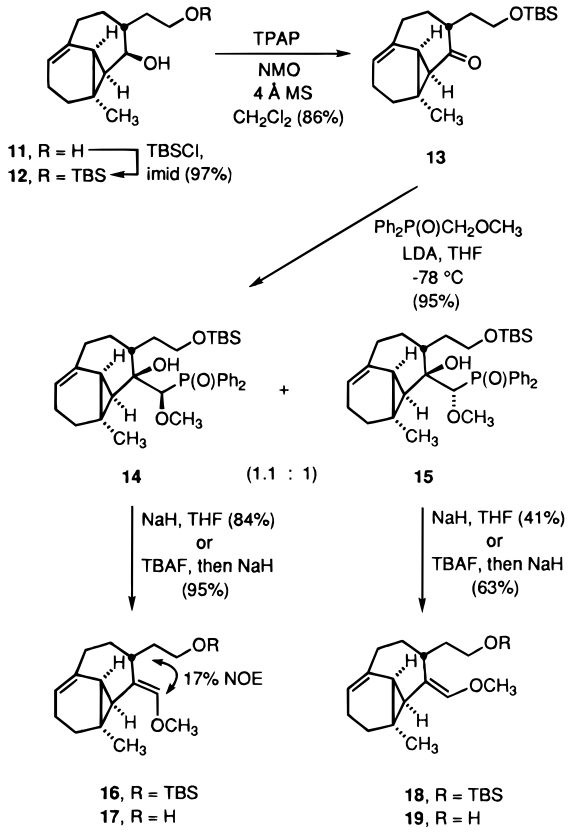
to be ideally suited to the construction of ring D. However, the adaptation of a Diels−Alder tactic for the elaboration of **5** was thwarted by the facility with which epimerization to the trans-fused isomer **6** occurs.[1d,7] The lessons learned from attempts to bring about extraannular (as in **7**)[1c] and intraannular (as in **8**)[1b] Robinson annulation were that no diastereomer was suited to dehydrative cyclization under any of the basic or acidic conditions examined. Analogously, the crucial six-membered cyclization of intermediates of type **9** by metal-mediated means was not kinetically favored.[1a]

Herein, we record the first total synthesis of cerorubenic acid-III methyl ester (**2**) in its naturally occurring levorotatory configuration. Worthy of advance notice is the fact that a radical cyclization protocol was deployed in order to generate a properly functionalized D ring. Significantly, the route that elaborates the necessary intermediate is short, highly efficient, and

Scheme 1

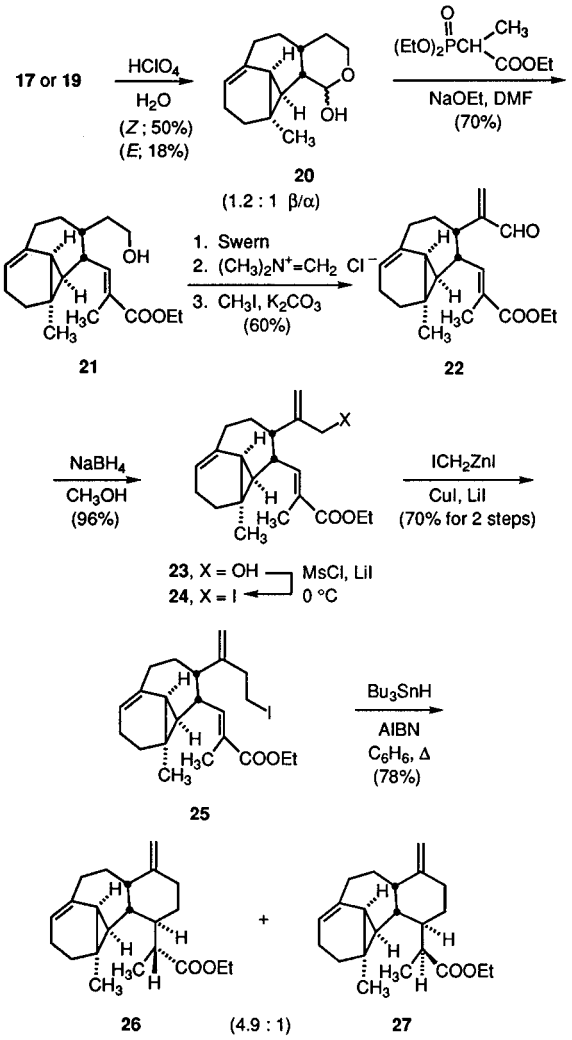


effectively stereocontrolled. Furthermore, the synthesis serves to confirm Naya's original assignment.

Results and Discussion

The strategic selection of levorotatory diol **11**, readily available by alkylation of **4** with ethyl iodoacetate with ensuing lithium aluminum hydride reduction,[1a] was seen as the cornerstone of the present approach in that it was anticipated that the resident dual functionality would lend itself conveniently to regiochemical control. In fact, the two hydroxyl groups in **11** are easily distinguished as is evident in its efficient conversion to the monosilyl ether **12** (Scheme 1). The viability of this selective protection step provided for the elaboration of ketone **13** via perruthenate oxidation.[8] When attempts to homologate

Scheme 2



13 with (methoxymethylene)triphenylphosphorane[9] in the presence of HMPA and 18-crown-6 were found to provide only modest yields of enol ether, a more advantageous route was pursued which involved the lithium salt of (methoxymethyl)-diphenylphosphine oxide.[10] Nucleophilic attack on **13** was expected to occur exclusively from the exterior of the cup-shaped tricyclic nucleus. Indeed, only the diastereomeric adducts **14** and **15** were produced in a 1.1:1 ratio and 95% combined yield. The chromatographic separation of **14** from **15** was straightforward. The stereochemical assignments of these diastereomers rest on the stereoselectivity of their base-promoted elimination reactions which are recognized to proceed in cis fashion. Strikingly, whereas **14** underwent smooth conversion (84%) to the (*Z*)-enol ether **16**, the identical elimination of its epimer **15** to the (*E*)-enol ether **18** proved sluggish and less efficient (41%).

In an attempt to facilitate this important transformation, the primary hydroxyl substituents were unmasked prior to exposure to sodium hydride. Under these circumstances, a substantial improvement in the yield of both enol ethers was observed. The

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(8) Griffith, W. P.; Ley, S. V. *Aldrichim. Acta* **1990**, *23*, 13.

(9) Soderquist, J. A.; Ramos-Veguilla, J. *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; Wiley: Chichester, 1995; pp 3363−3365.
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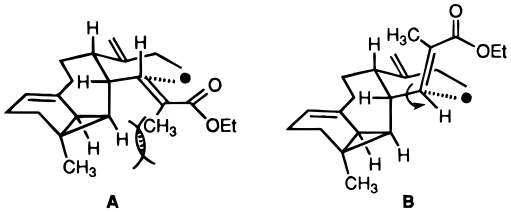
intense NOE interaction exhibited between the vinylic and allylic methine protons in **16** (see formula) attests to their close proximity.

We had now arrived at the stage where the extension of both side chains required consideration. The plan called for initial homologation of the enol ether segment to an α-methyl α,β-unsaturated ester, whose ultimate role was to serve as the radical acceptor.[11] Central to this scenario was the availability of lactol **20**. Although both epimers of this key intermediate proved to be rather labile,[12] it was ultimately found that 35% aqueous perchloric acid acted on **17** to deliver a nearly equimolar mixture of the β- and α-forms of **20** (Scheme 2). Convinced that the most kinetically feasible pathway for ring closure would involve that aldehyde isomer predisposed with cis functional groups, we directed our attention to establishing the cis fusion of the D ring by NMR methods. Although the chemical shifts of the relevant protons clearly parallel those known for **2**, a more definitive correlation was not possible due to the unresolved and overlapping features of selected proton signals. Notwithstanding, since the next step was to involve strongly basic reaction conditions, all indications suggested that equilibration would operate at the enolizable site if it had not already materialized in order to position this side chain on the exterior of the concave−convex ABC core.

When the lactols were treated with the sodium salt of triethyl 2-phosphonopropionate in DMF, three-carbon homologation was successfully accomplished. Only two geometric isomers were produced, with **21** predominating by a factor of 2:1. Since both the (*Z*)- and (*E*)-hydroxy esters are homogeneous compounds, the inference can be drawn that the starting lactols differed only as a consequence of configurational inhomogeneity at the carbinol carbon. As before, the chemical shifts and coupling constants exhibited by **21** were fully consistent with the stereochemical assignment drawn. Also, the specific rotations for **20**, **21**, and later intermediates all proved to be levorotatory as in **2**, thereby providing early suggestive evidence that the natural enantiomer was being pursued.

Adaptation of the one-pot Swern oxidation/methylenation sequence earlier developed by Takano *et al.*[13] to **21** afforded the triene aldehydo ester **22** in 60% yield. Reduction to give alcohol **23** was effectively accomplished by treatment of **22** with sodium borohydride in methanol. Replacement of the hydroxyl group in **23** by iodide was uncomplicated when mediated by transient formation of the mesylate. To set the stage for stereoselective radical cyclization, it was necessary to arrive at the homologated iodide **25**. In the event, reaction of **24** with iodomethylzinc iodide in the presence of copper(I) iodide and lithium iodide according to Knochel and co-workers[14] led directly to **25** in 70% yield from **23** when performed at room temperature. The minor geometrical isomer produced during the formation of **21** was transformed via the same sequence to the *Z* isomer of **25**.

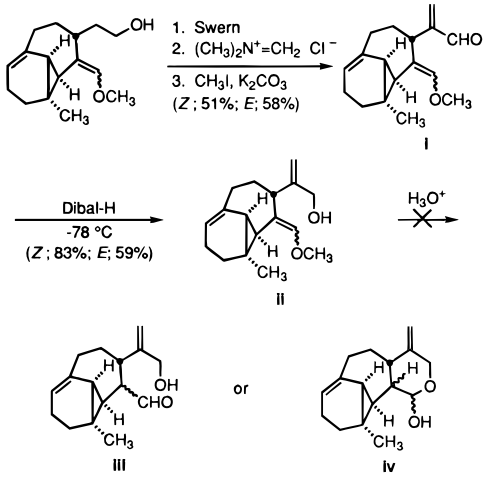
At this juncture, the time had arrived to explore the 6-exo cyclization of **25** under free radical conditions.[15] In light of the activated status of the alkene acceptor in **25**, the customary deceleration seen for these processes in the absence of an electron-withdrawing substituent[16,17] was not observed. The expectation was that the two low-energy transition states would be **A** and **B**, structures which are chairlike with one stretched bond. These two conformers, which can be interconverted simply by rotation around the exocyclic allylic bond specified



in **B**, possess distinctive structural features. When other energetic factors are more or less equal, it is recognized that the major product will derive from the transition state where the acceptor resides in an equatorial disposition.[15] In **A**, however, projection of the α,β-unsaturated ester into the equatorial plane is met with substantial nonbonded steric compression between the α-methyl substituent and cyclopropyl methine carbon. Since the axial alternative **B** experiences appreciably less nonbonded interaction, our expectation was that the major product would be formed via this rotamer to deliver **26** in highly stereoselective fashion. At the experimental level, two cyclized products were formed in a 4.9:1 ratio. That both stereoisomers reflect the preferred reaction pathway via **B** was supported by formation of the identical pair of tetracyclic esters in the same ratio upon comparable treatment of the *Z* isomer of **25**. Although **26** and **27** proved to be inseparable, several ^{1}H and ^{13}C NMR patterns exhibited by **26** were clearly seen to be comparable to those of **2**.

The remarkable capacity of **25** and its *Z* isomer to undergo cyclization with exclusive formation of radical **C** leads to a second stereoselectivity issue. In the present instance, the radical center is adjacent to a carbonyl group, the single occupied orbital is very likely sp^2-hybridized, and this orbital is most apt

(11) A reversal in the sequencing of the chain extensions was also accorded brief attention. As indicated below, the generation of both geometric isomers of **i** and **ii** was not at all problematic. However, proper conditions for the effective hydrolysis of **ii** to either **iii** or **iv** were not found.



(12) The sensitivity of the vinylcyclopropane moiety embedded in the ABC substructure of this structural type has previously been commented on.[1d,7] The lability of **20** to the acidic conditions necessary for hydrolysis of the enol ether functionality is attributed to competitive attack at the bridgehead site.

(13) Takano, S.; Inomata, K.; Samizu, K.; Shun'ichi, T.; Yanase, M.; Suzuki, M.; Iwabuchi, Y.; Sugihara, T.; Ogasawara, K. *Chem. Lett.* **1989**, 1283.

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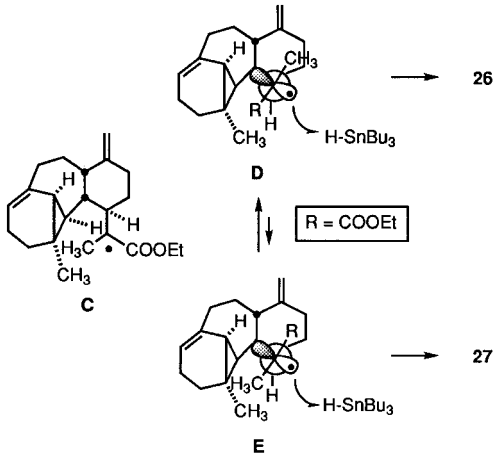
(15) Curran, D. P.; Porter, N. A.; Giese, B. *Stereochemistry of Radical Reactions*: *Concepts, Guidelines, and Synthetic Applications*; VCH Publishers: Weinheim; 1995.

(16) (a) Porter, N. A.; Roe, A. N.; McPhail, A. T. *J. Am. Chem. Soc.* **1980**, *102*, 7574. (b) Roe, A. N.; McPhail, A. T.; Porter, N. A. *J. Am. Chem. Soc.* **1983**, *105*, 1199.

(17) Hanessian, S.; Dhanoa, D. S.; Beaulieu, P. L. *Can. J. Chem.* **1987**, *65*, 1859.

to be aligned with the σ-bond of the largest α-substituent due to a combination of steric and electronic factors.[18] Given these requirements, the two possible conformations **D** and **E**, which differ with respect to orientation of the carboethoxy or methyl substituent over the cyclohexane ring, are plausibly adopted. The minimization of gauche interactions is achieved by positioning the smaller methyl group in this region as in **D**. Donation of a hydrogen atom to the more sterically accessible lobe in **D** leads preferentially to **26**. The observation that both

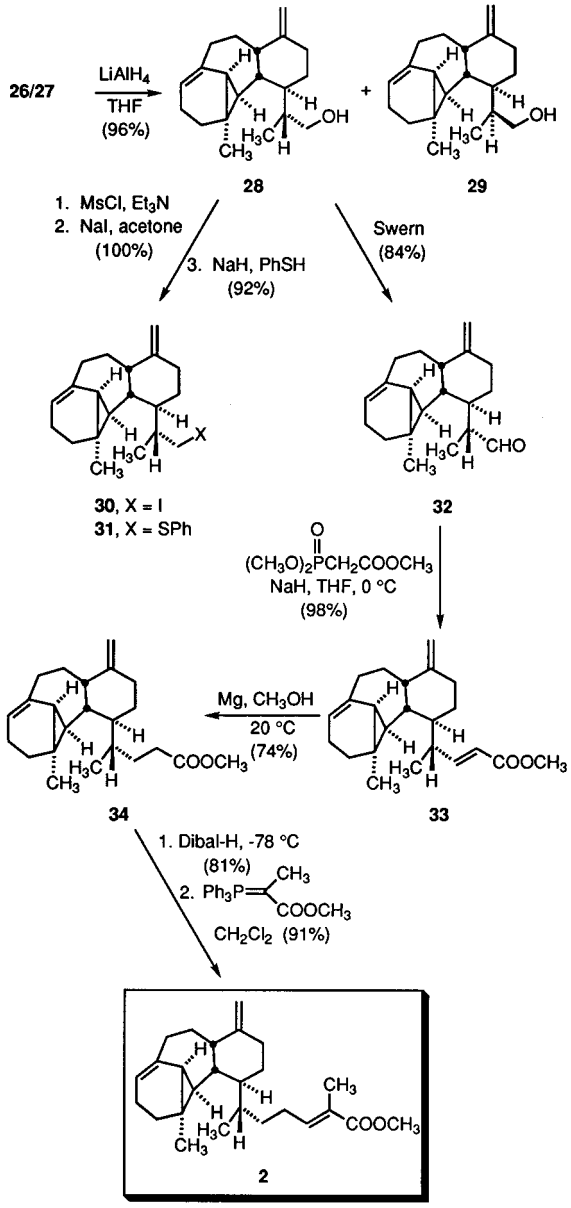


25 and its *Z* isomer preferentially give rise to **26** as the major product is consistent with the intervention of a relatively long-lived radical which has the opportunity to equilibrate as in **D** ⇄ **E** prior to capture by the tin hydride reagent.

The dominant formation of ester **26**, *precisely as required for arrival at cerorubenic acid-III*, is representative of a manner in which a customarily favored transition state model can become disfavored as a direct consequence of global structural considerations. Such crossovers in diastereoselection are not without precedent.[16,17,19−21]

Our final objective was to install the remaining carbon atoms of the pendant side chain as a single unit. Since the alkylation of extended enolates with alkyl halides is recognized to favor α-substitution overwhelmingly,[22] iodide **30** (Scheme 3) was not serviceable in this capacity. However, this intermediate proved to be highly crystalline, thereby permitting complete corroboration of the earlier stereochemical assignments by X-ray crystallographic analysis (Figure 1).[23]

Scheme 3



From a different vantage point, aldehydes are recognized to often give favorable γ/α ratios with extended enol silanes, including tiglate derivatives.[24] In the present context, however, subsequent deoxygenation of the resulting carbinol was predicted to be problematic,[25] and this route was not pursued. Alternatively, an α-chloro sulfide was viewed to be an attractive masked aldehyde equivalent since such electrophiles have been reported to give high γ/α ratios in alkylations involving extended enolate

(18) (a) Hart, D. J.; Krishnamurthy, R. *J. Org. Chem.* **1992**, *57*, 4457. (b) Guindon, Y.; Faucher, A.-M.; Bourque, É.; Caron, V.; Jung, G.; Landry, S. R. *J. Org. Chem.* **1997**, *62*, 9276 and relevant references therein.

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(22) (a) Herrmann, J. L.; Kieczykowski, G. R.; Schlessinger, R. H. *Tetrahedron Lett.* **1973**, 2433. (b) Savu, P. M.; Katzenellenbogen, J. A. *J. Org. Chem.* **1981**, *46*, 239.

(23) In actuality, the X-ray study was performed on *ent*-**30**, which was prepared from *ent*-**4** during the course of exploratory studies.

(24) See, for example: Patron, A. P.; Richter, P. K.; Tomaszewski, M. J.; Miller, R. A.; Nicolaou, K. C. *J. Chem. Soc., Chem. Commun.* **1994**, 1147.

(25) The difficulty lies in the fact that the great majority of deoxygenation maneuvers proceed via radical pathways. Radical intervention in the present instance would very likely evenuate in 6-exo cyclization by intramolecular attack at the methylene double bond.[15]

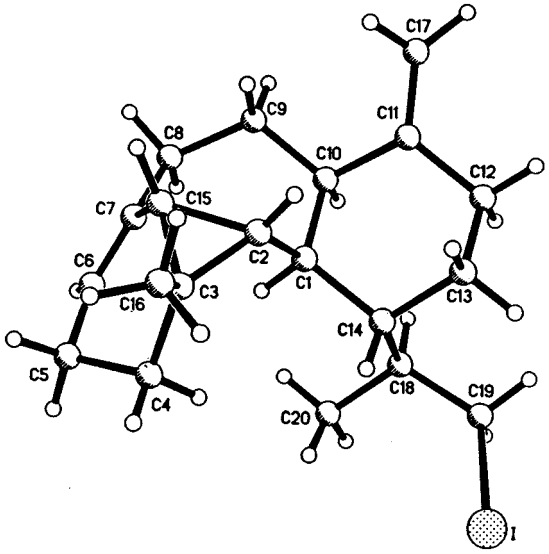

Figure 1. ORTEP diagram of *ent*-**30**.

equivalents.[26] Furthermore, reductive desulfurization of the product was expected to pose no problem. Unfortunately, however, the necessary α-chlorination of **31** could not be accomplished, as refluxing with *N*-chlorosuccinimide in CCl_4[27] only returned unreacted starting material, and reaction with sulfuryl chloride[28] induced its complete decomposition.

In light of the above developments, the side chain was introduced in stepwise fashion. Swern oxidation of the major alcohol **28**, which proved to be readily separable from **29**, led to **32**. Homologation according to the Wadsworth−Emmons protocol[29] gave rise to unsaturated ester **33** in a diastereomeric ratio of 7:1. Following chemoselective reduction of the conjugated double bond with magnesium in methanol,[30] low-temperature exposure of **34** to Dibal-H and condensation with α-(carbomethoxyethylidene)triphenylphosphorane[31] furnished ester **2** in very good yield. Synthetic **2** showed ^{1}H and ^{13}C NMR properties that were indistinguishable from those of the authentic material.

Summary

The first total synthesis of the methyl ester of (−)-cerorubenic acid-III was accomplished in 30 steps and with an overall yield of 0.3% from 3-methyl-2-cyclohexenone. The enantioselective route is characterized by two key strategic elements. The first is an oxyanionic Cope rearrangement of **3** which occurs in high yield and under complete stereocontrol. The formation of **4** in this manner constitutes a particularly expedient means for setting three of the four rings of the target. Fusion of a substituted methylenecyclohexane unit to **4** with proper setting of the four additional stereocenters is shown to be possible via a radical cyclization pathway. This remarkable aspect of our first-generation approach to the cerorubenic acid ring system has elucidated several stereocontrol elements that merit possible attention in other synthetic undertakings.

The route to **2** also makes use of the Knochel chain extension in the context of a total synthesis.[33] Importantly, the completed synthesis substantiates the original structural assignment to **1** and **2** while simultaneously establishing their absolute configuration.

Experimental Section

General Methods. Melting points are uncorrected. The column chromatographic separations were performed with Woelm silica gel (230−400 mesh). Solvents were reagent grade and in most cases dried prior to use. The purity of all compounds was shown to be >95% by TLC and high field ^{1}H and ^{13}C NMR. The high-resolution and fast-atom-bombardment spectra were recorded at The Ohio State University Campus Chemical Instrument Center. Elemental analyses were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark or at Atlantic Microlab, Inc., Norcross, GA.

(1*R*,2*R*,3*R*,4*R*,11*S*)-4-[2-(*tert*-Butyldimethylsiloxy)ethyl]-11-methyltricyclo[5.4.0.0^{2,11}]undec-7-en-3-ol (12). *tert*-Butyldimethylsilyl chloride (2.77 g, 18.4 mmol) was added to an ice-cooled solution of **11**[1a] (3.71 g, 16.7 mmol) and imidazole (2.00 g, 29.4 mmol) in CH_2Cl_2 (60 mL). After 30 min, the reaction mixture was washed with water, dried, and concentrated under reduced pressure. Chromatography of the residue on silica gel (elution with 5% ethyl acetate in hexanes) furnished 5.45 g (97%) of **12** as a colorless oil: IR (neat, cm^{-1}) 3459, 1101; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.72 (d, J = 6.4 Hz, 1 H), 4.16 (dd, J = 13.2, 6.4 Hz, 1 H), 3.72−3.57 (m, 2 H), 2.36−2.25 (m, 1 H), 2.22−2.11 (m, 2 H), 2.09−1.97 (m, 2 H), 1.94−1.41 (series of m, 7 H), 1.14 (s, 3 H), 1.00−0.93 (m, 2 H), 0.87 (s, 9 H), 0.04 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 140.2, 127.1, 75.8, 61.8, 39.2, 35.2, 33.2, 31.3, 29.1, 28.4, 28.2, 25.9, 25.8, 23.5, 22.6, 18.3, −5.3, −5.4; MS *m*/*z* (M^+) calcd 336.2485, obsd 336.2491; $[\alpha]^{20}_D$ −130 (*c* 0.33, $CHCl_3$).

Anal. Calcd for $C_{20}H_{36}O_2Si$: C, 71.37; H, 10.78. Found: C, 71.47; H, 10.86.

(1*R*,2*R*,4*R*,11*S*)-4-[2-(*tert*-Butyldimethylsiloxy)ethyl]-11-methyltricyclo[5.4.0.0^{2,11}]undec-7-en-3-one (13). Alcohol **12** (7.57 g, 22.5 mmol), *N*-methylmorpholine *N*-oxide (3.16 g, 27.0 mmol), and 4 Å molecular sieves (7.6 g) were stirred in CH_2Cl_2 (150 mL) for 15 min, at which time TPAP (240 mg, 0.67 mmol) was introduced in portions. After 2 h, more NMO (1.05 g, 8.97 mmol) was added, and the mixture was stirred for 1 h, concentrated under reduced pressure, taken up in 5% ethyl acetate in hexanes, and poured directly atop a silica gel column. Elution with the same solvent system provided 6.45 g (86%) of **13** as a colorless oil; IR (neat, cm^{-1}) 1696, 1108: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.71 (d, J = 6.9 Hz, 1 H), 3.69−3.58 (m, 1 H), 2.42−2.36 (m, 1 H), 2.26−1.96 (series of m, 5 H), 1.82−1.48 (series of m, 6 H), 1.27 (d, J = 9.5 Hz, 1 H), 1.18 (s, 3 H), 0.87 (s, 9 H), 0.030 (s, 3 H), 0.028 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 210.0, 137.7, 127.7, 61.3, 50.2, 38.9, 34.9, 33.2, 30.2, 27.7, 26.6, 25.9, 23.8, 22.9, 22.4, 18.3, −5.4; MS *m*/*z* (M^+) calcd 334.2328, obsd 334.2348; $[\alpha]^{20}_D$ +10.2 (*c* 0.31, $CHCl_3$).

Anal. Calcd for $C_{20}H_{34}O_2Si$: C, 71.80; H, 10.24. Found: C, 71.53; H, 10.25.

[(*R*)-[(1*R*,2*R*,3*R*,4*R*,11*S*)-4-[2-(*tert*-Butyldimethylsiloxy)ethyl]-3-hydroxy-11-methyltricyclo[5.4.0.0^{2,11}]undec-7-en-3-yl]methoxymethyl]-diphenylphosphine Oxide (14) and [(*S*)-[(1*R*,2*R*,3*R*,4*R*,11*S*)-4-[2-(*tert*-Butyldimethylsiloxy)ethyl]-3-hydroxy-11-methyltricyclo[5.4.0.0^{2,11}]undec-7-en-3-yl]methoxymethyl]diphenylphosphine Oxide (15). (Methoxymethyl)-diphenylphosphine oxide (5.70 g, 23.1 mmol) in dry THF (60 mL) was added to an ice-cooled solution of LDA [from *n*-butyllithium (14.8 mL, 19.2 mmol) and diisopropylamine (3.0 mL, 21 mmol) in THF (50 mL) at 0 °C for 20 min]. After 15 min at 0 °C, the solution was cooled to −78 °C, **13** (1.29 g, 3.86 mmol) dissolved in THF (10 mL) was introduced dropwise, and the resulting mixture was stirred for 30 min, quenched with saturated NH_4Cl solution, and warmed to room temperature. The aqueous phase was extracted with ether, the combined organic layers were dried and concentrated, and the residue was chromatographed on silica gel (elution

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with 10−20% ethyl acetate in hexanes). There was isolated 1.12 g (50%) of **14** followed by 1.00 g (45%) of **15**, both as white powders.

For 14: mp 153−154 °C; IR (CH_2Cl_2, cm^{-1}) 3346, 1470; ^1H NMR (300 MHz, $CDCl_3$) δ 8.21−8.14 (m, 2 H), 7.77−7.30 (m, 2 H), 7.54−7.40 (m, 6 H), 5.61 (d, J = 6.1 Hz, 1 H), 4.72 (br s, 1 H), 3.93 (d, J = 7.7 Hz, 1 H), 3.71−3.64 (m, 1 H), 3.58−3.50 (m, 1 H), 3.15 (s, 3 H), 2.38 (ddd, J = 13.1, 12.8, 4.9 Hz, 1 H), 2.23−1.74 (series of m, 8 H), 1.57−1.51 (m, 1 H), 1.33 (dd, J = 13.8, 3.5 Hz, 1 H), 0.87 (s, 9 H), 0.85−0.72 (m, 2 H), 0.29 (s, 3 H), 0.03 (s, 3 H), 0.02 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 139.5, 134.3 (d, $J_{C,P}$ = 93.9 Hz), 132.6 (d, $J_{C,P}$ = 8.4 Hz), 131.8, 131.7, 131.4, 130.0, 128.5 (d, $J_{C,P}$ = 11.0 Hz), 128.3 (d, $J_{C,P}$ = 11.1 Hz), 124.2, 91.9 (d, $J_{C,P}$ = 83.7 Hz), 80.5, 62.4, 61.8, 46.0, 31.9, 31.2, 29.6, 27.4, 27.1, 26.3, 26.0, 25.8, 25.4, 23.6, 18.4, −5.38, −5.41; MS m/z (M^+) calcd 580.3138, obsd 580.3170; $[\alpha]^{20}_D$ −96.4 (c 1.6, $CHCl_3$).

Anal. Calcd for $C_{34}H_{49}O_4PSi$: C, 70.31; H, 8.50. Found: C, 70.39; H, 8.48.

For 15: mp 190−192 °C; IR (CH_2Cl_2, cm^{-1}) 3366, 1472, 1437; ^1H NMR (300 MHz, $CDCl_3$) δ 8.02−7.87 (m, 4 H), 7.54−7.41 (m, 6 H), 5.58 (d, J = 6.6 Hz, 1 H), 3.97 (d, J = 5.8 Hz, 1 H), 3.70−3.65 (m,1 H), 3.53−3.45 (m, 1 H), 3.22 (br s, 1 H), 2.95 (s, 3 H), 2.33−2.28 (m, 1 H), 2.16−1.56 (series of m, 8 H), 1.10−0.90 (m, 3 H), 0.86 (s, 9 H), 0.85 (s, 3 H), 0.81−0.72 (m, 1 H), 0.01 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 140.0, 133.7 (d, $J_{C,P}$ = 93.4 Hz), 132.5 (d, $J_{C,P}$ = 9.0 Hz), 131.6, 131.5, 131.4 (d, $J_{C,P}$ = 8.8 Hz), 130.4, 128.4 (d, $J_{C,P}$ = 11.0 Hz), 127.7 (d, $J_{C,P}$ = 12.0 Hz), 124.2, 84.6 (d, $J_{C,P}$ = 85.0 Hz), 82.0, 62.4, 61.5, 41.0, 40.9, 31.4, 31.2, 29.4, 28.1, 27.0, 26.5, 26.0, 25.9, 23.5, 18.4, −5.40, −5.42; MS m/z (M^+) calcd 580.3138, obsd 580.3180; $[\alpha]^{20}_D$ −56.4 (c 0.64, $CHCl_3$).

Anal. Calcd for $C_{34}H_{49}O_4PSi$: C, 70.31; H, 8.50. Found: C, 70.38; H, 8.48.

***tert*-Butyl[2-[(1*R*,2*R*,4*R*,11*S*)-3-[(*Z*)-methoxymethylene]-11-methyltricyclo[5.4.0.0^{2,11}]undec-7-en-4-yl]ethoxy]dimethylsilane (16).** Sodium hydride (136 mg, 5.67 mmol) was added in portions to an ice-cooled solution of **14** (330 mg, 0.568 mmol) in dry THF (5 mL). After the addition was complete, the ice bath was removed and the reaction mixture was stirred at 20 °C for 3 h, carefully quenched with water, and extracted with ether. The combined organic phases were dried and concentrated to leave a residue that was purified by chromatography on silica gel (elution with 1% ethyl acetate in hexanes). There was obtained 172 mg (84%) of **16** as a colorless oil: IR (neat, cm^{-1}) 1661, 1472, 1255, 1132, 1102; ^1H NMR (300 MHz, $CDCl_3$) δ 5.89 (d, J = 2.1 Hz, 1 H), 5.64 (d, J = 6.9 Hz, 1 H), 3.65−3.50 (m, 2 H), 3.48 (s, 3 H), 2.32−2.27 (m, 1 H), 2.13−2.10 (m, 2 H), 2.04−1.93 (m, 2 H), 1.83−1.52 (m, 4 H), 1.26−0.98 (series of m, 4 H), 1.19 (s, 3 H), 0.90 (s, 9 H), 0. 0.05 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 145.7, 141.8, 126.3, 116.5, 61.8, 59.2, 39.9, 37.9, 34.5, 32.0, 30.8, 28.3, 26.54, 26.50, 26.0, 24.2, 24.0, 18.3, −5.3; MS m/z (M^+) calcd 362.2642, obsd 362.2643.

Anal. Calcd for $C_{22}H_{38}O_2Si$: C, 72.87; H, 10.56. Found: C, 73.03; H, 10.53.

***tert*-Butyl[2-[(1*R*,2*R*,4*R*,11*S*)-3-[(*E*)-methoxymethylene]-11-methyltricyclo[5.4.0.0^{2,11}]undec-7-en-4-yl]ethoxy]dimethylsilane (18).** Submission of **15** to the identical reaction conditions gave rise to **18** in 41% yield: colorless oil; IR (neat, cm^{-1}) 1663, 1462, 1254, 1218, 1125, 1104; ^1H NMR (300 MHz, $CDCl_3$) δ 5.61 (d, J = 7.1 Hz, 1 H), 5.56 (d, J = 1.9 Hz, 1 H), 3.68−3.54 (m, 2 H), 3.51 (s, 3 H), 2.98−2.93 (m, 1 H), 2.14−1.91 (m, 3 H), 1.81−1.72 (m, 2 H), 1.65−1.43 (m, 3 H), 1.29−1.09 (series of m, 3 H), 1.16 (s, 3 H), 1.04 (d, J = 9.0 Hz, 1 H), 0.90 (s, 9 H), 0.06 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 148.0, 140.6, 125.7, 115.9, 62.5, 59.4, 36.1, 34.3, 32.6, 31.9, 29.7, 29.6, 29.0, 27.2, 26.9, 26.0, 23.9, 23.8, −5.1, −5.2; MS m/z (M^+) calcd 362.2641, obsd 362.2648.

Anal. Calcd for $C_{22}H_{38}O_2Si$: C, 72.87; H, 10.56. Found: C, 72.96; H, 10.52.

(1*R*,2*R*,4*R*,11*S*)-3-[(*Z*)-Methoxymethylene]-11-methyltricyclo[5.4.0.0^{2,11}]undec-7-ene-4-ethanol (17). A solution of tetra-*n*-butylammonium fluoride in THF (0.17 mL, 0.17 mmol) was added to a magnetically stirred solution of **14** (65 mg, 0.11 mmol) in THF (3 mL). After 4 h, the mixture was cooled to 0 °C, treated with sodium hydride (15 mg, 0.63 mmol), stirred at 20 °C for 4 h, poured into water, and extracted with ether. The combined organic phases were dried and concentrated to leave a residue, purification of which by chromatography on silica gel (elution with 15% ethyl acetate in hexanes) gave **17** (26 mg, 95%) as a white solid: mp 58−62 °C; IR (neat, cm^{-1}) 3342, 1660, 1446, 1128; ^1H NMR (300 MHz, $CDCl_3$) δ 5.94 (d, J = 2.1 Hz, 1 H), 5.65 (d, J = 7.0 Hz, 1 H), 3.71−3.57 (m, 2 H), 3.48 (s, 3 H), 2.34−2.28 (m, 1 H), 2.14−1.93 (m, 4 H), 1.84−1.52 (m, 4 H), 1.44 (br s, 1 H), 1.25−0.99 (series of m, 4 H), 1.18 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 145.7, 141.5, 126.4, 116.5, 61.6, 59.2, 40.0, 38.1, 34.3, 31.9, 30.8. 28.2, 26.6, 26.4, 24.3, 24.0; MS m/z (M^+) calcd 248.1776, obsd 248.1767; $[\alpha]^{20}_D$ −104 (c 0.31, $CHCl_3$).

Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.36; H, 9.75. Found: C, 77.25; H, 9.69.

(1*R*,2*R*,4*R*,11*S*)-3-[(*E*)-Methoxymethylene]-11-methyltricyclo[5.4.0.0^{2,11}]undec-7-ene-4-ethanol (19). The title alcohol, prepared in an entirely similar manner, was obtained in 63% yield as a white solid: mp 69−70 °C: IR (CH_2Cl_2, cm^{-1}) 3613, 1449, 1121; ^1H NMR (300 MHz, $CDCl_3$) δ 5.63−5.62 (m, 2 H), 3.64 (dd, J = 7.4, 5.3 Hz, 2 H), 3.54 (s, 3 H), 3.02−2.93 (m, 1 H), 2.17−1.98 (m, 3 H), 1.92−1.73 (m, 4 H), 1.68−1.49 (m, 2 H), 1.31−1.19 (m, 3 H), 1.16 (s, 3 H), 1.06 (d, J = 9.0 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 148.4, 139.9, 125.7, 115.4, 61.5, 59.5, 35.4, 35.0, 32.2, 32.1, 29.1, 28.8, 27.2, 26.5, 23.7, 23.2; MS m/z (M^+) calcd 248.1776, obsd 248.1772; $[\alpha]^{20}_D$ −60.9 (c 0.23, $CHCl_3$).

Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.36; H, 9.75. Found: C, 77.17; H, 9.76.

(4a*R*,7a*R*,8*R*,8a*S*,8b*S*)-4,4a,5,6,7a,8,8a,8b-Octahydro-8-methyl-3*H*-8,7-[1]propanyl[3]ylidene-1*H*-cyclopropa[6,7]cyclohepta[1,2-*c*]-pyran-1-ol (20). Perchloric acid (35%, 0.50 mL) was added to a magnetically stirred solution of **17** (17 mg, 0.068 mmol) in 9:1 dioxane-water (2 mL), and the resulting mixture was stirred for 24 h, poured into saturated $NaHCO_3$ solution, and extracted with ether. The combined organic phases were dried and concentrated, and the residue was chromatographed on silica gel (elution with 10% ethyl acetate in hexanes). There was isolated 8 mg (50%) of a 1.2:1 mixture of β- and α-lactols **20** as a colorless oil. Attempts to purify these compounds resulted in decomposition; IR (neat, cm^{-1}) 3378, 1649, 1443, 1378; ^1H NMR (300 MHz, $CDCl_3$) δ (major epimer) 5.66−5.63 (m, 1 H), 4.58 (d, J = 7.1 Hz, 1 H), 4.05−3.96 (m, 1 H), 3.49 (ddd, J = 12.0, 12.0, 2.4 Hz, 1 H), 2.99 (d, J = 7.1 Hz, 1 H), 2.36−1.91 (series of m, 3 H), 1.89−1.24 (series of m, 9 H), 1.19 (s, 3 H), 1.10−0.83 (m, 2 H); (minor epimer) 5.01 (s, 1 H), 3.61 (ddd, J = 11.1, 4.9, 1.2 Hz, 1 H), 1.14 (s, 3 H), (the remaining signals were obscured); ^{13}C NMR (75 MHz, C_6D_6) ppm 139.9, 139.8, 125.0, 124.8, 98.2, 95.3, 66.1, 59.6, 39.6, 38.1, 37.5, 33.4, 33.3, 32.3, 32.2. 32.0, 31.5, 29.7, 29.4, 28.8, 28.2, 27.23, 27.18, 26.9, 24.5, 24.0, 23.7, 23.1, 21.1, 20.5; MS m/z (M^+) calcd 234.1620, obsd 234.1652; $[\alpha]^{20}_D$ −133 (c 0.20, $CHCl_3$).

Ethyl (α*E*,1*R*,2*R*,3*R*,4*R*,11*R*)-4-(2-Hydroxyethyl)-α,11-dimethyltricyclo[5.4.0.0^{2,11}]undec-7-ene-3-acrylate (21). Triethyl 2-phosphonopropionate (3.71 mL, 17.3 mmol) was added to a stirred suspension of sodium ethoxide (0.985 g, 14.5 mmol) in DMF (55 mL). After 1 h, the mixture was cooled to 0 °C, added to an ice-cooled solution of **20** (0.675 g, 2.88 mmol) in DMF (25 mL), stirred for 4.5 h, and poured into ether. The organic phase was washed with water and brine, dried, and concentrated under reduced pressure. The residue was chromatographed on silica gel (elution with 10% ethyl acetate in hexanes) to afford 0.220 g (24%) of the (*Z*)-isomer and 0.422 g (46%) of (*E*)-isomer **21**.

For the (*Z*)-isomer: colorless oil; IR (neat, cm^{-1}) 3394, 1712, 1642, 1451, 1375; ^1H NMR (300 MHz, $CDCl_3$) δ 6.05 (dd, J = 10.0, 1.1 Hz, 1 H), 5.63 (d, J = 6.7 Hz, 1 H), 4.24−4.06 (m, 2 H), 3.73−3.56 (m, 2 H), 3.05 (dd, J = 10.0, 10.0 Hz, 1 H), 2.21−1.91 (series of m, 6 H), 1.88 (s, 3 H), 1.85−1.65 (m, 2 H), 1.60 (dd, J = 13.7, 2.4 Hz, 1 H), 1.54−1.15 (series of m, 6 H), 1.11 (s, 3 H), 0.95 (d, J = 9.0 Hz, 1 H), 0.58 (dd, J = 9.6, 9.6 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 168.0, 146.5, 140.6, 125.5, 124.3, 61.9, 60.1, 40.7, 38.8, 35.7, 33.0, 31.7, 30.2, 28.3, 27.1, 26.6, 23.6, 23.2, 21.0, 14.3; MS m/z (M^+) calcd 318.2195, obsd 318.2232; $[\alpha]^{20}_D$ −208 (c 0.22, $CHCl_3$).

For the (*E*)-isomer 21: colorless oil; IR (neat, cm^{-1}) 3426, 1707, 1446, 1367; ^1H NMR (300 MHz, $CDCl_3$) δ 6.86 (dd, J = 9.6, 1.3 Hz, 1 H), 5.63 (d, J = 6.7 Hz, 1 H), 4.17 (q, J = 7.1 Hz, 2 H), 3.73−3.55 (m, 2 H), 2.34 (dd, J = 9.8, 9.8 Hz, 1 H), 2.20−2.14 (m, 2 H), 2.08−1.79 (series of m, 7 H), 1.77 (d, J = 1.2 Hz, 3 H), 1.65 (ddd, J = 13.7,

4.0, 1.8 Hz, 1 H), 1.33−1.16 (m, 5 H), 1.10 (s, 3 H), 0.98 (d, J = 9.0 Hz, 1 H), 0.70 (dd, J = 9.5, 9.5 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 168.6, 146.2, 140.5, 126.2, 124.7, 61.5, 60.5, 39.5, 39.1, 36.1, 32.0, 31.6, 30.0, 28.9, 27.0, 26.6, 23.6, 23.3, 14.2, 12.9; MS *m*/*z* (M^+) calcd 318.2195, obsd 318.2194; $[\alpha]^{20}_D$ −140 (*c* 0.32, $CHCl_3$).

Ethyl (α*E*,1*R*,2*R*,3*S*,4*S*,11*R*)-4-(1-Formylvinyl)-α,11-dimethyltricyclo[5.4.0.0^{2,11}]undec-7-ene-3-acrylate (22). Dimethyl sulfoxide (0.20 mL, 4.1 mmol) was added to a cold (−70 °C) solution of oxalyl chloride (0.18 mL, 2.1 mmol) in CH_2Cl_2 (10 mL). After 15 min, **21** (220 mg, 0.69 mmol) in CH_2Cl_2 (2 mL) and triethylamine (1.10 mL, 7.95 mmol) were added in succession, and the mixture was allowed to warm to 20 °C over 1 h. *N*,*N*,*N*-Dimethyl(methylene)ammonium chloride (123 mg, 1.31 mmol) was introduced, and the mixture was stirred for 48 h with more ammonium salt (2 × 150 mg) and triethylamine (2 × 0.2 mL) being added after 18 and 28 h, poured into water, and extracted with $CHCl_3$. The combined organic layers were dried, concentrated, and dissolved in 2:1 ether-chloroform (6 mL). Iodomethane (4 mL) was added and stirring was continued for 10 h. The resulting mixture was concentrated, taken up in $CHCl_3$ (15 mL), and stirred vigorously with aqueous K_2CO_3 solution (10 mL) for 6 h. Extraction with $CHCl_3$ preceded drying, concentration, and chromatography of the residue on silica gel. Elution with 5% ethyl acetate in hexanes furnished 135 mg (60%) of **22** as a colorless oil: IR (neat, cm^{-1}) 1711, 1691, 1644, 1453, 1366, 1278, 1236; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.40 (s, 1 H), 6.77 (s, 1 H), 6.40 (dd, J = 9.9, 1.3 Hz, 1 H), 6.15 (s, 1 H), 5.72 (d, J = 6.1 Hz, 1 H), 4.11 (br q, J = 7.1 Hz, 2 H), 3.18−3.12 (m, 1 H), 2.63 (dt, J = 4.5, 10.0 Hz, 1 H), 2.30−2.26 (m, 2 H), 2.03−1.79 (m, 3 H), 1.77 (d, J = 1.3 Hz, 3 H), 1.66 (ddd, J = 13.8, 4.4, 1.9 Hz, 1 H), 1.53−1.44 (m, 1 H), 1.32 (dd, J = 13.3, 4.7 Hz, 1 H), 1.23 (t, J = 7.1 Hz, 3 H), 1.12 (s, 3 H), 1.07 (d, J = 8.8 Hz, 1 H), 0.77 (dd, J = 9.4, 9.4 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 194.5, 168.2, 150.9, 144.0, 139.5, 136.4, 126.4, 125.3, 60.3, 37.4, 37.2, 34.3, 32.8, 31.7, 28.3, 27.0, 26.1, 23.5, 22.5, 14.2, 12.8; MS *m*/*z* (M^+) calcd 328.2038, obsd 328.1994; [α]S(22,D) −93.8 (*c* 0.15, $CHCl_3$).

Ethyl (α*E*,1*R*,2*R*,3*S*,4*S*,11*R*)-4-[1-(Hydroxymethyl)vinyl]-α,11-dimethyltricyclo[5.4.0.0^{2,11}]undec-7-ene-3-acrylate (23). Sodium borohydride (23 mg, 0.61 mmol) was added to a magnetically stirred solution of **22** (77 mg, 0.23 mmol) in methanol (5 mL), and the resulting mixture was stirred for 20 min, quenched with saturated NH_4Cl solution, and extracted with ethyl acetate. The combined organic phases were dried and concentrated to leave a residue, purification of which by chromatography on silica gel (elution with 15% ethyl acetate in hexanes) delivered 73 mg (96%) of **23** as a colorless oil: IR (neat, cm^{-1}) 3436, 1711, 1644, 1453, 1366, 1283, 1247; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.69 (dd, J = 9.9, 1.3 Hz, 1 H), 5.69 (d, J = 6.7 Hz, 1 H), 5.28 (s, 1 H), 5.24 (d, J = 1.1 Hz, 1 H), 4.16 (q, J = 7.1 Hz, 2 H), 3.95 (s, 2 H), 2.56 (dt, J = 4.2, 10.1 Hz, 1 H), 2.44−1.80 (series of m, 7 H), 1.77 (d, J = 1.3 Hz, 3 H), 1.64 (ddd, J = 13.8, 4.3, 1.7 Hz, 1 H), 1.55−1.32 (m, 1 H), 1.31−1.18 (m, 1 H), 1.27 (t, J = 7.1 Hz, 3 H), 1.12 (s, 3 H), 1.06−1.03 (m, 1 H), 0.84 (dd, J = 9.6, 9.6 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 168.5, 149.8, 145.6, 139.9, 126.0, 124.7, 111.2, 67.3, 60.5, 44.7, 37.7, 34.8, 33.2, 31.5, 28.4, 26.9, 26.1, 23.5, 22.3, 14.2, 12.8; MS *m*/*z* (M^+) calcd 330.2195, obsd 330.2197; $[\alpha]^{20}_D$ −93.9 (*c* 0.12, $CHCl_3$).

Ethyl (α*E*,1*R*,2*R*,3*S*,4*S*,11*R*)-4-(1-(2-Iodoethyl)vinyl)-α,11-dimethyltricyclo[5.4.0.0^{2,11}]undec-7-ene-3-acrylate (25). Methanesulfonyl chloride (0.035 mL, 0.45 mmol) was added to a stirred solution of **23** (75 mg, 0.23 mmol) and triethylamine (0.10 mL) in CH_2Cl_2 (10 mL) at 0 °C. After 20 min, lithium iodide (305 mg, 2.28 mmol) and THF (3 mL) were introduced, the ice bath was removed, and the mixture was stirred at room temperature for 30 min, poured into water, and extracted with hexanes. The combined extracts were dried and concentrated. The unpurified allylic iodide, together with copper(I) iodide (381 mg, 2.00 mmol) and lithium iodide (535 mg, 4.00 mmol), was taken up in dry THF (20 mL), cooled to −10 °C, treated during 25 min with a 1.4 M solution of iodomethylzinc iodide in THF[32] (3.0 mL, 4.2 mmol), and allowed to warm to room temperature during 2 h. The mixture was poured into saturated NH_4Cl solution and extracted with ether. The combined organic phases were dried and concentrated to leave a residue which was chromatographed on silica gel. Elution with 1% ethyl acetate in hexanes afforded 74 mg (70% overall) of **25** as a colorless oil: IR (neat, cm^{-1}) 1713, 1643, 1443, 1279, 1237; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.72 (dd, J = 9.9, 1.0 Hz, 1 H), 5.70 (d, J = 6.1 Hz, 1 H), 5.24 (s, 1 H), 4.97 (s, 1 H), 4.24−4.12 (m, 2 H), 3.20−3.14 (m, 2 H), 2.62−2.40 (m, 4 H), 2.33−2.21 (m, 2 H), 2.15−1.99 (m, 2 H), 1.86−1.82 (m, 1 H), 1.79 (d, J = 0.9 Hz, 3 H), 1.68−1.52 (m, 1 H), 1.51−1.45 (m, 1 H), 1.30 (t, J = 7.1 Hz, 3 H), 1.26−1.20 (m, 1 H), 1.13 (s, 3 H), 1.05 (d, J = 8.9 Hz, 1 H), 0.85 (dd, J = 9.6 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 168.3, 139.1, 145.4, 149.9, 126.0, 124.8, 113.4, 60.5, 47.5, 43.0, 37.8, 34.6, 33.0, 31.3, 28.3, 27.0, 25.9, 23.5, 22.2, 14.3, 12.9, 3.5; MS *m*/*z* (M^+) calcd 454.1369, obsd 454.1359; $[\alpha]^{20}_D$ −80.3 (*c* 0.12, $CHCl_3$).

Ethyl (α*R*,1*R*,1a*R*,4a*S*,8*R*,8a*S*,8b*R*)-1a,3,4,4a,5,6,7,8,8a,8b-Decahydro-α,1-dimethyl-5-methylene-1*H*-1,2[1]propanyl[3]ylidene-benzo[*a*]cyclopropa[*c*]cycloheptene-8-acetate (26) and Ethyl (α*R*,1*R*,1a*R*,4a*S*,8*R*,8a*S*,8b*R*)-1a,3,4,4a,5,6,7,8,8a,8b-Decahydro-α,1-dimethyl-5-methylene-1*H*-1,2-[1]propanyl[3]ylidenebenzo[*a*]cyclopropa[*c*]cycloheptene-8-acetate (27). Iodide **25** (44 mg, 0.097 mmol), tributyltin hydride (37 mg, 0.13 mmol), and AIBN (4 mg) were refluxed in benzene (4 mL) for 90 min, cooled to 20 °C, and concentrated. The residue was purified by chromatography on silica gel (elution with hexanes to remove tin residues, followed by 0.5% ethyl acetate in hexanes) to provide 25 mg (78%) of an inseparable mixture of **26** containing 17% of **27**.

For 26: IR (neat, cm^{-1}) 1731, 1637, 1455, 1173, 1153; ^{1}H NMR (800 MHz, C_6D_6) δ 5.66 (d, J = 6.6 Hz, 1 H), 4.91 (s, 1 H), 4.83 (s, 1 H), 4.02−3.94 (m, 2 H), 3.78 (dq, J = 10.9, 6.9 Hz, 1 H), 2.48−2.46 (m, 1 H), 2.37 (ddd, J = 13.2, 13.2, 4.4 Hz, 1 H), 2.24−2.15 (m, 4 H), 2.06−2.00 (m, 1 H), 1.94−1.91 (m, 2 H), 1.90−1.85 (m, 1 H), 1.74−1.70 (m, 1 H), 1.67−1.65 (m, 1 H), 1.55 (br d, J = 13.4 Hz, 1 H), 1.48−1.42 (m, 2 H), 1.13 (d, J = 6.9 Hz, 3 H), 0.98 (s, 3 H), 0.96 (t, J = 7.2 Hz, 3 H), 0.91 (d, J = 9.0 Hz, 1 H), 0.80 (dd, J = 10.0, 10.0 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 176.9, 151.0, 140.3, 124.4, 106.6, 60.0, 41.3, 40.5, 39.6, 35.1, 32.2, 32.0, 29.2, 28.7, 28.0, 27.1, 26.4, 24.8, 23.8, 20.8, 16.1, 14.3; MS *m*/*z* (M^+) calcd 328.2402, obsd 328.2393.

(α*R*,1*R*,1a*R*,4a*S*,8*R*,8a*S*,8b*R*)-1a,3,4,4a,5,6,7,8,8a,8b-Decahydro-α,1-dimethyl-5-methylene-1*H*-1,2-[1]propanyl[3]ylidenebenzo[*a*]-cyclopropa[*c*]cycloheptene-8-ethanol (28) and (α*S*,1*R*,1a*R*,4a*S*,8*R*,8a*S*,8b*R*)-1a,3,4,4a,5,6,7,8,8a,8b-Decahydro-α,1-dimethyl-5-methylene-1*H*-1,2-[1]propanyl[3]ylidenebenzo[*a*]cyclopropa[*c*]cycloheptene-8-ethanol (29). A solution of the **26/27** mixture (37 mg, 0.11 mol) in dry THF (1 mL) was added to a stirred suspension of lithium aluminum hydride (43 mg, 1.13 mmol) in THF (2 mL) at −78 °C. The mixture was allowed to warm to 20 °C during 1 h, treated sequentially with water (0.043 mL), 15% NaOH solution (0.043 mL), and water (0.13 mL), filtered, and concentrated. Chromatography of the residue on silica gel (elution with 5% ethyl acetate in hexanes) furnished 5.3 mg (16%) of **29** and 26 mg (80%) of **28**.

For 28: white solid, mp 107−109 °C; IR (CH_2Cl_2, cm^{-1}) 3390, 1637, 1455, 1020; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.67 (d, J = 6.6 Hz, 1 H), 4.79 (s, 1 H), 4.71 (d, J = 1.1 Hz, 1 H), 3.70 (dd, J = 10.6, 3.4 Hz, 1 H), 3.47 (dd, J = 10.6, 6.8 Hz, 1 H), 2.50−2.41 (m, 1 H), 2.35−2.27 (m, 1 H), 2.25−2.12 (m, 4 H), 2.05−1.94 (m, 1 H), 1.92−1.69 (m, 4 H), 1.67−1.60 (m, 2 H), 1.58−1.42 (m, 1 H), 1.40−1.26 (m, 3 H), 1.10 (s, 3 H), 1.01−0.94 (m, 1 H), 0.98 (d, J = 6.8 Hz, 3 H), 0.75 (dd, J = 10.7, 9.3 Hz, 1 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 151.3, 140.6, 124.4, 106.7, 66.1, 40.9, 40.4, 36.3, 35.2, 32.9, 32.5, 30.4, 29.0, 28.5, 27.2, 25.1, 24.9, 24.2, 20.9, 16.2; MS *m*/*z* (M^+) calcd 286.2297, obsd 286.2329; $[\alpha]^{20}_D$ −161 (*c* 0.27, $CHCl_3$).

For 29: white solid, mp 61−64 °C; IR (neat, cm^{-1}) 3351, 1638, 1453, 1022; ^{1}H NMR (300 MHz, C_6D_6) δ 5.72−5.68 (m, 1 H), 4.94 (s, 1 H), 4.88 (d, J = 1.0 Hz, 1 H), 3.33 (dd, J = 10.3, 5.2 Hz, 1 H), 3.20 (dd, J = 10.3, 6.2 Hz, 1 H), 2.53−2.47 (m, 1 H), 2.28−2.02 (m, 5 H), 1.87−1.19 (series of m, 10 H), 1.05 (s, 3 H), 1.03−0.82 (m, 2 H), 0.79 (d, J = 6.8 Hz, 3 H), 0.72 (dd, J = 10.4, 9.2 Hz, 1 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 151.5, 140.2, 124.2, 106.5, 66.3, 40.5, 40.2, 36.3, 34.9, 32.5, 30.7, 30.2, 28.5, 28.2, 27.0, 24.5, 23.9, 23.6, 20.4, 14.2; MS *m*/*z* (M^+) calcd 286.2297, obsd 286.2280; $[\alpha]^{20}_D$ −139 (*c* 0.34, $CHCl_3$).

(1*R*,1a*R*,4a*S*,8*R*,8a*S*,8b*R*)-1a,3,4,4a,5,6,7,8,8a,8b-Decahydro-8-[(*R*)-2-iodo-1-methylethyl]-1-methyl-5-methylene-1*H*-1,2-[1]propanyl-[3]ylidenebenzo[*a*]cyclopropa[*c*]cycloheptene (30). Methanesulfonyl

chloride (0.005 mL, 0.07 mmol) was added to an ice-cold, stirred solution of **28** (12 mg, 0.042 mmol) and triethylamine (0.050 mL, 0.36 mmol) in CH_2Cl_2 (3 mL). After 30 min, the mixture was poured into water and extracted with $CHCl_3$. The combined organic layers were dried and concentrated to give 17 mg (100%) of the mesylate, which was directly heated with sodium iodide (132 mg, 0.88 mmol) in acetone (5 mL) for 10 h. After being cooled, the mixture was concentrated and chromatographed on silica gel (elution with hexanes) to afford 18 mg (100%) of **30** as a white powder. Crystals suitable for X-ray analysis were grown from methanol: mp 76−78 °C; IR (CH_2Cl_2, cm^{-1}) 1708, 1108, 1091; ^1H NMR (300 MHz, $CDCl_3$) δ 5.69−5.66 (m, 1 H), 4.80 (d, J = 0.9 Hz, 1 H), 4.72 (d, J = 1.5 Hz, 1 H), 3.38 (dd, J = 9.7, 2.7 Hz, 1 H), 3.14 (dd, J = 9.7, 6.7 Hz, 1 H), 2.47−2.45 (m, 1 H), 2.29−1.99 (m, 5 H), 1.87−1.80 (m, 2 H), 1.72−1.46 (m, 6 H), 1.37−1.26 (m, 2 H), 1.11 (s, 3 H), 1.01−0.96 (m, 1 H), 1.00 (d, J = 6.5 Hz, 3 H), 0.72 (dd, J = 10.8, 9.2 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 150.8, 140.3, 124.3, 106.8, 43.2, 40.5, 35.9, 33.6, 32.2, 32.0, 29.9, 28.3, 28.2, 27.1, 24.6, 24.0, 23.8, 20.7, 19.8, 17.7; MS m/z (M^+) calcd 396.1273, obsd 396.1326; $[\alpha]^{20}_D$ −109 (c 0.14, $CHCl_3$).

(1*R,1a*R**,4a*S**,8*R**,8a*S**,8b*R**)-1a,3,4,4a,5,6,7,8,8a,8b-Decahydro-1-methyl-5-methylene-8-[(*R**)-1-methyl-2-(phenylthio)ethyl]-1−1*H*-1,2-[1]propanyl[3]ylidenebenzo[*a*]cyclopropa[*c*]cycloheptene (31).** Thiophenol (0.050 mL, 0.49 mmol) was added to a stirred suspension of 80% sodium hydride mineral oil dispersion (13 mg, 0.43 mmol) in dry THF (1 mL). After 30 min, a solution of **30** (12 mg, 0.031 mmol) in THF (1 mL) was introduced, and the mixture was stirred for 1 h, poured into saturated NH_4Cl solution, and extracted with ether. The combined organic layers were dried and concentrated to leave a residue that was chromatographed on silica gel. Elution with hexanes afforded 11 mg (92%) of **31** as a colorless oil: IR (neat, cm^{-1}) 1639, 1583, 1478, 1436, 1376; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35−7.13 (m, 5 H), 5.66 (br d, J = 5.6 Hz, 1 H), 4.78 (s, 1 H), 4.71 (s, 1 H), 3.15 (dd, J = 12.2, 2.9 Hz, 1 H), 2.65 (dd, J = 12.2, 9.1 Hz, 1 H), 2.49−2.44 (m, 1 H), 2.31−2.11 (m, 5 H), 2.09−1.95 (m, 2 H), 1.89−1.59 (m, 5 H), 1.55−1.21 (m, 3 H), 1.10 (s, 3 H), 1.06 (d, J = 6.7 Hz, 3 H), 1.02−0.93 (m, 1 H), 0.71 (dd, J = 10.5, 9.3 Hz, 1 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 151.1, 140.3, 137.6, 129.1, 128.8, 125.7, 124.2, 106.4, 43.5, 40.1, 39.8, 36.1, 34.8, 32.8, 32.3, 30.3, 28.7, 28.3, 27.2, 24.8, 24.3, 23.8, 20.8, 18.0; MS m/z (M^+) calcd 378.2381, obsd 378.2378.

(α*R*,1*R*,1a*R*,4a*S*,8*R*,8a*S*,8b*R*)-1a,3,4,4a,5,6,7,8,8a,8b-Decahydro-α,1-dimethyl-5-methylene-1*H*-1,2-[1]propanyl[3]ylidenebenzo[*a*]-cyclopropa[*c*]cycloheptene-8-acetaldehyde (32). Dimethyl sulfoxide (0.035 mL, 0.49 mmol) was added to a stirred solution of oxalyl chloride (0.021 mL, 0.24 mmol) in CH_2Cl_2 (3 mL) at −70 °C. After 15 min, **28** (12 mg, 0.042 mmol) dissolved in CH_2Cl_2 (2 mL) was introduced, followed by triethylamine (0.13 mL, 0.93 mmol). The mixture was allowed to warm to room temperature over 2 h, quenched with saturated NH_4Cl solution, and extracted with ether. The combined organic phases were dried and concentrated, and the residue was chromatographed on silica gel (elution with 1% ethyl acetate in hexanes). There was isolated 10 mg (84%) of **32** as a colorless oil: IR (neat, cm^{-1}) 1725, 1455; ^1H NMR (300 MHz, C_6D_6) δ 9.30 (d, J = 3.3 Hz, 1 H), 5.66−5.64 (m, 1 H), 4.89 (s, 1 H), 4.82 (d, J = 1.6 Hz, 1 H), 2.49−2.42 (m, 1 H), 2.39−2.27 (m, 1 H), 2.27−1.99 (m, 6 H), 1.94−1.51 (m, 4 H), 1.50−1.21 (m, 4 H), 1.01 (s, 3 H), 0.90 (d, J = 9.4 Hz, 1 H), 0.77 (d, J = 6.9 Hz, 3 H), 0.69 (dd, J = 10.5, 9.4 Hz, 1 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 203.4, 150.4, 140.2, 124.6, 107.3, 46.7, 40.2, 39.6, 35.6, 32.4, 32.3, 29.8, 28.8, 28.5, 27.1, 25.9, 25.0, 24.1, 20.8, 12.4; MS m/z (M^+) calcd 284.2140, obsd 284.2165; $[\alpha]^{20}_D$ −130 (c 0.18, $CHCl_3$).

Methyl (α*E*,γ*S*,1*R*,1a*R*,4a*S*,8*S*,8a*S*,8b*R*)-1a,3,4,4a,5,6,7,8,8a,8b-Decahydro-γ,1-dimethyl-5-methylene-1*H*-1,2[1]propanyl[3]-ylidenebenzo[*a*]cyclopropa[*c*]cycloheptene-8-crotonate (33). Trimethyl phosphonoacetate (0.050 mL, 0.31 mmol) was added to an ice-cooled, stirred suspension of 80% sodium hydride mineral oil suspension (8.6 mg, 0.29 mmol) in dry THF (2 mL). The ice bath was removed, stirring was continued for 20 min, and the mixture was returned to 0 °C prior to the addition of **32** (10 mg, 0.035 mmol) dissolved in THF (2 mL). After 80 min at 0 °C, saturated NH_4Cl solution was introduced, the product was extracted into ether, and the combined extracts were dried and concentrated. Chromatography of the residue on silica gel (elution with 1% ethyl acetate in hexanes) afforded 12 mg (98%) of a 7.1:1 mixture of **33** and its *Z* isomer as a colorless oil.

For 33: IR (neat, cm^{-1}) 1725, 1655, 1455, 1267, 1179; ^1H NMR (300 MHz, $CDCl_3$) δ 6.84 (dd, J = 15.6, 9.2 Hz, 1 H), 5.79 (d, J = 15.6 Hz, 1 H), 5.67 (br d, J = 6.7 Hz, 1 H), 4.78 (s, 1 H), 4.71 (s, 1 H), 3.73 (s, 3 H), 2.64−2.54 (m, 1 H), 2.51−2.41 (m, 1 H), 2.35−1.22 (series of m, 14 H), 1.11 (s, 3 H), 1.02 (d, J = 6.7 Hz, 3 H), 0.99−0.97 (m, 1 H), 0.75 (dd, J = 11.6, 9.4 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 167.2, 154.3, 151.0, 140.3, 124.4, 119.9, 106.7, 51.4, 43.1, 39.9, 37.0, 35.6, 32.1, 31.9, 29.7, 28.5, 28.2, 27.1, 25.5, 24.8, 23.8, 20.7, 18.5; MS m/z (M^+) calcd 340.2402, obsd 340.2400; $[\alpha]^{20}_D$ −115 (c 0.17, $CHCl_3$).

Methyl (γ*S*,1*R*,1a*R*,4a*S*,8*S*,8a*S*,8b*R*)-1a,3,4,4a,5,6,7,8,8a,8b-Decahydro-γ,1-dimethyl-5-methylene-1*H*-1,2[1]propanyl[3]ylidenebenzo-[*a*]cyclopropa[*c*]cycloheptene-8-butyrate (34). The *E*/*Z* mixture of esters **33** (11.8 mg, 0.035 mmol) and magnesium (32 mg, 1.3 mg-at) was stirred in methanol (1 mL) for 4 h. Hydrochloric acid (1 N) was added with vigorous stirring until the mixture became homogeneous (ca. 5 mL). The product was extracted into ether, and the combined organic extracts were washed with saturated $NaHCO_3$ solution, dried, and concentrated. The residue was chromatographed on silica gel (elution with 0.5% ethyl acetate in hexanes) to afford 8.9 mg (74%) of **34** as a colorless oil: IR (neat, cm^{-1}) 1741, 1453; ^1H NMR (300 MHz, $CDCl_3$) δ 5.65 (dd, J = 6.0, 1.1 Hz, 1 H), 4.77 (s, 1 H), 4.70 (d, J = 1.5 Hz, 1 H), 3.66 (s, 3 H), 2.50−2.10 (m, 9 H), 2.04−1.92 (m, 1 H), 1.88−1.75 (m, 3 H), 1.74−1.41 (m, 6 H), 1.39−1.25 (m, 2 H), 1.22−1.14 (m, 1 H), 1.10 (s, 3 H), 0.95 (d, J = 9.0 Hz, 1 H), 0.86 (d, J = 6.7 Hz, 1 H), 0.69 (dd, J = 10.4, 9.3 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 174.5, 151.5, 140.4, 124.1, 106.2, 51.5, 44.1, 40.2, 35.9, 32.4, 32.3, 31.82, 31.76, 30.5, 29.0, 28.5, 28.4, 27.2, 24.6, 23.83, 23.78, 20.6, 17.7; MS m/z (M^+) calcd 342.2559, obsd 342.2559; $[\alpha]^{20}_D$ −126 (c 0.24, $CHCl_3$).

Cerorubenic Acid-III Methyl Ester (2). A 1.0 M solution of Dibal-H in hexanes (0.028 mL, 0.028 mmol) was added to a stirred solution of **34** (8.9 mg, 0.026 mmol) in toluene (2 mL) at −78 °C. After 1 h, 1 M HCl (3 mL) was added, the reaction mixture was warmed to room temperature, and the product was extracted into ether. The combined extracts were washed with saturated $NaHCO_3$ solution, dried, and concentrated. Chromatography of the residue on silica gel (elution with 0.5% ethyl acetate in hexanes) provided 6.6 mg (81%) of the aldehyde, which was directly stirred with α-(carbomethoxyethylidene)-triphenylphosphorane (14 mg, 0.040 mmol) in CH_2Cl_2 (2 mL) for 20 h, concentrated, and again chromatographed on silica gel. Elution with 0.5% ethyl acetate in hexanes gave 7.3 mg (91%) of **2** as a colorless oil, the spectral properties of which are indistinguishable from those of the natural sample: IR (neat, cm^{-1}) 1717, 1648, 1435, 1264; ^1H NMR (300 MHz, C_6D_6) δ 6.92 (dt, J = 1.4, 7.5 Hz, 1 H), 5.70−5.67 (m, 1 H), 4.95 (s, 1 H), 4.88 (d, J = 0.8 Hz, 1 H), 3.45 (s, 3 H), 2.55−2.48 (m, 1 H), 2.34−1.72 (series of m, 13 H), 1.65−1.30 (m, 8 H), 1.23−1.17 (m, 1 H), 1.05 (s, 3 H), 0.92 (d, J = 9.7 Hz, 1 H), 0.81 (d, J = 6.7 Hz, 3 H), 0.70 (dd, J = 10.2, 9.4 Hz, 1 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 168.1, 151.3, 142.6, 140.5, 124.4, 106.9, 51.2, 44.9, 40.6, 36.3, 32.8, 32.6, 32.2, 31.1, 30.0, 28.9, 28.7, 27.3, 26.5, 24.8, 24.2, 23.9, 20.7, 18.0, 12.5 (the signal for the enoate carbon is obscured by solvent peaks, in line with earlier observations[2]); MS m/z (M^+) calcd 382.2872, obsd 382.2852; $[\alpha]^{20}_D$ −139 (c 0.16, $CHCl_3$); −124 (c 0.001, $CHCl_3$) [lit[2] −60 (c 0.001, $CHCl_3$)].

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Supporting Information Available: Tables of X-ray crystal data, bond distances and angles, final atomic coordinates, and anisotropic/isotropic displacement parameters for *ent*-**30** (5 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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