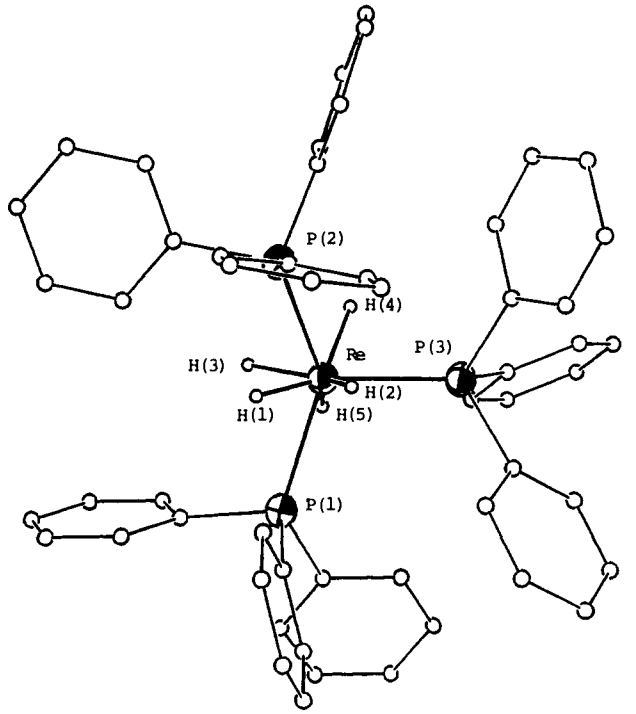

Figure 3. An ORTEP drawing of **1**. The ellipsoids represent thermal displacements and are drawn at the 50% probability level. Carbon atoms and the metal-bonded hydrogen atoms are represented by spheres of arbitrary size.

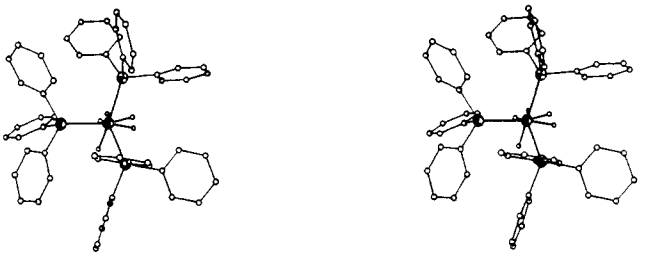

Figure 4. A stereopair representation of **1**.

important differences in their respective P–Re–P angles (107.43 (7)°, 108.38 (7)°, 133.28 (7)° in **1** to 100 [1]°, 102.5 [9]°, 147.3 [8]° in **2**, and 99.8(2)°, 101.9 (2)° and 149.5 (2)° in **3**). This may be attributed to steric interactions between the sterically bulkier pseudo-*cis*-PPh_3 ligands which would enlarge the P(1)-ReP(3) and P(2)ReP(3) angles while making the P(1)ReP(2) angle smaller in **1** as compared to the other molecules.

Conclusions

The T_1 (min) values for **1**, **2**, and **3** are well within the generally accepted range used to suggest that a complex contains a molecular hydrogen ligand. These results are at variance with the structure of **1** determined by X-ray crystallography and the structure of **2** determined by neutron diffraction methods as containing only classical hydride ligands. Although, there is no way of proving that some crystals did not contain a molecular hydrogen ligand, we believe that the problem of classification resides with the vagaries of the T_1 analytical technique. Perhaps, in the case of these polyhydride complexes, where the number of metal-bonded hydrogen atoms is greater than two, the suggested upper limit (100 ms at 250 MHz) of the T_1 value used to predict η^2-H_2 ligands is too high. Furthermore, the fluxional process for the hydrogen atoms may involve temporary molecular hydrogen formation that would lower T_1 values. Thus, it remains for future experiments to determine if merely taking a lower value as the upper limit will maintain the validity of the T_1 criterion or whether the results of this technique, per se, should always be viewed skeptically. Our results, needless to say, raise questions about the correctness of the assignment of other rhenium polyhydride complexes, such as $ReH_7(PPh_3)_2$, as nonclassical by this technique.

It is interesting that the recently reported neutron structure[18] of ReH_7(dppe), dppe = $Ph_2PCH_2CH_2PPh_2$, assigned as Re(η^2-H_2)H_5(dppe) by the T_1 method,[5] contained no short H–H contacts that would justify the η^2-H_2 formulation.

Acknowledgment. We thank the National Science Foundation for financial support and Professor J. P. Fackler, Jr., for the use of the diffractometer.

Supplementary Material Available: An ORTEP drawing of **1** showing the full atomic labeling scheme, a stereoview of the crystal packing of **1**, and tables listing the fractional atomic coordinates, bond distances and angles, and the anisotropic displacement parameters (18 pages); listings of observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

(18) Howard, J. A. K.; Mason, S. A.; Johnson, O.; Diamond, I. C.; Grennell, S.; Keller, P. A.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1988**, 1502.

Indole Diterpene Synthetic Studies. 5. Development of a Unified Synthetic Strategy; a Stereocontrolled, Second-Generation Synthesis of (−)-Paspaline

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Abstract: We record here a full account of a highly stereocontrolled, second-generation synthesis of (−)-paspaline (**1**). The synthesis proceeded via an initial nine-step conversion of (+)-Wieland–Miescher ketone to tricyclic cyclopentanone **5**, an intermediate that we anticipate will be useful for the construction of other members of this family of tremorgenic indole diterpene alkaloids. Completion of the synthetic scheme involved an eight-step transformation of **5** to **6**, the latter an advanced intermediate in our first total synthesis of paspaline (**1**).

In a recent paper,[1] we recorded a first-generation synthesis of (−)-paspaline (**1**),[2,3] the simplest member of a family of tremorgenic indole diterpenes. Notwithstanding the eventual success of this approach, considerable difficulty was encountered in

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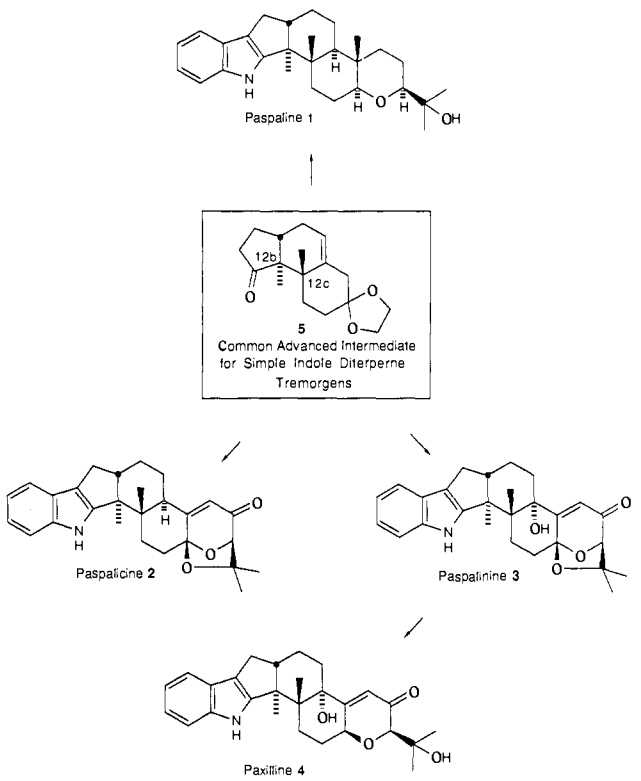
Scheme I

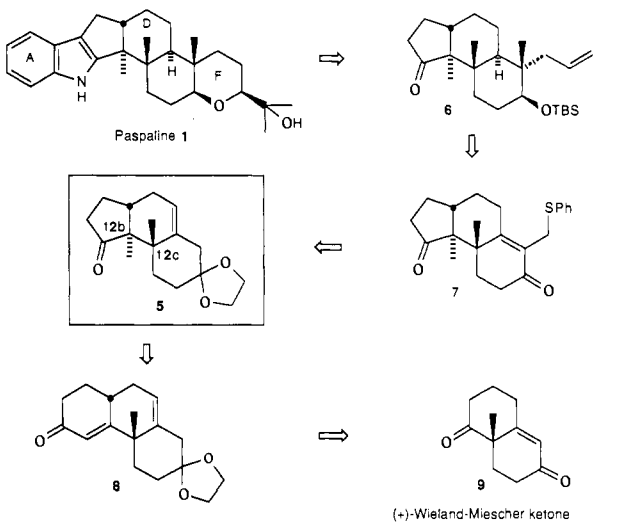


construction of the vicinal quaternary centers at C(12b) and C(12c), the central structural elements of the paspaline skeleton. During the earlier venture it also became apparent that the strategy would not be amenable to other members of the family. Accordingly, we felt compelled to reexamine the paspaline problem. The principal goal in this exercise was not simply to devise a more efficient, stereocontrolled synthesis of paspaline, but more importantly, to develop a unified strategy that would be applicable to the entire class of simple indole diterpenes. The cornerstone of this approach was the recognition that tricyclic ketone **5** could serve as a common, advanced synthetic intermediate (Scheme I).

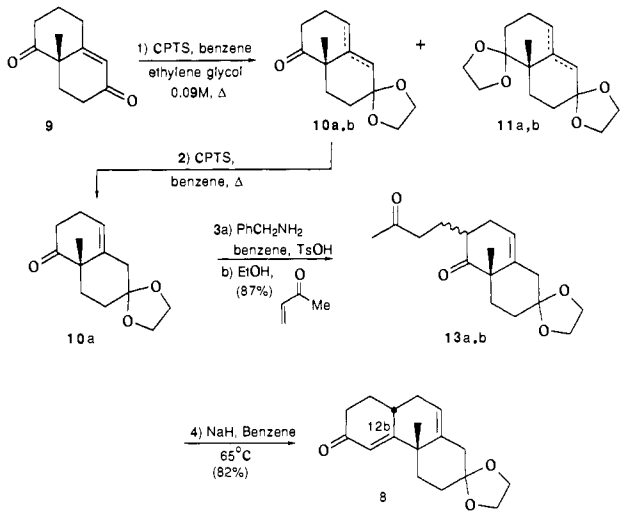
In this account we wish to record completion of the first phase of this effort, namely an efficient (nine steps, 9.4% overall yield), highly stereocontrolled approach to (−)-**5** from (+)-Wieland–Miescher ketone. In addition, we will describe a second-generation synthesis of paspaline from **5**. Full demonstration of the utility of this unified strategy awaits completion of our ongoing synthetic efforts with paspalicine (**2**),[2,3] paspalinine (**3**),[4] and paxilline (**4**).[5]

Development of a Unified Synthetic Strategy for the Simple Indole Diterpene Tremorgens. Our approach to common advanced intermediate **5**, and ultimately to paspaline (**1**), is outlined in Scheme II. From the retrosynthetic perspective, cleavage of the indole moiety and disconnection of the pyranyl ring leads to cyclopentanone **6**, a central intermediate in our first paspaline synthesis.[6] A stereocontrolled synthesis of cyclopentanone **6** would

Scheme II



Scheme III



therefore constitute a second-generation synthesis of (−)-paspaline.[7]

Further simplification of tricyclic ketone **6** leads to (phenylthio)methyl enone **7**, which was anticipated to arise from common advanced intermediate **5** via deketalization and a Petrow reaction.[8] Introduction of the allyl substituent was envisioned to take advantage of reductive alkylation of the (phenylthio)methyl enone moiety via a protocol previously developed in our laboratory for this purpose.[9] Analysis of **5** then led to tricyclic enone **8**, wherein incorporation of the quaternary methyl group at C(12b), as well as formation of the requisite trans-fused cyclopentanone ring, would be achieved via conjugate addition of a methyl group followed by ring contraction. Finally, **8** was envisioned to arise from (+)-Wieland–Miescher ketone (**9**),[10] via selective ketalization of the enone moiety followed by Robinson annulation.[11]

Results and Discussion

(1) Construction of Tricyclic Enone 8: Starting Material for Common Advanced Intermediate 5. Preparation of enone **8** began

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(2) (a) Fehr, Th.; Acklin, W. *Helv. Chim. Acta* **1966**, *49*, 1907. (b) Gysi, R. R. Dissertation No. 4990, Eidgenossiche Technische Hochschule, Zurich, Switzerland, 1973. (c) Leutwiler, A. Dissertation No. 5163, Eidgenossichen Technische Hochschule, Zurich, Switzerland, 1973.

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(6) Smith, A. B., III; Mewshaw, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 1769.

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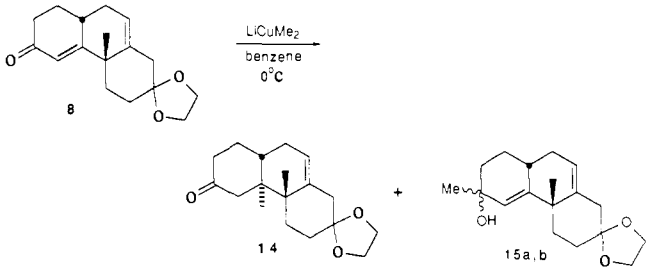
(8) Kirk, D. N.; Petrow, V. *J. Chem. Soc.* **1962**, 1091.

(9) Smith, A. B., III; Mewshaw, R. E. *J. Org. Chem.* **1984**, *49*, 3685.

(10) (a) Hajos, Z. G.; Parrish, D. R. *J. Org. Chem.* **1974**, *39*, 1615. (b) Eder, U.; Sauer, G.; Wiechert, R. *Angew. Chem.* **1971**, *83*, 492; *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 496. (c) Gutzwiller, J.; Buchschacher, P.; Furst, A. *Synthesis* **1977**, 167. (d) Buchschacher, P.; Furst, A. *Org. Synth.* **1984**, *63*, 37.

(11) For reviews, see: (a) Robinson, B. *Chem. Rev.* **1962**, *62*, 373. (b) Robinson, B. *Chem. Rev.* **1969**, *69*, 227.

Scheme IV

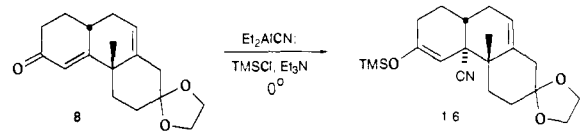


with ketal **10a**,[12] available from (+)-Wieland–Miescher ketone **9** (Scheme III). In 1984 Nitz and Paquette reported an improved procedure for the preparation of ketals **10a,b** using collidinium *p*-toluenesulfonate as catalyst.[13] In order to prepare ketal **10a** in half-mole quantities, we modified their conditions to include high dilution (~0.09 M); the resulting product was shown by GC analysis to be composed of a 1:1 mixture of ketals **10a** and **10b** (67%), along with diketals **11a,b** (4%) and starting ketone **9** (23%). Although **10a** could be isolated by flash chromatography, it was more convenient to equilibrate the mixture first to increase the amount of the thermodynamically more stable ketal **10a**.[14] This was achieved by exposing the mixture of **10a,b** to the same acidic conditions in the absence of ethylene glycol. In this fashion, ketal **10** was generated in 85% overall yield as a 9:1 mixture of **10a** to **10b**.

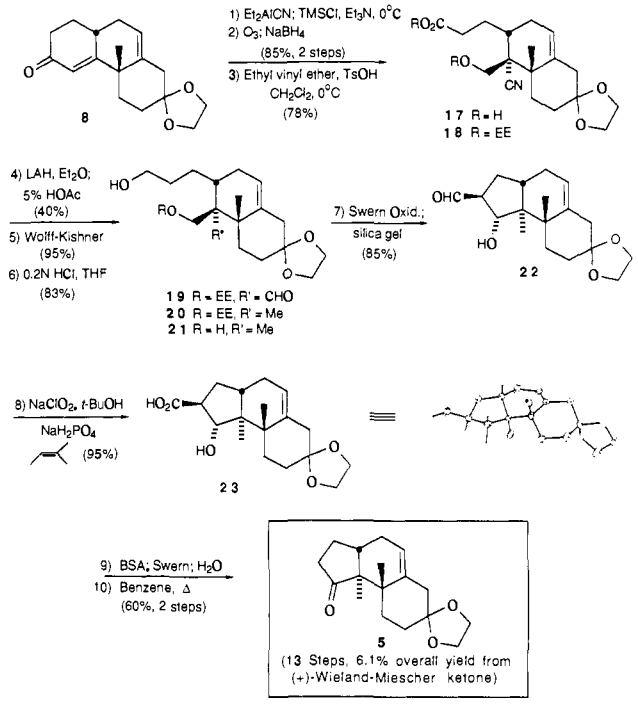
A two-step Robinson annulation[15] protocol then furnished tricyclic enone **8** (Scheme III). This procedure, performed on a 0.15-mol scale with readily available, inexpensive reagents, entailed an initial one-pot procedure for preparation of 1,5-diketones **13a,b**. Thus, ketal **10a** was exposed to a mixture of benzylamine[16] in benzene with catalytic *p*-toluenesulfonic acid, followed by heating for 24 h, to afford the corresponding imine (**12**).[17] Reaction of the latter with excess methyl vinyl ketone in dry ethanol for several hours then furnished a 2:1 epimeric mixture of **13a** and **13b** in 87% yield. Treatment of this mixture with excess sodium hydride in benzene at 65 °C completed the three-step construction of tricyclic enone **8**; the overall yield was 61%.

(2) Orchestration of the Vicinal Quaternary Centers: A Challenging Synthetic Problem. Having developed an efficient route to tricyclic enone **8**, we next required introduction of the quaternary methyl group at C(12b) adjacent and trans to the quaternary methyl substituent at C(12c). Although β,β-substituted enones such as **8** are known to be relatively unreactive Michael acceptors,[18] we were somewhat encouraged by the formation of the desired 1,4-adduct (**14**) in 25% yield upon treatment of enone **8** with 5 equiv of lithium dimethylcuprate in benzene at 0 °C (Scheme IV).[19] However, the major products (65% yield) were the diastereomeric 1,2-adducts **15a,b**. Attempts to improve the yield of the 1,4-addition product by exploiting a variety of protocols, including the Corey–Alexakis lithium dimethyl cuprate/trimethylsilyl chloride procedure,[20] Noyori's methylcopper

Scheme V



Scheme VI



tri-*n*-butylphosphine reagent,[21] Lipshutz's higher order cuprates,[22] or BF_3·Et_2O-catalyzed cuprate addition,[23] proved unsuccessful. The poor chemoselectivity in these reactions appeared to reflect not only the unreactive nature of β,β-substituted enone **8** but also the steric constraints imposed by the adjacent C(12c)-quaternary methyl group.

Due to the poor regioselectivity, we turned to diethylaluminum cyanide, a highly reactive reagent which effects selective conjugate additions, even in highly hindered systems.[24] We recognized, of course, that this was a less direct approach; a more efficient solution to this problem will be disclosed in the last section of this account. Treatment of tricyclic enone **8** with diethylaluminum cyanide (1 M in toluene, Aldrich), followed by capture of the resultant aluminum enolate with trimethylsilyl chloride[25] gave silyl enol ether **16** as a single product by 250-MHz ^{1}H NMR analysis (Scheme V). The stereochemical outcome, tentatively assigned on the basis of literature precedent, was subsequently confirmed by X-ray analysis of a more advanced intermediate (vide infra).

(3) Preparation of Cyclopentanone 5: The Common Advanced Intermediate for the Indole Diterpene Tremorgens. Having established the quaternary center at C(12b), attention next focused on the preparation of cyclopentanone **5**. Elaboration of the trans-fused cyclopentanone first entailed cleavage of the six-membered ring. Without purification, silyl enol ether **16** was subjected to ozonolysis (Scheme VI). Careful monitoring of the reaction by TLC permitted selective cleavage of the more electron rich double bond, to afford hydroxy acid **17** in 85% overall yield, after decomposition of the ozonide with sodium borohydride.[26]

(12) We were unable to prepare ketone **10b** by a previously reported method: De Leeuw, J. W.; DeWaard, E. D.; Beetz, T.; Huisman, H. O. *Recl. Trav. Chim. Pays-Bas.* **1973**, *92*, 1047.

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(16) Hickmott, P. W.; Rae, B. *Tetrahedron Lett.* **1985**, 2577.

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(19) Posner, G. H.; Sterling, J. J.; Whitten, C. E.; Lentz, C. M.; Brunnelle, D. J. *J. Am. Chem. Soc.* **1975**, *97*, 107.

(20) (a) Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* **1985**, 6015, 6019. (b) Alexakis, A.; Berlan, J.; Besace, Y. *Tetrahedron Lett.* **1986**, 1047. (c) For other references, see: Horiguchi, Y.; Matsuzawa, S.; Nakamura, E.; Kuwajima, I. *Tetrahedron Lett.* **1986**, 4025, 4029. Johnson, C. R.; Marren, T. J. *Tetrahedron Lett.* **1987**, 27.

(21) Suzuki, M.; Suzuki, T.; Kawagishi, T.; Noyori, R. *Tetrahedron Lett.* **1980**, 1247.

(22) Lipshultz, B. H.; Wilhelm, R. S.; Kozlowski, J. *Tetrahedron Lett.* **1982**, 3755. Lipshultz, B. H. *Tetrahedron Lett.* **1983**, 127.

(23) Smith, A. B., III; Jerris, P. J. *J. Org. Chem.* **1982**, *47*, 1845.

(24) Nagata, W.; Yoshioka, M. *Tetrahedron Lett.* **1966**, 1913. Nagata, W.; Narisada, M.; Sugasawa, T. *J. Chem. Soc. C* **1967**, 648.

(25) Samson, M.; Vanderwalle, M. *Synth. Commun.* **1978**, *8*, 231.

At this juncture, we found it most convenient to convert the axial cyano group to the requisite methyl substituent. However, in order to accomplish this operation, the relatively labile β-hydroxy nitrile moiety required protection. Moreover, it was essential that the chosen protecting group not only be resistant to strong base and hydride reduction but also sufficiently labile to undergo selective hydrolysis in the presence of the dioxolane moiety.[27a] Ideal in this regard appeared to be the ethoxyethyl protecting group. Treatment of alcohol **17** with ethyl vinyl ether and a catalytic amount of *p*-toluenesulfonic acid in dichloromethane effected the alcohol protection, in conjunction with esterification of the acid; the result was ethoxy ether **18**.[27b]

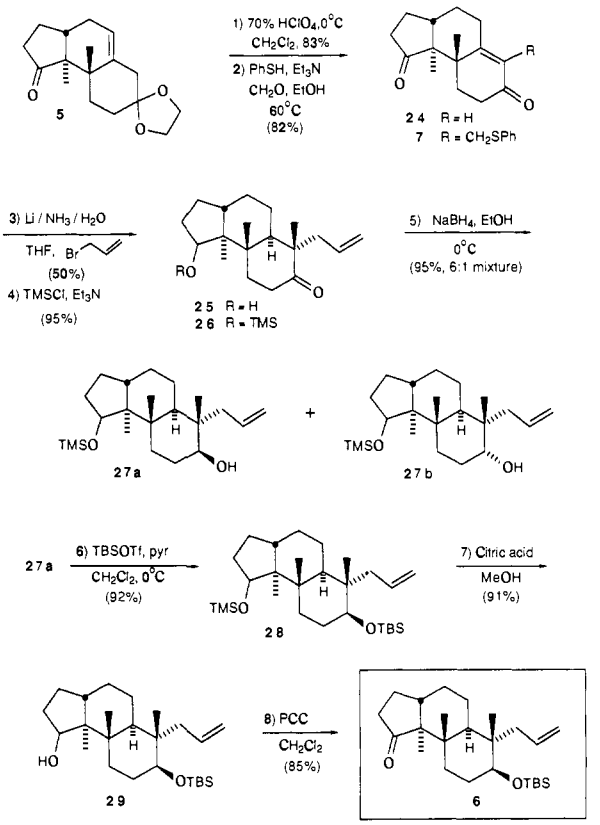
Turning next to the conversion of the cyano group to the corresponding aldehyde, reduction of **18** with an ethereal solution of lithium aluminum hydride, followed by heating the mixture at reflux for several hours, afforded the corresponding imino alcohol.[28a] Subsequent hydrolysis with 5% acetic acid then led to aldehyde **19**, albeit in modest yield (40%). Other methods for nitrile reduction, such as Redal,[28b] $Li(EtO)_3AlH$,[28c] and Dibal[28d] were also examined; however, these procedures resulted in either overreduction or recovery of starting material. Wolff–Kishner reduction[29] of **19** then gave alcohol **20**.

With the requisite trans diaxial quaternary methyl groups in place, mild acid hydrolysis (0.2 N HCl) of **20** provided diol **21**, which in turn was subjected to Swern oxidation.[30] Upon purification by flash chromatography,[31] the corresponding dialdehyde somewhat surprisingly underwent cyclization to aldol **22**. Oxidation of the aldehyde functionality was then effected in very high yield with sodium chlorite[32a] in *tert*-butyl alcohol, employing *trans*-2-methyl-2-butene as a chlorine scavenger,[32b] to provide carboxylic acid **23** as a crystalline solid.

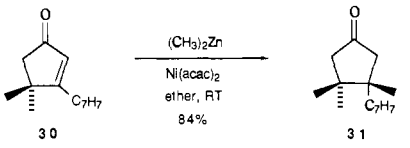
The relative configuration of the β-hydroxy acid moiety in **23** could not be determined by NMR.[33] To establish this structural point, as well as to confirm the tentative assignment of the trans disposition of the methyl substituents, we submitted **23** to single-crystal X-ray analysis. The derived ORTEP plot (Scheme VI) revealed (a) that the carboxylic acid and hydroxyl groups were trans, with both occupying pseudoequatorial positions on the five-membered ring, (b) that the critical C–D ring fusion was in fact trans, and (c) most notably that the vicinal, quaternary methyl groups at C(12b) and C(12c) were trans as required.

A number of oxidation methods were next investigated for the conversion of β-hydroxy acid **23** to the corresponding β-keto acid; we anticipated that the latter would decarboxylate readily to afford cyclopentanone **5**. Fetizon's reagent[34] in toluene at reflux gave the desired cyclopentanone (**5**), but the yield was quite low (31%). Best results were realized by treating **23** with bis(trimethylsilyl)acetamide[35] in dichloromethane to form in situ the corresponding silyl ester. After acid **23** went into solution, presumably as the silyl ester, the mixture was added directly to a preformed solution of the Swern oxalyl chloride–DMSO reagent,[30] followed by normal workup with triethylamine. Quenching the reaction mixture with water and acidification with 3 N HCl, followed by gentle heating to effect decarboxylation, completed construction of cyclopentanone **5**, the proposed common advanced intermediate for the indole diterpene tremorgens.

Scheme VII



Scheme VIII



(4) Preparation of Tricyclic Ketone 6: Completion of a Highly Stereocontrolled Total Synthesis of (−)-Paspaline. With a stereoselective synthesis of cyclopentanone **5** in hand, we focused attention on the preparation of ketone **6**, the advanced intermediate employed in our first paspaline synthesis.[6] This highly functionalized ketone (**6**) contains six of the seven contiguous stereogenic centers present in paspaline (**1**). Construction of **6** began with hydrolysis of ketal **5** to afford tricyclic enone **24** (Scheme VII).[36] Exposure of the latter to the Petrow reduction conditions[8] incorporated the (phenylthio)methyl substituent in the α-position of the enone.

We then executed the reductive alkylation protocol developed in our laboratories for the construction of *trans*-decalone ring systems.[9] Addition of a solution of enone **7** containing 1.95 equiv of water to a solution of lithium in liquid ammonia, followed by treatment with excess allyl bromide, provided keto alcohol **25** as a single compound in 50% yield.

It was now necessary to interchange the oxidation states at carbons C(12a) and C(14a). Toward this end, keto alcohol **25** was treated with excess trimethylsilyl chloride and triethylamine to give silyl ether **26**. Stereoselective reduction of the latter with sodium borohydride in ethanol[6,37] at 0 °C then provided a 6:1 mixture of equatorial and axial alcohols **27a** and **27b**, respectively, which were easily separable by flash column chromatography. Protection of the resultant secondary alcohol was achieved in 92% yield with *tert*-butyldimethylsilyl triflate[38] and pyridine. The more

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(27) (a) Greene, T. W. *Protective Groups in Organic Synthesis*; Wiley: New York, 1981; pp 10–86. (b) Meyers, A. I.; Comins, D. L.; Roland, D. M.; Henning, R.; Shimizu, K. *J. Am. Chem. Soc.* **1979**, *101*, 7104.
(28) (a) Dailey, O. D.; Fuchs, P. L. *J. Org. Chem.* **1980**, *45*, 216. (b) Schlosser, V. M.; Brich, Z. *Helv. Chim. Acta* **1978**, *61*, 1903. (c) Brown, H. C.; Garg, C. P. *J. Am. Chem. Soc.* **1964**, *86*, 1085. (d) Stevens, R. V.; DuPree, L. E., Jr.; Lowenstein, P. L. *J. Org. Chem.* **1972**, *37*, 977.
(29) Huang-Minlon *J. Am. Chem. Soc.* **1949**, *71*, 3301.
(30) Omura, K.; Swern, D. *Tetrahedron* **1978**, *34*, 1651. Mancuso, A. J.; Huang, S. L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480. For a recent review, see: Mancuso, A. J.; Swern, D. *Synthesis* **1981**, 165.
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(32) (a) Lingren, B. O.; Nilsson, T. *Acta Chem. Scand.* **1973**, *27*, 888. (b) Kraus, G. A.; Taschner, M. J. *J. Org. Chem.* **1980**, *45*, 1175.
(33) Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*; Pergamon: Oxford, 1969; Vol. 5, pp 195–200.
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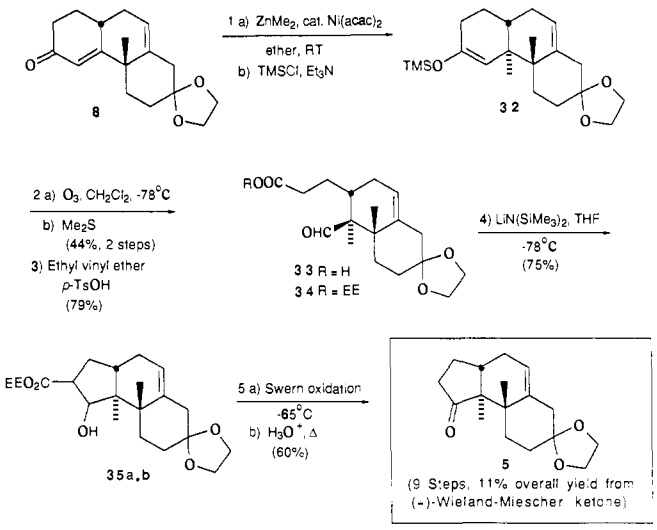
(36) Grieco, P.; Oguri, T.; Gilman, S. *J. Am. Chem. Soc.* **1978**, *100*, 1616.
(37) Otani, G.; Yamada, S. *Chem. Pharm. Bull.* **1973**, *21*, 2112.

Scheme IX



labile trimethylsilyl ether was then removed via exposure to citric acid in methanol to give **29**.[39] Oxidation with pyridinium chlorochromate[40] then afforded advanced intermediate **6**; the overall yield for this eight-step sequence was 17.5%. That the product was identical in all respects with cyclopentanone **6**, prepared in our first-generation paspaline synthesis, was demonstrated by careful comparison of spectroscopic (i.e., ^1H NMR, IR, and HRMS) and optical rotation data.[6] Thus, a highly stereocontrolled, second-generation synthesis of (-)-paspaline (**1**) had been achieved.[7]

(5) A More Efficient Route to Tricyclic Ketone 5. Whereas we had devised a stereocontrolled approach to cyclopentanone **5**, a shorter, more efficient synthesis would be realized if the quaternary methyl group at C(12b) could be introduced directly by conjugate addition, thereby avoiding the inherently inefficient cyano-methyl interconversion. We therefore reexamined this transformation.

Particularly attractive in this regard appeared to be the 1,4-addition reaction introduced by Luche et al. in 1984.[41] Specifically, treatment of enone **30** with dimethylzinc in ether containing a catalytic amount of nickel acetylacetonate afforded β-cuparenone (**31**) in high yield (Scheme VIII). Of the now numerous approaches to β-cuparenone,[42] this was the first successful route involving a conjugate-addition strategy. The failure of previous efforts in this area is not surprising, given the steric hindrance at the β-carbon.

With this transformation in mind, exposure of tricyclic enone **8** to the conditions described by Luche[41a] gave, after quenching the reaction mixture with excess trimethylsilyl chloride and triethylamine, the desired 1,4-adduct **32** in 90–95% yield (Scheme IX). The efficiency of the process presumably reflects the thermal stability of the organozinc reagent, which allows the addition process to proceed at room temperature.[41]

With gram quantities of silyl enol ether **32** available, we turned to the preparation of cyclopentanone **5**. Silyl enol ether **32** was subjected to ozonolysis and a dimethyl sulfide workup[43] to provide carboxy aldehyde **33** in 44% yield for two steps (**8** to **33**). Esterification was achieved upon exposure of **33** to ethyl vinyl ether and catalytic *p*-toluenesulfonic acid[27b] at 0 °C. Closure of the five-membered ring was then effected with lithium hexamethyldisilazide, to afford a 2:1 mixture of β-hydroxy esters **35a,b**. Finally, oxidation exploiting the Swern trifluoroacetic anhydride–DMSO protocol,[44,45] gave the corresponding β-keto ester. The latter was readily hydrolyzed with 0.2 N HCl in THF, whereupon decarboxylation provided cyclopentanone **5** in 45% yield for two steps. In this fashion a second, more efficient synthesis of the central advanced intermediate **5** was achieved (9 steps vs 14 from (+)-Wieland–Miescher ketone) via direct incorporation of the quaternary methyl group at C(12b).

(6) Summary. In this account we recorded a highly stereocontrolled synthesis of tricyclic ketone **6** in 1.7% overall yield, thereby completing a second generation route to (-)-paspaline (**1**). We anticipate that cyclopentanone **5**, an advanced intermediate enroute to **6**, can be advantageously employed for the construction of other simple indole diterpene tremorgens (i.e., **2–4**). Demonstration of the full utility of this unified synthetic strategy will be reported in due course.

Experimental Section[46]

4′,4′a,6′,7′-(+)-Tetrahydro-4′a*S-methylspiro[1,3-dioxolane-2,2′-(1′*H*)-naphthalen]-5′(3′*H*)-one (10a).** A mixture of (+)-Wieland–Miescher ketone (**9**) (39.1 g, 0.219 mol), collidinium *p*-toluenesulfonate (8.03 g, 27 mmol), and ethylene glycol (13.45 mL, 0.24 mol) in 2.3 L of benzene (~0.09 M) was heated at reflux for approximately 20 h, until GC monitoring of the reaction indicated that most of the starting material was consumed (<30%) or the amount of diketal **11a,b** exceeded 4%. After cooling to room temperature, the reaction mixture was quenched with brine and extracted with ether. The combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. Purification by flash chromatography (hexane–ethyl acetate, 7:1, 6:1, 4:1, 2:1) afforded 26.8 g (58%) of ketals **10a,b** as a mixture of double bond isomers and 11.71 g (30%) of recovered starting material (**9**).

A mixture of benzene (1.3 L) and collidinium *p*-toluenesulfonate (5.1 g, 17.4 mmol) was heated at reflux for 1 h to remove any traces of water. A solution of ketals **10a,b** (30.92 g, 0.139 mol) in 200 mL of benzene was then added. The reaction mixture was heated at reflux for several days until the ratio of double bond isomers (**10a**:**10b**) was greater than 8:1. The reaction mixture was worked up as described above and purified by flash chromatography (hexane–ethyl acetate, 4:1) to give 28.45 g (92%) of ketal **10a**: $[\alpha]^{25}_D$ +23.9° (*c* 1.49, $CHCl_3$); IR ($CHCl_3$) 2950 (m), 2870 (m), 1710 (s), 1450 (w), 1430 (m), 1360 (m), 1230 (m), 1100 (m), 1015 (m), 950 (m), 860 (m) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.30 (s, 3 H), 1.65–1.84 (complex m, 4 H), 2.25 (dd, J = 2.4, 13.8 Hz, 1 H), 2.39–2.71 (complex m, 5 H), 3.94 (m, 4 H), 5.58 (m, 1 H).

[4′a*S*-(4′aα,6β)]-4′,4′a,6′,7′-Tetrahydro-4′a-methyl-6′-(3-oxobutyl)-spiro[1,3-dioxolane-2,2′(1′*H*)-naphthalen]-5′(3′*H*)-one (13a) and the 6α-Epimer (13b). A mixture of ketone **10a** (32.6 g, 0.147 mol), benzylamine (16.5 g, 0.154 mol), *p*-toluenesulfonic acid (280 mg, 1.5 mmol), and 200 mL of benzene was heated at reflux for 24 h under a Dean–Stark water separator. After cooling to room temperature, the solvent was removed in vacuo. To the resultant imine were added 200 mL of dry ethanol and methyl vinyl ketone (14.6 mL, 0.176 mol), and the mixture was stirred at room temperature for 1 h. Additional methyl vinyl ketone (7.5 mL, 0.09 mol) was added and stirring was continued for 30 min. The solvent was removed in vacuo and the residue was partitioned be-

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(46) **Materials and Methods.** Melting points were determined on a Thomas-Hoover instrument and are corrected. All solvents were reagent grade. Ether and THF were distilled from sodium and benzophenone. Precoated silica gel plates (250 μm) with a fluorescent indicator (Merck) were used for analytical thin-layer chromatography (TLC). Visualization was achieved via ultraviolet light or ethanolic 12-molybdophosphoric acid [7% (w/v)]. Silica gel 60 (particle size 0.043–0.063 mm) supplied by Merck was used for flash chromatography. *n*-Butyllithium was standardized by titration with diphenylacetic acid. ^1H and ^{13}C NMR spectra were obtained in deuteriochloroform solutions on a Bruker WP250, AM250 (250 MHz), or AM500 (500 MHz) spectrometer. Chemical shifts are reported in δ values relative to tetramethylsilane. All infrared spectra were recorded on either a Perkin-Elmer Model 337 or Model 283B spectrophotometer. Optical rotations were obtained on a Perkin-Elmer 241 polarimeter. Microanalyses were determined by the Rockefeller University Microanalytical Laboratories under the direction of S. T. Bella. High-resolution mass spectra were obtained from the University of Pennsylvania Mass Spectrometer Service Center on a Hitachi Perkin-Elmer RMH-2 or a VG 70-70 Micromass double-focusing spectrometer interfaced with a Kratos DS-50-s system.

tween ether and brine. The aqueous layer was extracted with ether, and the combined organic layers were dried ($MgSO_4$) and evaporated in vacuo. The residue was subjected to flash chromatography (hexane–ethyl acetate, 7:1, 6:1, 3:1), furnishing 37.4 g (87%) of a 2.2:1 mixture of epimeric 1,5-diketones, **13a,b**.

13a: R_f = 0.4, hexane–ethyl acetate, 1:1; mp 55 °C; $[\alpha]^{22}_D$ −50.3° (*c* 0.65, $CHCl_3$); IR ($CHCl_3$) 3000 (s), 2950 (s), 2890 (s), 1710 (s), 1450 (w), 1430 (w), 1360 (m), 1230 (m), 1140 (m), 1120 (m), 1085 (m), 1000 (m), 950 (w), 860 (w), 810 (w) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.30 (s, 3 H), 1.51–2.26 (complex m, 8 H), 2.14 (s, 3 H), 2.37–2.66 (m, 4 H), 2.83–2.94 (m, 1 H), 3.95 (m, 4 H), 5.47 (m, 1 H).

Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27. Found: C, 70.13; H, 8.33.

13b: R_f = 0.29, hexane–ethyl acetate, 1:1; $[\alpha]^{22}_D$ +164.5° (*c* 0.78, $CHCl_3$); IR ($CHCl_3$) 3000 (s), 2950 (s), 2890 (s), 1710 (s), 1445 (w), 1425 (w), 1360 (m), 1230 (m), 1100 (s), 990 (w), 810 (w) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.22 (s, 3 H), 1.50–2.10 (complex m, 7 H), 2.11 (s, 3 H), 2.20–2.71 (complex m, 6 H), 3.96 (m, 4 H), 5.60 (d, J = 5 Hz, 1 H); high-resolution chemical-ionization mass spectrum, m/z 293.1791 (MH^+ calcd for $C_{17}H_{25}O_4$ 293.1752).

[4′aS-(4′aα,8′aα)]-4′,4′a,7′,8′,8′a,9′-Hexahydro-4′a-methylspiro[1,3-dioxolane-2,2′(1′H)-phenanthren]-6′(3′H)-one (8). To a slurry of 80% sodium hydride (11.5 g, 0.383 mol) in 350 mL of benzene was added a solution of diketones **13a,b** (37.36 g, 0.128 mol) in 450 mL of benzene. The mixture was heated at 65 °C (foaming) for 30 min. After cooling to 0 °C, the reaction was carefully quenched with water and extracted with ether. The combined organic layers were washed with brine and dried ($MgSO_4$), and the solvent was removed in vacuo. Flash chromatography (hexane–ethyl acetate, 4:1, 2:1) furnished 28.6 g (82%) of enone **8**: mp 82–83 °C; $[\alpha]^{22}_D$ −158.4° (*c* 0.85, $CHCl_3$); IR ($CHCl_3$) 3000 (s), 2950 (s), 2890 (s), 1665 (s), 1620 (m), 1455 (m), 1430 (w), 1360 (m), 1330 (w), 1260 (m), 1240 (m), 1085 (m), 1000 (w), 950 (w), 870 (m), 810 (w), 690 (w) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.33 (s, 3 H), 1.68–1.95 (complex m, 5 H), 2.16–2.48 (complex m, 6 H), 2.59 (m, 1 H), 2.78 (m, 1 H), 3.96 (m, **4** H), 5.50 (m, 1 H), 5.95 (s, 1 H).

Anal. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.14; H, 7.95.

[4′aS-(4′aα,4′bβ,8′aα)]-4′,4′a,7′,8′,8′a,9′-Hexahydro-4′a-methyl-6′-[(trimethylsilyl)oxy]spiro[1,3-dioxolane-2,2′(1′H)-phenanthrene]-4′b-(3′H)-carbonitrile (16). A solution of enone **8** (8.26 g, 30.1 mmol) in 100 mL of benzene–toluene (1:1) was treated at 0 °C with diethylaluminum cyanide in toluene (1.0 M, 45 mL, 45 mmol) and the mixture was stirred for 30 min. Triethylamine (16.7 mL, 120 mmol) and trimethylsilyl chloride (7.6 mL, 60 mmol) were then added, followed by stirring at room temperature for 1 h. After cooling to 0 °C, the mixture was carefully quenched with saturated aqueous sodium bicarbonate. The aqueous layer was extracted with ether, and the combined organic phases were washed with brine and dried ($MgSO_4$). Concentration in vacuo afforded 12.1 g of silyl enol ether **16**, which was used directly in the next reaction: IR ($CHCl_3$) 3000 (m), 2950 (s), 2220 (w), 1650 (s), 1450 (w), 1360 (m), 1250 (s), 1200 (m), 1090 (m), 880 (s), 845 (s) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.17 (s, 9 H), 1.01 (s, 3 H), 1.14–2.50 (complex m, 13 H), 3.90 (m, 4 H), 4.80 (m, 1 H), 5.39 (m, 1 H).

[4′aS-(4′aα,5′α,6′β)]-5′-Cyano-3′,4′,4′a,5′,6,7′-hexahydro-4′a-methylspiro[1,3-dioxolane-2,2′(1′H)-naphthalene]-6′-propanoic Acid (17). A stirred solution of silyl enol ether **16** (12.1 g, 30.1 mmol) in 500 mL of dichloromethane–methanol (3:1) was treated with ozone at −78 °C until TLC analysis showed the complete consumption of starting material. Excess sodium borohydride (3.4 g, 90 mmol) was added, followed by stirring for 3 h at −78 °C. After warming to room temperature, the solvent was removed in vacuo and the residue was partitioned between ether and water. The aqueous layer was carefully acidified with 3 N HCl (pH ~3–4) and extracted with six 100-mL portions of ethyl acetate. The combined ethyl acetate solutions were dried ($MgSO_4$) and evaporated in vacuo to afford 8.47 g (85%) of acid **17** as a white foam: $[\alpha]^{22}_D$ −29.3° (*c* 1.16, EtOH); IR ($CHCl_3$) 3650–2400 (br), 2960 (s), 2930 (s), 2230 (w), 1710 (s), 1450 (w), 1370 (w), 1230 (m), 1080 (m), 1035 (m), 860 (w) cm^{-1}; ^1H NMR (250 MHz, CD_3OD) δ 1.17 (s, 3 H), 1.48–2.52 (complex m, 13 H), 3.88 (s, 2 H), 3.91 (m, 4 H), 5.38 (m, 1 H), CO_2H, O*H* not observed; high-resolution chemical-ionization mass spectrum, m/z 336.1831 (MH^+ calcd for $C_{18}H_{26}O_5N$ 336.1811).

[4′aS-(4′aα,5′α,6′β)]-5′-Cyano-5′-[(1-ethoxyethoxy)methyl]-3′,4′,4′a,5′,6,7′-hexahydro-4′a-methylspiro[1,3-dioxolane-2,2′(1′H)-naphthalene]-6′-propanoic Acid 1-Ethoxyethyl Ester (18). To a stirred solution of acid **17** (5.65 g, 16.85 mmol) in 60 mL of dichloromethane at 0 °C were added ethyl vinyl ether (8.5 mL, 84 mmol) and *p*-toluenesulfonic acid (160 mg, 0.84 mmol). After stirring for 30 min, the reaction mixture was quenched with saturated aqueous sodium bicarbonate and extracted with dichloromethane. The organic layers were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. Purification by flash chromatography (hexane–ethyl acetate, 3:1, with 2% Et_3N) afforded 6.31 g (78%) of ester **18** as an oil: IR ($CHCl_3$) 2980 (m), 2940 (s), 2890 (m), 2240 (w), 1730 (s), 1450 (w), 1385 (m), 1230 (w), 1140 (s), 1090 (s), 1035 (s), 940 (m) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.19 (m, 9 H), 1.36 (m, 6 H), 1.60–2.38 (complex m, 11 H), 2.55 (m, 2 H), 3.49–4.00 (complex m, 10 H), 4.75 (m, 1 H), 5.44 (m, 1 H), 5.94 (m, 1 H); high-resolution chemical-ionization mass spectrum, m/z 480.2908 (MH^+ calcd for $C_{26}H_{42}O_7N$ 480.2961).

[4′aS-(4′aα,5′α,6′β)]-5′-[(1-Ethoxyethoxy)methyl]-5′-formyl-3′,4′,4′a,5′,6,7′-hexahydro-4′a-methylspiro[1,3-dioxolane-2,2′(1′H)-naphthalene]-6′-propanol (19). To a solution of ester **18** (4.24 g, 8.84 mmol) in 40 mL of ether at 0 °C was added an ethereal solution of lithium aluminum hydride (1 M, 22 mL, 22 mmol). The reaction was heated at reflux for 3.5 h and then cooled and carefully quenched with 5 mL of methanol followed by 120 mL of 5% acetic acid solution. After stirring for 2 h at room temperature, solid potassium sodium tartrate was added and the product was extracted with ether. The combined ether layers were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. Flash column chromatography (hexane–ethyl acetate, 3:1) gave 1.4 g (40%) of aldehyde **19** as an oil: IR ($CHCl_3$) 3450 (br), 2980 (s), 2940 (s), 2890 (s), 2750 (w), 1710 (s), 1450 (m), 1370 (m), 1250 (s), 1100 (s), 950 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (m, 1 H), 1.24 (m, 9 H), 1.36–1.96 (complex m, 8 H), 2.32 (m, 3 H), 2.68 (m, 1 H), 3.58 (m, 5 H), 3.94 (m, 5 H), 4.58 (m, 1 H), 5.52 (m, 1 H), 9.70 (m, 1 H), O*H* not observed; high-resolution electron-impact mass spectrum, m/z 396.2477 (M^+ calcd for $C_{22}H_{36}O_6$ 396.2512).

[4′aS-(4′aα,5′α,6′β)]-5′-[(1-Ethoxyethoxy)methyl]-3′,4′,4′a,5′,6,7′-hexahydro-4′a,5′-dimethylspiro[1,3-dioxolane-2,2′(1′H)-naphthalene]-6′-propanol (20). A stirred solution of aldehyde **19** (1.4 g, 3.53 mmol) and hydrazine monohydrate (5.16 g, 0.10 mol) in 30 mL of triethylene glycol was heated at 120 °C. After 2 h, the excess hydrazine and water was removed by distillation. After cooling to room temperature, potassium hydroxide (1.98 g, 35.3 mmol) was added, followed by heating at 180 °C for 3–4 h. The reaction mixture was quenched with water at room temperature and the product was extracted with ether. The combined organic layers were washed with brine, dried ($MgSO_4$), and evaporated in vacuo. Purification by flash column chromatography (hexane–ethyl acetate, 3:1) afforded 1.28 g of **20** (95%) as a colorless oil: IR ($CHCl_3$) 3610 (w), 3450 (br), 2980 (s), 2940 (s), 2890 (s), 1450 (w), 1380 (m), 1240 (m), 1120 (s), 1085 (s), 1050 (s), 950 (w) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.73, 0.76 (s, s, diastereomers, 3 H), 0.96–1.98 (complex m, 19 H), 2.14 (m, 2 H), 2.57 (m, 1 H), 3.17–3.74 (complex m, 6 H), 3.95 (m, 4 H), 4.57 (m, 1 H), 5.34 (m, 1 H), O*H* not observed; high-resolution chemical-ionization mass spectrum, m/z 383.2730 (MH^+ calcd for $C_{22}H_{39}O_5$ 383.2797).

[4′aS-(4′aα,5′α,6′β)]-5′-(Hydroxymethyl)-3′,4′,4′a,5′,6,7′-hexahydro-4′a,5′-dimethylspiro[1,3-dioxolane-2,2′(1′H)-naphthalene]-6′-propanol (21). To a stirred solution of alcohol **20** (296 mg, 0.77 mmol) in 8 mL of THF at 0 °C was added 0.2 M HCl (0.5 mL, 0.1 mmol). The mixture was warmed to room temperature and stirred for 7 h, followed by quenching with saturated aqueous sodium bicarbonate and extraction with ethyl acetate. The combined organic layers were dried over $MgSO_4$ and evaporated in vacuo. Purification by flash column chromatography (hexane–ethyl acetate, 1:1), afforded 200 mg (83%) of diol **21**, which crystallized upon standing: mp 123–124 °C; $[\alpha]^{22}_D$ −95.9° (*c* 0.94, $CHCl_3$); IR ($CHCl_3$) 3600 (w), 3400 (br), 2970 (s), 2940 (s), 2890 (s), 2830 (m), 1420 (w), 1370 (m), 1250 (m), 1110 (s), 1080 (s), 1020 (s), 950 (w), 850 (w), 810 (w) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.68 (s, 3 H), 1.08–1.23 (m, 1 H), 1.22 (s, 3 H), 1.43–2.17 (complex m, 11 H), 2.58 (m, 1 H), 2.98 (br s, 2 H), 3.47–3.75 (m, 4 H), 3.93 (m, 4 H), 5.34 (m, 1 H).

Anal. Calcd for $C_{18}H_{30}O_4$: C, 69.64; H, 9.74. Found: C, 69.79; H, 9.82.

[1R-(1α,2β,3aβ,9aβ,9bα)]-1,2,3,3a,4,6,8,9,9a,9b-Decahydro-1-hydroxy-9a,9b-dimethylspiro[7H-benz[e]indene-7,2′-[1,3]dioxolane]-2-carboxaldehyde (22). A solution of DMSO (1.02 mL, 14.4 mmol) in 3 mL of dichloromethane was added dropwise to a solution of oxalyl chloride (0.572 mL, 6.55 mmol) in dichloromethane (6 mL) at −78 °C. After stirring for 10 min, a solution of diol **21** (814 mg, 2.62 mmol) in dichloromethane (10 mL) was then added and the resultant mixture was stirred for 30 min at −65 °C. Addition of triethylamine (2.2 mL, 15.7 mmol) was followed by warming to room temperature. The mixture was quenched with water and extracted with dichloromethane. The organic layers were dried ($MgSO_4$) and concentrated in vacuo. The resulting oil was adsorbed onto silica gel and subjected to flash chromatography (hexane–ethyl acetate, 4:1), furnishing 685 mg (85%) of aldol **22**: mp 140–142 °C; $[\alpha]^{24}_D$ −68.8° (*c* 1.1, $CHCl_3$); IR ($CHCl_3$) 3600 (w), 3450 (br), 3000 (m), 2980 (s), 2940 (s), 2890 (s), 2840 (w), 2710 (w), 1715 (s), 1460 (w), 1360 (m), 1230 (m), 1080 (m), 1020 (m), 940 (w), 900 (w), 850 (w) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.91 (s, 3 H), 1.18

(s, 3 H), 1.53–2.03 (complex m, 9 H), 2.25 (dd, J = 2.8, 14 Hz, 1 H), 2.57 (m, 1 H), 2.74 (m, 1 H), 3.94 (m, 4 H), 4.34 (d, J = 8.8 Hz, 1 H), 5.32 (m, 1 H), 9.82 (d, J = 1.8 Hz, 1 H), O*H* not observed; high-resolution electron-impact mass spectrum, m/z 307.1890 (M^+ calcd for $C_{18}H_{26}O_4$ 307.1909).

[1*R*-(1α,2β,3aβ,9aβ,9bα)]-1,2,3,3a,4,6,8,9,9a,9b-Decahydro-1-hydroxy-9a,9b-dimethylspiro[7*H*-benz[*e*]indene-7,2′-[1,3]dioxolane]-2-carboxylic Acid (23). Aldol **22** (252 mg, 0.82 mmol) and 2-methyl-2-butene (5.2 mL) were dissolved in 20 mL of *tert*-butyl alcohol, and a solution of 80% sodium chlorite (838 mg, 7.38 mmol) and monobasic sodium phosphate (795 mg, 5.74 mmol) in 8 mL of water was added dropwise. After stirring for 15 min at room temperature, the solvent was removed in vacuo, and the residue was diluted with water and extracted with three 50-mL portions of ethyl acetate. The combined organic layers were dried ($MgSO_4$), and the solvent was removed in vacuo. The resulting crystals were washed with hexane to yield 250 mg (95%) of pure acid **23**: mp 203–204 °C; $[\alpha]^{25}_D$ −6.0° (c 0.5, EtOH); IR (KBr) 3600–2500 (br), 3450 (w), 2980 (s), 2900 (s), 2840 (m), 1725 (s), 1450 (w), 1400 (m), 1220 (m), 1170 (m), 1020 (m), 940 (w), 840 (w), 810 (w) cm^{-1}; ^{1}H NMR (250 MHz, CD_3COCD_3) δ 0.87 (s, 3 H), 1.19 (s, 3 H), 1.56–2.21 (complex m, 10 H), 2.45 (m, 1 H), 2.70 (m, 1 H), 2.85 (br s, 1 H), 3.87 (m, 4 H), 4.38 (d, J = 8.6 Hz, 1 H), 5.23 (m, 1 H), CO_2H not observed.

Anal. Calcd for $C_{18}H_{26}O_5$: C, 67.06; H, 8.13. Found: C, 67.26; H, 8.25.

[3a*R*-(3aα,9aα,9bβ)]-3,3a,4,6,8,9,9a,9b-Octahydro-9a,9b-dimethylspiro[7*H*-benz[*e*]indene-7,2′-[1,3]dioxolan]-1(2*H*)-one (5). A solution of DMSO (0.19 mL, 2.7 mmol) in 2 mL of dichloromethane was added dropwise to a solution of oxalyl chloride (0.104 mL, 1.19 mmol) in dichloromethane (3 mL) at −78 °C. In a separate flask, bis(trimethylsilyl)acetamide (0.267 mL, 1.08 mmol) was added to a slurry of acid **23** (349 mg, 1.08 mmol) in dichloromethane (4 mL), and the flask was swirled until the acid dissolved. The latter solution was added to the oxalyl chloride–DMSO reagent. After stirring for 45 min at −65 °C, triethylamine (0.680 mL, 4.9 mmol) was added and the reaction mixture was stirred for an additional 15 min before warming to room temperature. The mixture was partitioned between water and ether, and the ether layer was discarded. The aqueous layer was acidified with 3 N HCl (pH ~3–4) and extracted with four 30-mL portions of ethyl acetate. The organic layers were dried ($MgSO_4$) and the solvent was evaporated in vacuo. The residue was dissolved in benzene (15 mL) and heated at 65 °C for 30 min to complete decarboxylation. After removal of the solvent in vacuo, the residue was purified by flash chromatography (hexane–ethyl acetate, 6:1) to give 178 mg (60%) of cyclopentanone **5**: mp 114–115 °C; $[\alpha]^{25}_D$ −196° (c 0.95, $CHCl_3$); IR (KBr) 3000 (m), 2980 (s), 2900 (s), 2840 (w), 1730 (s), 1365 (m), 1250 (m), 1120 (m), 1090 (m), 1040 (m), 1020 (m), 950 (w) cm^{-1}; ^{1}H NMR (250 MHz, CD_3COCD_3) δ 0.93 (s, 3 H), 1.13 (s, 3 H), 1.58–2.60 (complex m, 13 H), 3.94 (m, 4 H), 5.33 (m, 1 H); high-resolution chemical-ionization mass spectrum, m/z 277.1817 (MH^+ calcd for $C_{17}H_{25}O_3$ 277.1804).

Anal. Calcd for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. Found: C, 73.65; H, 8.66.

[3a*S*-(3aα,9aα,9bβ)]-3,3a,4,5,8,9,9a,9b-Octahydro-9a,9b-dimethyl-1*H*-benz[*e*]indene-1,7(2*H*)-dione (24). To a solution of cyclopentanone **5** (178 mg, 0.64 mmol) in dichloromethane (8 mL) at 0 °C was added 70% $HClO_4$ (50 μL). After stirring for 15 min, the reaction mixture was quenched with saturated aqueous sodium bicarbonate and extracted with dichloromethane. The organic layers were dried ($MgSO_4$) and evaporated in vacuo. Purification by flash chromatography (hexane–ethyl acetate, 4:1) afforded 125 mg (83%) of pure enone **24**: mp 128–130 °C; $[\alpha]^{25}_D$ +131° (c 1.14, $CHCl_3$); IR ($CHCl_3$) 3000 (w), 2950 (m), 2900 (m), 1730 (s), 1670 (s), 1610 (w), 1375 (w), 1330 (w), 1230 (m), 1170 (w), 1010 (w) cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.93 (s, 3 H), 1.29 (s, 3 H), 1.52–1.88 (complex m, 3 H), 1.94–2.60 (complex m, 10 H), 5.86 (m, 1 H); high-resolution chemical-ionization mass spectrum, m/e 233.1550 (MH^+ calcd for $C_{15}H_{21}O_2$ 233.1541).

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.39; H, 8.84.

[3a*S*-(3aα,9aα,9bβ)]-3,3a,4,5,8,9,9a,9b-Octahydro-9a,9b-dimethyl-6-[(phenylthio)methyl]-1*H*-benz[*e*]indene-1,7(2*H*)-dione (7). A solution of enone **24** (153 mg, 0.66 mmol), thiophenol (0.101 mL, 0.98 mmol), triethylamine (0.119 mL, 0.85 mmol), and 37% formalin solution (85 μL, 1.05 mmol) in 2 mL of ethanol was heated at 60 °C under argon for 24 h. After cooling to room temperature, the reaction mixture was quenched with 0.5 N KOH solution and the product was extracted with ether. The organic layers were washed with brine and dried ($MgSO_4$), and the solvent was removed in vacuo. The residue was purified by flash chromatography (hexane–ethyl acetate, 8:1) to provide 190 mg (82%) of enone **7**: mp 140–141 °C; $[\alpha]^{25}_D$ +76° (c 1.0, $CHCl_3$); IR ($CHCl_3$) 3000 (m), 2980 (s), 2900 (s), 1735 (s), 1670 (s), 1600 (w), 1480 (m), 1440 (m), 1380 (w), 1340 (w), 1220 (m), 1020 (m), 960 (w), 690 (w) cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.85 (s, 3 H), 1.25 (s, 3 H), 1.31–2.25 (complex m, 7 H), 2.34–2.56 (m, 5 H), 2.83 (m, 1 H), 3.92 (AB_q, J_{AB} = 11.6 Hz, $\Delta\nu_{AB}$ = 17.4 Hz, 2 H), 7.19–7.30 (m, 3 H), 7.37 (m, 2 H); high-resolution electron-impact mass spectrum, m/z 354.1677 (M^+ calcd for $C_{16}H_{26}O_2S$ 354.1653).

[3a*S*-(3aα,5aβ,6β,9aα,9bβ)]-Dodecahydro-1-hydroxy-6,9a,9b-trimethyl-6-(2-propenyl)-1*H*-benz[*e*]inden-7-one (25). A solution of enone **7** (92.8 mg, 0.26 mmol) and water (8.9 mg, 0.49 mmol) in 1.5 mL of THF was added dropwise to a stirred solution of lithium (12.5 mg, 1.8 mmol) in dry, distilled ammonia (7 mL) at −78 °C over 30 min. After stirring 45 min further, 1 mL of THF was added, followed by rapid addition of allyl bromide (0.360 mL, 4.16 mmol) dissolved in 0.5 mL of THF. The resulting mixture was stirred for 30 min at −78 °C, and the ammonia was then evaporated. After quenching with water, the residue was extracted with ether. The organic layers were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The product was purified by flash chromatography (hexane–ethyl acetate, 20:1), furnishing 38 mg (50%) of keto alcohol **25**, which crystallized upon standing: mp 99 °C; $[\alpha]^{25}_D$ +11.3° (c 1, $CHCl_3$); IR ($CHCl_3$) 3600 (w), 3450 (br), 2950 (s), 2870 (m), 1690 (s), 1640 (w), 1445 (m), 1380 (m), 1230 (w), 1110 (w), 1030 (w), 995 (w), 910 (w) cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.87 (s, 3 H), 1.05 (s, 3 H), 1.10 (s, 3 H), 1.24–2.60 (complex m, 16 H), 4.15 (m, 1 H), 5.06 (m, 2 H), 5.65 (m, 1 H), O*H* not observed; high-resolution chemical-ionization mass spectrum, m/z 291.2298 (MH^+ calcd for $C_{19}H_{31}O_2$ 291.2323).

[3a*S*-(3aα,5aβ,6β,9aα,9bβ)]-[[Dodecahydro-6,9a,9b-trimethyl-6-(2-propenyl)-7-oxo-1*H*-benz[*e*]inden-1-yl]oxy]trimethylsilane (26). Triethylamine (70 μL, 0.5 mmol) and trimethylsilyl chloride (0.130 mL, 1.0 mmol) were added to a solution of alcohol **25** (29.6 mg, 0.1 mmol) in 1 mL of THF and the mixture was stirred overnight. After cooling to 0 °C, the reaction mixture was quenched with saturated aqueous sodium bicarbonate and the product was extracted with ether. The organic layers were washed with brine and dried over $MgSO_4$, and the solvent was removed in vacuo. The residue was subjected to flash chromatography (hexane–ethyl acetate, 50:1) to give 34 mg (95%) of silyl ether **26**: mp 75 °C; $[\alpha]^{25}_D$ +7.6° (c 0.3, $CHCl_3$); IR ($CHCl_3$) 2960 (s), 2860 (s), 1695 (m), 1460 (m), 1445 (w), 1380 (w), 1250 (m), 1130 (m), 1060 (m), 900 (w), 840 (w) cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.06 (s, 9 H), 0.85 (s, 3 H), 1.03 (s, 3 H), 1.04 (s, 3 H), 1.12–2.06 (complex m, 10 H), 2.17–3.02 (m, 6 H), 4.05 (app t, J = 8.5 Hz, 1 H), 5.03 (m, 2 H), 5.62 (m, 1 H); high-resolution chemical-ionization mass spectrum, m/z 363.2754 (MH^+ calcd for $C_{22}H_{39}O_2Si$ 363.2719).

[3a*S*-(3aα,5aβ,6β,7α,9aα,6bβ)]-[[Dodecahydro-7-hydroxy-6,9a,9b-trimethyl-6-(2-propenyl)-1*H*-benz[*e*]inden-1-yl]oxy]trimethylsilane (27a) and Its 7β-Epimer (27b). To a solution of ketone **26** (34 mg, 0.094 mmol) in 3 mL of absolute ethanol at 0 °C was added sodium borohydride (7 mg, 0.19 mmol). After stirring for 24 h, the solvent was removed in vacuo and the residue was partitioned between ether and water. The organic phases were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. Flash chromatography (hexane–ethyl acetate, 20:1) afforded 26 mg (76%) of equatorial alcohol **27a** and 6 mg (18%) of axial alcohol **27b**.

27a: R_f = 0.44, hexane–ethyl acetate, 4:1; $[\alpha]^{25}_D$ −22.3° (c 0.7, $CHCl_3$); IR ($CHCl_3$) 3600 (w), 3400 (br), 2960 (s), 2880 (m), 1250 (m), 1120 (m), 1060 (m), 900 (m), 845 (m) cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$), δ 0.06 (s, 9 H), 0.80 (s, 3 H), 0.84 (s, 3 H), 0.99 (s, 3 H), 1.12–1.90 (complex m, 14 H), 2.01 (m, 1 H), 2.30 (m, 1 H), 3.43 (app t, J = 7.6 Hz, 1 H), 4.06 (m, 1 H), 5.07 (m, 2 H), 5.85 (m, 1 H), O*H* not observed; high-resolution electron-impact mass spectrum, m/z 364.2809 (M^+ calcd for $C_{22}H_{40}O_2Si$ 364.2797).

27b: R_f = 0.6, hexane–ethyl acetate, 4:1; $[\alpha]^{25}_D$ −60.8° (c 0.13, $CHCl_3$); IR ($CHCl_3$) 2960 (s), 1720 (w), 1380 (m), 1250 (m), 1120 (m), 1060 (m), 895 (m), 835 (m) cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.06 (s, 9 H), 0.87 (s, 3 H), 0.91 (s, 3 H), 1.01 (s, 3 H), 1.14–2.12 (complex m, 16 H), 3.49 (m, 1 H), 4.09 (m, 1 H), 5.11 (m, 2 H), 6.01 (m, 1 H), O*H* not observed; high-resolution electron-impact mass spectrum, m/z 364.2768 (M^+ calcd for $C_{22}H_{40}O_2Si$ 364.2797).

[3a*S*-(3aα,5aβ,6β,7α,9aα,9bβ)]-[[7-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]dodecahydro-6,9a,9b-trimethyl-6-(2-propenyl)-1*H*-benz[*e*]-inden-1-yl]oxy]trimethylsilane (28). To a stirred solution of alcohol **27a** (25 mg, 0.068 mmol) in 1.5 mL of dichloromethane at 0 °C were added pyridine (55 μL, 0.68 mmol) and then *tert*-butyldimethylsilyl triflate (78 μL, 0.34 mmol). After 15 min, the reaction was quenched with saturated aqueous sodium bicarbonate and the product was extracted with ether. The organic layers were dried ($MgSO_4$) and evaporated in vacuo, and the residue was subjected to flash chromatography (hexane), affording 30 mg (92%) of **28**: $[\alpha]^{25}_D$ +2.18° (c 0.6, $CHCl_3$); IR ($CHCl_3$) 2960 (s), 2860 (m), 1460 (w), 1360 (w), 1250 (s), 1085 (s), 900 (s), 840 (s) cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.06 (m, 15 H), 0.79 (s, 3 H), 0.86

(s, 3 H), 0.88 (s, 9 H), 0.98 (s, 3 H), 1.08–1.96 (complex m, 15 H), 2.30 (m, 1 H), 3.43 (dd, J = 4.7, 10.6 Hz, 1 H), 4.05 (app t, J = 7.9 Hz, 1 H), 5.03 (m, 2 H), 5.80 (m, 1 H); high-resolution electron-impact mass spectrum, m/z 478.3579 (M^+ calcd for $C_{28}H_{54}O_2Si_2$ 478.3662).

[3a*S*-(3aα,5aβ,6β,7aα,9aα,9bβ)]-7-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]dodecahydro-6,9a,9b-trimethyl-6-(2-propenyl)-1*H*-benz[*e*]inden-1-ol (29). A solution of **28** (27 mg, 0.056 mmol) in 5 mL of methanol was treated with citric acid (60 mg, 0.31 mmol), and the mixture was stirred for 2 h at room temperature. The solvent was removed in vacuo and the residue was partitioned between ether and water. The aqueous layer was extracted with ether, and the combined organic phases were washed with brine, dried ($MgSO_4$), and evaporated in vacuo. Purification by flash chromatography gave 21 mg (91%) of alcohol **29**: mp 90–92 °C; $[\alpha]^{25}_D$ –0.1° (c 0.77, $CHCl_3$); IR ($CHCl_3$) 3600 (w), 2960 (s), 2870 (m), 1475 (w), 1260 (m), 1090 (m), 920 (m), 875 (w), 840 (m) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.05 (s, 6 H), 0.80 (s, 3 H), 0.82 (s, 3 H), 0.88 (s, 9 H), 1.03 (s, 3 H), 1.13–1.76 (complex m, 13 H), 1.88–2.09 (m, 2 H), 2.31 (m, 1 H), 3.44 (m, 1 H), 4.16 (m, 1 H), 6.04 (m, 2 H), 6.80 (m, 1 H), O*H* not observed; high-resolution electron-impact mass spectrum, m/z 406.3328 (M^+ calcd for $C_{25}H_{46}O_2Si$ 406.3267).

[3a*S*-(3aα,5aβ,6β,7aα,9aα,9bβ)]-7-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]dodecahydro-6,9a,9b-trimethyl-6-(2-propenyl)-1*H*-benz[*e*]inden-1-one (6). Silyl alcohol **29** (23 mg, 0.056 mmol) was dissolved in 2 mL of dichloromethane and treated with sodium acetate (10 mg, 0.1 mmol) and pyridinium chlorochromate (24 mg, 0.11 mmol). The mixture was stirred for 1 h, whereupon dry ether was added and the solution was filtered through florisil. The solvent was evaporated in vacuo and the residue was purified by flash chromatography (hexane–ethyl acetate, 30:1), affording 19 mg (85%) of ketone **6**: $[\alpha]^{22}_D$ –33.9° (c 0.9, $CHCl_3$); IR ($CHCl_3$) 2865 (m), 2695 (s), 1735 (s), 1475 (w), 1390 (w), 1260 (m), 1090 (m), 920 (m), 845 (m) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.04 (s, 3 H), 0.05 (s, 3 H), 0.76 (s, 3 H), 0.87 (s, 3 H), 0.88 (s, 9 H), 0.99 (s, 3 H), 1.05–2.40 (complex m, 16 H), 3.43 (dd, J = 10.6, 5.1 Hz, 1 H), 5.05 (m, 2 H), 5.78 (m, 1 H); high-resolution electron-impact mass spectrum, m/z 404.3190 (M^+ calcd for $C_{25}H_{44}O_2Si$ 404.3110).

[4′a*S*-(4′aα,4′bβ,8′aα)]-3′,4′,4′a,4′b,7,8,8′a,9′-Octahydro-4′a,4′b-dimethyl-6′-[(trimethylsilyl)oxy]spiro[1,3-dioxolane-2,2′(1′*H*)-phenanthrene] (32). A mixture of methyl iodide (3.73 mL, 60 mmol), zinc bromide (6.75 g, 30 mmol), lithium wire (832 mg, 120 mmol), and 90 mL of ether was sonicated for 30 min at 0 °C under argon. A solution of enone **8** (2.40 g, 8.75 mmol) and nickel acetylacetonate (65 mg, 0.25 mmol) in 50 mL of ether was then added at 0 °C. After stirring for 20 h at room temperature, the reaction was quenched with triethylamine (7.3 mL, 52.5 mmol) and trimethylsilyl chloride (3.3 mL, 26.25 mmol), followed by stirring for an additional 1 h. The mixture was cooled to 0 °C, carefully treated with saturated aqueous sodium bicarbonate, and extracted with ether. The organic layers were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The resulting silyl enol ether **32** was used directly in the next reaction. Spectral data for **32**: IR ($CHCl_3$) 3000 (m), 2960 (s), 2890 (s), 2840 (m), 1660 (s), 1450 (m), 1425 (m), 1370 (s), 1250 (s), 1150 (m), 1090 (m), 885 (m), 845 (m) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.15 (s, 9 H), 0.83 (s, 3 H), 1.02 (s, 3 H), 1.15–2.17 (complex m, 12 H), 2.47 (m, 1 H), 3.90 (m, 4 H), 4.80 (d, J = 1.8 Hz, 1 H), 5.30 (m, 1 H).

[4′a*S*-(4′aα,5α,6β)]-5′-Formyl-3′,4′,4′a,5′,6′,7′-hexahydro-4′a,5′-dimethylspiro[1,3-dioxolane-2,2′(1′*H*)-naphthalene]-6′-propanoic Acid (33). A stirred solution of silyl enol ether **32** (11.48 g, 31.7 mmol) in 500 mL of dichloromethane was treated with ozone at –78 °C until TLC analysis indicated that the reaction was complete. Argon was then passed through the solution for 30 min, followed by the addition of dimethyl sulfide (3.5 mL, 47.5 mmol). After warming to room temperature, the reaction mixture was stirred overnight. The solvent was removed in vacuo and the residue was subjected to flash chromatography (dichloromethane–methanol, 50:1, 20:1) affording 4.49 g (44%) of aldehyde-acid **33** as an oil: $[\alpha]^{25}_D$ –124.5° (c 2.85, $CHCl_3$); IR ($CHCl_3$) 3500–2400 (br), 2980 (m), 2940 (m), 2890 (m), 1715 (s), 1450 (w), 1420 (w), 1370 (w), 1230 (w), 1115 (w), 1080 (w), 945 (w) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.98 (s, 3 H), 1.17–1.99 (complex m, 7 H), 1.27 (s, 3 H), 2.15–2.61 (complex m, 6 H), 3.95 (m, 4 H), 5.36 (m, 1 H), 9.79 (s, 1 H), CO_2H not observed; high-resolution chemical-ionization mass spectrum, m/z 340.2129 (MNH_4^+ calcd for $C_{18}H_{30}O_5N$ 340.2124).

Anal. Calcd for $C_{18}H_{26}O_5$: C, 67.06; H, 8.12. Found: C, 66.91; H, 7.98.

[4′a*S*-(4′aα,5α,6β)]-5′-Formyl-3′,4′,4′a,5′,6′,7′-hexahydro-4′a,5′-dimethylspiro[1,3-dioxolane-2,2′(1′*H*)-naphthalene]-6′-propanoic Acid 1-Ethoxyethyl Ester (34). To a stirred solution of acid **33** (2.45 g, 7.6 mmol) in 50 mL of dichloromethane at 0 °C were added ethyl vinyl ether (3.8 mL, 38 mmol) and p-toluenesulfonic acid (14 mg, 0.076 mmol). After stirring for 10 min, the mixture was quenched with saturated aqueous sodium bicarbonate and the aqueous layer was extracted with dichloromethane. The combined organic phases were dried ($MgSO_4$), and the solvent was removed in vacuo. The residue was purified by flash chromatography (hexane–ethyl acetate, 15:1, with 3% Et_3N), furnishing 2.36 g (79%) of ester **34** as an oil: IR ($CHCl_3$) 3000 (m), 2950 (s), 2900 (s), 2840 (m), 2730 (w), 1730 (s), 1450 (m), 1390 (m), 1370 (m), 1230 (s), 1120 (m), 1040 (w), 940 (w) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.98 (s, 3 H), 1.21 (t, J = 7.1 Hz, 3 H), 1.27 (s, 3 H), 1.39 (d, J = 5.2 Hz, 3 H), 1.44–1.97 (complex m, 6 H), 2.15–2.61 (complex m, 7 H), 3.56 (m, 1 H), 3.69 (m, 1 H), 3.93 (m, 4 H), 5.38 (m, 1 H), 5.93 (q, J = 5.2 Hz, 1 H), 9.79 (s, 1 H); high-resolution electron-impact mass spectrum, m/z 394.2399 (M^+ calcd for $C_{22}H_{34}O_6$ 394.2355).

[3a*S*-(3aα,9aα,9bβ)]-1,2,3,3a,4,6,8,9,9a,9b-Decahydro-1-hydroxy-9a,9b-dimethylspiro[7*H*-benz[*e*]indene-7,2′-[1,3]dioxolane]-2-carboxylic Acid 1-Ethoxyethyl Ester (35a,b). A stirred solution of hexamethyldisilazane (4.4 mL, 20.7 mmol) in 50 mL of THF was treated at –78 °C with n-butyllithium (2.5 M, 6.88 mL, 17.2 mmol). After 0.5 h, a solution of ethoxyethyl ester **34** (3.40 g, 8.60 mmol) in 40 mL of THF was added dropwise. The mixture was stirred for 4 h at –78 °C, quenched with pH 7 buffer, and extracted with ether. The combined organic layers were washed with brine and dried over $MgSO_4$. Removal of solvent in vacuo afforded an oil which was subjected to flash chromatography (hexane–ethyl acetate, 20:1 with 3% Et_3N), furnishing 3.17 g (93%) of a 1:1 mixture of β-hydroxy esters **35a,b**.

35a: R_f = 0.34, hexane–ethyl acetate, 2:1; IR ($CHCl_3$) 3470 (br), 2980 (s), 2900 (s), 1715 (s), 1465 (m), 1370 (m), 1270 (m), 1240 (m), 1180 (m), 1130 (m), 1090 (m), 1030 (m), 945 (w), 850 (w), 820 (w) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.83, 0.84 (s, s, diastereomers, 3 H), 1.16 (s, 3 H), 1.21 (m, 3 H), 1.41 (d, J = 5.1 Hz, 3 H), 1.51–2.05 (complex m, 9 H), 2.22 (m, 1 H), 2.56 (m, 1 H), 3.05 (m, 1 H), 3.47–3.61 (m, 2 H), 3.75 (m, 1 H), 3.94 (m, 4 H), 4.37 (dd, J = 7.8, 10 Hz, 1 H), 5.31 (m, 1 H), 5.97 (m, 1 H); high-resolution chemical-ionization mass spectrum, m/z 394.2371 (M^+ calcd for $C_{22}H_{34}O_6$ 394.2355).

35b: R_f = 0.24, hexane–ethyl acetate, 2:1; IR ($CHCl_3$) 3590 (w), 3490 (br), 2980 (s), 2940 (s), 1720 (s), 1450 (m), 1365 (m), 1235 (m), 1180 (m), 1140 (m), 1095 (m), 1020 (m), 945 (w), 855 (w), 830 (w) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.88 (s, 3 H), 1.18 (s, 3 H), 1.21 (m, 3 H), 1.43 (m, 3 H), 1.57–2.02 (complex m, 9 H), 2.22 (m, 1 H), 2.32 (br s, 1 H), 2.56 (m, 1 H), 2.74 (m, 1 H), 3.57 (m, 1 H), 3.72 (m, 1 H), 3.94 (m, 4 H), 4.28 (d, J = 8.8 Hz, 1 H), 5.31 (m, 1 H), 5.98 (m, 1 H); high-resolution chemical-ionization mass spectrum, m/z 394.2312 (M^+ calcd for $C_{22}H_{34}O_6$ 394.2355).

[3a*R*-(3aα,9aα,9bβ)]-3,3a,4,6,8,9,9a,9b-Octahydro-9a,9b-dimethylspiro[7*H*-benz[*e*]indene-7,2′-[1,3]dioxolan]-1(2*H*)-one (5). A solution of DMSO (6.57 mL, 92.6 mmol) in 30 mL of dichloromethane was added dropwise to a solution of trifluoroacetic anhydride (5.24 mL, 37.1 mmol) in 30 mL of dichloromethane at –78 °C. After stirring for 10 min, a solution of β-hydroxy esters **35a,b** (7.31 g, 18.53 mmol) in 50 mL of dichloromethane was added, and the resultant mixture was stirred for 1 h at –78 °C. Triethylamine (25.8 mL, 0.185 mol) was added, followed by stirring for 5 min before warming the mixture to room temperature. The mixture was quenched with saturated aqueous sodium bicarbonate and extracted with dichloromethane. The organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The resulting oil was dissolved in THF (100 mL) and treated with 0.2 N HCl (9.26 mL, 1.85 mmol). The mixture was stirred for 2 h, and was then diluted with brine and extracted with ethyl acetate. The organic layers were dried over $MgSO_4$, and the solvent was removed in vacuo. The resultant β-keto acid was dissolved in benzene (50 mL) and heated at reflux for 1 h. The solution was cooled to room temperature and washed with 60 mL of 0.5 N aqueous sodium hydroxide to remove any remaining carboxylic acid. The aqueous layer was extracted with ether, and the combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. Purification by flash chromatography (hexane–ethyl acetate, 10:1) gave 2.46 g (48%) of cyclopentanone **5**: mp 114–115 °C; $[\alpha]^{25}_D$ –196° (c 0.95, $CHCl_3$); IR ($CHCl_3$) 3000 (m), 2980 (s), 2900 (s), 2840 (w), 1730 (s), 1365 (m), 1250 (m), 1120 (m), 1090 (m), 1040 (m), 1020 (m), 950 (w) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.93 (s, 3 H), 1.13 (s, 3 H), 1.58–2.60 (complex m, 13 H), 3.94 (m, 4 H), 5.33 (m, 1 H); high-resolution chemical-ionization mass spectrum, m/z 277.1817 (MH^+ calcd for $C_{17}H_{25}O_3$ 277.1804).

Anal. Calcd for $C_{17}H_{24}O_3$: 73.88; H, 8.75. Found: C, 73.65; H, 8.66.

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