A Synthesis of (±)-Stemodinone: An Application of Organoiron Chemistry to the Construction of Sterically Congested Quaternary Carbon Centers

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A synthesis of racemic stemodinone is described, using tricarbonyl(1−5-η-4-methoxy-1,3-dimethylcyclohexadienyl)iron(I) hexafluorophosphate (**9**) as an electrophile that is the A-ring precursor. Reaction of **9** with the tin enolate from 4,4-(ethylenedioxy)cyclohexanecarbaldehyde proceeded with excellent regioselectivity and high yield to generate an intermediate representing the A and C rings of the target molecule. The B ring was constructed by introducing a two-carbon electrophilic group onto the A ring, followed by ring closure using an intramolecular enolate alkylation. Installation of the D ring and manipulation to give the final product followed transformations precedented with this series of compounds.

Introduction

Stemodinone (**1**) is a tetracyclic diterpenoid, isolated from the leaves of *Stemodia maritimal* L, a plant used on the Carribean island of Curacao for the treatment of venereal disease.[1,2] The structural elucidation of stemodinone was accomplished in 1973 by Manchand, White, and their co-workers.[1] This naturally occurring substance possesses an interesting arrangement of fused, spiro, and bridged rings, and especially noteworthy is the unique spiro center at C-9. Other natural diterpenoids[1,2] of the stemodane-type have also been obtained, including stemodin (**3**), 2-desoxystemodinone (**4**), and maritimol (**5**) (Figure 1).

The diterpenoid tetraol aphidicolin (**2**), isolated from *Cephalosporium aphidicolia petch*,[3,4] shows activity against Herpes simplex virus,[5,6] as well as antimitotic and antitumor activity.[7] The structure and absolute configuration of aphidicolin were determined by X-ray crystallographic analysis in 1973.[3,4]

Stemodinone and aphidicolin have similar tetracyclic skeleta with a different stereochemical relationship of the C and D rings. Owing to this structural resemblance, a methodology developed for a synthesis of stemodinone can be employed for synthesis of aphidicolin with some modifications, and *vice versa*.

Because of their unique molecular framework and the alleged medicinal properties of *S. maritima L*,[1,2a] stemodinone and its derivatives have received considerable attention as challenging targets for synthesis;[8] ap-

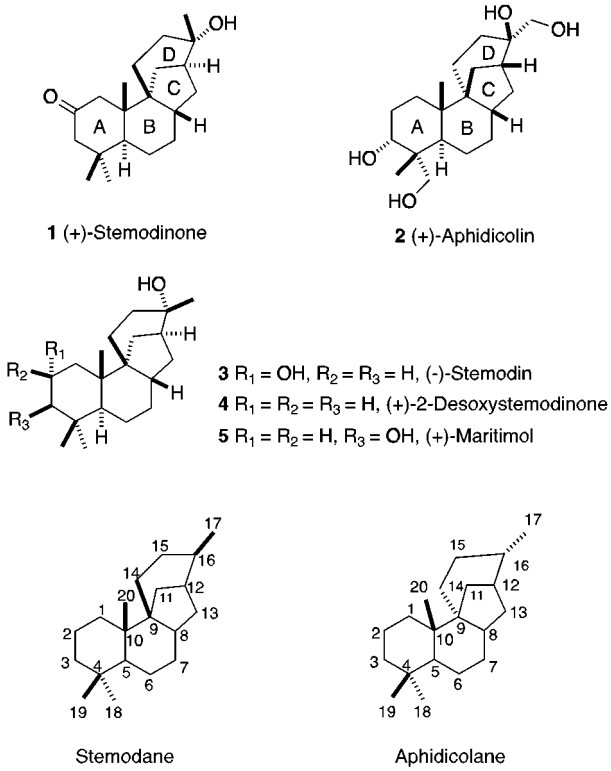

Figure 1. Aphidicolin and stemodinone and its derivatives; skeletal numbering of parent stemodane and aphidicolane.

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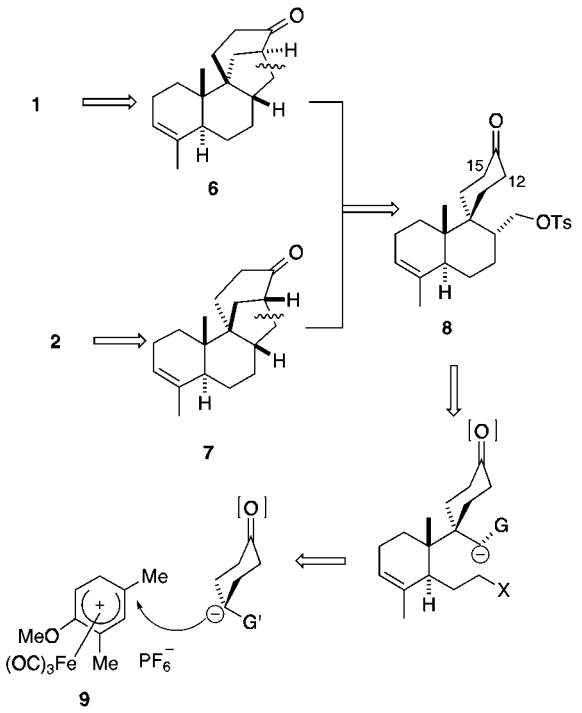
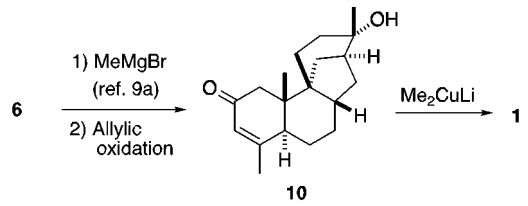
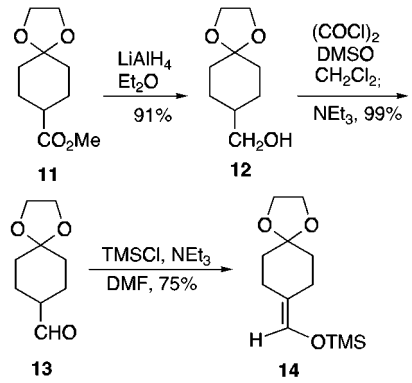
Scheme 1



Scheme 2



Scheme 3



proaches to aphidicolin have also been intensively studied.[9] One of the challenges associated with the construction of these molecules is the dense arrangement of quaternary carbon centers. We have previously found that the addition of nucleophiles to substituted cyclohexadienyliron complexes provides methodology that is well-suited to this task,[10] and we report herein an application of this chemistry to the synthesis of racemic stemodinone.

At the synthetic planning stage, it was conceived that both stemodinone and aphidicolin could be accessed from a common intermediate (**8**) (Scheme 1). Simplifications of **1** to **6** and **2** to **7** involve fuctional group removals (FGR) and interconversions (FGI). The C-ring disconnections on both **6** and **7** as shown are based on Corey's synthesis[8a,9d] of aphidicolin and stemodinone from related intermediates. Thus, reversible enolate formation (NaOMe or KOBu^t base) from **8** would lead to internal alkylation at C-15, to provide **6**, having the stemodinone BCD ring stereochemistry, while kinetically controlled deprotonation (LiN(Bu^t)$_2$) would occur at C-12, to give **7**, possessing aphidicolin stereochemistry. In this paper we report an investigation into the construction of the stemodinone ring system which uses the cyclohexadienyliron complex **9** as the A-ring precursor, coupled with an enolate (see later) that corresponds to the D ring, the remaining rings being elaborated by appropriate bond connections between residues incorporated into each subunit (Scheme 1).

In the synthetic direction, conversion of **7** into aphidicolin would require functionalization of the A-ring double bond *via* hydroboration and oxidation, followed by thermodynamic enolate formation and hydroxymethylation. This planned sequence is not shown here. The elaboration of **6** into stemodinone might be achieved according to Scheme II. It should be noted here that cuprate addition to enone **10** has been reported as the final step in a recently published synthesis of stemodinone,[8n] so production of this intermediate would constitute a formal synthesis of the natural product.

Results and Discussion

Our synthesis began with the known[11] cyclohexadienyliron complex **9**, which represents the A ring of stemodinone, and can be prepared on large scale (>200 g). We planned to connect the A and C rings of stemodinone by tin enolate nucleophile addition to **9**, and the requisite enolate was prepared by standard methods as follows (Scheme III). Reduction of ester **11** with lithium aluminum hydride afforded alcohol **12**, which was then converted into aldehyde **13** by Swern oxidation. Transformation of aldehyde **13** into silyl enol ether **14** was accomplished by reaction with chlorotrimethylsilane in the presence of triethylamine. Enolsilane **14** was purified by fractional distillation under reduced pressure and

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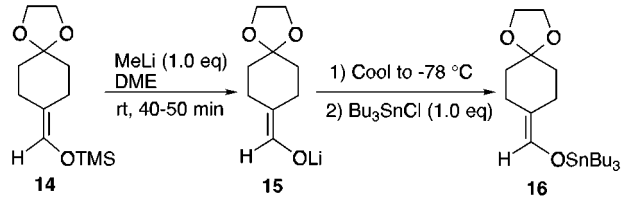
Scheme 4



provided a convenient precursor to its tin enolate derivative. The *in situ* generation of enolstannane **16** from enolsilane **14** was performed according to a modification of the procedure[12] described by Yamamoto (Scheme 4).

The reason for choosing a tin enolate as the nucleophile was based on the earlier discovery[10] made in our laboratory that these enolates react with dienyliron complexes such as **9** with excellent regioselectivity at the methylated terminus. Indeed, addition of tributyltin enolate **16** to dimethyl-substituted dienyl complex **9** proceeded smoothly to produce aldehyde **17** as a single product in high yield. This reaction provides a method of joining two six-membered rings at highly substituted positions, forming contiguous quaternary centers, appropriate for synthesis of the key intermediate **8**. There are 20 carbon atoms in both stemodane and aphidicolane skeleta (see Figure 1). Intermediate **17** contributes 15 of these skeletal carbons. Thus, a substantial portion of the stemodane and aphidicolane frameworks is set in place in a single nucleophile addition step.

The presence of aldehyde functionality in complex **17** allowed us to incorporate the required pro-C ring carbon unit at this stage, thus overcoming some of the problems encountered in earlier approaches where this residue is incorporated onto a later, sterically congested tricyclic intermediate.[9,10] Wittig methylenation in refluxing THF, using *n*-BuLi as base, afforded a high yield of olefin **18**, which was converted into primary alcohol **19** upon hydroboration/oxidation (Scheme 5); this intermediate was protected as its *tert*-butyldiphenylsilyl (TBDPS) ether **20** by treatment with *tert*-butyldiphenylsilyl chloride and imidazole in dimethylformamide.[13] It is noteworthy that a large number of synthetic transformations can be carried out without detriment to the diene−$Fe(CO)_3$ moiety, which acts as a protecting group for the masked A-ring enone.

Removal of the tricarbonyliron moiety from **20** was effected by using a large excess of trimethylamine *N*-oxide (10−15 equiv).[14] The resulting diene **21** was subjected to hydrolysis with aqueous oxalic acid in an 8:1 mixture of methanol and tetrahydrofuran, to give enone **22**. Cleavage of the ketal and silyl ether functions was not observed when the pH of the initial reaction mixture was around 2, and the reaction was permitted to proceed for 18 min before immediate neutralization with aqueous sodium bicarbonate solution.

Sodium borohydride reduction[15] of enone **22** afforded the allylic alcohol **23** *via* axial hydride delivery. The stereochemistry of product **23** was supported by ^{1}H NMR spectroscopy of its benzoyl derivative **24**, where the allylic proton showed a doublet of doublets around 5.70 ppm. The coupling constants (J_{aa} = 8.8 Hz, J_{ae} = 2.8 Hz) indicated that the allylic proton was in an axial position, as required.

In order to construct the B ring on **23**, it was necessary to introduce a two-carbon unit onto the molecule. This was achieved by converting allylic alcohol **23** into allyl vinyl ether **25**, followed by Claisen rearrangement to give **26**, as shown in Scheme 6. In view of the degree of steric hindrance in the substrate, this reaction was expected to be problematic, as was indeed the case. Uncatalyzed reaction in mesitylene at 165 °C gave only 8% yield of the desired product. After experimenting with numerous modifications of the procedure, we discovered that a substantial yield improvement (to 32%) was obtained when the reaction was conducted in the presence of ammonium chloride.

In order to complete the B-ring construction, intermediate **30** was prepared from aldehyde **26** *via* a three-step sequence (Scheme 6). Thus, reduction of **26**, followed by treatment of the resulting alcohol **27** with carbon tetrachloride and triphenylphosphine in dichloromethane[16] cleanly generated chloride **28**. Removal of the silyl protecting group on **28** using tetra-*n*-butylammonium fluoride released alcohol **29** in quantitative yield, which was readily oxidized to aldehyde **30**.

Ring closure of aldehyde−chloride **30** turned out to be a very facile reaction.[17] Thus, treatment of **30** with an excess of potassium hydride (to ensure equilibration of the product aldehyde to the thermodynamically more stable epimer) in tetrahydrofuran at ambient temperature provided the spiro tricyclic aldehyde **31** in 98% yield! The starting material was consumed in 1 h according to thin layer chromatography of the reaction mixture. In Corey's total synthesis of aphidicolin[10d] and stemodinone,[8a] only the thermodynamically more stable equatorial aldehydes were produced in both the cases, and the formation of their C-8 epimers was not observed, thus supporting our own stereochemical assignment.

In order to construct the tetracyclic skeleton of stemodinone, one more cyclization was to be conducted upon tricyclic keto−tosylate **8**, which was obtained from aldehyde **31** by a three-step manipulation (Scheme 7). The aldehyde was reduced to primary alcohol **32** by reaction with sodium borohydride in a 1:1 mixture of ethanol and THF. Treatment of alcohol **32** with *p*-toluenesulfonyl chloride (4 equiv) and triethylamine (10 equiv) in chloroform, in the presence of 4-(dimethylamino)pyridine (2 equiv),[18] afforded the crude ketal tosylate, which was hydrolyzed to **8** with dilute hydrochloric acid in THF (97% yield over two steps). Corey's earlier work had shown that treatment of a similar keto−tosylate with sodium methoxide in methanol at 0 °C led exclusively to the product that has the BCD ring stereochemistry of stemodinone. Reaction of **8** with 10 equiv of sodium methoxide in anhydrous methanol at 0 °C indeed afforded a single cyclization product (**6**), which was assigned the stemodinone stereochemistry based on Corey's observations.

Stereoselective addition of a methyl group to the carbonyl group in ketone **6** also follows the precedent set

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(13) Blanchette, M. A.; Kageyama, M.; Malamas, M. S.; Nantz, M. H.; Roberts, J. C.; Somfai, P.; Tamura, T.; Whritenour, D. C.; Masamune, S. *J. Org. Chem.* **1989**, *54*, 2817.
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(17) This observation is in contrast to the corresponding aldehyde−tosylate which did not give a reasonable cyclization yield under a variety of reaction conditions.
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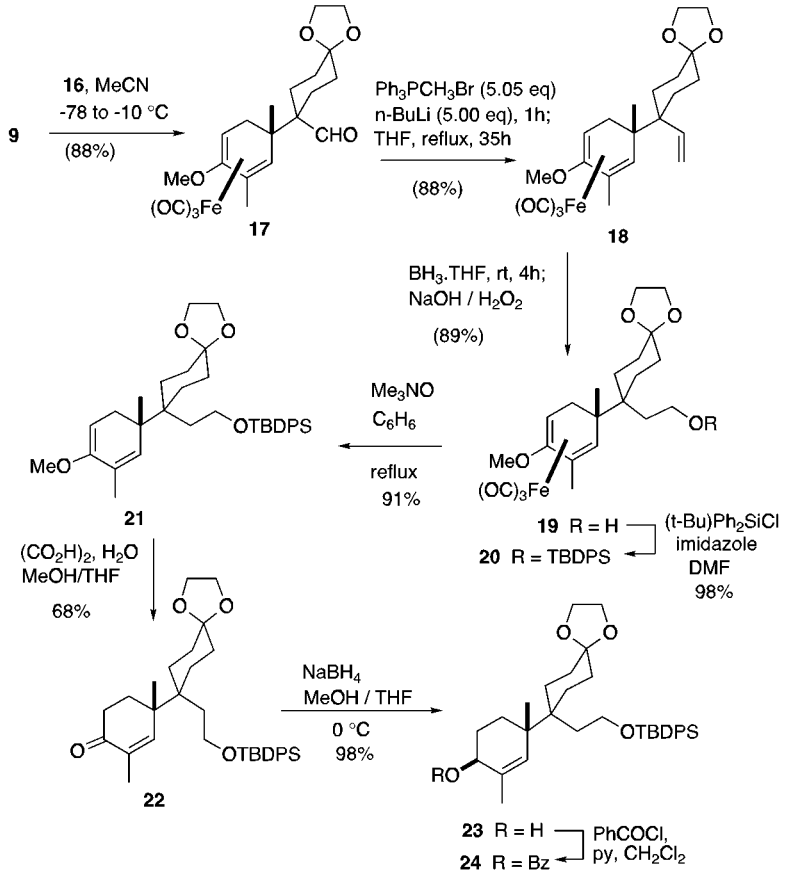
Scheme 5



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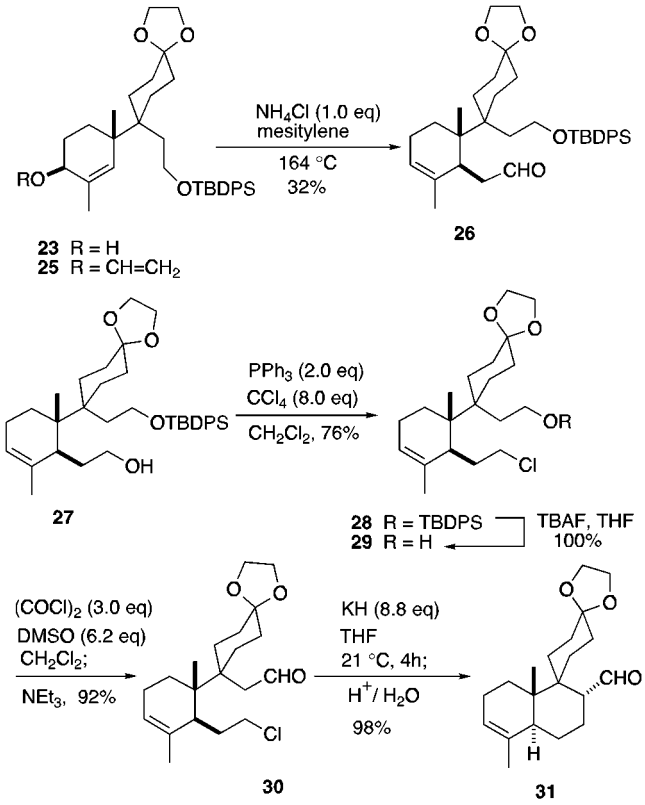
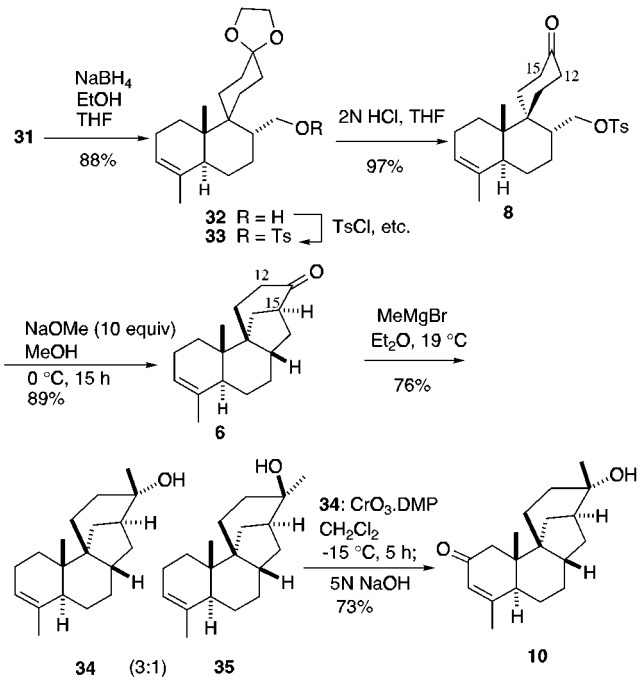


Scheme 7



by Corey's synthesis of stemodinone.[8a] Thus, reaction of **6** with 10 equiv of methylmagnesium bromide in diethyl ether at 19 °C generated epimeric alcohols **34** and **35** as a chromatographically separable 3:1 mixture, in favor of the desired product (Scheme 7). The stereochemistry of the tertiary alcohols **34** and **35** was assigned by comparison of the observed chemical shifts of the carbinol methyl groups with the data reported for Corey's epimers. It should be noted that some physical properties (R_f and mp) of these four alcohols are quite comparable: the desired isomers have higher R_f (less polar) and lower melting points than their epimers (see Experimental Section).

For generating the A-ring enone functionality from

olefin **34**, an allylic oxidation procedure described by Salmond and co-workers[19] was employed. Thus, treatment of **34** with 20 equiv of 3,5-dimethylpyrazole/chromium trioxide complex (CrO_3·DMP) in methylene chloride for 5 h afforded the desired enone **10** (Scheme 7).

The stereochemistry of intermediate **10** is supported by comparing its ^1H and ^{13}C NMR spectra with the corresponding spectra of (+)-stemodinone.[20] In the ^1H NMR spectrum of **10**, the chemical shifts for the angular methyl and the carbinol methyl are δ 1.09 and 1.14; for authentic stemodinone, the two corresponding resonances also occur at δ 1.09 and 1.14. In the ^{13}C NMR spectrum of **10**, the chemical shift for the unique carbon atom which carries a hydroxyl group is 72.16 ppm; for authentic stemodinone, the corresponding carbon resonance is at 72.15 ppm. Installation of the final methyl group, via cuprate addition, to produce stemodinone proceeds in very low yield, with poor conversion.[8n] A variety of alternate conjugate addition methods[21] were examined in our laboratory without success. In summary, the capability of dienyliron complexes for generating congested quaternary carbon centers provides a relatively straighforward route to the stemodinone and aphidicolin ring structures (18 steps from complex **9**). Since these types of cyclohexadienyliron complexes can be obtained optically pure,[22] the methodology would also provide access to stemodinone in its natural form.

Experimental Section

General methods for purification and characterization of reaction products are described elsewhere.[23]

Tricarbonyl(1−5-η-2-methoxy-3,5-dimethylcyclohexadienyl)iron(I) hexafluoro-phosphate (9). This compound was reported earlier by Curtis *et al.*[11] We prepared **9** on large scale using a somewhat different procedure: Di-*n*-butyl ether was filtered through basic alumina prior to use. The 1,4-diene resulting from Birch reduction of 2,4-dimethylanisole (91 g, 0.66 mol, prepared according to Curtis *et al.*[11]) was refluxed with pentacarbonyliron (240 mL) in di-*n*-butyl ether (500 mL) under argon for 5 days. After being cooled to rt, the reaction mixture was filtered through a Celite pad, and the pad was washed through with dibutyl ether. The filtrate was evaporated on a rotary evaporator fitted with a dry ice−acetone condenser, and the resulting residue was filtered through a pad of silica gel eluting with diethyl ether. Evaporation to near dryness gave a mixture of three isomeric diene−iron complexes[11] (138 g, 75%) as a clear orange oil, which, without being separated, was used for hydride abstraction as follows. $Ph_3C^+PF_6^-$ (102 g, 0.25 mol) in 800 mL of methylene chloride was stirred over solid K_2CO_3 (5 g) for 30 min prior to use. This acid-free trityl solution was added, *via* cannula, to a solution of the mixture of diene−iron complexes (138 g) in 200 mL of CH_2Cl_2, with vigorous stirring. After the addition, the reaction mixture was continually stirred at rt for 1 h and then poured into 2 L of *wet* diethyl ether. The resulting precipitate was collected and washed with wet ether and then with dry ether and air-dried overnight. Recrystallization from methanol twice provided 77 g (35%) of the desired dienyl−iron complex **9** as yellow needles: mp 206 °C (dec); IR (MeCN) 2100, 2050, 1250, 855−825 cm^{-1}; ^1H NMR (200 MHz, CD_3CN) δ 5.74 (s, 1 H), 3.92−3.88 (dd, 1 H, J = 6.4, 1.3 Hz), 3.66 (s 3 H), 2.98−2.87 (ddd, 1 H, J = 16, 6.4, 1.3 Hz), 2.61 (s, 3 H), 2.3−2.1 (m, 1 H), 1.70 (s, 3 H).

Methyl 4,4-(Ethylenedioxy)cyclohexanecarboxylate (11). This compound was prepared according to a procedure used earlier in our laboratory.[24] A mixture of methyl 4-oxocyclohexanecarboxylate (143 g, 0.917 mol), ethylene glycol (220 mL), and *p*-toluenesulfonic acid (2 g) in 500 mL of benzene was agitated *via* overhead stirring at rt under nitrogen atmosphere for 20 h (it was not necessary to heat or to use a Dean−Stark apparatus for azeotropic removal of the water formed during the reaction). After being poured into 2 L of diethyl ether, the mixture was washed with water (1 L × 2), dilute sodium bicarbonate solution (800 mL × 2), and brine. The organic solution was dried over $MgSO_4$, filtered, and evaporated *in vacuo* to furnish 174 g (95%) of ketal **11** as a colorless oil which gave a clean ^1H NMR spectrum and was not further purified: IR ($CHCl_3$) 2955, 1729 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.85 (s, 4 H), 3.58 (s, 3 H), 2.27 (m, 1 H), 1.9−1.3 (m, 8 H).

4,4-(Ethylenedioxy)cyclohexanemethanol (12). To a stirred solution of the ketal−ester **11** (5.88 g, 29.4 mmol) in 25 mL of diethyl ether was added 1 M solution of $LiAlH_4$ in diethyl ether (30 mL, 30 mmol) dropwise at such a rate as to maintain a gentle reflux. After complete addition, the resulting white suspension was heated to reflux under nitrogen atmosphere for 15 h. Upon cooling, the reaction was carefully quenched by slowly adding water (20 mL) dropwise, followed by addition of 15% aqueous sodium hydroxide (20 mL). After the solution was stirred at rt for 1 h, 10 g of solid sodium chloride was added in order to facilitate the subsequent workup, and the mixture was then filtered through a pad of cotton wool and washed through with diethyl ether. The filtrate was extracted with diethyl ether. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash chromatography on a silica gel column (EtOAc/hexane, 50/50) to afford 4.58 g (91%) of alcohol **12** as a colorless liquid: R_f 0.27 (EtOAc/hexane, 50/50); IR (neat) 3640−3250 (br, OH), 2940, 2865 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.95 (s, 4 H), 3.50 (d, 2 H, J = 6.4 Hz), 1.8−1.2 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 109.1, 67.3, 64.1, 39.0, 34.0, 26.6; HRMS calcd for $C_9H_{16}O_3$ (M) 172.1010, found 172.1009.

4,4-(Ethylenedioxy)cyclohexanecarbaldehyde (13). To a stirred solution of oxalyl chloride (16.1 mL, 182 mmol) in 185 mL of dichloromethane at −78 °C under a nitrogen atmosphere was added dropwise, over a period of 30 min, dimethyl sulfoxide (26.7 mL, 365 mmol). After 10 min, the primary alcohol **12** (12.5 g, 72.7 mmol) in 100 mL of dichloromethane was added dropwise over a period of 40 min. After 10 min the initially clear solution became white and cloudy. The mixture was stirred at −78 °C for an additional hour. Triethylamine (68 mL, 0.48 mol) was added dropwise while the reaction temperature was maintained at −78 °C. Upon complete addition, the reaction mixture was slowly warmed to −10 °C in 2 h and then quenched by addition of 50 mL of water. The organic layer (lower layer) was separated and washed with water and brine. The aqueous layers were combined and extracted with CH_2Cl_2. The combined organics were dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The residual oil was purified by flash chromatog-

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raphy on a silica gel column (EtOAc/hexane, 20/80) to give 12.4 g (99%) of aldehyde **13** as a pale yellow liquid: R_f 0.36 (EtOAc/hexane, 25/75); IR (neat) 2925, 2855, 2706, 1720 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.58 (s, 1 H), 3.88 (s, 4 H), 2.19 (quintet, 1 H, J = 4.5 Hz), 1.91−1.47 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.9, 107.9, 64.2, 48.1, 33.2, 23.2; HRMS calcd for $C_9H_{14}O_3$ (M) 170.0943; found 170.0941.

1′-(((Trimethylsilyl)oxy)methylene)-4,4-(ethylenedioxy)cyclohexane (14). Chlorotrimethylsilane (23.2 mL, 183 mmol) was added *via* syringe to a stirred solution of aldehyde **13** (12.4 g, 72.9 mmol) and triethylamine (51.0 mL, 365 mmol) in *N*,*N*-dimethylformamide (150 mL) at rt under nitrogen atmosphere. The reaction mixture was then heated to reflux for 24 h. After cooling, the mixture was diluted with diethyl ether (350 mL) and washed successively with saturated sodium bicarbonate solution, cold 1 N hydrochloric acid (to remove the triethylamine), and aqueous $NaHCO_3$ again. The ethereal layer was dried ($MgSO_4$) and concentrated *in vacuo*. Fractional distillation of the resultant residue at 80−85 °C/0.35 mmHg yielded 12.2 g (75%) of the expected product **14** as a pale yellow liquid: R_f 0.75 (EtOAc/hexane, 25/75); IR (neat) 2970, 2850, 1710, 1660 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.04 (s, 1 H), 3.96 (s, 4 H,), 2.32 (t, 2 H, J = 6.4 Hz), 2.11 (t, 2 H, J = 6.3 Hz), 1.68−1.60 (m, 4 H), 0.16 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.1, 119.4, 109.3, 64.2 (2 coincident), 36.1, 34.8, 27.2, 21.9, −0.6; HRMS calcd for $C_{12}H_{22}O_3Si$ (M) 242.1338, found 242.1378.

Tricarbonyl[5-(1-formyl-4,4-ethylenedioxy)cyclohexyl)-2-methoxy-3,5-dimethyl-1−4-η-cyclohexa-1,3-diene]-iron(0) (17). To a stirred solution of silyl enol ether **14** (9.29 g, 9.0 mL, 38.39 mmol) in 40 mL of 1,2-dimethoxyethane under a nitrogen atmosphere was added dropwise methyllithium solution (1.4 M in diethyl ether, 27.42 mL, 38.39 mmol) over a period of 15 min, and the resulting solution was continually stirred at rt for 1 h. After the solution was cooled to −78 °C, tri-*n*-butyltin chloride (10.42 mL, 38.39 mmol) was added *via* syringe over a period of 3 min and the solution was stirred at −78 °C for 90 min. The dienyl−iron salt **9** (16.20 g, 38.39 mmol) dissolved in 150 mL of dry acetonitrile was added *via* cannula over a period of 20 min. After complete addition, the reaction mixture was gradually warmed to −14 °C in 3 h and then quenched by addition of 30 mL of 50% aqueous tetrahydrofuran. The resulting mixture was extracted with diethyl ether (200 mL × 3). The combined organic extracts were successively washed with a saturated aqueous ammonium chloride solution, saturated sodium bicarbonate, and brine. The organics were dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* to give a brown liquid. Flash chromatography (twice) on silica gel (EtOAc/hexane, 35/65) afforded 15.1 g (88%) of the desired addition product **17** as an orange viscous oil: R_f 0.78 (EtOAc/hexane, 50/50); IR ($CHCl_3$) 2950, 2040, 1962, 1712 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.55 (s, 1 H), 3.91 (s, 4 H), 3.56 (s, 3 H), 3.23 (t, 1 H, J = 2.9 Hz), 2.48 (s, 1 H), 2.16 (s, 3 H), 2.10 (dd, 1 H, J = 15.4, 2.8 Hz), 1.7−1.3 (m, 8 H), 1.28 (dd, 1 H, J = 15.4, 3.0 Hz), 1.02 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.5, 207.7, 139.5, 108.0, 84.9, 65.9, 64.2, 55.5, 55.4, 45.6, 43.4, 38.2, 31.7, 26.1, 25.3, 25.1, 17.3; HRMS calcd for $C_{21}H_{26}FeO_7$ (M) 446.1028, found 446.1035. Anal. Calcd for $C_{21}H_{26}FeO_7$: C, 56.52; H, 5.87. Found: C, 56.11; H, 5.64.

Tricarbonyl[5-(1-vinyl-4,4-(ethylenedioxy)cyclohexyl)-2-methoxy-3,5-dimethyl-1−4-η-cyclohexa-1,3-diene]-iron(0) (18). To a stirred mixture of methyltriphenylphosphonium bromide (6.73 g, 18.8 mmol, 5.05 equiv) in 60 mL of THF under nitrogen atmosphere at rt, was added, dropwise, *n*-butyllithium (1.29 M solution in hexanes, 14.6 mL, 18.6 mmol, 5.00 equiv). The resultant orange suspension was stirred at rt for 40 min, and then aldehyde **17** (1.66g, 3.72 mmol) in 20 mL of THF was added dropwise. Upon complete addition, the mixture was heated to reflux for 35 h. After being cooled to rt, the mixture was poured into water (20 mL) and extracted with diethyl ether (40 mL x 3), and the combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered, and evaporated. The crude product was purified by flash chromatography on silica gel column (EtOAc/Hexane, 15/85) to give 1.45 g (88%) of olefin **18** as a yellow oil: R_f 0.25 (EtOAc/hexane, 15/85); IR (neat) 2930, 2860, 2020, 1940, 1725 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.46 (dd, 1 H, J = 17.6, 11.0 Hz), 5.28 (dd, 1 H, J = 11.0, 1.5 Hz), 4.92 (dd, 1 H, J = 17.6, 1.5 Hz), 3.90 (s, 4 H), 3.55 (s, 3 H), 3.20, (t, 1 H, J = 2.5 Hz), 2.49 (s, 1 H), 2.14 (s, 3 H), 1.91 (dd, 1 H, J = 15.2, 2.5 Hz), 1.62−1.43 (m, 8 H), 1.28 (dd, 1 H, J = 15.2, 3.1 Hz), 0.97 (s 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.1 141.3, 139.5, 116.2, 108.9, 85.1, 68.1, 64.1, 55.2, 46.7, 45.8, 43.8, 38.4, 31.2, 28.6, 27.5, 26.1, 17.5; HRMS calcd for $C_{22}H_{28}FeO_6$ (M) 444.1235, found 444.1230. Anal. Calcd for $C_{22}H_{28}FeO_6$: C, 59.47; H, 6.35. Found: C, 58.98; H, 6.32.

Tricarbonyl[5-[1-(2-hydroxyethyl)-4,4-(ethylenedioxy)cyclohexyl]-2-methoxy-3,5-dimethyl-1−4-η-cyclohexa-1,3-diene]iron (19). To a stirred solution of olefin **18** (6.40 g, 14.4 mmol) in 100 mL of dry tetrahydrofuran at 0 °C was added a borane−tetrahydrofuran solution (1.0 M, 28.8 mL, 28.8 mmol) dropwise via a pressure-equalizing funnel. After complete addition, the cooling bath was removed and the reaction solution was continually stirred under nitrogen atmosphere for 4 h. Water (60 mL), 15% aqueous NaOH (80 mL), and a 30% aqueous H_2O_2 solution (100 mL) were added sequentially, and the resultant mixture was stirred for 2 h. The mixture was filtered to remove some orange precipitate, and the filtrate was extracted with diethyl ether. The ethereal extracts were combined and dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* to give a vicous oil, which was purified by flash chromatography on silica gel (EtOAc/Hexane, 40/60) to afford 5.9 g (89%) of alcohol **19** as yellow crystals: mp 124− 126 °C; R_f 0.13 (EtOAc/hexane, 50/50); IR ($CHCl_3$) 3618, 2928, 2897, 2038, 1959, 1640 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.92 (s, 4 H), 3.65 (t, 2 H, J = 8.5 Hz), 3.55 (s, 3 H), 3.20 (t, 1 H, J = 2.9 Hz), 2.55 (s, 1 H), 2.18 (s, 3 H), 1.91 (dd, 1 H, J = 15.0, 2.8 Hz), 1.86 (s, 1 H), 1.8 - 1.3 (m, 10 H), 1.26 (dd, 1 H, J = 15.0, 3.0 Hz), 1.03 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.1, 139.3, 108.5, 85.4, 77.2, 68.0, 64.2, 64.1, 60.3, 55.2, 45.5, 43.4, 41.5, 39.6, 35.0, 31.0, 26.6, 17.3; HRMS calcd for $C_{22}H_{30}FeO_7$ (M) 462.1341, found 462.1378. Anal. Calcd for $C_{22}H_{30}FeO_7$: C, 57.13; H, 6.54. Found: C, 57.05; H, 6.62.

Tricarbonyl[5-(1-(2-((*tert*-butyldiphenylsilyl)oxy)ethyl)-4,4-(ethylenedioxy)cyclohexyl)−2-methoxy-3,5-dimethyl-1−4-η-cyclohexa-1, 3-diene]iron(0) (20). To a stirred solution of alcohol **19** (5.90 g, 12.8 mmol) in 100 mL of DMF were added imidazole (2.60 g, 38.0 mmol) and *tert*-butylchlorodiphenylsilane (6.70 mL, 25.6 mmol). The mixture was stirred at rt under nitrogen for 24 h, then diluted with diethyl ether (200 mL), and washed with water and brine. The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. Flash chromatography of the residue on silica gel (EtOAc/hexane, 15/85) gave 8.81 g (98%) of silyl ether **20** as a viscous yellow oil: R_f 0.24 (EtOAc/hexane, 15/85); IR ($CHCl_3$) 2036, 1966 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.73−7.61 (m, 4 H), 7.46−7.36 (m, 6 H), 3.92 (s, 4 H), 3.64 (m, 2 H), 3.49 (s, 3 H), 3.11 (t, 1 H, J = 2.8 Hz), 2.38 (br, 1 H), 2.2−1.1 (m, 12 H), 1.56 (s, 3 H), 1.03 (s, 9 H), 0.83 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.1, 135.5, 134.8, 133.8, 133.7, 129.7, 129.5, 127.7, 108.7, 73.5, 68.2, 64.2, 64.0, 61.5, 55.1, 45.6, 41.5, 39.7, 39.6, 30.9, 26.8, 26.5, 19.1, 17.2; HRMS calcd for $C_{27}H_{44}FeO_6Si$ (M−CO): 548.2256, found 548.2260. The molecular ion was not observed.

2-Methoxy-3,5-dimethyl-5-[1-(2-((*tert*-butyldiphenylsilyl)oxy)ethyl)-4,4-(ethylene-dioxy)cyclohexyl]cyclohexa-1,3-diene (21). Trimethylamine *N*-oxide (12.4 g, 165 mmol) was refluxed in 550 mL of dry benzene under a nitrogen atmosphere until all the oxide was dissolved. After cooling, the diene−iron complex **20** (7.71 g, 11.0 mmol) in 150 mL of benzene was added *via* cannula, and the mixture was refluxed for 18 h (the reaction was monitored by IR, and disappearance of the $Fe(CO)_3$ bands at 2036, 1966 cm^{-1} indicated its completion). After cooling, the mixture was diluted with diethyl ether (200 mL) and washed with water and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered through Celite, and concentrated *in vacuo* to yield 5.01 g (91%) of crude diene **21** as an oil, which was used for the next step without further purification: IR ($CHCl_3$) 2959, 2860, 1727 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.67 (m, 4 H), 7.36 (m, 6 H), 5.27 (s, 1 H), 4.30

(dd, 1 H, J = 7.0, 3.0 Hz), 3.90 (s, 4 H), 3.70 (m, 2 H), 3.45 (s, 3 H), 2.3−1.1 (m, 12 H), 1.54 (br, 3 H), 1.01 (s, 9 H), 0.78 (s, 3 H).

4-[1-(2-((*tert*-butyldiphenylsilyl)oxy)ethyl)-4,4-(ethylenedioxy)cyclohexyl]-2,4-di-methylcyclohex-2-en-1-one (22). To a solution of the dienyl methyl ether **21** (32.0 g, 57.1 mmol) in a mixture of THF (100 mL) and methanol (800 mL) was added aqueous oxalic acid (18.1 g, 200 mmol, in 500 mL of water). The resultant mixture was vigorously stirred *via* overhead stirring at rt for *18* min and poured into water (1 L) and *immediately* neutralized with aqueous sodium bicarbonate solution. The mixture was extracted with diethyl ether. The combined ethereal layers were dried over anhydrous $MgSO_4$, filtered through Celite, and evaporated. Purification of the residual oil by column chromatography on silica gel (EtOAc/Hexane, 25/75) afforded 21.2 g (68%) of the desired enone **22** as a foam: R_f 0.45 (EtOAc/hexane, 25/75); IR ($CHCl_3$) 1667 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.65−7.38 (m, 10 H), 6.50 (s, 1 H), 3.93 (br s, 4 H), 3.70 (t, 2 H, J = 8.0 Hz), 2.38 (ddd, 1 H, J = 17.0, 13.9, 5.4 Hz), 2.27 (ddd, 1 H, J = 17.0, 5.2, 2.6 Hz), 1.86−1.25 (m, 12 H), 1.58 (s, 3 H), 1.04 (s, 9 H), 0.95 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.5, 152.3, 135.5, 133.7, 133.6, 132.7, 129.7, 127.7, 108.4, 64.2, 61.1, 41.7, 39.7, 34.3, 33.3, 30.9, 30.7, 29.3, 27.3, 26.9, 19.1, 19.0, 16.3; HRMS calcd for $C_{34}H_{46}O_4Si$ (M) 546.3165, found 546.3160.

2,4-Dimethyl-4-[1-(2-((*tert*-butyldiphenylsilyl)oxy)ethyl)-4,4-(ethylenedioxy)cyclohexyl]cyclohex-2-en-1-ol (23). To a stirred solution of enone **22** (190 mg, 0.347 mmol) in 6 mL of 1:1 THF and methanol at 0 °C was added sodium borohydride (20 mg, 0.529 mmol) in portions. After the solution was stirred at 0 °C for 45 min, 5 mL of water was added, and the resultant mixture was stirred for 5 min. The mixture was then poured into 20 mL of ethyl acetate and washed with water and brine. The aqueous layers were combined and extracted with EtOAc. The combined organics were dried over anhydrous $MgSO_4$, filtered, and evaporated to give a yellow oil. Flash chromatography on silica gel (EtOAc/hexane, 25/75) and subsequent recrystallization from chloroform provided 186 mg (98%) of the desired allylic alcohol **23** as pale yellow rods: mp 152−153 °C; R_f 0.35 (EtOAc/hexane, 25/75); IR ($CHCl_3$) 3609, 1663 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.66−7.38 (m, 10 H), 5.17 (s, 1 H), 3.9 (br s, 4H), 3.84−3.60 (m, 3 H), 1.9−1.1 (m, 15 H), 1.56 (s, 3 H), 1.04 (s, 9 H), 0.83 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.4, 134.6, 133.9, 133.8, 131.1, 129.5, 127.6, 108.7, 69.6, 64.0, 61.4, 41.0, 39.7, 33.5, 30.8, 30.7, 30.2, 28.8, 27.1, 26.8, 22.1, 19.2, 19.0; HRMS calcd for $C_{34}H_{48}O_4Si$ (M) 548.3322, found 548.3318.

1-(Benzoyloxy)-2,4-dimethyl-4-[1-(2-((*tert*-butyldiphenylsilyl)oxy)ethyl)-4,4-(ethylenedioxy)cyclohexyl]-2-cyclohexene (24). To a stirred solution of allylic alcohol **23** (50 mg, 0.091 mmol) and pyridine (22.1 μL, 0.373 mmol) in dichloromethane (2 mL) at 0 °C under nitrogen atmosphere was added benzoyl chloride (16.0 μL, 0.137 mmol) *via* syringe. The reaction solution was stirred at 0 °C for 15 min, and then at rt for 5 h. The mixture was transferred into a separatory funnel, diluted with 15 mL of diethyl ether, and washed successively with aqueous sodium bisulfate (0.15 N, 5 mL x 2), water, and saturated sodium bicarbonate. The organics were dried over anhydrous $MgSO_4$, filtered, and evaporated. The resulting crude product was purified by column chromatography on silica gel (EtOAc/hexane, 15/85) to afford 58 mg (98%) of benzoyl derivative **24** as an oil: R_f 0.50 (EtOAc/hexane, 25/75); ^1H NMR (300 MHz, $CDCl_3$) δ 8.17−7.35 (m, 15 H), 5.70 (dd, J = 8.8, 2.8 Hz, 1 H), 5.33, (br s, 1 H), 3.92 (br s, 4 H), 3.77−3.68 (m, 2 H), 1.98 −1.18 (m, 14 H), 1.56 (s, 3 H), 1.04 (s, 9 H), 0.87 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 135.5, 134.5, 133.9, 133.2, 132.8, 130.5, 129.6, 128.9, 128.3, 127.7, 108.7, 72.9, 64.1, 61.5, 41.0, 39.7, 33.5, 30.9, 30.7, 29.7, 28.4, 27.3, 26.9, 26.3, 22.0, 19.4, 19.1; HRMS calcd for $C_{36}H_{43}O_5Si$ (M − C_4H_9) 583.2880, found 583.2879. The molecular ion was not observed.

1-(Vinyloxy)-2,4-dimethyl-4-[1-(2-((*tert*-butyldiphenylsilyl)oxy)ethyl)-4,4-(ethylenedioxy)cyclohexyl]-2-cyclohexene (25). To a solution of allylic alcohol **23** (180 mg, 0.328 mmol) in 8 mL of *n*-butyl vinyl ether were added mercuric acetate (210 mg, 0.656 mmol) and vinyl acetate (60.5 μL, 0.656 mmol) at rt under a nitrogen atmosphere. The mixture was stirred at reflux for 3 h. After cooling, the mixture was diluted with 20 mL of diethyl ether, washed with an aqueous sodium thiosulfate solution (for removal of $Hg(OAc)_2$), water, and brine. The organics were dried over anhydrous sodium carbonate, filtered through Celite, and concentrated *in vacuo*. Column chromatography on basic alumina (this vinyl ether underwent hydrolysis on silica gel) (EtOAc/hexane, 15/85) provided 160 mg (85%) of allyl vinyl ether **25** as a viscous liquid: R_f 0.78 (EtOAc/hexane, 25/75); ^1H NMR (200 MHz, $CDCl_3$) δ 7.62−7.38 (m, 10 H), 6.23 (dd, 1 H, J = 14.0, 6.5 Hz), 5.22 (s, br, 1 H), 4.26 (dd, 1 H, J = 14.0, 1.4 Hz), 3.93 (dd, 1 H, J = 6.5, 1.4 Hz), 3.90 (s, 4 H), 3.87−3.47 (m, 3 H), 2.15−1.14 (m, 14 H), 1.54, (s, 3 H), 1.01 (s, 9 H), 0.81 (s, 3 H); HRMS calcd for $C_{36}H_{50}O_4Si$ (M) 574.3478, found 574.3482.

2,4-Dimethyl-3-(2-oxoethyl)-4-[1-(2-((*tert*-butyldiphenylsilyl)oxy)ethyl)-4,4-ethylenedioxy)cyclohexyl]cyclohexene (26). To a degassed solution of allyl vinyl ether **25** (710 mg, 1.24 mmol) in 10 mL of mesitylene was added ammonium chloride (67 mg, 1.24 mmol). The reaction mixture was refluxed at 164 °C with stirring under a nitrogen atmosphere for 17 h (or until the starting material was completely consumed according to TLC). The solvent was then removed from the mixture on a rotary evaporator at 85 °C (bath), and the residual oil was diluted with diethyl ether (50 mL) and filtered through Celite. The filtrate was washed with water (10 mL) and brine (10 mL), dried over magnesium sulfate, filtered, and concentrated *in vacuo*. Flash chromatography on silica gel (EtOAc/hexane, 15/85) afforded 230 mg (32%) of the expected aldehyde product **26** as an oil: R_f 0.18 (EtOAc/hexane, 15/85); IR ($CHCl_3$) 1722 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.71 (s, 1 H), 7.67−7.37 (m, 10 H), 5.38 (s br, 1 H), 3.91 (s, 4 H), 3.78 (m, 2 H), 2.55 (dd, 1 H, J = 16.9, 6.8 Hz), 2.35 (dd, 1 H, J = 16.9, 8.4 Hz), 1.9−1.1 (m, 15 H), 1.55 (s, 3 H), 1.05 (s, 9 H), 0.64 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.8, 136.4, 135.5, 133.9, 129.6, 127.6, 123.4, 108.5, 64.1, 61.6, 46.4, 41.7, 40.9, 38.0, 33.6, 31.1, 30.9, 28.5, 28.2, 26.9, 23.1, 22.7, 21.3, 19.1, 14.0; HRMS calcd for $C_{36}H_{50}O_4Si$ (M) 574.3478, found 574.3484.

2,4-Dimethyl-3-(2-hydroxyethyl)-4-[1-(2-((*tert*-butyldiphenylsilyl)oxy)ethyl)-4-ethylenedioxy)cyclohexyl]cyclohexene (27). To a cold (0 °C), stirred solution of aldehyde **26** (5.00 g, 8.70 mmol) in 100 mL of ethanol was added sodium borohydride (0.795 g, 21.0 mmol) in small portions. After the addition, the ice bath was removed, and the reaction mixture was stirred at ambient temperature under a nitrogen atmosphere for 50 min and then quenched with water (30 mL). After being stirred for 5 min, the mixture was extracted with diethyl ether. The combined extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered, and evaporated *in vacuo*. The residual liquid was purified by flash chromatography (EtOAc/hexane, 28/72) to provide 3.90 g (78%) of alcohol **27** as a clear oil: R_f 0.21 (EtOAc/hexane, 28/72); IR ($CHCl_3$) 3618 (OH) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.67−7.39 (m, 10 H), 5.34 (br s, 1 H), 3.91 (br s, 4 H), 3.74 (t, 2 H, J = 8.4 Hz), 3.49 (t, 2 H, J = 7.1 Hz), 2.0−1.1 (m, 18 H), 1.62 (s, 3 H), 1.04 (s, 9 H), 0.73 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.4, 135.4, 133.8, 129.5, 127.6, 122.4, 108.6, 63.9, 62.6, 61.6, 41.4, 41.2, 40.1, 34.4, 33.9, 31.6, 31.1, 31.0, 28.7, 27.9, 26.8, 23.6, 23.1, 22.1, 19.0; HRMS calcd for $C_{36}H_{52}O_4Si$ (M) 576.3635, found 576.3633.

2,4-Dimethyl-3-(2-chloroethyl)-4-[1-(2-((*tert*-butyldiphenylsilyl)oxy)ethyl)-4,4-ethylenedioxy)cyclohexyl]-1-cyclohexene (28). To a solution of alcohol **27** (2.55 g, 4.42 mmol) and triphenylphosphine (2.32 g, 8.84 mmol, 2.0 equiv) in 20 mL of methylene chloride at rt under nitrogen atmosphere was added freshly distilled carbon tetrachloride (3.42 mL, 35.4 mmol, 8.0 equiv) *via* syringe. The reaction mixture was stirred at ambient temperature (19 °C) for 24 h. After removal of the solvent on a rotary evaporator, the residue was directly purified by flash chromatography on silica gel, eluting with 5% and then 8% EtOAc in hexane, to afford 2.04 g (76%) of chloride **28** as a colorless oil: R_f 0.49 (EtOAc/hexane, 15/85); IR ($CHCl_3$) 2959, 2933, 2890, 1589 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.65−7.36 (m, 10 H), 5.35 (t, br, 1 H, J = 0.62 Hz), 3.89 (s, 4 H), 3.71 (t, br, 2 H, J = 7.8 Hz), 3.33 (t, br, 2 H,

8.0 Hz), 1.9−1.2 (m, 17 H), 1.59 (d, 3 H, J = 1.0 Hz), 1.02 (s, 9 H), 0.68 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.9, 135.1, 134.2, 130.0, 129.8, 128.0, 123.7, 109.0, 64.4, 61.9, 44.7, 42.1, 41.9, 41.7, 35.3, 34.4, 32.2, 31.5, 29.0, 28.4, 27.2, 26.9, 23.9, 23.4, 19.4; HRMS calcd for $C_{36}H_{51}ClO_3Si$ (M) 594.3296, found 594.3301.

2,4-Dimethyl-3-(2-chloroethyl)-4-[1-(2-hydroxyethyl)-4,4-(ethylenedioxy)cyclohexyl]-1-cyclohexene (29). To a stirred solution of silyl ether **28** (1.79 g, 3.00 mmol) in 25 mL of tetrahydrofuran at 0 °C under a nitrogen atmosphere was added tetra-*n*-butylammonium fluoride (1.0 M solution in THF, 3.3 mL, 1.1 equiv) dropwise over 10 min. After the addition, the ice bath was removed, and the reaction mixture was stirred at ambient temperature (20 °C) for 5 h. Upon removal of the solvent on a rotary evaporator, the residue was directly subjected to flash chromatographic purification on silica gel, eluting with 15% and then 50% ethyl acetate in hexane, to yield 1.09 g (100%) of alcohol **29** as a colorless liquid: R_f 0.31 (EtOAc/hexane, 50/50); IR ($CHCl_3$) 3618 (OH) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.47 (s, br, 1 H), 3.92 (s, 4 H), 3.83−3.71 (m, 2 H), 3.57 (dt, 1 H, J = 17.2, 3.7 Hz), 3.50 (dt, 1 H, J = 17.2, 4.9 Hz), 2.10−1.21 (m, 17 H), 1.57 (s, 3 H), 0.93 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.4, 123.5, 108.5, 64.1, 63.7, 60.4, 44.6, 41.6, 35.0, 34.4, 32.0, 31.2, 28.6, 28.1, 23.7, 23.6, 23.2, 22.3; HRMS calcd for $C_{20}H_{33}ClO_3$ (M) 356.2118, found 356.2121.

2,4-Dimethyl-3-(2-chloroethyl)-4-[1-(2-oxoethyl)-4,4-(ethylenedioxy)cyclohexyl]-1-cyclohexene (30). To a stirred solution of oxalyl chloride (814 μL, 9.18 mmol, 3.0 equiv) in 10 mL of dry methylene chloride at −78 °C under a nitrogen atmosphere, was added, dropwise, dimethyl sulfoxide (1.35 mL, 19.0 mmol, 6.2 equiv) in 4 mL of CH_2Cl_2 over 10 min. After the solution was stirred for an additional 10 min, alcohol **29** (1.09 g, 3.06 mmol) in 8 mL of dichloromethane was added dropwise over a period of 8 min, and the resulting solution was continually stirred for 70 min. Triethylamine (4.5 mL) was added dropwise while the reaction temperature was maintained at −78 °C. After the addition, the reaction mixture was allowed to warm to −10 °C in 2 h, and then 5 mL of water was added. The mixture was extracted with CH_2Cl_2, and the combined organics were washed with brine, dried over anhydrous $MgSO_4$, filtered, and evaporated. Flash chromatography on silica gel (EtOAc/hexane, 25/75) furnished 0.998 g (92%) of aldehyde **30** as a pale yellow oil: R_f 0.35 (EtOAc/hexane, 25/75); IR ($CHCl_3$) 1733 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.95 (t, 1 H), 5.48 (s br, 1 H), 3.94 (s, 4 H), 3.53 (m, 1 H), 2.57 (dd, 1 H, J = 15.8, 3.2 Hz), 2.45 (dd, 1 H, J = 15.8, 3.2 Hz), 2.15−1.25 (m, 16 H), 1.72 (s, 3 H), 0.94 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.6, 137.2, 123.6, 108.1, 64.2, 44.6, 44.3, 42.0, 41.6, 34.9, 31.8, 31.3, 31.1, 30.9, 28.6, 28.2, 23.3, 23.1, 22.4; HRMS calcd for $C_{20}H_{31}ClO_3$ (M) 354.1962, found 354.1959.

Spiro[4,10β-Dimethyl-8α-formyl-$\Delta^{3,4}$-*trans*-decalin-9,1′-[3,3′-(ethylenedioxy)cyclohexane] (31). Potassium hydride (35 wt % dispersion in mineral oil, 122 mg, 1.06 mmol, 8.8 equiv) was placed in a 10 mL flask and washed with dry pentane (0.5 mL × 2) and THF (0.5 mL) under a nitrogen atmosphere before addition of 4 mL of dry tetrahydrofuran. To this stirred KH suspension in THF was introduced a solution of the aldehyde−chloride **30** (42 mg, 0.12 mmol) in 1.5 mL of THF *via* syringe over a period of 2 min. The reaction mixture was stirred at ambient temperature (21 °C) under a nitrogen atmosphere for 4 h and then carefully quenched with an aqueous ammonium chloride solution (3 mL). The mixture was extracted with diethyl ether, and the combined ethereal extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to give a white powder (44 mg). Flash chromatography on silica gel (EtOAc/hexane, 25/75) and subsequent recrystallization from chloroform afforded 37 mg (98%) of the desired tricyclic aldehyde **31** as white needles: mp 188−189 °C; R_f 0.39 (EtOAc/hexane, 25/75); IR ($CHCl_3$) 1705 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.10 (s, 1 H), 5.32 (s br, 1 H), 3.96 (s, 4 H), 2.68 (dd, 1 H, J = 5.1, 1.5 Hz), 2.29 (m, 2 H), 2.10−1.41 (m, 13 H), 1.59 (s, 3 H), 1.39−1.15 (m, 2 H), 0.71 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.1, 135.5 120.9, 108.4, 64.3, 64.2, 45.8, 43.1, 41.6, 39.0, 31.2, 30.4, 28.7, 26.4, 24.5, 23.1, 21.6, 20.8, 20.3, 14.6; HRMS calcd for $C_{20}H_{30}O_3$ (M) 318.2195, found 318.2194. Anal. Calcd for $C_{20}H_{30}O_3$: C, 75.43; H, 9.50. Found: C, 75.88; H, 9.52.

Spiro[4,10-dimethyl-8-(hydroxymethyl)-$\Delta^{3,4}$-*trans*-decalin-9,1′-(3,3′-(ethylenedioxy)cyclohexane] (32). To a stirred solution of the aldehyde **31** (7.0 mg, 0.022 mmol) in 1.5 mL of a 1:1 mixture of ethanol and tetrahydrofuran was added sodium borohydride (8.3 mg, 0.22 mmol) in portions. The reaction mixture was stirred at rt under a nitrogen atmosphere for 50 min, followed by addition of water (2 mL) and extraction with diethyl ether. The organic extracts were combined and washed with brine, dried over anhydrous $MgSO_4$, filtered, and evaporated to give 9 mg of residue. Flash chromatography on silica gel, eluting with 25% and then 50% ethyl acetate in hexane, yielded 6.2 mg (88%) of the alcohol **32** as a clear oil: R_f 0.10 (EtOAc/hexane, 25/75); IR ($CHCl_3$) 3616 (OH) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.30 (s, br, 1 H), 3.91 (s, 4 H), 3.76 (m, 2 H), 2.3−0.8 (m, 19 H), 1.60 (s, 3 H), 0.66 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.8, 120.9, 108.8, 64.2, 64.1, 63.0, 42.5, 40.6, 38.5, 38.1, 30.9, 30.2, 29.5, 25.9, 25.1, 23.6, 23.2, 21.8, 19.9, 14.9; HRMS calcd for $C_{20}H_{32}O_3$ (M) 320.2351, found 320.2348.

Spiro[4,10-dimethyl-8-((*para*-toluenesulfonyloxy)-methyl)-$\Delta^{3,4}$-*trans*-decalin-9,1′-3′-oxocyclohexane] (8). To a cold (0 °C) solution of the alcohol **32** (20.0 mg, 0.0625 mmol) in 2 mL of chloroform, were successively added *p*-toluenesulfonyl chloride (48 mg, 0.25 mmol, 4.0 equiv), triethylamine (87 μL, 0.625 mmol, 10 equiv), and 4-(dimethylamino)pyridine (15.3 mg, 0.125 mmol, 2.0 equiv). After the addition, the cooling bath was removed and the reaction mixture was stirred under a nitrogen atmosphere at rt for 3 h. Aqueous sodium bicarbonate (5%, 4 mL) was added to hydrolyze the unreacted *p*-TsCl. After being stirred for 30 min, the mixture was extracted with chloroform. The combined chloroform layers were sequentially washed with a 0.15 N aqueous $NaHSO_4$ solution, water, and a saturated $NaHCO_3$ solution, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting crude tosylate (36 mg) was, without further purification, carried through to the next step as follows. To a solution of this crude ketal tosylate in 5 mL of THF was added 1.5 mL of 2 N hydrochloric acid. The resulting mixture was stirred under a nitrogen atmosphere at ambient temperature for 16 h. After being diluted with brine (5 mL), the mixture was extracted with diethyl ether. The extracts were combined and washed with water and aqueous $NaHCO_3$, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. Flash chromatography of the residual liquid on silica gel column (EtOAc/hexane, 14/86) gave 26 mg (97% over two steps) of the desired keto tosylate **8** as a pale yellow oil: R_f 0.30 (EtOAc/Hexane, 25/75); IR ($CHCl_3$) 1705, 1662 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.79 (d, 2 H, J = 8.3 Hz), 7.34 (d, 2 H, J = 8.3 Hz), 5.29 (s, br, 1 H), 4.4−4.1 (m, 2 H), 2.43 (s, 3 H), 2.3−0.8 (m, 18 H), 1.57 (s, 3 H), 0.65 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.3, 135.0, 130.9, 129.9, 129.8, 128.8, 127.8, 127.0, 120.9, 71.0, 41.9, 41.0, 38.3, 37.1, 36.3, 36.0, 29.8, 29.3, 28.7, 27.3, 23.6, 22.9, 21.6, 19.4, 14.1; HRMS calcd for $C_{25}H_{34}O_4S$ (M) 430.2178, found 430.2181.

4,16-Nor-$\Delta^{3,4}$-2-Desoxystemodinone (6). To a stirred solution of the keto−tosylate **8** (26 mg, 0.0625 mmol) in 4 mL of anhydrous methanol at 0 °C under an argon atmosphere was added 138 μL of sodium methoxide−methanol solution (25 wt % solution, 0.605 mmol, 10 equiv) *via* syringe. The resulting yellowish solution was stirred at 0 °C for 15 h, and the keto− tosylate was completely consumed according to TLC. The reaction was then quenched by addition of a saturated aqueous solution of ammonium chloride (2 mL). After being transferred into a test tube, the mixture was extracted with diethyl ether (3 mL × 3). The combined ethereal layers were washed with a saturated aqueous NaCl solution (3 mL), dried over anhydrous $MgSO_4$, filtered, and evaporated *in vacuo*. The crude product was purified by flash chromatography on silica gel (EtOAc/hexane, 2/98 and 15/85) using a Pasteur pipet as the column. This reaction gave a single cyclization product **6** (14 mg, 89%): mp 108−109 °C; R_f 0.37 (EtOAc/hexane, 15/85); IR ($CHCl_3$) 1710 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.35 (s br, 1 H), 2.67 (m, 1 H), 2.46−2.33 (m, 2 H), 2.26−1.10 (m, 16 H), 1.62 (s, 3 H), 0.97 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$)

δ 215.2, 136.3, 120.8, 55.5, 51.2, 47.1, 40.2, 38.0, 37.2, 36.4, 35.3, 34.3, 32.2, 28.0, 23.2, 22.7, 21.5, 18.5; HRMS calcd for $C_{18}H_{26}O$ (M) 258.1984, found 258.1986.

Tetracyclic Tertiary Alcohols 34 and 35. To a stirred and precooled solution of the tetracyclic ketone **6** (10.0 mg, 0.039 mmol) in 1.2 mL of diethyl ether at 0 °C under an argon atmosphere was added a methylmagnesium bromide solution (3.0 M in Et_2O, 130 μL, 0.39 mmol, 10 equiv) *via* syringe. After the addition, the cooling bath was removed and the reaction mixture was stirred at ambient temperature (19 °C) for 150 min. The reaction was quenched by addition of saturated aqueous ammonium chloride (1 mL) and water (1 mL). After being transferred into a test tube, the mixture was extracted with diethyl ether. The organic extracts were combined and washed with water (2 mL), dried over anhydrous $MgSO_4$, filtered, and evaporated on a rotary evaporator to give 12 mg of residual solid. The TLC and ^{1}H NMR of this residue indicated it was a mixture of two epimeric alcohols, as expected. Gravity chromatography on silica gel (EtOAc/Hexane, 10/90) afforded the desired alcohol **34** (6.0 mg, white solid), along with its epimer **35** (2.1 mg, white solid) in 76% total yield **4-Nor-$\Delta^{3,4}$-2-Desoxystemodinone (34)**: mp 114−115.5 °C; R_f 0.28 (EtOAc/hexane, 15/85); IR ($CHCl_3$) 3571, 3421 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.36 (s br, 1H), 2.18−1.20 (m, 20 H), 1.61 (s, 3 H), 1.13 (s, 3 H), 0.91 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.7, 120.7, 72.4, 47.6, 46.1, 39.1, 37.8, 36.5, 33.6, 31.9, 30.9, 30.7, 29.7, 28.6, 27.9, 23.4, 22.8, 21.4, 18.0; HRMS calcd for $C_{19}H_{30}O$ (M) 274.2297, found 274.2280. **4-Nor-$\Delta^{3,4}$-16-epi-2-desoxystemodinone (35)**: mp 135−137 °C; R_f 0.23 (EtOAc/hexane, 15/85); IR ($CHCl_3$) 3569, 3426 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.33 (s, br, 1 H), 2.2−0.9 (m, 20 H), 1.60 (s, 3 H), 1.25 (s, 3 H), 0.89 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.8, 120.6, 72.6, 48.2, 46.6, 39.7, 37.8, 34.6, 34.4, 33.4, 31.9, 29.7, 27.9, 27.3, 26.5, 23.4, 22.8, 21.4, 18.0; HRMS calcd for $C_{19}H_{30}O$ (M) 274.2297, found 274.2296.

4-Nor-$\Delta^{3,4}$-Stemodinone (10). Chromium trioxide was dried over P_2O_5 in a vacuum desiccator overnight prior to use. To a stirred suspension of chromium trioxide (74.4 mg, 0.744 mmol, 20 equiv) in 980 μL of dry methylene chloride at −20 °C under a dry argon atmosphere was added 3,5-dimethylpyrazole (71.6 mg, 0.744 mmol) in one portion. After the solution was stirred at −20 °C for 15 min, the tetracyclic olefin **34** (10.2 mg, 0.0372 mmol) in 120 μL of dichloromethane was introduced *via* syringe over a period of 3 min. Upon addition, the reaction mixture was warmed to −15 °C and stirred at this temperature for 5 h. An aqueous sodium hydroxide solution (5 N, 500 μL) was added, the resulting mixture was stirred at 0 °C for 1 h, and two layers were separated. After being transferred into a test tube, the mixture was extracted with dichloromethane. The combined organic layers were washed with 1 N hydrochloric acid to remove the 3,5-dimethylpyrazole, then washed with water and saturated sodium bicarbonate solution, dried over anhydrous Na_2SO_4, filtered, and evaporated. Column chromatography of the residue on silica gel (EtOAc/hexane, 15/85) yielded 7.8 mg (73%) of the expected A-ring enone **10** as an off-white solid: mp 195−196 °C; R_f 0.22 (EtOAc/hexane, 50/50); IR ($CHCl_3$) 3560, 3380, 1661 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 5.81 (s, br, 1 H), 2.65−2.45 (m, 2 H), 2.30−1.20 (m, 16 H), 1.89 (s, 3 H), 1.14 (s, 3 H), 1.09 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.5, 162.2, 125.5, 72.16, 49.1, 48.1, 46.2, 40.8, 40.0, 39.8, 34.3, 34.1, 33.6, 33.0, 27.0, 26.5, 23.0, 21.9, 19.0; HRMS calcd for $C_{19}H_{28}O_2$ (M) 288.2089, found 288.2093.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for all new compounds (43 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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