Organoiron-Templated Stereocontrolled Alkylation of Enolates: Functionalization of Cycloheptadienones To Give Useful Synthetic Building Blocks

Anthony J. Pearson* and Kieyoung Chang

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

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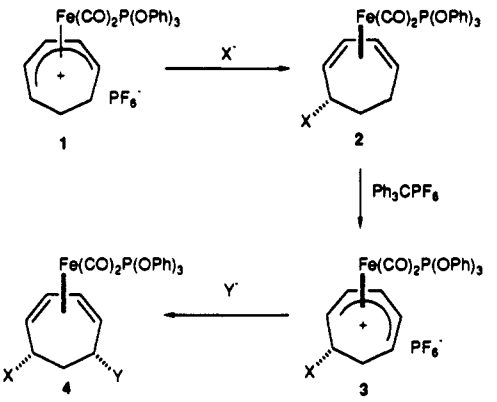
Conversion of η^4-cycloheptatriene–$Fe(CO)_2P(OPh)_3$ to ketocycloheptadiene–$Fe(CO)_2P(OPh)_3$ complex **7** was accomplished by hydroboration followed by Swern oxidation. Methylation and hydroxylation of the enolate from **7** proceeds with complete stereoselectivity, anti to the metal moiety, and introduction of two methyl or hydroxyl groups at the α and α' positions was accomplished in high overall yield. Reduction of the ketone group on these complexes occurs with high stereoselectivity and is controlled by the boat conformation adopted by these complexes. The product of these reaction sequences were demetalated to give cycloheptadiene derivatives that were further functionalized to give a C(9)–C(14) subunit of calyculin A_1 and a C(19)–C(25) subunit of swinholide A.

During the past 10 years we have developed methodology[1] for the stereocontrolled functionalization of cycloheptadiene via sequential nucleophile additions to the cycloheptadieneiron complex **1** and the derived alkyl-substituted dienyl complex **3** (Scheme I). This chemistry has been applied to syntheses of the (+)-Prelog–Djerassi lactone[2] as well as subunits for the macrolide antibiotics tylosin[2,3] and carbomycin B.[3] We have developed similar nucleophile addition sequences for molybdenum complexes of cyclic dienes,[4] and more recently we have shown that excellent stereocontrol can be achieved during the alkylation of enolates on cyclic π-allylmolybdenum complexes[5] and functionalization of uncomplexed double bonds on η^4-triene–$Fe(CO)_2L$ complexes (L = trialkylphosphine or trialkyl phosphite).[6,8] The potential for using this approach in constructing synthetic building blocks for, e.g., macrolide and ionophore antibiotics depends on the stereochemical homogeneity of the products, on the facility with which decomplexation of the organometallic can be effected, and also on the ease with which the so-formed organic ligand can be manipulated. The organomolybdenum systems that we have used previously are somewhat problematic during decomplexation of the π-allyl moiety, especially with cycloheptenyl systems,[7] and so we have undertaken the studies described herein, which

Scheme I



are aimed at utilizing a diene–$Fe(CO)_2L$ as the stereodirector during functionalization of seven-membered-ring enolates.[8]

While this paper is not primarily concerned with applications in synthesis, we have attempted to point out important potential target molecules to which this chemistry might be applied. With this in mind, we have undertaken additional studies on controlled functionalization of trisubstituted cycloheptadienes that can be obtained via this methodology.

Results and Discussion

(1) Enolate Alkylations and Hydroxylations. Deprotonation of complex **1**, using Et_3N/CH_2Cl_2, afforded the η^4-triene complex **5** in quantitative yield, hydroboration of which afforded the alcohol **6** (92%). Swern oxidation[9] of **6** gave the ketone **7** in 81% yield. Noteworthy features of this reaction sequence are as follows: (1) The $Fe(CO)_2L$ group controls the stereochemical outcome during hydroboration, since the triene–Fe system is quite flat and attack on the uncomplexed double is controlled by the steric bulk of the metal moiety. (2) The hydroboration is completely regioselective owing to stabilization of incipient positive charge in the transition state by the neighboring dieneiron moiety. (3) Oxidation of the alkylborane

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(2) Pearson, A. J.; Lai, Y. S.; Lu, W.; Pinkerton, A. A. *J. Org. Chem.* **1989**, *54*, 3882.

(3) Pearson, A. J.; Ray, T. *Tetrahedron Lett.* **1986**, *27*, 3111.

(4) Pearson, A. J.; Khan, M. N. I.; Clardy, J. C.; Cun-heng, H. *J. Am. Chem. Soc.* **1985**, *107*, 2748. Pearson, A. J.; Khan, M. N. I. *J. Org. Chem.* **1985**, *50*, 5276.

(5) Pearson, A. J.; Mallik, S.; Mortezaei, R.; Perry, M. W. D.; Shively, R. J., Jr.; Youngs, W. J. *J. Am. Chem. Soc.* **1990**, *112*, 8034. Pearson, A. J.; Mallik, S.; Pinkerton, A. A.; Adams, J. P.; Zheng, S. *J. Org. Chem.* **1992**, *57*, 2910.

(6) Pearson, A. J.; Srinivasan, K. *J. Org. Chem.* **1992**, *57*, 3965. For $Fe(CO)_3$ complexes, see also: Banthorpe, D. V.; Fitton, H.; Lewis, J. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2051. Evans, G.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1975**, *102*, 507. Grée, R. *Synthesis* **1989**, 341. Barton, D. H. R.; Gunatilaka, A. A. L.; Nakanishi, T.; Patin, H.; Widdowson, D. A.; Worth, B. R. *J. Chem. Soc., Perkin Trans. 1* **1976**, 821. Rosenblum, M.; Watkins, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 6316. Franck-Neumann, M.; Martina, D. *Tetrahedron Lett.* **1975**, 1759. Rigby, J. H.; Ogbu, C. O. *Tetrahedron Lett.* **1990**, *31*, 3385 and references cited therein.

(7) Mallik, S. Ph.D. Dissertation, Case Western Reserve University, 1992.

(8) Preliminary communication: Pearson, A. J.; Chang, K. *J. Chem. Soc., Chem. Commun.* **1991**, 394.

(9) Mancuso, A. J.; Huang, S. L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480.

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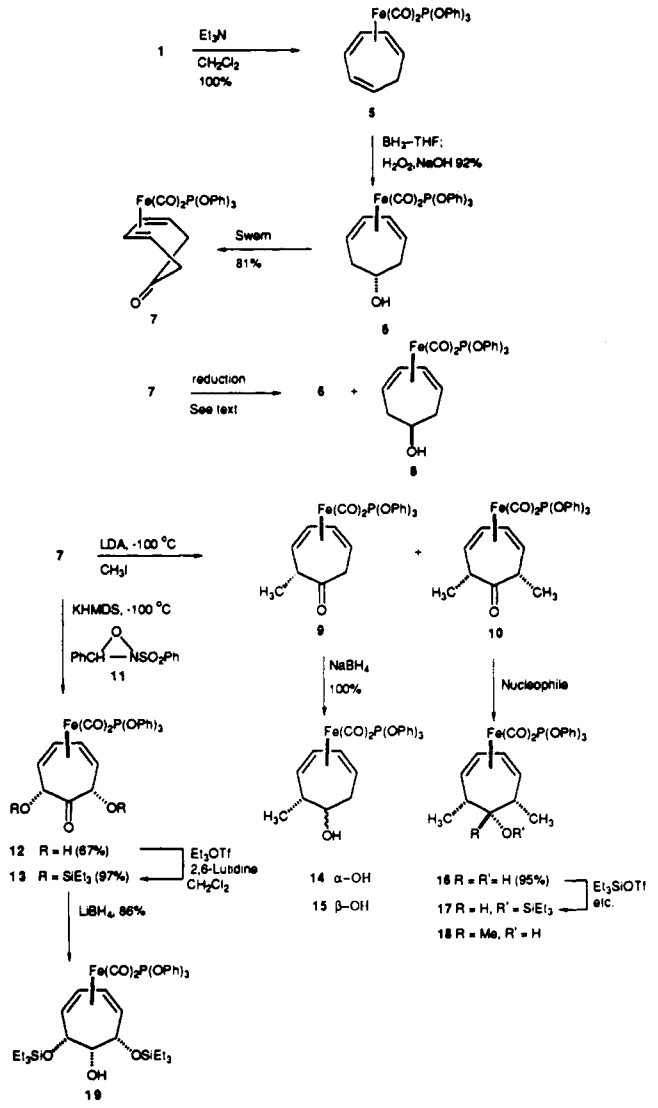
Scheme II



intermediate causes no decomposition of the organometallic, as was also shown in earlier work.[10]

The ketone 7 appears to exist predominantly in the boat conformation shown, as demonstrated earlier for substituted cycloheptadieneiron complexes.[11] This allows conformationally controlled nucleophilic addition to the ketone carbonyl. Thus, sodium borohydride reduction of 7 gave a 3:5 mixture of 6 and the epimeric alcohol 8 in 98% yield, while use of the sterically more demanding L-Selectride (Aldrich), gave exclusively 6 in quantitative yield. This result is consistent with preferred approach of the reagent from the more accessible convex face of 7, an effect which becomes magnified to considerable advantage with the substituted compounds to be described.

Treatment of 7 in tetrahydrofuran with LDA at −100 °C, followed by reaction of the enolate with methyl iodide, gave a mixture of monomethylated (9) and dimethylated (10) products in 86% and 8% yields, respectively (Scheme II). We were unable to effect clean monoalkylation of 7, even when LDA was used as the limiting reagent, but 9 and 10 could be separated by chromatography. Alkylation of the mixture of 9 and 10 (LDA, THF, −100 °C, MeI) gave 10 as a single product in 84% overall yield from 7. No evidence for epimeric compounds or products of *gem*-dialkylation was found in the ^{1}H NMR spectrum of the crude product. The cis orientation of the two methyl groups was evidenced by their coincidence in the NMR spectrum (6 H, d, see the Experimental Section), and the anti stereochemical relationship with the metal was initially assumed by analogy with the hydroboration reaction described above.

Double hydroxylation of 7 was readily accomplished by sequential treatment with potassium hexamethyldisilazide (KHMDS) at −100 °C, and the Davis oxaziridine[12] reagent 11, giving 12 as a single diastereomer in 67% yield. Clean monohydroxylation of 7 could not be effected, again reflecting the enhanced acidity of protons α to the ketone as a result of their "pseudoallylic" nature (allylic except that the C=C double bond is not free). Protection of 12 as its bis(triethylsilyl) ether 13 was accomplished in 97% yield as shown in Scheme II.

Reduction of complexes 9, 10, and 13 with borohydride was studied. Complex 9 gave a 4:1 mixture of 14 and 15, the stereochemistry of the major product being assigned by analogy with the reduction of 7 and (later) 10. The latter complex gave 16 in 95% yield, and no stereoisomeric compounds could be detected in the ^{1}H NMR spectrum. Protection of 16 as its triethylsilyl ether 17 provided material suitable for further elaboration (later). Owing to overlap between the key peaks in the NMR spectra of both 16 and 17, confirmation of the stereochemical course of the borohydride reduction was not possible at this stage. Indeed, it was not until after conversion to the later cycloheptenone derivatives that the stereochemistry of these compounds could be confirmed spectroscopically (vide infra). Reaction of 10 with methylmagnesium bromide also proceeded with complete stereoselectivity to give 18, although this reaction was more sluggish and gave a poorer mass balance (44% yield of 18 at 95% conversion). Reduction of 13 with sodium borohydride was rather slow, but lithium borohydride effected its clean conversion to 19 (86%), again as a single stereoisomer (NMR). In this way, *three contiguous chiral centers can be set in place with no stereochemical ambiguity* by taking advantage of the steric effects of the organoiron system as well as the previously discussed[11] conformational rigidity of the cycloheptadieneiron system. This methodology can only be useful, however, if the metal can be disengaged from the products and if the resulting cycloheptadienes can be functionalized in a controlled manner.

(2) Decomplexation and Further Reactions. We have focused our efforts on manipulations of the dimethyl derivatives 16 and 17 to give potentially useful acyclic building blocks. Direct decomplexation of 16 using copper(II) chloride[13] afforded the cycloheptadiene 20 in 96% yield, which was readily protected as the triethylsilyl ether 21 (Scheme III). Decomplexation of 17 to give 21 was best effected using Collins' reagent in refluxing methylene chloride.[2] Either of these methods allowed access to material that could be used in studies on diene functionalization. Reaction of 21 with singlet oxygen[2,14] gave a

(10) The oxidative workup during hydroboration does not cause decomposition of diene–$Fe(CO)_3$ or diene–$Fe(CO)_2PR_3$, although it should be noted that treatment with alkaline hydrogen peroxide is known to cause demetalation of such complexes, see: Franck-Neumann, M.; Hertz, D.; Martina, D. *Tetrahedron Lett.* **1983**, *24*, 1615.

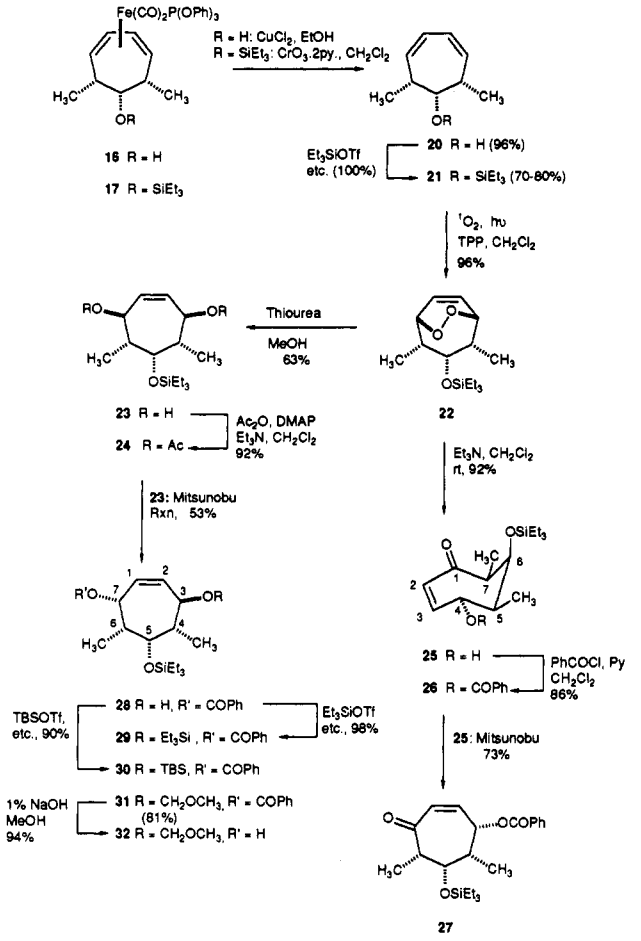
(11) Pearson, A. J.; Kole, S. L.; Ray, T. *J. Am. Chem. Soc.* **1984**, *106*, 6060.

(12) Davis, F. A.; Billmers, J. M.; Gosciniak, D. J.; Towson, J. C.; Bach, R. D. *J. Org. Chem.* **1986**, *51*, 4240 and referenced cited therein.

(13) Thompson, D. J. *J. Organomet. Chem.* **1976**, *108*, 381.

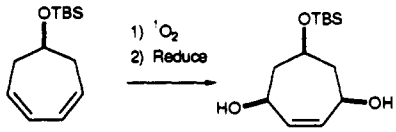
(14) Denny, R. W.; Nickon, A. *Org. React.* **1973**, *20*, 133.

Scheme III



single endoperoxide **22**, the stereochemical assignment of which was based on subsequent transformations. Thus, reduction of **22** with thiourea gave a single diol **23**, which was readily converted to the diacetate **24**. The ^{1}H NMR spectrum of **23** showed diaxial coupling (9.1 Hz) between H(1) and H(7) [H(4) and H(5)] as expected for the conformation shown and by comparison with our earlier assignments in related compounds, in which both diasteromeric series were available.[2] Treatment of the endoperoxide **22** with triethylamine gave the hydroxy enone **25** in 92% yield, which also showed the expected diaxial coupling (7.0 Hz) between H(4) and H(5). Further confirmation of this came from a comparison of the benzoate **26** with the epimeric compound **27**, the latter being produced by Mitsunobu reaction[15] on **25**. Compound **26** showed $J_{4,5}$ = 12.3 Hz, while **27** gave H(4) as a broadened singlet, although these were difficult to assign unambiguously owing to the partial overlap of the H(4) resonance with vinyl resonances. In addition to these NMR observations, both **25** and **26** showed H(6) as a *singlet*, indicating a dihedral angle with H(5) and H(7) of ca. 90° and thereby confirming the earlier stereochemical assignment of complex **16**. The consistency between all of these observations and our own earlier conformational analysis of cycloheptadiene–Fe(CO)$_2$L complexes[11] leaves no doubt about their stereochemistry.

Formation of the endoperoxide from **21** appears to be under steric control from the methyl groups, since Johnson has shown[16] that 6-((*tert*-butyldimethylsilyl)oxy)-1,3-cycloheptadiene reacts with singlet oxygen syn to the OTBS group (eq 1). Thus, the stereodirecting effects of methyl groups and triethylsilyl ether in **21** are in opposition, and the proximity of the methyls to the diene makes them the dominant controlling feature in this reaction.



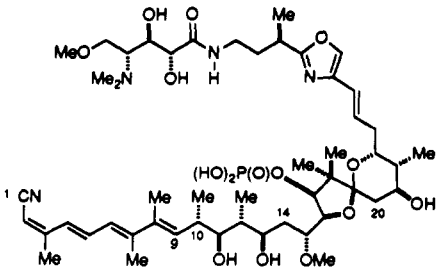
Eq. 1

Adjustment of the stereochemistry of the diol **23** may be an important consideration for the further applications of these compounds in synthesis.[2] We have found that mono-Mitsunobu inversion of **23** can be effected to give **28** in reasonable yield (53%). We did not observe any doubly inverted compounds in this reaction, but we were unable to improve the yield[17] or explain the poor mass balance. Protection of **28** as triethylsilyl ether **29**, TBDMS ether **30** or methoxymethyl ether **31** proceeded satisfactorily, and alkaline hydrolysis of **31** could be accomplished to give **32**. Further evidence for the stereochemistry assigned to diol **23** was available from the ^{1}H NMR spectra of **29–32** which showed H(3) as a broad doublet with $J_{3,4}$ = 8 Hz, while H(7) was a broad singlet with no discernable coupling to H(6), indicating the chair conformation shown in the structure.

(3) Conversion of Cycloheptene Derivatives to Acyclic Systems. As potential target molecules for this chemistry, we had in mind a C(9)–C(14) subunit of calyculin A (**48**),[18] a C(19)–C(25) subunit of swinholide A (**49**),[19] and a C(7)–C(12) subunit of tirandamycin (**50**).[20] What follows is a discussion of the chemical transformations that are necessary to reach these targets and how they were accomplished.

The product **27** of Mitsunobu inversion on **25** has relative stereochemistry corresponding to C(10)–C(13) of calyculin A and requires C=C double bond cleavage together with excision of the C(2) carbon α to the ketone. The same relationship holds between enone **25** and the tirandamycin subunit so that the methods used for **27** can in principle be applied to this target molecule. Direct ozonolytic cleavage of **27** proved troublesome, and so an indirect route was chosen (Scheme IV). Thus, osmylation of **27** gave the diol **33** in 95% yield as a mixture of diastereomers. Cleavage of **33** with lead tetraacetate in benzene/methanol[21] gave a mixture of **34** and the lactol **35** (resulting from partial in situ hydrolysis of the triethylsilyl ether), which was treated directly with 10% hydrochloric acid/tetrahydrofuran to effect conversion to the lactol. Since this was obtained as a mixture of anomers, it was oxidized

(15) Mitsunobu, O. *Synthesis* **1981**, 1.
(16) Johnson, C. R.; Senanayake, C. H. *J. Org. Chem.* **1989**, *54*, 735.
(17) The modification reported by Martin and Dodge did not give any improvement in the present reaction. See: Martin, S. F.; Dodge, J. A. *Tetrahedron Lett.* **1991**, *32*, 3017.
(18) Kato, Y.; Fusetani, N.; Matsunaga, S.; Hashimoto, K.; Fujita, S.; Furuya, T. *J. Am. Chem. Soc.* **1986**, *108*, 2780. Kato, Y.; Fusetani, N.; Matsunaga, S.; Hashimoto, K.; Koseki, K. *J. Org. Chem.* **1988**, *53*, 3830. Matsunaga, S.; Fusetani, N. *Tetrahedron Lett.* **1991**, *32*, 5605. For recent synthetic studies, see: Evans, D. A.; Gage, J. R. *Tetrahedron Lett.* **1990**, *31*, 6129.
(19) Doi, M.; Ishida, T.; Kobayashi, M.; Kitagawa, I. *J. Org. Chem.* **1991**, *56*, 3629 and references cited therein.
(20) Duchamp, D. J.; Branfman, A. R.; Button, A. C.; Rinehart, K. L., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 4077. MacKellar, K. L.; Grostic, M. F.; Olson, E. C.; Wnuk, R. J.; Branfman, A. R.; Rinehart, K. L., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 4943. For a summary of recent synthetic literature, see: Paterson, I.; Lister, M. A.; Ryan, G. R. *Tetrahedron Lett.* **1991**, *32*, 1749, and references cited therein.
(21) Danishefsky, S.; Schuda, P. F.; Kitahara, T.; Etheridge, S. *J. Am. Chem. Soc.* **1977**, *99*, 6066.



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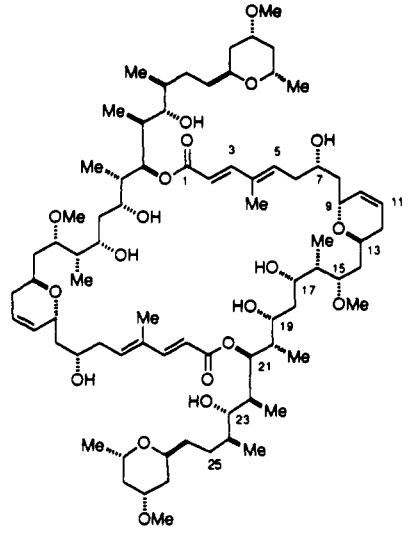

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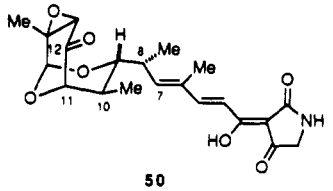

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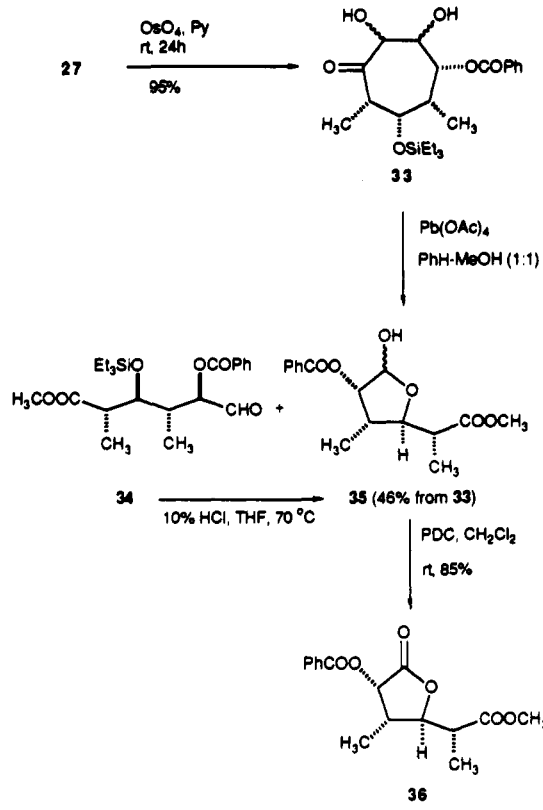
to the lactone **36** for characterization purposes. Formation of the latter compound demonstrates that the cycloheptenones obtained using our methodology can be converted to potentially viable building blocks for important biologically active molecules, although the sequence (12 steps from **7** to give racemic compound) requires some improvement.

Conversion of **25** into a swinholide A C(19)–C(25) subunit requires stereoselective introduction of a methyl substituent at C(3), syn to the hydroxyl. Initial experiments were based on our earlier observations[2] that reactions of dimethylcuprate with cycloheptenyl acetates proceed with anti stereochemistry.[22] Compounds **29–31** and the acetates **41** and **42** (Scheme V) appeared to be appropriate substrates for this reaction, since it was anticipated that displacement of the allylic benzoate or acetate would give molecules of structure **37**. In the event, however, none of these substrates gave any of the desired products. Therefore, our attention turned to cuprate additions on suitably protected hydroxycycloheptenones, since we have shown previously[2] that hydroxyl protecting groups such as benzoyl and methoxymethyl ether tend to direct syn during these reactions.

Reaction of **39** with Me_2CuLi under the usual conditions gave a single conjugate addition product **43** in 88% yield.

Scheme IV



The stereochemistry was assigned by comparison of NMR coupling constant data with a series of related cycloheptenones for which both diastereomers were available and for which the stereochemistry has been confirmed by X-ray structure determination.[2,23] Thus, the ^1H NMR spectrum of **43** showed H(5) as a doublet of doublets (J = 8.6, 3.4 Hz) with only one diaxial coupling; analogous compounds prepared earlier give this proton as a doublet of doublets ($J \sim 6$–8 and ~ 3 Hz) while the anti diastereomer typically shows a dd or triplet with two diaxial coupling constants (~ 8 Hz). The NMR data for **44** is therefore consistent with the conformation depicted for this molecule. It may be noted that the stereodirecting effect observed with **39** is much more pronounced than with our earlier, simpler compounds. This may be due in part to the presence of the axial OTES group (see structure) which assists by shielding the α-face of the molecule.

In order to open the cycloheptane ring regioselectively, it was necessary to trap the enolate during cuprate addition to give the enol silane **44** and cleave the double bond. This turned out to be more difficult than expected, since **44** was rather unstable, undergoing very facile hydrolysis to give **43**, and direct ozonolysis gave mixtures of products that were difficult to separate. Accordingly, crude **44** was treated with *m*-chloroperoxybenzoic acid[24] to give the α-ketol **45**. Attempted direct cleavage of **45** with lead tetraacetate was again unsuccessful, so it was converted to the diastereomeric mixture of diols **46**. Treatment of **46** with lead tetraacetate gave **47**, having relative stereochemistry corresponding to the C(20)–C(24) stereocenters of swinholide A.

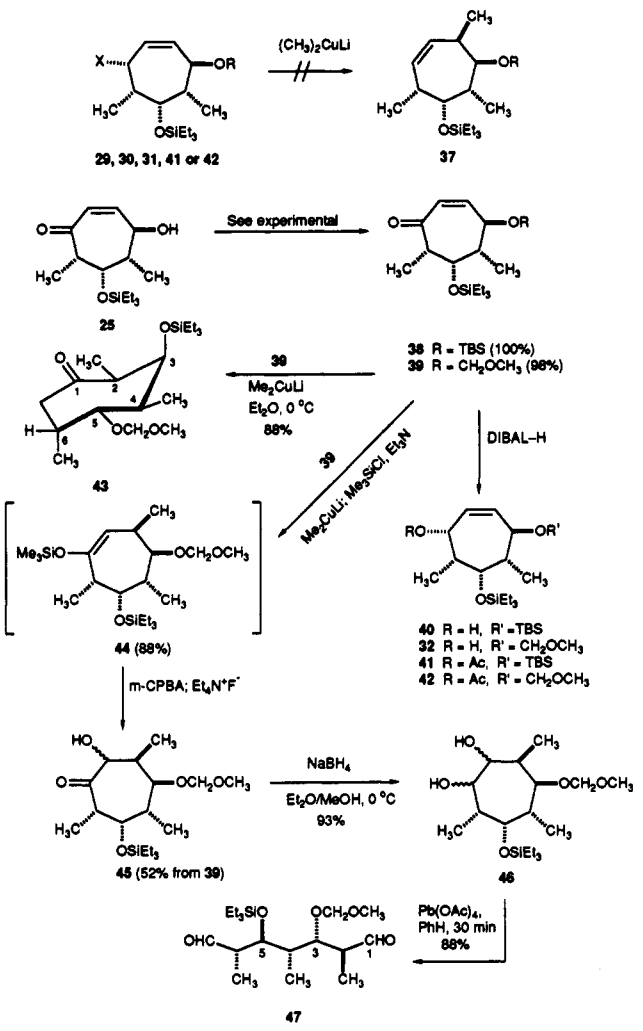
The sequence from complex **7**, which is readily prepared on large scale, to **47** requires 12 steps and produces racemic

(22) Goering, H. L.; Tseng, C. C. *J. Org. Chem.* **1983**, *48*, 3986 and references cited therein.

(23) Lai, Y. S. Ph.D. Dissertation, Case Western Reserve University, 1989.

(24) Rubottom, G. M.; Gruber, J. M. *J. Org. Chem.* **1978**, *43*, 1599.

Scheme V



material in ca. 13% overall yield. In order for this to be synthetically useful, optically pure **47** is required, and in this context it may be noted that we[2] and Johnson's group[16] have shown that asymmetrization of cycloheptene meso diacetates is readily accomplished by enzyme hydrolysis. In principle, therefore, nonracemic **47** is available from the meso diacetate **24** via its treatment with lipase and subsequent conversion to enones such as **39**.[25]

Experimental Section

General procedures are as reported elsewhere.[1,2,8]

Dicarbonyl(η^4-cyclohepta-1,3,5-triene)(triphenyl phosphite)iron (5). To a solution of 1.98 g (3 mmol) of dicarbonyl(η^5-cyclohepta-1,3-dienylium)(triphenyl phosphite)iron hexafluorophosphate[11] in 10 mL of CH_2Cl_2 at rt was added triethylamine (15 mL, 10.6 mmol). The solution was stirred for 20 min, water (10 mL) was added, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated, and the residue was purified by flash chromatography (10% EtOAc–hexane) to give the triene complex **5** (1.45 g, 100%) as a pale yellow solid. Mp: 83–85 °C. R_f: 0.57 (20% EtOAc–hexane). IR: 3005, 2950, 2000, 1950, 1450 cm^{-1}. ^{1}H NMR (200 MHz): δ 7.35–7.10 (m, 15 H, aromatic), 5.62 (ddt, J = 2.6, 4.6, 9.4 Hz, 1 H, C_1-H), 4.98 (m, 1 H, C_2-H), 4.68–4.59 (m, 2 H, C_1-H, C_4-H), 3.06 (ddd, J = 1.4, 3.8, 4.3 Hz, 1 H, C_6-H), 2.76 (m, 1 H, C_3-H), 2.17–1.93 (m, 2 H, C_7-endo and exo). ^{13}C NMR (75 MHz): δ 214.8, 151.5, 129.7, 129.1, 124.8, 124.6, 121.3, 92.1, 86.8, 59.3, 54.7, 30.6. HRMS: calcd for $C_{25}H_{23}O_3Fe$ P (M^+ – 2CO) 458.0734, found 458.0732.

Dicarbonyl(η^4-6-*exo*-hydroxycyclohepta-1,3-diene)(triphenyl phosphite)iron (6). To a solution of 7.3 g (14.19 mmol) of triene complex **5** in 60 mL of THF was added BH_3–THF (1.0 M solution, 31.22 mL, 31.22 mmol) at 0 °C. The solution was stirred for 2 h at rt and then cooled to 0 °C. Water (20 mL) was added, followed by NaOH (30% aqueous solution, 29.2 mL) and H_2O_2 (30% aqueous solution, 29.2 mL). The reaction mixture was stirred for 45 min at 0 °C and then diluted with Et_2O (100 mL). The organic layer was separated, and aqueous layer was extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with H_2O (2 × 40 mL) and brine (1 × 40 mL), dried ($MgSO_4$), filtered, and evaporated. The residue was purified by flash chromatography (30% petroleum ether–Et_2O) to give the alcohol **6** (6.95 g, 92%) as pale yellow solid. Mp: 90–91 °C. R_f: 0.16 (50% Et_2O–hexane). IR: 3603, 3030, 2000, 1950, 1590, 1190 cm^{-1}. ^{1}H NMR (200 MHz): δ 7.36–7.12 (m, 15 H, aromatic), 4.80–4.74 (m, 2 H, C_2-H, C_3-H), 3.55–3.52 (m, 1 H, C_6-H), 2.52–2.45 (m, 2 H, C_1-H, C_4-H), 2.06 (ddd, 2 H, $J_{endo-exo}$ = 16.7, $J_{exo-exo}$ = 5.1, 4.3 Hz, C_5-exo H, C_7-exo H), 1.09 (ddd, 2 H, $J_{endo-exo}$ = 16.7, $J_{endo-exo}$ = 5.1, 4.3 Hz, C_5-endo H, C_7-endo H), 1.54 (d, 1 H, J = 8.3 Hz, OH). ^{13}C NMR (75 MHz): δ 215.5, 151.4, 129.8, 125.0, 121.4, 88.2, 68.9, 52.4, 35.1. HRMS: calcd for $C_{25}H_{23}O_3Fe$ P (M^+ – 2CO – H_2O) 458.0734, found 458.0738.

Dicarbonyl(η^4-6-oxocyclohepta-1,3-diene)(triphenyl phosphite)iron (7). To a stirred solution of 1.40 g (10.98 mmol) of oxalyl chloride in 16 mL of CH_2Cl_2 at −78 °C was added DMSO (1.72 g, 21.96 mmol) in 10 mL of CH_2Cl_2 over 3 min. The turbid reaction mixture was stirred for 5 mim. A solution of 2.63 g (4.98 mmol) of the alcohol **6** in 60 mL of CH_2Cl_2 was added to the reaction mixture over 5 mim. The solution was stirred 45 min at −78 °C, and Et_3N (2.52 g, 24.9 mmol) was added. The resulting solution was warmed to −20 °C and stirred for 2 h. Water (30 mL) was added, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 30 mL), and the combined organic layers were washed with brine (40 mL), dilute HCl (40 mL), water, and 6% K_2CO_3 (40 mL). The organic layer was dried ($MgSO_4$), filtered, and evaporated, and the residue was purified by flash chromatography (35% hexane–CH_2Cl_2) to give the ketone **7** (2.12 g, 81%). Mp: 117.5 °C dec. R_f: 0.43 (20% EtOAc–hexane). IR: 3015, 2000, 1950, 1710, 1595, 1195 cm^{-1}. ^{1}H NMR (200 MHz): δ 7.4–7.2 (m, 15 H, aromatic), 4.74–4.68 (m, 2 H, C_2-H, C_3-H), 2.76–2.50 (m, 6 H, C_1-H, C_4-H, C_5-exo H, C_7-exo H). ^{13}C NMR (75 MHz): δ 214.2, 207.2, 151.7, 129.8, 125.2, 121.4, 88.5, 51.9, 44.4.

Reduction of 7 by $NaBH_4$. To a solution of 48.7 mg (0.09 mmol) of **7** in a mixture of Et_2O (8 mL) and MeOH (2 mL) was added 10.4 mg (0.276 mmol) of $NaBH_4$ in small portions at 0 °C. The reaction mixture was stirred for 1.5 h at 0 °C. The organic solvents were removed. EtOAc (20 mL) was added. The organic layer was washed with brine (2 × 10 mL). The separated organic layer was dried ($MgSO_4$), filtered, and evaporated. The residue was purified by flash chromatography (29% EtOAc–Hex) to give a 5:3 (by ^{1}H NMR) mixture of **6** and **8**. ^{1}H NMR (200 MHz): δ 7.42–720 (m, aromatic), 4.83 (ddd, J = 6.6, 4.1, 2.5 Hz, C_2-H, C_4-H), 4.60 (ddd, J = 6.5, 4.1, 2.4 Hz, C_2-H, C_4H), 3.61–3.55 (m, C_6-H), 3.13–3.02 (m, C_6-H), 2.82–2.72 (m, C_1-H, C_4-H), 2.59–2.50 (m, C_1-H, C_4-H), 2.76–2.11 (m, C_5-H, C_7-H), 2.09–1.91 (m, C_5-H, C_7-H), 1.71 (s, OH), 1.64 (s, OH).

Reduction of 7 by L-Selectride. To a solution of 97.4 mg (0.18 mmol) of **7** in 6 mL of THF was added 368 μL of L-Selectride (1 M soln in THF, 0.36 mmol) slowly at −78 °C. The reaction mixture was stirred for 2 h at −78 °C. H_2O (3 mL) was added, followed by 30% aqueous NaOH (3 mL) and 30% aqueous H_2O_2 (3 mL) with stirring at 0 °C. The resulting reaction mixture was stirred for 20 min at rt. The solution was extracted with EtOAc (30 mL). The aqueous layer was extracted with EtOAc (2 × 15 mL), and the combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The residue was purified by flash chromatography (30% EtOAc–hexane) to give alcohol **6** exclusively. The spectroscopic data were the same as **6** from **5**.

Dicarbonyl(η^4-5-*exo*-methyl-6-oxocyclohepta-1,3-diene)(triphenyl phosphite)iron (9). To a stirred solution of i-Pr_2-

(25) We have successfully carried out the enzymatic hydrolysis of **24** to give optically active hydroxyacetate, but this is not included here because full characterization and determination of absolute stereochemistry have not been undertaken.

NH (190.9 mg, 1.89 mmol) in 4 mL of THF at −78 °C was added *n*-BuLi (1.27 M, 1.34 mL, 1.742 mmol). The solution was stirred for 20 min. The ketone (796.6 mg, 1.45 mmol) in 15 mL of THF was added to the LDA solution at −100 °C. The reaction mixture was stirred for 45 min at −100 °C, and then CH_3I (6 mL) was added. The resulting solution was warmed to −20 °C with a cooling bath and then quenched with saturated NH_4Cl solution (10 mL). The reaction mixture was stirred for 30 min at rt, and Et_2O (20 mL) was added. Organic layer was separated, and then the aqueous layer was extracted with Et_2O (2 × 15 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The residue was purified by flash chromatography (35% hexane–CH_2Cl_2) to give the monomethylated product **9** (703 mg, 86%) and dimethylated product **10** (67 mg, 8%). For **9**: Mp: 115–120.5 °C dec. R_f: 0.57 (20% EtOAc–Hex). IR: 2320, 1995, 1940, 1720, 1595, 1185 cm^{-1}. ^{1}H NMR (200 MHz): δ 7.41–7.20 (m, 15 H, aromatic), 4.76 (dd, 1 H, J = 6.8, 4.2 Hz, C_2-H), 4.68 (dd, 1 H, J = 11.2, 4.1 Hz, C_3-H), 2.86–2.56 (m, 4 H, C_1-H, C_4-H, C_5-exo H, C_7-exo H), 1.38–1.22 (m, 1 H, C_7-endo H), 1.0 (d, 3 H, J = 6.8 Hz, CH_3). ^{13}C NMR (75 MHz): δ 214.5, 207.0, 151.4, 129.8, 125.0, 121.3, 88.7, 87.0, 60.3, 52.1, 57.9, 44.9, 19.6. HRMS: calcd for $C_{27}H_{25}O_5FeP$ (M^+ − CO) 516.0789, found 516.1794.

Reduction of 9 by $NaBH_4$. To a solution of 80 mg (0.15 mmol) of **9** in mixture solvents of Et_2O (6 mL) and MeOH (2 mL) was added 16 mg (0.44 mmol) of $NaBH_4$ at 0 °C. The reaction solution was stirred for 3 h at 0 °C. Organic solvents were removed. EtOAc (20 mL) was added. The resulting solution was washed with brine (2 × 10 mL). The organic layer was dried ($MgSO_4$), filtered, and evaporated. The residue was purified by flash chromatography (30% EtOAc–Hex) to give 4:1 mixture (by ^{1}H NMR) of **14** and **15**. ^{1}H NMR (200 MHz): δ 7.41–7.17 (m, aromatic protons), 4.86–4.74 (m, C_2-H, C_3-H), 4.61–4.59 (m, C_2-H, C_3-H), 3.38–3.36 (m, C_6-H), 2.55–2.49 (m, C_1-H, C_4-H), 2.28–2.06 (m, C_5-H, C_7-H), 1.02 (d, J = 6.8 Hz, CH_3), 0.95 (d, J = 6.9 Hz, CH_3).

Dicarbonyl(η^4-5,7-*exo*-dimethyl-6-oxocyclohepta-1,3-diene)(triphenyl phosphite)iron (10). To a stirred solution of i-Pr_2NH (142.7 mg, 1.89 mmol) in 6 mL of THF at −78 °C was added *n*-BuLi (1.29 M, 1.33 mL, 1.324 mmol). The solution was stirred for 20 min. The ketone mixture **9** and **10** from above in 20 mL of THF was added to the LDA solution at −100 °C over 20 min. The reaction solution was stirred for 45 min at −100 °C, and then CH_3I (4 mL) was added. The residue workup as above followed by flash chromatography (10% EtOAc–hexane) gave the dimethylated product **10** (469.7 mg, 84% for two steps). Mp: 133.5–139 °C dec. R_f: 0.66 (20% EtOAc–hexane). IR: 3000, 2000, 1950, 1720, 1600, 1495, 1195 cm^{-1}. ^{1}H NMR (200 MHz): δ 7.37–7.13 (m, 15 H, aromatic), 4.62 (ddd, 2 H, J = 6.2, 4.1, 2.5 Hz, C_2-H, C_3-H), 2.84 (dd, 2 H, J = 6.2, 4.1 Hz, C_1-H, C_4-H), 2.51 (ddd, 2 H, J = 8.0, 5.1, 1.6 Hz, C_5-H, C_7-H), 0.93 (d, 6 H, J = 6.6 Hz, 2 CH_3). ^{13}C NMR (75 MHz): δ 207, 151.4, 151.3, 129.9, 125.1, 121.3, 87.4, 61.0, 48.3, 19.1. HRMS: calcd for $C_{27}H_{27}O_4FeP$ (M^+ − 2CO) 502.0996, found 502.0981.

Dicarbonyl(η^4-5,7-*exo*-dihydroxy-6-oxocyclohepta-1,3-diene)(triphenyl phosphite)iron (12). To a solution of 165 mg (0.827 mmol, 1.65 mL, 0.5 M solution in toluene) of potassium bis(trimethylsilyl)amide in 6 mL of THF was added 200 mg of **7** (0.376 mmol) in 10 mL of THF over 15 min at −100 °C. The red solution was stirred for 25 min, and then 393 mg (1.503 mmol) of **11** in 6 mL of THF was added over 10 min at −100 °C. The reaction mixture was allowed to warm to −20 °C with a cooling bath and stirred for a further 30 min after adding saturated NH_4Cl solution (10 mL). Et_2O (25 mL) was added, and the organic layer was separated. The aqueous layer was extracted with Et_2O (2 × 15 mL), and the combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The residue was purified by flash chromatography (4% CH_2Cl_2–MeOH) to give **12** (141.7 mg, 67%) as colorless oil. R_f: 0.20 (33% EtOAc–hexane). IR: 3683, 3510, 3019, 2011, 1959, 1716, 1590, 1489, 1192, 1163 cm^{-1}. ^{1}H NMR (200 MHz): δ 7.32–7.09 (m, 15 H, aromatic), 4.68–4.59 (m, 4 H, C_2-H, C_3-H, C_5-H, C_7-H), 3.48 (d, 2 H, J = 5.5 Hz, 2 OH), 2.79–2.71 (m, 2 H, C_1-H, C_4-H), ^{13}C NMR (75 MHz): δ 204.1, 151.2, 129.8, 125.7, 121.2, 87.8, 74.5, 57.6. HRMS: calcd for $C_{25}H_{23}O_6FeP$ (M^+ − 2CO) 506.0582, found 506.0576.

Dicarbonyl[η^4-5,7-bis((triethylsilyl)oxy)-6-oxocyclohepta-1,3-diene](triphenyl phosphite)iron (13). To a solution of 123 mg (0.22 mmol) of **12** in 8 mL of CH_2Cl_2 was added 187 mg (1.74 mmol) of 2,6-lutidine and 345 mg (1.31 mmol) of triethylsilyl trifluoromethanesulfonate at 0 °C. The reaction mixture was stirred for 2 h at 0 °C. The organic solvent was removed. Et_2O (20 mL) and H_2O (10 mL) were added. The combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The residue was purified by flash chromatography (15% EtOAc–hexane) to give **13** (143 mg, 97%) as a colorless oil. R_f: 0.53 (15% EtOAc–hexane). IR: 2950, 2050, 1955, 1755, 1585, 1495, 1195, 1030 cm^{-1}. ^{1}H NMR (200 MHz): δ 7.31–7.06 (m, 15 H, aromatic), 4.72–4.65 (m, 2 H, C_2-H, C_3-H), 4.54 (t, 2 H, J = 1.7 Hz, C_5-H, C_7-H), 2.64–2.57 (m, 2 H, C_1-H, C_4-H), 0.82 (t, 18 H, J = 7.8 Hz, 2 $OSi(CH_2CH_3)_3$), 0.48 (q, 12 H, J = 7.9 Hz, 2 $OSi(CH_2CH_3)_3$). ^{13}C NMR (75 MHz): δ 198.6, 151.2, 130.0, 125.3, 121.2, 88.3, 77.5, 58.8, 6.9, 4.9.

Dicarbonyl(η^4-6-*exo*-hydroxy-5,7-*exo*-dimethylcyclohepta-1,3-diene)(triphenyl phosphite)iron (16). To a stirred solution of 206.5 mg (0.37 mmol) of the ketone **10** in a mixture of Et_2O (8 mL) and MeOH (2 mL) at 0 °C was added $NaBH_4$ (42 mg, 1.11 mmol) in small portions. The reaction mixture was stirred for 2 h at 0 °C, and then the solvent was removed by rotary evaporation. EtOAc (15 mL) was added, and the solution was washed with brine (2 × 5 mL). The organic layer was separated, dried ($MgSO_4$), and evaporated. The residue was purified by flash chromatography (40% hexane–Et_2O) to give the alcohol **16** (191 mg, 95%) as yellowish oil. R_f: 0.23 (20% EtOAc–hexane). IR: 3688, 2962, 1998, 1942, 1590, 1220 cm^{-1}. ^{1}H NMR (200 MHz): δ 7.36–7.11 (m, 15 H, aromatic), 4.76–4.70 (m, 2 H, C_2-H, C_3-H), 3.07–3.02 (br d, 1 H, C_6-H), 2.20–2.09 (m, 4 H, C_1-H, C_4-H, C_5-H, C_7-H), 1.00 (d, 1 H, J = 9.8 Hz, OH), 0.92 (d, 6 H, J = 7.1 Hz, 2 CH_3). ^{13}C NMR (75 MHz): δ 151.4, 129.8, 124.9, 121.3, 87.2, 76.5, 58.8, 23.4. HRMS: calcd for $C_{28}H_{29}O_5FeP$ (M^+ − CO) 532.1102, found 532.1108.

Dicarbonyl(η^4-5,7-*exo*-dimethyl-6-*exo*-((triethylsilyl)oxy)cyclohepta-1,3-diene)(triphenyl phosphite)iron (17). To a stirred solution of the alcohol **16** (122.8 mg, 0.22 mmol) in 10 mL of CH_2Cl_2 was added 2,6-lutidine (140.8 mg, 1.31 mmol) and triethylsilyl triflate (231.8 mg, 0.88 mmol) at 0 °C. The reaction solution was stirred for 1.5 h at 0 °C. Hexane (30 mL) and H_2O (10 mL) were added, and the organic layer was separated. The aqueous layer was extracted with hexane (2 × 15 mL), and the combined organic layers were dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash chromatography (2% EtOAc–Hex) to give the title compound **17** (147.8 mg, 100%). Mp: 89.5–90.5 °C. R_f: 0.51 (5% EtOAc–hexane). IR: 2960, 1996, 1940, 1595, 1492, 1195 cm^{-1}. ^{1}H NMR (200 MHz): δ 7.35–7.09 (m, 15 H, aromatic), 4.73 (br, 2 H, C_2-H), 2.07 (br, 4 H, C_1-H, C_4-H, C_5-H, C_7-H), 0.90 (t, 9 H, J = 7.9 Hz, $OSi(CH_2CH_3)_3$), 0.82 (d, 6 H, J = 7.1 Hz, 2 CH_3), 0.48 (q, 6 H, J = 7.9 Hz, $OSi(CH_2CH_3)_3$). ^{13}C NMR (75 MHz): δ 216.3, 151.6, 129.6, 124.6, 121.4, 87.7, 76.3, 58.3, 40.9, 23.9, 7.2, 5.6. HRMS: calcd for $C_{34}H_{43}O_5SiFeP$ (M^+ − CO) 618.2017, found 618.2022.

Dicarbonyl(6-hydroxy-5α,6β,7α-trimethylcyclohepta-1,3-diene)(triphenyl phosphite)iron (18). To a solution of methylmagnesium bromide (3 M solution in THF, 0.72 mmol) in 4 mL of THF was added 133 mg (0.24 mmol) of **10** in 8 mL of THF at 0 °C. The reaction mixture was warmed to 65 °C and stirred for 4 h. Saturated aqueous NH_4Cl (3 mL) was added. The reaction solution was extracted with Et_2O (2 × 10 mL). The organic layer was dried ($MgSO_4$), filtered, and evaporated. The residue was purified by flash chromatography (20% EtOAc–Hex) to give **18** (60.5 mg, 44%) and **10** (5.5 mg). R_f: 0.23 (20% EtOAc–Hex). IR: 3605, 3010, 2005, 1950, 1495, 1170 cm^{-1}. ^{1}H NMR (300 MHz): δ 7.42–7.17 (m, 15 H, aromatic), 4.82–4.75 (m, 2 H, C_2-H, C_3-H), 2.27 (dd, 2 H, J = 7.6, 5.3 Hz, C_1-H, C_4-H), 2.01 (q, 2 H, J = 6.9 Hz, C_{5endo}-H, C_{7endo}-H), 1.22 (s, 1 H, OH), 0.95 (d, 6 H, J = 6.9 Hz, 2 CH_3), 0.90 (s, 3 H, $C(CH_3)OH$). ^{13}C NMR (75 MHz): δ 235.8, 151.4, 129.8, 124.9, 121.3, 86.6, 74.4, 60.6, 43.5, 25.7, 20.3. HRMS: calcd for $C_{28}H_{31}O_4FeP$ (M^+ − 2CO) 518.1309, found 518.1306.

Dicarbonyl[η^4-5,7-bis((triethylsilyl)oxy)-6-hydroxycyclohepta-1,3-diene](triphenyl phosphite)iron (19). To a solution of 78 mg (0.1 mmol) of **13** in 5 mL of Et_2O was added 6.5 mg (0.3 mmol) of $LiBH_4$ at 0 °C. The reaction mixture was stirred for 30 min at 0 °C. H_2O (2 mL) was added. The organic layer was separated, and the aqueous layer was extracted with Et_2O (2 ×

10 mL). The combined organic layers were washed with H_2O (2 × 5 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash chromatography (20% EtOAc–Hex) to give **19** (67.6 mg, 86%) as colorless oil. R_f: 0.49 (20% EtOAc–Hex). IR: 3583, 2956, 1997, 1942, 1724, 1590, 1489, 1192, 1002 cm^{-1}. ^1H NMR (200 MHz): δ 7.37–7.11 (m, 15 H, aromatic), 4.85–4.78 (m, 2 H, C_2-H, C_3-H), 4.11–4.08 (m, 2 H, C_5-H, C_7-H), 3.56–3.53 (m, 1 H, C_6-H), 2.39–2.31 (m, 2 H, C_1-H, C_4-H), 2.11 (d, 1 H, J = 0.9 Hz, OH), 0.90 (t, 18 H, J = 8.0 Hz, 2 $OSi(CH_2CH_3)_3$), 0.54 (q, 12 H, J = 8.2 Hz, 2 × $OSi(CH_2CH_3)_3$). ^{13}C NMR (75 MHz): δ 224.6, 151.4, 129.9, 125.1, 121.2, 88.0, 75.1, 73.2, 56.3, 6.9, 4.9.

6α-Hydroxy-5α,7α-dimethylcyclohepta-1,3-diene (20). To a stirred solution of the iron complex **16** (331.5 mg, 0.60 mmol) in 7 mL of absolute EtOH was added $CuCl_2$ (224.5 mg, 1.78 mmol) in small portions. The reaction mixture was stirred for 3 h at rt and filtered through a Celite pad with pentane (30 mL). The solution was washed with H_2O (10 mL), and the aqueous layer was extracted with 25% Et_2O–pentane (3 × 5 mL). The combined organic layers were dried ($MgSO_4$) and filtered, and the solvent was removed by careful distillation. The residue was purified by flash chromatography (10% Et_2O–pentane) to give the title compound **20** (78.7 mg, 96%), which was used in the next step without further purification (considerable loss occurs under high vacuum). R_f: 0.24 (10% Et_2O–pentane). IR: 3625, 3016, 2945, 1270, 1130, 1015 cm^{-1}. ^1H NMR (200 MHz): δ 5.82–5.75 (m, 2 H, C_2-H, C_3-H), 5.37–5.30 (m, 2 H, C_1-H, C_4-H), 3.61 (dt, 1 H, J = 11.7, 1.8 Hz, C_6-H), 2.72–2.68 (m, 2 H, C_5-H, C_7-H), 1.54 (d, 1 H, J = 11.8 Hz, OH), 1.19 (d, 6 H, J = 7.4 Hz, 2 CH_3).

6α-((Triethylsilyl)oxy)-5α,7α-dimethylcyclohepta-1,3-diene (21). To a stirred solution of 545 mg (0.807 mmol) of the diene complex **17** in 6 mL of CH_2Cl_2 at 0 °C was added Collins reagent (912 mg, 3.232 mmol) in small portions. The reaction mixture was stirred for 1 h at 0 °C then heated and stirred under reflux for 24 h. The resulting mixture was filtered through a Celite pad with pentane, and the solvent was removed by careful distillation. The residue was purified by flash chromatography (pentane only) to give the diene **21** (165 mg, 81%) as colorless oil. This compound is relatively volatile and was used in the next step without purification. R_f: 0.68 (pentane only). IR: 2980, 1506, 1195, 1165, 1047 cm^{-1}. ^1H NMR (200 MHz): δ 5.71–5.62 (m, 2 H, C_2-H, C_3-H), 5.38–5.29 (m, 2 H, C_1-H, C_4-H), 3.9 (dd, 1 H, J = 2.4, 1.2 Hz, C_6-H), 2.70–2.60 (m, 2 H, C_5-H, C_7-H), 1.11 (d, 6 H, J = 7.3 Hz, 2 CH_3), 0.95 (t, 9 H, J = 8.3 Hz, $OSi(CH_2CH_3)_3$), 0.60 (q, 6 H, J = 8.1 Hz, $OSi(CH_2CH_3)_3$).

2α,4α-Dimethyl-3α-((triethylsilyl)oxy)-6β,7β-dioxabicyclo[3.2.2]non-8-ene (22). To a stirred solution of 1.15 g (5.10 mmol) of diene **21** in 60 mL of CH_2Cl_2 was added tetraphenylporphine (26 mg). The deep purple solution was irradiated with 100-W tungsten–halogen lamp at rt for 2 h while oxygen was continuously bubbled through. Organic solvent was removed, and the residue was purified by flash chromatography (10% EtOAc–hexane) to give the endoperoxide **22** (1.24 g, 96%) as a colorless oil. R_f: 0.28 (10% EtOAc–hexane). IR: 3028, 2950, 2920, 2460, 1260, 1125, 1010 cm^{-1}. ^1H NMR (200 MHz): δ 6.44 (dd, 2 H, J = 5.2, 3.1 Hz, C_8-H, C_9-H), 4.59 (ddd, 2 H, J = 11.0, 5.5, 2.0 Hz, C_1-H, C_5-H), 4.05 (t, 1 H, J = 6.0 Hz, C_3-H), 2.49 (ddq, 2 H, J = 8.3, 6.1, 2.8 Hz, C_1-H, C_5-H), 0.93 (d, 6 H, J = 8.5 Hz, 2 CH_3), 0.91 (t, 9 H, J = 7.8 Hz, $OSi(CH_2CH_3)_3$), 0.60 (q, 6 H, J = 8.0 Hz, $OSi(CH_2CH_3)_3$). ^{13}C NMR (75 MHz): δ 130.0, 79.0, 70.8, 43.5, 13.0, 7.0, 5.0. HRMS: calcd for $C_{13}H_{23}O_3Si$ ($M^+ - C_2H_5$) 255.1416, found 255.1417.

5α,7α-Dimethyl-6α-((triethylsilyl)oxy)cyclohept-2-ene-1β,4β-diol (23). To a solution of 356 mg (1.26 mmol) of **22** in 12 mL of MeOH was added 124 mg (1.62 mmol) of thiourea at room temperature. The reaction mixture was stirred for 13 h at rt then filtered and evaporated. The residue was purified by flash chromatography (12% EtOAc-Hex) to give **23** (224 mg, 63%) as a white solid. Mp: 133.5–135 °C. R_f: 0.3 (12% EtOAc–Hex). IR: 3628, 2959, 1458, 1265, 1222, 1010 cm^{-1}. ^1H NMR (300 MHz): δ 5.75 (s, 2 H, C_2-H, C_3-H), 4.23 (d, 2 H, J = 9.1 Hz, C_1-H, C_4-H), 4.04 (s, 1 H, C_6-H), 2.01 (s, 2 H, 2 OH), 1.85 (qd, 2 H, J = 9.1, 7.0 Hz, C_5-H, C_7-H), 1.03 (d, 6 H, J = 6.9 Hz, 2 CH_3), 0.96 (t, 9 H, J = 7.8 Hz, $OSi(CH_2CH_3)_3$), 0.63 (q, 6 H, J = 7.9 Hz, $OSi(CH_2CH_3)_3$). ^{13}C NMR (75 MHz): δ 135.1, 77.4, 70.2, 45.9, 16.4, 7.2, 5.5. HRMS: calcd for $C_{15}H_{28}O_2Si$ ($M^+ - H_2O$) 268.1859, found 268.1858.

3β,7β-Diacetoxy-5α-((triethylsilyl)oxy)-4α,6α-dimethylcycloheptene (24). To a solution of 132 mg (0.46 mmol) of diol **23** in 15 mL of CH_2Cl_2 was added 13 mg (10 wt %) of (dimethylamino)pyridine and 465 mg (4.62 mmol) of triethylamine. After 15 min of stirring, 378 mg (3.7 mmol) of acetic anhydride was added. The reaction solution was stirred for 10 h at rt, and then H_2O (5 mL) was added. The separated organic layer was dried ($MgSO_4$), filtered, and evaporated. The residue was purified by flash chromatography (5% EtOAc–Hex) to give **24** (171 mg, 92%). R_f: 0.48 (10% EtOAc–Hex). IR: 3029, 2879, 1736, 1601, 1458, 1371, 1244 cm^{-1}. ^1H NMR (300 MHz): δ 5.59 (d, 2 H, J = 10.3 Hz, C_3-H, C_7-H), 5.48 (s, 2 H, C_1-H, C_2-H), 3.91 (s, 1 H, C_5-H), 2.07 (s, 6 H, 2 OAc). 1.94 (dq, 2 H, J = 10.3, 6.7 Hz, C_4-H, C_6-H), 1.02 (d, 6 H, J = 6.8 Hz, 2 CH_3), 0.98 (t, 9 H, J = 8.0 Hz, $OSi(CH_2CH_3)_3$), 0.68 (q, 6 H, J = 8.0 Hz, $OSi(CH_2CH_3)_3$). ^{13}C NMR (75 MHz): δ 170.2, 132.0, 80.5, 72.7, 43.9, 21.1, 17.7, 7.1, 5.7. HRMS: calcd for $C_{17}H_{29}O_5Si$ ($M^+ - C_2H_5$) 341.1784, found 341.1778.

5α,7α-Dimethyl-4β-hydroxy-6α-((triethylsilyl)oxy)cyclohept-2-en-1-one (25). To a stirred solution of 620 mg (2.18 mmol) of the endoperoxide **22** in 20 mL of CH_2Cl_2 at 0 °C was slowly added 440.8 mg (4.36 mmol) of Et_3N. The solution was stirred for 1 h and then was warmed to rt and stirred for 18 h. Et_2O (40 mL) was added, and the resulting solution was washed with 10% aqueous HCl (15 mL) and H_2O (15 mL). The aqueous layer was extracted with Et_2O (2 × 10 mL), and the combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The residue was purified by flash chromatography (40% EtOAc–hexane) to give the product **25** (595 mg, 96%) as colorless oil. R_f: 0.32 (20% EtOAc–hexane). IR: 3628, 2960, 2360, 1734, 1506, 1047, 1019 cm^{-1}. ^1H NMR (300 MHz): δ 6.34 (dd, 1 H, J = 13.3, 2.2 Hz, C_3-H), 5.84 (dd, 1 H, J = 13.3, 1.9 Hz, C_2-H), 4.29 (broad t, 1 H, J = 7.0 Hz, C_4-H), 3.86 (s, 1 H, C_6-H), 2.79 (q, 1 H, J = 7.0 Hz, C_7-H), 2.2–2.1 (m, 2 H, C_5-H, OH), 1.24 (d, 3 H, J = 6.9 Hz, CH_3), 1.14 (d, 3 H, J = 7.0 Hz, CH_3), 0.92 (t, 9 H, J = 8.0 Hz, $OSi(CH_2CH_3)_3$), 0.60 (q, 6 H, J = 8.0 Hz, $OSi(CH_2CH_3)_3$). ^{13}C NMR (75 MHz): δ 201.6, 145.3, 28.9, 80.3, 72.4, 54.0, 47.1, 18.9, 15.2, 7.0, 5.5. HRMS: calcd for $C_{15}H_{28}O_3Si$ 284.1807, found 284.1805.

4β-(Benzoyloxy)-5α,7α-dimethyl-6α-((triethylsilyl)oxy)-cyclohept-2-en-1-one (26). To a solution of 56.4 mg (0.19 mmol) of **25** and 157 mg (1.9 mmol) of pyridine in 5 mL of CH_2Cl_2 was added 55.7 mg (1.14 mmol) of benzoyl chloride slowly at 0 °C. The reaction mixture was stirred for 1 h at 0 °C and then stirred further for 15 h at rt. Et_2O (20 mL) and H_2O (5 mL) were added. The organic layer was washed with 5% aqueous HCl solution, 10% aqueous $NaHCO_3$ solution, and H_2O sequentially, dried ($MgSO_4$), filtered, and evaporated. The residue was purified by flash chromatography (10% EtOAc–Hex) to give **26** (67.8 mg, 86%) as a colorless oil. R_f: 0.38 (20% EtOAc–Hex). IR: 3028, 2879, 1717, 1673, 1268, 1112, 1011 cm^{-1}. ^1H NMR (300 MHz): δ 8.09 (d, 2 H, J = 7.4 Hz, aromatic), 7.60 (t, 1 H, J = 7.4 Hz, aromatic), 7.47 (t, 2 H, J = 7.4 Hz, aromatic), 6.24 (dd, 1 H, J = 13.2, 2.2 Hz, C_3-H), 5.98 (dd, 1 H, J = 13.2, 1.9 Hz, C_2-H), 5.90 (d, 1 H, J = 12.3 Hz, C_4-H), 3.98 (s, 1 H, C_6-H), 2.88 (q, 1 H, J = 6.9 Hz, C_7-H), 2.59 (dq, 1 H, J = 12.3, 6.8 Hz, C_5-H), 1.23 (d, 3 H, J = 6.9 Hz, C_7-CH_3), 1.19 (d, 3 H, J = 6.9 Hz, C_5-CH_3), 0.97 (t, 9 H, J = 7.9 Hz, $OSi(CH_2CH_3)_3$), 0.66 (q, 6 H, J = 7.9 Hz, $OSi(CH_2CH_3)_3$). ^{13}C NMR (75 MHz): δ 201.0, 164.8, 141.0, 133.3, 130.2, 130.0, 129.8, 128.5, 80.0, 75.0, 54.1, 44.7, 18.6, 15.2, 7.0, 5.5. HRMS: calcd for $C_{22}H_{32}O_4Si$ 388.2070, found 388.2071.

4α-(Benzyloxy)-5α,7α-dimethyl-6α-((triethylsilyl)oxy)cyclohept-2-en-1-one (27). To a stirred solution of 308 mg (1.08 mmol) of hydroxy enone **25** in 25 mL of Et_2O at rt was added a solution of 568 mg (2.16 mmol) of triphenylphosphine and 264 mg (2.16 mmol) of benzoic acid, followed by a solution of 377.1 mg (2.16 mmol) of diethyl azodicarboxylate (DEAD) in 6 mL of Et_2O. The reaction mixture was stirred for 28 h at room temperature. H_2O (5 mL) was added, and the separated organic layer was dried ($MgSO_4$), filtered, and evaporated. The residue was purified by flash chromatography (10% EtOAc–hexane) to give the inverted ester **27** (306.4 mg, 73%). IR: 3027, 2958, 1716, 1676, 1378, 1316, 1097 cm^{-1}. ^1H NMR (200 MHz): δ 8.12–8.07 (m, 2 H, aromatic), 7.61–7.51 (m, 3 H, aromatic), 6.54–6.46 (m, 1 H, C_2-H), 6.19–6.10 (m, 2 H, C_3-H, C_4-H), 4.28 (dd, 1 H, J = 7.6, 3.3 Hz, C_6-H), 2.92 (dq, 1 H, J = 6.8, 3.3 Hz, C_7-H), 2.77 (m, 1 H, C_5-H), 1.22 (d, 3 H, J = 6.7 Hz, CH_3), 1.0 (d, 3 H, J = 7.1

Hz, CH_3), 0.90 (t, 9 H, J = 7.5 Hz, $OSi(CH_2CH_3)_3$), 0.61 (q, 6 H, J = 7.5 Hz, $OSi(CH_2CH_3)_3$). ^{13}C NMR (75 MHz): δ 200.7, 165.8, 143.7, 133.5, 133.0, 129.8, 128.6, 77.3, 73.7, 72.9, 51.2, 42.2, 13.9, 10.6, 7.0, 5.0. HRMS: calcd for $C_{22}H_{32}O_4Si$ 388.2070, found 388.2067.

3α-(Benzoyloxy)-4α,6α-dimethyl-5α-((trimethylsilyl)oxy)cyclohept-1-en-7β-ol (28). To a solution of 252 mg (0.89 mmol) of **23** in 30 mL of Et_2O was added 462 mg (1.76 mmol) of triphenylphosphine and 215 mg (1.76 mmol) of benzoic acid. Diethyl azadicarboxylate (307 mg, 1.76 mmol) in 8 mL of Et_2O was added slowly to the reaction mixture at rt. The reaction mixture was stirred for 22 h, and H_2O (15 mL) was added. Organic layer was separated, and the aqueous layer was extracted with Et_2O (2 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The residue was purified by flash chromatography (12% EtOAc–Hex) to give **28** (182 mg, 53%) as an oil. R_f: 0.70 (30% EtOAc–Hex). IR: 3733, 2955, 1716, 1452, 1176, 1070 m^{-1}. ^1H NMR (200 MHz): δ 7.96 (d, 2 H, J = 9.4 Hz, aromatic), 7.46 (d, 1 H, J = 8.1 Hz, aromatic), 7.34 (t, 2 H, J = 9.3 Hz, aromatic protons), 5.71 (m, 1 H, C_3-H), 5.64 (dd, 1 H, J = 4.3, 2.0 Hz, C_2-H), 5.41 (dd, J = 6.1 Hz, 4.3 Hz, C_1-H), 3.81 (d, 1 H, J = 6.8 Hz, C_7-H), 3.79 (broad s, 1 H, C_5-H), 2.74–2.6 (m, 1 H, C_6-H or C_4-H), 2.11 (dq, 1 H, J = 7.1, 2.6 Hz, C_6-H or C_4-H), 1.98 (d, 1 H, J = 6.8 Hz, OH), 1.11 (d, 3 H, J = 7.1 Hz, CH_3), 1.08 (d, 3 H, J = 7.4 Hz, CH_3) 0.89 (t, 9 H, J = 7.8 Hz, $OSi(CH_2CH_3)_3$), 0.55 (q, 6 H, J = 7.8 Hz, $OSi(CH_2CH_3)_3$). ^{13}C NMR (75 MHz): δ 162.2, 137.9, 133.1, 129.8, 128.4, 124.6, 78.2, 75.0, 74.0, 44.2, 39.8, 29.7, 20.2, 17.6, 7.6, 5.4. HRMS: calcd for $C_{20}H_{29}O_4Si$ ($M^+ - C_2H_5$) 361.1835, found 361.1840.

3α-(Benzoyloxy)-5α,7β-bis((triethylsilyl)oxy)-4α,6α-dimethylcyclohept-1-ene (29). To a solution of 27.5 mg (0.07 mmol) of **28** in 5 mL of CH_2Cl_2 at 0 °C was added 74.5 mg (0.28 mmol) of 2,6-lutidine. After 10 min of stirring, 45.3 mg (0.42 mmol) of triethylsilyl trifluoromethanesulfonate was added to the reaction solution at 0 °C. The reaction mixture was stirred for 2 h at 0 °C, the organic solvent was removed, and Et_2O (10 mL) and H_2O (4 mL) were added. The organic layer was separated, and the aqueous layer was extracted with Et_2O (2 × 6 mL). The combined organic layers were dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash chromatography (15% EtOAc–Hex) to give **29** (33.4 mg, 94%). R_f: 0.68 (20% EtOAc–Hex). IR: 3029, 2959, 1712, 1602, 1315, 1110 cm^{-1}. ^1H NMR (200 MHz): δ 8.03 (d, 2 H, J = 7.0 Hz, aromatic), 7.50 (d, 1 H, J = 7.2 Hz, aromatic), 7.41 (t, 2 H, J = 6.9 Hz, aromatic), 5.78–5.71 (m, 1 H, C_2-H), 5.55 (d, 1 H, J = 6.2 Hz, C_3-H), 5.42 (dd, 1 H, J = 11.2, 4.4 Hz, C_1-H), 3.95 (dd, 1 H, J = 7.7, 1.4 Hz, C_7-H), 3.93 (broad s, 1 H, C_5-H), 2.96–2.72 (m, 1 H, C_4-H), 2.37–2.32 (m, 1 H, C_6-H), 1.11 (d, 3 H, J = 7.0 Hz, CH_3), 1.08 (d, 3 H, J = 7.3 Hz, CH_3), 0.95 (t, 9 H, J = 8.0 Hz, $OSi(CH_2CH_3)_3$), 0.89 (t, 9 H, J = 7.8 Hz, $OSi(CH_2CH_3)_3$), 0.61 (q, 6 H, J = 7.7 Hz, $OSi(CH_2CH_3)_3$), 0.56 (q, 6 H, J = 7.9 Hz, $OSi(CH_2CH_3)_3$). This compound was not further characterized.

3α-(Benzoyloxy)-5α-((triethylsilyl)oxy)-4α,6α-dimethyl-7β-(*tert*-butyldimethylsiloxy)cyclohept-1-ene (30). To a solution of 9.8 mg (0.025 mmol) of **28** in 5 mL of CH_2Cl_2 was added 16.1 mg (0.15 mmol) of 2,6-lutidine at 0 °C. After 10 min of stirring, 26.4 mg (0.1 mmol) of *tert*-butyldimethylsilyl trifluoromethanesulfonate was added to the reaction mixture at 0 °C. Stirring was continued for 1 h at 0 °C and for a further 1 h at rt. The organic solvent was removed, and the residue was purified by flash chromatography (10% EtOAc–Hex) to give **30** (11.1 mg, 90%). R_f: 0.7 (12% EtOAc–Hex). IR: 3032, 2958, 1712, 16602, 1231, 1109, 1007 cm^{-1}. ^1H NMR: δ 8.03 (d, 2 H, J = 7.4 Hz, aromatic protons), 7.52 (d, 1 H, J = 6.9 Hz, aromatic proton), 7.41 (t, 2 H, J = 7.5 Hz, aromatic protons), 5.76–5.60 (m, 2 H, C_2-H, C_3-H), 5.42 (dd, 1 H, J = 11.1, 4.2 Hz, C_1-H), 3.92 (bd, 1 H, J = 6.8 Hz, C_7-H), 3.85 (broad s, 1 H, C_5-H), 2.76 (m, 1 H, C_4-H), 2.30 (td, 1 H, J = 6.9, 2.5 Hz, C_6-H), 1.10 (d, 3 H, J = 7.9 Hz, CH_3), 0.98 (d, 3 H, J = 7.5 Hz, CH_3), 0.96 (t, 9 H, J = 7.8 Hz, $OSi(CH_2CH_3)_3$), 0.81 (s, 9 H, $(CH_3)_3CSi$), 0.61 (q, 6 H, J = 7.8 Hz, $OSi(CH_2CH_3)_3$), 0.01 (d, 6 H, J = 3.9 Hz, $(CH_3)_2Si$). This compound was not further characterized.

3α-(Benzoyloxy)-5α-((triethylsilyl)oxy)-4α,6α-dimethyl-7β-(methoxymethoxy)cyclohept-1-ene (31). To a stirred solution of 14.7 mg (0.038 mmol) of **28** in 4 mL of CH_2Cl_2 at rt was added 50.0 mg (0.37 mmol) of diisopropylethylamine (Hünig base) and 24.5 mg (0.30 mmol) of chloromethyl methyl ether (MOM-Cl). The reaction mixture was stirred for 2 h at reflux temperature. After cooling, the solution was diluted with CH_2Cl_2 (15 mL) and H_2O (5 mL). The organic layer was separated and extracted with saturated aqueous $NaHCO_3$ (2 × 6 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash chromatography (12% EtOAc–Hex) to give **31** (13.2 mg, 81%) as colorless oil. R_f: 0.73 (20% EtOAc–Hex). IR: 3021, 2955, 1720, 1455, 1232, 1148, 1021 cm^{-1}. ^1H NMR (200 MHz): δ 8.04 (d, 2 H, J = 6.9 Hz, aromatic), 7.52 (d, 1 H, J = 7.3 Hz, aromatic), 7.41 (t, 2 H, J = 7.3 Hz, aromatic), 5.84–5.77 (m, 2 H, C_2-H, C_3-H), 5.41 (dd, 1 H, J = 12, 4.0 Hz, C_1-H), 4.68 (dd, 2 H, J = 18.1, 7.1 Hz, OCH_2OCH_3), 3.90 (broad s, 1 H, C_5-H), 3.84 (d, 1 H, J = 12.8 Hz, C_7-H), 3.35 (s, 3 H, OCH_3), 2.86–2.70 (m, 1 H, C_4-H), 2.45 (td, 1 H, J = 6.9, 4.0 Hz, C_6-H), 1.17 (d, 3 H, J = 7.1 Hz, CH_3), 1.12 (d, 3 H, J = 7.5 Hz, CH_3), 0.97 (t, 9 H, J = 7.8 Hz, $Si(CH_2CH_3)_3$), 0.70 (q, 6 H, J = 7.7 Hz, $OSi(CH_2CH_3)_3$). This compound was not further characterized.

5-((Triethylsilyl)oxy)-3-hydroxy-4,6-dimethyl-7-(methoxymethoxy)cyclohept-1-ene (32). **31** (13.5 mg, 0.03 mmol) was dissolved in solution of 1% NaOH in MeOH (4 mL). The reaction solution was stirred for 24 h at rt. The organic solvent was removed, and EtOAc (10 mL) and H_2O (4 mL) were added. The organic layer was separated, and the aqueous layer was extracted with EtOAc (2 × 4 mL). The combined organic layers were dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash chromatography (20% EtOAc–Hex) to give **32** (9.6 mg, 94%). R_f: 0.27 (20% EtOAc–Hex). IR: 3614, 3028, 2959, 1460, 1239, 1078, 1004 cm^{-1}. ^1H NMR (300 MHz): δ 5.92 (dd, 1 H, J = 12.1, 6.0 Hz, C_1-H), 5.80 (dd, 1 H, J = 12.1, 3.8 Hz, C_2-H), 4.74 (d, 1 H, J = 6.6 Hz, OCH_2OCH_3), 4.59 (d, 1 H, J = 6.6 Hz, OCH_2OCH_3), 4.33 (dd, 1 H, J = 8.4, 3.6 Hz, C_7-H), 4.24 (br, 1 H, C_3-H), 4.13 (s, 1 H, C_5-H), 3.38 (s, 3 H, MOM), 3.10 (d, 1 H, J = 7.3 Hz, OH), 2.03–1.90 (m, 2 H, C_4-H, C_6-H), 1.16 (d, 3 H, J = 7.2 Hz, CH_3), 1.06 (d, 3 H, J = 7.2 Hz, CH_3), 1.00 (t, 9 H, J = 7.9 Hz, $OSiEt_3$), 0.68 (q, 3 H, J = 7.9 Hz, $OSiEt_3$). ^{13}C NMR (75 MHz): δ 134.7, 133.0, 95.5, 78.8, 74.5, 71.6, 55.8, 43.7, 43.5, 16.4, 15.5, 7.0, 5.3. HRMS: calcd for $C_{17}H_{32}O_3Si$ ($M - H_2O$) 312.2120, found 312.2116.

4α-(Benzoyloxy)-2α,3α-dihydroxy-5α,7α-dimethyl-6-((triethylsilyl)oxy)cycloheptan-1-one (33). To a solution of 429 mg (1.1 mmol) of **27** in 20 mL of pyridine was added 33 mg (1.42 mmol) of osmium tetraoxide at rt. The dark red solution was stirred for 20 h at rt. Sodium metabisulfite ($Na_2S_2O_5$) (550 mg) dissolved in 5 mL of H_2O was added to the reaction mixture which was allowed to stir an additional 24 h at rt. Et_2O (40 mL) was added, and the organic layer was washed with 10% aqueous HCl solution (20 mL), saturated aqueous $NaHCO_3$ (20 mL), and H_2O (10 mL) sequentially, dried ($MgSO_4$), filtered, and evaporated. The residue was purified by flash chromatography (20% EtOAc–Hex) to give **33** (443 mg, 95%) as colorless oil. R_f: 0.42 (40% EtOAc–Hex). IR: 3629, 3578, 2958, 1722, 1671, 1220, 1052 cm^{-1}. ^1H NMR (300 MHz): δ 8.10 (d, 2 H, J = 7.4 Hz, aromatic), 7.60 (t, 1 H, J = 7.4 Hz, aromatic), 7.47 (t, 2 H, J = 7.4 Hz, aromatic), 5.52 (dd, J = 11.0, 1.9 Hz, C_4-H), 4.62 (d, 1 H, J = 1.9 Hz, C_2-H), 4.40 (s, 1 H, OH), 4.02 (d, 1 H, J = 2.5 Hz, C_3-H), 3.94 (s, 1 H, C_6-H), 2.75 (q, 3 H, J = 7.2 Hz, C_7-H), 2.50 (dq, 1 H, J = 6.9, 2.8 Hz, C_5-H), 2.31 (broad s, 1 H, OH), 1.34 (d, 3 H, J = 7.3 Hz, C_7-CH_3), 1.17 (d, 3 H, J = 7.0 Hz, C_5-CH_3), 0.98 (t, 9 H, J = 8.0 Hz, $OSi(CH_2CH_3)_2$), 0.66 (q, 6 H, J = 8.0 Hz, $OSi(CH_2CH_3)_2$). ^{13}C NMR (75 MHz): 211.0, 166.4, 133.3, 130.0, 129.8, 128.3, 79.3, 75.3, 73.6, 50.8, 39.5, 16.9, 16.0, 7.1, 5.6 (one carbon peak not detected). HRMS: calcd for $C_{20}H_{29}O_6Si$ ($M^+ - C_2H_5$) 393.1733, found 393.1709.

Cleavage of Diol 33 with Lead Tetraacetate. To a solution of 105 mg (0.25 mmol) of **33** in 10 mL of benzene and 10 mL of MeOH was added 661 mg (1.49 mmol) of freshly recrystallized lead tetraacetate at rt. The reaction mixture turned to a bright orange, and the solution was stirred for 6 h at rt. The solvent was removed, EtOAc (30 mL) and H_2O (10 mL) were added, and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 5 mL), and the combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The crude product was used for the next reaction without purification.

Lactol 35. To a solution of 76 mg (crude) of mixture of **34** and **35** in 5 mL of THF was added 5 mL of 10% aqueous HCl. The reaction mixture was stirred for 2 h at 70 °C and then diluted with EtOAc (15 mL). The organic layer was washed with saturated aqueous $NaHCO_3$, and the aqueous layer was extracted with EtOAc (2 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The residue was purified by flash chromatography (40% EtOAc–Hex) to give **35** (51 mg, 49% from **33**) as colorless oil. R_f: 0.23 (40% EtOAc–Hex). IR: 3600, 2980, 1721, 1452, 1223, 1116 cm^{-1}. ^1H NMR (200 MHz): δ 8.06 (d, 2 H, J = 7.3 Hz, aromatic), 7.51 (d, 1 H, J = 7.2 Hz, aromatic), 7.46 (t, 2 H, J = 7.4 Hz, aromatic), 5.37–5.34 (m, 1 H, C_1-H or C_2-H), 5.35 (d, 1 H, J = 4.7 Hz, C_1-H or C_2-H), 4.08 (dd, J = 9.1, 5.8 Hz, C_4-H), 3.74 (s, 3 H, $COOCH_3$), 3.23 (d, 1 H, J = 4.3 Hz, OH), 2.80–2.66 (m, 2 H, C_3-H, C_5-H), 1.32 (d, 3 H, J = 7.3 Hz, CH_3), 1.13 (d, 3 H, J = 6.8 Hz, CH_3). ^{13}C NMR (75 MHz): δ 175.0, 165.8, 133.3, 129.8, 128.5, 100.4, 86.8, 81.0, 77.3, 52.0, 44.5, 37.5, 14.5, 11.2. HRMS: calcd for $C_{14}H_{17}O_5$ ($M^+ - OCH_3$) 277.1075, found 277.1076.

Lactone 36. To a solution of 73 mg (0.25 mmol) of **35** in 5 mL of CH_2Cl_2 was added 111 mg (0.29 mmol) of pyridium dichlorochromate (PDC) slowly at rt. The reaction mixture was stirred for 2 h at rt and then filtered through a Celite pad with 20 mL of CH_2Cl_2. The filtrate was concentrated and purified by flash chromatography (15% EtOAc–Hex) to give **36** (62 mg, 85%) as an oil. R_f: 0.52 (20% EtOAc–Hex). IR: 3030, 1794, 1731, 1453, 1268, 1198 cm^{-1}. ^1H NMR (300 MHz): δ 8.10 (d, 2 H, J = 7.4 Hz, aromatic), 7.63 (t, 1 H, J = 7.4 Hz, aromatic), 7.54 (t, 2 H, J = 7.5 Hz, aromatic), 5.73 (d, 1 H, J = 8.2 Hz, C_2-H), 4.50 (dd, 1 H, J = 7.4, 3.1 Hz, C_4-H), 3.76 (s, 3 H, $COOCH_3$), 2.91–2.85 (m, 2 H, C_2-H, C_4-H), 1.32 (d, 3 H, J = 7.2 Hz, CH_3), 1.14 (d, 3 H, J = 7.2 Hz, CH_3). ^{13}C NMR (75 MHz): 173.0, 171.8, 165.4, 133.9, 130.1, 128.6, 85.8, 77.3, 70.2, 52.3, 43.3, 35.3, 13.6, 13.1. HRMS: calcd for $C_{16}H_{18}O_6$ 306.1103, found 306.1134.

4β-((*tert*-Butyldimethylsilyl)oxy)-5α,7α-dimethyl-6α-((triethylsilyl)oxy)cyclohept-2-en-1-one (38). To a solution of 265 mg (0.93 mmol) of **25** in 10 mL of CH_2Cl_2 was added 599 mg (5.59 mmol) of 2,6-lutidine at 0 °C. The reaction mixture was stirred for 20 min at 0 °C, and then 986 mg (3.73 mmol) of *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBSOTF) was added slowly. The reaction mixture was stirred for 2 h at 0 °C. The solvent was removed, and Et_2O (20 mL) and H_2O (10 mL) were added. The aqueous layer was separated and extracted with Et_2O (2 × 8 mL). The combined organic layers were dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash chromatography (4% EtOAc–Hex) to give **38** (372 mg, 100%) as a colorless oil. R_f: 0.86 (12% EtOAc–Hex). IR: 3030, 2957, 1726, 1472, 1257, 1065, 1006 cm^{-1}. ^1H NMR (300 MHz): δ 6.17 (dd, 1 H, J = 6.0, 1.7 Hz, C_3-H)), 5.99 (d, 1 H, J = 6.0 Hz, C_2-H), 4.43 (broad s, 1 H, C_4-H), 3.94 (t, 1 H, J = 4.3 Hz, C_6-H), 2.18–2.13 (m, 1 H, C_7-H), 2.02–1.98 (m, 1 H, C_5-H), 0.95 (d, 3 H, J = 8.4 Hz, CH_3), 0.93 (d, 3 H, J = 8.0 Hz, CH_3), 0.90 (s, 9 H, $C(CH_3)_3$), 0.85 (t, 9 H, J = 7.5 Hz, $OSi(CH_2CH_3)_3$), 0.56 (q, 6 H, J = 7.6 Hz, $OSi(CH_2CH_3)_3$), 0.93 (s, 3 H, $Si(CH_3)_2$), 0.87 (s, 3 H, $Si(CH_3)_2$). ^{13}C NMR (75 MHz): δ 136.2, 134.1, 109.2, 82.5, 73.8, 45.2, 39.6, 25.9, 18.1, 13.8, 12.9, 7.8, 5.4, −1.8. HRMS: calcd for $C_{19}H_{38}O_3Si_2$ ($M^+ - C_2H_5$) 370.2359, found 370.2364.

4β-(Methoxymethoxy)-5α,7α-dimethyl-6α-((triethylsilyl)oxy)cyclohept-2-en-1-one (39). To a solution of 718 mg (2.53 mmol) of **25** in 15 mL of CH_2Cl_2 was added 3.28 g (25.3 mmol) of diisopropylethylamine (Hünig base) and 1.62 g (20.2 mmol) of chloromethyl methyl ether at rt. The reaction mixture was stirred for 36 h at reflux temperature and then diluted with CH_2Cl_2 (20 mL). The organic layer was washed with 10% aqueous HCl (2 × 10 mL). Saturated aqueous $NaHCO_3$ (2 × 10 mL) and H_2O (2 × 10 mL), dried ($MgSO_4$), filtered, and evaporated. The residue was purified by flash chromatography (10% EtOAc–Hex) to give **39** (801 mg, 98%) as a colorless oil. R_f: 0.36 (10% EtOAc–Hex). IR: 3057, 2963, 1673, 1460, 1220, 1160, 1060 cm^{-1}. ^1H NMR (300 MHz): δ 6.36 (dd, 1 H, J = 13.3, 2.4 Hz, C_3-H), 5.89 (dd, 1 H, J = 13.3, 1.9 Hz, C_2-H), 4.72 (dd, 2 H, J = 12.6, 9.6 Hz, OCH_2OCH_3), 4.23 (br d, 1 H, J = 9.9 Hz, C_4-H), 3.90 (s, 1 H, C_6-H), 3.42 (s, 3 H, OCH_2OCH_3), 2.80 (q, 1 H, J = 6.8 Hz, C_7-H), 2.29 (dq, 1 H, J = 9.9, 7.0 Hz, C_5-H), 1.21 (d, 3 H, J = 7.0 Hz, CH_3), 1.16 (d, 3 H, J = 7.0 Hz, CH_3), 0.92 (t, 9 H, J = 7.9 Hz, $OSi(CH_2CH_3)_3$), 0.60 (q, 6 H, J = 7.9 Hz, $OSi(CH_2CH_3)_3$). ^{13}C NMR (75 MHz): δ 201.6, 143.3, 129.7, 97.1, 80.0, 78.5, 56.1, 53.8, 45.6, 18.6, 15.1, 6.9, 5.5. HRMS: calcd for $C_{15}H_{27}O_4Si$ ($M^+ - C_2H_5$) 299.1678, found 299.1650.

Reduction of 39 with DIBAL-H. To a solution of 72 mg (0.22 mmol) of **39** in 3 mL of CH_2Cl_2 was added diisobutylaluminum hydride (1.54 M in toluene, 0.33 mmol) slowly at −78 °C. The reaction mixture was stirred for 45 min at −78 °C. Aqueous HCl (5%) (1 mL) was added, and the reaction mixture was stirred for 30 min without the cooling bath. CH_2Cl_2 (15 mL) and H_2O (5 mL) were added, the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The residue was purified by flash chromatography (25% EtOAc–Hex) to give **32** (67 mg, 92%) as a colorless oil (spectroscopic data: see earlier).

3β-((*tert*-Butyldimethylsilyl)oxy)-4α,6α-dimethyl-7α-hydroxy-5α-((triethylsilyl)oxy)cycloheptene (40). To a solution of 160 mg (0.4 mmol) of **38** in 8 mL of CH_2Cl_2 at −78 °C was added DIBAL-H (1.54 M in toluene, 0.6 mmol). The reaction mixture was stirred for 45 min at −78 °C and quenched with 5% aqueous HCl (2 mL). The resulting solution was stirred for 1 h at rt and diluted with CH_2Cl_2 (20 mL) and H_2O (5 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 8 mL), and the combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The residue was purified by flash chromatography (20% EtOAc–Hex) to give (150 mg, 93%) as a colorless oil. R_f: 0.33 (20% EtOAc–Hex). IR: 3629, 3011, 2878, 1463, 1315, 1276, 1232, 1108, 1070 cm^{-1}. ^1H NMR (300 MHz): δ 5.75 (d, 2 H, J = 3.6 Hz, C_1-H, C_2-H), 4.80 (d, 1 H, J = 3.0 Hz, C_7-H), 4.32 (t, 1 H, J = 4.8 Hz, C_3-H), 4.22–4.7 (broad, 1 H, C_5-H), 2.15–2.06 (m, 2 H, C_4-H, C_6-H), 0.98 (t, 9 H, J = 7.9 Hz, $OSi(CH_2CH_3)_3$), 0.94 (d, 3 H, J = 7.1 Hz, C_6-CH_3), 0.83 (d, 3 H, J = 7.3 Hz, C_4-CH_3, 0.90 (s, 9 H, *tert*-butyl), 0.61 (q, 6 H, J = 7.9 Hz, $OSi(CH_2CH_3)_3$), 0.06 (s, 3 H, $SiCH_3$), 0.05 (s, 3 H, $SiCH_3$). ^{13}C NMR (75 MHz): 141.8, 127.4, 70.7, 70.5, 70.1, 47.8, 43.7, 25.9, 18.2, 13.4, 8.6, 7.0, 5.0, −4.8, −4.9. HRMS: calcd for $C_{21}H_{44}O_3Si_2$ (M^+) 400.2829, found 400.2796.

7α-Acetoxy-3β-((*tert*-butyldimethylsilyl)oxy)-4α,6α-dimethyl-5α-((triethylsilyl)oxy)cycloheptene (41). To a solution of 69.3 mg (0.171 mmol) of **40** in 8 mL of CH_2Cl_2 were added sequentially 135.3 mg (1.71 mmol) of pyridine, 1.5 mg of (dimethylamino)pyridine (DMAP), and 106 mg (1.04 mmol) of acetic anhydride. The reaction mixture was stirred for 14 h at rt, and then CH_2Cl_2 (20 mL) and H_2O (5 mL) were added. The organic layer was dried (Na_2SO_2), filtered, and evaporated. The residue was purified by flash chromatography (10% EtOAc–Hex) to give **41** (71 mg, 93%) as a colorless oil. R_f: 0.65 (20% EtOAc–Hex). IR: 3015, 2856, 1730, 1472, 1472, 1463, 1373, 1257, 1065, 837 cm^{-1}. ^1H NMR (300 MHz): δ 5.76–5.72 (m, 2 H, C_2-H, C_7-H), 5.10 (t, 1 H, J = 5.5 Hz, C_3-H), 4.71 (dd, 1 H, J = 5.2, 2.9 Hz, C_1-H), 4.21 (t, 1 H, J = 4.8 Hz, C_5-H), 2.17–2.08 (m, 2 H, C_4-H, C_6-H), 2.04 (s, 3 H, OAc), 0.97 (t, 9 H, J = 7.9 Hz, $OSi(CH_2CH_3)_3$), 0.96 (d, 3 H, J = 7.8 Hz, CH_3), 0.93 (d, 3 H, J = 7.8 Hz, CH_3), 0.90 (s, 9 H, *tert*-butyl), 0.59 (q, 6 H, J = 7.8 Hz, $OSi(CH_2CH_3)_3$), 0.04 (s, 3 H, $OSiCH_3$), 0.05 (s, 3 H, $OSiCH_3$). ^{13}C NMR (75 MHz): 142.6, 130.7, 123.7, 72.5, 70.7, 70.4, 47.8, 41.5, 25.9, 20.9, 18.3, 12.9, 8.5, 7.0, 5.0, −3.8, −4.0. HRMS: calcd for $C_{21}H_{44}O_2Si_2$ ($M^+ - C_2H_4O_2$) 382.2723, found 382.2731.

7α-Acetoxy-4α,6α-dimethyl-3β-(methoxymethoxy)-5α-((triethylsilyl)oxy)cyclohept-1-ene (42). To a solution of 168 mg (0.51 mmol) of **32** in 5 mL of CH_2Cl_2 was added 6 mg (0.051 mmol) of (dimethylamino)pyridine and 402 mg (5.07 mmol) of pyridine. After 15 min of stirring, 415 mg (4.08 mmol) of acetic anhydride was added to the reaction mixture slowly. The resulting reaction mixture was stirred for 12 h at rt. CH_2Cl_2 (20 mL) and H_2O (5 mL) were added. The organic layer was washed with 5% aqueous HCl (5 mL), saturated aqueous $NaHCO_3$, and H_2O sequentially, then dried ($MgSO_4$), filtered, and evaporated. The residue was purified by flash chromatography (12% EtOAc–Hex) to give **42** (177 mg, 94%) as colorless oil. R_f: 0.6 (15% EtOAc–Hex). IR: 3011, 2952, 1722, 1458, 1367, 1263, 1145, 1040 cm^{-1}. ^1H NMR (300 MHz): δ 5.80–5.73 (m, 3 H, C_1-H, C_2-H, C_7-H), 4.70 (d, 1 H, J = 6.6 Hz, OCH_2OCH_3), 4.55 (d, 1 H, J = 6.6 Hz, OCH_2OCH_3), 4.35 (t, 1 H, J = 4.7 Hz, C_3-H or C_5-H), 4.07 (t, 1 H, J = 5.5 Hz, C_3-H or C_5-H), 3.35 (s, 3 H, OCH_2OCH_3), 2.20–2.16 (m, 2 H, C_4-H, C_6-H), 2.06 (s, 3 H, $COOCH_3$), 0.97 (d,

3 H, J = 7.8 Hz, CH_3), 0.95 (d, 3 H, J = 7.8 Hz, CH_3) 0.93 (t, 9 H, J = 7.9 Hz, $OSi(CH_2CH_3)_3$), 0.59 (q, 6 H, J = 7.9 Hz, $OSi(CH_2CH_3)_3$). ^{13}C NMR (75 MHz): 170.4, 136.2, 127.1, 94.8, 73.9, 73.1, 69.9, 55.5, 43.7, 42.6, 21.3, 13.0, 9.3, 6.9, 5.0. HRMS: calcd for $C_{17}H_{32}O_3Si$ ($M^+ - CH_3COOH$) 321.2121, found 312.2109.

2α,4α,6β-Trimethyl-5β-(methoxymethoxy)-3α-((triethylsilyl)oxy)cycloheptanone (43). To a stirred suspension of 278 mg (1.4 mmol) of cuprous iodide in 6 mL of Et_2O at 0 °C was added CH_3Li (2.8 mmol) slowly. The solution was stirred for 20 min at 0 °C, and 240 mg (0.73 mmol) of **29** in 6 mL of Et_2O was added slowly. The reaction mixture was stirred for 40 min at 0 °C. Saturated aqueous NH_4Cl (5 mL) was added. The reaction mixture was stirred for 30 min at rt, and then Et_2O (15 mL) and H_2O (5 mL) were added. The organic layer was separated, and the aqueous layer was extracted with Et_2O (2 × 6 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The residue was purified by flash chromatography (10% EtOAc–Hex) to give **43** (221 mg, 88%). R_f: 0.45 (15% EtOAc–Hex). IR: 3029, 2959, 1693, 1382, 1218, 1148, 1097 cm^{-1}. ^1H NMR (300 MHz): δ 4.69 (dd, 2 H, J = 9.8, 6.9 Hz, OCH_2OCH_3), 3.93 (s, 1 H, C_3-H), 3.65 (dd, 1 H, J = 8.6, 3.4 Hz, C_5-H), 3.41 (s, 3 H, OCH_2OCH_3), 2.66–2.51 (m, 3 H, C_2-H, C_7-H), 2.34 (dq, 1 H, J = 6.9, 3.4 Hz, C_6-H), 2.04 (dq, 1 H, J = 8.4, 7.0 Hz, C_4-H), 1.17 (d, 3 H, J = 7.1 Hz, CH_3), 1.13 (d, 3 H, J = 7.1 Hz, CH_3), 1.03 (d, 3 H, J = 7.1 Hz, CH_3), 0.90 (t, 9 H, J = 8.0 Hz, $OSi(CH_2CH_3)_3$), 0.61 (q, 6 H, J = 8.0 Hz, $OSi(CH_2CH_3)_3$). ^{13}C NMR (75 MHz): δ 212.1, 96.6, 82.5, 77.6, 56.0, 52.4, 46.4, 42.3, 31.5, 17.9, 15.4, 14.7, 7.0, 5.4. HRMS: calcd for $C_{16}H_{31}O_4Si$ ($M^+ - C_2H_5$) 315.2016, found 315.2016.

Silyl Enol Ether 44. To a stirred suspension of 306 mg (1.61 mmol) of CuI in 6 mL of Et_2O at 0 °C was added slowly CH_3Li (1.49 M in Et_2O, 3.2 mmol). After 20 min of stirring, 240 mg (0.73 mmol) of **39** in 5 mL of Et_2O was added to the cuprate solution, and then the reaction mixture was stirred for 45 min at 0 °C. Freshly distilled Et_3N (797 mg, 7.3 mmol) and 793 mg (7.3 mmol) of chlorotrimethylsilane (TMS-Cl) were added to the reaction mixture. Stirring was continued for 4 h at rt, and the reaction mixture was filtered through short plug of silica gel using pentane (30 mL). The filtrate was evaporated and dried under high vacuum. The crude product was used for the next reaction without purification or spectroscopic analysis, owing to its extreme lability.

2-Hydroxy-4β-(methoxymethoxy)-3β,5α,7α-trimethyl-6α-((triethylsilyl)oxy)cycloheptan-1-one (45). To a solution of crude **44** from above in 6 mL of CH_2Cl_2 at 0 °C was added slowly 189 mg (1.1 mmol) of *m*-chloroperbenzoic acid in 5 mL of CH_2Cl_2. The reaction mixture was stirred for 2 h at 0 °C, tetra-*n*-butylammonium fluoride (1 M in THF 1.1 mmol) was added, and stirring was continued for 1 h at rt. EtOAc (20 mL) and H_2O (10 mL) were added, and the aqueous layer was extracted with EtOAc (2 × 5 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated, and the residue was purified by flash chromatography (15% EtOAc–Hex) to give an inseparable mixture (3:1 by NMR) of diastereomers **45** (144 mg, 54% from **39**). R_f: 0.34 (20% EtOAc–Hex). IR: 3474, 3028, 2959, 1693, 1462, 1229, 1218, 1209, 1153, 1036 cm^{-1}. Major diastereomer. ^1H NMR (300 MHz): δ 4.75 (d, 1 H, J = 6.9 Hz, OCH_2OCH_3), 4.63 (d, 1 H, J = 6.9 Hz, OCH_2OCH_3), 4.58 (t, 1 H, J = 3.0 Hz, C_2-H), 3.94–3.92 (m, 1 H, C_4-H), 3.84 (s, 1 H, C_6-H), 3.39 (s, 3 H, OCH_2OCH_3), 2.58–2.53 (m, 1 H, C_3-H), 2.37 (q, 1 H, J = 7.7 Hz, C_7-H), 1.90 (dq, 1 H, J = 10.6, 7.2 Hz, C_5-H), 1.28 (d, 3 H, J = 7.7 Hz, C_7-CH_3), 1.20 (d, 3 H, J = 6.8 Hz, C_3-OH_3), 0.95 (t, 9 H, J = 7.8 Hz, $OSi(CH_2CH_3)_3$), 0.82 (d, 3 H, J = 7.2 Hz, C_5-CH_3), 0.63 (q, 6 H, J = 7.8 Hz, $OSi(CH_2CH_3)_3$). Minor diastereomer. ^1H NMR (300 MHz): δ 4.72 (d, 1 H, J = 6.9 Hz, OCH_2OCH_3), 4.62 (d, 1 H, J = 6.9 Hz, OCH_2OCH_3), 4.08 (dd, 1 H, J = 9.4, 2.6 Hz, C_4-H), 3.51 (broad s, 1 H, C_6-H), 3.41 (s, 3 H, OCH_2OCH_3), 3.25–3.17 (m, 1 H, C_2-H), 2.17–2.14 (m, 2 H, C_5-H, C_7-H), 1.25 (d, 3 H, J = 7.5 Hz, CH_3), 1.20 (d, 3 H, J = 7.0 Hz, CH_3), 0.98 (d, 3 H, J = 7.6 Hz, CH_3), 0.93 (t, 9 H, J = 7.9 Hz, $OSi(CH_2CH_3)_3$), 0.59 (q, 6 H, J = 7.8 Hz, $OSi(CH_2CH_3)_3$). Major diastereomer. ^{13}C NMR (75 MHz): δ 213.3, 96.2, 83.8, 79.2, 78.5, 56.3, 56.1, 50.5, 40.6, 39.9, 18.6, 17.0, 7.1, 5.5. Minor diastereomer. ^{13}C NMR (75 MHz): 211.1, 96.5, 79.4, 76.0, 56.4, 47.5, 42.7, 36.7, 17.6, 14.3, 7.3, 5.2 (2 carbon peaks are not observed). HRMS: calcd for $C_{16}H_{29}O_4Si$ ($M^+ - C_2H_5 - H_2O$) 313.1835, found 313.1881.

3β,5α,7α-Trimethyl-6α-((triethylsilyl)oxy)cycloheptane-1,2-diol (46). To a stirred solution of 109 mg (0.3 mmol) of **45** in a mixture of Et_2O (6 mL) and MeOH (2 mL) at 0 °C was added 34 mg (0.6 mmol) of $NaBH_4$ in small portions. The reaction mixture was stirred for 1 h at 0 °C, warmed to rt, and stirred for 1 h. EtOAc (10 mL) and H_2O (4 mL) were added, and the aqueous layer was extracted with EtOAc (2 × 5 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated, and the residue was purified by flash chromatography (30% EtOAc–Hex) to give one separable diastereomer (34 mg) and inseparable diastereomeric mixtures (68 mg) of **46**. The combined yield of **46** is 93% (102 mg). R_f: 0.41, 0.34 (40% EtOAc–Hex). IR: 3713, 3657, 3028, 1521, 1231, 1224, 1196 cm^{-1}. ^1H NMR (300 MHz) for separable diastereomer: δ 4.65 (dd, 2 H, J = 8.3, 6.9 Hz, OMOM), 3.88–3.75 (m, 3 H, C_1-H, C_2-H, C_6-H), 3.56 (dd, 1 H, J = 6.1, 2.8 Hz, C_4-H), 3.49 (broad d, 1 H, J = 8.8 Hz, OH), 3.39 (s, 3 H, OCH_2OCH_3), 3.07 (broad d, 1 H, J = 10.4 Hz, OH), 2.45 (ddq, 1 H, J = 7.3, 7.0, 2.8 Hz, C_3-H), 1.97–1.91 (m, 1 H, C_7-H), 1.87 (ddq, 1 H, J = 7.1, 6.8, 2.7 Hz, C_5-H), 1.26 (d, 3 H, J = 7.4 Hz, CH_3), 1.11 (d, 3 H, J = 7.1 Hz, CH_3), 1.10 (d, 3 H, J = 7.2 Hz, CH_3), 1.00 (t, 9 H, J = 7.9 Hz, $OSi(CH_2CH_3)_3$). 0.70 (q, 6 H, J = 7.9 Hz, $OSi(CH_2CH_3)_3$). ^{13}C NMR (75 MHz) for separable diastereomer: 97.1, 82.7, 81.8, 76.4, 73.6, 55.9, 43.5, 40.3, 36.6, 18.9, 18.6, 15.2, 7.0, 5.3. HRMS: calcd for $C_{18}H_{34}O_3Si$ ($M^+ - H_2O$) 326.2277, found 326.2253.

Preparation of Heptanediol Derivative (47). To a stirred solution of 36 mg (0.10 mmol) of **46** in 4 mL of PhH at rt was added 66 mg (0.15 mmol) of lead tetraacetate in small portions. The reaction mixture was stirred for 1.5 h at rt. EtOAc (15 mL) and H_2O (5 mL) were added. The aqueous layer was extracted with EtOAc (2 × 5 mL), and the combined organic layers were washed with saturated $NaHCO_3$ solution (10 mL) and H_2O (10 mL), dried ($MgSO_4$), filtered, and evaporated. The residue was purified by flash chromatography (15% EtOAc–Hex) to give **47** (31.5 mg, 88%) as colorless oil. R_f: 0.34 (20% EtOAc–Hex) IR: 3019, 2958, 1721, 1458, 1228, 1216, 1200, 1036 cm^{-1}, ^1H NMR (300 MHz): δ 9.79 (d, 1 H, J = 1.5 Hz, CHO), 9.71 (d, 1 H, J = 2.9 Hz, CHO), 4.66 (dd, 2 H, J = 16.8, 7.0 Hz, OCH_2OCH_3), 4.16 (dd, 1 H, J = 7.9, 2.9 Hz, C_3-H), 4.04 (dd, 1 H, J = 7.6, 2.2 Hz, C_5-H), 3.35 (s, 3 H, OCH_2OCH_3), 2.64 (ddq, 1 H, J = 7.9, 7.2, 2.9 Hz, C_2-H), 2.62 (ddq, 1 H, J = 7.6, 7.2, 2.2 Hz, C_6-H), 1.80 (ddq, 1 H, J = 7.5, 7.2, 2.3 Hz, C_4-H), 1.16 (d, 3 H, J = 7.1 Hz, CH_3), 1.06 (d, 3 H, J = 7.2 Hz, CH_3), 0.98 (t, 9 H, J = 8.0 Hz, $OSi(CH_2CH_3)_3$), 0.80 (d, 3 H, J = 7.2 Hz, CH_3), 0.67 (q, 6 H, J = 8.0 Hz, $OSi(CH_2CH_3)_3$). ^{13}C NMR (75 MHz): 203.7, 203.6, 98.0, 79.9, 74.9, 55.9, 51.4, 50.2, 40.2, 11.5, 10.6, 9.8, 7.0, 5.3. HRMS: calcd for $C_{16}H_{31}O_5Si$ ($M^+ - C_2H_5$) 331.1941, found 331.1948.

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Supplementary Material Available: ^1H and/or ^{13}C NMR spectra for all new compounds (70 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.