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Studies toward the Total Synthesis of Dumsin. 2. A Second Generation Approach Resulting in Enantioselective Construction of a Functionalized ABC Subunit of the Tetranortriterpenoid Insect Antifeedant

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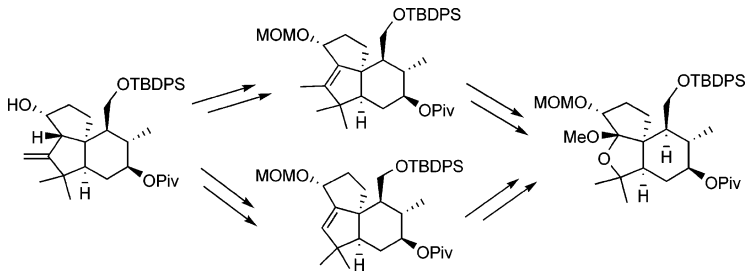

A synthesis of the ABC framework of dumsin is described. The optically active intermediate **9b**, which is expeditiously assembled from 5-oxobornyl pivalate by the sequential implementation of an oxy-Cope rearrangement and an intramolecular ene reaction, proved to be suitably functionalized for ultimate conversion to **5**. The synthesis plan relies on two approaches to this targeted intermediate. In the first, the exocyclic double bond introduced during $EtAlCl_2$-promoted closure of aldehyde **10b** is cleaved to leave a carbonyl group that is amenable to hydride reduction and elimination of water. Cleavage of the resulting double bond with ruthenium tetroxide provided the seco ketoacid. The same advanced intermediate was obtained by initially positioning the double bond internal to the five-membered ring in advance of transient ring expansion via diketone formation and intramolecular aldolization. Both of these approaches bypass the complications arising from the substantial steric congestion prevailing in these structural networks. The task of covalently positioning an oxygen atom adjacent to the *gem*-dimethyl-substituted carbon in **5** was properly realized by oxidative decarboxylation. The stereochemical assignments to many of the intermediates were confirmed by an X-ray crystallographic analysis of **43**.

Introduction

In 1990, Kubo et al. reported the isolation from *Croton jatrophoides* Pax of the tetranortriterpene limonoid called dumsin (**1**).[1] In line with the wide range of biological effects discovered in members of the limonoid family, **1** was found to exhibit potent insect antifeedant properties in several studies.[2,3] Additional antifeedant limonoids were also disclosed by Nakatani and co-workers in 1996 and 1997.[4] As a group, this class of natural products is recognized to display antimalarial activity,[5] cell adhesion inhibitory indications,[6] H^+-ATPase inhibitory effects,[7] and cytotoxic properties against select human breast cancer cell lines.[8]

(1) Kubo, I.; Hanke, F. J.; Asaka, Y.; Matsumoto, T.; Cun-Heng, H.; Clardy, J. *Tetrahedron* **1990**, *46*, 1515.

(2) (a) Nihei, K.-I.; Hanke, F. J.; Asaka, Y.; Matsumoto, T.; Kubo, I. *J. Agric. Food Chem.* **2002**, 5048. See also (b) Nihei, K.; Asaka, Y.; Mine, Y.; Ito, C.; Furukawa, H.; Ju-Ichi, M.; Kubo, I. *J. Agric. Food Chem.* **2004**, *52*, 3325. (c) Nihei, K.; Asaka, Y.; Mine, Y.; Kubo, I. *J. Nat. Prod.* **2005**, *68*, 244.

(3) (a) Chan, B. G.; Waiss, A. C.; Jr.; Stanley, W. L.; Goodban, A. E. *J. Econ. Entomol.* **1978**, *71*, 366. (b) Kubo, I.; Klocke, J. A. In *Plant Resistance To Insects*; Hedin, P. A., Ed; ACS Symposium Series 208; Washington, DC, 1983; pp 329−346. (c) Kubo, I. In *Methods In Plant Biochemistry*; Hostettmann, K., Ed; Academic Press: London, U.K., 1991; Vol. 6; pp 179−193.

(4) (a) Zhou, J.-B.; Minami, Y.; Yagi, F.; Tadera, K.; Nakatani, M. *Heterocycles* **1997**, *45*, 1781. (b) Zhou, J.-B.; Minami, Y.; Yagi, F.; Tadera, K.; Nakatani, M. *Heterocycles* **1996**, *43*, 1477.

(5) (a) Bickii, J.; Njifutie, N.; Foyere, J. A.; Basco, L. K.; Ringwald, P. J. *Ethnopharmacology* **2000**, *69*, 27. (b) Mackinnon, S.; Durst, T.; Arnason, J. T.; Angerhofer, C.; Pezzuto, J.; Sanchez-Vindas, P. E.; Poveda, J.; Gbeassor, M. *J. Nat. Prod.* **1997**, *60*, 336.

(6) Musza, L. L.; Killar, L. M.; Speight, P.; McElhiney, S.; Barrow, C. J.; Gillum, A. M.; Cooper, R. *Tetrahedron* **1994**, *50*, 11369.

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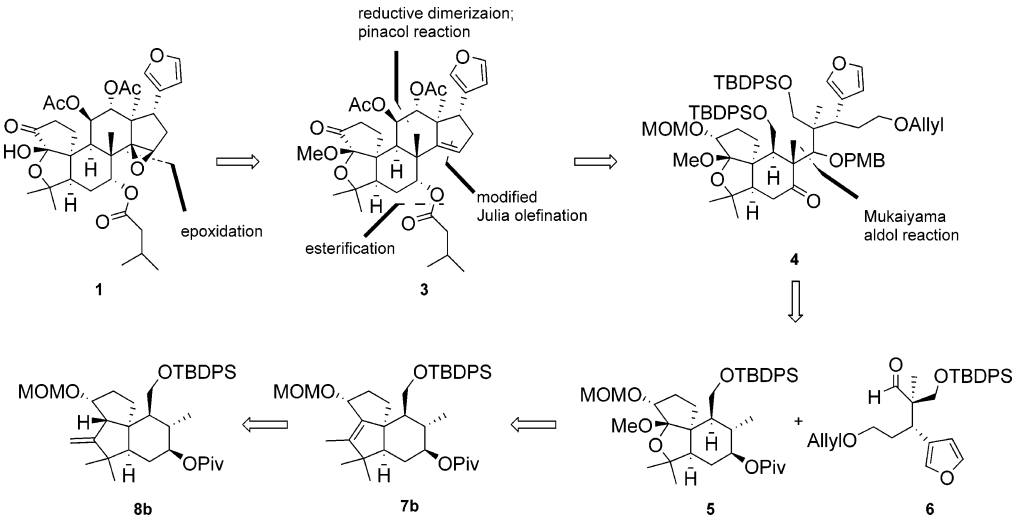
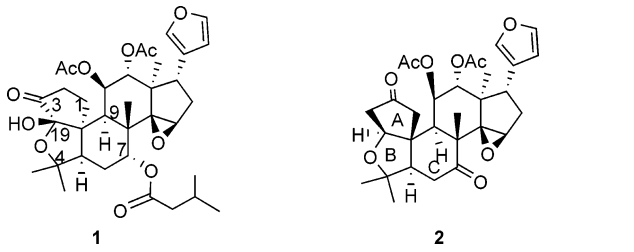
SCHEME 1



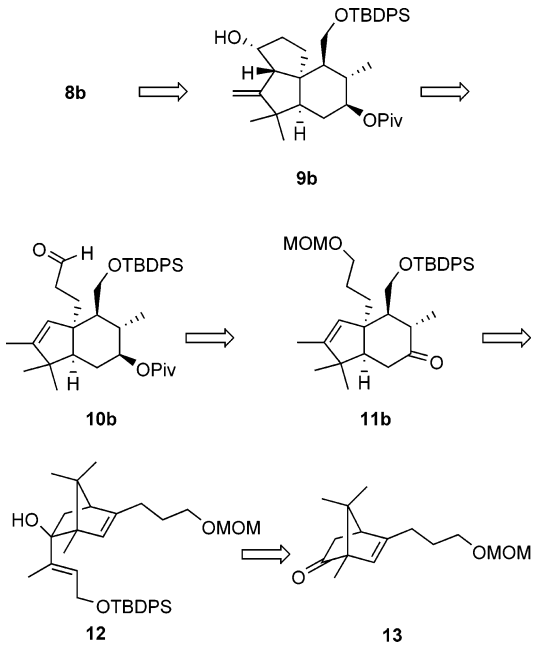
Continuing studies of the same East African plant by the Kubo team resulted more recently in their characterization of zumsin (**2**), which possesses structural features similar to those resident in **1**.[2a] Differences are found in the orientation of the A ring, which results in a *trans* fusion across the B/C sector in **2** in contrast to the *cis*-B/C arrangement in **1**. Furthermore, zumsin has no hemiketal functionality at C19, the carbonyl functionality at C3 in dumsin is shifted to C2 in **2**, and the esterified hydroxyl group at C7 in **1** is oxidized to a ketone carbonyl in **2**. Notwithstanding these structural variations, zumsin exhibits potent insect antifeedant activity similar to the effects displayed by **1**.[2]



The first synthetic studies aimed at **1** were undertaken in this laboratory by Hong and dealt largely with the enantioselective elaboration of key intermediates derived from (−)-bornyl acetate.[9] Presently, we detail an improved strategy that targets the highly complex ABC ring scaffold resident in dumsin.

Retrosynthetic Analysis. Our thinking regarding assembly of the ABC ring system of **1** was guided from the beginning by the presence therein of a hemiketal subunit. The projected stability of the *O*-methyl acetal thereof prompted us to consider its installation at a point roughly midway in the total synthesis

SCHEME 2



(Scheme 1). This perception led us back via **3** to **4**, whose further processing in the forward direction would ultimately involve a Mukaiyama aldol reaction[10] followed by suitable implementation of an intramolecular coupling step[11] and a modified Julia olefination.[12] Of more immediate significance was our concern over proper insertion of the oxygen atom in ring B as defined, for example, by **5**. Although methods are, of course, available for oxidative cleavage of the double bond in both **7b** and **8b**, neither process installs the requisite functionality directly. As a result, acetal **5** emerged as a key tricyclic intermediate and became the central target of the present study.

One abbreviated plan for generating **8b** was to rely first on an enantiodefined oxy-Cope rearrangement within the *exo*-norbornenol **12** (Scheme 2). It was our ambition to exploit the

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(8) (a) Guthrie, N.; Morley, K.; Hasegawa, S.; Manners, G. D.; Vandenberg, T. In *Citrus Limonoids-Functional Chemicals in Agriculture and Foods*; Berhow, M. A.; Hasegawa, S.; Manners, G. D., Eds.; ACS Symposium Series 758; American Chemical Society: Washington, DC, 2000; pp 165−184. (b) Lam, L. K. T.; Hasegawa, S.; Bergstrom, C.; Lam, S. H.; Kenney, P. In *Citrus Limonoids-Functional Chemicals in Agriculture and Foods*; Berhow, M. A.; Hasegawa, S.; Manners, G. D., Eds; ACS Symposium Series 758; American Chemical Society: Washington, DC, 2000; pp 185−200.

(9) (a) Hong, F.-T.; Paquette, L. A. *Tetrahedron Lett.* **1994**, *35*, 9153. (b) Paquette, L. A.; Hong, F.-T. *J. Org. Chem.* **2003**, *68*, 6905.

(10) Mikami, K.; Matsukawa, S. *J. Am. Chem. Soc.* **1993**, *115*, 7039.

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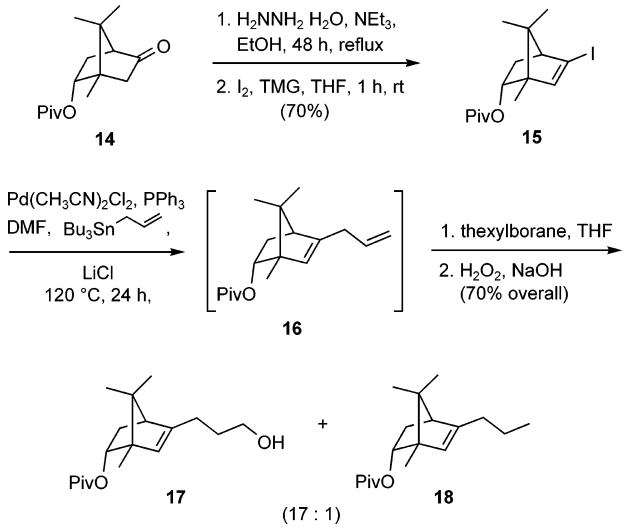
(12) (a) Blakemore, P. R. *J. Chem. Soc. Perkin Trans. 1* **2002**, 2563. (b) Blakemore, P. R.; Cole, W. J.; Kocienski, P. J.; Morley, A. *Synlett.* **1998**, 26. (c) Julia, M.;. Paris, J.-M. *Tetrahedron Lett.* **1973**, 4833.

SCHEME 3



well-defined transition state that would be utilized by this strained bicyclic framework to set the four stereogenic centers as desired in **11b**. Beyond that, the projection was made that aldehyde **10b** would be amenable to an intramolecular ene reaction,[13,14] whose role was to fashion the second cyclopentane ring resident in **9b**.

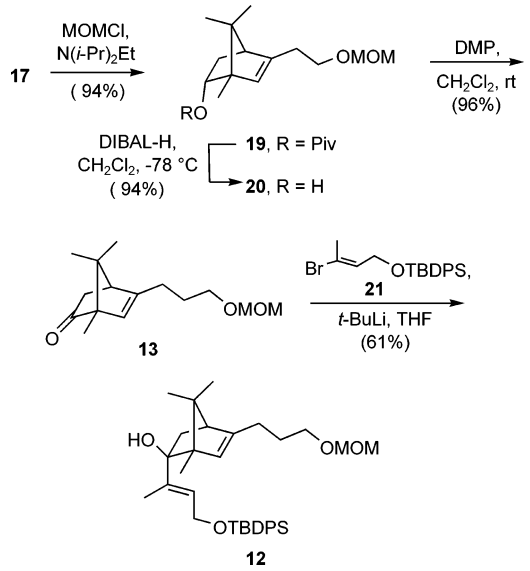
Results and Discussion

Keto pivalate **14** was prepared efficiently by saponification of the known (−)-5-oxobornyl acetate[15] followed by re-esterification of the alcohol so formed with pivaloyl chloride (Scheme 3).

Adaptation of the Barton method for generating vinyl iodides from ketone hydrazones[16] to **14** furnished **15** thereby allowing for Stille coupling[17] with allyltributylstannane. The ensuing regioselective hydroboration of **16** with thexylborane resulted in the predominant formation of primary carbinol **17**. A lesser quantity of the dihydro byproduct **18** was simultaneously generated.

The route continued by protection of the primary hydroxyl group in **17** as the MOM ether. This tactic allowed for uncomplicated reductive removal of the pivaloyl group and Dess−Martin oxidation[18] of norbornenol **20** so formed (Scheme 4). The coupling of **13** with the lithiated derivative of alkenyl bromide **21**, whose three-step synthesis was based on Corey's protocol,[19] proceeded as expected from the *endo* face to deliver the *exo* allylic alcohol **12**. The evaluation of **12** as a feasible substrate for the projected anionic oxy-Cope rearrangement[20] followed.

SCHEME 4



When the key [3,3] sigmatropic shift was induced by way of the lithium alkoxide in THF, a chromatographically separable mixture of the epimeric ketones **11a** and **11b** resulted, with **11a** predominating by a ratio of 5:1 (Scheme 5). *The carbon indicated by an "x" in these products must ultimately be made quaternary, thereby minimizing stereochemical concerns at this stage.* Notwithstanding, the stereoselectivity of protonation in the enolate intermediate proved to be subject to alkali metal counterion control. For example, generation of the potassium enolate led instead almost exclusively to **11b**. The potential significance of these results has been outlined elsewhere.[21]

Treatment of **11a** with DIBAL-H at −78 °C resulted in predominant conversion to β-alcohol **23a** (15:1), the acylation of which with pivaloyl chloride gave rise to the desired **24a**. Subsequently, the MOM group was cleaved chemoselectively with 9-bromo-9-borabicyclo[3.3.1]nonane[22] to provide the primary carbinol **27a** whose oxidation with the Dess−Martin periodinane (DMP) reagent served to provide aldehyde **10a** in near-quantitative yield. The intramolecular ene cyclization now had to be confronted. After numerous experiments with different Lewis acids, it was determined that ethylaluminum dichloride[14] constitutes the most efficient reagent for this transformation. As with many of its precursors, the stereostructure of **9a** was established by 2D-NMR spectroscopy. The product of simple ethylation, *viz*. **28a**, was formed concomitantly in variable low yields that peaked at 15%.

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(14) Marshall, J. A.; Andersen, M. W. *J. Org. Chem.* **1993**, *58*, 3912.

(15) (a) Allen, M. S.; Darby, N.; Salisbury, P.; Sigurdson, E. R.; Money, T. *Can. J. Chem.* **1979**, *57*, 733. (b) Meinwald, J.; Shelton, J. C.;Buchanan, G. L.; Courtin, A. *J. Org. Chem.* **1968**, *33*, 99. (c) Fabris, F.; Bellotto, L.; De Lucchi, O. *Tetrahedron Lett.* **2003**, *44*, 1211.

(16) (a) Barton, D. H. R.; Bashiardes, G.; Fourrey, J.-L. *Tetrahedron Lett.* **1983**, *24*, 1605. (b) Williams, D. R.; Heidebrecht; R. W., Jr. *J. Am. Chem. Soc.* **2003**, *125*, 1843. (c) Helliwell, M.; Thomas, E. J.; Townsend, L. A. *J. Chem. Soc., Perkin Trans. 1* **2002**, 1286. (d) Peña-Cabrera, E.; Norrby, P.-O.; Sjögren, M.; Vitagliano, A.; De Felice, V.; Oslob, J.; Ishii, S.; O'Neill, D.; Åkermark, B.; Helquist, P. *J. Am. Chem. Soc.* **1996**, *118*, 4299.

(17) Ritter, K. *Synthesis* **1993**, 735. (b) Espinet, P.; Echavarren, A. M. *Angew. Chem.* **2004**, *116*, 4808. (c) Stille, J. K.; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (d) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 363.

(18) (a) Boeckman, R. K.; Shao, P.; Mullins, J. *J. Org. Synth.* **1999**, *77*, 141. (b) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155. (c) Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 7277. (d) Ireland, R. E.; Liu, L. *J. Org. Chem.* **1993**, *58*, 2899.

(19) (a) Corey, E. J.; Bock, M. G.; Kozikowski, A. V.; Rao, R.; Floyd, D.; Lipshutz, B. *Tetrahedron Lett.* **1978**, *12*, 1051. (b) Roush, R. W.; Brown, B. B. *J. Am. Chem. Soc.* **1993**, *115*, 2268. (c) Corey, E. J.; Kania, R. S. *J. Am. Chem. Soc.* **1996**, *118*, 1229.

(20) (a) Paquette, L. A. *Tetrahedron* **1997**, *53*, 13971. (b) Paquette, L. A. *Chem. Soc. Rev.* **1995**, 9. (c) Paquette, L. A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 609.

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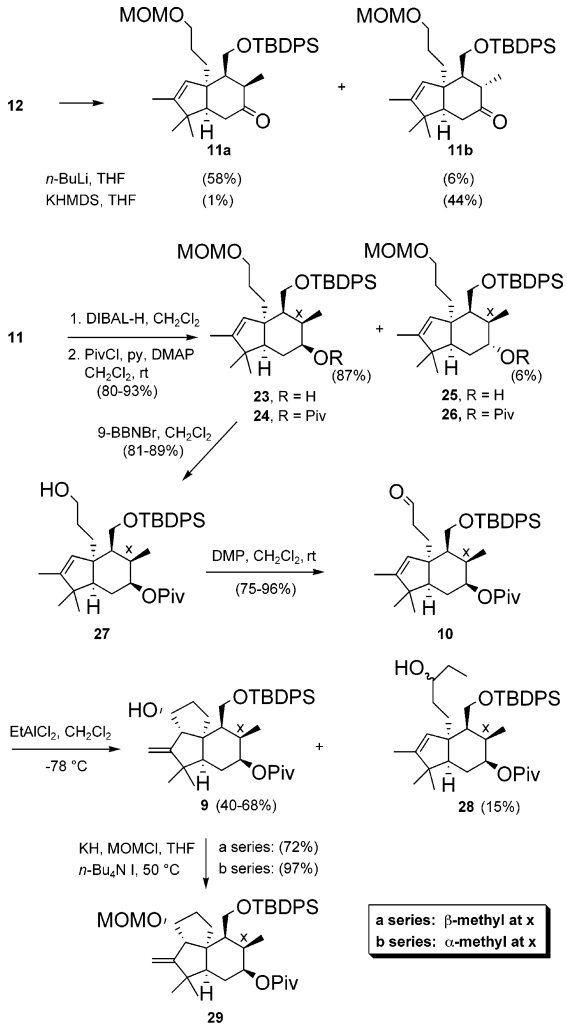
SCHEME 5

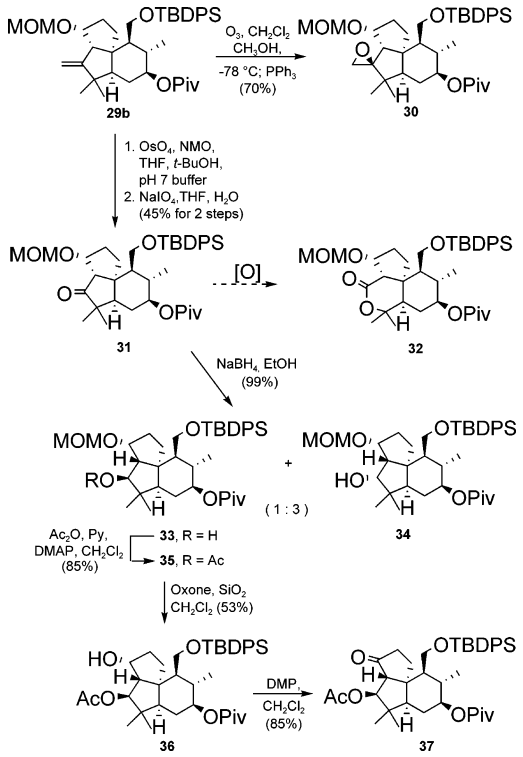


As we undertook to explore the chemistry of **9a**, we were made increasingly aware of the steric congestion present in this tricyclic framework. The first reflection of this fact was the unreactivity of **9a** to the action of MOM chloride in the presence of Hünig's base. The successful implementation of this step required the use of potassium hydride and a catalytic quantity of tetrabutylammonium iodide in THF at 50 °C.[23] The discovery of additional reactivity differences prompted us to undertake a parallel series of steps that would eventuate in the acquisition of **29b** from **11b** (Scheme 5). In this way, comparative analysis of the responses of **29a** and **29b** to more advanced chemical transformations would be made possible as warranted. Thus, co-exploration of the α/β stereoisomers (or series a and b) was likewise undertaken.

From this point, the cause of synthetic directness could be well served in one of two ways. The first would consist of introducing a double bond in ring B with subsequent excision of the unneeded carbon atom. This variant is exemplified by the structural features present in **38** and **39**. A pathway along these lines might facilitate elaboration of the challenging tetrahydrofuran substructural unit while also allowing for the application of more direct routes exemplified by the hypothetical

(23) Ireland, R. E.; Anderson, R. C.; Badoud, R.; Fitzsimmons, B. J.; McGarvey, G. J.; Thaisrivongs, S.; Wilcox, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 1988.

SCHEME 6



generation of lactone **32**. Alternatively, the heterocyclic B ring might arise via precursors such as **41**−**44**. In this approach, the loss of two carbons might be effected in a single maneuver, causing the route to be more economic in synthetic steps.

Customarily, the ozonolysis of alkenes proceeds with full involvement of all three atoms of the O_3 molecule in product formation. Examples exist, however, where only one oxygen of the ozone becomes incorporated with resultant epoxide formation.[24] Exocyclic olefin **29b** happens to share in the latter pattern of reactivity. Its response to a broad range of ozonolysis conditions was to produce **30** in good yield with the co-formation of only small levels (5−9%) of **31** (Scheme 6).

This ketone was made available in satisfactory quantities by alternative application of Johnson−Lemieux conditions.[25] At this juncture, our quest for lactone **32** was cut short by virtue of the complete unreactivity of **31** to reagents such as MCPBA,[26] TFAA/30% H_2O_2,[27] Oxone/$NaHCO_3$,[28] MMPP,[29] and the like. Evidently, the substantive steric compression that deters operation of the "normal" ozonolytic pathway for **29b** acts comparably to prevent key 1,2-addition of the oxidizing species to the carbonyl group of **31**.

Experiments of a different type proved to be substantially more encouraging. Thus, ketone **31** was smoothly reduced with sodium borohydride. Reaction proceeded slowly and required the use of ethanol as the medium to minimize the rate of competing degradation of the $NaBH_4$ by solvent. Carbinols **33** and **34** (ratio 1:3) were formed in quantitative yield. β-Face

(24) Bailey, P. S. *Ozonization in Organic Chemistry*; Academic Press: New York, 1978; Vol. 1.
(25) Pappo, R.; Allen, D. S., Jr.; Lemieux, R. U.; Johnson, W. S. *J. Org. Chem.* **1956**, *21*, 478.
(26) Krow, G. R. *Org. React.* **1993**, *43*, 251.
(27) Emmons, W. D.; Lucas, G. B. *J. Am. Chem. Soc.* **1955**, *77*, 2287.
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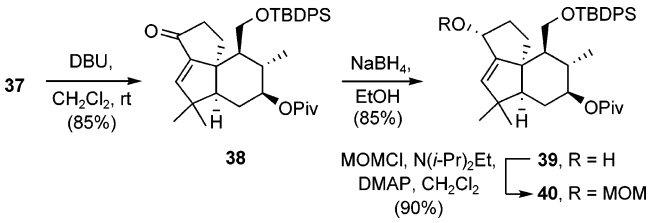
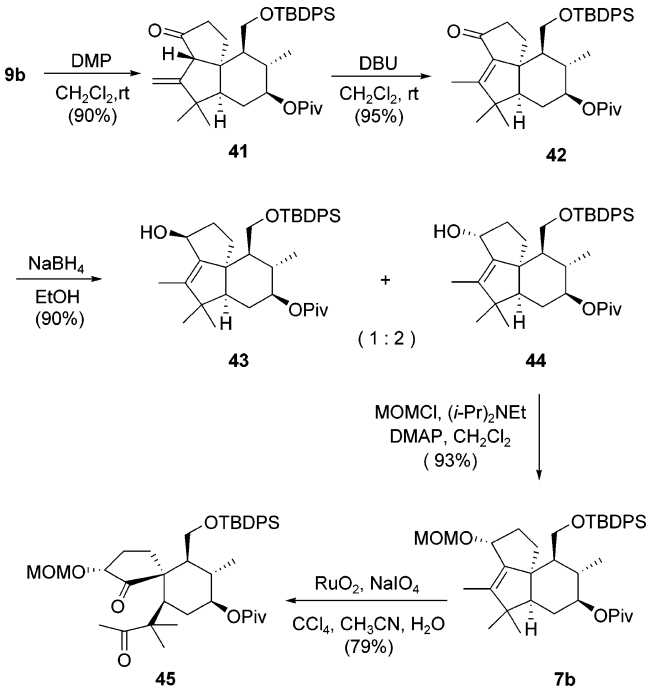
(29) Harmata, M.; Rashatasakhon, P. *Org. Lett.* **2000**, *2*, 2913.

SCHEME 7



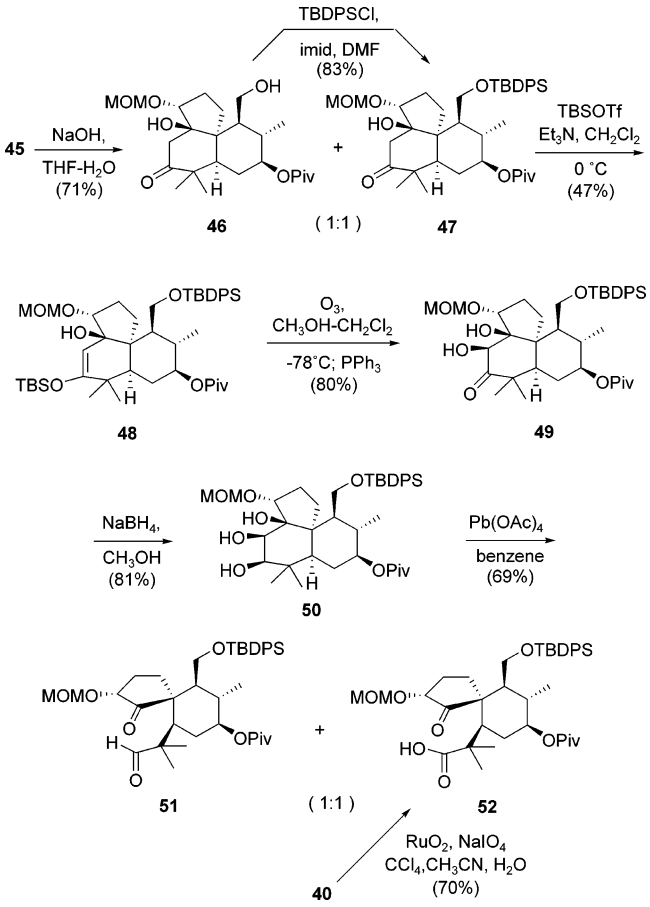
SCHEME 8



attack corresponds to hydride delivery from the less hindered direction, thereby giving rise to **34** as the major component. Although no attempts have been made to invert this product distribution, a simplification subsequently presented itself. Whereas the hydroxyl substituent in β-alcohol **33** could be routinely functionalized as in **35**, its α-epimer **34** proved resistant to either *O*-acylation or *O*-alkylation. Consequently, acetate **35** could be readily accessed, freed of its MOM protecting group with Oxone on silica gel,[30] and subjected to the action of the Dess−Martin periodinane in CH_2Cl_2. The assumption was made that the *syn* elimination envisaged for **37** (Scheme 7) would not prove problematic in light of the possible operation of the E_{1cb} mechanistic option. At the experimental level, the **37** → **38** conversion proceeded efficiently. When **38** was admixed with sodium borohydride in ethanol, β-face attack leading predominantly to **39** was substantially favored (85% yield). Moreover, no tendency on the part of **38** to experience 1,4-hydride addition was noted. In any case, a straightforward synthetic route to **40** had been opened.

The plan for generating the tricyclic methyl-bearing homologues **43** and **44** called for oxidizing **9b** to **41**, the isomerization of which to the conjugated counterpart **42** was expected to take place readily (Scheme 8). Such was indeed the case in near-quantitative yield. When enone **42** was next subjected to

SCHEME 9



borohydride reduction, the chromatographically separable allylic alcohols **43** and **44** resulted. The crystallinity of β-stereoisomer **43** provided the opportunity for stereochemical corroboration by X-ray crystallographic analysis. Although the corresponding acetates proved readily available, this protecting group was insufficiently robust in later steps. Consequently, the MOM ether **7b** was selected in the expectation that it would be more well suited to the task at hand. At this juncture, the tetrasubstituted double bond in **7b** was readily cleaved with ruthenium tetroxide as generated from RuO_2 and $NaIO_4$.[30] As in the case of **31**, the resulting diketone **45** proved not to be amenable to Baeyer−Villiger oxidation under a broad selection of conditions. A more circuitous means for proper insertion of the ring B oxygen atom had to be devised.

To meet this challenge, advantage was taken of the ease with which **45** undergoes intramolecular base-promoted aldol ring closure to give **46** and **47** (Scheme 9). Following reprotection of the primary carbinol, it proved easy to generate the silyl enol ether as found to be present in **48** concurrently.[31] Ozonolysis of **48** at −78 °C delivered in 80% yield the α,β-dihydroxy ketone **49**, a compound whose ^{1}H and ^{13}C NMR spectra are very broad and ill-defined because of multiple hydrogen bond ineractions.[32] Reduction of **49** with sodium borohydride gave exclusively the triol **50**. Although attempts to cleave this highly functionalized intermediate with sodium periodate resulted in

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(31) Kocienski, P.; Narquizian, R.; Raubo, P.; Smith, C. Farrugia, L. J.; Muir, K.; Boyle, F. T. *J. Chem. Soc. Perkin Trans. 1* **2000**, 2357.

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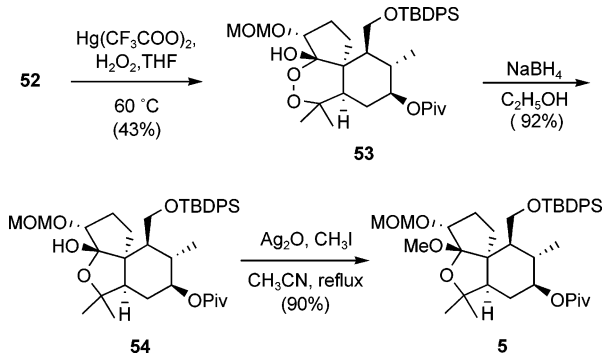
SCHEME 10



no reaction, lead tetraacetate proved to be quite effective[33] and delivered in 69% yield the keto aldehyde **51** and keto acid **52** in a 1:1 ratio. Before proceeding with elaboration of the key subtarget, we decided to establish that **52** could also be prepared by the ruthenium tetroxide oxidation of **40**. This was indeed the case, thus opening two complementary routes to this substance. This interconversion also served to substantiate the stereochemical assignments accorded to all of the intermediates. In line with our earlier observations, it was not possible to transform **51** to the keto formate upon treatment with *m*-chloroperbenzoic acid.

The task of covalently positioning an oxygen atom adjacent to the *gem*-dimethyl-substituted carbon as in **5** was properly realized by making recourse to the process known as oxidative decarboxylation.[34] For the present purposes, **52** was admixed with hydrogen peroxide and mercuric trifluoroacetate in THF.[35] These conditions resulted in generation of the nor derivative through the loss of carbon dioxide, with subsequent capture by H_2O_2 to give the hydroperoxide. In the present context, intramolecular cyclization subsequently operates to form **53** (Scheme 10). This result is in accord with prevailing steric congestion, which is expediently released by ring formation. The weak peroxidic linkage in **53** is conducive to efficient reduction with sodium borohydride, thus producing hemiketal **54**. *O*-Methylation was ultimately accomplished with silver(I) oxide and methyl iodide in refluxing acetonitrile as solvent.[36]

Conclusion

The ABC ring skeleton of dumsin has been constructed in optically active form from (+)-5-oxobornyl pivalate, whose structural elements proved adequate for introduction of the additional necessary stereogenic centers present in **5**. Our objectives in the design and execution of this synthesis were (i) to utilize the mild conditions underlying application of anionic [3,3] sigmatropy to build a suitable bicyclic scaffold, (ii) to deploy an intramolecular ene reaction for assembly of the A-ring, and (iii) to involve oxidative decarboxylation as the means for introducing the oxygen atom in ring B. This last tactic has received little attention in total synthesis.

The access routes to keto acid **52** were realized via tricyclic allylic alcohol **39** on the one hand and triol **50** on the other. The relative stereochemistry of both advanced intermediates was corroborated by X-ray crystallographic analysis of **43**. The shorter of the two sequences involves 22 steps and is preferred. We expect that the anticipated adaptability of **5** to structural modification will enable the rational arrival at dumsin (**1**) which is currently being pursued in this laboratory.

Experimental Section

1,7,7-Trimethyl-5-oxobicyclol[2.2.1]heptan-2-yl Pivalate (14). 5-Hydroxy-4,7,7- trimethylbicyclo[2.2.1] heptan-2-one[15] (75.0 g. 446 mmol) was dissolved in dry CH_2Cl_2 (1200 mL) and dry pyridine (72.7 mL, 892 mmol). The solution was cooled to 0 °C before pivaloyl chloride (219 mL, 1.78 mol) and DMAP (54.5 g. 446 mmol) were introduced. The reaction mixture was warmed to rt, stirred for 72 h, returned to 0 °C, and treated dropwise with concentrated $NaHCO_3$ solution (100 mL). Water (800 mL) was added, the separated aqueous layer was extracted three times with CH_2Cl_2, and the combined organic layers were washed with water and brine, dried, and concentrated *in vacuo*. The residue distilled at 120−121 °C and 0.2 mm to yield 100 g (89%) of **14** as a colorless solid, mp 46−48 °C; IR (film, cm^{-1}) 1748, 1480, 1457; ^1H NMR (300 MHz, CDC1$_3$) δ 5.10−5.04 (m, 1H), 2.69−2.58 (m, 1H), 2.54 (d, J = 18.7 Hz, 1H), 2.19 (d, J = 5.3 Hz, 1H), 2.01 (d, J = 18.7 Hz, 1H), 1.26 (dd, J = 14.8, 3.6 Hz, 1H), 1.19 (s, 9H), 1.03 (s, 3H) 1.00 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.9, 178.3, 77.0, 59.7, 49.5, 47.0, 41.9, 38.7, 31.8, 27.0, 20.0, 17.5, 12.7; HRMS (EI) *m*/*z* calcd for $C_{15}H_{24}O_3Na^+$ 252.1720, obsd 252.1725; $[\alpha]^{24}_D$ +88.8 (*c* 1.09, $CHCl_3$).

5-Iodo-1,7,7-trimethylbicyclo[2.2.1]hept-5-en-2-yl Pivalate (15). To a mixture of hydrazine monohydrate (125 mL), triethylamine (125 mL), and ethanol (250 mL) was added dropwise a solution of **14** (25 g, 99 mmol) in ethanol (150 mL). After 3 d of reflux, most of the ethanol and triethylamine were distilled off. The residue was cooled to rt, poured into cold water (400 mL), and extracted with ether (3 × 400 mL). The combined organic layers were washed with brine, dried, and concentrated to afford crude hydrazone (24 g, 91%) as a light yellow oil; IR (film, cm^{-1}) 3388, 3216, 1729, 1674, 1627; ^1H NMR (300 MHz, $CDCl_3$) δ 4.99 (ddd, J = 9.8, 3.6, 2.0 Hz, 1H), 2.61−2.48 (m, 1H), 2.45 (d, J = 17.1 Hz, 1H), 2.31 (d, J = 4.6 Hz, 1H), 1.93 (dd, J = 17.1, 1.6 Hz, 1H), 1.24−1.18 (m, 1H), 1.19 (s, 9H), 0.97 (s, 3H), 0.96 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.4, 160.6, 77.7, 53.3, 49.9, 48.2, 38.8, 34.1, 30.7, 27.1, 19.8, 18.0, 13.2.

To a solution of iodine (98.5 g, 387mmol) in dry ether (360 mL) was added slowly 1,1,3,3-tetramethylguanidine (109 mL, 870 mmol) at rt. A solution of the hydrazone (24 g, 90 mmol) in dry ether (100 mL) was then introduced dropwise at rt. After 4 h of stirring, the reaction mixture was cooled to 0 °C and treated slowly with 10% aqueous hydrochloric acid (200 mL). The organic phase was separated and washed with saturated $Na_2S_2O_3$ (2 × 200 mL) and saturated $NaHCO_3$ (200 mL) solutions and brine. After drying, the solvent was evaporated and the residue was purified by flash chromatography to give iodide **15** (27 g, 82%) as a red-brown oil; IR (film, cm^{-1}) 1730, 1572, 1479; ^1H NMR (300 MHz, $CDCl_3$) δ 6.07 (s, 1H), 5.04 (dd, J = 7.2, 2.6 Hz, 1H), 2.48 (d, J = 3.6 Hz 1H), 2.46−2.37 (m,1H), 1.14 (s, 9H), 1.05 (s, 3H), 0.95 (dd, J = 13.1, 2.6 Hz 1H), 0.94 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.7, 144.5, 97.4, 80.3, 62.8, 59.7, 58.7, 38.7, 35.2, 27.0, 19.8, 19.0, 10.5; HRMS *m*/*z* calcd for $C_{15}H_{23}IO_2Na^+$ 385.0635, obsd 385.0629; $[\alpha]^{24}_D$ +61.3 (*c* 0.88, $CHCl_3$).

5-Allyl-1,7,7-trimethylbicyclo[2.2.1]hept-5-en-2-yl Pivalate (l6). A round-bottomed flask was charged with $Pd(CH_3CN)_2Cl_2$ (1.78 g, 7.4 mmol), PPh_3 (5.84 g, 22.2 mmol), and a solution of **15** (27 g, 74 mmol) in dry DMF (400 mL). After 15 min, allyltributyltin

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(23 mL, 74 mmol) and LiCl (9.43 g, 222 mmol) was introduced. The resulting mixture was heated to 100 °C for 24 h, taken up in water (400 mL), and extracted with hexane (3 × 400 mL). The organic layers were combined, and most of the solvent was evaporated. The residue was treated with a saturated KF solution (100 mL) at rt. The precipitate so formed was filtered off and washed with hexane (50 mL). The organic layer was washed with brine, dried, and evaporated. The residue was purified by column chromatography (silica gel, ethyl acetate/hexane 1:100) to give **16** (17 g, 83%) as a colorless oil; IR (film, cm^{-1}) 1728, 1480, 1461; ^1H NMR (300 MHz, $CDCl_3$) δ 5.87−5.72 (m,1H) 5.24 (d, $J = 1.3$ Hz, 1H), 5.11−4.98 (m, 3H), 2.85 (dd, $J = 6.9$, 1.3 Hz, 2H), 2.51−2.41 (m, 1H), 2.17 (d, $J = 3.6$ Hz, 1H), 1.13 (s, 9H), 1.00 (s, 3H) 0.85, (dd, $J = 13.1$, 3.0 Hz, 1H), 0.844 (s, 3H), 0.838 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.8, 147.6, 135.5, 128.7, 115.8, 81.3, 57.5, 56.8, 54.7, 38.7, 35.6, 35.0, 27.0, 19.9, 11.1; HRMS (ES) *m*/*z* calcd for $C_{18}H_{28}O_2Na^+$ 299.1981, obsd 299.1962; $[\alpha]^{24}_D$ +52.7 (*c* 0.97, $CHCl_3$).

5-(3-Hydroxypropyl)-1,7,7-trimethylbicyclo[2.2.1]hept-5-en-2-yl Pivalate (17). To a solution of 2,3-dimethyl-2-butene (1 M in THF, 66 mL) at 0 °C was added a solution of BH_3 (1 M in THF, 66 mL). After 1 h of stirring at 0 °C, a solution of **16** (17 g, 61 mmol) in dry THF (100 mL) was introduced by cannula and the resulting reaction mixture was stirred for 3 h at 0 °C, treated with hydrogen peroxide (30%, 66 mL) followed by the slow addition of a 15% aqueous NaOH solution (66 mL) in the cold. After a further 1 h of stirring at 0 °C, water (100 mL) was added and the whole was extracted several times with ether. The combined organic layers were washed with brine, dried, and concentrated. The residue was purified by flash chromatography (silica gel, ethyl acetate/hexanes 1:9 to 1:3) to give 15 g (85%) of **17** as a colorless oil. In addition, 854 mg (5%) of **18** was also isolated as a colorless oil.

For **17**: IR (film, cm^{-1}) 3435, 1727, 1708; ^1H NMR (300 MHz, $CDCl_3$) δ 5.24 (d, $J = 1.3$ Hz, 1H), 5.11 (dd, $J = 7.6$, 2.6 Hz, 1H), 3.69 (t, $J = 6.6$ Hz, 2H) 2.52−2.42 (m, 1H), 2.22−2.13 (m, 3H), 1.84−1.62 (m. 2H), 1.34 (br s, 1H, OH), 1.13 (s, 9H), 1.00 (s, 3H), 0.84 (s, 3H), 0.84 (dd, $J = 13.1$, 2.6, Hz, 1H): ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.9, 149.0, 127.8, 81.2, 62.7, 57.5, 56.5, 55.0, 38.6, 35.5, 30.2, 27.0, 26.4, 19.9, 19.2, 11.2; HRMS (ES) *m*/*z* calcd for $C_{18}H_{30}O_3Na^+$ 317.2087, obsd 317.2080; $[\alpha]^{24}_D$ + 21.6 (*c* 1.23, $CHCl_3$).

For **18**: IR (film, cm^{-1}) 1728, 1480, 1458; ^1H NMR (300 MHz, $CDCl_3$) δ 5.19 (d, $J = 1.0$ Hz, 1H), 5.09 (dd, $J = 7.6$, 2.6 Hz, 1H) 2.50−2.40 (m, 1H), 2.13 (d, $J = 3.6$ Hz, 1H), 2.11−2.02 (m, 2H), 1.55−1.38 (m, 2H), 1.25 (br s, 1H, OH), 1.13 (s, 9H), 0.99 (s, 3H), 0.93 (t, $J = 7.2$ Hz, 3H), 0.84 (s, 3H), 0.83 (s, 3H), 0.83 (dd, $J = 13.1$, 2.6 Hz 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.9, 149.6, 127.5, 81.3, 57.4, 56.4, 55.0, 38.5, 32.5, 27.0, 20.4, 19.9, 19.3, 14.1, 11.2; HRMS (ES) *m*/*z* calcd for $C_{18}H_{30}O_2Na^+$ 301.2138, obsd 301.2141; $[\alpha]^{24}_D$ +43.3 (*c* 1.17, $CHCl_3$).

5-(3-(Methoxymethoxy)propyl)-1,7,7-trimethylbicyclo[2.2.1]-hept-5-en-2-yl Pivalate (19). A solution of **17** (680 mg, 2.31 mmol) and diisopropylethylamine (0.46 mL, 2.77 mmol) in dry CH_2Cl_2 (10 mL) was cooled to 0 °C, treated dropwise with MOMCl (0.19 mL, 2.54 mmol), allowed to warm to rt, and stirred overnight prior to quenching with saturated $NaHCO_3$ solution (3.5 mL) and water (40 mL), and extraction with ether (1 × 20 mL and 2 × 15 mL). The combined ethereal layers were washed with brine, dried, and concentrated. The residue was purified by flash column chromatography (silica gel, ethyl acetate/hexanes 1:32) to provide 735 mg (94%) of **19** as a colorless oil; IR (film, cm^{-1}) 1728, 1480, 1457; ^1H NMR (300 MHz, $CDCl_3$) δ 5.22 (d, $J = 1.3$ Hz, 1H), 5.09 (dd, $J = 7.6$, 2.6 Hz, 1H), 4.61 (s, 2H), 3.55 (td, $J = 6.6$, 1.6 Hz, 2H), 3.35 (s, 3H), 2.51−2.41 (m, 1H), 2.21−2.12 (m, 3H), 1.86−1.63 (m, 2H), 1.12 (s, 9H), 0.99 (s, 3H), 0.83 (s, 3H), 0.83 (dd, $J = 12.8$, 2.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.8, 149.0, 127.8, 96.4, 81.2, 67.5, 57.5, 56.5, 55.1, 55.0, 38.7, 35.5, 27.4, 27.0, 26.7, 19.9, 19.3, 11.2; HRMS (ES) *m*/*z* calcd for $C_{20}H_{34}O_4Na^+$ 361.2349, obsd 361.2385; $[\alpha]^{24}_D$ +38.9 (*c* 1.26, $CHCl_3$).

5-(3-(Methoxymethoxy)propyl-1,7,7-trimethylbicyclo[2.2.1]-hept-5-en-2-ol (20). A solution of **19** (735 mg, 2.17 mmol) in dry CH_2Cl_2 (30 mL) was cooled to −78 °C and DIBAL-H (1.0 M in hexanes, 2.40 mL, 2.40 mmol) was added dropwise. After complete deprotection (TLC analysis), the reaction mixture was quenched with saturated $NaHCO_3$ solution (1.5 mL), and saturated K−Na tartrate solution (3 mL) was added. The mixture was warmed to rt, stirred overnight, and diluted with water (40 mL). The separated aqueous layer was extracted with ether (3 × 20 mL). The combined organic layers were washed with brine, dried, and concentrated. The crude product was purified by flash column chromatography (silica gel, ethyl acetate/hexanes 1:9 to 1:3) to give 520 mg (94%) of **20** as a colorless oil; IR (film, cm^{-1}) 3447, 1472, 1463; ^1H NMR (300 MHz, $CDCl_3$) δ 5.25 (s, 1H), 4.61 (s, 2H), 4.09 (dd, $J = 7.6$, 2.3 Hz, 1H), 3.56 (t, $J = 6.6$ Hz, 2H), 3.35 (s, 3H), 2.46−2.36 (m, 1H), 2.21 (td, $J = 7.6$, 1.6 Hz, 2H), 2.13 (d, $J = 3.6$ Hz, 1H), 1.87−1.65 (m, 2H), 1.04 (s, 3H), 0.82 (s, 3H), 0.76 (s, 3H), 0.76 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.0, 126.0, 96.4, 78.9, 67.6, 58.2, 57.7, 55.3, 55.1, 38.0, 27.3, 27.1, 20.4, 19.0, 10.8; HRMS *m*/*z* calcd for $C_{20}H_{34}O_4Na^+$ 254.1882, obsd 254.1873; $[\alpha]^{24}_D$ +33.8 (*c* 0.855, $CHCl_3$).

5-(3-(Methoxymethoxy)propyl)-1,7,7-trimethylbicyclo[2.2.1]-hept-5-en-2-on e (13). To a solution of **20** (519 mg, 2.04 mmol) in dry CH_2Cl_2 (35 mL) was added Dess−Martin periodinane (1.30 g, 3.06 mmol) portionwise at 0 °C. After being stirred at rt for 24 h, the reaction mixture was cooled again to 0 °C, treated with saturated $NaHCO_3$ (14 mL) and $Na_2S_2O_3$ (14 mL) solutions, and stirred for a further 15 min at 0 °C. The separated aqueous layer was extracted another two times with CH_2Cl_2. The organic layers were combined, washed with brine, dried, and evaporated to leave a residue that was purified by flash chromatography (silica gel, ethyl acetate/hexanes 1:9) to yield 494 mg (96%) of **13** as a colorless oil; IR (film, cm^{-1}) 1742, 1469, 1447; ^1H NMR (300 MHz, $CDCl_3$) δ 4.86 (s,1H), 4.46 (s, 2H), 3.35 (t, $J = 1.7$ Hz, 2H), 3.17 (s, 3H), 2.00−1.88 (m, 4H), 1.66−1.49 (series of m, 3H), 0.98 (s, 3H), 0.83 (s, 3H), 0.63 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.4, 156.5, 124.3, 96.4, 67.2, 65.6, 59.2, 55.1, 52.0, 36.2, 27.7, 26.6, 19.5, 19.1, 7.0; HRMS (ES) *m*/*z* calcd for $C_{15}H_{24}O_3Na^+$ 252.1725, obsd 252.1724; $[\alpha]^{24}_D$ +594.1 (*c* 0.41, $CHCl_3$).

2-[3-(*tert*-Butyldiphenylsilyloxy)-1-methyl-propenyl]-5(3-methoxymethoxypropyl-1,7,7-trimethylbicyclo[2.2.1]hept-5-en-2-ol (12). To a solution of **21** (26.3 g, 67.6 mmol) in dry THF (175 mL) was added *t*-BuLi (1.7 M in pentane, 79.6 mL, 135.3 mmol) dropwise at −78 °C. The mixture was stirred for another 30 min at −78 °C and was subsequently transferred with vigorous stirring into a solution of **13** (5.69 g, 22.6 mmol) in dry THF (260 mL) which was cooled to −40 °C. After being stirred for another 4 h at −40 °C, the reaction mixture was quenched with saturated NH_4Cl solution (88 mL) and allowed to warm to rt. Water (350 mL) was added, the separated aqueous layer was extracted with ether (1 × 200 mL and 2 × 50 mL) and the organic layers were combined, washed with brine, dried, and concentrated. The residue was purified by flash chromatography (silica gel, ethyl acetate/hexanes 1:32, 1:19 and 1:9) to yield 7.67 g (61%) of **12** as a colorless oil; IR (film, cm^{-1}) 3482, 1472, 1463; ^1H NMR (300 MHz, $CDCl_3$) δ 7.71−7.65 (m, 4H), 7.44−7.34 (m, 6H), 5.44 (dt, $J = 5.9$, 1.0 Hz, 1H), 5.06 (d, $J = 1.3$ Hz, 1H), 4.60 (s, 2H), 4.24 (d, $J = 5.9$ Hz, 1H) 3.50 (dt, $J = 6.6$, 1.0 Hz, 2H), 3.34 (s, 3H), 2.13 (d, $J = 1.3$ Hz, 1H), 2.08−1.97 (m, 3H), 1.82−1.60 (m, 3H), 1.40 (s, 3H), 1.13 (s, 3H), 1.04 (s, 9H), 1.02 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.2, 140.7, 135.6, 134.0, 133.9, 131.1, 129.6, 127.6, 126.1, 96.4, 86.3, 67.6, 61.6, 60.7, 59.9, 55.1, 54.2, 38.4, 27.1, 26.85, 26.77, 22.2, 21.5, 19.1, 15.4, 8.8; HRMS (ES) *m*/*z* calcd for $C_{35}H_{50}O_4Na^+$ 585.3371, obsd 585.3419; $[\alpha]^{24}_D$ +42.5 (*c* 1.09, $CHCl_3$).

(3a*R*,5*S*,6*R*,7*S*,7a*R*)-7-((*tert*-Butyldiphenylsilyloxy)methyl)-7a-(3-(methoxy methoxy)propyl)-2,3,3,6-tetramethyl-3a,4,5,6,7,7a-hexahydro-3*H*-inden-5-ol (23a). To a solution of **11a**[21] (7.25 g, 12.9 mmol) in dry CH_2Cl_2 (725 mL) was added DIBAL-H (1.0 M

in hexane, 28.3 mL, 28.3 mmol) dropwise at −78 °C. After being stirred for 3 h at this temperature, the reaction mixture was quenched with saturated Na−K tartrate solution (100 mL), allowed to warm to rt, and diluted with water (400 mL). The separated aqueous layer was extracted with CH_2Cl_2 (3 × 200 mL). The combined organic phases were washed with brine, dried, and evaporated, and the crude product was purified by flash chromatography (silica gel, ethyl acetate/hexanes 1:19) to provide 6.35 g (87%) of **23a** as a colorless oil. In addition, 422 mg (6%) of **25a** also was isolated.

For **23a**: IR (film, cm^{-1}) 3446, 1472, 1462; ^1H NMR (300 MHz, $CDCl_3$) δ 7.71−7.65 (m, 4H), 7.45−7.33 (m, 6H), 5.25 (d, J = 1.3 Hz, 2H), 4.59 (s, 2H), 3.77−3.64 (m, 2H), 3.48−3.36 (m, 2H), 3.35 (s, 3H), 2.16−2.03 (m, 1H), 1.82−1.34 (series of m, 8H) 1.55 (d, J = 1.3 Hz, 3H), 1.10 (s, 3H), 1.04 (s, 9H), 0.94−089 (m, 3H), 0.91 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.4, 135.6, 135.6, 133.8, 129.5, 129.5, 128.8, 127.6, 96.3, 70.8, 68.5, 62.6, 55.1, 51.0. 50.9, 47.4, 46.9, 38.4, 33.9, 31.9, 29.6, 26.8, 25.6, 23.4, 19.1, 12.5, 10.9; HRMS (EI) m/z calcd for $C_{35}H_{50}O_4-C_4H_9$ 507.2931, obsd 507.2970; $[\alpha]^{24}_D$ +15.5 (c 1.30, $CHCl_3$).

For **25a**: IR (film, cm^{-1}) 3359, 1472, 1438; ^1H NMR (500 MHz, $CDCl_3$) δ 7.68−7.64 (m, 4H), 7.44−7.34 (m, 6H), 5.23 (d, J = 1.3 Hz, 1H), 4.62 (s, 2H), 3.57−3.44 (m, 4H), 3.36 (s, 3H), 3.55−3.28 (m, 1H), 1.86 (t, J = 6.9 Hz, 2H), 1.77−1.69 (m, 1H), 1.65−1.41 (m, 8H), 1.55 (d, J = 1.3 Hz, 3H), 1.04 (d, J = 6.9 Hz, 3H), 1.03 (s, 9H) 1.02 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.7, 135.6, 133.8, 133.8, 129.5, 129.3, 127.6, 127.5, 96.4, 71.6, 68.6, 62.3, 55.1, 51.6, 50.8, 47.5, 38.1, 37.4, 32.9, 30.0, 26.7, 25.6, 21.9, 19.0, 16.6, 12.4; HRMS (ES) m/z calcd for $C_{35}H_{52}O_4SiNa^+$ 587.3527, obsd 585.3510; $[\alpha]^{24}_D$ +9.15 (c 1.11, $CHCl_3$).

(3a*R*,5*S*,6*R*,7*S*,7a*R*)-7-((*tert*-Butyldiphenylsilyloxy)methyl)-7a-(3-(methoxy methoxy)propyl)-2,3,3,6-tetramethyl-3a,4,5,6,7,7a-hexahydro-3*H*-inden-5-yl Pivalate (24a). To a solution of **23a** (6.35 g, 11.2 mmol) in dry CH_2Cl_2 (450 mL) at 0 °C was added pyridine (1.83 mL, 22.5 mmol), pivaloyl chloride (5.53 mL, 45 mmol), and DMAP (1.37 g, 11.2 mmol). The reaction mixture was allowed to warm to rt, stirred for 24 h, returned to 0 °C, and quenched with saturated $NaHCO_3$ solution (100 mL) and water (200 mL). The separated aqueous layer was extracted with CH_2Cl_2 (3 × 80 mL). The organic layers were combined, washed with brine, dried, and freed of solvent. The residue was chromatographed on silica gel (ethyl acetate/hexanes 1:49 and 1:19) to yield 7.13 g (98%) of **24a** as a colorless oil; IR (film, cm^{-1}) 1725, 1479, 1472; ^1H NMR (500 MHz, $CDCl_3$) δ 7.71−7.63 (m, 4H), 7.43−7.33 (m, 6H), 5.47 (s, 1H), 4.83 (dd, J = 13.6, 7.6 Hz, 1H), 4.62 (s, 2H), 3.70 (dd, J = 10.4, 3.2 Hz, 1H), 3.56 (dd, J = 10.4, 6.9 Hz, 1H), 3.53−3.43 (m, 2H), 3.37 (s, 3H), 2.09−2.00 (m, 1H), 1.93−1.84 (m, 1H), 1.80−1.73 (m, 1H), 1.73−1.44 (overlapping signals: d, J = 1.3 Hz, 3H and m, 5H), 1.11 (s, 3H), 1.06 (s, 9H), 0.97 (s, 9H), 0.87−0.81 (m, 3H), 0.85 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.0, 144.9, 135.7, 133.9, 129.5, 129.4, 128.4, 127.5, 96.4, 72.5, 68.6, 63.2, 55.1, 52.4, 50.8, 47.8, 47.3, 38.7, 38.6, 31.9, 30.1, 29.5, 27.0, 26.9, 25.5, 23.2, 19.1, 13.3, 12.5; HRMS (ES) m/z calcd for $C_{40}H_{60}O_5SiNa^+$ 671.4102, obsd 671.4095; $[\alpha]^{24}_D$ +31.5 (c 1.33, $CHCl_3$).

(3a*R*,5*R*,6*R*,7*S*,7a*R*)-7-((*tert*-Butyldiphenylsilyloxy)methyl)-7a-(3-(methoxy methoxy)propyl)-2,3,3,6-tetramethyl-3a,4,5,6,7,7a-hexahydro-3*H*-inden-5-yl Pivalate (26a). A solution of **25a** (104 mg, 0.185 mmol) and pyridine (31 μL, 0.369 mmol) in dry CH_2Cl_2 (10 mL) was treated with pivaloyl chloride (91 μL, 0.739 mmol) and DMAP (22.6 mg, 0.185 mmol) according to the procedure described above to yield 101 mg (84%) of **26a** as a colorless oil; IR (film, cm^{-1}) 1724, 1479, 1472; ^1H NMR (500 MHz, $CDCl_3$) δ 7.66−7.63 (m, 4H), 7.44−7.34 (m, 6H), 5.15 (d, J = 1.3 Hz, 1H), 4.62 (s, 2H), 4.48−4.41 (m, 1H), 3.60 (dd, J = 10.4, 4.4 Hz, 1H), 3.56 (dd, J = 10.4, 5.7 Hz, 1H), 3.52−3.45 (m, 2H), 3.37 (s, 3H), 2.04−1.96 (m, 1H), 1.89 (dd, J = 10.1, 5.0 Hz, 1H), 1.82 (t, J = 6.6 Hz, 1H), 1.68−1.50 (overlapping signals: 1.53, d, J = 1.3 Hz, 1H and m, 5H), 1.48−1.39 (m, 1H), 1.18 (s, 9H), 1.03 (s, 9H), 0.99 (s, 3H), 0.95 (d, J = 6.9 Hz, 3H), 0.85 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.4, 144.9, 135.7, 135.6, 133.8, 133.8, 129.5, 129.2, 127.6, 127.6, 96.4, 74.6, 68.6, 62.3, 55.1, 51.4, 50.9, 48.7, 47.7, 38.7, 38.3, 34.3, 29.9, 29.2, 27.1, 26.8, 25.7, 21.9, 19.1, 16.4, 12.4; HRMS (ES) m/z calcd for $C_{40}H_{60}O_5SiNa^+$ 671.4102, obsd 671.4132; $[\alpha]^{24}_D$ −15.7 (c 1.02, $CHCl_3$).

(3a*R*,5*S*,6*R*,7*S*,7a*R*)-7-((*tert*-Butyldiphenylsilyloxy)methyl)-7a-(3-hydroxypr opyl)-2,3,3,6-tetramethyl-3a,4,5,6,7,7a-hexahydro-3*H*-inden-5-yl Pivalate (27a). A solution of **24a** (102 mg, 0.157 mmol) in dry CH_2Cl_2 (10 mL) was cooled to −40 °C and 9-BBNBr (1.0 M in CH_2Cl_2, 0472 mL, 0.472 mmol) was added dropwise. After being stirred for 3 h at −40 °C, the reaction mixture was quenched with saturated $NaHCO_3$ solution (2.5 mL) and water (15 mL), and the separated aqueous layer was extracted with CH_2Cl_2 (3 × 8 mL). The combined organic layers were washed with brine, dried, and concentrated. The residue so obtained was purified by flash chromatography (silica gel, ethyl acetate/hexanes 1:19 and 1:9) to yield 72 mg (76%) of **27a** as a colorless oil; IR (film, cm^{-1}) 3450, 1724, 1709; ^1H NMR (400 MHz, $CDCl_3$) δ 7.70−7.65 (m, 4H), 7.44−7.33 (m, 6H), 5.46 (d, J = 1.0 Hz, 1H), 4.82 (dd, J = 15.2, 7.1 Hz, 1H) 3.71 (dd, J = 10.6, 3.5 Hz, 1H), 3.62−3.53 (m, 3H), 2.09−2.00 (m, 1H), 1.92−1.84 (m, 1H), 1.77−1.72 (m, 1H), 1.71−1.39 (m, 8H), 1.59 (d, J = 1.5 Hz, 3H) 1.11 (s, 3H), 1.06 (s, 9H) 0.97 (s, 9H), 0.86−0.82 (m, 3H), 0.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.0, 145.0, 135.7, 133.9, 129.5, 129.5, 128.3, 127.6, 72.5, 63.7, 63.1, 52.2, 50.7, 47.7, 47.2, 38.6, 38.2, 31.9, 30.1, 29.4, 28.6, 27.0, 26.9, 23.2, 19.1, 13.2, 12.6; HRMS (ES) m/z calcd for $C_{38}H_{56}O_4SiNa^+$ 627.3840, obsd 627.3795; $[\alpha]^{24}_D$ +14.6 (c 0.93, $CHCl_3$).

(3a*R*,5*S*,6*R*,7*S*,7a*R*)-7-((*tert*-Butyldiphenylsilyloxy)methyl)-2,3,3,6-tetramethyl-7a-(3-oxopropyl)-3a,4,5,6,7,7a-hexahydro-3*H*-inden-5-yl Pivalate (10a). To a solution of **27a** (500 mg, 0.827 mmol) in dry CH_2Cl_2 (210 mL) was added Dess−Martin periodinane (526 mg, 1.24 mmol) portionwise at 0 °C. The reaction mixture was stirred overnight at rt, returned to 0 °C, and diluted with saturated $NaHCO_3$ (50 mL) and $Na_2S_2O_3$ solutions (50 mL). The mixture was stirred until all suspended solids had dissolved, at which point the separated aqueous phase was extracted with CH_2Cl_2 (3 × 35 mL). The combined organic layers were washed with brine, dried, and concentrated. The residue was purified by flash column chromatography (silica gel, ethyl acetate/hexanes 1:19) to give 442 mg (89%) of **10a** as a colorless oil; IR (film, cm^{-1}) 1725, 1478, 1472; ^1H NMR (400 MHz, $CDCl_3$) δ 9.78 (t, J = 1.5 Hz, 1H), 7.69−7.63 (m, 4H), 7.44−7.33 (m, 6H), 5.45 (d, J = 1.0 Hz, 1H), 4.83 (dd, J = 14.2, 8.1 Hz, 1H), 6.70 (dd, J = 10.6, 3.0 Hz, 1H), 3.52 (dd, J = 10.6, 7.1 Hz, 1H), 2.49 (dt, J = 1.5, 8.1 Hz, 2H), 2.04−19.0 (m, 2H), 1.88−1.71 (s, 2H), 1.61 (d, J = 1.5 Hz, 3H), 1.60−1.57 (m, 2H), 1.12 (s, 3H) 1.07 (s, 9H), 0.95 (s, 9H), 0.86 (s, 3H), 0.82 (d, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.9, 178.0, 146.5, 135.6, 133.7, 129.6, 129.5, 127.6, 127.1, 72.1, 63.0, 52.2, 50.7, 48.2, 47.3, 40.4, 38.6, 33.6, 31.9, 30.1, 29.7, 27.0, 26.9, 23.2, 19.1, 13.5, 12.6; HRMS (ES) m/z calcd for $C_{38}H_{54}O_4SiNa^+$ 625.3684, obsd 625.3666; $[\alpha]^{24}_D$ +30.7 (c 1.08, $CHCl_3$).

Ene Reaction Involving 10a. (3*R*,3a*R*,5a*R*,7*S*,8*R*,9*S*,9a*R*)-9-((*tert*-Butyldiphenylsilyloxy)methyl)-3-hydroxy-5,5,8-trimethyl-4-methylene-decahydro-1*H*-cyclopenta[*i*]inden-7-yl Pivalate (9a). A flask containing dry CH_2Cl_2 (35 mL) was cooled to −78 °C, and $EtAlCl_2$ (1 M in hexanes, 0.71 mL, 0.705 mmol) was added. In a separate flask, aldehyde **10a** (106 mg, 0.176 mmol) was dissolved in dry CH_2Cl_2 (31 mL), 4 Å molecular sieves were added, and the mixture was cooled to −78 °C. At this point, the aldehyde solution was cannulated slowly into the $EtAlCl_2$ solution in the cold. The mixture was stirred for 3 h, quenched with saturated $NaHCO_3$ (5.6 mL) and Na−K tartrate solutions (12 mL) at −78 °C, allowed to warm to rt, and stirred overnight. Water (10 mL) was introduced, the separated aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL), and the combined organic layers were washed with brine, dried, and concentrated. The residue was purified by

flash chromatography (silica gel, ethyl acetate/hexanes 1:32) to yield 72 mg (68%) of **9a** and 16 mg (14%) of **28a**, both as colorless oils.

For **9a**: IR (film, cm^{-1}) 3548, 1726, 1471; ^1H NMR (500 MHz, $CDCl_3$) δ 7.66−7.62 (m, 4H), 7.44−7.34 (m, 6H), 5.06 (d, J = 1.6 Hz, 1H), 4.89 (d, J = 1.6 Hz, 1H), 4.83 (dt, J = 9.8, 6.0 Hz, 1H), 4.24−4.18 (m, 1H), 3.71 (dd, J = 10.7, 5.0 Hz, 1H), 3.56 (dd, J = 10.7, 6.6 Hz, 1H), 3.44 (d, J = 6.0 Hz, 1H), 2.21−2.13 (m, 1H), 1.94−1.83 (m, 4H), 1.71 (dd, J = 13.9, 5.0 Hz, 1H) 1.68−1.60 (m, 1H), 1.53−1.46 (m, 1H), 1.21 (s, 3H), 1.05 (s, 9H), 1.01 (s, 12H), 0.99−0.94 (m, 1H), 0.84 (d, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.0, 161.7, 135.6, 135.6, 133.5, 129.7, 129.7, 127.7, 127.7, 108.6, 74.6, 72.9, 62.7, 56.6, 54.5, 53.3, 52.1, 46.2, 40.5, 38.7, 33.9, 32.9, 32.2, 29.6, 27.0, 26.9, 26.8, 19.2; HRMS (ES) m/z calcd for $C_{38}H_{54}O_4SiNa^+$ 625.3684, obsd 625.3712; $[\alpha]^{24}_D$ +9.5 (c 0.67, $CHCl_3$).

For **28a**: IR (film, cm^{-1}) 3504, 1725, 1710; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72−7.64 (m, 4H), 7.44−7.33 (m, 6H), 5.47 (s, 1H), 4.86−4.78 (m, 1H), 3.70 (dd, J = 10.6, 3.5 Hz, 1H), 3.56 (dd, J = 10.6, 7.1 Hz, 1H), 3.48−3.40 (m, 1H), 2.08−1.98 (m, 1H), 1.81−1.62 (m, 2H), 1.59 (s, 3H), 1.58−1.36 (m, 8H, 1.12 (s, 3H), 1.06 (s, 9H), 0.99−0.93 (m, 3H), 0.97 (s, 9H), 0.85 (s, 3H), 0.82 (d, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.0, 145.0, 145.0, 135.7, 133.9, 129.5, 129.5, 128.3, 128.2, 127.8, 127.5, 74.1, 73.9, 72.5, 72.5, 63.1, 63.0, 52.4, 52.3, 50.8, 47.9, 47.6, 47.2, 38.6, 38.0, 37.9, 32.5, 31.9, 30.2, 30.1, 30.1, 29.5, 29.5, 27.0, 26.9, 23.3, 19.2, 13.3, 13.2, 12.6, 9.8; HRMS (ES) m/z calcd for $C_{40}H_{60}O_4SiNa^+$ 655.4153, obsd 655.4164.

(3*R*,3a*R*,5a*R*,7*S*,8*R*,9*S*,9a*R*)-9-((*tert*-Butyldiphenylsilyloxy)-methyl)-3-(methoxymethoxy)-5,5,8-trimethyl-4-methylene-decahydro-1*H*-cyclopenta[*i*]inden-7-yl Pivalate (29a). Potassium hydride (30% in mineral oil; 16.6 mg, 0.124 mmol) was suspended in dry THF (7 mL), and a solution of **9a** (15 mg, 0.025 mmol) in dry THF (3 mL) was added via cannula at rt. After 30 min of stirring, MOMCl (0.04 mL, 5.27 mmol) was introduced, and the reaction mixture was stirred for 48 h at 50 °C. The same amount of MOMCl was introduced again and agitation with heating was continued for another 48 h. If necessary, more MOMCl was added and the reaction time was extended to complete the conversion. The reaction mixture was cooled to 0 °C, quenched with saturated $NaHCO_3$ solution (3 mL) and water (15 mL), and extracted with ether (3 × 10 mL). The organic layers were combined, washed with brine, dried, and freed of solvent. The residue was purified by column chromatography (silica gel, ethyl acetate/hexanes 1:32) to yield 9.5 mg (63%) of **29a** as a colorless oil; IR (film, cm^{-1}) 1726, 1472, 1461; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68−7.64 (m, 4H), 7.45−7.34 (m, 6H), 5.01−4.99 (m, 1H), 4.94 (dd, J = 2.0, 1.0 Hz, 1H), 4.82 (dt, J = 9.6, 5.6 Hz, 1H), 4.60 (d, J = 6.6 Hz, 1H), 4.74 (d, J = 6.6 Hz, 1H), 4.15 (dd, J = 13.1, 6.6 Hz, 1H), 3.66 (dd, J = 10.6, 5.6 Hz, 1H), 3.62 (dd, J = 10.6, 6.1 Hz, 1H), 3.31 (s, 3H), 3.29 (d, J = 6.6 Hz, 1H), 2.24−2.14 (m, 1H), 1.86−1.66 (m, 6H), 1.63−1.51 (m, 2H), 1.89 (s, 3H), 1.06 (s, 9H), 1.03 (s, 9H), 0.97 (s, 3H), 0.83 (d, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.0, 160.0, 135.6, 133.6, 133.6, 129.6, 127.7, 108.2, 95.9, 81.0, 73.1, 63.0, 55.3, 54.0, 53.1, 51.6, 45.6, 40.5, 38.7, 32.9, 31.2, 30.8, 29.1, 27.2, 27.1, 26.9, 19.1, 11.4; HRMS (ES) m/z calcd for $C_{40}H_{58}O_5SiNa^+$ 669.3946; obsd 699.3966; $[\alpha]^{24}_D$ +15.8 (c 0.61, $CHCl_3$).

(3a*R*,5*S*,6*S*,7*S*,7a*R*)-7-((*tert*-Butyldiphenylsilyloxy)methyl)-7a-(3-(methoxymethoxy)propyl)-2,3,3,6-tetramethyl-3a,4,5,6,7,7a-hexahydro-3*H*-inden-5-ol (23b). Ketone **11b**[21] (3.38 g, 6.01 mmol) dissolved in dry CH_2Cl_2 (340 mL) was treated with DIBAL-H (1.0 M in hexane, 13.2 mL, 13.2 mmol) according to the procedure detailed above to yield 2.86 g (84%) of **23b** as a colorless oil; IR (film, cm^{-1}) 3423, 1472, 1447; ^1H NMR (500 MHz, $CDCl_3$) δ 7.69−7.62 (m, 4H), 7.45−7.35 (m, 6H), 4.80 (d, J = 1.3 Hz, 1H), 4.60 (s, 2H), 3.61 (dd, J = 10.1, 5.0 Hz, 1H), 3.50−3.42 (m, 3H), 3.35 (s, 3H), 3.31 (t, J = 9.8 Hz, 1H), 1.83 (dd, J = 12.3, 7.3 Hz, 1H), 1.69−1.61 (m, 3H), 1.54−1.31 (overlapping signals: 1.46, d, J = 1.3 Hz, 3H and m, 5H), 1.17 (d, J = 6.9 Hz, 3H), 1.13 (d, J = 12.0 Hz, 1H), 1.06 (s, 9H), 0.99 (s, 3H), 0.72 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 135.7, 135.7, 134.1, 134.0, 129.6, 129.5, 128.2, 127.6, 96.4, 74.3, 68.4, 68.3, 55.1, 52.7, 51.2, 50.4, 47.8, 41.4, 40.2, 33.4, 29.3, 26.9, 25.6, 23.5, 21.3, 19.2, 12.0; HRMS (ES) m/z calcd for $C_{35}H_{52}O_4SiNa^+$ 587.3527, obsd 587.3523; $[\alpha]^{24}_D$ +13.5 (c, 1.11, $CHCl_3$).

(3a*R*,5*S*,6*S*,7*S*,7a*R*)-7-((*tert*-Butyldiphenylsilyloxy)methyl)-7a-(3-(methoxymethoxy)propyl)-2,3,3,6-tetramethyl-3a,4,5,6,7,7a-hexahydro-3*H*-inden-5-yl Pivalate (24b). A solution of alcohol **23b** (3.09 g, 5.47 mmol) and pyridine (0.892 mL, 10.9 mmol) in dry CH_2Cl_2 (220 mL) was treated with pivaloyl chloride (2.69 mL, 21.9 mmol) and DMAP (668 mg, 5.47 mmol) according to the procedure described above to provide 3.29 g (93%) of **24b** as a colorless oil; IR (film, cm^{-1}) 1724, 1479, 1472; ^1H NMR (500 MHz, $CDCl_3$) δ 7.69−7.64 (m, 4H), 7.45−7.34 (m, 6H), 4.80 (d, J = 1.3 Hz, 1H), 4.67 (dt, J = 10.4, 3.8 Hz, 1H), 4.69 (s, 2H), 3.61 (dd, J = 10.4, 5.0 Hz, 1H), 3.49−3.39 (m, 2H), 3.35 (s, 3H), 3.32 (t, J = 9.8 Hz, 1H), 2.07−1.98 (m, 1H), 1.90 (dd, J = 11.4, 7.3 Hz, 1H), 1.75−1.69 (m, 1H), 1.67−1.62 (m, 1H), 1.52−1.45 (overlapping signals: 1.46, d, J = 1.3 Hz, 3H and m, 3H), 1.22 (s, 9H), 1.07−1.04 (overlapping signals: 1.06, s, 9H and m, 3H), 0.97 (s, 3H), 0.67 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.6, 145.1, 135.7, 135.6, 133.9, 133.7, 129.6, 127.7, 127.6, 96.3, 76.8, 68.3, 67.7, 55.1, 52.0, 51.4, 49.7, 47.8, 40.8, 38.7, 35.8, 29.5, 29.3, 27.2, 26.8, 25.5, 23.4, 20.7, 19.2, 12.1; HRMS (ES) m/z calcd for $C_{40}H_{60}O_5SiNa^+$ 671.4102, obsd 671.4133; $[\alpha]^{24}_D$ +21.5 (c 1.05, $CHCl_3$).

(3a*R*,5*S*,6*S*,7*S*,7a*R*)-7-((*tert*-Butyldiphenylsilyloxy)methyl)-7a-(3-hydroxypropyl)-2,3,3,6-tetramethyl-3a,4,5,6,7,7a-hexahydro-3*H*-inden-5-yl Pivalate (27b). Compound **24b** (3.73 g, 5.73 mmol) dissolved in dry CH_2Cl_2 (324 mL) was deprotected with 9-BBNBr (1.0 M in CH_2Cl_2, 17.2 mL, 17.2 mmol) following the procedure described above so that 2.80 g (81%) of **27b** was isolated as a colorless oil; IR (film, cm^{-1}) 3448, 1724, 1706, 1664; ^1H NMR (400 MHz, $CDCl_3$) δ 7.69−7.64 (m, 4H), 7.46−7.34 (m, 6H), 4.80 (d, J = 1.5 Hz, 1H), 4.66 (dt, J = 10.1, 4.0 Hz, 1H), 3.61, (dd, J = 10.1, 5.1 Hz, 1H), 3.59−3.51 (m, 2H), 3.33 (t, J = 10.1 Hz, 1H), 2.07−1.96 (m, 2H), 1.89 (dd, J = 11.1, 7.1 Hz, 1H), 1.77−1.69 (m, 1H), 1.66−1.60 (m, 1H), 1.46 (d, J = 1.5 Hz, 3H), 1.46−1.40 (m, 3H), 1.22 (s, 9H), 1.06, (s, 9H), 1.06 (d, J = 7.1 Hz, 3H), 0.97 (s, 3H), 0.68 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.6, 145.2, 135.7, 135.7, 133.9, 133.7, 129.6, 127.6, 76.7, 67.6, 63.5, 52.2, 51.4, 49.6, 47.9, 40.4, 38.7, 35.8, 29.5, 29.3, 38.6, 27.2, 26.9, 23.4, 20.6, 19.2, 12.1; HRMS (ES) m/z calcd for $C_{38}H_{56}O_4SiNa^+$ 627.3840, obsd 627.3836; $[\alpha]^{24}_D$ +18.8 (c 0.895, $CHCl_3$).

(3a*R*,5*S*,6*S*,7*S*,7a*R*)-7-((*tert*-Butyldiphenylsilyloxy)methyl)-2,3,3,6-tetramet hyl-7a-(3-oxopropyl)-3a,4,5,6,7,7a-hexahydro-3*H*-inden-5-yl Pivalate (10b). Alcohol **27b** (2.76 g, 4.57 mmol) dissolved in dry CH_2Cl_2 (500 mL) was oxidized by the portionwise addition of DMP (4.23 g, 9.97 mmol) according to the procedure described above to yield 2.07 g (75%) of **10b** as a colorless oil; IR (film, cm^{-1}) 1724, 1479, 1474; ^1H NMR (400 MHz, $CDCl_3$) δ 9.68 (t, J = 1.8 Hz, 1H), 7.71−7.59 (m, 4H), 7.48−7.33 (m, 6H), 4.70 (d, J = 1.0 Hz, 1H), 4.64 (td, J = 10.1, 4.0 Hz, 1H), 3.61 (dd, J = 10.1, 5.1 Hz, 1H), 3.33 (t, J = 10.1 Hz, 1H), 2.28 (dt, J = 8.1, 1.5 Hz, 2H), 2.08−1.96 (m, 1H), 1.87−1.52 (m, 6H), 1.47 (d, J = 1.5 Hz, 3H), 1.22 (s, 9H), 1.06 (s, 9H), 1.06 (d, J = 7.1 Hz, 3H), 0.97 (s, 3H), 0.69 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.5, 178,5, 146.6, 135.7, 135.6, 133.8, 133.6, 129.6, 127.7, 126.9, 76.4, 67.4, 51.5, 51.2, 50.3, 48.0, 40.3, 38.7, 35.6, 35.6, 29.2, 29.1, 27.1, 26.9, 23.4, 20.7, 19.2, 12.1; HRMS (ES) m/z calcd for $C_{38}H_{54}O_4$-$SiNa^+$ 625.3684, obsd 625.3693; $[\alpha]^{24}_D$ +22.3 (c 1.02, $CHCl_3$).

(3*R*,3a*R*,5a*R*,7*S*,8*S*,9*S*,9a*R*)-9-((*tert*-Butyldiphenylsilyloxy)-methyl)-3-hydrox y-5,5,8-trimethyl-4-methylene-decahydro-1*H*-cyclopenta[*i*]inden-7-yl Pivalate (9b). Aldehyde **10b** (115 mg, 0.183 mmol) was dissolved in dry CH_2Cl_2 (33 mL) and reacted with a solution of $EtAlCl_2$ (1 M in hexane, 0.762 mL, 0.762 mmol) in dry CH_2Cl_2 (37 mL) according to the protocol detailed earlier

to give 42.9 mg (25%, or 40% based on recovered material) of **9b** as a colorless oil; IR (film, cm^{-1}) 3548, 1725, 1480; ^1H NMNR (500 MHz, $CDCl_3$) δ 7.69−7.64 (m, 4H), 7.46−7.35 (m, 6H), 4.98 (d, J = 1.6 Hz, 1H), 4.85 (d, J = 1.6 Hz, 1H), 4.56 (ddd, J = 13.6, 10.1, 3.5 Hz, 1H), 4.07 (quint, J = 7.6 Hz, 1H), 3.69 (dd, J = 10.4, 3.8 Hz, 1H), 3.58 (dd, J = 10.4, 6.6 Hz, 1H), 2.94 (d, J = 8.2 Hz, 1H), 1.89−1.71 (m, 6H), 1.56−1.49 (m, 1H), 1.47−1.35 (m, 2H), 1.20 (s, 9H), 1.12 (s, 3H), 1.09 (s, 9H), 0.96 (d, J = 6.9 Hz, 3H), 0.90 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.4, 161.7, 135.8, 133.6, 133.5, 129.7, 127.7, 127.6, 109.0, 76.5, 73.7, 66.0, 56.7, 55.8, 54.1, 53.9, 45.9, 40.2, 38.8, 37.3, 33.9, 32.0, 31.1, 27.3, 27.2, 27.0, 19.2, 18.4; HRMS (ES) m/z calcd for $C_{38}H_{54}O_4SiNa^+$ 625.3684; obsd 625.3712; $[\alpha]^{24}_D$ −2.76 (c 0.61, $CHCl_3$).

(3*R*,3a*R*,5a*R*,7*S*,8*S*,9*S*,9a*R*)-9-((*tert*-Butyldiphenylsilyloxy)-methyl)-3-(metho xymethoxy)-5,5,8-trimethyl-4-methylene-decahydro-1*H*-cyclopenta[*i*]inden-7-yl Pivalate (29b). Compound **9b** (33.6 mg, 0.056 mmol) dissolved in dry THF (20 mL) was treated with potassium hydride (30% in mineral oil, 37.5 mg, 0.279 mmol), MOMCl (0.25 mL, 3.29 mmol), and a catalytic amount of n-Bu_4-NI at 50 °C according to the procedure described earlier. Flash chromatography (silica gel, ethyl acetate/hexanes 1:32) provided 35.1 mg (97%) of **29b** as a colorless oil; IR (film, cm^{-1}) 1725, 1644, 1590, 1479; ^1H NMR (300 MHz, $CDCl_3$) δ 7.69−7.63 (m, 4H), 7.47−7.34 (m, 6H), 4.83 (s, 1H), 4.79 (s, 1H), 4.62 (s, 2H), 4.55 (m, 1H), 3.67 (dd, J = 10.2, 4.3 Hz, 1H), 3.53 (dd, J = 10.2, 7.5 Hz, 1H), 3.30 (s, 3H), 2.81 (d, J = 7.9 Hz, 1H), 1.89 (dd, J = 12.8, 6.9 Hz, 1H), 1.85−1.55 (m, 6H), 1.46−1.37 (m, 1H), 1.99 (s, 9H), 1.12 (s, 3H), 1.07 (s, 9H), 0.97 (d, J = 6.9 Hz, 3H), 0.84 (s, 3H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.4, 160.7, 135.8, 135.7, 133.7, 129.7, 127.6, 108.0, 95.4, 80.0, 77.2, 66.9, 56.8, 55.2, 55.0, 54.3, 53.2, 45.6, 40.9, 38.8, 37.5, 31.5, 31.3, 31.3, 29.7, 27.1, 26.9, 19.3, 19.2; HRMS (ES) m/z calcd for $C_{40}H_{58}O_5SiNa^+$ 669.3946, obsd 669.3917; $[\alpha]^{24}_D$ +15.7 (c 1.59, $CHCl_3$).

Ozonolytic Epoxidation of 29b. Compound **29b** (35.7 mg, 0.552 mmol) was dissolved in dry CH_2Cl_2 (4 mL) and anhydrous methanol (4 mL). The solution was treated with ozone at −78 °C for 1 h and followed by the addition of triphenylphosphine and column chromatography. There was isolated 31.9 mg (87%) of epoxide **30** as a colorless oil; IR (film, cm^{-1}) 1724, 1479, 1462; ^1H NMR (400 MHz, $CDCl_3$) δ 7.70−7.65 (m, 4H), 7.44−7.34 (m, 6H), 4.61 (ddd, J = 11.6, 10.1, 3.5 Hz, 1H), 4.56 (d, J = 6.6 Hz, 1H), 4.49 (d, J = 6.6 Hz, 1H), 3.94 (dd, J = 13.6, 7.1 Hz, 1H), 3.89 (dd, J = 10.6, 4.6 Hz, 1H), 3.58 (dd, J = 10.1, 9.1 Hz, 1H), 3.31 (s, 3H), 3.13 (d, J = 4.6 Hz, 1H), 2.59 (d, J = 4.6 Hz, 1H), 2.30 (d, J = 7.6 Hz, 1H), 2.08−1.97 (m, 1H), 1.89 (dd, J = 12.1, 7.1 Hz, 1H), 1.79−1.62 (m, 5H), 1.52−1.45 (m, 1H), 1.21 (s, 9H), 1.09 (s, 9H), 1.04 (d, J = 7.1 Hz, 3H), 0.96 (s, 3H), 0.54 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.5, 135.7, 135.8, 135.7, 133.8, 133.7, 129.6, 129.6, 127.6, 95.8, 79.6, 76.5, 69.5, 67.3, 56.5, 55.5, 54.0, 53.5, 52.5, 48.7, 42.6, 41.9, 38.7, 36.8, 31.2, 30.1, 27.9, 27.1, 27.0, 26.9, 20.6, 20.2, 19.3; HRMS (ES) m/z calcd for $C_{40}H_{58}O_6SiNa^+$ 685.3895, obsd 685.3851; $[\alpha]^{24}_D$ +7.1 (c 0.67, $CHCl_3$).

(3*R*,3a*S*,5a*R*,7*S*,8*S*,9*S*,9a*R*)-9-((*tert*-Butyldiphenylsilyloxy)-methyl)-3-(metho xymethoxy)-5,5,8-trimethyl-4-oxo-decahydro-1*H*-cyclopenta[*i*]inden-7-yl Pivalate (31). A solution of OsO_4 (20 mg, 0.08 mmol) in t-BuOH (4 mL) was treated with a solution of **29b** (140 mg, 0.2 mmol) in THF/pH 7 buffer (5 mL/2 mL). N-Methylmorpholine N-oxide (60 mg, 0.44 mmol) was added in one portion, and the reaction mixture was stirred at rt for 4 days, cooled to 0 °C, and treated with 1.5 g of $NaHSO_3$. After 15 min of stirring, ethyl acetate and water were introduced. The separated aqueous layer was extracted with ethyl acetate (3 × 20 mL), and the combined organic layers were washed with brine, dried, and concentrated. The residue was purified by flash chromatography on silica gel (elution with ethyl acetate/hexane 1:2) to provide the diol (71 mg, 45%) as a colorless oil.

The diol was subsequently dissolved in THF (5 mL) and treated with a solution of sodium periodate (120 mg, 0.56 mmol) in water (1 mL). The reaction mixture was stirred for 2 days and diluted with water and ethyl acetate. The separated aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine, dried, and concentrated. The residue was purified by flash chromatography on silica gel (ethyl acetate/hexane 1:8) to provide ketone **31** (70 mg, 98%) as a colorless oil; IR (neat, cm^{-1}) 1727, 1161, 1039; ^1H NMR (300 MHz, $CDCl_3$) δ 7.66−7.61 (m, 4H), 7.46−7.35 (m, 6H), 4.74−4.65 (m, 1H), 4.59 (d, J = 6.9 Hz, 1H), 4.52 (d, J = 6.9 Hz, 1H), 4.27−4.24 (m, 1H), 3.57−3.44 (m, 2H), 3.30 (s, 3H), 2.79 (d, J = 8.4 Hz, 1H), 2.15 (dd, J = 12.0, 7.5 Hz, 1H), 1.93−1.73 (m, 6H), 1.55−1.52 (m, 1H), 1.21 (s, 9H), 1.08−1.04 (m, 13H), 0.72 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 222.3, 135.6, 133.2, 133.1, 129.8, 129.8, 177.8, 98.7, 95.4, 79.6, 75.6, 67.5, 58.9, 55.4, 53.6, 53.4, 50.2, 49.6, 43.1, 38.7, 37.5, 32.4, 30.1, 29.3, 27.1, 26.9, 26.8, 21.9, 20.4, 19.1; HRMS (ES) m/z calcd for $C_{39}H_{56}O_6SiNa^+$ 671.3744, obsd 671.3751; $[\alpha]^{24}_D$ + 26 (c 0.6, $CHCl_3$).

(3*R*,3a*R*,4*S*,5a*R*,7*S*,8*S*,9*S*,9a*R*)-9-((*tert*-Butyldiphenylsilyloxy)-methyl)-4-hydroxy-3-(methoxymethoxy)-5,5,8-trimethyl-decahydro-1*H*-cyclopenta[*i*]inden-7 -yl Pivalate (33). To a solution of **31** (20 mg, 0.03 mmol) in anhydrous ethanol (6 mL) was added sodium borohydride (100 mg, 2.63 mmol) at 0 °C. The reaction mixture was stirred overnight at rt, freed of solvent on a rotary evaporator, and diluted with ethyl acetate and water. The separated aqueous phase was extracted with ethyl acetate (3 × 20 mL), washed with brine, dried, and concentrated. The residue was purified by flash chromatography on silica gel (ethyl acetate/hexane 1:4) to give 5 mg (25%) of the more polar **33** and 14 mg (74%) of the less polar **34**, both as colorless oils.

For **33**: IR (neat, cm^{-1}) 3518, 1160; ^1H NMR (300 MHz, $CDCl_3$) δ 7.69−7.65 (m, 4H), 7.47−7.41 (m, 6H), 4.63−4.56 (m, 3H), 4.01 (dd, J = 15.0, 7.5 Hz, 1H), 3.85−3.77 (m, 2H), 3.50 (t, J = 9.3 Hz, 1H), 3.30 (s, 3H), 2.55 (d, J = 1.8 Hz, 1H), 2.48 (dd, J = 9.0, 6.9 Hz, 1H), 1.97−1.89 (m, 2H), 1.73−1.49 (m, 7H), 1.21 (s, 9H), 1.08 (s, 9H), 1.04 (d, J = 7.2 Hz, 3H), 0.96 (s, 3H), 0.62 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.5, 135.7, 135.6, 133.6, 129.7, 127.7, 96.2, 80.2, 80.1, 68.7, 55.7, 55.4, 53.7, 52.9, 49.3, 44.4, 43.5, 38.7, 37.3, 29.7, 29.4, 27.7, 27.4, 27.1, 26.9, 21.7, 19.2, 16.6; HRMS (ES) m/z calcd for $C_{39}H_{58}O_6SiNa^+$ 673.3900, obsd 673.3898; $[\alpha]^{24}_D$ +4 (c 0.5, $CHCl_3$).

For **34**: IR (neat, cm^{-1}) 3532, 1725, 1164, 1035; ^1H NMR (300 MHz, $CDCl_3$) δ 7.69−7.66 (m, 4H), 7.45−7.37 (m, 6H), 4.62−4.57 (m, 3H), 4.27−4.25 (m, 1H), 3.72−3.67 (m, 1H), 3.58 (s, 1H), 3.44 (t, J = 8.7 Hz, 1H), 3.34 (s, 3H), 2.80 (dd, J = 8.4, 4.8 Hz, 1H), 2.24 (dd, J = 12.8, 6.6 Hz, 1H), 2.00−1.83 (m, 4H), 1.67−1.59 (m, 2H), 1.49−1.43 (m, 1H), 1.21 (s, 9H), 1.07 (s, 9H), 1.04 (d, J = 6.9 Hz, 3H), 1.01 (s, 3H), 0.66 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.4, 135.7, 135.6, 133.5, 133.4, 129.9, 129.8, 127.8, 96.0, 83.0, 80.4, 77.3, 68.6, 55.6, 55.2, 55.1, 53.4, 50.7, 47.1, 44.5, 38.7, 37.8, 33.0, 28.3, 27.2, 26.9, 23.4, 23.0, 22.0, 19.2; HRMS (ES) m/z calcd for $C_{39}H_{58}O_6SiNa^+$ 673.3900, obsd 673.3890; $[\alpha]^{24}_D$ +7.5 (c 5.0, $CHCl_3$).

(3*R*,3a*S*,4*S*,5a*R*,7*S*,8*S*,9*S*,9a*R*)-4-Acetoxy-9-((*tert*-butyldiphenylsilyloxy)methyl)-3-(methoxymethoxy)-5,5,8-trimethyl-decahydro-1*H*-cyclopenta[*i*]inden-7-yl Pivalate (35). A solution of **33** (27 mg, 0.04 mmol) and pyridine (0.065 mL, 0.8 mmol) in dry CH_2Cl_2 (4 mL) was cooled to 0 °C, treated dropwise with acetic anhydride (0.04 mL, 0.4 mmol), and admixed with DMAP (10 mg). The reaction mixture was stirred overnight at rt, quenched with saturated $NaHCO_3$ solution (2 mL) and water, and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried, and concentrated to leave a residue that was chromatographed on silica gel (ethyl acetate/hexane 1:4) to furnish 24 mg (85%) of **35** as a colorless oil; IR (neat, cm^{-1}) 1725, 1046; ^1H NMR (300 MHz, $CDCl_3$) δ 7.70−7.67 (m, 4H), 7.45−7.38 (m, 6H), 5.14 (d, J = 9.0 Hz, 1H), 4.67−4.58 (m, 1H), 4.50 (d, J = 6.6 Hz, 1H), 4.47 (d, J = 6.6 Hz, 1H), 4.01 (dd, J = 10.2, 5.7 Hz, 1H), 3.82 (dd, J = 10.2, 8.1 Hz, 1H), 3.51 (t, J = 9.0 Hz, 1H), 3.29 (s, 3H), 2.81 (dd, J = 9.0, 7.2 Hz, 1H), 1.98 (s, 3H), 1.90−1.51 (m, 9H), 1.19 (s, 9H), 1.08 (s, 9H), 1.02 (d, J = 7.2 Hz, 3H),

0.92 (s, 3H), 0.62 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.4, 169.9, 135.7, 135.6, 133.5, 133.4, 129.8, 129.7, 127.7, 98.7, 95.1, 80.3, 68.3, 55.1, 52.8, 50.4, 49.8, 44.1, 43.7, 38.7, 37.2, 31.9, 29.7, 29.6, 29.5, 29.3, 27.7, 27.6, 27.1, 26.8, 22.6, 21.2, 21.1, 19.1, 17.9, 14.1; HRMS (ES) *m*/*z* calcd for $C_{41}H_{60}O_7SiNa^+$ 715.4006, obsd 715.3993; $[\alpha]^{24}_D$ +32 (*c* 0.15, $CHCl_3$).

(3*R*,3a*S*,4*S*,5a*R*,7*S*,8*S*,9*S*,9a*R*)-4-Acetoxy-9-((*tert*-butyldiphenylsilyloxy)methyl)-3-hydroxy-5,5,8-trimethyl-decahydro-1*H*-cyclopenta[*i*]inden-7-yl Pivalate (36). To a solution of **35** (24 mg, 0.034 mmol) in CH_2Cl_2 (4 mL) was added Oxone-silica gel (360 mg, 2 mmol) in CH_2Cl_2 (4 mL) in one portion at rt. Two hours later, the solvent was evaporated and the residue was purified by flash chromatography on silica gel (ethyl acetate/hexane 1:2) to provide **36** (12 mg, 53%) as a colorless oil; IR (neat, cm^{-1}) 3733, 1718, 1164; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69−7.65 (m, 4H), 7.45−7.37 (m, 6H), 4.91 (d, J = 8.4 Hz, 1H), 4.60 (m, 1H), 4.20 (m, 1H), 3.80 (dd, J = 10.2, 5.7 Hz, 1H), 3.51 (dd, J = 10.2, 8.1 Hz, 1H), 2.72−2.67 (m, 2H), 2.05 (s, 3H), 1.85−1.50 (m, 9H), 1.21 (s, 9H), 1.08 (s, 9H), 1.00 (d, J = 7.2 Hz, 3H), 0.95 (s, 3H), 0.71 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.4, 172.1, 135.7, 135.6, 133.5, 133.4, 129.8, 127.7, 81.2, 76.1, 73.2, 67.7, 55.1, 53.1, 52.9, 51.5, 44.5, 43.5, 38.7, 37.3, 32.8, 31.9, 29.7, 29.6, 29.3, 28.2, 27.8, 27.1, 26.8, 22.7, 21.2, 20.7, 19.2, 18.3, 14.1; $[\alpha]^{24}_D$ +40 (*c* 0.1, $CHCl_3$).

(3a*R*,4*S*,5a*R*,7*S*,8*S*,9*S*,9a*R*)-4-Acetoxy-9-((*tert*-butyldiphenylsilyloxy)methyl)-5,5,8-trimethyl-3-oxo-decahydro-1*H*-cyclopenta[*i*]inden-7-yl Pivalate (37). To a solution of **36** (12 mg, 0.018 mmol) in CH_2Cl_2 (4 mL) was added Dess−Martin periodinane (52 mg, 0.12 mmol) portionwise at 0 °C. The reaction mixture was allowed to warm to rt, stirred for 5 h, recooled to 0 °C, and diluted with saturated $NaHCO_3$ (1 mL) and $Na_2S_2O_3$ solutions (1 mL). Stirring was maintained until all suspended solids had dissolved. The aqueous phase was extracted with CH_2Cl_2 (3 × 4 mL), and the organic layers were combined, washed with brine, dried, and concentrated. The residue was purified by flash chromatography on silica gel (ethyl acetate/hexane 1:8) to furnish **37** (10 mg, 85%) as a colorless oil; IR (neat, cm^{-1}) 1745, 1727; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66−7.60 (m, 4H), 7.46−7.36 (m, 6H), 5.01 (d, J = 7.6 Hz, 1H), 4.53−4.49 (m, 1H), 3.70 (dd, J = 10.5, 6.3 Hz, 1H), 3.50 (dd, J = 10.5, 9.6 Hz, 1H), 2.94 (d, J = 7.4 Hz, 1H), 2.42−2.31 (m, 1H), 2.20−2.13 (m, 1H), 2.05 (s, 3H), 1.96 (dd, J = 12.6, 6.0 Hz, 1H), 1.88−1.78 (m, 2H), 1.72−1.65 (m, 2H), 1.62−1.53 (m, 2H), 1.19 (s, 9H), 1.05 (s, 9H), 0.98 (d, J = 6.8 Hz, 3H), 0.93 (s, 3H), 0.75 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 217.3, 178.3, 170.1, 135.7, 135.6, 133.1, 133.0, 129.9, 127.8, 80.9, 76.4, 66.6, 58.5, 56.4, 50.8, 50.1, 46.3, 41.3, 37.9, 37.2, 29.7, 29.4, 29.3, 27.3, 27.1, 26.8, 22.7, 20.1, 19.1, 18.4, 14.1; HRMS (ES) *m*/*z* calcd for $C_{39}H_{54}O_6SiNa^+$ 669.3587; obsd 669.3579; $[\alpha]^{24}_D$ +18 (*c* 4.0, $CHCl_3$).

(5a*S*,7*S*,8*S*,9*S*,9a*R*)-9-((*tert*-Butyldiphenylsilyloxy)methyl)-5,5,8-trimethyl-3 -oxo-2,3,5,5a,6,7,8,9-octahydro-1*H*-cyclopenta-[*i*]inden-7-yl Pivalate (38). To a solution of **37** (10 mg, 0.015 mmol) in CH_2Cl_2 (3 mL) was added 5 drops of DBU. The reaction mixture was stirred overnight before the solvent was evaporated, and the residue was purified by flash chromatography on silica gel (ethyl acetate/hexane 1:16) to provide **38** (7 mg, 85%) as a colorless oil; IR (neat, cm^{-1}) 1725, 1162; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64−7.59 (m, 4H), 7.43−7.34 (m, 6H), 6.03 (s, 1H), 4.59−4.52 (m, 1H), 3.53 (dd, J = 10.2, 5.7 Hz, 1H), 3.38 (t, J = 10.2 Hz, 1H), 2.41−2.33 (m, 2H), 2.25−2.16 (m, 2H), 2.01−1.95 (m, 1H), 1.85−1.78 (m, 1H), 1.58−1.45 (m, 3H), 1.20 (s, 9H) 1.13 (d, J = 7.2 Hz, 3H), 1.10 (s, 3H), 1.02 (s, 9H), 0.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 178.5, 147.8, 142.4, 135.7, 135.5, 133.5, 133.5, 129.8, 129.7, 127.8, 127.7, 76.2, 68.6, 57.2, 56.3, 52.0, 48.3, 41.0, 39.6, 38.8, 36.6, 31.7, 28.4, 27.2, 26.9, 24.0, 22.1, 19.1; HRMS (ES) *m*/*z* calcd for $C_{37}H_{50}O_4SiNa^+$ 609.3376, obsd 609.3373; $[\alpha]^{24}_D$ −122 (*c* 0.1, $CHCl_3$).

(3*R*,5a*S*,7*S*,8*S*,9*S*,9a*R*)-9-((*tert*-Butyldiphenylsilyloxy)methyl)-3-hydroxy-5,5,8-trimethyl-2,3,5,5a,6,7,8,9-octahydro-1*H*-cyclopenta[*i*]inden-7-yl Pivalate (39). To a solution of **38** (7 mg, 0.012 mmol) in anhydrous ethanol (3 mL) was added $NaBH_4$ (50 mg) at 0 °C. The reaction mixture was allowed to warm to rt, stirred for 4 h, and evaporated. The residue was diluted with ethyl acetate and water, and the separated aqueous layer was extracted with ethyl acetate (3 × 4 mL). The combined organic layers were washed with brine, dried, and concentrated. The residue was purified by flash chromatography on silica gel (ethyl acetate/hexane 1:4) to give **39** (6 mg, 85%) as a colorless oil; IR (neat, cm^{-1}) 3429, 1725, 1163; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69−7.64 (m, 4H), 7.46−7.36 (m, 6H), 5.11 (d, J = 1.8 Hz, 1H), 4.53 (ddd, J = 12.3, 10.2, 3.0 Hz, 1H), 4.02−3.96 (m, 1H), 3.45−3.43 (m, 2H), 2.28−2.18 (m, 1H), 2.11−2.03 (m, 2H), 1.86−1.79 (m, 1H), 1.70−1.53 (m, 5H), 1.23 (s, 9H), 1.12 (d, J = 6.8 Hz, 3H), 1.08 (s, 9H), 1.02 (s, 3H), 0.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 153.4, 135.7, 135.6, 133.9, 133.6, 129.9, 129.8, 129.7, 127.7, 127.7, 68.6, 68.4, 58.5, 55.7, 51.5, 47.8, 41.4, 38.8, 36.5, 35.7, 32.2, 31.6, 28.4, 27.2, 26.9, 25.0, 22.4, 19.2; HRMS (ES) *m*/*z* calcd for $C_{37}H_{52}O_4SiNa^+$ 611.3533, obsd 611.3530; $[\alpha]^{24}_D$ −2.0 (*c* 2.0, $CHCl_3$).

(3*R*,5a*S*,7*S*,8*S*,9*S*,9a*R*)-9-((*tert*-Butyldiphenylsilyloxy)methyl)-3-(methoxym ethoxy)-5,5,8-trimethyl-2,3,5,5a,6,7,8,9-octahydro-1*H*-cyclopenta[*i*]inden-7-yl Pivalate (40). A solution of **39** (26 mg, 0.044 mmol) and diisopropylethylamine (0.28 mL, 1.6 mmol) in dry CH_2Cl_2 (4 mL) was cooled to 0 °C, treated dropwise with MOMCl (0.1 mL, 1.3 mmol), followed by DMAP (20 mg). The reaction mixture was allowed to warm to rt, stirred overnight, quenched with saturated $NaHCO_3$ solution (3 mL) and water, and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine, dried, and concentrated. The residue was purified by flash chromatography on silica gel (elution with ethyl acetate/hexane 1:16) to provide **40** (25 mg, 90%) as a colorless oil; IR (neat, cm^{-1}) 3071, 1725, 1162; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72−7.68 (m, 4H), 7.48−7.39 (m, 6H), 5.17 (d, J = 1.6 Hz, 1H), 4.61 (d, J = 6.8 Hz, 1H), 4.55 (d, J = 6.8 Hz, 1H), 4.56−4.54 (m, 1H), 4.07 (dd, J = 6.4, 2.0 Hz, H), 3.53−3.45 (m, 2H), 3.34 (s, 3H), 2.28−2.04 (m, 3H), 1.87 (dd, J = 11.2, 8.0 Hz, 1H), 1.80−1.72 (m, 1H), 1.69−1.53 (m, 2H), 1.42−1.32 (m, 2H), 1.25 (s, 9H), 1.16 (d, J = 6.4 Hz, 3H), 1.09 (s, 9H), 1.07 (s, 3H), 0.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 149.9, 135.7, 135.6, 133.9, 133.7, 130.6, 129.7, 129.7, 127.7, 96.1, 77.1, 73.2, 68.5, 58.0, 55.5, 55.4, 51.4, 47.8, 41.5, 38.8, 36.5, 32.7, 32.2, 28.4, 27.2, 26.9, 25.0, 22.5, 19.2; HRMS (ES) *m*/*z* calcd for $C_{39}H_{56}O_5SiNa^+$ 643.3795, obsd 643.3790; $[\alpha]^{24}_D$ +4.7 (*c* 1.6, $CHCl_3$).

(3a*R*,5a*R*,7*S*,8*S*,9*S*,9a*R*)-9-((*tert*-Butyldiphenylsilyloxy)methyl)-5,5,8-trimet hyl-4-methylene-3-oxo-decahydro-1*H*-cyclopenta-[*i*]inden-7-yl Pivalate (41). A solution of **9b** (900 mg, 1.5 mmol) in CH_2Cl_2 (100 mL) was treated with Dess−Martin periodinane (954 mg, 2.25 mmol) portionwise at 0 °C. The reaction mixture was allowed to warm to rt, stirred for 3 h, recooled to 0 °C, and diluted with saturated $NaHCO_3$ (20 mL) and NaS_2O_3 solutions (20 mL) prior to stirring until all suspended solids were dissolved. The aqueous phase was extracted with CH_2Cl_2 (3 × 40 mL), and the combined organic layers were washed with brine, dried, and concentrated. The residue was purified by flash chromatography on silica gel (ethyl acetate/hexane 1:16) to provide **41** (810 mg, 90%) as a colorless oil; IR (neat, cm^{-1}) 1736, 1724, 1167; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.59 (m, 4H), 7.47−7.38 (m, 6H), 5.09 (d, J = 2.0 Hz, 1H), 4.90 (d, J = 2 Hz, 1H), 4.50 (ddd, J = 12.0, 11.2, 3.2 Hz, 1H), 3.62 (dd, J = 11.2, 4.8 Hz, 1H), 3.57 (dd, J = 11.2, 3.6 Hz, 1H), 3.24 (s, 1H), 2.43−2.36 (m, 1H), 2.25−2.17 (m, 1H), 2.01−1.79 (m, 4H), 1.66−1.54 (m, 1H), 1.49−1.45 (m, 1H), 1.40−1.37 (m, 1H), 1.20 (s, 9H), 1.14 (s, 3H), 1.08 (s, 9H), 1.01 (s, 3H), 0.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 218.0, 178.3, 158.1, 135.9, 135.8, 133.2, 133.1, 129.9, 129.8, 127.7, 108.2, 76.3, 64.3, 60.5, 56.0, 54.9, 51.6, 46.6, 38.8, 37.4, 36.8, 36.7, 33.8, 31.9, 31.6, 27.2, 27.0, 25.8, 19.1, 16.2, 14.1; HRMS (ES) *m*/*z* calcd for $C_{38}H_{52}O_4SiNa^+$ 623.2533, obsd 623.3529; $[\alpha]^{24}_D$ −11 (*c* 0.71, $CHCl_3$).

(5a*S*,7*S*,8*S*,9*S*,9a*R*)-9-((*tert*-Butyldiphenylsilyloxy)methyl)-4,5,5,8-tetrameth yl-3-oxo-2,3,5,5a,6,7,8,9-octahydro-1*H*-cyclopenta[*i*]inden-7-yl Pivalate (42). A solution of **41** (290 mg, 0.48 mmol) in CH_2Cl_2 (20 mL) was treated dropwise with DBU (0.35 mL, 2.3 mmol) and stirred overnight prior to dilution with CH_2Cl_2 (40 mL) and water (10 mL). The organic layer was separated, washed with brine, dried, and concentrated. The residue was purified by flash chromatography on silica gel (ethyl acetate/hexane 1:16) to furnish **42** (275 mg, 95%) as a colorless oil; IR (neat, cm^{-1}) 1714, 1164; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68−7.59 (m, 4H), 7.48−7.35 (m, 4H), 4.61 (dt, J = 11.2, 1.4 Hz, 1H), 3.53 (dd, J = 10.0, 6.0 Hz, 1H), 3.35 (t, J = 10.0 Hz, 1H), 2.50−2.40 (m, 1H), 3.53 (dd, J = 10.0, 6.0 Hz, 1H), 3.35 (t, J = 10.0 Hz, 1H), 2.50−2.40 (m, 1H), 2.32 (dd, J = 10.2, 5.7 Hz, 1H), 2.23−2.15 (m, 2H), 2.00−1.93 (m, 2H), 1.82 (s, 3H), 1.75−1.69 (m, 1H), 1.59−1.48 (m, 2H), 1.26 (s, 3H), 1.23 (s, 9H), 1.15 (d, J = 6.4 Hz, 1H), 1.07 (s, 9H), 0.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 178.4, 154.6, 140.8, 135.7, 135.5, 133.6, 133.5, 129.7, 127.7, 127.7, 76.2, 69.6, 56.5, 54.6, 53.9, 49.6, 41.5, 40.3, 38.8, 36.9, 31.9, 29.8, 29.7, 29.7, 29.4, 28.4, 27.2, 26.9, 23.1, 22.7, 22.0, 19.1, 14.1, 10.3; HRMS (ES) m/z calcd for $C_{38}H_{52}O_4SiNa^+$ 623.3533, obsd 623.3532; $[\alpha]^{24}_D$ −29 (c 0.8, $CHCl_3$).

(3*S*,5a*S*,7*S*,8*S*,9*S*,9a*R*)-9-((*tert*-Butyldiphenylsilyloxy)methyl)-3-hydroxy-4,5,5,8-tetramethyl-2,3,5,5a,6,7,8,9-octahydro-1*H*-cyclopenta[*i*]inden-7-yl Pivalate (43) and (3*R*,5a*S*,7*S*,8*S*,9*S*,9a*R*)-9-((*tert*-Butyldiphenylsilyloxy)methyl)-3-hydroxy-4,5,5,8-tetramethyl-2,3,5,5a,6,7,8,9-octahydro-1*H*-cyclopenta[*i*]inden-7-yl Pivalate (44). To a solution of **42** (330 mg, 0.55 mmol) in anhydrous ethanol (15 mL) was added $NaBH_4$ (105 mg, 2.8 mmol) at 0 °C. The reaction mixture was allowed to warm to rt, stirred for 4 h, and evaporated. The residue was treated with ethyl acetate and water. The separated aqueous layer was extracted with ethyl acetate (3 × 10 mL), and the combined organic layers were washed with brine, dried and concentrated. The residue was purified by flash chromatography on silica gel (ethyl acetate/hexane 1:8) to provide **43** (100 mg) as a colorless oil. An increase in solvent polarity to ethyl acetate/hexane 1:4 gave **44** (205 mg, combined yield 90%) as a colorless oil.

For **43**: IR (neat, cm^{-1}) 3462, 1725; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68−7.62 (m, 4H), 7.48−7.38 (m, 6H), 4.58 (dt, J = 11.2, 2.8 Hz, 1H), 4.51 (dd, J = 7.2, 3.6 Hz, 1H), 3.74 (dd, J = 10.0, 6.4 Hz, 1H), 3.39 (t, J = 10.0 Hz, 1H), 2.39−2.32 (m, 2H), 2.13−1.82 (m, 6H), 1.70−1.63 (m, 1H), 1.59 (s, 3H), 1.22 (s, 9H), 1.16 (d, J = 6.4 Hz, 3H), 1.09 (s, 9H), 0.98 (s, 3H), 0.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 144.3, 141.2, 135.7, 133.5, 133.3, 129.7, 127.7, 127.7, 76.9, 70.0, 67.0, 56.1, 56.0, 52.5, 49.3, 42.9, 38.8, 38.3, 37.2, 33.8, 33.8, 30.3, 29.7, 28.6, 27.2, 26.8, 23.0, 22.1, 19.1, 10.2; HRMS (ES) m/z calcd for $C_{38}H_{54}O_4SiNa^+$ 625.3689, obsd 625.3679; $[\alpha]^{24}_D$ +34 (c 2.8, $CHCl_3$).

Details pertaining to the crystallographic analysis of **43** are provided in Supporting Information.

For 44: IR (neat, cm^{-1}) 3498, 1725; ^1H NMR (400 MHz, $CDCl_3$) δ 7.70−7.65 (m, 4H) 7.48−7.38 (m, 6H), 4.58 (dt, J = 11.2, 2.8 Hz, 1H), 4.21 (d, J = 8.4 Hz, 1H), 3.47−3.37 (m, 2H), 3.39−3.29 (m, 1H), 2.03−1.93 (m, 2H), 1.79 (dd, J = 12.0, 7.6 Hz, 1H), 1.70−1.58 (m, 4H), 1.57 (s, 3H), 1.43 (m, 1H), 1.20 (s, 9H), 1.13 (d, J = 6.4 Hz, 3H), 1.08 (s, 9H), 0.99 (s, 3H), 0.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 144.4, 137.7, 135.7, 135.6, 133.9, 133.7, 129.7, 129.6, 127.7, 69.2, 68.8, 57.5, 54.5, 53.7, 48.1, 41.1, 38.8, 37.4, 37.2, 30.5, 28.5, 27.2, 26.9, 22.8, 22.3, 19.2, 9.8; HRMS (ES) m/z calcd for $C_{38}H_{54}O_4SiNa^+$ 625.3689, obsd 625.3676; $[\alpha]^{24}_D$ +12 (c 1.8, $CHCl_3$).

(3*R*,5a*S*,7*S*,8*S*,9*S*,9a*R*)-9-((*tert*-Butyldiphenylsilyloxy)methyl)-3-(methoxymethoxy)-4,5,5,8-tetramethyl-2,3,5,5a,6,7,8,9-octahydro-1*H*-cyclopenta[*i*]inden-7-yl Pivalate (7b). A solution of **44** (420 mg, 0.7 mmol) and diisopropylethylamine (0.73 mL, 4.2 mmol) in dry CH_2Cl_2 (15 mL) was cooled to 0 °C and treated dropwise with MOMCl (0.2 mL, 2.6mmol), followed by DMAP (85 mg, 0.7 mmol). The reaction mixture was allowed to warm to rt, stirred overnight, quenched with saturated $NaHCO_3$ solution (5 mL) and water, and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried, and concentrated. The residue was purified by flash chromatography on silica gel (elution with ethyl acetate/hexane 1:16) to provide **7b** (400 mg, 93%) as a colorless oil; IR (neat, cm^{-1}) 1725, 1163; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74−7.70 (m, 4H), 7.48−7.40 (m, 6H), 4.65 (d, J = 6.8 Hz, 1H), 4.63 (m, 1H), 4.58 (d, J = 6.8 Hz, 1H), 4.27 (d, J = 8.4 Hz, 1H), 3.51 (dd, J = 10.0, 4.8 Hz, 1H), 3.44 (d, J = 10.0 Hz, 1H), 3.39 (s, 3H), 2.32−2.23 (m, 2H), 1.88−1.80 (m, 2H), 1.73−1.65 (m, 2H), 1.42−1.38 (m, 2H), 1.27 (s, 9H), 1.17 (d, J = 7.2 Hz, 3H), 1.11 (s, 9H), 1.03 (s, 3H), 0.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 141.0, 138.1, 135.7, 135.6, 133.9, 133.7, 129.7, 129.7, 127.7, 95.9, 73.8, 68.7, 56.9, 55.7, 54.4, 53.7, 48.1, 41.2, 38.8, 37.2, 33.6, 30.4, 28.5, 27.2, 26.9, 22.9, 22.4, 19.2, 14.2, 9.8; HRMS (ES) m/z calcd for $C_{40}H_{58}O_5SiNa^+$ 669.3951, obsd 669.3947; $[\alpha]^{24}_D$ +8.4 (c 1.0, $CHCl_3$).

Diketone 45. Compound **7b** (263 mg, 0.40 mmol) was dissolved in a mixture of CCl_4 (6 mL), acetonitrile (6 mL), and water (9 mL). To this mixture was added sodium periodate (1.08 g, 5 mmol) and ruthenium dioxide (15 mg, 0.1 mmol). The resulting yellow solution was stirred vigorously for 15 min and then diluted with CH_2Cl_2 (60 mL) and water (5 mL). The organic layer was separated, washed with 10% $NaHSO_3$ solution and brine, dried, and concentrated. The residue was purified by flash chromatography on silica gel (elution with ethyl acetate/hexane 1:4) to provide **45** (219 mg, 79%) as a colorless oil; IR (neat, cm^{-1}) 1723, 1702, 1152; ^1H NMR (400 MHz, $CDCl_3$) δ 7.66−7.60 (m, 4H), 7.47−7.28 (m, 6H), 4.61 (s, 2H), 4.50−4.43 (m, 1H), 3.86 (t, J = 10.0 Hz, 1H), 3.74 (dd, J = 11.6, 2.8 Hz, 1H), 3.52 (dd, J = 11.6, 3.2 Hz, 1H), 3.32 (s, 3H), 2.35−2.23 (m, 2H), 2.22 (s, 3H), 2.22−2.13 (m, 1H), 1.95−1.76 (m, 3H), 1.70−1.60 (m, 1H), 1.53−1.43 (m, 1H), 1.38−1.28 (m, 1H), 1.23 (s, 9H), 1.07 (s, 9H), 0.98 (s, 3H), 0.94 (s, 3H), 0.79 (d, J = 5.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 218.8, 212.2, 178.4, 135.9, 135.7, 133.0, 132.8, 130.0, 129.9, 127.8, 127.8, 96.0, 79.4, 77.6, 63.2, 55.6, 55.5, 51.8, 51.4, 50.5, 38.9, 34.7, 28.4, 27.7, 27.2, 27.0, 26.9, 26.3, 24.7, 21.7, 19.3, 15.8; HRMS (ES) m/z calcd for $C_{40}H_{58}O_7SiNa^+$ 701.3850, obsd 701.3839; $[\alpha]^{24}_D$ +13 (c 0.6, $CHCl_3$).

(3*R*,3a*R*,6a*R*,8*S*,9*S*,10*S*,10a*R*)-3a-Hydroxy-10-(hydroxymethyl)-3-(methoxymethoxy)-6,6,9-trimethyl-5-oxo-dodecahydrocyclopenta[*j*]naphthalen-8-yl Pivalate (46) and (3*R*,3a*R*,6a*R*,8*S*,9*S*,10*S*,10a*R*)-10-((*tert*-Butyldiphenylsilyloxy)methyl)-3a-hydroxy-3-(methoxymethoxy)-6,6,9-trimethyl-5-oxo-dodecahydrocyclopenta[*j*]nap hthalen-8-yl Pivalate (47). A solution of diketone **45** (300 mg, 0.44 mmol) in THF (10 mL) was treated with a solution of NaOH (600 mg, 15 mmol) in water (4 mL). The reaction mixture was stirred overnight, treated with 1 M HCl (15 mL), and diluted with ether (50 mL). The aqueous layer was extracted with ether (20 mL × 3). The combined organic layers were washed with brine, dried, and concentrated. The residue was purified by flash chromatography on silica gel (elution with ethyl acetate/hexane 1:4) to provide **47** (110 mg, 37%) as a colorless oil. An increase in solvent polarity to ethyl acetate/ hexane 1:2 gave **46** (66 mg, 34%) as a colorless oil.

For **46**: ^1H NMR (400 MHz, CDCl) δ 5.07 (s, 1H), 4.76 (d, J = 6.8 Hz, 1H), 4.72 (d, J = 6.8 Hz, 1H), 4.51 (dt, J = 10.8, 4.0 Hz, 1H), 4.26 (t, J = 10.0 Hz, 1H), 3.97−3.91 (m, 1H), 3.88 (t, J = 12.0 Hz, 1H), 3.64 (d, J = 5.2 Hz, 1H), 3.45 (s, 3H), 3.06 (d, J = 12.8 Hz, 1H), 2.74 (d, J = 12.8 Hz, 1H), 2.53−2.46 (m, 1H), 2.15−2.10 (m, 1H), 1.98−1.66 (m, 4H), 1.48−1.38 (m, 2H), 1.38−1.30 (m, 4H), 1.22 (s, 9H), 1.16 (s, 3H), 0.98 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 216.8, 178.5, 97.7, 87.8, 86.0, 78.3, 58.3, 56.0, 55.8, 52.3, 49.6, 47.0, 42.6, 38.9, 34.3, 32.2, 2.99, 27.9, 27.2, 26.1, 15.9.

For **47**: IR (neat, cm^{-1}) 3423, 1721, 1112; ^1H NMR (400 MHz, $CDCl_3$) δ 7.71−7.66 (m, 4H), 7.50−7.38 m, 6H), 4.66 (d, J = 6.8 Hz,1H), 4.58 (s, 1H), 4.55 (d, J = 6.8 Hz, 1H), 4.25 (br, 1 H), 4.02−3.91 (m, 2H), 3.88 (dd, J = 11.6, 4.0 Hz, 1H), 3.39 (s, 3H),

3.04 (d, J = 13.2 Hz, 1H), 2.76 (d, J = 13.2 Hz, 1H), 2.37 (br, 1H), 2.11−2.08 (m, 1H), 1.98−1.71 (m, 5H), 1.65−1.38 (m, 2 H), 1.30 (s, 3H), 1.23 (s, 9H), 1.14 (s, 9H), 1.13 (s, 3H), 0.69 (d, J = 5.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 217.2, 178.4, 136.2, 135.9, 132.7, 132.3, 130.2, 130.0, 127.8, 96.9, 87.9, 85.8, 55.8, 52.2, 49.9, 46.9, 42.9, 38.8, 36.2, 34.7, 32.2, 31.6, 29.5, 28.2, 27.2, 27.0, 25.3, 22.6, 20.7, 19.2, 14.1; HRMS (ES) *m*/*z* calcd for $C_{40}H_{58}O_8SiNa^+$ 701.3850, obsd 701.3839; $[\alpha]^{24}_D$ +4.1 (*c* 3.0, $CHCl_3$).

Conversion of 46 to 47. Alcohol **46** (70 mg, 0.16 mmol) was taken up in DMF (1 mL) and treated with imidazole (39 mg, 0.58 mmol) and *tert*-butyldipenylchlorosilane (0.1 mL, 0.38 mmol) at rt. The reaction mixture was allowed to stir overnight prior to being partitioned between hexane (30 mL) and water (10 mL). The combined organic phases were washed with brine, dried, and concentrated. The residue was purified by flash chromatography on silica gel (elution with ethyl acetate/hexane 1:4) to provide **47** (90 mg, 83%) as a colorless oil.

(3*R*,3a*R*,6a*S*,8*S*,9*S*,10*S*,10a*R*)-5-(*tert*-Butyldimethylsilyloxy)-10-((*tert*-butyld iphenylsilyloxy)methyl)-3a-hydroxy-3-(methoxymethoxy)-6,6,9-trimethyl-1,2,3 ,3a,6,6a,7,8,9,10-decahydrocyclopenta[*j*]naphthalen-8-yl Pivalate (48). To a solution of **47** (130 mg, 0.19 mmol) in CH_2Cl_2 (6 mL) was added triethylamine (0.22 mL, 1.72 mmol) under argon. The mixture was cooled to 0 °C, and *tert*-butyldimethylsilyl triflate (0.2 mL, 0.85 mmol) was added dropwise. After 30 min, the reaction mixture was quenched with saturated $NaHCO_3$ solution (5 mL) and allowed to warm to rt. The aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were washed with brine, dried, and concentrated. The residue was purified by flash chromatography on silica gel (elution with ethyl acetate/hexane 1:32) to provide **48** (65 mg, 47%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73−7.68 (m, 4H), 7.48−7.36 (m, 6H), 4.80 (s, 1H), 4.70 (d, J = 6.8 Hz, 1H), 4.58 (d, J = 6.8 Hz, 1H), 4.17−4.12 (m, 2H), 3.97−3.89 (m, 2H), 3.40 (s, 3H), 2.43−2.37 (m, 1H), 2.02−1.36 (m, 8H), 1.29 (s, 3H), 1.19 (s, 9H), 1.15 (s, 9H), 1.10 (s, 3H), 0.97 (s, 9H), 0.62 (d, J = 6.4 Hz, 3H), 0.25 (s, 3H), 0.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 156.0, 136.3, 136.0, 133.0, 132.5, 130.1, 129.9, 127.7, 127.6, 102.8, 97.0, 88.7, 82.1, 78.8, 63.0, 57.4, 55.6, 51.5, 48.5, 38.9, 38.8, 35.8, 31.6, 30.1, 27.2, 27.1, 25.8, 25.3, 22.6, 19.3, 18.2, 16.6, 14.1, −3.4, −5.0.

(3*R*,3a*S*,4*S*,6a*R*,8*S*,9*S*,10*S*,10a*R*)-10-((*tert*-Butyldiphenylsilyloxy)methyl)-3a,4-dihydroxy-3-(methoxymethoxy)-6,6,9-trimethyl-5-oxo-dodecahydrocyclopenta[*j*]naphthalen-8-yl Pivalate (49). A solution of silyl enol ether **48** (60 mg, 0.075 mmol) in CH_2Cl_2 (1 mL) and methanol (4 mL) was treated with excess ozone at −78 °C for 30 min. The blue solution was purged with N_2 until the color faded. Triphenylphosphine (64 mg) was added, and the reaction mixture was allowed to warm to rt. The solvent was evaporated, and the residue was purified by flash chromatography on silica gel (elution with ethyl acetate/hexane 1:4) to provide **49** (43 mg, 80%) as a colorless oil; IR (neat, cm^{-1}) 3425, 1721, 1159; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69−7.67 (m, 4H), 7.44−7.37 (m, 6H), 4.58 (d, J = 6.4 Hz, 1H), 4.54 (s, 1H), 4.50 (d, J = 6.4 Hz, 1H), 4.51−4.48 (m, 1H), 4.10−3.72 (m, 5H), 3.32 (s, 3H), 2.37−2.26 (m, 1H), 2.06−1.83 (m, 4H), 1.72−1.62 (m, 2H), 1.45−1.33 (m, 4H), 1.l8 (s, 9H), 1.12 (s, 3H), 1.08 (s, 9H), 1.00 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.4, 178.4, 135.8, 135.7, 133.5, 133.5, 129.8, 127.8, 96.8, 87.1,83.3, 65.8, 55.7, 53.0, 48.2, 46.9, 38.8, 37.8, 31.9, 30.8, 29.7, 29.6, 29.4, 27.8, 27.2, 26.9, 24.5, 22.7, 19.2, 14.1; HRMS (ES) *m*/*z* calcd for $C_{40}H_{58}O_8SiNa^+$ 717.3799; obsd 717.3818; $[\alpha]^{24}_D$ + 46 (*c* 1.0, $CHCl_3$).

(3*R*,3a*S*,4*R*,5*R*,6a*S*,8*S*,9*S*,10*S*,10a*R*)-10-((*tert*-Butyldiphenylsilyloxy)methyl)-3a,4,5-trihydroxy-3-(methoxymethoxy)-6,6,9-trimethyldodecahydrocyclopent a[*j*]naphthalen-8-yl Pivalate (50). A solution of **49** (43 mg, 0.06 mmol) in methanol (4 mL) was treated with sodium borohydride (38 mg, 1.0 mmol) at rt. One hour later, the methanol was evaporated and the residue was diluted with EtOAc (10 mL) and water (5 mL). The aqueous layer was separated and extracted with EtOAc (5 mL × 2). The combined organic layers were washed with brine, dried, and concentrated. The residue was purified by flash chromatography on silica gel (elution with ethyl acetate/hexane 1:2) to provide the triol **50** (35 mg, 81%) as a colorless oil; IR (neat, cm^{-1}) 3476, 1720, 1112; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70−7.68 (m, 4H), 7.46−7.38 (m, 6H), 4.52 (d, J = 6.4 Hz, 1H), 4.47 (d, J = 6.4 Hz, 1H), 4.36 (dt, J = 10.8, 4.4 Hz, 1H), 4.08 (m, 1H), 3.91 (s, 1H), 3.91−3.80 (m, 3H), 3.60 (s, 1H), 3.54 (br s, 1H), 3.31 (s, 3H), 2.57 (br s, 1H), 2.50−2.42 (m, 1H), 2.24−2.14 (m, 1H), 2.05−1.95 (m, 2H), 1.61-(s, 1H), 1.53 (dd, J = 13.6, 4.4 Hz, 1H), 1.46−1.33 (m, 3H), 1.22 (s, 9H), 1.17 (s, 3H), 1.15 (s, 3H), 1.11 (s, 9H), 0.95 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 135.9, 135.8, 133.6, 133.5, 129.8, 129.7, 127.7, 96.5, 87.9, 82.3, 78.7, 68.6, 64.7, 59.9, 55.7, 49.2, 47.8, 38.8, 37.9, 37.3, 34.1, 32.8, 31.3, 29.7, 27.6, 27.2, 27.0, 26.5, 19.2, 16.7; HRMS (ES) *m*/*z* calcd for $C_{40}H_{60}O_8SiNa^+$ 719.3955, obsd 719.3948; $[\alpha]^{24}_D$ +22 (*c* 3.6, $CHCl_3$).

Keto Aldehyde 51 and Keto Acid 52. A solution of triol **50** (35 mg, 0.05 mmol) in benzene (4 mL) was allowed to react with lead tetraacetate (66 mg, 0.15 mmol) at rt for 10 min. At this time, the reaction mixture was filtered through Celite, and the filtrate was concentrated. The residue was passed through a plug of silica gel (elution with ethyl acetate/hexane 1:8) to provide aldehyde **51** (12 mg, 35%). An increase in solvent polarity to ethyl acetate/hexane (1:2) gave **52** (13 mg, 34%) as a colorless oil.

For **51**: IR (neat, cm^{-1}) 1720; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (s, 1H), 7.68−7.58 (m, 4H), 7.47−7.36 (m, 6H), 4.63 (d, J = 6.4 Hz, 1H), 4.59 (d, J = 6.4 Hz, 1H), 4.46 (dt, J = 10.8, 4.4 Hz, 1H), 3.88 (t, J = 10.4 Hz, 1H), 3.76 (dd, J = 11.6, 2.8 Hz, 1H), 3.51 (dd, J = 11.6, 3.2 Hz, 1H), 3.32 (s, 3H), 2.28−2.15 (m, 2H), 2.07−1.80 (m, 5H), 1.57−1.51 (m, 1H), 1.45−1.39 (m, 1H), 1.25 (s, 9H), 1.08 (s, 9H), 0.98 (s, 3H), 0.86 (s, 3H), 0.80 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 218.3, 202.4, 178.4, 135.9, 135.7, 133.0, 132.8, 130.0, 139.9, 127.8, 127.8, 96.1, 80.0, 63.3, 55.6, 55.0, 51.6, 50.1, 49.7, 38.9, 34.7, 28.2, 27.2, 27.1, 27.0, 26.1, 25.3, 25.0, 19.3, 18.1, 15.8; HRMS (ES) *m*/*z* calcd for $C_{39}H_{56}O_7SiNa^+$ 687.3693, obsd 687.3693; $[\alpha]^{24}_D$ +33 (*c* 0.2, $CHCl_3$).

For **52**: IR (neat, cm^{-1}) 3566−3150 (br), 1724, 1698; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.61 (m, 4H), 7.47−7.38 (m, 6H), 4.63 (d, J = 8.0 Hz, 1H), 4.61 (d, J = 8.0 Hz, 1H), 4.47 (dt, J = 10.4, 4.4, 1H), 3.93 (t, J = 9.2 Hz, 1H), 3.79 (dd, J = 11.6, 2.4 Hz, 1H), 3.56 (dd, J = 11.6, 2.8 Hz, 1H), 3.32 (s, 3H), 2.36−2.17 (m, 3H), 2.05−1.85 (m, 5H), 1.43−1.38 (m, 1H), 1.23 (s, 9H), 1.18 (s, 3H), 1.08 (s, 9H), 1.02 (s, 3H), 0.78 (d, J = 5.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 218.8, 184.1, 178.4, 136.0, 135.7, 133.0, 132.8, 130.0, 129.9, 127.8, 127.8, 96.0, 79.6, 77.6, 62.9, 55.5, 55.2, 51.6, 50.5, 45.1, 38.9, 34.5, 31.9, 29.8, 29.7, 29.4, 27.4, 27.2, 27.0, 26.8, 26.5, 22.7, 21.6, 19.3, 15.8, 14.1; HRMS (ES) *m*/*z* calcd for $C_{39}H_{56}O_8SiNa^+$ 703.3642, obsd 703.3640; $[\alpha]^{24}_D$ +28 (*c* 0.3, $CHCl_3$).

Conversion of 40 to 52. Olefin **40** (12 mg, 0.019 mmol) was dissolved in a mixture of CCl_4 (1 mL), acetonitrile (1 mL), and water (1.5 mL). To this mixture was added sodium periodate (42 mg, 0.19 mmol) and ruthenium dioxide (1.5 mg). The resulting yellow solution was stirred vigorously for 15 min and then diluted with CH_2Cl_2 (20 mL) and water (5 mL). The organic layer was separated, washed with 10% $NaHSO_3$ solution and brine, dried, and concentrated. The residue was purified by flash chromatography on silica gel (elution with ethyl acetate/hexane 1:2) to provide **52** (9 mg, 70%) as a colorless oil identical in all respects with the keto acid described above.

Hydroxy Peroxide 53. A solution of Na_2CO_3 (93 mg, 0.88 mmol) in water (0.5 mL) was cautiously added dropwise to a hot solution (50−60 °C) of **52** (30 mg, 0.044 mmol) and mercuric trifluoroacetate (187.7 mg, 0.44 mmol) in a mixture of THF (4 mL) and 30% H_2O_2 (0.25 mL). The reaction mixture was kept at the same temperature for 30 min and then cooled to rt. A solution of NaOH (8.8 mg, 0.22 mmol) was introduced followed by addition of a solution of $NaBH_4$ (38 mg) in water (2 mL) until a black

precipitate formed. The reaction mixture was diluted with ether (20 mL) and water (2 mL), the aqueous layer was separated and extracted with ether (5 mL × 2), and the combined organic layers were washed with brine, dried, and concentrated. The residue was purified by flash chromatography on silica gel (elution with ethyl acetate/hexane 1:8) to provide peroxide **53** (13 mg, 43%) as a colorless oil; IR (neat, cm^{-1}) 3356, 1720, 1108; ^1H NMR (400 MHz, $CDCl_3$) δ 7.69−7.66 (m, 4H), 7.49−7.42 (m, 6H), 5.44 (br s, 1H), 4.61 (d, J = 6.8 Hz, 1H), 4.42 (d, J = 6.8 Hz, 1H), 4.40 (dt, J = 10.8, 4.0 Hz, 1H), 3.84 (dd, J = 10.8, 4.8 Hz, 1H), 3.59 (d, J = 10.8 Hz, 1H), 3.47 (s, 3H), 3.21 (br s, 1H), 2.20 (br s, 1H), 2.08−1.75 (m, 6H), 1.55−1.48 (m, 1H), 1.38−1.35 (m, 1H), 1.33 (s, 3H), 1.29 (s, 3H), 1.24 (s, 9H), 1.10 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 135.9, 135.7, 133.7, 133.6, 129.9, 129.7, 127.7, 127.7, 107.6, 98.8, 91.2, 81.1, 77.8, 66.3, 56.7, 48.7, 47.8, 38.9, 38.5, 33.9, 33.8, 29.7, 29.0, 28.3, 27.2, 26.9, 25.8, 19.1, 16.6; HRMS (ES) m/z calcd for $C_{38}H_{56}O_8SiNa^+$ 691.3642, obsd 691.3660; $[\alpha]^{24}_D$ +19 (c 0.8, $CHCl_3$).

Hemiketal 54. A solution of **53** (13 mg, 0.02 mmol) in ethanol (4 mL) was treated with sodium borohydride (76 mg, 2.0 mmol) at rt. After 30 min, another portion of sodium borohydride (76 mg) was added, and the reaction mixture was stirred for another 3 h until reaction was complete. The ethanol was evaporated, and the residue was diluted with EtOAc (10 mL) and water (5 mL). The aqueous layer was separated and extracted with EtOAc (5 mL × 2). The combined organic layers were washed with brine, dried, and concentrated. The residue was purified by flash chromatography on silica gel (elution with ethyl acetate/hexane 1:8) to provide **54** (12 mg, 92%) as a colorless oil; IR (neat, cm^{-1}) 3398, 1721, 1112; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73−7.66 (m, 4H), 7.48−7.38 (m, 6H), 4.88 (s, 1H), 4.65 (d, J = 6.8 Hz, 1H), 4.50 (d, J = 6.8 Hz, 1H), 4.41 (dt, J = 10.8, 4.4 Hz, 1H), 3.89 (d, J = 4.4 Hz, 2H), 3.67 (t, J = 8.4 Hz, 1H), 3.43 (s, 3H), 2.04 (dd, J = 12.0, 6.8 Hz, 1H), 1.98−1.92 (m, 1H), 1.85−1.62 (m, 6H), 1.49−1.43 (m, 1H), 1.35 (s, 3H), 1.28 (s, 3H), 1.21 (s, 9H), 1.09 (s, 9H), 0.83 (d, J = 5.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 135.9, 135.8, 133.4, 133.4, 129.9, 129.8, 127.8, 127.7, 111.2, 97.6, 87.5, 83.5, 77.2, 64.5, 55.6, 54.6, 54.1, 53.8, 38.8, 32.4, 30.6, 27.9, 27.6, 27.2, 26.9, 19.1, 16.3; HRMS (ES) m/z calcd for $C_{38}H_{56}O_7SiNa^+$ 675.3693, obsd 675.3696; $[\alpha]^{24}_D$ −12 (c 0.5, $CHCl_3$).

***O*-Methylation of 54.** A solution of **54** (10 mg, 0.015 mmol) in acetonitrile (2 mL) and methyl iodide (2 mL) was stirred at reflux in the presence of silver(I) oxide (700 mg). The solids were removed by filtration, and the filtrate was concentrated. The residue was purified by flash chromatography on silica gel (elution with ethyl acetate/hexane 1:8) to provide ketal **5** (9 mg, 90%) as a colorless oil; IR (neat, cm^{-1}) 1722, 1041; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73−7.69 (m, 4H), 7.47−7.40 (m, 6 H), 4.60 (s, 2H), 4.40 (dt, J = 10.8, 4.0 Hz, 1H), 3.95 (dd, J = 9.2, 2.8 Hz, 1H), 3.88 (dd, J = 11.2, 4.0 Hz, 1H), 3.81 (dd, J = 11.2, 5.6 Hz, 1H), 3.39 (s, 3H), 3.33 (s, 3H), 2.00 (dd, J = 12.4, 6.0 Hz, 1H), 1.88−1.81 (m, 1H), 1.75−1.60 (m, 6H), 1.47−1.42 (m, 1H), 1.39 (s, 3H), 1.28 (s, 3H), 1.21 (s, 9H), 1.09 (s, 9H), 0.83 (d, J = 5.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 135.8, 135.8, 133.7, 133.6, 129.7, 129.7, 127.7, 127.7, 114.2, 95.9, 84.4, 83.0, 76.8, 64.8, 55.6, 54.5, 53.7, 50.5, 38.8, 37.6, 35.9, 32.0, 30.5, 29.7, 28.2, 27.2, 27.0, 26.9, 19.1, 16.5; HRMS (ES) m/z calcd for $C_{39}H_{58}O_7SiNa^+$ 689.3850, obsd 689.3835; $[\alpha]^{24}_D$ −12 (c 0.7, $CHCl_3$).

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Supporting Information Available: Details of the X-ray crystallographic analysis of **43** and high-field ^1H and ^{13}C NMR spectra for all stable new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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