Application of an S → O Allylic Transposition in the Context of a Bridgehead Olefinic System. New Opportunities for the Structural Modification of Bicyclo[6.2.1]undecanes via Transannular Ring Closure

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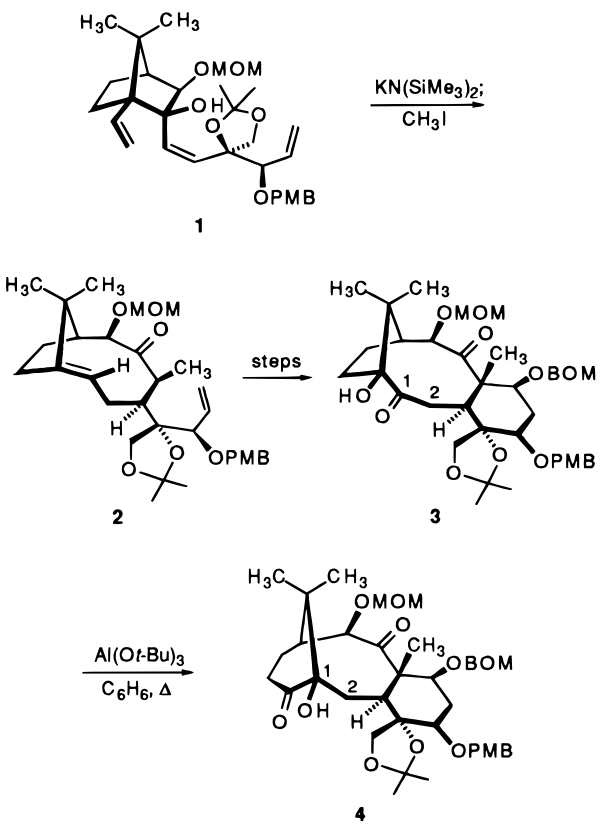
A practical route is described for the preparation of allylic sulfide **8,** whose double bond resides at a bridgehead site. Following hydride reduction of the ketone carbonyl and sulfoxidation, exposure to trifluoroacetic anhydride results in the operation of an intermolecular S → O allylic transposition. This central step leads to **14a**, an intermediate useful for probing the consequences associated with epoxidation of its *cis*-cyclononene double bond. A total of three different transannular cyclizations are described in order to demonstrate the ease with which ring closures can operate in a medium-ring setting of this type. Represented are transformations that generate tetrahydrofuran, oxetane, and cyclopropane subunits. The kinetic biases favoring these transformations are highlighted.

The exploratory studies that we have conducted to date have established the feasibility of obtaining taxane systems in concise fashion by proper deployment of an anionic oxy-Cope rearrangement and an α-ketol isomerization in sequence.[2] The pathway outlined in Scheme 1 is illustrative. Alcohol **1**, which is readily derived from D-camphor, undergoes anionically promoted [3.3] sigmatropy to deliver an enolate. In situ methylation of this reactive product leads to **2**, a convenient precursor to **3**. Exposure of this highly functionalized α-hydroxy ketone to aluminum tri-*tert*-butoxide in benzene results in equilibration to the thermodynamically more stable isomer **4**. As part of a broader program directed toward the synthesis of Taxol and heretofore unknown congeners thereof, we have now focused on the need to introduce a critical oxygen substituent at C-2 (Taxol numbering). A particularly attractive and economic resolution was believed to reside in the introduction of $\Delta^{1,2}$-unsaturation in **3** and analogues thereof in advance of oxygenation and bridge migration.

Our first investigations were designed with the intention of not prolonging the synthetic sequence. We wondered whether the Evans−Mislow allyl sulfoxide−allyl sulfenate rearrangement[3] might be suitably deployed for hydroxylation of the bridgehead position with *simultaneous* generation of a C-1/C-2 double bond. To our knowledge, this [2,3] sigmatropic rearrangement has not previously been applied in the context of bridgehead unsaturation. Herein, the feasibility of a variant of the classical sulfur−oxygen transposition is demonstrated in this somewhat unusual setting. Further, the exceptional proclivity of highly oxygenated bicyclo[6.2.1]undecanes derived from this intermediate to transannular cyclization is detailed in three rather different contexts.

Scheme 1



Results and Discussion

Thiophenyl as an Oxygen Surrogate. To arrive at enantiomerically pure ketone **5**, advantage was taken of

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(2) Paquette, L. A.; Montgomery, F. J.; Wang, T.-Z. *J. Org. Chem.* **1995**, *60*, 7857 and the earlier references therein.

(3) (a) Evans, D. A.; Andrews, G. C. *Acc. Chem. Res* **1974**, *7*, 147. (b) Hoffmann, R. W. *Angew Chem., Int. Ed. Engl.* **1979**, *18*, 563. (c) Braverman, S. In *The Chemistry of Sulfones and Sulfoxides*; Patai, S., Rappoport Z., Stirling, C., Eds.: Wiley: New York, 1988; p 665. (d) Altenbach, H.-J. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: Oxford, England, 1991; p 834. (e) Brückner, R. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.: Pergamon: Oxford, England, 1991; p 899.

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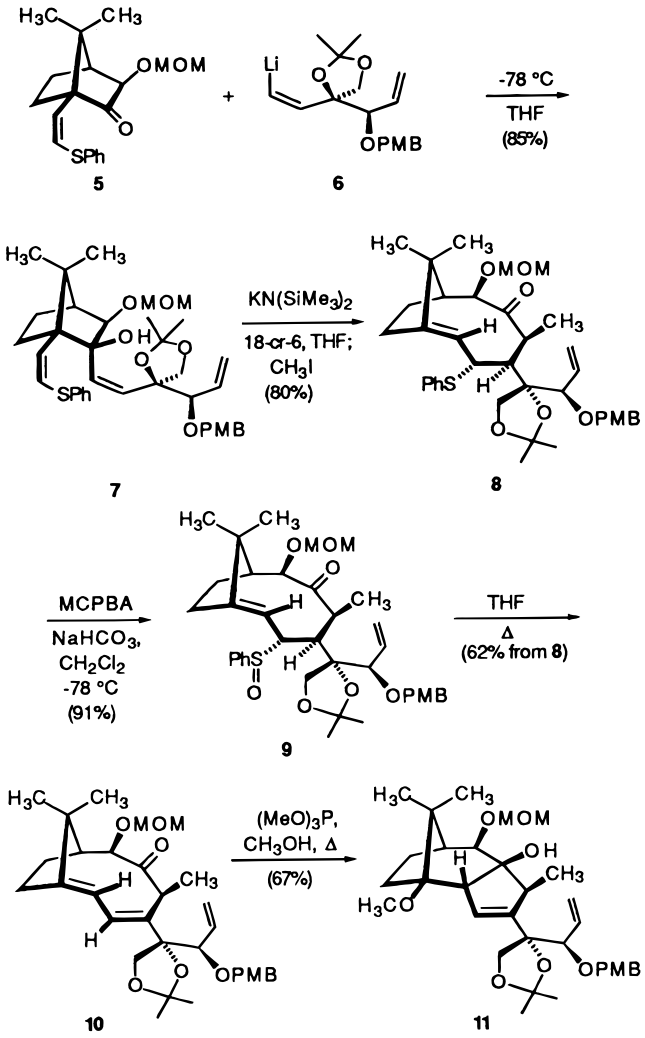
Scheme 2



the chemoselectivity with which the known keto aldehyde[4] reacts with $Ph_3P{=}CHSPh$[5] to give predominantly the *Z*-isomer. Condensation of **5** with alkenyllithium **6**[2] is relegated exclusively to approach from the endo direction because of the bevy of substituents that are projected onto the exo surface (Scheme 2). Treatment of the resulting 2-norbornanol **7** with potassium hexamethyldisilazide and 18-crown-6 in THF resulted in smooth, regiospecific conversion to an enolate anion, capture of which with methyl iodide led to **8** in 80% yield. The α-orientation of the thiophenyl substituent indicated that the presence of a sulfur atom had not altered adoption of the transition state geometry universally preferred by these systems.[6] Oxidation of **8** with 1.2 equiv of *m*-chloroperbenzoic acid under buffered ($NaHCO_3$) conditions at −78 °C furnished a 2.2:1 mixture of diastereomeric sulfoxides **9**.

The time had arrived to explore the Evans−Mislow protocol. However, various attempts to bring about this transformation proved unsuccessful. The consequences of heating **9** with trimethyl phosphite in methanol are illustrative. Instead of arrival at the transposed allylic alcohol, the tricyclic ether **11** was unexpectedly formed instead in good yield. Within the limits of detection by 300 MHz ^{1}H NMR, this transannularly ring-contracted product had formed exclusively. Its genesis became apparent when the sensitivity of sulfoxides **9** to the thermal extrusion of phenylsulfenic acid was noted. This elimination, which occurs slowly at room temperature, can be significantly accelerated in refluxing THF to deliver **10**. Acid-catalyzed addition of methanol to **10** with bonding between sp^2-hybridized carbons proximally positioned across the nine-membered ring leads to **11**. The structural assignment to **11** rests firmly on spectroscopic grounds, with ^{1}H and ^{13}C/DEPT, COSY, and NOE studies proving particularly informative (see Supporting Information).

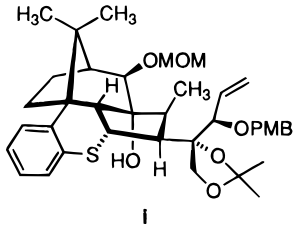
Since the conversion just described is presumably dependent on the presence of a ketone carbonyl for its operation,[7] **8** was next subjected to hydride reduction in advance of sulfoxidation (Scheme 3). With lithium aluminum hydride in ether, a chromatographically separable 11:1 mixture of β- and α-alcohols **12a** and **12b** were obtained. This stereochemical outcome is a direct consequence of the "carbonyl-up" conformation preferentially adopted by **8**.[8] Each alcohol was subjected in turn to MCPBA oxidation and to the action of excess trifluoroacetic anhydride in CH_2Cl_2 at −78 °C. These conditions resulted in the formation of **13a** and **13b**, respectively. These products were routinely transformed into their bis(trifluoroacetylated) counterparts by addition of pyridine to the reaction mixture *prior to workup*. The structural assignment to **14a** was corroborated by single-crystal X-ray analysis of the derived alcohol **14b**. The ORTEP diagram (Figure 1) clearly delineated the conformation

(4) Elmore, S. W.; Paquette, L. A. *J. Org. Chem.* **1995**, *60*, 889.

(5) (a) Marino, J. P.; Kaneko, T. *Tetrahedron Lett.* **1973**, 3975. (b) Vlattas, I.; Lee, A. O. *Tetrahedron Lett.* **1974**, 4451. (c) Muthikrishnan, R.; Schlosser, M. *Helv. Chim. Acta* **1976**, *59*, 13.

(6) Paquette, L. A.; Teleha, C. A.; Taylor, R. T.; Maynard, G. D.; Rogers, R. D.; Gallucci, J. C; Springer, J. P. *J. Am. Chem. Soc.* **1990**, *112*, 265.

(7) Somewhat related chemical behavior was noted during attempts to hydrolyze the acetonide functionality in **8** and related intermediates. For example, treatment of **8** with 80% aqueous acetic acid was adequate to effect conversion to **i**, itself the result of tandem intramolecular alkylation/Friedel−Crafts alkylation: colorless oil; IR (film, cm^{-1}) 1612, 1514; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.8, 1.3 Hz, 1 H), 7.50 (dd, *J* = 7.4, 1.6 Hz, 1 H), 7.14 (d, *J* = 8.7 Hz, 2 H), 7.03 (ddd, *J* = 7.4, 7.4, 1.6 Hz, 1 H), 6.95 (ddd, *J* = 7.4, 7.4, 1.4 Hz, 1 H), 6.75 (d, *J* = 8.7 Hz, 2 H), 6.15 (ddd, *J* = 17.4, 10.6, 5.2 Hz, 1 H), 5.47 (ddd, *J* = 17.4, 1.8, 1.8 Hz, 1 H), 5.31 (ddd, *J* = 10.6, 1.6, 1.6 Hz, 1H), 4.53 (d, *J* = 6.5 Hz, 1 H), 4.50 (d, *J* = 11.1 Hz, 1 H), 4.35 (d, *J* = 6.5 Hz, 1 H), 4.21 (d, *J* = 9.2 Hz, 1 H), 4.16 (d, *J* = 11.1 Hz, 1 H), 4.11 (br d, *J* = 5.2 Hz, 1 H), 3.76 (d, *J* = 3.8 Hz, 1 H), 3.65 (d, *J* = 9.1 Hz, 1 H), 3.53 (ddd, *J* = 13.6, 9.3, 3.9 Hz, 1 H), 3.28 (s, 3 H), 3.18 (s, 3 H), 3.24−3.17 (m, 1 H), 2.96 (dd, *J* = 14.1, 10.3 Hz, 1 H), 2.85 (dd, *J* = 9.2, 5.4 Hz, 1 H), 2.63 (qd, *J* = 6.7, 5.1 Hz, 1 H), 2.29 (ddd, *J* = 14.1, 4.3, 4.3 Hz, 1 H), 1.75 (dd, *J* = 7.1, 3.6 Hz, 1 H), 1.64 (s, 3 H), 1.59−1.52 (m, 1 H), 1.49 (s, 3 H), 1.48 (s, 3 H), 1.46−1.37 (m, 1 H), 1.29 (s, 3 H), 1.04 (d, *J* = 6.9 Hz, 3 H), 0.88−0.79 (m, 1 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 159.7, 146.8, 140.1, 134.9, 132.2, 130.8, 129.6, 126.1, 125.8, 125.7, 117.6, 114.0, 108.6, 95.2, 86.3, 83.5, 80.3, 72.3, 67.3, 55.5, 55.3, 54.7, 54.1, 53.5, 46.4, 46.0, 43.8, 43.3, 38.1, 30.1, 28.9, 28.7, 26.7, 26.0, 25.8, 21.1; MS *m/z* (M^+) calcd 634.3328, obsd 634.3348; $[\alpha]^{20}_D$ −66.3 (*c* 0.65, $CHCl_3$).



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(8) (a) Paquette, L. A.; Combrink, K. D.; Elmore, S. W.; Rogers, R. W. *J. Am. Chem. Soc.* **1991**, *13*, 1335. (b) Paquette, L. A.; Elmore, S. W.; Combrink, K. D.; Hickey, E. R. *Helv. Chim. Acta* **1992**, *75*, 1755. (c) Paquette, L. A.; Combrink, K. D.; Elmore, S. W.; Zhao, M. *Helv. Chim. Acta* **1992**, *75*, 1772.

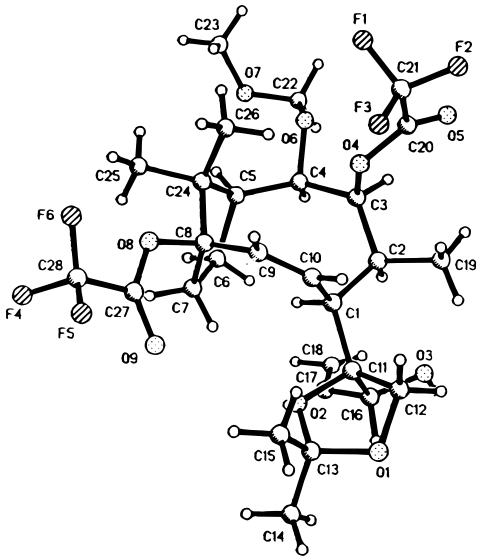
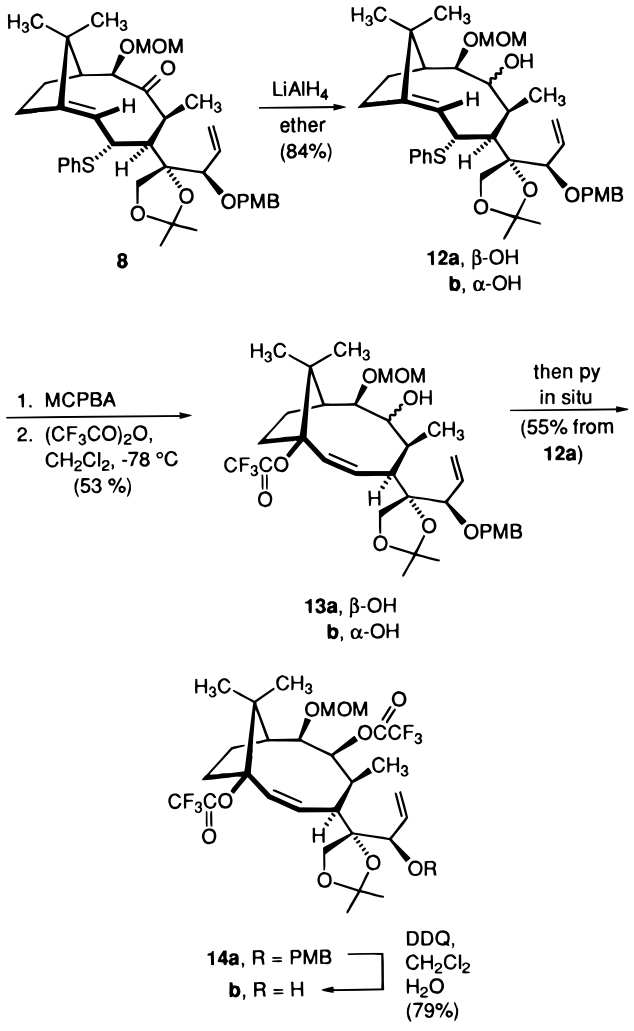


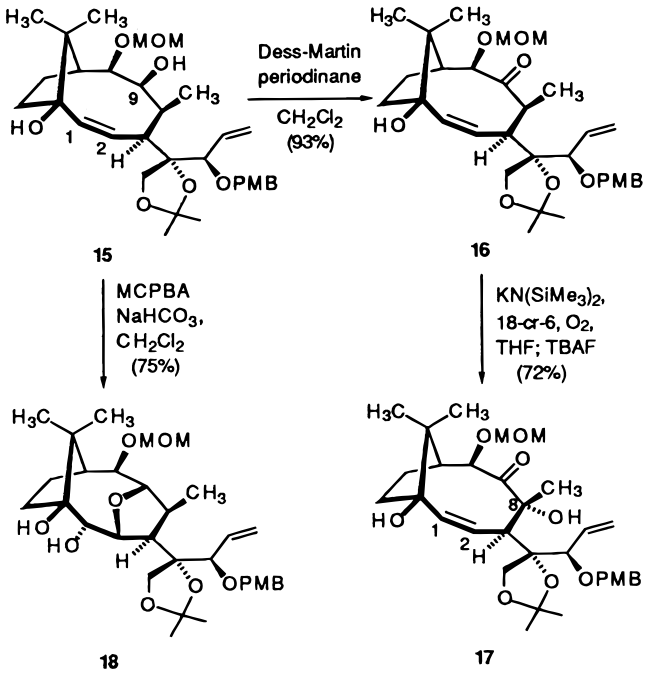
Figure 1. Computer-generated perspective drawing of the final X-ray model of **14b**.

Scheme 3



adopted by the bicyclic core, confirmed that a formal Evans−Mislow reaction has taken place, and convincingly demonstrated that the double bond within the medium-sized ring is open to attack only from the endo direction. The modest yield for the conversion of **12a,b** into **13a,b** may be due to an elimination problem similar to that observed in the conversion of **9** to **10**.

Scheme 4

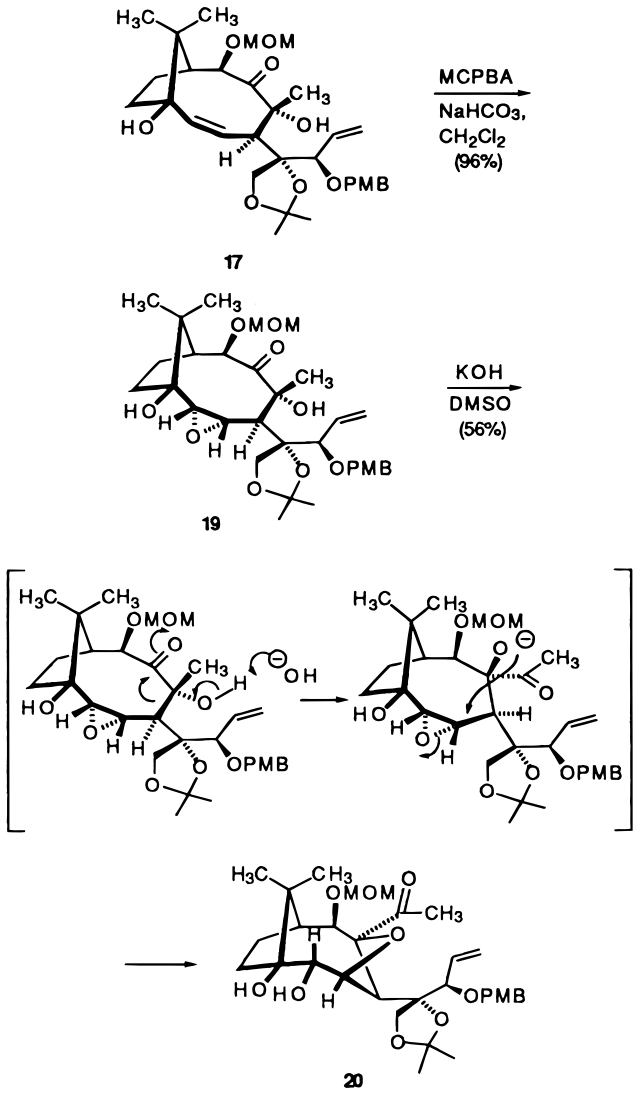


The mechanistic details associated with the conversion of **12** into **13** were probed to a limited degree by surveying several electrophilic activators. While trichloroacetic anhydride provided a product whose spectral characteristics were nearly identical with those of **13a**, trichloroacetyl chloride failed to function analogously. This distinction would appear to rule out intramolecular acetyl transfer via a cyclic transition state and suggests the possible operation of an intermolecular S_N2' process. Perhaps relevantly, benzene and chloroform provided results comparable to those observed in dichloromethane, while tetrahydrofuran, ether, and acetonitrile gave rise to little or no **13**. Neither the coaddition of 1,1-diphenylethylene nor solvent degassing prior to the introduction of trifluoroacetic anhydride facilitated the reaction. Obviously, the configuration of the hydroxyl group on the northern rim of the nine-membered ring plays no important role in the reaction.

As expected, bis(trifluoracetate) **14a** could be chemoselectively deprotected without difficulty. Arrival at **14b** was routinely achieved by DDQ oxidation to remove the *p*-methoxybenzyl protecting group. In contrast, diol **15** was obtained by saponification with potassium carbonate in methanol.

Structural Changes Leading to Transannular Cyclization. The ready formation of **15** permitted its exploitation as a probe of front-rim oxygenation chemistry. In the illustrative examples that follow, it will become clear that transannular bonding occurs with considerable facility within the medium-sized ring of these bicyclic frameworks. As a first example, it was quickly recognized that peracid oxidation of **15** occurs to deliver diol **18** directly (Scheme 4). A reasonable interpretation of this phenomenon involves neighboring group participation by the β-hydroxyl at C-9 as the peroxidation is initiated on the sterically accessible α-face of the π-bond linking C-1 to C-2. The regioselectivity of this process likely derives from the disubstituted nature of

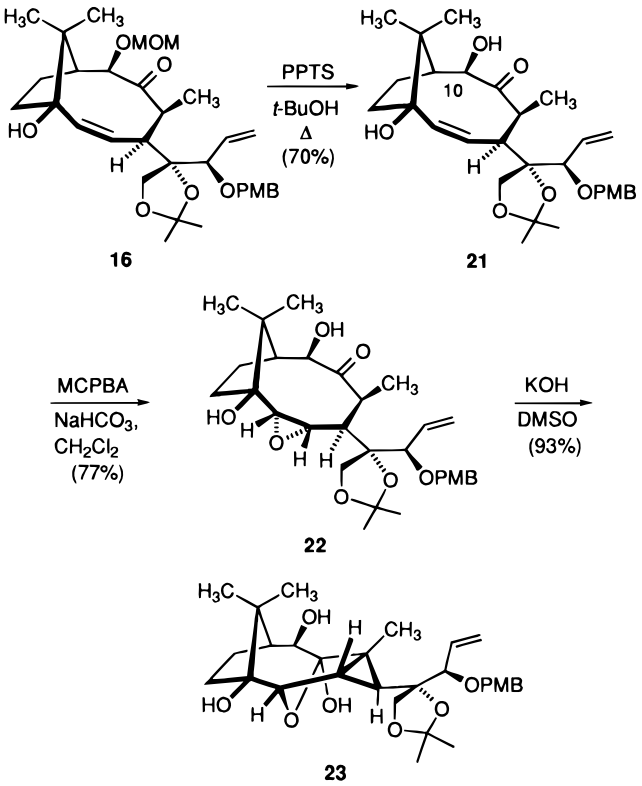
Scheme 5



this olefinic site (the other alternative is a terminal double bond).

Next to be addressed was the conversion of **15** to ketone **16** in advance of the regiocontrolled deprotonation of this intermediate for the purpose of α-oxygenation as in **17**. This two-step sequence places C-9 at a different oxidation level than in **15** while introducing a new hydroxyl group in an α-orientation at C-8. This significant change in position and stereochemistry did indeed allow for the formation and isolation of epoxide **19** in near quantitative yield (Scheme 5). Notwithstanding, transannular cyclization with generation of oxetane **20** materialized when **19** was exposed to solutions of potassium hydroxide in dimethyl sulfoxide. Highlighted by this transformation is an uncommon method for the preparation of a four-membered oxygen-containing ring by nucleophilic attack on a more strained smaller ring analogue. Of particular interest is the finding that ring closure does not materialize via the direct transannular cyclization of **19**. Rather, this compound first experiences an α-ketol ring contraction, an equilibrium process that gives rise in stereocontrolled fashion to an alkoxide much better aligned for backside attack at C-2 with cleavage of the oxirane subunit. The structural assignment to **20**, initially inferred by the appearance of an acetyl singlet at

Scheme 6



δ 2.32, was fully corroborated by extended NMR studies on **20** itself as well as its hydroboration products.

To define whether a C-10 β-hydroxyl could similarly enter into related chemistry, the MOM group in **16** was hydrolytically released with pyridinium *p*-toluenesulfonate in hot *tert*-butyl alcohol (Scheme 6). Following peracid oxidation to generate **22**, the fate of this epoxide in strongly basic media was explored. In this instance, intramolecular ring closure with generation of a cyclopropane ring was the kinetically preferred reaction pathway. Once the three-membered ring had been generated, the liberated oxido anion became positioned in adequate proximity to the carbonyl group to form a second ring via transannular acetalization.

It is especially noteworthy that in no instance was direct conversion of a 1,2-epoxide to an unrearranged 1,2-diol observed. If such a process is to be adapted to a synthesis of Taxol, one needs to give serious attention to curtailing transannular bonding. In the accompanying paper,[9] an alternative means for bringing about the C-2 oxygenation of advanced intermediates as demanded by the target molecule is delineated. In effect, a reversal of polarity at C-2 from an electrophilic reaction center as in an epoxide to one that is nucleophilic as in an enolate anion is adequate to the task.

Experimental Section

General Methods. Melting points are uncorrected. The column chromatographic separations were performed with Woelm silica gel (230−400 mesh). Solvents were reagent grade and in most cases dried prior to use. The purity of all compounds was shown to be >95% by TLC and high-field ^{1}H and ^{13}C NMR. The high-resolution and fast-atom-bombardment spectra were recorded at The Ohio State University

(9) Zeng, Q.; Bailey, S.; Wang, T.-Z.; Paquette, L. A. *J. Org. Chem.* **1998**, *63*, 135−141.

Campus Chemical Instrumentation Center. Elemental analyses were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark, or at Atlantic Microlab, Inc., Norcross, GA.

(1*S*,3*R*,4*S*)-3-(Methoxymethoxy)-7,7-dimethyl-1-[(*Z*)-2-(phenylthio)vinyl]-2-norbornanone (5). A solution of potassium hexamethyldisilazide (95.0 mL of 0.5 M in toluene, 0.047 mol) was added dropwise to a chilled (0 °C), magnetically stirred suspension of commercial [(phenylthio)methyl]triphenylphosphonium chloride (19.7 g, 0.047 mol) in dry THF (100 mL) under N_2. After 30 min at this temperature, a solution of the keto aldehyde[4] (8.7 g, 0.039 mol) in THF (20 mL) was introduced slowly into the yellow reaction mixture. The cooling bath was removed and stirring was maintained for an additional 2 h, at which point saturated NH_4Cl solution (100 mL) was poured in followed by hexanes (200 mL). The separated organic layer was dried and concentrated to leave an oil, which was purified by chromatography on silica gel. Elution with 7% ethyl acetate in hexanes gave pure **5** (8.1 g, 63%) and the slightly impure trans isomer (2.7 g, 21%), which was not completely purified.

For **5**: white solid, mp 70−70.5 °C; IR (film, cm^{-1}) 1755, 1586; ^1H NMR (300 MHz, $CDCl_3$) δ 7.38−7.18 (m, 5 H), 6.57 (d, J = 10.6 Hz, 1 H), 5.68 (d, J = 10.6 Hz, 1 H), 4.85 (d, J = 6.6 Hz, 1 H), 4.72 (d, J = 6.6 Hz, 1 H), 3.75 (s, 1 H), 3.41 (s, 3 H), 2.37−2.27 (m, 1 H), 2.17−2.03 (m, 3 H), 1.54−1.45 (m, 1 H), 1.12 (s, 3 H), 1.04 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 213.3, 136.5, 129.7, 129.2, 128.9, 126.5, 124.0, 96.6, 81.1, 62.7, 55.5, 49.0, 47.8, 25.4, 25.3, 21.3, 20.7; MS m/z (M^+) calcd 332.1446, obsd 332.1448; $[\alpha]^{20}_D$ −68.3 (*c* 1.26, $CHCl_3$). Anal. Calcd for $C_{19}H_{24}O_3S$: C, 68.64; H, 7.28. Found: C, 68.91; H, 7.33.

(1*S*,2*S*,3*R*,4*S*)-2-[(*Z*)-2-[(4*S*)-4-[(1*R*)-1-[(*p*-Methoxybenzyl)oxy]allyl]-2,2-dimethyl-1,3-dioxolan-4-yl]vinyl]-3-(methoxymethoxy)-7,7-dimethyl-1-[(*Z*)-2-(phenylthio)-vinyl]-2-norbornanol (7). *n*-Butyllithium (3.07 mL of 1.5 M in hexanes, 4.60 mmol) was added to a solution of (4*S*)-4-[(*Z*)-2-iodovinyl]-4-[(1*R*)-1-[(*p*-methoxybenzyl)oxy]allyl]-2,2-dimethyl-1,3-dioxolane[2] (1.98 g, 4.60 mmol) in anhydrous ether (12 mL) at −78 °C. After 1 min of stirring, a solution of **5** (1.39 g, 4.18 mmol) in dry ether (5 mL) was cannulated into the reaction mixture, which was agitated for another 2 min at −78 °C before being diluted with water, allowed to warm to rt, and extracted with ether. The combined organic layers were dried and concentrated to leave a residue that was chromatographed on silica gel (elution with 10% ethyl acetate in hexanes) to furnish **7** (2.25 g, 85%) as a colorless oil: IR (film, cm^{-1}) 3423, 1612, 1586; ^1H NMR (300 MHz, $CDCl_3$) δ 7.29−7.13 (m, 7 H), 6.87−6.83 (m, 2 H), 6.32 (d, J = 10.9 Hz, 1 H), 5.90 (d, J = 10.9 Hz, 1 H), 5.79 (ddd, J = 6.6, 10.0, 17.9 Hz, 1 H), 5.63 (d, J = 13.4 Hz, 1 H), 5.59 (d, J = 13.4 Hz, 1 H), 5.27 (d, J = 16.7 Hz, 1 H), 5.26 (d, J = 11.8 Hz, 1 H), 4.58 (s, 1 H), 4.52 (d, J = 11.3 Hz, 1 H), 4.45 (d, J = 11.3 Hz, 1 H), 4.35 (d, J = 6.6 Hz, 1 H), 4.30−4.20 (m, 3 H), 4.01 (d, J = 6.3 Hz, 1 H), 3.78 (s, 3 H), 3.37 (s, 1 H), 3.23 (s, 3 H), 2.12−2.07 (m, 2 H), 1.87−1.79 (m, 2 H), 1.40 (s, 3 H), 1.38 (s, 3 H), 1.32 (s, 3 H), 1.29−1.10 (m, 1 H), 0.86 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 159.3, 137.9, 137.3, 134.6, 130.8, 130.0, 129.4, 128.8, 128.7, 126.1, 125.8, 118.6, 113.6, 108.6, 96.5, 90.4, 84.6, 84.0, 83.2, 72.6, 71.4, 60.4, 55.2, 55.0, 52.4, 49.3, 27.0, 26.7, 25.7, 24.9, 22.33, 22.26; MS m/z (M^+) calcd 636.3120, obsd 636.3141; $[\alpha]^{20}_D$ −205 (*c* 0.81, $CHCl_3$). Anal. Calcd for $C_{37}H_{48}O_7S$: C, 69.78; H, 7.60. Found: C, 69.81; H, 7.63.

(1*S*,2*R*,4*S*,5*S*,6*R*,7*E*)-5-[(4*S*)-4-[(1*R*)-1-[(*p*-Methoxybenzyl)oxy]allyl]-2,2-dimethyl-1,3-dioxolan-4-yl]-2-(methoxymethoxy)-4,11,11-trimethyl-6-(phenylthio)bicyclo-[6.2.1]undec-7-en-3-one (8). Nitrogen was bubbled through a solution of **7** (816 mg, 1.28 mmol) and 18-crown-6 (1.00 g, 3.85 mmol) in dry THF (20 mL) for 30 min. The reaction mixture was cooled to −78 °C, treated dropwise with potassium hexamethyldisilazide (7.7 mL in toluene, 3.85 mmol), and allowed to stir at −78 °C for 15 min prior to the introduction of methyl iodide (0.80 mL, 12.8 mmol) in one portion. After a final hour of agitation at −78 °C, the white suspension was quenched with saturated NH_4Cl solution (10 mL), allowed to warm to rt, and diluted with ethyl acetate (20 mL). The separated organic layer was dried and concentrated, leaving a residue that was purified by chromatography on silica gel. Elution with 15% ethyl acetate in hexanes gave **8** as a white foam (667 mg, 80%); IR (film, cm^{-1}) 1613, 1584, 1514; ^1H NMR (300 MHz, $CDCl_3$) δ 7.31−7.13 (m, 7 H), 6.86−6.81 (m, 2 H), 6.05 (br s, 1 H), 5.40 (br m, 1 H), 5.29 (d, J = 11.6 Hz, 1 H), 5.24 (d, J = 6.8 Hz, 1 H), 4.61 (d, J = 6.9 Hz, 1 H), 4.54 (d, J = 11.3 Hz, 1 H), 4.36−4.25 (m, 3 H), 4.23 (d, J = 9.1 Hz, 1 H), 4.09 (s, 1 H), 3.79 (s, 3 H), 3.30 (s, 3 H), 3.01−2.97 (m, 1 H), 2.85 (br s, 1 H), 2.33−2.15 (m, 2 H), 2.13 (d, J = 8.2 Hz, 1 H), 1.49 (s, 3 H), 1.41 (s, 3 H), 1.21 (d, J = 7.5 Hz, 3 H), 1.13 (s, 3 H), 0.99 (s, 3 H) (3 protons not observed due to site exchange within ring B); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 217.8, 159.3, 137.3, 134.6, 130.8, 130.1, 129.5, 128.9, 128.84, 128.77, 126.2, 125.9, 118.7, 113.7, 108.7, 99.8, 98.2, 96.5, 90.4, 84.6, 84.1, 83.3, 72.7, 71.5, 60.5, 55.2, 55.1, 52.5, 49.3, 27.0, 26.7, 25.7, 24.9, 22.4, 22.3; FAB MS m/z (M^+ + H) calcd 651.33, obsd 651.22; $[\alpha]^{20}_D$ −105 (*c* 0.77, $CHCl_3$). Anal. Calcd for $C_{38}H_{50}O_7S$: C, 70.12; H, 7.75. Found: C, 69.90; H, 7.92.

(1*S*,2*R*,4*S*,5*S*,6*R*,7*R*)-5-[(4*S*)-4-[(1*R*)-1-[(*p*-Methoxybenzyl)oxy]allyl]-2,2-dimethyl-1,3-dioxolan-4-yl]-2-(methoxymethoxy)-4,11,11-trimethyl-6-(phenylsulfinyl)bicyclo-[6.2.1]undec-7-en-3-one (9). *m*-Chloroperbenzoic acid (35 mg, 0.20 mmol) dissolved in CH_2Cl_2 was added to a solution of **8** (111 mg, 0.17 mmol) in CH_2Cl_2 (10 mL) containing sodium bicarbonate (2 mg, 24 μmol) at −78 °C. After 10 min of stirring at this temperature, the reaction mixture was diluted with water (10 mL) and CH_2Cl_2 (10 mL). The separated organic phase was dried and concentrated to leave an oil that was purified by chromatography on silica gel (elution with 40% ethyl acetate in hexanes). The less polar sulfoxide (71 mg, 62%) was isolated as a colorless oil; the more polar diastereomer (33 mg, 29%) exhibited the same physical characteristics. These sulfoxides are unstable at rt, readily undergoing elimination to **10**. Consequently, no characterization was undertaken.

(1*S*,2*R*,4*S*,5*Z*,7*E*)-5-[(4*S*)-4-[(1*R*)-1-[(*p*-Methoxybenzyl)-oxy]allyl]-2,2-dimethyl-1,3-dioxolan-4-yl]-2-(methoxymethoxy)-4,11,11-trimethylbicyclo[6.2.1]undeca-5,7-dien-3-one (10). Reaction of MCPBA (232 mg, 1.35 mmol) with **8** (727 mg, 1.12 mmol) in the predescribed manner gave an oily mixture of sulfoxides, which was taken up in THF (20 mL), heated to relfux for 3 h, cooled to rt, and concentrated. Purification of the residue by chromatography on silica gel (elution with 20% ethyl acetate in hexanes) afforded triene **10** as a colorless oil (374 mg, 62%): IR (film, cm^{-1}) 1705, 1613, 1586; ^1H NMR (300 MHz, C_6D_6, 60 °C) δ 7.29−7.25 (m, 2 H), 6.85−6.82 (m, 2 H), 6.59 (br s, 1 H), 6.09 (ddd, J = 6.9, 10.7, 17.4 Hz, 1 H), 5.65 (s, 1 H), 5.37 (d, J = 17.4 Hz, 1 H), 5.31 (d, J = 10.4 Hz, 1 H), 4.60−4.55 (m, 3 H), 4.35−4.30 (m, 2 H), 4.19−4.08 (m, 3 H), 3.39 (s, 3 H), 3.31−3.27 (m, 1 H), 3.22 (s, 3 H), 2.60−2.52 (m, 1 H), 2.16−2.15 (m, 1 H), 2.14−1.98 (m, 2 H), 1.60−1.58 (m, 1 H), 1.54 (s, 6 H), 1.39 (s, 3 H), 1.34 (d, J = 6.9 Hz, 3 H), 1.06 (s, 3 H); ^{13}C NMR (75 MHz, C_6D_6, 25 °C) ppm 209.2, 159.8, 146.7, 135.5, 130.7, 129.8, 126.5, 118.5, 114.0, 109.0, 95.2, 85.3, 71.5, 55.4, 54.7, 54.0, 47.0, 46.5, 26.9, 25.5,25.0, 24.9, 21.7, 17.5; MS molecular ion too fleeting for accurate mass measurement; $[\alpha]^{20}_D$ −219 (*c* 1.70, $CHCl_3$).

(1*S*,3a*S*,4*R*,7*S*,8*R*,8a*S*)-3a,4,5,6,7,8-Hexahydro-4-methoxy-2-[(4*S*)-4-[(1*R*)-1-[(*p*-methoxybenzyl)oxy]allyl]-2,2-dimethyl-1,3-dioxolan-4-yl]-8-(methoxymethoxy)-1,9,9-trimethyl-4,7-methanoazulen-8a(1*H*)-ol (11). Trimethyl phosphite (4 drops) was added to a solution of sulfoxides **9** (90 mg, 0.14 mmol) in methanol (5 mL), and the reaction mixture was heated at reflux for 2 h, cooled to rt, and freed of solvent. The residue was subjected to chromatography on silica gel (elution with 20% ethyl acetate in hexanes) to give **11** (52 mg, 67%) as a colorless oil; IR (film, cm^{-1}) 3510, 1586, 1514; ^1H NMR (300 MHz, $CDCl_3$) δ 7.24−7.17 (m, 2 H), 6.87−6.78 (m, 2 H), 5.90 (ddd, J = 7.1, 10.5, 17.2 Hz, 1 H), 5.81 (t, J = 2.7 Hz, 1 H), 5.36 (d, J = 10.2 Hz, 1 H), 5.32 (d, J = 17.1 Hz, 1 H), 4.75 (d, J = 6.8 Hz, 1 H), 4.61 (d, J = 6.8 Hz, 1 H), 4.55 (d, J = 11.3 Hz, 1 H), 4.31 (d, J = 11.3 Hz, 1 H), 4.13 (d, J = 8.7 Hz, 1 H), 3.87 (d, J = 8.7 Hz, 1 H), 3.85 (d, J = 7.2 Hz, 1 H),

3.80 (s, 3 H), 3.75 (br s, 1 H), 3.45 (s, 3 H), 3.40 (s, 3 H), 3.34 (s, 3 H), 3.11 (s, 1 H), 2.48−2.40 (br q, J = 7.2 Hz, 1 H), 1.97−1.74 (m, 3 H), 1.55−1.50 (m, 1 H), 1.48 (s, 3 H), 1.34 (s, 3 H), 1.15 (s, 3 H), 1.13−1.02 (m, 1 H), 0.98 (s, 3 H), 0.97 (d, J = 7.1 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 159.0, 146.9, 134.7, 130.1, 129.7, 126.6, 119.2, 113.6, 109.3, 96.2, 85.8, 85.1, 83.0, 81.2, 80.9, 70.9 (2 C), 60.1, 55.9, 55.2, 53.5, 52.3, 49.4, 45.1, 26.7, 25.6, 25.4, 24.3, 23.4, 21.5, 10.1; MS molecular ion too fleeting for accurate measurement; $[\alpha]^{20}_D$ +47.7 (*c* 0.83, $CHCl_3$).

(1*S*,2*R*,3*S*,4*S*,5*S*,6*R*,7*E*)-5-[(4*S*)-4-[(1*R*)-1-[(*p*-Methoxybenzyl)oxy]allyl]-2,2-dimethyl-1,3-dioxolan-4-yl]-2-(methoxymethoxy)-4,11,11-trimethyl-6-(phenylthio)bicyclo-[6.2.1]undec-7-en-3-one (12a) and (1*S*,2*R*,3*R*,4*S*,5*S*,6*R*,7*E*)-5-[(4*S*)-4-[(1*R*)-1-[(*p*-Methoxybenzyl)oxy]allyl]-2,2-dimethyl-1,3-dioxolan-4-yl]-2-(methoxymethoxy)-4,11,11-trimethyl-6-(phenylthio)bicyclo[6.2.1]undec-7-en-3-one (12b). Lithium aluminum hydride (141 mg, 3.72 mmol) was added to a cold (0 °C) solution of **8** (2.02 g, 3.10 mmol) in anhydrous ether (30 mL). The suspension was stirred for 2 h, treated with saturated Rochelle's salt solution, and stirred for an additional 12 h. Following extraction with ethyl acetate, the combined organic layers were dried and concentrated. The residue was chromatographed on silica gel (elution with 20% ethyl acetate in hexanes) to furnish 1.57 g (77%) of **12a** and 134 mg (7%) of **12b**, both as colorless oils.

For **12a**: IR (film, cm^{-1}) 3485, 1613; ^{1}H NMR (300 MHz, C_6D_6) δ 7.33 (d, J = 7.3 Hz, 2 H), 7.22 (d, J = 8.6 Hz, 2 H), 7.04 (dd, J = 7.2 Hz, 2 H), 6.93 (dd, J = 7.3 Hz, 1 H), 6.73 (dd, J = 8.6 Hz, 2 H), 6.28 (ddd, J = 17.3, 10.4, 6.8 Hz, 1 H), 5.78 (d, J = 7.5 Hz, 1 H), 5.39 (d, J = 10.3 Hz, 1 H), 5.34 (br d, J = 17.3 Hz, 1 H), 4.53 (d, J = 11.1 Hz, 1 H), 4.45 (d, J = 6.4 Hz, 2 H), 4.37 (d, J = 11.1 Hz, 1 H), 4.33 (d, J = 6.5 Hz, 1 H), 4.31 (d, J = 11.1 Hz, 1 H), 4.19 (d, J = 6.9 Hz, 1 H), 4.16 (d, J = 11.2 Hz, 1 H), 3.92−3.85 (m, 2 H), 3.77 (d, J = 5.7 Hz, 1 H), 3.36 (d, J = 11.5 Hz, 1 H), 3.25 (s, 3 H), 3.10 (s, 3 H), 3.08−2.97 (m, 1 H), 2.79 (br s, 1 H), 2.31 (br dd, J = 12.3 Hz, 1 H), 1.87 (dd, J = 6.9 Hz, 1 H), 1.64 (ddd, J = 12.4, 12.4, 5.4 Hz, 1H), 1.45 (s, 3 H), 1.44 (s, 3 H), 1.41 (d, J = 6.8 Hz, 3 H), 1.33 (s, 3 H), 1.16−1.07 (m, 2 H), 0.82 (s, 3 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 159.8, 148.5, 148.4, 136.1, 131.4, 130.3, 130.2, 128.6, 126.1, 120.4, 118.9, 114.2, 109.7, 97.7, 90.3, 87.5, 83.9, 80.7, 72.0, 71.3, 55.7, 54.6, 52.2, 45.8, 45.2, 44.9 (2 C), 27.4, 27.3, 26.9, 26.0, 23.1, 22.5, 13.2; $[\alpha]^{21}_D$ −284 (*c* 1.10, $CHCl_3$).

For **12b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, J = 6.9 Hz, 2 H), 7.26−7.15 (m, 5H), 6.85 (d, J = 8.7 Hz, 2 H), 5.97 (ddd, J = 17.6, 10.2, 7.1 Hz, 1 H), 5.42 (d, J = 6.6 Hz, 1 H), 5.32 (d, J = 17.6 Hz, 1 H), 5.26 (d, J = 10.2 Hz, 1 H), 4.72 (d, J = 6.7 Hz, 1 H), 4.66 (d, J = 6.7 Hz, 1 H), 4.55 (d, J = 11.6 Hz, 1 H), 4.54 (d, J = 6.6 Hz, 1 H), 4.41 (d, J = 9.2 Hz, 1 H), 4.32 (d, J = 11.6 Hz, 1 H), 4.14 (d, J = 9.5 Hz, 1 H), 4.07 (d, J = 9.2 Hz, 1 H), 4.07 (d, J = 7.1 Hz, 1 H), 3.78 (s, 3 H), 3.77−3.71 (m, 2 H), 3.41 (s, 1 H), 3.39 (s, 3 H), 3.31 (d, J = 9.5 Hz, 1 H), 2.59 (br s, 1 H), 2.25 (q, J = 7.6 Hz, 1 H), 2.21−2.16 (m, 3 H), 1.41 (s, 3 H), 1.40 (s, 3 H), 1.31 (s, 3 H), 1.36−1.28 (m, 1 H), 1.09 (d, J = 7.6 Hz, 3 H), 1.03 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 159.0, 152.0, 136.8, 134.6, 130.7, 130.1, 129.3, 128.4, 126.2, 119.5, 116.8, 113.6, 108.4, 97.6, 88.3, 88.1, 82.5, 70.7, 69.8, 68.0, 55.8, 55.2, 51.8, 50.2, 47.1, 46.3, 33.0, 27.7, 27.5, 26.7, 26.1, 25.2, 21.7, 16.2; MS m/z (M^+) calcd 652.3434, obsd 652.3451; $[\alpha]^{21}_D$ −103 (*c* 0.64, $CHCl_3$).

(1*R*,2*Z*,4*S*,5*S*,6*S*,7*R*,8*S*)-4-[(4*S*)-4-[(1*R*)-1-[(*p*-Methoxybenzyl)oxy]allyl]-2,2-dimethyl-1,3-dioxolan-4-yl]-7-(methoxymethoxy)-5,11,11-trimethylbicyclo[6.2.1]undec-2-ene-1,6-diol 1-(Trifluoroacetate) (13a). A mixture of **12a** (231 mg of 80% purity, 0.28 mmol) and sodium bicarbonate (29 mg, 0.35 mmol) in dry CH_2Cl_2 (5 mL) at −78 °C was treated with MCPBA (79 mg, 0.46 mmol), stirred for 1.5 h, diluted with water, and extracted with ether. The combined organic layers were dried and concentrated to give a foam that was immediately dissolved in cold (−78 °C) CH_2Cl_2 (5 mL) and treated with trifluoroacetic anhydride (100 μL, 0.71 mmol). After an additional 30 min of stirring, the reaction mixture was diluted with water and extracted with ether. The combined organic layers were dried and concentrated to leave a residue that was subjected to chromatography on silica gel. Elution with 20% ethyl acetate in hexanes furnished **13a** (97 mg, 53%) as a colorless oil; IR (film, cm^{-1}) 3498, 1783, 1613; ^{1}H NMR (300 MHz, C_6D_6) δ 7.14 (d, J = 8.6 Hz, 2 H), 6.79 (d, J = 8.6 Hz, 2 H), 6.15 (ddd, J = 17.3, 10.5, 5.7 Hz, 1 H), 5.67 (dd, J = 12.2, 12.2 Hz, 1 H), 5.37 (d, J = 17.5 Hz, 1 H), 5.36 (d, J = 12.2 Hz, 1 H), 5.27 (d, J = 10.5 Hz, 1 H), 4.47 (d, J = 11.0 Hz, 1 H), 4.31 (d, J = 6.9 Hz, 1 H), 4.26 (d, J = 7.0 Hz, 1 H), 4.09 (d, J = 11.0 Hz, 1 H), 4.04 (d, J = 9.2 Hz, 1 H), 3.98 (d, J = 9.2 Hz, 1 H), 3.95 (d, J = 5.6 Hz, 1 H), 3.75 (dd, J = 3.4, 3.4 Hz, 1 H), 3.47−3.37 (m, 2 H), 3.29 (s, 3 H), 3.32−3.24 (m, 1 H), 3.06 (s, 3 H), 2.42 (br d, J = 11.8 Hz, 1 H), 2.17−2.09 (m, 1 H), 2.08−1.71 (series of m, 4 H), 1.50 (s, 6 H), 1.46 (s, 3 H), 1.10 (s, 3 H), 1.08 (d, J = 7.0 Hz, 3 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 159.9, 135.5, 132.6, 130.4, 130.3, 129.5, 117.9, 114.1, 109.3, 97.8, 95.8, 87.5, 87.0, 84.2, 79.9, 72.3, 66.4, 55.5, 54.7, 53.4, 51.6, 39.6, 35.0, 32.7, 30.1, 27.9, 26.9, 25.6, 20.4, 15.7 (CF_3CO carbons not observed); FAB MS m/z (M^+ + H) calcd 657.33, obsd 657.32; $[\alpha]^{23}_D$ −6.9 (*c* 0.71, $CHCl_3$).

(1*R*,2*Z*,4*S*,5*S*,6*S*,7*R*,8*S*)-4-[(4*S*)-4-[(1*R*)-1-[(*p*-Methoxybenzyl)oxy]allyl]-2,2-dimethyl-1,3-dioxolan-4-yl]-7-(methoxymethoxy)-5,11,11-trimethylbicyclo[6.2.1]undec-2-ene-1,6-diol Bis(trifluoroacetate) (14a). MCPBA (231 mg, 1.34 mmol) was added to a cold (0 °C) mixture of **12a** (796 mg of 80% purity, 0.98 mmol) and $NaHCO_3$ (51 mg, 0.61 mmol) in CH_2Cl_2 (15 mL). This mixture was stirred for 1.5 h and treated with trifluoroacetic anhydride (0.86 mL, 6.1 mmol) followed by pyridine (0.69 mL, 8.5 mmol). After 1 h, water was introduced and the separated aqueous layer was further extracted with CH_2Cl_2. The combined organic layers were dried and concentrated. Purification of the residue by chromatography on silica gel (elution with 8−20% ethyl acetate in hexanes) provided **14a** as a colorless oil (403 mg, 55%); IR (film, cm^{-1}) 1783, 1613, 1515; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, J = 8.7 Hz, 2 H), 6.91 (d, J = 8.6 Hz, 2 H), 6.08 (ddd, J = 17.2, 10.6, 5.6 Hz, 1 H), 5.62 (dd, J = 12.1, 12.1 Hz, 1 H), 5.49 (m, 2 H), 5.45 (d, J = 10.2 Hz, 1 H), 5.29 (dd, J = 3.4, 3.4 Hz, 1 H), 4.61 (d, J = 11.2 Hz, 1 H), 4.58 (d, J = 7.4 Hz, 1 H), 4.51 (d, J = 7.4 Hz, 1 H), 4.33 (d, J = 11.2 Hz, 1 H), 3.97 (d, J = 9.2 Hz, 1 H), 3.93 (d, J = 9.2 Hz, 1 H), 3.92 (d, J = 5.7 Hz, 1 H), 3.82 (s, 3 H), 3.57 (dd, J = 3.6, 3.6 Hz, 1 H), 3.41 (s, 3 H), 3.55−3.37 (m, 1 H), 3.20 (ddd, J = 13.7, 11.4, 4.5 Hz, 1 H), 2.47 (br d, J = 12.9 Hz, 1 H), 2.43−2.29 (m, 1 H), 2.29−2.20 (m, 1 H), 2.07−1.82 (series of m, 2 H),1.45 (s, 3 H), 1.31 (s, 3 H), 1.20 (s, 3 H), 1.16 (s, 3 H), 0.77 (d, J = 7.0 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 159.5, 134.4, 133.8, 130.1, 129.5, 127.2, 118.6, 113.9, 109.3, 96.6, 95.2, 86.7, 83.0, 82.9, 82.4, 71.8, 66.0, 56.3, 55.2, 52.8, 51.4, 38.9, 34.7, 32.2, 29.8, 27.5, 26.5, 25.5, 18.8, 13.7 (CF_3CO carbons not observed); FAB MS m/z (M^+ + H) calcd 753.31, obsd 753.43; $[\alpha]^{21}_D$ +28.4 (*c* 1.33, $CHCl_3$). Anal. Calcd for $C_{36}H_{46}F_6O_{10}$: C, 57.44; H, 6.16. Found: C, 57.55; H, 6.23.

(1*R*,2*Z*,4*S*,5*S*,6*S*,7*R*,8*S*)-4-[(4*S*)-4-[(1*R*)-1-Hydroxyallyl]-2,2-dimethyl-1,3-dioxolan-4-yl]-7-(methoxymethoxy)-5,-11,11-trimethylbicyclo[6.2.1]undec-2-ene-1,6-diol 1,6-Bis-(trifluoroacetate) (14b). A solution of **14a** (12.5 mg, 0.017 mmol) and DDQ (10 mg, 0.046 mmol) in CH_2Cl_2 (1 mL) containing water (2 drops) was stirred vigorously at rt for 3 h, treated with saturated $NaHCO_3$ solution, and extracted with ether. The combined organic layers were dried and concentrated to leave a residue that was chromatographed on silica gel. Elution with 30% ethyl acetate in hexanes yielded 8.3 mg (79%) of **14b** as colorless crystals: mp 155−156 °C; IR (film, cm^{-1}) 3414, 1784, 1217, 1167; ^{1}H NMR (300 MHz, C_6D_6) δ 6.09 (ddd, J = 17.3, 10.7, 4.0 Hz, 1 H), 5.84−5.40 (m, 2 H), 5.37 (dd, J = 3.7, 3.7 Hz, 1 H), 5.22 (ddd, J = 17.3, 1.8, 1.8 Hz, 1 H), 5.11 (ddd, J = 10.7, 1.8, 1.8 Hz, 1 H), 4.36 (d, J = 7.3 Hz, 1 H), 4.28 (d, J = 7.3 Hz, 1 H), 3.78 (br s, 1 H), 3.64 (s, 2 H), 3.52 (dd, J = 3.8, 3.8 Hz, 1 H), 3.42 (m, 1 H), 3.30−3.19 (m, 2 H), 3.15 (s, 3 H), 2.37 (br d, J = 12.8 Hz, 1 H), 2.08−1.98 (m, 2 H), 1.85−1.74 (m, 2 H), 1.41 (s, 3 H), 1.39 (s, 3 H), 1.36 (s, 3 H), 1.04 (s, 3 H), 0.52 (d, J = 7.0 Hz, 3 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 137.8, 134.3, 127.3, 115.7, 109.5, 97.0, 95.4, 87.0, 83.2, 82.8, 74.8, 65.6, 56.1, 53.2, 51.6, 38.9, 35.4, 32.6, 29.9, 27.4, 26.8, 25.5, 19.2, 13.4 (CF_3CO carbons not observed); FAB MS m/z (M^+ + H) calcd 633.25, obsd 633.33;

$[\alpha]^{21}_D$ +44.2 (*c* 0.79, $CHCl_3$). Anal. Calcd for $C_{28}H_{38}F_6O_9$: C, 53.16; H, 6.05. Found: C, 53.22; H, 6.06.

The structural assignment to **14b** was corroborated by X-ray crystallographic analysis (Figure 1).

(1*R*,2*Z*,4*S*,5*S*,6*S*,7*R*,8*S*)-4-[(4*S*)-4-[(1*R*)-1-[(*p*-Methoxybenzyl)oxy]allyl]-2,2-dimethyl-1,3-dioxolan-4-yl]-7-(methoxymethoxy)-5,11,11-trimethylbicyclo[6.2.1]undec-2-ene-1,6-diol (15). A solution of **14a** (37 mg, 49 μmol) in methanol (0.5 mL) was added to a suspension of K_2CO_3 (75 mg, 540 μmol) in methanol (2.5 mL). The reaction mixture was stirred at rt for 30 min, diluted with water, and extracted with ether. The combined ethereal layers were dried and concentrated, and the residue was purified by flash chromatography (SiO_2, elution with 30% ethyl acetate in hexanes) to furnish **15** (23.6 mg, 86%) as a colorless oil; IR (film, cm^{-1}) 3488, 1614, 1515; ^1H NMR (300 MHz, C_6D_6) δ 7.14 (d, J = 8.6 Hz, 2 H), 6.81 (d, J = 8.6 Hz, 2 H), 6.12 (ddd, J = 17.2, 10.5, 6.3, Hz, 1 H), 5.64−5.62 (m, 2 H), 5.30 (br d, J = 11.3 Hz, 1 H), 5.26 (dd, J = 3.2, 1.2 Hz, 1 H), 4.47 (d, J = 11.3 Hz, 1 H), 4.44 (d, J = 7.0 Hz, 1 H), 4.38 (d, J = 7.0 Hz, 1 H), 4.08 (d, J = 9.2 Hz, 1 H), 4.05 (d, J = 11.2 Hz, 1 H), 3.94 (d, J = 9.2 Hz, 1 H), 3.86 (br d, J = 5.9 Hz, 2 H), 3.51 (dd, J = 5.9, 5.9 Hz, 1 H), 3.42 (dd, J = 3.4, 3.4 Hz, 1 H), 3.30 (s, 4 H), 3.14 (s, 3 H), 2.92 (ddd, J = 14.1, 10.3, 3.7 Hz, 1 H), 2.57 (ddd, J = 12.2, 2.7, 2.7 Hz, 1 H), 2.34 (d, J = 5.1 Hz, 1 H), 2.17−2.11 (m, 2 H), 1.97−1.85 (m, 1 H), 1.80−1.70 (m, 1 H), 1.49 (s, 3 H), 1.37 (s, 6 H), 1.16 (s, 3 H), 1.14 (d, J = 7.1 Hz, 3 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 160.0, 139.2, 135.7, 130.5, 130.3, 126.8, 118.5, 114.1, 108.7, 95.8, 87.8, 87.6, 84.2, 84.0, 80.5, 71.9, 66.9, 55.4, 55.1, 54.7, 50.3, 39.5, 35.7, 35.6, 29.7, 27.6, 27.3, 25.3, 20.6, 15.9; FAB MS m/z (M^+ + H) calcd for 561.34, obsd 561.45; $[\alpha]^{21}_D$ −35 (*c* 0.5, $CHCl_3$).

(1*R*,2*R*,4*S*,5*S*,6*Z*,8*R*)-8-Hydroxy-5-[(4*S*)-4-[(1*R*)-1-[(*p*-methoxybenzyl)oxy]allyl]-2,2-dimethyl-1,3-dioxolan-4-yl]-2-(methoxymethoxy)-4,11,11-trimethylbicyclo[6.2.1]-undec-6-en-3-one (16). A solution of 15 (73 mg, 130 μmol) in CH_2Cl_2 (5 mL) was stirred with the Dess−Martin periodinane (113 mg, 260 μmol) for 30 min, filtered through Celite, and concentrated. The resulting oil was chromatographed on silica gel (elution with 30% ethyl acetate in hexanes) to provide 66.4 mg (91%) of 16 and 3.5 mg (5%) of unreacted 15.

For **16**: colorless oil; IR (film, cm^{-1}) 3495, 1714, 1614, 1515; ^1H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, J = 8.6 Hz, 2 H), 6.88 (d, J = 8.6 Hz, 2 H), 6.11 (ddd, J = 17.4, 10.5, 6.8 Hz, 1 H), 5.56 (d, J = 10.4 Hz, 1 H), 5.48 (d, J = 12.1 Hz, 1 H), 5.45 (d, J = 17.4 Hz, 1 H), 5.40 (dd, J = 12.1, 12.1 Hz, 1 H), 4.65 (d, J = 11.2 Hz, 1 H), 4.50 (d, J = 7.0 Hz, 1 H), 4.31 (d, J = 7.0 Hz, 1 H), 4.28 (d, J = 11.2 Hz, 1 H), 4.07 (d, J = 9.3 Hz, 1 H), 3.95 (d, J = 2.2 Hz, 1 H), 3.85−3.80 (m, 3 H), 3.79 (s, 3 H), 3.31 (s, 3 H), 2.79−2.73 (m, 1 H), 2.71 (ddd, J = 13.9, 9.9, 3.3 Hz, 1 H), 2.49 (d, J = 11.9 Hz, 1 H), 2.43−2.37 (m, 1 H), 2.07−1.94 (m, 1 H), 1.94−1.88 (m, 1 H), 1.65 (br s, 1 H), 1.36 (s, 3 H), 1.33 (s, 3 H), 1.03 (s, 3 H), 1.00 (s, 3 H), 0.86 (d, J = 6.7 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 210.2, 159.5, 140.1, 134.9, 130.4, 129.3, 125.0, 119.9, 113.8, 109.0, 95.3, 88.1, 86.5, 83.9, 82.8, 71.2, 66.6, 56.1, 55.7, 55.2, 51.8, 46.6, 36.0, 35.8, 29.2, 26.92, 26.89, 26.3, 18.1, 10.8; FAB MS m/z (M^+ + H) calcd 559.33, obsd 559.24; $[\alpha]^{19}_D$ +0.38 (*c* 0.80, $CHCl_3$).

(1*R*,2*R*,4*R*,5*S*,6*Z*,8*R*)-4,8-Dihydroxy-5-[(4*S*)-4-[(1*R*)-1-[(*p*-methoxybenzyl)oxy]allyl]-2,2-dimethyl-1,3-dioxolan-4-yl]-2-(methoxymethoxy)-4,11,11-trimethylbicyclo[6.2.1]-undec-6-en-3-one (17). A solution of **16** (30.8 mg, 55 μmol) and 18-crown-6 (15 mg, 55 μmol) in cold (0 °C) THF (3 mL) was oxygenated while being treated with potassium hexamethyldisilazide in toluene (0.23 mL of 0.5 M, 115 μmol). Oxygen was bubbled through the solution for an additional 20 min before triphenylphosphine (16 mg, 61 μmol) was introduced. The reaction mixture was stirred for 20 min at rt, diluted with water, and extracted with ether. The combined organic layers were dried and concentrated to leave a residue that was chromatographed on silica gel (elution with 30% ethyl acetate in hexanes) to give bridgehead-silylated **17** (2.0 mg, 6%) and **17** (20.8 mg, 66%), both as colorless oils.

Deprotection of the silylated product (17.9 mg, 28.4 μmol) was effected by stirring with tetra-*n*-butylammonium fluoride (142 μL of 1 M in THF) in THF (4 mL) for 24 h at rt. The reaction mixture was concentrated and the residue was chromatographed on silica gel as above to give **17** (15.4 mg, 94%).

For the silylated derivative: IR (film, cm^{-1}) 3416, 1722, 1614, 1515; ^1H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, J = 8.7 Hz, 2 H), 6.89 (d, J = 8.7 Hz, 2 H), 6.11 (ddd, J = 16.8, 11.0, 5.6 Hz, 1 H), 5.50−5.41 (series of m, 3 H), 5.28 (s, 1 H), 5.08 (dd, J = 12.5, 12.5 Hz, 1 H), 4.99 (d, J = 4.0 Hz, 1 H), 4.70 (d, J = 10.9 Hz, 1 H), 4.51 (d, J = 6.9 Hz, 1 H), 4.42 (d, J = 10.9 Hz, 1 H), 4.29 (d, J = 6.9 Hz, 1 H), 4.17 (d, J = 5.6 Hz, 1 H), 4.09 (d, J = 9.2 Hz, 1 H), 3.93 (d, J = 9.2 Hz, 1 H), 3.81 (s, 3 H), 3.74 (d, J = 12.5 Hz, 1 H), 3.30 (s, 3 H), 2.51−2.26 (series of m, 4 H), 1.93−1.86 (m, 1 H), 1.39 (s, 3 H), 1.24 (s, 3 H), 1.13 (s, 3 H), 1.02 (s, 3 H), 0.96 (s, 3 H), 0.03 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 211.7, 159.8, 139.7, 132.7, 130.1, 128.1, 124.5, 119.9, 114.1, 108.4, 95.5, 86.5, 85.8, 82.5, 81.0, 80.1, 72.8, 66.3, 55.6, 55.2, 52.9, 51.9, 43.7, 34.7, 29.1, 28.2, 26.4, 23.5, 22.5, 18.2, 2.0; FAB MS m/z (M^+ + H) calcd 631.37, obsd 631.41; $[\alpha]^{20}_D$ +10.4 (*c* 1.10, $CHCl_3$).

For **17**: IR (film, cm^{-1}) 3390, 1717, 1614, 1516; ^1H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, J = 8.6 Hz, 2 H), 6.89 (d, J = 8.6 Hz, 2 H), 6.13 (ddd, J = 17.2, 10.8, 6.2 Hz, 1 H), 5.49 (d, J = 12.4 Hz, 1 H), 5.44 (d, J = 17.7 Hz, 1 H), 5.41 (d, J = 10.9 Hz, 1 H), 5.26 (s, 1 H), 5.15 (dd, J = 12.4, 12.4 Hz, 1 H), 5.01 (d, J = 3.8 Hz, 1 H), 4.69 (d, J = 11.0 Hz, 1 H), 4.51 (d, J = 6.9 Hz, 1 H), 4.40 (d, J = 11.0 Hz, 1 H), 4.30 (d, J = 6.9 Hz, 1 H), 4.12 (d, J = 6.2 Hz, 1 H), 4.04 (d, J = 9.4 Hz, 1 H), 3.98 (d, J = 9.4 Hz, 1 H), 3.81 (s, 3H), 3.72 (d, J = 12.4 Hz, 1 H), 3.31 (s, 3 H), 2.57−2.52 (m, 1 H), 2.50−2.20 (series of m, 3 H), 1.91 (ddd, J = 12.8 Hz, 12.8 Hz, 6.4 Hz, 1 H), 1.38 (s, 3 H), 1.25 (s, 1 H), 1.23 (s, 3 H), 1.16 (s, 3 H), 1.07 (s, 3 H), 1.04 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 211.2, 159.8, 138.6, 132.8, 130.2, 128.1, 125.5, 120.5, 114.1, 108.6, 95.5, 86.2, 83.5, 83.2, 80.8, 80.0, 72.5, 66.5, 55.7, 55.2, 54.5, 50.6, 43.8, 34.6, 28.6, 28.0, 26.4, 23.5, 22.0, 18.1; FAB MS m/z (M^+ + H) calcd 575.32, obsd 575.43; $[\alpha]^{22}_D$ −15.4 (*c* 0.36, $CHCl_3$).

(1*R*,2*R*,3*S*,6*S*,7*R*,8*S*,9*S*,10*R*)-10-[(4*S*)-4-[(1*R*)-1-[(*p*-Methoxybenzyl)oxy]allyl]-2,2-dimethyl-1,3-dioxolan-4-yl]-7-(methoxymethoxy)-9,12,12-trimethyl-11-oxatricyclo-[6.2.1.1^{3,6}]dodecane-2,3-diol (18). A mixture of **15** (100 mg, 0.18 mmol), MCPBA (123 mg, 0.71 mmol), and $NaHCO_3$ (30 mg, 0.36 mmol) was stirred in CH_2Cl_2 (8 mL) at rt for 24 h, treated with triphenylphosphine (140 mg, 0.53 mmol), diluted with saturated $NaHCO_3$ solution, and extracted with ether. The combined organic layers were dried and concentrated, leaving a residue that was subjected to chromatography (SiO_2, elution with 20% ethyl acetate in hexanes). There was isolated 77 mg (75%) of **18** as a colorless oil; IR (film, cm^{-1}) 3389, 1614, 1515; ^1H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, J = 8.7 Hz, 2 H), 6.89 (d, J = 8.7 Hz, 2 H), 5.97 (ddd, J = 17.4, 10.7, 4.5 Hz, 1 H), 5.48 (ddd, J = 17.4, 1.7, 1.7 Hz, 1 H), 5.40 (ddd, J = 10.7, 1.5, 1.5 Hz, 1 H), 4.68 (d, J = 7.8 Hz, 1 H), 4.64 (d, J = 7.0 Hz, 1 H), 4.58 (d, J = 11.0 Hz, 1 H), 4.55 (d, J = 7.0 Hz, 1 H), 4.45 (dd, J = 8.0, 4.8 Hz, 1 H), 4.31 (d, J = 11.0 Hz, 1 H), 4.19 (d, J = 9.5 Hz, 1 H), 4.12 (ddd, J = 4.5, 1.3, 1.3 Hz, 1 H), 4.02 (s, 1 H), 3.99 (dd, J = 7.8, 4.8 Hz, 1 H), 3.85 (d, J = 9.4 Hz, 1 H), 3.82 (s, 3 H), 3.57 (s, 1 H), 3.36 (d, J = 5.3 Hz, 1 H), 3.35 (s, 3 H), 3.09 (dd, J = 8.2, 8.2 Hz, 1 H), 2.43−2.34 (m, 2 H), 2.12−1.96 (m, 2 H), 1.82−1.78 (m, 1 H), 1.49 (s, 3 H), 1.40 (s, 3 H), 1.33 (s, 3 H), 1.11 (s, 3 H), 1.07 (d, J = 7.0 Hz, 3 H), 1.09−1.04 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 159.3, 133.3, 129.7, 129.5, 118.2, 113.8, 108.9, 95.0, 93.0, 86.6, 85.2, 83.3, 81.8, 81.5, 73.5, 72.4, 67.2, 55.4, 55.2, 49.4, 45.8, 41.6, 41.5, 32.0, 31.60, 31.57, 28.2, 26.3, 21.2, 20.7; FAB MS m/z (M^+ + H) calcd 577.34, obsd 577.39; $[\alpha]^{20}_D$ +38.6 (*c* 0.92, $CHCl_3$). Anal. Calcd for $C_{32}H_{48}O_9$: C, 66.64; H, 8.39. Found: C, 66.37; H, 8.45.

(1*S*,2*R*,4*R*,5*S*,6*S*,7*S*,8*S*)-6,7-Epoxy-4,8-dihydroxy-5-[(4*S*)-4-[(1*R*)-1-[(*p*-methoxybenzyl)oxy]allyl]-2,2-dimethyl-1,3-dioxolan-4-yl]-2-(methoxymethoxy)-4,11,11-trimethylbicyclo[6.2.1]undecan-3-one (19). A magnetically stirred mixture of **16** (13 mg, 23 μmol) and $NaHCO_3$ (3.8 mg, 45 μmol) in CH_2Cl_2 (0.5 mL) was treated with MCPBA (16 mg, 91 μmol), stirred for 16 h prior to the introduction of triphenylphosphine (18 mg, 69 μmol), and concentrated. Chromatography of the residue (SiO_2, elution with 30% ethyl acetate in hexanes)

furnished **19** (12.8 mg, 96%) as a colorless oil: IR (film, cm^{-1}) 3397, 1716, 1613, 1515; ^1H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, J = 8.6 Hz, 2 H), 6.89 (d, J = 8.6 Hz, 2 H), 5.99−5.89 (m, 1 H), 5.44 (br d, J = 10.9 Hz, 1 H), 5.39 (d, J = 18.0 Hz, 1 H), 5.04 (d, J = 4.7 Hz, 1 H), 4.67 (d, J = 11.2 Hz, 1 H), 4.53 (d, J = 6.8 Hz, 1 H), 4.41 (d, J = 11.2 Hz, 1 H), 4.37 (d, J = 6.8 Hz, 1 H), 4.27−4.24 (br m, 1 H), 4.21 (br s, 2 H), 3.82 (s, 3 H), 3.29 (s, 3 H), 2.96 (dd, J = 11.7, 4.2 Hz, 1 H), 2.80 (d, J = 4.2 Hz, 1 H), 2.57 (d, J = 11.7 Hz, 1 H), 2.46 (ddd, J = 10.0, 4.3, 4.3 Hz, 1 H), 2.24−2.11 (m, 2 H), 1.99−1.62 (series of m, 2 H), 1.47 (s, 3 H), 1.44 (s, 2 H), 1.31 (s, 3 H), 1.27 (s, 6 H), 1.09 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 213.5, 159.6, 133.0, 132.5, 130.1, 120.3, 114.0, 109.1, 96.1, 87.8, 83.1, 81.3, 79.5, 71.9, 67.4, 60.0, 55.7, 55.2, 52.2, 47.2, 43.5, 31.6, 30.7, 29.3, 26.2, 25.4, 22.6, 20.1, 17.8, 14.1; FAB MS m/z (M^+) calcd 591.32, obsd 591.22; $[\alpha]^{19}_D$ +0.29 (c 0.35, $CHCl_3$).

(1*S*,2*S*,3*S*,4*R*,5*R*,7*R*,8*S*)-1,2-Dihydroxy-4-[(4*S*)-4-[(1*R*)-1-[(*p*-methoxybenzyl)oxy]allyl]-2,2-dimethyl-1,3-dioxolan-4-yl]-7-(methoxymethoxy)-5,11,11-trimethyl-12-oxatricyclo[6.2.1.1^{3,5}]dodecan-6-one (20). A solution of **19** (18 mg, 31 μmol) and aqueous potassium hydroxide (0.40 mL of a 3 M solution) in DMSO (4 mL) was warmed to 55 °C for 2 h, cooled, and diluted with water. Following exhaustive extraction with ethyl acetate, the organic layers were dried and concentrated to leave a crude oil that was purified by means of silica gel chromatography (30% ethyl acetate in hexanes) to give **20** as a colorless oil (10 mg, 56%); IR (film, cm^{-1}) 3467, 1712, 1615, 1516; ^1H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, J = 8.6 Hz, 2 H), 6.86 (d, J = 8.6 Hz, 2 H), 6.08 (ddd, J = 17.7, 10.5, 7.7 Hz, 1 H), 5.47 (d, J = 10.5, Hz, 1 H), 5.37 (d, J = 17.3 Hz, 1 H), 4.88 (dd, J = 5.0, 3.6 Hz, 1 H), 4.57 (d, J = 10.8 Hz, 1 H), 4.52 (d, J = 6.9 Hz, 1 H), 4.33 (d, J = 6.9 Hz, 1 H), 4.31 (d, J = 10.8 Hz, 1 H), 4.09 (d, J = 7.7 Hz, 1 H), 3.96 (dd, J = 8.4, 3.6 Hz, 1 H), 3.94 (d, J = 8.7 Hz, 1 H), 3.80 (s, 3 H), 3.65 (d, J = 5.0 Hz, 1 H), 3.64 (d, J = 3.7 Hz, 1 H), 3.60 (d, J = 8.7 Hz, 1 H), 3.31 (s, 3 H), 2.73 (s, 1 H), 2.60 (d, J = 8.4 Hz, 1 H), 2.45 (dd, J = 10.5, 3.7 Hz, 1 H), 2.32 (s, 3 H), 2.19−2.04 (m, 3 H), 1.60−1.46 (m, 1 H), 1.44 (s, 3 H), 1.42 (s, 3 H), 1.40 (s, 3 H), 1.12 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 214.3, 159.6, 134.7, 130.5, 129.3, 120.6, 113.8, 111.2, 97.0, 90.4, 86.5, 86.0, 84.2, 82.6, 76.7, 75.9, 71.5, 68.3, 56.2, 55.2, 50.8, 46.5, 40.0, 31.2, 30.7, 29.5, 28.0, 26.4, 24.6, 20.1; FAB MS m/z (M^+ + H) calcd 591.32, obsd 591.16; $[\alpha]^{21}_D$ +10.0 (c 0.89, $CHCl_3$).

(1*S*,2*R*,4*S*,5*S*,6*Z*,8*R*)-2,8-Dihydroxy-5-[(4*S*)-4-[(1*R*)-1-[(*p*-methoxybenzyl)oxy]allyl]-2,2-dimethyl-1,3-dioxolan-4-yl]-4,11,11-trimethylbicyclo[6.2.1]undec-6-en-3-one (21). A solution of **16** (57 mg, 100 μmol) and pyridinium *p*-toluenesulfonate (128 mg, 510 μmol) in *tert*-butyl alcohol (3 mL) was warmed to 80 °C, stirred for 48 h, cooled, diluted with water, and extracted with ether. The combined organic layers were dried and evaporated to leave a residue, chromatography of which on silica gel (elution with 30% ethyl acetate in hexanes) furnished **21** (36.5 mg, 70%) as a colorless oil: IR (film, cm^{-1}) 3478, 1694, 1615, 1515; ^1H NMR (300 MHz, $CDCl_3$) δ 7.22 (d, J = 8.6 Hz, 2 H), 6.86 (d, J = 8.6 Hz, 2 H), 6.13 (ddd, J = 17.2, 10.6, 6.0 Hz, 1 H), 5.54 (ddd, J = 10.6, 1.1, 1.1 Hz, 1 H), 5.47 (ddd, J = 17.2, 1.5, 1.5 Hz, 1 H), 5.47 (d, J = 12.2 Hz, 1 H), 5.41 (dd, J = 12.2 Hz, 1 H), 4.63 (d, J = 11.1 Hz, 1 H), 4.29 (d, J = 11.1 Hz, 1 H), 4.08 (d, J = 9.3 Hz, 1 H), 3.91 (d, J = 6.0 Hz, 1 H), 3.89 (d, J = 9.3 Hz, 1 H), 3.87−3.82 (m, 3 H), 3.79 (s, 3H), 2.87 (qd, J = 6.6, 6.5 Hz, 1 H), 2.72 (ddd, J = 14.3, 10.0, 4.0 Hz, 1 H), 2.62 (ddd, J = 11.7, 2.1, 2.1 Hz, 1 H), 2.39−2.30 (m, 1 H), 2.09−1.99 (m, 1 H), 1.88 (ddd, J = 13.3, 13.3, 5.9 Hz, 1 H), 1.37 (s, 3 H), 1.32 (s, 3 H), 1.25 (br s, 1 H), 1.04 (s, 3 H), 0.95 (d, J = 6.6 Hz, 3 H), 0.90 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 214.9, 159.5, 140.1, 134.6, 130.0, 129.4, 124.6, 119.2, 113.8, 109.0, 86.3, 83.8 (2 C), 83.1, 71.7, 66.7, 57.0, 55.3, 51.6, 46.2, 36.0, 35.6, 28.7, 27.1, 26.8, 24.6, 18.0, 10.9; MS m/z (M^+) calcd 514.2931, obsd 514.2903; $[\alpha]^{21}_D$ −15.4 (c 0.65, $CHCl_3$).

(1*S*,2*R*,4*S*,5*R*,6*S*,7*S*,8*S*)-6,7-Epoxy-2,8-dihydroxy-5-[(4*S*)-4-[(1*R*)-1-[(*p*-methoxybenzyl)oxy]allyl]-2,2-dimethyl-1,3-dioxolan-4-yl]-4,11,11-trimethylbicyclo[6.2.1]undecan-3-one (22). A mixture of **21** (12 mg, 23 μmol), MCPBA (16 mg, 93 μmol), and $NaHCO_3$ (3.9 mg, 47 μmol) in CH_2Cl_2 (0.75 mL) was stirred for 22 h at rt, diluted with saturated $NaHCO_3$ solution, and extracted with ether. Following the predescribed workup and chromatography (SiO_2, elution with 30% ethyl acetate in hexanes), there was isolated 9.5 mg (77%) of **22** as a colorless oil: IR (film, cm^{-1}) 3460, 1695, 1614, 1515; ^1H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, J = 8.6 Hz, 2 H), 6.87 (d, J = 8.6 Hz, 2 H), 6.05 (ddd, J = 17.2, 10.6, 5.5 Hz, 1 H), 5.45 (ddd, J = 17.2, 1.5, 1.5 Hz, 1 H), 5.43 (ddd, J = 10.6, 1.3, 1.3 Hz, 1 H), 4.59 (d, J = 11.1 Hz, 1 H), 4.36 (d, J = 11.1 Hz, 1 H), 4.16 (s, 2 H), 4.12 (br d, J = 5.5 Hz, 1 H), 3.99 (dd, J = 6.2, 4.3 Hz, 1 H), 3.80 (s, 3 H), 3.56 (d, J = 6.3 Hz, 1 H), 3.21 (dq, J = 6.4, 6.4 Hz, 1 H), 3.08 (dd, J = 11.7, 4.2 Hz, 1 H), 2.73 (dd, J = 4.1, 1.1 Hz, 1 H), 2.66 (dd, J = 11.7, 5.9 Hz, 1 H), 2.59−2.53 (m, 1 H), 2.32−2.22 (m, 1 H), 2.14−2.03 (m, 1 H), 1.95 (s, 1 H), 1.77−1.57 (series of m, 2 H), 1.48 (s, 3 H), 1.44 (s, 3 H), 1.10 (s, 3 H), 1.10 (d, J = 6.4 Hz, 3 H), 1.09 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 216.2, 159.3, 134.4, 129.7, 129.6, 118.4, 113.8, 109.4, 86.7, 83.7, 83.0, 81.8, 72.0, 67.2, 59.5, 57.5, 55.3, 54.4, 46.9, 45.7, 34.9, 30.7, 29.3, 27.3, 26.6, 22.5, 17.3, 13.2; FAB MS m/z (M^+ + H) calcd 531.30, obsd 531.37; $[\alpha]^{21}_D$ +8.9 (c 0.98, $CHCl_3$).

(1*S*,2*S*,5*S*,6*R*,7*R*,8*S*,9*S*,10*S*)-9-[(4*S*)-4-[(1*R*)-1-[(*p*-Methoxybenzyl)oxy]allyl]-2,2-dimethyl-1,3-dioxolan-4-yl]-7-(methoxymethoxy)-8,12,12-trimethyl-11-oxatetracyclo[5.3.1.1^{2,5}.0^{8,10}]-dodecane-2,6,7-triol (23). Aqueous KOH (5.5 μL of 3 M) was added to a solution of **22** (8.7 mg, 16 μmol) in DMSO (0.5 mL) and the reaction mixture was stirred for 30 min, diluted with water, and extracted with ether. The combined organic layers were dried and concentrated to leave a residue that was purified by chromatography on silica gel (elution with 40% ethyl acetate in hexanes) to give **23** as a colorless oil (8.1 mg, 93%): IR (film, cm^{-1}) 3474, 1614, 1515; ^1H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, J = 8.7 Hz, 2 H), 6.86 (d, J = 8.7 Hz, 2 H), 6.06 (ddd, J = 17.4, 10.5, 6.8 Hz, 1 H), 5.47 (d, J = 10.5 Hz, 1 H), 5.35 (d, J = 17.4 Hz, 1 H), 4.61 (d, J = 11.1 Hz, 1 H), 4.28 (d, J = 11.1 Hz, 1 H), 4.03 (br s, 1 H), 3.86 (d, J = 6.8 Hz, 1 H), 3.85 (s, 1 H), 3.80 (s, 3 H), 3.74 (d, J = 8.8 Hz, 1 H), 3.61 (d, J = 8.8 Hz, 1 H), 3.29 (s, 1 H), 2.12−2.04 (m, 1 H), 1.97 (dd, J = 9.6, 1.5 Hz, 1 H), 1.85 (d, J = 4.0 Hz, 1 H), 1.83 (d, J = 3.9 Hz, 1 H), 1.87−1.78 (m, 1 H), 1.62 (s, 1 H), 1.68−1.56 (m, 2 H), 1.51 (d, J = 3.9 Hz, 1 H), 1.47 (s, 3 H), 1.38 (s, 3 H), 1.37 (s, 3 H), 1.33 (s, 3 H), 1.05 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 159.4, 135.1, 130.0, 129.4, 119.4, 113.9, 109.0, 105.8, 87.2, 85.7, 83.7, 83.2, 82.0, 70.9, 68.6, 55.2, 52.0, 46.1, 35.7, 34.8, 29.4, 27.6, 27.02, 26.98, 26.4, 19.6, 12.0; EI MS m/z (M^+− OH) calcd 513.2852, obsd 513.2884; $[\alpha]^{21}_D$ −7.1 (c 0.72, $CHCl_3$).

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Supporting Information Available: Spectroscopic details for **11** and the hydroboration products of **20**, X-ray crystallographic details for **14b**, together with high-field ^1H and ^{13}C NMR spectra of all compounds reported herein (79 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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