Opening the [4 + 2 + 2] Cycloadducts of Bicyclo[2.2.1]hepta-2,5-dienes (Norbornadienes) to Cis-Fused Bicyclo[5.3.0]decanes[1]

Yan Chen and John K. Snyder*

Department of Chemistry, Boston University, 590 Commonwealth Avenue, Boston, Massachusetts 02215

jsnyder@chem.bu.edu

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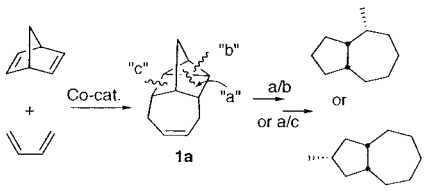
Tetracyclo[5.4.0.0.^{2,4}0^{3,7}]undec-9-enes, prepared by the transition-metal-catalyzed [4 + 2 + 2] homo-Diels−Alder reactions of norbornadiene and 1,3-butadienes, can be opened using either acid-promoted or Zeise's dimer-mediated cyclopropane ring cleavage, ultimately leading to cis-fused bicyclo[5.3.0]decanes (perhydroazulenes). Stereoselective functionalization of the olefin unit in the tetracycloundecenes to an alcohol or diol prior to ring opening is tolerated by the Zeise's dimer ($[Pt(C_2H_4)Cl_2]_2$) catalyst to yield highly functionalized bicyclo[5.3.0]decanes, which form the core structure of numerous sesquiterpenes.

The transition-metal-catalyzed [4 + 2 + 2] homo-Diels−Alder reaction of norbornadiene and substituted derivatives with 1,3-butadienes is an intriguing higher order cycloaddition with the potential to create numerous stereocenters in a single step.[2] In the previous paper, we reported the results of our studies into this cycloaddition in order to probe the regioselectivity of the reaction of 2-substituted norbornadienes as well as to optimize the catalyst. The ultimate goal of this work was to develop protocols to open the highly caged adducts to cis-fused bicyclo[5.3.0]decanes (Scheme 1), the core skeleton of numerous sesquiterpenes of biological interest.[3]

Only limited success scattered through the literature has been reported in opening the [2 + 2 + 2] cycloadducts of norbornadiene, and no reports other than our own preliminary communications[4] had dealt with the [4 + 2 + 2] adducts. Nickon had employed acidic conditions to open deltacyclane (**2**) to mixtures of brendane (**3**) and brexane (**4**) acetates with the former dominating (Figure 1, eq 1),[5] conditions which we had adopted to open other [2 + 2 + 2] adducts as well as a [4 + 2 + 2] cycloadduct.[4a] More recently, Lautens utilized an Hg(II)-promoted opening to form brendane derivatives from deltacyclanes (Figure 1, eq 2).[6] In both cases, subsequent conversion to the corresponding brendanones set the stage for the opening to the biquinanes, Nickon using Haller−Bauer chemistry,[5c,7] while Lautens followed a Baeyer−Villiger route with reductive opening of the lactone finally achieving the biquinane. Others have also reported the use of Baeyer−Villiger oxidations of brendanones to access biquinanes, though the brendanones were not prepared from deltacyclanes.[8,9] We now report the open-

Scheme 1



* To whom correspondence should be addressed. Tel: (617) 353-2621, 2575. Fax: (617) 353-6466.

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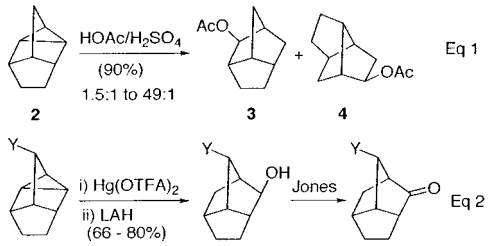
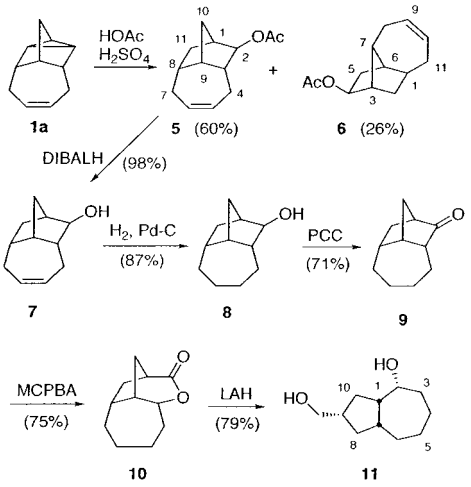


Figure 1. Nickon's acid-catalyzed opening of deltacyclane (**2**) to brendyl acetate **3** and brexyl acetate **4** (eq 1).[5] Lautens' Hg(II)-ptomoted opening of deltacyclanes to brendanes (**Eq 2**).[6]

Scheme 2

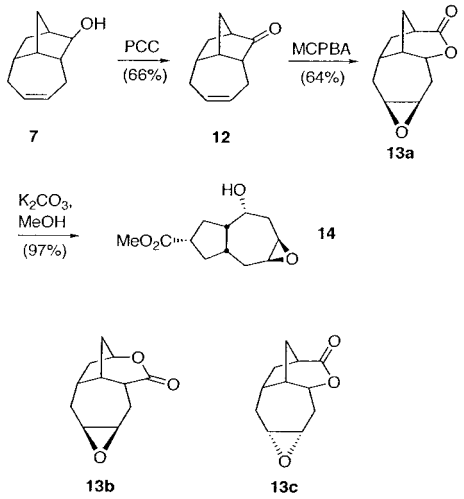


ing of [4 + 2 + 2] homo-Diels−Alder adducts of norbornadienes using either the Nickon conditions or $[Pt(C_2H_4)Cl_2]_2$ (Zeise's dimer)[4b] to yield the highly functionalized targets: cis-fused bicyclo[5.3.0]decanes.

Results and Discussion

Nickon Opening/Baeyer−Villiger Sequence to Bicyclo[5.3.0]decanes. As reported in the previous paper, the [4 + 2 + 2] adduct (**1a**) of norbornadiene and 1,3-butadiene was readily available from cobalt-catalyzed cycloadditions.[4,10] Unveiling of the bicyclo[5.3.0]decane system from **1a** was achieved by two key steps: acid-catalyzed opening of the cyclopropane ring and Baeyer−Villiger reaction of the ketone after subsequent functional group transformations. Under Nickon's conditions ([**1a**] = 0.17 M in acetic acid with 30 mol % sulfuric acid, rt), *exo*-2-tricyclo[6.2.1.0^{3,9}]undec-5-enyl acetate (**5**) with the brendane-like skeleton was obtained as the major product (60% isolated yield), accompanied by lesser amounts of the brexane-like compound *exo*-2-tricyclo[5.4.0.0^{3,7}]undec-9-enyl acetate (**6**, 26% isolated yield, Scheme 2). The ratio of these two products (**5**/**6** = 2.2:1, from ^{1}H NMR integration) remained constant during the consumption of the starting material (monitored from 2 to 17 h) and did not change after the starting material was gone with continuous monitoring of the product mixture for 189 h. Isolation and resubjection of either **5** or **6** to the reaction conditions also produced the same ratio of isomers. Thus, the equilibration of **5** and **6** is likely very rapid, and the favored brendane-like product **5** is the thermodynamically favored compound. Use of HCO_2H/H_2SO_4 to effect the acid-catalyzed opening produced the corresponding formates in an initial ratio of 4.4:1 in favor of the brendane-like product analogous to **5** (after 30 min at room temperature). Subsequent addition of formic acid across the double bonds, however, resulted in a more complex reaction mixture. Analogous addition of acetic acid across the double bonds was not observed under the Nickon conditions. The structures of **5** and **6** were established through extensive NMR experiments (see the Experimental Section).

Scheme 3



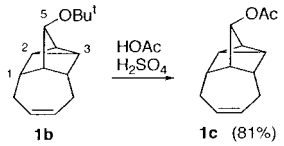
Reduction of **5** with DIBALH generated alcohol **7** (98% yield), and then the double bond was removed by hydrogenation (87%) to provide saturated alcohol **8** and thereby obviate possible complications due to diastereomeric epoxide formation during the Baeyer−Villiger oxidation (Scheme 2). Ketone **9** was obtained after PCC oxidation of **5** (71%). Then, Baeyer−Villiger reaction (*m*-CPBA−$NaHCO_3$) of **9** gave major lactone **10** in 75% isolated yield, accompanied by a very small amount of another compound, presumably the other regioisomeric lactone, detected in the ^{1}H NMR spectrum of the crude reaction mixture, though too little was obtained for characterization. Completion of the cis-fused bicyclo[5.3.0]decane system **11**, which marks the first example of the synthesis of a cis-fused 5,7-bicyclic ring skeleton from the opening of a [4 + 2 + 2] homo-Diels−Alder cycloadduct, was achieved by reduction of lactone **10** with LAH (79%).

If the double bond from the cycloaddition was left intact prior to the Baeyer−Villiger reaction, epoxidation also occurred. Thus, treatment of ketone **12**, which was prepared by PCC oxidation of alcohol **7** (66%), with *m*-CPBA−$NaHCO_3$ gave *exo*-epoxylactone **13a** as the major product in 64% isolated yield (Scheme 3, see the Experimental Section for characterization). Two other minor products, regioisomer **13b** (11%) and stereoisomer **13c** (trace), were also isolated from this reaction. Selective cleavage of the lactone by basic methanolysis gave the more functionalized cis-fused bicyclo[5.3.0]decane epoxide **14** (97%).

Similar ring opening of adducts formed from 7-*tert*-butoxynorbornadiene such as **1b** was an important goal since the *tert*-butoxy substituent was foreseen as the precursor to the oxygen functionalities in the five-membered rings of potential targets. Unfortunately, attempts to apply the Nickon acid-promoted opening to **1b** failed, leading only to replacement of the *tert*-butyl

(10) Preceding manuscript: Chen, Y.; Kiattansakul, R.; Ma, B.; Snyder, J. K. *J. Org. Chem.* **2001**, *66*, xxxx (JO010268O).

Scheme 4



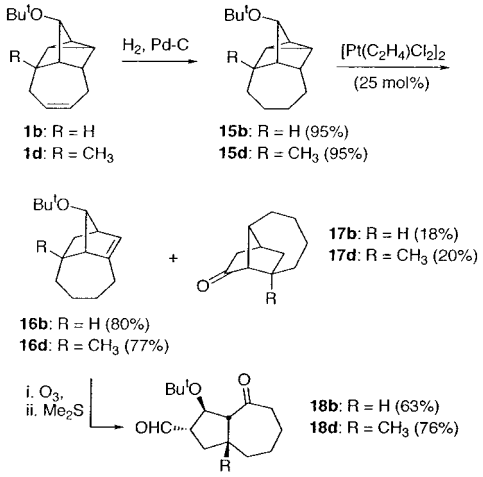
group with an acetyl group, yielding acetate **1c** (81%, Scheme 4). Presumably, the reduction in the electron density of the cyclopropane due to the presence of the oxygen at C5 either as the OBu^t or OAc group is sufficient to prevent cyclopropane protonation, thereby preventing acid-promoted opening. With this failure, we then turned to Zeise's dimer ($[(Pt(C_2H_4)Cl_2]_2$) to effect the cyclopropane cleavage of **1b**.

Zeise's Dimer/Ozonolysis Sequence to Bicyclodecanes. It is well-known that cyclopropanes upon treatment with stoichiometric Zeise's dimer ($[Pt(C_2H_4)Cl_2]_2$) form platina(IV)cyclobutanes via platinum insertion into the cyclopropane ring, and that subsequent ring opening may occur by rearrangement and reductive elimination to produce alkenes following heating or the addition of other ligands.[11] Treatment of **1b**, bearing both the double bond and a cyclopropane ring with Zeise's dimer in diethyl ether at room temperature, gave a platinum-containing compound as a white solid. Preliminary study of this compound indicated it to be Pt-dimer consisting of a chlorine-containing organic ligand derived from **1b**, though confirmation of this structure awaits the growth of crystals suitable for X-ray analysis.

Since it is known that the ethylene in Zeise's dimer can be readily replaced by higher boiling olefins to form stable complexes,[11,12] the assumption was that the alkene subunit in **1b** was the cause of the complicity in the reaction with Zeise's dimer. Therefore, the double bond in **1b** was removed via hydrogenation (95%) to give **15b** and the Zeise's dimer opening reexamined (Scheme 5). A new olefin **16b**, free of Pt, was isolated in 83% yield after treatment of **15b** with Zeise's dimer (50 mol %) in diethyl ether, along with lesser amounts of regioisomer **17b** with the brexane-like structure. Cis-fused bicyclo[5.3.0]decane **18b** with defined stereochemistry (63% yield) was then made from **16b** uneventfully by ozonolysis. The amount of Zeise's dimer could be reduced without compromising the yield of **16b**, though the reaction time increased significantly from 9 h (50 mol %) to 70 h (10 mol %). These longer reaction times, however, led to somewhat capricious results as precipitation of platinum-black from the reaction mixture frequently occurred, indicating the loss of active catalyst. Using 25 mol % Zeise's dimer, an 80% yield of **16b** was obtained, along with 18% **17b** in 21 h. The use of *n*-Bu_2O was comparable to Et_2O, but other solvents (THF, CH_2Cl_2) were not as effective.

Following the same procedure, another *tert*-butoxy-substituted cycloadduct **1d**[10] was hydrogenated, giving

Scheme 5



15d (95%). Treatment of **15d** with 50 mol % of Zeise's dimer in $CDCl_3$ led to alkene **16d** in 79% yield (rt, 8 h). The use of 25 mol % of Zeise's dimer gave 77% yield, along with regioisomer **17d** in 20% yield, within an extended, though still reasonable, time frame (25 h, rt, Scheme 5). The use of $CDCl_3$ for the optimal conversion from **15d** to **16d** was important since one major unidentified byproduct that derived from **16d** was obtained upon running the reaction in diethyl ether, and the reactions were not as clean when run in $CHCl_3$ or CH_2Cl_2, although **16d** was formed in these latter cases in lower yields. The use of $CDCl_3$ as the solvent in Zeise's dimer and other transition-metal-promoted cyclopropane opening has been previously noted.[13] Ozonolysis of **16d** gave pseudoguaianolide core skeleton **18d** with the methyl group at the ring fusion center in 76% yield.

The exclusive formation of regioisomers **16**, with the newly formed double bond anti to the *tert*-butoxyl group, was thought to arise via a Pt-insertion into the cyclopropane to form platinacyclobutane **A** (Scheme 6, path A). Rearrangement would then lead to Pt-stabilized anti-Bredt 1-norbornene intermediate **B**, with subsequent migration of the platinum to the "top" face (**C**) regiochemically controlled by the blockage of the other top face by the bulky *tert*-butoxy group. Double-bond migration mediated by the Pt-catalyst to the more stable bridgehead olefin **D** followed by Pt-elimination gives **16** with regeneration of the Pt-catalyst for further cyclopropane insertion. Transient 1-norbornene intermediates have been reported previously, though only indirectly detected,[14] and highly strained anti-Bredt olefins are known to be stabilized by transition-metal coordination,[15] as proposed here. The product bridgehead olefins **16** with the trans alkene configuration lying within a nine-membered ring is predicted to be stable by Wiseman's rules.[16]

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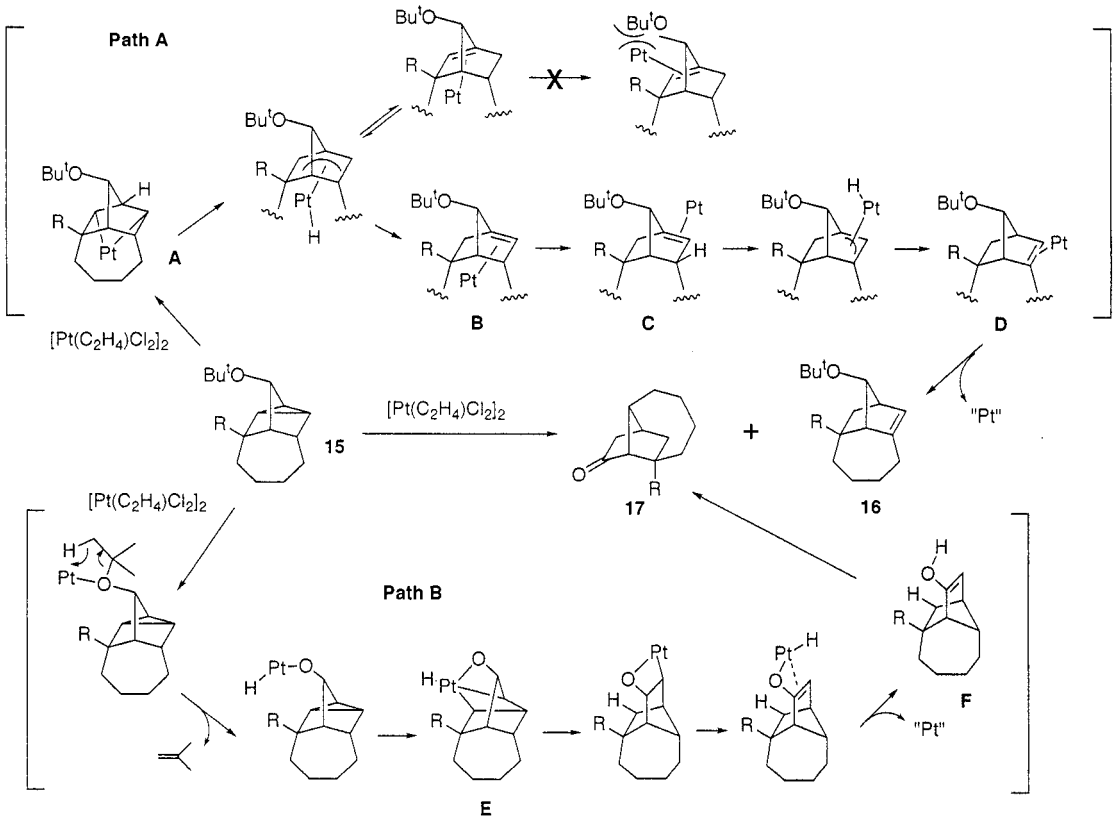
Scheme 6



From the Zeise's dimer reactions of **15b** and **15d**, minor side products, ketones **17b** and **17d**, respectively, resulting from the loss of the *tert*-butyl group and cleavage of a cyclopropane "top" bond located on the same side as the original *tert*-butoxyl group, were isolated. Presumably, after the loss of 2-methylpropene from the *tert*-butyl group mediated by Pt, the oxygen atom, by coordinating to Pt, directs the Pt-insertion into the cyclopropane ring causing the cleavage of a "top" bond of cyclopropane on the same side as the original *tert*-butoxyl group, forming intermediate platinacyclobutane **E** (Scheme 6, path B). A Pt-mediated hydride shift leads to enol **F**, with tautomerization generating **17b** and **17d** as single regioisomers.

An alternative regioisomer to **17d** is **19**, the product that results from cyclopropane ring cleavage at the "top" bond of the cyclopropane opposite to the *tert*-butoxyl group (Figure 2). Confirmation of the structure **17d** was achieved by the DNOE experiments. Irradiation of methyl group in **17d** induced significant enhancements of

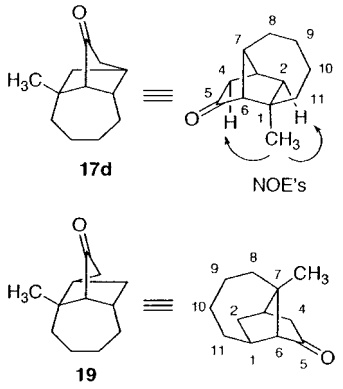


Figure 2. NOE distinction of ketone **17d** from its regioisomeric alternative **19**.

three well-resolved protons, of which one was a methine proton while the other two belonged to two different isolated methylene pairs (i.e., they were not part of the four coupled methylene pairs H8−H11) as determined by the scalar coupling systems delineated through ^{1}H,^{1}H-COSY and HMQC experiments. Of the two regioisomers **17d** and **19**, **19** was excluded since irradiation of methyl group in **19** could not cause an enhancement of an H2 proton, which is one of the isolated methylene pairs in the molecule. In **17d**, both $H2_{endo}$ and $H4_{endo}$ were within the NOE distance (2.45 Å for H2 and 3.11 Å for H4, from CS Chem3D Pro modeling).

Since the formation of ketone byproducts **17b** and **17d** from the Zeise's dimer opening of **1b** and **1d**, respectively, was thought to arise from the Pt-promoted loss of isobutylene, the absence of a β-hydrogen on the oxygen protecting group should prevent these byproducts from forming. To test this, cycloadduct **1e**[10] was hydrogenated (99%, Scheme 7) and then subjected to Zeise's dimer

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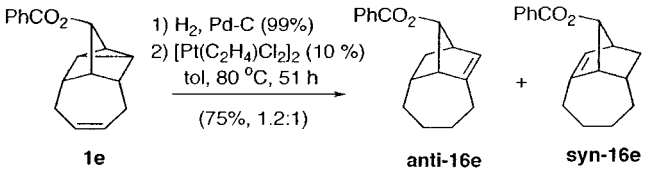
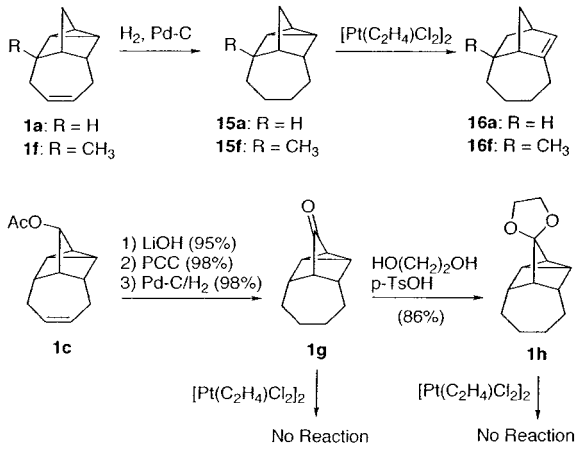
Scheme 7



Scheme 8



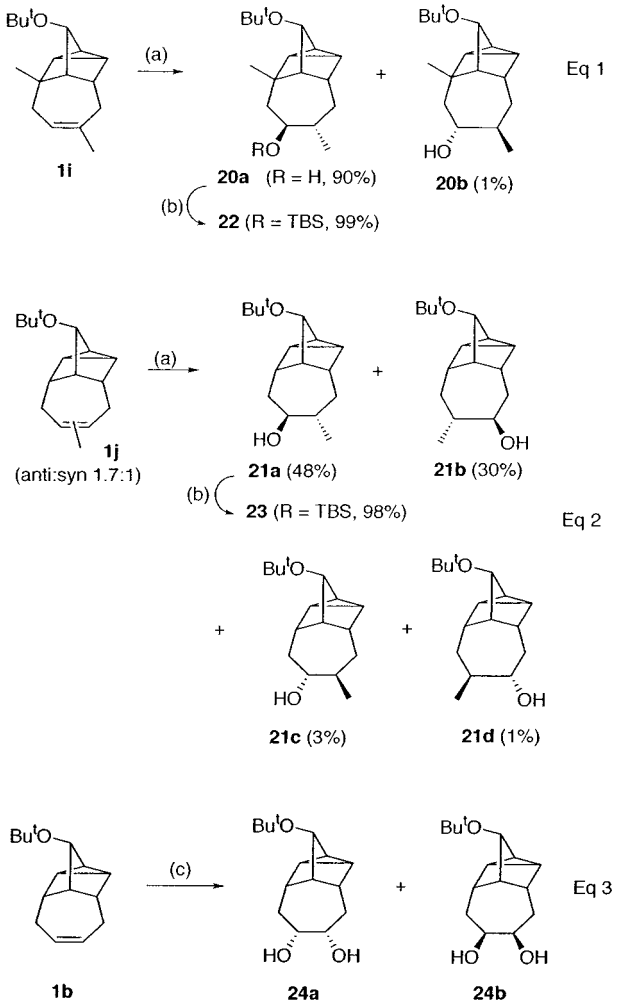
opening (10 mol %, 80 °C in tol, 51 h) to produce an inseparable mixture of stereoisomers *anti*-**16e** and *syn*-**16e** (75%, 1.2:1), which were distinguished from NOE studies (see the Experimental Section).[17] The nearly equal mixture of diastereomers indicated that the benzoyl group is not as effective as the *tert*-butyl group in blocking the top face of the cyclopropane. However, the absence of any detectable ketone products analogous to **17b** and **17d** also suggested that the benzoyl group was not directing the platinum to the alternative pathway either.

The platinum-catalyzed opening of the [4 + 2 + 2] cycloadducts without a *tert*-butoxyl group, hydrogenation products **15a** and **15f** prepared by hydrogenation of cycloadducts **1a** and **1f**, respectively, were unsuccessful, resulting in complicated product mixtures (Scheme 8). The expected olefinic products were detected in both reactions from ^{1}H NMR spectra of the crude product mixtures, which showed the characteristic olefin signal around δ 5.5 as broad singlets. Small amounts of the cyclopropane ring-opened product from **15f** was isolated from the reaction mixture by gas chromatography and was tentatively assigned as **16f** (Scheme 8). The attempted purification of an olefin product from the reaction of **15a** by gas chromatography was unsuccessful. In addition, treatment of ketone **1g** and **1h** with Zeise's dimer were also unsuccessful, returning only unreacted starting materials.

To take full advantage of the functionality present in the original [4 + 2 + 2] cycloadducts, efforts were made to use the double bond for further functionalization. The synthesis of bicyclo[5.3.0]decane **14** (Scheme 3) was quite successful with the conversion of the double bond in the original cycloadduct **1a** to an epoxide which was preserved in the final product. Having more functional groups in the tetracyclo[5.4.0.0.^{2,4}0^{3,7}]undecanes prior to the Zeise's dimer catalyzed cyclopropane opening not only would install essential functionalities required for later

(17) The production of *anti*-**16e** and *syn*-**16e** is an example of different regiochemical pathways producing diastereomers.

Scheme 9[a]



[a] Key: (a) BH_3·THF; Then H_2O_2, NaOH; (b) TBSCl, Im, DMF; (c) OsO_4 or $KMnO_4$ (see Table 1).

synthetic targets, but also would test the applicability of this Zeise's dimer chemistry on a greater variety of substrates. Two specific olefin transformations were examined: hydroboration and dihydroxylation.

Lauten's group has reported that hydroboration/oxidation of the double bond in [4 + 2 + 2] cycloadducts prepared from norbornadiene and 2-substituted 1,3-butadienes gave single stereoisomers: *exo*-alcohols.[18] This chemistry was applied to the 5-*tert*-butoxyl [4 + 2 + 2] cycloadduct **1i** to functionalize the seven-membered ring and simultaneously remove the interfering double bond prior to Zeise's dimer treatment. Hydroboration of cycloadduct **1i** (BH_3·THF, 0 °C, 20 min.), followed by oxidation (H_2O_2−NaOH, rt, 20 min), gave *exo*-alcohol **20a** in 90% isolated yield, accompanied by 1% of *endo*-alcohol **20b** (Scheme 9, eq 1). Similarly, the hydroboration of the inseparable stereoisomeric cycloadducts *anti*-**1j** and *syn*-**1j** (1.7:1)[10] gave four isomers **21a**−**d** (83% combined yield) with the *exo*-alcohols dominant (Scheme 9, eq 2). The major alcohol **21a** (48%) was easily isolated by flash chromatography. Both **20a** and **21a** were subsequently protected as their TBS ethers **22** and **23**, respectively.

(18) (a) Lautens, M.; Tam, W.; Sood, C. *J. Org. Chem.* **1993**, *58*, 4513−4515. (b) Lautens, M.; Tam, W.; Lautens, J. C.; Edwards, L. G.; Crudden, C. M.; Smith, A. C. *J. Am. Chem. Soc.* **1995**, *117*, 6863−6879.

Table 1. Dihydroxylations of Cycloadduct 1b

item	reagents	solvent	*T* (°C)	time (h)	% yield[a] (**24a**:**24b**)[b]	% yield **1b**[c]
1	OsO_4 (5%)/NMO (1.3 equiv)	*t*-BuOH/H_2O (1:1)	rt	21	89 (6.2:1)	0
2	OsO_4 (5%)/NMO (1.3 equiv)	*t*-BuOH/H_2O (1:1)	90	7	91 (5.6:1)	0
3	OsO_4 (5%)/NMO (1.3 equiv)	*t*-BuOH/H_2O (1:1)	0	48	56 (4.9:1)	22
4	OsO_4 (1%)/NMO (1.2 equiv)	acetone/H_2O (1:1)	rt	22	27 (3.0:1)	57
5	$KMnO_4$ (1 equiv) + $BnNEt_3Cl$ (1.5 equiv)	CH_2Cl_2	0	4	33 (1:2)	37
6	OsO_4 (1.1 equiv)	CH_2Cl_2	rt	48	14 (5.0:1)	66
7	OsO_4 (1.1 equiv)	THF	rt	45	39 (4.3:1)	37

[a] Combined isolated yields of **24a** + **24b**. [b] The ratio was obtained from ^{1}H NMR integration of crude product mixtures. [c] Recovered starting material.

In contrast to the hydroboration stereoselectivity, catalytic dihydroxylation with OsO_4 of **1b** gave a separable mixture of *endo*- and *exo*-diols **24a** and **24b**, surprisingly with the *endo*-diol dominant under a variety of conditions (Scheme 9, eq 3, Table 1). The optimized conditions for the production of **24a** (aqueous *t*-BuOH, rt, Table 1, entry 1) gave an endo/exo ratio of 6.2:1 in 89% combined yield, with temperature variations having little effect on the endo/exo ratio (Table 1, entries 1−3).[19] The reaction was noticeably more sluggish in aqueous acetone with a reduced amount of OsO_4 (1 mol %, Table 1, entry 4) in comparison to aqueous *t*-BuOH. Even more striking, the dihydroxylation of **1b** with $KMnO_4$[20] in the presence of the phase transfer reagent benzyltriethylammonium chloride in dry CH_2Cl_2[21] (Table 1, entry 5) produced *exo*-diol **24b** as the major product (endo/exo 1:2) although the reaction yield was relatively low (33%) and was accompanied by considerable unreacted starting material **1b** (37%). To mimic the permanganate conditions, OsO_4 dihydroxylation was repeated under stoichiometric conditions in both CH_2Cl_2 and THF (the solvent used in the hydroborations) without the addition of an accelerating nitrogen base (Table 1, entries 6 and 7).[22] While very slow, in both cases, predominance of the *endo*-diol **24a** was still observed (4.3:1 in THF, 5:1 in CH_2Cl_2).

The reason for the contrast in the facial selectivity in the dihydroxylation of **1b** using OsO_4 and $KMnO_4$, as well as in the comparison of the facial selectivity in the hydroboration and dihydroxylation, is not clear. Reversals in the facial selectivity of hydroboration in comparison to dihydroxylation of the same substrate have been previously noted.[23] Two different conformations are conceivable for **1b** (**1b-A** and **1b-B**, Figure 3) which expose either the exo (**1b-A**) or endo (**1b-B**) face. Simple calculations (Maestro with Amber* force field) indicate that **1b-A** is more stable by 2.6 kcal/mol both in the absence of solvent and in $CHCl_3$. The ^{1}H NMR analysis of **1b** is non-first order, but that of **1a**, which lacks the *tert*-butoxyl group, presents a simpler spectrum for easy interpretation due to symmetry. In a DNOE study of **1a**, one set of allylic protons (δ 2.24, H8/11) caused an enhancement of the "backside" proton H2/3 resonance upon saturation, while an NOE was also observed between H6 and the H8/11 exo protons, thereby indicating that both conformations are populated in **1a**. Since the remote *tert*-butoxyl group in cycloadduct **1b** should have little effect on the conformation of the seven-membered ring, analogous conformations should also exist in **1b**, thereby accounting for the exposure of the endo face to dihydroxylation. Nevertheless, the distinction in the stereoselectivities of the hydroborations and permanganate dihydroxylation with that of the OsO_4 dihydroxylation is difficult to explain at this point, with the modeling calculations correctly predicting the observed stereoselectivity of the hydroboration, but not the dihydroxylation.

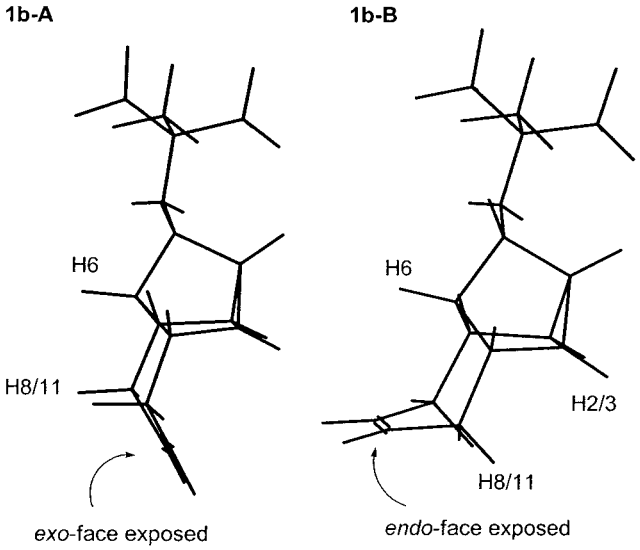


Figure 3. Two most stable conformations of cycloadduct **1b**.

With the functionalized 5-*tert*-butoxycycloadducts **20**−**24** in hand, Zeise's dimer opening of the cyclopropane was then examined. Initially, it was thought that the alcohols would have to be protected prior to Zeise's dimer opening in order to prevent interferring complexation with the platinum. The treatment of silyl ethers **22** or **23** with Zeise's dimer (25 mol % of Zeise's dimer, in $CDCl_3$, rt) gave the expected ring-opened products **25b** (64%) and **27b** (37%), respectively, accompanied by the rearranged ketone byproducts **26b** (31%) and **28b** (36%), respectively (Scheme 10). Surprisingly, treatment of the unprotected alcohol **21a** with Zeise's dimer (25 mol %) in $CDCl_3$ also gave desired ring-opened product **27a** accompanied by ketone byproduct **28a** (**27a**/**28a**, 2.5:1) in a preliminary experiment. Optimization for the production of **27a** (64%) was achieved with 10 mol % Zeise's dimer in toluene (80

(19) For reviews discussing reaction conditions for catalytic OsO_4 dihydroxylation conditions: (a) Kolb, H. C.; Van Nieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483−2547. (b) Beller, M.; Sharpless, K. B. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: Weinheim, Germany, 1996; Vol. 2, pp 1009−1024.

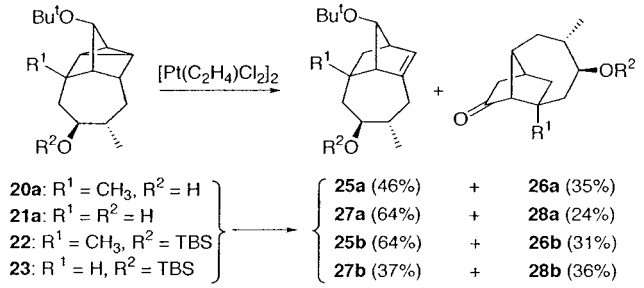
(20) (a) Fatiadi, A. J. *Synthesis* **1987**, 85−127 and references therein. (b) Houk, K. N.; Strassner, T. *J. Org. Chem.* **1999**, *64*, 800−802. (c) Strassner, Th.; Busold, M. *J. Org. Chem.* **2001**, *66*, 672−676.

(21) (a) Ogino, T.; Mochizuki, K. *Chem. Lett.* **1979**, 443−446. (b) Ogino, T. *Tetrahedron Lett.* **1980**, *21*, 177−180.

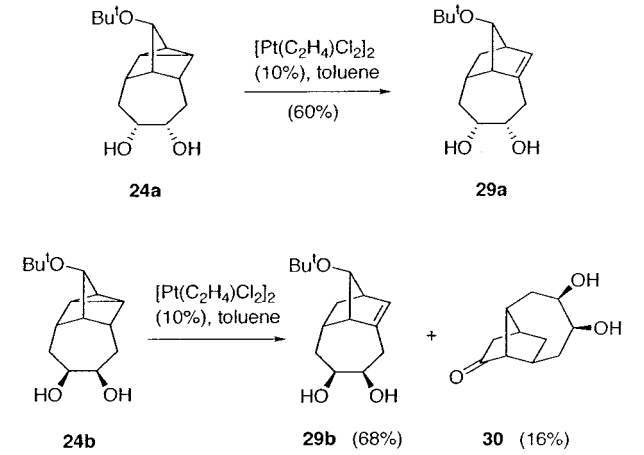
(22) (a) Schroeder, M. *Chem. Rev.* **1980**, *80*, 187−213. (b) Berrisford, D. J.; Bolm, C.; Sharpless, K. B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1059−1070.

(23) (a) Hanson, J. R.; Hitchcock, P. B.; Reese, P. B.; Truneh, A. *J. Chem. Soc., Perkins Trans. 1* **1988**, 1465−1468. (b) Vedejs, E.; Kruger, A. W. *J. Org. Chem.* **1999**, *64*, 4790−4797.

Scheme 10



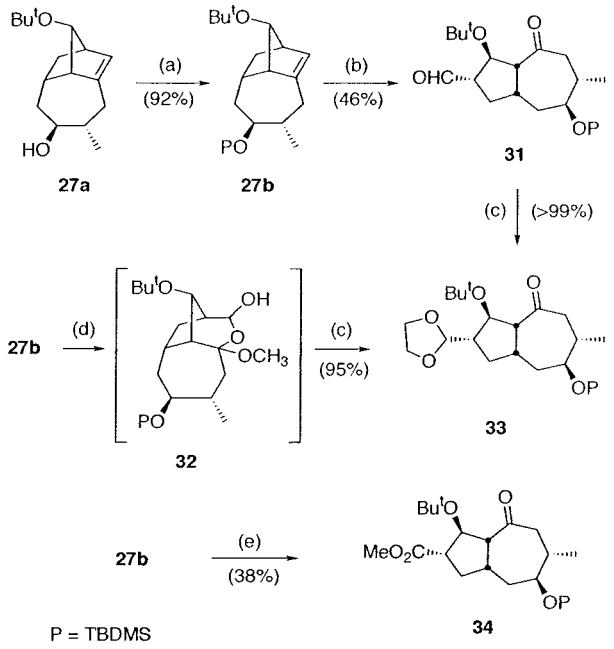
Scheme 11



°C, 19 h) with **28a** (24%) and unreacted **21a** (6%) also recovered. Higher temperature (refluxing toluene) did not accelerate the reaction as the precipitation of platinum black became noticeable. In ethereal solvents (THF, Et_2O, and *n*-Bu_2O) the reaction was considerably slower. Reduction of Zeise's dimer to 5 mol % left considerable amounts of starting material **21a** even after 48 h. However, application of these optimized conditions to **20a** indicated a faster reaction and the catalyst load could be reduced to 5 mol %, giving **25a** (46%) and **26a** (35%). Using Zeise's dimer, the cyclopropane opening of unprotected diols **24a** and **24b** generated desired alkenes **29a** (60%) and **29b** (68%), respectively (Scheme 11). The ketone byproduct **30** (16%) was also isolated from the reaction of **24b**, but in the reaction of **24a**, no analogous ketone was detected.

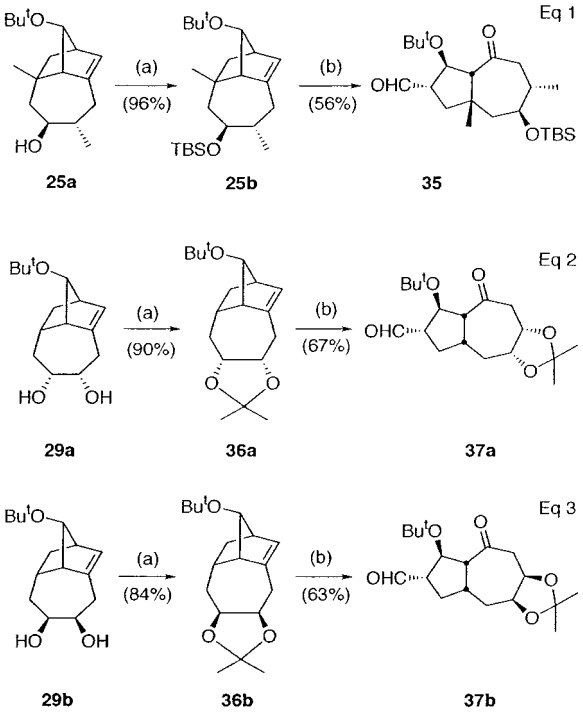
With the functionalized tricyclic olefins (**25**, **27**, and **29**) in hand, attention then turned to the final olefin cleavage via ozonolysis to complete the bicyclo[5.3.0]-decane formation, initially focusing on **27b** obtained directly from the Zeise's dimer opening of **23**, or from protection of **27a** (Scheme 12). Ozonolysis of alkene **27a** with the free hydroxyl group, did generate a bicyclic product as indicated by the ^1H NMR spectrum of the crude product mixture, but surprisingly, it was unstable to silica gel or alumina chromatography and was never obtained in pure form. Ozonolysis of **27b** in CH_2Cl_2 followed by Me_2S workup produced aldehyde **31** in only 46% yield. In CH_3OH, **32** was produced, which was stable to flash chromatography on silica gel but did not have a very long shelf life. Opening of **32** under acidic conditions with in situ trapping with ethylene glycol, gave cis-fused bicyclo[5.3.0]decane **33** (95% yield from **27b**), which could also be obtained from **32**. The ozonolysis of **27b** in basic medium (NaOH−MeOH) gave ring-opened ester **34** in 38% yield with no epimerization of the carbons adjacent

Scheme 12[a]



[a] Key: (a) TBDMSCl, Im, DMF; (b) (i) O_3,CH_2Cl_2; (ii) Me_2S; (c) $(CH_2OH)_2$, $CH(OCH_3)_3$, *p*-TsOH; (d) (i) O_3,CH_3OH (ii) Me_2S; (e) O_3, NaOH−MeOH, CH_2Cl_2.

Scheme 13[a]



[a] Key: TBDMSCl, Im, DMF; (b) (i) O_3, CH_2Cl_2, (ii) Me_2S; (c) $(CH_3O)_2C(CH_3)_2$, *p*-TsOH.

to the carbonyl groups based on the NOE studies (see the Experimental Section).

Using these protocols, the protected alcohol **25b** gave bicyclo[5.3.0]decane **35** in 56% yield after ozonolysis in CH_2Cl_2 (Scheme 13, eq 1). An attempt to use MeOH instead of CH_2Cl_2 in the ozonolysis of **25b**, by adapting the procedure applied to **27b**, was unsuccessful; the reaction generated a complex product mixture. Protection of diols **29a** and **29b** with 2,2-dimethoxypropane in the

presence of *p*-toluenesulfonic acid (*p*-TsOH) gave ketals **36a** (90%) and **36b** (84%), respectively (Scheme 13, eqs 2 and 3). Ozonolysis of **36a** and **36b** provided the highly oxygenated bicyclo[5.3.0]decanes **37a** (67%) and **37b** (63%), respectively. The protection of the diols prior to the ozonolysis also was necessary, since the treatment of unprotected *exo*-diol **29b** with ozone gave a messy reaction.

Conclusions

The successful utilization of Zeise's dimer in opening the cyclopropane ring of highly substituted [4 + 2 + 2] homo Diels−Alder cycloadducts of norbornadiene will hopefully lead the way to the synthesis of cis-fused bicyclo[5.3.0]decane natural products as found in guaianolides and pseudoguaianolides, research that is ongoing.

Experimental Section

General Methods. ^{1}H NMR and ^{13}C NMR spectra data were recorded at 93.94 kG (^{1}H 400 MHz), 70.5 kG (^{1}H 300 MHz, ^{13}C 75 MHz) or 63.41 kG (^{13}C 67.5 MHz) at ambient temperature in $CDCl_3$. Proton chemical shifts (in ppm) are referenced to the residual $CHCl_3$ resonance: δ 7.24. For ^{13}C NMR, the center line of the $CDCl_3$ triplet was used as the internal reference: δ 77.0. Unless otherwise noted, each carbon resonance represents a single carbon (relative intensity); carbon resonances of more than a single carbon in relative intensity were established from integration under inverse gated decoupled conditions (delay between transients of 10 s). Where given, ^{1}H and ^{13}C assignments were made on the basis of extensive 1D (DNOE, APT) and 2D (^{1}H,^{1}H-COSY, ^{1}H,^{13}C-COSY, NOESY, HMQC, HMBC) techniques. All O*H* protons were confirmed by D_2O exchange. Mass spectra (HRMS) were recorded in either CI (140 eV) or EI (70 eV) mode as noted. Infrared spectra were recorded on NaCl plates; solid samples were prepared by depositing a solution of the sample (typically in $CDCl_3$) on the plate and allowing the solvent to evaporate prior to recording the spectra.

All reaction solvents were dried and distilled immediately prior to use (toluene, Et_2O, and THF with sodium, $ClCH_2CH_2Cl$ and CH_2Cl_2 with CaH_2);[24] chromatography solvents were distilled prior to use. Commercially available reagents were used without further purification. All reactions were carried out in oven-dried (105 °C) glassware. Dry ice−acetone baths were used to maintain reactions at −78 °C, dry ice−50% aqueous acetone baths maintain temperatures of −30 °C. Flash chromatography was performed using silica gel-60 (43−60 μm); TLC was performed on silica gel plates, and visualization was accomplished with ammonium molybdate stain: ammonium molybdate (4 g)/H_2O (60 mL)/H_2SO_4 (4 mL). Workup of many reactions began as noted by passing the reaction mixture through a "silica gel plug"; this refers to vacuum filtration through a pad of silica gel approximately 2 cm in height, typically on a Hirsch funnel. For the preparation of **1e** and **1j**, see the previous paper in this issue.[10] For the preparation of **1c**, **16c**, **15a**, **15f**, **16f**, **1g**, and **1h**, see the Supporting Information. For the preparation and structure assignments of **1a**, **1b**, **1d**, **1f**, **1i**, **15b**, **16b**, and **18b**, see the Supporting Information of our previous communication.[4b] Molecular modeling calculations were performed using Maestro with the Amber* force field.

***exo*-2-Tricyclo[6.2.1.0^{3,9}]undec-5-enyl acetate (5) and *exo*-4-Tricyclo[5.4.0.0^{3,7}]undec-9-enyl acetate (6).** A solution of **1a** (49.9 mg, 0.3 mmol) in HOAc/H_2SO_4 (2.1 mL, H_2SO_4/HOAc 0.50 g/100 mL)[5c] was stirred at room temperature for 17 h. The reaction was quenched by the addition of aqueous Na_2CO_3 (saturated) solution until neutral to pH paper, and the mixture was then extracted with EtOAc (3 × 10 mL). The combined organic extracts were dried ($MgSO_4$), and the crude product obtained by evaporating the solvent in vacuo was purified by flash chromatography (hexanes/EtOAc, 20:1) to give **5** (R_f = 0.47, 42.2 mg, 60%) and **6** (R_f = 0.41, 18.2 mg, 26%) as colorless liquids (**5**/**6** = 2.2:1, from ^{1}H NMR integration of the crude product mixture). **5**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (ddd, J = 12.4, 6.4, 2.4 Hz, $H11_{endo}$), 1.20 (dd, J = 9.6, 1.2 Hz, *H*10), 1.50 (dd, J = 9.6, 1.6 Hz, *H*10′), 1.56 (ddd, J = 12.4, 12.4, 5.6 Hz, $H11_{exo}$), 1.91−1.98 (m, 2H, *H*1/3), 1.95 (s, 3H, CH_3), 2.04 (br s, *H*9), 2.11−2.30 (m, 4H, *H*8/4/7/7′), 2.41 (ddd, J = 15.2, 8.8, 6.0 Hz, *H*4′), 4.29 (dd, J = 2.8, 1.2 Hz, *H*2), 5.59−5.66 (m, *H*6), 5.71−5.78 (m, *H*5); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 21.4 (*C*H$_3$), 27.3 (*C*4), 28.1 (*C*11), 28.8 (*C*7), 33.9 (*C*1), 38.7 (*C*10), 43.2 (*C*8), 45.3 (*C*3), 48.0 (*C*9), 79.9 (*C*2), 129.9 (*C*6), 130.0 (*C*5), 171.0 (*C*OOCH$_3$); IR (NaCl) 1735 cm^{-1}; HRMS (EI, 70 eV) *m*/*z* 206.1294 ([M]$^+$, 0.4), calcd for $C_{13}H_{18}O_2$ 206.1307. The stereochemistry of C2 was confirmed after conversion to alcohol **7** (see characterization of **7**). **6**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (ddd, J = 12.8, 8.5, 1.0 Hz, $H2_{endo}$), 1.47 (ddd, J = 13.5, 3.6, 3.6 Hz, $H5_{exo}$), 1.63 (ddd, J = 12.8, 4.8, 4.8 Hz, $H2_{exo}$), 1.75−1.78 (m, *H*1), 1.80 (dd, J = 13.5, 7.3 Hz, $H5_{endo}$), 1.98 (s, 3H, CH_3), 2.03−2.14 (m, 4H, *H*3/6/7/11*), 2.22−2.42 (m, 3H, *H*11′*/8*/8′*), 4.52 (dd, J = 7.5, 3.0 Hz, *H*4), 5.22−5.26 (m, *H*9**), 5.42−5.47 (m, *H*10**); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 21.3, 28.4, 29.5, 34.9, 39.3, 41.6, 43.6, 44.2, 48.1, 77.4, 124.5, 128.7, 170.8; IR (NaCl) 1734 cm^{-1}; HRMS (EI, 70 eV) *m*/*z* 206.1306 ([M]$^+$, 0.4), calcd for $C_{13}H_{18}O_2$ 206.1307. The relative stereochemistry of C4 was confirmed by a DNOE experiment: H4 → $H5_{endo}$, $H2_{endo}$ and H3.

***exo*-Tricyclo[6.2.1.0^{3,9}]undec-5-en-2-ol (7).** To a solution of **5** (196.3 mg, 0.95 mmol) in THF (1.9 mL) at −78 °C was slowly added DIBAL (1.0 M in THF, 2.4 mL) with stirring. After 2 h, the reaction was quenched by the sequential addition of MeOH (1 mL) at −78 °C and 10% aqueous HCl (1 mL) at 0 °C, and the reaction mixture was allowed to warm to room temperature. Water (10 mL) was added, and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic extracts were dried ($MgSO_4$), and the solvent was evaporated in vacuo. Flash chromatography (hexanes/EtOAc, 2:1) of the crude product gave **7** (R_f = 0.7, 155.1 mg, 98%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 (ddd, J = 12.5, 5.8, 2.4 Hz, $H11_{endo}$), 1.21 (dd, J = 9.8, 1.2 Hz, *H*10), 1.45 (br s, O*H*), 1.53 (dd, J = 12.5, 5.2 Hz, H_{exo}), 1.58 (dd, J = 9.8, 2.7 Hz, *H*10′), 1.78−1.79 (br s, *H*3), 1.91−1.97 (m, *H*9), 2.04−2.05 (m, 2H, *H*1/8), 2.16 (ddd, J = 15.2, 8.8, 6.8 Hz, *H*7), 2.24−2.32 (m, 2H, *H*4/7′), 2.44 (ddd, J = 15.4, 8.8, 6.2 Hz, *H*4′), 3.41 (dd, J = 3.40, 1.8 Hz, *H*2), 5.59−5.64 (m, *H*6), 5.67−5.73 (m, *H*5); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 27.4 (*C*4), 28.4 (*C*11), 29.0 (*C*7), 33.8 (*C*8), 38.3 (*C*10), 46.1 (*C*1*), 48.0 (*C*9*), 48.4 (*C*3), 77.4 (*C*2), 129.89 (*C*6), 129.91(*C*5); IR (NaCl) 3287 cm^{-1}; HRMS (EI, 70 eV) *m*/*z* 164.1170 ([M]$^+$, 7.8), calcd for $C_{11}H_{16}O$ 164.1201. The relative stereochemistry of C2 was confirmed by a DNOE experiment: H2 → $H11_{endo}$, as well as H2 → H3 and H1.

***exo*-Tricyclo[6.2.1.0^{3,9}]undecan-2-ol (8).** A mixture of alcohol **7** (79.9 mg, 0.5 mmol) and Pd−C (10% Pd on C, 5.1 mg, 1 mol %) in THF (2 mL) was kept under an H_2 atmosphere (1 atm, balloon) at room temperature for 5 h with stirring. After removal of the catalyst by passing the reaction mixture through a silica gel plug eluting with CH_2Cl_2 (3 × 5 mL), the solution was concentrated in vacuo and the product purified by flash chromatography (hexanes/EtOAc, 2:1) to give **8** (R_f = 0.7, 70.4 mg, 87%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.72 (ddd, J = 12.1, 6.1, 2.4 Hz, 1H), 1.24 (dddd, J = 9.6, 2.0, 2.0, 2.0 Hz, 1H), 1.41−1.57 (m, 5H), 1.58 (dddd, J = 9.6, 2.0, 2.0, 2.0 Hz, 1H), 1.64−1.73 (m, 3H), 1.79, (dd, J = 12.1, 5.4 Hz, 1H), 1.78−1.88 (m, 2H), 2.01−2.06 (m, 2H), 2.18 (br s, 1H), 3.42 (br s, 1H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 23.9, 24.8, 28.5, 30.3, 33.3, 37.9, 38.1, 43.7, 45.3, 52.4, 82.5; IR (NaCl) 3313 cm^{-1}; HRMS (EI, 70 eV) *m*/*z* 166.1340 ([M]$^+$, 1.4), calcd for $C_{11}H_{18}O$ 166.1358.

Tricyclo[6.2.1.0^{3,9}]undecan-2-one (9). A mixture of **8** (98.4 mg, 0.6 mmol) and PCC (191.7 mg, 0.9 mmol) in CH_2Cl_2 (5 mL) was stirred under Ar at room temperature for 1.5 h. After

(24) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: New York, 1980.

the brownish reaction mixture was passed through a silica gel plug eluting with CH_2Cl_2 (3 × 5 mL), the clear solution was collected and most of the solvent evaporated in vacuo. Purification by flash chromatography (hexanes/EtOAc, 3:1), gave **9** (R_f = 0.8, 69.0 mg, 71%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (ddd, J = 12.8, 6.0, 1.6 Hz, 1H), 1.19−1.29 (m, 1H), 1.32−1.43 (m, 1H), 1.48−1.54 (m, 1H), 1.59−1.75 (m, 6H), 1.98−2.07 (m, 2H), 2.24−2.28 (m, 1H), 2.38−2.44 (m, 1H), 2.65−2.66 (m, 2H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 23.1, 24.4, 27.1, 31.1, 31.7, 37.6, 39.5, 43.8, 50.8, 53.6, 220.4; IR (NaCl) 1741 cm^{-1}; HRMS (EI, 70 eV) m/z 164.1201 ([M]$^+$, 1.9), calcd for $C_{11}H_{16}O$ 164.1201.

3-Oxatricyclo[7.2.1.0^{4,10}]dodecan-2-one (10). A solution of ketone **9** (7.5 mg, 0.05 mmol), *m*-CPBA (80−85% purity, 98.6 mg, 0.5 mmol), and $NaHCO_3$ (76.8 mg, 0.9 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature under Ar overnight (14 h). The reaction was quenched by the addition of saturated aqueous sodium sulfite solution and 10% aqueous HCl until no more bubbling ensued and the reaction mixture was neutral to pH paper. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried ($MgSO_4$), and concentrated by evaporating most of the solvent in vacuo. Flash chromatography (hexanes/EtOAc, 2:1) gave **10** (R_f = 0.7, 6.2 mg, 75%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33−1.46 (m, 2H), 1.54 (ddd, J = 13.2, 3.6, 3.6 Hz, 1H), 1.60−1.72 (m, 4H), 1.80 (ddd, J = 11.6, 5.2, 3.6 Hz, 1H), 2.01 (dd, J = 11.6, 2.4 Hz, 1H), 2.02−2.16 (m, 3H), 2.35 (br dd, J = 6.8, 5.6 Hz, 1H), 2.39−2.47 (m, 1H), 2.84 (dd, J = 6.8, 3.6 Hz, 1H), 4.60 (dd, J = 5.2, 2.8 Hz, 1H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 24.1, 24.3, 32.0, 33.3, 35.7, 37.7, 38.2, 41.8, 42.2, 85.3, 175.2; IR (NaCl) 1739 cm^{-1}; HRMS (EI, 70 eV) m/z 180.1151 ([M]$^+$, 14.4), calcd for $C_{11}H_{16}O_2$ 180.1150. Proof of the regiochemistry of the reaction was obtained following reduction to **11**.

(1*S,2*R**,7*R**,9*S**)-9-Hydroxymethylbicyclo[5.3.0]decan-2-ol (11).** A mixture of lactone **10** (36.7 mg, 0.2 mmol) and $LiAlH_4$ (7.7 mg, 0.2 mmol) in THF (2 mL) was refluxed under Ar for 1 h. After being cooled to room temperature, the reaction was quenched by the addition of 15% KOH aqueous solution (10 mL), and the mixture was extracted with EtOAc (3 × 10 mL). The combined extracts were dried ($MgSO_4$) and concentrated by evaporating most of the solvent in vacuo. Flash chromatography (hexanes/EtOAc, 1:2), gave **11** (R_f = 0.3, 29.8 mg, 79%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (ddd, J = 11.6, 11.6, 11.6 Hz, $H8_\alpha$), 1.21−1.30 (m, $H5$), 1.38−1.58 (m, 4H, $H10_\alpha$/6/3/4), 1.59−1.76 (m, 3H, $H4'$/5′/6′), 1.81−2.09 (m, 6H, $H8_\beta$/10_β/3′/9)/2 X OH), 2.12−2.29 (m, 2H, $H7$/1), 3.62 (d, J = 6.0 Hz, 2H, CH_2OH), 3.97 (ddd, J = 8.0, 2.8, 1.2 Hz, $H2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.2 (*C*4), 27.4 (*C*5), 33.1 (*C*6), 33.4 (*C*10), 35.4 (*C*3), 38.5 (*C*8), 42.0 (*C*7), 42.2 (*C*9), 47.0 (*C*1), 67.1 (*C*H$_2$OH), 73.9 (*C*2); IR (NaCl) 3313 cm^{-1}; HRMS (EI, 70 eV) m/z 184.1429 ([M]$^+$, 1.3), calcd for $C_{11}H_{20}O_2$ 184.1463. The locations of −OH and −CH_2OH groups were confirmed by long range ($^3J_{H,C}$) heteronuclear couplings observed in HMBC spectrum: H2 with C4, C7, C10, and CH_2-OH with C8, C10, thereby confirming the regiochemistry of the Baeyer−Villiger reaction. The stereochemistry was confirmed by NOESY and DNOE experiments: H2 ↔ H1, H1 ↔ H7; CH_2OH → H8$_\alpha$ and H10$_\alpha$.

Tricyclo[6.2.1.0^{3,9}]undec-5-en-2-one (12). A mixture of **7** (226.2 mg, 1.4 mmol) and PCC (446.0 mg, 2.1 mmol) in CH_2Cl_2 (14 mL) was stirred under Ar at room temperature for 1.5 h. After the reaction mixture was passed through a silica gel plug eluting with CH_2Cl_2 (3 × 5 mL), the clear solution was collected and most of the solvent evaporated in vacuo. Purification by flash chromatography (hexanes/EtOAc, 3:1), gave **12** (R_f = 0.8, 147.9 mg, 66%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (ddd, J = 12.8, 5.6, 1.2 Hz, 1H), 1.57−1.63 (AA′, 2H), 1.91 (ddd, J = 11.8, 11.8, 5.6 Hz, 1H), 2.17−2.29 (m, 4H), 2.37−2.42 (m, 1H), 2.51−2.58 (m, 3H), 5.54−5.61 (m, 1H), 5.76−5.83 (m, 1H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 24.7, 27.6, 28.4, 34.2, 38.2, 46.8, 49.9, 51.5, 128.6, 130.1, 217.5; IR (NaCl) 1738 cm^{-1}; HRMS (EI, 70 eV) m/z 162.1023 ([M]$^+$, 8.8), calcd for $C_{11}H_{14}O$ 162.1045.

***exo*-3,7-Dioxatetracyclo[8.2.1.0^{4,11}.0^{6,8}]tridecan-2-one (13a), *exo*-2,7-Dioxatetracyclo[8.2.1.0^{4,11}.0^{6,8}]tridecan-3-one (13b), and *endo*-3,7-Dioxatetracyclo[8.2.1.0^{4,11}.0^{6,8}]-tridecan-2-one (13c).** A mixture of ketone **12** (73.3 mg, 0.45 mmol), *m*-CPBA (80−85% purity, 976.0 mg, 4.5 mmol), and $NaHCO_3$ (760.2 mg, 0.9 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature under Ar overnight (14 h) and then quenched by the addition of saturated aqueous sodium sulfite solution and 10% HCl aqueous until no more bubbling ensued and the reaction mixture was neutral to pH paper. The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL), and the combined extracts were dried ($MgSO_4$) and then concentrated by evaporating most of the solvent in vacuo. Purification by flash chromatography (hexanes/EtOAc, 1:1) gave **13a** (R_f = 0.26, 56.5 mg, 64%), **13b** (R_f = 0.31, 10.0 mg, 11%) and **13c** (R_f = 0.15, < 1 mg, trace) as white solids. **13a**:^{1}H NMR (400 MHz, $CDCl_3$) δ 1.63 (dd, J = 14.8, 7.3 Hz, $H5$), 1.72−1.83 (m, 3H, $H9$/12/13), 1.96 (br d, J = 12.2 Hz, $H12'$), 2.18 (ddd, J = 14.1, 11.0, 7.9 Hz, $H13'$), 2.22−2.25 (m, $H11$), 2.35−2.41 (m, $H10$), 2.46 (ddd, J = 14.7, 6.1, 6.1 Hz, $H9'$), 2.78 (ddd, J = 14.8, 6.8, 6.8 Hz, $H5'$), 2.95 (dd, J = 7.9, 3.8 Hz, $H1$), 3.08−3.16 (m, 2H, $H8$/6), 4.67 (dd, J = 6.8, 3.6 Hz, $H4$); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 28.8 (*C*9), 30.6 (*C*13), 32.4 (*C*5), 32.6 (*C*12), 37.2 (*C*10), 41.2 (*C*1), 44.8 (*C*11), 51.1 (*C*6), 51.8 (*C*8), 81.2 (*C*4), 174.6 (*C*2); IR (NaCl) 1741 cm^{-1}; HRMS (EI, 70 eV) m/z 194.0955 ([M]$^+$, 2.1), calcd for $C_{11}H_{14}O_3$ 194.0943. The regiochemical identity of **13a** was assigned from the ^{1}H,^{1}H−COSY spectrum linking H4 through H6 and H8, and confirmed by long range ($^3J_{H,C}$) heteronuclear couplings observed in a selective INEPT experiment:[25] H4 → C6, as well as C2, C10 and C11. The relative stereochemistry of C6 and C8 was assigned by a NOESY experiment: H8 ↔ H1 and H13$_{endo}$. **13b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43 (ddd, J = 13.7, 7.6, 1.5 Hz, $H5$), 1.73−1.82 (m, 2H, $H12$/9), 1.97 (ddd, J = 14.6, 8.0, 2.4 Hz, $H13_{endo}$), 2.03 (br d, J = 12.8 Hz, $H12'$), 2.20 (ddd, J = 14.6, 11.6, 5.2 Hz, $H13_{exo}$), 2.29−2.38 (m, 2H, $H10$/11), 2.44 (ddd, J = 15.2, 6.1, 6.1 Hz, $H9'$), 2.89 (ddd, J = 13.7, 6.4, 6.4 Hz, $H5'$), 2.95 (dddd, J = 6.4, 5.0, 1.5, 1.2 Hz, $H4$), 3.03 (ddd, J = 7.6, 6.1, 4.4 Hz, $H8$), 3.20 (ddd, J = 7.6, 6.4, 4.4 Hz, $H6$), 4.83 (br s, $H1$); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 28.9 (*C*9), 29.9 (*C*5), 35.2 (*C*13), 38.4 (*C*12), 38.7 (*C*10), 43.9 (*C*11), 44.0 (*C*4), 52.0 (*C*8), 52.7 (*C*6), 80.9 (*C*1), 172.2 (*C*3); IR (NaCl) 1728 cm^{-1}; HRMS (CI, NH_3, 140 eV) m/z 195.1003 ([M + H]$^+$, 100), calcd for $C_{11}H_{15}O_3$ 195.1021. The regiochemical identity of **13b** was assigned by mapping the proton-coupled spin systems in the ^{1}H,^{1}H-COSY spectrum, supported by selective INEPT[25] experiments: H1 → C3, C10, and C11. The relative stereochemistry of C6 and C8 was assigned by a NOESY experiment: H8 ↔ H13$_{endo}$. **13c**: ^{1}H NMR (400 MHz, $CDCl_3$) 1.60 (ddd, J = 14.0, 9.6, 8.4 Hz, $H9$), 1.67 (ddd, J = 13.8, 5.0, 1.2 Hz, $H13_{endo}$), 1.81 (ddd, J = 11.6, 4.4, 4.4 Hz, $H12$), 1.95−2.02 (m, 2H, $H5$/12′), 2.21 (ddd, J = 13.8, 11.6, 7.2 Hz, $H13_{exo}$), 2.36−2.49 (m, 3H, $H9'$/10/11), 2.61 (ddd, J = 15.6, 8.0, 4.8 Hz, $H5'$), 2.89 (dd, J = 7.2, 4.4 Hz, $H1$), 3.02 (ddd, J = 7.2, 4.8, 4.8 Hz, $H6$), 3.15 (ddd, J = 8.4, 4.8, 4.8 Hz, $H8$), 4.73 (br dd, J = 8.0, 7.0, 7.0 Hz, $H4$); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 31.0, 32.8, 33.2, 34.9, 36.3, 40.5, 41.4, 50.4, 53.8, 80.5, 174.3. The regiochemical identity of **13c** was assigned by the observation in a COSY experiment: H4 only couples with one set of the methylene protons H5/5′, and this fact ruled out the possibility of the other regioisomer whose carbinol proton would couple with two sets of the methylene protons as in **13b**. Since the exo stereoisomer was already characterized as **13a**, this lactone must be endo.

Methyl (1*S,2*R**,4*R**,6*S**,7*S**,9*S**)-2-Hydroxy-5-oxa-10-tricyclo[6.3.0.0^{4,6}]undecylmethanoate (14).** Lactone **13a** (6.0 mg, 0.03 mmol) and K_2CO_3 (0.4 mg, 0.003 mmol) in CH_3-OH (0.5 mL) were stirred at room temperature for 48 h. After evaporation of the solvent in vacuo, flash chromatography (EtOAc) of the crude residue gave pure **14** (R_f = 0.6, 6.8 mg, 97%) as a colorless liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65

(25) (a) Bax, A. *J. Magn. Reson.* **1984**, *57*, 314−318. (b) Jakobsen, H. J.; Bildsoe, H.; Donstrup, S.; Sorensen, O. W. *J. Magn. Reson.* **1984**, *57*, 324−330.

(ddd, J = 12.8, 10.0, 8.4 Hz, *H*9), 1.79 (br d, J = 4.0 Hz, O*H*), 1.86−2.01 (m, 3H, *H*11/11′/7), 2.02−2.24 (m, 4H, *H*9′/3/1/8), 2.30−2.39 (m, 2H, *H*7′/3′), 2.74 (dddd, J = 9.6, 9.6, 8.4, 8.4 Hz, *H*10), 3.04−3.10 (m, 2H, *H*4/6), 3.67 (s, 3H, CH_3), 3.99−4.03 (m, *H*2); ^{13}C NMR (67.5 MHz, $CDCl_3$) 30.0 (*C*7), 30.9 (*C*11), 33.1 (*C*3), 35.6 (*C*8), 36.8 (*C*9), 42.5 (*C*10), 46.8 (*C*1), 51.8 (CH_3), 52.7 (*C*4), 55.1 (*C*6), 69.2 (*C*2), 176.9 (*C*OOCH_3); IR (NaCl) 3447, 1731 cm^{-1}; HRMS (CI, NH_3, 140 eV) *m*/*z* 227.1262 ([M + H]$^+$, 87), calcd for $C_{12}H_{19}O_4$ 227.1283. The regiochemistry of the Baeyer−Villiger reaction was further confirmed by long range ($^3J_{H,C}$) heteronuclear couplings observed in the HMBC spectrum: H2/C4, C8 and C11, indicating that the hydroxyl group and epoxide are on the same ring. The stereochemistry was confirmed by a DNOE experiment: irradiation of H4 and H6 (overlapped peaks) did not cause an NOE enhancement of H2, H1 or H8, while in a NOESY experiment, an NOE was observed between O*H* and H4 (H6).

***syn*-5-*tert*-Butoxy-1-methyltetracyclo[5.4.0.0^{2,4}.0^{3,7}]-undecane (15d).** A mixture of **1d**[10] (100.2 mg, 0.4 mmol) and Pd−C (10% Pd on C, 22.8 mg, 0.02 mmol) in THF (4 mL) was stirred under an H_2 atmosphere (balloon, 1 atm) at room temperature for 4.5 h. After passing through a silica gel plug to remove the catalyst, eluting with CH_2Cl_2 (3 × 5 mL), the crude product was obtained by evaporating the solvent in vacuo. Purification by flash chromatography (hexanes/EtOAc, 20:1) gave **15d** (R_f = 0.4, 105.2 mg, 95%) as a colorless liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (ddd, J = 4.2, 4.2, 1.2 Hz, 1H), 0.99−1.05 (m, 2H), 1.16 (s, 9H), 1.31 (s, 3H), 1.38−1.62 (m, 7H), 1.66−1.73 (m, 2H), 1.77 (br d, J = 7.0 Hz, 1H), 3.54 (br s, 1H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 16.2, 19.6, 22.6, 25.5, 25.9, 27.0, 28.4 (3C), 31.0, 42.3, 42.5, 46.9, 48.1, 73.2, 81.1; HRMS (CI, NH_3, 140 eV) *m*/*z* 234.1978 ([M]$^+$, 0.5), calcd for $C_{16}H_{26}O$ 234.1984.

(1*R,8*R**,9*S**,10*R**)-10-*tert*-Butoxytricyclo[6.2.1.0^{3,9}]-undec-2-ene (16b) and Tricyclo[5.4.0.0^{3,7}]undecan-5-one (17b).** A solution of **15b**[4b] (110.0 mg, 0.5 mmol) and Zeise's dimer ([Pt(C_2H_4)Cl$_2$]$_2$, 73.5 mg, 0.125 mmol) in $CDCl_3$ (1 mL) was stirred under Ar at room temperature for 21 h. After evaporation of the solvent in vacuo, the residue was purified by flash chromatography (hexanes/EtOAc, 20:1) to give **16b**[4b] (R_f = 0.7, 87.5 mg, 80%) and **17b** as a white solid (hexanes/EtOAc, 5:1, R_f = 0.6, 14.7 mg, 18% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26−1.31 (m, 2H), 1.48−1.77 (m, 7H), 1.86 (d, J_{AB} = 17.8 Hz, 1H), 1.95−2.02 (m, 1H), 2.06 (br ddd, J = 17.8$_{(AB)}$, 5.5, 2.8 Hz, 1H), 2.12−2.17 (m, 2H), 2.36 (br dd, J = 4.4, 4.4 Hz, 1H), 2.41 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.2, 26.5, 29.6, 30.3, 31.3, 36.2, 42.1, 46.3, 46.5, 58.6, 217.6; IR (NaCl) 1748 cm^{-1}; HRMS (CI, NH_3, 140 eV) *m*/*z* 165.1274 ([M + H]$^+$, 2.8), calcd for $C_{11}H_{17}O$ 165.1279.

(1*R,8*R**,9*S**,10*R**)-10-*tert*-Butoxy-8-methyltricyclo-[6.2.1.0^{3,9}]undec-2-ene (16d).** A solution of **15d** (29.2 mg, 0.12 mmol) and Zeise's dimer ([Pt(C_2H_4)Cl$_2$]$_2$, 36.7 mg, 0.06 mmol) in $CDCl_3$ (1.2 mL) was stirred under Ar at room temperature for 8 h. After evaporation of the solvent in vacuo, the residue was purified by flash chromatography (hexanes/EtOAc, 20:1) to give **16d** (R_f = 0.6, 22.9 mg, 79%) as a colorless liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (br d, J = 11.0 Hz, $H11_{endo}$), 1.14 (s, 9H, OC(CH_3)$_3$), 1.20−1.26 (m, *H*7), 1.29 (s, 3H, CH_3), 1.29−1.44 (m, 3H, *H*5/6/6′), 1.47−1.53 (m, *H*7′), 1.58−1.65 (m, *H*5′), 1.75 (dd, J = 11.0, 3.7 Hz, $H11_{exo}$), 1.99 (br s, *H*9), 2.13−2.25 (m, 2H, *H*4/4′), 2.40 (br s, *H*1), 3.36 (br s, *H*10), 5.48 (br m, *H*2); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 23.2 (*C*6), 27.5 (CH_3), 28.3 (3C, OC(CH_3)$_3$), 29.9 (*C*5), 30.8 (*C*4), 39.6 (*C*8), 40.2 (*C*11), 47.2 (*C*7), 47.8 (*C*1), 58.8 (*C*9), 73.2 (O*C*(CH$_3$)$_3$), 84.3 (*C*10), 125.0 (*C*2), 147.4 (*C*3); HRMS (CI, NH_3, 140 eV) *m*/*z* 235.2103 ([M + H]$^+$, 0.75), calcd for $C_{16}H_{27}O$ 235.2062. The retention of the stereochemistry of C10 was confirmed by a DNOE experiment: H10 → H2. Byproduct **17d** was not noticed in this run of the reaction, though its presence is presumed.

1-Methyltricyclo[5.4.0.0^{3,7}]undecan-5-one (17d). Following the above-described procedure, a solution of **15d** (13.7 mg, 0.06 mmol) and Zeise's dimer ([Pt(C_2H_4)Cl$_2$]$_2$, 8.6 mg, 0.015 mmol) in $CDCl_3$ (0.6 mL) was stirred under Ar at room temperature for 25 h to give **16d** (10.5 mg, 77%) and **17d**, which was purified by flash chromatography (hexanes/EtOAc/CH_2Cl_2, 10:1:0.1, R_f = 0.3, 2.1 mg, white solid, 20%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (s, 3H, CH_3), 1.13 (dd, J = 12.8, 1.2 Hz, *H*2), 1.27−1.62 (m, 6H, *H*9/8/10/11/11′/9′), 1.66−1.73 (m, *H*10), 1.81 (d, J = 17.7 Hz, *H*4), 1.95−2.05 (m, 2H, *H*8/2′), 2.07−2.15 (m, 2H, *H*4′/7), 2.21 (br s, *H*6), 2.30−2.32 (m, *H*3); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 25.5 (*C*9), 27.3 (*C*10), 30.1 (*C*8), 30.6 (CH_3), 38.0 (*C*2), 39.9 (*C*1), 41.7 (*C*11), 42.1 (*C*3), 46.1 (*C*4), 48.2 (*C*7), 63.2 (*C*6), 216.3 (*C*5); IR (NaCl) 1747 cm^{-1}; HRMS (CI, NH_3, 140 eV) *m*/*z* 178.1347 ([M]$^+$, 0.13), calcd for $C_{12}H_{18}O$ 178.1358. The regiochemical identity of **17d** was assigned by a DNOE experiment: CH_3 → H2 and H4 (one of each methylene pairs of the norbornyl skeleton), excluding the other possible regioisomer which anticipates an NOE between CH_3 and only one of the methylene groups on the norbornyl skeleton.

(1*R,7*R**,9*S**,10*R**)-10-*tert*-Butoxy-7-methyl-2-oxobicyclo[5.3.0]decane-9-carbaldehyde (18d).** Ozone was bubbled into a solution of **16d** (20.6 mg, 0.09 mmol) in CH_2Cl_2 (8 mL) at −78 °C until it became light blue. The reaction was quenched by adding Me_2S (10 drops) and the reaction mixture allowed to warm to room temperature. After evaporation of the solvent in vacuo, purification by flash chromatography (hexanes/EtOAc, 5:1), gave **18d** (R_f = 0.4, 17.8 mg, 76%) as a colorless liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (s, 9H, OC(CH_3)$_3$), 1.15−1.23 (m, *H*6), 1.28 (s, 3H, CH_3), 1.39−1.78 (m, 6H, *H*8/8′/6′/5/4/5′), 1.92−2.02 (m, *H*4′), 2.32−2.43 (m, 2H, *H*3/3′), 2.87−2.94 (m, 2H, *H*1/9), 4.95 (dd, J = 7.8, 3.2 Hz, *H*10), 9.68 (d, J = 3.7 Hz, C*H*O); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 22.3 (2C), 26.5, 28.4 (3C), 37.4, 39.7, 42.8, 44.0, 58.5, 68.3, 73.3, 74.2, 202.9, 212.0; IR (NaCl) 1732, 1704 cm^{-1}; HRMS (EI, 70 eV) *m*/*z* 266.1857 ([M]$^+$, 0.03), calcd for $C_{16}H_{26}O_3$ 266.1882. No epimerization of C9 occurred during the reaction and isolation, as confirmed by a DNOE experiment: H10 → CHO.

(1*S,2*S**,3*S**,4*S**,5*S**,6*R**,7*R**,9*S**,10*S**)-5-*tert*-Butoxy-7,10-dimethyltetracyclo[5.4.0.0^{2,4}.0^{3,7}]undecan-9-ol (20a) and (1*S**,2*S**,3*S**,4*S**,5*S**,6*R**,7*R**,9*R**,10*R**)-5-*tert*-Butoxy-7,10-dimethyltetracyclo[5.4.0.0^{2,4}.0^{3,7}]undecan-9-ol (20b).** To a solution of **1i**[10] (170.1 mg, 0.7 mmol) in THF (1.4 mL) at 0 °C under Ar was added BH_3·THF (1.0 M in THF, 0.7 mL, 0.7 mmol) dropwise with stirring. The reaction mixture was maintained at 0 °C for 20 min, and then 3 N NaOH (1 mL) was added, followed by the careful, dropwise addition of 30% H_2O_2 aqueous solution (1 mL). The cold bath was then removed and the reaction mixture stirred at room temperature for another 20 min. The reaction was then quenched by adding 10% HCl and saturated aqueous sodium sulfite solution until the mixture was neutral to pH paper and no more bubbling ensued. The aqueous mixture was extracted with CH_2Cl_2 (3 × 15 mL) and the extracts dried ($MgSO_4$). After concentrating in vacuo, final purification by flash chromatography (hexanes/EtOAc/CH_2Cl_2, 3:1:0.1) gave **20a** (R_f = 0.5, 164.4 mg, 90%) and **20b** (R_f = 0.6, 2.0 mg, 1% yield) as white solids. **20a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (d, J = 6.4 Hz, 3H, *H*13), 1.00 (br dd, J = 5.2, 5.2 Hz, *H*2), 1.06 (br d, J = 5.2 Hz, 2H, *H*3/4), 1.16 (s, 9H, OC(CH_3)$_3$), 1.21 (ddd, J = 14.7, 11.0, 1.5 Hz, *H*11), 1.35 (s, 3H, *H*12), 1.38−1.44 (m, *H*10), 1.45 (br s, *H*6), 1.59 (dd, J = 13.9, 10.6 Hz, *H*8), 1.75 (br d, J = 8.2 Hz, *H*1), 1.88 (ddd, J = 14.7, 8.2, 6.0 Hz, *H*11′), 1.95 (dd, J = 13.9, 3.1 Hz, *H*8′), 3.48−3.55 (m, overlapped with H5, *H*9), 3.51 (br s, overlapped with H9, *H*5), O*H* not observed; ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.2 (*C*4), 19.3 (*C*13), 20.2 (*C*2), 21.9 (*C*3), 25.2 (*C*12), 28.4 (3C, C(CH_3)$_3$), 37.1 (*C*11), 39.9 (*C*10), 41.2 (*C*1), 45.1 (*C*7), 47.1 (*C*6), 51.7 (*C*8), 73.0 (*C*9), 73.4 (O*C*(CH$_3$)$_3$), 80.8 (*C*5); IR (NaCl) 3382 cm^{-1}; HRMS (EI, 70 eV) *m*/*z* 264.2078 ([M]$^+$, 1.2), calcd for $C_{17}H_{28}O_2$ 264.2089. The stereochemistry of C9 and C10 was assigned by a NOESY experiment: H1 ↔ H10. **20b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (d, J = 6.7 Hz, 3H, *H*13), 1.10 (dddd, J = 6.1, 4.3, 1.2, 1.2 Hz, *H*2), 1.16 (s, 9H, OC(CH_3)$_3$), 1.19 (dddd, J = 6.1, 5.2, 1.2, 1.2 Hz, *H*4), 1.27 (ddd, J = 5.2, 4.3, 1.2 Hz, *H*3), 1.33 (s, 3H, *H*12), 1.47 (ddd, J = 14.3, 11.2, 0.9 Hz, *H*11), 1.57 (ddd, J = 1.2, 1.2, 1.2 Hz, *H*6), 1.59−1.65 (m, overlapped with H8, *H*10), 1.66 (dd, J = 15.3, 3.4 Hz, overlapped with H10, *H*8), 1.74 (ddd, J = 14.3, 8.9, 5.5 Hz, *H*11′), 1.84 (br d, J = 8.9 Hz, *H*1), 2.02 (dd, partially overlapped with OH, J = 15.3, 4.9 Hz, *H*8′), 2.03 (d, J = 10.1 Hz, partially

overlapped with H8′, O*H*), 3.57 (br s, *H*5), 3.62−3.66 (m, *H*9); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.1 (*C*4), 20.1 (*C*2), 20.7 (*C*13), 23.5 (*C*3), 26.0 (*C*12), 28.4 (3C, C(*C*H$_3$)$_3$), 33.5 (*C*11), 36.3 (*C*10), 40.8 (*C*1), 46.3 (*C*7), 47.3 (*C*8), 47.6 (*C*6), 73.5 (O*C*(CH$_3$)$_3$), 75.9 (*C*9), 80.5 (*C*5); IR (NaCl) 3454 cm^{-1}; HRMS (CI, CH_4, 140 eV) *m*/*z* 264.2076 ([M]$^+$, 0.8), calcd for $C_{17}H_{28}O_2$ 264.2089. The stereochemistry of C9 was assigned by a DNOE experiment: H9 → H1.

(1*S,2*S**,3*S**,4*S**,5*S**,6*R**,7*R**,9*S**,10*S**)-5-*tert*-Butoxy-10-methyltetracyclo[5.4.0.0^{2,4}.0^{3,7}]undecan-9-ol (21a), (1*R**,2*S**,3*S**,4*S**,5*S**,6*R**,7*S**,9*R**,10*R**)-5-*tert*-Butoxy-10-methyltetracyclo[5.4.0.0^{2,4}.0^{3,7}]undecan-9-ol (21b), and (1*R**,2*S**,3*S**,4*S**,5*S**,6*R**,7*S**,9*S**,10*S**)-5-*tert*-Butoxy-10-methyltetracyclo[5.4.0.0^{2,4}.0^{3,7}]undecan-9-ol (21d).** To a solution of **1j**[10] (ratio of 2 isomers, 1.7:1, 306.4 mg, 1.3 mmol) in THF (2.6 mL) at 0 °C under Ar was added BH_3·THF (1.0 M in THF, 1.3 mL, 1.3 mmol) dropwise with stirring. The reaction mixture was maintained at 0 °C for 20 min, and then 3 N NaOH (1 mL) was added, followed by the careful, dropwise addition of of 30% H_2O_2 aqueous solution (1 mL). The cold bath was then removed and the reaction mixture stirred at room temperature for another 20 min. Following the workup procedure as described above for **20a** and **20b**, final purification by flash chromatography (hexanes/EtOAc/CH_2Cl_2, 3:1:0.1) gave **21a** (R_f = 0.31, 158.9 mg, 48%), **21b** and **21c** (R_f = 0.38, **21b**/**21c** = 9:1 from ^{1}H NMR, 110.6 mg total, 33% combined yield; **21b** was finally separated from **21c** in pure form by repeated chromatography and characterized, but pure **21c** could not be obtained), and **21d** (R_f = 0.41, 4.4 mg, 1%) as white solids. **21a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (d, *J* = 6.7 Hz, 3H, C*H*$_3$), 0.97 (br dd, *J* = 5.8, 5.2 Hz, *H*4), 1.05 (br dd, *J* = 5.8, 4.9 Hz, *H*2), 1.12 (br dd, *J* = 5.2, 4.9 Hz, *H*3), 1.16 (s, 9H, OC(C*H*$_3$)$_3$), 1.16−1.20 (m, overlapped with *t*-Bu, *H*11), 1.25 (br d, *J* = 4.0 Hz, O*H*), 1.39−1.47 (m, *H*10), 1.53 (ddd, *J* = 13.7, 10.4, 3.3 Hz, *H*8), 1.67 (br s, *H*6), 1.76 (br d, *J* = 9.1 Hz, *H*1), 1.83 (ddd, *J* = 14.0, 9.1, 4.9 Hz, *H*11′), 2.16 (ddd, *J* = 13.7, 4.0, 4.0 Hz, *H*8′), 2.45−2.47 (m, *H*7), 3.47 (dddd, *J* = 10.4, 10.4, 4.0, 4.0 Hz, *H*9), 3.53 (br s, *H*5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.4 (*C*3), 17.3 (*C*4), 18.9 (*C*H$_3$), 21.2 (*C*2), 28.6 (3C, OC(*C*H$_3$)$_3$), 37.2 (*C*11), 37.3 (*C*7), 39.1 (*C*1), 40.1 (*C*10), 40.3 (*C*8), 42.6 (*C*6), 73.2 (O*C*(CH$_3$)$_3$), 73.3 (*C*9), 78.3 (*C*5); IR (NaCl) 3367 cm^{-1}; HRMS (EI, 70 eV) *m*/*z* 250.1909 ([M]$^+$, 7.6), calcd for $C_{16}H_{26}O_2$ 250.1933. The stereochemistry of C5 was assigned by a DNOE experiment (*t*-Bu ↔ H7) with H7 assigned by long range ($^3J_{H,C}$) heteronuclear couplings observed in the HMBC spectrum: H7/C9. The stereochemistry of C9 was assigned by a DNOE experiment: H9 → H3 and H2. **21b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (d, *J* = 6.4 Hz, 3H, C*H*$_3$), 0.95 (m, partially overlapped with CH$_3$, *H*4), 1.05−1.10 (m, 2H, *H*2/*H*3), 1.16 (s, 9H, OC(C*H*$_3$)$_3$), 1.31−1.46 (m, 3H, *H*11/10 and −O*H*), 1.46 (ddd, *J* = 13.4, 10.7, 2.9 Hz, *H*8), 1.66 (br s, *H*6), 1.81 (br dd, *J* = 3.7, 2.9 Hz, *H*7), 1.89 (ddd, *J* = 13.7, 9.3, 4.3 Hz, *H*11′), 1.98 (ddd, *J* = 13.4, 3.7, 3.7 Hz, *H*8′), 2.44 (br d, *J* = 9.3 Hz, *H*1), 3.45 (ddd, *J* = 10.7, 9.2, 3.7 Hz, *H*9), 3.58 (dd, *J* = 2.9, 2.9 Hz, *H*5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.2 (*C*4), 17.4 (*C*3), 18.9 (*C*H$_3$), 19.1 (*C*2), 28.6 (3C, OC(*C*H$_3$)$_3$), 35.6 (*C*11), 37.3 (*C*1), 38.7 (*C*7), 40.1 (*C*10), 40.9 (*C*8), 42.4 (*C*6), 73.1 (*C*9), 73.2 (O*C*(CH$_3$)$_3$), 78.2 (*C*5); IR (NaCl) 3234 cm^{-1}; HRMS (CI, CH_4, 140 eV) *m*/*z* 250.1936 ([M]$^+$, 4.2), calcd for $C_{16}H_{26}O_2$ 250.1933. The assignment of H1 and H7 was accomplished by long range ($^3J_{H,C}$) heteronuclear couplings observed in the HMBC spectrum: H1/C10 and H7/C9. With the assignment of H7 sured, the stereochemistry of C5 was established by a NOESY experiment: H5 ↔ H7. The stereochemistry of C9 was assigned by a DNOE experiment: H9 → H2 and H3, as well as H8′ and C*H*$_3$. **21d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (d, *J* = 6.5 Hz, 3H, C*H*$_3$), 1.08 (br dd, *J* = 5.5, 5.3 Hz, *H*4), 1.17 (s, 9H, OC(C*H*$_3$)$_3$), 1.19 (br dd, *J* = 5.5, 5.3 Hz, partially overlapped with *t*-Bu, *H*2), 1.32 (br dd, *J* = 5.5, 5.5 Hz, *H*3), 1.57−1.68 (m, 3H, *H*8/11/10), 1.72−1.77 (m, 2H, *H*6/11′), 1.77 (d, *J* = 10.3 Hz, O*H*), 1.86 (br dd, *J* = 3.8, 3.8 Hz, partially overlapped with H8′, *H*7), 1.92 (ddd, *J* = 14.6, 4.4, 3.8 Hz, partially overlapped with H7, *H*8′), 2.53 (dddd, *J* = 8.7, 1.0, 1.0, 1.0 Hz, *H*1), 3.56 (br s, *H*5), 3.68 (br ddd, *J* = 10.3, 4.4, 4.4 Hz, *H*9); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.5 (*C*2), 19.1 (*C*4), 19.7 (*C*3), 20.7 (*C*H$_3$), 28.6 (3C, OC(*C*H$_3$)$_3$), 31.3 (*C*11), 36.9 (*C*8), 37.3 (*C*1), 37.4 (*C*10), 39.7 (*C*7), 43.5 (*C*6), 73.3 (O*C*-(CH$_3$)$_3$), 75.9 (*C*9), 78.1 (*C*5); IR (NaCl) 3444 cm^{-1}; HRMS (EI, 70 eV) *m*/*z* 250.1932 ([M]$^+$, 6.2), calcd for $C_{16}H_{26}O_2$ 250.1933. The stereochemistry of C5 was assigned by a NOESY experiment, H7 ↔ H5 with H7 assigned by long range ($^3J_{H,C}$) heteronuclear couplings observed in the HMBC spectrum: H7/C9′. The stereochemistry of C9 was assigned by a DNOE experiment: H9 → H6 and CH$_3$.

(1*S,2*S**,3*S**,4*S**,5*S**,6*R**,7*R**,9*S**,10*S**)-5-*tert*-Butoxy-9-(*tert*-butyldimethylsiloxy)-7,10-dimethyltetracyclo-[5.4.0.0^{2,4}.0^{3,7}]undecane (22).** A solution of *tert*-butyldimethylchlorosilane (27.9 mg, 0.18 mmol), imidazole (26.2 mg, 0.38 mmol), and **20a** (40.7 mg, 0.15 mmol) in DMF (0.3 mL) was stirred under Ar at room temperature for 24 h. After removal of the solvent in vacuo, flash chromatography (hexanes/EtOAc/Et_3N, 20:1:0.1) of the residue gave pure **22** (R_f = 0.4, 58.1 mg, 99%) as a colorless liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.02 (s, 3H, SiC*H*$_3$), 0.05 (s, 3H, SiC*H*$_3$), 0.84 (d, *J* = 6.7 Hz, 3H, *H*13), 0.88 (s, 9H, SiC(C*H*$_3$)$_3$), 0.99−1.02 (m, 3H, *H*3/2), 1.04 (dddd, *J* = 5.9, 4.5, 1.4, 1.4 Hz, *H*4), 1.16 (s, 9H, OC(C*H*$_3$)$_3$, partially overlapped with H11), 1.16 (ddd, *J* = 14.6, 11.0, 1.7 Hz, partially overlapped with *t*-Bu, *H*11), 1.32 (s, 3H, *H*12), 1.42−1.47 (m, partially overlapped with H6, *H*10), 1.46 (br s, overlapped with H10, *H*6), 1.59 (dd, *J* = 14.3, 10.3 Hz, *H*8), 1.74 (br d, *J* = 8.3 Hz, *H*1), 1.84 (dd, *J* = 14.3, 2.8 Hz, partially overlapped with H11′, *H*8′), 1.86 (ddd, *J* = 14.6, 8.3, 5.6 Hz, partially overlapped with H8′, *H*11′), 3.49 (ddd, *J* = 10.3, 9.1, 2.8 Hz, partially overlapped with H5, *H*9), 3.51 (br s, overlapped with H9, *H*5); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.6 (Si*C*H$_3$), −4.3 (Si*C*′H$_3$), 17.1 (*C*4), 18.2 (Si*C*(CH$_3$)$_3$), 20.3 (2C, *C*2/13), 22.1 (*C*3), 25.4 (*C*12), 26.0 (3C, SiC(*C*H$_3$)$_3$), 28.4 (3C, OC(*C*H$_3$)$_3$), 37.1 (*C*11), 40.5 (*C*10), 41.3 (*C*1), 45.0 (*C*7), 47.1 (*C*6), 52.0 (*C*8), 73.4 (O*C*(CH$_3$)$_3$), 73.5 (*C*9), 80.8 (*C*5); HRMS (CI, CH_4, 140 eV) *m*/*z* 378.2947 ([M]$^+$, 0.4), calcd for $C_{23}H_{42}O_2$-Si 378.2954.

(1*S,2*S**,3*S**,4*S**,5*S**,6*R**,7*R**,9*S**,10*S**)-5-*tert*-Butoxy-9-(*tert*-butyldimethylsiloxy)-10-methyltetracyclo-[5.4.0.0^{2,4}.0^{3,7}]undecane (23).** A solution of **21a** (100.2 mg, 0.4 mmol), *tert*-butyldimethylsilyl chloride (72.5 mg, 0.5 mmol), and imidazole (68.2 mg, 1.0 mmol) in DMF (0.8 mL) was stirred under Ar at room temperature for 5 h. After removal of the solvent in vacuo, flash chromatography (hexanes/EtOAc/Et_3N, 20:1:0.1) of the residue gave pure **23** (R_f = 0.4, 142.4 mg, 98%) as a colorless liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.01 (s, 3H, SiC*H*$_3$), 0.03 (s, 3H, SiC*H*$_3$), 0.85 (d, *J* = 6.7 Hz, 3H, *H*12), 0.87 (s, 9H, SiC(C*H*$_3$)$_3$), 0.96 (br dd, *J* = 5.3, 5.3 Hz, *H*4), 1.05−1.16 (m, partially overlapped with *t*-Bu, 3H, *H*2/3/11), 1.16 (s, 9H, OC(C*H*$_3$)$_3$), 1.42−1.50 (m, *H*10), 1.54 (ddd, *J* = 14.0, 10.2, 3.6 Hz, *H*8), 1.68 (br s, *H*6), 1.75 (br d, *J* = 9.2 Hz, *H*1), 1.82 (ddd, *J* = 14.2, 9.2, 4.9 Hz, *H*11′), 2.04 (ddd, *J* = 14.0, 3.8, 3.3 Hz, *H*8′), 2.41 (br dd, *J* = 3.8, 3.6 Hz, *H*7), 3.45 (ddd, *J* = 10.2, 9.0, 3.3 Hz, *H*9), 3.52 (br dd, *J* = 1.8, 1.8 Hz, *H*5); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.7 (Si*C*H$_3$), −4.4 (Si*C*′H$_3$), 15.5 (*C*3), 17.4 (*C*4), 18.2 (Si*C*(CH$_3$)$_3$), 19.9 (*C*12), 21.2 (*C*2), 25.9 (3C, SiC(*C*H$_3$)$_3$), 28.6 (3C, OC(*C*H$_3$)$_3$), 37.0 (*C*11), 37.3 (*C*7), 39.3 (*C*1), 40.5 (*C*8), 40.6 (*C*10), 42.7 (*C*6), 73.2 (O*C*(CH$_3$)$_3$), 73.9 (*C*9), 78.3 (*C*5); HRMS (CI, NH_3, 140 eV) *m*/*z* 364.2778 ([M]$^+$, 0.3), calcd for $C_{22}H_{40}O_2Si$ 364.2798.

***endo*-5-*tert*-Butoxytetracyclo[5.4.0.0^{2,4}.0^{3,7}]undecane-9,-10-diol (24a) and *exo*-5-*tert*-Butoxytetracyclo[5.4.0.0^{2,4}.0^{3,7}]-undecane-9,10-diol (24b). By OsO_4 Dihydroxylation.** To a solution of **1b** (41.7 mg, 0.2 mmol) in *t*-BuOH (1 mL) was added OsO_4 (0.2 M in CH_2Cl_2, 48 μL, 0.01 mmol), followed by *N*-methylmorpholine *N*-oxide (29.1 mg, 0.25 mmol) and H_2O (1 mL). The greenish reaction mixture turned yellow after 21 h at room temperature, then most of the *t*-BuOH was evaporated in vacuo, H_2O (10 mL) was added, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The extracts were dried ($MgSO_4$) and then concentrated by evaporating most of the solvent in vacuo. Flash chromatography (hexanes/EtOAc/CH_2Cl_2, 1:2:0.1) gave **24a** and **24b** (42.8 mg, 89% combined yield, **24a**:**24b**, 6.2:1, from ^{1}H NMR integration). Pure **24a** (R_f = 0.2, white solid) and **24b** (R_f = 0.3, white solid) were

obtained by careful flash chromatography (hexanes/EtOAc/CH_2Cl_2, 1:2:0.1).

By $KMnO_4$ Dihydroxylation.[21a,b] To a solution of **1b** (139.2 mg, 0.6 mmol) in CH_2Cl_2 (1.3 mL) at 0 °C was added slowly a solution of $KMnO_4$ (201.8 mg, 1.3 mmol) and benzyltriethylammonium chloride (436.3 mg, 1.9 mmol) in CH_2Cl_2 (6.4 mL) with stirring. After 4 h, 3% aqueous NaOH (8.5 mL) was added dropwise, and the reaction mixture was allowed to warm to room temperature and kept for 14 h. The dark, cloudy reaction mixture was passed through a silica gel plug eluting with EtOAc (3 × 5 mL), and then the combined washings were concentrated, most of the organic solvent was evaporated, and dilute aqueous HCl (10%) was added to neutralize the mixture. The aqueous mixture was extracted with CH_2Cl_2 (3 × 10 mL), the extracts were dried ($MgSO_4$), and most of the solvent was then evaporated in vacuo. Flash chromatography as above gave **24a** and **24b** (53.0 mg, 33% combined yield, **24a**:**24b**, 1:2, from ^{1}H NMR integration); unreacted starting material **1b** was also recovered (51.6 mg, 37%). **24a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (br dd, J = 5.2, 5.2 Hz, *H*4), 1.15 (s, 9H, OC(CH_3)$_3$), 1.26 (br dd, J = 5.2, 5.2 Hz, *H*2*), 1.31 (br dd, J = 5.2, 5.2 Hz, *H*3*), 1.69 (br s, *H*6), 1.76−1.88 (m, partially overlapped with H11, 3H, *H*8/8′/7), 1.90 (ddd, J = 15.1, 6.6, 4.7 Hz, partially overlapped with H8′, *H*11), 2.00 (ddd, J = 15.1, 7.3, 2.7 Hz, *H*11′), 2.05 (br, 2 × O*H*), 2.51 (br d, J = 6.7 Hz, *H*1), 3.56 (dd, J = 0.8, 0.8 Hz, *H*5), 3.72−3.81 (m, 2H, *H*9/10); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.6, 18.9, 19.9, 28.5 (3C), 32.5, 33.5, 36.0, 37.3, 43.4, 73.5, 74.6, 75.1, 78.0; IR (NaCl) 3389 cm^{-1}; HRMS (CI, NH_3, 140 eV) m/z 253.1789 ([M + H]$^+$, 3.1), calcd for $C_{15}H_{25}O_3$ 253.1803. The stereochemistry of C9 and C10 were assigned by a DNOE experiment: H9/10 → H6. **24b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (br dd, J = 5.2, 5.2 Hz, *H*4), 1.08 (br dd, J = 5.2, 5.2 Hz, *H*3*), 1.13 (br dd, J = 5.2, 5.2 Hz, *H*2*), 1.16 (s, 9H, OC(CH_3)$_3$), 1.61−1.62 (m, O*H*), 1.70 (ddd, J = 14.5, 4.7, 2.7 Hz, *H*8), 1.76−1.78 (m, *H*7), 1.86−1.90 (m, 2H, *H*11/6), 1.95 (ddd, J = 14.5, 6.2, 6.2 Hz, partially overlapped with H11′, *H*8′), 2.01 (ddd, J = 14.8, 7.4, 5.5 Hz, partially overlapped with H8′, *H*11′), 2.43−2.45 (br m, *H*1), 3.55 (br s, *H*5), 3.96−4.02 (br m, 2H, *H*9/10); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.0, 17.2, 19.4, 28.6 (3C), 32.4, 33.6, 36.6, 38.1, 43.2, 73.27, 73.29, 73.4, 78.5; IR (NaCl) 3383 cm^{-1}; HRMS (CI, NH_3, 140 eV) m/z 252.1743 ([M]$^+$, 5.4), calcd for $C_{15}H_{24}O_3$ 252.1725. The stereochemistry of C9 and C10 were assigned by a DNOE experiment: H9/10 → H2/3.

(1*R,5*S**,6*S**,8*S**,9*S**,10*R**)-10-*tert*-Butoxy-5,8-dimethyltricyclo[6.2.1.0^{3,9}]undec-2-en-6-ol (25a) and (1*S**,3*S**,6*R**,7*S**,9*S**,10*S**)-10-Hydroxy-1,9-dimethyltricyclo-[5.4.0.0^{3,7}]undecan-5-one (26a).** A solution of **20a** (87.3 mg, 0.33 mmol) and Zeise's dimer ($[Pt(C_2H_4)Cl_2]_2$, 9.7 mg, 0.017 mmol) in toluene (3.3 mL) was heated under Ar at 80 °C for 48 h. After evaporation of the solvent in vacuo, the crude product was purified by flash chromatography (hexanes/EtOAc/CH_2Cl_2, 3:1:0.1) to give **25a** (R_f = 0.6, 40.4 mg, 46%) and **26a** (R_f = 0.2, 23.7 mg, 35%) as white solids. **25a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (d, J = 6.8 Hz, 3H, *H*12), 1.14 (s, overlapped with H11$_{endo}$, 9H, OC(CH_3)$_3$), 1.10−1.15 (m, overlapped with *t*-Bu, *H*11$_{endo}$), 1.38 (s, 3H, *H*13), 1.45 (dd, J = 14.2, 9.9 Hz, *H*7), 1.61−1.83 (m, 5H, *H*5/4/7′/11$_{exo}$, O*H*), 2.06 (br s, *H*9), 2.34 (br s, *H*1), 2.47 (ddd, J = 12.8, 7.0, 1.0 Hz, *H*4′), 3.25 (br dd, J = 9.9, 9.0 Hz, *H*6), 3.38 (br s, *H*10), 5.56 (br s, *H*2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.7 (*C*12), 28.3 (3C, OC(CH_3)$_3$), 29.7 (*C*13), 36.9 (*C*4), 38.5 (*C*5), 39.5 (*C*8), 40.5 (*C*11), 47.2 (*C*1), 54.7 (*C*7), 57.1 (*C*9), 72.2 (*C*6), 73.3 (O*C*-(CH_3)$_3$), 84.5 (*C*10), 128.8 (*C*2), 144.8 (*C*3); IR (NaCl) 3366 cm^{-1}; HRMS (CI, CH_4, 140 eV) m/z 264.2107 ([M]$^+$, 2.1), calcd for $C_{17}H_{28}O_2$ 264.2089. The stereochemistry of C6 was further confirmed by NOESY and DNOE experiments: H6 ↔ H11$_{endo}$, H6 → H2 and H11$_{endo}$. **26a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (d, J = 6.7 Hz, 3H, *H*13), 1.02 (s, 3H, *H*12), 1.07 (ddd, J = 15.5, 12.1, 3.4 Hz, *H*8), 1.18 (dd, J = 13.0, 1.4 Hz, *H*2), 1.39 (dd, J = 13.7, 10.4 Hz, partially overlapped with OH, *H*11), 1.38 (d, J = 5.2 Hz, overlapped with H11, O*H*), 1.47−1.55 (m, partially overlapped with H_2O, *H*9), 1.82 (br d, J = 18.0 Hz, *H*4), 1.91−1.99 (m, 2H, *H*8′/2′), 2.06 (dd, J = 13.7, 5.2 Hz, partially overlapped with H4′, *H*11′), 2.08 (ddd, J = 18.0, 4.9, 2.4 Hz, partially overlapped with H11′, *H*4′), 2.19−2.22 (m, 2H, *H*6/7), 2.28−2.30 (br m, *H*3), 3.32 (dddd, J = 10.4, 10.4, 5.2, 5.2 Hz, *H*10); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.5 (*C*13), 30.4 (*C*12), 34.1 (*C*8), 37.1 (*C*2), 37.4 (*C*9), 37.5 (*C*1), 42.3 (*C*3), 45.3 (*C*4), 46.6 (*C*7), 50.7 (*C*11), 63.1 (*C*6), 77.3 (*C*10), 215.9 (*C*5); IR (NaCl) 3453, 1740 cm^{-1}; HRMS (CI, NH_3, 140 eV) m/z 209.1561 ([M + H]$^+$, 1.2), calcd for $C_{13}H_{21}O_2$ 209.1541. The regiochemistry was assigned by long range ($^3J_{H,C}$) heteronuclear couplings observed in an HMBC experiment: H2/C12, this coupling between one of the methylene protons on the norbornyl skeleton and the CH_3 carbon ruled out the other regioisomer.

(1*R,5*S**,6*S**,8*S**,9*S**,10*R**)-10-*tert*-Butoxy-5-methyltricyclo[6.2.1.0^{3,9}]undec-2-en-6-ol(27a)and(1*S**,3*S**,6*R**,7*S**,9*S**,-10*S**)-10-Hydroxy-9-methyltricyclo[5.4.0.0^{3,7}]undecan-5-one (28a).** A solution of **21a** (84.0 mg, 0.3 mmol) and Zeise's dimer ($[Pt(C_2H_4)Cl_2]_2$, 19.8 mg, 0.03 mmol) in toluene (3.4 mL) was heated at 80 °C under Ar for 13 h. After evaporation of the solvent in vacuo, the crude product was purified by flash chromatography (hexanes/EtOAc/CH_2Cl_2, 3:1:0.1) to give **27a** (R_f = 0.5, 53.2 mg, 64%) and **28a** (R_f = 0.1, 15.6 mg, 24%) as white solids, along with recovered **21a** (2.5 mg, 3% recovery). **27a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.69 (ddd, J = 11.1, 4.3, 1.1 Hz, *H*11$_{endo}$), 0.98 (d, J = 6.4 Hz, 3H, CH_3), 1.12 (s, 9H, OC(CH_3)$_3$), 1.61−1.71 (m, 2H, *H*7/5), 1.74 (dd, J = 10.4, 10.4 Hz, *H*4), 1.92 (ddd, J = 13.9, 2.5, 2.5 Hz, *H*7′), 2.07 (ddd, J = 11.1, 9.0, 3.8 Hz, *H*11$_{exo}$), 2.29−2.32 (m, 2H, *H*1/9), 2.43−2.53 (m, 2H, *H*4′/8), 3.19 (ddd, J = 10.7, 8.5, 2.5 Hz, *H*6), 3.36 (br s, *H*10), 5.56 (dd, J = 2.5, 2.5 Hz, *H*2), O*H* not observed; ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.2 (*C*12), 28.5 (3C, OC(CH_3)$_3$), 31.1 (*C*8), 31.9 (*C*11), 37.5 (*C*4), 39.3 (*C*5), 43.5 (*C*7), 46.3 (*C*1), 51.7 (*C*9), 70.8 (*C*6), 73.1 (O*C*(CH_3)$_3$), 82.5 (*C*10), 129.1 (*C*2), 142.4 (*C*3); IR (NaCl) 3252 cm^{-1}; HRMS (CI, NH_3, 140 eV) m/z 250.1957 ([M]$^+$, 2.3), calcd for $C_{16}H_{26}O_2$ 250.1933. The stereochemistry of C6 (C5) and C10 were confirmed by a NOESY experiment: H2 ↔ H10, H11$_{endo}$ ↔ H6. **28a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (d, J = 6.7 Hz, 3H, CH_3), 1.04 (ddd, J = 15.3, 11.9, 3.4 Hz, *H*8), 1.44−1.56 (m, 4H, O*H* and *H*11/9/2), 1.67 (dddd, J = 13.1, 9.2, 4.5, 2.9 Hz, *H*2′), 1.85 (br d, J = 18.0 Hz, *H*4), 1.92 (ddd, J = 15.3, 11.3, 2.4 Hz, *H*8′), 2.04 (ddd, J = 18.0, 4.4, 2.9 Hz, *H*4′), 2.09−2.15 (m, *H*1), 2.19 (ddd, J = 13.4, 5.5, 5.2 Hz, overlapped with H7, *H*11′), 2.19−2.24 (br m, overlapped with *H*11′, *H*7), 2.33 (br dd, J = 4.5, 4.4 Hz, *H*3), 2.39 (br s, *H*6), 3.36 (br m, *H*10); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.6 (*C*H_3), 29.7 (*C*2), 33.4 (*C*1), 34.0 (*C*8), 38.2 (*C*9), 40.5 (*C*11), 42.1 (*C*3), 44.9 (*C*7), 45.6 (*C*4), 58.4 (*C*6), 76.1 (*C*10), 217.0 (*C*5); IR (NaCl) 3444, 1743 cm^{-1}; HRMS (CI, NH_3, 140 eV) m/z 194.1295 ([M]$^+$, 31.4), calcd for $C_{12}H_{18}O_2$ 194.1307. The regiochemistry was assigned by long range ($^3J_{H,C}$) heteronuclear couplings observed in an HMBC experiment between H2 and C11, which ruled out the possibility of the other regioisomer.

(1*R,5*S**,6*S**,8*S**,9*S**,10*R**)-10-*tert*-Butoxy-6-*tert*-butyldimethylsiloxy-5,8-dimethyltricyclo[6.2.1.0^{3,9}]undec-2-ene (25b) and (1*S**,3*S**,6*R**,7*S**,9*S**,10*S**)-10-*tert*-Butyldimethylsiloxy-1,9-dimethyltricyclo[5.4.0.0^{3,7}]undecan-5-one (26b).** A solution of **22** (39.4 mg, 0.1 mmol) and Zeise's dimer ($[Pt(C_2H_4)Cl_2]_2$, 15.3 mg, 0.026 mmol) in $CDCl_3$ (0.5 mL) was stirred under Ar at room temperature for 22 h. After evaporation of the solvent in vacuo, the crude product was purified by flash chromatography (hexanes/EtOAc/Et_3N, 20:1:0.1) to give **25b** (R_f = 0.5, 24.2 mg, 64%) as a colorless liquid and **26b** (R_f = 0.2, 10.4 mg, 31%) as a white solid. Silyl ether **25b** was also prepared from **25a**: to solution of **25a** (12.0 mg, 0.045 mmol) in a DMF (0.5 mL) at room temperature were added *tert*-butyldimethylchlorosilane (8.2 mg, 0.05 mmol) and imidazole (7.7 mg, 0.11 mmol) with stirring, and the reaction mixture was kept at room temperature for 3 h. After evaporation of the solvent in vacuo, the crude product was purified by flash chromatography (hexanes/EtOAc/Et_3N, 20:1:0.1) to give **25b** (16.5 mg, 96%). **25b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.01 (s, 3H, SiCH_3), 0.01 (s, 3H, SiCH_3), 0.83 (d, J = 6.4 Hz, 3H, *H*12), 0.88 (s, 9H, SiC(CH_3)$_3$), 1.05 (br d, J = 11.3 Hz, *H*11$_{endo}$), 1.14 (s, 9H, OC(CH_3)$_3$), 1.36 (s, 3H, *H*13), 1.47 (dd, J = 14.7, 9.3 Hz, *H*7), 1.60 (dd, J = 14.7, 2.0 Hz, *H*7′), 1.69−1.74 (m, 2H, *H*4/5), 1.79 (dd, J = 11.3, 3.4 Hz, *H*11$_{exo}$), 2.16 (br s, *H*9),

2.34 (br s, *H*1), 2.45−2.52 (m, *H*4′), 3.34 (ddd, J = 9.3, 7.5, 2.0 Hz, partially overlapped with H10, *H*6), 3.37 (br s, partially overlapped with H6, *H*10), 5.52−5.54 (m, *H*2); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.8 (Si*C*H$_3$), −4.4 (Si*C*′H$_3$), 18.1 (Si*C*(CH$_3$)$_3$), 18.9 (*C*12), 26.0 (3C, SiC(*C*H$_3$)$_3$), 28.3 (3C, OC(*C*H$_3$)$_3$), 29.6 (*C*13), 36.3 (*C*4), 38.6 (*C*5), 39.3 (*C*8), 41.3 (*C*11), 47.1 (*C*1), 52.8 (*C*7), 57.6 (*C*9), 73.2 (O*C*(CH$_3$)$_3$), 73.4 (*C*6), 84.4 (*C*10), 127.6 (*C*2), 145.5 (*C*3); HRMS (CI, NH_3, 140 eV) m/z 378.2930 ([M]$^+$, 2.1), calcd for $C_{23}H_{42}O_2Si$ 378.2954. The stereochemistry of H6 (C5) and C10 were further confirmed by a NOESY experiment: H6 ↔ H11$_{endo}$, H9 ↔ SiC(CH$_3$)$_3$, and H2 ↔ H10. **26b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.031 (s, 3H, SiC*H*$_3$), 0.034 (s, 3H, SiC*H*′$_3$), 0.87 (s, 9H, SiC(C*H*$_3$)$_3$), 0.89 (d, J = 6.6 Hz, 3H, *H*13), 0.99 (s, partially overlapped with H8, 3H, *H*12), 1.04 (ddd, J = 15.2, 11.9, 3.3 Hz, partially overlapped with H12, *H*8), 1.15 (dd, J = 12.8, 1.5 Hz, *H*2), 1.42 (dd, J = 13.9, 10.2 Hz, *H*11), 1.46−1.57 (m, *H*9), 1.81 (d, J = 17.9 Hz, *H*4), 1.87 (dd, J = 13.9, 5.1 Hz, partially overlapped with H8′, *H*11′), 1.89−1.96 (m, partially overlapped with H11′, 2H, *H*8′/2′), 2.07 (dddd, J = 17.9, 5.0, 2.5, 0.8 Hz, *H*4′), 2.19 (br d, J = 11.9 Hz, partially overlapped with H6, *H*7), 2.21 (br s, partially overlapped with H7, *H*6), 2.25−2.29 (m, *H*3), 3.28 (ddd, J = 10.2, 10.2, 5.1 Hz, *H*10); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.6 (Si*C*H$_3$), −4.2 (Si*C*′H$_3$), 18.1 (Si*C*(CH$_3$)$_3$), 20.6 (*C*13), 25.9 (3C, SiC(*C*H$_3$)$_3$), 30.6 (*C*12), 34.1 (*C*8), 37.1 (*C*2), 37.5 (*C*1), 37.8 (*C*9), 42.2 (*C*3), 45.4 (*C*4), 46.7 (*C*7), 51.3 (*C*11), 63.1 (*C*6), 77.3 (*C*10), 216.2 (*C*5); IR (NaCl) 1749 cm^{-1}; HRMS (CI, NH_3, 140 eV) m/z 322.2297 ([M]$^+$, 0.5), calcd for $C_{19}H_{34}O_2Si$ 322.2328. The regiochemistry was confirmed by long range ($^3J_{H,C}$) heteronuclear couplings observed in the HMBC spectrum: H2/C12, coupling between H2, which was assigned as one of the methylene groups in the norbornyl skeleton from the ^{1}H,^{1}H-COSY spectrum, to the methyl carbon (C12).

(1*R,5*S**,6*S**,8*S**,9*S**,10*R**)-10-*tert*-Butoxy-6-*tert*-butyldimethylsiloxy-5-methyltricyclo[6.2.1.0^{3,9}]undec-2-ene (27b) and (1*S**,3*S**,6*R**,7*S**,9*S**,10*S**)-10-*tert*-Butyldimethylsiloxy-9-methyltricyclo-[5.4.0.0^{3,7}]undecan-5-one (28b).** A solution of **23** (76.8 mg, 0.21 mmol) and Zeise's dimer ([Pt(C$_2$H$_4$)Cl$_2$]$_2$, 31.0 mg, 0.053 mmol) in $CDCl_3$ (0.4 mL) was stirred under Ar at room temperature for 19 h. After evaporation of the solvent in vacuo, the crude product was purified by flash chromatography (hexanes/EtOAc/Et$_3$N, 20:1:0.1) to give **27b** (R_f = 0.4, 28.3 mg, 37%) as a colorless liquid, **28b** (R_f = 0.2, 23.4 mg, 36%) as a white solid, and recovered **23** (7.9 mg, 10%). Silyl ether **27b** was also prepared from **27a**: to solution of **27a** (8.9 mg, 0.036 mmol) in a DMF (0.4 mL) at room temperature were added *tert*-butyldimethylchlorosilane (6.4 mg, 0.04 mmol) and imidazole (6.1 mg, 0.09 mmol) with stirring, and the reaction mixture was kept at room temperature for 3 h. After evaporation of the solvent in vacuo, the crude product was purified by flash chromatography (hexanes/EtOAc/Et$_3$N, 20:1:0.1) to give **27b** (11.9 mg, 92%). **27b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.03 (s, 3H, SiC*H*$_3$), −0.02 (s, 3H, SiC*H*$_3$), 0.65 (ddd, J = 11.0, 4.3, 1.2 Hz, *H*11$_{endo}$), 0.85 (s, 9H, SiC(C*H*$_3$)$_3$), 0.87 (d, J = 6.4 Hz, 3H, *H*12), 1.12 (s, 9H, OC(C*H*$_3$)$_3$), 1.63−1.72 (m, 3H, *H*4/5/7), 1.77 (ddd, J = 14.4, 2.4, 2.4 Hz, *H*7′), 2.07 (ddd, J = 11.0, 8.9, 3.7 Hz, *H*11$_{exo}$), 2.29 (br s, *H*1), 2.34 (br s, *H*9), 2.41−2.45 (m, 2H, *H*4′/8), 3.20 (ddd, J = 10.1, 7.9, 2.4 Hz, *H*6), 3.35 (br s, *H*10), 5.55 (br s, *H*2); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.7 (Si*C*H$_3$), −4.5 (Si*C*′H$_3$), 18.2 (Si*C*(CH$_3$)$_3$), 19.1 (*C*12), 25.9 (3C, SiC(*C*H$_3$)$_3$), 28.5 (3C, OC(*C*H$_3$)$_3$), 31.0 (*C*8), 32.2 (*C*11), 37.4 (*C*4), 39.8 (*C*5), 43.5 (*C*7), 46.3 (*C*1), 51.9 (*C*9), 71.4 (*C*6), 73.0 (O*C*(CH$_3$)$_3$), 82.5 (*C*10), 128.5 (*C*2), 143.1 (*C*3); HRMS (CI, CH_4, 140 eV) m/z 365.2864 ([M + H]$^+$, 1.0), calcd for $C_{22}H_{41}O_2Si$ 365.2876. The stereochemistry of C6 (C5) and C10 were further confirmed by a NOESY experiment: H11$_{endo}$ ↔ H6, and H2 ↔ H10. **28b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.02 (s, 6H, Si(C*H*$_3$)$_2$), 0.86 (s, 9H, SiC(C*H*$_3$)$_3$), 0.89 (d, J = 6.7 Hz, 3H, *H*12), 1.00 (ddd, J = 15.3, 11.9, 3.4 Hz, *H*8), 1.48−1.56 (m, 3H, *H*2/9/11), 1.65 (dddd, J = 12.9, 4.6, 3.6, 2.8 Hz, *H*2′), 1.84 (br d, J = 17.7 Hz, *H*4), 1.91 (ddd, J = 15.3, 11.3, 2.1 Hz, *H*8′), 2.00−2.08 (m, 3H, *H*4′/11/1), 2.20 (br d, J = 11.9 Hz, *H*7), 2.30−2.32 (br m, *H*3), 2.40 (br s, *H*6), 3.33 (ddd, J = 10.1, 10.1, 5.2 Hz, *H*10); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.7 (Si*C*H$_3$), −4.2 (Si*C*′H$_3$), 18.3 (Si*C*(CH$_3$)$_3$), 20.6 (*C*12), 25.9 (3C, SiC(*C*H$_3$)$_3$), 29.8 (*C*2), 33.5 (*C*1), 33.9 (*C*8), 38.6 (*C*9), 41.0 (*C*11), 42.0 (*C*3), 44.9 (*C*7), 45.7 (*C*4), 58.4 (*C*6), 76.8 (*C*10), 217.2 (*C*5); IR (NaCl) 1746 cm^{-1}; HRMS (CI, NH_3, 140 eV) m/z 308.2146 ([M]$^+$, 6.6), calcd for $C_{18}H_{32}O_2Si$ 308.5356. The $^3J_{H,C}$ correlation observed in HMBC spectrum between H2, which was assigned as one of the methylene groups in the norbornyl skeleton from the ^{1}H,^{1}H-COSY spectrum, and C11 confirmed the assignment of the regiochemistry.

***endo*-(1*R**,5*S**,6*R**,8*S**,9*S**,10*R**)-10-*tert*-Butoxytricyclo-[6.2.1.0^{3,9}]undec-2-ene-5,6-diol (29a).** To a solution of **24a** (17.5 mg, 0.07 mmol) in toluene (1.4 mL) under Ar was added Zeise's dimer ([Pt(C$_2$H$_4$)Cl$_2$]$_2$, 4.1 mg, 6.9 μmol), and the reaction mixture was heated to 80 °C with stirring for 15 h. After evaporation of the solvent in vacuo, the crude product was purified by flash chromatography (hexanes/EtOAc/CH_2Cl_2, 1:2:0.1) to give **29a** (R_f = 0.3, 10.5 mg, 60%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.72 (br dd, J = 11.4, 3.0 Hz, *H*11$_{endo}$), 1.12 (s, 9H, OC(C*H*$_3$)$_3$), 1.62 (ddd, J = 14.8, 9.6, 5.4 Hz, partially overlapped with 6-OH, *H*7), 1.67 (br s, partially overlapped with H7, 6-O*H*), 1.74 (br d, J = 6.6 Hz, 5-O*H*), 1.87 (ddd, J = 14.8, 9.6, 2.5 Hz, *H*7′), 2.24 (ddd, J = 11.4, 8.4, 3.4 Hz, partially overlapped with H9, *H*11$_{exo}$), 2.26−2.28 (m, partially overlapped with H11′ and H4, *H*9), 2.31 (dd, J = 13.7, 4.1 Hz, partially overlapped with H9, *H*4), 2.42 (br s, *H*1), 2.46−2.54 (m, partially overlapped with H4′, *H*8), 2.56 (br dd, J = 13.7, 4.4 Hz, partially overlapped with H8, *H*4′), 3.39 (br s, *H*10), 3.81 (br s, *H*6), 3.97−3.98 (br m, *H*5), 5.74 (br s, *H*2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.5 (3C, OC(C*H*$_3$)$_3$), 29.3 (*C*8), 35.3 (*C*11), 35.6 (*C*7), 36.1 (*C*4), 46.9 (*C*1), 53.5 (*C*9), 72.5 (*C*5), 73.3 (O*C*(CH$_3$)$_3$), 74.3 (*C*6), 83.1 (*C*10), 128.8 (*C*2), 140.3 (*C*3); IR (NaCl) 3397 cm^{-1}; HRMS (CI, CH_4, 140 eV) m/z 252.1722 ([M]$^+$, 2.1), calcd for $C_{15}H_{24}O_3$ 252.1725. The stereochemistry C6 and C10 were confirmed by a NOESY experiment: H6 ↔ H9 and H2 ↔ H10.

***exo*-(1*R**,5*R**,6*S**,8*S**,9*S**,10*R**)-10-*tert*-Butoxytricyclo-[6.2.1.0^{3,9}]undec-2-ene-5,6-diol (29b) and (1*S**,3*S**,6*R**,7*S**,9*R**,-10*S**)-9,10-Dihydroxytricyclo[5.4.0.0^{3,7}]undecan-5-one (30).** To a solution of **24b** (16.3 mg, 0.06 mmol) in toluene (1.3 mL) was added Zeise's dimer ([Pt(C$_2$H$_4$)Cl$_2$]$_2$, 3.8 mg, 6.5 μmol) under Ar, and the mixture was heated to 80 °C with stirring for 17 h. After evaporation of the solvent in vacuo, the crude product was purified by flash chromatography (hexanes/EtOAc/CH_2Cl_2, 1:2:0.1) to give **29b** (R_f = 0.4, 11.0 mg, 68% yield) and **30** (R_f = 0.2, 2.0 mg, 16% yield) as white solids. **29b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.69 (ddd, J = 11.2, 4.1, 1.1 Hz, *H*11$_{endo}$), 1.12 (s, 9H, OC(C*H*$_3$)$_3$), 1.41 (br d, J = 5.0 Hz, 6-O*H*), 1.52 (ddd, J = 14.2, 3.1, 3.1 Hz, *H*7), 1.82 (br d, J = 3.4 Hz, 5-O*H*), 2.07 (ddd, J = 11.2, 8.8, 3.7 Hz, *H*11$_{exo}$), 2.19 (ddd, J = 14.2, 11.0, 5.9 Hz, *H*7′), 2.31 (br s, partially overlapped with H4, *H*1), 2.34 (ddd, J = 14.0, 1.8, 1.8 Hz, partially overlapped with H1, *H*4), 2.45−2.54 (m, partially overlapped with H4′, 2H, *H*9/8), 2.48 (br dd, J = 14.0, 6.7 Hz, partially overlapped with H8/9, *H*4′), 3.34 (br s, *H*10), 3.61 (br ddd, J = 11.0, 5.0, 3.1 Hz, *H*6), 4.04−4 0.06 (br m, *H*5), 5.61 (br s, *H*2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.5 (3C, OC(C*H*$_3$)$_3$), 30.9 (*C*8), 31.4 (*C*11), 34.6 (*C*7), 36.3 (*C*4), 46.1 (*C*1), 53.0 (*C*9), 71.0 (*C*6), 73.1 (O*C*(CH$_3$)$_3$), 74.3 (*C*5), 83.1 (*C*10), 129.6 (*C*2), 140.9 (*C*3); IR (NaCl) 3375 cm^{-1}; HRMS (CI, CH_4, 140 eV) m/z 252.1707 ([M]$^+$, 9.6), calcd for $C_{15}H_{24}O_3$ 252.1725. The stereochemistry of C2, C5 and C6 were further confirmed by a NOESY experiment: H11$_{endo}$ ↔ H6, H2 ↔ H10. **30**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.51 (ddd, J = 15.7, 2.5, 2.5 Hz, *H*8), 1.59 (br d, J = 13.3 Hz, partially overlapped with H2′, *H*2), 1.64 (dddd, J = 13.3, 5.5, 4.1, 2.8 Hz, partially overlapped with H2, *H*2′), 1.71 (d, J = 5.2, 10-O*H*), 1.82 (br d, J = 17.9 Hz, partially overlapped with H11, *H*4), 1.86 (ddd, J = 14.0, 8.8, 3.6 Hz, partially overlapped with H4, *H*11), 1.91−1.97 (m, 2H, 9-O*H*/*H*11′), 2.05 (br ddd, J = 17.9, 5.1, 2.8 Hz, partially overlapped with H1/7, *H*4′), 2.07−2.14 (m, 2H, *H*1/7), 2.29 (ddd, J = 15.7, 9.6, 6.9 Hz, *H*8′), 2.40 (br dd, J = 4.1, 4.1 Hz, *H*3), 2.89 (br s, *H*6), 3.85−3.91 (br m, *H*10), 4.08−4.10 (br m, *H*9); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.8 (*C*2), 31.2 (*C*8), 33.0 (*C*1), 34.9 (*C*11), 42.1 (*C*3), 43.3 (*C*7), 45.7 (*C*4), 58.1 (*C*6), 73.1 (*C*10), 73.5 (*C*9), 217.4 (*C*5); IR (NaCl) 3415, 1738 cm^{-1}; HRMS (CI, CH_4, 140 eV) m/z 196.1112 ([M]$^+$, 16.5), calcd for $C_{11}H_{16}O_3$ 196.1099.

(1*R,4*S**,5*S**,7*S**,9*S**,10*R**)-10-*tert*-Butoxy-5-*tert*-butyldimethylsiloxy-4-methyl-2-oxobicyclo[5.3.0]decane-9-carbaldehyde (31).** Into a solution of **27b** (28.3 mg, 0.077 mmol) in CH_2Cl_2 (2 mL) at −78 °C was bubbled O_3 until the solution became light blue, and then Me_2S (0.1 mL) was added to quench the reaction. After evaporation of the solvent in vacuo, flash chromatography (hexanes/EtOAc/Et_3N, 5:1:0.1) of the crude product gave pure **31** (R_f = 0.6, 14.0 mg, 46%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.01 (s, 3H, SiCH_3), 0.03 (s, 3H, SiCH'_3), 0.88 (s, 9H, SiC(CH_3)$_3$), 1.01 (d, J = 6.1 Hz, 3H, CH_3), 1.08 (s, 9H, OC(CH_3)$_3$), 1.26 (ddd, J = 15.4, 12.4, 3.1 Hz, overlapped with H8, *H*6), 1.23 (ddd, J = 12.4, 12.4, 12.4 Hz, overlapped with H6, *H*8), 1.69 (ddd, J = 15.4, 3.1, 3.1 Hz, *H*6′), 1.78 (ddd, J = 12.4, 6.2, 6.2 Hz, *H*8′), 2.09 (dd, J = 16.2, 11.9 Hz, partially overlapped with H4, *H*3), 2.12−2.20 (m, partially overlapped with H3, *H*4), 2.30 (dd, J = 16.2, 2.6 Hz, *H*3′), 2.74 (dddd, J = 12.4, 8.6, 6.2, 3.5 Hz, *H*9), 2.87 (ddddd, J = 12.4, 12.4, 12.4, 6.2, 3.1 Hz, *H*7), 3.35 (dd, J = 12.4, 4.3 Hz, *H*1), 3.47 (ddd, J = 7.4, 3.1, 3.1 Hz, *H*5), 4.95 (dd, J = 8.6, 4.3 Hz, *H*10), 9.66 (d, J = 3.5 Hz, C*H*O); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.8 (Si*C*H$_3$), −4.4 (Si*C*′H$_3$), 18.0 (Si*C*(CH$_3$)$_3$), 19.0 (*C*H$_3$), 25.8 (3C, SiC(*C*H$_3$)$_3$), 28.4 (3C, OC(*C*H$_3$)$_3$), 31.9 (*C*6), 33.7 (*C*7), 36.2 (*C*4), 38.2 (*C*8), 47.6 (*C*3), 59.6 (*C*9), 61.3 (*C*1), 72.4 (*C*10), 74.3 (O*C*(CH$_3$)$_3$), 74.9 (*C*5), 202.7 (*C*HO), 210.6 (*C*2); IR (NaCl) 1728, 1706 cm^{-1}; HRMS (CI, NH_3, 140 eV) m/z 396.2698 ([M]$^+$, 0.12), calcd for $C_{22}H_{40}O_4Si$ 396.2696. The regiochemistry of the Zeise's dimer opening was further confirmed by long range ($^3J_{H,C}$) heteronuclear couplings observed in the HMBC spectrum: H3/C2, H4/C2 and H3/*C*H$_3$. The stereochemistry of C4 (C5) was confirmed by a NOESY experiment: H1 ↔ H4, H7 ↔ H9.

(1*S,6*S**,7*S**,9*S**,10*R**,11*R**)-11-*tert*-Butoxy-7-*tert*-butyldimethylsiloxy-4-methoxy-6-methyl-3-oxatricyclo-[6.2.1.0^{3,9}]dodecan-2-ol (32).** Into a solution of **27b** (8.2 mg, 0.02 mmol) in MeOH (2.3 mL) at −78 °C was bubbled O_3 until the solution became blue, and then Me_2S (1 mL) was added to quench the reaction. After evaporation of the solvent in vacuo, flash chromatography (hexanes/EtOAc/Et_3N, 5:1:0.1) gave **32** (R_f = 0.5) as a colorless liquid which proved to be unstable: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.02 (s, 6H), 0.87 (s, 9H), 0.97 (d, J = 6.8 Hz, 3H), 1.17 (s, 9H), 1.17−1.23 (m, 1H), 1.50−1.57 (m, overlapped with H_2O, 1H), 1.66−1.86 (m, 3H), 2.05 (ddd, J = 13.4, 10.2, 10.2 Hz, 1H), 2.36 (br d, J = 7.3 Hz, 1H), 2.39−2.44 (br m, 1H), 2.67−2.78 (br m, 1H), 2.94 (br d, J = 5.0 Hz, 1H), 3.26 (s, 3H), 3.50−3.53 (m, 1H), 4.44 (s, 1H), 5.24 (br dd, J = 5.0, 5.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.7, −4.4, 17.9, 22.1, 25.8 (3C), 28.3 (3C), 29.5, 32.1, 36.2, 36.3, 37.1, 48.3, 50.1, 56.2, 74.2, 75.4, 76.9, 97.1, 107.4.

(1*R,4*S**,5*S**,7*S**,9*S**,10*R**)-10-*tert*-Butoxy-5-*tert*-butyldimethylsiloxy-4-methyl-9-(2,5-dioxacyclopentyl)-bicyclo[5.3.0]decan-2-one (33).** To a solution of crude **32** (prior to flash chromatography from above) in benzene (1.1 mL) were added sequentially ethylene glycol (14 mg, 0.2 mmol), trimethylorthoformate (4.9 μL, 0.045 mmol), and *p*-TsOH (a few crystals). The reaction mixture was then heated to 80 °C for 30 min. After evaporation of the solvent in vacuo, flash chromatography (hexanes/EtOAc/Et_3N = 5:1:0.1) gave pure **33** (R_f = 0.6, 9.4 mg, 95%) as a colorless liquid. Compound **33** was also made from **31**. To a solution of **31** (4.8 mg, 0.012 mmol) in benzene (0.6 mL) were added ethylene glycol (1 drop), trimethylorthoformate (2.6 μL, 0.024 mmol), and *p*-TsOH (a few crystals) under Ar. After the mixture was refluxed for 1 h with stirring and then cooled to room temperature, the solvent was removed in vacuo. Flash chromatography as above gave pure **33** (5.3 mg, 99%) as a colorless liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.00 (s, 3H, SiCH_3), 0.02 (s, 3H, SiCH_3), 0.87 (s, 9H, SiC(CH_3)$_3$), 1.00 (d, J = 6.3 Hz, 3H, CH_3), 0.99−1.05 (m, overlapped with CH_3, *H*8), 1.08 (s, 9H, OC(CH_3)$_3$), 1.19−1.27 (m, *H*6), 1.61−1.69 (m, 2H, *H*8′/6′), 2.03−2.25 (m, 4H, *H*3/4/9/3′), 2.79 (ddddd, J = 12.2, 12.2, 12.2, 6.1, 3.1 Hz, *H*7), 3.28 (dd, J = 12.2, 4.4 Hz, *H*1), 3.44 (ddd, J = 7.7, 3.0, 3.0 Hz, *H*5), 3.80−3.96 (m, 4H, OCH_2CH_2O), 4.64 (dd, J = 9.4, 4.4 Hz, *H*10), 4.96 (d, J = 3.3 Hz, C*H*(OCH$_2$)$_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.8 (Si*C*H$_3$), −4.4 (Si*C*′H$_3$), 17.9 (Si*C*(CH$_3$)$_3$), 19.2 (*C*H$_3$), 25.8 (3C, SiC(*C*H$_3$)$_3$), 28.4 (3C, OC(*C*H$_3$)$_3$), 30.0 (*C*8), 33.2 (*C*7), 36.2 (*C*4), 38.4 (*C*6), 48.1 (*C*3), 49.8 (*C*9), 61.5 (*C*1), 65.1 (O*C*H$_2$C′H$_2$O), 65.2 (OCH$_2$*C*′H$_2$O), 72.6 (*C*10), 73.7 (O*C*(CH$_3$)$_3$), 75.3 (*C*5), 103.8 (*C*(OCH$_2$)$_2$), 211.2 (*C*2); IR (NaCl) 1706 cm^{-1}; HRMS (CI, CH_4, 140 eV) m/z 441.3076 ([M + H]$^+$, 1.0), calcd for $C_{24}H_{45}O_5Si$ 441.3036. The stereochemistry of C9 was further confirmed by a NOESY experiment: C*H*(OCH$_2$)$_2$ ↔ H10.

Methyl (1*R,4*S**,5*S**,7*S**,9*S**,10*R**)-10-*tert*-Butoxy-5-*tert*-butyldimethylsiloxy-4-methyl-2-oxobicyclo[5.3.0]-decane-9-carboxylate (34).** To a solution of **27b** (9.6 mg, 0.03 mmol) in CH_2Cl_2 (2.6 mL) was added NaOH in MeOH solution (0.1 mL, 2.5 N), and then the solution was cooled to −78 °C and O_3 was bubbled into this solution until the color changed from bright yellow to light blue. To the reaction mixture were added Et_2O (2 mL) and H_2O (2 mL), the reaction mixture becoming colorless. The solution was then allowed to warm to room temperature and neutralized with aqueous HCl (10%), and then the aqueous layer was separated and extracted with Et_2O (3 × 10 mL), and the combined organic layers were dried ($MgSO_4$). The solvent was evaporated in vacuo, and flash chromatography (hexanes/EtOAc/Et_3N, 5:1:0.1) gave pure **34** (R_f = 0.7, 4.1 mg, 38%) as a colorless liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.00 (s, 3H, SiCH_3), 0.02 (s, 3H, SiCH_3), 0.87 (s, 9H, SiC(CH_3)$_3$), 1.00 (d, J = 6.1 Hz, 3H, CH_3), 1.05 (s, 9H, OC(CH_3)$_3$), 1.22−1.36 (m, 2H, *H*6/8), 1.64 (ddd, J = 15.3, 3.1, 3.1 Hz, *H*6′), 1.86 (ddd, J = 12.4, 6.2, 6.2 Hz, *H*8′), 2.08 (dd, J = 15.9, 11.9 Hz, *H*3), 2.08−2.18 (m, partially overlapped with H3, *H*4), 2.28 (dd, J = 15.9, 2.4 Hz, *H*3′), 2.73 (ddd, J = 13.1, 8.7, 6.2 Hz, *H*9), 2.82 (ddddd, J = 12.4, 12.4, 12.4, 6.2, 3.1 Hz, *H*7), 3.26 (dd, J = 12.4, 4.9 Hz, *H*1), 3.45 (ddd, J = 7.6, 3.1, 3.1 Hz, *H*5), 3.66 (s, 3H, COOCH_3), 4.94 (dd, J = 8.7, 4.9 Hz, *H*10); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.8, −4.4, 17.9, 19.0, 25.8 (3C), 28.3 (3C), 33.6, 35.1, 36.1, 38.1, 47.7, 51.6, 52.2, 61.1, 73.9, 74.9, 75.0, 174.5, 210.2; IR (NaCl) 1739, 1707 cm^{-1}; HRMS (CI, CH_4, 140 eV) m/z 427.2893 ([M + H]$^+$, 0.5), calcd for $C_{23}H_{43}O_5Si$ 427.2880. The stereochemistry was confirmed by DNOE and NOESY experiments: H1 → H9, H4 and H7; H7 ↔ H4.

(1*R,4*S**,5*S**,7*S**,9*S**,10*R**)-10-*tert*-Butoxy-5-*tert*-butyldimethylsiloxy-4,7-dimethyl-2-oxobicyclo[5.3.0]decane-9-carbaldehyde (35).** Into a solution of **25b** (16.5 mg, 0.04 mmol) in CH_2Cl_2 (4.4 mL) at −78 °C was bubbled O_3 until it became light blue, and then Me_2S (5 drops) was added to quench the reaction. After evaporation of the solvent in vacuo, flash chromatography (hexanes/EtOAc/Et_3N, 5:1:0.1) of the crude product gave pure **35** (R_f = 0.6, 10.1 mg, 56%) as a colorless liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.13 (s, 3H, SiCH_3), −0.12 (s, 3H, SiCH_3), 0.89 (s, 9H, SiC(CH_3)$_3$), 1.03 (d, J = 6.4 Hz, 3H, *H*12), 1.05 (s, 9H, OC(CH_3)$_3$), 1.34 (dd, J = 13.1, 13.1 Hz, partially overlapped with H6, *H*8), 1.37 (dd, J = 15.8, 4.6 Hz, partially overlapped with H8, *H*6), 1.45 (s, 3H, *H*11), 1.49 (dd, J = 13.1, 6.8 Hz, *H*8′), 1.68 (dd, J = 15.8, 1.8 Hz, *H*6′), 2.14 (dd, J = 17.7, 12.8 Hz, *H*3), 2.27 (dd, J = 17.7, 3.8 Hz, *H*3′), 2.38 (qddd, J = 6.4, 12.8, 9.3, 3.8 Hz, *H*4), 2.89 (dddd, J = 13.1, 6.8, 6.8, 3.4 Hz, *H*9), 3.06 (d, J = 2.8 Hz, *H*1), 3.46 (ddd, J = 9.3, 4.6, 1.8 Hz, *H*5), 4.97 (dd, J = 6.8, 2.8 Hz, *H*10), 9.68 (d, J = 3.4 Hz, C*H*O); ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.1 (Si*C*H$_3$), −3.8 (Si*C*′H$_3$), 17.9 (Si*C*(CH$_3$)$_3$), 19.4 (*C*11), 25.8 (3C, SiC(*C*H$_3$)$_3$), 28.0 (*C*12), 28.3 (3C, OC(*C*H$_3$)$_3$), 35.2 (*C*4), 40.0 (*C*8), 44.6 (*C*7), 44.8 (*C*6), 48.6 (*C*3), 57.8 (*C*9), 67.7 (*C*1), 72.6 (*C*10), 74.2 (O*C*(CH$_3$)$_3$), 76.0 (*C*5), 202.9 (*C*HO), 210.6 (*C*2); IR (NaCl) 1726, 1702 cm^{-1}; HRMS (CI, CH_4, 140 eV) m/z 410.2812 ([M]$^+$, 1.6), calcd for $C_{23}H_{42}O_4Si$ 410.2852. The stereochemistry was confirmed by a NOESY experiment: H1 ↔ H9, H1 ↔ H4, and Si(CH$_3$)$_2$ ↔ H1.

(1*R,5*S**,9*R**,11*S**,12*S**,13*R**)-13-*tert*-Butoxy-7,7-dimethyl-6,8-dioxatetracyclo[9.2.1.0^{3,12}.0^{5,9}]tetradec-2-ene (36a).** To **29a** (12.2 mg, 0.05 mmol) was added a solution of *p*-TsOH/2,2-dimethoxypropane (4.8 mL, *p*-TsOH/2,2-dimethoxypropane = 4.3 mg/50 mL), and the mixture was stirred at room temperature until the starting material disappeared according to TLC (1 h). After evaporation of the volatiles in vacuo, purification by flash chromatography (hexanes/EtOAc, 10:1) gave **36a** (R_f = 0.5, 11.8 mg, 84%) as a colorless liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.58 (br d, J = 11.0 Hz, $H14_{endo}$), 1.04 (ddd, J = 13.3, 12.1, 10.4 Hz, *H*10), 1.12 (s, 9H, OC(CH_3)$_3$),

1.30 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 2.00 (ddd, J = 13.3, 7.1, 3.3 Hz, $H10'$), 2.08 (ddd, J = 11.0, 7.7, 3.3 Hz, $H14_{exo}$), 2.23 (br d, J = 3.8 Hz, $H12$), 2.27−2.33 (m, overlapped with H4, $H11$), 2.31 (dd, J = 15.9, 9.6 Hz, overlapped with H8, $H4$), 2.46 (br s, $H1$), 2.87 (ddd, J = 15.9, 7.0, 2.5 Hz, $H4'$), 3.39 (br s, $H13$), 4.25 (ddd, J = 12.1, 7.0, 3.3 Hz, $H9$), 4.52 (ddd, J = 9.6, 7.0, 7.0 Hz, $H5$), 5.45 (br dd, J = 2.5, 2.5 Hz, $H2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.1 (CH_3), 27.4 ($C'H_3$), 28.5 (3C, OC-(CH_3)$_3$), 30.0 ($C11$), 31.1 ($C14$), 32.9 ($C4$), 35.3 ($C10$), 46.6 ($C1$), 50.8 ($C12$), 73.2 (OC(CH$_3$)$_3$), 75.4 ($C5$), 77.2 ($C9$), 81.5 ($C13$), 106.9 ($C7$), 125.9 ($C2$), 139.0 ($C3$); HRMS (CI, CH_4, 140 eV) m/z 292.2046 ([M]$^+$, 3.2), calcd for $C_{18}H_{28}O_3$ 292.2038. The stereochemistry was further confirmed by a NOESY experiment: H5 ↔ H12, H9 ↔ H12 and *t*-Bu ↔ H11.

(1*R,5*R**,9*S**,11*S**,12*S**,13*R**)-13-*tert*-Butoxy-7,7-dimethyl-6,8-dioxatetracyclo[9.2.1.0^{3,12}.0^{5,9}]tetradec-2-ene (36b).** To **29b** (4.9 mg, 0.02 mmol) was added a solution of *p*-TsOH/2,2-dimethoxypropane (1.9 mL, *p*-TsOH/2,2-dimethoxypropane = 4.3 mg/50 mL), and the mixture was stirred at room temperature for 2 h. After evaporation of the volatiles in vacuo, purification by flash chromatography (hexanes/EtOAc, 10:1) gave **36b** (R_f = 0.5, 5.1 mg, 90%) as a colorless liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.71 (br dd, J = 11.0, 2.5 Hz, $H14_{endo}$), 1.12 (s, 9H, OC(CH_3)$_3$), 1.28 (s, 3H, CH_3), 1.46 (s, partially overlapped with H10, 3H, CH_3'), 1.46 (ddd, J = 14.8, 7.1, 2.5 Hz, partially overlapped with CH'_3, $H10$), 1.87−1.96 (m, 2H, $H10'$/14_{exo}), 2.38−2.43 (m, 2H, $H4$/1), 2.44−2.51 (m, $H11$), 2.53 (br s, $H12$), 2.73 (dd, J = 14.8, 7.1 Hz, $H4'$), 3.32 (br s, $H13$), 4.14 (ddd, J = 9.6, 7.1, 2.5 Hz, $H9$), 4.30 (ddd, J = 7.1, 7.1, 7.1 Hz, $H5$), 5.51 (br d, J = 2.2 Hz, $H2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.2 (CH_3), 27.37 ($C14$), 27.41 ($C'H_3$), 28.5 (3C, OC(CH_3)$_3$), 30.6 ($C11$), 31.1 ($C4$), 33.7 ($C10$), 47.3 ($C1$), 55.1 ($C12$), 73.1 (OC(CH$_3$)$_3$), 75.7 ($C5$), 76.8 ($C9$), 81.5 ($C13$), 107.5 ($C7$), 126.3 ($C2$), 140.6 ($C3$); HRMS (CI, CH_4, 140 eV) m/z 292.2060 ([M]$^+$, 0.1), calcd for $C_{18}H_{28}O_3$ 292.4174. The stereochemistry of the molecule was further confirmed by NOESY experiment: $H14_{endo}$ ↔ H9 and H2 ↔ H13.

(1*R,4*S**,8*R**,10*S**,12*S**,13*R**)-13-*tert*-Butoxy-6,6-dimethyl-2-oxo-5,7-dioxatricyclo[8.3.0.0^{4,8}]tridecane-12-carbaldehyde (37a).** Into a solution of **36a** (6.6 mg, 0.02 mmol) in CH_2Cl_2 (2.3 mL) at −78 °C was bubbled O_3 until the solution became light blue, and then Me_2S (5 drops) was added to quench the reaction. After evaporation of the solvent in vacuo, flash chromatography (hexanes/EtOAc/CH_2Cl_2, 2:1:0.1) of the residue gave **37a** (R_f = 0.4, 4.9 mg, 67%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (s, 9H, OC(CH_3)$_3$), 1.26−1.39 (m, partially overlapped with CH_3, 2H, $H9$/11), 1.34 (s, partially overlapped with H9/11, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.94 (ddd, J = 12.9, 6.6, 6.6 Hz, $H11'$), 2.24 (ddd, J = 13.7, 4.6, 4.6 Hz, $H9'$), 2.48 (dd, J = 18.9, 11.6 Hz, $H3$), 2.56−2.66 (m, partially overlapped with H3′, $H10$), 2.65 (dd, J = 18.9, 5.2 Hz, partially overlapped with H10 and H12, $H3'$), 2.70 (dddd, J = 11.5, 6.6, 6.6, 2.7 Hz, partially overlapped with H3′, $H12$), 2.88 (dd, J = 10.1, 2.6 Hz, $H1$), 4.42 (ddd, J = 11.2, 6.4, 4.6 Hz, $H8$), 4.64 (ddd, J = 11.6, 6.4, 5.2 Hz, $H4$), 4.95 (dd, J = 6.6, 2.6 Hz, $H13$), 9.70 (d, J = 2.7 Hz, CHO); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.1 (CH_3), 27.8 ($C'H_3$), 28.3 (3C, OC(CH_3)$_3$), 31.4 ($C11$), 31.5 ($C9$), 37.1 ($C10$), 45.2 ($C3$), 60.1 ($C12$), 62.6 ($C1$), 71.9 ($C13$), 72.8 ($C4$), 74.8 OC(CH$_3$)$_3$), 75.6 ($C8$), 109.0 ($C6$), 201.6 (CHO), 207.1 ($C2$); IR (NaCl) 1724, 1702 cm^{-1}; HRMS (CI, NH_3, 140 eV) m/z 324.1915 ([M]$^+$, 0.2), calcd for $C_{18}H_{28}O_5$ 324.1937. The stereochemistry was confirmed by a NOESY experiment: H1 ↔ H4, H1 ↔ H8 and CHO ↔ H13.

(1*R,4*R**,8*S**,10*S**,12*S**,13*R**)-13-*tert*-Butoxy-6,6-dimethyl-2-oxo-5,7-dioxatricyclo[8.3.0.0^{4,8}]tridecyl-12-carbaldehyde (37b).** Into a solution of **36b** (3.7 mg, 0.012 mmol) in CH_2Cl_2 (2 mL) at −78 °C was bubbled O_3 until the solution became light blue, and then Me_2S (5 drops) was added to quench the reaction. After evaporation of the solvent in vacuo, flash chromatography (hexanes/EtOAc/CH_2Cl_2, 3:1:0.1) of the residue gave **37b** (R_f = 0.2, 2.6 mg, 63%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (s, 9H, OC(CH_3)$_3$), 1.12−1.35 (m, 2H, $H9_\alpha$/11_α), 1.36 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), 1.85 (ddd, J = 12.6, 6.3, 6.3 Hz, $H11_\beta$), 2.15 (ddd, J = 15.1, 4.8, 4.8 Hz, $H9_\beta$), 2.53 (dd, J = 17.8, 3.8 Hz, $H3$), 2.71 (dddd, J = 11.3, 6.3, 6.3, 2.5 Hz, $H12$), 2.76−2.87 (m, partially overlapped with H3′, $H10$), 2.87 (dd, J = 17.8, 3.8 Hz, partially overlapped with H10, $H3'$), 3.63 (dd, J = 10.1, 2.5 Hz, $H1$), 4.39−4.47 (m, 2H, $H8$/4), 4.88 (dd, J = 6.3, 2.5 Hz, $H13$), 9.73 (d, J = 2.5 Hz, CHO); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.6 (CH_3), 26.0 ($C'H_3$), 28.3 (3C, OC(CH_3)$_3$), 30.6 ($C11$), 33.2 ($C9$), 34.7 ($C10$), 43.2 ($C3$), 60.2 ($C12$), 61.5 ($C1$), 72.3 ($C13$), 72.4 (OC(CH$_3$)$_3$), 74.1 ($C4$), 74.4 ($C8$), 107.6 ($C6$), 202.1 (CHO), 208.3 ($C2$); IR (NaCl) 1724, 1700 cm^{-1}; HRMS (CI, CH_4, 140 eV) m/z 324.1931 ([M]$^+$, 2.1), calcd for $C_{18}H_{28}O_5$ 324.1937. The stereochemistry was confirmed by a NOESY experiment: H10 ↔ H12, CHO ↔ H13.

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Supporting Information Available: Experimental procedures and characterization data for **1c**, **16c**, **15a**,**f**, **16f**, and **1g**,**h** and copies of ^{1}H and ^{13}C NMR spectra of previously unreported compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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