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Construction of Fused Bicyclic Cyclooctane Ring Frameworks

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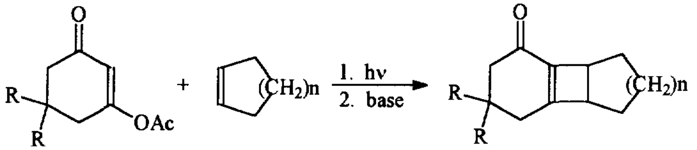
Abstract: A three step procedure beginning with cyclobutenyl ketones, prepared via a [2+2] cycloaddition-β-elimination sequence, provides fused bicyclic cyclooctane systems. This approach affords easy access to 1,4-cyclooctadione ring systems and complements the de Mayo reaction which generates 1,5-cyclooctadiones.

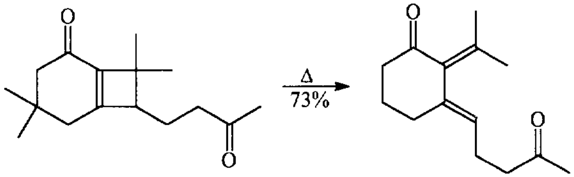
INTRODUCTION

The array of carbon skeletons Nature has endowed secondary metabolites isolated from natural sources is vast and continually expanding.[1] In particular, the number of known compounds possessing 8-membered rings has grown in recent years. This carbocyclic ring framework is found in a number of natural products of the following structural families: precapnellane, asteriscane, taxane, basmane, fusicoccane, ophiobolane and lignan.[2] The potent and varied biological activities exhibited by members of these natural product families has stimulated a great interest in the synthesis of these compounds. The construction of the 8-membered ring present in these compounds is one of the key aspects any synthesis would need to address. Due to enthalpic and entropic factors which hinder direct methods for their construction,[3] a variety of methods have been developed to circumvent direct preparation.[2]

We recently reported a tandem [2+2]-cycloaddition-β-elimination sequence[4] that could be used as a general procedure for the assembly of fused ring cyclobutenyl ketones (see reaction 1). At that time we also demonstrated the ability of a bicyclic derivative from this sequence to undergo, a thermal electrocyclic ring opening reaction to the corresponding dienyl system (see reaction 2). We felt that electrocyclic ring opening



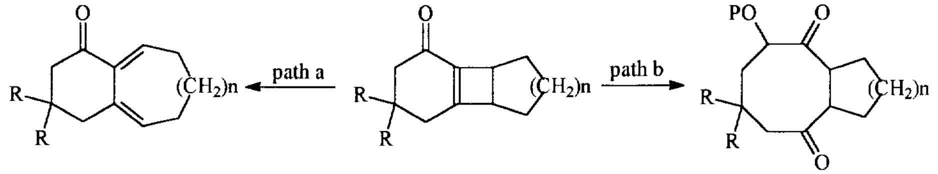
1



2

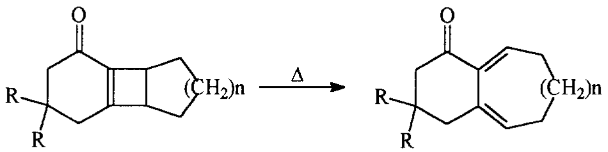
of the cyclobutene present in these tricyclic enones could provide access to medium sized rings, including cyclooctanes (scheme 1, path a). Alternatively, oxidative cleavage of the olefin in these enones could provide a direct route to cyclooctadiones (scheme 1, path b). Mehta[5] has investigated the use of RuO_2-$NaIO_4$ for the oxidative cleavage of olefins to 1,5-cyclooctadiones. These systems are also available from the de Mayo reaction.[6] More recently Blechert[7] has made use of similar chemistry in his synthetic approach to Taxol. This work would complement the existing approaches in that the predicted product would be a 1,4-cyclooctadione and would show the generality of this methodology. We now wish to present our findings dealing with the chemistry of these compounds.

SCHEME 1



RESULTS AND DISCUSSION

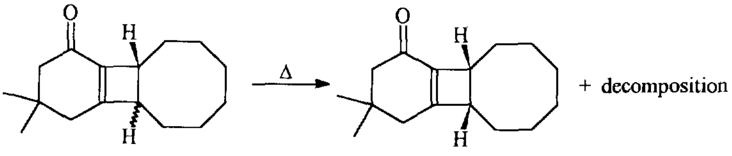
Our investigations began with an attempt to thermolyze cyclobutenyl ketone **2**. It should be noted that as a result of the photochemistry required for the construction of **1** and **2**, compounds of series **a** and **b** have a *cis* ring fusion, whereas, compounds of series **c** were an inseparable mixture of *cis* and *trans* ring fused isomers. Ring opening of the cyclobutene moiety would give rise to dienone **3**. Heating in a sealed tube to temperatures as high as 210 °C resulted only in recovery of **2a** or **2b**. In the case of **2c**, after thermolysis in refluxing toluene, the 200 MHz ^{1}H NMR of the crude reaction mixture indicated the presence of recovered



1 R = H **a** n = 1
2 R = Me **b** n = 2
c n = 4

3

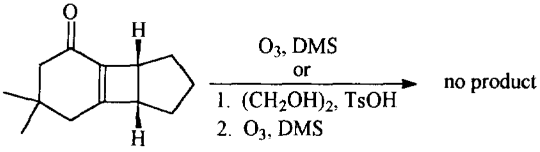
cis ring fused isomer **2c'** and decomposed material. Presumably for **2a** and **2b** in which the ring fusion is *cis*, the thermal four electron conrotatory electrocyclic ring opening would give rise to an **E-Z** diene moiety in an 8-membered ring which would be highly strained. While *trans*-cyclooctene is isolable, it is 9.2 kcal mol^{-1} less stable than its *cis* isomer.[9] For **2c** the *cis* fused isomer remained unreactive in an analogous manner to **2a** and **2b**. However, the *trans* fused isomer could undergo the ring opening but was labile and decomposed under the thermal conditions.



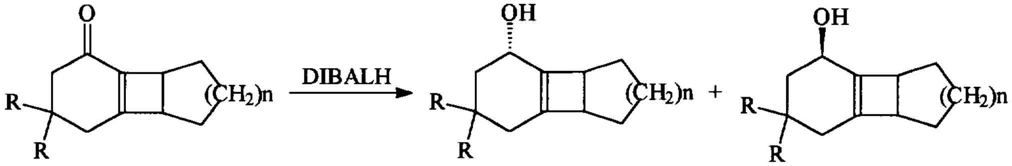
2c **2c'**

A four electron disrotatory electrocyclic ring opening of the cyclobutenyl system would give rise to a more stable **Z-Z** diene moiety. The Woodward-Hoffmann rules[8] predict that photochemical conditions would allow for this reaction manifold. Indeed, irradiation of **2**, using a 450 W medium pressure Hanovia lamp through pyrex at 0 °C, resulted in the formation of new products, however, these compounds were again labile either photochemically or thermally and resulted in an unidentifiable complex mixture of products. Since the ring opened product would be a dienone which should have a chromophore near the irradiating wavelength (> 300 nm), the potential for the products to also undergo photochemical reactions existed and this could have been the cause of the complex mixture of products observed.

In an effort to find an alternative method to fragment this system, it was thought that an oxidative cleavage of the olefin would give rise to a cyclooctane compound. Direct ozonolysis of **2a** did not produce any recognizable products. Furthermore, conversion of **2a** to the corresponding ketal followed by ozonolysis also resulted in decomposition of the starting material. Evidently the choice of protecting group was critical for success of the ozonolysis reaction. It was felt that protection of the alcohol obtained from reduction of the ketone would give the most synthetically useful derivative. Reduction of **1** and **2** with DIBALH proceeded in excellent yield, with two exceptions (*vide infra*), to afford allylic alcohols **4** and **5** (see table 1). There proved to be no stereochemical control over the reduction and a mixture of diastereomeric alcohols was formed which could be separated by chromatography. Each of these diastereomers was taken through the next set of steps in pure form.



2a

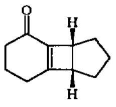
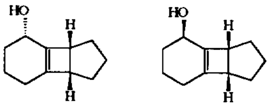
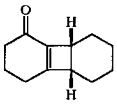
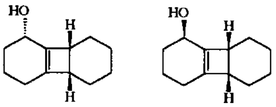
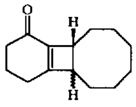
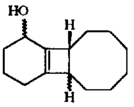
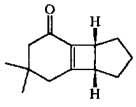
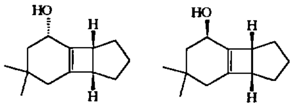
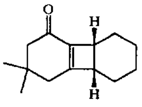
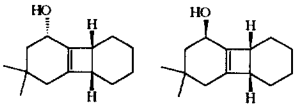
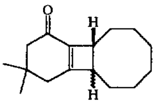
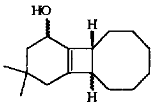


1 R = H **a** n = 1
2 R = Me **b** n = 2
c n = 4

4 R = H
5 R = Me

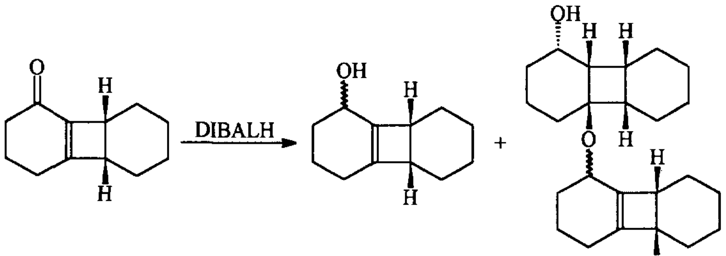
4' R = H
5' R = Me

Table 1. Summary of DIBALH Reduction Results

Entry	Substrate	Products	Yield (%)^a
1	 **1a**	 **4a/4'a**	85 (1.81)^b
2	 **1b**	 **4b/4'b**	67 (1:1.1)^{b,c}
3	 **1c**	 **4c**	100^d
4	 **2a**	 **5a/5'a**	98 (1.2:1)^b
5	 **2b**	 **5b/5'b**	90 (1.6:1)^b
6	 **2c**	 **5c**	69^{d,e}

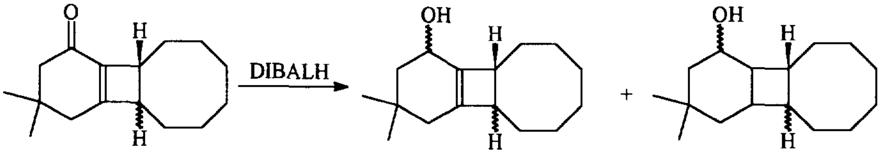
a) yield of isolated, chromatographically pure material. b) quoted diastereomeric ratio is based on chromatographically separated isomers. c) compound **6** also isolated in 25% yield. d) carried through as a mixture of diastereomers. e) compound **7** also isolated in 24% yield.

For the transformation of **1b** to **4b**, the diminished yield could be attributed to the formation of **6**. Presumably, this compound is formed by a Michael addition of **4b** with unreacted starting material followed



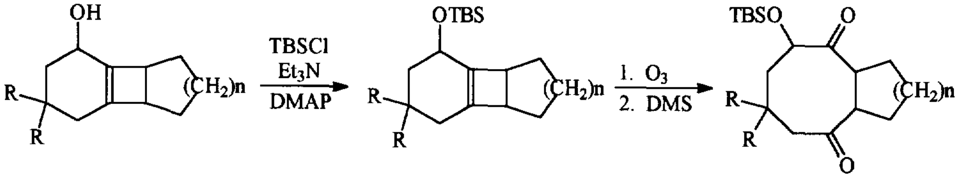
1b **4b** **6**

by reduction of the Michael adduct. The propensity for **1b** to undergo Michael additions was also noted in our earlier work.[4] While the reduction of **2c** produced the expected allylic alcohol **5c**, saturated alcohol **7** was also formed in this transformation but could be removed by chromatography.



2c **5c** **7**

The allylic alcohols thus produced were converted to *tert*-butyldimethylsilyl ethers **8** and **9** in excellent yield (see table 2) using the standard procedure. With the alcohol functional group protected, the compounds



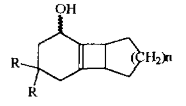
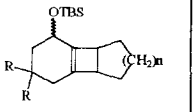
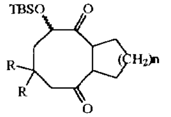
4 R = H
5 R = Me

8 R = H
9 R = Me

10 R = H
11 R = Me

were ready for cleavage of the double bond with ozone. Exposure of **8** and **9** to ozone followed by DMS work-up afforded the cyclooctadiones **10** and **11** (see table 2). As can be seen, the ozonolysis of the cyclobutene ring afforded cyclooctanes **10** and **11** in good to excellent yield.

TABLE 2. Summary of Protection and Ozonolysis Reaction Results

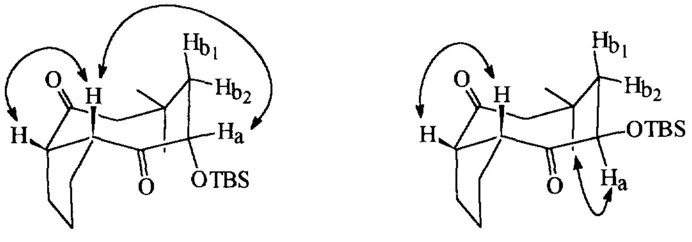
Entry	Substrate 	Silyl Ether 	Yield (%)^a	Cyclooctadione 	Yield (%)^a
1	**4a** (R=H, n=1)	**8a**	92	**10a**	79
2	**4'a** (R=H, n=1)	**8'a**	80	**10'a**	89
3	**4b** (R=H, n=2)	**8b**	78	**10b**	67
4	**4'b** (R=H, n=2)	**8'b**	86	**10'b**	91
5	**4c** (R=H, n=4)	**8c**	78	**10c**	82
6	**5a** (R=Me, n=1)	**9a**	93	**11a**	57
7	**5'a** (R=Me, n=1)	**9'a**	98	**11'a**	83
8	**5b** (R=Me, n=2)	**9b**	87	**11b**	66
9	**5'b** (R=Me, n=2)	**9'b**	91	**11'b**	93
10	**5c** (R=Me, n=4)	**9c**	79	**11c**	89

a) yield of isolated, chromatographically pure material.

The conditions for the ozonolysis were optimized based on the following observations. Ozonolysis of **5b** in CH_2Cl_2 using triphenylphosphine to work-up the ozonide gave rive to **11b** in 45% yield. Switching to DMS for the work-up improved the isolated yield to about the 65% level. Presumably this increase in yield is associated with purification problems in the former reaction that are known to occur with the removal of triphenylphosphine oxide. Furthermore, changing the solvent from CH_2Cl_2 to a mixed solvent system of CH_2Cl_2/MeOH (4:1) improved the yields further. Performing the ozonolysis reaction in CH_2Cl_2 afforded the desired cyclooctadione and an as yet unidentified compound. Switching to the mixed solvent system altered the reaction manifold preventing the formation of this unknown compound and therefore the improved yields. These latter conditions were then used for all ozonolyses.

The stereochemical assignments for compounds **4-11** were based on the following observations. As a result of the photochemistry used in their preparation, compounds **1c** and **2c** were inseparable mixtures of *cis* and *trans* fused isomers, while the ring fusion for compounds **1a-b** and **2a-b** was *cis*.[4] The chemistry described in this work resulted in the formation of four isomers for the **c** series of compounds which could not be separated and as a result stereochemistry was not determined for these compounds. For the other compounds, it was not until the cyclooctadiones were obtained could any assignment be made. Determination of the relative stereochemistry was initiated by an examination of compounds **11a** and **11'a**. The ^1H NMR signal of the carbinol hydrogen for **11a** appeared at δ 4.33 as a doublet of doublets (J = 5.6, 3.28 Hz), while the same signal for **11'a** appeared at δ 4.02 also as a doublet of doublets (J = 11.2, 4.4 Hz). Molecular mechanics calculations[10] predicted that the chair-boat conformation for the 8-membered ring (see figure 1) was the most stable conformation for both compounds. The calculated coupling constants for the spin-spin couplings noted above were 3.83 and 2.85 Hz for **11a** and 10.77 and 4.78 Hz for **11'a**. These

Figure 1



11a **11'a**

numbers are in good agreement with those observed (*vide supra*). Also, difference NOE measurements, indicated in figure 1, support the relative stereochemistry shown. Similar arguments leads one to conclude that **11b** and **11'b** have the analogous relative stereochemistry. Difference NOE measurements on **10a** and **10'a** were inconclusive. Presumably the lack of the geminal dimethyl moiety in these compounds allows the 8-membered ring to be more flexible which prevented unambiguous assignment of stereochemistry based on the enhancements. This conformational flexibility also prevented assignment based on the use of coupling constants. However, we assumed similar reactivity patterns for these compounds and have extrapolated the stereochemistry observed in the previous compounds to these compounds. Working backwards would then give the stereochemistry for the synthetic precursors. The relative stereochemistry for side-product **6** in the reduction of **1b** could not be completely determined. This compound consisted of two diastereomers and was deduced to be dimeric in nature from ^{13}C NMR and a high resolution mass spectrum. Since the reduction of **1b** forms two diastereomers for **4b**, it was felt that it was this stereocenter that resulted in the two isomers of **6**. The allylic alcohols **4b** both underwent a Michael addition to unreacted **1b** from the convex face with the following chemistry also occurring from the convex face resulting in the stereochemistry shown for **6**. Finally, due to the multi-isomeric nature of **7** its relative stereochemistry was not determined.

CONCLUSIONS

We have developed a three step sequence, from readily available material, for the construction of fused ring derivatives of 1,4-cyclooctadiones. These compounds provide an entry into the synthesis of a number of natural products that contain an 8-membered ring. In addition, the disposition of the carbonyl groups in these compounds complements that found in similar compounds derived from the de Mayo reaction.[6] In these compounds the carbonyl groups are 1,5-disposed.

EXPERIMENTAL SECTION

General Procedures and Materials. Melting points were taken on a Fischer-Johns melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 400 and 100 MHz respectively unless specified otherwise. Combustion analyses were performed by M-H-W Laboratories, Phoenix, AZ. Ozonolyses were carried out using a Welsbach Laboratory ozonator model T-816 operating with compressed air at 8 psig, 1 SLPM and 90 V. All solvents used for chromatography were distilled prior to use. Reactions were monitored by TLC using E. Merck precoated silica gel 60 F-250 (0.25 mm thickness) aluminum backed plates. The plates were visualized by immersion in p-anisaldehyde solution and warming on a hotplate. E. Merck silica gel 60 (70-230 mesh) was used for column chromatography. All solvents were reagent grade and anhydrous solvents were dried prior to use as follows: CH_2Cl_2 was distilled from CaH_2, while ether and THF were distilled from benzophenone ketyl. Compounds obtained from commercial sources were used directly as received.

General Procedure for DIBALH Reductions of Enones. To a solution of enone **1** or **2** in 10-80 mL of dry CH_2Cl_2 at -78 °C was added DIBALH (1.5 eq. of a 1M soultion in CH_2Cl_2). The reaction was stirred for 3 h before quenching at -78 °C with a saturated solution of sodium potassium tartrate. The reaction was warmed to RT and the aqueous phase extracted 5 times with CH_2Cl_2. The combined extracts were dried (anhydrous Na_2SO_4), filtered by suction and the solvent removed *in vacuo*. The crude products were purified by chromatography (40-300 g silica gel, 5-10% ethyl acetate/hexanes) to afford alcohols **4** and **5**. The diastereomers epimeric at the carbinol carbon could be separated at this point. Samples for combustion analysis were obtained by recrystallization from hexanes.

Reduction of Enone 1a. Enone **1a** (11.9 mmol, 1.99g) was reduced with DIBALH (17.9 mmol, 17.9 mL) following the general procedure to afford alcohols **4a** (1.11g, 55%) and **4'a** (0.61g, 30%): **(1β, 3β, 8β)-Tricyclo[6·3·0·0^{2,7}]undec-$\Delta^{2,7}$-ene-3-ol (4a)**: mp=56-57.5 °C; IR(CCl_4): 3622, 3476, 1688 cm^{-1}; ^1H NMR δ 4.09(s, 1H), 3.20(m, 1H), 3.09(m, 1H), 1.95-1.50(m, 10H), 1.40(m, 1H), 1.25-1.05(m, 2H); ^{13}C NMR δ 146.0, 142.2, 65.3, 47.8, 47.4, 33.0, 26.6, 24.8, 23.6, 22.5, 19.5; Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.31; H, 9.86. **(1β, 3α, 8β)-Tricyclo[6·3·0·0^{2,7}]undec-$\Delta^{2,7}$-ene-3-ol (4'a)**: IR(film): 3330 cm^{-1}; ^1H NMR δ 4.05(m, 1H), 3.29(m,1H), 3.09(dd, 1H, J=6.8, 2.4 Hz), 1.83-1.72(m, 4H), 1.68-1.40(m, 7H), 1.19-1.06(m, 2H); ^{13}C NMR δ 146.8, 142.5, 62.4, 47.9, 46.1, 32.8, 24.9, 24.7, 23.6, 22.5, 20.0; HRMS calcd for $C_{11}H_{16}O$: 164.1201; found: 164.1198.

Reduction of Enone 1b. Enone **1b** (5.1 mmol, 0.90g) was reduced with DIBALH (7.7 mmol, 7.7 mL) following the general procedure to afford alcohols **4b** (0.327g, 35%), **4'b** (0.293g, 32%), **6** (0.129g, 14%) and **6'** (0.10g, 11%): **(1β, 3β, 8β)-Tricyclo[6·4·0·0^{2,7}]dodec-$\Delta^{2,7}$-ene-3-ol (4b)**: IR(CCl_4): 3372 cm^{-1}; ^1H NMR δ 4.11(brs, 1H), 2.80(m, 1H), 2.86(m, 1H), 2.76(m, 1H), 2.00-1.30(m, 15H); ^{13}C NMR δ 149.2, 145.3, 65.0, 41.2, 32.9, 24.3, 23.3, 23.1, 19.7, 18.7, 18.5; HRMS calcd for $C_{12}H_{18}O$: 178.1358; found: 178.1357. **(1β, 3α, 8β)-Tricyclo[6·4·0·0^{2,7}]dodec-$\Delta^{2,7}$-ene-3-ol (4'b)**: IR(CCl_4): 3623, 3347, 1687 cm^{-1}; ^1H NMR δ 4.11(m, 1H), 2.99(m, 1H), 2.79(m, 1H), 1.95-1.25(m, 15H); ^{13}C NMR δ 149.5, 145.3, 63.2, 41.1, 39.1, 32.8, 23.5, 23.1, 23.0, 19.8, 18.4; HRMS calcd for $C_{12}H_{18}O$: 178.1358; found: 178.1358. **(6)**: mp=117-118 °C; IR(CCl_4): 3622, 3485 cm^{-1}; ^1H NMR δ 4.29(m, 1H), 4.17(m, 1H), 2.87(m, 1H), 2.68(t, 1H, J=8.0 Hz), 2.10-1.10(m, 31H); ^{13}C NMR δ 149.9, 145.8, 69.8, 66.2, 48.2, 48.1, 44.2, 42.7, 41.0, 40.7, 30.1, 29.4, 28.6, 27.7, 26.6, 25.2, 24.9, 24.4, 23.1, 21.4, 19.0, 18.7, 16.9; HRMS calcd for $C_{24}H_{36}O_2$: 338.2610 (M^+-H_2O); found: 338.2602. **(6')**: mp=155-156 °C; IR(CCl_4): 3615, 3590-3100 cm^{-1}; ^1H NMR δ 4.36(m, 1H), 3.92(m, 1H), 2.88(m, 1H), 2.80(m, 1H), 2.19(t, 1H, J=7.6 Hz), 2.09-1.98(m, 2H), 1.92-1.00(m, 29H); ^{13}C NMR δ 149.9, 145.5, 70.5, 66.1, 50.0, 49.2, 46.1, 41.5, 41.1, 40.7, 40.2, 32.5, 27.3, 27.3, 27.2, 26.6, 26.5, 24.8, 24.5, 23.1, 21.4, 21.3, 18.9, 18.7; HRMS calcd for $C_{24}H_{36}O_2$: 338.2610 (M^+-H_2O); found: 338.2608.

Reduction of Enone 1c. Enone **1c** (4.90 mmol, 1.00g), as a mixture of *cis* and *trans* isomers, was reduced with DIBALH (7.35 mmol, 7.4 mL) following the general procedure to afford alcohols **4c** (1.01g, 100%), as an inseparable mixture of 4 diastereomers: **Tricyclo[6·6·0·$0^{2,7}$]tetradec-$\Delta^{2,7}$-ene-3-ol (4c)**: IR(film): 3339 cm^{-1}; ^{1}H NMR δ 4.12(m, 4H), 2.78(brd, 2H, *J*=11.6 Hz), 2.66(brd, 2H, *J*=11.6 Hz), 2.53(brd, 2H, *J*=11.2 Hz), 2.46(brd, 2H, *J*=10.8 Hz), 2.10-1.09(m, 76H); ^{13}C NMR δ 148.3, 148.0, 147.8, 147.7, 144.1, 144.0, 64.9, 64.6, 62.0, 61.8, 51.6, 51.3, 49.3, 48.4, 48.3, 48.0, 45.9, 33.6, 33.1, 33.0, 32.8, 32.7, 32.2, 31.8, 30.3, 29.7, 29.6, 28.3, 28.2, 28.1, 26.8, 26.1, 26.0, 25.9, 25.5, 25.2, 22.4, 22.3, 22.1, 22.0, 19.8, 19.7, 19.5, 19.3; HRMS Calcd for $C_{14}H_{22}O$: 206.1671; found: 206.1673.

Reduction of Enone 2a. Enone **2a** (21.0 mmol, 4.00g) was reduced with DIBALH (31.6 mmol, 31.6 mL) following the general procedure to afford alcohols **5a** (2.19g, 54%) and **5'a** (1.76g, 44%): **(1β, 3β , 8β)-5,5-Dimethyltricyclo[6·3·0·$0^{2,7}$]undec-$\Delta^{2,7}$-ene-3-ol (5a)**: mp=50-51.5 °C; IR(CCl_4): 3631, 3486, 1684 cm^{-1}; ^{1}H NMR δ 4.14(m, 1H), 3.17(m, 1H), 3.03(m, 1H), 1.80-1.42(m, 8H), 1.30(dd, 1H, *J*=12.8, 7.6 Hz), 1.21-1.05(m, 2H), 0.98(s, 3H), 0.88(s, 3H); ^{13}C NMR δ 143.8, 140.5, 65.9, 47.3, 46.5, 36.6, 32.1, 30.9, 27.4, 26.8, 24.8, 23.8; Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.07; H, 10.51. **(1β, 3α, 8β)-5,5-Dimethyltricyclo[6·3·0·$0^{2,7}$]undec-$\Delta^{2,7}$-ene-3-ol (5'a)**: mp=89-90 °C; IR(CCl_4): 3617, 3465 cm^{-1}; ^{1}H NMR δ 4.12(m, 1H), 3.31(dt, 1H, *J*=3.6, 3.6 Hz), 3.07(brd, 1H, *J*=6.8 Hz), 1.78-1.41(m, 7H), 1.37(m, 1H), 1.32(dd, 1H, *J*=12.8, 8.8 Hz), 1.17(m, 2H), 0.99(s, 3H), 0.89(s, 3H); ^{13}C NMR δ 144.7, 141.2, 63.4, 47.2, 46.4, 45.3, 36.5, 33.4, 31.5, 26.7, 24.9, 24.6, 24.1; Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.40; H, 10.51.

Reduction of Enone 2b. Enone **2b** (2.4 mmol, 0.50g) was reduced with DIBALH (3.7 mmol, 3.7 mL) following the general procedure to afford alcohols **5b** (0.277g, 55%) and **5'b** (0.175g, 35%): **(1β, 3β, 8 β)-5,5-Dimethyltricyclo[6·4·0·$0^{2,7}$]dodec-$\Delta^{2,7}$-ene-3-ol (5b)**: mp=48.5-50 °C; IR(CCl_4): 3630, 3465, 1681 cm^{-1}; ^{1}H NMR δ 4.19(m, 1H), 2.91(m, 1H), 2.74(m, 1H), 1.88-1.34(m, 12H), 1.31(brs, 1H), 1.03(s, 3H), 0.91(s, 3H); ^{13}C NMR δ 147.4, 143.6, 66.0, 46.5, 41.0, 40.4, 37.7, 32.5, 30.9, 27.4, 24.4, 23.3, 18.8, 18.5; Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.60; H, 10.65. **(1β, 3α, 8 β)-5,5-Dimethyltricyclo[6·4·0·$0^{2,7}$]dodec-$\Delta^{2,7}$-ene-3-ol (5'b)**: mp=83-84 °C; IR(CCl_4): 3615, 3328, 1678 cm^{-1}; ^{1}H NMR δ 4.19(m, 1H), 3.00(m, 1H), 2.78(m, 1H), 1.84-1.37(m, 12H), 1.34(dd, 1H, *J*=12.8, 8.8 Hz), 1.01(s, 3H), 0.96(s, 3H); ^{13}C NMR δ 147.4, 143.9, 64.6, 46.6, 40.2, 38.3, 37.2, 33.4, 31.5, 26.5, 23.5, 22.8, 18.5, 18.3; Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.64; H, 10.57.

Reduction of Enone 2c. Enone **2c** (3.55 mmol, 0.824g), as a mixture of *cis* and *trans* isomers, was reduced with DIBALH (5.33 mmol, 5.3 mL) following the general procedure to afford alcohols **5c** (0.575g, 69%) and **7** (0.201g, 24%) each as an inseparable mixture of 4 diastereomers: **5,5-Dimethyltricyclo[6·6·0·$0^{2,7}$]tetradec-$\Delta^{2,7}$-ene-3-ol (5c)**: IR(film): 3324 cm^{-1}; ^{1}H NMR δ 4.19(m, 4H), 2.87(m, 1H), 2.80(brd, 1H, *J*=11.6 Hz), 2.64(m, 2H), 2.55-2.38(m, 4H), 2.15-1.10(m, 68H), 1.00(brs, 12H), 0.91(s, 3H), 0.89(brs, 9H); ^{13}C NMR δ 146.4, 146.2, 145.6, 145.5, 142.8, 142.7, 142.5, 142.4, 66.2, 66.0, 63.4, 63.0, 51.1, 50.8, 50.6, 48.7, 48.3, 47.6, 47.0, 46.8, 46.6, 46.5, 46.2, 45.2, 36.7, 36.4, 36.3, 35.9, 33.8, 33.0, 32.9, 32.8, 32.5, 31.9, 31.6, 31.3, 31.0, 30.9, 30.4, 30.3, 30.2, 29.8, 29.7, 29.6, 28.4, 28.3, 28.2, 28.1, 27.0, 26.9, 26.8, 26.4, 26.3, 26.1, 26.0, 25.9, 25.8, 25.7, 24.8; HRMS calcd for

$C_{16}H_{26}O$: 234.1984; found: 234.1990. **5,5-Dimethyltricyclo[6·6·0·0^{2,7}]tetradecan-3-ol (7)**: IR(film): 3365 cm^{-1}; ^{1}H NMR δ 4.20-4.05(m, 4H), 2.78(brs, 4H), 2.20-0.70(m, 104H); ^{13}C NMR δ 74.9, 73.2, 71.8, 69.5, 68.6, 68.5, 66.1, 66.0, 65.9, 64.4, 58.4, 56.6, 54.9, 54.7, 54.1, 52.1, 51.7, 50.2, 50.1, 49.0, 48.6, 44.1, 43.8, 43.4, 43.0, 42.9, 42.0, 37.8, 36.3, 34.8, 33.4, 33.1, 33.0, 32.9, 32.2, 31.5, 30.9, 30.8, 30.4, 30.3, 29.9, 29.6, 28.9, 28.8, 28.6, 28.5, 27.6, 27.5, 27.4, 27.0, 26.9, 26.3, 25.9, 25.8, 25.5, 25.4, 25.1, 25.0, 22.8, 22.7, 18.4; HRMS calcd for $C_{16}H_{28}O$: 235.2062 (M^+-H); found: 235.2054.

General Procedure For Silyl Ether Formation. To a solution of alcohol **4** or **5** in 10-30 mL of dry CH_2Cl_2 at 0 °C was added triethylamine (1.5 eq.) *tert*-butyldimethylsilyl chloride (1.2 eq.) and DMAP (0.1 eq.). After stirring for 10 min. the reaction was warmed to RT and stirred for an additional 41-44 h. The reaction was poured into water, extracted three times with CH_2Cl_2 and the combined extracts dried (Na_2SO_4). After filtration and removal of the solvent *in vacuo*, the crude product was purified by chromatography (20-45 g silica gel, 5-10% ethyl acetate/hexanes) to afford **8** and **9**. Analytical samples were obtained by recrystallization from hexanes.

(1β, 3β, 8β)-3-(tert-butyldimethylsilyloxy)-Tricyclo[6·3·0·0^{2,7}]undec-Δ^{2,7}-ene (8a). Alcohol **4a** (5.92 mmol, 1.00g) was treated with triethylamine (8.9 mmol, 1.2 mL), TBSCl (7.10 mmol, 1.07 g) and DMAP (0.59 mmol, 0.072 g) following the general procedure to afford 1.54 g of **8a** (92%): IR(film): 2936, 2856, 1474, 1461, 1444, 1359, 1255, 1089, 1059, 1006, 925, 881, 836, 774 cm^{-1}; ^{1}H NMR δ 4.12(m, 1H), 3.14(m, 1H), 3.06(m, 1H), 1.95-1.45(m, 10H), 1.09(m, 2H), 0.90(s, 9H), 0.07(s, 3H), 0.06(s, 3H); ^{13}C NMR δ 144.1, 143.1, 66.0, 47.6, 33.6, 26.4, 25.9, 24.9, 23.6, 22.4, 20.4, 18.2, -4.6, -4.7; HRMS calcd for $C_{17}H_{30}OSi$: 278.2066; found: 278.2076.

(1β, 3α, 8β)-3-(tert-butyldimethylsilyloxy)-Tricyclo[6·3·0·0^{2,7}]undec-Δ^{2,7}-ene (8'a). Alcohol **4'a** (2.4 mmol, 0.40g) was treated with triethylamine (3.56 mmol, 0.496 mL), TBSCl (2.84 mmol, 0.429 g) and DMAP (0.24 mmol, 0.029 g) following the general procedure to afford 0.534 g of **8'a** (80%): IR(film): 2933, 2860, 1475, 1369, 1263, 1104, 1071, 1018, 846, 780 cm^{-1}; ^{1}H NMR δ 4.10(m,1H), 3.27(m, 1H), 3.10(m,1H), 1.86-1.70(m, 4H), 1.66-1.43(m, 6H), 1.14(m, 2H), 0.90(s, 9H), 0.08(s, 3H), 0.07(s, 3H); ^{13}C NMR δ 145.6, 143.1, 63.5, 47.6, 46.2, 33.6. 25.9, 25.1, 24.8, 23.7, 22.5, 20.9, 18.4, -4.6, -4.7; HRMS calcd for $C_{17}H_{30}OSi$: 278.2066; found: 278.2071.

(1β, 3β, 8β)-3-(tert-butyldimethylsilyloxy)-Tricyclo[6·4·0·0^{2,7}]dodec-Δ^{2,7}-ene (8b). Alcohol **4b** (1.50 mmol, 0.267g) was treated with triethylamine (2.25 mmol, 0.314 mL), TBSCl (1.80 mmol, 0.271 g) and DMAP (0.15 mmol, 0.018 g) following the general procedure to afford 0.342 g of **8b** (78%): IR(film): 2936, 2863, 1473, 1463, 1363, 1258, 1070, 1020, 1004, 954, 910, 835, 776 cm^{-1}; ^{1}H NMR δ 4.15(m, 1H), 2.83(m, 1H), 2.74(m, 1H), 1.96-1.20(m, 14H), 0.88(s, 9H), 0.06(s, 3H), 0.04(s, 3H); ^{13}C NMR δ 147.3, 146.3, 66.0, 41.4, 41.2, 33.7, 25.9, 24.1, 23.5, 23.1, 20.8, 18.3, 18.2, 18.1, -4.7, -4.8; HRMS calcd for $C_{18}H_{32}OSi$: 292.2222; found: 292.2237.

(1β, 3α, 8β)-3-(tert-butyldimethylsilyloxy)-Tricyclo[6·4·0·0^{2,7}]dodec-Δ^{2,7}-ene (8'b). Alcohol **4'b** (1.90 mmol, 0.339g) was treated with triethylamine (2.86 mmol, 0.398 mL), TBSCl (2.29 mmol, 0.344 g) and DMAP (0.19 mmol, 0.023 g) following the general procedure to afford 0.476 g of **8'b** (86%): IR(film): 2943, 2907, 2856, 1472, 1462, 1362, 1255, 1082, 1010, 838, 774 cm^{-1}; ^{1}H NMR δ 4.15(m, 1H), 2.97(m, 1H), 2.79(m, 1H), 1.92-1.74(m, 4H), 1.73-1.33(m, 10H), 0.89(s, 9H), 0.07(s, 3H), 0.06(s, 3H);

^{13}C NMR δ 148.3, 146.1, 64.5, 40.8, 39.3, 33.6, 25.9, 23.5, 23.4, 23.1, 20.7, 18.6, 18.5, 18.4, -4.6, -4.8; HRMS calcd for $C_{18}H_{32}OSi$: 292.2222; found: 292.2226.

3-(tert-butyldimethylsilyloxy)-Tricyclo[6·6·0·0^{2,7}]tetradec-Δ^{2,7}-ene (8c). Alcohol **4c** (2.43 mmol, 0.50g), as a mixture of 4 diastereomers, was treated with triethylamine (3.64 mmol, 0.508 mL), TBSCl (2.91 mmol, 0.439 g) and DMAP (0.24 mmol, 0.030 g) following the general procedure to afford 0.603 g of **8c** (78%) as an inseparable mixture of 4 diastereomers: IR(film): 2929, 2863, 1473, 1458, 1362, 1255, 1085, 1061, 1015, 1004, 938, 836, 775 cm^{-1}; ^{1}H NMR δ 4.25-4.09(m, 4H), 2.83(m, 1H), 2.76-2.56(m, 4H), 2.52-2.36(m, 3H), 2.20-1.12(m, 72H), 0.89(s, 36H), 0.06(s, 24H); ^{13}C NMR δ 146.9, 146.7, 146.6, 146.5, 145.0, 144.8, 144.7, 144.6, 66.6, 66.5, 63.4, 63.1, 51.4, 51.2, 51.1, 49.6, 48.6, 48.5, 48.0, 46.0, 33.8, 33.7, 33.6, 33.4, 32.6, 32.0, 31.8, 30.5, 30.4, 30.3, 29.8, 29.7, 29.6, 28.6, 28.4, 26.3, 26.2, 26.1, 26.0, 25.9, 25.8, 25.7, 25.6, 22.6, 22.2, 22.1, 20.9, 20.4, 20.3, 18.3, 18.2, -4.4, -4.5, -4.6, -4.7, -4.8; HRMS calcd for $C_{20}H_{36}OSi$: 320.2535; found: 320.2540.

(1β, 3β, 8β)-3-(tert-butyldimethylsilyloxy)-5,5-dimethyltricyclo[6·3·0·0^{2,7}]undec-Δ^{2,7}-ene (9a). Alcohol **5a** (5.21 mmol, 1.00 g) was treated with triethylamine (7.8 mmol, 1.1 mL), TBSCl (6.25 mmol, 0.942 g) and DMAP (0.52 mmol, 0.064 g) following the general procedure to afford 1.47 g of **9a** (93%): IR(film): 2959, 2933, 2900, 2854, 2827, 1473, 1460, 1366, 1258, 1085, 1055, 999, 886, 836 cm^{-1}; ^{1}H NMR δ 4.16(m, 1H), 3.13(m, 1H), 3.03(m, 1H), 1.84(dd, 1H, *J*=11.6, 5.6 Hz), 1.81-1.67(m, 2H), 1.66-1.46(m, 4H), 1.36(dd, 1H, *J*=12.8, 7.6 Hz), 1.11(m, 2H), 1.00(s, 3H), 0.91(s, 3H), 0.90(s, 9H), 0.07(s, 6H); ^{13}C NMR δ 142.6, 141.1, 65.9, 47.3, 46.9, 46.7, 36.7, 32.1, 31.0, 27.8, 26.5, 26.0, 24.9, 23.8, 18.2, -4.6, -4.7; HRMS calcd for $C_{19}H_{34}OSi$: 306.2379; found: 306.2389.

(1β, 3α, 8β)-3-(*tert*-butyldimethylsilyloxy)-5,5-dimethyltricyclo[6·3·0·0^{2,7}]undec-Δ^{2,7}-ene (9'a). Alcohol **5'a** (5.21 mmol, 1.00 g) was treated with triethylamine (7.8 mmol, 1.1 mL), TBSCl (6.25 mmol, 0.942 g) and DMAP (0.52 mmol, 0.064 g) following the general procedure to afford 1.56 g of **9'a** (98 %): mp(hexanes)=27-28 °C; IR(film): 2963, 2930, 2897, 2850, 1476, 1370, 1264, 1093, 1059, 881, 841, 775 cm^{-1}; ^{1}H NMR δ 4.14(m,1H), 3.28(m, 1H), 3.06(brd, 1H, *J*=6.8 Hz), 1.74(brd, 1H, *J*=17.2 Hz), 1.70-1.39(m, 6H), 1.39(dd, 1H, *J*=12.8, 8.8 Hz), 1.15(m, 2H), 0.97(s, 3H), 0.90(s, 9H), 0.89(s, 3H), 0.08(s, 3H), 0.07(s, 3H); ^{13}C NMR δ 143.9, 141.6, 63.9, 47.0, 46.6, 36.5, 33.3, 31.6, 26.7, 25.9, 25.1, 24.7, 24.2, 18.3, -4.5, -4.6; Anal. Calcd for $C_{19}H_{34}OSi$: C, 74.44; H, 11.18. Found: C, 74.50; H, 11.06.

(1β, 3β, 8β)-3-(*tert*-butyldimethylsilyloxy)-5,5-dimethyltricyclo[6·4·0·0^{2,7}]dodec-Δ^{2,7}-ene (9b). Alcohol **5b** (1.27 mmol, 0.262 g) was treated with triethylamine (1.91 mmol, 0.266 mL), TBSCl (1.53 mmol, 0.230 g) and DMAP (0.13 mmol, 0.016 g) following the general procedure to afford 0.355 g of **9b** (87 %): IR(film): 2942, 2896, 2856, 1482, 1376, 1258, 1073, 894, 835, 775 cm^{-1}; ^{1}H NMR δ 4.18(m, 1H), 2.83(m, 1H), 2.72(m, 1H), 1.81(brd, 1H, *J*=16.8 Hz), 1.78-1.30(m, 11H), 1.02(s, 3H), 0.92(s, 3H), 0.89(s, 9H), 0.06(s, 3H), 0.05(s, 3H); ^{13}C NMR δ 145.9, 144.2, 65.9, 46.6, 40.9, 40.7, 37.8, 32.4, 30.9, 27.7, 25.9, 24.2, 23.2, 18.2, 18.1, -4.7, -4.9; HRMS Calcd for $C_{20}H_{36}OSi$: 320.2535; found: 320.2539.

(1β, 3α, 8β)-3-(*tert*-butyldimethylsilyloxy)-5,5-dimethyltricyclo[6·4·0·0^{2,7}]dodec-Δ^{2,7}-ene (9'b). Alcohol **5'b** (1.23 mmol, 0.255 g) was treated with triethylamine (1.86 mmol, 0.259 mL), TBSCl (1.49 mmol, 0.224 g) and DMAP (0.12 mmol, 0.015 g) following the general procedure to afford 0.257 g of **9'b** (91%): mp(hexanes)=28.5-30 °C; IR(CCl_4): 2933, 2900, 2867, 1482, 1376, 1257, 1078, 899, 839 cm^{-1};

^{1}H NMR δ 4.20(m, 1H), 2.97(m, 1H), 2.76(m, 1H), 1.83-1.34(m, 12H), 0.99(s, 3H), 0.95(s, 3H), 0.89(s, 9H), 0.07(s, 3H), 0.07(s, 3H); ^{13}C NMR δ 146.6, 144.4, 65.1, 46.8, 40.1, 38.5, 37.3, 33.4, 31.6, 26.6, 25.9, 23.8, 22.9, 18.7, 18.3, -4.6, -4.7; Anal. Calcd for $C_{20}H_{36}OSi$: C, 74.93; H, 11.32. Found: C, 75.11; H, 11.11.

3-(*tert*-butyldimethylsilyloxy)-5,5-dimethyltricyclo[6·6·0·$0^{2,7}$]tetradec-$\Delta^{2,7}$-ene (9c). Alcohol **5c** (2.38 mmol, 0.557 g), as a mixture of 4 diastereomers, was treated with triethylamine (3.57 mmol, 0.498 mL), TBSCl (2.86 mmol, 0.430 g) and DMAP (0.24 mmol, 0.029 g) following the general procedure to afford 0.655 g of **9c** (79%) as an inseparable mixture of 4 diastereomers: IR(film): 2954, 2929, 2856, 1474, 1464, 1363, 1258, 1092, 1059, 868, 841, 775 cm^{-1}; ^{1}H NMR δ 4.21(m, 4H), 2.82(m, 1H), 2.72(m, 1H), 2.62(m, 3H), 2.44(d, 2H, *J*=11.6 Hz), 2.35(m, 1H), 2.22-1.10(m, 64H), 0.98(s, 12H), 0.90(s, 36H), 0.88(s, 12H), 0.07(s, 24H); ^{13}C NMR δ 145.5, 145.3, 145.2, 144.9, 143.3, 143.0, 142.7, 142.6, 66.6, 64.1, 63.7, 51.0, 50.7, 50.6, 48.8, 48.5, 47.8, 47.1, 46.9, 46.8, 46.6, 45.3, 36.8, 36.4, 36.3, 36.1, 33.4, 33.0, 32.9, 32.8, 31.6, 31.4, 31.0, 30.6, 30.4, 30.3, 29.8, 29.7, 29.6, 28.6, 28.5, 28.4, 28.3, 27.5, 27.0, 26.8, 26.5, 26.3, 26.4, 26.2, 26.1, 26.0, 25.9, 25.8, 25.6, 25.3, 18.3, 18.2, 18.2, 18.1, -4.3, -4.4, -4.5, -4.6, -4.7; HRMS Calcd for $C_{22}H_{40}OSi$: 348.2845; found: 348.2855.

General Procedure For Ozonolysis Reactions. To a solution of either **8** or **9** in 5 mL of dry CH_2Cl_2:MeOH = 4:1 at -78 °C was bubbled O_3 until a pale blue color persisted. The excess O_3 was allowed to evaporate and methyl sulfide (1.5 eq.) was added. The reaction was stirred at RT for 1 h before removing the solvent *in vacuo*. The crude product was purified by chromatography (20 g silica gel, 10% ethyl acetate/hexanes) to afford the cyclooctanediones **10** and **11**. Analytical samples were prepared by recrystallization from hexanes.

(1β, 3β, 8β)-3-(*tert*-butyldimethylsilyloxy)-bicyclo[6·3·0]undecane (10a). Alkene **8a** (0.71 mmol, 0.20 g) was treated with O_3 according to the general procedure and worked up with DMS (1.07 mmol, 0.078 mL) to afford 0.178 g of **10a** (79%): mp=65-66 °C; IR(CCl_4): 1718, 1701 cm^{-1}; ^{1}H NMR δ 4.25(dd, 1H, *J*=6.0, 2.4 Hz), 3.28(m, 1H), 3.00(dt, 1H, *J*=11.6, 8.0 Hz), 2.46(dt, 1H, *J*=17.6, 12.8 Hz), 2.22-1.60(m, 11H), 0.90(s, 9H), 0.13(s, 3H), 0.00(s, 3H); ^{13}C NMR δ 214.0, 213.5, 77.2, 60.8, 49.6, 36.2, 30.7, 29.1, 28.2, 25.8, 24.3, 20.2, 18.4, -4.5, -5.6; Anal. Calcd for $C_{17}H_{30}O_3Si$: C, 65.76; H, 9.74. Found: C, 65.75; H, 9.79.

(1β, 3α, 8β)-3-(*tert*-butyldimethylsilyloxy)-bicyclo[6·3·0]undecane (10'a). Alkene **8'a** (0.66 mmol, 0.19 g) was treated with O_3 according to the general procedure and worked up with DMS (0.99 mmol, 0.073 mL) to afford 0.185 g of **10'a** (89%): mp=36-37 °C; IR(CCl_4): 1704 cm^{-1}; ^{1}H NMR δ 4.17(t, 1H, *J*=4.4 Hz), 3.61(dt, 1H, *J*=9.6, 8.0 Hz), 3.50(dt, 1H, *J*=10.0, 7.6 Hz), 2.30-1.45(m, 12H), 0.90(s, 9H), 0.05(s, 3H), 0.02(s, 3H); ^{13}C NMR δ 217.0, 212.4, 77.3, 55.6, 51.2, 39.6, 35.0, 28.9, 26.4, 25.6, 24.6, 18.9, 17.9, -4.9, -5.4; Anal. Calcd for $C_{17}H_{30}O_3Si$: C, 65.76; H, 9.74. Found: C, 65.67; H, 9.85.

(1β, 3β, 8β)-3-(*tert*-butyldimethylsilyloxy)-bicyclo[6·4·0]dodecane (10b). Alkene **8a** (0.74 mmol, 0.22 g) was treated with O_3 according to the general procedure and worked up with DMS (1.11 mmol, 0.082 mL) to afford 0.160 g of **10b** (67%): mp=66-67 °C; IR(CCl_4): 1717, 1700 cm^{-1}; ^{1}H NMR δ 4.20(dd, 1H, *J*=6.4, 2.8Hz), 2.98(m, 1H), 2.65(m, 1H), 2.40(dt, 1H, *J*=17.6, 12.8 Hz), 2.18(m, 1H), 2.05-1.64(m, 8H), 1.50-1.38(m, 3H), 1.24(m, 1H), 0.86(s, 9H), 0.10(s, 3H), -0.04(s, 3H); ^{13}C NMR δ 214.9, 213.9, 76.9, 57.2, 40.8, 35.2, 30.9, 27.4, 25.7, 24.3, 23.7, 21.3, 20.3, 18.4, -4.6, -5.7; Anal. Calcd for $C_{18}H_{32}O_3Si$: C, 66.62; H, 9.94. Found: C, 66.66; H, 10.00.

(1β, 3α, 8β)-3-(*tert*-butyldimethylsilyloxy)-bicyclo[6·4·0]dodecane (10'b). Alkene **8'b** (0.68 mmol, 0.20 g) was treated with O_3 according to the general procedure and worked up with DMS (1.0 mmol, 0.075 mL) to afford 0.200 g of **10'b** (91%): mp=87-88 °C; IR(CCl_4): 1703 cm^{-1}; ^{1}H NMR δ 4.31(dd, 1H, *J*=5.2, 3.2 Hz), 4.03(m, 1H), 3.05(m, 1H), 2.46(dd, 1H, *J*=15.6, 9.2 Hz), 2.08-1.56(m, 9H), 1.50-1.18(m, 4H), 0.94(s, 9H), 0.08(s, 3H), 0.07(s, 3H); ^{13}C NMR δ 217.4, 213.1, 78.2, 47.3, 44.9, 42.2, 36.7, 26.4, 25.6, 24.6, 23.7, 22.1, 18.4, 17.9, -4.9, -5.3; Anal. Calcd for $C_{18}H_{32}O_3Si$: C, 66.62; H, 9.94. Found: C, 66.60; H, 9.98.

(1β, 3α, 8β)-3-(*tert*-butyldimethylsilyloxy)-bicyclo[6·6·0]tetradecane (10c). Alkene **8c** (0.94 mmol, 0.30 g), as a mixture of 4 diastereomers, was treated with O_3 according to the general procedure and worked up with DMS (1.41 mmol, 0.104 mL) to afford 0.273 g of **10c** (82%) as an inseparable mixture of 4 diastereomers: IR(film): 1738, 1708 cm^{-1}; ^{1}H NMR δ 4.21(m, 3H), 4.08(m, 1H), 3.84(m, 1H), 3.71(m, 3H), 3.49(m, 4H), 2.60-1.10(m, 72H), 0.96-0.84(m, 36H), 0.12 to -0.05(m, 24H); ^{13}C NMR δ 221.4, 221.4, 219.5, 219.4, 217.5, 213.8, 213.7, 87.5, 85.8, 84.5, 79.3, 77.5, 77.2, 76.7, 74.3, 66.8, 60.0, 58.3, 56.5, 56.2, 53.8, 53.1, 48.7, 48.6, 47.0, 46.9, 45.9, 41.4, 40.8, 35.8, 34.7, 34.0, 33.6, 33.2, 28.0, 27.6, 27.0, 26.8, 26.5, 26.4, 26.1, 25.9, 25.8, 25.7, 25.6, 25.5, 25.4, 25.3, 24.1, 23.7, 22.1, 20.3, 18.4, 18.0, -3.7, -3.9, -5.1, -5.6, -5.8; HRMS Calcd for $C_{20}H_{36}O_3Si$: 337.2197 (M^+-Me); found: 337.2192.

(1β, 3α, 8β)-3-(*tert*-butyldimethylsilyloxy)-5,5-dimethylbicyclo[6·3·0]undecane (11a). Alkene **9a** (0.65 mmol, 0.20 g) was treated with O_3 according to the general procedure and worked up with DMS (0.98 mmol, 0.072 mL) to afford 0.164 g of **11a** (75%): mp=40-41.5 °C; IR(CCl_4): 1728, 1700 cm^{-1}; ^{1}H NMR δ 4.33(dd, 1H, *J*=5.6, 3.2 Hz), 3.17(m, 1H), 2.86(dt, 1H, *J*=11.2, 7.2 Hz), 2.55(d, 1H, *J*=12.8 Hz), 2.12-1.56(m, 9H), 1.09(s, 3H), 0.99(s, 3H), 0.87(s, 9H), 0.07(s, 3H), -0.06(s, 3H); ^{13}C NMR δ 213.1, 211.8, 78.7, 60.6, 49.1, 47.9, 42.6, 34.4, 30.9, 29.2, 28.6, 25.7, 23.7, 18.3, -4.7, -5.8; Anal. Calcd for $C_{19}H_{34}OSi$: C, 67.40; H, 10.12. Found: C, 67.46; H, 9.90.

(1β, 3β, 8β)-3-(*tert*-butyldimethylsilyloxy)-5,5-dimethylbicyclo[6·3·0]undecane (11'a). Alkene **9'a** (0.65 mmol, 0.20 g) was treated with O_3 according to the general procedure and worked up with DMS (0.98 mmol, 0.072 mL) to afford 0.183 g of **11'a** (83%): IR(film): 1701 cm^{-1}; ^{1}H NMR δ 4.02(dd, 1H, *J*=11.2, 4.4 Hz), 3.69(dt, 1H, *J*=8.4, 2.8 Hz), 2.89(dt, 1H, *J*=10.4, 8.4 Hz), 2.38(d, 1H, *J*=12.8 Hz), 2.05-1.50(m, 9H), 1.04(s, 3H), 0.97(s, 3H), 0.81(s, 9H), 0.00(s, 3H), -0.05(s, 3H); ^{13}C NMR δ 214.3, 211.4, 76.9, 60.8, 47.6, 45.8, 44.9, 33.1, 31.1, 29.1, 29.1, 28.6, 25.5, 24.1, 17.9, -5.0, -5.2; HRMS Calcd for $C_{19}H_{34}OSi$: 323.2036 (M^+-Me); found: 323.2036.

(1β, 3α, 8β)-3-(*tert*-butyldimethylsilyloxy)-5,5-dimethylbicyclo[6·4·0]dodecane (11b). Alkene **9b** (0.61 mmol, 0.20 g) was treated with O_3 according to the general procedure and worked up with DMS (0.92 mmol, 0.067 mL) to afford 0.142 g of **11b** (66%): mp=105-106 °C; IR(CCl_4): 1734, 1712 cm^{-1}; ^{1}H NMR δ 4.37(dd, 1H, *J*=4.0, 2.8 Hz), 2.57(d, 1H, *J*=13.6 Hz), 2.52(dt, 1H, *J*=14.8, 11.6 Hz), 2.36(dt, 1H, *J*=15.2, 11.6 Hz), 2.01(dd, 1H, *J*=16.0, 3.6 Hz), 1.90(d, 1H, *J*=13.6 Hz, 1.81-1.57(m, 6H), 1.43(m, 1H), 1.31-1.12(m, 2H), 1.09(s, 6H), 0.90(s, 9H), 0.10(s, 3H), -0.05(s, 3H); ^{13}C NMR δ 214.6, 212.0, 78.7, 56.0, 51.0, 48.0, 42.5, 35.1, 31.6, 30.9, 29.8, 26.0, 25.7, 24.8, 24.2, 18.4, -4.8, -5.9; Anal. Calcd for $C_{20}H_{36}OSi$: C, 68.13; H, 10.29. Found: C, 67.95; H, 10.15.

(1β, 3β, 8β)-3-(*tert*-butyldimethylsilyloxy)-5,5-dimethylbicyclo[6•4•0]dodecane (11'b). Alkene **9'b** (0.50 mmol, 0.16 g) was treated with O_3 according to the general procedure and worked up with DMS (0.75 mmol, 0.055 mL) to afford 0.163 g of **11'b** (93%): mp=79-80 °C; IR(CCl_4): 1707 cm^{-1}; ^1H NMR δ 4.02(dd, 1H, *J*=10.4, 5.2 Hz), 3.40(dt, 1H, *J*=8.4, 4.0 Hz), 2.72(m, 1H), 2.39(d, 1H, *J*=12.8 Hz), 2.00(m, 2H), 1.75(m, 4H), 1.65-1.40(m, 4H), 1.30(m, 1H), 1.09(s, 3H), 1.04(s, 3H), 0.86(s, 9H), 0.04(s, 6H); ^{13}C NMR δ 213.4, 212.4, 77.2, 56.0, 48.6, 46.5, 33.6, 31.4, 28.6, 27.5, 25.6, 24.5, 24.4, 22.0, 18.0, -4.8, -5.0; Anal. Calcd for $C_{20}H_{36}OSi$: C, 68.13; H, 10.29. Found: C, 68.15; H, 10.12.

3-(*tert*-butyldimethylsilyloxy)-5,5-dimethylbicyclo[6•6•0]tetradecane (11c). Alkene **9c** (0.47 mmol, 0.162 g), as a mixture of 4 diastereomers, was treated with O_3 according to the general procedure and worked up with DMS (0.70 mmol, 0.051 mL) to afford 0.159 g of **11c** (89%) as an inseparable mixture of 4 diastereomers: IR(film): 1710 cm^{-1}; ^1H NMR δ 4.38(m, 1H), 4.27(m, 1H), 4.05(m, 1H), 3.97(m, 1H), 3.68(m, 4H), 3.30(m, 1H), 3.08(m, 1H), 2.92-2.72(m, 4H), 2.62-2.30(m, 6H), 2.12-1.28(m, 56H), 1.25-0.96(m, 24H), 0.90-0.82(m, 36H), 0.09 to -0.07(m, 24H); ^{13}C NMR δ 216.7, 215.6, 213.8, 213.4, 213.2, 213.1, 212.9, 212.6, 78.7, 78.2, 76.8, 58.3, 58.1, 56.9, 55.1, 55.1, 51.4, 51.1, 47.6, 47.4, 47.4, 46.3, 45.2, 44.9, 43.9, 43.4, 43.1, 42.7, 35.2, 33.2, 32.9, 32.0, 31.5, 31.4, 30.8, 30.5, 28.9, 28.8, 28.6, 28.5, 28.3, 27.8, 27.5, 27.4, 27.3, 27.01, 26.8, 26.4, 26.1, 26.0, 25.9, 25.8, 25.7, 25.6, 25.5, 25.3, 25.1, 24.9, 24.6, 24.5, 24.4, 23.9, 18.4, 18.3, 18.0, -4.8, -4.9, -5.0, -5.1, -5.9, -6.0; HRMS Calcd for $C_{22}H_{40}OSi$: 365.2512 (M^+-Me); found: 365.2507.

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