A New Strategy to Bicyclo[5.3.0]decenes via Anionic Intramolecular Ring Opening of Oxabicyclo[3.2.1] Compounds

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Abstract: Intramolecular anionic ring opening of oxabicyclo[3.2.1] systems has been achieved and leads to an efficient route to bicyclo[5.3.0]decenes which are trans fused. Tethers containing heteroatoms (X = O, S, NMe) as well as all-carbon derivatives have been successfully cyclized under these conditions. It is not necessary to take any special precautions (high dilution, slow addition etc.) when carrying out the transmetalation−cyclization since intermolecular ring opening does not occur under these conditions.

Introduction

The development of methods that efficiently construct polycyclic, multifunctional systems which are stereochemically rich is of great interest in synthetic chemistry. Our objective was to design a strategy which would rapidly assemble the trans-fused bicyclo[5.3.0] ring system and be sufficiently flexible to incorporate substitution within the rings and/or at the periphery. The 5,7-fused ring system is found in many natural products.[2] A recent review on sesquiterpenes states that of the more than 500 new sesquiterpenes, about 100 possess the 5,7-fused ring framework.[3] The biological activity of the tumor promoting phorbols (tigliane skeleton), the structurally related daphnane as well as the broadly active grayanotoxins, provided further impetus for these studies (Figure 1).[4]

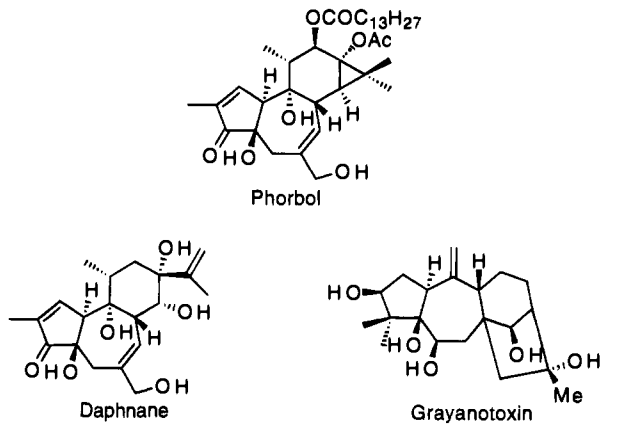

Figure 1.

A survey of strategies for the construction of the bicyclo-[5.3.0] carbon framework has been reported by Heathcock.[5a] The major strategy employed was an annulation of either the cyclopentane ring or the cycloheptane ring. The transannular cyclization of appropriately constructed cyclodecanes and the rearrangements of either the bicyclo[4.3.1]decanes or a hydronaphthalene are other ways to prepare the 5,7-fused ring system.[5]

In spite of the efforts reported to date, few of the methods give the trans-fused bicyclo[5.3.0] system.[4m,n,6] Our overall plan, outlined in Scheme 1, relies on an intramolecular cyclization process in which the C−C bond formation is accompanied by the rupture of a C−O bond. There exists a significant body of work on anionic, cationic, or radical cyclization reactions as a means of creating and/or appending a new ring onto an existing framework.[7] The ability to further functionalize a radical or carbanion which is formed following cyclization, by addition of a radical acceptor or an electrophile, enhances the utility of these approaches.[8,9] The notion of coupling the anionic cyclization with a fragmentation was attractive since the reappearance of unsaturation in the product introduces a site for subsequent reactions. Previous work in our laboratory on the nucleophilic ring opening reaction of oxabicyclic compounds suggested that an appropriate cyclization precursor would be an organolithium species.[10] In this first report on the feasibility of this opening,

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0002-7863/95/1517-1954$09.00/0

Scheme 1

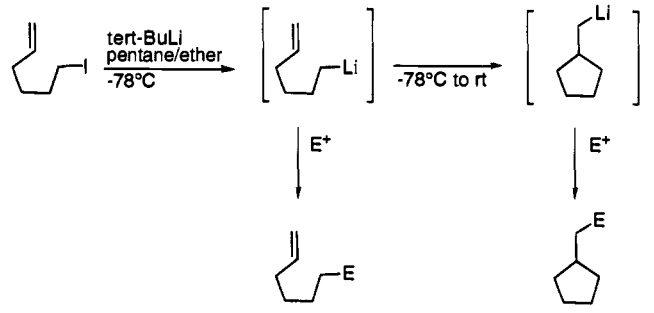
we have addressed the issue of regio- and stereocontrol in the bond-forming reaction, the efficiency of the openings, and ease of access to the starting materials.

Parenthetically, we note that while the focus of the current work is toward the [5.3.0] systems, the products of the ring opening can also be envisaged as precursors to a wide variety of mono- and tricyclic compounds.

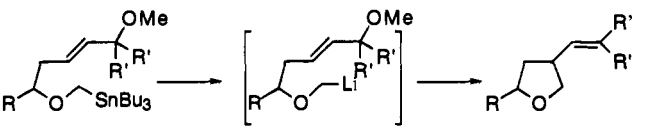
Background

Bailey, Chamberlin, and Cooke have carried out important investigations on anionic cyclization reactions.[9ag,11-13] For example, Bailey showed that primary 5-hexenyllithiums, which are prepared in excellent yield by metal−halogen exchange between the iodide and *t*-BuLi at −78 °C in pentane/ether, can be trapped by various electrophiles. However, on warming to room temperature, they undergo a 5-*exo-trig* cyclization providing the five-membered carbocycles, Scheme 2. These observations conclusively establish that the carbanion is the reactive species rather than a one-electron cyclization pathway which undergoes a second one-electron transfer. The diastereoselectivity of alkyl and alkenyllithium addition to terminal olefins

Scheme 2



Scheme 3



was also investigated.[14] Cyclizations of Grignard, organozinc, and organoalanes have also been described with recent advances reported by Normant, Marek, and Knochel.[15-17]

Broka developed a route to substituted tetrahydrofurans by anionic cyclization of an α-alkoxy anion of a homoallylic ether, Scheme 3.[9h,i] Whereas a terminal olefin gave a good yield of the cyclized product, a 1,2-disubstituted alkene did not cyclize unless a leaving group such as a methoxy was positioned at the allylic carbon. *Cis* isomers predominated with selectivities approaching 15:1.

These studies formed the foundation of our investigations which are described herein and which illustrate that the leaving group can be constrained within a ring in order to form bicyclic products. Of the two stereochemical options which are possible (syn or anti displacement), a single stereoisomer was isolated in all cases and the structure of one of the cyclized adducts was unambiguously determined by X-ray crystallography, *inter alia*.

Results and Discussion

(a) Preparation of Oxabicyclo[3.2.1] Compounds Bearing α-Alkylheterotin Tether 3a−l. The oxabicyclo[3.2.1] substrates **3a**−**l** employed in this study were prepared in three to five steps using the [4 + 3] cycloaddition of an oxyallyl cation with a variety of new substituted furan partners as the key step, Table 1 and Scheme 4.[18-21] The α-(tributylstannyl)methyl ether of furfuryl alcohol **1a**, 5-methyl-2-furanmethanol **1b** (prepared by the reduction of 5-methylfurfural), furfuryl-2-ethanol **1c** (prepared by trapping 2-lithiofuran with ethylene oxide[22]), and furfuryl mercaptan **1d** were prepared by the method of Still (KH, Bu_3SnCH_2I).[23-26] Furfurylamine was acylated with methyl chloroformate and then alkylated with Bu_3SnCH_2I (**1e**) prior to the cycloaddition.[27]

Noyori's [4 + 3] cycloaddition[9] was employed for the synthesis of oxabicyclo[3.2.1] substrates **2a**,**b**,**d**−**g**, Table 1. The method involves the generation of an oxyallyl cation from a di- or tetrabromo ketone[18,20] and Zn/Ag couple[20], followed by

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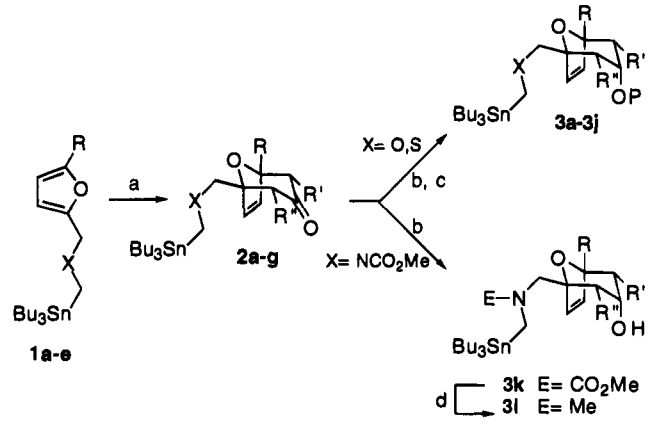
Scheme 4[a]



[a] (a) [4 + 3] cycloaddition, details in the Experimental Section. (b) L-selectride, THF, −78 °C. (c) KH, THF; PX = MeI, BnBr, or TBDMSCl. (d) $LiAlH(OMe)_3$, THF.

Table 1. [4 + 3] Cycloaddition

Entry	Substrate		Product [a]			Yield [b]
(i) *α-alkyl hetero tether*						
1	1a X= O	R= H	2a	R'= Me	R"= Me	22%
2	1a	R= H	2b	R'= H	R"= H	13%
3	1a	R= H	2c	R'= H	R"= OMe	33%
4	1b	R= Me	2d	R'= Me	R"= Me	-[c]
5	1c n= 2	R= H	2e	R'= Me	R"= Me	43%
6	1d X= S	R= H	2f	R'= Me	R"= Me	24%
7	1e X= NCO_2Me	R= H	2g	R'= Me	R"= Me	55%
(ii) *α-alkyl tether*						
8	1f		2h	R'= Me	R"= Me	35%
9	1f		2i	R', R"= $(CH_2)_3$		50%

[a] [4 + 3] cycloaddition, details in the Experimental Section. [b] Isolated yield of analytically pure product. [c] Product was carried out to the next step without any further purification.

cycloaddition to the furan derivatives. In the case of **2b**, cycloaddition produces an α,α′-dibromo product which was reduced with Zn/Cu couple in a methanol/ammonium chloride solution. Compound **2c** was prepared according to Albizati's method[21a] utilizing a silyloxyallyl cation with furan **1a**. The cycloaddition generated a mixture of stereoisomers (which were carried through the next step). Following cycloaddition (13−55% yield) under the appropriate conditions, the ketones **2a−g** were stereoselectively reduced with L-selectride.[28,29] Previous studies in our laboratory showed that oxabicyclo[3.2.1]octenones react with L-selectride to furnish the axial alcohols exclusively.[29]

(28) The substituted furans and the oxyallyl cations (produced from α,α-dihalo ketones[18] using Noyori's zinc−silver couple[19,20] or from the silyl enol ether using Albizati's method[21]) were submitted to a [4 + 3] cycloaddition using methodology discovered by Noyori,[19] Fohlisch,[31] or Albizati[21] yielding the oxabicyclic [3.2.1] precursors.

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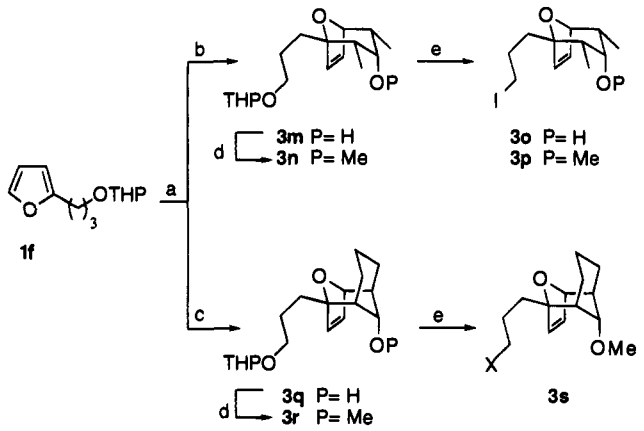
Scheme 5[a]



[a] (a) [4 + 3] cycloaddition, details in the Experimental Section. (b) L-selectride, THF, −78 °C. (c) $LiAlH_4$, THF, −78 °C. (d) KH, THF; MeI. (e) I_2, dppe, CH_2Cl_2.

The free alcohols as well as the methyl **3b,j**, silyl **3d**, or benzyl **3c** ethers were investigated in the cyclization reaction.[30]

(b) Preparation of Oxabicyclo[3.2.1] Compounds Bearing α-Alkyliodo Tether 3p and 3s. In a similar fashion, the oxabicyclo[3.2.1]octenones **2h−i** were prepared from the corresponding substituted tetrahydropyranyl protected furan **1f** and oxyallyl cations under the conditions described by Noyori and Fohlisch (Scheme 5).[19,31,32] The furan derivative **1f** was prepared by trapping 2-lithiofuran with allyl bromide followed by hydroboration and finally protection of the resulting alcohol as the tetrahydropyranyl ether. Furan **1f** undergoes a [4 + 3] cycloaddition with an oxyallyl cation (either from α,α′-dibromo ketone[18] or from the α-chlorocyclohexanone[32]) to give **2h** and **2i**. Reduction of the ketones **2h** and **2i** respectively with L-selectride and lithium aluminum hydride, protection of the alcohol as the methyl ether, and direct conversion of the THP protected alcohol to the iodide (I_2, dppe, CH_2Cl_2) afforded the desired starting materials **3p** and **3s**.[33]

(c) Intramolecular Ring Opening of the α-Alkoxytin Substituted Series. The feasibility of the intramolecular ring opening of the oxabicyclo[3.2.1] compounds was first explored on the stannyl ethers **3a−h**, Table 2. MeLi was chosen as the transmetalation agent since we had previously established that it did not induce ring opening in bridgehead substituted [3.2.1] systems.[10c,d] This eliminated any intermolecular coupling and avoided the need for high dilution or other precautions during the transmetalation. In a typical experiment, **3a** was treated with 5 equiv of MeLi in THF at −78 °C for 5 min to generate the α-oxy organolithium species. Upon warming to 0 °C and stirring for minutes (**3b,d**) to hours (**3a,c,e−g**), the bicyclo[5.3.0] tetrahydrofurans are produced in 71−86% yield. In the case of the protected substrates **3b** and **3d**, anionic cyclization yielded unstable bicyclo[5.3.0] compounds since longer reaction times led to degradation of products and decreased yields. Furthermore, substrates **3e,f** and even the doubly substituted substrates **3g** undergo reaction with equal facility to furnish the

(30) The alcohol may be protected as its methyl, benzyl, or *tert*-butyldimethylsilyl ethers (KH, 18-c-6, PX = MeI, BnBr or TBDMSCl, THF).

(31) (a) Fohlisch, B.; Gehrlach, E.; Herter, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 137. (b) Fohlisch, B.; Gottstein, W.; Kaiser, R.; Wanner, I. *Tetrahedron Lett.* **1980**, 3005. (c) Fohlisch, B.; Gottstein, W.; Herter, R.; Wanner, I. *J. Chem. Res. (S)* **1981**, 246.

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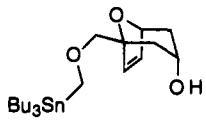
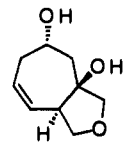
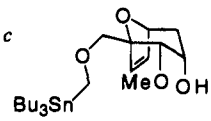
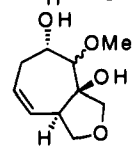
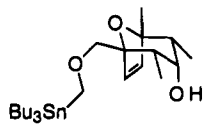
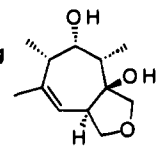
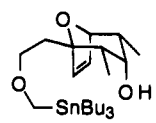
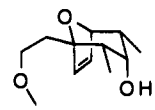
Table 2. Intramolecular Ring Opening of the Alkyloxy Tether Series

Entry	Substrate		Product [a]		Yield [b]
1	**3a**	R= H	**4a**	R= H	85%
2	**3b**	R= Me	**4b**	R= Me	82%
3	**3c**	R= Bn	**4c**	R= Bn	80%
4	**3d**	R= TBDMS	**4d**	R= TBDMS	83%
5	**3e**		**4e**		88%
6	**3f** [c]		**4f**		80%
7	**3g**		**4g**		71%
8	**3h**		**4h**		[d]

[a] Reaction with 5 equiv of MeLi in THF at −78 °C for 5 min then warming to 0 °C. [b] Isolated yield of analytically pure product. [c] A mixture (4−5:1) of the equatorial−axial methoxy isomers was isolated from the cycloaddition. [d] Product not purified, undetermined yield.

bicyclo[5.3.0] **4e−g**. Last of all, in the case of **3h**, increasing the chain length by one carbon leads to transmetalation but no cyclization in accord with previous observations.[9h]

The ^{13}C NMR spectrum of **4g** deserves further comment since it was poorly resolved at ambient temperature and the number of signals were less than expected. When the spectrum was obtained in toluene-d_8 at 90 °C the intensity of some signals increased and the resolution improved which indicates that several conformations are of similar energy and are interconverting slowly on the NMR time scale. Even at 90 °C, two quaternary carbons still appeared as broad signals.

The stereochemistry of the bicyclo[5.3.0] compound **4a** was established by X-ray crystallography and is consistent with an intramolecular anionic attack of the olefin in an exo S_N2' fashion. The other adducts were assumed to have cyclized in an analogous fashion. The product contains five contiguous stereocenters, a new ring, and a tertiary bridgehead hydroxyl moiety.

We attempted the *inter*molecular ring opening of an unsymmetrical oxabicyclic [3.2.1] with methoxymethyllithium under identical conditions (Scheme 6). After 1 h at 0 °C, and an additional 22 h at room temperature, no ring opening product was observed. This illustrates that intramolecular cyclization is much more facile and otherwise unreactive nucleophiles can now induce ring opening.

The scope of the methodology was determined by examining

Scheme 6

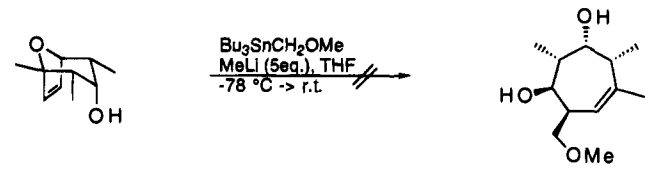
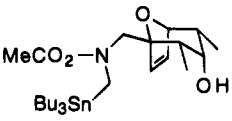
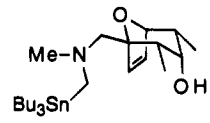
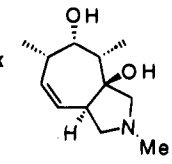


Table 3. Intramolecular Ring Opening of the Alkylhetero Tether Series

Entry	Substrate		Product [a]		Yield [b]
1	**3i**	R= H	**4i**	R= H	88%
2	**3j**	R= Me	**4j**	R= Me	80%
3	**3k**				[c]
4	**3l**		**4k**		80%

[a] Reaction with 5 equiv of MeLi in THF at −78 °C for 5 min then warming to 0 °C. [b] Isolated yield of analytically pure product. [c] No cyclized product was observed; ^1H NMR showed a complex mixture.

other α-heterostabilized carbanions, Table 3. A successful five-membered annulation of the α-alkylthio **3i,j** was achieved. The corresponding amide derivative **3k** did not cyclize. The change in bond angle associated with the amide or the additional stabilization of the anion[34] was considered to be responsible for its reluctance to undergo closure. Following conversion of the amide **3k** to the methyl amine **3l** by reduction with $LiAlH_4$ or $LiAlH(OMe)_3$ and treatment with MeLi under the usual conditions, the [5.3.0] cyclized product **4k** was obtained in good yield.[35]

(d) Intramolecular Ring Opening of the α-Alkyliodo Series. Use of this approach in a synthesis of the phorbols requires that an all-carbon chain must cyclize efficiently. Intramolecular cyclization of oxabicyclic [3.2.1] compounds **3o** and **3p** was therefore investigated. Lithium−iodide exchange (*t*-BuLi in pentane/ether at −78 °C) was rapid, but cyclization did not occur until the mixture was warmed to room temperature. Substrate **3o**, containing a free hydroxyl group, failed to cyclize but following protection as its methyl ether, **3p** cyclized in 80% yield, Table 4.

We also investigated the behavior of a more complex oxatricyclic [3.2.1] compound **3s**. Treatment of the latter under identical conditions (-78 °C for 5 min and then room temperature for 1 h) resulted in a mixture of the desired cyclized product

(34) (a) Beak, P.; Reitz, D. B. *Chem. Rev.* **1978**, *78*, 275. (b) Rondan, N. G.; Houk, K. N.; Beak, P.; Zajdel, W. J.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Org. Chem.* **1981**, *46*, 4108.

(35) Initially, the reduction of **3k** had been effected with $LiAlH_4$ (Maryanoff, B. E.; Almond, H. R., Jr. *J. Org. Chem.* **1986**, *51*, 3295). However, less destannylation was observed using $LiAlH(OMe)_3$ (Malek, J.; Cerny, M. *Synthesis* **1972**, 229).

Table 4. Intramolecular Ring Opening of the Carbon Tether Series

Entry	Substrate	Product [a]	Yield [b]
1	**3o** R= H	**4m** R= H	trace
2	**3p** R= Me	**4n** R= Me	80%
3	**3s**	**4o**	90%

[a] Reaction with 2.2 equiv of *t*-BuLi in THF at −78 °C for 5 min then warming to 0 °C for **4o** and room temperature for **4n**. [b] Isolated yield of analytically pure product.

accompanied by considerable amount of product tentatively identified as diene **4p** (Figure 2). However, by keeping the

4p

Figure 2.

temperature below 0 °C the desired cyclized product **4o** was obtained in excellent yield.

(e) Comparison of Inter- and Intramolecular Ring Opening. The *inter*molecular ring opening of symmetrical [3.2.1] system utilizes 5 equiv of RLi in ether at 0 °C for 1−3 h thus providing the cycloheptenediols (R = *n*-Bu, *s*-Bu, *t*-Bu), yields ranging from 70−90%. MeLi is often unreactive under the standard conditions and requires addition of TMEDA to induce ring opening. Unsymmetrical [3.2.1] adducts usually require excess organolithium. In contrast, the *intra*molecular ring opening occurred readily at 0 °C in minutes to a few hours and requires only "1" equiv of the nucleophile in order to react and give the desired bicyclo [5.3.0] system in yields of 70−90%.

Conclusion

We have shown that oxabicyclo[3.2.1] compounds bearing a three-atom tether (α-heteroalkyltin or α-alkyliodo) are available in 3−7 steps starting from available furans via a [4 + 3] cycloaddition. The anionic intramolecular ring opening of oxabicyclic compounds is efficient for tethers with a variety of substituents in the tether. Bicyclo[5.3.0] systems are generated with complete regio- and stereocontrol. Studies are in progress on the application of this process to the synthesis of natural products.

Experimental Section

General. Analytical thin-layer chromatography (TLC) was performed on precoated aluminum-backed silica gel (Merck 60F-254). Flash chromatography was performed using 230−400 mesh silica gel or as indicated otherwise using 80−200 mesh alumina.[36] Infrared spectra were recorded on a Nicolet 8210E FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 or VXR-400 spectrometer. Chemical shifts are reported in parts per million (δ) using tetramethylsilane as a reference. High-resolution mass spectra were obtained on a VG 70−250S spectrometer. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN. All glassware was flame dried under an inert atmosphere of dry nitrogen. Unless stated otherwise, commercial reagents were used without purification. Tetrahydrofuran and diethyl ether were distilled immediately prior to use from sodium/benzophenone. Pyrrolidine and dichloromethane were distilled immediately prior to use from calcium hydride.

General Procedure for the Preparation of α-Alkylhetero Organostannanes from Furan Derivatives. ((Furfuryloxy)methyl) tri-*n*-butylstannane (1a). Potassium hydride (1.13 g, 14 mmol, 50% in oil), which was washed three times with pentane, was suspended in THF (35 mL). A solution of furfuryl alcohol (1.17 g, 12 mmol) in THF (10 mL) was added dropwise (over a period of 0.5 h). The mixture was stirred at room temperature for 0.5 h before the dropwise addition of (iodomethyl)tributyltin[25] (4.00 g, 9 mmol) in THF (5 mL). After the addition was complete, stirring was continued for an additional 22 h. The reaction was quenched with a little methanol and poured into hexanes (140 mL). The organic phase was washed with water followed by brine, dried over Na_2SO_4, and concentrated *in vacuo*. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 20:1, **1a** (2.91 g, 80%) was obtained as a colorless oil. R_f = 0.75 on silica gel (hexanes−ethyl acetate 10:1); IR (neat) 2959, 2924, 2875, 2853, 1504, 1462, 1377, 1152, 1060 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.40 (1H, s), 6.34 (1H, s), 6.29 (1H, d, J = 3.2 Hz), 4.34 (2H, s), 3.72 (2H, s), 1.54−1.41 (6H, m), 1.37−1.21 (6H, m), 0.94−0.84 (15H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 142.9, 110.6, 109.4, 86.7, 69.4, 61.7, 29.6, 27.8, 14.3, 9.5; HRMS calcd for $C_{18}H_{34}O_2Sn$ [M − Bu]$^+$ 345.0876, found 345.0891.

(((5-Methyl-2-furfuryl)oxy)methyl)-tri-*n*-butylstannane (1b). A solution of 5-methylfurfural (1.00 g, 9 mmol) in diethyl ether (10 mL) was cooled to 0 °C, treated portionwise with lithium aluminum hydride (0.200 g, 4.7 mmol), and stirred at 0 °C for 30 min. The reaction was quenched cautiously with 1.0 M Rochelle's salt and stirred for an additional 5 h. The mixture was extracted with ether. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 2:1, 5-methyl-2-furanmethanol (0.963 g, 94%) was obtained as a colorless oil. R_f = 0.70 on silica gel (hexanes−ethyl acetate 10:5); ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.2 (1H, d), 5.9 (1H, d), 4.5 (2H, br s), 2.3 (3H, s), 1.75 (1H, br s).

To a suspension of potassium hydride (0.826 g, 10.3 mmol, 50% in oil) in THF (10 mL) was added 5-methyl-2-furanmethanol (0.963 g, 8.6 mmol) in THF (8 mL). The mixture was stirred at room temperature for 0.5 h before the dropwise addition of (iodomethyl)tributyltin (2.965 g, 6.9 mmol). After purification by flash chromatography on silica gel with 100% hexanes, **1b** (1.95 g, 68%) was obtained as a colorless oil. R_f = 0.54 on silica gel (hexanes); IR (neat) 3107, 2959, 2924, 2875, 2846, 1560, 1462, 1377, 1222, 1054 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.17 (1H, d, J = 3.0 Hz), 5.91 (1H, d, J = 3.0 Hz), 4.28 (2H, s), 3.73 (2H, s), 2.29 (3H, s), 1.55−1.43 (6H, m), 1.35−1.24 (6H, m), 0.95−0.85 (15H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 152.7, 150.9, 110.5, 106.5, 69.4, 61.4, 29.6, 27.8, 14.1, 9.4; HRMS calcd for $C_{19}H_{36}O_2Sn$ [M − Bu]$^+$ 359.1033, found 359.1047.

((2-Furylethoxy)methyl)-tri-*n*-butylstannane (1c). To a suspension of potassium hydride (1.5 g, 18.7 mmol, 50% in oil) in THF (25 mL) was added furan-2-ethanol (1.5 g, 13 mmol) in THF (10 mL). The mixture was stirred at room temperature for 0.5 h before the dropwise addition of (iodomethyl)tributyltin (4.59 g, 10.1 mmol) in THF (5 mL). After purification by flash chromatography on silica gel with hexanes−ethyl acetate 100:1 to 20:1, **1c** (4.04 g, 91%) was obtained as a colorless oil. R_f = 0.86 on silica gel (hexanes−ethyl acetate 10:1); IR (neat) 2959, 2924, 2875, 2854, 1595, 1462, 1377, 1089 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.25 (1H, s), 6.22 (1H, m),

(36) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(37) The relative stereochemistry of **4a** was established by X-ray crystallography. The details of the structure determination will be published elsewhere: Lough, A. J.; Lautens, M.; Kumanovic, S. *Acta Cryst. C*, in preparation.

5.99 (1H, m), 3.69 (2H, s), 3.52 (2H, t, J = 6.9 Hz), 2.83 (2H, t, J = 6.7 Hz), 1.49−1.27 (6H, m), 1.26−1.19 (6H, m), 0.88−0.80 (15H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 154.1, 141.5, 110.8, 106.3, 73.9, 62.6, 29.8, 29.3, 27.9, 14.3, 9.6.

((2-Furylthio)methyl)-tri-*n*-butylstannane (1d). To a suspension of sodium hydride (0.80 g, 26.6 mmol, 80% in oil) in DMF (30 mL) was added dropwise furfurylmercaptan (2.2 mL, 22 mmol). The mixture was stirred at room temperature for 0.5 h before the dropwise addition of (iodomethyl)tributyltin (10.0 g, 23 mmol). After the addition was complete, stirring was continued for 22 h. The reaction was quenched with a little methanol, diluted in water, and extracted with ether. The combined organic layers were washed with water followed by brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 10:1, **1d** (6.99 g, 76%) was obtained as a colorless oil. R_f = 0.89 on silica gel (hexanes−ethyl acetate 10:1); IR (neat) 3114, 2952, 2924, 2853, 1595, 1462, 1377, 1250, 1068 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.36 (1H, d, J = 1.8 Hz), 6.31 (1H, dd, J = 3.1, 1.9 Hz), 6.17 (1H, d, J = 2.3 Hz), 3.67 (2H, s), 1.87 (2H, s), 1.53−1.41 (6H, m), 1.40−1.23 (6H, m), 0.96−0.84 (15H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 142.4, 110.7, 107.8, 86.7, 35.1, 29.5, 27.8, 14.2, 10.1, 9.3; HRMS calcd for $C_{18}H_{34}OSSn$ [M − Bu]$^+$ 361.0648, found 361.0632.

2-((*N*-(methoxycarbonyl)-*N*-[(tri-*n*-butylstannyl)methyl]amino)-methyl)furan (1e). A suspension of potassium carbonate (171 g, 1.23 mol) and furfurylamine (18.1 mL, 0.21 mol) in acetone (400 mL) was treated with methyl chloroformate (63 mL, 0.82 mol) at room temperature. After the addition was complete, stirring at reflux was continued for an additional 18 h. The reaction mixture was filtered through silica gel and evaporated *in vacuo*. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 10:1, 2-furfurylmethyl carbamate (25.02 g, 90%) was obtained as a yellow oil. R_f = 0.24 on silica gel (hexanes−ethyl acetate 10:1); IR (neat) 3339, 3156, 3121, 2995, 2952, 1708, 1532, 1250 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.29 (1H, d, J = 1.8 Hz), 6.26 (1H, dd, J = 3.2, 1.9 Hz), 6.16 (1H, d, J = 3.0 Hz), 5.38 (1H, br s), 4.29 (2H, d, J = 5.9 Hz), 3.62 (3H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 157.4, 152.3, 142.6, 110.8, 107.6, 52.7, 38.5.

A solution of 2-furfurylmethyl carbamate (6.02 g, 38 mmol) in DMF (10 mL) was added dropwise over a period of 0.2 h to a suspension of sodium hydride (1.39 g, 46 mmol, 80% in oil) in DMF (10 mL). The black mixture was stirred at room temperature for 2 h before the dropwise addition of (iodomethyl)tributyltin (14.7 g, 34 mmol) in DMF (5 mL). After the addition was complete, stirring was continued at room temperature for an additional 22 h. The reaction was quenched with a little methanol, diluted in water, and extracted with ether. The combined organic layers were washed with water followed by brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 10:1, **1e** (12.0 g, 77%) was obtained as a colorless oil. R_f = 0.66 on silica gel (hexanes−ethyl acetate 10:1); IR (neat) 3121, 2959, 2924, 2875, 2854, 1694, 1469, 1377, 1209, 1103 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.34 (1H, d, J = 1.8 Hz), 6.31 (1H, dd, J = 3.2, 1.8 Hz), 6.22 (1H, dd, J = 12.7, 2.9 Hz), 4.41 (2H, d, J = 8.5 Hz), 3.69 (3H, s), 2.90 (2H, d, J = 17.0 Hz), 1.51−1.40 (6H, m), 1.39−1.17 (6H, m), 0.93−0.83 (15H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 157.0, 151.9, 142.6, 110.8, 108.8, 108.2, 53.3, 53.1, 47.1, 46.9, 34.2, 33.0, 29.5, 27.9, 14.2, 10.8, 10.1; HRMS calcd for $C_{20}H_{37}NO_3Sn$ [M − Bu]$^+$ 402.1091, found 402.1091.

2-[(3-(2′-Furyl)propyl)oxy]tetrahydro-2*H*-pyran (1f). A solution of furan (20 mL, 0.28 mol) in THF (100 mL) at −78 °C was treated with *n*-BuLi (100 mL, 2.5 M solution in hexanes, 0.25 mol) and then stirred at 0 °C for an additional 3 h. The reaction was then cooled to −78 °C for the dropwise addition of allyl bromide (19.8 mL, 0.23 mol) in THF (22 mL). After the addition was complete, stirring was continued at 0 °C for an additional hour. The reaction was quenched with brine, diluted with water, and extracted with ether. The combined organic layers were subsequently washed with water followed by brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The product was fractionally distilled under nitrogen at 110−119 °C, at atmospheric pressure. 2-(1-Propenyl)furan was obtained as a clear colorless liquid (15 g, 62%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.35 (1H, s), 6.30 (1H, s), 6.05−5.80 (2H, m), 5.22−5.05 (2H, m), 3.40 (2H, d).

A solution of 9-BBN (309 mL, 0.5 M solution in THF, 0.15 mol) was added over 75 min to a solution of 2-(1-propenyl)furan (15.19 g, 0.14 mol) in THF (25 mL) at 0 °C. After the addition was complete, stirring was continued at 0 °C for an additional 22 h. The reaction was quenched cautiously at 0 °C with 5 M NaOH (170 mL), stirred 10 min, treated with 30% H_2O_2 (91 mL), and extracted with ether. The combined organic layers were dried over $MgSO_4$, filtered and evaporated *in vacuo*. The product was fractionally distilled at 145−155 °C, at P = 10 mmHg. 2-Furanpropanol was obtained as a colorless oil (10.6 g, 62%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.31 (1H, s), 6.28 (1H, m), 6.01 (1H, m), 3.69 (2H, t, J = 6.5 Hz), 2.74 (2H, t, J = 1.51 Hz), 1.90 (2H, q), 1.48 (1H, br s).

A solution of 2-furanpropanol (11.33 g, 89 mmol) in dichloromethane (90 mL) was treated with pyridinium *p*-toluenesulfonate (PPTS) (2.25 g, 8.9 mmol) followed by 3,4-dihydro-2*H*-pyran (DHP) (19.7 mL, 215 mmol) and then stirred at room temperature for 12 h. The reaction mixture was diluted in ether. The ether layer was washed with sodium bicarbonate and brine, dried over $MgSO_4$, filtered, and evaporated *in vacuo*. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 20:1, **1f** (15.0 g, 80%) was obtained as a colorless oil. R_f = 0.58 on silica gel (hexanes−ethyl acetate 10:1); IR (neat) 3114, 2938, 2875, 1595, 1448, 1384, 1131 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.28 (1H, d, J = 1.8 Hz), 6.26 (1H, dd, J = 3.1, 1.9 Hz), 5.98 (1H, d, J = 3.0 Hz), 4.58 (1H, t, J = 2.9 Hz), 3.87−3.73 (2H, m), 3.53−3.40 (2H, m), 2.72 (2H, t, J = 7.3 Hz), 2.05−1.49 (8H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 156.3, 141.3, 110.5, 105.3, 99.3, 67.1, 62.7, 31.2, 28.7, 26.0, 25.3, 20.1; HRMS calcd for $C_{12}H_{18}O_3$ [M]$^+$ 210.1255, found 210.1255.

General Procedure for the Preparation of Oxabicyclo[3.2.1] Compounds. (*1S*,2R*,4S*,5R)-2,4-Dimethyl-1-[(((tri-*n*-butylstannyl)methyl)oxy)methyl]-8-oxabicyclo[3.2.1]oct-6-en-3-one (2a).** A suspension of Zn−Ag couple[20] (0.5 g) and furan **1a** (9.99 g, 25 mmol) in THF (5 mL) was cooled to −10 °C, and a solution of 2,4-dibromopentan-3-one[18] (2.60 g, 10 mmol) in THF (10 mL) was added dropwise over a period of 1 h. After the addition was complete, the mixture was allowed to warm to room temperature and stirring was continued for an additional 22 h. The reaction mixture was filtered through Celite, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 50:1 to 10:1, **2a** (1.186 g, 22%) was obtained as a colorless oil. R_f = 0.51 on silica gel (hexanes−ethyl acetate 10:1); IR (neat) 3010, 2980, 1740, 1485, 1400, 1370 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.30 (1H, dd, J = 6.1, 1.8 Hz), 6.07 (1H, d, J = 6.1 Hz), 4.88 (1H, dd, J = 4.7, 1.7 Hz), 3.91 (1H, d, J = 10.4 Hz), 3.77 (1H, d, J = 10.3 Hz), 3.69 (1H, d, J = 10.6 Hz), 3.55 (1H, d, J = 10.6 Hz), 2.90−2.75 (2H, m), 1.58−1.44 (6H, m), 1.39−1.21 (6H, m), 1.04−0.85 (21H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 134.6, 134.2, 90.9, 83.5, 76.8, 63.9, 51.7, 50.1, 29.6, 27.8, 14.2, 10.8, 10.1, 9.6; HRMS calcd for $C_{23}H_{42}O_3Sn$ [M − Bu]$^+$ 429.1451, found 429.1451.

(*1R*,5S)-1-[(((Tri-*n*-butylstannyl)methyl)oxy)methyl]-8-oxabicyclo-[3.2.1]oct-6-en-3-one (2b).** A suspension of Zn−Ag couple (0.510 g) and furan **1a** (10.0 g, 25 mmol) in THF (5 mL) was cooled to −10 °C, and a solution of tetrabromoacetone[18] (3.73 g, 10 mmol) in THF (10 mL) was added dropwise over a period of 1 h. After the addition was complete, the mixture was allowed to warm to room temperature and stirring was continued for an additional 22 h. The reaction mixture was filtered through celite, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Afterward, the crude product was fully debrominated by dissolving it in methanol (2.0 M) saturated in NH_4Cl. The Zn−Cu couple was added to the reaction and was allowed to stir at room temperature for 2 days. The reaction mixture was filtered through Celite and extracted with ether. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 30:1 to 10:1, **2b** (0.59 g, 13%) was obtained as a colorless oil. R_f = 0.35 on silica gel (hexanes−ethyl acetate 10:1); IR (neat) 2956, 2924, 2871, 2854, 1771, 1717, 1464, 1405, 1375, 1289, 1181, 1096 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.20 (1H, dd, J = 6.0, 1.7 Hz), 6.07 (1H, d, J = 6.0 Hz), 5.06 (1H, br s), 3.80 (2H, d, J = 2.4 Hz), 3.53 (2H, s), 2.67 (1H, dd, J = 16.8, 5.1 Hz), 2.64 (1H, d, J = 16.8 Hz), 2.35 (1H, d, J = 15.6 Hz), 2.23 (1H, d, J = 15.8 Hz), 1.56−1.43 (6H, m), 1.41−1.22 (6H, m), 0.92−0.83 (15H, m); ^{13}C NMR (50 MHz,

$CDCl_3$) δ 206.4, 134.4, 134.1, 86.3, 78.8, 64.0, 48.8, 45.9, 29.6, 27.8, 14.2, 9.6; HRMS calcd for $C_{21}H_{38}O_3Sn$ [M − Bu]$^+$ 401.1138, found 401.1138.

(*1R*,2S*,5S)-2-Methoxy-1-[(((tri-*n*-butylstannyl)methyl)oxy)methyl]-8-oxabicyclo[3.2.1]oct-6-en-3-one (2c).** To a solution of furan **1a** (2.016 g, 5.03 mmol) and nitroethane (5 mL) containing molecular sieves 3Å was added at −78 °C the silylenol ether of α,α-dimethoxyacetone[21] (0.862 g, 4.57 mmol) followed by a catalytic amount of trimethylsilyl trifluoromethanesulfonate (0.1 mL, 0.50 mmol). After the addition was complete, stirring was continued at −78 °C for 2.5 h. The reaction mixture was warmed to 0 °C, quenched with $NaHCO_3$ (saturated), and stirred vigorously. The mixture was then extracted with dichloromethane. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 20:1 to 10:1, **2c** (0.740 g, 33%) was obtained as a colorless oil. R_f = 0.38 on silica gel (hexanes−ethyl acetate 10:1); IR (neat) 2957, 2922, 2871, 1725, 1464, 1412, 1375, 1334, 1306, 1256, 1200, 1147, 1084 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$, mixture of isomers) δ 6.20 (1H, dd, J = 5.8, 1.8 Hz), 5.97 (1H, d, J = 5.9 Hz), 4.98 (1H, br d), 3.95−3.46 (5H, m), 3.53 (3H, s), 2.74 (1H, dd, J = 15.4, 4.8 Hz), 2.30 (1H, d, J = 15.4 Hz), 1.52−1.40 (6H, m), 1.39−1.16 (6H, m), 0.91−0.80 (15H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 206.8, 135.7, 132.4, 87.3, 79.3, 74.9, 63.9, 61.4, 46.3, 29.7, 27.9, 14.3, 9.6; HRMS calcd for $C_{22}H_{40}O_4Sn$ [M − Bu]$^+$ 431.1244, found 431.1244.

(*1S*,2R*,4S*,5R)-1-[(((Tri-*n*-butylstannyl)methyl)oxy)methyl]-2,4,5-trimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (2d).** To Zn−Ag couple (0.4 g) was added furan **1b** (1.80 g, 4.3 mmol) in THF (4 mL). The mixture was then cooled to −10 °C and a solution of 2,4-dibromopentan-3-one (0.732 g, 3.0 mmol) in THF (1 mL) was added dropwise. After a partial purification by flash chromatography on silica gel with hexanes−ethyl acetate 10:1, **2d** was directly used in the next step. R_f = 0.64 on silica gel (hexanes−ethyl acetate 10:1).

(*1S*,2R*,4S*,5R)-2,4-Dimethyl-1-[(((tri-*n*-butylstannyl)methyl)oxy)ethyl]-8-oxabicyclo[3.2.1]oct-6-en-3-one (2e).** To Zn−Ag couple (0.20 g) was added furan **1c** (4.00 g, 9.6 mmol) in THF (2 mL). The mixture was then cooled to −10 °C and a solution of 2,4-dibromopentan-3-one (0.936 g, 4.8 mmol) in THF (4 mL) was added dropwise. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 20:1, **2e** (0.817 g, 43%) was obtained as a colorless oil. R_f = 0.47 on silica gel (hexanes−ethyl acetate 10:1); IR (neat) 3072, 2952, 2931, 2875, 2854, 1708, 1588, 1469, 1377, 1082 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.16 (1H, dd, J = 6.0, 1.6 Hz), 6.09 (1H, d, J = 6.1 Hz), 4.79 (1H, dd, J = 4.7, 1.6 Hz), 3.66−3.49 (2H, m), 3.46−3.37 (2H, m), 2.71−2.56 (2H, m), 2.06−1.98 (2H, m), 1.55−1.39 (6H, m), 1.39−1.17 (6H, m), 0.99−0.85 (21H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 217.0, 136.6, 132.9, 89.7, 82.9, 71.4, 62.6, 55.0, 50.2, 34.6, 29.6, 27.8, 14.2, 10.9, 10.3, 9.5.

(*1S*,2R*,4S*,5R)-2,4-Dimethyl-1-[(((tri-*n*-butylstannyl)methyl)thio)methyl]-8-oxabicyclo[3.2.1]oct-6-en-3-one (2f).** To Zn−Ag couple (1.7 g) was added furan **1d** (6.9 g, 16 mmol) in THF (1 mL). The mixture was then cooled to −10 °C and a solution of 2,4-dibromopentan-3-one (2.20 g, 9 mmol) in THF (1 mL) was added dropwise. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 50:1 to 5:1, **2f** (1.09 g, 24%) was obtained as a colorless oil. R_f = 0.54 on silica gel (hexanes−ethyl acetate 10:1); IR (neat) 3114, 2959, 2924, 2875, 2853, 1721, 1595, 1461, 1384, 1075 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.3 (1H, dd), 6.1 (1H, d), 4.9 (1H, m), 3.0−2.7 (4H, m), 2.2−2.0 (2H, q), 1.6−1.2 (12H, m), 1.0−0.8 (21H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 142.4, 135.9, 133.9, 110.7, 107.8, 83.4, 53.5, 49.9, 43.6, 35.1, 29.5, 27.7, 14.2, 10.0, 9.3; HRMS calcd for $C_{23}H_{42}O_2SSn$ [M]$^+$ 502.1927, found 502.1927.

(*1S*,2R*,4S*,5R)-2,4-Dimethyl-1-{[*N*-(methoxycarbonyl)-*N*-(((tri-*n*-butylstannyl)methyl)amino)methyl}-8-oxabicyclo[3.2.1]oct-6-en-3-one (2g).** To Zn−Ag couple (0.89 g) was added furan **1e** (10.23 g, 22 mmol) followed by THF (5 mL). The mixture was then cooled to −10 °C and a solution of 2,4-dibromopentan-3-one (2.19 g, 8 mmol) in THF (10 mL) was added dropwise. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 50:1 to 2:1, **2g** (2.39 g, 55%) was obtained as a colorless oil. R_f = 0.41 on silica gel (hexanes−ethyl acetate 10:1); IR (neat) 3079, 2959, 2924, 2854, 1701, 1476, 1377, 1195 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.23 (1H, s), 6.18 (1H, m), 4.81 (1H, d, J = 4.5 Hz), 3.95−3.45 (2H, m), 3.66 (3H, s), 3.18−3.04 (2H, m), 2.74 (1H, m), 2.54 (1H, m), 1.55−1.42 (6H, m), 1.40−1.19 (6H, m), 1.07−0.78 (21H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 209.3, 157.8, 135.2, 134.7, 134.3, 82.8, 53.4, 53.2, 53.0, 50.1, 37.2, 36.1, 29.6, 27.9, 14.3, 11.0, 10.9, 10.3; HRMS calcd for $C_{25}H_{45}O_4NSn$ [M − Bu]$^+$ 486.1666, found 486.1685.

(*1S*,2R*,4S*,5R)-2,4-Dimethyl-1-[3-(2′-tetrahydro-2*H*-pyranyloxy)propyl]-8-oxabicyclo[3.2.1]oct-6-en-3-one (2h).** To Zn−Ag couple (2.56 g) was added furan **1f** (15.0 g, 71 mmol) in THF (20 mL). The mixture was then cooled to −10 °C and a solution of 2,4-dibromopentan-3-one (8.66 g, 35.5 mmol) in THF (20 mL) was added dropwise. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 50:1 to 10:1, **2h** (3.6 g, 35%) was obtained as a colorless oil. R_f = 0.24 on silica gel (hexanes−ethyl acetate 10:1); IR (neat) 3514, 3072, 2945, 2875, 1743, 1715, 1455, 1377, 1201 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.20 (1H, d, J = 6.2 Hz), 6.05 (1H, d, J = 6.2 Hz), 4.80 (1H, br d, J = 4.5 Hz), 4.55 (1H, br t), 3.93−3.72 (2H, m), 3.49−3.38 (2H, m), 2.72 (1H, m), 2.57 (1H, m), 1.91−1.51 (10H, m), 0.96 (3H, d, J = 7.2 Hz), 0.92 (3H, d, J = 7.1 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 210.0, 136.3, 133.8, 99.3, 90.7, 82.9, 67.9, 62.9, 62.8, 54.6, 54.5, 50.2, 31.3, 31.2, 25.9, 24.4, 24.4, 20.2, 20.1, 10.8, 10.2; HRMS calcd for $C_{17}H_{26}O_4$ [M]$^+$ 294.1831, found 294.1831.

(*1S*,2S*,6R*,7R)-1-[3-(2′-Tetrahydro-2*H*-pyranyloxy)propyl]-10-oxatricyclo[5.2.1^{1,7}.1^{2,6}]undec-8-en-11-one (2i).** Silver tetrafluoroborate (1.3 g, 67 mmol) was suspended in dichloromethane (10 mL). The mixture was then cooled to −78 °C. Furan **1f** (0.768 g, 3.6 mmol) in dichloromethane (1 mL) was added dropwise followed by the chloroenamine[31] (0.850 g, 4.5 mmol) in dichloromethane (1 mL). After the addition was complete, the reaction was stirred at room temperature for an additional 22 h. The reaction mixture was filtered through celite and concentrated *in vacuo*. The product was then treated with 5 M NaOH (aq) and methanol, stirred 3 h, and concentrated *in vacuo*. The residue was extracted with ether. The combined organic layers were washed with NH_4Cl (saturated) and brine, dried over $MgSO_4$, filtered, and evaporated *in vacuo*. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 10:1 to 2:1, **2i** (550 mg, 50%) was obtained as a colorless oil. R_f = 0.59 on silica gel (hexanes−ethyl acetate 10:4); IR (neat) 3093, 2938, 2868, 1729, 1455, 1349, 1117, 1075, 1033 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.26 (1H, d, J = 5.9 Hz), 6.14 (1H, d, J = 5.9 Hz), 4.90 (1H, br s), 4.55 (1H, br s), 3.83−3.67 (2H, m), 3.49−3.33 (2H, m), 2.62−1.30 (18H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 216.0, 138.1, 136.4, 99.3, 91.0, 84.0, 67.9, 62.9, 56.4, 52.3, 31.8, 31.2, 29.8, 29.3, 25.9, 25.1, 21.2, 20.1; HRMS calcd for $C_{18}H_{26}O_4$ [M]$^+$ 306.1831, found 306.1837.

General Procedure for the Reduction of Oxabicyclo[3.2.1]-octenones with L-Selectride. (*1S*,2S*,3S*,4R*,5R)-2,4-Dimethyl-1-[(((tri-*n*-butylstannyl)methyl)oxy)methyl]-8-oxabicyclo[3.2.1]oct-6-en-3-ol (3a).** The oxabicyclic compound **2a** (1.234 g, 2.54 mmol) was dissolved in THF (7 mL), cooled to −78 °C and L-selectride (3.8 mL, 1.0 M solution in THF, 3.80 mmol) was added dropwise. After the addition was complete, stirring was continued for an additional 2 h at −78 °C (the reaction was monitored by TLC). The reaction was then warmed to 0 °C, quenched cautiously with 5 M NaOH (6.6 mL), stirred 10 min, and treated with 30% H_2O_2 (5.3 mL). The reaction mixture was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 20:1 to 10:1, **3a** (0.91 g, 73%) was obtained as a colorless oil. R_f = 0.24 on silica gel (hexanes−ethyl acetate 10:1); IR (neat) 3605, 3500, 2960, 2920, 2840, 1460, 1380 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.46 (1H, dd, J = 6.1, 1.8 Hz), 6.20 (1H, d, J = 6.0 Hz), 4.51 (1H, dd, J = 3.3, 1.7 Hz), 3.83 (1H, d, J = 10.5 Hz), 3.72 (1H, d, J = 10.5 Hz), 3.68 (1H, m), 3.55 (1H, d, J = 10.4 Hz), 3.39 (1H, d, J = 10.4 Hz), 2.26−2.22 (2H, m), 1.57 (1H, d, J = 11.1 Hz), 1.54−1.40 (6H, m), 1.39−1.17 (6H, m), 0.98−0.81 (21H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 136.8, 136.3, 88.7, 83.5, 76.8, 73.5, 63.3, 38.9, 38.7, 29.1, 27.3, 13.7, 12.9, 12.8, 9.1; HRMS calcd for $C_{23}H_{44}O_3Sn$ [M − Bu]$^+$ 431.1608, found 431.1608.

(*1S*,3S*,5S)-1-[(((Tri-*n*-butylstannyl)methyl)oxy)methyl]-8-oxabicyclo[3.2.1]oct-6-en-3-ol (3e).** The oxabicyclic compound **2b** (0.577 g, 1.26 mmol) in THF (3.5 mL) was cooled to −78 °C, treated with L-selectride (2.5 mL, 1.0 M solution in THF, 2.5 mmol), and stirred

for 3 h at −78 °C. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 10:1 to 2:1, **3e** (0.382 g, 66%) was obtained as a colorless oil. R_f = 0.12 on silica gel (hexanes−ethyl acetate 10:1); IR (neat) 3555, 3082, 2955, 2926, 2872, 2854, 1599, 1463, 1376, 1113, 1087 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.43 (1H, dd, J = 6.1, 1.6 Hz), 6.28 (1H, d, J = 6.0 Hz), 4.80 (1H, br s), 3.98 (1H, m), 3.80 (2H, s), 3.41 (2H, s), 2.24−2.03 (4H, m), 1.84−1.42 (7H, m), 1.38−1.20 (6H, m), 0.93−0.80 (15H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 137.1, 136.7, 85.8, 79.4, 79.3, 66.2, 64.1, 38.7, 36.2, 29.7, 27.9, 14.3, 9.7; HRMS calcd for $C_{21}H_{40}O_3Sn$ [M − Bu]$^+$ 403.1295, found 403.1295.

(*1R*,2S*,3S*,5S)-2-Methoxy-1-[(((tri-*n*-butylstannyl)methyl)oxy)methyl]-8-oxabicyclo[3.2.1]oct-6-en-3-ol (3f).** The oxabicyclic compound **2c** (0.658 g, 1.35 mmol) in THF (3 mL) was cooled to −78 °C, treated with L-selectride (2.70 mL, 1.0 M solution in THF, 2.70 mmol) and stirred for 2.5 h at −78 °C. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 10:1 to 5:1, **3f** (0.512 g, 78%) was obtained as a colorless oil. R_f = 0.22 on silica gel (hexanes−ethyl acetate 10:1); IR (neat) 3551, 2955, 2925, 2871, 2853, 2614, 1456, 1375, 1350, 1085 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$, mixture of isomers) δ 6.30 (1H, dd, J = 6.1, 1.8 Hz), 5.92 (1H, d, J = 6.2 Hz), 4.73 (1H, br s), 4.24 (1H, m), 3.89−3.33 (5H, m), 3.39 (3H, s), 2.48 (1H, d, J = 2.3 Hz), 2.18−1.78 (2H, m), 1.53−1.41 (6H, m), 1.40−1.18 (6H, m), 0.92−0.82 (15H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 137.7, 132.2, 81.6, 80.0, 78.2, 76.6, 75.8, 64.8, 63.8, 58.2, 35.3, 33.8, 29.7, 27.9, 14.2, 9.6; HRMS calcd for $C_{22}H_{42}O_4Sn$ [M − Bu]$^+$ 433.1400, found 433.1400.

(*1S*,2S*,3S*,4R*,5R)-1-[(((Tri-*n*-butylstannyl)methyl)oxy)methyl]-2,4,5-trimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-ol (3g).** A mixture of oxabicyclic compound **2d** and furan **1b** (1.78 g, 3.5 mmol) in THF (30 mL) was cooled to −78 °C, treated with L-selectride (7.5 mL, 1.0 M solution in THF, 7.5 mmol), and stirred for 2 h at −78 °C. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 20:1 to 2:1, **3g** (0.740 g, 49%, two steps) was obtained as a colorless oil. R_f = 0.36 on silica gel (hexanes−ethyl acetate 10:1); IR (neat) 3606, 3508, 3072, 2917, 1455, 1377, 1335, 1089 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.24 (1H, d, J = 5.9 Hz), 6.16 (1H, d, J = 5.9 Hz), 3.90−3.60 (1H, m), 3.85 (1H, d, J = 10.4 Hz), 3.74 (1H, d, J = 10.4 Hz), 3.52 (1H, d, J = 10.2 Hz), 3.67 (1H, d, J = 10.3 Hz), 2.28 (1H, m), 2.03 (1H, m), 1.69 (1H, d, J = 11.3 Hz), 1.61−1.42 (6H, m), 1.41−1.21 (9H, m), 0.99−0.84 (21H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 140.2, 136.6, 89.9, 87.9, 77.6, 74.7, 63.8, 44.5, 40.3, 29.6, 27.9, 22.3, 14.1, 13.7, 13.4, 9.6; HRMS calcd for $C_{24}H_{46}O_3Sn$ [M − H]$^+$ 501.2390, found 501.2398.

(*1S*,2S*,3S*,4R*,5R)-2,4-Dimethyl-1-[(((tri-*n*-butylstannyl)methyl)oxy)ethyl]-8-oxabicyclo[3.2.1]oct-6-en-3-ol (3h).** The oxabicyclic compound **2e** (0.731 g, 1.46 mmol) in THF (4 mL) was cooled to −78 °C, treated with L-selectride (2.9 mL, 1.0 M solution in THF, 2.90 mmol), and stirred for 3 h at −78 °C. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 30:1 to 10:1, **3h** (0.658 g, 90%) was obtained as a colorless oil. R_f = 0.25 on silica gel (hexanes−ethyl acetate 10:1); IR (neat) 3430, 3086, 2959, 2931, 2868, 2854, 1588, 1462, 1377, 1075 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.38 (1H, dd, J = 6.0, 1.7 Hz), 6.28 (1H, d, J = 6.0 Hz), 4.48 (1H, dd, J = 3.4, 1.7 Hz), 3.68−3.30 (5H, m), 2.30−1.01 (17H, m), 0.98−0.83 (21H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 138.7, 135.4, 87.8, 82.9, 73.5, 70.9, 62.0, 42.3, 38.9, 33.9, 29.1, 27.3, 13.7, 13.1, 12.9, 8.9.

(*1S*,2S*,3S*,4R*,5R)-2,4-Dimethyl-1-[(((tri-*n*-butylstannyl)methyl)thio)methyl]-8-oxabicyclo[3.2.1]oct-6-en-3-ol (3i).** The oxabicyclic compound **2f** (0.852 g, 1.70 mmol) in THF (10 mL) was cooled to −78 °C, treated with L-selectride (4.2 mL, 1.0 M solution in THF, 4.2 mmol) and stirred for 4 h at −78 °C. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 20:1 to 3:1, **3i** (0.700 g, 81%) was obtained as a colorless oil. R_f = 0.60 on silica gel (hexanes−ethyl acetate 10:3); IR (neat) 3606, 3494, 3064, 2966, 2917, 2875, 2853, 1455, 1377, 1075 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.48 (1H, dd, J = 5.9, 1.8 Hz), 6.28 (1H, d, J = 6.0 Hz), 4.54 (1H, br s), 3.70 (1H, m), 2.87 (2H, d, J = 2.9 Hz), 2.26 (2H, m), 2.03 (2H, d, J = 2.2 Hz), 1.63 (1H, d, J = 10.6 Hz), 1.54−1.42 (6H, m), 1.38−1.12 (6H, m), 0.98−0.79 (21H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 138.5, 136.5, 89.7, 83.8, 73.8, 43.9, 41.6, 39.3, 29.5, 27.8, 14.2, 13.6, 13.4, 11.6, 9.9; HRMS calcd for $C_{23}H_{44}O_2SSn$ [M − Bu]$^+$ 447.1379, found 447.1379.

(*1S*,2S*,3S*,4R*,5R)-2,4-Dimethyl-1-{[*N*-(methoxycarbonyl)-*N*-((tri-*n*-butylstannyl)methyl)amino]methyl}-8-oxabicyclo[3.2.1]oct-6-en-3-ol (3k).** The oxabicyclic compound **2g** (2.39 g, 4.40 mmol) in THF (50 mL) was cooled to −78 °C, treated with L-selectride (8.8 mL, 1.0 M solution in THF, 8.8 mmol), and stirred for 2 h at −78 °C. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 5:1, **3k** (1.73 g, 72%) was obtained as a colorless oil. R_f = 0.33 on silica gel (hexanes−ethyl acetate 10:3); IR (neat) 3478, 3079, 2959, 2924, 2875, 2847, 1694, 1476, 1377, 1195, 1019 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.38 (1H, d, J = 2.3 Hz), 6.42−6.26 (1H, m), 4.43 (1H, br s), 3.99−3.61 (3H, m), 3.62 (3H, d, J = 3.9 Hz), 3.22−2.95 (2H, m), 2.35−2.12 (1H, m), 2.10−1.92 (1H, m), 1.66 (1H, d, J = 11.3 Hz), 1.54−1.39 (6H, m), 1.37−1.22 (6H, m), 1.02−0.80 (21H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 163.2, 157.5, 137.7, 137.4, 90.5, 83.0, 73.6, 53.4, 53.1, 41.1, 39.3, 37.4, 36.3, 29.5, 27.9, 14.2, 13.8, 13.5, 13.3, 10.9, 10.3; HRMS calcd for $C_{25}H_{47}O_4NSn$ [M − Bu]$^+$ 488.1822, found 488.1819.

(*1S*,2S*,3S*,4R*,5R)-2,4-Dimethyl-1-[3-(2′-tetrahydro-2*H*-pyranyloxy)propyl]-8-oxabicyclo[3.2.1]oct-6-en-3-ol (3m).** The oxabicyclic compound **2h** (3.17 g, 10.7 mmol) in THF (50 mL) was cooled to −78 °C, treated with L-selectride (21.4 mL, 1.0 M solution in THF, 21.4 mmol), and stirred for 3 h at −78 °C. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 20:1 to 2:1, **3m** (2.20 g, 70%) was obtained as a colorless oil. R_f = 0.26 on silica gel (hexanes−ethyl acetate 10:3); IR (neat) 3508, 3072, 2938, 2875, 1448, 1356 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.41 (1H, dd, J = 6.0, 1.8 Hz), 6.20 (1H, d, J = 5.9 Hz), 4.53 (1H, dd, J = 3.7, 2.9 Hz), 4.46 (1H, t, J = 1.6 Hz), 3.89−3.61 (3H, m), 3.48−3.35 (2H, m), 2.22−2.13 (1H, m), 2.08−1.98 (1H, m), 1.80−1.46 (11H, m), 0.95 (3H, d, J = 7.3 Hz), 0.93 (3H, d, J = 7.4 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 138.9, 136.6, 99.2, 88.9, 83.5, 73.9, 68.2, 62.8, 62.8, 42.4, 39.5, 31.3, 31.2, 26.0, 24.1, 20.2, 13.6, 13.5; HRMS calcd for $C_{17}H_{28}O_4$ [M]$^+$ 296.1987, found 296.1987.

(*1S*,2R*,6S*,7R*,11S)-1-[3-(2′-Tetrahydro-2*H*-pyranyloxy)-propyl]-10-oxatricyclo[5.2.1^{1,7}.1^{2,6}]undec-8-en-11-ol (3q).** A solution of oxabicyclic compound **2i** (388 mg, 1.27 mmol) in THF (1 mL) was added dropwise to a suspension of lithium aluminum hydride (96 mg, 2.53 mmol) in THF (13 mL) at −78 °C. The reaction was stirred for 2 h at room temperature. The reaction was then cooled to 0 °C, quenched cautiously with 1.0 M Rochelle's salt, and stirred overnight. The mixture was extracted with ether. The combined extracts were washed with brine, dried over $MgSO_4$, filtered, and evaporated *in vacuo*. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 20:1 to 2:1, **3q** (232 mg, 60%) was obtained as a colorless oil. R_f = 0.32 on silica gel (hexanes−ethyl acetate 10:4); IR (neat) 3599, 3466, 3079, 2938, 2860, 1469, 1448, 1349, 1257, 1131, 1060, 1032 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.59 (1H, d, J = 6.0 Hz), 6.43 (1H, d, J = 5.9 Hz), 4.76 (1H, br s), 4.55 (1H, br s), 3.85−3.65 (3H, m), 3.51−3.33 (2H, m), 2.75 (1H, d, J = 11.4 Hz), 2.45−2.25 (1H, m), 2.05−1.35 (17H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 140.7, 138.6, 99.4, 89.6, 84.4, 77.4, 68.2, 62.9, 43.7, 40.7, 31.7, 31.2, 31.1, 28.4, 26.0, 24.9, 21.3, 20.1; HRMS calcd for $C_{18}H_{28}O_4$ [M]$^+$ 308.1985, found 308.1992.

(*1S*,2S*,3S*,4R*,5R)-2,4-Dimethyl-1-{[*N*-methyl-*N*-((tri-*n*-butylstannyl)methyl)amino]methyl}-8-oxabicyclo[3.2.1]oct-6-en-3-ol (3l).** A suspension of $LiAlH(OMe)_3$ (3.6 mL, 0.5 M suspension in THF, 1.83 mmol) was cooled to 0 °C and treated dropwise with a solution of oxabicyclic compound **3k** (249 mg, 0.46 mmol) in THF (1 mL). After the addition was complete, stirring was continued at 0 °C for 30 min then at room temperature for 18 h. The reaction was cooled to 0 °C, quenched with Rochelle's salt, stirred at room temperature for an additional 3 h, and filtered. After purification by chromatography on alumina eluting with hexanes−ethyl acetate 100:0 to 5:1, **3l** (143 mg, 63%) was obtained as a colorless oil. R_f = 0.26 on silica gel (hexanes−ethyl acetate 3:1); IR (neat) 3431, 3079, 2959, 2924, 2875, 2854, 1659, 1595, 1462, 1377, 1075, 1019 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.46 (1H, dd, J = 6.0, 1.8 Hz), 6.24 (1H, d, J = 6.0 Hz), 4.52 (1H, br s), 3.69 (1H, m), 2.70 (2H, dd, J = 12.3, 12.4 Hz), 2.52 (2H, dd, J = 13.6, 13.7 Hz), 2.33−2.20 (2H, m), 2.28 (3H, s), 1.61 (1H, d, J = 12.0 Hz), 1.54−1.41 (6H, m), 1.38−1.02 (6H, m), 0.99−

0.79 (21H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 138.7, 136.5, 83.8, 74.1, 64.2, 48.9, 48.6, 40.4, 39.3, 29.7, 27.9, 17.9, 14.2, 13.7, 13.4, 10.8; HRMS calcd for $C_{24}H_{47}NO_2Sn$ [M − Bu]$^+$ 444.1924, found 444.1926.

General Procedure for the Protection of the Alcohol as Its Ether. (*1S*,2S*,3S*,4R*,5R)-2,4-Dimethyl-3-methoxy-1-[(((tri-*n*-butylstannyl)methyl)oxy)methyl]-8-oxabicyclo[3.2.1]oct-6-ene (3b).** Potassium hydride (30 mg, 0.26 mmol, 35% in oil), which was washed three times with pentane, was suspended in THF (1 mL). The mixture was then cooled to 0 °C. The oxabicyclic compound **3a** (101 mg, 0.21 mmol) in THF (1 mL) was added. The reaction mixture was then allowed to stir to room temperature for 1 h before the addition of 18-C-6 (5 mg, 0.02 mmol) followed by iodomethane (30 mg, 0.21 mmol). After the addition was complete, stirring was continued for an additional 22 h. The reaction was quenched by the addition of water and extracted with ether. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and evaporated *in vacuo*. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 100:1 to 10:1, **3b** (87 mg, 84%) was obtained as a colorless oil. R_f = 0.44 on silica gel (hexanes−ethyl acetate 10:1); IR (neat) 3079, 2959, 2931, 2875, 1461, 1377, 1103, 1068 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.29 (1H, dd, J = 6.0, 1.7 Hz), 6.03 (1H, d, J = 6.1 Hz), 4.43 (1H, br s), 3.88 (1H, d, J = 10.6 Hz), 3.74 (1H, d, J = 10.5 Hz), 3.58 (1H, d, J = 10.5 Hz), 3.37 (1H, d, J = 10.4 Hz), 3.31 (3H, s), 3.24 (1H, t), 2.40−2.25 (2H, m), 1.55−1.43 (6H, m), 1.38−1.20 (6H, m), 0.96−0.85 (21H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 135.1, 134.6, 88.9, 84.4, 84.0, 77.5, 63.8, 63.5, 39.8, 29.7, 27.9, 14.3, 13.1, 12.9, 9.7; HRMS calcd for $C_{24}H_{46}O_3Sn$ [M − Bu]$^+$ 445.1764, found 445.1764.

(*1S*,2S*,3S*,4R*,5R)-3-(Benzyloxy)-2,4-dimethyl-1-[(((tri-*n*-butylstannyl)methyl)oxy)methyl]-8-oxabicyclo[3.2.1]oct-6-ene (3c).** To a suspension of potassium hydride (60 mg, 0.30 mmol, 50% in oil) in THF (1 mL) at 0 °C was added the oxabicyclic compound **3a** (109 mg, 0.22 mmol). The reaction mixture was stirred 1 h at room temperature before the addition of 18-C-6 (5 mg, 0.02 mmol) followed by benzyl bromide (50 mg, 0.29 mmol) in THF (1 mL). After purification by flash chromatography on silica gel with hexanes−ethyl acetate 100:1 to 10:1, **3c** (82 mg, 64%) was obtained as a colorless oil. R_f = 0.56 on silica gel (hexanes−ethyl acetate 10:1); IR (neat) 2952, 1690, 1458, 1371, 1264, 1192, 1095 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.34−7.29 (5H, m), 6.31 (1H, dd, J = 6.1, 1.7 Hz), 6.04 (1H, d, J = 6.1 Hz), 4.48 (1H, br s), 4.45 (2H, s), 3.90 (1H, d, J = 10.6 Hz), 3.76 (1H, d, J = 10.5 Hz), 3.62 (1H, d, J = 10.5 Hz), 3.55 (1H, t), 3.34 (1H, d, J = 10.4 Hz), 2.42−2.26 (2H, m), 1.57−1.45 (6H, m), 1.45−1.22 (6H, m), 0.98−0.86 (21H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 139.9, 135.1, 134.5, 128.6, 127.5, 127.3, 89.0, 84.2, 81.7, 78.2, 76.9, 63.7, 40.1, 40.0, 29.7, 27.9, 14.2, 13.3, 13.2, 9.6; HRMS calcd for $C_{30}H_{50}O_3Sn$ [M − Bu]$^+$ 521.2077, found 521.2071.

(*1S*,2S*,3S*,4S*,5R)-2,4-Dimethyl-3-(*tert*-butyldimethylsiloxy)-1-[(((tri-*n*-butylstannyl)methyl)oxy)methyl]-8-oxabicyclo[3.2.1]oct-6-ene (3d).** To a suspension of potassium hydride (119 mg, 1.34 mmol, 50% in oil) in THF (5 mL) cooled to 0 °C was added the oxabicyclic compound **3a** (220 mg, 0.45 mmol). The reaction mixture was stirred for 1 h at room temperature before the addition of *tert*-butyldimethylsilyl chloride (201 mg, 1.34 mmol) in THF (1 mL). After purification by flash chromatography on silica gel with hexanes−ethyl acetate 10:1, **3d** (230 mg, 85%) was obtained as a colorless oil. R_f = 0.50 on silica gel (hexanes−ethyl acetate 10:1) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.19 (1H, dd, J = 6.0, 1.7 Hz), 5.92 (1H, d, J = 6.0 Hz), 4.41 (1H, br s), 3.86 (1H, d, J = 10.5 Hz), 3.85 (1H, br t), 3.71 (1H, d, J = 10.5 Hz), 3.56 (1H, d, J = 10.3 Hz), 2.26−2.06 (2H, m), 1.53−1.41 (6H, m), 1.40−1.18 (6H, m), 0.91−0.81 (30H, m), −0.04 (6H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 134.8, 134.3, 84.4, 77.9, 73.6, 63.7, 39.8, 29.7, 27.9, 26.7, 14.7, 14.4, 14.3, 9.6, −2.8; HRMS calcd for $C_{29}H_{58}O_3SiSn$ [M − Bu]$^+$ 545.2472, found 545.2458.

(*1S*,2S*,3S*,4R*,5R)-2,4-Dimethyl-3-methoxy-1-[(((tri-*n*-butylstannyl)methyl)thio)methyl]-8-oxabicyclo[3.2.1]oct-6-ene (3j).** A suspension of potassium hydride (80 mg, 0.49 mmol, 50% in oil) in THF (1 mL) was cooled to 0 °C and the oxabicyclic compound **3i** (100 mg, 0.20 mmol) was added. The reaction mixture was then allowed to stir to room temperature for 1 h before the addition of 18-C-6 (5 mg, 0.02 mmol) followed by iodomethane (28 mg, 0.19 mmol). After purification by flash chromatography on silica gel with hexanes−ethyl acetate 20:1 to 3:1, **3j** (81 mg, 79%) was obtained as a colorless oil. R_f = 0.53 on silica gel (hexanes−ethyl acetate 10:1); IR (neat) 3086, 2959, 2924, 2875, 2854, 1595, 1455, 1384, 1096 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.27 (1H, dd, J = 6.0, 1.8 Hz), 6.08 (1H, d, J = 5.9 Hz), 4.44 (1H, br m), 3.31 (3H, s), 3.24 (1H, br t), 2.86 (2H, d, J = 4.0 Hz), 2.29 (2H, m), 2.03 (2H, d, J = 5.7 Hz), 1.58−1.42 (6H, m), 1.41−1.20 (6H, m), 0.97−0.84 (21H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 136.2, 134.6, 89.2, 84.2, 83.8, 63.5, 44.3, 41.9, 39.8, 29.5, 27.8, 14.2, 13.0, 11.5, 9.9; HRMS calcd for $C_{24}H_{46}O_2SSn$ [M − Bu]$^+$ 461.1536, found 461.1529.

(*1S*,2S*,3R*,4R*,5R)-2,4-Dimethyl-3-methoxy-1-[3-(2′-tetrahydro-2*H*-pyranyloxy)propyl]-8-oxabicyclo[3.2.1]oct-6-ene (3n).** To a suspension of potassium hydride (880 mg, 10.9 mol, 50% in oil) in THF (40 mL) cooled to 0 °C was added the oxabicyclic compound **3m** (2.20 g, 7.4 mmol). The reaction mixture was then allowed to stir to room temperature for 1 h before the addition of 18-C-6 (0.220 g, 0.80 mmol) followed by iodomethane (39 mg, 9.8 mmol). After purification by flash chromatography on silica gel with hexanes−ethyl acetate 20:1 to 5:1, **3n** (1.85 g, 81%) was obtained as a colorless oil. R_f = 0.26 on silica gel (hexanes−ethyl acetate 10:1); IR (neat) 3079, 2938, 2875, 1455, 1370, 1082 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.14 (1H, dd, J = 6.1, 1.8 Hz), 5.95 (1H, d, J = 5.9 Hz), 4.50 (1H, br t), 4.31 (1H, br t), 3.85−3.64 (2H, m), 3.43−3.33 (2H, m), 3.23 (3H, s), 3.15 (1H, t, J = 5.1 Hz), 2.25−2.12 (1H, m), 2.08−1.93 (1H, m), 1.75−1.45 (10H, m), 0.86 (6H, dd, J = 7.3 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 136.6, 134.2, 99.1, 88.4, 84.2, 83.4, 68.2, 63.4, 62.6, 62.5, 42.8, 39.9, 31.2, 25.9, 24.1, 24.1, 20.1, 20.0, 13.0, 12.9; HRMS calcd for $C_{18}H_{30}O_4$ [M − H]$^+$ 309.2065, found 309.2065.

(*1S*,2R*,6S*,7R*,11S)-11-Methoxy-1-[3-(2′-tetrahydro-2*H*-pyranyloxy)propyl]-10-oxatricyclo[5.2.1^{1,7}.1^{2,6}]undec-8-ene (3r).** To a suspension of potassium hydride (85 mg, 0.94 mmol, 50% in oil) in THF (7 mL) cooled to 0 °C was added the oxabicyclic compound **3q** (232 mg, 0.75 mmol) in THF (1 mL). The reaction mixture was then allowed to stir to room temperature for 1 h before the addition of iodomethane (133 mg, 0.94 mmol). After purification by flash chromatography on silica gel with hexanes−ethyl acetate 20:1 to 5:1, **3r** (150 mg, 60%) was obtained as a colorless oil. R_f = 0.76 on silica gel (hexanes−ethyl acetate 10:4); IR (neat) 3079, 2931, 2868, 2804, 1446, 1350, 1110, 1026 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.23 (1H, dd, J = 5.8, 1.7 Hz), 6.08 (1H, d, J = 5.9 Hz), 4.66 (1H, br s), 4.55 (1H, br t), 3.89−3.65 (2H, m), 3.52−3.31 (3H, m), 3.13 (3H, s), 2.51−2.30 (1H, m), 2.11−1.44 (17H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 137.5, 135.4, 99.3, 89.1, 86.1, 84.2, 68.3, 62.8, 58.9, 38.8, 36.1, 31.8, 31.2, 30.9, 28.2, 26.0, 25.0, 21.7, 20.1; HRMS calcd for $C_{19}H_{30}O_4$ [M]$^+$ 322.2144, found 322.2130.

General Procedure for the Conversion of the OTHP Group to the Iodide. (*1S*,2S*,3S*,4R*,5R)-2,4-Dimethyl-3-methoxy-1-(3-iodopropyl)-8-oxabicyclo[3.2.1]oct-6-ene (3p).** A solution of iodine (3.58 g, 1.4 mmol) in dichloromethane (50 mL) was added dropwise to a solution of 1,2-bis(diphenylphosphino)ethane (dppe) (2.79 g, 7.0 mmol) in dichloromethane (50 mL) at 0 °C. After the addition was complete, a solution of oxabicyclic compound **3n** (1.75 g, 5.60 mmol) in dichloromethane (50 mL) was added and the reaction mixture was warmed to room temperature and stirred for 4 h. The reaction was then treated with ether (250 mL) followed by pentane (500 mL). The mixture was filtered through silica gel and the filtrate evaporated *in vacuo*. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 10:1, **3p** (0.79 g, 42%) was obtained as a colorless oil. R_f = 0.40 on silica gel (hexanes−ethyl acetate 10:1); IR (neat) 2959, 2924, 2882, 2826, 1462, 1377, 1089 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.18 (1H, dd, J = 5.9, 1.7 Hz), 5.97 (1H, d, J = 5.9 Hz), 4.33 (1H, br s), 3.26 (3H, s), 3.17 (3H, m), 2.30−2.13 (1H, m), 2.05−1.60 (5H, m), 0.90 (3H, d, J = 7.3 Hz), 0.89 (3H, d, J = 7.3 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 136.2, 134.6, 88.2, 84.2, 83.5, 63.6, 43.1, 40.0, 35.6, 28.3, 13.1, 12.9, 8.5; HRMS calcd for $C_{13}H_{21}IO_2$ [M]$^+$ 336.0586, found 336.0571.

(*1S*,2S*,6S*,7R*,11S)-11-Methoxy-1-(3-iodopropyl)-10-oxatricyclo[5.2.1^{1,7}.1^{2,6}]undec-8-ene (3s).** A solution of iodine (550 mg, 2.20 mmol) in dichloromethane (10 mL) was added dropwise to a solution of 1,2-bis(diphenylphosphino)ethane (dppe) (640 mg, 1.6 mmol) in dichloromethane (10 mL) at 0 °C. After the addition was complete, a solution of oxabicyclic compound **3r** (420 mg, 1.28 mmol) in dichloromethane (10 mL) was added. After purification by flash

chromatography on silica gel with hexanes−ethyl acetate 10:1, **3s** (317 mg, 68%) was obtained as a colorless oil. R_f = 0.73 on silica gel (hexanes−ethyl acetate 10:4); IR (neat) 3072, 2973, 2924, 2861, 2812, 1595, 1462, 1391, 1335, 1230, 1188, 1103, 1026, 906 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.25 (1H, dd, J = 5.9, 1.7 Hz), 6.05 (1H, d, J = 5.9 Hz), 4.70 (1H, br s), 3.38−3.15 (3H, m), 3.16 (3H, s), 2.55−1.40 (12H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 135.4, 88.2, 85.5, 83.8, 55.5, 38.9, 35.5, 35.4, 30.4, 28.3, 27.8, 21.2, 7.9; HRMS calcd for $C_{14}H_{21}IO_2$ $[M]^+$ 348.0586, found 348.0587.

General Procedure for the Anionic Intramolecular Ring Opening of Oxabicyclo[3.2.1] Compounds. Tin−Lithium Exchange with MeLi. (*1S*,2S*,3S*,4S*,7R)-2,4-Dimethyl-9-oxabicyclo[5.3.0]dec-5-en-1,3-diol (4a).**[37] A solution of oxabicyclic compound **3a** (206 mg, 0.42 mmol) in THF (4 mL) was cooled to −78 °C and stirred while MeLi (1.6 mL, 1.4 M solution in diethyl ether, 2.12 mmol) was added dropwise. After 5 min, the reaction was warmed to 0 °C and stirred for an additional 3 h. The reaction was quenched by the addition of water and the solvent was evaporated. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 20:1 to 0:100, **4a** (73 mg, 85%) was obtained as a colorless oil. R_f = 0.33 on silica gel (ethyl acetate); IR (neat) 3605, 3500, 2960, 2920, 2840, 1460, 1380 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.43 (1H, br d, J = 11.3 Hz), 5.32 (1H, br d, J = 11.4 Hz), 4.12 (1H, dd, J = 7.9, 7.9 Hz), 3.80−3.59 (4H, m), 3.31 (1H, br t, J = 9.4 Hz), 2.89 (1H, m), 2.50 (1H, s), 2.15 (1H, m), 1.93 (1H, d, J = 6.4 Hz), 1.16 (3H, d, J = 7.5 Hz), 0.98 (3H, d, J = 7.5 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 134.4, 125.3, 82.6, 78.4, 78.1, 72.5, 45.1, 43.8, 39.7, 21.2, 14.9; HRMS calcd for $C_{11}H_{18}O_3$ $[M - H]^+$ 197.1177, found 197.1179. Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 65.75; H, 9.17.

(*1S*,2S*,3S*,4S*,7R)-2,4-Dimethyl-3-methoxy-9-oxabicyclo-[5.3.0]dec-5-en-1-ol (4b).** The oxabicyclic compound **3b** (40 mg, 0.08 mmol) in THF (2 mL) was treated with MeLi (0.23 mL, 1.4 M solution in diethyl ether, 0.32 mmol) at −78 °C and then stirred at 0 °C for 20 min. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 20:1 to 2:1, **4b** (14 mg, 82%) was obtained as a colorless oil. R_f = 0.41 on silica gel (hexanes−ethyl acetate 100:40); IR (neat) 3444, 3016, 2966, 2931, 2875, 1462, 1377, 1089 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.78 (1H, ddd, J = 11.2, 5.7, 2.9 Hz), 5.31 (1H, dd, J = 11.3, 1.7 Hz), 4.17 (1H, dd, J = 7.8, 7.7 Hz), 3.93−3.69 (3H, m), 3.49−3.39 (2H, m), 3.42 (3H, s), 2.90−2.78 (1H, m), 2.53−2.40 (1H, m), 2.33 (1H, s), 1.17 (3H, d, J = 7.5 Hz), 1.08 (3H, d, J = 7.5 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 135.9, 124.9, 83.6, 82.3, 77.9, 72.7, 60.3, 43.9, 43.5, 39.3, 18.3, 13.7; HRMS calcd for $C_{12}H_{20}O_3$ $[M - H - H_2O]^+$ 193.1228, found 193.1218.

(*1S*,2S*,3S*,4S*,7R)-3-(Benzyloxy)-2,4-dimethyl-9-oxabicyclo-[5.3.0]dec-5-en-1-ol (4c).** The oxabicyclic compound **3c** (50 mg, 0.09 mmol) in THF (1 mL) was cooled to -78 °C and treated with MeLi (0.31 mL, 1.4 M solution in diethyl ether, 0.43 mmol) and then stirred at 0 °C for 3 h. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 20:1 to 2:1, **4c** (20 mg, 80%) was obtained as a colorless oil. R_f = 0.59 on silica gel (hexanes−ethyl acetate 100:40); IR (neat) 3423, 3072, 3008, 2966, 2938, 2882, 1651, 1504, 1455, 1377, 1068 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.35−7.29 (5H, m), 5.83 (1H, ddd, J = 11.1, 6.2, 2.9 Hz), 5.31 (1H, dd, J = 11.1, 2.5 Hz), 4.58 (2H, s), 4.17 (1H, dd, J = 7.7, 7.9 Hz), 3.94−3.70 (4H, m), 3.44 (1H, br t), 2.85 (1H, m), 2.51 (1H, m), 2.23 (1H, s), 1.21 (3H, d, J = 7.6 Hz), 1.13 (3H, d, J = 7.5 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 139.1, 135.5, 128.4, 128.3, 127.3, 127.0, 124.6, 81.8, 80.4, 77.4, 73.1, 72.2, 43.5, 43.1, 39.0, 17.6, 13.3.

(*1S*,2S*,3S*,4S*,7R)-2,4-Dimethyl-3-(*tert*-butyldimethylsiloxy)-9-oxabicyclo[5.3.0]dec-5-en-1-ol (4d).** The oxabicyclic compound **3d** (74 mg, 0.12 mmol) in THF (3 mL) was treated with MeLi (0.35 mL, 1.4 M solution in diethyl ether, 0.49 mmol) at −78 °C and then stirred at 0 °C for 20 min. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 20:1 to 2:1, **4d** (29 mg, 83%) was obtained as a colorless oil. R_f = 0.83 on silica gel (hexanes−ethyl acetate 10:4); IR (neat) 3445, 3016, 2959, 2931, 2889, 2860, 1462, 1377, 1251, 1075, 1033 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.88 (1H, m), 5.29 (1H, dd, J = 11.2, 2.9 Hz), 4.20−3.72 (5H, m), 3.56 (1H, br t), 2.70−2.50 (1H, m), 2.34−2.21 (1H, m), 1.62 (1H, br s), 1.14 (3H, d, J = 7.6 Hz), 1.09 (3H, d, J = 7.5 Hz), 0.90 (9H, s), 0.05 (6H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 136.5, 125.1, 82.2, 77.9, 72.8, 71.8, 46.3, 43.3, 42.2, 26.4, 18.7, 16.5, 13.1, −4.0. Anal. Calcd for $C_{17}H_{32}O_3Si$: C, 65.33; H, 10.32. Found: C, 65.43; H, 10.35.

(*1R*,3S*,7R)-9-Oxabicyclo[5.3.0]dec-5-en-1,3-diol (4e).** The oxabicyclic compound **3e** (42 mg, 0.09 mmol) in THF (1 mL) was treated with MeLi (0.33 mL, 1.4 M solution in diethyl ether, 0.46 mmol) at −78 °C and then stirred at 0 °C for 2.5 h. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 2:1 to 0:100, **4e** (13 mg, 86%) was obtained as a colorless oil. R_f = 0.13 on silica gel (ethyl acetate); IR (neat) 3360, 3310, 3022, 2931, 2868, 1645, 1427, 1356, 1033 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.04 (1H, m), 5.53 (1H, m), 4.19 (1H, dd, J = 8.5, 8.1 Hz), 3.95−3.66 (4H, m), 3.04 (1H, br t), 2.48 (3H, br t), 1.84−1.54 (3H, br s, dd, br s, J = 10.9, 11.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 131.2, 128.7, 80.3, 77.6, 72.3, 65.1, 48.7, 47.6, 38.8; HRMS calcd for $C_9H_{14}O_3$ $[M - H_2O]^+$ 152.0837, found 152.0830. Anal. Calcd for $C_9H_{14}O_3$: C, 63.49; H, 8.3. Found: C, 63.20; H, 8.39.

(*1R*,2S*,3S*,7R)-2-Methoxy-9-oxabicyclo[5.3.0]dec-5-en-1,3-diol (4f).** The oxabicyclic compound **3f** (40 mg, 0.09 mmol) in THF (1 mL) was treated with MeLi (0.31 mL, 1.4 M solution in diethyl ether, 0.44 mmol) at −78 °C and then stirred at 0 °C for 3 h. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 2:1 to 0:100, **4f** (14 mg, 80%) was obtained as a colorless oil. R_f = 0.48 on silica gel (ethyl acetate); IR (neat) 3409, 3030, 2945, 2882, 2833, 1652, 1441, 1363, 1103, 1040 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.97 (1H, m), 5.40 (1H, dt, J = 10.3, 3.2 Hz), 4.16 (1H, dd, J = 8.1, 8.8 Hz), 3.99−3.53 (5H, m), 3.56 (3H, s), 3.43 (1H, tm), 2.79 (1H, tm), 2.14 (1H, m), 1.96 (2H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 131.4, 128.4, 84.4, 81.5, 76.7, 72.1, 68.5, 63.1, 42.6, 31.6; HRMS calcd for $C_{10}H_{16}O_4$ $[M - H]^+$ 199.0970, found 199.0975.

(*1S*,2S*,3S*,4S*,7R)-2,4,5-Trimethyl-9-oxabicyclo[5.3.0]dec-5-en-1,3-diol (4g).** The oxabicyclic compound **3g** (200 mg, 0.39 mmol) in THF (5 mL) was treated with MeLi (1.1 mL, 1.4 M solution in diethyl ether, 1.60 mmol) at −78 °C and then stirred at 0 °C for 30 min. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 2:1 to 0:100, **4g** (60 mg, 71%) was obtained as a colorless oil. R_f = 0.43 on silica gel (ethyl acetate); IR (neat) 3416, 3036, 2959, 2924, 2882, 1651, 1448, 1377, 1250, 1089 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.02 (1H, br s), 4.11 (1H, dd, J = 8.5, 8.1 Hz), 3.95−3.66 (4H, m), 3.22 (1H, br t), 2.51−2.31 (4H, br m), 1.79 (3H, s), 1.16 (3H, d, J = 7.6 Hz), 1.10 (3H, d, J = 7.4 Hz); ^{13}C NMR (100 MHz, toluene-d_8, 90 °C) δ 143.3, 119.3, 81.5, 77.8, 72.6, 69.3, 47.5, 45.4, 42.3, 25.7, 13.7, 11.7; HRMS calcd for $C_{12}H_{20}O_3$ $[M - H]^+$ 211.1334, found 211.1337. Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.88; H, 9.5. Found: C, 68.07; H, 9.27.

(*1S*,2S*,3S*,4R*,5R)-2,4-Dimethyl-1-(2-methoxyethyl)-8-oxabicyclo[3.2.1]oct-6-en-3-ol (4h).** The oxabicyclic compound **3h** (23 mg, 0.05 mmol) in THF (1 mL) was treated with MeLi (0.14 mL, 1.4 M solution in diethyl ether, 0.18 mmol) at −78 °C and stirred at 0 °C for 3 h. The reaction was quenched with water and evaporated, followed by an extraction with acetonitrile and pentane. The acetonitrile layer was washed with brine, dried over $MgSO_4$, filtered, and evaporated *in vacuo*. ^{1}H NMR (**4h** crude, 200 MHz, $CDCl_3$) 6.44 (1H, dd, J = 5.9, 1.7 Hz), 6.30 (1H, d, J = 6.1 Hz), 4.49 (1H, br s), 3.70−3.33 (3H, m), 3.31 (3H, s), 2.23−1.86 (5H, m), 1.01 (3H, d, J = 6.6 Hz), 0.98 (3H, d, J = 7.0 Hz).

(*1R*,2S*,3S*,4S*,7S)-2,4-Dimethyl-9-thiabicyclo[5.3.0]dec-5-en-1,3-diol (4i).** The oxabicyclic compound **3i** (97 mg, 0.19 mmol) in THF (2 mL) was treated with MeLi (0.69 mL, 1.4 M solution in diethyl ether, 0.96 mmol) at −78 °C and then stirred at 0 °C for 2.5 h. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 10:1 to 0:100, **4i** (37 mg, 88%) was obtained as a colorless oil. R_f = 0.24 on silica gel (hexanes−ethyl acetate 10:4); IR (neat) 3445, 3008, 2959, 2931, 2882, 2875, 1455, 1377, 1173, 1019 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.44 (2H, br s), 3.79 (1H, br m), 3.30−3.09 (3H, m), 2.85−2.66 (3H, m), 2.42 (1H, s), 2.19 (1H, ddd, J = 7.5, 7.5, 3.1 Hz), 1.74 (1H, d, J = 6.1 Hz), 1.14 (6H, d, J = 7.4 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 133.6, 127.1, 85.2, 76.7, 46.5, 45.6, 43.9, 40.3, 35.2, 19.3, 15.9; HRMS calcd for $C_{11}H_{18}O_2S$ $[M]^+$ 214.1027, found 214.1027.

(*1R*,2S*,3S*,4S*,7S)-2,4-Dimethyl-3-methoxy-9-thiabicyclo-[5.3.0]dec-5-en-1-ol (4j).** The oxabicyclic compound **3j** (37 mg, 0.07 mmol) in THF (1 mL) was treated with MeLi (0.24 mL, 1.4 M solution in diethyl ether, 0.33 mmol) at −78 °C and then stirred at 0 °C for 3

h. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 10:1 to 0:100, **4j** (13 mg, 80%) was obtained as a colorless oil. R_f = 0.83 on silica gel (ethyl acetate); IR (neat) 3438, 3009, 2966, 2931, 2882, 2826, 1652, 1455, 1377, 1096 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.62 (1H, ddd, J = 11.3, 6.6, 2.5 Hz), 5.31 (1H, dd, J = 11.4, 3.3 Hz), 3.46 (1H, dd, J = 4.8, 2.6 Hz), 3.42 (3H, s), 3.28 (1H, br t), 3.25 (1H, d, J = 11.0 Hz), 3.06 (1H, dd, J = 9.9, 10.2 Hz), 2.86 (1H, dd, J = 10.2, 10.2 Hz), 2.68 (1H, d, J = 11.0 Hz), 2.65 (1H, br m), 2.26 (1H, ddd, J = 7.7, 7.7, 2.6 Hz), 2.17 (1H, s), 1.17 (3H, d, J = 7.3 Hz), 1.08 (3H, d, J = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.3, 125.3, 84.8, 83.2, 60.5, 46.0, 44.2, 42.5, 40.2, 34.7; HRMS calcd for $[M]^+$ $C_{12}H_{20}O_2S$ 228.1183, found 228.1184. Anal. Calcd for $C_{12}H_{20}O_2S$: C, 63.12; H, 8.83. Found: C, 62.92; H, 8.87.

***(1S*,2S*,3S*,4S*,7R*)*-*N*-Methyl-2,4-dimethyl-9-azabicyclo[5.3.0]-dec-5-en-1,3-diol (4k).** The oxabicyclic compound **3l** (110 mg, 0.21 mmol) in THF (2 mL) was treated with MeLi (0.63 mL, 1.4 M solution in diethyl ether, 0.88 mmol) at −78 °C and then stirred at 0 °C for 1 h. After purification by chromatography on alumina with hexanes−ethyl acetate 10:1 to 0:100, **4k** (36 mg, 78%) was obtained as a colorless oil. R_f = 0.32 on silica gel (methanol); IR (neat) 3409, 3008, 2959, 2931, 2882, 2846, 1652, 1455, 1384, 1166, 1103, 1019 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 (2H, br d, J = 12.1 Hz, and br d, J = 12.4 Hz), 3.71 (1H, d, J = 4.4 Hz), 3.28 (1H, br t), 2.98 (2H, br m), 2.79 (1H, dd, J = 9.1, 9.2 Hz), 2.68 (1H, d, J = 9.2 Hz), 2.64 (1H, d, J = 9.6 Hz), 2.52 (1H, d, J = 9.5 Hz), 2.36 (3H, s), 2.31 (1H, s), 2.10 (1H, m), 1.18 (3H, d, J = 7.3 Hz), 1.03 (3H, d, J = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.9, 128.5, 82.9, 78.2, 66.9, 59.8, 44.5, 42.7, 42.1, 38.9, 20.7, 13.8; HRMS calcd for $[M]^+$ $C_{12}H_{21}NO_2$ 211.1572, found 211.1569.

General Procedure for the Anionic Intramolecular Ring Opening of Oxabicyclo[3.2.1] Compounds. Lithium−Halogen Exchange with *t*-BuLi. *(1S*,2S*,3S*,4S*,7S*)*-2,4-Dimethyl-3-methoxybicyclo-[5.3.0]dec-5-en-1-ol (4n). A solution of 0.1 M of oxabicyclic compound **3p** (206 mg, 0.61 mmol) in pentane−ether (3:2, 6 mL) was cooled to −78 °C and treated with a solution of *t*-BuLi (0.79 mL, 1.7 M solution in pentane, 1.35 mmol). The reaction was stirred 5 min at -78 °C and then the reaction was allowed to stir to room temperature for 50 min. The reaction was quenched by the addition of methanol and the volatiles were evaporated. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 20:1 to 2:1, **4n** (90 mg, 80%) was obtained as a colorless oil. R_f = 0.19 on silica gel (hexanes−ethyl acetate 10:1); IR (neat) 3494, 2966, 2931, 2882, 1729, 1461, 1377, 1265, 1096 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.77 (1H, ddd, J = 11.3, 6.9, 2.9 Hz), 5.38 (1H, dd, J = 11.4, 2.8 Hz), 3.50 (1H, dd, J = 4.4, 3.4 Hz), 3.37 (3H, s), 2.91 (1H, br t), 2.72 (1H, m), 2.40 (1H, m), 2.02 (1H, s), 2.02−1.54 (6H, m), 1.10 (3H, d, J = 7.5 Hz), 1.05 (3H, d, J = 7.5 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 134.7, 131.2, 81.9, 83.7, 59.0, 45.9, 43.4, 38.8, 38.3, 32.1, 22.0, 17.2, 13.5; HRMS calcd for $C_{13}H_{22}O_2$ $[M - H]^+$ 209.1541, found 209.1541. Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 73.52; H, 10.53.

***(1S*,2S*,6S*,9S*,13S*)*-13-Methoxytricyclo[7.3.1^{2,6}.0^{1,9}]tridec-7-en-1-ol (4o).** The oxabicyclic compound **3s** (60 mg, 0.17 mmol) in pentane−ether (1:1, 3 mL) was treated with *t*-BuLi (0.25 mL, 1.5 M solution in pentane, 0.38 mmol) at −78 °C and then stirred at 0 °C for 1.5 h. After purification by flash chromatography on silica gel with hexanes−ethyl acetate 100:0 to 10:1, **4o** (35 mg, 90%) was obtained as a colorless oil. R_f = 0.42 on silica gel (hexanes−ethyl acetate 10:1); IR (neat) 3521, 3002, 2931, 2868, 1448, 1384, 1251, 1188, 1103 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.49 (1H, dd, J = 11.4, 1.5 Hz), 5.42 (1H, dm, J = 11.3 Hz), 3.65 (1H, br t), 3.36 (3H, s), 3.30 (1H, m), 2.82 (1H, br s), 2.49 (1H, br m), 2.12 (1H, dm, J = 12.6 Hz), 1.95−1.90 (2H, m), 1.80−1.27 (10H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.1, 130.1, 88.7, 85.8, 56.1, 44.8, 43.6, 41.2, 40.4, 31.7, 29.7, 27.8, 20.8, 20.1; HRMS calcd for $C_{14}H_{22}O_2$ $[M - CH_3OH]^+$ 190.1357, found 190.1354.

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