Samarium(II) Iodide-Mediated Reductive Annulations of Ketones Bearing a Distal Vinyl Epoxide Moiety

Gary A. Molander* and Sagar R. Shakya

Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0215

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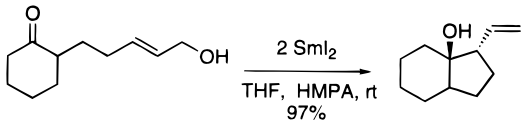
Samarium(II) iodide in the presence of hexamethylphosphoramide (HMPA) efficiently promotes the intramolecular coupling of ketones with distal epoxy olefins. The reaction appears to proceed by a mechanism wherein a ketyl couples with the unsaturated epoxide. Subsequent fragmentation of the epoxide ring in compounds **1a**−**k** yields carbocycles **2a**−**k** with an allyl alcohol side chain in good yields, and often with high diastereoselectivity. When tetramethylguanidine was used as an additive instead of HMPA, the desired carbocycle was obtained in good yield, but the diastereoselectivity was diminished. A palladium(0)-catalyzed SmI_2 reaction provided the expected product in modest yield, but the sense of diastereoselectivity was reversed. In the latter case, a different reaction mechanism may be involved. Thus, formation of an allylsamarium species may be invoked, with nucleophilic carbonyl addition leading to the observed facial selectivity.

Introduction

Intramolecular radical cyclizations leading to the formation of carbocycles or heterocycles have been extensively utilized in a large number of important synthetic applications.[1] Compared to simple radical cyclizations, the cyclizations of ketyls are relatively new and have many advantages. One of the most appealing features of ketyl−olefin cyclizations is the diastereoselective introduction of a hydroxyl group at the newly formed carbon−carbon bond of the cyclic products. Our earlier work[2] and results from other laboratories[3] have unveiled useful aspects of ketyl−olefin coupling reactions using samarium(II) iodide as a reductant.[4] The oxophilicity of samarium ions permits the addition of chelating additives such as HMPA,[5] thereby increasing the steric bulk around the ketyl oxygen. As a result, cyclizations under these conditions provide inherently higher diastereoselectivities when compared to methods employing ketyl formation via electrochemical,[6] photochemical,[7] and other chemical[8] reductants.

Earlier observations have revealed that a number of allylically functionalized units, including allyl alcohols, can successfully couple with ketones under SmI_2−HMPA-promoted reductive coupling conditions (eq 1).[9] Although



(1)

allylstannanes,[10] allyl sulfides, and allyl sulfones[11] have been used in similar reactions, olefins bearing an epoxide terminus have not been studied until recently. Vinyl-

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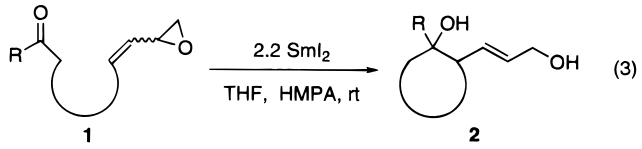
substituted epoxides would appear to be excellent substrates for the reaction because they can be readily reduced by SmI_2[12] and because the epoxide moiety can be opened under both radical and anionic β-elimination processes.[13] Furthermore, in contrast to the above-mentioned leaving groups, the functionality remains appended to the product in the epoxide ring-opening process. Thus, successful coupling of ketones with vinyl epoxides would provide access to functionalized carbocycles having an allyl alcohol side chain,[14] a structural pattern found in many biologically active compounds.[15]

In a recent study, the intermolecular coupling of ketones with a variety of vinyl epoxides was communicated (eq 2).[16] In that contribution, it was postulated that the process transpired exclusively via an allylsamarium species that subsequently added to the ketone. Herein we report the results of our initial studies on intramolecular reactions and stereochemical studies that suggest that a ketyl−olefin coupling reaction may be involved in the intramolecular version of the reaction (eq 3).

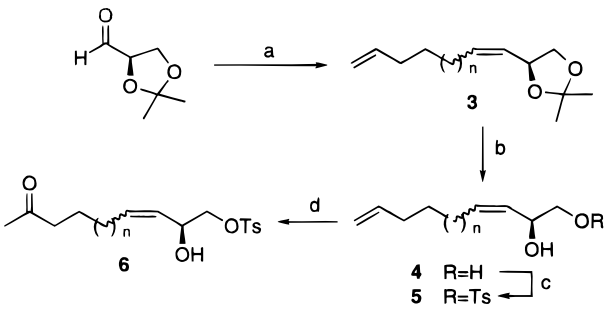


(3)

Results and Discussion

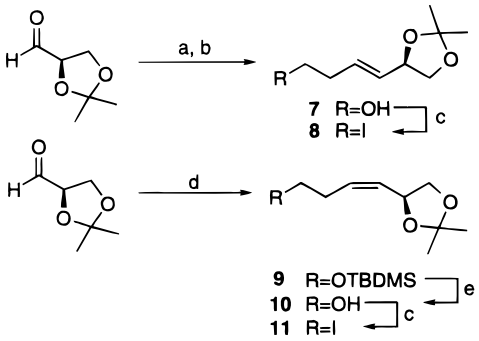
The substrates required for the study (**1a**−**k**) were readily obtained in several steps utilizing standard procedures. The sensitivity of the requisite unsaturated epoxides toward both acids and strong bases demanded careful, strategic sequencing of the reactions leading to their synthesis. In all cases, the epoxide moiety was assembled in the last step (eq 4). We incorporated enantiopure (2*R*)-bis-*O*-methylethylideneglyceraldehyde into the synthesis of many of the substrates simply for the sake of convenience. For example, **1a**,**c**,**e** were constructed from the glyceraldehyde derivative utilizing a Wittig reaction in the initial step, which led to **3** (Scheme 1). Deprotection of the acetal, followed by selective conversion of the primary alcohol to the tosylate, provided **5**, which was subjected to a Wacker oxidation to afford ketones **6**. Treatment with base at low temperatures, as indicated in eq 4, led to the desired substrates.

Scheme 1[a]

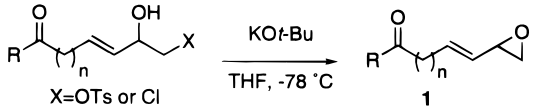


[a] Key: (a) $R'PPh_3^+I^-$ (R′ = 5-hexenyl or 6-heptenyl), 2PhLi·LiBr, THF, −78 °C (for **3a**) or $NaNH_2$, THF, −78 °C (for **3c** and **3e**); (b) 10% aqueous HCl, THF; (c) TsCl, pyridine, −25 to −20 °C; (d) 10 mol % $PdCl_2$, 1.1 equiv of CuCl, O_2, DMF/H_2O (7:1).

Scheme 2[a]



[a] Key: (a) $HO(CH_2)_3PPh_3^+I^-$; *n*-BuLi, TMSCl, THF, −78 °C; (b) 2 mol % PhSSPh, hexane, *hν*; (c) Ph_3P, I_2, imidazole, CH_3CN; (d) $TBDMSO(CH_2)_3PPh_3^+I^-$, *n*-BuLi, THF, −78 °C; (e) TBAF, THF.



(4)

For alkyl ketones wherein a Wacker oxidation could not be utilized, an alkylative coupling strategy was pursued. The alkylating agents were synthesized from the acetonide of glyceraldehyde (Scheme 2), and these were subsequently coupled to the appropriate ketone dimethylhydrazones to afford the desired intermediates (Scheme 3). Acidic workup, selective conversion to the tosylate, and ring closure as in eq 4 provided **1b**,**d**,**h**−**k**.

Compounds **1f**,**g** required a more customized approach. These substrates were synthesized by chloromethylation of the butenyl-substituted cycloalkenones, followed by a Wacker oxidation (Scheme 4), with epoxide ring formation as described previously (eq 4) completing the synthesis.

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(17) The lithio species was obtained by tin−lithium exchange of the corresponding tributyltin derivative.

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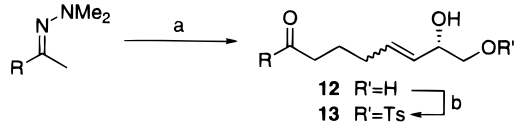
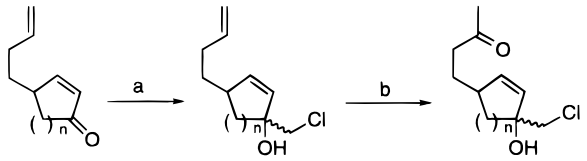
Scheme 3[a]



[a] Key: (a) *n*-BuLi or LDA, **8** or **11**, then aqueous HCl, MeOH; (b) TsCl, pyridine, −25 to −20 °C.

Scheme 4[a]

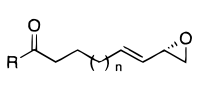
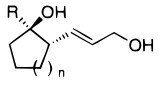
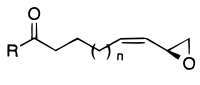
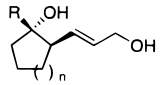
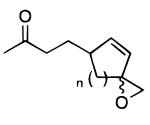
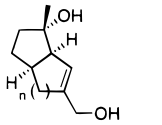
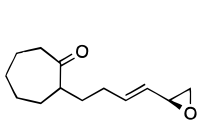
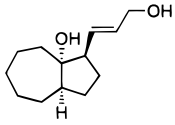
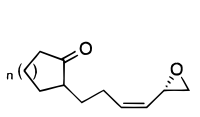
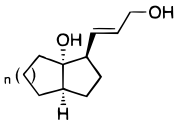


[a] Key: (a) 1.3 equiv of $ClCH_2I$, 1.3 equiv of *n*-BuLi, THF, −78 °C; (b) 10 mol % $PdCl_2$, 1.1 equiv of CuCl, O_2, DMF/H_2O (7:1).

With the substrates in hand, studies were initiated on the SmI_2-promoted cyclization reactions (Table 1). The initial experiments with **1a**,**c** provided rather interesting results. As indicated in entries 1 and 3 of Table 1, only one diastereomer was obtained. The *trans* relationship between the hydroxyl group and the allyl alcohol side chain was established by comparison of the ^1H NMR spectrum of an authentic sample prepared by an unambiguous synthetic route. Thus, methylcyclopentene oxide was treated with the (3*E*)-lithio species of the TBDMS ether of 2-propen-1-ol[17] in the presence of $BF_3{\cdot}OEt_2$.[18] The major adduct from this reaction was treated with TBAF in THF to provide the comparison sample. Furthermore, **2a**,**c** were found to differ only in their handedness and enantiomeric enrichment. Thus, double bond geometry has a slight influence on the enantiotopic facial selectivity of the addition. Unfortunately, the asymmetric induction was very low (**2a**,**c** were generated with <10% ee),[19] and the absolute stereochemistry of the products was, therefore, not determined. These results indicate that the stereogenicity of the epoxide has very little influence on the facial bias of addition, in contrast to the stereoselective reactions of vinyl epoxides with cuprates.[20] The conversion with partial enantiomeric enrichment suggests that some portion of the reaction probably proceeds via a ketyl−olefin coupling pathway. Conversion via an allylsamarium species would most likely result in racemic material; furthermore, there is some evidence to suggest that the opposite diastereomer would probably be generated (vide infra).

The generality of the intramolecular coupling reaction was examined utilizing the diverse substrates displayed in Table 1. In the case of more highly hindered ketone substrates, competing reactions led to a number of side products. For example, reductive ring opening of the vinyl epoxide terminus of **1b** competed with the desired reductive cyclization, and thus several acyclic compounds could be isolated. In an attempt to improve this situation, two different reductive coupling protocols were tested with substrate **1d**. The best yield of the cyclic product **2d** was realized when HMPA was replaced by tetramethylguanidine (TMG).[21] Unfortunately, in this case, a 1:1 mixture of diastereomers was obtained, perhaps owing to the decreased steric bulk of the complexed ketyl when using this additive. Compound **1d** was also subjected to a palladium-catalyzed SmI_2 reaction.[22] This reaction provided only a modest yield (41%) of the cyclized product, but interestingly, the sense of diastereoselectivity was reversed (4:1 in favor of the minor diastereomer from the HMPA reaction). The *cis* stereochemistry of the final product was established by an X-ray crystal structure determination. The results of this experiment indicate a dramatic change in the mechanism of the reaction. The palladium-catalyzed reaction is believed to proceed via initial formation of a π-allyl palladium complex, which undergoes reductive transmetalation to provide an allylsamarium species. Subsequent carbonyl addition through this allylsamarium species would afford the observed product. Again, in contrast to these palladium-catalyzed SmI_2 reactions, the

Table 1. Ketyl Coupling Reactions of Vinyl Epoxides Promoted by Samarium(II) Iodide

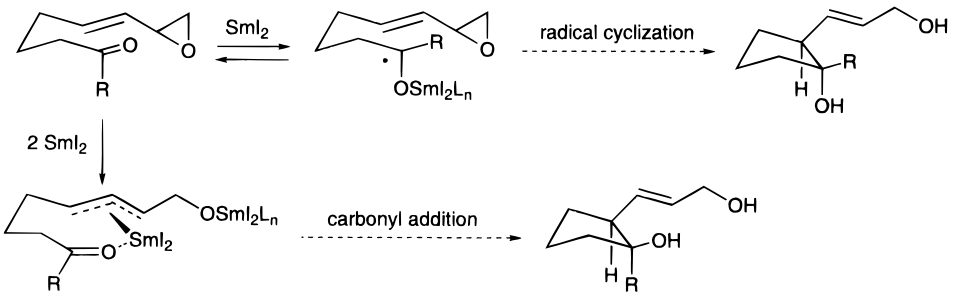
entry	substrates	products	% yield	diastereoselectivity
				
1	**1a** R=Me, n=1	**2a** R=Me, n=1	52	>200 : 1
2	**1b** R=*i*-Bu, n=1	**2b**R=*i*-Bu, n=1	48 [a]	3 : 1
				
3	**1c** R=Me, n=1	**2c** R=Me, n=1	72	>200 : 1
4	**1d** R=*i*-Bu, n=1	**2d** R=*i*-Bu, n=1	71	1:1 [b]
5	**1e** R=Me, n=2	**2e** R=Me, n=2	17	>200 : 1
				
6	**1f** n=1	**2f** n=1	72	>200 : 1
7	**1g** n=2	**2g** n=2	78	>200 : 1
				
8	**1h**	**2h**	69	10 : 1
				
9	**1i** n=1	**2i** n=1	78	>200 : 1
10	**1j** n=2	**2j** n=2	76	>200 : 1
11	**1k** n=4	**2k** n=4	83 [a]	1.5 : 1.2 : 1 [c]

[a] Characterized as the mono-TBDMS ether. [b] 19 equiv of TMG was used. [c] By GLC analysis.

(21) Cabri, W.; Candiani, I.; Colombo, M.; Franzoi, L.; Bedeschi, A. *Tetrahedron Lett.* **1995**, *36*, 949.

(22) The reaction was performed using 5 mol % of the Pd(0) catalyst generated in situ from $Pd(OAc)_2$ and Ph_3P. A solution of the epoxide was slowly added to a mixture of the Pd(0) catalyst and SmI_2 at −30 °C over 1 h. For examples of Pd(0)-catalyzed SmI_2 reactions, see: (a) Fukuzawa, S.; Fujinami, T.; Sakai, S. *Chem. Lett.* **1990**, 927. (b) Tabuchi, T.; Inanaga, J.; Yamaguchi, M. *Tetrahedron Lett.* **1986**, *27*, 1195. (c) Tabuchi, T.; Inanaga, J.; Yamaguchi, M. *Tetrahedron Lett.* **1986**, *27*, 601. (d) Tabuchi, T.; Inanaga, J.; Yamaguchi, M. *Tetrahedron Lett.* **1986**, *27*, 5237.

Scheme 5



SmI_2–HMPA-promoted reactions may well proceed via a ketyl–olefin pathway. Ketyl–olefin coupling reactions mediated by SmI_2 are known to lead to products enriched in the *trans* isomers.[2,9a]

In this vein, it is interesting to note the analogy between the SmI_2-promoted reactions of vinyl epoxides with carbonyl substrates and analogous reactions involving allyl sulfones and sulfides.[11] In the latter, the mixture of regioisomers observed in the intermolecular reactions provides sufficient evidence that a significant fraction of the process occurs via an allylsamarium species. In the intramolecular reactions, the results are much more ambiguous. A single regioisomer is generated in the examples reported, but this result is expected regardless of whether an allylsamarium intermediate is involved or the process occurs via the ketyl. However, the sense and magnitude of diastereoselection varies dramatically in the various substrates examined to date. A possible explanation may involve the reversible nature of the reaction of SmI_2 with ketones.[23] In intermolecular coupling reactions, SmI_2 can reversibly reduce the ketone to a ketyl, but ketyl coupling with the olefinic substrate is a relatively slow bimolecular process. This may provide ample time for competitive reduction of the allylic substrate to an allylsamarium species by the SmI_2, with subsequent addition of the resulting allylsamarium species to the ketone, leading to the observed product. In the intramolecular version of the reactions, any ketyl formed can be rapidly trapped by addition to the activated alkene. Consequently, a greater proportion of the reaction may proceed via the ketyl coupling process (Scheme 5).

Further synthetic studies revealed that the cyclization reaction is generally restricted to five-membered ring formation. As indicated in entry 5, of Table 1, the corresponding six-*exo* annulation/fragmentation reaction provides a low yield of the expected cyclic product. Significant amounts of uncyclized material were obtained as side products.

Substrates **1f**,**g** provided further confirmation that the stereochemistry of the epoxide stereogenic center does not dramatically influence facial selectivity in the carbon–carbon bond-forming event. Starting with a mixture of diastereomers of **1f** or **1g**, only one isomer of **2f** or **2g** was obtained in excellent yield. The formation of a single diastereomer in these reactions must be due to the topographical bias of the conformationally fixed cyclic olefin.

Finally, high diastereoselectivity was observed in the synthesis of the bicyclo[3.3.0]alkanols and bicyclo[4.3.0]-alkanols **2i** and **2j**, respectively. The relative stereochemistry of **2i** was established by single-crystal X-ray diffractometry. In conformationally more flexible systems, the diastereomeric purity is again diminished. Thus, a 10:1 mixture of diastereomers is generated when a cycloheptanone substrate is utilized (Table 1, entry 8), and a mixture of at least three diastereomers was isolated from a cyclooctanone precursor (Table 1, entry 11).

(23) Curran, D. P.; Fevig, T. L.; Jasperse, C. P.; Totleben, M. J. *Synlett* **1992**, 943.

Conclusions

A versatile new method for the construction of carbocycles has been demonstrated. The reductive coupling reaction of ketones with vinyl epoxides, mediated by SmI_2–HMPA, leads to highly functionalized diols in high yields. Evidence has been presented that suggests that the reaction proceeds via an initial radical cyclization route, although reaction through an allylsamarium species cannot be ruled out at this stage. Reaction with SmI_2–catalytic Pd(0), on the other hand, presumably transpires via allylsamarium species, with nucleophilic carbonyl addition completing the process.

Experimental Section

Details concerning the preparation of the SmI_2–HMPA solution are provided in the experimental sections of our earlier publications.[2,24] KO*t*-Bu was sublimed and handled under argon using Schlenk techniques. A suspension of $NaNH_2$ in toluene was purchased from Aldrich. The solvent was removed in vacuo, and the $NaNH_2$ was handled under argon. $PdCl_2$, CuCl, and DMF were used as received. TsCl was recrystallized before use. Pyridine was distilled from KOH and stored over 4 Å molecular sieves. Chloroiodomethane (Aldrich) was distilled prior to use. *n*-BuLi was titrated using diphenylacetic acid.

(2*S*,3*E*)-1,2-Bis-*O*-methylethylidene-3,8-nonadiene-1,2-diol (3a). Freshly prepared phenyllithium[25] (0.95 M, 5.26 mL, 5.0 mmol) was added to a suspension of 5-hexenyltriphenylphosphonium iodide[26] (2.36 g, 5.0 mmol). After being stirred for 1 h at rt, the clear solution of ylide was cooled to −78 °C. A solution of (2*R*)-2,3-bis-O-methylethylideneglyceraldehyde[27] (0.715 g, 5.50 mmol) in 5 mL of THF was added dropwise to the ylide solution at −78 °C. The reaction mixture was stirred at −30 °C for 30 min, and an additional equivalent of phenyllithium was added to it.[28] After the mixture was stirred for 30 min at 25 °C and 15 min at −78 °C, *t*-BuOH (0.37 g, 5.0 mmol) and KO*t*-Bu (0.672 g, 6.0 mmol) were sequentially added to it. The mixture was warmed to rt and stirred for 1.5 h. Aqueous workup gave a crude product, which was taken up in pentane. The pentane layer was decanted

(24) Molander, G. A. *Org. React.* **1994**, *46*, 211.
(25) Preparation: Gilman, H.; Morton, J. W. In *Organic Reactions*; J. Wiley & Sons: New York, 1954; Vol. 8, p 286.
(26) Prepared from 5-hexenol (Aldrich) by treatment with (a) Ph_3P, I_2, imidazole, CH_3CN. Lange, G. L.; Gottardo, C. *Synth. Commun.* **1990**, *20*, 1473. (b) Ph_3P, CH_3NO_2, heated at reflux.
(27) Schmid, C. R.; Bryant, J. D. *Org. Synth.* **1993**, *72*, 6.
(28) Schlosser, M.; Tuong, H. B.; Schaub, B. *Tetrahedron Lett.* **1985**, *26*, 311.

and concentrated to give an oil, which was purified by flash silica gel columm chromatography to provide 0.492 g (50%) of the desired product **3a** (98% *E* by GLC): Kugelrohr distilled ot 80−90 °C/1.0 mmHg; R_f 0.18 (1:20 ether/pentane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (s, 3H), 1.40 (s, 3 H), 1.42−1.53 (m, 2H), 2.00−2.08 (m, 4H), 3.53 (t, J = 8.0 Hz, 1H), 4.04 (dd, J = 6.0, 8.1 Hz, 1H), 4.44 (m, 1H), 4.92−5.01 (m, 2H), 5.38−5.45 (m, 1H), 5.72−5.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.9, 26.7, 28.0, 31.6, 33.1, 69.4, 77.3, 109.0, 114.6, 127.5, 135.5, 138.4.

(2*S*,3*Z*)-1,2-Bis-*O*-methylethylidene-3,8-nonadiene-1,2-diol (3c). A mixture of 5-hexenyltriphenylphosphonium iodide (12.0 g, 25.42 mmol) and $NaNH_2$ (0.992 g, 25.42 mmol) in 80 mL of THF was stirred for 4 h to afford a reddish-orange solution.[29] Argon was bubbled through this solution to remove residual ammonia. A solution of freshly distilled (2*R*)-2,3-bis-*O*-methylethylideneglyceraldehyde (3.97 g, 30.51 mmol) in 20 mL of THF was added dropwise to the ylide solution at −78 °C and stirred for 2 h. The cooling bath was removed, and the reaction mixture was stirred for an additional 16 h. Pentane was added to bring the final volume of the reaction mixture to 400 mL; the mixture was then filtered and the filtrate concentrated. Flash silica gel column chromatography yielded 2.92 g (59%) of **3c** (>97% *Z* by GLC): R_f 0.33 (1:20 ether/pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.44 (s, 3H), 1.47 (s, 3H), 1.51−1.60 (m, 2H), 2.07−2.22 (m, 4H), 3.56 (t, J = 8.1 Hz, 1H), 4.10 (dd, J = 6.1, 8.1 Hz, 1H), 4.84−4.92 (m, 1H), 5.00−5.09 (m, 2H), 5.43−5.50 (m, 1H), 5.63−5.69 (m, 1H), 5.79−5.88 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.0, 26.7, 27.0, 28.7, 33.1, 69.4, 71.9, 109.0, 114.8, 127.4, 134.6, 138.3.

(2*S*,3*Z*)-1,2-Bis-*O*-methylethylidene-3,9-decadiene-1,2-diol (3e). A mixture of 6-heptenyltriphenylphosphonium iodide[30] (1.70 g, 3.50 mmol) and $NaNH_2$ (0.141 g, 3.61 mmol) in 10 mL of THF was stirred for 4 h to afford a reddish-orange solution. As described in the preparation of **3c**, this mixture was treated with a solution of freshly distilled (2*R*)-2,3-bis-*O*-methylethylideneglyceraldehyde (0.550 g, 4.23 mmol) in 10 mL of THF. The usual workup and purification of the crude product by flash silica gel column chromatography yielded 0.298 g (41%) of **3e**: R_f 0.34 (1:20 ether/pentane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32−1.40 (m with two overlapping s at 1.38 and 1.40, 10H), 1.95−2.11 (m, 4H), 3.49 (t, J = 8.0 Hz, 1H), 4.37 (dd, J = 6.1, 8.0 Hz, 1H), 4.82 (q, J = 8.0 Hz, 1H), 4.91−5.00 (m, 2H), 5.38 (dd, J = 8.8, 10.9 Hz, 1H), 5.58−5.64 (m, 1H), 5.72−5.83 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.0, 26.8, 27.5, 28.3, 29.0, 33.5, 69.4, 71.9, 109.0, 114.4, 127.2, 134.9, 138.7.

(2*S*,3*E*)-3,8-Nonadiene-1,2-diol (4a). A solution of **3a** (0.470 g, 2.40 mmol) in 12 mL of THF/10% aqueous HCl (4:1) was stirred for 18 h at ambient temperature. The reaction mixture was quenched with anhydrous K_2CO_3, filtered, and concentrated. Kugelrohr distillation of the crude product gave the desired diol **4a** (0.355 g, 95%): Kugelrohr distilled ot 120 °C/1.0 mmHg; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.41−1.51 (m, 2H), 1.95−2.29 (m, 6H), 3.42−3.51 (m, 1H), 3.58−3.65 (m, 1H), 4.18 (br s, 1H), 4.91−5.02 (m, 2H), 5.40−5.48 (m, 1H), 5.70−5.84 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.1, 31.6, 33.1, 66.6, 73.1, 114.7, 128.6, 133.8, 138.5.

(2*S*,3*Z*)-3,8-Nonadiene-1,2-diol (4c). A solution of **3c** (2.473 g, 12.62 mmol) was hydrolyzed as described for **3a** to provide 1.899 g (96%) of the diol **4c**: Kugelrohr distilled ot 120 °C/0.1 mmHg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.42−1.50 (m, 2H), 1.96 (br s, 2H), 2.02−2.16 (m, 4H), 3.48 (dd, J = 8.0, 11.1 Hz, 1H), 3.56 (dd, J = 3.7, 11.1 Hz, 1H), 4.53 (dt, J = 3.7, 8.5 Hz, 1H), 4.93−5.02 (m, 2H), 5.38 (dd, J = 8.8, 10.8 Hz, 1H), 5.54−5.61 (m, 1H), 5.72−5.82 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.2, 28.6, 33.1, 66.3, 68.6, 114.8, 128.1, 134.1, 138.4.

(2*S*,3*Z*)-3,9-Decadiene-1,2-diol (4e). Compound **3e** (0.298 g, 1.419 mmol) was hydrolyzed as described for **3a** to provide 0.208 g (86%) of the diol **4e**: Kugelrohr distilled ot 130−140 °C/1.5 mmHg; R_f 0.22 (1:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36−1.43 (m, 4H), 1.90−2.12 (m, 6H), 3.48 (dd, J = 8.0, 11.1 Hz, 1H), 3.57 (dd, J = 3.7, 11.1 Hz, 1H), 4.51−4.56 (m, 1H), 4.91−5.00 (m, 2H), 5.33−5.38 (m, 1H), 5.55−5.61 (m, 1H), 5.72−5.83 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.7, 28.4, 29.0, 33.5, 66.4, 68.6, 114.5, 127.9, 134.5, 138.7.

(2*S*,3*E*)-1-[(4-Methylbenzenesulfonyl)oxy]-3,8-nonadien-2-ol (5a). Diol **4a** (0.350 g, 2.24 mmol) in 3 mL of dry pyridine was treated with TsCl (0.427 g, 2.24 mmol) in 2 mL of pyridine at −25 to −20 °C for 2 d.[31] Aqueous workup using CH_2Cl_2 afforded the crude tosylate, which was purified by flash silica gel column chromatography to give 0.498 g (72%) of the desired tosylate **5a**: R_f 0.33 (3:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39−1.46 (m, 2H), 1.98−2.06 (m, 5H), 2.43 (s, 3H), 3.87 (dd, J = 7.7, 10.1 Hz, 1H), 4.02 (dd, J = 3.3, 10.1 Hz, 1H), 4.32−4.33 (br m, 1H), 4.92−4.99 (m, 2H), 5.33 (dd, J = 6.5, 15.4 Hz, 1H), 5.72−5.79 (m, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 27.9, 31.6, 33.0, 70.2, 73.3, 114.7, 126.5, 127.9, 129.9, 132.7, 135.0, 138.3, 145.0.

(2*S*,3*Z*)-1-[(4-Methylbenzenesulfonyl)oxy]-3,8-nonadien-2-ol (5c). Diol **4c** (1.87 g, 12.0 mmol) was treated with TsCl (2.286 g, 11.99 mmol) as described for **5a** to give 2.63 g (71%) of tosylate **5c**: R_f 0.33 (1:3 ethyl acetate/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38−1.47 (m, 2H), 1.94−2.10 (m, 5H), 2.43 (s, 3H), 3.88 (dd, J = 7.8, 10.2 Hz, 1H), 3.96 (dd, J = 3.4, 10.2 Hz, 1H), 4.62−4.69 (m, 1H), 4.92−5.02 (m, 2H), 5.23−5.30 (m, 1H), 5.53−5.62 (m, 1H), 5.68−5.82 (m, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 27.2, 28.4, 33.0, 66.0, 73.0, 114.9, 126.2, 128.0, 129.9, 132.7, 135.4, 138.2, 145.1.

(2*S*,3*Z*)-1-[(4-Methylbenzenesulfonyl)oxy]-3,9-decadien-2-ol (5e). Diol **4e** (0.197 g, 1.16 mmol) was treated with TsCl (0.221 g, 1.16 mmol) as described for **5a** to give 0.280 g (75%) of the desired tosylate **5e**: R_f 0.44 (3:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33−1.39 (m, 4H), 1.95−2.02 (m, 5H), 2.44 (s, 3H), 3.88 (dd, J = 8.0, 10.3 Hz, 1H), 3.96 (dd, J = 3.4, 10.3 Hz, 1H), 4.67 (dt, J = 3.5, 8.1 Hz, 1H), 4.92−5.00 (m, 2H), 5.25 (t, J = 10.9 Hz, 1H), 5.55−5.61 (m, 1H), 5.71−5.81 (m, 1H), 7.34 (d, J = 8.1 Hz, 2H), 7.79 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 27.8, 28.4, 28.8, 33.5, 66.0, 73.0, 114.5, 125.9, 128.0, 129.9, 132.7, 135.7, 138.6, 145.0.

(8*S*,6*E*)-8-Hydroxy-9-[(4-methylbenzenesulfonyl)oxy]-6-nonen-2-one (6a). A suspension of $PdCl_2$ (0.0246 g, 0.139 mmol) and CuCl (0.1516 g, 1.53 mmol) in 4 mL of a mixture of DMF/H_2O (7:1) was stirred under oxygen (using an oxygen-filled balloon) for 1 h.[32] The precursor **5a** (0.454 g, 1.46 mmol) in 4 mL of DMF was added to this catalyst mixture, and the mixture was stirred under oxygen for an additional 20 h. Aqueous workup was followed by purification of the crude product by flash silica gel column chromatography to yield 0.354 g (74%) of **6a**: R_f 0.33 (1:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.59−1.66 (m, 2H), 1.98−2.04 (m, 3H), 2.11 (s, 3H), 2.40 (t, J = 7.3 Hz, 2H), 2.44 (s, 3H), 3.87 (dd, J = 7.4, 10.1 Hz, 1H), 4.00 (dd, J = 3.5, 10.2 Hz, 1H), 4.30−4.34 (br m, 1H), 5.35 (dd, J = 6.4, 15.5 Hz, 1H), 5.69−5.77 (m, 1H), 7.34 (d, J = 8.1 Hz, 2H), 7.78 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 22.6, 29.9, 31.4, 42.7, 70.1, 73.2, 127.2, 127.9, 129.9, 132.6, 134.2, 145.0, 208.8.

(8*S*,6*Z*)-8-Hydroxy-9-[(4-methylbenzenesulfonyl)oxy]-6-nonen-2-one (6c). The toluenesulfonate **5c** (2.60 g, 8.39 mmol) was oxidized as described for **6a** to give 1.90 g (70%) of ketone **6c**: R_f 0.33 (1:1 hexanes/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.57−1.68 (m, 2H), 1.98−2.11 (m, 3H), 2.12 (s, 3H), 2.41 (t, J = 7.1 Hz, 2H), 2.43 (s, 3H), 3.89 (dd, J = 7.3, 10.2 Hz, 1H), 3.94 (dd, J = 3.9, 10.2 Hz, 1H), 4.60−4.67 (m, 1H), 5.27−5.34 (m, 1H), 5.50−5.59 (m, 1H), 7.34 (d, J = 8.6 Hz, 2H), 7.78 (d, J = 8.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$)

(29) Schaub, B.; Blaser, G.; Schlosser, M. *Tetrahedron Lett.* **1985**, *26*, 307.

(30) Prepared from 6-heptenoic acid (Aldrich) in three steps: (a) $LiAlH_4$, THF, 0 °C. López-Tudanca, P. L.; Jones, K.; Brownbridge, P. *Tetrahedron Lett.* **1991**, *32*, 2261. (b) Ph_3P, I_2, imidazole, CH_3CN. (c) Ph_3P, CH_3NO_2, heated at reflux.

(31) For selective monotosylation of a primary alcohol in the presence a secondary alcohol, see: Gerlach, H.; Oertle, K.; Thalmann, A. *Helv. Chim. Acta* **1976**, *59*, 755.

(32) Tsuji, J.; Nagashima, H.; Nemoto, H. *Org. Synth.* **1984**, *62*, 9.

δ 21.6, 23.1, 27.0, 29.8, 42.5, 65.7, 72.9, 127.1, 127.9, 129.9, 132.6, 134.5, 145.1, 209.0.

(9*S*,7*Z*)-9-Hydroxy-10-[(4-methylbenzenesulfonyl)oxy]-7-decen-2-one (6e). The monotosylate **5e** (0.270 g, 0.833 mmol) was oxidized as described for **6a** to yield 0.134 g (47%) of the desired ketone **6e**: R_f 0.25 (1.5:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29−1.36 (m, 2H), 1.50−1.57 (m, 2H), 1.95−2.11 (m with an overlapping s at 2.11, 6H), 2.42 (t with an overlapping s at 2.43, 5H), 3.88 (dd, J = 9.5, 7.7 Hz, 1H), 3.95 (dd, J = 2.0, 10.3 Hz, 1H), 4.63−4.67 (m, 1H), 5.26 (t, J = 9.6 Hz, 1H), 5.23−5.59 (m, 1H), 7.34 (d, J = 7.9 Hz, 2H), 7.78 (d, J = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 23.1, 27.6, 28.7, 29.9, 43.3, 65.9, 73.0, 126.4, 127.9, 129.9, 132.7, 135.0, 145.0, 209.0.

(2*S*,3*E*)-1,2-Bis-*O*-methylethylidene-3-hexene-1,2,6-triol (7). *n*-BuLi (139.55 mL, 1.38 M, 192.58 mmol) was added dropwise to a suspension of (3-hydroxypropyl)triphenylphosphonium iodide[33] (43.14 g, 96.29 mmol) in 150 mL of THF at −78 °C. The reaction mixture was gradually warmed to −10 °C over 3 h. TMSCl (10.443 g, 96.125 mmol) was added to the mixture at −78 °C. After 1 h, (2*R*)-2,3-bis-*O*-methylethylideneglyceraldehyde (13.77 g, 105.92 mmol) was added to the ylide solution, and the resultant mixture was stirred for 18 h without further cooling. The crude product obtained after aqueous workup was stirred with 24 g of silica gel in 120 mL of MeOH for 0.5 h. Removal of the silica gel, followed by purification of the concentrated residue by silica gel flash column chromatography, afforded 5.86 g (35%) of **7** ($E/Z \approx$ 1:1) as an oil.

The *E*-enriched **7** was obtained by irradiation of a solution of a 1:1 (*E*/*Z*) mixture of **7** (5.86 g, 34.1 mmol) and 2 mol % of diphenyl disulfide (0.149 g, 0.682 mmol) in 341 mL of hexane in a Pyrex flask for 6 h, to provide 2.00 g (34%) of **7** ($E/Z \approx$ 9:1 by ^{1}H NMR): Kugelrohr distilled ot 120 °C/1 mmHg; R_f 0.25 (1:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (s, 3H), 1.41 (s, 3H, contains 2 s at 1.43 and 1.46 due to minor isomer of OH, 1H), 2.32 (q, J = 6.2 Hz, 2H, overlapping with m from minor isomer), 3.56 (t, J = 7.7 Hz, 1H), 3.67 (t, J = 6.4 Hz, 2H), 4.04−4.09 (m, 1H), 4.46 (q, J = 7.5 Hz, 0.9H), 4.83 (q, J = 6.4 Hz, 0.1H), 5.52−5.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.86, 25.89, 26.66, 26.72, 31.2, 35.6, 61.6, 63.0, 69.37, 69.39, 71.7, 109.16, 109.2, 130.04, 130.26, 131.0, 131.5.

(2*S*,3*Z*)-1,2-Bis-*O*-methylethylidene-3-hexene-1,2,6-triol (10). *n*-BuLi (16.5 mL, 1.38 M, 22.78 mmol) was added to a suspension of {[(*tert*-butyldimethylsilyl)oxy]propyl}-triphenylphosphonium iodide[34] (12.80 g, 22.78 mmol) in 150 mL of THF at −78 °C. The reaction mixture was warmed to rt and stirred for 30 min to give an orange solution. A solution of (2*R*)-2,3-bis-*O*-methylethylideneglyceraldehyde (4.50 g, 34.610 mmol) in 10 mL of THF was added to the ylide solution at −78 °C, and the mixture was stirred for 3 h at −78 to 25 °C. Aqueous workup and purification of the crude product by flash silica gel column chromatography yielded 4.71 g (72%) of the *tert*-butyldimethylsilyl ether **9**.

Tetrabutylammonium fluoride (TBAF) in THF (19.76 mL, 1 M, 19.76 mmol) was added to the *tert*-butyldimethylsilyl ether **9** (4.71 g, 16.5 mmol) in 20 mL of wet THF, and the reaction mixture was stirred for 5 h at 25 °C. After removal of THF, the residue was subjected to aqueous workup using saturated NH_4Cl and EtOAc. The crude product was purified by silica gel column chromatography to provide 2.10 g (74%) of **10**: Kugelrohr distilled ot 100−110 °C/1 mmHg; R_f 0.25 (1:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (s, 3H), 1.41 (s, 3H), 1.60 (s, 1H), 2.33−1.46 (m, 2H), 3.54 (t, J = 8.0 Hz, 1H), 3.65 (t, J = 6.3 Hz, 2H), 4.07 (t, J = 6.1 Hz, 1H), 4.83 (q, J = 6.2 Hz, 1H), 5.59 (dd, J = 11.2, 8.3 Hz, 1H), 5.67 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.9, 26.7, 31.2, 61.6, 69.4, 71.7, 109.2, 130.0, 131.0.

(2*S*,3*E*)-1,2-Bis-*O*-methylethylidene-6-iodo-3-hexene-1,2-diol (8). Iodine (3.54 g, 13.9 mmol) was added in portions to a mixture of **7** (2.00 g, 11.6 mmol), Ph_3P (3.66 g, 13.9 mmol), and imidazole (1.186 g, 17.44 mmol) in 20 mL of CH_3CN at 0 °C. The reaction mixture was stirred for 4 h at 25 °C. After removal of CH_3CN, ether was added to the residue, and the insoluble Ph_3PO was removed by filtration. Purification of the crude product by silica gel column chromatography gave 2.76 g (84%) of **8**: R_f 0.32 (8:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (s, 3H), 1.41 (s, 3H), 2.56−2.64 (m, 2H), 3.09−3.18 (m, 2H), 3.55−3.59 (m, 1H), 4.6−4.09 (m, 1H), 4.46 (q, J = 7.4 Hz, 0.9H), 4.74−4.80 (m, 0.1H), 5.50−5.57 (m, 1H), 5.68−5.75 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.2, 4.6, 25.8, 25.9, 26.66, 26.71, 31.6, 36.1, 69.3, 69.4, 71.8, 109.3, 129.8, 130.2, 132.5, 133.0.

(2*S*,3*Z*)-1,2-Bis-*O*-methylethylidene-6-iodo-3-hexene-1,2-diol (11). Alcohol **10** (0.432 g, 2.51 mmol) was converted by the method described for **8** to 0.681 g (96%) of iodide **11**: R_f 0.32 (8:1 hexanes/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.37 (s, 3H), 1.40 (s, 3H), 2.64−2.76 (m, 2H), 3.04−3.22 (m, 2H), 3.54 (t, J = 8.0 Hz, 1H), 4.08 (dd, J = 6.1, 8.1 Hz, 1H), 4.73−4.80 (m, 1H), 5.50−5.60 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 4.5, 25.9, 26.7, 31.6, 69.4, 71.8, 109.3, 129.8, 132.5.

(10*S*,8*E*)-10,11-Dihydroxy-2-methyl-8-undecen-4-one (12b). A solution of lithium diisopropylamide [LDA, prepared from diisopropylamine (0.339 g, 3.35 mmol) and *n*-BuLi (2.4 mL, 1.38 M, 3.3 mmol) in 10 mL of THF] was slowly added to a solution of the *N*,*N*-dimethylhydrazone of 4-methylpentan-2-one (0.468 g, 3.30 mmol) in 10 mL of THF at −78 °C. The reaction mixture was warmed to 0 °C and stirred for 20 min. A solution of iodide **8** (0.846 g, 3.00 mmol) in 5 mL of THF was added to the solution of the anion at 0 °C.[35] The resultant reaction mixture was stirred for 5 h at 0−25 °C, concentrated in vacuo, and treated with 10 mL of a 1:1 mixture of aqueous HCl (10%) and methanol for 18 h. The water layer was saturated with K_2CO_3 and extracted with EtOAc. The crude product was purified by silica gel flash column chromatography to provide 0.538 g (84%) of **12b**: R_f 0.3 (1:4 hexanes/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (s, 3H), 0.89 (s, 3H), 1.64 (p, J = 7.3 Hz, 2H), 1.97−2.17 (m, 5H), 2.24−2.27 (overlapping 2 d, J = 6.9 Hz, 2H), 2.36 (t, J = 7.3 Hz, 2H), 3.47 (dd, J = 7.3, 11.0 Hz, 1H, overlapping with m from minor isomer), 3.62 (dd, J = 11.2, 3.7 Hz, 1H), 4.15−4.21 (m, 1H, m for minor isomer is observed near 4.45 ppm), 5.45 (dd, J = 6.6, 15.6 Hz, 1H), 5.68−5.77 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.6, 22.9, 23.4, 24.6, 27.1, 31.6, 42.3, 42.4, 51.75, 51.85, 66.3, 66.5, 68.3, 73.0, 129.0, 129.3, 132.9, 133.3, 211.0.

(5*S*,3*E*)-2-(5,6-Dihydroxy-3-hexenyl)cycloheptan-1-one (12h). The *N*,*N*-dimethylhydrazone of cycloheptanone (0.473 g, 3.07 mmol) was treated with *n*-BuLi (2.23 mL, 1.38 M, 3.08 mmol) at −78 °C for 40 min. The anion solution was reacted with iodide **8** as described for **12b** to yield 0.427 g (62%) of **12h**: R_f 0.25 (1:3 hexanes/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23−1.41 (m, 4H), 1.44−1.63 (m, 1H), 1.70−1.80 (m, 5H), 2.01 (q, J = 7.5 Hz, 2H), 2.17 (s with overlapping m, 2H), 2.37−2.52 (m, 3H), 3.46 (dd, J = 7.3, 11.2 Hz, 1H, overlapping with m from minor isomer), 3.60 (dd, J = 3.7, 11.0 Hz, 1H), 4.14−4.19 (m, 0.8H), 4.47−4.50 (m, 0.2H), 5.38−5.51 (m, 1H), 5.66−5.76 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.4, 28.4, 29.4, 29.9, 31.3, 31.45, 31.47, 42.78, 42.80, 51.4, 66.5, 72.95, 72.98, 129.1, 133.1, 133.2, 216.4.

(5*S*,3*Z*)-2-(5,6-Dihydroxy-3-hexenyl)cyclopentan-1-one (12i). The hydrazone of cyclopentanone (0.658 g, 5.222 mmol) was coupled with iodide **11** (1.473 g, 5.222 mmol), and the crude product was hydrolyzed as described for **12b** to yield 0.54 g (52%) of diol **12i**: R_f 0.24 (1:4 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30−1.59 (m, 2H), 1.72−1.86 (m, 2H), 1.96−2.45 (m, 9H), 3.45−3.59 (m, 2H), 4.51−4.56 (m, 1H), 5.36−5.43 (m, 1H), 5.51−5.59 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6, 25.6, 25.7, 29.5, 29.6, 29.7, 38.14, 38.17, 48.0, 48.4, 66.27, 66.31, 68.3, 68.5, 128.9, 129.0, 133.16, 133.24, 215.7, 216.1.

(5*S*,3*Z*)-2-(5,6-Dihydroxy-3-hexenyl)cyclohexan-1-one (12j). Iodide **11** (0.524 g, 1.858 mmol) and the hydrazone of cyclohexanone (0.26 g, 1.857 mmol) were coupled and

(33) Prepared from 3-iodopropanol and Ph_3P. Maryanoff, B. E.; Reitz, A. B.; Duhl-Emswiler, B. A. *J. Am. Chem. Soc.* **1985**, *107*, 217.

(34) Prepared from the TBDMS ether of 3-iodopropanol and Ph_3P in nitromethane. When ethanol was used as a solvent, desilylation occurred during the reaction.

(35) Corey, E. J.; Enders, D. *Tetrahedron Lett.* **1976**, 3.

hydrolyzed as described for **12b** to provide 0.220 g (56%) of **12j**: R_f 0.22 (4:1 ethyl acetate/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19−1.48 (m, 2H), 1.56−1.89 (m, 4H), 1.94−2.18 (m, 4H), 2.22−2.50 (m, 4H), 2.74−2.84 (br t, 1H), 3.43−3.54 (m, 2H), 4.49 (br s, 1H), 5.33−5.40 (m, 1H), 5.48−5.59 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.5, 24.7, 25.4, 27.89, 27.90, 29.3, 29.4, 33.93, 33.99, 41.8, 41.9, 49.7, 49.9, 66.2, 68.32, 68.34, 128.7, 128.8, 133.0, 133.1, 213.9, 214.1.

(5*S*,3*Z*)-2-(5,6-Dihydroxy-3-hexenyl)cyclooctan-1-one (12k). The hydrazone of cyclooctanone (0.34 g, 2.02 mmol) and iodide **11** were coupled and hydrolyzed as described for **12h** to afford 0.11 g (23%) of **12k**: R_f 0.28 (1:1 hexanes/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.20−2.58 (m, 19H), 3.46−3.58 (m, 2H), 4.18−4.52 (m, 1H), 5.32−5.55 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.6, 25.4, 25.58, 25.63, 25.9, 26.1, 26.8, 27.0, 32.1, 32.2, 32.3, 32.5, 40.9, 41.7, 50.15, 50.20, 66.1, 66.2, 68.0, 68.3, 128.9, 129.2, 132.7, 132.9, 221.0, 221.4.

(10*S*,8*E*)-10-Hydroxy-2-methyl-11-[(4-methylbenzenesulfonyl)oxy]-8-undecen-4-one (13b). Diol **12b** (0.520 g, 2.43 mmol) was treated with TsCl (0.463 g, 2.43 mmol) as described for **5a** to give 0.605 g (68%) of **13b**: R_f 0.29 (2:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (s, 3H), 0.89 (s, 3H), 1.61 (p, J = 7.3 Hz, 2H), 2.00 (q, J = 7.2 Hz, 2H), 2.05−2.15 (m, 2H), 2.24 (d, J = 6.9 Hz, 2H, overlapping with d from minor isomer), 2.34 (t, J = 7.3 Hz, 2H, overlapping with t from minor isomer), 2.44 (s, 3H), 3.86 (dd, J = 7.6, 10.2 Hz, 1H, overlapping with m from minor isomer), 4.01 (dd, J = 3.1, 10.1 Hz, 1H), 4.32 (m, 0.8H), 4.64 (m, 0.2H), 5.34 (dd, J = 3.4, 15.5 Hz, 1H, overlapping with peaks from minor isomer), 5.51−5.58 (m, 0.2H), 5.70−5.77 (m, 0.8H), 7.34 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 22.5, 22.6, 23.1, 24.53, 24.55, 27.1, 31.5, 42.2, 42.3, 51.7, 51.8, 65.7, 70.1, 72.9, 73.2, 127.0, 127.1, 127.9, 129.9, 132.6, 134.3, 134.6, 145.0, 210.7.

(10*S*,8*Z*)-10-Hydroxy-2-methyl-11-[(4-methylbenzenesulfonyl)oxy]-8-undecen-4-one (13d). A solution of iodide **11** (8.20 g, 29.1 mmol) in 15 mL of THF was added to a solution of the anion derived from the *N*,*N*-dimethylhydrazone of 4-methylpentanone (4.54 g, 32.0 mmol) in 30 mL of THF at 0 °C. The reaction mixture was worked up and purified as described in the case of **12b** to provide 5.2 g (84%) of diol **12d**, contaminated with an inseparable impurity, which was removed by careful column chromatography after the tosylation step described below.

Diol **12d** (5.20 g, 24.3 mmol) was treated with TsCl (4.633 g, 24.30 mmol) in 10 mL of pyridine as described for **5a** to give 5.89 g (66%) of **13d**: R_f 0.25 (1:1 hexanes/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (d, J = 6.6 Hz, 6H), 1.56−1.66 (m, 2H), 1.99−2.15 (m, 3H), 2.24−2.26 (m with overlapping d, J = 6.6 Hz, 3H), 2.36 (t, J = 7.3 Hz, 2H), 2.43 (s, 3H), 3.89 (dd, J = 7.6, 10.3 Hz, 1H), 3.96 (dd, J = 3.9, 10.2 Hz, 1H), 4.61−4.67 (m, 1H), 5.26−5.33 (m, 1H), 5.50−5.59 (m, 1H), 7.34 (d, J = 8.5 Hz, 2H), 7.80 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 22.5, 23.1, 24.5, 27.1, 42.2, 51.7, 65.7, 72.9, 127.0, 127.9, 129.9, 132.6, 134.6, 145.0, 210.9.

(5*S*,3*E*)-2-{5-Hydroxy-6-[(4-methylbenzenesulfonyl)oxy]-3-hexenyl}-cycloheptan-1-one (13h). Diol **12h** (0.42 g, 1.86 mmol) was treated with TsCl (0.354 g, 1.86 mmol) as described for **5a** to yield 0.458 g (65%) of **13h**: R_f 0.3 (1:2 hexanes/ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27−1.36 (m, 4H), 1.56−1.59 (m, 1H), 1.70−1.82 (m, 6H), 1.98 (q, J = 7.2 Hz, 2H), 2.44 (s with overlapping m, 6H), 3.86 (dd, J = 7.6, 10.2 Hz, 1H, overlapping with m from minor isomer), 3.99 (dd, J = 4.4, 10.1 Hz, 1H), 4.31 (m, 0.8H), 4.60 (m, 0.2H), 5.33 (dd, J = 6.5, 15.5 Hz, 1H, overlapping with m from minor isomer), 5.69−5.76 (m, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 24.4, 28.5, 29.4, 29.9, 31.26, 31.30, 42.9, 51.3, 70.2, 73.2, 126.8, 128.0, 129.9, 132.7, 134.7, 145.0, 216.0.

(5*S*,3*Z*)-2-{5-Hydroxy-6-[(4-methylbenzenesulfonyl)oxy]-3-hexenyl}-cyclopentan-1-one (13i). Diol **12i** (0.469 g, 2.37 mmol) was treated with TsCl (0.452 g, 2.37 mmol) in pyridine as described for **5a** to give 0.65 g (78%) of **13i**: R_f 0.25 (1:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28−1.37 (m, 1H), 1.45−1.53 (m, 1H), 1.55 (s, 0.5 H), 1.73−1.83 (m, 2H), 1.96−2.30 (m, 7.5H), 2.44 (s, 3H), 3.86−3.97 (m, 2H), 4.68−4.70 (m, 1H), 5.27−5.33 (m, 1H), 5.52−5.59 (m, 1H), 7.34 (d, J = 8.1 Hz, 2H), 7.78 (d, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6, 21.6, 25.7, 25.8, 29.3, 29.4, 29.5, 29.7, 38.08, 38.10, 48.0, 48.3, 65.7, 65.9, 72.9, 73.0, 126.8, 127.0, 127.93, 127.94, 129.9, 132.6, 134.70, 134.72, 145.01, 145.04, 216.3, 216.6.

(5*S*,3*Z*)-2-{5-Hydroxy-6-[(4-methylbenzenesulfonyl)oxy]-3-hexenyl}cyclohexan-1-one (13j). Diol **12j** (0.209 g, 0.986 mmol) was treated with TsCl (0.188 g, 0.986 mmol) in pyridine as described for **5a** to give 0.26 g (71%) of **13j**: R_f 0.2 (1:1.5 hexanes/ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22−1.34 (m, 1H), 1.37−1.40 (m, 1H), 1.54 (s, 1H), 1.62−1.67 (m, 2H), 1.79−1.87 (m, 2H), 2.02−2.05 (m, 4H), 2.20−2.38 (m, 3H), 2.43 (s, 3H), 3.86−3.97 (m, 2H), 4.61−4.68 (m, 1H), 5.25−5.31 (m, 1H), 5.52−5.60 (m, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 24.6, 24.8, 25.5, 25.6, 27.9, 28.0, 29.2, 29.3, 34.0, 41.8, 42.0, 49.6, 49.9, 65.6, 65.7, 72.9, 73.0, 126.6, 126.7, 127.9, 129.9, 132.6, 134.98, 135.08, 144.94, 144.96, 213.3, 213.6.

(5*S*,3*Z*)-2-{5-Hydroxy-6-[(4-methylbenzenesulfonyl)oxy]-3-hexenyl}cyclooctan-1-one (13k). Diol **12k** (0.100 g, 0.417 mmol) was treated with TsCl (0.0795 g, 0.417 mmol) in pyridine as described for **5a** to give 0.110 g (67%) of **13k**: R_f 0.48 (1.5:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21−1.46 (m, 5H), 1.53−2.03 (m, 9.5H), 2.19−2.53 (m with overlapping s at 2.51, 6H), 2.98 (d, J = 3.7 Hz, 0.5 H), 3.86−3.95 (m, 2H), 4.56−4.64 (m, 1H), 5.23−5.34 (m, 1H), 5.44−5.54 (m, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 24.6, 25.3, 25.5, 25.6, 25.7, 25.9, 26.3, 26.7, 27.0, 31.7, 31.8, 32.0, 32.3, 40.7, 41.7, 50.1, 65.1, 65.5, 72.7, 72.8, 126.8, 127.4, 127.8, 129.76, 129.77, 132.51, 132.53, 134.1, 134.4, 144.8, 144.9, 216.8, 217.4.

4-(3-Butenyl)-1-(chloromethyl)-2-cyclopenten-1-ol (14f). *n*-BuLi (1.12 mL, 1.4 M, 1.57 mmol) was added to a solution of 4-(3-butenyl)-2-cyclopentenone[36] (0.164 g, 1.21 mmol) and chloroiodomethane (0.277 g, 1.57 mmol) in 5 mL of THF at −78 °C.[37] The reaction mixture was stirred for 8.5 h at −78 °C and quenched with saturated aqueous NH_4Cl solution. Aqueous workup and purification of the crude product by flash silica gel column chromatography gave 0.145 g (65%) of **14f** as a mixture of diastereomers, contaminated with traces of starting enone: R_f 0.2−0.25 (8:1 hexanes/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.33−1.65 (m, 3H), 2.02−2.20 (m, 2H), 2.31−2.39 (m, 2H), 2.61−2.69 (m, 1H), 3.55 (d, J = 10.8 Hz, 0.8H), 3.60 (d, J = 10.7 Hz, 0.8H), 3.64 (s, 0.4H), 4.91−5.04 (m, 2H), 5.67−5.82 (m, 2H), 5.83−5.97 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.7, 32.0, 34.6, 35.0, 42.4, 42.5, 43.7, 52.5, 53.1, 84.6, 84.8, 114.7, 114.8, 132.0, 132.6, 138.2, 138.3, 139.5, 140.6.

4-(3-Butenyl)-1-(chloromethyl)-2-cyclohexen-1-ol (14g). *n*-BuLi (3.59 mL, 1.38 M, 4.95 mmol) was added to a solution of 4-(3-butenyl)-2-cyclohexenone[38] (0.576 g, 3.84 mmol) and chloroiodomethane (0.874 g, 4.95 mmol) in 10 mL of THF at −78 °C. According to the procedure described for **14f**, 0.66 g (86%) of **14g** was obtained as a mixture of diastereomers: R_f 0.27 (3:1 hexanes/ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20−1.92 (m, 6H), 1.99−2.20 (m, 4H), 3.52−3.59 (m, 2H), 4.93−5.03 (m, 2H), 5.56−5.84 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.8, 25.6, 31.0, 31.1, 31.9, 32.9, 34.3, 34.5, 34.7, 35.3, 53.1, 54.3, 69.1, 70.0, 114.7, 114.8, 127.7, 128.5, 136.5, 137.5, 138.3, 138.4.

4-(3-Oxobutyl)-1-(chloromethyl)-2-cyclopenten-1-ol (15f). Chlorohydrin **14f** (0.1444 g, 0.776 mmol) was oxidized as described for **6a** to yield 0.104 g (66%) of **15f** (10% of impure product was also obtained): R_f 0.24 (1:2 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.49−1.60 (m, 1H), 1.62−1.82 (m, 2H), 2.13 (s, 3H), 2.32 (dd, J = 7.9, 13.8 Hz, 1H), 2.43−2.47 (m, 3H), 2.62−2.69 (m plus a m for the minor diastereomer at 2.9 ppm, 1H), 3.57 (d, J = 10.9 Hz, 0.45H), 3.59 (d, J = 11.3 Hz, 0.45H), 3.63 (s, 0.1H), 5.70 (dd, J = 2.2, 5.6 Hz, 0.9H), 5.74 (dd, J = 2.4, 5.6 Hz, 0.1H), 5.86 (dd, J = 2.0, 5.7

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(38) Schinzer, D.; Solyom, S.; Becker, M. *Tetrahedron Lett.* **1985**, *26*, 1831.

Hz, 0.9H), 5.92 (dd, J = 2.0, 5.6 Hz, 0.1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.0, 29.2, 29.9, 41.2, 41.6, 42.0, 42.2, 43.5, 43.6, 52.4, 52.9, 84.5, 84.8, 132.6, 133.2, 138.7, 139.8, 208.5, 208.7.

4-(3-Oxobutyl)-1-(chloromethyl)-2-cyclohexen-1-ol (15g). Chlorohydrin **14g** (0.64 g, 3.19 mmol) was oxidized as described for **6a** to give 0.474 g (69%) of **15g**: R_f 0.3 (2:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19−1.28 (m, 1H), 1.42−1.74 (m, 4H), 1.83−1.91 (m, 1H), 1.98−2.04 (m, 1H), 2.14 (s, 3H), 2.22 (s, 1H), 2.44−2.50 (m, 2H), 3.51−3.58 (m, 2H), 5.61−5.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.5, 25.5, 28.6, 28.9, 30.0, 31.7, 32.8, 34.6, 35.2, 40.7, 40.9, 53.0, 54.2, 68.9, 69.8, 128.3, 129.1, 135.6, 136.7, 208.5, 208.6.

General Method of Epoxide Preparation. Base-washed glassware was used as a precaution in all cases. The use of silica gel chromatography and deuteriochloroform as an NMR solvent was avoided.

(8*S*,6*E*)-8,9-Epoxy-6-nonen-2-one (1a). The tosylate **6a** (0.310 g, 0.951 mmol) in 5 mL of THF was added to a solution of KO*t*-Bu[39] (0.1065 g, 0.951 mmol) in 5 mL of THF at −78 °C. After being stirred for 0.25−0.5 h, the reaction mixture was diluted with 40 mL of pentane, filtered, and concentrated. The crude epoxide was again dissolved in pentane, and the insoluble material was filtered to provide 0.142 g (97%) of **1a**: ^{1}H NMR of crude product (400 MHz, C_6D_6) δ 1.43−1.48 (m, 2H), 1.59 (s, 3H), 1.73−1.82 (m, 6H), 2.24 (dd, J = 2.5, 5.4 Hz, 1H), 2.49 (dd, J = 4.0, 5.4 Hz, 1H), 2.98−3.02 (m, 1H), 4.96−5.02 (m, 1H), 5.52−5.60 (m, 1H).

(10*S*,8*E*)-10,11-Epoxy-2-methyl-8-undecen-4-one (1b). The tosylate **13b** (0.188 g, 0.511 mmol) was converted, by the method described for **1a**, to 0.074 g (74%) of **1b**: ^{1}H NMR (300 MHz, C_6D_6) δ 0.79 (s, 3H), 0.81 (s, 3H), 1.46−1.57 (m, 2H), 1.78−2.05 (m, 6H), 2.05−2.14 (m, 1H), 2.24 (dd, J = 2.7, 5.6 Hz, 1H), 2.48−2.52 (m, 1H), 2.99−3.04 (m, 0.8H), 3.36−3.40 (m, 0.2H), 4.98−5.07 (m, 1H), 5.55−5.64 (m, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 22.6, 23.0, 23.5, 24.5, 27.1, 31.9, 41.9, 42.1, 47.6, 48.0, 48.1, 51.6, 51.9, 129.0, 129.4, 135.3, 135.4, 208.1.

(8*S*,6*Z*)-8,9-Epoxy-6-nonen-2-one (1c). The precursor tosylate **6c** (0.452 g, 1.39 mmol) was converted, by the method described for **1a**, to 0.175 g (82%) of **1c**: ^{1}H NMR (300 MHz, C_6D_6) δ 1.37−1.59 (m, 2H), 1.62 (s, 3H), 1.82−1.97 (m, 4H), 2.23 (dd, J = 2.7, 5.6 Hz, 1H), 2.51 (dd, J = 4.1, 5.4 Hz, 1H), 3.29−3.34 (m, 1H), 4.94−5.00 (m, 1H), 5.34−5.41 (m, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 23.5, 26.9, 29.4, 42.0, 47.5, 48.0, 129.0, 135.4, 205.9.

(10*S*,8*Z*)-10,11-Epoxy-2-methyl-8-undecen-4-one (1d). Tosylate **13d** (0.50 g, 1.36 mmol) was converted, by the method described for **1a**, to 0.260 g (98%) of **1d**: ^{1}H NMR (400 MHz, C_6D_6) δ 0.80−0.83 (overlapping d, J = 6.7 Hz, 6H), 1.46−1.59 (m, 2H), 1.87 (d, J = 7.5 Hz, 2H), 1.92−2.02 (m with overlapping t, J = 7.3 Hz, 4H), 2.09−2.15 (m, 1H), 2.25 (dd, J = 2.5, 5.5 Hz, 1H), 2.52 (dd, J = 4.0, 5.4 Hz, 1H), 3.34−3.37 (m, 1H), 4.99 (dd, J = 9.2, 10.9 Hz, 1H), 5.44 (dt, J = 7.6, 11.0 Hz, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 23.0, 23.9, 24.8, 27.4, 42.3, 48.0, 48.4, 52.0, 129.4, 135.8, 208.6.

(9*S*,7*Z*)-9,10-Epoxy-7-decen-2-one (1e). The tosylate **6e** (0.114 g, 0.335 mmol) was treated with KO*t*-Bu (0.0376 g, 0.335 mmol) in THF as described for **1a** to yield 0.056 g (99%) of **1e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35−1.44 (m, 2H), 1.53−1.64 (m, 2H), 2.12 (s, 3H), 2.15−2.39 (m, 2H), 2.43 (t, J = 7.4 Hz, 2H), 2.63 (dd, J = 2.7, 5.3 Hz, 1H), 2.96 (dd, J = 4.2, 5.0 Hz, 1H), 3.55−3.59 (m, 1H), 5.00 (dd, J = 9.2, 10.5 Hz, 1H), 5.66−5.70 (m, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 23.3, 27.5, 29.13, 29.22, 42.9, 47.6, 47.9, 128.5, 135.8, 206.1.

6-(3-Oxobutyl)-1-oxaspiro[2.4]-4-heptene (1f). Compound **15f** (0.093 g, 0.46 mmol) was treated with KO*t*-Bu (0.051 g, 0.46 mmol) in THF as described for **1a** to provide 0.047 g (62%) of **1f**: ^{1}H NMR (400 MHz, C_6D_6) δ 1.41 (dd, J = 4.2, 14.3 Hz, 1H), 1.48−1.65 (m with overlapping s at 1.62 ppm, 5H), 1.88−2.62 (m, 3H), 2.46 (s, 1H), 2.60−2.65 (m, 2H), 5.28 (dd, J = 1.9, 5.6 Hz, 1H), 5.68 (dd, J = 1.3, 5.7 Hz, 1H); ^{13}C NMR (75 MHz, C_6D_6) δ 29.5, 29.7, 30.1, 35.2, 35.9, 40.6, 41.4, 43.3, 43.6, 52.8, 53.2, 68.0, 68.3, 132.0, 132.2, 141.7, 142.4, 206.6.

(39) Use of KO*t*-Bu in the preparation of vinyl epoxides: Tanis, S. P.; McMills, M. C.; Herrinton, P. M. *J. Org. Chem.* **1985**, *50*, 5887.

6-(3-Oxobutyl)-1-oxaspiro[2.5]-4-octene (1g). Compound **15g** (0.1082 g, 0.5 mmol) was treated with KO*t*-Bu (0.056 g, 0.5 mmol) as described for **1a** to yield 0.073 g (81%) of **1g**: ^{1}H NMR (400 MHz, C_6D_6) δ 1.10−1.18 (m, 1H), 1.28−1.48 (m, 4H), 1.51−1.76 (m with overlapping s at 1.61 and 1.62 ppm, 4H), 1.83−1.89 (m, 3H), 2.44 and 2.46 (s, 2H), 5.17−5.22 (m, 1H), 5.64 (dd, J = 3.0, 10.1 Hz, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 27.0, 27.8, 28.99, 29.03, 29.3, 29.5, 30.3, 34.5, 34.8, 40.2, 40.6, 54.3, 54.4, 55.0, 55.7, 128.8, 129.8, 137.9, 139.0, 205.7.

(5*S*,3*E*)-2-(5,6-Epoxy-3-hexenyl)cycloheptan-1-one (1h). Tosylate **13h** (0.273 g, 0.718 mmol) was treated with KO*t*-Bu (0.0804 g, 0.718 mmol) in THF as described for **1a** to provide 0.122 g (82%) of **1h**: ^{1}H NMR (400 MHz, C_6D_6) δ 0.93−1.12 (m, 3H), 1.15−1.30 (m, 2H), 1.38−1.59 (m, 4H), 1.74−1.92 (m, 3H), 1.96−2.27 (m, 4H), 2.48−2.54 (m, 1H), 3.00−3.04 (m, 0.8H), 3.38−3.42 (m, 0.2H), 4.96−5.08 (m, 1H), 5.45−5.70 (m, 1H), with m from minor isomer; ^{13}C NMR (100 MHz, C_6D_6) δ 24.8, 29.1, 29.9, 30.7, 31.9, 32.0, 43.2, 43.3, 48.5, 51.5, 51.6, 52.3, 129.5, 129.6, 135.9, 136.0, 213.5.

(5*S*,3*E*)-2-(5,6-Epoxy-3-hexenyl)cyclopentan-1-one (1i). Tosylate **13i** (0.242 g, 0.69 mmol) was treated with KO*t*-Bu (0.077 g, 0.69 mmol) in THF as described for **1a** to give 0.100 g (81%) of **1i**: ^{1}H NMR (300 MHz, C_6D_6) δ 0.86−0.96 (m, 1H), 1.07−1.19 (m, 2H), 1.34−1.44 (m, 1H), 1.56−2.15 (m, 7H), 2.15−2.27 (m, 1H), 2.51−2.55 (m, 1H), 3.37−3.46 (m, 1H), 5.00 (t, J = 10.0 Hz, 1H), 5.46 (m, 1H); ^{13}C NMR (75 MHz, C_6D_6) δ 20.61, 20.63, 25.5, 25.8, 29.4, 29.6, 29.8, 29.9, 37.69, 37.71, 47.53, 47.58, 47.85, 47.92, 47.94, 47.96, 128.87, 128.9, 135.55, 135.57, 218.4.

(5*S*,3*E*)-2-(5,6-Epoxy-3-hexenyl)cyclohexan-1-one (1j). Tosylate **13j** (0.460 g, 1.26 mmol) was treated with KO*t*-Bu (0.140 g, 1.26 mmol) as described for **1a** to provide 0.222 g (91%) of **1j**: ^{1}H NMR (400 MHz, C_6D_6) δ 0.95−1.38 (m, 5H), 1.50−1.66 (m, 2H), 1.78−2.28 (m, 7H), 2.54 (dd, J = 5.2, 9.4 Hz, 1H), 3.45−3.48 (m, 1H), 4.99−5.04 (m, 1H), 5.50−5.57 (m, 1H); ^{13}C NMR (75 MHz, C_6D_6) δ 25.4, 25.5, 25.7, 26.1, 28.2, 28.4, 30.1, 30.3, 34.2, 34.8, 42.3, 42.5, 48.0, 48.3, 48.4, 49.86, 49.91, 129.1, 129.2, 136.3, 136.4, 210.8, 211.0.

(5*S*,3*E*)-2-(5,6-Epoxy-3-hexenyl)cyclooctan-1-one (1k). Tosylate **13k** (0.100 g, 0.254 mmol) was treated with KO*t*-Bu (0.0284 g, 0.254 mmol) in THF as described for **1a** to provide 0.046 g (82%) of **1k**: ^{1}H NMR (400 MHz, C_6D_6) δ 1.12−1.54 (m, 10H), 1.68−2.39 (m, 8H), 2.51−2.55 (m, 1H), 3.34−3.39 (m, 1H), 4.95−5.00 (m, 1H), 5.43−5.50 (m, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 25.3, 26.17, 26.22, 26.9, 28.0, 28.2, 32.8, 33.0, 33.3, 34.0, 34.1, 42.5, 43.2, 47.9, 48.0, 48.4, 49.7, 50.0, 129.13, 129.15, 135.9, 136.1, 217.5, 217.7.

General Method of Annulation. [1*R,2*S**,(1*E*)]-2-(3-Hydroxy-1-propenyl)-1-methylcyclopentan-1-ol (2a).** A solution of epoxide **1a** (0.140 g, 0.909 mmol) in 40 mL of THF was added dropwise to a solution of freshly prepared SmI_2 [obtained from Sm (0.375 g, 2.50 mmol) and CH_2I_2 (0.535 g, 1.999 mmol)] in 20 mL of THF and HMPA (2.812 g, 17.26 mmol) over 1 h by a syringe pump. After being stirred for an additional 15−30 min at rt, the reaction mixture was quenched with 5 mL of saturated K_2CO_3. The resulting slurry was extracted repeatedly with EtOAc. The organic phase was decanted from the flask to another receiver, and the combined organic extracts were dried with anhydrous $MgSO_4$ and concentrated. Purification of the crude product by flash silica gel column chromatography gave 0.081 g (57%) of **2a**: Kugelrohr distilled ot 100−120 °C/1.0 mmHg; R_f 0.2 (1:8 hexanes/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.13 (s, 3H), 1.40−1.89 (m, 8H), 1.92−2.02 (m, 1H), 2.36−2.45 (m, 1H), 4.10 (d, J = 6.6 Hz, 2H), 5.57 (dd, J = 7.3, 15.4 Hz, 1H), 5.68 (dt, J = 5.4, 15.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.4, 23.4, 29.3, 40.2, 53.8, 63.4, 80.9, 130.5, 132.8; IR (neat) 3356 cm^{-1}; HRMS calcd for $C_9H_{14}O$ $(M - H_2O)^+$ 138.1045, found 138.1058; LRMS (EI) m/z 156 (0.1), 138 (33), 123 (11), 95 (35), 80 (100); CI^+ using NH_3 gave M^+ ion peak at 156; $[\alpha]^{20}_D$ −41.9° (c = 0.7, $CHCl_3$).

[1*R,2*R**,(2*E*)]-2-{3-[(*tert*-Butyldimethylsilyl)oxy]-1-propenyl}-1-(2-methyl)propylcyclopentan-1-ol (2b).** The epoxide **1b** (0.090 g, 0.459 mmol) was treated with a solution of SmI_2−HMPA in THF as described for **2a** to give 0.050 g (55%) of impure annulated product. ^{1}H NMR of the crude

product indicated the presence of 10% of the open-chain diol and a 3:1 mixture of diastereomeric cyclic diols (3:1 determined by GLC and isolation). To facilitate separation, this impure fraction (0.050 g, ~0.252 mmol) was treated with TBDMSCl (0.047 g, 0.303 mmol) and imidazole (0.0258 g, 0.379 mmol) in 2 mL of CH_2Cl_2. Aqueous workup, followed by purification of the crude product by silica gel flash column chromatography, provided 0.017 g (22%) of the impure minor diastereomer and 0.044 g (56%) of **2b**: Kugelrohr distilled ot 135−140 °C/l mmHg; R_f 0.19 (12:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 6H), 0.89 (s, 9H), 0.94 (apparent t due to overlapping d, J = 6.4 Hz, 6H), 1.25 (s, 1H), 1.32 (d, J = 6.0 Hz, 2H), 1.40−1.49 (m, 1H), 1.60−1.86 (m, 5H), 1.97−2.06 (m, 1H), 2.37−2.42 (m, 1H), 4.12 (d, J = 4.1 Hz, 2H), 5.43−5.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −5.1, 18.4, 21.1, 24.5, 24.7, 24.8, 25.9, 29.6, 37.1, 45.4, 55.1, 63.8, 84.3, 130.0, 131.3; IR (neat) 3451 cm^{-1}; HRMS calcd for $C_{18}H_{35}O_2Si$ (M − H)$^+$ 311.2406, found 311.2404; LRMS (EI) *m/z* 311 (9), 295 (37), 255 (10), 180 (99), 163 (65).

[1*S,2*R**,(1*E*)]-2-(3-Hydroxy-1-propenyl)-1-methylcyclopentan-1-ol (2c).** Epoxide **1c** (0.015 g, 0.0974 mmol) was added over a period of 0.5 h to a solution of SmI_2−HMPA in THF as described for **2a**. Purification of the crude product by flash silica gel column chromatography gave 0.011 g (72%) of **2c**: Kugelrohr distilled ot 100−120 °C/1.0 mmHg; R_f 0.25 (ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.13 (s, 3H), 1.45−1.49 (m, 1H), 1.51−1.78, (m, 6H), 1.92−1.96 (m, 1H), 2.36−2.44 (m, 1H), 4.10 (d, J = 5.3 Hz, 2H), 5.57 (dd, J = 8.3, 15.4 Hz, 1H), 5.68 (dt, J = 4.4, 15.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.6, 23.7, 29.5, 40.3, 53.9, 63.6, 81.0, 130.4, 132.8; IR (neat) 3300 cm^{-1}; HRMS calcd for $C_9H_{14}O$ (M − H_2O)$^+$ 138.1045, found 138.1062; LRMS (EI) *m/z* 138 (15), 95 (24), 80 (100), 67 (24), 55 (18); CI$^+$ using NH_3 gave M$^+$ ion peak at 156; $[\alpha]^{20}_D$ +21.4° (*c* = 0.7, $CHCl_3$).

(1*E*)-2-(3-Hydroxy-1-propenyl)-1-(2-methylpropyl)cyclopentan-1-ol (2d). A solution of epoxide **1d** (0.084 g, 0.429 mmol) in 20 mL of THF was added to a mixture of SmI_2 solution in THF (9.43 mL, 0.1 M, 0.943 mmol) and tetramethylguanidine (TMG, 0.956 g, 8.30 mmol) at rt over 2.3 h by a syringe pump. A standard workup after stirring the reaction mixture for 15 min and purification of the product by silica gel flash column chromatography afforded 0.06 g (71%) of a 1:1 mixture of diastereomers of **2d**: R_f 0.35 (1:1 hexanes/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.85−0.97 (m, 6H), 1.08 (s, 0.5H), 1.22−1.87 (m, 10H), 1.96−2.06 (m, 0.5H), 2.14−2.21 (m, 0.5H), 2.41 (q, J = 7.8 Hz, 0.5H), 4.09−4.13 (m, 2H), 5.51 (dd, J = 8.5, 15.1 Hz, 0.5H), 5.63 (dt, J = 15.4, 5.6 Hz, 0.5H), 5.69−5.76 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.8, 21.4, 24.4, 24.55, 24.61, 24.8, 29.0, 29.4, 36.8, 38.1, 44.8, 48.3, 52.9, 55.1, 63.3, 63.4, 83.2, 84.1, 129.9, 131.3, 131.5, 133.0; IR (CH_2Cl_2) 3354 cm^{-1}; HRMS calcd for $C_{12}H_{20}O$ (M − H_2O)$^+$ 180.1514, found 180.1518; LRMS (EI) *m/z* 197 (2), 180 (62), 165 (46), 137 (48), 123 (62).[40]

[1*S,2*R**,(1*E*)]-2-(3-Hydroxy-1-propenyl)-1-methylcyclohexan-1-ol (2e).** The epoxide **1e** (0.071 g, 0.423 mmol) was treated with a solution of SmI_2−HMPA in THF as described for **2a** to afford 0.012 g (17%) of **2e**: R_f 0.14 (1:4 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (s, 3H), 1.19−1.42 (m, 5H), 1.65−1.78 (m, 5H), 2.03−2.06 (br m, 1H), 4.11 (d, J = 4.3 Hz, 2H), 5.63−5.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.9, 23.7, 25.1, 29.6, 40.5, 51.4, 63.6, 72.3, 131.1, 132.8; IR (neat) 3358 cm^{-1}; HRMS calcd for $C_{10}H_{16}O$ (M − H_2O)$^+$ 152.1201, found 152.1199; LRMS (EI) *m/z* 169 (0.2), 152 (5), 109 (25), 94 (15), 79 (57); CI$^+$ using NH_3 gave M$^+$ ion peak at 170.

(1*R,5*S**,8*S**)-3-(Hydroxymethyl)-8-methylbicyclo[3.3.0]-2-octen-8-ol (2f).** A solution of epoxide **1f** (0.047 g, 0.283 mmol) in 15 mL of THF was added dropwise to a solution of SmI_2−HMPA in THF over 3 h. The reaction mixture was worked up and purified as described for **2a** to yield 0.034 g (72%) of **2f**: mp 125−126 °C; R_f 0.34 (1:1.5 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (s, 3H), 1.30−1.37 (m, 1H), 1.44−1.51 (m, 3H), 1.88 (s, 1H), 1.98−2.15 (m, 2H), 2.63 (dd, J = 8.9, 16.7 Hz, 1H), 2.91−2.95 (m, 2H), 4.10 (s, 2H), 5.38 (d, J = 1.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.1, 32.6, 39.0, 39.6, 41.6, 62.0, 63.4, 81.7, 124.8, 145.8; IR ($CDCl_3$) 3316 cm^{-1}; HRMS calcd for $C_{10}H_{14}O$ (M − H_2O)$^+$ 150.1045, found 150.1017; LRMS (EI) *m/z* 150 (20), 135 (6), 119 (6), 107 (14), 92 (100); CI$^+$ using NH_3 gave M$^+$ ion peak at 168.

(1*R,6*S**,9*S**)-3-(Hydroxymethyl)-9-methylbicyclo[4.3.0]-2-nonen-9-ol (2g).** The epoxide **1g** (0.070 g, 0.389 mmol) in 20 mL of THF was added to a solution of SmI_2−HMPA in THF over 3 h. Usual workup and purification of the crude product by flash silica gel column chromatography provided 0.055 g (78%) of **2g**: Kugelrohr distilled ot 150−160 °C/1 mmHg; R_f 0.3 (1:4 hexanes/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25 (s, 3H), 1.31−1.55 (m, 4H), 1.58−1.71 (m, 3H), 1.87−2.03 (m, 3H), 2.31−2.33 (m, 1H), 2.47−2.59 (m, 1H), 4.01 (s, 2H), 5.63 (t, J = 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.6, 25.4, 26.0, 27.3, 34.8, 39.8, 50.4, 67.4, 81.9, 121.9, 139.3; IR (neat) 3345 cm^{-1}; LRMS (EI) *m/z* 164 (5), 122 (8), 106 (100), 91 (22); CI$^+$ using NH_3 gave a peak at 182 (M$^+$). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.40; H, 9.98.

[1*S,7*R**,10*R**,(1*E*)]-10-(3-Hydroxy-1-propenyl)bicyclo[5.3.0]decan-1-ol (2h).** A solution of epoxide **1h** (0.120 g, 0.577 mmol) in 25 mL of THF was added to a solution of SmI_2−HMPA in THF over 3 h by a syringe pump as described for **2a**. Usual workup and purification of the crude product by flash silica gel column chromatography provided 0.075 g (62%) of **2h** [8 mg (~7%) of a minor diastereomer was obtained as an impure fraction and was not characterized; these isolated amounts are in agreement with a 1:10 diastereomeric ratio determined by GC]: Kugelrohr distilled ot 160 °C/1 mmHg; R_f 0.2 (1:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22−1.65 (m, 12H), 1.77−1.81 (m, 2H), 1.93−2.09 (m, 3H), 2.41 (m, 1H), 4.12 (d, J = 13.3 Hz, 2H), 5.48−5.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.9, 29.0, 30.0, 30.8, 32.0, 33.9, 36.1, 52.4, 57.8, 63.6, 85.8, 129.9, 132.7; IR ($CDCl_3$) 3346 cm^{-1}; LRMS (EI) *m/z* 210 (0.1), 192 (25), 161 (4), 149 (6), 112 (100); CI$^+$ using NH_3 gave a peak at 210 (M$^+$). Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.66; H, 10.98.

[1*R,2*S**,5*S**,(1*E*)]-2-(3-Hydroxy-1-propenyl)bicyclo[3.3.0]octan-1-ol (2i).** A solution of epoxide **1i** (0.099 g, 0.55 mmol) in 30 mL of THF was added to a solution of SmI_2−HMPA in THF over 5 h as described for **2a**. The usual workup and purification of the crude product by silica gel flash column chromatography afforded 0.078 g (78%) of **2i**: mp 95−96 °C; R_f 0.21 (1:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03−1.12 (m, 1H), 1.23−1.76 (m, 9H), 1.83−1.94 (m, 1H), 2.06−2.21 (m, 2H), 2.43−2.49 (m, 1H), 4.11 (s, 2H), 5.67−5.77 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.8, 30.0, 30.1, 34.8, 37.3, 50.8, 54.1, 63.5, 92.8, 130.3, 132.2; IR ($CDCl_3$) 3385 cm^{-1}; HRMS calcd for $C_{11}H_{16}O$ (M − H_2O)$^+$ 164.1204, found 164.1224; LRMS (EI) *m/z* 164 (12), 97 (19), 84 (100), 67 (15), 55 (18); CI$^+$ using NH_3 gave a peak at 182 (M$^+$).[40]

[1*R,6*S**,9*S**,(1*E*)]-9-(3-Hydroxy-1-propenyl)bicyclo[4.3.0]nonan-1-ol (2j).** A solution of epoxide **1j** (0.220 g, 1.13 mmol) in 57 mL of THF was added to a solution of SmI_2−HMPA in THF over 5 h as described for **2a**. Usual workup and purification of the crude product provided 0.170 g (76%) of **2j**: mp 110−111 °C; R_f 0.24 (1:1.5 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29−1.37 (m, 4H), 1.40−1.52 (m, 6H), 1.50−1.70 (m, 3H), 1.81−1.97 (m, 2H), 2.42 (q, J = 9.3 Hz, 1H), 4.10 (t, J = 5.4 Hz, 2H), 5.62 (dd, J = 7.0, 15.4 Hz, 1H), 5.68 (dt, J = 15.4, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.2, 20.9, 23.5, 24.0, 26.0, 28.9, 44.0, 54.6, 63.6, 79.2, 130.9, 132.3; IR ($CDCl_3$) 3378 cm^{-1}; LRMS (EI) *m/z* 178 (14), 98 (100), 83 (19), 70 (22), 55 (17); CI$^+$ using NH_3 gave a peak at 196 (M$^+$). Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.15; H, 10.42.

[1*R,8*S**,11*S**,(1*E*)]-11-{3-[(*tert*-Butyldimethylsilyl)oxy]-1-propenyl}bicyclo[6.3.0]undecan-1-ol (2k).** A solution of epoxide **1k** (0.040 g, 0.180 mmol) in 10 mL of THF was added dropwise to a solution of SmI_2−HMPA over 1 h as described for **2a**. Usual workup and purification of the crude product by silica gel flash column chromatography gave 0.037 g of

(40) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

impure product, which was silylated as described for **2b**. TLC showed the presence of six spots, four of which after silica gel flash column chromatography appeared to have the features of the desired product on the basis of the ^{1}H NMR spectra of partially separated fractions. These four fractions when combined gave 0.050 g (83% overall yield) of **2k**. GLC analysis of **2k** gave only three peaks (1.5:1.2:1): R_f 0.2−0.35 (25:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 6H), 0.88 (s, 9H), 1.22−2.03 (m, 17.5H), 2.12−2.41 (m, 1.5H), 4.07−4.20 (m, 2H), 5.32−5.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −5.12, −5.08, 18.4, 21.2, 21.6, 23.6, 23.7, 25.55, 25.65, 25.74, 25.94, 26.5, 26.88, 26.91, 27.4, 27.8, 28.0, 28.9, 29.2, 30.37, 30.45, 31.2, 32.0, 33.3, 34.4, 34.5, 34.6, 36.7, 43.2, 49.8, 50.1, 52.6, 57.9, 58.2, 63.76, 63.80, 64.1, 81.5, 82.3, 83.8, 84.8, 129.1, 129.7, 130.1, 130.2, 131.6, 132.2, 132.6, 132.8; IR (neat) 3454 cm^{-1}; HRMS calcd for $C_{20}H_{37}O_2Si$ $(M - 1)^+$ 337.2563, found 337.2563; LRMS (EI) *m*/*z* 337 (0.1), 320 (0.8), 281 (4), 263 (4), 206 (35).

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Supporting Information Available: Copies of ^{1}H and ^{13}C NMR spectra of compounds synthesized (107 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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