Formation of *trans* Ring-Fused Compounds by an Alkylation–Radical Cyclization Sequence

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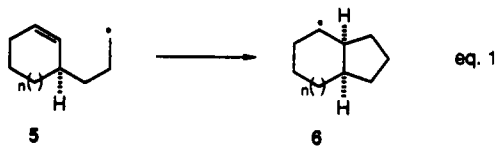
Enolates derived from bicyclic lactones of type 1 (Scheme I) can be alkylated with 2-propynylic halides to give products 2, in which the unsaturated alkyl group is *syn* to the adjacent ring-fusion hydrogen. Reaction of 2 with sodium phenyl selenide and then with diazomethane produces esters 3, and these give *trans* ring-fused bicyclic compounds 4 when treated with triphenyltin hydride in the presence of a radical initiator. The bicyclic compounds afford ketones on double-bond cleavage, and the angular ester function can be converted into a methyl group. Similar processes occur if an aldehyde is used in the first step instead of a halide. The methodology is general.

The formation of *trans* ring-fused bicyclic compounds is a problem that has been approached by a number of methods.[1,2] We report full details of a procedure based on radical cyclization[3] (Scheme I).

The principle behind our method rests on the observation that radical cyclizations of the type 5 → 6 (eq 1)



eq. 1

give exclusively or predominantly *cis* ring-fused products.[4] Therefore, in order to use radical closure to generate *trans* ring-fused compounds, the last bond to be formed must not be a bond to a ring-fusion atom. Accordingly, it is necessary to attach to an existing ring two pendants—one carrying a radical trap, such as a multiple bond, and the other a source of carbon radicals. This requirement can be met by alkylation of lactones of type 1 (see Scheme I). Such alkylations proceed so as to place the alkyl group *syn* to the adjacent ring-fusion position.[5] The stereochemical course of alkylation of endocyclic enolates has been examined in some detail,[6] and, in the present case, the result is probably due to an inherent pyramidalization of the carbon being attacked and to some steric impediment to approach from one face of the enolate.

After lactone opening with phenyl selenide anion and esterification (2 → 3), the radical source (the CH_2–SePh bond) and the radical trap (the triple bond) are *trans*; consequently, radical cyclization gives *trans* ring-fused products 4.

Preparation of the Starting Lactones. Lactones of type 1 are available by a number of methods, but generally, we used partial reduction ($NaBH_4$ or $LiAlH_4$) of anhydrides[7] as summarized in Table I. The anhydrides fused to 5-,7-, and 8-membered rings were made by dehydration[8] (acetic anhydride) of the corresponding diacids, and these, in turn, were generated by Favorskii rearrangement of β-keto esters,[9] as shown in Table I. Anhydrides fused to 6-membered rings were, of course, readily accessible[10] by Diels–Alder reaction.

Another general route is by cyclization of acyl radicals,[11] and we used this method in one case (Scheme II).

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(1) For review, see: Kocovsky, P.; Turecek, F.; Hájíček, J. *Synthesis of Natural Products: Problems of Stereoselectivity*; CRC Press: Boca Raton, FL, 1986; Vol. I.

(2) For methods based on catalytic hydrogenation, see: (a) Hajos, Z. G.; Parrish, D. R. *J. Org. Chem.* **1973**, *38*, 3239. (b) Micheli, R. A.; Hajos, Z. G.; Cohen, N.; Parrish, D. R.; Portland, L. A.; Sciamanna, W.; Scott, M. A.; Wehrli, P. A. *J. Org. Chem.* **1975**, *40*, 675. (c) Banerjee, D. K.; Kasturi, T. R.; Govindan, G. *Indian J. Chem., Sect. B.* **1976**, *14B*, 312. For methods based on conjugate reduction, see: (d) Fraisse-Jullien, R.; Frejaville, C.; Toure, V. *Bull. Soc. Chim. Fr.* **1966**, 3725. (e) Caine, D. *Org. React.* **1976**, *23*, 33. (f) Tsuda, T.; Kawamoto, T.; Kumamoto, Y.; Saegusa, T. *Synth. Commun.* **1986**, *16*, 639. For methods based on allylic alcohols, see: (g) Stork, G.; Kahn, M. *J. Am. Chem. Soc.* **1985**, *107*, 500. (h) Stork, G.; Sofia, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 6826. (i) Mandai, T.; Matsumoto, T.; Kawada, M.; Tsuji, J. *J. Org. Chem.* **1992**, *57*, 1326. (j) Corey, E. J.; Engler, T. A. *Tetrahedron Lett.* **1984**, *25*, 149. For Diels–Alder approaches, see, *e.g.*: (k) Jung, M. E.; Halweg, K. M. *Tetrahedron Lett.* **1981**, *22*, 3929. (l) Bal, S. A.; Helquist, P. *Tetrahedron Lett.* **1981**, *22*, 3933. (m) Roush, W. R.; Gillis, H. R.; Ko, A. I. *J. Am. Chem. Soc.* **1982**, *104*, 2269. (n) Boeckman, R. K., Jr.; Ko, S. S. *J. Am. Chem. Soc.* **1982**, *104*, 1033. (o) Wilson, S. R.; Haque, M. S. *J. Org. Chem.* **1982**, *47*, 5411. (p) Jung, M. E.; Halweg, K. M. *Tetrahedron Lett.* **1984**, *25*, 2121. (q) Wilson, S. R.; Haque, M. S. *Tetrahedron Lett.* **1984**, *25*, 3147. (r) Fallis, A. G. *Can. J. Chem.* **1984**, *62*, 183. (s) Hudlicky, T.; Radesca-Kwart, L.; Li, L.; Bryant, T. *Tetrahedron Lett.* **1988**, *29*, 3283. (t) Furuta, K.; Kanematsu, A.; Yamamoto, H. *Tetrahedron Lett.* **1989**, *30*, 7231. (u) Kametani, T.; Matsumoto, H.; Honda, T.; Fukumoto, K. *Tetrahedron Lett.* **1980**, *21*, 4847. (v) Attah-Poku, S. K.; Yadav, F. C. V. K.; Fallis, A. G. *J. Org. Chem.* **1985**, *50*, 3418. (w) Nemoto, H.; Nagai, M.; Fukumoto, K.; Kametani, T. *Tetrahedron* **1985**, *41*, 2361. (x) Stork, G.; Stotter, P. L. *J. Am. Chem. Soc.* **1969**, *91*, 7780. For methods based on conjugate addition, see: (y) Denmark, S. E.; Germanas, J. P. *Tetrahedron Lett.* **1984**, *25*, 1231. (z) Horiguchi, Y.; Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1989**, *111*, 6257. (aa) Doi, T.; Shimizu, K.; Takahashi, T.; Tsuji, J.; Yamamoto, K. *Tetrahedron Lett.* **1990**, *31*, 3313. (bb) Zoretic, P. A.; Yu, B. C.; Caspar, M. L. *Synth. Commun.* **1989**, *19*, 1859. (cc) Yamada, H.; Shimizu, K.; Nisar, M.; Takahashi, T.; Tsuji, J. *Tetrahedron Lett.* **1990**, *31*, 2407. (dd) Fukuzaki, K.; Nakamura, E.; Kuwajima, I. *Tetrahedron Lett.* **1984**, *25*, 3591. (ee) Stork, G.; Logusch, E. W. *Tetrahedron Lett.* **1979**, 3361. (ff) Bernstein, P. R.; Stork, G. *Tetrahedron Lett.* **1979**, 1967. (gg) Yamamoto, K.; Iijima, M.; Ogimura, Y.; Tsuji, J. *Tetrahedron Lett.* **1984**, *25*, 2813. For methods based on intermolecular Michael addition–aldol condensation, see: (hh) Stork, G.; Winkler, J. D.; Shiner, C. S. *J. Am. Chem. Soc.* **1982**, *104*, 310. (ii) Stork, G.; Winkler, J. D.; Shiner, C. S. *J. Am. Chem. Soc.* **1982**, *104*, 3767. (jj) Stork, G.; Winkler, J. D.; Saccomano, N. A. *Tetrahedron Lett.* **1983**, *24*, 465. (kk) Stork, G.; Atwal, K. S. *Tetrahedron Lett.* **1983**, *24*, 3819. (ll) Stork, G.; Saccomano, N. A. *Tetrahedron Lett.* **1987**, *28*, 2087. (mm) Ihara, M.; Suzuki, S.; Taniguchi, N.; Fukumoto, K. *J. Chem. Soc., Perkin Trans. I* **1992**, 2527. For methods based on fragmentation of bicycloheptanes, see: (nn) Stevens, R. V.; Gaeta, F. C. A. *J. Am. Chem. Soc.* **1977**, *99*, 6105. (oo) Trost, B. M.; Bernstein, P. R.; Funfschilling, P. C. *J. Am. Chem. Soc.* **1979**, *101*, 4378. (pp) Grieco, P. A.; Takigawa, T.; Moore, D. R. *J. Chem. Soc.* **1979**, *101*, 4380. (qq) Hutchinson, J. H.; Money, T.; Piper, S. E. *J. Chem. Soc., Chem. Commun.* **1984**, 455. (rr) Naurla, A. S.; Sethi, S. P. *Tetrahedron Lett.* **1984**, *25*, 685. (ss) Hutchinson, J. H.; Money, T. *J. Chem. Soc., Chem. Commun.* **1986**, 288. For miscellaneous methods, see: (tt) Mikami, K.; Takahashi, K.; Nakai, T. *J. Am. Chem. Soc.* **1990**, *112*, 4035. (uu) Kim, D.; Kim, S.; Lee, J. J.; Kim, H. S. *Tetrahedron Lett.* **1990**, *31*, 4027. (vv) Kim, D.; Lee, Y. K. *Tetrahedron Lett.* **1991**, *32*, 6885. (ww) Snider, B. B.; Kirk, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 2364. (xx) Hart, D. J.; Huang, H.-C. *J. Am. Chem. Soc.* **1988**, *110*, 1634. (yy) Hart, D. J.; Huang, H.-C.; Krishnamurthy, R.; Schwartz, T. *J. Am. Chem. Soc.* **1989**, *111*, 7507. (zz) Satoh, S.; Sodeoka, M.; Sasai, H.; Shibasaki, M. *J. Org. Chem.* **1991**, *56*, 2278.

0022-3263/93/1958-6857$04.00/0

Scheme I

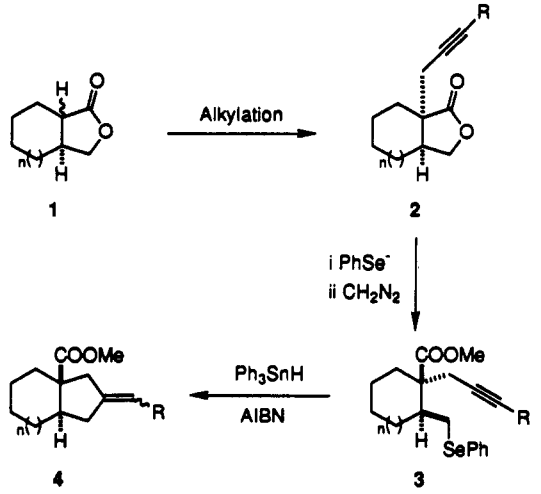
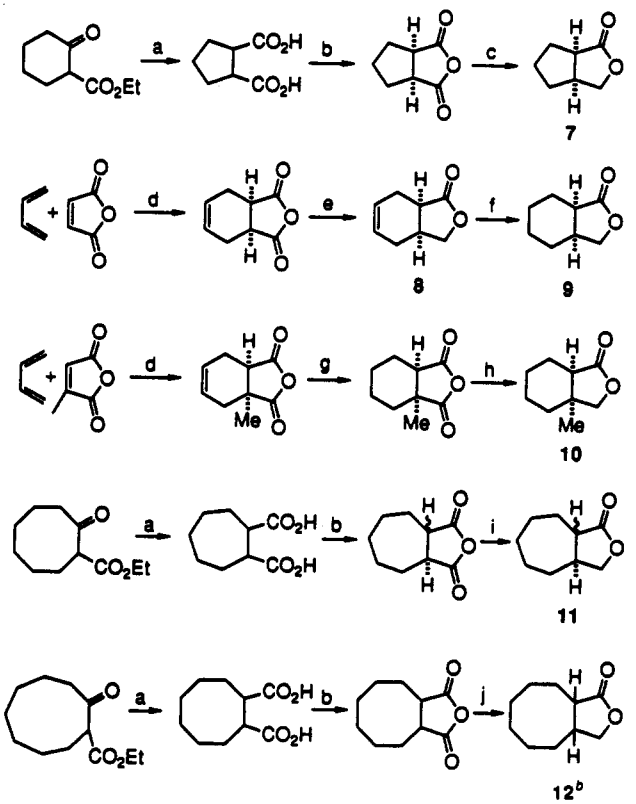


Table I[a]



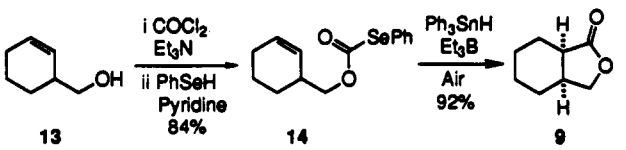
[a] References for procedures are given in the experimental section. Reagents: (a) Br_2, KOH; (b) Ac_2O; (c) $NaBH_4$, H_3O^+; 78%; (d) heat; (e) $LiAlH_4$, H_3O^+; 67%; (f) Pd/C, H_2; 98%; (g) Pd/C, H_2; (h) $LiAlH_4$, H_3O^+; 72%; (i) $NaBH_4$, H_3O^+; 79%; and (j) $NaBH_4$, H_3O^+; 74%. [b] One isomer of undefined stereochemistry.

All of our experiments were done using racemic materials, but it should be noted that lactones of type 1 can also be made optically pure by chemoenzymatic procedures.[12]

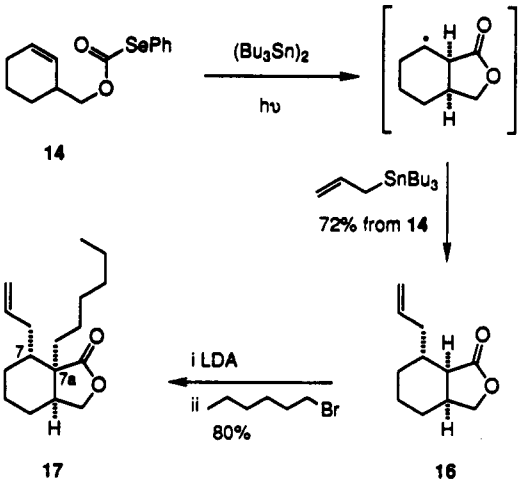
Alkylation and Aldol Condensation of the Lactones. Alkylation of the lactones (see Scheme I, 1 → 2) is a key step in our overall sequence because it is at this stage that the ring-fusion stereochemistry is determined. We believe that in all the cases we have examined (Table II), alkylation occurs exclusively or largely *syn* to the adjacent ring-fusion hydrogen.

(3) For a preliminary communication, see: Clive, D. L. J.; Manning, H. W.; Boivin, T. L. B. *J. Chem. Soc., Chem. Commun.* **1990**, 972.

Scheme II



Scheme III



In our first experiment (Table II, entry 2), we used allyl bromide as the electrophile, but acetylenes are more useful because the final radical cyclization product contains an exocyclic double bond, which can be cleaved to a carbonyl group on the 5-membered ring.

The alkylations were carried out under standard conditions by converting each lactone into its enolate with LDA at a low temperature followed by addition of the alkylating agent. We have sometimes used 3-bromo-1-phenylpropyne[13] (Table II, entries 3, 4, and 5) but prefer 1-bromo-2-hexyne[14] because it can be stored (refrigerator) longer without deterioration.

Only in one case (Table II, entry 6) was a small amount (0.6%) of the *trans* alkylated product isolated. The crude alkylation mixtures were not examined spectroscopically, and so we cannot be certain that no *trans* isomers were formed in the other experiments. However, significant byproducts were not detected by thin layer chromatography, and it is evident that the method is a reliable and efficient way of forming the desired *cis* alkylation products.

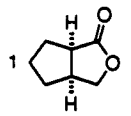
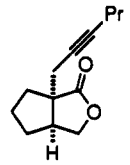
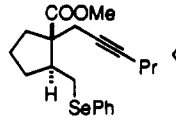
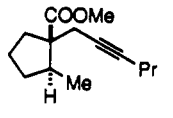
(4) Clive, D. L. J.; Cheshire, D. R.; Set, L. *J. Chem. Soc., Chem. Commun.* **1987**, 353.

(5) *cf.*: (a) de Jong, J. C.; Feringa, B. L. *Tetrahedron Lett.* **1989**, *30*, 7239. (b) Corbera, J.; Font, J.; Monsalvatje, M.; Ortuño, R. M.; Sánchez-Ferrando, F. *J. Org. Chem.* **1988**, *53*, 4394. (c) Cannone, P.; Akssira, M.; Lemay, G. *Tetrahedron Lett.* **1983**, *24*, 1929. (d) Evans, D. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: Orlando, FL, 1984; Vol. 3, Chapter 1.

(6) (a) Tomioka, K.; Cho, Y.-S.; Sato, F.; Koga, K. *J. Org. Chem.* **1988**, *53*, 4094. (b) Herradón, B.; Seebach, D. *Helv. Chim. Acta* **1989**, *72*, 690. (c) Tomioka, K.; Kawasaki, H.; Yasuda, K.; Koga, K. *J. Am. Chem. Soc.* **1988**, *110*, 3597. (d) Tomioka, K.; Yasuda, K.; Kawasaki, H.; Koga, K. *Tetrahedron Lett.* **1986**, *27*, 3247. (e) Matassa, V. G.; Jenkins, P. R.; Kûmin, A.; Damm, L.; Schreiber, J.; Felix, D.; Zass, E.; Eschenmoser, A. *Isr. J. Chem.* **1989**, *29*, 321. (f) Meyers, A. I.; Wallace, R. H. *J. Org. Chem.* **1989**, *54*, 2509. (g) Durkin, K. A.; Liotta, D. *J. Am. Chem. Soc.* **1990**, *112*, 8162. (h) Seebach, D.; Boes, M.; Naef, R.; Schweizer, W. B. *J. Am. Chem. Soc.* **1983**, *105*, 5390. (i) House, H. O ; Umen, M. J. *J. Org. Chem.* **1972**, *37*, 2841. (j) House, H. O.; Nomura, G. S.; VanDerveer, D.; Wissinger, J. E. *J. Org. Chem.* **1986**, *51*, 2408. (k) Tomioka, K.; Kawasaki, H.; Koga, K. *Tetrahedron Lett.* **1985**, *26*, 3027. (l) Meyers, A. I.; Harre, M.; Garland, R. *J. Am. Chem. Soc.* **1984**, *106*, 1146. (m) Meyers, A. I.; Lefker, B. A. *Tetrahedron* **1987**, *43*, 5663.

(7) (a) For $NaBH_4$ reduction of anhydrides, see: Bailey, D. M.; Johnson, R. E. *J. Org. Chem.* **1970**, *35*, 3574. (b) For $LiAlH_4$ reduction of anhydrides, see: Bloomfield, J. J.; Lee, S. L. *J. Org. Chem.* **1967**, *32*, 3919.

Table II[a]

entry	lactone	alkylated lactone or aldol product	selenide	cyclized product
1				
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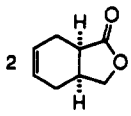
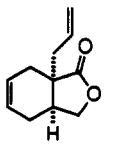
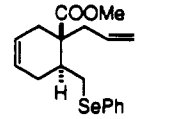
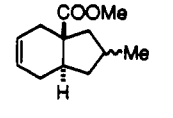
2				
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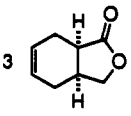
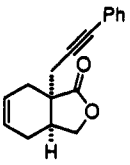
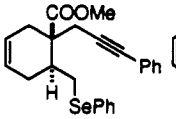
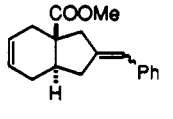
3				
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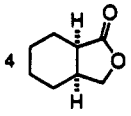
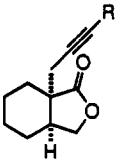
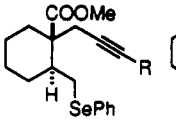
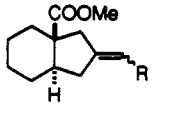
4				
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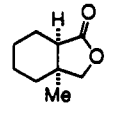
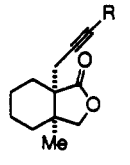
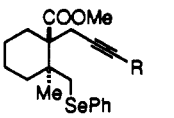
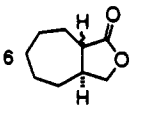
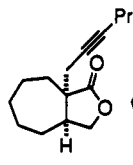
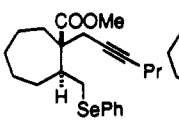
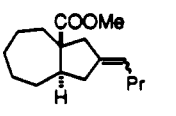
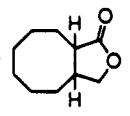
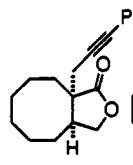
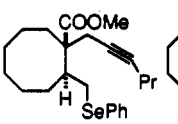
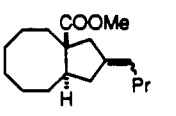
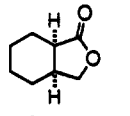
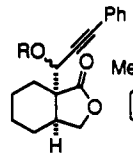
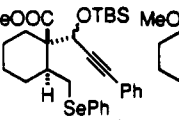
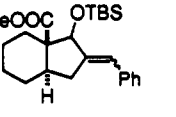
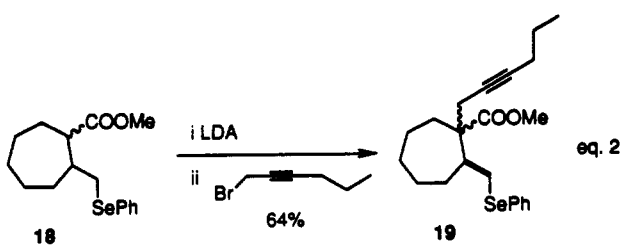
5				
	10	10a R = Ph 90% 10a' R = Pr 90%	10b' R = Pr 14% (79%)	
6				
	11	11a (89%)	11b 66% (86%)	11c 79%[d]; 95%[b]
7				
	12	12a 72%	12b 69% (55%)	12c 77%[d]; 87%[b]
8				
	9	85% → 15 R = H 95%; 15a R = TBS[f]	15b 65%[e]	15c 78%

[a] Where two yields are given, the second value is that corrected for recovered starting material, unless stated to the contrary. [b] Ph_3SnH/Et_3B used for radical cyclization. [c] Experiment not performed. [d] Ph_3SnH/AIBN used for radical cyclization. [e] Only one isomer of **15a** was used. [f] TBS = $SiMe_2$-*t*-Bu.

This stereochemical result is seen not only with the angularly substituted lactone **10** (see Table II) but also with lactone **16**, which was prepared and alkylated as summarized in Scheme III. For this alkylation (**16** → **17**), we used 1-bromohexane; an unsaturated electrophile was unnecessary as we were interested only in the stereochemistry of the alkylation, and use of a saturated halide made it easier to prove the stereochemistry by chemical degradation (see later).

By way of contrast with the result for alkylation of lactone **11** (i.e., isolation of only a very small amount of the *trans* alkylated product), we examined alkylation of ester **18**, and obtained products **19** as an approximately 1:1 mixture of *cis* and *trans* isomers (see eq 2).[15]



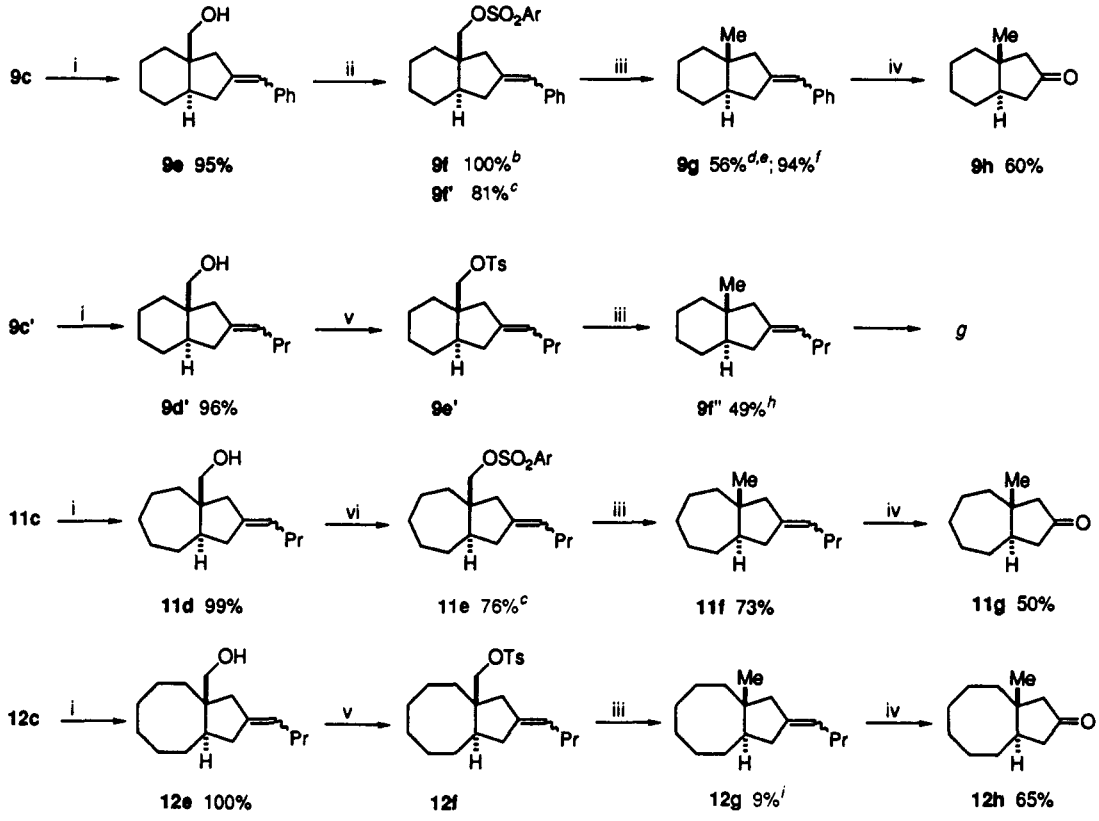
18 19 eq. 2

We also examined briefly an aldol condensation (Table II, entry 8) and found that the reaction (**9** → **15**) proceeds without incident.

Lactone Opening with Phenyl Selenide Anion. Each of the alkylated lactones shown in Table II was treated with PhSeNa, generated from diphenyl diselenide and sodium hydride.[16a] The lactone opening was done in refluxing THF containing some HMPA, and the crude products were esterified with diazomethane. With some

(8) *cf.*: Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Longman: Harlow, 1989; p 695.
(9) (a) Svendsen, A.; Boll, P. M. *Tetrahedron* **1973**, *29*, 4251. (b) Wilkening, D.; Mundy, B. P. *Synth. Commun.* **1984**, *14*, 227.
(10) *cf.*: Sample, T. E., Jr.; Hatch, L. F. *J. Chem. Educ.* **1968**, *45*, 55.
(11) Bachi, M. D.; Bosch, E. *Hetereocycles* **1989**, *28*, 579.
(12) (a) Jakovac, I. J.; Goodbrand, H. B.; Lok, K. P.; Jones, J. B. *J. Am. Chem. Soc.* **1982**, *104*, 4659. (b) Jones, J. B.; Jakovac, I. J. *Organic Syntheses*; Wiley: New York, 1984; Vol. 63, p 10.
(13) Tchoa Yin Lai. *Bull. Soc. Chim. Fr.* **1933**, *53*, 1533. For preparation of the starting 3-phenyl-2-propyn-1-ol, see: Denis, J.-N.; Greene, A. E.; Serra, A. A.; Luche, M. J. *J. Org. Chem.* **1986**, *51*, 46.
(14) Cologne, J.; Descotes, G. *Bull. Soc. Chim. Fr.* **1959**, 815.
(15) *cf.*: Shimada, M.; Kobayashi, S.; Ohno, M. *Tetrahedron Lett.* **1988**, *29*, 6961.

Table III[a]



[a] Reagents: (i) $LiAlH_4$; (ii) for Ar = 4-methylphenyl, TsCl, pyridine; for Ar = 2,4,6-triisopropylphenyl, 2,4,6-*i*-$Pr_3C_6H_2SO_2Cl$, pyridine; (iii) $LiEt_3BH$; (iv) O_3, MeOH–CH_2Cl_2; Ph_3P; (v) TsCl, pyridine; and (vi) 2,4,6-*i*-$Pr_3C_6H_2SO_2Cl$, pyridine. [b] Ar = 4-methylphenyl. [c] Ar = 2,4,6-triisopropylphenyl. [d] From **9f**, Ar = Ph. [e] **9e** recovered in 42% yield. [f] From **9f'**, Ar = 2,4,6-triisopropylphenyl. [g] Experiment not performed. [h] From **9d'**. [i] Overall yield from **12e**, which was itself recovered in 75% yield.

lactones (Table II, entries 4, 5, and 6), it was difficult to drive the ring opening to completion and in these experiments, some of the unopened lactone was recovered. With **10a'** the desired process (**10a'** → **10b**) is an S_N2 displacement at a neopentyl center, and, not surprisingly, the yield was low, even after prolonged heating (4 days) in the presence of 18-crown-6. In general, however, the lactone opening and esterification were efficient.

Aldols **15** (Table I, entry 8) had to be protected by silylation (**15** → **15a**) in order to avoid regeneration of the original lactone (**9**) by a retroaldol process. The diastereoisomeric silyl ethers **15a** were separated chromatographically. We assume, by analogy with the other examples, that the ring-fusion stereochemistry in **15a** is *cis*, but the remaining stereocenter was not assigned, and only one of the isomers was taken forward; it reacted smoothly (65%) with PhSeNa.

Radical Cyclization to *trans* Ring-Fused Compounds. The final step in the sequence involves stannane reduction of the selenide and 5-*exo* closure of the resulting radical. The process can be done thermally by simultaneous addition of benzene solutions of triphenyltin hydride and azobis(isobutyronitrile) (AIBN) to a refluxing benzene solution of the selenide.[17] A more convenient procedure[18] involves addition of triethylborane to a solution of the selenide and triphenyltin hydride in hexane and in the presence of air. Reaction occurs at room temperature and generally leads to higher yields than the thermal method.

The radical closure proved to be very suitable for making *trans* ring-fused 5,6-, 5,7-, and 5,8-bicyclic systems, the cyclized products being obtained in 73–96% yield. Only in the case of **7b** (Table II, entry 1), where the two 5-membered rings would be fused in a *trans* manner, was the process unsuccessful.

Closure onto the triple bond always afforded mixtures of *Z* and *E* isomers, but this is of no consequence, as the double bond would normally be cleaved to a ketone.

Modification of the Cyclization Products. Acetylenes were chosen as the radical trap since the cyclization products, being olefins, should be cleavable to ketones, and this transformation was carried out in two cases (Scheme IV). With **9c**, we tried both epoxidation (*m*-chloroperbenzoic acid) and vicinal hydroxylation (OsO_4) of the double bond followed by periodate cleavage,[19] but neither process was as efficient as direct ozonolysis, and so this was the only method used with **12c**.

We also examined conversion of the angular methoxycarbonyl into a methyl group. Several methods are available for this purpose;[20] we used hydride reduction (COOMe → CH_2OH) and derivatization as a tosylate or

(16) (a) Dowd, P.; Kennedy, P. *Synth. Commun.* **1981**, *11*, 935. *cf.*: (b) Scarborough, R. M., Jr.; Smith, A. B., III. *Tetrahedron Lett.* **1977**, 4361. (c) Liotta, D.; Santiesteban, H. *Tetrahedron Lett.* **1977**, 4369. (d) Ley, S. V.; O'Neil, I. A.; Low, C. M. R. *Tetrahedron* **1986**, *42*, 5363.

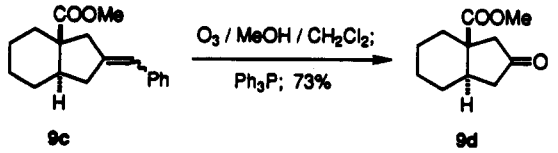
(17) *cf.*: Clive, D. L. J.; Boivin, T. L. B. *J. Org. Chem.* **1989**, *54*, 1997.

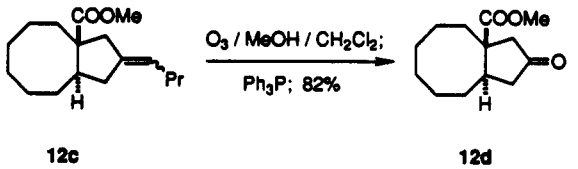
(18) (a) Nozaki, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1988**, *29*, 6125. (b) Nozaki, K.; Oshima, K.; Utimoto, K. *J. Am. Chem. Soc.* **1987**, *109*, 2547. (c) Barton, D. H. R.; Jang, D. O.; Jaszberenyi, J. Cs. *Tetrahedron Lett.* **1990**, *31*, 4681.

(19) (a) Goldbach, M.; Jäkel, E.; Scheider, M. P. *J. Chem. Soc., Chem. Commun.* **1987**, 1434. (b) Sklartz, B. *Quart. Rev. Chem. Soc.* **1967**, *21*, 3.

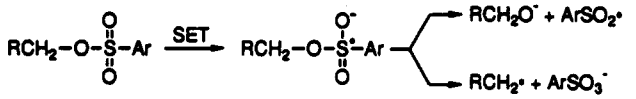
(20) (a) Roush, W. R.; Peseckis, S. M. *J. Am. Chem. Soc.* **1981**, *103*, 6696. (b) Meyers, A. I.; Busacca, C. A. *Tetrahedron Lett.* **1989**, *30*, 6977. (c) Krishnamurthy, S. *J. Organomet. Chem.* **1978**, *156*, 171. (d) Kido, F.; Tsutsumi, K.; Maruta, R.; Yoshikoshi, A. *J. Am. Chem. Soc.* **1979**, *101*, 6420. (e) Marshall, J. A.; Wuts, P. G. M. *J. Org. Chem.* **1977**, *42*, 1794. (f) Fujimoto, Y.; Tatsuno, T. *Tetrahedron Lett.* **1976**, 3325.

Scheme IV





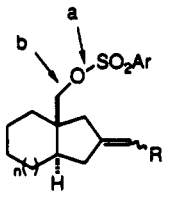
Scheme V



2,4,6-triisopropylbenzenesulfonate followed by hydride displacement ($CH_2OSO_2Ar \rightarrow CH_3$). Our results are shown in Table III.

In early experiments, based on tosylates, the hydride-displacement step gave significant amounts of the parent alcohol by cleavage of bond a (see diagram **20**), but with 2,4,6-triisopropylbenzenesulfonates (**9f'** and **11e**), the undesired cleavage was suppressed.

We did not establish whether the two pathways—cleavage of bonds a or b in **20**—represent competitive hydride displacements on sulfur and carbon, respectively, or are



20

the result of competitive fragmentation pathways of a radical anion that results from single-electron transfer (Scheme V).[21]

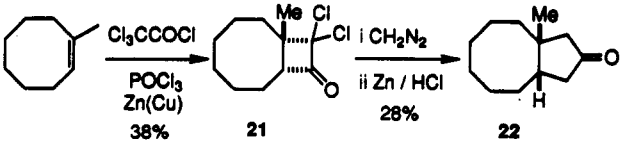
As shown in Table III, we combined the ester → methyl group reduction with double-bond cleavage in a few cases.

Stereochemical Proof for Critical Intermediates. The stereochemical assignments made to the initial alkylation products are based on a number of considerations.

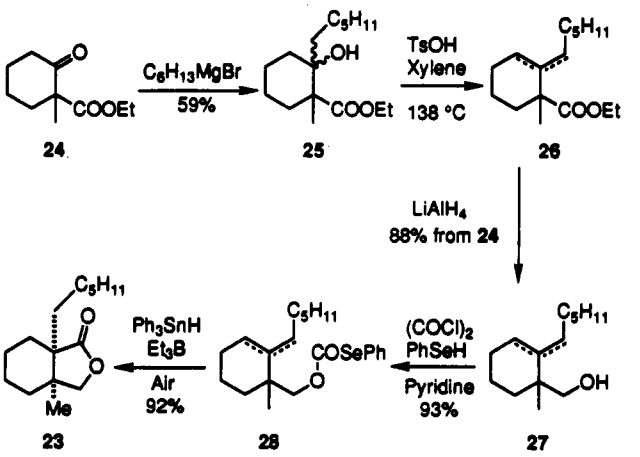
Alkylated lactone **7a** (Table II) was assumed to be *cis*-fused due to the high strain that would develop in forming the isomeric *trans* compound.[22] Our assumption is supported by the fact that attempted cyclization of derived selenide **7b** failed, and reduced uncyclized material was isolated instead. If the original alkylation had gone in a stereochemical sense opposite to that shown in Table I, there would be no obvious impediment to the radical closure.

The stereochemistry of lactone **9a** was established by conversion to ketone **9h** (Table III), which was spectroscopically distinguishable from the corresponding *cis* isomer—a known compound available by an unambiguous route.[23] We have assumed that the aldol condensation **9** → **15** (Table II, entry 8) proceeded in the same stereochemical sense as the analogous alkylations.

Scheme VI

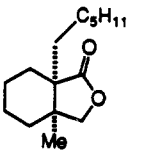


Scheme VII



As described above, the compounds **11c** and **12c**, with 7- and 8-membered rings (Table II, entries 6 and 7), were degraded into ketones **11g** and **12h**, respectively (see Table III). The former (**11g**) is known;[24] its spectroscopic properties have been reported, and so the identity of our product was easily established. For characterization of ketone **12h**, we prepared the corresponding *cis* isomer **22** by adapting a standard method[25] (see Scheme VI) and confirmed that it is different from our ketone **12h**. The latter must, therefore, have *trans* ring fusion.

Nuclear Overhauser measurements with **10a'** (see Table II, entry 5) were not sufficiently clear-cut, and so we hadto use chemical methods. The compound was hydrogenated to saturated lactone **23**, which was found to be identical



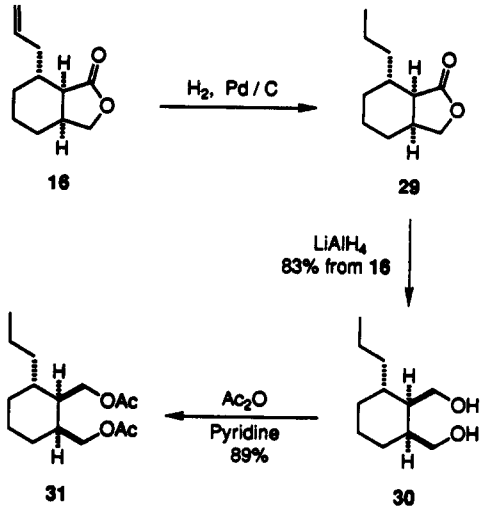
23

to material made from the known keto ester **24**[26] by the route summarized in Scheme VII. The final step (**28** → **23**) is an acyl radical closure that produces a bicyclic compound. Here, the last bond formed is to a ring-fusion position, and so the stereochemical outcome can confidently be taken[4] as shown.

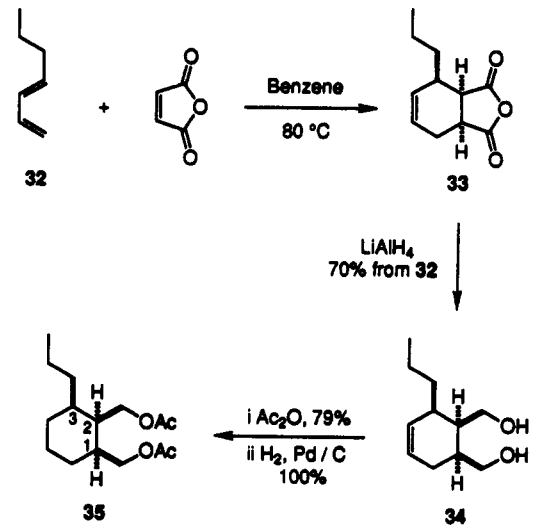
Lactone **17** (see Scheme III) has two centers, C(7) and C(7a), whose stereochemistries had to be determined. The former, which is set up by radical addition to allyltribu-

(21) *cf.*: Della, E. W.; Janowski, W. K.; Pigou, P. E. *Aust. J. Chem.* **1992**, *45*, 1205.
(22) *cf.*: Eliel, E. L. *Stereochemistry of Carbon Compounds*; McGraw-Hill: New York, 1962; p 273.
(23) (a) Dave, V.; Stothers, J. B.; Warnhoff, E. W. *Can. J. Chem.* **1984**, *62*, 1965. (b) Sellers, P. *Acta Chem. Scand.* **1970**, *24*, 2453.
(24) Ito, Y.; Aoyama, H.; Saegusa, T. *J. Am. Chem. Soc.* **1980**, *102*, 4519.
(25) Greene, A. E.; Deprés, J.-P. *J. Am. Chem. Soc.* **1979**, *101*, 4003.
(26) Hodgson, A.; Marshall, J.; Hallett, P.; Gallagher, T. *J. Chem. Soc., Perkin Trans. I* **1992**, 2169.

Scheme VIII



Scheme IX

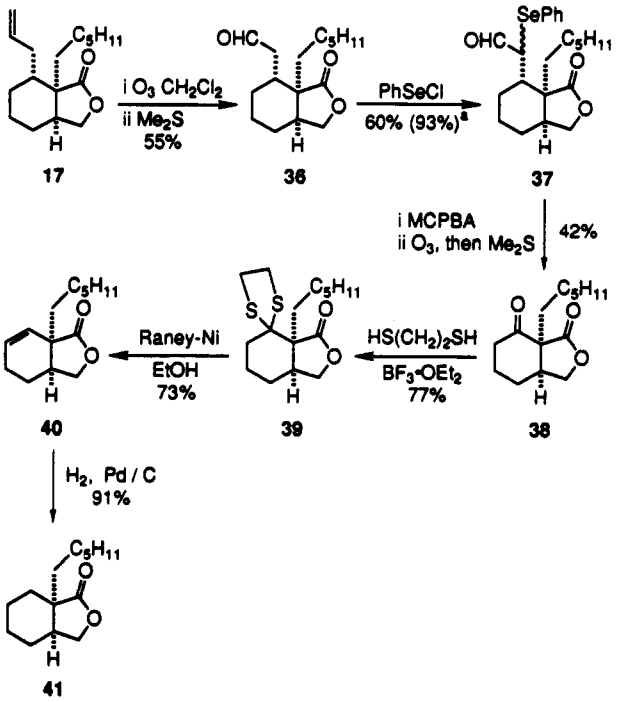


tyltin,[27] was established by degradation of **16** to diacetate **31** (Scheme VIII). An isomeric diacetate was readily made (Scheme IX) by Diels–Alder reaction of diene **32**[28] with maleic anhydride followed by reduction ($LiAlH_4$), acetylation, and hydrogenation. Diacetate **35** was different from **31**. The method used to prepare **35** ensures that **35** and **31** have the same relative stereochemistry at C(1) and C(2) and so must differ at C(3). The C(3) stereochemistry [relative to that at C(2)] of **35** is defined by the method of formation; consequently, the assignment to **31** is as shown.

Finally, the stereochemistry at the angular position [C(7a)] of **17** was determined as follows (see Scheme X).

The olefinic chain was first removed oxidatively by sequential ozonolysis (**17** → **36**), phenylselenenylation (**36** → **37**), selenoxide elimination, and ozonolysis (**37** → **38**). The resulting ketone (**38**) was then converted into its ethylene dithioacetal, and this was desulfurized with Raney nickel to olefin **40**.[29] Hydrogenation gave material (**41**) identical to that obtained by hydrogenation of lactone **9a′**.

Scheme X[a]



[a]Yield corrected for recovered **36**.

Experimental Section

The same general procedures were followed as described previously.[30] For ^{13}C NMR spectra, the symbols s′, d′, t′, q′ indicate zero, one, two, and three attached hydrogens, respectively.

General Procedure for Radical Cyclization. The substrate was placed in a round-bottomed flask equipped with a Teflon-coated stirring bar and a reflux condenser sealed with a rubber septum. The system was flushed with argon for 5–10 min, and dry benzene was injected into the flask. The flask was placed in an oil bath preheated to 85 °C, and solutions of Ph_3SnH and AIBN in benzene were injected simultaneously by syringe pump over 8 h. Refluxing was continued for an arbitrary period of 2–4 h after the addition. The reaction mixture was cooled, and the solvent was evaporated to give a residue which was processed as described for the individual experiments.

***cis*-6a-(2-Hexynyl)hexahydro-1*H*-cyclopenta[*c*]furan-1-one (7a).** Lithium bis(trimethylsilyl)amide was prepared by rapid addition of *n*-BuLi (1.45 mL, 1.57 M in hexanes, 2.27 mmol) to a stirred and cooled (−78 °C) solution of bis(trimethylsilyl)-amine (0.50 mL, 2.37 mmol) in THF (5 mL). The reagent was used immediately. Lactone **7**[9,12a] (260 mg, 2.06 mmol) in THF (2 mL plus 1 mL rinse) was injected dropwise over 5 min, and the resulting solution was stirred at −78 °C. After 40 min, 1-bromo-2-hexyne[14] (0.39 mL, 3.09 mmol) was injected neat and the cooling bath was removed. Stirring was continued overnight. The mixture was quenched with saturated aqueous NH_4Cl (10 mL) and extracted with ether (3 × 30 mL). The combined ether extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (3 × 20 cm), using 10% EtOAc–hexane, gave **7a** (268 mg, 63%) as a pure (^1H NMR), colorless oil: FTIR ($CHCl_3$ cast) 2956, 2200, 1765 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.96 (t, J = 7.0 Hz, 3 H), 1.44–1.81 (m, 6 H), 1.94–2.05 (m, 1 H), 2.07–2.16 (m, 3 H), 2.41 (dt, J = 16.5, 2.5 Hz, 1 H), 2.66 (dt, J = 16.5, 2.5 Hz, 1 H), 2.83–2.90 (m, 1 H), 3.94 (dd, J = 9.0, 3.5 Hz, 1 H), 4.47 (dd, J = 9.0, 4.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 13.45, 20.64, 22.34, 25.70, 26.32, 34.60, 37.37, 43.52, 55.35, 73.11, 75.74, 82.23, 181.89; exact mass *m/z* calcd for $C_{13}H_{18}O_2$ 206.1307, found 206.1290. An analytical sample was prepared by Kugelrohr distillation (140 °C, 8 mmHg). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.63; H, 8.70.

Methyl *cis*-1-(2-Hexynyl)-2-[(phenylseleno)methyl]cyclopentanecarboxylate (7b). A literature procedure for the cleavage of lactones using phenyl selenide anion[16a] was followed

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(28) Diene **32** was prepared by Wittig methylenation of *trans*-2-hexenal (Aldrich). *cf.*: Claesson, A. *Acta Chem. Scand., Ser. B*, **1975**, *29*, 609.
(29) *cf.*: Fishman, J.; Torigoe, M.; Guzik, H. *J. Org. Chem.* **1963**, *28*, 1433.
(30) Clive, D. L. J.; Boivin, T. L. B.; Angoh, A. G. *J. Org. Chem.* **1987**, *52*, 4943.

with slight modification: PhSeSePh (293 mg, 0.94 mmol) and NaH (68 mg, 60% dispersion in oil, 1.69 mmol) in THF (2.5 mL) were refluxed for 50 min. Hexamethylphosphoramide (HMPA) (0.15 mL) was added to the cooled mixture followed by lactone **7a** (257 mg, 1.25 mmol) in THF (0.5 mL plus 0.5 mL rinse). The mixture was refluxed for 4 h, cooled to room temperature, and quenched by addition of MeOH (1 mL). The solvents were evaporated, and water (4 mL) was added to the residue. The mixture was extracted with ether (1 × 20 mL), and the aqueous layer was then acidified with 6 N hydrochloric acid. The acidic solution was extracted with ether (3 × 50 mL), and the combined ethereal extracts were dried ($MgSO_4$) and evaporated. The residue was dissolved in ether (5 mL), and CH_2N_2 in ether was added until nitrogen evolution ceased. Evaporation of the solution and flash chromatography of the residue over silica gel (2 × 20 cm), using 5% EtOAc–hexane, gave selenide **7b** (381 mg, 81%) as a pale yellow oil: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.95 (t, J = 7.5 Hz, 3 H), 1.36–2.00 (m, 6 H), 2.00–2.36 (m, 5 H), 2.42 (dt, J = 16.5, 2.5 Hz, 1 H), 2.63 (dt, J = 16.5, 2.2 Hz, 1 H), 2.65 (d, J = 11.0 Hz, 1 H), 3.12 (dd, J = 11.0 Hz, 1 H), 3.71 (s, 3 H), 7.22–7.35 (m, 3 H), 7.45–7.58 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ13.42, 20.71, 22.41, 22.63, 26.70, 29.30, 32.14, 34.72, 48.77, 51.67, 56.66, 76.73, 82.07, 126.69, 129.04, 130.66, 132.23, 175.44. An analytical sample was prepared by Kugelrohr distillation (120 °C, 0.005 mmHg). Anal. Calcd for $C_{20}H_{26}O_2Se$: C, 63.65; H, 6.94; O, 8.48. Found: C, 63.85; H, 6.84; O, 8.76.

***cis*-3a,4,7,7a-Tetrahydro-7a-(2-propenyl)-1(3*H*)-isobenzofuranone (8a).** LDA was prepared by dropwise addition of *n*-BuLi (47.1 mL, 1.4 M in hexanes, 6.60 mmol) to a stirred and cooled (0 °C) solution of *i*-Pr_2NH (1.00 mL, 7.14 mmol) in dry THF (20 mL). Stirring was continued for 20 min, the mixture was cooled to −78 °C, and lactone **8**[10,7b] (830 mg, 6.01 mmol) in THF (5 mL plus 1 mL rinse) was injected over 10 min. After a further 30 min, freshly distilled allyl bromide (0.78 mL, 9.0 mmol) was added dropwise. Stirring was continued at −78 °C for 1.5 h, the dry ice–acetone bath was then replaced by an ice bath, and the mixture was stirred for an additional 2 h. Saturated aqueous NH_4Cl (10 mL) was added, and the mixture was allowed to warm to room temperature and then extracted with ether (3 × 15 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (2 × 15 cm), using 15% EtOAc–hexane, gave **8a** (961 mg, 89%) as a colorless liquid: FTIR (CCl_4 cast) 1770, 1175, 1010 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.88–2.70 (m, 7 H), 3.87 (t, J = 8.5 Hz, 1 H), 4.26 (dd, J = 7.5, 8.5 Hz, 1 H), 5.08 (m, 2 H), 5.74 (m, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 22.89 (t′), 28.91 (t′), 36.03 (d′), 39.89 (t′), 43.60 (s′), 70.29 (t′), 119.05 (t′), 124.58 (d′), 124.77 (d′), 132.95 (d′), 180.98 (s′); exact mass m/z calcd for $C_{11}H_{14}O_2$ 178.0994, found 178.0988. An analytical sample was prepared by Kugelrohr distillation (75–78 °C, 0.3 mmHg). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.91; H, 7.93.

***cis*-3a,4,7,7a-Tetrahydro-7a-(3-phenyl-2-propynyl)-1(3*H*)-isobenzofuranone (8a′).** The procedure employed for **8a** was followed, using *n*-BuLi (2.40 mL, 1.4 M in hexanes, 3.36 mmol), *i*-Pr_2NH (0.52 mL, 3.70 mmol) in THF (20 mL), lactone **8**[10,7b] (419 mg, 3.03 mmol) in THF (4 mL plus 1 mL rinse), and 3-bromo-1-phenylpropyne[13] (878 mg, 4.50 mmol) in THF (4 mL plus 1 mL rinse). Flash chromatography of the crude product over silica gel (2 × 15 cm), using 10% EtOAc–hexane, gave **8a′** (728 mg, 95%) as a white solid: FTIR (CCl_4 cast) 1763, 1490, 1160, 995 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.92–2.20 (m, 2 H), 2.38 (m, 2 H), 2.60–2.90 (m, 2 H), 2.98 (m, 1 H), 3.88 (t, J = 8.0 Hz, 1 H), 4.34 (t, J = 8.0 Hz, 1 H), 5.75 (m, 2 H), 7.22 (m, 3 H), 7.32 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHZ) δ 23.29 (t′), 26.67 (t′), 28.98 (t′), 36.55 (d′), 44.21 (s′), 70.65 (t′), 83.31 (s′), 85.02 (s′), 123.16 (s′), 124.74 (d′), 125.00 (d′), 128.09 (d′), 128.27 (d′), 131.70 (d′), 180.29 (s′); exact mass m/z calcd for $C_{17}H_{16}O_2$ 252.1150, found 252.1155. An analytical sample was prepared by recrystallization from CH_2Cl_2–hexane: mp 79 °C. Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.77; H, 6.32.

Methyl *cis*-6-[(Phenylseleno)methyl]-1-(2-propenyl)-3-cyclohexenecarboxylate (8b). The procedure for **7b** was followed, using PhSeSePh (468 mg, 1.50 mmol) and NaH (108 mg, 60% in oil, 2.70 mmol) in THF (5 mL) and a reflux period of 60 min. The mixture was cooled to room temperature, and freshly distilled, dry HMPA (0.2 mL) was added by syringe followed by lactone **8a** (356 mg, 2.00 mmol) in THF (1 mL plus 1 mL rinse). The mixture was refluxed for 11.5 h, cooled, and quenched with MeOH (1 mL). The solvents were evaporated, and the residue was taken up in water (10 mL) and extracted with ether (3 × 10 mL). The aqueous solution was acidified with 10% hydrochloric acid and reextracted with ether (3 × 10 mL). The extracts were combined, dried ($MgSO_4$), and cooled to 0 °C. Freshly prepared CH_2N_2 in ether was added dropwise until no further reaction could be detected by TLC. The ether and excess of CH_2N_2 were evaporated, and flash chromatography of the residue over silica gel, using first 2% EtOAc–hexane and then an increasingly more polar mixture (up to 20% EtOAc–hexane), gave **8b** (516 mg, 74%) as a colorless oil: FTIR ($CHCl_3$ cast) 1732, 1435, 1214, 1100 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.96–1.45 (m, 7 H), 2.74 (m, 2 H), 3.55 (s, 3 H), 4.97 (m, 2 H), 5.56 (m, 3 H), 7.20 (m, 3 H), 7.45 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 26.41 (t′), 27.39 (t′), 30.48 (t′), 39.53 (d′), 40.65 (t′), 49.61 (s′), 51.96 (q′), 118.76 (t′), 124.32 (d′), 124.86 (d′), 127.30 (d′), 129.43 (d′), 130.97 (s′), 133.16 (d′), 133.79 (d′), 176.39 (s′); exact mass m/z calcd for $C_{18}H_{22}O_2Se$ 350.0785, found 350.0791. Anal. Calcd for $C_{18}H_{22}O_2Se$: C, 61.89; H, 6.34; O, 9.16. Found: C, 62.11; H, 6.34; O, 9.07.

Methyl *cis*-6-[(Phenylseleno)methyl]-1-(3-phenyl-2-propynyl)-3-cyclohexenecarboxylate (8b′). The procedure employed for **8b** was followed, using PhSeSePh (468 mg, 1.50 mmol) and NaH (108 mg, 60% in oil, 2.70 mmol) in THF (5 mL), HMPA (0.20 mL), and lactone **8a′** (502 mg, 1.99 mmol) in THF (5 mL plus 2 mL as rinse). Flash chromatography of the crude product over silica gel (2 × 15 cm), using 5% EtOAc–hexane, gave **8b′** (699 mg, 83%) as a colorless syrup which solidified on cooling: mp 52 °C; FTIR (CCl_4 cast) 1734, 1488, 1478, 1436, 1204, 1290, 1059, 756, 736, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.13–2.97 (m, 9 H), 3.60 (s, 3 H), 5.57 (m, 2 H), 7.19 (m, 8 H), 7.42 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 26.16 (t′), 27.00 (t′), 28.10 (t′), 29.80 (t′), 38.64 (d′), 49.35 (s′), 51.95 (q′), 83.22 (s′), 85.58 (s′), 123.47 (s′), 123.95 (d′), 124.50 (d′), 126.93 (d′), 127.86 (d′), 128.20 (d′), 129.04 (d′), 130.32 (s′), 131.67 (d′), 132.77 (d′), 175.11 (s′); exact mass m/z calcd for $C_{24}H_{24}O_2Se$ 424.0941, found 424.0934. Anal. Calcd for $C_{24}H_{24}O_2Se$: C, 68.08; H, 5.71; O, 7.56. Found: C, 68.12; H, 5.70; O, 7.49.

Methyl (2α,3aα,7aβ)- and (2α,3aβ,7aα)-1,2,3,4,7,7a-Hexahydro-2-methyl-3a*H*-indene-3a-carboxylate (8c). The general procedure for radical cyclization was followed, using selenide **8b** (350 mg, 1.00 mmol) in benzene (50 mL), Ph_3SnH (557 mg, 1.58 mmol) in benzene (10 mL), and AIBN (10 mg, 0.06 mmol) in benzene (10 mL). Kugelrohr distillation (55 °C, 0.2 mmHg) of the crude product gave **8c** (179 mg, 92%) as a colorless oil which was a chromatographically (TLC) inseparable mixture of two isomers in a 3:1 ratio (^{1}H NMR): FTIR (CCl_4 cast) 2950, 1730, 1194, 1174 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.95–1.12 (m, 1 H), 1.02 (d, J = 6.0 Hz, 3 H), 1.38 (m, 1 H), 1.80–2.10 (m, 3 H), 2.10–2.36 (m, 4 H), 2.67–2.90 (m, 1 H), 3.61 (s) and 3.63 (s) (both signals together correspond to 3 H), 5.62 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) (signals assigned to major isomer) δ 22.91 (q′), 28.71 (t′), 30.39 (d′), 36.80 (t′), 37.04 (t′), 43.74 (d′), 46.80 (t′), 51.25 (q′), 52.99 (s′), 125.88 (d′), 128.06 (d′), 176.35 (s′), (signals assigned to minor isomer) δ 22.03 (q′), 25.19 (d′), 28.38 (t′), 31.18 (d′), 37.55 (t′), 38.06 (t′), 44.82 (t′), 46.14 (q′), 126.06 (d′), 128.75 (d′), several signals overlapped; exact mass m/z [(M−H)$^+$] calcd for $C_{12}H_{17}O_2$ 193.1228, found 193.1223. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.54; H, 9.35.

Methyl (2*E*,3aα,7aβ)- and (2*Z*,3aα,7aβ)-1,2,3,4,7,7a-Hexahydro-2-(phenylmethylene)-3a*H*-indene-3a-carboxylate (8c′). The general procedure for radical cyclization was followed, using selenide **8b′** (117 mg, 0.276 mmol) in benzene (40 mL), Ph_3SnH (116 mg, 0.331 mmol) in benzene (10 mL), and AIBN (5 mg, 0.03 mmol) in benzene (10 mL). The residue was distilled (Kugelrohr, 90 °C, 0.100 mmHg) three times to afford **8c′** (54 mg, 73%) as a colorless oil which was a chromatographically (TLC) inseparable mixture of two isomers in a 1:1 ratio (^{1}H NMR): FTIR (CCl_4 cast) 1728, 1440, 1205, 1192, 1174 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.94–3.15 (m, 9 H), 3.54 (s, 1.5 H), 3.60 (s, 1.5 H), 5.67 (m, 2 H), 6.30 (m, 1 H), 7.04–7.34 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 28.10 (t′), 28.38 (t′), 35.47 (t′), 36.17 (t′), 36.69 (t′), 38.51 (t′), 43.35 (t′), 43.68 (d′), 45.13 (d′), 47.33 (t′), 50.51 (s′), 51.50 (q′), 52.05 (s′), 122.38 (d′), 122.69 (d′), 125.93 (d′), 125.98 (d′), 127.83 (d′), 127.91 (d′), 128.05 (d′), 128.23 (d′), 138.43 (s′), 138.48 (s′),

142.72 (s'), 142.60 (s'), 175.62 (s'), 175.68 (s'), several signals overlapped; exact mass m/z calcd for $C_{18}H_{20}O_2$ 268.1463, found 268.1463.

***cis*-Hexahydro-1(3*H*)-isobenzofuranone (9).** Et_3B (1.0 mL, 1 M in hexane, 1.0 mmol) was added dropwise to a stirred solution of selenocarbonate **14** (296 mg, 1.0 mmol) and Ph_3SnH (527 mg, 1.5 mmol) in hexane (100 mL) (protection from moisture by a drying tube packed with Drierite). The resulting solution was stirred at room temperature for 24 h and then evaporated. Flash chromatography of the residue over silica gel (2 × 16 cm), using 20% EtOAc–hexane, gave **9** (129 mg, 92%) as a pure (^{1}H NMR), colorless oil, identical to material prepared by reduction of the corresponding anhydride.[7]

***cis*-Hexahydro-7a-(3-phenyl-2-propynyl)-1(3*H*)-isobenzofuranone (9a).** The procedure employed for **7a** was followed, using *n*-BuLi (5.7 mL, 1.57 M in hexanes, 8.93 mmol), *i*-Pr_2NH (1.3 mL, 9.32 mmol), THF (20 mL), lactone **9**[7] (1.088 g, 7.76 mmol) in THF (4 mL plus 1 mL rinse), and 3-bromo-1-phenylpropyne[13] (1.7 mL, 11.6 mmol) in THF (4 mL plus 1 mL rinse). Flash chromatography of the crude product over silica gel (5 × 18 cm), using 15% EtOAc–hexane, gave **9a** (1.911 g, 97%) as a pure (^{1}H NMR), pale yellow oil which solidified on standing: FTIR ($CHCl_3$ cast) 2934, 1769, 1490, 1164, 1111, 1072, 1024, 757, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.35–1.97 (m, 8 H), 2.60–2.86 (m, 3 H), 4.00 (dd, J = 9.0, 5.5 Hz, 1 H), 4.34 (dd, J = 9.0, 6.5 Hz, 1 H), 7.18–7.42 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 21.88, 21.93, 25.11, 25.71, 29.32, 37.72, 45.45, 69.43, 83.80, 85.17, 123.07, 128.26, 131.67, 179.69; exact mass m/z calcd for $C_{17}H_{18}O_2$ 254.1307, found 254.1304. An analytical sample was prepared by recrystallization from CH_2Cl_2–hexane (mp 65 °C). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.21; H, 6.92.

***cis*-7a-(2-Hexynyl)hexahydro-1(3*H*)-isobenzofuranone (9a').** The procedure employed for **7a** was followed, using *n*-BuLi (4.84 mL, 1.56 M in hexanes, 7.55 mmol), *i*-Pr_2NH (1.10 mL, 7.88 mmol) in THF (8 mL), lactone **9** (920 mg, 6.57 mmol) in THF (5 mL plus 1 mL rinse), and 1-bromo-2-hexyne[14] (1.25 mL, 9.85 mmol). Flash chromatography of the crude product over silica gel (4 × 17 cm), using 8% EtOAc–hexane, gave **9a'** (1.270 g, 88%) as a pure (^{1}H NMR), colorless oil: FTIR ($CHCl_3$ cast) 2924, 1772, 1020 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.97 (t, J = 7.0 Hz, 3 H), 1.32–1.70 (m, 8 H), 1.72–1.87 (m, 2 H), 2.14 (tt, J = 7.0, 2.5 Hz, 2 H), 2.41 (dt, J = 8.0, 2.5 Hz, 1 H), 2.52 (dt, J = 8.0, 2.5 Hz, 1 H), 2.66–2.75 (m, 1 H), 3.98 (dd, J = 9.0, 6.0 Hz, 1 H), 4.34 (dd, J = 9.0, 6.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.44, 20.70, 21.91, 22.00, 22.30, 25.12, 25.19, 29.15, 37.48, 45.45, 69.44, 75.34, 83.71, 179.92; exact mass m/z calcd for $C_{14}H_{20}O_2$ 220.1463, found 220.1458. An analytical sample was prepared by Kugelrohr distillation (98 °C, 0.005 mmHg). Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.17; H, 9.30.

Methyl *cis*-1-(3-Phenyl-2-propynyl)-2-[(phenylseleno)methyl]cyclohexanecarboxylate (9b). The procedure employed for **7b** was followed, using PhSeSePh (1.800 g, 5.77 mmol) and NaH (415 mg, 60% in oil, 10.38 mmol) in THF (15 mL), a reflux period of 50 min, HMPA (0.90 mL, 5.2 mmol), and lactone **9a** (1.907 g, 7.50 mmol) in THF (5 mL plus 1 mL rinse). Flash chromatography of the crude product over silica gel (5 × 16 cm), using first 8% EtOAc–hexane and then 15% EtOAc–hexane, gave unreacted lactone **9a** (542 mg, 27%) and selenide **9b** (2.296 g, 72%; 100% corrected for recovered starting material) as a pure (^{1}H NMR), pale yellow oil: FTIR (CCl_4 cast) 2936, 1729, 1210, 1135, 1070, 1046, 1023, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.20–1.80 (m, 6 H), 1.91–2.10 (m, 3 H), 2.79 (dd, J = 27.0, 17.0 Hz, 2 H), 3.0 (t, J = 11.0 Hz, 1 H), 3.29 (dd, J = 11.0, 2.0 Hz, 1 H), 3.68 (s, 3 H), 7.12–7.40 (m, 8 H), 7.44–7.58 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 22.63, 24.16, 27.04, 28.15, 30.16, 32.53, 43.59, 50.72, 51.63, 83.67, 85.74, 123.46, 126.67, 127.82, 128.98, 130.91, 131.63, 132.46, 174.98; exact mass m/z calcd for $C_{24}H_{26}O_2Se$ 426.1097, found 426.1091. Anal. Calcd for $C_{24}H_{26}O_2Se$: C, 67.76; H, 6.16. Found: C, 68.12; H, 6.18.

Methyl *cis*-1-(2-Hexynyl)-2-[(phenylseleno)methyl]cyclohexanecarboxylate (9b'). The procedure employed for **7b** was followed, using PhSeSePh (234 mg, 0.75 mmol) and NaH (54 mg, 60% in oil, 1.35 mmol) in THF (10 mL), HMPA (0.15 mL, 0.86 mmol), and lactone **9a'** (215 mg, 0.97 mmol) in THF (3 mL plus 1 mL rinse). Flash chromatography of the crude product over silica gel (3 × 18 cm), using first 5% EtOAc–hexane and then 10% EtOAc–hexane, gave recovered lactone **9a'** (24 mg, 11%) and selenide **9b'** (294 mg, 77%; 87% corrected for recovered starting material) as a pure (^{1}H NMR), pale yellow oil: FTIR ($CHCl_3$ cast) 2933, 1730, 1209 cm^{-1}; ^{1}H NMR($CDCl_3$, 300 MHz) δ 0.94 (t, J = 7.0 Hz, 3 H), 1.20–1.35 (m, 1 H), 1.40–1.68 (m, 7 H), 1.84–1.98 (m, 3 H), 2.07 (tt, J = 7.0, 2.5 Hz, 2 H), 2.45 (dt, J = 17.0, 2.5 Hz, 1 H), 2.58 (dt, J = 17.0, 2.5 Hz, 1 H), 2.95 (dd, J = 12.0, 11.0 Hz, 1 H), 3.20 (dd, J = 12.0, 2.5 Hz, 1 H), 7.20–7.30 (m, 3 H), 7.45–7.55 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 13.53, 20.79, 22.44, 22.64, 24.14, 26.99, 27.59, 30.21, 32.16, 43.47, 50.66, 51.54, 75.74, 83.51, 126.65, 128.99, 131.10, 132.47, 175.31; exact mass m/z calcd for $C_{21}H_{28}O_2Se$ 392.1254, found 392.1251. An analytical sample was prepared by Kugelrohr distillation (127 °C, 0.005 mmHg). Anal. Calcd for $C_{21}H_{28}O_2Se$: C, 64.44; H, 7.21; O, 8.18. Found: C, 64.38; H, 7.22; O, 8.40.

Methyl (2*E*,3aα,7aβ)- and (2*Z*,3aα,7aβ)-Octahydro-2-(phenylmethylene)-3a*H*-indene-3a-carboxylate (9c). (a) The general procedure for radical cyclization was followed, using selenide **9b** (852 mg, 2.0 mmol) in benzene (80 mL), Ph_3SnH (1.054 g, 3.0 mmol) in benzene (20 mL), and AIBN (33 mg, 0.2 mmol) in benzene (20 mL). The crude product was taken up in ether (20 mL), and a saturated solution of iodine in ether was added until the iodine color persisted. The solution was washed with 10% aqueous $Na_2S_2O_3$ (10 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (3 × 18 cm), using first 5% CH_2Cl_2–hexane and then mixtures of CH_2Cl_2 and hexane containing increasing amounts (up to 20%) of CH_2Cl_2, followed by Kugelrohr distillation (97 °C, 0.01 mmHg) gave **9c** (520 mg, 96%) as a pure (^{1}H NMR), colorless oil which was a chromatographically (TLC) inseparable mixture of two isomers in a 1.3:1 ratio (^{1}H NMR): FTIR (CCl_4 cast) 2920, 2848, 1730, 1444, 1132, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.18–1.48 (m, 3 H), 1.59–1.97 (m, 5 H), 2.37–3.12 (m, 5 H), 3.59 (s, 1.5 H), 3.65 (s, 1.5 H), 6.30–6.42 (m, 1 H), 7.14–7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 23.79, 25.67, 25.92, 26.31, 35.52, 36.02, 36.53, 36.36, 44.07, 48.05, 48.28, 49.61, 51.32, 52.95, 54.20, 122.69, 122.97, 125.83, 125.88, 128.02, 128.20, 138.44, 138.55, 142.55, 142.64, 175.85; exact mass m/z calcd for $C_{18}H_{22}O_2$ 270.1620, found 270.1620. Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.59; H, 7.89.

(b) Et_3B (1.0 mL, 1 M in hexane, 1.0 mmol) was added dropwise to a stirred solution of selenide **9b** (426 mg, 1.0 mmol) and Ph_3SnH (421 mg, 1.2 mmol) in hexane (100 mL) at room temperature (protection from moisture by a drying tube packed with Drierite). Stirring was continued for 48 h, and the solvent was then evaporated. Flash chromatography of the residue over silica gel (2 × 16 cm), using 10% CH_2Cl_2–hexane, followed by Kugelrohr distillation (102 °C, 0.01 mmHg) gave **9c** (236 mg, 87%) as a colorless oil, identical (^{1}H NMR) to material obtained by the general procedure for radical cyclization.

Methyl (2*E*,3aα,7aβ)- and (2*Z*,3aα,7aβ)-2-Butylideneoctahydro-3a*H*-indene-3a-carboxylate (9c'). The general procedure for radical cyclization was followed, using selenide **9b'** (751 mg, 1.92 mmol) in benzene (75 mL), Ph_3SnH (110 mg, 2.88 mmol) in benzene (20 mL), and AIBN (32 mg, 0.19 mmol) in benzene (20 mL). The crude product was dissolved in ether (15 mL), and a saturated solution of iodine in ether was added until the iodine color persisted. The solution was washed with 10% aqueous $Na_2S_2O_3$ (25 mL) and brine (25 mL), and the combined aqueous washes were extracted once with ether (25 mL). The combined extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (3 × 21 cm), using first 0.5% CH_2Cl_2–hexane and then 10% CH_2Cl_2–hexane, gave **9c'** (372 mg, 82%) as a pure (^{1}H NMR), colorless oil which was a chromatographically (TLC) inseparable mixture of two isomers in a 1.3:1 ratio (^{1}H NMR): FTIR ($CHCl_3$ cast) 2961, 2926, 1734, 1136 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.82–0.90 (m, 3 H), 1.13–1.40 (m, 5 H), 1.47–2.06 (m, 7.5 H), 2.15–2.75 (m, 4.5 H), 3.63 (2 s, 3 H), 5.19–5.30 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 13.77, 13.83, 22.71, 22.77, 23.88, 25.91, 26.08, 26.42, 26.45, 31.56, 32.74, 36.17, 36.22, 36.48, 41.91, 46.15, 48.76, 48.82, 51.19, 53.45, 53.53, 122.46, 122.53, 138.80, 138.99, 176.17, 176.30; exact mass m/z calcd for $C_{15}H_{24}O_2$ 236.1776, found 236.1780. An analytical sample was prepared by Kugelrohr distillation (71 °C, 0.01 mmHg). Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.23. Found: C, 76.45; H, 10.24.

Methyl *trans*-Octahydro-2-oxo-3a*H*-indene-3a-carboxylate (9d). This experiment was done using the apparatus described by Rubin[31] but with a pear-shaped reagent bulb. Ozonized oxygen, cooled by passage through a glass coil immersed in a dry ice–acetone bath, was bubbled for 4 min into dry CH_2Cl_2 (19.5 mL) at −78 °C. The resulting solution was transferred into the other bulb of the apparatus, which contained a cold (−78 °C) solution of **9c** (58 mg, 0.25 mmol) in CH_2Cl_2 (4 mL) and MeOH (6 mL). The resulting mixture was stirred for 5 min, and Ph_3P (200 mg, 0.75 mmol) was added. The cold bath was removed, and stirring was continued for 1.5 h. Evaporation of the solvent and flash chromatography of the residue over silica gel (2 × 17 cm), using 15% EtOAc–hexane followed by 20% EtOAc–hexane, gave **9d** (35 mg, 73%) as a pure (^{1}H NMR) oil: FTIR (CCl_4 cast) 2924, 2860, 1750, 1729, 1220, 1136 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.23–2.32 (m, 10 H), 2.40–2.70 (m, 3 H), 3.69 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 23.43, 25.76, 26.23, 35.70, 41.97, 47.13, 51.46, 51.72, 175.25, 215.77; exact mass *m/z* calcd for $C_{11}H_{16}O_3$ 196.1099, found 196.1100. Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.63; H, 8.26.

(2*E*,3aα,7aβ)- and (2*Z*,3aα,7aβ)-Octahydro-2-(phenylmethylene)-3a*H*-indene-3a-methanol (9e). A solution of ester **9c** (508 mg, 1.88 mmol) in THF (5 mL plus 2 mL rinse) was added dropwise to a stirred and cooled (ice bath) suspension of $LiAlH_4$ (142 mg, 3.75 mmol) in THF (10 mL). The ice bath was removed, and stirring was continued for 5 h. The mixture was recooled to ca. 0 °C (ice bath) and quenched by successive dropwise addition of water (0.14 mL), 15% aqueous NaOH (0.14 mL), and water (0.42 mL). The mixture was stirred for 10 min and filtered through a pad (2 × 5 cm) of Celite. The pad was washed with EtOAc, and the combined filtrates were evaporated. Flash chromatography of the residue over silica gel (3 × 18 cm), using 15% EtOAc–hexane, gave **9e** (433 mg, 95%) as a pure (^{1}H NMR), colorless oil which was a mixture of two diastereomers in a 1:1 ratio (^{1}H NMR). The diastereomers were separated by flash chromatography over silica gel, using 75% EtOAc–hexane. **Faster moving diastereomer:** FTIR ($CHCl_3$ cast) 3324, 2926, 2848, 1442, 1030, 740, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.05–1.23 (m, 2 H), 1.23–1.42 (m, 2 H), 1.42–1.74 (m, 4 H), 1.78–1.88 (m, 1 H), 2.03 (dd, *J* = 16.0, 2.5 Hz, 1 H), 2.11–2.30 (m, 2 H), 2.51 (ddd, *J* = 16.0, 7.5, 1.0 Hz, 1 H), 2.94 (d, *J* = 16.0 Hz, 1 H), 3.21 (d, *J* = 11.0 Hz, 1 H), 3.79 (d, *J* = 11.0 Hz, 1 H), 6.38 (m, 1 H), 7.10–7.20 (m, 1 H), 7.26–7.35 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 21.37, 24.84, 26.42, 33.03, 38.09, 42.19, 45.68, 47.24, 60.42, 123.66, 125.86, 128.03, 128.22, 138.65, 143.47; exact mass *m/z* calcd for $C_{17}H_{22}O$ 242.1671, found 242.1675. An analytical sample was prepared by Kugelrohr distillation (125 °C, 0.005 mmHg). Anal. Calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found: C, 84.39; H, 9.18.

Slower moving diastereomer: FTIR ($CHCl_3$ cast) 3328, 2925, 2848, 1442, 1030, 790 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.00–1.41 (m, 4 H), 1.46–1.90 (m, 5 H), 2.05–2.27 (m, 3 H), 2.68 (dd, *J* = 17.0, 8.0 Hz, 1 H), 2.75 (d, *J* = 16.0 Hz, 1 H), 3.29 (d, *J* = 11.0 Hz, 1 H), 3.83 (dd, *J* = 11.0, 2.0 Hz, 1 H), 6.40 (br s, 1 H), 7.10–7.20 (m, 1 H), 7.26–7.35 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 21.36, 25.06, 26.43, 32.62, 35.06, 44.25, 46.27, 48.70, 60.25, 123.38, 125.84, 127.96, 128.27, 138.61, 143.50; exact mass *m/z* calcd for $C_{17}H_{22}O$ 242.1671, found 242.1667. An analytical sample (mp 91–93 °C) was prepared by recrystallization from hexane. Anal. Calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found: C, 83.98; H, 8.87.

(2*E*,3aα,7aβ)- and (2*Z*,3aα,7aβ)-[Octahydro-2-(phenylmethylene)-3a*H*-inden-3a-yl]methyl 4-Methylbenzenesulfonate (9f). *p*-Toluenesulfonyl chloride (682 mg, 3.58 mmol) was added to a stirred and cooled (ice bath) solution of alcohol **9e** (433 mg, 1.79 mmol) in pyridine (7 mL). The resulting solution was allowed to stand in the refrigerator (ca. 5 °C) for 4 days. The mixture was poured onto ice and extracted with ether (3 × 30 mL). The combined ether extracts were washed with 10% hydrochloric acid (2 × 10 mL) and water (20 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (3 × 17 cm), using 10% EtOAc–hexane, gave a white solid (**9f**) which was not characterized but used directly for conversion to **9g**.

(31) Rubin, M. B. *J. Chem. Educ.* **1964**, *41*, 388.

(2*E*,3aα,7aβ)- and (2*Z*,3aα,7aβ)-[Octahydro-2-(phenylmethylene)-3a*H*-inden-3a-yl]methyl 2,4,6-Tris(1-methylethyl)benzenesulfonate (9f′). 2,4,6-Triisopropylbenzenesulfonyl chloride (606 mg, 2.00 mmol) was added to a solution of alcohol **9e** (162 mg, 0.67 mmol) in pyridine (5 mL). The solution was stirred at 80 °C (oil bath temperature) overnight, cooled, poured onto ice, and extracted with ether (3 × 30 mL). The combined ethereal extracts were washed with 10% hydrochloric acid (2 × 15 mL) and water (15 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (3 × 16 cm), using 5% EtOAc–hexane, gave **9f′** (274 mg, 81%) as a viscous oil which was not characterized but used directly for conversion to **9g**.

(2*E*,3aα,7aβ)- and (2*Z*,3aα,7aβ)-Octahydro-3a-methyl-2-(phenylmethylene)-1*H*-indene (9g). (a) From 9f. Lithium triethylborohydride (8.9 mL, 1.0 M in THF, 8.9 mmol) was added dropwise to a stirred and cooled (ice bath) solution of tosylate **9f** (1.79 mmol; assuming 100% conversion of the alcohol to the tosylate) in THF (5 mL). The cold bath was removed, and the solution was refluxed for 15 h, cooled, quenched with 3 N aqueous NaOH (20 mL), and extracted with ether (3 × 10 mL). The combined ether extracts were dried ($MgSO_4$) and evaporated. The residue was filtered through a pad (3 × 5 cm) of silica gel, using first pentane and then EtOAc. The pentane filtrate was evaporated, and Kugelrohr distillation (90 °C, 0.01 mmHg) of the residue gave **9g** (226 mg, 56%) as a pure (^{1}H NMR), colorless oil which was a chromatographically (TLC) inseparable mixture of two isomers in a 1:1.4 ratio (^{1}H NMR): FTIR ($CHCl_3$ cast) 2925, 2855, 1446, 693 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.75 (s, 1.2 H), 0.80 (s, 1.8 H), 1.15–1.185 (m, 9 H), 2.07–2.73 (m, 4 H), 6.30–6.40 (m, 1 H), 7.08–7.20 (m, 1 H), 7.20–7.38 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 16.57, 17.03, 21.90, 25.32, 25.56, 26.63, 35.03, 37.99, 38.68, 39.13, 39.48, 40.98, 47.03, 47.88, 48.51, 51.82, 122.73, 123.00, 125.61, 127.89, 127.93, 128.13, 128.20, 138.85, 138.96, 144.54, 144.79; exact mass *m/z* calcd for $C_{17}H_{22}$ 226.1721, found 226.1714. Anal. Calcd for $C_{17}H_{22}$: C, 90.20; H, 9.80. Found: C, 90.28; H, 9.58.

Evaporation of the EtOAc filtrate and flash chromatography of the residue over silica gel (2 × 18 cm), using 15% EtOAc–hexane, gave recovered alcohol **9e** (182 mg, 42%).

(b) From 9f′. Lithium triethylborohydride (2.7 mL, 1.0 M in THF, 2.7 mmol) was added dropwise to a stirred solution of sulfonate **9f′** (274 mg, 0.54 mmol) in THF (2 mL). The solution was refluxed for 12 h. Additional lithium triethylborohydride (1.1 mL, 1.0 M in THF, 1.1 mmol) was added, and refluxing was continued for 12 h. The mixture was cooled, quenched with 3 N aqueous NaOH (20 mL), and extracted with ether (3 × 20 mL). The combined ether extracts were dried ($MgSO_4$) and evaporated. The residue was filtered through a pad (4 × 4 cm) of silica gel with pentane. Evaporation of the filtrate gave **9g** (115 mg, 94%) as a pure (^{1}H NMR), colorless oil, identical to material obtained from tosylate **9f**.

***trans*-Octahydro-3a-methyl-2*H*-inden-2-one (9h) from 9g.** The apparatus described in the procedure for **9d** was used. Ozonized oxygen, cooled by passage through a glass coil immersed in a dry ice–acetone bath, was bubbled for 4 min into dry CH_2Cl_2 (19.6 mL) at −78 °C. The resulting solution was transferred into the other bulb of the apparatus, which contained a cold (−78 °C) solution of **9g** (54.1 mg, 0.24 mmol) in CH_2Cl_2 (4 mL) and MeOH (6 mL). The resulting solution was stirred for 5 min, and Ph_3P (188 mg, 0.72 mmol) was added. The cold bath was removed, and stirring was continued for 2 h. Evaporation of the solvent and flash chromatography of the residue over silica gel (2 × 18 cm), using 50% CH_2Cl_2–hexane, gave **9h** (22 mg, 60%) as a pure (^{1}H NMR), colorless oil: FTIR (CH_2Cl_2 solution) 2930, 2858, 1710, 1448, 1407, 1380, 1269, 1260, 1191, 1093 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.90 (s, 3 H), 1.25–1.98 (m, 10 H), 1.98–2.29 (m, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 17.16, 21.69, 24.91, 26.48, 38.52, 39.03, 41.39, 45.73, 55.68, 218.67; exact mass *m/z* calcd for $C_{10}H_{16}O$ 152.1201, found 152.1204. A satisfactory combustion analysis could not obtained.

(2*E*,3aα,7aβ)- and (2*Z*,3aα,7aβ)-2-Butylideneoctahydro-3a*H*-indene-3a-methanol (9d′). A solution of ester **9c′** (50.9 mg, 0.21 mmol) in THF (1 mL plus 1.5 mL rinse) was added dropwise to a stirred and cooled (ice bath) suspension of $LiAlH_4$ (16.3 mg, 0.43 mmol) in THF (1 mL). The ice bath was removed, and stirring was continued for 9 h. The mixture was recooled to ca. 0 °C (ice bath) and quenched by successive dropwise addition

of water (0.0165 mL), 15% aqueous NaOH (0.0165 mL), and water (0.05 mL). The mixture was stirred for 10 min and filtered through a pad (5 × 2 cm) of Celite. The pad was washed with EtOAc, and the combined filtrates were evaporated. Flash chromatography of the residue over silica gel (1 × 19 cm), using 15% EtOAc–hexane, gave **9d′** (42.9 mg, 96%) as a pure (^{1}H NMR), colorless oil which was a mixture of two diastereomers in a 1:1 ratio (^{1}H NMR): FTIR ($CHCl_3$ cast) 3324, 2925, 2859, 1456, 1055, 424 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.82–0.93 (t, 3 H), 0.95–1.14 (m, 2 H), 1.70–1.15 (br m, 9 H), 1.71–1.87 (m, 1 H), 2.56 (dd, J = 42.0, 17.0 Hz, 1 H), 3.24 (d, J = 12 Hz, 1 H), 3.79 (t, J = 10.0 Hz, 1 H), 5.24–5.48 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 13.90, 21.42, 21.47, 22.75, 22.89, 25.02, 25.17, 26.49, 26.53, 31.67, 32.37, 32.76, 33.01, 36.01, 39.59, 43.93, 44.61, 44.70, 47.78, 47.84, 60.36, 60.69, 123.13, 123.25, 139.41, 139.53; exact mass m/z calcd for $C_{14}H_{24}O$ 208.1827, found 208.1832. An analytical sample was prepared by Kugelrohr distillation (96 °C, 0.01 mmHg). Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 81.07; H, 11.50.

(2*E*,3a*α*,7a*β*)- and (2*Z*,3a*α*,7a*β*)-[2-Butylideneoctahydro-3a*H*-inden-3a-yl]methyl 4-Methylbenzenesulfonate (9e′). *p*-Toluenesulfonyl chloride (28 mg, 0.14 mmol) was added to a stirred and cooled (ice bath) solution of alcohol **9d′** (15 mg, 0.07 mmol) in pyridine (1 mL). The resulting solution was allowed to stand in a refrigerator (ca. 5 °C) for 4 days. The mixture was poured onto ice and extracted with ether (2 × 25 mL). The combined ether extracts were washed with 3 N hydrochloric acid (2 × 10 mL) and water (20 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (1 ×15 cm), using 5% EtOAc–hexane, gave a colorless oil (**9e′**) which was used directly in the next experiment without characterization.

(2*E*,3a*α*,7a*β*)- and (2*Z*,3a*α*,7a*β*)-2-Butylideneoctahydro-3a-methyl-1*H*-indene (9f″). Lithium triethylborohydride (0.15 mL, 1.0 M in THF, 0.15 mmol) was added dropwise to a stirred and cooled (ice bath) solution of tosylate **9e′** (0.07 mmol; assuming 100% conversion of the alcohol to the tosylate) in THF (1 mL). The cold bath was removed, and the solution was refluxed for 2 h. At this stage, only starting material was present (TLC). Lithium triethylborohydride (0.15 mL, 1.0 M in THF, 0.15 mmol), from a new bottle, was added to the above solution, and the mixture was refluxed for 4 h, cooled, quenched with water (2 mL), and extracted with ether (2 × 10 mL). The combined ether extracts were dried ($MgSO_4$) and evaporated. The residue was filtered through a pad (2 × 3 cm) of silica gel, using first pentane and then EtOAc. The pentane filtrate was evaporated, and Kugelrohr distillation (106 °C, 10 mmHg) of the residue gave **9f″** (48.2 mg, 49%) as a pure (^{1}H NMR), colorless oil which was a chromatographically (TLC) inseparable mixture of two isomers in a 1.1:1 ratio (^{1}H NMR): FTIR ($CHCl_3$ cast) 2957, 2925, 2858 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.72 (s, 1.8 H), 0.73 (s, 1.2 H), 1.10–1.83 (m, 12 H), 1.86–2.33 (m, 5 H), 5.20–5.31 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 13.90, 16.50, 17.09, 22.02, 22.05, 22.86, 22.94, 25.55, 25.71, 26.75, 26.80, 31.66, 32.31, 35.96, 38.93, 39.22, 39.81, 39.99, 45.33, 47.54, 47.69, 49.56, 122.28, 122.42, 140.40, 140.70; exact mass m/z calcd for $C_{14}H_{24}$ 192.1878, found 192.1875. Anal. Calcd for $C_{14}H_{24}$: C, 87.42; H, 12.58. Found: C, 87.28; H, 12.61.

Evaporation of the EtOAc filtrate and flash chromatography of the residue over silica gel (2 x 18 cm), using 15% EtOAc–hexane, gave recovered alcohol **9d′** (37.5 mg, 35%).

***cis*-Hexahydro-3a-methyl-7a-(3-phenyl-2-propynyl)-1(3*H*)-isobenzofuranone (10a).** The procedure employed for **8a** was followed, using *n*-BuLi (2.40 mL, 1.4 M in hexanes, 3.36 mmol), *i*-Pr_2NH (0.52 mL, 3.70 mmol) in THF (15 mL), lactone **10**[7b] (470 mg, 3.05 mmol) in THF (4 mL plus 1 mL rinse), and 3-bromo-1-phenylpropyne[13] (875 mg, 4.49 mmol) in THF (4 mL plus 1 mL rinse). Flash chromatography of the crude product over silica gel (2 × 15 cm) twice, using 10% EtOAc–hexane, afforded **10a** (742 mg, 90%) as a white solid: mp 40 °C; FTIR (CCl_4 cast) 1772, 1510, 1440, 1140, 1090, 1012 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.20 (s, 3 H), 1.22–1.82 (m, 7 H), 2.05 (m, 1 H), 2.57 (d, J = 1.0 Hz, 2 H), 3.88 (d, J = 8 Hz, 1 H), 4.14 (d, J = 8.5 Hz, 1 H), 7.21 (m, 3 H), 7.32 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 18.67 (q′), 21.38 (t′), 22.80 (t′), 25.17 (t′), 29.69 (t′), 35.59 (t′), 41.07 (s′), 48.55 (s′), 75.90 (t′), 83.54 (s′), 85.47 (s′), 123.25 (s′), 128.00 (d′), 128.24 (d′), 131.49 (d′), 179.45 (s′); exact mass m/z calcd for $C_{18}H_{20}O_2$ 268.1463, found 268.1453. Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.67; H, 7.68.

***cis*-7a-(2-Hexynyl)hexahydro-3a-methyl-1(3*H*)-isobenzofuranone (10a′).** The procedure employed for **7a** was followed, using *n*-BuLi (5.03 mL, 1.56 M in hexane, 7.85 mmol), *i*-Pr_2NH (1.15 mL, 8.19 mmol) in THF (8 mL), lactone **10** (1.053 g, 6.83 mmol) in THF (5 mL plus 1 mL rinse), and 1-bromo-2-hexyne[14] (1.3 mL, 10.2 mmol). Flash chromatography of the crude product over silica gel (4 x 18 cm), using 10% EtOAc–hexane, gave **10a′** (1.432 g, 90%) as a pure (^{1}H NMR), colorless oil: FTIR ($CHCl_3$ cast) 2933, 1773, 1013 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.97 (t, J = 7.0 Hz, 3 H), 1.16 (s, 3 H), 1.23–1.74 (m, 9 H), 1.96–2.06 (m, 1 H), 2.12 (tt, J = 7.0, 2.5 Hz, 2 H), 2.31 (dt, J = 17.0, 2.5 Hz, 1 H), 2.38 (dt, J = 17.0, 2.5 Hz, 1 H), 3.85 (d, J = 8.5 Hz, 1 H), 4.15 (d, J = 8.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 13.57, 18.26, 20.84, 21.45, 22.22, 22.95, 24.86, 29.54, 35.99, 41.05, 48.53, 75.46, 76.07, 83.53, 179.69; exact mass m/z calcd for $C_{15}H_{22}O_2$ 234.1620, found 234.1619. An analytical sample was prepared by Kugelrohr distillation (100 °C, 0.005 mmHg). Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 77.08; H, 9.46.

Methyl *cis*-1-(2-Hexynyl)-2-methyl-2-[(phenylseleno)-methyl]cyclohexanecarboxylate (10b′). The procedure employed for **7b** was followed, using PhSeSePh (175 mg, 0.56 mmol) and NaH (40 mg, 60% dispersion in oil, 1.0 mmol), THF (2 mL), 18-crown-6 (10 mg, 0.04 mmol), and lactone **10a′** (171 mg, 0.73 mmol) in THF (1 mL plus 0.5 mL rinse). The mixture was refluxed for 90 h. Flash chromatography of the crude product over silica gel (2 × 18 cm), using first 3% EtOAc–hexane and then 10% EtOAc–hexane, gave unreacted lactone **10a′** (140 mg, 82%) and selenide **10b′** (42 mg, 14%; 79% corrected for recovered starting material) as a pure (^{1}H NMR), pale yellow oil: FTIR ($CHCl_3$ cast) 2931, 1726, 1201, 734 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.92 (t, J = 7.5 Hz, 3 H), 1.09 (s, 3 H), 1.14–1.52 (m, 6 H), 1.55–1.65 (m, 1 H), 1.70–1.80 (m, 1 H), 1.97–2.13 (m, including tt (J = 7.0, 2.5 Hz) at δ 2.07, 4 H), 2.49 (dt, J = 15.0, 2.5 Hz, 1 H), 2.73 (br d, J = 12.0 Hz, 1 H), 2.88 (br d, J = 16.0 Hz, 1 H), 3.45 (br d, J = 12.0 Hz, 1 H), 3.70 (s, 3 H), 7.20–7.30 (m, 3 H), 7.44–7.55 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 13.34, 20.74, 21.04, 21.31, 22.13, 22.43, 23.00, 27.03, 33.65, 38.11, 39.54, 51.64, 53.06, 76.66, 82.64, 126.85, 129.03, 131.32, 133.01, 175.15; exact mass m/z calcd for $C_{22}H_{30}O_2Se$ 406.1410, found 406.1419. An analytical sample was prepared by Kugelrohr distillation (137 °C, 0.008 mmHg). Anal. Calcd for $C_{22}H_{30}O_2Se$: C, 65.17; H, 7.46; O, 7.89. Found: C, 65.24; H, 7.43; O, 7.73.

***cis*- and *trans*-Octahydro-1*H*-cyclohepta[*c*]furan-1-one (11).** A solution of *cis*- and *trans*-hexahydro-1*H*-cyclohepta[*c*]-furan-1,3-dione[32] (980 mg, 5.83 mmol) in THF (2 mL plus 1 mL rinse) was added dropwise (ca. 5 min) to a stirred and cooled (0 °C) suspension of $NaBH_4$ (232 mg, 95%, 5.83 mmol) in THF (4 mL). The ice bath was removed, and stirring was continued for 1 h. Hydrochloric acid (3 mL, 6 N) and then water (10 mL) were added, and the mixture was extracted with ether (3 × 30 mL). The combined extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (3 × 20 cm), using 15% EtOAc–hexane, gave lactone **11**[33] (558 mg, 62%) as a pure (^{1}H NMR), colorless oil and a mixed fraction of the *cis* and *trans* isomers (160 mg) in a 1.3:1 ratio (^{1}H NMR). The following data are for the mixed fraction: FTIR ($CHCl_3$ cast) 2928, 1771, 1171 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.23–2.47 (m, 11 H), 2.65–2.85 (m, 1 H), 3.71 (dd, J = 10.5, 9.0 Hz, 0.4 H), 3.90 (dd, J = 9.0, 5.0 Hz, 0.6 H), 4.32–4.44 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 26.25, 27.15, 28.13, 28.31, 30.50, 42.47, 45.01, 71.48, 179.69; exact mass m/z calcd for $C_9H_{14}O_2$ 154.0994, found 154.0996. An analytical sample was prepared by Kugelrohr distillation (100 °C, 10 mmHg). Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.93; H, 9.14.

***cis*-8a-(2-Hexynyl)octahydro-1*H*-cyclohepta[*c*]furan-1-one (11a).** Lithium bis(trimethylsilyl)amide was prepared by rapid addition of *n*-BuLi (8.84 mL, 1.6 M solution in hexane, 14.1 mmol) to a stirred and cooled (−78 °C) solution of bis-(trimethylsilyl)amine (3.11 mL, 14.7 mmol) in THF (20 mL).

(32) The corresponding diacids were made by Favorskii rearrangement (see ref 9), and the anhydrides were obtained by treatment with acetic anhydride (see ref 8). The individual *cis* and *trans* anhydrides have been reported; see: (a) Sicher, J.; Sipos, F.; Jonas, J. *Collect. Czech. Chem. Commun.* **1961**, *26*, 262. (b) Eberson, L.; Landström, L. *Acta Chem. Scand.* **1972**, *26*, 239.

(33) *cf.*: Iwasa, S.; Yamamoto, M.; Kohmoto, S.; Yamada, K. *J. Chem. Soc., Perkin Trans. I* **1991**, 1173.

The reagent was used immediately. Lactone **11** (1.817 g, 11.8 mmol) in THF (10 mL plus 3 mL rinse) was injected dropwise over 5 min, and the resulting solution was stirred for 40 min at −78 °C. 1-Bromo-2-hexyne[14] (2.23 mL, 17.7 mmol) was injected neat, and the cooling bath was removed. Stirring was continued overnight. The mixture was quenched with saturated aqueous NH_4Cl (10 mL) and extracted with ether (3 × 30 mL). The combined ethereal extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (5 × 15 cm), using 5% EtOAc–hexane, gave the *cis* isomer **11a** (2.451 g, 89%) as a pure (^1H NMR), colorless liquid: FTIR ($CHCl_3$ cast) 2920, 1766, 430 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.97 (t, J = 7.0 Hz, 3 H), 1.43–1.78 (m, 10 H), 1.79–1.87 (m, 2 H), 2.13 (tt, J = 7.0, 2.4 Hz, 2 H), 2.43 (dt, J = 17.0, 3.0 Hz, 1 H), 2.50 (dt, J = 17.0, 3.0 Hz, 1 H), 2.68–2.78 (m, 1 H), 3.95 (dd, J = 9.0, 4.5 Hz, 1 H), 4.47 (dd, J = 9.0, 9.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 13.52, 20.76, 22.33, 24.75, 26.63, 29.99, 30.92, 31.76, 34.73, 43.15, 50.86, 71.58, 75.52, 82.96, 181.53; exact mass m/z calcd for $C_{15}H_{22}O_2$ 234.1620, found 234.1616. An analytical sample was prepared by Kugelrohr distillation (72 °C, 0.075 mmHg). Anal Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 77.04; H, 9.35.

The *trans* isomer of **11a** (17 mg, 0.6%) was also isolated as a colorless oil which contained trace impurities (^1H NMR): FTIR (CCl_4 cast) 2961, 2932, 2064, 1772, 1174, 1164, 1114, 1025 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.96 (t, J = 7.5 Hz, 3 H), 1.30–2.00 (m, 12 H), 2.12 (tt, J = 7.0, 2.5 Hz, 2 H), 2.41 (dt, J = 16.0, 2.5 Hz, 1 H), 2.60 (dt, J = 16.0, 2.5 Hz, 1 H), 2.63–2.77 (m, 1 H), 4.09–4.24 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 13.52, 20.80, 21.27, 22.14, 22.26, 25.58, 26.02, 26.23, 36.68, 43.38, 49.01, 70.48, 75.12, 83.38, 180.76; exact mass m/z calcd for $C_{15}H_{22}O_2$ 234.1620, found 234.1616.

Methyl *cis*-1-(2-Hexynyl)-2-[(phenylseleno)methyl]cycloheptanecarboxylate (11b). The procedure employed for **7b** was followed, using PhSeSePh (387 mg, 1.24 mmol) and NaH (89 mg, 60% dispersion in oil, 2.23 mmol) in THF (4 mL), HMPA (0.20 mL, 1.15 mmol), and lactone **11a** (368 mg, 1.57 mmol) in THF (1 mL plus 0.5 mL as rinse). Flash chromatography of the crude product over silica gel (3 x 20 cm), using 3% EtOAc–hexane followed by 10% EtOAc–hexane, gave unreacted lactone **11a** (89 mg, 24%) and selenide **11b** (417 mg, 66%; 86% corrected for recovered starting material) as a pure (^1H NMR), pale yellow oil: FTIR ($CHCl_3$ cast) 2928, 1727, 1437, 1195, 1175, 737 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.95 (t, J = 7.0 Hz, 3 H), 1.30–1.97 (m, 11 H), 1.97–2.20 (m, 4 H), 2.28 (dt, J = 16.0, 2.5 Hz, 1 H), 2.47–2.70 (m, 2 H), 3.15 (dd, J = 12.0, 2.0 Hz, 1 H), 3.68 (s, 3 H), 7.21–7.34 (m, 3 H), 7.46–7.60 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 13.44, 20.76, 22.36, 22.62, 27.27, 28.31, 28.35, 29.41, 32.18, 34.67, 46.41, 51.57, 53.39, 76.83, 82.57, 126.96, 129.00, 130.38, 133.09, 175.55; exact mass m/z calcd for $C_{22}H_{30}O_2Se$ 406.1410, found 406.1423. An analytical sample was prepared by Kugelrohr distillation (104 °C, 0.005 mmHg). Anal. Calcd for $C_{22}H_{30}O_2Se$: C, 65.17; H, 7.46; O, 7.89. Found: C, 65.21; H, 7.21; O, 8.14.

Methyl (2*E*,3aα,8aβ)- and (2*Z*,3aα,8aβ)-2-Butylideneoctahydro-3a(1*H*)-azulenecarboxylate (11c). **(a)** The general procedure for radical cyclization was followed, using selenide **11b** (417 mg, 1.03 mmol) in benzene (30 mL), Ph_3SnH (542 mg, 1.55 mmol) in benzene (10 mL), and AIBN (17 mg, 0.10 mmol) in benzene (10 mL). At the end of the reaction the solvent was evaporated and Kugelrohr distillation (125–135 °C, 0.05 mmHg) of the residue followed by flash chromatography over silica gel (2 × 18 cm), using 2% EtOAc–hexane, gave **11c** (202 mg, 79%) as a pure (^1H NMR), colorless oil which was a chromatographically (TLC) inseparable mixture of two isomers in about a 1:1.2 ratio (^{13}C NMR): FTIR ($CHCl_3$ cast) 2926, 2856, 1729, 1452, 1195, 1158 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.82–0.91 (m, 3 H), 1.15–2.10 (m, 14 H), 2.15–2.74 (m, 5 H), 3.67 (two s, 3 H), 5.07–5.20 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 13.80, 13.82, 22.75, 22.79, 26.21, 27.25, 27.31, 27.96, 28.12, 29.55, 30.09, 31.45, 31.51, 37.31, 39.18, 39.79, 41.07, 45.46, 47.99, 48.20, 49.68, 51.14, 51.18, 54.96, 55.01, 120.66, 120.80, 139.77, 139.93, 176.93, 177.17; exact mass m/z calcd for $C_{16}H_{26}O_2$ 250.1933, found 250.1934. Anal. Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47. Found: C, 76.96; H, 10.49.

(b) Et_3B (1.0 mL, 1 M in hexane, 1.0 mmol) was added dropwise to a stirred solution of selenide **11b** (406 mg, 1.0 mmol) and Ph_3SnH (422 mg, 1.2 mmol) in hexane (100 mL) at room temperature (protection from moisture by a drying tube packed with Drierite). The mixture was stirred for 24 h and then evaporated. The residue was taken up in ether (10 mL), and a saturated solution of iodine in ether was added dropwise until the iodine color persisted. The resulting solution was washed with 10% aqueous $Na_2S_2O_3$ (15 mL) and brine (15 mL), and the combined aqueous washes were extracted with ether (15 mL). The combined ether extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (2 x 17 cm), using 5% CH_2Cl_2–hexane followed by 10% CH_2Cl_2–hexane, gave **11c** (237 mg, 95%) as a pure (^1H NMR), colorless oil, identical (^1H NMR) to material obtained by the general procedure for radical cyclization.

(2*E*,3aα,8aβ)- and (2*Z*,3aα,8aβ)-2-Butylidenedecahydroazulene-3a-methanol (11d). Ester **11c** (171 mg, 0.68 mmol) in THF (3 mL plus 1 mL rinse) was added dropwise to a stirred and cooled (ice bath) suspension of $LiAlH_4$ (54 mg, 1.4 mmol) in THF (3 mL). The cooling bath was removed, and stirring was continued for 14 h. The reaction mixture was recooled to 0 °C and quenchedby successive dropwise addition of water (0.055 mL), 15% aqueous NaOH (0.055 mL), and water (0.165 mL). The mixture was stirred for 10 min more and filtered through a pad (2 × 3 cm) of Celite. The pad was washed with EtOAc, and the combined filtrates were evaporated. Flash chromatography of the residue over silica gel (2 × 17 cm), using 15% EtOAc–hexane, gave **11d** (151 mg, 99%) as a pure (^1H NMR), colorless oil which was a chromatographically (TLC) inseparable mixture of two isomers in a 1:1 ratio (^1H NMR): FTIR (CH_2Cl_2 cast) 3334, 2955, 2922, 2858, 1465, 1452, 1377, 1035, 1021 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.87 (t, J = 7.5 Hz, 1.5 H), 0.88 (t, J = 7.5 Hz, 1.5 H), 0.96–1.13 (m, 1 H), 1.17–1.60 (m, 7 H), 1.60–2.20 (m, 10 H), 2.37–2.53 (m, 1 H), (2.55 (d, J = 16 Hz) and 2.69 (d, J = 17.0 Hz), 1 H), 3.40–3.52 (m, 1 H), 3.71 (br t, J = 10.5 Hz, 1 H), 5.10–5.26 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 13.89, 22.76, 22.90, 26.77, 26.82, 26.96, 27.05, 27.08, 27.36, 27.81, 31.49, 31.52, 36.68, 37.37, 37.93, 40.59, 41.76, 45.67, 46.38, 48.57, 48.80, 62.98, 63.24, 121.07, 121.09, 140.41, 140.52; exact mass m/z calcd for $C_{15}H_{26}O$ 222.1984, found 222.1984. An analytical sample was prepared by Kugelrohr distillation (102 °C, 0.005 mmHg). Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.78. Found: C, 81.11; H, 11.98.

(2*E*,3aα,8aβ)- and (2*E*,3aα,8aβ)-[2-Butylidenedecahydroazulen-3a-yl]methyl 2,4,6-Tris(1-methylethyl)benzenesulfonate (11e). 2,4,6-Triisopropylbenzenesulfonyl chloride (811 mg, 2.68 mmol) was added to a solution of alcohol **11d** (198 mg, 0.89 mmol) in pyridine (5 mL) at room temperature, and the solution was stirred at 90 °C (oil bath temperature) for 6 h, cooled, and poured onto ice. The resulting mixture was extracted with ether (3 × 20 mL), and the combined ether extracts were washed with 10% hydrochloric acid (10 mL) and brine (10 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (2 × 16 cm), using first hexane and then 5% EtOAc–hexane, gave **11e** as a colorless oil (334 mg, 76%) which was used directly in the next experiment without characterization.

(2*E*,3aα,8aβ)- and (2*E*,3aα,8aβ)-2-Butylidenedecahydro-3a-methylazulene (11f). Lithium triethylborohydride (3.4 mL, 1.0 M in THF, 3.4 mmol) was added dropwise to a stirred solution of sulfonate **11e** (334 mg, 0.68 mmol) in THF (2 mL), and the resulting solution was refluxed for 24 h. Additional lithium triethylborohydride (1.36 mL, 1.0 M in THF, 1.36 mmol) was added, and refluxing was continued for another 24 h. The mixture was cooled, quenched with 3 N aqueous NaOH (15 mL), and extracted with ether (3 × 20 mL). The combined ether extracts were dried ($MgSO_4$) and evaporated. The residue was filtered through a pad (3 × 5 cm) of silica gel with hexane. The hexane filtrate was evaporated, and Kugelrohr distillation (127 °C, 17 mmHg) of the residue gave **11f** (102 mg, 73%) as a pure (^1H NMR), colorless oil which was a chromatographically (TLC) inseparable mixture of two isomers in a 1.4:1 ratio (^1H NMR): FTIR (CCl_4 cast) 2955, 2923, 2859, 1464, 1449, 1376 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.79 (s, 1.75 H), 0.82 (s, 1.25 H), 0.87 (t, J = 7.5 Hz, 3 H), 1.15–2.22 (m, 18 H), 2.30–2.45 (m, 1 H), 5.09–5.19 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 13.90, 18.11, 18.80, 22.88, 22.97, 24.18, 26.68, 26.76, 26.80, 26.87, 28.07, 28.50, 31.52, 36.39, 40.22, 43.02, 43.53, 43.79, 44.03, 46.22, 46.31, 48.31, 52.65, 120.46, 120.55, 141.09, 141.31; exact mass m/z calcd for $C_{15}H_{26}$ 206.2034, found 206.2037. Anal. Calcd for $C_{15}H_{26}$: C, 87.30; H, 12.70. Found: C, 87.26; H, 12.79.

***trans*-Octahydro-3a-methyl-2(1*H*)-azulenone (11g).** The apparatus described in the procedure for **9d** was used. Ozonized oxygen, cooled by passage through a glass coil immersed in a dry ice–acetone bath, was bubbled for 4 min into dry CH_2Cl_2 (7.7 mL) at −78 °C. The resulting solution was transferred into the other bulb of the apparatus, which contained a cold (−78 °C) solution of **11f** (19.4 mg, 0.094 mmol) in CH_2Cl_2 (2 mL) and MeOH (2.5 mL). The resulting mixture was stirred for 5 min, and dimethyl sulfide (0.5 mL) was added. The cold bath was removed, and stirring was continued overnight. Evaporation of the solvent and flash chromatography of the residue over silica gel (2 × 15 cm), using 5% EtOAc–hexane, gave **11g**[24] (8.0 mg, 50%) as a pure (^{1}H NMR) oil: FTIR (CH_2Cl_2 cast) 2923, 2858, 1744, 1448, 1402, 1183 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.95 (s, 3 H), 1.25–1.90 (m, 10 H), 1.95 (dd, *J* = 18.0, 12.0 Hz, 1 H), 2.10 (s, 2 H), 2.13–2.23 (m, 1 H), 2.32 (dd, *J* = 18.0, 7.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 18.56, 26.43, 26.80, 28.19, 42.48, 43.41, 43.77, 44.99, 57.90, 218.98; exact mass *m/z* calcd for $C_{11}H_{18}O$ 166.1358, found 166.1355.

Octahydrocycloocta[*c*]furan-1(3*H*)-one (12). A solution of hexahydro-1*H*-cycloocta[*c*]furan-1,3-dione[34] (4.710 g, 25.8 mmol) in THF (20 mL) was added dropwise over 10 min to a stirred and cooled (0 °C) suspension of $NaBH_4$ (1.115 g, 95%, 28 mmol) in THF (6 mL). After 1 h, the ice bath was removed and, after a further 2 h, the reaction was quenched by cautious addition of 6 N hydrochloric acid (11 mL). The mixture was diluted with water (50 mL) and extracted with ether (3 × 50 mL). The combined ether extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (5 × 18 cm), using 15% EtOAc–hexane, gave **12** (3.234 g, 74%), of undefined stereochemistry, as a pure (^{1}H NMR), colorless oil: FTIR ($CHCl_3$ cast) 2920, 1771, 1168, 1040, 1015 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.27–1.60 (m, 6 H), 1.63–1.90 (m, 5 H), 2.20–2.45 (m, 3 H), 3.65 (dd, *J* = 9.5, 9.0 Hz, 1 H), 4.37 (dd, *J* = 9.0, 8.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 25.21, 25.39, 27.08, 27.28, 30.12, 32.30, 41.64, 44.89, 71.94, 180.40; exact mass *m/z* calcd for $C_{10}H_{16}O_2$ 168.1150, found 168.1149. An analytical sample was prepared by Kugelrohr distillation (130 °C, 11 mmHg). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.10; H, 9.43.

***cis*-9a-(2-Hexynyl)octahydrocycloocta[*c*]furan-1(3*H*)-one (12a).** Lithium diisopropylamide was prepared by rapid addition of *n*-BuLi (3.5 mL, 1.56 M solution in hexanes, 5.5 mmol) to a stirred and cooled (−78 °C) solution of *i*-Pr_2NH (0.84 mL, 6.0 mmol) in THF (6 mL). The reagent was used immediately. Lactone **12** (841 mg, 5.0 mmol) in THF (4 mL plus 1 mL rinse) was added dropwise over 5 min, and the resulting solution was stirred for 40 min at −78 °C. 1-Bromo-2-hexyne[14] (1.0 mL, 7.6 mmol) was added neat. Stirring was continued at −78 °C for 2 h and then at ca. 0 °C (ice bath) for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (10 mL), and the mixture was extracted with ether (3 × 30 mL). The combined ether extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (4 × 18 cm), using 5% EtOAc–hexane, gave **12a** (900 mg, 72%) as a pure (^{1}H NMR), colorless oil: FTIR ($CHCl_3$ cast) 2928, 2860, 1772, 1464, 1190, 1158 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.97 (t, *J* = 7.5 Hz, 3 H), 1.20–1.93 (m, including q at δ 1.51 (*J* = 14.5 Hz), 13 H), 1.98–2.09 (m, 1 H), 2.13 (tt, *J* = 7.0, 2.5 Hz, 2 H), 2.35–2.44 (m, 1 H), 2.45 (dt, *J* = 17.0, 2.2 Hz, 1 H), 2.53 (dt, *J* = 17.0, 2.2 Hz, 1 H), 3.88 (dd, *J* = 9.0, 2.2 Hz, 1 H), 4.57 (dd, *J* = 9.0, 7.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 13.46, 20.74, 22.21, 23.64, 25.10, 25.61, 25.92, 27.64, 30.142, 32.10, 44.69, 48.95, 74.62, 75.09, 83.37, 180.60; exact mass *m/z* calcd for $C_{16}H_{24}O_2$ 248.1776, found 248.1774. An analytical sample was prepared by Kugelrohr distillation (110 °C, 0.01 mmHg). Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.37; H, 9.66.

Methyl *cis*-1-(2-Hexynyl)-2-[(phenylseleno)methyl]cyclooctanecarboxylate (12b). The procedure for **7b** was followed, using PhSeSePh (767 mg, 2.46 mmol) and NaH (177 mg, 60% dispersion in oil, 4.43 mmol) in THF (8 mL). HMPA (0.50 mL, 2.9 mmol) was added to the cooled mixture followed by lactone **12a** (796 mg, 3.20 mmol) in THF (2 mL plus 1 mL rinse). The mixture was refluxed for 13 h (TLC control), cooled to room temperature, and quenched by addition of MeOH (4 mL). The solvents were evaporated, and water was added. The mixture was extracted with ether (1 × 20 mL), and the aqueous layer was acidified with 6 N hydrochloric acid and extracted with ether (3 × 50 mL). The combined ether extracts were dried ($MgSO_4$) and evaporated. The residue was dissolved in ether (5 mL), and CH_2N_2 in ether was added until nitrogen evolution ceased. Evaporation of the solvent and flash chromatography of the residue over silica gel (4 × 18 cm), using 3% EtOAc–hexane followed by 10% EtOAc–hexane, gave unreacted lactone **12a** (159 mg, 19%) and selenide **12b** (983 mg, 69%; 85% corrected for recovered starting material) as a pure (^{1}H NMR), pale yellow oil: FTIR ($CHCl_3$ cast) 2926, 1728, 1204, 738 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.93 (t, *J* = 7.5 Hz, 3 H), 1.20–1.72 (m, including q at δ 1.46 (*J* = 7.5 Hz), 10 H), 1.72–1.87 (m, 2 H), 1.87–2.13 (m, 5 H), 2.16–2.28 (m, 1 H), 2.35 (t, *J* = 11.5 Hz, 1 H), 2.72 (br d, *J* = 12.0 Hz, 1 H), 3.23 (dd, *J* = 12.0, 2.0 Hz, 1 H), 3.68 (s, 3 H), 7.22–7.31 (m, 3 H), 7.46–7.55 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 13.44, 20.80, 22.41, 23.36, 25.38, 25.84, 27.03, 30.19, 30.27, 30.44, 33.98, 43.23, 51.53, 52.98, 76.91, 82.53, 127.08, 129.07, 130.22, 133.28, 175.06; exact mass *m/z* calcd for $C_{23}H_{32}O_2Se$ 420.1567, found 420.1575. An analytical sample was prepared by Kugelrohr distillation (145 °C, 0.01 mmHg). Anal. Calcd for $C_{23}H_{32}O_2Se$: C, 65.86; H, 7.69; O, 7.63. Found: C, 66.01; H, 7.67; O, 7.80.

Methyl (2*E*,3aα,9aβ)- and (2*Z*,3aα,9aβ)-2-Butylidenedecahydro-3a*H*-cyclopentacyclooctene-3a-carboxylate (12c). (a) The general procedure for radical cyclization was followed, using selenide **12b** (426 mg, 1.0 mmol) in benzene (40 mL), Ph_3SnH (534 mg, 1.5 mmol) in benzene (10 mL), and AIBN (17 mg, 0.1 mmol) in benzene (10 mL). The crude product was taken up in ether (25 mL), and a saturated solution of iodine in ether was added dropwise until the iodine color persisted. The solution was washed with 10% aqueous $Na_2S_2O_3$ (10 mL) and brine (10 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (3 × 20 cm), using first 5% CH_2Cl_2–hexane followed by 10% CH_2Cl_2–hexane, gave **12c** (206 mg, 77%) as a pure (^{1}H NMR), colorless oil which was a chromatographically (TLC) inseparable mixture of two isomers in a 1:1 ratio (^{1}H NMR): FTIR ($CHCl_3$ cast) 2952, 2925, 2870, 1727, 1202, 1166 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.88 (t, *J* = 7.5 Hz, 1.5 H), 0.89 (t, *J* = 7.5 Hz, 1.5 H), 1.24–1.77 (m, 13 H), 1.86–1.97 (m, 2 H), 2.06–2.51 (m, 5 H), (2.59 (d, *J* = 16.0 Hz) and 2.71 (d, *J* = 17.0 Hz), 1 H), 3.65 (s, 1.5 H), 3.66 (s, 1.5 H), 5.12–5.23 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 13.83, 13.85, 22.75, 22.78, 22.80, 24.94, 25.10, 26.60, 30.70, 30.77, 30.81, 30.96, 31.39, 35.69, 36.02, 37.12, 40.82, 42.52, 42.73, 42.78, 46.99, 51.23, 51.29, 54.45, 54.71, 120.41, 120.54, 139.18, 177.16, 177.26; exact mass *m/z* calcd for $C_{17}H_{28}O_2$ 264.2089, found 264.2089. An analytical sample was prepared by Kugelrohr distillation (85 °C, 0.01 mmHg). Anal. Calcd for $C_{17}H_{28}O_2$: C, 77.22; H, 10.67. Found: C, 77.38; H, 10.97.

(b) Et_3B (1.3 mL, 1 M in hexane, 1.3 mmol) was added dropwise to a stirred solution of selenide **12b** (559 mg, 1.33 mmol) and Ph_3SnH (561 mg, 1.6 mmol) in hexane (130 mL) at room temperature (protection from moisture by a drying tube packed with Drierite). After 24 h, the solvent was evaporated and the residue was taken up in ether (25 mL). A saturated solution of iodine in ether was added dropwise until the iodine color persisted. The solution was washed with 10% aqueous $Na_2S_2O_3$ (10 mL) and brine (10 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (3 × 14 cm), using 3% EtOAc–hexane, gave **12c** (306 mg, 87%) as a colorless oil which was a chromatographically (TLC) inseparable mixture of two isomers identical (^{1}H NMR) to material obtained by the general procedure for radical cyclization.

Methyl *trans*-Decahydro-2-oxo-3a*H*-cyclopentacyclooctene-3a-carboxylate (12d). The apparatus described in the procedure for **9d** was used. Ozonized oxygen, cooled by passage through a glass coil immersed in a dry ice–acetone bath, was bubbled for 4 min into dry CH_2Cl_2 (21 mL) at −78 °C. The resulting solution was transferred into the other bulb of the apparatus, which contained a cold (−78 °C) solution of **12c** (67 mg, 0.25 mmol) in CH_2Cl_2 (4 mL) and MeOH (6 mL). The resulting mixture was stirred for 5 min, and Ph_3P (200 mg, 0.75

(34) The corresponding diacid was made by Favorskii rearrangement (see ref 9), and the anhydride was obtained by treatment with acetic anhydride (see ref 8). The material was used without stereochemical characterization. *cis*- and *trans*-cyclooctane-1,2-dicarboxylic acids are known; see ref 32a.

mmol) was then added. The cold bath was removed, and stirring was continued for 1.5 h. Evaporation of the solvent and flash chromatography of the residue over silica gel (2 × 19 cm), using 20% EtOAc–hexane, gave **12d** (47 mg, 82%) as a pure (^{1}H NMR), colorless oil: FTIR ($CHCl_3$ cast) 2922, 1751, 1729, 1204 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.20–1.35 (m, 1 H), 1.39–1.90 (m, 5 H), 2.12–2.46 (m, 4 H), 2.50–2.67 (m, 2 H), 3.70 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 22.31, 24.45, 26.34, 31.21, 31.31, 34.19, 39.20, 44.48, 51.41, 51.90, 53.04, 215.50; exact mass *m/z* calcd for $C_{13}H_{20}O_3$ 224.1412, found 224.1411. An analytical sample was prepared by Kugelrohr distillation (85 °C, 0.12 mmHg). Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.41; H, 8.73.

(2*E*,3aα,9aβ)- and (2*Z*,3aα,9aβ)-2-Butylidenedecahydro-3a*H*-cyclopentacyclooctene-3a-methanol (12e). Ester **12c** (302 mg, 1.14 mmol) in THF (5 mL plus 1 mL rinse) was added dropwise to a stirred and cooled (ice bath) suspension of $LiAlH_4$ (92 mg, 2.3 mmol) in THF (3 mL). The ice bath was removed, and stirring was continued for 20 h. The reaction was quenched by successive dropwise addition of water (0.09 mL), 15% aqueous NaOH (0.09 mL), and water (0.30 mL). The mixture was stirred for 20 min and filtered through a pad (2 × 3 cm) of Celite. The pad was washed with EtOAc, and the combined filtrates were evaporated. Flash chromatography of the residue over silica gel (2 × 15 cm), using 10% EtOAc–hexane, gave **12e** (269 mg, 100%) as a pure (^{1}H NMR), colorless oil which was a chromatographically (TLC) inseparable mixture of two isomers in a ratio of ca. 1:1 (^{13}C NMR): FTIR (CCl_4 cast) 3330, 2923, 2860, 1470, 1449, 1045, 1037 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.89 (t, *J* = 7.5 Hz, 3 H), 1.20–2.06 (m, 18 H), 2.10–2.46 (m, 4 H), 3.40–3.63 (m, 2 H), 5.16–5.28 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 13.92, 22.21, 22.77, 22.90, 25.76, 26.57, 29.62, 29.97, 31.47, 31.55, 32.34, 32.40, 34.41, 34.84, 36.32, 39.50, 39.55, 39.94, 40.07, 44.34, 46.03, 46.25, 66.36, 66.55, 121.47, 121.63, 139.39, 139.53; exact mass *m/z* calcd for $C_{16}H_{28}O$ 236.2140, found 236.2143. Anal. Calcd for $C_{16}H_{28}O$: C, 81.29; H, 11.94. Found: C, 81.33; H, 12.03.

(2*E*,3aα,9aβ)- and (2*Z*,3aα,9aβ)-[2-Butylidenedecahydro-3a*H*-cyclopentacycloocten-3a-yl]methyl 4-Methylbenzenesulfonate (12f). *p*-Toluenesulfonyl chloride (384 mg, 2.0 mmol) was added to a solution of alcohol **12e** (238 mg, 1.0 mmol) in pyridine (5 mL) at 0 °C (ice bath). Stirring was continued for 24 h, the cooling bath being allowed to attain room temperature. The mixture was poured onto ice and extracted with ether (3 × 25 mL). The combined ether extracts were washed with 10% hydrochloric acid (2 × 10 mL) and water (20 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (2 × 15 cm), using 5% EtOAc–hexane, gave the product as a viscous oil which was used directly in the next experiment without characterization.

(2*E*,3aα,9aβ)- and (2*Z*,3aα,9aβ)-2-Butylidenedecahydro-3a-methyl-1*H*-cyclopentacyclooctene (12g). Lithium triethylborohydride (5.0 mL, 1.0 M in THF, 5.0 mmol) was added dropwise to a stirred solution of tosylate **12f** (1.0 mmol; assuming 100% conversion of the alcohol into the tosylate) in THF (2 mL). The resulting solution was refluxed for 17 h. An additional quantity of lithium triethylborohydride (6.0 mL, 1.0 M in THF, 6.0 mmol) was added, and refluxing was continued for another 48 h. The mixture was cooled, quenched with 3 N aqueous NaOH (20 mL), and extracted with ether (3 × 20 mL). The combined ether extracts were washed with brine, dried ($MgSO_4$), and evaporated. The residue was filtered through a pad (3 × 5 cm) of silica gel, using first hexane (100 mL) and then EtOAc (100 mL). The hexane filtrate was evaporated, and the residue was chromatographed over silica gel (three times) (2 × 16 cm), using 100% hexane, to give **12g** (21 mg, 9%) as a pure (^{1}H NMR), colorless oil which was a chromatographically (TLC) inseparable mixture of two isomers in a 1.5:1 ratio (^{1}H NMR): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.76 (d, *J* = 0.7 Hz, 1.8 H), 0.79 (s, 1.2 H), 0.88 (t, *J* = 7.5 Hz, 1.2 H), 0.89 (t, *J* = 7.5 Hz, 1.8 H), 1.24–1.82 (m, 15 H), 1.84–2.40 (m, 6 H), 5.10–5.23 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 13.91, 20.54, 21.16, 22.52, 22.87, 22.96, 25.63, 26.41, 29.80, 30.18, 31.47, 31.53, 32.31, 32.35, 36.01, 39.63, 40.05, 41.46, 41.71, 46.13, 50.18, 120.87, 121.07, 140.19, 140.40. A satisfactory combustion analysis could not be obtained.

***trans*-Decahydro-3a-methyl-2*H*-cyclopentacycloocten-2-one (12h).** The apparatus described in the procedure for **9d** was used but with one modification. Ozonized oxygen, cooled by passage through a glass coil immersed in a dry ice acetone bath, was bubbled for 4 min into dry CH_2Cl_2 (7.5 mL) at −78 °C. The resulting solution was transferred into the other bulb of the apparatus, which contained a cold (−78 °C) solution of **12g** (20 mg, 0.09 mmol) in CH_2Cl_2 (2 mL) and MeOH (2.5 mL). The resulting mixture was stirred for 5 min, and dimethyl sulfide (instead of Ph_3P, 0.05 mL) was then added. The cold bath was removed, and stirring was continued for 12 h. Flash chromatography of the crude product over silica gel (2 × 15 cm), using 5% EtOAc–hexane, gave **12h** (11 mg, 65%) as a colorless oil: FTIR ($CHCl_3$ cast) 2922, 1751, 1729, 1204 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.94 (d, *J* = 0.8 Hz, 3 H), 1.30–1.94 (m, 13 H), 2.05 (ddd, *J* = 18.5, 12.5, 1.5 Hz, 1 H), 2.23 (d, *J* = 16.5 Hz, 1 H), 2.31 (d, *J* = 18.0 Hz, 1 H), 2.30–2.46 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 21.07, 22.27, 25.35, 26.16, 29.77, 32.02, 39.51, 40.62, 44.48, 55.77, 218.59; exact mass *m/z* calcd for $C_{12}H_{20}O$ 180.1514, found 180.1512. Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.22; H, 11.55.

***Se*-Phenyl *O*-(2-Cyclohexen-1-ylmethyl) Selenocarbonate (14).** Phosgene (ca. 6 mL) was condensed in a cooled (−78 °C) three-necked 200-mL flask. A solution of 2-cyclohexenemethanol[35] (2.241 g, 20 mmol) and triethylamine (3.3 mL, 24 mmol) in THF (20 mL) was added dropwise (ca. 10 min). The cold bath was removed, and stirring was continued for 40 min. The mixture was then concentrated under reduced pressure to about half its original volume, and a solution of benzeneselenol (2.76 mL, 26 mmol) and pyridine (1.9 mL, 24.6 mmol) in THF (20 mL) was added with stirring (argon atmosphere). After 45 min, the mixture was quenched with water (30 mL) and extracted with ether (3 × 25 mL). The combined ether extracts were washed with brine (25 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (4 × 16 cm), using 5% CH_2Cl_2–hexane, gave **14** (4.952 g, 84%) as a pure (^{1}H NMR), pale yellow oil: FTIR (neat film) 2931, 1729, 1478, 1439, 1121, 1074, 1022, 739, 723, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.25–1.40 (m, 1 H), 1.46–1.62 (m, 1 H), 1.65–1.82 (m, 2 H), 1.94–2.40 (m, 2 H), 2.40–2.54 (m, 1 H), 4.18 (d, *J* = 13.5 Hz, 2 H), 5.47–5.55 (m, 1 H), 5.75–5.84 (m, 1 H), 7.30–7.45 (m, 3 H), 7.58–7.68 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 20.50, 25.13, 25.49, 34.95, 71.60, 126.13, 126.34, 129.10, 129.27, 129.94, 135.83, 166.96; exact mass *m/z* calcd for $C_{14}H_{16}O_2Se$ 296.0315, found 296.0321. An analytical sample was prepared by Kugelrohr distillation (135 °C, 12 mmHg). Anal. Calcd for $C_{14}H_{16}O_2Se$: C, 56.96; H, 5.46; O, 10.84. Found: C, 57.20; H, 5.58; O, 10.74.

[3aα,7aα (*R)]- and [3aα,7aα(*S**)]-Hexahydro-7a-(1-hydroxy-3-phenyl-2-propynyl)-1(3*H*)-isobenzofuranone (15).** The procedure employed for **7a** was followed, using *n*-BuLi (1.40 mL, 1.6 M in hexanes, 2.24 mmol), *i*-Pr_2NH (0.35 mL, 2.5 mmol) in THF (10 mL), lactone **9** (280 mg, 2.00 mmol) in THF (3 mL plus 1 mL as a rinse), and 3-phenyl-2-propynal[36] (380 mg, 2.92 mmol) in THF (3 mL plus 1 mL as a rinse). The mixture was stirred at −78 °C for 1.5 h and quenched with saturated aqueous NH_4Cl (10 mL). Flash chromatography of the crude product over silica gel (3 × 16 cm), using 25% EtOAc–hexane, followed by Kugelrohr distillation (125–130 °C, 0.05 mmHg) gave **15** (513 mg, 95%) as a pure (^{1}H NMR), colorless oil which was a chromatographically (TLC) inseparable mixture of two isomers in a 1:1 ratio (^{1}H NMR): FTIR (CCl_4 cast) 3440, 2933, 1763, 1753, 1490, 1211, 1070, 1052, 1021, 758, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.35–2.05 (m, 7 H), 2.05–2.25 (m, 1 H), 2.70–2.85 (m, 0.5 H), 2.95–3.15 (m, 1 H), 3.45–3.55 (m, 0.5 H), 4.0–4.17 (m, 1 H), 4.35–4.50 (m, 1 H), 4.72–4.87 (m, 1 H), 7.22–7.50 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 20.54, 20.71, 21.38, 23.54, 24.88, 25.33, 25.52, 35.88, 36.68, 49.67, 65.05, 66.22, 69.71, 69.90, 86.50, 87.08, 87.20, 87.30, 122.04, 128.33, 128.79, 131.76, 179.48, 180.44; exact mass *m/z* calcd for $C_{17}H_{18}O_3$ 270.1256, found 270.1255. Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.24; H, 6.77.

[3aα,7aα(*R)]- and [3aα,7aα(*S**)]-7a-[1-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-3-phenyl-2-propynyl]hexahydro-1(3*H*)-isobenzofuranone (15a).** Triethylamine (1.3 mL, 9.5 mmol) and 4-(*N*,*N*-dimethylamino)pyridine (25 mg, 0.20 mmol) were added to a stirred solution of alcohols **15** (511 mg, 1.9 mmol) in DMF (2 mL). *tert*-Butyldimethylsilyl chloride (1.430 g, 9.5

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mmol) in DMF (1.5 mL plus 0.5 mL rinse) was added, and the resulting suspension was stirred for 66 h. More 4-(*N,N*-dimethylamino)pyridine (25 mg, 0.20 mmol) was added, and the mixture was heated at 50 °C (oil bath temperature) for 24 h, cooled, quenched with water (5 mL), and extracted with ether (3 × 20 mL). The combined ether extracts were washed with saturated aqueous NH_4Cl (1 × 10 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (4 × 19 cm), using 5% EtOAc–hexane, gave **15a** (621 mg, 85%) as a pure (^1H NMR), colorless oil which was a mixture of two diastereomers in a 1.2:1 ratio (^1H NMR). The diastereomers were separated by flash chromatography over silica gel, using 5–7% EtOAc–hexane mixtures of increasing polarity. **Faster moving diastereomer**: FTIR ($CHCl_3$ cast) 2930, 2857, 1770, 1088, 1082, 840, 783, 758, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.15 (s, 3 H), 0.20 (s, 3 H), 0.90 (s, 9 H), 1.22–1.41 (m, 3 H), 1.52–1.63 (m, 1 H), 1.66–1.83 (m, 2 H), 1.89–2.06 (m, 2 H), 2.93–3.02 (m, 1 H), 3.88 (dd, J = 8.0, 3.5 Hz, 1 H), 4.53 (dd, J = 8.0, 6.5 Hz, 1 H), 4.63 (s, 1 H), 7.30–7.48 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ -5.49, -4.56, 18.06, 21.53, 21.65, 25.67, 27.36, 26.03, 35.51, 52.17, 69.38, 72.05, 86.71, 88.20, 122.44, 128.43, 128.66, 131.47, 179.27; exact mass m/z (M - t-Bu) calcd for $C_{19}H_{23}O_3Si$ 327.1416, found 327.1415. An analytical sample was prepared by Kugelrohr distillation (143 °C, 0.008 mmHg). Anal. Calcd for $C_{23}H_{32}O_3Si$: C, 71.83; H, 8.39. Found: C, 71.52; H, 8.44.

Slower moving diastereomer: FTIR ($CHCl_3$ cast) 2929, 1772, 1070, 839 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.17 (s, 3 H), 0.22 (s, 3 H), 0.94 (s, 9 H), 1.30–1.47 (m, 3 H), 1.47–1.60 (m, 1 H), 1.66–1.80 (m, 1 H), 1.80–2.04 (m, 3 H), 2.86–2.97 (m, 1 H), 3.95 (dd, J = 9.0, 5.0 Hz, 1 H), 4.50 (dd, J = 9.0, 7.0 Hz, 1 H), 4.76 (s, 1 H), 7.29–7.45 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ -5.02, -4.38, 18.25, 21.10, 21.69, 25.84, 26.52, 27.40, 36.11, 51.70, 68.15, 70.57, 86.72, 87.73, 122.43, 128.37, 128.62, 131.61, 178.35; exact mass m/z (M - t-Bu) calcd for $C_{19}H_{23}O_3Si$ 327.1416, found 327.1418. An analytical sample was prepared by Kugelrohr distillation (140 °C, 0.010 mmHg). Anal. Calcd for $C_{23}H_{32}O_3Si$: C, 71.83; H, 8.39. Found: C, 71.91; H, 8.33.

Methyl [1α,1(*R),2α]- and [1α,1(*S**),2α]-1-[1-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-3-phenyl-2-propynyl]-2-[(phenylseleno)methyl]cyclohexanecarboxylate (15b).** The procedure employed for **7b** was followed, using PhSeSePh (237 mg, 0.76 mmol) and NaH (55 mg, 60% dispersion in oil, 1.37 mmol), THF (2.5 mL), HMPA (0.18 mL, 1.0 mmol), and lactone **15a** (slow isomer) (379 mg, 1.0 mmol) in THF (2 mL plus 1 mL rinse). The mixture was refluxed for 12 h, cooled to room temperature, and quenched by addition of MeOH (2 mL). The solvents were evaporated, and water (5 mL) was added to the residue. The mixture was extracted with ether (1 × 20 mL), and the aqueous layer was then acidified with 3 N hydrochloric acid. The acidic solution was extracted quickly with ether (2 × 15 mL), and the combined ethereal extracts were dried ($MgSO_4$) and evaporated. The residue was dissolved in ether (5 mL), and CH_2N_2 in ether was added until nitrogen evolution ceased. Evaporation of the solution and flash chromatography of the residue over silica gel (a) (4 × 18 cm), using EtOAc–hexane mixtures (from 0% to 15% EtOAc), (b) (4 × 18 cm), using EtOAc–hexane mixtures (from 3% to 5% EtOAc), and (c) (3 × 18 cm), using first 10% CH_2Cl_2–hexane (to remove PhSeSePh) and then 5% EtOAc–hexane, gave selenide **15b** (356 mg, 65%) as a pure (^1H NMR), pale yellow oil: FTIR ($CHCl_3$ cast) 2928, 2855, 1738, 1215, 1136, 1081, 838, 778, 756, 735, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.12 (s, 3 H), 0.18 (s, 3 H), 0.88 (s, 9 H), 1.05–1.36 (m, 2 H), 1.53–1.79 (m, 4 H), 2.03–2.16 (m, 2 H), 2.23–2.32 (m, 1 H), 2.98 (dd, J = 12.0, 11.5 Hz, 1 H), 3.54 (dd, J = 12.5, 2.5 Hz, 1 H), 3.70 (s, 3 H), 5.12 (s, 1 H), 7.07–7.14 (m, 3 H), 7.29–7.37 (m, 4 H), 7.46–7.54 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ -5.31, -4.23, 18.10, 23.07, 25.69, 25.95, 28.84, 29.45, 31.08, 43.11, 51.42, 57.41, 68.00, 87.55, 87.69, 122.68, 126.49, 128.31, 128.45, 128.95, 131.32, 131.60, 132.34, 173.93; exact mass m/z calcd for $C_{30}H_{40}O_3SiSe$ 556.1911, found 556.1920. An analytical sample was prepared by Kugelrohr distillation (158 °C, 0.005 mmHg). Anal. Calcd for $C_{30}H_{40}O_3SiSe$: C, 64.84; H, 7.26. Found: C, 65.10; H, 7.00.

Methyl [2*E*,3α,3aα,7aβ]-, [2*Z*,3α,3aα,7aβ]-, [2*E*,3α,3aβ,7aα]-, and [2*Z*,3α,3aβ,7aα]-3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]octahydro-2-(phenylmethylene)-3a*H*-indene-3a-carboxylate (15c). The general procedure for radical cyclization was followed, using selenide **15b** (327 mg, 0.59 mmol) in benzene (25 mL), Ph_3SnH (310 mg, 0.88 mmol) in benzene (10 mL), and AIBN (10 mg, 0.06 mmol) in benzene (10 mL). The crude product was taken up in ether (15 mL), and a saturated solution of iodine in ether was added until the iodine color persisted. The solution was washed with 10% aqueous $Na_2S_2O_3$ (10 mL) and brine (10 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (3 × 19 cm), using 15% CH_2Cl_2–hexane, gave **15c** (185 mg, 78%) as a pure (^1H NMR), colorless oil which was a chromatographically (TLC) inseparable mixture of two isomers in a 1.6:1 ratio (^1H NMR): FTIR ($CHCl_3$ cast) 2950, 2928, 2855, 1735, 1250, 1205, 1172, 1129, 1105, 1087, 1069, 854, 775 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ -0.43 (s, 1.8 H), -0.30 (s, 1.8 H), 0.10 (s, 1.2 H), 0.17 (s, 1.2 H), 0.77 (s, 5.4 H), 0.89 (s, 3.6 H), 1.08–1.36 (m, 2 H), 1.57–1.82 (m, 4 H), 1.88–2.10 (m, 2 H), 2.13–2.30 (m, 1 H), 2.38–2.69 (m, 2 H), 3.60 (s, 1.2 H), 3.71 (s, 1.8 H), 4.49 (s, 0.4 H), 5.10 (s, 0.6 H), 6.40 (s, 0.6 H), 6.45 (t, J = 2.5 Hz, 0.4 H), 7.10–7.38 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) -5.10, -5.03, -4.25, -3.75, 18.30, 23.32, 25.54, 25.73, 25.90, 25.98, 26.29, 26.45, 30.30, 30.50, 33.55, 34.54, 40.80, 43.22, 51.43, 59.41, 60.61, 74.31, 82.77, 126.56, 126.72, 127.07, 128.31, 128.52, 137.80, 138.25, 145.13, 145.29, 174.96, 175.10; exact mass m/z calcd for $C_{24}H_{36}O_3Si$ 400.2434, found 400.2428. An analytical sample was prepared by Kugelrohr distillation (123 °C, 0.010 mmHg). Anal. Calcd for $C_{24}H_{36}O_3Si$: C, 71.95; H, 9.06. Found: C, 71.72; H, 9.23.

(3aα,7aα,7aα)-Hexahydro-7-(2-propenyl)-1(3*H*)-isobenzofuranone (16). A solution of selenide **14** (1.471 g, 5.0 mmol), allyltributyltin (7.7 mL, 25 mmol), and hexabutylditin (0.26 mL, 0.51 mmol), in benzene (10 mL), was irradiated for 24 h with a sun lamp (General Electric, 275 W) placed about 5 cm from the reaction flask. Evaporation of the solvents and flash chromatography of the residue over silica gel (5 x 14 cm), using 10% EtOAc–hexane, gave **16** (647 mg, 72%) as a colorless oil containing slight impurities (^1H NMR): FTIR ($CHCl_3$ cast) 2928, 1769, 1172, 1136, 988 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.24–1.59 (m, 5 H), 1.70–1.83 (m, 1 H), 2.05–2.23 (m, 2 H), 2.23–2.38 (m, 1 H), 2.43 (dd, J = 7.0, 3.5 Hz, 1 H), 2.47–2.60 (m, 1 H), 3.99 (dd, J = 9.0, 3.5 Hz, 1 H), 4.19 (dd, J = 9.0, 5.5 Hz, 1 H), 5.00–5.13 (m, 2 H), 5.69–5.83 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 18.84, 26.18, 27.08, 31.80, 33.50, 37.46, 43.40, 71.39, 116.96, 136.48, 178.29; exact mass m/z calcd for $C_{11}H_{16}O_2$ 180.1150, found 180.1149. An analytical sample was prepared by Kugelrohr distillation (140 °C, 13 mmHg). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.41; H, 8.65.

(3aα,7aα,7aα)-7a-Hexylhexahydro-7-(2-propenyl)-1(3*H*)-isobenzofuranone (17). The procedure employed for **7a** was followed, using *n*-BuLi (2.32 mL, 1.60 M in hexanes, 3.71 mmol), *i*-Pr_2NH (0.54 mL, 3.87 mmol) in THF (3 mL), lactone **16** (581 mg, 3.23 mmol) in THF (3 mL plus 1 mL rinse), and 1-bromohexane (0.72 mL, 5.13 mmol). HMPA (0.60 mL, 3.45 mmol) was added, and the resulting solution was allowed to warm to room temperature. After 4 h, the mixture was quenched with saturated aqueous NH_4Cl (10 mL) and extracted with ether (2 × 15 mL). The combined ether extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (5 × 14 cm), using 10% EtOAc–hexane, gave **17** (681 mg, 80%) as a colorless oil containing trace impurities (^1H NMR): FTIR (CCl_4 cast) 2929, 2858, 1768, 1211, 1087, 1020, 1001, 910 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.90 (t, J = 7.0 Hz, 3 H), 1.00–1.90 (m, 18 H), 2.42–2.75 (m, 2 H), 4.14 (d, J = 2.0 Hz, 1 H), 4.19 (s, 1 H), 4.95–5.09 (m, 2 H), 5.55–5.78 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 14.07, 20.79, 21.55, 22.62, 24.84, 25.07, 26.20, 29.86, 31.76, 33.80, 36.66, 37.36, 47.53, 67.19, 116.59, 137.22, 180.14; exact mass m/z calcd for $C_{17}H_{28}O_2$ 264.2089, found 264.2106. An analytical sample was prepared by Kugelrohr distillation (145–148 °C, 11 mmHg). Anal. Calcd for $C_{17}H_{28}O_2$: C, 77.22; H, 10.67. Found: C, 77.23; H, 10.56.

Methyl *cis*- and *trans*-2-[(Phenylseleno)methyl]cycloheptanecarboxylate (18). The procedure for **7b** was followed, using PhSeSePh (0.7210 g, 2.31 mmol), NaH (60%, 0.1664 g, 4.16 mmol), THF (10 mL), and a reflux period of 2 h. The mixture was cooled to room temperature, and dry HMPA (1.0 mL) was injected in one portion to form a dark orange solution. Lactone **11** (0.4752 g, 3.08 mmol) in THF (5 mL) was then added by cannula; the mixture was refluxed for 12 h, cooled, carefully quenched with MeOH (3 mL), poured into 2 N hydrochloric acid,

and extracted with ether (4 × 25 mL). The combined organic extracts were dried ($MgSO_4$) and evaporated. The resulting thick oil was titrated with ethereal CH_2N_2 until bubbling ceased, and the solvent was then evaporated. Flash chromatography of the thick, orange residue over silica gel (2 × 30 cm), using 5% CH_2Cl_2–hexane, gave recovered starting material **11** (57.0 mg, 12%) (^1H NMR, 200 MHz) along with selenide **18** (687.3 mg, 69%; 78% corrected for recovered **11**) as a yellow oil: FTIR ($CHCl_3$ cast) 2824, 1730, 1105 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.32–2.00 (br m, 10 H), 2.01–2.22 (m, 1 H), 2.83–3.13 (m, 2 H), 3.63 (s, 3H), 7.18–7.30 (m, 3 H), 7.40–7.86 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) (signals assigned to major isomer) δ 26.30, 28.16, 28.42, 31.39, 32.45, 40.78, 45.21, 51.31, 126.78, 129.02, 130.54, 132.62, 175.52 (signals assigned to minor isomer) δ 25.11, 26.10, 27.18, 27.49, 28.00, 30.67, 46.42, 173.88; exact mass *m/z* calcd for $C_{16}H_{22}SeO_2$ 326.0794, found 326.0781. Anal. Calcd for $C_{16}H_{22}SeO_2$: C, 58.88; H, 6.80; O, 9.81. Found: C, 58.95; H, 6.76; O, 9.51.

Methyl *cis*- and *trans*-1-(2-Hexynyl)-2-[(phenylseleno)methyl]cycloheptanecarboxylate (19). *n*-BuLi (1.6 M in hexanes, 0.30 mL, 0.480 mmol) was added dropwise by syringe to a magnetically stirred and cooled (ice bath) solution of *i*-Pr_2NH (0.065 mL, 0.0465 mmol) in THF (7 mL). The solution was then cooled to −78 °C, and, after a further 10 min, a solution of ester **18** (0.1261 g, 3.88 mmol) in THF (3 mL) was added by cannula. After 30 min, the halide (0.1 mL, 0.790 mmol) was added in one portion. The cold bath was removed, and stirring was continued for 12 h. Saturated aqueous NH_4Cl (5 mL) was then added, and the mixture was extracted with ether (3 × 20 mL). The combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the yellow residue over silica gel (3 × 20 cm), using 5% EtOAc–hexane, gave **19** (1.0131, 64%) as a mixture (^1H NMR and ^{13}C NMR) of two isomers: FTIR ($CHCl_3$ cast) 2927, 1727, 1136 cm^{-1}; exact mass *m/z* calcd for $C_{22}H_{30}O_2Se$ 406.1409, found 406.1412.

***cis*-10,10-Dichloro-1-methylbicyclo[6.2.0]decan-9-one (21).** A solution of trichloroacetyl chloride (1.17 mL, 10.5 mmol) and phosphorus oxychloride (0.98 mL, 10.5 mmol) in ether (10 mL) was added dropwise over 1 h to a stirred suspension of activated zinc/copper couple (0.72 g) and *cis* 1-methylcycloocetene[37] (1.25 g, 10.1 mmol) in ether (20 mL). The resulting suspension was refluxed for 24 h, cooled, and filtered through a pad (2 × 5 cm) of Celite with ether (30 mL). The filtrate was evaporated to approximately 25% of its original volume and diluted with an equal volume of pentane. The solution was stirred for a few minutes to precipitate the zinc salts, then decanted from the dark brown residue, washed with water (10 mL), saturated aqueous $NaHCO_3$ (10 mL), and brine (10 mL), and evaporated. Flash chromatography of the residue over silica gel (4 × 16 cm), using 10% CH_2Cl_2–hexane, gave **21** (904 mg, 38%) as a pure (^1H NMR), colorless oil: ^1H NMR ($CDCl_3$, 200 MHz) δ 1.05–1.38 (m, 3H), 1.40 (s, 3H), 1.50–2.32 (m, 9 H), 3.84 (dd, *J* = 6.5, 2.5 Hz, 1 H). The material was used directly in the next step without full characterization.

***cis*-Decahydro-3a-methyl-2*H*-cyclopentacycloocten-2-one (22).** Ethereal CH_2N_2 (30 mL, 0.2 M, ca. 6.0 mmol) was added to **21** (0.9000 g, 3.8 mmol) followed by MeOH (2 mL). The solution was stirred for 12 h, the remaining CH_2N_2 was destroyed with a few drops of AcOH, and the solvent was evaporated. Flash chromatography of the residue over silica gel (4 × 16 cm), using 10% CH_2Cl_2–hexane, gave the ring-expansion product. This was dissolved in AcOH (5 mL), and Zn powder (1 g) was added. The stirred mixture was heated for 2 h at 65 °C, cooled, and filtered through a pad (2 × 5 cm) of Celite with EtOAc (70 mL). Evaporation of the filtrate and flash chromatography of the residue over silica gel (3 × 15 cm), using 5% EtOAc–hexane, gave **22** (196 mg, 28%) as a pure (^1H NMR), colorless oil: FTIR (CCl_4 cast) 2920, 2855, 1744, 1467, 1445, 1404, 1378, 1165, 514 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.08 (s, 3 H), 1.20–1.50 (m, 6 H), 1.60–2.20 (m, 10 H), 2.75 (ddd, *J* = 21.0, 9.0, 1.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 24.67, 25.38, 25.58, 25.84, 31.31, 33.30, 33.44, 41.48, 45.25, 49.46, 52.42, 219.74; exact mass *m/z* calcd for $C_{12}H_{20}O$ 180.15, found 180.1515. Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.01; H, 11.35.

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***cis*-7a-Hexylhexahydro-3a-methyl-1(3*H*)-isobenzofuranone (23) from 10a'.** Palladium (10 mg, 5% on carbon) was added to a solution of acetylene **10a'** (96 mg, 0.41 mmol) in EtOAc (2 mL). The flask was flushed with hydrogen, and the suspension was stirred under a hydrogen atmosphere (balloon) for 8 h. The mixture was filtered through a pad (3 × 2 cm) of Celite, and the pad was washed with EtOAc. Evaporation of the filtrate and flash chromatography of the residue over silica gel (2 × 14 cm), using 8% EtOAc–hexane, gave **23** (94 mg, 96%) as a pure (^1H NMR), colorless oil: FTIR (CCl_4 cast) 2932, 2859, 1773, 1106, 1012 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.87 (t, *J* = 7.0 Hz, 3 H), 1.06 (s, 3 H), 1.10–1.44 (m, 12 H), 1.44–1.64 (m, 5 H), 2.06–2.20 (m, 1 H), 3.76 (d, *J* = 8.5 Hz, 1 H), 3.99 (d, *J* = 8.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 14.06, 16.81, 21.38, 22.63, 23.23, 23.52, 27.82, 29.99, 31.66, 33.50, 36.35, 41.30, 48.44, 75.91, 180.04. Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 11.00. Found: C, 75.93; H, 11.24.

Ethyl *cis*- and *trans*-2-Hexyl-2-hydroxy-1-methylcyclohexanecarboxylate (25). A solution of 1-bromohexane (2.4 mL, 16.8 mmol) in THF (15 mL) was added dropwise to a stirred suspension of Mg turnings (490 mg, 20.2 mmol) in THF (5 mL). The mixture was then refluxed for 2 h, cooled to 0 °C (ice bath), and added by cannula to a stirred and cooled (−78 °C) solution of keto ester **24** (2.500 g, 14.0 mmol) in THF (20 mL). The resulting solution was stirred at −78 °C for 1 h, and the cold bath was then removed. After ca. 30 min, the mixture was quenched with saturated aqueous NH_4Cl (10 mL), extracted with ether (3 × 40 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (5 × 15 cm), using 5% EtOAc–hexane, gave **25** (2.15 g, 59%) as a colorless oil: ^1H NMR (80 MHz) δ 0.7–2.2 (m, 27 H), 3.0 (s, 1 H), 4.23 (q, *J* = 5.2 Hz, 2 H). The material was used directly in the next step without further characterization.

2-Hexyl-1-methyl-2-cyclohexene-1-methanol and (2*Z*)- and (2*E*)-2-Hexylidene-1-methylcyclohexanemethanol (27). *p*-Toluenesulfonic acid monohydrate (60 mg, 0.32 mmol) was added to a solution of alcohols **25** (1.76 g, 6.5 mmol) in xylene (65 mL). The solution was refluxed for 1 h. The condenser was removed and replaced by a setup for distillation, and most of the xylene was distilled off. Solid Na_2CO_3 (500 mg) was added to the residue which was then filtered through a pad (4 × 5 cm) of silica gel, and the filtrate was evaporated. The crude product in THF (5 mL) was added dropwise to a stirred and cooled (ice bath) suspension of $LiAlH_4$ (260 mg, 6.5 mmol) in THF (10 mL). The ice bath was removed and stirring was continued for 1.5 h. The reaction was quenched by successive dropwise addition of water (0.26 mL), 15% aqueous NaOH (0.26 mL), and water (0.78 mL). The mixture was stirred for 15 min and filtered through a pad (2 × 5 cm) of Celite. The pad was washed with ether (75 mL), and the filtrate was evaporated. Flash chromatography of the residue over silica gel (4 × 15 cm), using 10% EtOAc–hexane, gave the isomer mixture **27** (1.20 g, 88%). This material was used directly for the next step.

***Se*-Phenyl *O*-[(2-Hexyl-1-methyl-2-cyclohexen-1-yl)methyl] Selenocarbonate and *Se*-Phenyl *O*-[(2-Hexylidene-1-methylcyclohex-1-yl)methyl] Selenocarbonate (28).** A solution of alcohol **27** (1.14 g, 5.4 mmol) and triethylamine (0.91 mL, 6.5 mmol) in THF (20 mL) was added dropwise to an excess of phosgene (ca. 2 mL) at −78 °C. The cold bath was removed, and the mixture was stirred for 30 min. The mixture was then concentrated under reduced pressure to approximately half its original volume, and a solution of benzeneselenol (0.75 mL, 7.0 mmol) and pyridine (0.52 mL, 6.5 mmol) in THF (8 mL) was added. The mixture was stirred at room temperature for 45 min, quenched with water (15 mL), and extracted with ether (3 × 25 mL). The combined ether extracts were washed with brine (25 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (5 × 15 cm), using 5% CH_2Cl_2–hexane, gave **28** (1.97 g, 93%) as a colorless oil which was a chromatographically (TLC) inseparable mixture of two isomers in a 2.8:1 ratio (^1H NMR). The material was used directly in the next and final step of the sequence.

Conversion of 28 into *cis*-7a-Hexylhexahydro-3a-methyl-1(3*H*)-isobenzofuranone (23). Et_3B (1.0 mL, 1.0 M in hexane, 1.0 mmol) was added to a solution of selenocarbonates **28** (398 mg, 1.01 mmol) and Ph_3SnH (532 mg, 1.2 mmol) in hexane (100 mL) at room temperature (protection from moisture by a drying

tube packed with Drierite). After 24 h, the solvent was evaporated and flash chromatography of the residue over silica gel (4 × 16 cm), using 8% EtOAc–hexane, gave **23** (223 mg, 92%) as a colorless oil, identical to material obtained from **10a'**.

(1α,2α,3β)-3-Propyl-1,2-cyclohexanedimethanol (30). Palladium (2.0 mg, 5% on carbon) was added to a solution of olefin **16** (17 mg, 0.094 mmol) in EtOAc (1 mL). The flask was flushed with hydrogen, and the suspension was stirred under a hydrogen atmosphere (balloon) for 20 h. The mixture was filtered through a pad (3 × 2 cm) of Celite, and the pad was washed with ether. The filtrate was dried ($MgSO_4$) and evaporated. The residue was dissolved in tetrahydrofuran, and $LiAlH_4$ (10 mg, 0.25 mmol) was added. The mixture was stirred at room temperature for 3 h and quenched by successive dropwise addition of water (0.01 mL), 15% aqueous NaOH (0.01 mL), and water (0.03 mL). The mixture was stirred for 20 min and filtered through a pad (2 × 3 cm) of Celite. The pad was washed with ether, and the combined filtrates were evaporated. Flash chromatography of the residue over silica gel (2 × 14 cm), using 60% EtOAc–hexane, gave **30** (14.5 mg, 83%) as a pure (^1H NMR), colorless oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 0.90 (t, J = 7.0 Hz, 3 H), 1.10–1.72 (m, 12 H), 1.95–2.05 (m, 1 H), 3.20 (s, 2 H), 3.50–3.66 (m, 2 H), 3.74–3.94 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 14.44, 20.05, 21.28, 27.72, 28.91, 34.95, 35.05, 37.81, 44.13, 63.79, 65.04.

(1α,2α,3β)-3-Propyl-1,2-cyclohexanedimethanol Diacetate (31). Acetic anhydride (0.022 mL, 0.23 mmol) was added to a solution of diol **30** (14.5 mg, 0.078 mmol) and 4-(*N,N*-dimethylamino)pyridine (2 mg, 0.016 mmol) in pyridine (1.0 mL). The mixture was stirred for 4.5 h at room temperature, quenched by addition of saturated aqueous NH_4Cl (5 mL), and extracted with ether (2 × 15 mL). The combined ether extracts were washed with 2 N aqueous hydrochloric acid (2 × 5 mL) and brine (5 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (2 × 14 cm), using 15% EtOAc–hexane, gave **31** (18.8 mg, 89%) as a pure (^1H NMR), colorless oil: FTIR (CH_2Cl_2 cast) 2958, 2925, 2853, 1744, 1257, 1235 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.90 (s, 3 H), 1.16–1.68 (m, 11 H), 1.79–1.88 (m, 1 H), 2.05 (s, 6 H), 2.10–2.20 (m, 1 H), 4.00–4.21 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 13.98, 19.80, 20.19, 20.62, 25.89, 27.51, 33.72, 34.29, 34.57, 39.99, 64.24, 65.27, 170.66. Anal. Calcd for $C_{15}H_{26}O_4$: C, 66.63; H, 9.69. Found: C, 66.89; H, 9.87.

(1α,2α,3α)-3-Propyl-4-cyclohexene-1,2-dimethanol (34). Maleic anhydride (630 mg, 6.4 mmol) was added to a solution of diene **32**[28] (517 mg, 5.4 mmol) in benzene (5 mL), and the solution was refluxed for 3.5 h, cooled, and concentrated under reduced pressure to give a waxy solid which was taken up in THF (20 mL). $LiAlH_4$ (520 mg, 13 mmol) was added in small portions over 10 min (stirring), and the resulting suspension was refluxed for 24 h. The mixture was cooled to room temperature and quenched by successive dropwise addition (stirring) of water (0.5 mL), 15% aqueous NaOH (0.5 mL), and water (1.5 mL). Stirring was continued for 20 min, and the mixture was filtered through a pad (2 × 4 cm) of Celite. The pad was washed with EtOAc (100 mL), and the combined filtrates were evaporated. Flash chromatography of the residue over silica gel (4 × 14 cm), using 70% EtOAc–hexane, gave **34** (690 mg, 70%) as a colorless oil: FTIR (CH_2Cl_2 cast) 3299, 2957, 2928, 2896, 2873, 1655, 1034 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.94 (t, J = 7.0 Hz, 3 H), 1.20–1.50 (m, 4 H), 1.90–2.10 (m, 4 H), 2.10–2.40 (m, 1 H), 3.25 (br s, 1 H), 3.50–3.79 (m, 4 H), 5.40 (br d, J = 10 Hz, 1 H), 5.54–5.66 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 14.23, 20.49, 24.75, 35.30, 39.67, 40.53, 41.33, 57.83, 65.90, 125.87, 130.52; exact mass m/z calcd for $C_{11}H_{20}O_2$ 184.1463, found 184.1458.

(1α,2α,3α)-3-Propyl-1,2-cyclohexanedimethanol Diacetate (35). (a) Acetic anhydride (0.17 mL, 1.8 mmol) was added to a solution of diol **34** (110 mg, 0.6 mmol) and 4-(*N,N*-dimethylamino)pyridine (10 mg, 0.08 mmol) in pyridine (1.5 mL). The mixture was stirred for 5 h at room temperature, quenched by addition of saturated aqueous NH_4Cl (10 mL), and extracted with ether (2 × 15 mL). The combined ether extracts were washed with 2 M aqueous hydrochloric acid (2 × 5 mL) and brine (5 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (2 × 16 cm), using 15% EtOAc–hexane, gave (1α,2α,3α)-3-propyl-4-cyclohexene-1,2-dimethanol diacetate (127 mg, 79%) as a pure (^1H NMR), colorless oil: FTIR ($CHCl_3$ cast) 2958, 2924, 1742, 1369, 1235, 1037 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.93 (t, J = 7.0 Hz, 3 H), 1.20–1.50 (m, 4 H), 1.74–1.90 (m, 1 H), 2.00–2.30 (m, including at δ 2.04 and 2.07, 9 H), 3.92–4.20 (m, 4 H), 5.45 (br d, J = 10.0 Hz, 1 H), 5.58–5.67 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 14.18, 20.43, 20.96, 21.08, 25.87, 34.99, 35.86, 37.65, 39.54, 61.20, 67.42, 125.17, 130.47, 171.05; exact mass m/z calcd for $C_{15}H_{24}O_4$ 224.1776, found 224.1776. Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.14; H, 9.01. Found: C, 67.08; H, 9.23.

(b) Palladium (10 mg, 5% on carbon, 0.005 mmol) was added to a solution of the above olefin diacetate (120 mg, 0.45 mmol) in EtOAc (5 mL). The flask was flushed with hydrogen, and the suspension was stirred under a hydrogen atmosphere (balloon) for 4 h. The mixture was filtered through a pad (2 × 4 cm) of Celite, and the pad was washed with EtOAc. Evaporation of the filtrate and flash chromatography of the residue over silica gel (2 × 14 cm), using 15% EtOAc–hexane, gave **35** (121 mg, 100%) as a pure (TLC), colorless oil: FTIR (CH_2Cl_2 cast) 2927, 1741, 1369, 1244, 1037 cm^{-1}; ^1H NMR ($CDCl_3$ 300 MHz) δ 0.84–1.10 (m, including t at δ 0.90 (t, J = 7.0 Hz), 4 H), 1.10–1.40 (m, 6 H), 1.40–1.63 (m, 3 H), 1.74–1.96 (m, 2 H), 1.96–2.14 (m, including s at δ 2.02 and 2.05, 7 H), 3.92 (dd, J = 17.5, 7.5 Hz, 1 H), 4.01–4.18 (m, 3 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 14.31, 20.47, 20.97, 21.10, 24.41, 25.78, 28.28, 36.50, 38.15, 40.81 (two signals), 60.76, 67.54, 171.09 (two signals); mass (CI) m/z calcd for $C_{15}H_{26}O_4$ 270, found 271. Anal. Calcd for $C_{15}H_{26}O_4$: C, 66.64; H, 9.69. Found: C, 66.39; H, 9.81.

(3aα,7α,7aα)-7a-Hexylhexahydro-7-(2-oxoethyl)-1(3*H*)-isobenzofuranone (36). Ozone, precooled by passage through a glass coil immersed in a dry ice–acetone bath, was bubbled through a cold (−78 °C) solution of alkene **17** (633 mg, 2.4 mmol) in CH_2Cl_2 (50 mL). After the starting material had been consumed (6.5 min, TLC control), dimethyl sulfide (0.5 mL) was added and the resulting solution was stirred overnight at room temperature. Evaporation of the solvent and flash chromatography of the residue over silica gel (4 × 13 cm), using 15% EtOAc–hexane, gave **36** (356 mg, 55%) as a pure (TLC), colorless oil: ^1H NMR ($CDCl_3$, 200 MHz) δ 0.89 (t, J = 6.0 Hz, 3 H), 1.00–1.43 (m, 9 H), 1.43–1.75 (m, 7 H), 2.19–2.40 (m, 2 H), 2.58–3.00 (m, 2 H), 4.21 (d, J = 10.0 Hz, 2 H), 9.71 (d, J = 2.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 14.06, 20.68, 20.99, 22.59, 24.84, 26.50, 26.59, 29.79, 31.54, 31.71, 36.42, 44.33, 46.67, 67.28, 179.91, 201.03. The material was used directly without further characterization.

(3aα,7α,7aα)-7a-Hexylhexahydro-7-[2-oxo-1-(phenylseleno)ethyl]-1(3*H*)-isobenzofuranone (37). Concentrated hydrochloric acid (1 drop) was added to a stirred solution of aldehyde **36** (104 mg, 0.39 mmol) and benzeneselenenyl chloride (90 mg, 0.47 mmol) in EtOAc (4 mL). The mixture was stirred at room temperature for 9 h, and the solvent was then evaporated. Flash chromatography of the residue over silica gel (2 × 16 cm), using 15% EtOAc–hexane, gave unreacted aldehyde **36** (38 mg, 37%) and selenide **37** (96 mg, 60%; 93% corrected for recovered starting material) as a pure (^1H NMR), colorless oil which was a chromatographically (TLC) inseparable mixture of two isomers in a 1.4:1 ratio (^1H NMR): FTIR (CCl_4 cast) 2928, 2857, 1761, 1705, 1107, 1021, 741 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.80–0.94 (m, 3 H), 1.00–2.00 (m, 16 H), 2.26–2.35 (m, 0.4 H), 2.51 (dt, J = 21.5, 2.5 Hz, 0.6 H), 2.65–2.80 (m, 1 H), 4.07–4.26 (m, 3 H) 7.25–7.70 (m, 5 H), 9.36 (d, J = 2.0 Hz, 0.6 H), 9.52 (d, J = 6.0 Hz, 0.4 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 14.02, 14.09, 20.98, 21.09, 21.12, 21.75, 22.53, 22.62, 23.17, 25.06, 25.13, 25.96, 27.64, 27.71, 29.54, 29.82, 31.64, 31.68, 34.10, 36.40, 26.80, 42.76, 47.69, 48.87, 52.81, 54.71, 67.11, 67.28, 127.10, 127.75, 128.77, 128.90, 129.51, 129.67, 134.66, 135.02, 191.10, 191.89; exact mass m/z calcd for $C_{22}H_{30}O_3Se$ 422.1360, found 422.1359. An analytical sample was prepared by Kugelrohr distillation (150–155 °C, 0.20 mmHg). Anal. Calcd for $C_{22}H_{30}O_3Se$: C, 62.70; H, 7.17; O, 11.39. Found: C, 62.80; H, 7.00; O, 11.14.

***cis*-7a-Hexyltetrahydro-1,7(3*H*,6*H*)-isobenzofurandione (38).** 3-Chloroperoxybenzoic acid (100 mg, 80–85%, ca. 0.48 mmol) was added to a stirred solution of selenide **37** (126 mg, 0.30 mmol) in CH_2Cl_2 (4 mL) at room temperature. After 20 min, the mixture was quenched by addition of saturated aqueous $NaHCO_3$ (5 mL) and extracted with CH_2Cl_2 (10 mL). The organic extract was dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (2 × 14 cm), using 20% EtOAc–hexane, gave the expected unsaturated aldehyde (58 mg, 74%) as a mixture of *Z* and *E* isomers which were oxidized directly without characterization.

Ozone, precooled by passage through a glass coil immersed in a dry ice–acetone bath, was bubbled through a cold (−78 °C) solution of the above unsaturated aldehyde (58 mg, 0.22 mmol) in CH_2Cl_2–MeOH (4:1, 25 mL) until a blue color appeared (2 min). Dimethyl sulfide (4 mL) was added, and the solution was stirred overnight at room temperature. Evaporation of the solvents and flash chromatography of the residue over silica gel (2 × 15 cm), using 20% EtOAc–hexane, gave **38** (28 mg, 54%) as a pure (^{1}H NMR), colorless oil: FTIR (CCl_4 cast) 2954, 2927, 2859, 1781, 1769, 1712, 1206, 1189, 1162, 1095, 1021 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.87 (t, J = 6.0 Hz, 3 H), 1.15–1.50 (m, 8 H), 1.60–2.15 (m, 6 H), 2.25–2.60 (m, 2 H), 2.78–2.93 (m, 1 H), 4.02 (dd, J = 9.5, 6.0 Hz, 1 H), 4.34 (dd, J = 9.5, 7.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 14.02, 22.38, 22.54, 24.92, 29.49, 31.49, 32.01, 39.23, 42.09, 60.27, 69.56, 174.47, 205.30; exact mass m/z calcd for $C_8H_{10}O_3$ (M − C_6H_{12}) 154.0624, found 154.0631. An analytical sample was prepared by Kugelrohr distillation (120–122 °C, 0.50 mmHg). Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30. Found: C, 70.62; H, 9.04.

***cis*-7a-Hexyltetrahydro-1,7(3*H*,6*H*)-isobenzofurandione 7-(Ethanediyl dithioacetal) (39).** Boron trifluoride etherate (37 μL, 0.30 mmol) was added to a stirred and cooled (0 °C) solution of ketone **38** (48 mg, 0.20 mmol) and 1,2-ethanedithiol (34 μL, 0.40 mmol) in CH_2Cl_2 (3 mL). The cold bath was removed, and the solution was stirred for 2 h. More 1,2-ethanedithiol (15 μL, 0.12 mmol) was added, and, after 2 h, the mixture was quenched with aqueous NaOH (5 mL, 2.5 M) and extracted with CH_2Cl_2 (10 mL). The organic extract was washed with brine (5 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (2 × 15 cm), using 10% EtOAc–hexane, gave **39** (49 mg, 77%) as a pure (^{1}H NMR), colorless oil: FTIR (CCl_4 cast) 2923, 1757, 1023, 997 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.88 (t, J = 6.5 Hz, 3 H), 1.20–1.39 (br s, 8 H), 1.54–1.85 (m, 5 H), 2.20–2.30 (m, 3 H), 2.64–2.75 (m, 1 H), 3.05–3.15 (m, 1 H), 3.23–3.33 (m, 3 H), 4.17–4.27 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 14.06, 20.90, 22.24, 22.60, 26.60, 29.74, 31.64, 34.83, 37.93, 38.98, 39.93, 41.61, 54.18, 68.42, 71.77, 177.34; exact mass m/z calcd for $C_{16}H_{26}O_2S_2$ 314.1374, found 314.1373.

***cis*-7a-Hexyl-3a,4,5,7a-tetrahydro-1(3*H*)-isobenzofuranone (40).** Raney nickel (W-2, suspension in EtOH, settled volume 0.6 mL) was added to a solution of dithioacetal **39** (35 mg, 0.11 mmol) in ethanol (4 mL) and benzene (0.3 mL). The suspension was refluxed for 20 h, cooled, and filtered through a pad (2 × 4 cm) of Celite. The pad was washed with EtOAc, and the combined filtrates were evaporated. Flash chromatography of the residue over silica gel (2 × 15 cm), using 5% EtOAc–hexane, gave olefin **40** (18 mg, 73%) as a pure (^{1}H NMR), colorless oil: FTIR (CCl_4 cast) 2953, 2932, 2858, 1767, 1194, 1180, 1107, 1023 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.88 (t, J = 6.5 Hz, 3 H), 1.17–1.44 (br s, 8 H), 1.57–1.70 (m, 3 H), 1.70–1.85 (m, 1 H), 1.98–2.10 (m, 2 H), 2.55–2.66 (m, 1 H), 3.98 (dd, J = 9.0, 7.5 Hz, 1 H), 4.33 (dd, J = 9.0, 7.5 Hz, 1 H), 5.54 (dt, J = 10.0, 4.0 Hz, 1 H), 5.94 (dt, J = 10.0, 7.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 14.07, 20.94, 21.27, 22.60, 24.42, 29.60, 31.67, 36.31, 37.41, 46.93, 68.72, 126.49, 129.39, 179.62; exact mass m/z calcd for $C_{14}H_{22}O_2$ 222.1620, found 222.1611.

***cis*-7a-Hexylhexahydro-1(3*H*)-isobenzofuranone (41).** Palladium (4 mg, 5% on carbon) was added to a solution of olefin **40** (18 mg, 0.08 mmol) in EtOAc (3 mL) at room temperature. The flask was flushed with hydrogen, and the suspension was stirred under a hydrogen atmosphere (balloon) for 4 h. The mixture was filtered through a pad (2 x 4 cm) of Celite, and the pad was washed with EtOAc. Evaporation of the filtrate and flash chromatography of the residue over silica gel (2 × 17 cm), using 10% EtOAc–hexane, gave **41** (16 mg, 91%) as a pure (^{1}H NMR), colorless oil: FTIR (CCl_4 cast) 2931, 2858, 1769, 1451, 1204, 1113, 1021 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.88 (t, J = 7.0 Hz, 3 H), 1.20–1.95 (m, 18 H), 2.26–2.36 (m, 1 H), 3.95 (dd, J = 9.0, 5.0 Hz, 1 H), 4.30 (dd, J = 9.0, 6.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 14.07, 22.10, 22.36, 22.60, 24.10, 25.80, 29.63, 29.73, 31.68, 34.93, 38.66, 38.90, 45.30, 69.50, 180.82; exact mass m/z calcd for $C_{14}H_{24}O_2$ 224.1776, found 224.1776.

***cis*-7a-Hexylhexahydro-1(3*H*)-isobenzofuranone (41) from 9a′.** Palladium (4 mg, 5% on carbon) was added to a solution of alkyne **9a′** (22.6 mg, 0.10 mmol) in EtOAc (1.5 mL) at room temperature. The flask was flushed with hydrogen, and the suspension was stirred under a hydrogen atmosphere (balloon) for 4 h. The mixture was filtered through a pad (2 × 3 cm) of Celite, and the pad was washed with EtOAc. Evaporation of the filtrate and flash chromatography of the residue over silica gel (2 × 15 cm), using 7% EtOAc–hexane, gave **41** (17.7 mg, 77%) as a pure (^{1}H NMR), colorless oil, identical to material obtained from **40**.

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Supplementary Material Available: NMR spectra for compounds **8c′**, **9h**, **11g**, **12g**, **30**, **34**, and **39–41** (25 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.