Preparation of Polycyclic Systems by Sequential 5-*Exo-Digonal* Radical Cyclization, 1,5-Hydrogen Transfer from Silicon, and 5-*Endo-Trigonal* Cyclization

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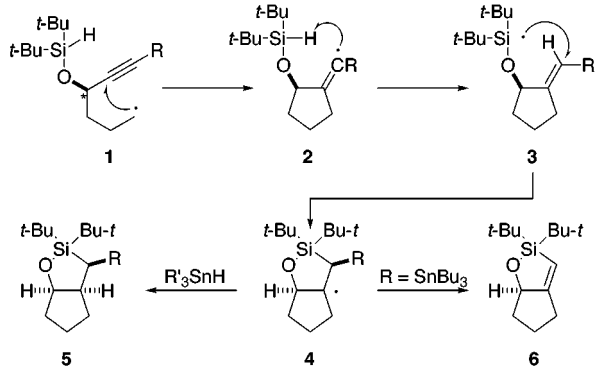
Radicals of type **1** undergo 5-*exo* diagonal cyclization, and the resulting vinyl radical abstracts hydrogen from silicon to afford a silicon-centered radical. This radical closes in a 5-*endo trigonal* manner to generate radicals of type **4**, which are reduced (**4** → **5**) by stannane, except when the starting acetylene carries a terminal trimethylstannyl group. In this case, radicals **4** expel trimethylstannyl radical to afford vinyl silanes **6**. The stereochemical outcome of the radical cascade **1** → **5** is controlled by the stereochemistry of the oxygen-bearing carbon in **1** (see starred atom). The sequence can be initiated by carbon-, α-substituted carbon-, oxyacyl-, and carbamoyl radicals and generates a silicon-containing ring fused onto a carbocycle or heterocycle. Numerous examples are described, as well as a number of transformations of the final cyclization products, especially their response to *n*-Bu_4NF and to $BF_3{\cdot}OEt_2$, reagents that cleave the newly formed carbon−silicon bond.

The sequence of radical reactions outlined in Scheme 1 provides a route to unusual bicyclic or polycyclic compounds. Earlier publications[1] from this laboratory illustrated the method for a variety of examples that followed the pathway **1** → **5** and in which the radical appendage—which is shown in Scheme 1 for a particular case—was varied in length, carried substituents, was part of an aromatic system, or included heteroatoms; here, full details and additional examples are described, as well as some simple transformations of the products, and a method for diverting the intermediates of type **4** to vinylsilanes such as **6**.

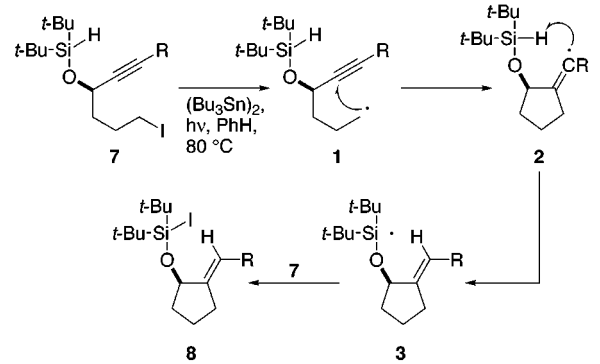
The first step of the sequence (see **1** → **2**) involves 5-*exo-digonal* cyclization, but the notable features of the process are, of course, the intramolecular transfer of hydrogen from *silicon* to carbon (**2** → **3**) and the 5-*endo* nature of the subsequent *trigonal* closure (**3** → **4**). While many intramolecular 1,5-hydrogen transfers are known, we were not aware of any prior examples of transfer from silicon when our work began,[1] although a number have now been reported.[2,3] The penultimate carbon radical in our cascade (see **4**) can be intercepted (Scheme 2) to produce **8**, by iodine atom transfer, when the starting radical **1** is generated ($Bu_3SnSnBu_3$, light) from an iodide (e.g., **7**) instead of a selenide.[2d,e]

5-*Endo-trigonal* cyclizations are encountered much less frequently than their 5-*exo* counterparts—in accordance with the Baldwin rules[4] and Beckwith guidelines.[5] In the present case,[6] the increased length of the bonds to silicon, as compared to bonds between first-row elements, lowers the stereoelectronic barrier that normally hinders such

Scheme 1



Scheme 2



(1) (a) Clive, D. L. J.; Cantin, M. *J. Chem. Soc., Chem. Commun.* **1995**, 319−320. (b) Clive, D. L. J.; Yang, W. *J. Chem. Soc., Chem. Commun.* **1996**, 1605−1606. (c) Sannigrahi, M.; Mayhew, D. L.; Clive, D. L. J. *J. Org. Chem.* **1999**, *64*, 2776−2788.

(2) (a) Curran, D. P.; Xu, J. *J. Chem. Soc., Perkin Trans. 1* **1995**, 3061−3063. (b) Curran, D. P.; Xu, J.; Lazzarini, E. *J. Am. Chem. Soc.* **1995**, *117*, 6603−6604. (c) Curran, D. P.; Xu, J.; Lazzarini, E. *J. Chem. Soc., Perkin Trans. 1* **1995**, 3049−3059. (d) Martinez-Grau, A.; Curran, D. P. *J. Org. Chem.* **1995**, *60*, 8332−8333. (e) Martinez-Grau, A.; Curran, D. P. *Tetrahedron* **1997**, *53*, 5679−5698.

(3) Review on silicon radicals: Chatgilialoglu, C. *Chem. Rev.* **1995**, *95*, 1229−1251.

(4) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734−736.

(5) Beckwith, A. L. J.; Easton, C. J.; Serelis, A. K. *J. Chem. Soc., Chem. Commun.* **1980**, 482−483.

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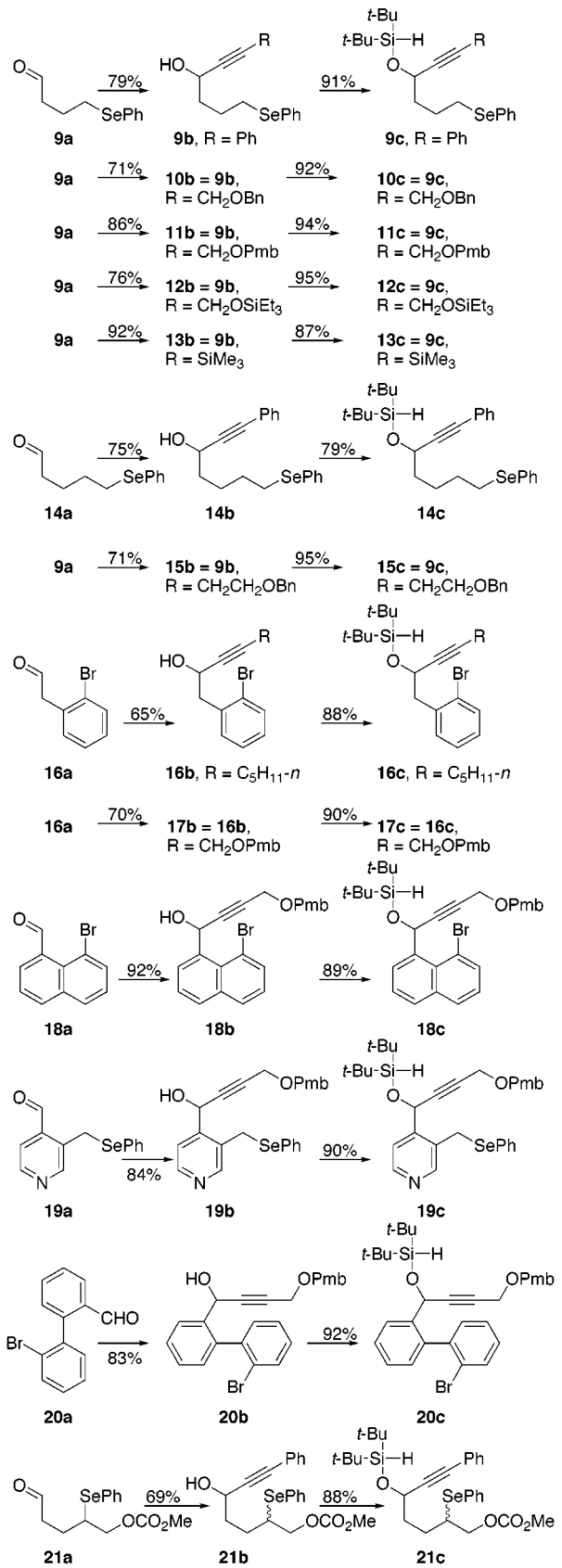
endo cyclizations. However, in first-row element chemistry, there is a growing number of 5-*endo trigonal* closures. Enamides are particularly prone to follow this pathway,[7] and a number of other specialized systems have also been found to undergo efficient 5-*endo trigonal* cyclization.[8]

Preparation of Starting Materials. Radicals of type **1**, and related species, were generated by stannane-induced homolysis of carbon−bromine or carbon−selenium bonds, and most of the radical precursors we used are shown in Table 1 (compounds **9c**−**21c**) and Table 2, (compounds **29c**−**34c**).

This subdivision is made according to whether the homolyzable group is connected to the acetylene by an all-carbon chain (Table 1) or by a chain containing a heteroatom (Table 2). Table 3 shows several steps in the preparation of those starting materials (compounds **35d**−**39d**) used for the pathway **1** → **6** of Scheme 1.

Most of the sequences summarized in the tables begin with readily available aldehydes, and of these, compounds **9a**,[9] **14a**,[10] **16a**,[11] **18a**,[12] and **20a**[13,14] (all shown in Table 1) were known and easily prepared by the literature methods. Aldehydes **19a** and **21a** of Table 1

Table 1



(6) Cf. (a) Cai, Y.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 1* **1998**, 467−475. (b) Barton, T. J.; Revis, A. *J. Am. Chem. Soc.* **1984**, *106*, 3802−3805. (c) Chatgilaloglu, C.; Woynar, H.; Ingold, K. U.; Davies, A. G. *J. Chem. Soc., Perkin Trans. 2* **1983**, 555−561. (d) Sarasa, J. P.; Igual, J.; Poblett, J. M. *J. Chem. Soc., Perkin Trans. 2* **1986**, 861−865. (e) For an example of 5-*endo trigonal* cyclization involving sulfur, see: Journet, M.; Rouillard, A.; Cai, D.; Larsen, R. D. *J. Org. Chem.* **1997**, *62*, 8630−8632.

(7) E.g. (a) Clark, A. J.; Dell, C. P.; Ellard, J. M.; Hunt, N. A.; McDonagh, J. P. *Tetrahedron Lett.* **1999**, *40*, 8619−8623. (b) Ishibashi, H.; Nakamura, N.; Sato, T.; Takeuchi, M. *Tetrahedron Lett.* **1991**, *32*, 1725−1728. (c) Sato, T.; Machigashira, N.; Ishibashi, H.; Ikeda, M. *Heterocycles* **1992**, *33*, 139−142. (d) Sato, T.; Nakamura, N.; Ikeda, K.; Okada, M.; Ishibashi, H.; Ikeda, M. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2399−2407. (e) Sato, T.; Chona, N.; Ishibashi, H.; Ikeda, M. *J. Chem. Soc., Perkin Trans. 1* **1995**, 1115−1120. (f) Ishibashi, H.; Kameoka, C.; Kodama, K.; Ikeda, M. *Tetrahedron Lett.* **1996**, *52*, 489−502. (g) Ikeda, M.; Ohtani, S.; Yamamoto, T.; Sato, T.; Ishibashi, H. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1763−1768. (h) Ishibashi, H.; Higuchi, M.; Ohba, M.; Ikeda, M. *Tetrahedron Lett.* **1998**, *39*, 75−78. (i) Ikeda, M.; Hamada, M.; Yamashita, T.; Matsui, K.; Sato, T.; Ishibashi, H. *J. Chem. Soc., Perkin Trans. 1* **1999**, 1949−1956. (j) Goodall, K.; Parsons, A. F. *J. Chem. Soc., Perkin Trans. 1* **1994**, 3257−3259. (k) Goodall, K.; Parsons, A. F. *Tetrahedron Lett.* **1997**, *38*, 491−494. (l) Baker, S. R.; Parsons, A. F.; Pons, J.-F.; Wilson, M. *Tetrahedron Lett.* **1998**, *39*, 7197−7200. (m) Baker, S. R.; Parsons, A. F.; Wilson, M. *Tetrahedron Lett.* **1998**, *39*, 2815−2818. (n) Baker, S. R.; Burton, K. I.; Parsons, A. F.; Pons, J.-F.; Wilson, M. *J. Chem. Soc., Perkin Trans. 1* **1999**, 427−436. (o) Davies, D. T.; Kapur, N.; Parsons, A. F. *Tetrahedron Lett.* **1999**, *40*, 8615−8618. (p) Cassayre, J.; Quiclet-Sire, B.; Saunier, J.-B.; Zard, S. Z. *Tetrahedron Lett.* **1998**, *39*, 8955−8998. (q) Cassayre, J.; Dauge, D.; Zard, S. Z. *Synlett* **2000**, 471−474.

(8) E.g. (a) Bogen, S.; Gulea, M.; Fensterbank, L.; Malacria, M. *J. Org. Chem.* **1999**, *64*, 4920−4925. (b) Gimisis, T.; Chatgilialoglu, C. *J. Org. Chem.* **1996**, *61*, 1908−1909. (c) Chatgilialoglu, C.; Gimisis, T.; Spada, G. P. *Chem. Eur. J.* **1999**, *5*, 2866−2876. (d) Kittaka, A.; Asakura, T.; Kuze, T.; Tanaka, H.; Yamada, N.; Nakamura, K. T.; Miyasaka, T. *J. Org. Chem.* **1999**, *64*, 7081−7093. (e) Rao, A. V. R.; Singh, A. K.; Rao, B. V.; Reddy, K. M. *Tetrahedron Lett.* **1993**, *34*, 2665−2668. (f) Schmalz, H.-G.; Siegel, S.; Bats, J. W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2383−2385. (g) Mendenhall, G. D.; Protasiewicz, J. D.; Brown, C. E.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **1994**, *116*, 1718−1724. (h) Yamamoto, Y.; Ohno, M.; Eguchi, S. *J. Am. Chem. Soc.* **1995**, *117*, 9653−9661. (i) Nonami, Y.; Baran, J.; Sosnicki, J.; Mayr, H.; Masuyama, A.; Nojima, M. *J. Org. Chem.* **1999**, *64*, 4060−4063.

(9) Clive, D. L. J.; Bergstra, R. J. *J. Org. Chem.* **1990**, *55*, 1786−1792.

(10) Bowman, W. R.; Stephenson, P. T.; Terrett, N. K.; Young, A. R. *Tetrahedron* **1995**, *51*, 7959−7980.

(11) Hartman, G. D.; Phillips, B. T.; Halczenko, W. *J. Org. Chem.* **1985**, *50*, 2423−2427.

(12) (a) Bailey, R. J.; Card, P. J.; Schechter, H. *J. Am. Chem. Soc.* **1983**, *105*, 6096−6103. (b) Luckenbach, R.; Jensen, A. *Zeit. Naturforsch. B.* **1977**, *32b*, 912−933.

(13) (a) Corresponding acid: Gilman, H.; Gorsich, R. D. *J. Am. Chem. Soc.* **1956**, *78*, 2217−2222. (b) Esterification (EtOH, HCl, 74%) and DIBAL-H reduction (1 equiv., CH_2Cl_2, −78 °C, 1 h, 86%) gave the aldehyde (see ref 14).

(14) Shuttleworth, R. G.; Rapson, W. S.; Stewart, E. T. *J. Chem. Soc.* **1944**, 71−73.

Table 2

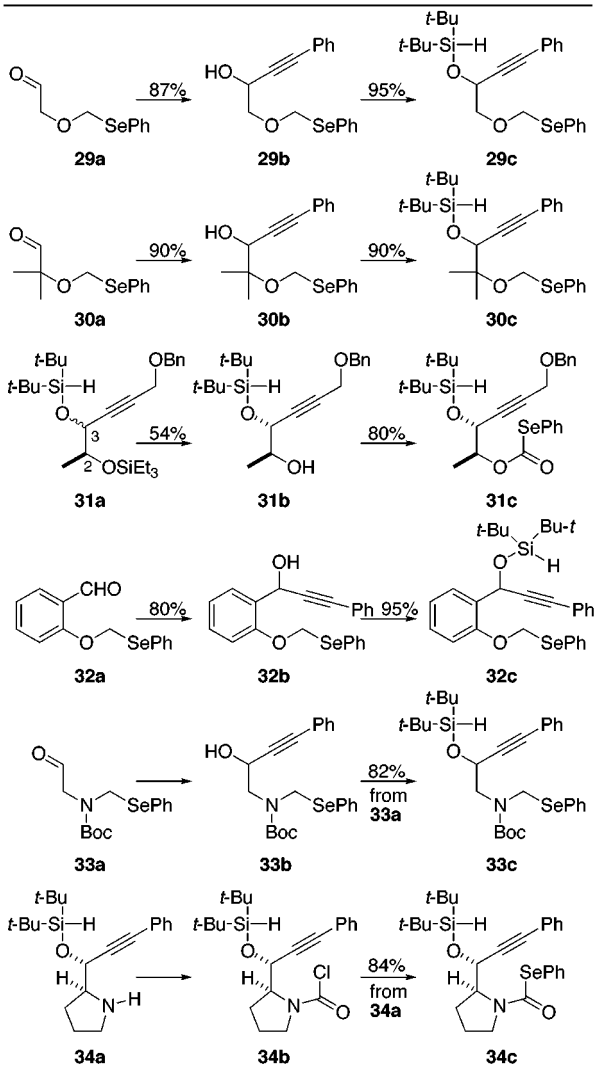
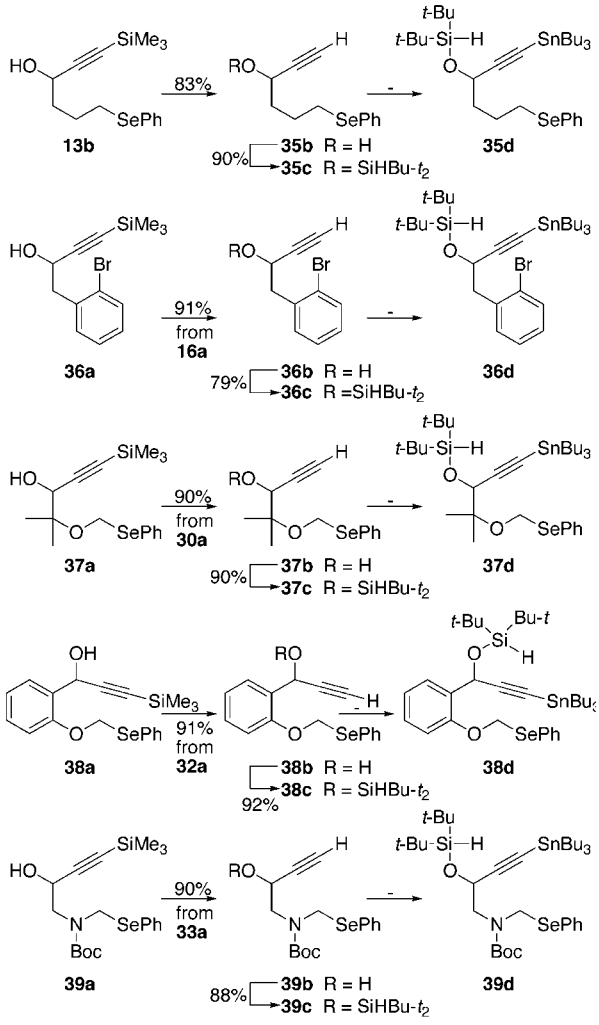
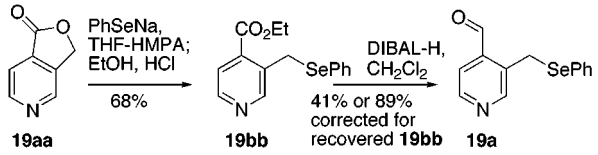


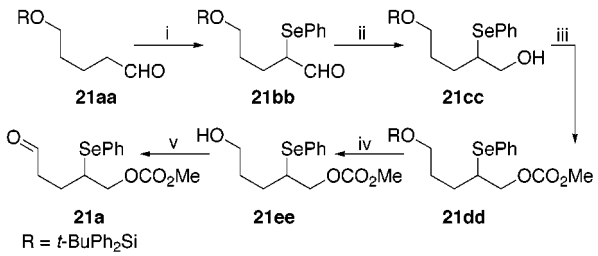
Table 3



Scheme 3



Scheme 4[a]



[a] Key: (i) Et_2NH, PhSeCl, hexane; (ii) $NaBH_4$, MeOH, 49% from **21aa**; (iii) MeOC(O)Cl, pyridine, CH_2Cl_2, 84%; (iv) *n*-Bu_4NF, AcOH, THF, 95%; (v) Swern oxidation, 67%.

are new; they were prepared by the conventional methods summarized in Schemes 3 and 4, respectively.

The aldehydes shown in Table 2 were also readily prepared, as were the two silylated starting materials **31a** and **34a** also listed in Table 2. For the preparation of **29a**, advantage was taken of the ability of the PhSeNa to open γ-lactone-like structures,[15] and in the present case (Scheme 5), the dioxolanone **29bb**, made by treatment of glycolic acid with formaldehyde, smoothly gave the desired ring-opened selenide acid **29cc**. This was esterified (**29cc** → **29dd**), and DIBAL-H reduction then afforded aldehyde **29a**. The dimethyl analogue **30a** was made in exactly the same way (Scheme 6).

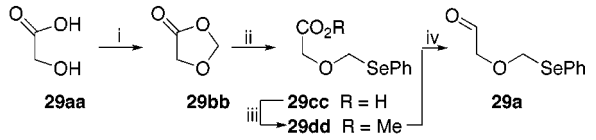
Silane **31a** [as an ca. 3.6:1 (^{1}H NMR on **31bb**) mixture of C(3) epimers that were separated at a later stage] was made (Scheme 7) from (*S*)-2-(triethylsilyloxy)propanal (**31aa**)[16] by acetylide addition (**31aa** → **31bb**) and silylation (**31bb** → **31a**). Although we used optically pure starting material we did not monitor the optical integrity of the derived products, but have no reason[17] to suspect any loss of stereochemical integrity.

(15) (a) Liotta, D.; Sunay, U.; Santiesteban, H.; Markiewicz, W. *J. Org. Chem.* **1981**, *46*, 2605−2610. (b) Zima, G.; Liotta, D. *Synth. Commun.* **1979**, *9*, 697−703. (c) Scarborough, R. M., Jr.; Smith, A. B., III. *Tetrahedron Lett.* **1977**, 4361−4364. (d) Dowd, P.; Kennedy, P. *Synth. Commun.* **1981**, *11*, 935−941. (e) Pedersen, M. L.; Berkowitz, D. B. *Tetrahedron Lett.* **1992**, *33*, 7315−7318.

(16) (a) Ishibashi, T.; Nagisa, O.; Miwako, M. *Tetrahedron Lett.* **1996**, *37*, 6165−6168. (b) Cainelli, G.; Panunzio, M.; Bandini, E.; Martelli, G.; Spunta, G. *Tetrahedron* **1996**, *52*, 1685−1698.

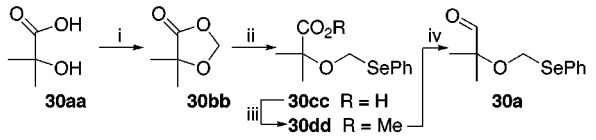
(17) Cf. Hirama, M.; Shigemoto, T.; Itô, S. *J. Org. Chem.* **1987**, *52*, 3342−3346.

Scheme 5[a]



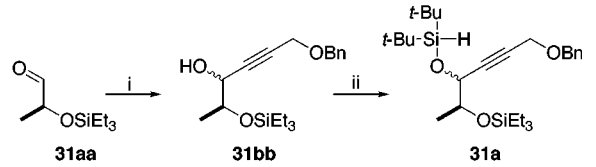
[a] Key: (i) $(CH_2O)_n$, $TsOH\cdot H_2O$, PhH, reflux, Dean−Stark apparatus, 14%; (ii) PhSeNa, THF−HMPA, reflux; (iii) MeOH, concd H_2SO_4, 80% from **29bb**; (iv) DIBAL-H, CH_2Cl_2, 80%.

Scheme 6[a]



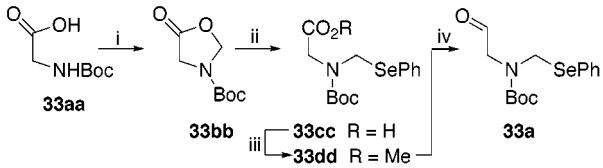
[a] Key: (i) *s*-trioxane, $TsOH\cdot H_2O$, PhH, reflux, Dean−Stark apparatus, 82%; (ii) PhSeNa, THF−HMPA, reflux; (iii) MeOH, concd H_2SO_4, 70% from **30bb**; (iv) DIBAL-H, CH_2Cl_2, 90%.

Scheme 7[a]



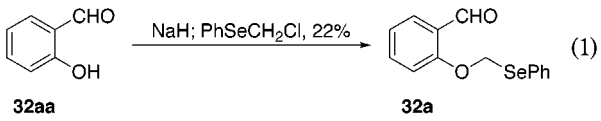
[a] Key: (i) $BnOCH_2C{\equiv}CH$, *n*-BuLi, THF, −78 °C, then add **31aa**; (ii) *t*-Bu_2SiHCl, Et_3N, CH_2Cl_2, DMAP (for overall yield from **31aa**, see preparation of **31b**).

Scheme 8[a]



[a] Key: (i) $(CH_2O)_n$, $TsOH\cdot H_2O$, PhH, reflux, Dean−Stark apparatus, 61%; (ii) PhSeNa, THF−HMPA, reflux; (iii) CH_2N_2, Et_2O, 80% from **33aa**; (iv) DIBAL-H, Et_2O, 83%.

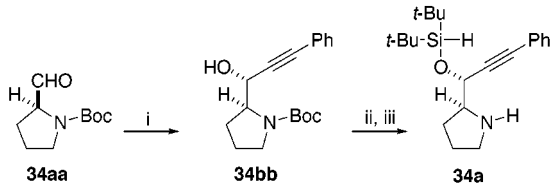
Aldehyde **32a** (see Table 2) was formed (22%) by alkylation of salicylaldehyde with $PhSeCH_2I$,[18] as summarized in eq 1, and aldehyde **33a** (see Table 2) was



prepared (see Scheme 8) in a manner similar to that of **29a**, once again using PhSeNa to open a type of γ-lactone ring (**33bb** → **33cc**).

Silane **34a** (see Table 2) was derived from *S*-proline, as shown in Scheme 9, by way of the known aldehyde **34aa**,[19] which was treated with lithium phenylacetylide (**34aa** → **34bb**) to afford a 1:1 mixture[20] of two separable isomers; that having the stereochemistry shown as **34bb**—an assignment established at a later stage by

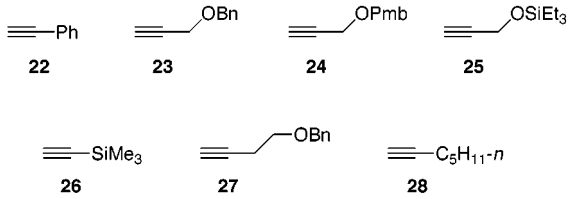
Scheme 9[a]



[a] Key: (i) PhC≡CH, *n*-BuLi, THF, −78 °C, then add **34aa**, chromatographic separation of isomer **34bb**, 41%; (ii) TFA, CH_2Cl_2; (iii) *t*-Bu_2SiHCl, imidazole, CH_2Cl_2, 60% from **34bb**.

X-ray analysis—was treated with TFA to remove the nitrogen protecting group and then the hydroxyl was silylated (**34bb** → **34a**).

The aldehydes listed in Tables 1 and 2 were each treated with the lithium acetylide derived from one of the acetylenes **22**−**28**.



Of these, **22**, **26**, and **28** were commercially available, and the others were made by the literature method of O-alkylation (**23**,[21] **24**,[21] **27**[22]) or, in the case of **25**,[23] by silylation with Et_3SiCl. Both alcohol **20b** (Table 1) and the derived silane **20c** displayed atropisomerism, revealed by a doubling of many signals in the NMR spectra. As expected, the acetylenic alcohol **21b** (Table 1) was obtained as a mixture of diastereoisomers (ca. 1:1). The acetylenic alcohols **36a**, **37a**, **38a**, and **39a** (Table 3) were made in the same general way from the appropriate aldehydes, except that in the preparation of **36a** the cerium salt of the acetylene was arbitrarily used.

The acetylenic alcohols shown in Tables 1 and 2 were silylated using *t*-Bu_2SiHCl in the presence of a base, usually imidazole, but sometimes Et_3N and a catalytic amount of DMAP. Reactions were generally complete after a few hours at the reflux temperature of THF or benzene, with yields usually well above 80%. The *t*-Bu_2Si group of **31a** (Table 2) was stable enough to hydrolytic conditions (H_2O−AcOH-THF) to allow selective removal of the Et_3Si group also present (**31a** → **31b**). Compound **31a** is an isomer mixture but, after the hydrolysis, the stereoisomer **31b**, having the indicated absolute configuration, could be isolated in 54% yield; the isomeric alcohol was discarded. Treatment with $COCl_2$ and PhSeNa then served to afford the required selenocarbonate **31c**, as shown in Table 2.

The amine **34a** (Table 2) was treated with $COCl_2$, and the resulting carbamoyl chloride (**34b**), which was stable to chromatography, reacted with PhSeNa to give the radical precursor **34c** (84% overall from **34a**).

The acetylenic trimethylsilyl groups (see Table 3) of **13b**, **36a**, **37a**, **38a**, and **39a** were removed efficiently by

(18) (a) Beckwith, A. L. J.; Pigou, P. E. *Aust. J. Chem*. **1986**, *39*, 77−87. (b) Nakanishi, W. *Chem. Lett*. **1993**, 2121−2122.

(19) Reed, P. E.; Katzenellenbogen, J. A. *J. Org. Chem*. **1991**, *56*, 2624−2634.

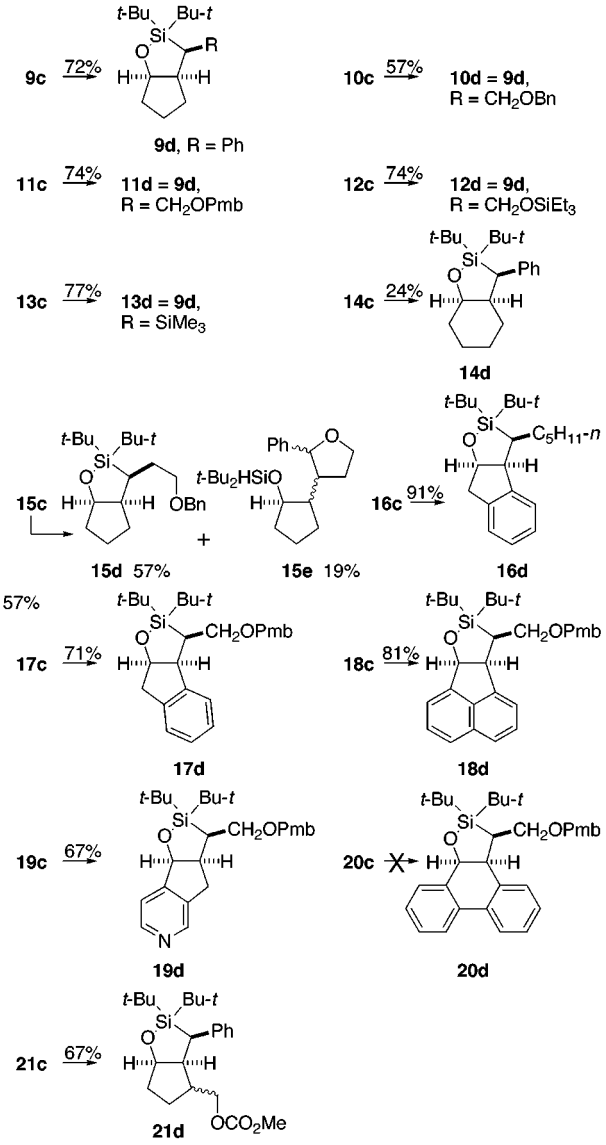
(20) Cf. Reference 19 and Koskinen, A. M. P.; Paul, J. M. *Tetrahedron Lett*. **1992**, *33*, 6853−6856.

(21) (a) Montevecchi, P. C.; Navacchia, M. L. *J. Org. Chem*. **1998**, *63*, 537−542. (b) We used refluxing THF-DMF, instead of heating the mixture in a sealed tube.

(22) Kobayashi, Y.; Mizojiri, R.; Ikeda, E. *J. Org. Chem*. **1996**, *61*, 5391−5399.

(23) Cf. Lorenz, C.; Schubert, U. *Chem. Ber*. **1995**, *128*, 1267−1269.

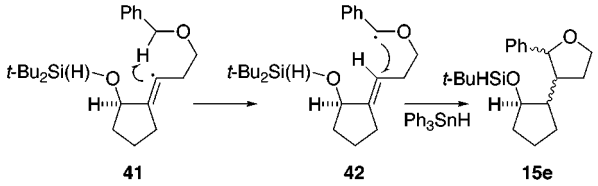
Table 4

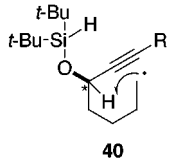


the action of *n*-Bu_4NF in THF at 0 °C, and the resulting alcohols were silylated on oxygen with *t*-Bu_2SiHCl, under our standard conditions. The resulting O-silylated terminal acetylenes **35c**−**39c** (Table 3) were deprotonated by treatment with *n*-BuLi and then stannylated by reaction with Bu_3SnCl. The acetylenic stannanes formed by this sequence were unstable to chromatography, and so they were used directly for radical cyclization.

Formation of Radical Cyclization Products. The radical cyclizations (cf. Scheme 1) were conducted by slow addition of separate solutions of Ph_3SnH (or Bu_3SnH) and AIBN, each in dry PhH, to a refluxing solution of the substrate in the same solvent, and our results with the radical precursors of Table 1 are shown in Table 4. For those reactions involving an initial 5-*exo* digonal cyclization, yields varied between 57% and 91%. The cyclization of **14c** afforded **14d** in poor yield (24%). This reaction involves initial 6-*exo digonal* cyclization, which might, like the corresponding *trigonal* reaction,[24] be inherently slower than 5-*exo digonal* closures, so affording greater opportunities for competing pathways—possibly, intramolecular transfer of a propargylic hydrogen (see **40**). 6-*Exo-digonal* closures that have been reported cover a wide range of yields.[25] Those that proceed poorly often afford extensive amounts of material in which simple reduction has occurred (replacement of the homolyzed group by hydrogen), but—at least in the research familiar to us—no control experiments have been done that would establish whether these formal reduction products arise by way of intramolecular hydrogen transfer, followed by reduction of the resulting propargylic radical.[26]

Scheme 10





The biphenyl derivative **20c** of Table 1 gave a complex mixture (see Table 4), and appeared to afford little, if any, of the desired product. This is the only case where the radical cascade failed.

Selenide **15c** also gave a yield at the lower end of the range (see Table 4), possibly because of the intervention of the hydrogen abstraction pathway (via a six-membered transition state) shown in Scheme 10 (**41** → **42** → **15e**). Although we did isolate a byproduct with the anticipated accurate mass corresponding to **15e**, it was not further characterized.[27] The high yield of **16d** (Table 4) establishes that this type of intramolecular hydrogen transfer from the side chain does not intervene if the hydrogens are unactivated. Cyclization product **21d** (Table 4) was obtained as an ca. 1:2 mixture of two isomers, this ratio being lower than we have subsequently observed[1c] in a related cyclization, where a value of 7:1 was found. We assume, on the basis of related work,[1c] that the major isomer has the carbonate appendage syn to the adjacent ring fusion hydrogen.

(24) Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron* **1985**, *41*, 3925−3941.

(25) E.g. (a) Gómez, A. M.; Danelón, G. O.; Moreno, E.; Valverde, S.; López, J. C. *Chem. Commun.* **1999**, 175−176. (b) Crich, D.; Chen, C.; Hwang, J.-T.; Yuan, H.; Papadatos, A.; Walter, R. I. *J. Am. Chem. Soc.* **1994**, *116*, 8937−8951. (c) Schinzer, D.; Jones, P. G.; Obierey, K. *Tetrahedron Lett.* **1994**, *35*, 5853−5856. (d) Audin, C.; Lancelin, J.-M.; Beau, J.-M. *Tetrahedron Lett.* **1988**, *29*, 3691−3694. (e) Honda, T.; Satoh, M.; Kobayashi, Y. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1557−1558. (f) Parsons, P. J.; Penkett, C. S.; Cramp, M. C.; West, R. I.; Warrington, J.; Saraiva, M. C. *Synlett* **1995**, 507−509. (g) Sha, C.-K.; Jean, T.-S.; Wang, D.-C. *Tetrahedron Lett.* **1990**, *30*, 3745−3748. (h) Sha, C.-K.; Shen, C.-Y.; Jean, T.-S.; Chiu, R.-T.; Tseng, W.-H. *Tetrahedron Lett.* **1993**, *34*, 7641−7644. (i) Pike, K. G.; Destabil, C.; Anson, M.; Kilburn, J. D. *Tetrahedron Lett.* **1998**, *39*, 5877−5880. (j) Maudru, E.; Singh, G.; Wightman, R. H. *Chem. Commun.* **1998**, 1505−1506. (k) Zhou, S.-Z.; Anné, S.; Vandewalle, M. *Tetrahedron Lett.* **1996**, *37*, 7637−7640. (l) Cossy, J.; Cases, M.; Pardo, D. G. *Bull. Soc. Chim. Fr.* **1997**, *134*, 141−144.

(26) Cf. For radical reduction of a propargylic alcohol without formation of an allene, see: Clive, D. L. J.; Yeh, V. S. C. *Tetrahedron Lett.* **1998**, *39*, 4789−4792.

(27) Cf. Reference 2e.

Table 5

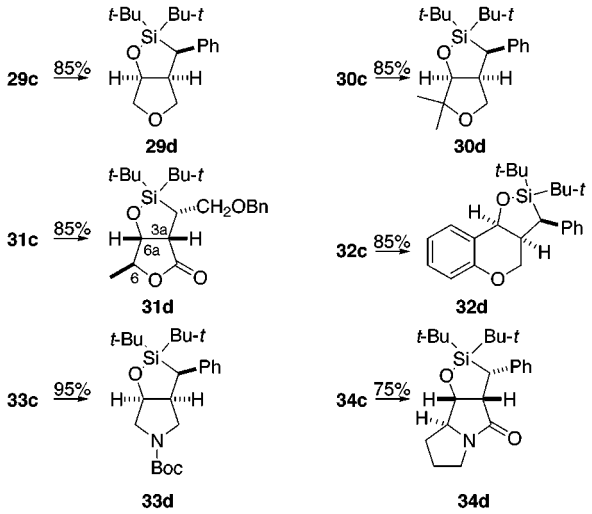
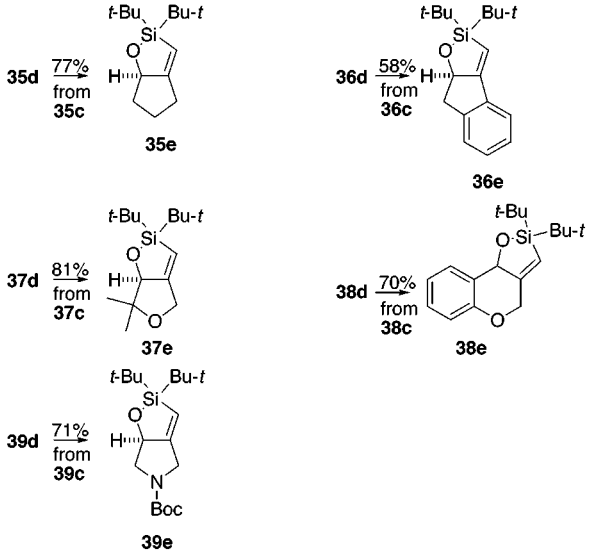


Table 6



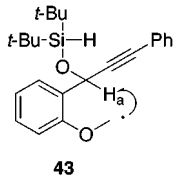
The cyclizations shown in Table 5 represent those cases in which the radical source is connected to the acetylenic unit by a chain incorporating a heteroatom. As can be seen, the sequence is very efficient in these examples. Cyclization of **34c**[28] proceeds via a carbamoyl radical, a species that has been investigated in greater detail by others.[29] Evidently, closure of these radicals is faster than decarbonylation, as is the case with alkoxycarbonyl radicals.[30]

The cyclization results collected in Table 6 correspond to the pathway **4** → **6** of Scheme 1, and the yields shown refer to two steps—stannylation of the acetylene (see Table 3) as well as the radical cascade. In all these cases, the final carbon radical (cf. **4**) expels a stannyl radical, so as to generate a vinylsilane.

Stereochemistry of Radical Cascade Products. The stereochemistry of the radical cascade products follows from the mechanistic pathway summarized in Scheme 1. However, X-ray analyses were obtained for **34d** (see Table 5) and for **9f** (see Table 8, which is discussed later). The structures found confirm the mechanistic prediction that the product stereochemistry is determined by the stereochemistry of the starting alcohol and, in the case of **34d** (Table 5), served to identify which isomer from the original acetylide addition (see Scheme 9) had been selected.

Some comment is also necessary about the stereochemistry of **31d** (Table 5). The precursor alcohol **31b** (see Table 2) was separated from an isomer mixture, and the stereochemistry shown was established by examining the ^{1}H NMR spectrum of the final radical cyclization product **31d** (Table 5). The $CH_3C(6)H-$ signal is a quartet (δ 4.65), and there is no coupling to the adjacent C(6a)*H*. Dreiding models show the two hydrogens at C(6) and C(6a) must be anti, because a syn relationship would result in a large coupling.

It is noteworthy that, in the formation of **32d** (see Table 5), intramolecular hydrogen abstraction (see **43**) does not occur to any appreciable extent, if at all, even though the hydrogen that would be removed is both benzylic and propargylic. However, the factors responsible for the



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small, or nonexistent, extent of hydrogen abstraction have not been identified. The facility of such hydrogen transfers would depend not only on the accessible geometries[31] of the system and the strength of the C—H_a bond (see **43**) but also on certain characteristics of the radical (here $ArOCH_2^{\cdot}$), such as resonance stabilization and polarity.[32] The relative importance of these factors is unknown, but we note that efficient 6-*exo*-*trigonal* closures of alkoxymethyl radicals have also been observed in systems that lack the additional activating features of the propargylic hydrogen in **43**,[33] and the absence of intramolecular transfer during these reactions or in the 6-*exo*-*digonal* closure described here[1a,2d] may be a general and synthetically useful characteristic of alkoxymethyl radicals. Hydrogen transfer is also insignificant or absent in the cyclization of acyl[34] or 1,1-difluoroalkyl[35] radicals.

Compound **32d** (Table 5) was converted into the known alcohol **32e** (see Table 9), a result that again supports the stereochemical assignment to **32d**.

Use of Different Silicon Substituents. We examined briefly the use of *i*-Pr, Ph, and Me substituents on

(28) Yang, W. Ph.D. Thesis, University of Alberta, Edmonton, Canada, January, 1998.

(29) (a) Rigby, J. H.; Danca, D. M.; Horner, J. H. *Tetrahedron Lett.* **1998**, *39*, 8413−8416. (b) Keck, G. E.; Grier, M. C. Abtracts of Papers. *214th National Meeting of the American Chemical Society*, Las Vegas, NV, Sep 1997; American Chemical Society: Washington, DC, 1997; ORGN 337.

(30) Cf. Forbes, J. E.; Zard, S. Z. *J. Am. Chem. Soc.* **1990**, *112*, 2034−2036 and references therein.

(31) Cf. Stork, G.; Mook, Jr., R.; Biller, S. A.; Rychnovsky, S. D. *J. Am. Chem. Soc.* **1983**, *105*, 3741−3742.

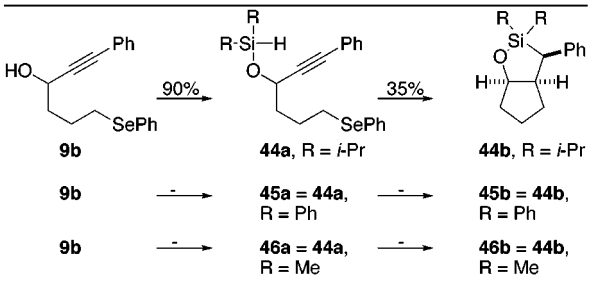
(32) (a) Beckwith, A. L. J.; Glover, S. A. *Aust. J. Chem.* **1987**, *40*, 157−173. (b) Roberts, B. P. *Chem. Soc. Rev.* **1999**, *28*, 25−35.

(33) (a) Rawal, V. H.; Singh, S. P.; Dufour, C.; Michoud, C. *J. Org. Chem.* **1991**, *56*, 5245−5247. (b) Burke, S. D.; Rancourt, J. *J. Am. Chem. Soc.* **1991**, *113*, 2335−2336. (c) Bachi, M. D.; Frolow, F.; Hoornaert, C. *J. Org. Chem.* **1983**, *48*, 1841−1849.

(34) (a) Chen, C.; Crich, D.; Papadatos, A. *J. Am. Chem. Soc.* **1992**, *114*, 8313−8314. (b) Bachi, M. D.; Denenmark, D. *Heterocycles* **1989**, *28*, 583−588.

(35) Arnone, A.; Bravo, P.; Frigerio, M.; Viani, F.; Cavicchio, G.; Crucianelli, M. *J. Org. Chem.* **1994**, *59*, 3459−3466.

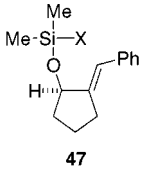
Table 7



silicon, and our results for the radical cascades are summarized in Table 7.

The diisopropyl silane **44a** gave a poor yield in the cyclization, possibly due to undesired hydrogen transfer[2c] from the isopropyl groups. The diphenyl- and dimethylsilyl compounds decomposed on silica gel and on alumina; the cyclization products were difficult to purify and appeared to be formed in poor yield. For the dimethylsilyl series, the intramolecular hydrogen transfer step (cf. **2** → **3** of Scheme 1) is not as efficient as with the di-*tert*-butyl series, since an appreciable amount of olefinic product was formed. Surprisingly, the diphenylsilane **45a** also gave a poor yield, but it was not clear if this reflected the difficulty of handling the compound.

Modifications of the Radical Cyclization Products. As shown in Table 8, the crude products **45b** and **46b** from radical cyclization experiments were treated with fluoride ion under conditions of the Tamao oxidation[36] (30% H_2O_2, $KHCO_3$, $KF{\cdot}2H_2O$ in 1:1 MeOH−THF at 60 °C) to yield diols. Diol **45c** was isolated in the first case (14%) and both **46c** (= **45c**) (27%) and **46d** (29%) in the second. The olefinic alcohol **46d** most probably arises from an *O*-silyl precursor of type **47** in the crude radical cyclization product, suggesting, as mentioned above, that hydrogen transfer from silicon is not particularly efficient in the dimethylsilyl case.



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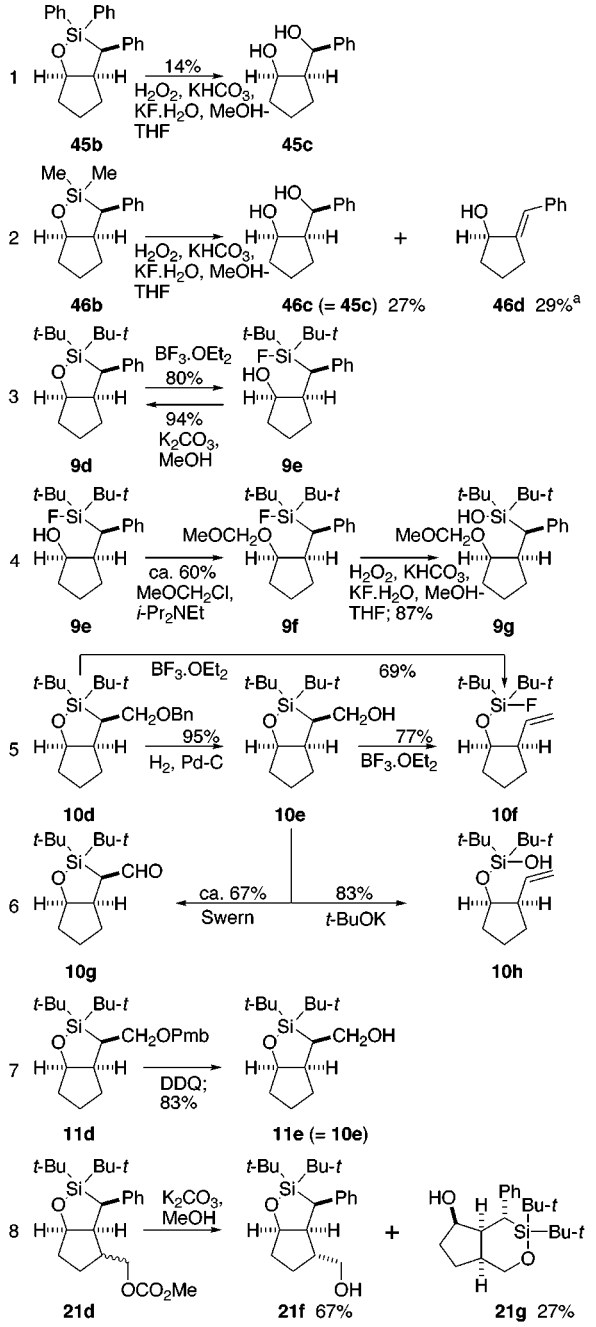
Using several cyclization products of the di-*tert*-butyl series, a number of experiments (Table 8) were done to modify the structures and, especially, to break the newly formed carbon−silicon bond. Treatment of **9d** with $BF_3{\cdot}OEt_2$ (Table 8, entry 3) produced a hydroxyfluorosilane (**9d** → **9e**). The hydroxyl group could be protected and the fluorine replaced by OH (**9e** → **9f** → **9g**, entry 4). When an *O*-benzyl side chain is present (**10d**, entry 5), hydrogenolysis releases the free hydroxyl group (**10d** → **10e**), and treatment with $BF_3{\cdot}OEt_2$ gives an olefinic fluorosilane (**10e** → **10f**). The same compound (**10f**) is obtained directly from the *O*-benzyl precursor by the action of $BF_3{\cdot}OEt_2$ (**10d** → **10f**). Alcohol **10e** was oxidized (Swern) to the corresponding aldehyde (**10g**, see entry 6) and converted by treatment with *t*-BuOK into the olefinic hydroxysilane **10h**. Compound **11d** (entry 7) was treated with DDQ, and the expected alcohol (**11e**) (= **10e**) was released. Hydrolysis of carbonate **21d** (entry 8) gave

Table 8



[a] As indicated in the text, **46d** probably arises from **47** present in crude **46b**.

mainly the desired alcohol **21f**, but a small amount of the silicon O → O migration product **21g** was isolated.

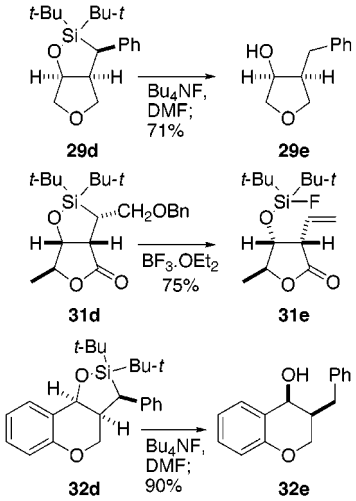
Several of the radical cyclization products shown in Table 5 were also modified, as summarized in Table 9. Treatment of **29d** with *n*-Bu_4NF in DMF[37] gave **29e** (Table 9), and **32d** gave the known compound **32e**[38] under the same conditions. Comparison of the ^1H NMR spectrum of our material with the data published for **32e**[38] served to confirm the stereochemistry of **32d**. Lactone **31d** was transformed into the olefinic fluorosilane **31e** on treatment with $BF_3{\cdot}OEt_2$ (Table 9).

(36) Jones, G. R.; Landais, Y. *Tetrahedron* **1996**, *52*, 7599−7662

(37) Koreeda, M.; Wu, J. *Synlett* **1995**, 850−852, and references therein.

(38) Gomis, M.; Kirkiacharian, B. S.; Likforman, J.; Mahuteau, J. *Bull. Soc. Chim. Fr.* **1988**, 585−590.

Table 9



Finally, some comment is appropriate about the chemical properties of the vinyl silanes shown above in Table 6. A proper study of their reaction with electrophiles was not undertaken, as a cursory examination, using dimethyldioxirane or $AcCl/AlCl_3$ gave rather complex mixtures.

Conclusion

The radical cascade summarized in Scheme 1, and illustrated by the examples collected in the Tables, represents a method for making unusual heterocycles containing silicon. The new asymmetric centers that are generated have a predictable stereochemistry relative to the initial stereogenic center (the hydroxyl-bearing carbon). The carbon−silicon bond in the products can be cleaved and, in previous work from this laboratory,[1c] the sequence of Scheme 1 has been used in formal syntheses of Corey lactones and methyl *epi*-jasmonate. The cyclization of selenocarbamate **34c** (see Table 5), together with other more extensive published work,[29] illustrates the utility of carbamoyl radicals.

Experimental Section

General Procedures. Unless stated to the contrary, the general procedures used previously[39] were followed. The symbols s′, d′, t′, and q′ used for ^{13}C NMR signals indicate 0, 1, 2, or 3 attached hydrogens, respectively, the assignments being made from APT spectra.

General Procedure for Addition of an Acetylide to an Aldehyde. The acetylene was placed in a round-bottomed flask sealed with a septum and equipped with a Teflon-coated stirring bar. The system was flushed with Ar for 2−5 min, and dry THF was injected. The solution was lowered into a cooling bath (−78 °C) and stirred for 5 min. A solution of *n*-BuLi (1.6 M in hexanes) was injected dropwise, the mixture was stirred at −78 °C for 5−15 min, and a solution of the aldehyde in dry THF was then injected at a rapid dropwise rate. Stirring at −78 °C was continued for 15−60 min, and the mixture was then quenched, usually with saturated aqueous NH_4Cl. The cooling bath was removed, and the mixture was allowed to reach room temperature, and then processed as described for the individual experiments.

General Procedure for Silylation of Alcohols. The alcohol and imidazole were placed in a round-bottomed flask equipped with a Teflon-coated stirring bar and a reflux condenser that was sealed with a septum. The system was flushed with Ar for 2−5 min, and dry THF or dry PhH was injected. A solution of the dialkylchlorosilane in dry THF or PhH was injected. A white precipitate formed rapidly, and the reaction mixture was refluxed, usually for several hours, and then cooled and processed as described for the individual experiments.

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 that was sealed with a septum. The system was flushed with Ar for 5−10 min, and dry PhH was injected. The solution was refluxed, and separate solutions of Ph_3SnH (or Bu_3SnH) and AIBN, each in dry PhH, were injected simultaneously by syringe pump over several h. Refluxing was continued for an arbitrary time after the addition was complete. The reaction mixture was cooled, and the solvent was evaporated to give a residue that was processed as described for the individual experiments.

1-Phenyl-6-(phenylseleno)-1-hexyn-3-ol (9b). The general procedure for addition of an acetylide to an aldehyde was followed, using **22** (2.96 mg, 2.90 mmol) in THF (15 mL), *n*-BuLi (1.6 M in hexanes, 1.64 mL, 2.62 mmol), an initial reaction time of 15 min, and **9a**[9] (379.5 mg, 1.750 mmol) in THF (1.5 mL plus 1 mL as a rinse). Stirring at −78 °C was continued for 45 min, water (50 mL) was added, and the mixture was allowed to attain room temperature and was extracted with CH_2Cl_2. The combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (1.8 × 20 cm), using 1:9 EtOAc−hexane, gave **9b** (454.7 mg, 79%) as a colorless oil: FTIR ($CDCl_3$ cast) 3362, 2936, 1578, 1489, 1477, 1437, 757, 735, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.86−2.01 (m, 4 H), 2.08 (br s, 1 H), 2.89−3.03 (m, 2 H), 4.60 (br s, 1 H), 7.17−7.33 (m, 6 H), 7.33−7.42 (m, 2 H), 7.45−7.60 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 25.8 (t′), 27.5 (t′), 37.7 (t′), 62.4 (d′), 85.2 (s′), 89.7 (s′), 122.5 (s′), 126.8 (d′), 128.3 (d′), 128.5 (d′), 129.1 (d′), 130.2 (s′), 131.7 (d′), 132.7 (d′); exact mass *m*/*z* calcd for $C_{18}H_{18}O^{80}Se$ 330.0522, found 330.0527. Anal. Calcd for $C_{18}H_{18}OSe$: C, 65.65; H, 5.51. Found: C, 65.48; H, 5.53.

Bis(1,1-dimethylethyl)[[3-phenyl-1-[3-(phenylseleno)-propyl]-2-propynyl]oxy]silane (9c). The general procedure for silylation of alcohols was followed, using **9b** (239.3 mg, 1.00 mmol) in THF (8 mL), imidazole (136.2 mg, 2.00 mmol), *t*-Bu_2-SiHCl (223.5 mg, 1.25 mmol) in THF (1 mL plus 1 mL as a rinse), and a reflux time of 2.5 h.[40] The mixture was cooled, diluted with water (50 mL), and extracted with Et_2O. The combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (2 × 15 cm), using 3:47 CH_2Cl_2−hexane, gave **9c** (427.8 mg, 91%) as a colorless oil: FTIR ($CHCl_3$ cast) 2929, 2856, 2096, 1470, 1084, 826 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.00 (s, 9 H), 1.05 (s, 9 H), 1.88−2.04 (m, 4 H), 2.99 (t, J = 7.0 Hz, 2 H), 4.14 (s, 1 H), 4.70 (t, J = 5.5 Hz, 1 H), 7.20−7.25 (m, 3 H), 7.26−7.34 (m, 3 H), 7.35−7.41 (m, 2 H), 7.48−7.54 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 19.8 (s′), 20.2 (s′), 25.7 (t′), 27.38 (q′), 27.43 (q′), 27.8 (t′), 38.4 (t′), 66.3 (d′), 85.2 (s′), 99.0 (s′), 123.0 (s′), 126.8 (d′), 128.2 (d′), 128.3 (d′), 129.0 (d′), 130.4 (s′), 130.6 (d′), 132.8 (d′); exact mass *m*/*z* calcd for $C_{26}H_{36}O^{80}SeSi$ 472.1701, found 472.1696. Anal. Calcd for $C_{26}H_{36}OSeSi$: C, 66.22; H, 7.69. Found: C, 66.08; H, 7.82.

(3α,3a*β*,6a*β*)-2,2-Bis(1,1-dimethylethyl)hexahydro-3-phenyl-2*H*-cyclopent[*d*]-1,2-oxasilole (9d). The general procedure for radical cyclization was followed, using **9c** (141.5 mg, 0.30 mmol) in PhH (45 mL), Ph_3SnH (210.6 mg, 0.60 mmol) in PhH (7.5 mL), AIBN (24.6 mg, 0.5 mmol) in PhH (7.5 mL), and an addition time of 6 h. Refluxing was continued for 0.5 h after the stannane addition. Evaporation of the solvent and flash chromatography of the residue over silica

(39) Clive, D. L. J.; Wickens, P. L.; Sgarbi, P. W. M. *J. Org. Chem.* **1996**, *61*, 7426−7437.

(40) McCombie, S. W.; Ortiz, C.; Cox, B.; Ganguly, A. K. *Synlett* **1993**, 541−547.

gel (1.8 × 14 cm), using increasing amounts of CH_2Cl_2 in hexane (from 5% to 7%), gave an oil that was purified by filtration through a pad (1 × 6 cm) of neutral alumina (Grade I), using 1:199 Et_2O−hexane, to give **9d** (68.5 mg, 72%) as a white solid: mp 49−51 °C; FTIR ($CDCl_3$ cast) 2960, 2938, 2859, 1475, 820 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.04 (s, 9 H), 1.15 (s, 9 H), 1.54−2.03 (m, 6 H), 2.89−3.01 (m, 1 H), 3.40 (d, J = 7.5 Hz, 1 H), 4.48−4.53 (m, 1 H), 7.10−7.15 (m, 1 H), 7.23−7.33 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 21.1 (s′), 22.6 (s′), 24.1 (t′), 28.0 (t′), 28.5 (q′), 28.8 (q′), 35.1 (t′), 36.6 (d′), 47.5 (d′), 83.7 (d′), 124.7 (d′), 128.1 (d′), 129.5 (d′), 142.2 (s′); exact mass m/z calcd for $C_{20}H_{32}OSi$ 316.2222, found 316.2220. Anal. Calcd for $C_{20}H_{32}OSi$: C, 75.88; H, 10.19. Found: C, 75.53; H, 10.25.

[1α,2α(*R)]-2-[[Bis(1,1-dimethylethyl)fluorosilyl]phenylmethyl]cyclopentanol (9e).** $BF_3{\cdot}Et_2O$ (0.10 mL, 0.81 mmol) was added dropwise to a stirred and cooled (0 °C) solution of **9d** (72.4 mg, 0.229 mmol) in dry CH_2Cl_2 (2.3 mL), and the mixture was stirred at 0 °C for 7 h. Saturated aqueous $NaHCO_3$ (1 mL) was added, and stirring was continued for 10 min. The cooling bath was removed, and the mixture was extracted with CH_2Cl_2. The combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (1 × 10 cm), using increasing amounts of EtOAc in hexane (5% to 10%), gave **9e** (61.7 mg, 80%) as a white, crystalline solid: mp 115−118 °C; FTIR (CH_2Cl_2 cast) 3459, 2939, 2861, 1474, 823, 809, 703, 579 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.97 (d, J = 0.5 Hz, 9 H), 1.11 (d, $J_{H,F}$ = 1.0 Hz, 10 H), 1.50−1.79 (m, 4 H), 1.80−1.96 (m, 1 H), 1.96−2.10 (m, 1 H), 2.38−2.52 (m, 1 H), 2.88 (d, $J_{H,F}$ = 12.0 Hz, 1 H), 3.81−3.89 (m, 1 H), 7.11−7.18 (m, 1 H), 7.24−7.36 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 22.1 (s′, J_{CF} = 12.2 Hz), 22.7 (t′), 22.8 (s′, J_{CF} = 12.6 Hz), 28.4 (q′), 28.8 (q′), 29.4 (t′, J = 5.8 Hz), 32.7 (t′), 35.4 (d′, J_{CF} = 12.6 Hz), 48.4 (d′), 73.6 (d′), 125.6 (d′), 128.6 (d′), 129.6 (d′), 141.8 (s′, J = 5.5 Hz); exact mass m/z calcd for $C_{16}H_{24}FOSi$ (M − C_4H_9) 279.1581, found 279.1579. Anal. Calcd for $C_{16}H_{24}FOSi$: C, 71.37; H, 9.88. Found: C, 71.37; H, 9.88.

Crystallographic data for **9e**: $C_{20}H_{33}FOSi$, MW 336.55, crystal size 0.59 × 0.58 × 0.58 mm, tetragonal space group $P4_2/n$ (No. 86), a = 21.1751(15) Å, c = 8.8012(8) Å, V = 3946.3(5) Å^3, Z = 8, D_{calc} = 1.133 g cm^{-3}, μ = 0.131 mm^{-1}, T = 223(1) K, λ = 0.710 73 Å (Mo Kα), $2\theta_{max}$ = 55.86°, absorption correction by Gaussian integration (indexing of crystal faces), range of transmission factors 0.9352−0.9243, $R_1(F)$ = 0.0473 (for 3038 data with $F_o^2 \geq 2\sigma(F_o^2)$) and $wR_2(F^2)$ = 0.1341 (for all 4738 independent data), goodness-of-fit (S) = 1.105, largest difference peak and hole 0.227 and −0.262 e Å^{-3}.

(3α,3a*β*,6a*β*)-2,2-Bis(1,1-dimethylethyl)hexahydro-3-phenyl-2*H*-cyclopent[*d*]-1,2-oxasilole (9d). Anhydrous K_2CO_3 (19.7 mg, 0.140 mmol) was added to a stirred solution of **9e** (47.8 mg, 0.142 mmol) in MeOH (1.4 mL). Stirring was continued for 45 min, and the mixture was evaporated. Flash chromatography of the residue over silica gel (1 × 10 cm), using 1:99 EtOAc−hexane, gave **9d** (42.2 mg, 94%) as a white solid, identical [^1H NMR (400 MHz)] to that obtained from radical cyclization.

[1α(1*R),2α]-Bis(1,1-dimethylethyl)fluoro[[2-(methoxymethoxy)cyclopentyl]phenylmethyl]silane (9f).** A solution of $MeOCH_2Cl$ (23.8 mg, 0.295 mmol) in CH_2Cl_2 (0.5 mL) was added at a fast dropwise rate to a stirred solution of **9e** (24.8 mg, 0.074 mmol) and *i*-Pr_2NEt (47.6 mg, 0.370 mmol) in CH_2Cl_2 (3 mL). Stirring was continued for 24 h, at which point the reaction was half complete (TLC control, 1:9 silica, EtOAc−hexane). More $MeOCH_2Cl$ (23.8 mg, 0.295 mmol), *i*-Pr_2NEt (47.6 mg, 0.370 mmol), and CH_2Cl_2 (3.6 mL) were added, and stirring was continued for 24 h. Water (10 mL) was added, and the mixture was extracted with CH_2Cl_2. The combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (1 × 10 cm), using 1:99 EtOAc−hexane, gave **9f** (16.7 mg, 60%) as a colorless oil, which was used directly for conversion into **9g**.

[1α(*R),2α]-Bis(1,1-dimethylethyl)[[2-(methoxymethoxy)-cyclopentyl]phenylmethyl]silanol (9g).** H_2O_2 (30% in H_2O, 0.18 mL, 1.6 mmol) was added to a stirred mixture of KF·$2H_2O$ (4.1 mg, 0.043 mmol), K_2CO_3 (6.0 mg, 0.043 mmol), and **9f** (16.5 mg, 0.043 mmol) in 1:1 MeOH−THF (2 mL). The mixture was heated at 65 °C overnight, cooled, diluted with water (20 mL), and extracted with CH_2Cl_2. The combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (0.5 × 5 cm), using 1:19 EtOAc−hexane, gave **9g** (14.3 mg, 87%) as a yellowish solid: mp 106−111 °C; FTIR (CH_2Cl_2 cast) 3649, 3501, 2937, 2858, 1474, 1044, 821 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.00 (s, 9 H), 1.11 (s, 9 H), 1.56−1.93 (m, 6 H), 2.01−2.11 (m, 1 H), 2.44−2.55 (m, 1 H), 2.87 (d, J = 11.5 Hz, 1 H), 3.11 (s, 3 H), 3.58−3.62 (m, 1 H), 3.78 (d, J = 6.5 Hz, 1 H), 4.30 (d, J = 6.5 Hz, 1 H), 7.03−7.11 (m, 1 H), 7.17−7.27 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 22.1 (s′), 22.6 (t′), 23.0 (s′), 29.1 (q′), 29.2 (q′), 31.0 (t′), 31.1 (t′), 35.8 (d′), 47.5 (d′), 55.3 (q′), 81.0 (d′), 96.9 (t′), 124.9 (d′), 128.2 (d′), 129.5 (d′), 144.2 (s′); exact mass m/z calcd for $C_{20}H_{33}O_2Si$ (M − C_2H_5O) 333.2250, found 333.2246; mass (CI) m/z calcd for $C_{22}H_{39}O_3Si$ (M + H) 379, found 379.

(3α,3a*β*,6a*β*)-2,2-Bis(1,1-dimethylethyl)hexahydro-2*H*-cyclopent[*d*]-1,2-oxasilole-3-methanol (10e). A solution of **10d** (40.7 mg, 0.113 mmol) in 98% EtOH (1.1 mL) was shaken with Pd/C (5−10%, 40.7 mg) under H_2 (50 psi) in a Parr shaker for 3 h. The mixture was evaporated, and flash chromatography of the residue over silica gel (1 × 10 cm), using 1:9 EtOAc−hexane, gave **10e** (28.9 mg, 95%) as a white solid: mp 64.5−66 °C; FTIR ($CDCl_3$ cast) 3388, 2960, 2934, 2859, 1474, 1030, 1004, 822 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.04 (s, 9 H), 1.05 (s, 9 H), 1.39−1.65 (m, 3 H), 1.65−1.78 (m, 2 H), 1.78−1.89 (m, 1 H), 2.01−2.11 (m, 2 H), 2.50−2.60 (m, 1 H), 3.97 (s, 1 H), 3.97−4.02 (m, 1 H), 4.49 (ddd, J = 6.0, 6.0, 2.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 20.6 (s′), 22.0 (s′), 25.1 (t′), 26.2 (t′), 27.9 (q′), 28.6 (q′), 31.9 (d′), 35.6 (t′), 46.0 (d′), 62.3 (t′), 83.8 (d′); exact mass m/z calcd for $C_{11}H_{21}O_2Si$ (M − C_4H_9) 213.1311, found 213.1307. Anal. Calcd for $C_{15}H_{30}O_2Si$: C, 66.61; H, 11.18. Found: C, 66.85; H, 11.27.

***cis*-Bis(1,1-dimethylethyl)[(2-ethenylcyclopentyl)oxy]-fluorosilane (10f) from 10e.** $BF_3{\cdot}Et_2O$ (0.10 mL, 0.8 mmol) was added to a stirred and cooled (0 °C) solution of **10e** (27.4 mg, 0.100 mmol) in dry CH_2Cl_2 (2.5 mL).[41] Stirring at 0 °C was continued for 1 h, saturated aqueous $NaHCO_3$ (1 mL) was added, and the cooling bath was removed. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (0.5 × 5 cm), using hexane, gave **10f** (19.9 mg, 77%) as a colorless oil: FTIR ($CDCl_3$ cast) 2966, 2935, 2862, 1473, 1137, 1066, 842, 830 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.02 (d, J = 0.5 Hz, 9 H), 1.04 (d, J = 0.5 Hz, 9 H), 1.55−1.92 (m, 6 H), 2.37 (dddd, J = 9.0, 9.0, 9.0, 4.0 Hz, 1 H), 4.48−4.53 (m, 1 H), 4.99−5.09 (m, 2 H), 5.99 (ddd, J = 17.5, 10.0, 8.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 20.1 (s′, J_{CF} = 14.5 Hz), 20.7 (s′, J_{CF} = 16.0 Hz), 21.8 (t′), 27.0 (s′), 27.2 (s′), 28.9 (t′), 35.3 (t′), 50.6 (d′), 78.6 (d′), 114.8 (s′), 139.3 (d′); exact mass m/z calcd for $C_{11}H_{20}FOSi$ (M − C_4H_9) 215.1267, found 215.1267.

***cis*-Bis(1,1-dimethylethyl)[(2-ethenylcyclopentyl)oxy]-fluorosilane (10f) from 10d.** $BF_3{\cdot}Et_2O$ (0.10 mL, 0.8 mmol) was added to a stirred and cooled (0 °C) solution of **10d** (23.8 mg, 0.066 mmol) in dry CH_2Cl_2 (2.5 mL).[41] Stirring at 0 °C was continued for 1 h, saturated aqueous $NaHCO_3$ (1 mL) was added, and the cooling bath was removed. The mixture was stirred for 15 min, the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (0.5 × 5 cm), using hexane, gave **10f** (11.6 mg, 69%) as a colorless oil, whose ^1H NMR spectrum was identical to that obtained with material derived from **10e**.

***cis*-Bis(1,1-dimethylethyl)[(2-ethenylcyclopentyl)oxy]-silanol (10h).** Alcohol **10e** (13.5 mg, 0.050 mmol) was added to a stirred slurry of *t*-BuOK (8.8 mg, 0.075 mmol) in dry THF (1 mL). Stirring at room temperature was continued for 10 min, saturated aqueous NH_4Cl (ca. 5 drops) and water (2 mL)

(41) Tamao, K.; Ishida, N. *Tetrahedron Lett.* **1984**, *25*, 4245−4248.

were added sequentially, and the mixture was extracted with CH_2Cl_2. The combined organic extracts were dried (Na_2SO_4) and evaporated to give **10h** (11.2 mg, 83%) as a colorless oil: FTIR ($CHCl_3$ cast) 3492, 2965, 2934, 2859, 1473, 1136, 1056, 911, 828 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.00 (s, 18 H), 1.53−1.91 (m, 7 H), 2.36 (dddd, J = 9.0, 9.0, 9.0, 4.0 Hz, 1 H), 4.41−4.46 (m, 1 H), 5.00−5.09 (m, 2 H), 6.01 (ddd, J = 17.5, 10.0, 8.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 20.5 (s′), 20.8 (s′), 21.9 (t′), 27.7 (q′), 27.8 (q′), 28.9 (t′), 35.5 (t′), 50.7 (d′), 77.8 (d′), 114.8 (t′), 140.2 (d′); exact mass m/z calcd for $C_{15}H_{30}O_2Si$ (M − C_4H_9) 303.1780, found 303.1782.

(3α,3aβ,6aβ)-[2,2-Bis(1,1-dimethylethyl)hexahydro-2*H*-cyclopent[*d*]-1,2-oxasilol-3-yl]carboxaldehyde (10g). Dry DMSO (0.17 mL, 2.2 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of $(COCl)_2$ (0.10 mL, 1.1 mmol) in CH_2Cl_2 (3.5 mL).[42] Stirring was continued for 15 min, and a portion of this solution (ca. 0.3 mL) was quickly withdrawn into a syringe and transferred to a stirred and cooled (−78 °C) solution of **10e** (18.5 mg, 0.068 mmol) in CH_2Cl_2 (1 mL). Stirring at −78 °C was continued for 15 min, and dry Et_3N (0.1 mL) was added. Stirring was continued for 5 min, the cooling bath was removed, and the mixture was allowed to reach room temperature. Water (1 mL) was added, the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (1 × 5 cm), using 1:9 EtOAc−hexane, gave **10g** (12.4 mg, 67%) as a slightly impure [^1H NMR (300 MHz)], colorless oil: FTIR ($CDCl_3$ cast) 2936, 2860, 1692, 1474, 1069, 823 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.03 (s, 9 H), 1.09 (s, 9 H), 1.29−2.13 (m, 6 H), 3.03 (dd, J = 8.0, 3.5 Hz, 1 H), 4.53 (ddd, J = 6.0, 6.0, 2.5 Hz, 1 H), 9.92 (d, J = 3.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 20.8 (s′), 22.5 (s′), 25.7 (t′), 27.7 (q′), 27.8 (t′), 28.3 (q′), 34.7 (t′), 45.5 (d′), 47.2 (d′), 84.4 (d′), 203.6 (d′); exact mass m/z calcd for $C_{15}H_{28}O_2Si$ 268.1859, found 268.1854.

1-Methoxy-4-[(2-propynyloxy)methyl]benzene (24). The following procedure differs from that given in the literature.[21]

NaH (80% dispersion in mineral oil, 1.602 g, 53.51 mmol) was suspended in a mixture of THF (20 mL) and DMF (2.5 mL), and the mixture was stirred at 0 °C for 10 min. Propargyl alcohol (1.504 g, 26.76 mmol) was added dropwise over 10 min, to give a light brown slurry, which was stirred for 2 h. *p*-Methoxybenzyl chloride (4.193 g, 26.76 mmol) was added over 15 min, after which time the ice bath was removed and stirring was continued overnight. The mixture was poured into water (150 mL) and extracted with Et_2O. The combined organic extracts were washed with brine and dried ($MgSO_4$). Evaporation of the solvent and flash chromatography of the residue over silica gel (5 × 25 cm), using hexane (750 mL), followed by 1:19 EtOAc−hexane (1500 mL), gave **24**[21] (3.254 g, 69%) as an oil: FTIR (CH_2Cl_2 cast) 3289, 3001, 2937, 2115, 1442, 819 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.53 (t, J = 2.3 Hz, 1 H), 3.78 (s, 3 H), 4.17 (d, J = 2.5 Hz, 2 H), 4.55 (s, 2 H), 6.84 (d, J = 8.7 Hz, 2 H), 7.36 (d, J = 8.7 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 55.18 (q′), 56.96 (t′), 71.10 (t′), 74.7 (d′), 79.93 (s′), 113.86 (d′), 129.40 (s′), 129.81 (d′), 159.45 (s′); exact mass m/z calcd for $C_{11}H_{12}O_2$ 176.08372, found 176.08372.

(3α,3aβ,6aβ)-2,2-Bis(1,1-dimethylethyl)hexahydro-2*H*-cyclopent[*d*]-1,2-oxasilole-3-methanol (11e = 10e) from 11d. Compound **11d** (214.4 mg, 0.55 mmol) and a Teflon-coated stirring bar were placed in a round-bottomed flask that was sealed with a septum. The system was flushed with Ar for 20 min, and CH_2Cl_2 (7.5 mL) and water (0.35 mL) were injected. DDQ[43] (187.2 mg, 0.82 mmol) was added to produce a dark green mixture, which quickly changed to a light beige color. Stirring was continued for 1 h. The mixture was poured into saturated aqueous $NaHCO_3$ (10 mL) and water (30 mL) and extracted with CH_2Cl_2. The combined organic extracts were washed with brine and dried ($MgSO_4$). Evaporation of the solvent and flash chromatography of the residue over silica gel (2 × 25 cm), using 3:17 EtOAc−hexane, gave **11e** (122.8 mg, 83%) as an oil: FTIR ($CHCl_3$ cast) 3362, 1474, 1034, 822 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.24 (s, 18 H), 1.38−1.91 (m, 6 H), 1.98−2.11 (m, 2 H), 2.47−2.60 (m, 1 H), 3.97 (d, J = 8.5 Hz, 2 H), 4.47 (td, J = 6.0, 2.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 20.5 (s′), 21.9 (s′), 25.0 (t′), 26.2 (t′), 27.9 (q′), 28.6 (q′), 31.8 (d′), 35.5 (t′), 45.9 (d′), 62.2 (t′), 83.7 (d′); exact mass m/z calcd for $C_{11}H_{21}O_2Si$ (M − C_4H_9) 213.13109, found 213.13068.

Triethyl(2-propynyloxy)silane (25). Compound **25** was prepared by a method different from that given in the literature.[23] Propargyl alcohol (987.1 mg, 17.64 mmol) and imidazole (2.396 g, 35.23 mmol) were dissolved in THF (25 mL). Neat Et_3SiCl (332.4 mg, 22.03 mmol) was added dropwise over 15 min to produce a white slurry, which was refluxed for 12 h. The mixture was cooled, poured into water (100 mL), extracted with EtOAc, and dried ($MgSO_4$). Evaporation of the solvent and flash chromatography of the residue over silica gel (4 × 25 cm), using hexane, gave **25**[23] as an oil, characterized by spectroscopic comparison with published data.

Ethyl 3-[(Phenylseleno)methyl]-4-pyridinecarboxylate (19bb). PhSeSePh (188.2 mg, 0.60 mg) and NaH (80% dispersion in mineral oil, 32.2 mg, 1.07 mmol) and a Teflon-coated stirring bar were placed in a round-bottomed flask carrying a condenser sealed with a septum. The system was flushed with Ar for 10 min, and THF (2 mL) was injected. The solution was stirred and heated at 60 °C for 1 h to give a bright yellow suspension, which was then allowed to cool. A solution of HMPA (0.1 mL) and **19aa**[44] (100.3 mg, 0.83 mmol) in THF (2 mL) was added with stirring, to produce a bright orange mixture, which was stirred and heated at 60 °C for 22 h, and then cooled. MeOH (1 mL) was added to quench the reaction, and the solvents were evaporated. Water (30 mL) was added to the residue, and the mixture was extracted with Et_2O. The aqueous phase was evaporated to dryness, and the residue was dissolved in EtOH that had been saturated with HCl (50 mL). The resulting solution was refluxed for 5 h, cooled, and evaporated. Saturated aqueous $NaHCO_3$ (20 mL) and water (25 mL) were added to the residue, and the mixture was extracted with EtOAc. Evaporation of the solvent and flash chromatography of the residue over silica gel (2.5 × 25 cm), using 1:1 EtOAc−hexane, gave **19bb** (180.2 mg, 68%) as an oil: FTIR ($CHCl_3$ cast) 2979, 1723 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.29 (t, J = 7.1 Hz, 3 H), 4.26 (q, J = 7.2 Hz, 2 H), 4.30 (s, 2 H), 7.05−7.22 (m, 3 H), 7.25−7.30 (m, 2 H), 7.58 (d, J = 5.0 Hz, 1 H), 8.12 (s, 1 H), 8.44 (d, J = 5.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 13.9 (q′), 27.5 (t′), 61.5 (t′), 123.4 (d′), 127.8 (d′), 128.8 (d′), 134.7 (d′), 135.2 (s′), 135.4 (s′), 148.5 (d′), 151.5 (d′), 165.4 (s′); exact mass m/z calcd for $C_{15}H_{15}NO_2$-Se 321.02679, found 321.026118.

3-[(Phenylseleno)methyl]-4-pyridinecarboxaldehyde (19a). Ester **19bb** (126.1 mg, 0.39 mmol) and a Teflon-coated stirring bar were placed in a round-bottomed flask sealed with a septum. The system was flushed with Ar for 10 min, and CH_2Cl_2 (4 mL) was injected. The solution was cooled to −78 °C, and after 10 min, DIBAL-H (1.0 M in CH_2Cl_2, 0.43 mL, 0.43 mmol) was injected over 2 min with stirring. Stirring was continued for an additional 25 min, the cooling bath was removed, and stirring was continued for 10 min. The solution was then filtered through a pad (1.5 × 4 cm) of Celite, using CH_2Cl_2. Evaporation of the solvent and flash chromatography of the residue over silica gel (2 × 25 cm), using 2:3 EtOAc−hexane, gave **19a** (44.6 mg, 41%, 89% corrected for recovered **19bb**) as an oil: FTIR ($CHCl_3$ cast) 2794, 1704 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.35 (s, 2 H), 7.16−7.40 (m, 5 H), 7.57 (d, J = 4.9 Hz, 1 H), 8.29 (s, 1 H), 8.68 (d, J = 4.9 Hz, 1 H), 10.16 (s, 1 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 25.6 (t′), 123.8 (d′), 128.2 (s′), 128.6 (d′), 129.3 (d′), 134.8 (s′), 135.5 (d′), 138.1 (s′), 149.6 (d′), 152.3 (d′), 191.2 (d′); exact mass m/z calcd for $C_{13}H_{11}$-$NO^{80}Se$ 277.00058, found 277.00039.

5-[(1,1-Dimethylethyl)diphenylsilyl)oxy]-2-(phenylseleno)pentanal (21bb). Dry Et_2NH (1.80 mL, 1.27 g, 1.7 mmol) was added to a stirred and cooled (0 °C) solution of PhSeCl

(42) Mancuso, A. J.; Swern, D. *Synthesis* **1981**, 165−185.
(43) Cf. Horita, K.; Yoshioka, T.; Tanaka, T.; Oikawa, Y.; Yonemitsu, O. *Tetrahedron*, **1986**, *42*, 3021−3028.
(44) Epsztajn, J.; Jozwiak, A.; Szczesniak, A. K. *Synth. Commun.* **1994**, *24*, 1789−1798.

(1.64 g, 8.56 mmol) in dry hexane (40 mL).[45] The red solution turned yellow, and a precipitate formed. Stirring at 0 °C was continued for 15 min, the cooling bath was removed, and the mixture was allowed to stand for 15 min so that the precipitate settled. The supernatant layer was transferred by syringe to a stirred and cooled (−78 °C) solution of **21aa**[46] (2.62 g, 7.70 mmol) in dry CH_2Cl_2 (40 mL). The residual salts were washed with dry hexane (20 mL), and the rinsings were transferred, again by syringe, into the reaction mixture. Stirring at −78 °C was continued for 30 min, and brine (100 mL) was added. The cooling bath was removed, and the mixture was allowed to reach room temperature. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (2 × 15 cm), using first 2:49 EtOAc−hexane, and then 1:9 EtOAc−hexane, gave **21bb** as an impure [^{1}H NMR (300 MHz)] oil, suitable for the next step (formation of **21cc**).

5-[(1,1-Dimethylethyl)diphenylsilyl)oxy]-2-(phenylseleno)-1-pentanol (21cc). $NaBH_4$ (1.17 g, 3.1 mmol) was added in 10 portions (over ca. 10 min) to a stirred and cooled (0 °C) solution of **21bb** and **21aa** in MeOH (75 mL). Stirring at 0 °C was continued for 1 h. Water (100 mL) was then added, the cooling bath was removed, and the mixture was acidified to ca. pH 6, using AcOH (ca. 1 mL). The mixture was extracted with Et_2O and the combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (2.8 × 30 cm), using 1:9 EtOAc−hexane, gave **21cc** (1.890 g, 49%) as a slightly yellow oil: FTIR ($CDCl_3$ cast) 3432, 3070, 2931, 2857, 1111, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.00 (s, 9 H), 1.58−1.94 (m, 4 H), 2.25 (br s, 1 H), 3.15−3.26 (m, 1 H), 3.50 (dd, J = 11.5, 6.5 Hz, 1 H), 3.60 (dd, J = 11.5, 5.0 Hz, 1 H), 3.64−3.72 (m, 2 H), 7.19−7.45 (m, 9 H), 7.49−7.56 (m, 2 H), 7.62−7.70 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 19.2 (s′), 26.9 (q′), 28.1 (t′), 30.7 (t′), 50.2 (d′), 63.4 (t′), 64.4 (t′), 127.3 (s′), 127.7 (d′), 128.0 (d′), 129.1 (d′), 129.6 (d′), 133.9 (s′), 135.5 (d′), 135.6 (d′); exact mass m/z calcd for $C_{27}H_{34}O_2{}^{80}SeSi$ 498.1493, found 498.1493. Anal. Calcd for $C_{27}H_{34}O_2SeSi$: C, 65.17; H, 6.89. Found: C, 65.34; H, 6.96.

5-[(1,1-Dimethylethyl)diphenylsilyl)oxy]-2-(phenylseleno)pentyl Methyl Carbonate (21dd). MeOCOCl (0.55 mL, 7.1 mmol) was added dropwise to a stirred and cooled (0 °C) solution of alcohol **21cc** (1.798 g, 3.61 mmol) and dry pyridine (0.58 mL, 7.2 mmol) in dry CH_2Cl_2 (36 mL). Stirring at 0 °C was continued for 1 h, and the cooling the bath was then removed. CH_2Cl_2 (100 mL) was added, and the mixture was washed with 10% aqueous $KHSO_4$. The organic layer was dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (2.8 × 25 cm), using 1:19 EtOAc−hexane, gave **21dd** (1.755 g, 84%) as a slightly yellow oil: FTIR ($CDCl_3$ cast) 2931, 1750, 1263, 1111, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.05 (s, 9 H), 1.54−1.77 (m, 2 H), 1.85−1.98 (m, 2 H), 3.28−3.37 (m, 1 H), 3.64−3.70 (m, 2 H), 3.74 (s, 3 H), 4.19 (dd, J = 11.5, 8.5 Hz, 1 H), 4.33 (dd, J = 11.5, 5.5 Hz, 1 H), 7.23−7.32 (m, 3 H), 7.35−7.46 (m, 6 H), 7.53−7.58 (m, 2 H), 7.64−7.69 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 19.3 (s′), 26.0 (q′), 28.1 (t′), 30.5 (t′), 43.0 (q′), 54.8 (d′), 63.4 (t′), 70.6 (t′), 127.7 (d′), 127.8 (s′), 128.0 (d′), 129.2 (d′), 129.6 (d′), 133.9 (s′), 135.2 (d′), 135.6 (d′), 155.6 (s′); exact mass m/z calcd for $C_{29}H_{36}O_4{}^{80}SeSi$ 556.1548, found 556.1553. Anal. Calcd for $C_{29}H_{36}O_4SeSi$: C, 62.69; H, 6.53. Found: C, 62.68; H, 6.50.

5-Hydroxy-2-(phenylseleno)pentyl Methyl Carbonate (21ee). n-Bu_4NF (3.88 mL, 1.0 M in THF, 3.88 mmol) was added to a stirred solution of **21dd** (1.707 g, 3.07 mmol) and glacial AcOH (0.22 mL, 3.84 mmol) in dry THF (28 mL). Stirring was continued for 22 h, and the mixture was evaporated. Flash chromatography of the residue over silica gel (2.8 × 19 cm), using 2:3 EtOAc−hexane, gave **21ee** (928.8 mg, 95%) as a slightly yellow oil: FTIR ($CHCl_3$ cast) 3382, 2953, 1748, 1439, 1265 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.54−1.78 (m, 3 H), 1.83−1.97 (m, 2 H), 3.30−3.49 (m, 1 H), 3.66 (t, J = 6.0 Hz, 2 H), 3.75 (s, 3 H), 4.22 (dd, J = 11.0, 8.5 Hz, 1 H), 4.36 (dd, J = 11.0, 5.0 Hz, 1 H), 7.24−7.34 (m, 3 H), 7.56−7.62 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 28.1 (t′), 30.7 (t′), 42.9 (d′), 54.8 (q′), 62.4 (t′), 70.6 (t′), 127.7 (s′), 128.0 (d′), 128.1 (d′), 135.1 (d′), 155.5 (s′); exact mass m/z calcd for $C_{13}H_{18}O_4{}^{80}Se$ 318.0370, found 318.0369. Anal. Calcd for $C_{13}H_{18}O_4Se$: C, 49.22; H, 5.72. Found: C, 49.10; H, 5.71.

5-Oxo-2-(phenylseleno)pentyl Methyl Carbonate (21a). Dry DMSO (0.49 mL, 6.88 mmol) was added dropwise to a stirred and cooled (−63 °C) solution of $(COCl)_2$ (0.30 mL, 3.44 mmol) in dry CH_2Cl_2 (10 mL). Stirring was continued for 10 min, and a solution of **21ee** (876.7 mg, 2.76 mmol) in CH_2Cl_2 (2.5 mL plus 2.5 mL as a rinse) was added over 5 min. Stirring was continued for 15 min, and dry Et_3N (2.07 mL, 14.9 mmol) was added. Stirring was continued for 5 min, the cooling bath was removed, and the mixture was allowed to reach room temperature. Water (50 mL) was added, and the mixture was extracted with CH_2Cl_2. The combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (2.8 × 18 cm), using 1:4 EtOAc−hexane, gave **21a** (585.7 mg, 67%) as a slightly yellow oil: FTIR ($CHCl_3$ cast) 1749, 1723, 1439, 1264 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.73−1.86 (m, 1 H), 2.13−2.25 (m, 1 H), 2.65−2.76 (m, 1 H), 2.77−2.87 (m, 1 H), 3.30−3.37 (m, 1 H), 3.76 (s, 3 H), 4.09 (dd, J = 11.0, 8.5 Hz, 1 H), 4.40 (dd, J = 11.0, 5.0 Hz, 1 H), 7.25−7.36 (m, 3 H), 7.54−7.60 (m, 2 H), 9.79 (t, J = 1.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 24.1 (t′), 42.0 (t′), 42.4 (d′), 54.9 (t′), 70.4 (t′), 127.2 (s′), 128.3 (d′), 129.3 (d′), 135.2 (d′), 155.5 (s′), 201.0 (d′); exact mass m/z calcd for $C_{13}H_{16}O_4{}^{80}Se$ 316.0214, found 316.0212. Anal. Calcd for $C_{13}H_{16}O_4Se$: C, 49.53; H, 5.12. Found: C, 49.74; H, 5.22.

5-Hydroxy-7-phenyl-2-(phenylseleno)-6-heptynyl Methyl Carbonate (21b). The general procedure for addition of an acetylide to an aldehyde was followed, using **22** (210 mg, 2.06 mmol) in THF (12 mL), n-BuLi (1.6 M in hexanes, 1.18 mL, 1.89 mmol), an initial reaction time of 15 min, and **21a** (540.9 mg, 1.72 mmol) in THF (2.5 mL plus 2.5 mL as a rinse). Stirring at −78 °C was continued for 45 min, 10% aqueous $KHSO_4$ (5 mL) and water (50 mL) were added, and the mixture was allowed to attain room temperature and extracted with CH_2Cl_2. The combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (2.8 × 20 cm), using increasing amounts of EtOAc in hexane (from 15% to 25%), gave **21b** (493.5 mg, 69%) as an inseparable (TLC, silica, 1:9 EtOAc−hexane) 1:1 mixture of isomers [^{1}H NMR (400 MHz)]: FTIR ($CHCl_3$ cast) 3440, 3056, 1748, 1441, 1266, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.68−1.85 (m, 1 H), 1.91−2.23 (m, 3 H), 2.30 (br s, 1 H), 3.32−3.43 (m, 1 H), 3.72 (two s, 3 H), 4.21 and 4.22 (two dd, J = 11.0, 6.5 Hz, 1 H), 4.36 and 4.37 (two dd, J = 11.0, 5.0 Hz, 1 H), 4.60−4.68 (m, 1 H), 7.19−7.35 (m, 6 H), 7.38−7.46 (m, 2 H), 7.57−7.63 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 27.1 (t′), 27.3 (t′), 35.6 (t′), 35.7 (t′), 42.6 (d′), 42.7 (d′), 54.8 (q′), 62.3 (d′), 62.5 (d′), 70.5 (t′), 85.2 (s′), 85.3 (s′), 89.6, 89.6 (two s′), 122.4 (s′), 127.4 (s′), 127.5 (s′), 128.0 (d′), 128.3 (d′), 128.4 (d′), 129.1 (d′), 132.0 (d′), 135.2 (d′), 135.3 (d′), 155.5 (s′); exact mass m/z calcd for $C_{21}H_{22}O_4{}^{80}Se$ 418.0683, found 418.0667. Anal. Calcd for $C_{21}H_{22}O_4Se$: C, 60.43; H, 5.31. Found: C, 60.29; H, 5.28.

5-[[Bis(1,1-dimethylethyl)silyl]oxy]-7-phenyl-2-(phenylseleno)-6-heptynyl Methyl Carbonate (21c). The general procedure for silylation of alcohols was followed, using **21b** (443.5 mg, 1.06 mmol) in THF (9 mL), imidazole (144.7 mg, 2.13 mmol), t-Bu_2SiHCl (228.0 mg, 1.28 mmol) in THF (1 mL plus 1 mL as a rinse), and a reflux time of 1.75 h. The mixture was cooled, diluted with water (50 mL), and extracted with CH_2Cl_2. The combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (2 × 15 cm), using 3:97 EtOAc−hexane, gave **21c** (522.3 mg, 88%) as a mixture of isomers [^{1}H NMR (400 MHz)]: FTIR ($CHCl_3$ cast) 2957, 2930, 2856, 2096, 1751, 1263, 826 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.01 and 1.02 (two s, 9 H), 1.06 (two s, 9 H), 1.73−1.86 (m, 1 H), 1.90−2.00 (m, 1 H), 2.05−2.23 (m, 2 H), 3.34−3.43 (m, 1 H), 3.72 and 3.73 (two s, 3 H),

(45) Jefson, M.; Meinwald, J. *Tetrahedron Lett.* **1981**, *22*, 3561−3564.

(46) Barrett, A. G. M.; Flygare, J. A. *J. Org. Chem.* **1991**, *56*, 638−642.

4.14 (two s, 1 H), 4.22 and 4.24 (two dd, J = 11.0, 3.0 Hz, 1 H), 4.38 (dd, J = 11.0, 5.5 Hz, 1 H), 4.70−4.76 (m, 1 H), 7.20−7.33 (m, 6 H), 7.38−7.44 (m, 2 H), 7.57−7.63 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 19.9 (s′), 20.2 (s′), 27.0 (t′), 27.2 (t′), 27.37 (q′), 27.40 (q′), 36.3 (t′), 36.4 (t′), 42.8 (d′), 42.9 (d′), 54.8 (q′), 66.3 (d′), 66.3 (d′), 70.3 (t′), 85.4 (s′), 89.9 (s′), 123.0 (s′), 127.6 (s′), 128.1 (d′), 128.3 (d′), 129.2 (d′), 131.7 (d′), 135.35 (d′), 135.38 (d′), 155.6 (s′); exact mass m/z calcd for $C_{29}H_{40}O_4{}^{80}SeSi$ 560.1861, found 560.1856. Anal. Calcd for $C_{29}H_{40}O_4SeSi$: C, 62.24; H, 7.20. Found: C, 62.27; H, 7.37.

[2,2-Bis(1,1-dimethyl)hexahydro-3-phenyl-2*H*-cyclopent-[*d*]-1,2-oxasilol-4-yl]methyl Methyl Carbonate (21d). The general procedure for radical cyclization was followed, using **21c** (167.9 mg, 0.30 mmol) in PhH (45 mL), Ph_3SnH (210.6 mg, 0.60 mmol) in PhH (7.5 mL), AIBN (24.6 mg, 0.15 mmol) in PhH (7.5 mL), and an addition time of 6 h. Refluxing was continued for 30 min after the stannane addition. Evaporation of the solvent, and flash chromatography of the residue over silica gel (1.8 × 17 cm), using increasing amounts of CH_2Cl_2 in hexane (from 1% to 5%, 1% increments), gave **21d** (82.1 mg, 67%) as a mixture of two isomers [^{1}H NMR (400 MHz)]: FTIR ($CHCl_3$ cast) 2956, 2859, 1749, 1269 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.03 (s, 1.5 H), 1.07 (s, 6.5 H), 1.08 (s, 2.5 H), 1.13 (s, 6.5 H), 1.47−2.68 (m, 6 H), 3.16−3.33 (m, 1 H), 3.61−3.81 (m, 5 H), 4.52−4.58 (m, 0.72 H), 4.66−4.70 (m, 0.28 H), 7.12−7.20 (m, 1 H), 7.21−7.33 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) (signals associated with the minor isomer are marked by an asterisk) δ 21.2 (s′), 21.6* (s′), 22.5* (s′), 22.7 (s′), 28.25* (q′), 28.30 (t′), 28.4 (q′), 28.7 (q′), 29.3* (q′), 33.4* (t′), 33.7 (t′), 34.3* (d′), 37.1 (d′), 39.2 (d′), 41.0* (t′), 48.6* (d′), 51.3 (d′), 54.5* (d′), 54.6 (d′), 68.9* (t′), 71.8 (t′), 83.6* (d′), 84.2 (d′), 125.4* (d′), 125.5 (d′), 128.3* (d′), 128.4 (d′), 129.9* (d′), 130.4 (d′), 140.4 (s′), 141.0* (s′), 155.5* (s′), 155.8 (s′); exact mass m/z calcd for $C_{23}H_{36}O_4Si$ 404.2383, found 404.2388. Anal. Calcd for $C_{23}H_{36}O_4Si$: C, 68.27; H, 8.97. Found: C, 68.18; H, 9.01.

(3α,3a*β*,4*β*,6a*β*)-2,2-Bis(1,1-dimethylethyl)hexahydro-3-phenyl-2*H*-cyclopent[*d*]-1,2-oxasilole-4-methanol (21f) and (4α,4aα,5*β*,7aα)-3,3-Bis(1,1-dimethylethyl)octahydro-5-hydroxy-4-phenylcyclopent[*d*][1,2]oxasilin (21g). Anhydrous K_2CO_3 (24.5 mg, 0.18 mmol) was added to a stirred solution of **21d** (71.7 mg, 0.18 mmol) in MeOH (18 mL). Stirring at room temperature was continued for 3 days, and the mixture was evaporated. Flash chromatography of the residue over silica gel (1 × 10 cm), using increasing amounts of EtOAc in hexane (from 5% to 20%), gave **21g** (16.7 mg, 27%) and **21f** (41.3 mg, 67%).

Alcohol **21g**: mp 120−121.5 °C; FTIR ($CHCl_3$ cast) 3447, 2950, 2933, 2858, 1472, 1076, 1065, 821, 760, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.04 (s, 1 H), 1.07 (s, 1 H), 1.24−1.55 (m, 3 H), 1.68−1.77 (m, 1 H), 1.77−1.86 (m, 1 H), 2.43−2.57 (m, 1 H), 2.65 (ddd, J = 13.0, 11.5, 4.0 Hz, 1 H), 3.19 (d, J = 13.0 Hz, 1 H), 3.63 (dd, J = 11.5, 11.5 Hz, 1 H), 4.87−4.95 (m, 2 H), 7.09−7.16 (m, 1 H), 7.22−7.30 (m, 2 H), 7.36−7.43 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 22.4 (s′), 23.1 (s′), 26.1 (t′), 26.7 (d′), 28.7 (q′), 28.8 (q′), 33.7 (t′), 40.4 (d′), 47.8 (d′), 67.5 (t′), 73.9 (d′), 125.1 (d′), 128.4 (d′), 129.2 (d′), 143.2 (s′); exact mass m/z calcd for $C_{21}H_{34}O_2Si$ 346.2328, found 346.2332.

The stereochemistry assignment to alcohol **21f** was made by analogy to results with related cyclization products.[1c] Alcohol **21f** had: FTIR ($CHCl_3$ cast) 3418, 2936, 2859, 1475, 1036, 990, 820, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.08 (s, 9 H), 1.12 (s, 9 H), 1.21 (br s, 1 H), 1.47−1.57 (m, 1 H), 1.77−1.88 (m, 1 H), 1.88−1.97 (m, 1 H), 2.02−2.15 (m, 1 H), 2.21−2.32 (m, 1 H), 2.45−2.53 (m, 1 H), 3.09 (dd, J = 10.5, 8.0 Hz, 1 H), 3.26 (dd, J = 10.5, 5.5 Hz, 1 H), 3.29 (d, J = 8.0 Hz, 1 H), 4.54 (ddd, J = 5.0, 5.0, 2.5 Hz, 1 H), 7.13−7.18 (m, 1 H), 7.23−7.36 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 21.3 (s′), 22.7 (s′), 27.9 (t′), 28.4 (q′), 28.7 (q′), 33.7 (t′), 37.3 (d′), 42.4 (d′), 67.1 (t′), 84.4 (d′), 125.4 (t′), 128.3 (t′), 130.5 (t′), 141.0 (s′); exact mass m/z calcd for $C_{21}H_{34}O_2Si$ 346.2328, found 346.2336.

Methyl [(Phenylseleno)methoxy]acetate (29dd). NaH (80% dispersion in mineral oil, 142.0 mg, 3.56 mmol) was added in one portion to a stirred solution of PhSeSePh (623.0 mg, 1.98 mmol) in THF (10 mL) (Ar atmosphere). The suspension was stirred and refluxed for 1 h and then cooled to room temperature. HMPA (0.30 mL, 1.7 mmol) was added, followed by a solution of **29bb**[47] (280.0 mg, 2.64 mmol) in THF (1 mL plus 1 mL as a rinse). The resulting mixture was refluxed for 6 h. Water (2 mL) and 6 N HCl (2 mL) were added, and the mixture was extracted with CH_2Cl_2. The organic layer was washed with brine, dried ($MgSO_4$), and evaporated. The residue (crude **29cc**) was redissolved in MeOH (40 mL), concentrated H_2SO_4 (five drops) was added, and the solution was refluxed overnight. The solvent was evaporated, and the residue was dissolved in EtOAc (40 mL), washed with saturated aqueous $NaHCO_3$ and brine, and dried (Na_2SO_4). Evaporation of the solvent and flash chromatography of the residue over silica gel (2 × 20 cm), using 1:10 EtOAc−hexane, gave **29dd** (547.0 mg, 80%) as a colorless oil: FTIR ($CHCl_3$, cast) 2951, 1754 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.78 (s, 3 H), 4.29 (s, 2 H), 5.4 (t, J = 9.7 Hz, 2 H), 7.22−7.35 (m, 3 H), 7.53−7.70 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 52.0 (q′), 65.5 (t′), 72.5 (t′), 127.4 (d′), 129.2 (d′), 130.0 (s′), 132.9 (d′), 169.9 (s′); exact mass m/z calcd for $C_{10}H_{12}O_3{}^{80}Se$ 259.99518, found 259.99503.

[(Phenylseleno)methoxy]acetaldehyde (29a). DIBAL-H (0.80 mL, 1.0 M in CH_2Cl_2, 0.80 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of **29dd** (130.0 mg, 0.5 mmol) in CH_2Cl_2 (20 mL). The solution was stirred at −78 °C for 1.5 h after the addition. Water (1 mL) was added, and the cold bath was removed. Stirring was continued for 1 h, the solvent was evaporated, and the residue was dissolved in Et_2O (30 mL), washed with 3 N HCl (3 × 20 mL), and saturated aqueous Na_2CO_3, and dried (Na_2SO_4). Evaporation of the solvent and flash chromatography of the residue over silica gel (2 × 20 cm), using 1:4 EtOAc−hexane, gave **29a** (91.0 mg, 80%) as a colorless oil: FTIR (CH_2Cl_2, cast) 3051, 2987, 2814, 1736 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.21 (s, 2 H), 5.35 (s, 2 H), 7.25−7.35 (m, 3 H), 7.55−7.65 (m, 2 H), 9.71 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 72.9 (t′), 74.2 (t′), 127.6 (d′), 129.2 (d′), 129.7 (s′), 132.9 (d′), 203.9 (s′); exact mass m/z calcd for $C_9H_{10}O_2{}^{80}Se$ 229.98460, found 229.98376.

4-Phenyl-1-[(phenylseleno)methoxy]-3-butyn-2-ol (29b). The general procedure for addition of an acetylide to an aldehyde was followed, using **22** (40.0 mg, 0.38 mmol) in THF (15 mL), *n*-BuLi (1.6 M solution in hexanes, 0.20 mL, 0.32 mmol), an initial reaction time of 30 min, and **29a** (72.5 mg 0.32 mmol) in THF (4 mL plus 1 mL as a rinse). Stirring at −78 °C was continued for 1 h, saturated aqueous NH_4Cl (10 mL) was added, and the mixture was allowed to attain room temperature and was extracted with Et_2O. The combined organic extracts were washed with brine, dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (2 cm × 20 cm), using 1:4 EtOAc−hexane, gave **29b** (92.0 mg, 87%) as a colorless oil: FTIR ($CHCl_3$, cast) 3422, 3055, 2232 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.46 (d, J = 5.4 Hz, 1 H), 3.81 (dd, J = 9.8, 6.9 Hz, 1 H), 3.89 (dd, J = 9.8, 3.6 Hz, 1 H), 4.81−4.89 (m, 1 H), 5.39 (dd, J = 11.3, 10.0 Hz, 2 H), 7.19−7.70 (m, 10 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 6l.9 (d′), 72.87 (t′), 72.91 (t′), 85.9 (s′), 86.5 (s′), 122.2 (s′), 127.4 (d′), 127.8 (d′), 128.3 (d′), 128.6 (d′), 129.2 (d′), 130.0 (s′), 131.8 (d′), 133.3 (d′); exact mass m/z calcd for $C_{17}H_{16}O_2{}^{80}Se$ 332.03156, found 332.03159.

Bis(1,1-dimethylethyl)[[3-phenyl-1-[[(phenylseleno)-methoxy]methyl]-2-propynyl]oxy]silane (29c). *t*-Bu_2SiHCl (16.0 mg, 0.089 mmol) was added in one portion to a stirred solution of **29b** (20.4 mg, 0.06 mmol) and Et_3N (0.10 mL, 0.09 mmol) in CH_2Cl_2 (1.5 mL), followed by a small crystal of DMAP. The mixture was refluxed for 2 h, cooled, and evaporated. Flash chromatography of the residue over silica gel (1 × 10 cm), using 1:10 EtOAc−hexane, gave **29c** (28.5 mg, 95%) as a colorless oil: FTIR ($CHCl_3$, cast) 2104 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.05 (s, 9 H), 1.10 (s, 9 H), 3.79−3.92 (m, 2 H), 4.20 (s, 1 H), 4.90 (dd, J = 6.5, 4.9 Hz, 1 H), 5.20 (d, J = 9.9 Hz, 1 H), 5.31 (d, J = 9.9 Hz, 1 H), 7.20−7.34 (m, 6 H), 7.40−7.45 (m, 2 H), 7.60−7.70 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5

(47) (a) Salomaa, P.; Laiho, S. *Acta Chem. Scand.* **1963**, *17*, 103−110. (b) Farines, M.; Soulier, J. *Bull Soc. Chim. Fr.* **1970**, 332−340.

MHz) δ 19.8 (s′), 20.2 (s′), 27.3 (q′), 65.9 (d′), 73.1 (t′), 73.5 (t′), 85.8 (s′), 87.7 (s′), 127.1 (d′), 128.2 (d′), 128.3 (d′), 129.0 (d′), 131.7 (d′), 133.1 (d′). We did not obtain a mass spectrum for **29c**.

(3α,3a*β*,6a*β*)-2,2-Bis(1,1-dimethylethyl)hexahydro-3-phenylfuro[3,4-*d*]-1,2-oxasilole (29d). The general procedure for radical cyclization was followed, using **29c** (64.3 mg, 0.135 mmol) in PhH (25 mL), Ph_3SnH (90.9 mg, 0.25 mmol) in PhH (4 mL), AIBN (5.0 mg, 0.03 mmol) in PhH (4 mL), and an addition time of 6 h. Refluxing was continued for 1 h after the stannane addition. Evaporation of the solvent, and flash chromatography of the residue over silica gel (2 × 20 cm), using 1:3 EtOAc−hexane, gave **29d** (36.0 mg, 85%) as a white solid: mp 106−108 °C; FTIR ($CHCl_3$, cast) 2965, 2931, 1600 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.05 (s, 9 H), 1.14 (s, 9 H), 3.30−3.37 (m, 1 H), 3.47 (d, J = 7.9 Hz, 1 H), 3.85 (dd, J = 9.8, 3.2 Hz, 1 H), 3.92 (dd, J = 9.2, 7.5 Hz, 1 H), 4.05 (t, J = 9.3 Hz, 2 H), 4.62−4.68 (m, 1 H), 7.10−7.30 (m, 5 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) 21.2 (s′), 22.3 (s′), 28.2 (q′), 28.4 (q′), 35.1 (d′), 46.8 (d′), 70.2 (t′), 75.6 (t′), 81.9 (d′), 125.2 (d′), 128.4 (d′), 128.8 (d′), 140.9 (s′); exact mass m/z calcd for $C_{19}H_{30}O_2Si$ 318.20151, found 318.20106.

***cis*-3-Hydroxy-4-(phenylmethyl)tetrahydrofuran (29e).** *n*-Bu_4NF (1.0 M in THF, 0.75 mL, 0.75 mmol) was added to a stirred solution of **29d** (20.0 mg, 0.063 mmol) in DMF (1 mL), and stirring was continued for 2 h. Evaporation of the solvent and flash chromatography of the residue over silica gel (2 × 10 cm), using EtOAc, gave **29e** (8.0 mg, 71%) as a colorless oil: FTIR ($CHCl_3$, cast) 3387, 3083 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 1.59 (d, J = 1.9 Hz, 1 H), 2.45−2.57 (m, 1 H), 2.75 (dd, J = 13.9, 7.27 Hz, 1 H), 2.95 (dd, J = 13.9, 8.3 Hz, 1 H), 3.65 (dd, J = 10.3, 8.1 Hz, 1 H), 3.82 (dd, J = 10.0, 0.9 Hz, 1 H), 3.90−4.00 (m, 2 H), 4.24 (dd, J = 8.6, 4.1 Hz, 1 H), 7.18−7.36 (m, 5 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) 31.8 (t′), 46.6 (d′), 71.2 (t′), 72.6 (d′), 76.3 (t′), 126.3 (d′), 128.6 (two d′), 140.4 (s′); exact mass m/z calcd for $C_{11}H_{14}O_2$ 178.09938, found 178.09902.

Methyl 2-Methyl-2-[(phenylseleno)methoxy]propanoate (30dd). NaH (80% dispersion in mineral oil, 1.00 g, 33.3 mmol) was added in portions to a stirred solution of PhSeSePh (5.800 g, 18.55 mmol) in THF (100 mL) (Ar atmosphere). The mixture was refluxed for 1 h and then cooled to room temperature. HMPA (2.5 mL, 14.38 mmol) was added, followed by a solution of **30bb**[47] (2.8728 g, 24.74 mmol) in THF (3 mL plus 3 mL as a rinse). Refluxing was resumed and continued overnight. The solution was cooled to room temperature, and MeOH (2 mL) was added. The solvent was evaporated, and the residue was partitioned between water (50 mL) and Et_2O (50 mL). The aqueous layer was acidified (3 N HCl) and extracted with Et_2O. The combined organic extracts were washed with brine and dried ($MgSO_4$). The solvent was evaporated and the residue (crude **30cc**) was redissolved in MeOH (50 mL). Concentrated H_2SO_4 (five drops) was added and the mixture was refluxed overnight. Most of the solvent was evaporated and the residue was dissolved in Et_2O (50 mL). The solution was washed with saturated aqueous $NaHCO_3$, and brine, and dried (Na_2SO_4). Evaporation of the solvent and flash chromatography of the residue over silica gel (3 × 30 cm), using 1:5 EtOAc−hexane, gave **30dd** (5.0 g, 70%) as a colorless oil: FTIR ($CHCl_3$, cast) 1738, 1478 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.45 (s, 6 H), 3.68 (s, 3 H), 5.20 (s, 2 H), 7.23−7.32 (m, 3 H), 7.55−7.65 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 24.6 (q′), 52.2 (q′), 65.6 (s′), 79.0 (t′), 127.2 (d′), 129.0 (d′), 130.9 (s′), 132.8 (d′), 174.5 (s′); exact mass m/z calcd for $C_{12}H_{16}O_3{}^{80}Se$ 288.02646, found 288.02598.

2-Methyl-2-[(phenylseleno)methoxy]propanal (30a). DIBAL-H (1.0 M in CH_2Cl_2, 12.0 mL, 0.012 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of **30dd** (3.45 g, 11.9 mmol) in CH_2Cl_2 (100 mL). The solution was stirred at −78 °C for 4 h, and 2 N HCl (20 mL) was then added. The aqueous phase was extracted with CH_2Cl_2, and the combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (3 × 30 cm), using 1:3 EtOAc−hexane, gave **30a** (2.78 g, 90%) as a colorless oil: FTIR ($CHCl_3$, cast) 3071, 3057, 2983, 2804, 1735 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.30 (s, 6 H), 5.29 (s, 2 H), 7.25−7.35 (m, 3 H), 7.58−7.70 (m, 2 H), 9.65 (s, 1 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 21.0 (q′), 65.6 (s′), 81.9 (t′), 127.5 (d′), 129.3 (d′), 130.2 (s′), 132.7 (d′), 203.4 (d′); exact mass m/z calcd for $C_{11}H_{14}O_2{}^{80}Se$ 258.01590, found 258.01589.

(2*S*,3*R*)- and (2*S*,3*S*)-6-(Phenylmethoxy)-2-[(triethylsilyl)oxy]-4-hexyn-3-ol (31bb). *n*-BuLi (1.6 M solution in hexanes, 10.0 mL, 16.0 mmol) was added slowly to a stirred and cooled (−78 °C) solution of **23**[21] (2.45 g, 16.78 mmol) in THF (30 mL). The cold bath was removed and, when the mixture had reached −30 °C (ca. 30 min), the solution was cooled to −78 °C. A solution of **31aa**[16] (2.743 g, 14.5 mmol) in THF (3 mL plus 1 mL as a rinse) was added dropwise to the acetylide solution, and the mixture was stirred for 3 h at −78 °C. Saturated aqueous NH_4Cl (2 mL) was then added, most of the solvent was evaporated and the residue was mixed with EtOAc (60 mL). The organic phase was washed with brine and dried ($MgSO_4$). Evaporation of the solvent and flash chromatography of the residue over silica gel (2 × 20 cm), using 1:3 EtOAc−hexane, gave **31bb** (3.88 g, 80%) as a mixture of two isomers which were used directly for the next step (formation of **31a**).

(5*R*,6*S*)-3-(1,1-Dimethylethyl)-8,8-diethyl-2,2,6-trimethyl-5-[3-(phenylmethoxy)-1-propynyl]-4,7-dioxa-3,8-disiladecane (31a). *t*-Bu_2SiHCl (1.65 g, 9.22 mmol) was added in one portion to a stirred solution of **31bb** (2.60 g, 7.77 mmol) in CH_2Cl_2 (5 mL). Et_3N (2.50 mL, 10 mmol) was then added, followed by DMAP (ca. 120 mg), and the solution was refluxed for 2 h (TLC control, silica, 1:10 EtOAc−hexane). Evaporation of the solvent and flash chromatography of the residue over silica gel (3 × 30 cm), using increasing amounts of EtOAc in hexane (100% hexane to 1:10 EtOAc−hexane), gave crude **31a** (3.32 g,), which was used directly for the next step (formation of **31b**).

(2*S*,3*R*)-3-[[Bis(1,1-dimethylethyl)silyl]oxy]-6-(phenylmethoxy)-4-hexyn-2-ol (31b). Water (0.5 mL) and glacial AcOH (4 mL) were added to a stirred solution of **31a** (100.0 mg, 0.21 mmol) in THF (4 mL). Stirring at room temperature was continued for ca. 7 h (TLC control, silica, 1:3 EtOAc−hexane). Water (10 mL) was added, and the mixture was extracted with CH_2Cl_2. The combined organic extracts were washed with saturated aqueous Na_2CO_3 and dried ($MgSO_4$). Evaporation of the solvent and flash chromatography of the residue over silica gel (2 cm × 20 cm), using 1:5 EtOAc−hexane, gave two isomers (85.0 mg, 72%, assuming crude **31a** was pure). The major (less polar) isomer (**31b**) (41.2 mg, 54%) was fully characterized and used in the next step (formation of **31c**): FTIR ($CHCl_3$, cast) 3431, 3032, 2100 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.02 (s, 9 H), 1.04 (s, 9 H), 1.29 (d, J = 6.3 Hz, 3 H), 2.32 (d, J = 4.7, 1 H), 3.84−3.90 (m, 1 H), 4.20 (s, 1 H), 4.25 (d, J = 1.6 Hz, 1 H), 4.40−4.50 (m, 1 H), 4.62 (s, 2 H), 7.30−7.42 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 17.8 (q′), 19.8 (s′), 20.2 (s′), 27.2 (q′), 27.3 (q′), 57.3 (t′), 70.6 (d′), 71.1 (d′), 71.4 (t′), 82.9 (s′), 84.0 (s′), 127.9 (d′), 128.1 (d′), 128.4 (d′), 137.5 (s′); exact mass m/z calcd for $C_{20}H_{30}O_3Si$ (M − C_4H_9) 330.20151, found 330.20129. The polar isomer had: ^1H NMR ($CDCl_3$, 300 MHz) δ 1.02 (s, 18 H), 1.33 (d, J = 6.4 Hz, 3 H), 2.50 (d, J = 4.7, 1 H), 4.05−4.15 (m, 2 H), 4.25 (s, 2 H), 4.40−4.45 (m, 1 H), 4.60 (s, 2 H), 7.30−7.42 (m, 5 H).

***Se*-Phenyl (1*S*,2*R*)-*O*-[2-[[Bis(1,1-dimethylethyl)silyl]-oxy]-1-methyl-5-(phenylmethoxy)-3-pentynyl]carbonoselenoate (31c).** A solution of $COCl_2$ in PhMe (ca. 1:1 v/v) was added by pipet in small portions to a stirred solution of **31b** (300.0 mg, 0.82 mmol) in THF (5 mL) until all the starting material had reacted (several min) (TLC control, silica, 1:10 EtOAc−hexane). The solution was then concentrated to half its original volume, using a rotary evaporator in which the receiving flask contained aqueous $NaHCO_3$ solution. A freshly prepared solution of PhSeNa [from PhSeSePh (256.0 mg, 0.82 mmol) and $NaBH_4$ (65.0 mg, 1.72 mmol) in EtOH (10 mL)] was added, and stirring was continued for 4 h (TLC control, silica, 1:10 EtOAc−hexane). The mixture was then diluted with Et_2O (30 mL) and washed with water and brine. The organic extract was dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (2 cm × 20 cm), using 1:10 EtOAc−hexane, gave **31c** (358.0 mg, 80%) as a

slightly yellowish oil: FTIR ($CHCl_3$, cast) 2963, 2097 (Si−H), 1728 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.06−1.11 (two close s, 18 H), 1.45 (d, J = 6.4 Hz, 3 H), 4.18 (s, 1 H), 4.24 (d, J = 1.6 Hz, 2 H), 4.61 (s, 2 H), 4.72−4.78 (m, 1 H), 5.09−5.21 (m, 1 H), 7.25−7.45 (m, 8 H), 7.59−7.72 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 14.5 (q′), 20.0 (s′), 20.3 (s′), 27.2 (q′), 27.4 (q′), 57.2 (t′), 68.0 (d′), 71.4 (t′), 77.4 (d′), 82.6 (s′), 83.7 (s′), 126.1 (s′), 127.9 (d′), 128.2 (d′), 128.5 (d′), 129.1 (d′), 129.3 (d′), 135.8 (d′), 137.4 (s′), 166.6 (s′); exact mass m/z calcd for $C_{24}H_{29}O_4{}^{80}SeSi$ (M − C_4H_9) 489.10004, found 489.09938. Anal. Calcd for $C_{28}H_{38}O_4{}^{80}SeSi$: C 61.63, H 7.02. Found: C 61.56, H 6.76.

(3α,3a*β*,6*β*,6a*β*)-2,2-Bis(1,1-dimethylethyl)tetrahydro-6-methyl-3-[(phenylmethoxy)methyl]furo[3,4-*d*]-1,2-oxasilol-4(2*H*)-one (31d). The general procedure for radical cyclization was followed, using **31c** (268.0 mg, 0.49 mmol) in PhH (60 mL), Ph_3SnH (256.0 mg, 0.73 mmol) in PhH (8 mL), AIBN (10.0 mg, 0.06 mmol) in PhH (8 mL), and an addition time of 6 h. Refluxing was continued for 1 h after the stannane addition. Evaporation of the solvent and flash chromatography of the residue over silica gel (2 × 20 cm), using 1:9 EtOAc−hexane, gave **31d** (169.0 mg, 85%) as an oil: FTIR ($CHCl_3$, cast) 3087, 1769 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.05 (two close s, 18 H), 1.30 (d, J = 6.9 Hz, 3 H), 2.20−2.28 (m, 1 H), 3.38 (dd, J = 9.9, 5.3 Hz, 1 H), 3.95 (dd, J = 9.1, 6.4 Hz, 1 H), 4.29 (d, J = 5.3 Hz, 1 H), 4.40 (dd, J = 10.2, 9.1 Hz, 1 H), 4.54 (d, J = 11.5 Hz, 1 H), 4.61 (AB q, $\Delta\nu_{AB}$ = 35.1 Hz, J = 11.5 Hz, 2 H)), 7.19−7.42 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) 18.9 (q′), 20.4 (s′), 21.4 (s′), 25.2 (d′), 26.9 (q′), 27.7 (q′), 43.7 (d′), 66.7 (t′), 73.2 (t′), 82.1 (d′), 82.6 (d′), 127.5 (d′), 128.0 (d′), 128.3 (d′), 138.9 (s′), 175.7 (s′); exact mass m/z calcd for $C_{22}H_{34}O_4Si$ 390.22263, found 390.22092.

(3*S*,4*R*,5*S*)-4-[[Bis(1,1-dimethylethyl)fluorosilyl]oxy]-3-ethenyldihydro-5-methyl-2(3*H*)-furanone (31e). $BF_3{\cdot}OEt_2$ (0.34 mL, 2.73 mmol) was added to a stirred solution of **31d** (88.0 mg, 0.225 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred for 8 h, transferred to a separatory funnel, washed with brine, and dried (Na_2SO_4). Evaporation of the solvent and flash chromatography of the residue over silica gel (2 × 10 cm), using 1:3 EtOAc−hexane, gave **31e** (51.0 mg, 75%) as a colorless oil: FTIR ($CHCl_3$, cast) 3066, 1765 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.05 (s, 18 H), 1.40 (d, J = 6.8 Hz, 3 H), 3.40 (dd, J = 7.9, 5.7 Hz, 1 H), 4.50 (dd, J = 5.6, 2.0 Hz, 1 H), 4.56 (d of q, J = 6.7, 1.9 Hz, 1 H), 5.34−5.45 (m, 2 H), 5.70−5.86 (m, 1 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) 17.8 (q′), 19.6, 19.9 (two s′, J_{C-F} = 12.8 Hz), 20.5, 20.9 (two s′, J_{C-F} = 15.9 Hz), 26.7 (q′), 26.9 (q′), 48.9 (d′), 77.2 (d′), 82.3 (d′), 121.9 (t′), 128.3 (d′), 175.0 (s′); exact mass m/z calcd for $C_{11}H_{18}FO_3Si$ (M − C_4H_9) 245.10092, found 245.10098.

2-[(Phenylseleno)methoxy]benzaldehyde (32a). Dry acetone (20 mL) was added to $PhSeCH_2Cl$[18a] (3.16 g, 15.4 mmol) and NaI (11.52 g, 76.9 mmol), and the mixture was stirred and refluxed for 3 h, cooled to room temperature, and evaporated. Et_2O (20 mL) was added and the solid was filtered off, and washed with Et_2O. The combined washings were evaporated to give crude $PhSeCH_2I$,[18b] which was used directly for the next step.

Salicylaldehyde (**32aa**) (1.22 g, 10.0 mmol) in THF (2 mL) was added by cannula over ca. 1 min to a stirred and cooled (0 °C) suspension of NaH (60% dispersion in mineral oil, 0.45 g, 12 mmol) in THF (40 mL). The mixture was stirred at 0 °C for 20 min, and then a solution of crude $PhSeCH_2I$ in THF (5 mL) was added by cannula over ca. 1 min. The mixture was refluxed for 4 h, and then cooled to room temperature. Water (10 mL) was added, and the mixture was extracted with CH_2Cl_2. The combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (3 × 25 cm), using increasing amounts of EtOAc in hexane (from 5% to 15%), gave **32a** (650.0 mg, 22%) as a colorless oil: FTIR (CH_2Cl_2 cast) 3072, 3057, 2859, 2759, 1689, 1598 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 5.80 (t, J_{C-Se} = 8.7 Hz, 2 H), 7.02 (d, J = 8.4 Hz, 1 H), 7.11 (t, J = 7.5 Hz, 1 H), 7.21−7.40 (m, 3 H), 7.49−7.64 (m, 3 H), 7.86 (dd, J = 7.7, 1.8 Hz, 1 H), 10.38 (d, J = 0.5 Hz, 1 H); ^{13}C NMR (CD_2Cl_2, 75.5 MHz) 68.6 (t′), 114.8 (d′), 122.4 (d′), 126.7 (s′), 128.3 (d′), 128.7 (d′), 129.0 (s′), 129.7 (d′), 133.8 (d′), 135.9 (d′), 159.6 (s′), 189.5 (d′); exact mass m/z calcd for $C_{14}H_{12}O_2{}^{80}Se$ 292.00024, found 292.00048. Anal. Calcd for $C_{14}H_{12}O_2{}^{80}Se$: C 57.96, H 3.92. Found: C 57.74, H 4.15.

(3α,3a*β*,9b*β*)-2,2-Bis(1,1-dimethylethyl)-2,3,3a,9b-tetrahydro-3-phenyl-4*H*-1,2-oxasilolo[4,5-*c*][1]benzopyran (32d). The general procedure for radical cyclization was followed, using **32c** (110.0 mg, 0.252 mmol) in PhH (40 mL), Ph_3SnH (116.0 mg, 0.328 mmol) in PhH (5 mL), AIBN (5.0 mg, 0.03 mmol) in PhH (5 mL), and an addition time of 4.5 h. Refluxing was continued for 1 h after the stannane addition. Evaporation of the solvent, and flash chromatography of the residue over silica gel (2 × 20 cm), using 1:10 CH_2Cl_2−hexane, gave **32d** (60.0 mg, 85%) as a white solid: mp 128.0−131.0 °C; FTIR ($CHCl_3$, cast) 3035, 1610, 1586 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.10 (s, 9 H), 1.20 (s, 9 H), 2.90−3.09 (m, 1 H), 3.49 (d, J = 7.4 Hz, 1 H), 3.95 (dd, J = 12.4, 11.0 Hz, 1 H), 4.25 (dd, J = 10.7, 3.2 Hz, 1 H), 4.85 (d, J = 4.1 Hz, 1 H), 6.88 (d, J = 8.2 Hz, 1 H), 6.99 (dd, J = 7.5, 1.0 Hz, 1 H), 7.16−7.40 (m, 6 H), 7.47 (dd, J = 7.6, 1.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) 23.0 (s′), 28.7 (q′), 29.1 (q′), 35.3 (d′), 42.1 (d′), 64.7 (t′), 71.6 (d′), 116.7 (d′), 120.7 (d′), 123.7 (s′), 125.6 (d′), 128.5 (d′), 129.1 (d′), 130.2 (d′), 131.7 (d′), 138.8 (s′), 154.9 (s′); exact mass m/z calcd for $C_{24}H_{32}O_2Si$ 380.21716, found 380.21579.

***cis*-3,4-Dihydro-3-(phenylmethyl)-2*H*-1-benzopyran-4-ol (32e).** *n*-Bu_4NF (1.0 M in THF, 1.0 mL, 1.0 mmol) was injected in one portion into a stirred solution of **32d** (40.0 mg, 0.10 mmol) in DMF (3 mL). The color of the solution quickly changed to brownish red. Stirring was continued for 30 min, and then Et_2O (20 mL) and water (10 mL) were added. The organic phase was separated, and the aqueous layer was extracted with Et_2O. The combined organic extracts were washed with water and brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (2 × 20 cm), using 1:3 EtOAc−hexane, gave **32e**[38] (21.5 mg, 90%) as a white solid: mp 103.0−105.0 °C; FTIR ($CHCl_3$ cast) 3439, 3061, 3026, 772 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.70 (s, 1 H), 2.29−2.41 (m, 1 H), 2.68 (dd, J = 13.7, 7.3, 1 H), 2.90 (dd, J = 13.7, 8.4, 1 H), 4.05−4.15 (m, 2 H), 4.52 (d, J = 2.0, 1 H), 6.82−6.94 (m, 2 H), 7.17−7.41 (m, 7 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) 32.9 (t′), 40.0 (d′), 64.97 (d′), 65.00 (t′), 117.0 (d′), 120.6 (d′), 124.2 (s′), 126.4 (d′), 128.6 (d′), 129.1 (d′), 130.0 (d′), 130.2 (d′), 139.2 (s′), 154.4 (s′); exact mass m/z calcd for $C_{16}H_{16}O_2$ 240.11504, found 240.11534.

1,1-Dimethylethyl 5-Oxo-3-oxazolidinecarboxylate (33bb). *N*-Boc-glycine (**33aa**) (4.38 g, 25.0 mmol) and paraformaldehyde (1.0 g, 28 mmol) were dissolved in PhH (120 mL). *p*-$TsOH{\cdot}H_2O$ (250 mg, 1.5 mmol) was added, and the mixture was refluxed for 1 h, using a Dean−Stark apparatus, and then cooled to room temperature. Evaporation of the solvent and flash chromatography of the residue over silica gel (2 × 20 cm), using 1:3 EtOAc−hexane, gave **33bb**[48] (2.85 g, 61%) as a colorless oil, which solidified on standing: mp 39−40 °C; FTIR ($CHCl_3$, cast) 2979, 1809, 1759, 1712 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.36 (s, 9 H), 3.88 (s, 2 H), 5.24 (s, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) 28.4 (q′), 44.0 (t′), 78.7 (s′), 82.2 (t′), 151.9 (s′), 170.1 (s′); exact mass m/z calcd for $C_8H_{13}NO_4$ 187.08446, found 187.08414.

Methyl *N*-[(1,1-Dimethylethoxy)carbonyl]-*N*-[(phenylseleno)methyl]glycinate (33dd). NaH (80% dispersion in mineral oil, 190.0 mg, 6.3 mmol) was added in small portions to a stirred solution of PhSeSePh (1.10 g, 3.50 mmol) in THF (10 mL) (Ar atmosphere). The suspension was refluxed for 2 h and then cooled to room temperature. HMPA (0.56 mL, 3.22 mmol) was added in one portion, followed by a solution of **33bb** (871.4 mg, 4.65 mmol) in THF (2 mL plus 1 mL as a rinse). The solution was refluxed for 5 h (TLC control, silica, 1:3 EtOAc−hexane), cooled to room temperature, and diluted with water (1 mL). The THF was evaporated under water pump vacuum, and the residue was partitioned between water (20 mL) and Et_2O (20 mL). The organic extract was washed with

(48) Cf. Walter, M. W.; Adlington, R. M.; Baldwin, J. E.; Chuhan, J.; Schofield, C. J. *Tetrahedron Lett.* **1995**, *36*, 7761−7764.

water, and the combined aqueous extracts were acidified with 3 N HCl to ca. pH 2. The acidic solution was extracted with EtOAc, and the combined organic extracts were washed with water and brine, and filtered through a column [4 (diameter) x 7 cm] of anhydrous $MgSO_4$. The filtrate was evaporated and the residue (crude **33cc**) was redissolved in Et_2O (10 mL), and cooled to 0 °C in an ice−water bath. Ethereal CH_2N_2 was added dropwise with stirring until all the acid had been esterified (TLC control, silica, 1:3 EtOAc−hexane). Evaporation of the solvent and flash chromatography of the residue over silica gel (3 × 30 cm), using 1:3 EtOAc−hexane, gave **33dd** (1.33 g, 80%) as a colorless oil: FTIR ($CHCl_3$, cast), 1753, 1703 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.3 (two s, 9 H), 3.69 (two s, 3 H), 3.99 (two s, 2 H), 4.90 (two s, 2 H), 7.20−7.32 (m, 3 H), 7.53−7.65 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 28.1 (three q′ from rotamers), 47.7 (four t′ from rotamers), 52.1 (d′), 81.2 (t′), 127.9 (two d′ from rotamers), 128.4 (two s′ from rotamers), 129.1 (d′), 135.0 (two d′ from rotamers), 154.1 (two s′ from rotamers), 169.8 (s′); exact mass *m*/*z* calcd for $C_{15}H_{21}NO_4{}^{80}Se$ 359.06357, found 359.06256.

***N*-[(1,1-Dimethylethoxy)carbonyl]-*N*-[(phenylseleno)methyl]glycinal (33a).** DIBAL-H (1.0 M solution in CH_2Cl_2, 3.0 mL, 3.0 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of **33dd** (510.0 mg, 1.42 mmol) in dry Et_2O (20 mL). After 30 min, little starting material remained (TLC control, silica, 1:5 EtOAc−hexane). More DIBAL-H (1.0 M solution in CH_2Cl_2, 1.5 mL, 1.5 mmol) was added, and stirring was continued for 15 min. MeOH (1 mL) was then added, and the solution was poured into saturated aqueous potassium sodium tartrate (30 mL). The mixture was extracted with Et_2O, and the combined organic extracts were washed with water and brine and dried ($MgSO_4$). Evaporation of the solvent and flash chromatography of the residue over silica gel (3 × 20 cm), using 1:5 EtOAc−hexane, gave **33a** (279.0 mg, 83%) as a colorless oil: FTIR (CH_2Cl_2 cast) 3071, 3057, 2977, 2931, 2872, 2819, 2720, 1735, 1698, 1579 cm^{-1}; ^1H NMR (CD_2Cl_2, 400 MHz) δ 1.30 (two close s, 9 H), 3.92 (two close s, 2 H), 4.92 (two close s, 2 H), 7.21−7.39 (m, 3 H), 7.55−7.65 (m, 2 H), 9.45−9.50 (two close s, 1 H); ^{13}C NMR (CD_2Cl_2, 100.6 MHz) δ 28.0 (q′), 28.1 (q′), 47.9 (t′), 48.5 (t′), 56.6 (t′), 57.2 (t′), 81.6 (s′), 81.8 (s′), 128.1 (d′), 128.5 (d′), 128.6 (s′), 128.7 (s′), 129.5 (d′), 129.6 (d′), 134.9 (d′), 135.8 (d′), 154.2 (s′), 154.7 (s′), 198.5 (d′), 198.5 (d′); exact mass (HR electrospray) *m*/*z* calcd for $C_{14}H_{20}NO_3{}^{80}Se$ (M + H) 330.060839, found 330.059420.

1,1-Dimethylethyl (2-Hydroxy-4-phenyl-3-butynyl)-[(phenylseleno)methyl]carbamate (33b). The general procedure for addition of an acetylide to an aldehyde was followed, using **22** (224.0 mg, 2.19 mmol) in THF (10 mL), *n*-BuLi (1.6 M in hexanes, 1.30 mL, 2.08 mmol), an initial reaction time of 10 min, and **33a** in THF (2 mL plus 1 mL as a rinse), added in two equal portions. Stirring at −78 °C was continued for 3 h, several drops of saturated aqueous NH_4Cl were then added, and the mixture was allowed to attain room temperature. The THF was evaporated, and the residue was dissolved in CH_2Cl_2 and dried ($MgSO_4$). Evaporation of the solvent gave crude **33b**, which was used directly in the next step (formation of **33c**).

1,1-Dimethylethyl [2-[[Bis(1,1-dimethylethyl)silyl]oxy]-4-phenyl-3-butynyl][(phenylseleno)methyl]carbamate (33c). Imidazole (118.0 mg, 1.70 mmol) and *t*-Bu_2SiHCl (193.5 mg, 1.10 mmol) were added successively to a stirred solution of crude **33b** in THF (10 mL), and stirring was continued for 3 h. Evaporation of the solvent and flash chromatography of the residue over silica gel (3 × 30 cm), using increasing amounts of EtOAc in hexane (from 10% to 25%), gave **33c** (503.0 mg, 82%) as an oil: FTIR ($CHCl_3$, cast), 2101, 1703 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.99 (s, 9 H), 1.03 (s, 9 H), 1.29 (s, 4.6 H), 1.39 (s, 4.4 H), 3.48−3.70 (m, 2 H), 4.10−4.20 (m, 1 H), 4.80−5.23 (m, 3 H), 7.18−7.36 (m, 6 H), 7.37−7.42 (m, 2 H), 7.55−7.70 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) (mixture of rotamers) 19.6 (s′), 20.3 (s′), 27.3 (q′), 28.1 (q′), 28.3 (q′), 48.1 (t′), 49.9 (t′), 52.5 (s′), 65.2 (d′), 65.4 (d′), 80.6 (t′), 80.8 (t′), 86.4 (s′), 88.2 (s′), 127.7 (d′), 128.0 (d′), 128.3 (d′), 128.8 (s′), 131.6 (d′), 135.0 (d′), 135.8 (d′), 154.4 (s′); exact mass *m*/*z* calcd for $C_{20}H_{29}NO_3Si$ (M − PhSe − C_4H_9) 360.19949, found 360.19932.

1,1-Dimethylethyl (3α,3a*β*,6a*β*)-2,2-Bis(1,1-dimethylethyl)hexahydro-3-phenyl-5*H*-1,2-oxasilolo[4,5-*c*]pyrrole-5-carboxylate (33d). The general procedure for radical cyclization was followed, using **33c** (150.0 mg, 0.262 mmol) in PhH (40 mL), Ph_3SnH (140.0 mg, 0.40 mmol) in PhH (8 mL), AIBN (5.0 mg, 0.03 mmol) in PhH (8 mL), and an addition time of 8 h. Refluxing was continued for 1 h after the stannane addition. Evaporation of the solvent and flash chromatography of the residue over silica gel (3 × 30 cm), using 1:3 EtOAc−hexane, gave **33d** (105.0 mg, 95%) as a white solid, which was a mixture of rotamers in solution (NMR): mp 126.0−128.0 °C; FTIR ($CHCl_3$, cast) 2971, 2895, 1697 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz, 55 °C) δ 1.05 (s, 9 H), 1.16 (s, 9 H), 1.43 (s, 9 H), 3.15−3.32 (m, 1 H), 3.39 (d, J = 7.3 Hz, 1 H), 3.51 (dd, J = 7.5, 4.3 Hz, 2 H), 3.59−3.90 (m, 2 H), 4.55 (t, 4.2 Hz, 1 H), 7.05−7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) 21.0 (s′), 22.5 (s′), 23.4 (q′), 25.2 (q′), 28.4 (q′), 28.5 (q′), 28.7 (q′), 35.9 (d′), 36.1 (d′), 45.0 (d′), 45.8 (d′), 48.3 (t′), 53.7 (s′), 54.0 (s′), 79.2 (t′), 79.9 (d′), 80.8 (d′), 125.3 (d′), 128.4 (d′), 128.8 (d′), 140.3 (s′), 140.5 (s′), 154.5 (s′); exact mass *m*/*z* calcd for $C_{24}H_{39}NO_3Si$ 417.26993, found 417.26881.

1,1-Dimethylethyl [2*R(*S**)]-2-(1-Hydroxy-3-phenyl-2-propynyl)-1-pyrrolidinecarboxylate (34bb).** The general procedure for addition of an acetylide to an aldehyde was followed, using **22** (320.0 mg, 3.13 mmol) in THF (10 mL), *n*-BuLi (1.6 M in hexane, 1.90 mL, 3.04 mmol), an initial reaction time of 15 min, and freshly prepared **34aa**[19] (292.9 mg, 1.56 mmol) in THF (4 mL plus 1 mL as a rinse). Stirring at −78 °C was continued for 2 h, water (five drops) was added, and the mixture was allowed to attain room temperature. Evaporation of the solvent and flash chromatography of the residue over silica gel (2 × 20 cm), using 1:3 EtOAc−hexane, gave equal amounts of two isomers (^1H NMR, 300 MHz). The less polar diastereomer **34bb** (192.0 mg, 41%) was carried on to the next step (formation of **34a**). The compound had: FTIR ($CHCl_3$, cast) 3380, 2976, 1737, 1693 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.50 (s, 9 H), 1.70−2.20 (m, 4 H), 3.30−3.60 (m, 2 H), 4.10 (dd, J = 12.6 Hz, 6.0 Hz, 1 H), 4.62 (d, J = 5.9 Hz, 1 H), 7.21−7.33 (m, 3 H), 7.34−7.50 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 23.9 (t′), 28.5 (q′), 28.7 (t′), 47.7 (t′), 62.8 (d′), 67.4 (d′), 80.7 (s′), 85.1 (s′), 88.7 (s′), 122.8 (s′), 128.2 (d′), 128.3 (d′), 131.7 (d′), 157.5 (s′); exact mass *m*/*z* calcd for $C_{14}H_{15}NO_3$ (M − C_4H_9) 245.10519, found 245.10452.

The more polar isomer had: ^1H NMR ($CDCl_3$, 300 MHz) δ 1.49 (s, 9 H), 1.70−2.19 (m, 4 H), 3.29−3.60 (m, 2 H), 4.01−4.19 (br t, J = 6.81 Hz, 1 H), 4.54−4.70 (br s, 1 H), 7.21−7.31 (m, 3 H), 7.32−7.47 (m, 2 H).

[2*R(*S**)]-2-[1-[[Bis(1,1-dimethylethyl)silyl]oxy]-3-phenyl-2-propynyl]pyrrolidine (34a).** TFA (3.0 mL) was added to a stirred solution of **34bb** (181.0 mg, 0.60 mmol) in CH_2Cl_2 (5 mL). Stirring was continued for 1 h, and the mixture was diluted with CH_2Cl_2 (30 mL), washed with saturated aqueous $NaHCO_3$, and dried (Na_2SO_4). The solvent was evaporated, and the residue was redissolved in dry THF (5 mL). Imidazole (43.0 mg, 0.63 mmol) was added, followed by *t*-Bu_2SiHCl (112.8 mg, 0.63 mmol), and the solution was refluxed overnight. The mixture was cooled and evaporated, and flash chromatography of the residue over silica gel (2 × 20 cm), using 1:4 EtOAc−hexane, gave **34a** (122.0 mg, 60%) as a slightly yellowish oil: FTIR ($CHCl_3$, cast) 3336, 3179, 3081, 2103 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.02 (s, 4.5 H), 1.05 (s, 4.5 H), 1.70−2.09 (m, 4 H), 2.60 (br s, 1 H), 2.85−3.21 (m, 2 H), 3.40 (dd, J = 12.0 Hz, 6.0 Hz, 2 H), 4.22 (s, 1 H), 4.64 (d, J = 6.1 Hz, 1 H), 7.25−7.36 (m, 3 H), 7.37−7.50 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) 19.8 (s′), 20.3 (s′), 25.3 (t′), 27.4 (t′), 27.5 (q′), 46.5 (t′), 64.0 (d′), 69.9 (d′), 85.9 (s′), 88.6 (s′), 123.0 (s′), 128.3 (d′), 131.6 (d′); exact mass *m*/*z* calcd for $C_{17}H_{24}NOSi$ (M − C_4H_9) 286.16268, found 286.16249.

***Se*-Phenyl [2*R**(*S**)]-2-[1-[[Bis(1,1-dimethylethyl)silyl]-oxy]-3-phenyl-2-propynyl]-1-pyrrolidineselenocarboxylate (34c).** A solution of $COCl_2$ in PhMe (ca. 1:1 v/v) was added dropwise to a stirred solution of **34a** (120.0 mg, 0.35 mmol) in

THF (4 mL). Acylation was complete in 10 min (TLC control, silica, 1:10 EtOAc−hexane). Evaporation of the solvent, using a rotary evaporator in which the receiving flask contained aqueous $NaHCO_3$, and flash chromatography of the residue over silica gel (2 × 20 cm), using 1:20 EtOAc−hexane, gave **34b**. This was dissolved in dry THF (2 mL plus 1 mL as a rinse) and added by syringe to a stirred solution of freshly prepared PhSeNa [from PhSeSePh (244.0 mg, 0.78 mmol) and $NaBH_4$ (59.0 mg, 1.56 mmol) in EtOH (10 mL)]. Stirring at room temperature was continued for 6 h. The mixture was diluted with EtOAc (30 mL), washed with brine, and dried (Na_2SO_4). Evaporation of the solvent and flash chromatography of the residue over silica gel (2 × 20 cm), using 1:10 EtOAc−hexane, gave **34c** (154.4 mg, 84%) as a slightly yellowish solid: mp 94.5−95.5 °C; FTIR ($CHCl_3$, cast) 3059, 2961, 2098, 1732 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.01 (s, 7.5 H), 1.09 (s, 7.5 H), 1.14 (two close s, 3 H), 1.88−2.02 (m, 1 H), 2.05−2.21 (m, 1 H), 2.26−2.51 (m, 2 H), 3.52−3.70 (m, 2 H), 4.15 (s, 1 H), 4.29−4.39 (m, 1 H), 5.20 (d, J = 5.4 Hz, 1 H), 5.40 (d, J = 4.9 Hz, 1 H), 7.30−7.49 (m, 8 H), 7.60−7.70 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) 19.9 (s′), 20.0 (s′), 24.0 (t′), 26.2 (t′), 27.3 (q′), 48.0 (t′), 63.0 (d′), 66.0 (d′), 85.8 (s′), 88.1 (s′), 122.9 (s′), 126.7 (s′), 128.4 (d′), 128.8 (d′), 129.2 (d′), 131.5 (d′), 136.5 (d′), 162.9 (s′); exact mass m/z calcd for $C_{28}H_{37}NO_2{}^{80}SeSi$ 527.17590, found 527.17611.

(3α,3a*β*,8aα,8b*β*)-Octahydro-3-phenyl-1,2-oxasilolo[4,5-*a*]pyrrolizin-4(4*H*)-one (34d). The general procedure for radical cyclization was followed, using **34c** (43.0 mg, 0.082 mmol) in PhH (30 mL), Ph_3SnH (60.0 mg, 0.17 mmol) in PhH (5 mL), AIBN (5.0 mg, 0.03 mmol) in PhH (5 mL), and an addition time of 6 h. Refluxing was continued for 1 h after the stannane addition. Evaporation of the solvent and flash chromatography of the residue over silica gel (2 × 20 cm), using 1:1 EtOAc−hexane, gave **34d** (22.8 mg, 75%) as a white solid: FTIR (CH_2Cl_2, cast) 3056, 2933, 1692, 1495 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.81 (s, 9 H), 1.06 (s, 9 H), 2.05−2.09 (m, 2 H), 2.30−2.41 (m, 1 H), 3.06−3.15 (m, 1 H), 3.20 (d, J = 12.0 Hz, 1 H), 3.50−3.65 (m, 1 H), 3.75 (dd, J = 12.1, 9.3 Hz, 1 H), 3.89−4.01 (m, 1 H), 4.67 (dd, J = 9.3, 4.2 Hz, 1 H), 7.02−7.31 (m, 5 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) 21.3 (s′), 21.9 (s′), 26.2 (t′), 27.8 (q′), 28.6 (q′), 30.5 (t′), 31.8 (d′), 41.6 (t′), 55.1 (d′), 69.6 (d′), 81.6 (d′), 125.2 (d′), 128.0 (d′), 129.1 (d′), 139.4 (s′), 173.0 (s′); exact mass m/z calcd for $C_{22}H_{33}NO_2Si$ 371.22806, found 371.22862.

Crystallographic data for compound **34d**: $C_{22}H_{33}NO_2Si$, MW 371.58, crystal size 0.81 × 0.66 × 0.09 mm, triclinic space group $P\bar{1}$ (No. 1), a = 8.907(3) Å, b = 8.906(2) Å, c = 27.566(8) Å, α = 90.182(5)°, β = 81.585(5)°, γ = 83.519(5)°, V = 2149.0(11) $Å^3$, Z = 4, D_{calc} = 1.148 g cm^{-3}, μ = 0.124 mm^{-1}, T = 193(1) K, λ = 0.71073 Å (Mo Kα), $2\theta_{max}$ = 53.14°, absorption correction by Gaussian integration (indexing of crystal faces), range of transmission factors 0.9887−0.9175, $R_1(F)$ = 0.1401 (for 14300 data with $F_o^2 \geq 2\sigma(F_o^2)$) and $wR_2(F^2)$ = 0.3816 (for all 17271 independent data), goodness-of-fit (S) = 1.595, largest difference peak and hole 2.334 and −0.837 e $Å^{-3}$. Because of the poor quality of the final model this structure should not be used for determination of precise geometrical parameters (e.g., bond lengths, bond angles, conformational angles); however, the results do allow the relative stereochemistry of the product to be assigned satisfactorily.

6-(Phenylseleno)-1-hexyn-3-ol (35b). *n*-Bu_4NF (1.0 M in THF, 7.5 mL, 7.5 mmol) was injected over 3 min to a stirred and cooled (0 °C) solution of crude **13b** (1.627 g, 6.40 mmol) in dry THF (10 mL). Stirring at 0 °C was continued for 2 h. Water (5 mL) was added, and the mixture was extracted with CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (4.5 × 30 cm), using 1:99 Et_2O−CH_2Cl_2, gave **35b** (1.047 g, 83%) as a colorless oil: FTIR (CH_2Cl_2 cast) 3385, 3289, 3071, 3056, 2940, 2860, 2114, 1578, 1478, 737 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.78−1.95 (m, 5 H), 2.46 (d, J = 2.0 Hz, 1 H), 2.91−2.98 (m, 2 H), 4.35−4.43 (m, 1 H), 7.19−7.32 (m, 3 H), 7.45−7.55 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 25.6 (t′), 27.4 (t′), 37.4 (t′), 61.8 (d′), 73.3 (d′), 84.5 (s′), 126.8 (d′), 129.0 (d′), 130.1 (s′), 132.7 (d′); exact mass m/z calcd for $C_{12}H_{14}O^{80}Se$ 254.02089, found 254.02117.

Bis(1,1-dimethylethyl)[[1-[3-(phenylseleno)propyl]-2-propynyl]oxy]silane (35c). The general procedure for silylation of alcohols was followed, using **35b** (1.040 g, 4.1 mmol) in THF (30 mL), imidazole (559.0 mg, 8.2 mmol), neat *t*-Bu_2SiHCl (1.24 mL, 6.15 mmol), and a reflux time of 2 h. The mixture was cooled, diluted with water (10 mL), and extracted with Et_2O. The combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (4.5 × 30 cm), using 1:49 EtOAc−hexane, gave **35c** (1.452 g, 90%) as a colorless oil: FTIR (CH_2Cl_2 cast) 3309, 2962, 2929, 2890, 2856, 2094, 1580, 1471, 826, 735 cm^{-1}; ^1H NMR (CD_2Cl_2, 300 MHz) δ 0.98 (s, 9 H), 1.02 (s, 9 H), 1.75−1.93 (m, 4 H), 2.46 (d, J = 2.0 Hz, 1 H), 2.96 (t, J = 6.9 Hz, 2 H), 4.06 (s, 1 H), 4.5 (ddd, J = 5.7, 5.7, 2.0, Hz, 1 H), 7.21−7.30 (m, 3 H), 7.46−7.53 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 19.7 (s′), 20.0 (s′), 25.4 (t′), 27.2 (q′), 27.6 (t′), 38.1 (t′), 65.5 (d′), 73.0 (d′), 84.3 (s′), 126.8 (d′), 129.0 (d′), 130.3 (s′), 132.7 (d′) (two peaks overlap in this spectrum); exact mass m/z calcd for $C_{20}H_{32}O^{80}SeSi$ 396.13876, found 396.13842.

Bis(1,1-dimethylethyl)[[1-[3-(phenylseleno)propyl]-3-tributylstannyl-2-propynyl]oxy]silane (35d). *n*-BuLi (1.6 M in hexanes, 0.33 mL, 0.53 mmol) was injected dropwise over ca. 20 s to a stirred and cooled (−78 °C) solution of **35c** (197.8 mg, 0.50 mmol) in THF (1 mL). The mixture was stirred at −78 °C for 15 min, and a solution of Bu_3SnCl (0.15 mL, 0.53 mmol) in THF (0.5 mL plus 0.5 mL as a rinse) was then added by cannula at a rapid dropwise rate. Stirring at −78 °C was continued for 20 min after the addition, and the mixture was then quenched with water (1 mL). The cooling bath was removed, stirring was continued while the mixture reached room temperature (ca. 30 min), and the mixture was then extracted with Et_2O. The combined organic extracts were dried (Na_2SO_4) and evaporated, to give crude **35d** (350 mg, ca. 0.51 mmol) as a colorless oil, which was used in the next step (formation of **35e**) without further purification. The compound was not stable to silica chromatography.

2,2-Bis(1,1-dimethylethyl)-4,5,6,6a-tetrahydro-2*H*-cyclopent[*d*]-1,2-oxasilole (35e). The general procedure for radical cyclization was followed, using crude stannane **35d** (350 mg) in PhH (50 mL), Bu_3SnH (0.14 mL, 0.50 mmol) in PhH (7 mL), AIBN (82.1 mg, 0.50 mmol) in PhH (7 mL), and an addition time of 2 h. Refluxing was continued for 3 h after the stannane addition. Evaporation of the solvent and flash chromatography of the residue over silica gel (1 × 20 cm), using 3:7 CH_2Cl_2−hexane, gave **35e** (92.0 mg, 77%) as a colorless oil: FTIR (CH_2Cl_2 cast) 2960, 2931, 2890, 2857, 1612, 1108, 1076, 824 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.99 (s, 9 H), 1.02 (s, 9 H), 1.19−1.35 (m, 1 H), 1.75−1.92 (m, 2 H), 2.00−2.12 (m, 1 H), 2.20−2.45 (m, 2 H), 4.72−4.82 (m, 1 H), 5.50−5.56 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 19.9 (s′), 21.6 (s′), 21.7 (t′), 25.5 (t′), 27.3 (q′), 27.7 (q′), 31.8 (t′), 87.5 (d′), 113.8 (d′), 170.1 (s′); exact mass m/z calcd for $C_{14}H_{26}OSi$ 238.17529, found 238.17610. Anal. Calcd for $C_{14}H_{26}OSi$: C, 70.52; H, 10.99. Found: C, 70.72; H, 10.99.

2,2-Bis(dimethylethyl)-8,8a-dihydro-2*H*-indeno[1,2-*d*]-1,2-oxasilole (36e). The general procedure for radical cyclization was followed, using crude **36d** (221 mg, ca. 0.34 mmol) in PhH (40 mL), Bu_3SnH (99.0 mg, 0.33 mmol) in PhH (5 mL), AIBN (54.2 mg, 0.33 mmol) in PhH (5 mL), and an addition time of 2 h. Refluxing was continued for 1 h after the stannane addition. Evaporation of the solvent, and flash chromatography of the residue over silica gel (1 × 20 cm), using 1:19 EtOAc−hexane, and rechromatography over silica gel (0.6 × 15 cm), using 3:97 EtOAc−hexane, gave **36e** (55.0 mg, 58%) as a colorless oil: FTIR (CH_2Cl_2 cast) 2957, 2930, 2890, 2856, 1612, 1601, 832, 824 748 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.00 (s, 9 H), 1.09 (s, 9 H), 2.67 (dd, J = 14.4, 8.2 Hz, 1 H), 3.20 (dd, J = 14.4, 7.7 Hz, 1 H), 5.28 (ddd, J = 8.2, 7.7, 2.6 Hz, 1 H), 6.02 (d, J = 2.6 Hz, 1 H), 7.20−7.30 (m, 3 H), 7.45−7.52 (m, 1 H); ^{13}C NMR (CD_2Cl_2, 75.5 MHz) δ 20.3 (s′), 22.3 (s′), 27.6 (q′), 28.0 (q′), 38.6 (t′), 88.7 (d′), 113.3 (d′), 122.6 (d′), 126.6 (d′), 127.6 (d′), 129.6 (d′), 136.8 (s′), 145.1 (s′), 167.7 (s′); exact mass m/z calcd for $C_{18}H_{26}OSi$ 286.17529, found 286.17561.

2,2-Bis(1,1-dimethylethyl)-2,4,6,6b-tetrahydro-6,6-dimethylfuro[3,4-*d*]-1,2-oxasilole (37e). The general procedure for radical cyclization was followed, using crude **37d** (370 mg, ca. 0.56 mmol) in PhH (50 mL), Bu_3SnH (0.14 mL, 0.5 mmol) in PhH (7 mL), AIBN (82.1 mg, 0.5 mmol) in PhH (7 mL), and an addition time of 2 h. Refluxing was continued for 2 h after the addition. Evaporation of the solvent, and flash chromatography of the residue over silica gel (1 × 20 cm), using 7:95 EtOAc−hexane, and rechromatography over silica gel (0.6 × 15 cm), using 1:31 EtOAc−hexane, gave **37e** (108 mg, 81%) as a colorless oil: FTIR (CH_2Cl_2 cast) 3032, 2971, 2932, 2894, 2858, 1620, 1474, 1092, 824 cm^{-1}; ^1H NMR (CD_2Cl_2, 400 MHz) δ 0.97 (s, 3 H), 1.03 (s, 9 H), 1.04 (s, 9 H), 1.33 (s, 3 H), 4.18−4.25 (m, 1 H), 4.35−4.45 (m, 1 H), 4.58−4.62 (m, 1 H), 5.80−5.83 (m, 1 H); ^{13}C NMR (CD_2Cl_2, 100.6 MHz) δ 20.2 (q′), 21.1 (s′), 22.7 (s′), 26.8 (q′), 27.4 (q′), 28.2 (q′), 64.8 (t′), 79.6 (s′), 92.4 (d′), 115.6 (d′), 167.3 (s′); exact mass *m*/*z* calcd for $C_{14}H_{25}O_2Si$ (M − CH_3) 253.16238, found 253.16268. Anal. Calcd for $C_{15}H_{28}O_2Si$: C, 67.11; H, 10.51. Found: C, 67.09; H, 10.62.

2,2-Bis(1,1-dimethylethyl)-2,9b-dihydro-4*H*-1,2-oxasilolo-[4,5-*c*][1]benzopyran (38e). The general procedure for radical cyclization was followed, using crude **38d** (310 mg, ca. 0.41 mmol) in PhH (40 mL), Bu_3SnH (0.11 mL, 0.40 mmol) in PhH (6 mL), AIBN (65.7 mg, 0.40 mmol) in PhH (6 mL), and an addition time of 2 h. Refluxing was continued for 7 h after the stannane addition. Evaporation of the solvent, and flash chromatography of the residue over silica gel (2 × 25 cm), using 3:97 EtOAc−hexane, and rechromatography over silica gel (1 × 20 cm), using 3:7 CH_2Cl_2-hexane, gave **38e** (85.0 mg, 70%) as a white solid: mp 80.5−81.5 °C; FTIR (CH_2Cl_2 cast) 3074, 3037, 1610, 1582, 1055, 824 cm^{-1}; ^1H NMR (CD_2Cl_2, 300 MHz) δ 0.88 (s, 9 H), 1.08 (s, 9 H), 4.78−4.94 (m, 2 H), 5.60−5.66 (m, 1 H), 5.90−5.96 (m, 1 H), 6.79 (dd, J = 8.1, 1.2 Hz, 1 H), 6.95 (ddd, J = 7.4, 7.4, 1.2 Hz, 1 H), 7.10−7.18 (m, 1 H), 7.42−7.50 (m, 1 H); ^{13}C NMR (CD_2Cl_2, 75.5 MHz) δ 20.2 (s′), 21.6 (s′), 27.5 (q′), 27.7 (q′), 68.6 (t′), 78.5 (d′), 116.4 (d′), 118.9 (d′), 121.2 (d′), 126.4 (d′), 128.3 (s′), 128.6 (d′), 153.5 (s′), 156.5 (s′); exact mass *m*/*z* calcd for $C_{18}H_{26}O_2Si$ 302.17020, found 302.16948.

1,1-Dimethylethyl 2,2-Bis(1,1-dimethylethyl)-2,4,6,6a-tetrahydro-5*H*-1,2-oxasilolo[4,5-*c*]pyrrole-5-carboxylate (39e). The general procedure for radical cyclization was followed, using crude **39d** (151 mg, ca. 0.21 mmol) in PhH (20 mL), Bu_3SnH (60.0 mg, 0.20 mmol) in PhH (3 mL), AIBN (32.8 mg, 0.20 mmol) in PhH (3 mL), and an addition time of 2 h. Refluxing was continued for 1 h after the stannane addition. Evaporation of the solvent, and flash chromatography of the residue over silica gel (1 × 20 cm), using 1:9 EtOAc−hexane, and rechromatography over silica gel (0.6 × 15 cm), using 1:19 EtOAc−hexane, gave **39e** (48.0 mg, 71%) as a colorless oil: FTIR (CH_2Cl_2 cast) 2960, 2931, 2858, 1704, 1629, 1473, 1158, 1103, 823 cm^{-1}; ^1H NMR (CD_2Cl_2, 400 MHz) δ 0.99 (s, 9 H), 1.02 (s, 9 H), 1.42 (s, 9 H), 2.70−2.80 (m, 1 H), 3.85−4.03 (m, 3 H), 4.92−4.98 (m, 1 H), 5.86 (s, 1 H); ^{13}C NMR (CD_2Cl_2, 50.3 MHz) δ 20.2 (s′), 21.8 (s′), 27.0 (q′), 27.3 (q′), 27.7 (q′), 28.5 (q′), 46.8 (t′), 47.3 (t′), 50.5 (t′), 51.3 (t′), 79.6 (s′), 83.0 (d′), 83.4 (d′), 116.9 (d′), 117.1 (d′), 154.6 (s′), 154.8 (s′), 162.5 (s′), 163.0 (s′) (several peaks overlap in this spectrum); exact mass (HRES) *m*/*z* calcd for $C_{18}H_{34}NO_3Si$ (M + H) 340.230798, found 340.231100.

Bis(1-methylethyl)[[3-phenyl-1-[3-(phenylseleno)propyl]-2-propynyl]oxy]silane (44a). The general procedure for silylation of alcohols was followed, using **9b** (329.3 mg, 1.00 mmol) in THF (8 mL), imidazole (136.2 mg, 2.00 mmol), *i*-Pr_2-SiHCl (188.1 mg, 1.25 mmol) in THF (1 mL plus 1 mL as a rinse), and a reflux time of 2.5 h. The mixture was cooled, diluted with water (50 mL), and extracted with Et_2O. The combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (1.8 × 20 cm), using 1:9, and then 3:17 CH_2Cl_2-hexane, gave **44a** (397.1 mg, 90%) as a colorless oil: FTIR ($CHCl_3$ cast) 2942, 2863, 2101, 1089, 836 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.98−1.13 (m, 14 H), 1.88−2.02 (m, 4 H), 2.94−3.03 (m, 2 H), 4.26 (s, 1 H), 4.60−4.68 (m, 1 H), 7.17−7.27 (m, 3 H), 7.27−7.33 (m, 3 H), 7.33−7.42 (m, 2 H), 7.46−7.55 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 12.5 (d′), 12.6 (d′), 17.4 (q′), 17.5 (q′), 17.6 (q′), 25.9 (t′), 27.7 (t′), 37.4 (t′), 65.1 (d′), 85.1 (s′), 89.9 (s′), 122.9 (s′), 126.8 (d′), 128.3 (d′), 129.0 (d′), 130.3 (s′), 131.6 (d′), 132.8 (d′); exact mass *m*/*z* calcd for $C_{24}H_{32}O^{80}SeSi$ 444.1389, found 444.1404. Anal. Calcd for $C_{24}H_{32}OSeSi$: C, 64.99; H, 7.27. Found: C, 65.18; H, 7.17.

(3α,3a*β*,6a*β*)-2,2-Bis(1-methylethyl)hexahydro-3-phenyl-2*H*-cyclopent[*d*]-1,2-oxasilole (44b). The general procedure for radical cyclization was followed, using **44a** (158.9 mg, 0.30 mmol) in PhH (45 mL), Ph_3SnH (210.6 mg, 0.60 mmol) in PhH (7.5 mL), AIBN (24.6 mg, 0.15 mmol) in PhH (7.5 mL), and an addition time of 6 h. Refluxing was continued for 0.5 h after the stannane addition. Evaporation of the solvent, and flash chromatography of the residue over silica gel (1.8 × 19 cm), using increasing amounts of CH_2Cl_2 in hexane (from 10% to 40%), gave an oil that was purified by filtration through a pad of neutral alumina (grade I) (0.5 × 2.5 cm), using hexane (ca. 5 mL), to give **44b** (30.1 mg, 35%) as a colorless oil: FTIR ($CDCl_3$ cast) 2959, 2942, 2866, 1495, 1465, 1027, 757 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.94 (d, J = 7.0 Hz, 3 H), 1.06 (d, J = 7.0 Hz, 3 H), 1.07 (d, J = 7.0 Hz, 3 H), 1.10 (d, J = 7.0 Hz, 3 H), 1.13−1.28 (m, 2 H) 1.48−1.68 (m, 2 H), 1.69−1.80 (m, 1 H), 1.81−1.98 (m, 2 H), 1.65−1.75 (m, 1 H), 3.07 (d, J = 7.0 Hz, 1 H), 4.46 (td, J = 4.5, 1.5 Hz, 1 H), 7.11−7.17 (m, 1 H), 7.21−7.30 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 13.0 (d′), 14.5 (d′), 17.7 (q′), 17.8 (q′), 17.9 (q′), 18.0 (q′), 24.6 (t′), 28.6 (t′), 34.7 (t′), 35.5 (d′), 49.6 (d′), 83.9 (d′), 124.9 (d′), 128.2 (d′), 129.3 (d′), 141.8 (s′); exact mass *m*/*z* calcd for $C_{18}H_{28}OSi$ 288.1910, found 288.1908.

Diphenyl[[3-phenyl-1-[3-(phenylseleno)propyl]-2-propynyl]oxy]silane (45a). The general procedure for silylation of alcohols was followed, using **9b** (98.8 mg, 0.30 mmol) in PhH (2 mL), imidazole (24.5 mg, 0.36 mmol), Ph_2SiHCl (72.2 mg, 0.33 mmol) in PhH (0.5 mL plus 0.5 mL as a rinse), and a reflux time of 2 h. The white solid was removed by filtration of the cooled mixture through glass wool. The clear filtrate containing **45a** was used directly for the next step (formation of **45b**). The ^1H NMR spectrum of the product from a similar experiment, using C_6D_6 as solvent, indicated that reaction was complete.

(3aα,3a*β*,6a*β*)-Hexahydro-2,2,3-triphenyl-2*H*-cyclopent-[*d*]-1,2-oxasilole (45b). The general procedure for radical cyclization was followed, using crude **45a** in PhH (45 mL), Ph_3-SnH (210.6 mg, 0.60 mmol) in PhH (7.5 mL), AIBN (24.6 mg, 0.5 mmol) in PhH, and an addition time of 6 h. Refluxing was continued for 2 h after the stannane addition. The crude product was used directly for the next step (formation of **45c**), because of the difficulty of obtaining it free of stannane residues.

[1α,2α(*R)]-2-[Hydroxy(phenyl)methyl]cyclopentanol (45c).** H_2O_2 (30% solution in H_2O, 0.70 mL, 6.2 mmol) was added to a stirred mixture of crude **45b**, $KHCO_3$ (60 mg, 0.6 mmol) and $KF{\cdot}2H_2O$ (56.4 mg, 0.6 mmol) in 1:1 MeOH-THF (12 mL) at room temperature. The mixture was heated at 60 °C overnight, cooled to room temperature, diluted with water (5 mL), and extracted with CH_2Cl_2. The combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (1.8 × 9 cm), using increasing amounts of EtOAc in hexane (from 15% to 25%), gave **45c** (11.0 mg, 14%) as a colorless oil (R_f 0.30, silica, 3:7 EtOAc−hexane): FTIR ($CDCl_3$ cast) 3345, 2960, 1451, 1031, 999 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.43−1.72 (m, 3 H), 1.73−2.10 (m, 4 H), 2.51 (br s, 1 H), 3.48 (br s, 1 H), 4.33 (td, J = 4.5, 2.0 Hz, 1 H), 5.17 (d, J = 3.5 Hz, 1 H), 7.21−7.29 (m, 1 H), 7.30−7.41 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 21.8 (t′), 22.0 (t′), 36.0 (t′), 51.7 (d′), 73.9 (d′), 76.6 (d′), 125.8 (d′), 127.1 (d′), 128.3 (d′), 144.2 (s′); exact mass *m*/*z* calcd for $C_{12}H_{14}O$ (M − H_2O) 174.1045, found 174.1043; mass (CI) *m*/*z* calcd for $C_{12}H_{16}O_2$ (M + NH_4) 210, found 210.

Dimethyl[[3-phenyl-1-[3-(phenylseleno)propyl]-2-propynyl]oxy]silane (46a). Solid NH_4Cl (ca. 1 mg) was added to a homogeneous mixture of $(Me_2SiH)_2NH$ (60 mg, 0.45 mmol) and **9b** (98.8 mg, 0.30 mmol) in a round-bottomed flask

equipped with a septum.[49] The mixture was swirled to distribute the material uniformly over the walls of the flask, and the flask was allowed to stand at room-temperature overnight. The mixture was placed under oil-pump vacuum for 1 h [in order to remove the excess of $(Me_2SiH)_2NH$], and the residual crude **46a** was used directly for the next step (formation of **46b**). A sample from a similar experiment [NH_4-Cl (ca. 1 mg), $(Me_2SiH)_2NH$ (20.1 mg, 0.15 mmol), **9b** (32.9 mg, 0.10 mmol)] was dissolved in C_6D_6 and filtered through glass wool, to give **46a** as a colorless oil: FTIR (C_6D_6 cast) 2946, 2123, 1489, 1252, 1086, 1073, 900 cm^{-1}; ^1H NMR (C_6D_6, 400 MHz) δ 0.19 (d, J = 2.8 Hz, 3 H), 0.24 (d, J = 2.8 Hz, 3 H), 1.88−1.93 (m, 4 H), 2.63−2.72 (m, 2 H), 4.51−4.58 (m, 1 H), 4.97−5.04 (m, 1 H), 6.89−7.00 (m, 6 H), 7.34−7.47 (m, 4 H); ^{13}C NMR (C_6D_6, 100 MHz) δ −1.0 (q′), −0.8 (q′), 26.1 (t′), 27.5 (t′), 38.6 (t′), 64.4 (d′), 85.7 (s′), 90.4 (s′), 123.3 (s′), 126.8 (d′), 128.4 (d′), 128.5 (d′), 129.2 (d′), 131.0 (s′), 131.9 (d′), 133.0 (d′); exact mass m/z calcd for $C_{20}H_{24}O^{80}SeSi$ 388.0762, found 388.0762.

(3α,3a*β*,6a*β*)-2,2-Dimethylhexahydro-3-phenyl-2*H*-cyclopent[*d*]-1,2-oxasilole (46b). The general procedure for radical cyclization was followed, using crude **46a** in PhH (45 mL), Ph_3SnH (210.6 mg, 0.60 mmol) in PhH (7.5 mL), AIBN (24.6 mg, 0.5 mmol) in PhH (7.5 mL), and an addition time of 6 h. Refluxing was continued for 2 h after the stannane addition. The crude product (**46b**) was used directly for the next step (formation of **46d** and **45c**).

(*E*)-2-(Phenylmethylene)cyclopentanol (46d) and [1α,2α-(*R)]-2-[Hydroxy(phenyl)methyl]cyclopentanol (45c).** H_2O_2 (30% solution in H_2O, 0.70 mL, 6.2 mmol) was added to a stirred mixture of crude **46b**, $KHCO_3$ (60 mg, 0.6 mmol) and $KF{\cdot}2H_2O$ (56.4 mg, 0.6 mmol) in 1:1 MeOH-THF (12 mL) at room temperature. The mixture was heated at 60 °C overnight, cooled to room temperature, and diluted with aqueous 5% $KHSO_4$ (10 mL). Water (10 mL) was added, and the mixture was extracted with EtOAc. The combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (1.8 × 10 cm), using increasing amounts of EtOAc in hexane (from 15% to 25%), gave **46d**[2e] (15.1 mg, 29%) as a colorless solid, and **45c** (15.4 mg, 27%) as a colorless oil. Alcohol **46d**, had: R_f 0.45, silica, 3:7 EtOAc−hexane; mp 115−118 °C; FTIR ($CDCl_3$ cast) 3346, 2958, 1491, 1447, 1384, 1200, 1093, 1076, 1029, 753, 694, 517 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.59−1.78 (m, 3 H), 1.89−2.05 (m, 2 H), 2.51−2.62 (m, 1 H), 2.68−2.79 (m, 1 H), 4.55−4.62 (m, 1 H), 6.56−6.61 (m, 1 H), 7.07−7.25 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 22.6 (t′), 29.4 (t′), 34.9 (t′), 77.4 (d′), 123.7 (d′), 126.6 (d′), 128.3 (d′), 128.4 (d′), 137.8 (s′), 147.9 (s′); exact mass m/z calcd for $C_{12}H_{14}O$ 174.1045, found 174.1042.

Diol **45c** was spectroscopically identical to the diol obtained from oxidation of **45b**.

The same three reactions were repeated, but using a nonaqueous workup in the last step. This procedure improved the yields. After the oxidation, the mixture was cooled to 0 °C, and well-crushed $Na_2S_2O_4{\cdot}5\ H_2O$ (ca. 1 g) was added. The mixture was diluted with Et_2O (20 mL), and filtered through a pad of Celite (3 × 2 cm). The pad was washed with Et_2O (2 × 20 mL), and the filtrate was evaporated. Flash chromatography of the residue over silica gel (1.8 × 8 cm), using increasing amounts of EtOAc in hexane (from 10% to 30%), gave **46d** (23.3 mg, 45%) and **45c** (19.0 mg, 33%).

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Supporting Information Available: All experimental procedures not given above, NMR spectra of compounds for which combustion analytical values were not obtained, and X-ray data for **9f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(49) Tamao, K.; Nakagawa, Y.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 3712−3714.