A Tin Hydride Designed To Facilitate Removal of Tin Species from Products of Stannane-Mediated Radical Reactions

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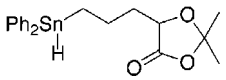
The stannane **1**, which is simple to prepare, behaves like the conventional reagents Bu_3SnH and Ph_3SnH in standard free radical reactions, but with the special characteristic that the tin-containing byproducts are easily and very largely removed by mild hydrolysis (LiOH−water−THF or TsOH−water−THF), which converts them into base-soluble (aqueous $NaHCO_3$) materials. The performance of stannane **1** was evaluated for a range of radical reactions involving halides, selenides, Barton−McCombie deoxygenation, and enyne cyclization. In several cases the effectiveness of the workup procedure in removing tin species was monitored by ^1H NMR.

Introduction

It is well-known that there are occasional difficulties in removing tin species from the products of stannane-mediated radical reactions. These reactions are important in organic synthesis; consequently, a number of methods have had to be developed to facilitate product isolation. We report the preparation and use of stannane **1**—a substance whose structural features simplify product isolation.



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Prior work on the problem of removing tin-containing impurities, and the alternative approach of avoiding the use of tin reagents, includes

(1) development of various workup procedures for reactions involving stoichiometric R_3SnH,[1]

(2) use of catalytic amounts of a tin hydride or its precursor and stoichiometric amounts of another hydride ($NaBH_4$,[2] $NaCNBH_3$,[3] polymethylhydrosiloxane,[4] $PhSiH_3$[5]),

(3) use of modified stannanes,[6] including fluorous stannanes,[7]

(4) use of solid-supported stannanes either stoichiometric[8] or catalytic,[8c,i,9]

(5) use of alternatives to stannanes,[10] especially silanes,[11,12] dialkyl phosphites and hypophosphorous acid,[13] and, more recently, R_2GaCl_2,[14] and

(6) use of xanthates.[15]

Results and Discussion

In connection with some free radical experiments done in this laboratory, a need developed for a readily acces-

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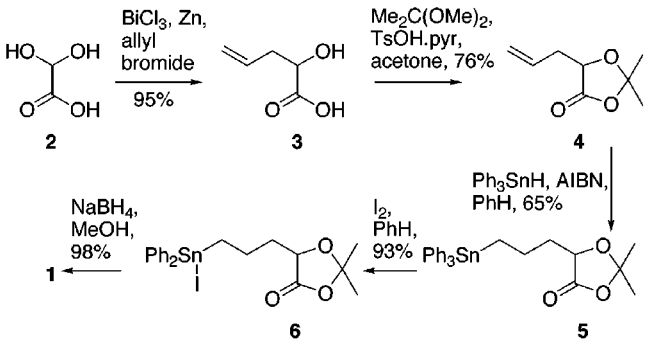
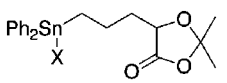
Scheme 1



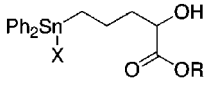
sible stannane, RR′R″SnH, whose derivatives, RR′R″SnX (X = halogen or SePh), could be converted by acid or base treatment under mild conditions to a carboxylic acid that is soluble in aqueous $NaHCO_3$. After some exploratory work to this end, we settled on compound **1**, which satisfies these requirements. This stannane is made by the straightforward route summarized in Scheme 1.

The known hydroxy acid **3**[16] was easily prepared (95%) by a literature procedure that calls for treatment of glyoxylic acid hydrate (**2**) with $BiCl_3$, Zn, and allyl bromide. Ketalization under standard conditions (2,2-dimethoxypropane, TsOH·pyridine, acetone) gave the derived ketal **4**. When this was heated with an excess (1.5 equiv) of Ph_3SnH in PhH in the presence of a catalytic amount of AIBN, the hydrostannylated product **5** could be isolated in 65% yield. Treatment with 1 equiv of I_2[17] served to replace (93%) one of the phenyl groups by I (**5** → **6**), and then reduction with $NaBH_4$ gave the required stannane **1** (98%) as a colorless oil, which was obtained pure by chromatography over silica gel. We store the compound under N_2 in a refrigerator; the material is stable for at least two months under these conditions, but we have not tested older samples.

To establish the properties of the anticipated tin-containing reaction products, the bromide **7** and the selenide **8** were also prepared, the former by reaction of **1** with 1-bromopropane under standard conditions (see the Experimental Section), and the latter by reaction of **1** with selenide **15a** (see later). In addition, compounds **6** and **8** (we did not examine **7**) were stirred in an aqueous THF solution of LiOH (ca. 10 equiv) for several hours, and the presumed products **9a** and **9b**, obtained by acidification, were esterified with CH_2N_2 to give **10a** (16%) and **10b** (31%), respectively. Compound **6** was also hydrolyzed, using acidic conditions (TsOH·H_2O) in MeOH, to obtain **10a** (50%) directly. Both **10a** and **10b** were characterized.



7 X = Br
8 X = SePh



9a R = H, X = I
9b R = H, X =SePh
10a R = Me, X = I
10b R = Me, X =SePh

We have evaluated the performance of reagent **1** by using it in typical radical reactions, as summarized in Table 1.

The table shows reduction of bromides (entries 1−4), a benzylic chloride (entry 5), and selenides (entries 6 and 7), radical cyclization onto a carbon−carbon double bond (entries 9, 10, 11, and 16), radical cyclization onto a triple bond (entries 12 and 13), stannane addition to a triple bond, followed by cyclization of the resulting vinyl radical and subsequent protodestannylation (entry 14), and cyclization onto an oxime (entry 15). Entry 8 shows an example of Barton−McCombie deoxygenation.

The reactions with **1** can be initiated by AIBN in refluxing PhH or PhMe, or by Et_3B and air at room temperature. In all cases, except those of entries 1 (procedure giving 85% yield), 7, 15, and 16, the crude reaction mixture was stirred with a solution of LiOH in aqueous THF for 1.5−3 h (TLC control), and the organic-soluble product was purified by flash chromatography. For reduction of **11a** (entry 1) we also tried acidic workup, the crude reaction mixture, in this case, being stirred with an aqueous THF solution of TsOH. The product **11b** was then isolated in 85% yield. In one case (entry 2), the ^1H NMR spectrum of the organic-soluble product after LiOH treatment was measured before and after flash chromatography. In two cases (entries 1 and 6) the same two measurements were again made, but in addition, the

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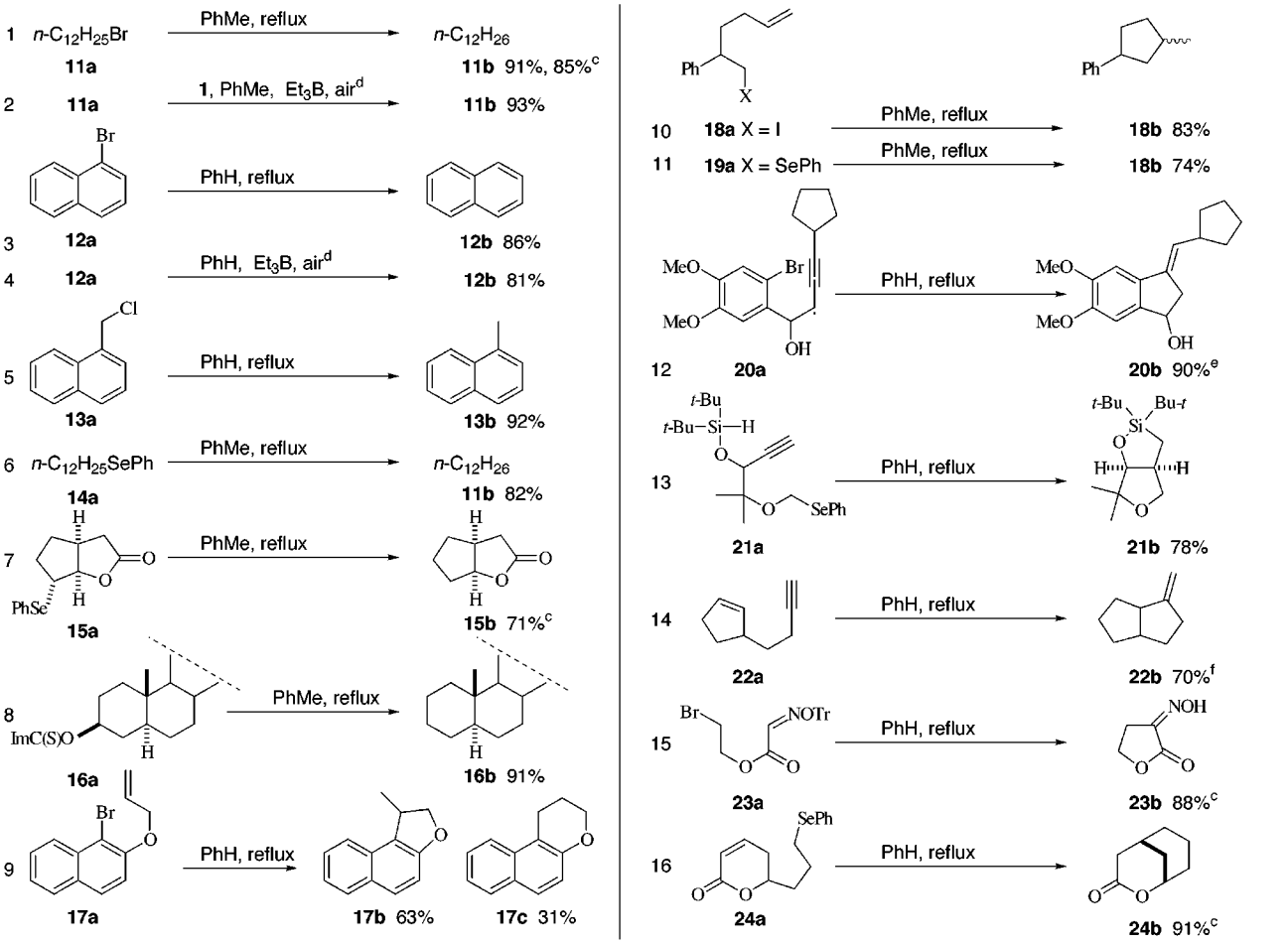
Table 1[a,b]



[a] Reaction conditions, unless indicated otherwise: **1**, AIBN, PhH or toluene, reflux. [b] Workup, unless indicated otherwise: LiOH, water–THF, extract with Et_2O, wash with $NaHCO_3$, flash chromatography. [c] Workup: $TsOH·H_2O$, aqueous THF, extract with Et_2O, wash with $NaHCO_3$, flash chromatography. [d] Room temperature. [e] A single isomer of unestablished geometry. [f] The initial radical cyclization product was treated with CF_3CO_2H before LiOH.

^1H NMR spectrum was run before workup. The three spectra for entry 1 (91% yield) are shown in Figure 1.

These spectra establish that the LiOH treatment removes all but traces of aryl-containing species, but leaves slight impurities (signals at δ 1.4, 1.5, and 3.6). All these impurities are removed by flash chromatography (in this case, using hexane as eluant). When acidic workup was used after reduction of **11a** (entry 1, 85% yield), the three ^1H NMR spectra (see the Supporting Information) were very similar to those shown in Figure 1. The three ^1H NMR spectra obtained from the experiment in entry 6 (see the Supporting Information) were comparable to those obtained from the experiment of entry 1.

While most of the experiments listed in Table 1 give products that are stable to mild base (LiOH and $NaHCO_3$), for the examples of entries 7, 15, and 16 we used acidic conditions for workup, followed by extraction of the tin species into saturated aqueous $NaHCO_3$.

Conclusion

Overall, our experiments show that reagent **1** behaves similarly to the standard Bu_3SnH of Ph_3SnH, with the additional characteristic that the tin-containing byproducts are easily removed.

Experimental Section

General Procedures. Unless stated to the contrary, all reactions were done under dry N_2, and the general procedures used previously[18] were followed. The symbols s′, d′, t′, and q′ used for ^{13}C NMR signals indicate zero, one, two, and three attached hydrogens, respectively, the assignments being made from APT spectra. Known reaction products were identified by comparison of their NMR spectra (usually both ^1H NMR and ^{13}C NMR) with reported values.

General Procedures for Radical Reactions and Workup. (a) Thermal Radical Reactions. The substrate (0.2 mmol) was placed in a round-bottomed flask carrying a reflux condenser closed by a septum. The flask was flushed with N_2, and the contents were kept under a slight positive pressure of N_2. PhH or PhMe (3 mL) was injected, and the flask was lowered into a preheated oil bath set at 85 °C, or at 125 °C in the case of PhMe. A solution of both stannane **1** (0.28 mmol, 1.4 equiv) and AIBN (1 mg) in the same solvent (3 mL, plus 1 mL as a rinse) was injected in one portion (except for the radical cyclizations, in which case the addition was made over 6 h). Refluxing was continued for 2–10 h after the addition. The mixture was cooled and evaporated. Aqueous LiOH (1 M, 2 mL) in THF (2 mL) or aqueous TsOH (0.25 M, 2 mL) in THF (2 mL) was added to the residue, and the mixture was stirred at room temperature for 1.5–3 h (TLC control). After all the tin dioxolanone had been hydrolyzed, Et_2O (20 mL) was added,

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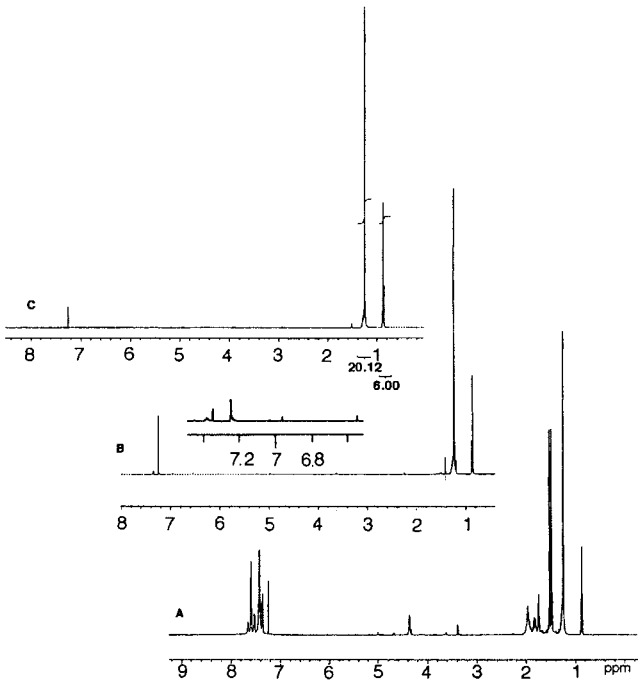

Figure 1. Trace A: spectrum measured after evaporation of reaction solvent for entry 1 of Table 1. Trace B: spectrum measured after LiOH treatment. Inset: expansion (ca. 4×) of region δ 6.5−7.4. The chloroform signal is truncated. Trace C: spectrum measured after flash chromatography.

and the organic layer was washed with saturated $NaHCO_3$ (3 × 20 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel then gave the product.

(b) Room Temperature Radical Reactions. Stannane **1** (1.4 mmol) in PhH (4 mL) and Et_3B (1 M in hexane, 1.1 mL) were added to a stirred solution of the substrate (1.0 mmol) in hexane (5 mL) contained in a flask fitted with a calcium sulfate guard tube. The mixture was stirred for 11 h with exposure to air (via the guard tube), and the same workup procedure was followed as for the thermal method.

2,2-Dimethyl-5-(2-propenyl)-1,3-dioxolan-4-one (4). 2-Hydroxy-4-pentenoic acid[16] (6.00 g, 51.7 mmol) was dissolved in 2,2-dimethoxypropane (150 mL). Pyridinium *p*-toluenesulfonate (0.50 g, 1.99 mmol) was added, and the mixture was stirred for 5 h (TLC control, silica, 1:4 EtOAc−hexane). Evaporation of the solvent and flash chromatography of the residue over silica gel (2.5 × 20 cm), using 1:19 EtOAc−hexane, gave acetonide **4** (6.14 g, 76%) as a colorless oil: FTIR ($CDCl_3$, cast) 2918, 1797 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.53 (s, 3 H), 1.60 (s, 3 H), 2.45−2.54 (m, 1 H), 2.62−2.70 (m, 1 H), 4.45 (q, J = 4.6, 6.6 Hz, 1 H), 5.16−5.26 (m, 2 H), 5.77−5.88 (m, 1 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 25.9 (q′), 27.2 (q′), 35.8 (t′), 73.8 (d′), 110.7 (s′), 119.2 (d′), 131.9 (t′), 172.6 (s′); exact mass *m*/*z* calcd for $C_8H_{12}O_3$ 156.07864, found 156.07834. Anal. Calcd for $C_8H_{12}O_3$: C, 61.47; H, 7.74. Found: C, 60.82; H, 7.94.

2,2-Dimethyl-5-[3-(triphenylstannyl)propyl]-1,3-dioxolan-4-one (5). A solution of **4** (1.56 g, 10.0 mmol) in dry PhH (10 mL) was added to freshly prepared Ph_3SnH (5.26 g, 15.0 mmol, made from Ph_3SnCl and $LiAlH_4$[19]). AIBN (10 mg) was added to the mixture, which was then heated at 90 °C for 10−24 h (TLC control; N_2 atmosphere). Evaporation of the solvent and rapid (no more than 30 min) flash chromatography of the residue over silica gel (3 × 25 cm), using 1:49 EtOAc−hexane, gave stannane **5** (3.29 g, 65%) as a colorless oil: FTIR ($CDCl_3$, cast) 3063, 1792, 1429 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.477 (s, 3 H), 1.481 (s, 3 H), 1.50−1.53 (m, 2 H), 1.75−1.97 (m, 4 H), 4.33−4.36 (m, 1 H), 7.33−7.39 (m, 9 H), 7.46−7.59 (m, 6 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 10.4 (t′), 22.3 (t′), 25.8 (q′), 27.1 (q′), 35.9 (t′), 73.6 (d′), 110.4 (s′), 128.5 (d′), 130.0 (d′), 137.0 (d′), 138.6 (s′), 173.2 (s′); exact mass *m*/*z* calcd for $C_{26}H_{28}O_3{}^{120}Sn$ 508.10605, found 508.10564. Anal. Calcd for $C_{26}H_{28}O_3Sn$: C, 61.57; H, 5.56. Found: C, 61.43; H, 5.45.

2,2-Dimethyl-5-[3-[iodo(diphenyl)stannyl]propyl]-1,3-dioxolan-4-one (6). A solution of I_2 (0.64 g, 2.5 mmol) in PhH (30 mL) was added over 30 min to a stirred solution of **5** (1.28 g, 2.5 mmol) in PhH (20 mL). Stirring was continued for 5−10 h (TLC control), and the solvent was evaporated. Rapid (less than 30 min) flash chromatography of the residue over silica gel (2 × 15 cm), using 1:4 EtOAc−hexane, gave **6** (1.31 g, 93%) as a colorless oil: FTIR (CH_2Cl_2, cast) 3065, 1790, 1430 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.49 (s, 3 H), 1.53 (s, 3 H), 1.72−2.04 (m, 6 H), 4.34−4.39 (m, 1 H), 7.35−7.70 (m, 10 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 16.2 (t′), 22.7 (t′), 25.8 (q′), 27.2 (q′), 35.0 (t′), 73.6 (d′), 110.6 (s′), 129.0 (d′), 130.1 (d′), 136.1 (d′), 137.0 (s′), 173.0 (s′); exact mass *m*/*z* calcd for $C_{20}H_{23}IO_3{}^{120}Sn$ 557.97137, found 557.97294. Anal. Calcd for $C_{20}H_{23}IO_3Sn$: C, 43.13; H, 4.16; I, 22.78. Found: C, 43.23; H, 4.11; I, 22.41.

2,2-Dimethyl-5-[3-(diphenylstannyl)propyl]-1,3-dioxolan-4-one (1). $NaBH_4$ (44 mg, 1.1 mmol) was added to a stirred and cooled (0 °C) solution of **6** (636 mg, 1.1 mmol) in dry MeOH (20 mL). Stirring was continued for 3 h at 0 °C, and the mixture was then quenched with EtOAc (20 mL), followed by water (20 mL). The mixture was extracted with EtOAc (3 × 20 mL), and the combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (2 × 10 cm), using 1:4 EtOAc−hexane, gave stannane **1** (484.2 mg, 98%) as a colorless oil which we store under N_2 in a refrigerator: FTIR (CD_2Cl_2, cast) 3068, 1792, 1429 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.35−1.41 (m, 2 H), 1.49 (s, 3 H), 1.52 (s, 3 H), 1.75−1.97 (m, 4 H), 4.34−4.38 (m, 1 H), 6.16 (t, J = 1.8 Hz, 1 H), 7.31−7.37 (m, 6 H), 7.45−7.56 (m, 4 H); ^{13}C NMR (CD_2Cl_2, 75.5 MHz) δ 10.2 (t′), 23.2 (t′), 25.9 (q′), 27.4 (q′), 36.1 (t′), 74.0 (d′), 110.8 (s′), 129.1 (d′), 129.2 (d′), 137.6 (d′), 138.3 (s′), 173.5 (s′); exact mass *m*/*z* calcd for $C_{20}H_{24}NaO_3{}^{120}Sn$ 455.06451, found 455.06535. Anal. Calcd for $C_{20}H_{24}O_3Sn$: C, 55.74; H, 5.56. Found: C, 55.99; H, 5.42.

2,2-Dimethyl-5-[3-[bromo(diphenyl)stannyl]propyl]-1,3-dioxolan-4-one (7). 1-Bromopropane (0.5 mL) was added to a solution of **1** (217 mg, 0.5 mmol) and AIBN (3 mg, 0.02 mmol) in PhMe (8 mL). The mixture was then heated at 110 °C for 3 h, cooled to room temperature, and evaporated. Flash chromatography of the residue over silica gel (1 × 15 cm), using 1:4 EtOAc−hexane, gave bromide **7** (152.5 mg, 60%) as a colorless oil: FTIR ($CHCl_3$, cast) 3066, 1789, 1430 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.49 (s, 3 H), 1.54 (s, 3 H), 1.66−2.04 (m, 6 H), 4.34−4.39 (m, 1 H), 7.38−7.68 (m, 10 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 16.7 (t′), 21.8 (t′), 25.7 (q′), 27.1 (q′), 35.0 (t′), 73.5 (d′), 110.6 (s′), 129.0 (d′), 130.2 (d′), 135.8 (d′), 137.9 (s′), 173.0 (s′); exact mass *m*/*z* calcd for $C_{20}H_{23}{}^{81}BrO_3{}^{120}Sn$ 511.98322, found 511.98251. Anal. Calcd for $C_{20}H_{23}BrO_3Sn$: C, 47.10; H, 4.55. Found: C, 47.45; H, 4.59.

2,2-Dimethyl-5-[3-[phenylseleno(diphenyl)stannyl]-propyl]-1,3-dioxolan-4-one (8). Stannane **1** (227 mg, 0.5 mmol) and AIBN (5 mg, 0.03 mmol) in PhMe (5 mL, plus 3 mL as a rinse) were added in one portion to a refluxing solution of (3aα,6α,6aα)-hexahydro-6-(phenylseleno)-2*H*-cyclopenta[*b*]-furan-2-one (**15a**)[20] (106 mg, 0.4 mmol) in PhMe (3 mL). Refluxing was continued overnight, and the solvent was then evaporated. Flash chromatography of the residue over silica gel (1 × 15 cm), using 1:9 EtOAc−hexane, gave **8** (152 mg, 69%) as a colorless oil: FTIR (CH_2Cl_2, cast) 3064, 2925, 1791, 1576, 1474 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.40−1.45 (m, 2 H), 1.48 (s, 3 H), 1.50 (s, 3 H), 1.65−1.88 (m, 4 H), 4.28 (q, J = 4.0, 7.0 Hz, 1 H), 7.02 (t, J = 7.5 Hz, 2 H), 7.12 (t, J = 7.4 Hz, 1 H), 7.30−7.50 (m, 12 H); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 13.9 (t′), 22.2 (t′), 25.9 (q′), 27.2 (q′), 35.5 (t′), 73.5 (d′), 110.4 (s′), 124.6 (s′), 126.6 (d′), 128.6 (d′), 128.7 (d′), 129.4 (d′), 136.4 (d′), 136.5 d′), 138.2 (s′), 172.9 (s′); exact mass *m*/*z* calcd for $C_{26}H_{28}NaO_3{}^{80}Se^{120}Sn$ 611.01233, found 611.01175.

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Methyl 5-[Iodo(diphenyl)stannyl]-2-hydroxypentanoate (10a). (a) Aqueous LiOH (1 M, 2 mL) was added to a stirred solution of compound **6** (133 mg, 0.24 mmol) in THF (2 mL). Stirring was continued for 1 h, and the mixture was acidified with concentrated hydrochloric acid. The precipitate was collected, washed with CH_2Cl_2, and dried under an oil pump vacuum. The solid (62 mg) was then suspended in a mixture of MeOH (2 mL) and PhMe (5 mL), and Me_3SiCHN_2 (2 M in hexane, 0.3 mL, 0.6 mmol) was added dropwise with stirring. Stirring was continued for 15 min. AcOH (0.5 mL) was added to destroy the excess Me_3SiCHN_2, and the mixture was extracted with EtOAc. The combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (1 × 10 cm), using EtOAc, gave **10a** (20 mg, 16%). See the following experiment for characterization data.

(b) Compound **6** (40 mg, 0.07 mmol) was stirred for 1.5 h in MeOH (3 mL) containing $TsOH·H_2O$ (3 mg). Evaporation of the solvent and flash chromatography of the residue over silica gel (1 × 15 cm), using EtOAc, gave **10a** (19.6 mg, 50%) as a colorless oil: FTIR ($CDCl_3$, cast) 3425 (br), 3064, 1733, 1429 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.65−2.00 (m, 6 H), 2.72 (br s, 1 H), 3.72 (s, 3 H), 4.15 (d, J = 7.1 Hz, 1 H), 7.33−7.43 (m, 6 H), 7.54−7.62 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 17.2 (t′), 22.5 (t′), 37.4 (t′), 52.6 (q′), 70.0 (d′), 128.9 (d′), 130.0 (d′), 136.1 (d′), 137.5 (s′), 175.3 (s′); exact mass m/z calcd for $C_{18}H_{21}INaO_3{}^{120}Sn$ 554.94497, found 554.94539.

Methyl 5-[(Diphenyl)(phenylseleno)stannyl]-2-hydroxypentanoate (10b). Conversion of **8** to **10b** was done in two slightly different ways: (a) After the LiOH hydrolysis of the crude reaction mixture from reduction of **14a** (59 mg) (see later), the aqueous LiOH layer was acidified with concentrated hydrochloric acid, and the precipitate was collected, washed with CH_2Cl_2, and dried under an oil pump vacuum. The solid (63 mg) was then suspended in a mixture of MeOH (2 mL) and PhMe (5 mL), and Me_3SiCHN_2 (2 M in hexane, 0.25 mL, 0.5 mmol) was added dropwise with stirring. Stirring was continued for 15 min. AcOH (0.5 mL) was added to destroy the excess Me_3SiCHN_2, and the mixture was extracted with EtOAc. The combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (1 × 10 cm), using 1:9 EtOAc−hexane, gave **10b** (20 mg, 31%) as a yellow oil: FTIR ($CHCl_3$, cast) 3485, 3063, 1958, 1735, 1576, 1429 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.37−1.85 (m, 6 H), 2.57 (d, J = 5.7 Hz, 1 H), 3.71 (s, 3 H), 4.07−4.13 (m, 1 H), 7.02 (t, J = 7.4 Hz, 2 H), 7.12 (tt, J = 1.2, 7.4 Hz, 1 H), 7.30−7.54 (m, 12 H); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 14.1 (t′), 22.0 (t′), 38.2 (t′), 52.5 (q′), 69.9 (d′), 124.7 (s′), 126.5 (d′), 128.6 (d′), 128.6 (d′), 129.3 (d′), 136.4 (d′), 136.5 (d′), 138.4 (s′), 175.4 (s′); exact mass m/z calcd for $C_{18}H_{21}O_3{}^{120}Sn$ (M − PhSe) 405.05127, found 405.05229. Anal. Calcd for $C_{24}H_{26}O_3SeSn$: C, 51.42; H, 4.68. Found: C, 51.34; H, 4.69.

(b) Anhydrous K_2CO_3 (3 mg, 0.02 mmol) was added to a stirred solution of **8** (94 mg, 0.16 mmol) in MeOH (5 mL), and stirring was continued for 3 h. Evaporation of the solvent and flash chromatography of the residue over silica gel (1 × 15 cm), using 1:19 EtOAc−hexane, gave **10b** (65 mg, 72%) as a yellow oil.

Dodecane (11b) from 11a. (a) Thermal Radical Reaction and Basic Workup. The general thermal procedure for radical reactions was followed, using 1-bromododecane (**11a**) (64 mg, 0.26 mmol) in PhMe (1 mL), stannane 1 (155 mg, 0.36 mmol) and AIBN (2 mg, 0.01 mmol) in PhMe (5 mL, plus 1 mL as a rinse), an addition time of 1 h, and an arbitrary reflux time of 3 h after the addition. The general basic workup procedure was followed, using aqueous LiOH (1 M, 2 mL) in THF (2 mL) and a reaction time of 3 h. Flash chromatography of the crude product over silica gel (1 × 10 cm), using hexane, gave **11b** (40.1 mg, 91%).

In this experiment the ^1H NMR spectra of the crude product, of the material obtained after LiOH treatment, and of the final product were measured (see Figure 1 and the Supporting Information).

(b) Thermal Radical Reaction and Acidic Workup. The general thermal procedure for radical reactions was followed, using **11a** (70 mg, 0.28 mmol) in PhMe (3 mL), stannane **1** (170 mg, 0.39 mmol) and AIBN (2 mg, 0.01 mmol) in PhMe (5 mL, plus 2 mL as a rinse), an addition time of 5 min, and an arbitrary reflux time of 5 h after the addition. The general acidic workup procedure was followed, using aqueous TsOH (0.25 M, 1 mL) in THF (2 mL) and a reaction time of 3 h. Flash chromatography of the crude product over silica gel (1 × 10 cm), using hexane, gave **11b** (41.1 mg, 85%).

In this experiment the ^1H NMR spectra of the crude product, of the material obtained after TsOH treatment (and washing with aqueous $NaHCO_3$), and of the final product were measured (see the Supporting Information).

(c) Room Temperature Radical Reaction and Basic Workup. The general room temperature procedure for radical reactions was followed, using **11a** (66 mg, 0.27 mmol) in PhH (2 mL), stannane **1** (160 mg, 0.37 mmol) in PhH (3 mL, plus 1 mL as a rinse), Et_3B (1 M in hexane, 0.35 mL, 0.35 mmol), and an arbitrary reaction time of 10 h after the addition. The general basic workup procedure was followed, using aqueous LiOH (1 M, 3 mL) in THF (3 mL) and a reaction time of 3 h. Flash chromatography of the crude product over silica gel (1 × 10 cm), using hexane, gave **11b** (42.0 mg, 93%).

Naphthalene (12b). (a) Thermal Reaction. The general thermal procedure for radical reactions was followed, using 1-bromonaphthalene (**12a**) (47.0 mg, 0.23 mmol) in PhH (4 mL), stannane **1** (132 mg, 0.31 mmol) and AIBN (1 mg, 0.006 mmol) in PhH (4 mL, plus 2 mL as a rinse), an addition time of 5 min, and an arbitrary reflux time of 3 h after the addition. The general basic workup procedure was followed, using aqueous LiOH (1 M, 2 mL) in THF (2 mL) and a reaction time of 3 h. Flash chromatography of the crude product over silica gel (1 × 10 cm), using hexane, gave **12b** (25.1 mg, 86%).

(b) Room Temperature Reaction. The general room temperature procedure for radical reactions was followed, using **12a** (42 mg, 0.20 mmol) in PhH (4 mL), stannane **1** (121 mg, 0.28 mmol) in PhH (3 mL, plus 1 mL as a rinse), Et_3B (1 M in hexane, 0.3 mL, 0.3 mmol), and an arbitrary reaction time of 10 h after the addition. The general basic workup procedure was followed, using aqueous LiOH (1 M, 2 mL) in THF (2 mL) and a reaction time of 3 h. Flash chromatography of the crude product over silica gel (1 × 10 cm), using hexane, gave naphthalene **12b** (20.8 mg, 81%).

1-Methylnaphthalene (13b). The general thermal procedure for radical reactions was followed, using 1-chloromethylnaphthalene (**13a**) (43.0 mg, 0.24 mmol) in PhH (4 mL), stannane **1** (147 mg, 0.34 mmol) and AIBN (2 mg, 0.01 mmol) in PhH (5 mL, plus 3 mL as a rinse), an addition time of 5 min, and an arbitrary reflux time of 10 h after the addition. The general basic workup procedure was followed, using aqueous LiOH (1 M, 2 mL) in THF (2 mL) and a reaction time of 1.5 h. Flash chromatography of the crude product over silica gel (1 × 10 cm), using 1:49 EtOAc−hexane, gave 1-methylnaphthalene **13b** (32.0 mg, 92%).

11b from 14a. The general thermal procedure for radical reactions was followed, using (1-phenylseleno)dodecane (**14a**) (59 mg, 0.18 mmol) in PhMe (1.5 mL), stannane **1** (103 mg, 0.24 mmol) and AIBN (2 mg, 0.01 mmol) in PhMe (4 mL, plus 1 mL as a rinse), an addition time of 5 min, and an arbitrary reflux time of 5 h after the addition. The general basic workup procedure was followed, using aqueous LiOH (1 M, 2 mL) in THF (3 mL) and a reaction time of 2 h. Flash chromatography of the crude product over silica gel (1 × 10 cm), using hexane, gave **11b** (25.2 mg, 82%).

***cis*-Hexahydro-2*H*-cyclopenta[*b*]furan-2-one (15b).** The general thermal procedure for radical reactions was followed, using **15a**[20] (89 mg, 0.32 mmol) in PhMe (4 mL), stannane **1** (157 mg, 0.36 mmol) and AIBN (3 mg, 0.02 mmol) in PhMe (4 mL, plus 2 mL as a rinse), an addition time of 5 min, and an arbitrary reflux time of 10 h after the addition. The general acidic workup procedure was followed, using aqueous TsOH (0.25 M, 1 mL) in THF (3 mL) and a reaction time of 3 h. Flash chromatography of the crude product over silica gel (1 × 15

cm), using 1:19 EtOAc−hexane, gave **15b**[21] (28.6 mg, 71%) as a colorless oil.

5α-Cholestane (16b). The general thermal procedure for radical reactions was followed, using **16a** (37.0 mg, 0.074 mmol) in PhMe (1.5 mL), stannane **1** (48 mg, 0.11 mmol) and AIBN (2 mg, 0.01 mmol) in PhMe (1.5 mL, plus 1.5 mL as a rinse), an addition time of 5 min, and an arbitrary reflux time of 10 h after the addition. The general basic workup procedure was followed, using aqueous LiOH (1 M, 1 mL) in THF (1 mL) and a reaction time of 1.25 h. Flash chromatography of the crude product over silica gel (1 × 10 cm), using hexane, gave **16b** (25.2 mg, 91%).

1-Methyl-1,2-dihydronaphtho[2,1-*b*]furan (17b) and 2,3-Dihydro-1*H*-naphtho[2,1-*b*]pyran (17c). The general thermal procedure for radical cyclization was followed, using **17a**[22] (57 mg, 0.2 mmol) in PhH (3 mL), stannane **1** (131 mg, 0.3 mmol) and AIBN (1 mg, 0.006 mmol) in PhH (3 mL, plus 2 mL as a rinse), an addition time of 5 h, and an arbitrary reflux time of 6 h after the addition. The general basic workup procedure was followed, using aqueous LiOH (1 M, 2 mL) in THF (2 mL) and a reaction time of 1.5 h. Flash chromatography of the crude product over silica gel (1 × 10 cm), using 1:19 EtOAc−hexane, gave **17b**[23] (23.7 mg, 63%) and **17c**[23] (14 mg, 31%).

[1-(Iodomethyl)-4-pentenyl]benzene (18a). Ph_3P (1.44 g, 5.5 mmol) and imidazole (375 mg, 5.5 mmol) were added to a stirred solution of 2-phenyl-5-hexen-1-ol[24] (485 mg, 2.8 mmol) in CH_2Cl_2 (20 mL).[25] Stirring was continued for 10 min, and I_2 (1.40 g, 5.5 mmol) was tipped into the mixture. Stirring was continued for 3 h, and the mixture was then washed with saturated aqueous $Na_2S_2O_3$ (20 mL) and extracted with CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (2 × 15 cm), using 1:99 EtOAc−hexane, gave **18a** (751 mg, 95%) as a colorless oil: FTIR ($CDCl_3$, cast) 3062, 2929, 1640, 1494 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.67−1.76 (m, 1 H), 1.85−2.03 (m, 3 H), 2.82−2.89 (m, 1 H), 3.32−3.41 (m, 2 H), 4.92−4.97 (m, 2 H), 5.69−5.78 (m, 1 H), 7.13−7.16 (m, 2 H), 7.22−7.34 (m, 3 H); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 13.7 (t′), 31.6 (t′), 34.9 (t′), 47.6 (d′), 115.0 (t′), 127.0 (d′), 127.4 (d′), 128.5 (d′), 137.8 (d′), 142.7 (s′); exact mass *m*/*z* calcd for $C_{12}H_{15}I$ 286.02185, found 286.02149. Anal. Calcd for $C_{12}H_{15}I$: C, 50.37; H, 5.28. Found: C, 50.39; H, 5.30.

***cis*- and *trans*-3-Methyl-1-phenylcyclopentane (18b) from 18a.** The general thermal procedure for radical cyclization was followed, using **18a** (81.5 mg, 0.29 mmol) in PhH (2 mL), stannane **1** (180 mg, 0.42 mmol) and AIBN (4 mg, 0.02 mmol) in PhH (5 mL, plus 3 mL as a rinse), an addition time of 5 h, and an arbitrary reflux time of 3 h after the addition. The general basic workup procedure was followed, using aqueous LiOH (1 M, 3 mL) in THF (3 mL) and a reaction time of 2 h. Flash chromatography of the crude product over silica gel (1 × 10 cm), using hexane, gave **18b**[26] (38.1 mg, 83%): ^1H NMR ($CDCl_3$, 500 MHz) δ 1.05 (q, J = 6.5 Hz, 3 H), 1.17−2.28 (m, 7 H), 3.00−3.19 (m, J = 8.4 Hz, 1 H), 7.12−7.29 (m, 5 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 21.0 (q′), 33.8 (d′), 34.1 (t′), 35.4 (t′), 42.5 (d′), 44.5 (d′), 125.5 (d′), 127.0 (d′), 128.1 (d′), 147.0 (s′).

In this experiment the ^1H NMR spectra of the crude product, of the material obtained after LiOH treatment, and of the final product were measured (see the Supporting Information).

[(2-Phenylhex-5-enyl)seleno]benzene (19a). $NaBH_4$ (52 mg, 1.35 mmol) was added to a stirred solution of **18a** (250 mg, 0.87 mmol) and PhSeSePh (136 mg, 0.44 mmol) in MeOH (7 mL) (N_2 atmosphere), MeOH (3 mL) being used as a rinse to transfer all the $NaBH_4$. The mixture was stirred overnight, and then evaporated. Flash chromatography of the residue over silica gel (1 × 20 cm), using hexane, gave **19a** (230 mg, 83%) as colorless oil: FTIR ($CDCl_3$, cast) 3072, 3027, 2926, 1640, 1579, 1477 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.68−1.76 (m, 1 H), 1.82−2.00 (m, 3 H), 2.82−2.88 (m, 1 H), 3.12−3.19 (m, 2 H), 4.87−4.94 (m, 2 H), 5.67−5.76 (m, 1 H), 7.10−7.44 (m, 10 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 31.5 (t′), 35.2 (t′), 35.3 (t′), 45.6 (d′), 114.7 (t′), 126.62 (d′), 126.64 (d′), 127.5 (d′), 128.4 (d′), 128.9 (d′), 130.8 (s′), 132.5 (d′), 138.1 (d′), 143.9 (s′); exact mass *m*/*z* calcd for $C_{18}H_{20}{}^{80}Se$ 316.07303, found 316.07266. Anal. Calcd for $C_{18}H_{20}Se$: C, 68.57; H, 6.39. Found: C, 68.35; H, 6.47.

18b from 19a. The general thermal procedure for radical cyclization was followed, using **19a** (77.8 mg, 0.25 mmol) in PhH (3 mL), stannane **1** (150 mg, 0.35 mmol) and AIBN (4 mg, 0.02 mmol) in PhH (8 mL, plus 2 mL as a rinse), an addition time of 5 h, and an arbitrary reflux time of 5 h after the addition. The general basic workup procedure was followed, using aqueous LiOH (1 M, 2 mL) in THF (2 mL) and a reaction time of 2 h. Flash chromatography of the crude product over silica gel (1 × 10 cm), using hexane, gave **18b** (29.5 mg, 74%).

3-Cyclopentylmethylene-2,3-dihydro-5,6-dimethoxy-1*H*-inden-1-ol (20b). The general thermal procedure for radical cyclization was followed, using **20a**[27] (see below for characterization data) (83.5 mg, 0.23 mmol) in PhH (10 mL), stannane **1** (143 mg, 0.33 mmol) and AIBN (2 mg, 0.01 mmol) in PhH (8 mL, plus 2 mL as a rinse), an addition time of 5 h, and an arbitrary reflux time of 5 h after the addition. The general basic workup procedure was followed, using aqueous LiOH (1 M, 2 mL) in THF (2 mL) and a reaction time of 3 h. Flash chromatography of the crude product over silica gel (1 × 15 cm), using 3:7 EtOAc−hexane, gave **20b** (58.8 mg, 90%) as a single isomer of unestablished stereochemistry: FTIR (CH_2Cl_2, cast) 3383 (br), 2949, 1605, 1500 cm^{-1}; ^1H NMR (C_6D_6, 300 MHz) δ 1.25−2.00 (m, 9 H), 2.46−2.56 (m, 1 H), 2.58−2.73 (m, 1 H), 2.96−3.08 (m, 1 H), 3.41 (2 s, each 3 H), 5.05 (dd, J = 3.2, 7.3 Hz, 1 H), 5.82 (dt, J = 2.3, 9.1 Hz, 1 H), 6.80 (s, 1 H), 6.91 (s, 1 H); ^{13}C NMR (C_6D_6, 75.5 MHz) (two signals overlap in this spectrum) δ 25.5 (t′), 33.7 (t′), 40.2 (t′), 40.8 (d′), 55.3 (q′), 73.4 (d′), 102.8 (d′), 107.9 (d′), 123.1 (d′), 133.7 (s′), 137.9 (s′), 139.5 (s′), 150.9 (s′), 151.1 (s′); exact mass *m*/*z* calcd for $C_{17}H_{22}O_3$ 274.15689, found 274.15712.

Data for **20a**: FTIR (CH_2Cl_2, cast) 3513, 2956, 2868, 1959, 1603, 1503.5, 1463, 1439 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.45−1.61 (m, 4 H), 1.64−1.78 (m, 2 H), 1.83−1.95 (m, 2 H), 2.40−2.50 (m, 1 H), 2.52−2.68 (m, 2 H), 2.68−2.79 (m, 1 H), 3.85 (2 s, each 3 H), 5.05 (q, J = 5 Hz, 1 H), 6.95 (s, 1 H), 7.10 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 25.0 (t′), 28.6 (t′), 30.3 (d′), 34.0 (t′), 56.0 (q′), 56.2 (q′), 71.0 (d′), 75.0 (s′), 88.3 (s′), 109.8 (d′), 115.6 (s′), 115.2 (d′), 133.8 (s′), 148.6 (s′), 148.9 (s′); exact mass *m*/*z* calcd for $C_{17}H_{21}{}^{79}BrNaO_3$ 375.05718, found 375.05716.

***cis*-2,2-Bis(1,1-dimethylethyl)hexahydro-6,6-dimethylfuro[3,4-*d*]-1,2-oxasilole (21b).** The general thermal procedure for radical cyclization was followed, using **21a**[28] (42.5 mg, 0.10 mmol) in PhH (3 mL), stannane **1** (65 mg, 0.15 mmol) and AIBN (2 mg, 0.01 mmol) in PhH (6 mL, plus 1 mL as a rinse), an addition time of 7 h, and an arbitrary reflux time of 5 h after the addition. The general basic workup procedure was followed, using aqueous LiOH (1 M, 1 mL) in THF (2 mL) and a reaction time of 1 h. Flash chromatography of the crude product over silica gel (1 × 10 cm), using 1:19 EtOAc−hexane, gave **21b** (20.9 mg, 78%) as a colorless oil: FTIR (CH_2Cl_2, cast) 2931, 2857, 1472, 1057 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.62 (q, J = 2.8, 15.5 Hz, 1 H), 1.00 (s, 9 H), 1.06 (s, 9 H), 1.06−1.10 (m, 1 H), 1.14 (s, 3 H), 1.28 (s, 3 H), 2.90−3.00 (m, 1 H), 3.46 (q, J = 6.6, 9.0 Hz, 1 H), 4.00 (t, J = 8.9 Hz, 1 H),

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4.08 (d, $J = 6.6$ Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 10.1 (s′), 19.7 (s′), 21.2 (t′), 22.4 (q′), 25.6 (q′), 27.5 (q′), 27.9 (t′), 41.9 (d′), 73.1 (t′), 84.2 (s′), 89.1 (d′); exact mass *m*/*z* calcd for $C_{15}H_{30}O_2Si$ 270.20151, found 270.20174.

4-(2-Cyclopenten-1-yl)-1-butyne (22a). (a) [4-(2-Cyclopenten-1-yl)but-1-ynyl]trimethylsilane. *n*-BuLi (2.5 M in hexane, 7.10 mL, 17.7 mmol) was added dropwise over ca. 10 min to a stirred and cooled (−78 °C) solution of ethynyltrimethylsilane (2.45 mL, 17.0 mmol) in THF (100 mL). Stirring at −78 °C was continued for 1.5 h, and neat 3-(2-iodoethyl)-cyclopentene[29] (see below for characterization data) (4.00 g, 18.1 mmol) was added dropwise over ca. 30 min (syringe pump). The cold bath was removed, and stirring was continued overnight. The mixture was quenched with water (100 mL) and extracted with Et_2O. The combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (2.5 × 20 cm), using hexane, gave starting material (2.67 g) and [4-(2-cyclopenten-1-yl)but-1-ynyl]-trimethylsilane (1.02 g, 88% corrected for recovered starting material): FTIR (CH_2Cl_2, cast) 3051, 2956, 2175, 1614, 1450, 1249 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.12 (s, 9 H), 1.35−1.42 (m, 1 H), 1.45−1.53 (m, 1 H), 1.58−1.66 (m, 1 H), 1.99−2.07 (m, 1 H), 2.20−2.36 (m, 4 H), 2.69−2.77 (m, 1 H), 5.63−5.73 (m, 2 H); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 0.3 (q′), 18.4 (t′), 29.5 (t′), 32.0 (t′), 34.9 (t′), 44.9 (d′), 84.3 (s′), 107.6 (s′), 130.7 (d′), 134.3 (d′); exact mass *m*/*z* calcd for $C_{12}H_{20}Si$ 192.13342, found 192.13369.

Data for 3-(2-iodoethyl)cyclopentene: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.33−1.41 (m, 1 H), 1.76−1.85 (m, 1 H), 1.90−1.98 (m, 1 H), 2.01−2.09 (m, 1 H), 2.24−2.36 (m, 2 H), 2.70−2.78 (m, 1 H), 3.13−3.22 (m, 2 H), 5.61−5.65 (m, 1 H), 5.72−5.76 (m, 1 H); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 4.9 (t′), 29.1 (t′), 32.0 (t′), 40.0 (t′), 46.5 (d′), 131.2 (d′), 133.1 (d′).

(b) 4-(2-Cyclopenten-1-yl)-1-butyne (22a). Aqueous NaOH (2 N, 20 mL) was added to a stirred solution of [4-(2-cyclopenten-1-yl)but-1-ynyl]trimethylsilane (1.00 g, 5.2 mmol) in MeOH (30 mL), stirring was continued for 3 h, and the mixture was then extracted with pentane. Evaporation of the solvent at 1 atm (short Vigreux column) and flash chromatography of the residue over silica gel (1 × 15 cm), using pentane, gave **22a**[30] (0.30 g, 49%) as a colorless oil: ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 16.8 (t′), 29.4 (t′), 31.9 (t′), 34.6 (t′), 44.6 (d′), 68.0 (d′), 84.7 (s′), 130.9 (d′), 134.2 (d′).

***cis*-Octahydro-1-methylenepentalene (22b).** The general thermal procedure for radical cyclization was followed, using **22a** (40.0 mg, 0.33 mmol) in PhH (3 mL), stannane **1** (200 mg, 0.46 mmol) and AIBN (7 mg, 0.04 mmol) in PhH (7 mL, plus 2 mL as a rinse), an addition time of 5 h, and an arbitrary reflux time of 3 h after the addition. After evaporation of the solvent, CF_3CO_2H (0.2 mL) and THF (5 mL) were added, and the mixture was stirred at room temperature for 3 h. The general basic workup procedure was then followed, using aqueous LiOH (1 M, 4 mL) and a reaction time of 3 h. Flash chromatography of the crude product over silica gel (1 × 10 cm), using pentane, gave **22b**[31] (28.6 mg, 70%) as a colorless oil.

Dihydro-2,3-furandione 3-Oxime (23b). The general thermal procedure for radical cyclization was followed, using **23a**[32] (51 mg, 0.12 mmol) in PhH (3 mL), stannane **1** (73 mg, 0.17 mmol) and AIBN (2 mg, 0.01 mmol) in PhH (6 mL, plus 2 mL as a rinse), an addition time of 5 h, and an arbitrary reflux time of 10 h after the addition. The general acidic workup procedure was followed, using aqueous TsOH (0.25 M, 1 mL) in THF (2 mL) and a reaction time of 3 h. Flash chromatography of the crude product over silica gel (1 × 10 cm), using 1:1 EtOAc−hexane, gave **23b**[32] (12.2 mg, 88%) as a white solid. After a CD_3OD solution of **23b** had been stored overnight while the ^{13}C NMR spectrum was being measured, a new set of signals appeared, which we arbitrarily attribute to a geometrical isomer. The isomers could not be separated, but by comparison with spectra run on fresh samples, the signals corresponding to each isomer could be identified. Data for the original isomer: ^{1}H NMR (CD_3OD, 400 MHz) δ 3.01 (t, $J = 7.3$ Hz, 2 H), 4.48 (t, $J = 7.3$ Hz, 2 H); ^{13}C NMR (CD_3OD, 100.6 MHz) δ 24.9 (t′), 67.0 (t′), 147.8 (s′), 168.7 (s′). Data for the new isomer: ^{1}H NMR (CD_3OD, 400 MHz) δ 2.80 (t, $J = 7.3$ Hz, 2 H), 3.65 (t, $J = 7.3$ Hz, 2 H); ^{13}C NMR (CD_3OD, 100.6 MHz) δ 29.4 (t′), 59.2 (t′), 150.8 (s′), 166.2 (s′).

2-Oxabicyclo[3.3.1]nonan-3-one (24b). The general thermal procedure for radical cyclization was followed, using **24a**[33] (90 mg, 0.31 mmol) in PhH (10 mL), stannane **1** (185 mg, 0.43 mmol) and AIBN (7 mg, 0.04 mmol) in PhH (8 mL, plus 2 mL as a rinse), an addition time of 5 h, and an arbitrary reflux time of 3 h after the addition. The general acidic workup procedure was followed, using aqueous TsOH (0.25 M, 3 mL) in THF (3 mL) and a reaction time of 1.5 h. Flash chromatography of the crude product over silica gel (1 × 10 cm), using 3:7 EtOAc−hexane, gave **24b**[33,34] (392 mg, 91%) as a white solid.

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Supporting Information Available: NMR spectra of **1**, **8**, **10a**, **20a**, **20b**, **21b**, 3-(2-iodoethyl)cyclopentene, and [4-(2-cyclopenten-1-yl)but-1-ynyl]trimethylsilane and ^{1}H NMR spectra that monitor the purification process for the experiments of entries 1, 2, and 6 of Table 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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