The study of intramolecular tandem radical cyclizations of acylsilanes with radicalphiles attached on silicon

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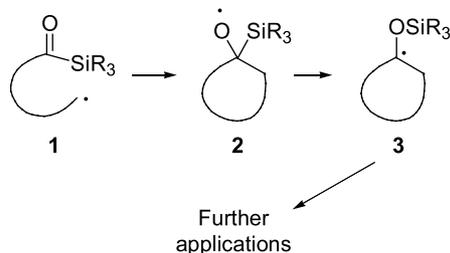
Abstract—Radical cyclizations of acylsilanes with radicalphilic pendant introduced on silicon proceeded in a tandem fashion to give spiro products containing a cyclic silyl ether skeleton. Because the alkoxysilyl group can be replaced with a hydroxy group through oxidation, the spiro silyl ethers can be converted into diols. In the case with a radical intermediate carrying 2-oxa-3-sila-6-heptenyl skeleton, products derived from 1,7-*endo* cyclization were obtained in good yields.
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1. Introduction

Radical reactions are now widely used as important tools to construct carbon–carbon bonds.[1] Among various radical reactions, radical additions to carbonyl generate alkoxy radicals that are prone to undergo β-scission to regenerate the carbonyl functionality.[2] Yet this seemingly deleterious property can be manipulated to yield ring-expansion[3,4] and acylation[4–7] products. The cyclized alkoxy radicals can also be trapped intermolecularly or intramolecularly by hydrogen,[8] phosphorous,[9] boron[10] and tin.[11,12]

Several years ago, we initiated a study of intramolecular radical cyclizations of acylsilanes (Scheme 1).[13] In this type of cyclizations, radical **1** adds intramolecularly to the carbonyl of the acylsilane functionality[14] to give a β-silyl substituted alkoxy radical **2**. A facile radical-Brook
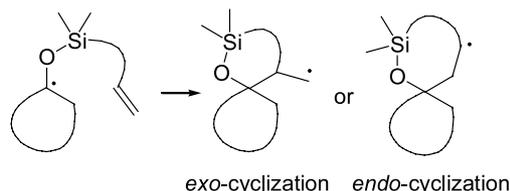
Scheme 1.

rearrangement[15,16] occurs to afford an α-silyloxy radical **3**. In this fashion, the radical carbonyl cyclization reaction can also be driven irreversibly towards ring formation. Depending on the reaction conditions[13c] and structural features[13b,d,f,j] the intermediate α-silyloxy radical **3** can be converted to different products. One possibility (Scheme 2) involves the design of a radicalphile tethered to the silicon atom in such a way that the α-silyloxy radical can undergo further cyclization.[13f] The alkoxy silane moiety in the resulting silacycles can be considered as a hydroxy group equivalent.[17] Through oxidative hydrolysis, the silacycles can be opened to give diols. Now we wish to report the full investigation of this approach.
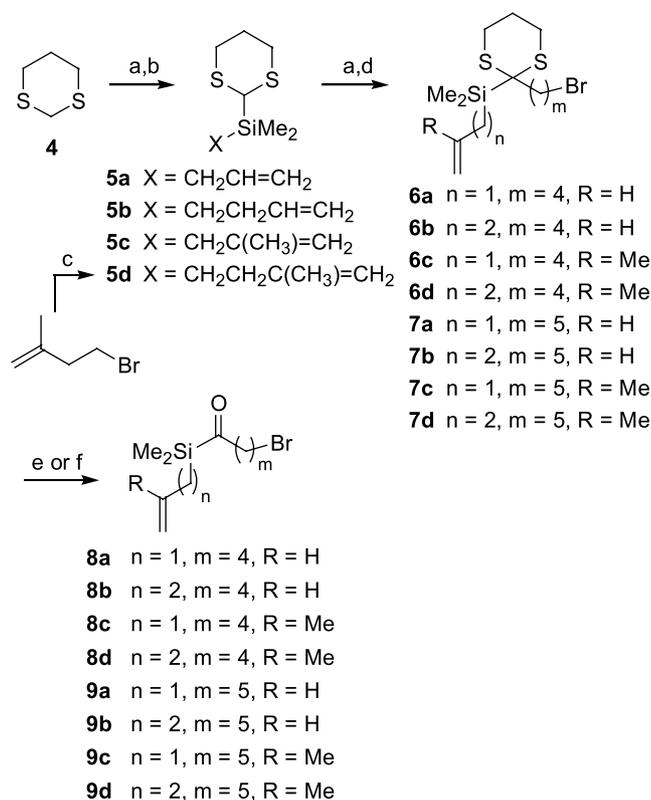
Scheme 2.

2. Results and discussion

As shown in Scheme 3, we choose to synthesize acylsilanes **8** and **9**. These acylsilanes contain allyl and homoallyl group attached on silicon. The strategy developed by Brook[18] and Corey[19] was used in the synthesis. We first prepared 2-silyl-1,3-dithianes **5a** (83%), **5b** (64%) and **5c** (68%) from the silylation of 1,3-dithiane (**4**) with the corresponding chlorosilanes. However when we used the same method for the preparation of dithiane **5d**, small amount of double

bond positional isomerization product was always present and difficult to remove. This was probably caused by the presence of small amount of hydrochloric acid in chloro-dimethyl(3-methyl-3-butenyl)silane. We therefore switched to use an in situ generation method for the preparation of the chlorosilane under a slightly basic condition.[20] The Grignard reagent prepared from 4-bromo-2-methylbutene in THF was treated with chlorodimethyl(dimethylamino)-silane followed by the addition of acetyl chloride. To the chlorodimethyl(3-methyl-3-butenyl)silane solution thus prepared was added the anion generated from 1,3-dithiane to afford pure 2-silyldithiane **5d** in 38% without the formation of its double bond positional isomer.


Scheme 3. Reagents and conditions: (a) BuLi, THF, 0 °C; (b) (CH$_2$=CHCH$_2$)Me$_2$SiCl for **5a** (83%), (CH$_2$=CHCH$_2$CH$_2$)Me$_2$SiCl for **5b** (64%), and (CH$_2$=CMeCH$_2$)Me$_2$SiCl for **5c** (68%); (c) (i) Mg, THF, (ii) Me$_2$NSiMe$_2$Cl, (iii) AcCl, (iv) **4**, BuLi (**5d**, 39%); (d) Br(CH$_2$)$_m$Br, −20 °C, 1 h, for **6c** (52%), **6d** (51%), **7c** (66%), and **7d** (85%); (e) CAN (4 equiv), H$_2$O/MeOH/CH$_2$Cl$_2$, −20 °C, for **8a** (33% from **5a**); CAN (3 equiv), H$_2$O/CH$_3$CN, NaHCO$_3$, 0 °C, 10 min, for **8c** (37%), **8d** (80%), **9c** (38%), and **9d** (64%); (f) (CF$_3$COO)$_2$IPh (1.7 equiv), NaHCO$_3$, CH$_3$CN/H$_2$O, −20 °C, for **8b** (36% from **5b**), **9a** (52% from **5a**), and **9b** (43% from **5b**).

The 2-silyl-1,3-dithianes were then alkylated with 1,4-dibromobutane or 1,5-dibromopentane to afford bromides **6** and **7**. Due to the presence of nucleophilic sulfur atoms in the molecule, the bromides are not stable. Although these bromides can be isolated and purified, it is best to hydrolyze the dithiane moiety once the crude bromides are obtained. In the case of the hydrolysis of **6a**, **6c**, **6d**, **7c**, and **7d**, ceric ammonium nitrate (CAN)[21] in wet methanol or acetonitrile was used as the reagent to give acylsilane **8a**, **8c**, **8d**, **9c**, and **9d**. Iodobenzene bistrifluoroacetate[22] was used in the hydrolysis of **6b**, **7a**, and **7b** to give **8b**, **9a**, and **9b**,

respectively. The yields for the preparation of acylsilanes **8** are lower. This probably reflects the lower stability of the corresponding bromides **6** because in these compounds intramolecular attack of sulfur at the bromo-substituted carbon goes through a favored six-membered ring transition state. In contrast, the homologous bromides **7** contain one more methylene unit and the intramolecular nucleophilic attack by sulfur is more difficult.

The radical cyclization of acylsilane **8a** (Scheme 4) was performed by slow addition (1 h) of a benzene solution of tributyltin hydride (1.2 equiv) and AIBN (0.05 equiv) to a solution of **8a** in refluxing benzene. The concentration with respect to **8a** was 0.05 M. Although there may be four possible products **10–13**, acylsilane **10**, derived from hydrogen abstraction of the initial radical **14**, was not observed. This is expected, because radical 1,5-cyclizations of acylsilanes are very fast processes, and straight reduction products are generally not observed.[13h,i] Cyclopentyl ether **11** derived from hydrogen abstraction of α-silyloxy radical **15** was observed in 8% by GC analysis. For the purpose of GC comparison, an authentic sample of ether **11** was prepared from the silylation of cyclopentyl alcohol with allyldimethylsilyl chloride. Radical intermediate **15** can undergo *endo-* and *exo-*cyclization to give spiro silyl ethers **12** and **13**, respectively. However, due to the volatility of these silyl ethers, we were only able to isolate the major product **12** in 46% yield. We believe some portion of **12** was lost during concentration. As mentioned earlier, the C–Si bond of the alkoxysilyl group can be oxidatively cleaved to result in the replacement of the silyl group with a hydroxy group.[17] Therefore, we decided to treat the crude cyclization product mixture directly with hydrogen peroxide and potassium hydrogen carbonate in a mixture of methanol
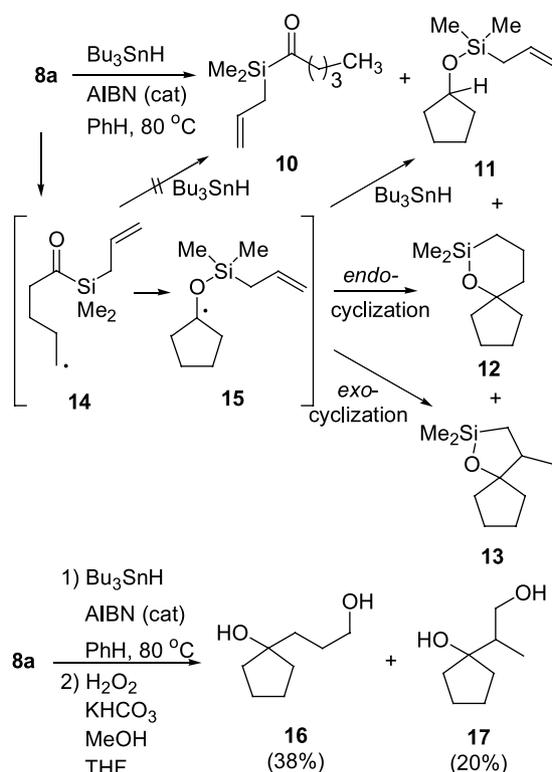
Scheme 4.

and THF.[23] In this way, we isolated 38% of diol **16** and 20% of diol **17**. Since diols **16** and **17** must be derived from silyl ethers **12** and **13**, respectively, this result showed that the *endo*-cyclization mode is the preferred process for the cyclization of α-silyloxy radical **15**. The ratio of the yields of the two diols, **16/17**=1.9/1, then reflects the *endo/exo* cyclization rate ratio of radical **15**.

In the cyclization of 5-hexenyl radical it is well-known that 5-*exo* cyclization is preferred over 6-*endo* cyclization.[1] In contrast, it was found that the replacement of C-3 of 5-hexenyl radical with a silicon atom directed the cyclization to 6-*endo* cyclization almost exclusively.[24] This preference is actually derived from the diminished 5-*endo* cyclization rate of the β-dimethylsilyl substituted radical.[24a] It was proposed by Wilt et al.[24a] that this phenomenon was due to the longer Si–C bond and the preferred ground state conformation making the radical more difficult to approach the internal carbon of the olefin. Our cyclization belongs to a 2-oxa-3-sila-5-hexenyl radical system that is rarely found in the literature. The cyclization results of acylsilane **8a** indicate that the presence of the silicon atom in this system also affects the mode of ring closure in favor of 6-*endo* cyclization albeit in a lower *endo/exo* ratio comparing with the 3-sila-5-hexenyl radical system. Although there is no adequate information in the literature to estimate the effect of the conformation of the silyloxy substituted radical, it can be speculated that the shorter C–O and Si–O bonds have important contribution influencing the *endo/exo* cyclization ratio of 2-oxa-3-sila-5-hexenyl radical.

Similarly, the reaction of acylsilane **9a** (Scheme 5) with tributyltin hydride at a concentration of 0.05 M gave a mixture of straight reduction product **18**, monocyclic product **19**, and two tandem cyclization products **20** and **21**. Direct treatment of the crude cyclization mixture under the oxidation conditions stated above afforded diols **22** and

23 in 55 and 25% yields, respectively. Gas chromatographic analysis of the crude cyclization mixture showed the straight reduction product **18** was present in about 7%, and the monocyclic product **19** was present in about 5%. For the purpose of comparison, authentic sample of **18** was isolated in 51% yield by performing the cyclization reaction at a more concentrated condition of 0.5 M. The silyl ether **19** was prepared from the reaction of cyclohexanol with allyldimethylsilyl chloride.

For the cyclization of acylsilane **9a**, the ratio of *endo/exo* cyclizations of the intermediate α-silyloxy substituted radical extrapolated from the ratio of diols **22/23** is 2.2/1. This *endo/exo* cyclization ratio is about the same as in the case of the cyclization of acylsilane **8a**. Therefore, the regioselectivity of the second ring formation is not strongly influenced by the pre-existing five- or six-membered ring. In the cyclization of **9a**, more straight reduction product was obtained. This reflects the slower 1,6-cyclization rate for acylsilanes as observed previously.[13i]

With a homoallyl group attached to the silicon atom, the two-step radical cyclization–oxidation sequences performed on acylsilanes **8b** and **9b** (Scheme 6) gave diols **24** (67%) and **26** (78%), respectively, as the major products. Small amount of diol **25** (3%) was isolated for the reaction of acylsilane **8b**. For the homologous acylsilane **9b**, diol **27** was not detected. These results indicate that the 2-oxa-3-sila-6-heptenyl radical intermediates **28** undergo 1,7-*endo* cyclization in preference. In the case of acylsilane **9b**, GC analysis of the crude radical cyclization product indicated the presence of 10% of straight reduction product and 12% of monocyclic silyl ether. Since the amount of monocyclic product is not much different from those obtained in the case of **8a** and **9a**, the 1,7-*endo* cyclization appears to be quite efficient. Previously, a similar 2,4-dioxa-3-sila-6-heptenyl radical system has also been reported by Myers, Gin and Rogers to give 1,7-*endo* cyclization predominantly.[25]

We also studied the cyclization of acylsilane **8c** (Scheme 6) having 2-methylallyl substituent on silicon. The methyl group attached on the internal carbon of the olefin directed the radical cyclization of **8c** to afford the spiro silyl ether **30** in 74% yield as the only product. We did not detect the presence of monocyclic ether **31** or acylsilane **32**. Apparently the methyl group on the allyl moiety retarded the attack of the radical appreciably such that the 5-*exo* cyclization mode was completely suppressed.[26] In addition, the 6-*endo* cyclization led to the formation of a more stabilized tertiary radical. This factor may contribute an acceleration effect that makes this tandem cyclization so efficient.

In comparison, the homologous acylsilane **9c** under our standard radical cyclization condition gave 23% of the tandem cyclization product **33**. Again, 6-*endo* cyclization of the second cyclization step was the predominate process. Analysis of the crude cyclization mixture via ^{1}H NMR revealed the presence of monocyclic product **34** and straight reduction product **35**. The ratio of **33/34/35** determined by NMR integration was 87/8/5. The low yield of the spiro product **33** was due to the volatility and the extensive chromatographic processes for its purification. When the
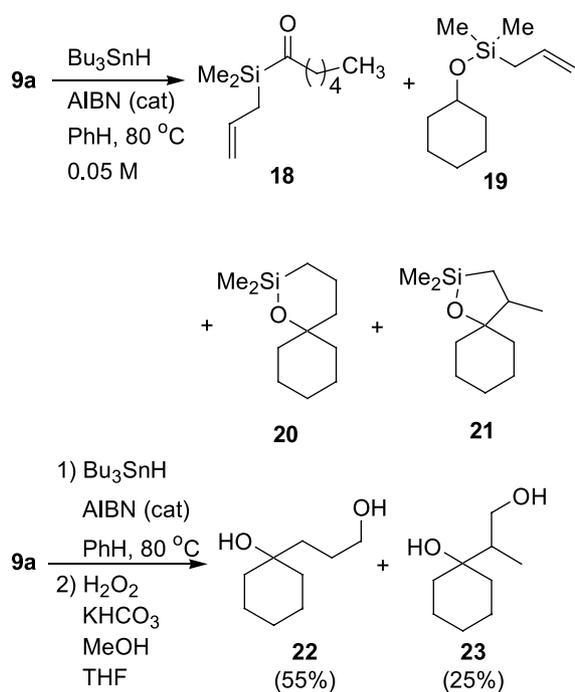
Scheme 5.
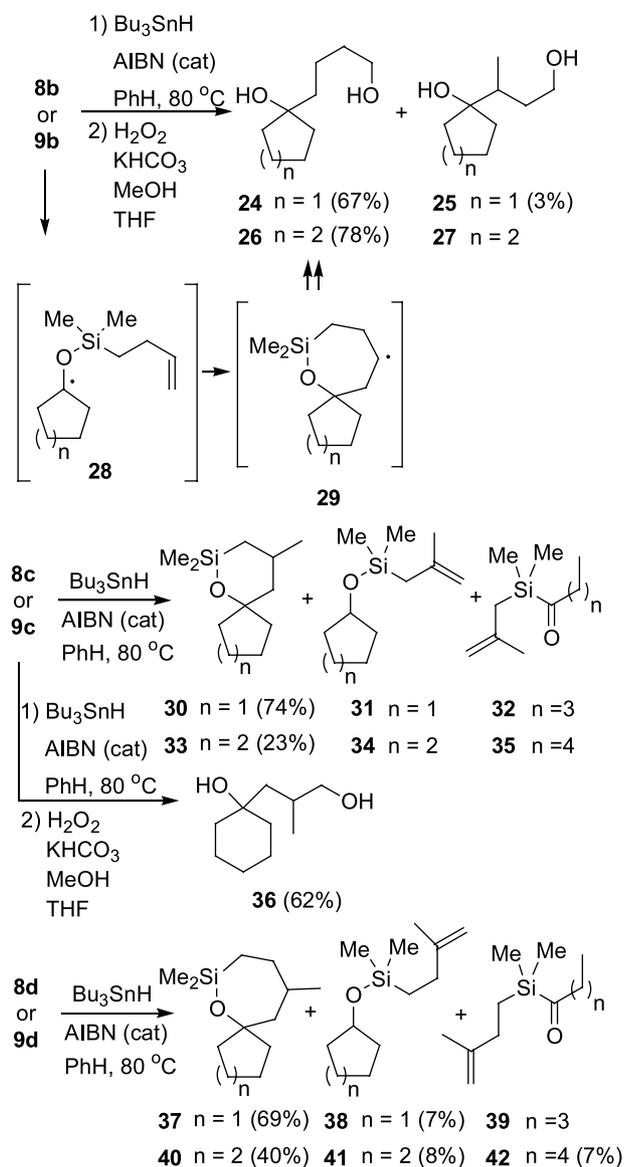
Scheme 6.

crude product of the cyclization of **9c** was directly oxidized under the Tamao oxidation condition,[23] we were able to obtain the diol **36** in 62% yield. The formation of small amount of monocyclic silyl ether **34** in this system seems to indicate that the cyclization rate of the intermediate cyclohexyl radical is slightly slower than the corresponding cyclopentyl radical as in the case of acylsilane **8c**. We suspect that the allylic methyl group may exhibit repulsive interaction with the C(3)-methylene unit of the cyclohexyl group in the transition state (Fig. 1) of the second cyclization and thus slows down the rate.
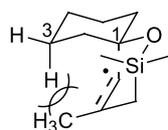

Figure 1. The proposed 1,6-*endo* cyclization transition state of the (2-methylallyl)silyloxy substituted cyclohexyl radical.

With a 3-methyl-3-butenyl group attached on silicon, the cyclizations of acylsilanes **8d** and **9d** gave exclusively 7-*endo* cyclization product for the second cyclization step. In the case of acylsilane **8d**, spiro silyl ether **37** was isolated in 69% yield in addition to 7% of monocyclic product **38**. Analysis of the crude product by ^{1}H NMR showed that straight reduction product **39** was not formed. The ratio of spiro silyl ether **37** and monocyclic silyl ether **38** in the crude product was 9/1 (**37**/**38**). The reaction of acylsilane **9d** with tributyltin hydride gave a 74/10/9 crude mixture of spiro silyl ether **40**, monocyclic silyl ether **41** and straight reduction product **42**, respectively. The spiro silyl ether **40** was isolated in 40% through silica gel column chromatography in addition to 6% of monocyclic product **41** and 7% of straight reduction product **42**. The presence of **42** reflected the slower rate of the initial 1,6-cyclization as described above. The lower ratio of spiro product **40** and monocyclic product **41** (74/10 by NMR) also showed that the pre-existing six-membered ring might influence the second 7-*endo* cyclization.

In summary, we have demonstrated that by introducing radicalphilic pendant on silicon, the radical cyclizations of acylsilanes can proceed in a tandem fashion. Because the alkoxysilyl group can be replaced with a hydroxy group through oxidation, the final cyclization products can be converted to give diols. In the case with a radical intermediate carrying 2-oxa-3-sila-6-heptenyl skeleton, products derived from 1,7-*endo* cyclization were obtained in good yields.

3. Experimental

3.1. General

Melting points are uncorrected. ^{1}H NMR spectra were recorded at 200, 300 or 400 MHz; ^{13}C NMR spectra were recorded at 50, 75 or 100 MHz. Tetramethysilane ($\delta = 0$ ppm) or $CHCl_3$ ($\delta = 7.24$ ppm) were used as internal standards and $CDCl_3$ was used as the solvent. Benzene and THF were distilled from sodium benzophenone ketyl under N_2. Diisopropylamine and acetonitrile were dried with CaH_2 and distilled. The benzene used for cyclization reactions was deoxygenated by passing a gentle stream of argon through for 0.5 h before use. All reactions were performed under a blanket of N_2 or Ar. Lobar LiChroprep Si 60 (40–63 μm) pre-packed columns purchased from Merck were used for medium pressure liquid chromatography (MPLC). Gas chromatography was performed on a Shimadzu GC-8A apparatus with TCD using a 3.3 mm × 2 m column of 10% SE-30 on Chromosorb W (AW-DMCS), 80–100 mesh, and hydrogen as carrier gas.

3.1.1. 2-(Allyldimethylsilyl)-1,3-dithiane (5a). To a solution of 0.800 g (6.67 mmol) of 1,3-dithiane in 4.7 mL of dry THF cooled at 0 °C was added dropwise over 20 min a 1.64 N solution of butyllithium in hexane (5.29 mL, 8.67 mmol). The resulting solution was stirred at the same temperature for 40 min and then added over 30 min to a solution of 1.08 mL (7.38 mmol) of allylchlorodimethylsilane in 4.0 mL of dry THF cooled at 0 °C. The reaction mixture was stirred at the same temperature for 1 h and then

partitioned between 100 mL of ether and 50 mL of water. The organic layer was washed with brine (50 mL), dried (MgSO$_4$), and concentrated in vacuo. The residue was chromatographed with MPLC using Lobar size B column (eluted with hexane/ethyl acetate, 99/1) to give 1.20 g (83%) of **5a** as a pale yellow liquid: IR (neat) 1625 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 0.11 (s, 6H), 1.65 (d, $J=$ 8 Hz, 2H), 1.88–2.15 (m, 2H), 2.68 (dt, $J=14$, 4 Hz, 2H), 2.84 (td, $J=14$, 4 Hz, 2H), 3.71 (s, 1H), 4.85 (br d, $J=$ 10 Hz, 1H), 4.90 (br d, $J=18$ Hz, 1H), 5.76 (ddt, $J=18$, 10, 8 Hz, 1H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ -5.4, 21.0, 26.1, 31.0, 33.0, 114.0, 133.7; HRMS calcd for C$_9$H$_{18}$S$_2$Si m/z 218.0619, found 218.0621.

3.1.2. 2-((3-Buten-1-yl)dimethylsilyl)-1,3-dithiane (5b).

According to the procedure for the preparation of **5a**, 1,3-dithiane (0.48 g, 4.0 mmol) reacted with 0.65 mL (4.0 mmol) of (3-buten-1-yl)chlorodimethylsilane[27] to afford 595 mg (64%) of **5b** as a pale yellow liquid: IR (neat) 1633 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 0.12 (s, 6H), 0.70–0.82 (m, 2H), 1.88–2.15 (m, 4H), 2.68 (dt, $J=14$, 4 Hz, 2H), 2.85 (td, $J=14$, 4 Hz, 2H), 3.70 (s, 1H), 4.87 (br d, $J=11$ Hz, 1H), 4.98 (br d, $J=17$ Hz, 1H), 5.84 (ddt, $J=$ 17, 11, 6 Hz, 1H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ -4.8, 12.5, 26.2, 27.6, 31.1, 33.5, 113.0, 141.0; HRMS calcd for C$_{10}$H$_{20}$S$_2$Si m/z 232.0775, found 232.0785.

3.1.3. 2-[Dimethyl(2-methyl-2-propenyl)silyl]-1,3-dithiane (5c).

According to the procedure for the preparation of **5a**, 1,3-dithiane (0.217 g, 1.81 mmol) reacted with 0.35 mL (2.0 mmol) of chlorodimethyl(2-methyl-2-propen-1-yl)silane[28] to afford 275 mg (65%) of **5c** as a colorless liquid: IR (neat) 1639 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.14 (s, 6H, SiCH$_3$), 1.70 (s, 2H, SiCH$_2$), 1.72 (s, 3H, =CCH$_3$), 1.93–2.16 (m, 2H, SCH$_2$CH_2CH$_2$S), 2.71 (dt, $J=$ 14, 4 Hz, 2H, SCH$_{2(eq)}$), 2.87 (td, $J=14$, 2.4 Hz, 2H, SCH$_{2(ax)}$), 3.73 (s, 1H, SCHS), 4.55 (br s, 1H, =CH$_2$), 4.63 (br s, 1H, =CH$_2$); ^{13}C NMR (CDCl$_3$, 100 MHz) δ -4.5 (CH$_3$), 24.8 (CH$_2$), 25.4 (CH$_3$), 26.3 (CH$_2$), 31.2 (CH$_2$), 33.6 (CH), 109.4 (CH$_2$), 142.3 (C); HRMS (FAB) calcd for C$_{10}$H$_{21}$S$_2$Si (M+H)$^+$ m/z 233.0854, found 233.0836.

3.1.4. 2-[Dimethyl(3-methyl-3-butenyl)silyl]-1,3-dithiane (5d).

A mixture of 0.358 g (14.9 mmol) of magnesium turnings and a few crystals of iodine in 1 mL of dry THF was stirred under argon until the iodine color disappeared. A solution of 1.38 mL (11.1 mmol) of 4-bromo-2-methyl-1-butene in 10 mL of dry THF was added to the mixture over a period of 25 min and stirred for another 15 min. The Grignard reagent prepared above was added dropwise over a period of 15 min to a cooled (0 °C) solution of 1.2 mL (6.93 mmol) of chlorodimethyl(dimethylamino)silane in 8 mL of dry THF. The reaction mixture was stirred for another 10 min at 0 °C followed by the addition of a solution of 0.50 mL (6.9 mmol) of acetyl chloride in 7 mL of dry THF over a period of 20 min at the same temperature. The resulting mixture was stirred for another 2.5 h at 0 °C to furnish a solution of dimethyl(3-methyl-3-buten-1-yl)silyl chloride. To another solution of 1.42 g (11.9 mmol) of 1,3-dithiane in 13 mL of dry THF cooled in an ice-water bath was added dropwise over 20 min a 1.5 N solution of butyllithium in hexane (9.40 mL, 14.1 mmol). This anion solution was then added to the silyl chloride solution

prepared above at 0 °C over a period of 20 min, and the reaction mixture was stirred for 1.5 h at room temperature. The resulting mixture was poured into 20 mL of sat. ammonium chloride solution and extracted with 100 mL of ether. The organic layer was washed with water (100 mL × 2), brine (100 mL), dried (MgSO$_4$) and concentrated in vacuo to give 2.31 g of a yellow residue. The residue was chromatographed with MPLC using Lobar size B column (eluted with hexane/ethyl acetate, 98/2) to give 0.659 g (39%) of **5d** as a colorless liquid: IR (neat) 1652 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.14 (s, 6H, SiCH$_3$), 0.80–0.85 (m, 2H, SiCH$_2$), 1.72 (s, 3H, =CCH$_3$), 1.95–2.14 (m, 4H, SCH$_2$CH_2CH$_2$S, and =CCH$_2$), 2.71 (dt, $J=14$, 4 Hz, 2H, SCH$_{2(eq)}$), 2.86 (td, $J=14$, 2.8 Hz, 2H, SCH$_{2(ax)}$), 3.73 (s, 1H, SCHS), 4.66 (br s, 1H, =CH$_2$), 4.70 (br s, 1H, =CH$_2$); ^{13}C NMR (CDCl$_3$, 100 MHz) δ -4.8 (CH$_3$), 11.6 (CH$_2$), 22.3 (CH$_3$), 26.3 (CH$_2$), 31.2 (CH$_2$), 31.5 (CH$_2$), 33.6 (CH), 108.6 (CH$_2$), 147.7 (C); HRMS (FAB) calcd for C$_{11}$H$_{22}$S$_2$Si m/z 246.0932, found 246.0928.

3.1.5. 5-Bromo-1-(allyldimethylsilyl)-1-pentanone (8a).

To a solution of 300 mg (1.38 mmol) of **5a** in 4.0 mL of dry THF cooled at 0 °C was added dropwise over 10 min a 1.46 N solution of butyllithium in hexane (1.23 mL, 1.79 mmol). The resulting solution was stirred at the same temperature for another 40 min and then added dropwise over 40 min to a solution of 0.33 mL (2.8 mmol) of 1,4-dibromobutane in 4.0 mL of dry THF cooled at -20 °C. The reaction mixture was stirred at -20 °C for 1 h and then partitioned between ether (60 mL) and water (30 mL). The organic layer was washed with brine (30 mL), dried (MgSO$_4$), and concentrated in vacuo. The residue was dissolved in a mixture of 2 mL of methanol and 2 mL of dichloromethane. To the resulting solution cooled at -20 °C was added over 7 min a solution of 3.10 g (5.66 mmol) of CAN in 6 mL of methanol and 0.31 mL of water. The resulting mixture was stirred at the same temperature for 5 min and then diluted with ether. The resulting mixture was filtered, and the filtrate was partitioned between 80 mL of ether and 35 mL of water. The organic phase was washed with brine (35 mL), dried (MgSO$_4$), and concentrated in vacuo to give 658 mg of a residual oil. The oil was chromatographed with MPLC over a Lobar size B column (eluted with hexane/ethyl acetate, 98/2) to give 120 mg (33%) of **8a** as a pale yellow liquid: IR (neat) 1637 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 0.19 (s, 6H), 1.53–1.72 (m, 4H), 1.72–1.87 (m, 2H), 2.60 (t, $J=7$ Hz, 2H), 3.36 (t, $J=6.5$ Hz, 2H), 4.81–4.93 (m, 2H), 5.72 (ddt, $J=18$, 10, 8 Hz, 1H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ -5.2, 20.5, 21.1, 32.2, 33.4, 48.0, 114.5, 133.0, 246.2; HRMS calcd for C$_{10}$H$_{19}$^{81}BrOSi m/z 264.0368, found 264.0357.

3.2. General procedure for the preparation of acylsilanes 8b, 9a and 9b using iodobenzenebistrifluoroacetate for hydrolysis: 5-bromo-1-((3-buten-1-yl)dimethylsilyl)-1-pentanone (8b)

According to the procedure for the synthesis of **8a**, 0.70 g of **5b** (3.0 mmol) was alkylated with 0.72 mL (6.0 mmol) of 1,4-dibromobutane. The crude alkylation product was mixed with 1.76 g of sodium bicarbonate, 10 mL of acetonitrile, and 3 mL of water. To the resulting mixture

cooled at $-20\,^\circ\text{C}$ was added slowly a solution of 2.2 g (5.1 mmol) of iodobenzenebistrifluoroacetate in 10 mL of acetonitrile. The reaction mixture was stirred at the same temperature for 5 min and then partitioned between 100 mL of ether and 50 mL of water. The organic layer was washed with brine (50 mL), dried (MgSO_4), and concentrated in vacuo to give 1.7 g of a residual oil. The oil was chromatographed with MPLC over a Lobar size B column (eluted with hexane/ethyl acetate, 97/3) to give 298 mg (36%) of **8b** as a pale yellow oil: IR (neat) 1642 cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 0.16 (s, 6H), 0.70–0.85 (m, 2H), 1.51–1.87 (m, 4H), 1.93–2.13 (m, 2H), 2.59 (t, $J=7$ Hz, 2H), 3.34 (t, $J=7$ Hz, 2H), 4.70–5.03 (m, 2H), 5.79 (ddt, $J=17, 11, 6$ Hz, 1H); ^{13}C NMR (CDCl$_3$, 50 MHz) δ -4.8, 12.5, 20.6, 27.5, 32.2, 33.3, 47.6, 113.5, 140.4, 246.9; HRMS calcd for C$_{11}$H$_{21}^{81}$BrOSi m/z 278.0524, found 278.0524.

3.2.1. 6-Bromo-1-(allyldimethylsilyl)-1-hexanone (9a).
A pale yellow oil: IR (neat) 1635 cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 0.18 (s, 6H), 1.25–1.73 (m overlapped with d, $J=8$ Hz, 6H), 1.82 (quintet, $J=7$ Hz, 2H), 2.58 (t, $J=7$ Hz, 2H), 3.37 (t, $J=7$ Hz, 2H), 4.80–4.93 (m, 2H), 5.70 (ddt, $J=18, 10, 8$ Hz, 1H); ^{13}C NMR (CDCl$_3$, 50 MHz) δ -5.2, 21.0, 21.2, 27.8, 32.6, 33.5, 48.8, 114.4, 133.1, 246.6; HRMS calcd for C$_{11}$H$_{21}^{81}$BrSi m/z 278.0525, found 278.0512.

3.2.2. 6-Bromo-1-((3-buten-1-yl)dimethylsilyl)-1-hexanone (9b).
A pale yellow oil: IR (neat) 1642 cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 0.16 (s, 6H), 0.70–0.82 (m, 2H), 1.27–1.59 (m, 4H), 1.81 (quintet, $J=7$ Hz, 2H), 1.97–2.12 (m, 2H), 2.57 (t, $J=7$ Hz, 2H), 3.36 (t, $J=7$ Hz, 2H), 4.80–5.03 (m, 2H), 5.79 (ddt, $J=16, 10, 6$ Hz, 1H); ^{13}C NMR (CDCl$_3$, 50 MHz) δ -4.7, 12.6, 21.0, 27.5, 27.8, 32.6, 33.5, 48.5, 113.5, 140.5, 247.4; HRMS calcd for C$_{12}$H$_{23}^{81}$BrSi m/z 292.0681, found 292.0691.

3.2.3. 2-(4-Bromobutyl)-2-[dimethyl(2-methyl-2-propenyl)silyl]-1,3-dithiane (6c).
According to the procedure for the synthesis of **8a**, 3.0 g (13 mmol) of **5c** was alkylated with 3.85 mL (32.3 mmol) of 1,4-dibromobutane to give 2.5 g (52%) of **6c** as a pale yellow liquid: IR (neat) 1639 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.20 (s, 6H, SiCH$_3$), 1.60–1.69 (m, 2H), 1.71 (s, 3H, =CCH$_3$), 1.79 (s, 2H, SiCH$_2$), 1.81–1.94 (m, 3H), 1.99–2.08 (m, 1H), 2.16–2.25 (m, 2H), 2.44 (dt, $J=14, 3.6$ Hz, 2H, SCH$_{2(eq)}$), 3.00 (td, $J=14, 2.8$ Hz, 2H, SCH$_{2(ax)}$), 3.44 (t, $J=6.8$ Hz, 2H, CH$_2$Br), 4.53 (br s, 1H, =CH$_2$), 4.63 (br s, 1H, =CH$_2$); ^{13}C NMR (CDCl$_3$, 100 MHz) δ -4.0 (CH$_3$), 23.6 (CH$_2$), 24.6 (CH$_2$), 25.1 (CH$_2$), 25.5 (CH$_3$), 26.4 (CH$_2$), 33.1 (CH$_2$), 33.6 (CH$_2$), 38.7 (C), 109.6 (CH$_2$), 142.6 (C); HRMS (FAB) calcd for C$_{14}$H$_{27}^{79}$BrS$_2$Si m/z 366.0507, found 366.0500.

3.2.4. 5-Bromo-1-[dimethyl(2-methyl-2-propenyl)silyl]-pentan-1-one (8c).
To a vigorously stirred cold ($0\,^\circ\text{C}$) mixture of 0.392 g (1.07 mmol) of **6c** and 0.553 g (6.59 mmol) of sodium bicarbonate in 10 mL of acetonitrile and 1 mL of water was added 1.47 g (2.69 mmol) of ceric ammonium nitrate in one portion. The resulting mixture was stirred for another 3 min at the same temperature and then quickly filtered over Celite. The filtrate was partitioned between 100 mL of ethyl acetate and 100 mL of water. The

organic layer was dried (MgSO_4) and concentrated in vacuo to give 0.428 g of a residual oil. The oil was chromatographed with MPLC over a Lobar size B column (eluted with hexane/ethyl acetate, 98/2) to give 109 mg (37%) of **8c** as a pale yellow oil: IR (neat) 1645 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.18 (s, 6H, SiCH$_3$), 1.60–1.72 (m overlapped with two s at 1.67 and 1.70, 7H, =CCH$_3$, SiCH$_2$ and others), 1.76–1.85 (m, 2H), 2.62 (t, $J=7$ Hz, 2H, COCH$_2$), 3.37 (t, $J=6.8$ Hz, 2H, CH$_2$Br), 4.50 (br s, 1H, =CH$_2$), 4.62 (br s, 1H, =CH$_2$); ^{13}C NMR (CDCl$_3$, 100 MHz) δ -0.92 (CH$_3$), 20.8 (CH$_2$), 24.3 (CH$_3$), 32.3 (CH$_2$), 33.5 (CH$_2$), 46.7 (CH$_2$), 110.3 (CH$_2$), 142.2 (C), 244.5 (C); MS (rel intensity) m/z 277 (M$^+$, 2), 263 (6), 211 (11), 157 (24), 139 (38), 113 (90), 85 (40), 75 (100), 59 (92); HRMS calcd for C$_{11}$H$_{22}^{81}$BrOSi (M+H)$^+$ m/z 279.0597, found 279.0602.

3.2.5. 2-(4-Bromobutyl)-2-[dimethyl(3-methyl-3-butenyl)silyl]-1,3-dithiane (6d).
According to the procedure for the synthesis of **8a**, 1.56 g (6.34 mmol) of **5d** was alkylated with 5.00 mL (37.3 mmol) of 1,4-dibromobutane to give 1.23 g (51%) of **6d** as a pale yellow liquid: IR (neat) 1651 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.19 (s, 6H, SiCH$_3$), 0.84–0.92 (m, 2H, SiCH$_2$), 1.60–1.73 (m, 2H), 1.73 (s, 3H, =CCH$_3$), 1.85–1.96 (m, 3H), 2.02–2.08 (m, 3H), 2.17–2.24 (m, 2H, =CCH$_2$), 2.43 (dt, $J=14, 3.6$ Hz, 2H, SCH$_{2(eq)}$), 3.00 (td, $J=14, 2.8$ Hz, 2H, SCH$_{2(ax)}$), 3.44 (t, $J=6.4$ Hz, 2H, CH$_2$Br), 4.66 (br s, 1H, =CH$_2$), 4.70 (br s, 1H, =CH$_2$); ^{13}C NMR (CDCl$_3$, 100 MHz) δ -4.2 (CH$_3$), 11.8 (CH$_2$), 22.4 (CH$_3$), 23.6 (CH$_2$), 25.2 (CH$_2$), 26.4 (CH$_2$), 32.1 (CH$_2$), 33.2 (CH$_2$), 33.6 (CH$_2$), 36.6 (CH$_2$), 38.8 (C), 108.6 (CH$_2$), 148.0 (C); HRMS (FAB) calcd for C$_{15}$H$_{30}^{79}$BrS$_2$Si (M+H)$^+$ m/z 381.0742, found 381.0741.

3.2.6. 5-Bromo-1-[dimethyl(3-methyl-3-butenyl)silyl]-pentan-1-one (8d).
According to the procedure for the synthesis of **8c**, 0.12 g (0.31 mmol) of **6d** was hydrolyzed with 0.52 g (0.95 mmol) of ceric ammonium nitrate to give 72.3 mg (80%) of **8d** as a pale yellow liquid: IR (neat) 1645 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.18 (s, 6H, SiCH$_3$), 0.81–0.87 (m, 2H, SiCH$_2$), 1.60–1.71 (m overlapped with a s at 1.70, 5H, CCH$_3$ and others), 1.76–1.84 (m, 2H), 1.95–2.01 (m, 2H, =CCH$_2$), 2.61 (t, $J=7$ Hz, 2H, COCH$_2$), 3.37 (t, $J=6.8$ Hz, 2H, CH$_2$Br), 4.67 (br s, 2H, =CH$_2$); ^{13}C NMR (CDCl$_3$, 100 MHz) δ -4.6 (CH$_3$), 11.7 (CH$_2$), 20.8 (CH$_2$), 22.2 (CH$_3$), 31.5 (CH$_2$), 32.3 (CH$_2$), 33.5 (CH$_2$), 47.7 (CH$_2$), 109.0 (CH$_2$), 147.2 (C), 246.6 (C); HRMS (FAB) calcd for C$_{12}$H$_{24}^{79}$BrOSi (M+H)$^+$ m/z 291.0780, found 291.0785.

3.2.7. 2-(5-Bromopentyl)-2-[dimethyl(2-methyl-2-propenyl)silyl]-1,3-dithiane (7c).
According to the procedure for the synthesis of **8a**, 3.1 g (13.3 mmol) of **5c** was alkylated with 5.00 mL (37.3 mmol) of 1,5-dibromopentane to give 3.36 g (66%) of **7c** as a pale yellow liquid: IR (neat) 1651 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.18 (s, 6H, SiCH$_3$), 1.42–1.55 (m, 4H), 1.70 (s, 3H, =CCH$_3$), 1.76 (s, 2H, SiCH$_2$), 1.86–1.95 (m, 3H), 1.98–2.06 (m, 1H), 2.15–2.21 (m, 2H), 2.43 (dt, $J=14, 3.2$ Hz, 2H, SCH$_{2(eq)}$), 2.99 (td, $J=14, 2.8$ Hz, 2H, SCH$_{2(ax)}$), 3.41 (t, $J=7.2$ Hz, 2H, CH$_2$Br), 4.51 (br s, 1H, =CH$_2$), 4.62 (br s, 1H, =CH$_2$); ^{13}C NMR (CDCl$_3$, 100 MHz) δ -4.0 (CH$_3$), 23.6 (CH$_2$), 24.6 (CH$_2$), 25.1 (CH$_2$), 25.5 (CH$_3$), 27.1 (CH$_2$), 28.8 (CH$_2$), 32.7 (CH$_2$), 33.9 (CH$_2$), 37.5 (CH$_2$), 38.8 (C), 109.5 (CH$_2$), 142.6

(C); HRMS (FAB) calcd for $C_{15}H_{29}{}^{79}BrS_2Si$ m/z 380.0663, found 380.0663.

3.2.8. 6-Bromo-1-[dimethyl(2-methyl-2-propenyl)silyl]-hexan-1-one (9c).

According to the procedure for the synthesis of **8c**, 3.31 g (8.68 mmol) of **7c** was hydrolyzed with 12.2 g (22.3 mmol) of ceric ammonium nitrate to give 0.97 g (38%) of **9c** as a pale yellow liquid: IR (neat) 1644 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.19 (s, 6H, SiCH$_3$), 1.33–1.42 (m, 2H), 1.47–1.57 (m, 3H), 1.66 (s, 3H, =CCH$_3$), 1.69 (s, 2H, SiCH$_2$), 1.83 (quintet, $J=7.2$ Hz, 2H), 2.60 (t, $J=7$ Hz, 2H, COCH$_2$), 3.37 (t, $J=6.8$ Hz, 2H, CH$_2$Br), 4.48 (br s, 1H, =CH$_2$), 4.61 (br s, 1H, =CH$_2$); ^{13}C NMR (CDCl$_3$, 100 MHz) δ −4.3 (CH$_3$), 21.2 (CH$_2$), 25.1 (CH$_2$), 25.2 (CH$_3$), 27.9 (CH$_2$), 32.7 (CH$_2$), 33.7 (CH$_2$), 48.8 (CH$_2$), 109.6 (CH$_2$), 141.7 (C), 246.4 (C); HRMS (FAB) calcd for $C_{12}H_{24}{}^{79}BrOSi$ (M+H)$^+$ m/z 291.0780, found 291.0774.

3.2.9. 2-(5-Bromopentyl)-2-[dimethyl(3-methyl-3-butenyl)-silyl]-1,3-dithiane (7d).

According to the procedure for the synthesis of **8a**, 1.44 g (5.84 mmol) of **5c** was alkylated with 2.2 mL (16 mmol) of 1,5-dibromopentane to give 1.97 g (85%) of **7d** as a pale yellow liquid: IR (neat) 1653 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.17 (s, 6H, SiCH$_3$), 0.85–0.91 (m, 2H, SiCH$_2$), 1.44–1.56 (m, 4H), 1.72 (s, 3H, =CCH$_3$), 1.85–1.94 (m, 3H), 1.95–2.07 (m, 3H), 2.16–2.22 (m, 2H, =CCH$_2$), 2.43 (dt, $J=13.5$, 4 Hz, 2H, SCH$_{2(eq)}$), 3.00 (td, $J=13.5$, 2.8 Hz, 2H, SCH$_{2(ax)}$), 3.41 (t, $J=6.8$ Hz, 2H, CH$_2$Br), 4.66 (br s, 1H, =CH$_2$), 4.70 (br s, 1H, =CH$_2$); ^{13}C NMR (CDCl$_3$, 100 MHz) δ −4.1 (CH$_3$), 11.9 (2°), 22.3 (CH$_3$), 23.6 (CH$_2$), 25.2 (CH$_2$), 27.1 (CH$_2$), 28.8 (CH$_2$), 32.1 (CH$_2$), 32.7 (CH$_2$), 33.9 (CH$_2$), 37.5 (CH$_2$), 38.9 (C), 108.6 (CH$_2$), 148.0 (C); HRMS (FAB) calcd for $C_{16}H_{32}{}^{81}BrS_2Si$ (M$^+$+H) m/z 397.0878, found 397.0878.

3.2.10. 6-Bromo-1-[dimethyl(3-methyl-3-butenyl)silyl]-hexan-1-one (9d).

According to the procedure for the synthesis of **8c**, 0.24 g (0.61 mmol) of **7d** was hydrolyzed with 0.99 g (1.8 mmol) of ceric ammonium nitrate to give 119 mg (64%) of **9d** as a pale yellow liquid: IR (neat) 1645 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.19 (s, 6H, SiCH$_3$), 0.81–0.87 (m, 2H, SiCH$_2$), 1.38 (quintet, $J=7$ Hz, 2H), 1.53 (quintet, $J=7$ Hz, 2H), 1.70 (s, 3H, =CCH$_3$), 1.83 (quintet, $J=7$ Hz, 2H), 1.95–2.01 (m, 2H, =CCH$_2$), 2.60 (t, $J=7$ Hz, 2H, COCH$_2$), 3.38 (t, $J=7$ Hz, 2H, CH$_2$Br), 4.67 (br s, 2H, =CH$_2$); ^{13}C NMR (CDCl$_3$, 100 MHz) δ −4.6 (CH$_3$), 11.7 (CH$_2$), 21.2 (CH$_2$), 22.2 (CH$_3$), 28.0 (CH$_2$), 31.6 (CH$_2$), 32.8 (CH$_2$), 33.7 (CH$_2$), 48.7 (CH$_2$), 108.9 (CH$_2$), 147.3 (C), 247.1 (C); HRMS (FAB) calcd for $C_{13}H_{26}{}^{79}BrOSi$ (M+H)$^+$ m/z 305.0936, found 305.0934.

3.3. General procedure for intramolecular radical cyclizations and oxidations: cyclization of 8a followed by oxidation. 1-(2-Hydroxy-1-methyl)ethylcyclopentanol (17)

To a refluxing solution of 150 mg (0.57 mmol) of **8a** in 2.5 mL of benzene was added via syringe pump over 2.5 h a solution of 0.18 mL (0.68 mmol) of tributyltin hydride and 5.0 mg (0.031 mmol) of AIBN in 6 mL of benzene. The resulting solution was heated for another 2 h and then

cooled to room temperature. Gas chromatographic analysis (oven temperature=130 °C; flow rate=28 mL/min) of the reaction mixture showed the presence of **11** ($t_R=6.4$ min), **13** ($t_R=7.3$ min), and **12** ($t_R=8.1$ min) in a ratio of 1:3:8.3, respectively. The reaction mixture was concentrated in vacuo. The residue was mixed with 626 mg (6.26 mmol) of potassium bicarbonate, 0.68 mL (23 mmol) of hydrogen peroxide, 8 mL of methanol, and 8 mL of THF. The resulting mixture was stirred at 66 °C for 19 h and then partitioned between 50 mL of dichloromethane and 30 mL of water. The aqueous phase was extracted with dichloromethane (50 mL), and the combined organic layers were dried (MgSO$_4$), and concentrated in vacuo. The residue was chromatographed over silica gel (eluted with hexane/ethyl acetate, 7/3, 6/4, 4/6 in sequence) to give 16 mg (20%) of the less polar **17** as a colorless oil: IR (neat) 3431 (br) cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 0.98 (d, $J=7$ Hz, 3H), 1.38–1.95 (m, 9H), 3.00 (br s, 2H), 3.62 (dd, $J=10.5$, 5 Hz, 1H), 3.84 (dd, $J=10.5$, 4 Hz, 1H); ^{13}C NMR (CDCl$_3$, 50 MHz) δ 12.8, 23.5, 23.8, 37.2, 39.2, 42.3, 66.9, 86.1; HRMS calcd for $C_8H_{16}O_2$ m/z 144.1150, found 144.1140. Continued elution gave 31 mg (38%) of the more polar **16**[12] as a pale yellow oil.

3.3.1. Cyclization of 9a followed by oxidation: 1-(3-hydroxypropyl)cyclohexanol (22) and 1-(2-hydroxy-1-methylethyl)cyclohexanol (23).

According to the general procedure for cyclization and oxidation, the reaction of 100 mg (0.36 mmol) of **9a** afforded 14 mg (25%) of **23** as a colorless oil, and 31 mg (55%) of the more polar **22**.[29] **22**: ^{13}C NMR (CDCl$_3$, 50 MHz) δ 22.3, 25.8, 26.1, 37.5, 38.8, 63.3, 71.1. **23**: IR (neat) 3347 (br) cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 0.91 (d, $J=7$ Hz, 3H), 1.02–1.75 (m, 11H), 2.56 (br s, 2H), 3.66 (dd, $J=11$, 6 Hz, 1H), 3.77 (dd, $J=11$, 4 Hz, 1H); ^{13}C NMR (CDCl$_3$, 50 MHz) δ 12.1, 21.6, 21.7, 25.7, 32.7, 36.5, 42.9, 65.4, 74.8; HRMS calcd for $C_9H_{18}O_2$ m/z 158.1307, found 158.1305.

3.3.2. Cyclization of 8b followed by oxidation: 1-(4-hydroxybutyl)cyclopentanol (24) and 1-(3-hydroxy-1-methylpropyl)cyclopentanol (25).

According to the general procedure for cyclization and oxidation, the reaction of 250 mg (0.90 mmol) of **8b** afforded 4 mg (3%) of **25** as a colorless oil, and 96 mg (67%) of the more polar **24**.[12] **24**: ^{13}C NMR (CDCl$_3$, 75 MHz) δ 20.9, 23.8, 33.1, 39.7, 41.0, 62.7, 82.5. **25**: IR (neat) 3370 (br) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 0.98 (d, $J=7$ Hz, 3H), 1.20–1.95 (m, 13H), 3.55–3.70 (m, 1H), 3.73–3.87 (m, 1H); ^{13}C NMR (CDCl$_3$, 50 MHz) δ 14.7, 23.8, 23.9, 35.3, 38.3, 38.8, 39.7, 60.5, 85.2; HRMS calcd for $C_9H_{16}O$ (M−H$_2$O) m/z 140.1201, found 140.1207.

3.3.3. Cyclization of 9b followed by oxidation: 1-(4-hydroxybutyl)cyclohexanol (26).

According to the general procedure for cyclization and oxidation, the reaction of 70 mg (0.24 mmol) of **9b** afforded 31 mg (78%) of **26**[29]: ^{13}C NMR (CDCl$_3$, 75 MHz) δ 22.2, 25.8, 29.7, 33.0, 37.4, 41.7, 62.7, 71.7.

3.3.4. Cyclization of 8c: 7,7,9-trimethyl-6-oxa-7-sila-spiro-[4.5]decane (30).

According to the general procedure for cyclization, 181 mg (0.653 mmol) of **8c** reacted with 0.24 mL (0.85 mmol) of tributyltin hydride to give 95 mg

(74%) of **30** as a pale yellow liquid: IR (neat) 1456, 1252, 1029, 1004 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.08 (s, 3H, SiCH$_3$), 0.10 (s, 3H, SiCH$_3$), 0.23 (t, $J=14$ Hz, 1H, SiCH$_2$), 0.67 (br d, $J=14$ Hz, 1H, SiCH$_2$), 0.98 (d, $J=6.4$ Hz, 3H, CHCH_3), 1.29 (t, $J=13$ Hz, 1H, CHCH_2), 1.41–1.59 (m, 5H, CHCH_2 and others), 1.62–1.79 (m, 4H), 1.81–1.95 (m, 1H, CHCH$_3$); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 1.20 (CH$_3$), 22.8 (CH$_2$), 23.2 (CH$_2$), 24.3 (CH$_2$), 26.4 (CH), 27.5 (CH$_3$), 38.5 (CH$_2$), 43.3 (CH$_2$), 47.8 (CH$_2$), 84.8 (C); MS (rel intensity) m/z 198 (M$^+$, 10), 183 (43), 169 (80), 156 (63), 141 (65), 127(81), 113 (14), 75 (100), 61 (23); HRMS calcd for C$_{11}$H$_{22}$OSi 198.1434, found 198.1439.

3.3.5. Cyclization of 9c: 2,2,4-trimethyl-1-oxa-2-sila-spiro[5.5]undecane (33).

According to the general procedure for cyclization, 353 mg (1.21 mmol) of **9c** reacted with 0.45 mL (1.7 mmol) of tributyltin hydride to give 58 mg (23%) of **33** as a pale yellow liquid: IR (neat) 1450, 1252, 1041, 1015 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.07 (s, 3H, SiCH$_3$), 0.16 (s, 3H, SiCH$_3$), 0.19 (t, $J=13$ Hz, 1H, SiCH), 0.66 (dq, $J=13$, 2 Hz, 1H, SiCH), 0.95 (d, $J=6.4$ Hz, 3H, CHCH_3), 1.00 (dd, $J=13$, 2 Hz, 1H, CHCH$_3$), 1.18–1.40 (m, 6H), 1.42–1.77 (m, 5H), 1.84–1.97 (m, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 1.50 (CH$_3$), 1.55 (CH$_3$), 22.2 (CH$_2$), 22.4 (CH$_2$), 23.1 (CH$_2$), 24.1 (CH), 26.3 (CH$_2$), 27.6 (CH$_3$), 36.6 (CH$_2$), 42.1 (CH$_2$), 48.4 (CH$_2$), 74.1 (C); MS (rel intensity) m/z 212 (M$^+$, 40), 197 (27), 183 (37), 169 (100), 156 (81), 141 (45), 127 (89); 75 (66); HRMS calcd for C$_{12}$H$_{24}$OSi 212.1591, found 212.1595.

3.3.6. Cyclization of 9c followed by oxidation: 1-(3-hydroxy-2-methylpropyl)cyclohexanol (36).[30]

According to the general procedure for cyclization followed by direct oxidation, 308 mg (1.05 mmol) of **9c** reacted with 0.38 mL (1.4 mmol) of tributyltin hydride to give 112 mg (62%) of **36** as a pale yellow liquid: IR (neat) 3306 (br) cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.76 (d, $J=6.8$ Hz, 3H, CH$_3$), 1.06–1.65 (m, 13H), 1.76–1.88 (m, 1H), 2.59 (br s, 1H, OH), 3.22 (dd, $J=10.4$, 9.2 Hz, 1H, OCH$_2$), 3.46 (dd, $J=10.4$, 3.6 Hz, 1H, OCH$_2$); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 19.8 (CH$_3$), 22.3 (CH$_2$), 22.6 (CH$_2$), 25.9 (CH$_2$), 30.9 (CH), 36.0 (CH$_2$), 40.1 (CH$_2$), 48.1 (CH$_2$), 69.2 (CH$_2$), 71.6 (C).

3.3.7. Cyclization of 8d: 7,7,10-trimethyl-6-oxa-7-sila-spiro[4.6]undecane (37) and (cyclopentyloxy)(dimethyl)(3-methyl-3-butenyl)silane (38).

According to the general procedure for cyclization, 289 mg (0.99 mmol) of **8d** reacted with 0.35 mL (1.3 mmol) of tributyltin hydride to give 144 mg (69%) of **37** as a pale yellow liquid: IR (neat) 1457, 1251, 1048 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.02 (s, 3H, SiCH$_3$), 0.08 (s, 3H, SiCH$_3$), 0.62–0.67 (m, 2H, SiCH$_2$), 0.92 (d, $J=6$ Hz, 3H, CHCH_3), 1.22–1.33 (m, 1H, CHCH$_3$), 1.37–1.58 (m, 5H), 1.64–1.84 (m, 7H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 0.5 (CH$_3$), 1.1 (CH$_3$), 16.4 (CH$_2$), 23.5 (CH$_2$), 23.8 (CH$_2$), 25.3 (CH$_3$), 32.4 (CH$_2$), 33.1 (CH), 38.7 (CH$_2$), 43.6 (CH$_2$), 50.2 (CH$_2$), 84.8 (C); MS (rel intensity) m/z 212 (M$^+$, 26), 197 (23), 183 (100), 169 (61), 155 (41), 142 (44), 127 (64); 75 (57); HRMS calcd for C$_{12}$H$_{24}$OSi 212.1591, found 212.1597. We also isolated 15 mg (7%) of **38** as a pale yellow liquid: IR (neat) 1653 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.09 (s, 6H, SiCH$_3$), 0.68–0.75 (m, 2H, SiCH$_2$), 1.41–1.56 (m, 4H), 1.66–1.78 (m overlapped with a s at 1.71, 7H, CCH$_3$ and others), 1.96–2.03 (m, 2H, CH$_2$C=), 4.19 (quintet, $J=4.8$ Hz, 1H, OCH), 4.64 (br s, 1H, =CH$_2$), 4.68 (br s, 1H, =CH$_2$); ^{13}C NMR (CDCl$_3$, 100 MHz) δ −1.4 (CH$_3$), 15.0 (CH$_2$), 22.3 (CH$_3$), 23.3 (CH$_2$), 31.3 (CH$_2$), 35.7 (CH$_2$), 74.3 (CH), 108.3 (CH$_2$), 148.3 (C); MS (rel intensity) m/z 212(M$^+$, 3), 197 (13), 143 (97), 111 (39), 101 (21), 85 (11), 75 (100), 67 (8), 59 (38); HRMS calcd for C$_{12}$H$_{24}$OSi 212.1591, found 212.1595.

3.3.8. Cyclization of 9d: 8,8,11-trimethyl-7-oxa-8-sila-spiro[5.6]dodecane (40), (cyclohexyloxy)(dimethyl)(3-methyl-3-butenyl)silane (41) and 1-[dimethyl(3-methyl-3-butenyl)silyl]hexan-1-one (42).

According to the general procedure for cyclization, 250 mg (0.82 mmol) of **9d** reacted with 0.29 mL (1.1 mmol) of tributyltin hydride to give 74 mg (40%) of **40** as a pale yellow liquid: IR (neat) 1449, 1252, 1053, 1029 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.03 (s, 3H, SiCH$_3$), 0.08 (s, 3H, SiCH$_3$), 0.57–0.63 (m, 2H, SiCH$_2$), 0.91 (d, $J=6.4$ Hz, 3H, CHCH_3), 1.16–1.50 (m, 10H), 1.54–1.68 (m, 3H), 1.71–1.85 (m, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 1.07 (CH$_3$), 1.14 (CH$_3$), 16.0 (CH$_2$), 22.5 (CH$_2$), 22.8 (CH$_2$), 25.2 (CH$_3$), 26.3 (CH$_2$), 30.0 (CH), 32.4 (CH$_2$), 37.1 (CH$_2$), 41.7 (CH$_2$), 50.2 (CH$_2$), 74.1 (C); MS (rel intensity) m/z 226 (M$^+$, 56), 211 (14), 183 (100), 170 (33), 157 (72), 142 (28), 127 (37); 75 (81); HRMS calcd for C$_{13}$H$_{26}$OSi 226.1747, found 226.1753. We also isolated 15 mg (8%) of **41** as a pale yellow liquid: IR (neat) 1653 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.09 (s, 6H, SiCH$_3$), 0.68–0.75 (m, 2H, SiCH$_2$), 1.05–1.33 (m, 6H), 1.45–1.54 (m, 2H), 1.65–1.80 (m overlapped with a s at 1.71, 5H, =CCH$_3$ and others), 1.96–2.04 (m, 2H, CH$_2$C=), 3.49–3.57 (m, 1H, OCH), 4.64 (br s, 1H, =CH$_2$), 4.68 (br s, 1H, =CH$_2$); ^{13}C NMR (CDCl$_3$, 100 MHz) δ −1.3 (CH$_3$), 15.2 (CH$_2$), 22.3 (CH$_3$), 24.6 (CH$_2$), 25.7 (CH$_2$), 31.3 (CH$_2$), 36.2 (CH$_2$), 71.1 (CH), 108.3 (CH$_2$), 148.3 (C); MS (rel intensity) m/z 226 (M$^+$, 3), 211 (12), 157 (100), 143 (9), 127 (12), 111 (30), 99 (16), 75 (100), 59 (25); HRMS calcd for C$_{13}$H$_{26}$OSi 226.1747, found 226.1754. In addition was isolated 13 mg (7%) of **42** as a pale yellow liquid: IR (neat) 1646 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.18 (s, 6H, SiCH$_3$), 0.80–0.89 (m, 5H, SiCH$_2$ and others), 1.16–1.33 (m, 4H), 1.49 (quintet, $J=7.6$ Hz, 2H), 1.70 (s, 3H, =CCH$_3$), 1.94–2.02 (m, 2H, =CCH$_2$), 2.56 (t, $J=7.2$ Hz, 2H, COCH$_2$), 4.64–4.68 (two overlapped br s at 4.65 and 4.67, 2H, =CH$_2$); ^{13}C NMR (CDCl$_3$, 100 MHz) δ −4.5 (CH$_3$), 11.8 (CH$_2$), 14.1 (CH$_3$), 21.9 (CH$_2$), 22.2 (CH$_3$), 22.7 (CH$_2$), 31.6 (CH$_2$), 31.7 (CH$_2$), 49.0 (CH$_2$), 108.9 (CH$_2$), 147.3 (C), 247.8 (C); HRMS (FAB) calcd for C$_{13}$H$_{27}$OSi (M+H)$^+$ m/z 227.1831, found 227.1833.

Acknowledgements

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