Tris(trimethylsilyl)silyl Radical Induced Bicyclization of 1,6-Dienes and 1,6-Enynes Providing 3,3-Bis(trimethylsilyl)-3-silabicyclo[3.3.0]octanes and 3-Silabicyclo[3.3.0]oct-1-enes

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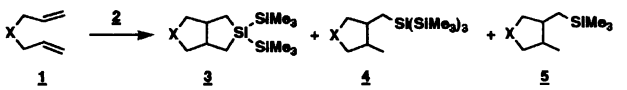
Treatment of 1,6-dienes with tris(trimethylsilyl)silane in the presence of Et_3B or α,α'-azobis(isobutyronitrile) afforded 3,3-bis(trimethylsilyl)-3-silabicyclo[3.3.0]octanes in addition to monocyclized cyclopentanes. Bicyclization of 1,6-enynes provided the corresponding 3-silabicyclo[3.3.0]oct-1-enes.

The formation of carbocyclic and heterocyclic compounds from diene[1] or enyne[2] by free-radical processes has received considerable attention in recent years.[3] We have reported that Et_3B induced a radical cyclization of enyne by the use of triphenylstannane[2a] or triphenylgermane[2b] under mild conditions. Recently, tris(trimethylsilyl)silane (TTMSS) as an alternative to tributylstannane has become more popular, being a superior reagent from both ecological and practical perspectives. This silane can be used as a reducing agent for organic compounds or a hydrosilylating agent for alkenes and alkynes.[4,5] Then, we examined Et_3B induced radical cyclization of diene and enyne mediated by TTMSS. To our surprise, the radical reaction gave a silabicyclic compound along with expected cyclopentane derivatives. Here, we present an efficient method for the preparation of bicyclic compounds such as 3,3-bis(trimethylsilyl)-3-silabicyclo[3.3.0]octane or 3,3-bis(trimethylsilyl)-3-silabicyclo[3.3.0]oct-1-ene based on the tandem radical cyclization of diene or enyne promoted by tris(trimethylsilyl)silyl radical.[6] In addition, a recent publication[7] on homolytic substitution reaction at a silicon atom prompts us to report our independent results[8] along similar lines.

(1) The Reaction of Diene with TTMSS. When a benzene solution of diene **1a** and TTMSS (**2**) was treated at room temperature with a catalytic amount of Et_3B (Method A), bicyclized product **3a** (11%) was obtained along with monocyclized product **4a** (87%).[9] In an effort to increase both the yield and the ratio of **3a** to **4a**, the reaction was repeated under various reaction conditions. The yields of **3a** and **4a** were 71 and 17%, respectively, and the ratio **3a**/**4a** had increased to 81/19 upon treatment of **1a** (1.00 mmol) with **2** (1.30 mmol) at 80 °C using an initial concentration of **1a** of 0.02 M (1 M=1 mol dm^{-3}) with intermittent addition of α,α'-azobis(isobutyronitrile) (AIBN, 0.10 mmol×5) over 5 h (Method B). Under these reaction conditions monocyclized product **4a** was *trans*-rich (*trans*-**4a**/*cis*-**4a**=2/1), and trimethylsilylmethyl-substituted cyclopentane **5a** was obtained in 8% yield in addition to the formation of **3a** and **4a** (Table 1).

In a similar manner, dienes **1b** and **1c** were converted into the corresponding bicyclized products **3b** and **3c**.

Table 1. Reaction of Dienes with TTMSS[a]

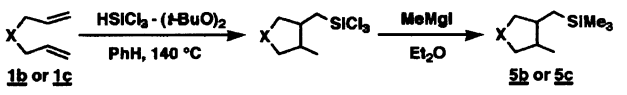


1 3 4 5

	X	Yield/% (*cis*/*trans*)[b] 3	4	5
1a:	$C(COOMe)_2$	71 (15/1)	17 (1/2)	8 (5/1)
1b:	CH_2	62 (6/1)	27 (1/5)	4 (3/1)
1c:	O	53 (cis only)	26 (1/8)	3 (3/1)

a) Diene (1.00 mmol), TTMSS (1.30 mmol), AIBN (0.10 mmol×5) and benzene (50 mL) were employed (Method B). b) Yields and isomeric ratios were determined by the examination of ^1H NMR of the mixture of **3**, **4**, and **5** after purification.

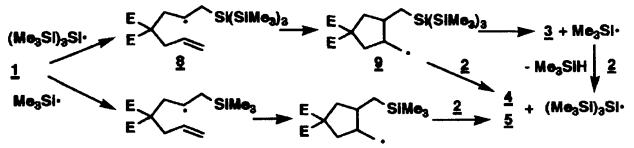
Two types of monocyclized products **4** and **5** were also obtained as a mixture of *cis* and *trans* compounds.[10] Trimethylsilylmethyl-substituted cyclopentane **5b** and tetrahydrofuran **5c** were synthesized independently by another procedure to prove the structure of these compounds (Eq. 1).[11]



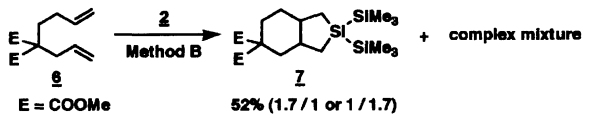
1b or 1c 5b or 5c (1)

Whereas **3c** was produced in an isomerically pure form (*cis*-fused compound), **3a** and **3b** were obtained as isomeric mixtures of *cis*-fused and *trans*-fused 3-silabicyclooctanes.[12] Formation of a negligible amount of highly strained *trans*-**3c** is predicted by calculations on MacroModel,[13] which indicate that *cis*-**3c** is about 2.4 kcal mol^{-1} more stable than *trans*-**3c**. Meantime, the calculations show that an energy difference between *cis*-**3b** and *trans*-**3b** is 1.2 kcal mol^{-1}.

A 1,7-diene **6** afforded a bicyclized product **7** as the isomeric mixture of *cis*- and *trans*-fused compounds in 52% yield. The stereoselectivity of **7** was low and the ratio of two isomers was 1.7/1 (Eq. 2).



Scheme 1.

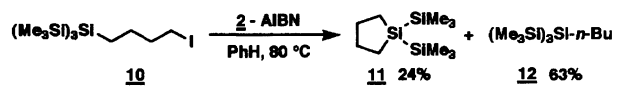


(2)

These results support the following reaction mechanism for bicyclization of dienes (Scheme 1). The tris(trimethylsilyl)silyl radical, generated by the action of radical initiator on **2** attacks terminal olefinic carbon of 1,6-diene to give a carbon radical **8**, which cyclizes to cyclopentylmethyl radical **9**. The carbon radical attacks silicon having three trimethylsilyl groups to produce **3** under elimination of trimethylsilyl radical. Trimethylsilyl radical abstracts hydrogen of **2**, and regenerates tris(trimethylsilyl)silyl radical.

In the homolytic substitution, *cis*-**9** reacts much faster than *trans*-**9** to provide **3** because of facile approach of the radical center to tris(trimethylsilyl)silyl group. Meantime, the intramolecular reaction of *trans*-**9** is slow, and this radical abstracts hydrogen of **2** to give monocyclized product **4** predominantly. For this reason, Method B affords *trans*-rich cyclopentane **4**. Moreover, the formation of **5** certifies the intermediacy of trimethylsilyl radical.

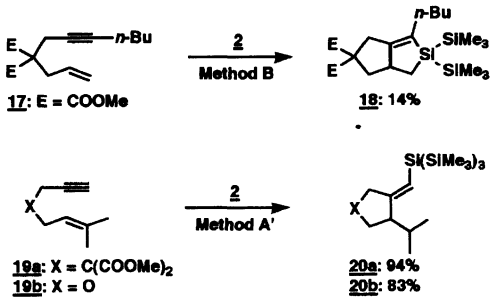
The Si–Si bond fission by the intermolecular attack of carbon radical was confirmed by the expriment shown below (Eq. 3). Treatment of iodoalkylsilane **10** with **2** gave silacyclopentane **11** in 24% yield along with the reduced product **12** (63%).



(3)

(2) The Reaction of Enyne with TTMSS. In order to demonstrate the applicability of this bicyclization, the reaction of 1,6-enyne with **2** has been examined. Treatment of a hexane (2 mL) solution of enyne **13** (1.00 mmol) and **2** (1.30 mmol) with Et_3B (0.10 mmol) (Method A′) gave 3-silabicyclo[3.3.0]oct-1-ene **14** (53%) as a major product in addition to methylenecyclopentane **15** (17%) and methylenecyclohexane **16** (20%). The changes of radical initiator and concentrations of enyne **13** were not effective for increase of the yield of **14** (Table 2).

The use of enyne **17** provided the corresponding bicyclized product **18** in only 14% yield along with unidentified complex products even under high dilution conditions (Eq. 4). In the case of enynes **19a** and **19b**, methylenecyclopentane **20a** (94%) and **20b** (83%) were formed and no trace of bicyclized products was detected in the reaction mixture (Eq. 5).

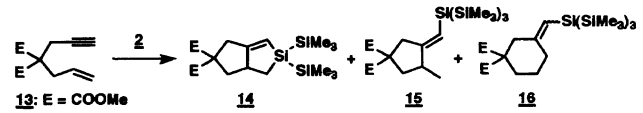


(4)

(5)

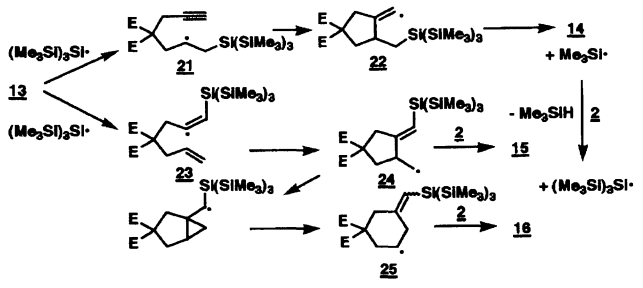
Based on these facts we assume the following reaction mechanism for the reaction of enyne **13** with **2** (Scheme 2). Tris(trimethylsilyl)silyl radical, given by the reaction of **2** with radical initiator, can attack either terminal olefinic carbon or terminal acetylenic carbon.[14] The attack on terminal olefinic carbon gives olefinic radical **22** via radical **21**. Intramolecular homolytic substitution of **22** affords **14** accompanying with the elimination of trimethylsilyl radical, which regenerate tris(trimethylsilyl)silyl radical by the abstraction of hydrogen from **2**. On the other hand, an addition of tris(trimethylsilyl)silyl radical to terminal acetylenic carbon provides alkenyl radical **23**. The intramolecular addition of carbon radical to double bond in **23**

Table 2. Reaction of Enyne **13** with TTMSS[a)]

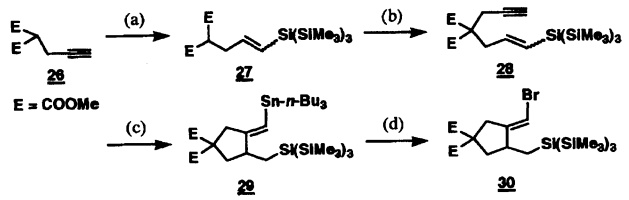


Method	Yield/%[b)]		
	14	**15**	**16**
A′	53	17	20
C	47	5	36
B	50	<1	38

a) **13** (1.00 mmol) and TTMSS (1.30 mmol) were employed. Method A′: Et_3B (0.10 mmol), hexane (2 mL), r.t.; Method C: AIBN (0.10 mmol), benzene (5 mL), reflux; Method B: See Table 1. b) Yields were determined by the examination of ^1H NMR.



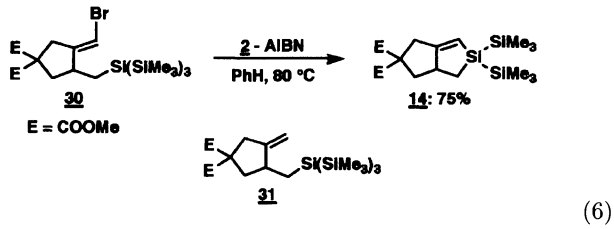
Scheme 2.



Scheme 3. (a) **2**, AIBN, benzene, reflux, 2 h. (b) NaH, THF, r.t., 30 min, then propargyl bromide, r.t., 4 h. (c) *n*-Bu_3SnH, AIBN, benzene, reflux, 2 h. (d) Br_2, CH_2Cl_2, −78 °C, 25 min.

proceeds on the opposite side of tris(trimethylsilyl)silyl group to avoid the steric hindrance, and gives cyclopentylmethyl radical **24** with (*E*)-stereochemistry.[2a] Therefore, **24** can not afford **14** because of its geometry, and abstracts hydrogen from **2** to provide **15**. Alternatively, **24** rearranges to cyclohexyl radical **25** which reacts with **2** to give **16**.[15]

To confirm this mechanism, alkenyl bromide **30** was synthesized from **26** as shown in Scheme 3. Treatment of **30** with **2** in the presence of AIBN gave **14** in good yield, and this result supports the homolytic substitution of **22** (Eq. 6). The reduced product **31** could not be observed in the reaction mixture. Thus, the intramolecular cyclization of **22** was much faster than an abstraction of hydrogen from **2**.



(6)

In conclusion, the addition of tris(trimethylsilyl)silyl radical to diene or enyne provides us with a new synthetic method for silabicyclo compounds and the reaction proceeds via homolytic substitution at silicon by carbon radical.[7,16]

Experimental

Distillation of the products was performed by use of Kugelrohr (Büchi), and boiling points are indicated by air-bath temperature without correction. Melting point was obtained on a Yanako MP-50929 melting point apparatus and are uncorrected, too. ^{1}H NMR and ^{13}C NMR spectra were taken on a Varian GEMINI 300 spectrometer, $CDCl_3$ was used as solvent, and chemical shifts being given in δ with tetramethylsilane as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer and the mass spectra on a Hitachi M-80 machine. When m/z is less than 100, mass spectra are described in only case where its relative intensity is more than 50. The analyses were carried out at the Elemental Analyses Center of Kyoto University.

General Procedure for the Reaction of Diene or Enyne with TTMSS. Method A: Typical procedure is as follows. Et_3B (0.96 M hexane solution, 1 M=1 mol dm^{-3}, 0.10 mL, 0.10 mmol) was added to a benzene (5 mL) solution of diene **1a** (0.212 mg, 1.00 mmol) and TTMSS (0.323 g, 1.30 mmol) at room temperature under argon atmosphere. After stirring for 1.3 h, the reaction mixture was concentrated in vacuo. The residual oil was purified by silica-gel column chromatography (hexane/AcOEt=20/1) to give a mixture of bicyclized product **3a** and monocyclized product **4a**. The yield and the diastereomeric ratio of **3a** or **4a** were determined by the examination of ^{1}H NMR.

Method A′: In Method A, hexane is used as a solvent instead of benzene.

Method B: A benzene solution of diene **1** (1.00 mmol) and TTMSS (0.323 g, 1.30 mmol) was stirred and heated at reflux under argon atmosphere. AIBN (0.10 M benzene solution, 1.0 mL, 0.10 mmol) was added to the mixture five times at intervals of 1 h. After the last addition of AIBN followed by stirring for 1 h, the reaction mixture was cooled to room temperature and concentrated in vacuo. The crude product was purified by silica-gel column to give a mixture of **3**, **4**, and **5**. The yield and the diastereomeric ratio of **3**, **4**, or **5** were determined by the examination of ^{1}H NMR.

Method C: AIBN (0.016 g, 0.10 mmol) was added to a benzene (5 mL) solution of enyne (1.00 mmol) and **2** (0.323 g, 1.30 mmol). The mixture was heated at reflux for 2.5 h with stirring. Work-up is similar to Method B.

Dimethyl *cis*-3,3-Bis(trimethylsilyl)-3-silabicyclo-[3.3.0]octane-7,7-dicarboxylate (*cis*-3a): Bp 101—105 °C (0.28 Torr, 1 Torr=133.322 Pa, bath temp); IR (neat) 2946, 1736, 1259, 1246, 1195, 1154, 834, 687, 621 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.09 (s, 9H), 0.13 (s, 9H), 0.71 (dd, J=14.9, 5.6 Hz, 2H), 1.01 (dd, J=14.9, 7.1 Hz, 2H), 1.95—2.05 (m, 2H), 2.38—2.49 (m, 4H), 3.71 (s, 6H); ^{13}C NMR ($CDCl_3$) δ=−0.93, −0.74, 12.57, 41.30, 46.20, 52.69 (two carbons), 60.06, 173.48; MS (20 eV) m/z (rel intensity) 372 (M^++1−Me, 0.8), 371 (M^+−Me, 3.2), 355 (1.6), 316 (M^++3−$SiMe_3$, 1.8), 315 (M^++2−$SiMe_3$, 12), 314 (M^++1−$SiMe_3$, 22), 313 (M^+−$SiMe_3$, 100), 163 (23). Found: C, 52.73; H, 9.13%. Calcd for $C_{17}H_{34}O_4Si_3$: C, 52.80; H, 8.86%.

Dimethyl *trans*-3,3-Bis(trimethylsilyl)-3-silabicyclo[3.3.0]octane-7,7-dicarboxylate (*trans*-3a): Bp 97—101 °C (0.27 Torr, bath temp); IR ($CHCl_3$) 2948, 2888, 1727, 1245, 836 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.11 (s, 18H), 0.39—0.49 (m, 2H), 0.90—0.98 (m, 2H), 1.50—1.63 (m, 4H), 2.51—2.56 (m, 2H), 3.72 (s, 6H); ^{13}C NMR ($CDCl_3$) δ=−0.91, 10.73, 39.90, 52.63, 52.99, 63.16, 173.42; MS (70 eV) m/z (rel intensity) 387 (M^++1, 5.5), 386 (M^+, 7.4), 314 (M^++1−$SiMe_3$, 4.3), 313 (M^+−$SiMe_3$, 17), 133 (14), 113 (14), 73 (100). Found: C, 52.53; H, 9.15%. Calcd for $C_{17}H_{34}O_4Si_3$: C, 52.80; H, 8.86%.

Dimethyl *cis*-4-Methyl-3-[tris(trimethylsilyl)silylmethyl]cyclopentane-1,1-dicarboxylate (*cis*-4a): Bp 107—111 °C (0.26 Torr, bath temp); IR (neat) 2948, 2890, 1735, 1435, 1246, 1199, 1149, 834, 684, 622 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.17 (s, 27H), 0.64 (dd, J=14.3, 9.5 Hz, 1H), 0.85 (d, J=6.8 Hz, 3H), 0.93 (dd, J=14.3, 3.5 Hz, 1H), 1.94 (dd, J=12.8, 9.3 Hz, 1H), 1.98 (dd, J=13.5, 4.9 Hz, 1H), 2.00—2.15 (m, 2H), 2.41 (dd, J=12.8, 6.3 Hz, 1H), 2.42 (dd, J=13.5, 6.6 Hz, 1H), 3.70 (s, 3H), 3.71 (s, 3H); ^{13}C NMR ($CDCl_3$) δ=1.25, 7.37, 14.81, 37.91, 40.93, 41.15, 42.04, 52.64 (two carbons), 58.77, 173.32, 173.47; MS (20 eV) m/z (rel intensity) 446 (M^++1−Me, 2.3), 445 (M^+−Me,

3.4), 389 (M^++2−$SiMe_3$, 13), 388 (M^++1−$SiMe_3$, 31), 387 (M^+−$SiMe_3$, 88), 207 (15), 206 (19), 205 (100), 175 (14), 173 (15). Found: C, 52.11; H, 9.88%. Calcd for $C_{20}H_{44}O_4Si_4$: C, 52.12; H, 9.62%.

Dimethyl *trans*-4-Methyl-3-[tris(trimethylsilyl)silylmethyl]cyclopentane-1,1-dicarboxylate (*trans*-4a): Bp 105—109 °C (0.23 Torr, bath temp); IR (neat) 2948, 2890, 1737, 1435, 1246, 1169, 1144, 834, 684, 622 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.17 (s, 27H), 0.49 (dd, J=14.3, 11.0 Hz, 1H), 0.99 (d, J=6.1 Hz, 3H), 1.21 (dd, J=14.3, 2.4 Hz, 1H), 1.33—1.56 (m, 2H), 1.71 (dd, J=13.2, 11.0 Hz, 1H), 1.79 (dd, J=13.6, 10.7 Hz, 1H), 2.47 (dd, J=13.6, 7.0 Hz, 1H), 2.60 (dd, J=13.2, 6.4 Hz, 1H), 3.71 (s, 3H), 3.72 (s, 3H); ^{13}C NMR ($CDCl_3$) δ=1.26, 11.00, 17.44, 42.29, 43.55, 43.76, 46.63, 52.60 (two carbons), 57.94, 173.27, 173.36; MS (20 eV) m/z (rel intensity) 446 (M^++1−Me, 2.1), 445 (M^+−Me, 4.5), 389 (M^++2−$SiMe_3$, 11), 388 (M^++1−$SiMe_3$, 26), 387 (M^+−$SiMe_3$, 79), 207 (12), 206 (18), 205 (100), 175 (13). Found: C, 51.92; H, 9.61%. Calcd for $C_{20}H_{44}O_4Si_4$: C, 52.12; H, 9.62%.

Dimethyl *cis*-4-Methyl-3-[(trimethylsilyl)methyl]-cyclopentane-1,1-dicarboxylate (*cis*-5a): Bp 66—70 °C (0.31 Torr, bath temp); IR (neat) 2950, 2900, 1735, 1435, 1250, 1219, 1202, 1151, 858, 838 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.01 (s, 9H), 0.46 (dd, J=14.6, 9.1 Hz, 1H), 0.58 (dd, J=14.6, 5.0 Hz, 1H), 0.82 (d, J=6.6 Hz, 3H), 1.89 (dd, J=13.3, 3.7 Hz, 1H), 2.02—2.13 (m, 3H), 2.33—2.40 (m, 2H), 3.72 (s, 6H); ^{13}C NMR ($CDCl_3$) δ=−0.87, 14.87, 16.64, 37.69, 39.02, 40.64, 41.21, 52.65 (two carbons), 58.85, 173.47, 173.66; MS (20 eV) m/z (rel intensity) 286 (M^+, 0.7), 272 (M^++1−Me, 5.6), 271 (M^+−Me, 25), 229 (12), 185 (14), 151 (13), 145 (100), 140 (10), 113 (15), 108 (31), 73 (53). Found: C, 58.47; H, 9.35%. Calcd for $C_{14}H_{26}O_4Si$: C, 58.70; H, 9.15%.

Dimethyl *trans*-4-Methyl-3-[(trimethylsilyl)methyl]cyclopentane-1,1-dicarboxylate (*trans*-5a): Bp 68—72 °C (0.30 Torr, bath temp); IR (neat) 2950, 1736, 1436, 1251, 1212, 1195, 1171, 1144, 858, 839 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.01 (s, 9H), 0.29 (dd, J=14.5, 10.8 Hz, 1H), 0.86 (dd, J=14.5, 2.4 Hz, 1H), 0.95 (d, J=6.1 Hz, 3H), 1.34—1.55 (m, 2H), 1.65 (d, J=13.2 Hz, 1H), 1.68 (d, J=13.4 Hz, 1H), 2.52 (dd, J=13.2, 6.6 Hz, 1H), 2.58 (dd, J=13.4, 6.5 Hz, 1H), 3.72 (s, 6H); ^{13}C NMR ($CDCl_3$) δ=−0.86, 17.15, 20.21, 42.15, 42.69, 43.50, 43.55, 52.64 (two carbons), 58.11, 173.48 (two carbons); MS (20 eV) m/z (rel intensity) 286 (M^+, 1.1), 272 (M^++1−Me, 4.3), 271 (M^+−Me, 25), 217 (16), 146 (15), 145 (100), 113 (27), 108 (31), 89 (55), 73 (85). Found: C, 58.57; H, 9.45%. Calcd for $C_{14}H_{26}O_4Si$: C, 58.70; H, 9.15%.

***cis*-3,3-Bis(trimethylsilyl)-3-silabicyclo[3.3.0]octane (*cis*-3b):** Bp 55—59 °C (0.33 Torr, bath temp); IR (neat) 2944, 2894, 2866, 1243, 832, 686, 621 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.10 (s, 9H), 0.12 (s, 9H), 0.66 (dd, J=14.6, 6.3 Hz, 2H), 0.97 (dd, J=14.6, 8.1 Hz, 2H), 1.22—1.35 (m, 2H), 1.44—1.61 (m, 1H), 1.65—1.81 (m, 3H), 2.22—2.35 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−0.80, −0.60, 13.28, 23.50, 33.32, 44.66; MS (70 eV) m/z (rel intensity) 272 (M^++2, 3.0), 271 (M^++1, 4.5), 270 (M^+, 14), 197 (M^+−$SiMe_3$, 35), 169 (11), 137 (22), 117 (25), 103 (18), 73 (76), 40 (100). Found: C, 57.72; H, 10.89%. Calcd for $C_{13}H_{30}Si_3$: C, 57.69; H, 11.17%.

***trans*-3,3-Bis(trimethylsilyl)-3-silabicyclo[3.3.0]octane (*trans*-3b):** Bp 62—66 °C (0.44 Torr, bath temp); 2946, 2888, 2858, 1244, 833, 778, 688, 620 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.11 (s, 18H), 0.40 (dd, J=13.4, 12.1 Hz, 2H), 0.91 (dd, J=13.4, 5.6 Hz, 2H), 0.99—1.13 (m, 2H), 1.34—1.51 (m, 2H), 1.67—1.77 (m, 2H), 1.86—1.96 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−0.86, 11.15, 27.48, 31.05, 54.39; MS (70 eV) m/z (rel intensity) 272 (M^++2, 4.4), 271 (M^++1, 8.2), 270 (M^+, 24), 197 (M^+−$SiMe_3$, 24), 182 (10), 137 (34), 136 (15), 123 (10), 122 (11), 117 (33), 103 (24), 73 (100). Found: C, 57.53; H, 11.40%. Calcd for $C_{13}H_{30}Si_3$: C, 57.69; H, 11.17%.

2-Methyl-1-[(trimethylsilyl)methyl]cyclopentane (5b, *cis*/*trans*=3/1): Bp 70—74 °C (43 Torr, bath temp); IR (neat) 2948, 2896, 2864, 1248, 860, 836, 688 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.01 (s, 9H), 0.27 (dd, J=14.3, 10.4 Hz, 0.25H), 0.42 (dd, J=14.5, 9.5 Hz, 0.75H), 0.59 (dd, J=14.5, 4.7 Hz, 0.75H), 0.77 (d, J=6.8 Hz, 2.25H), 0.85 (dd, J=14.3, 2.9 Hz, 0.25H), 0.93 (d, J=6.2 Hz, 0.75H), 1.02—1.34 (m, 3H), 1.43—1.95 (m, 5H); ^{13}C NMR ($CDCl_3$), *cis*-isomer δ=−0.79, 14.81, 17.41, 22.50, 32.08, 32.98, 38.12, 39.33, *trans*-isomer δ=−0.79, 18.47, 21.49, 23.06, 33.96, 34.62, 44.11, 44.29; MS (70 eV) m/z (rel intensity) 171 (M^++1, 0.2), 170 (M^+, 1.5), 156 (M^++1−Me, 1.3), 155 (M^+−Me, 8.1), 73 (100). Found: C, 70.64; H, 13.29%. Calcd for $C_{10}H_{22}Si$: C, 70.50; H, 13.02%.

***cis*-7,7-Bis(trimethylsilyl)-3-oxa-7-silabicyclo[3.3.0]octane (*cis*-3c):** Bp 71—74 °C (0.78 Torr, bath temp); IR (neat) 2944, 2890, 2848, 1244, 1068, 833, 773, 688, 621 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.12 (s, 9H), 0.13 (s, 9H), 0.76 (dd, J=14.8, 6.2 Hz, 2H), 1.04 (dd, J=14.8, 8.0 Hz, 2H), 2.57—2.70 (m, 2H), 3.43 (dd, J=8.2, 5.4 Hz, 2H), 3.93 (dd, J=8.2, 6.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=−0.92, −0.75, 10.54, 46.25, 74.64; MS (70 eV) m/z (rel intensity) 273 (M^++1, 0.3), 272 (M^+, 0.6), 258 (M^++1−Me, 0.3), 257 (M^+−Me, 1.0), 189 (19), 157 (18), 143 (13), 131 (23), 117 (20), 73 (100). Found: C, 52.57; H, 10.55%. Calcd for $C_{12}H_{28}OSi_3$: C, 52.87; H, 10.35%.

***cis*-4-Methyl-3-[(trimethylsilyl)methyl]tetrahydrofuran (*cis*-5c):** Bp 87—91 °C (29 Torr, bath temp); IR (neat) 2952, 2916, 2852, 1249, 1062, 1031, 910, 860, 839, 689 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.02 (s, 9H), 0.48 (dd, J=14.7, 9.5 Hz, 1H), 0.64 (dd, J=14.7, 5.4 Hz, 1H), 0.91 (d, J=7.0 Hz, 3H), 2.12—2.35 (m, 2H), 3.31 (dd, J=8.7, 8.0 Hz, 1H), 3.49 (dd, J=8.1, 3.4 Hz, 1H), 3.89 (dd, J=8.1, 2.4 Hz, 1H), 3.91 (dd, J=8.0, 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=−1.02, 13.19, 13.89, 37.32, 38.48, 73.30, 75.08; MS (20 eV) m/z (rel intensity) 158 (M^++1−Me, 1.1), 157 (M^+−Me, 7.9), 130 (7.2), 129 (13), 116 (8), 115 (80), 103 (12), 73 (100). Found: C, 62.67; H, 11.93%. Calcd for $C_9H_{20}OSi$: C, 62.72; H, 11.70%.

***trans*-4-Methyl-3-[(trimethylsilyl)methyl]tetrahydrofuran (*trans*-5c):** Bp 88—92 °C (30 Torr, bath temp); IR (neat) 2952, 2918, 2892, 2866, 1249, 1044, 925, 859, 839, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.00 (s, 9H), 0.38 (dd, J=14.6, 10.4 Hz, 1H), 0.88 (dd, J=14.6, 3.4 Hz, 1H), 0.99 (d, J=6.4 Hz, 3H), 1.62—1.83 (m, 2H), 3.27 (t, J=8.1 Hz, 1H), 3.30 (t, J=8.0 Hz, 1H), 3.97 (dd, J=8.1, 7.2 Hz, 1H), 4.03 (dd, J=8.0, 7.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=−1.05, 15.26, 18.63, 43.28, 43.46, 74.67, 75.26; MS (20 eV) m/z (rel intensity) 158 (M^++1−Me, 1.2), 157 (M^+−Me, 10), 130 (7.0), 129 (12), 116 (5), 115 (47), 103 (15), 73 (100). Found: C, 62.78; H, 11.88%. Calcd for $C_9H_{20}OSi$: C, 62.72; H, 11.70%.

Synthesis of 5b and 5c by Hydrosilylation of 1,6-Heptadiene or Diallyl Ether with Cl_3SiH. Preparation of **5c** is representative. A benzene (20 mL) solution of di-*t*-butyl peroxide (0.73 g, 5.0 mmol), diallyl ether **1c** (0.98 g, 10 mmol), and Cl_3SiH (4.1 mL, 40 mmol) was heated at 140 °C in a sealed tube under argon atmosphere. After stirring for 8 h, the reaction mixture was cooled to room temperature and concentrated in vacuo. The residual oil was diluted with Et_2O (10 mL) under argon atmosphere. MeMgI (0.96 M Et_2O solution, 37 mL, 36 mmol) was added dropwise over 10 min to this solution at 0 °C. After addition of MeMgI, the mixture was stirred for 13 h at room temperature. The reaction mixture was poured into ice (50 g) and 1 M aqueous HCl (50 mL), and extracted with Et_2O (30 mL×2). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated, the residual oil was purified by silica-gel column (hexane/Et_2O=10/1) to give **5c** (0.64 g, *cis*/*trans*=1.7/1) in 37% yield. **5b** was also obtained by this procedure in 22% yield.

Dimethyl 8,8-Bis(trimethylsilyl)-8-silabicyclo-[4.3.0]nonane-3,3-dicarboxylate (7, Major Isomer): Bp 101—105 °C (0.29 Torr, bath temp); IR (neat) 2946, 1734, 1258, 1243, 1218, 1157, 1139, 836, 777, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.09 (s, 9H), 0.10 (s, 9H), 0.37—0.50 (m, 2H), 0.85—1.26 (m, 5H), 1.45 (dd, J=13.4, 11.1 Hz, 1H), 1.64 (td, J=13.5, 3.9 Hz, 1H), 1.93 (dm, J=13.1 Hz, 1H), 2.37 (dm, J=13.4 Hz, 1H), 2.58 (dt, J=13.3, 2.6 Hz, 1H), 3.70 (s, 3H), 3.73 (s, 3H); ^{13}C NMR ($CDCl_3$) δ=−0.90 (two carbons), 15.41, 15.73, 32.00, 32.65, 40.83, 43.15, 46.13, 52.33, 52.61, 55.91, 171.74, 173.14; MS (70 eV) m/z (rel intensity) 402 (M^++2, 1.9), 401 (M^++1, 4.4), 400 (M^+, 13), 163 (14), 149 (11), 133 (14), 119 (11), 117 (13), 73 (100). Found: C, 53.76; H, 9.08%. Calcd for $C_{18}H_{36}O_4Si_3$: C, 53.95; H, 9.05%.

Dimethyl 8,8-Bis(trimethylsilyl)-8-silabicyclo-[4.3.0]nonane-3,3-dicarboxylate (7, Minor Isomer): Bp 110—114 °C (0.40 Torr, bath temp); IR (neat) 2946, 1735, 1245, 1152, 834, 621 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.10 (s, 9H), 0.15 (s, 9H), 0.59 (dd, J=14.6, 2.0 Hz, 1H), 0.68 (dd, J=14.5, 6.6 Hz, 1H), 0.95 (dd, J=14.5, 12.0 Hz, 1H), 1.05 (dd, J=14.6, 5.9 Hz, 1H), 1.48—2.15 (m, 8H), 3.69 (s, 3H), 3.74 (s, 3H); ^{13}C NMR ($CDCl_3$) δ=−0.92, −0.41, 9.11, 14.67, 25.32, 26.59, 33.38, 37.83, 40.04, 52.33, 52.58, 55.30, 171.85, 173.07; MS (20 eV) m/z (rel intensity) 385 (M^+−Me, 2), 328 (M^++1−$SiMe_3$, 26), 327 (M^+−$SiMe_3$, 100), 163 (28). Found: C, 53.71; H, 9.29%. Calcd for $C_{18}H_{36}O_4Si_3$: C, 53.95; H, 9.05%.

4-[Tris(trimethylsilyl)silyl]butyl *p*-Toluenesulfonate. AIBN (0.14 g, 0.85 mmol) was added to a benzene (17 mL) solution of 3-butenyl *p*-toluenesulfonate (1.93 g, 8.53 mmol) and **2** (2.85 mL, 9.38 mmol) under argon atmosphere. The mixture was heated at reflux and stirred for 3 h. The reaction did not complete, then AIBN (0.14 g, 0.85 mmol) was added again. After stirring for another 2 h, the reaction mixture was cooled to room temperature and concentrated in vacuo. The crude product was purified by silica-gel column chromatography (hexane/AcOEt=10/1) to give the title compound (2.32 g, 57%): Mp 45.8—46.9 °C (Hexane); IR ($CDCl_3$) 2948, 1358, 1245, 1189, 1177, 927, 836, 814 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.13 (s, 27H), 0.65—0.71 (m, 2H), 1.33—1.44 (m, 2H), 1.63—1.72 (m, 2H), 2.45 (s, 3H), 4.03 (t, J=6.4 Hz, 2H), 7.32—7.36 (m, 2H), 7.77—7.81 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=1.09, 7.04, 21.64, 24.87, 32.93, 69.93, 127.84, 129.81, 133.15, 144.59; MS (20 eV) m/z (rel intensity) 403 (M^++2−$SiMe_3$, 11), 402 (M^++1−$SiMe_3$, 4.4), 401 (M^+−$SiMe_3$, 21), 347 (22), 346 (34), 345 (100), 287 (15). Found: C, 50.29; H, 9.13%. Calcd for $C_{20}H_{42}O_3Si_4S$: C, 50.58; H, 8.91%.

1-Iodo-4-[tris(trimethylsilyl)silyl]butane (10). A solution of 4-[tris(trimethylsilyl)silyl]butyl *p*-toluenesulfonate (2.32 g, 4.89 mmol), prepared as shown above, and NaI (2.19 g, 14.6 mmol) in acetone (15 mL) was stirred for 20 h at room temperature. Resulting white precipitate was filtered through Na_2SO_4, and the filtrate was concentrated in vacuo. The crude product was diluted with water (30 mL), and extracted with hexane (30 mL×2). The combined organic layer was dried over Na_2SO_4, followed by concentration and purification by silica-gel column (hexane) to give the title compounds (1.95 g, 93%): Bp 102—106 °C (0.48 Torr, bath temp); IR (neat) 2944, 2888, 1257, 1244, 834, 686, 621 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.17 (s, 27H), 0.72—0.78 (m, 2H), 1.43—1.54 (m, 2H), 1.79—1.89 (m, 2H), 3.21 (t, J=6.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=1.15, 6.49, 6.95, 29.90, 37.36; MS (20 eV) m/z (rel intensity) 415 (M^+−Me, 1.2), 359 (M^++2−$SiMe_3$, 26), 358 (M^++1−$SiMe_3$, 19), 357 (M^+−$SiMe_3$, 69), 303 (13), 302 (27), 301 (100). Found: C, 36.11; H, 8.34%. Calcd for $C_{13}H_{35}Si_4I$: C, 36.26; H, 8.19%.

The Reaction of 10 with TTMSS. AIBN (0.10 M benzene solution, 2.0 mL, 0.20 mmol) was added to a benzene (100 mL) solution of **10** (0.861 g, 2.00 mmol) and **2** (0.547 g, 2.20 mmol) at 80—85 °C. After stirring for 2 h, MeI (0.32 mL, 5.0 mmol) and AIBN (0.20 mmol) were added to the mixture. After stirring for another 2 h, the reaction mixture was cooled to room temperature and concentrated in vacuo. The residual oil was diluted with THF (5 mL) and treated with aqueous NaOH (3 M, 2.0 mL) for 10 min. The mixture was poured into saturated aqueous NH_4Cl (30 mL), and extracted with hexane (30 mL×2). The combined organic layer was dried over Na_2SO_4, followed by concentration and purification by silica-gel column (hexane) to give a mixture (0.504 g, **11**/**12**=1/2.3) of **11** (27%) and **12** (62%). Analytical pure sample of **11** or **12** was obtained by preparative GLPC.

1,1-Bis(trimethylsilyl)-1-silacyclopentane (11): Bp 68—72 °C (10 Torr, bath temp); IR (neat) 2944, 2890, 2848, 1244, 856, 833, 776, 687, 651, 620 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.10 (s, 18H), 0.74—0.81 (m, 4H), 1.51—1.58 (m, 4H); ^{13}C NMR ($CDCl_3$) δ=−0.87, 8.02, 29.44; MS (70 eV) m/z (rel intensity) 232 (M^++2, 1.7), 231 (M^++1, 3.9), 230 (M^+, 13), 157 (M^+−$SiMe_3$, 28), 142 (11), 129 (18), 117 (19), 103 (10), 73 (100). Found: C, 52.01; H, 11.63%. Calcd for $C_{10}H_{26}Si_3$: C, 52.09; H, 11.37%.

1-[Tris(trimethylsilyl)silyl]butane (12): Bp 74—78 °C (0.70 Torr, bath temp); IR (neat) 2950, 2920, 2890, 1244, 831, 685, 621 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.15 (s, 27H), 0.73—0.79 (m, 2H), 0.88 (t, J=7.2 Hz, 3H), 1.26—1.43 (m, 4H); ^{13}C NMR ($CDCl_3$) δ=1.17, 7.17, 13.67, 27.14, 31.45; MS (70 eV) m/z (rel intensity) 306 (M^++2, 2.1), 305 (M^++1, 3.8), 304 (M^+, 11), 176 (12), 175 (58), 174 (11), 173 (11), 160 (30), 131 (12), 117 (14), 73 (100). Found: C, 51.04; H, 12.16%. Calcd for $C_{13}H_{36}Si_4$: C, 51.23; H, 11.91%.

Dimethyl 3,3-Bis(trimethylsilyl)-3-silabicyclo-[3.3.0]oct-1-ene-7,7-dicarboxylate (14): Bp 95—100 °C (0.28 Torr, bath temp); IR (neat) 2948, 1737, 1435,

1274, 1245, 1198, 1163, 836 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.09 (s, 9H), 0.10 (s, 9H), 0.71 (dd, J=13.8, 8.9 Hz, 1H), 1.19 (dd, J=13.8, 7.5 Hz, 1H), 1.67 (dd, J=12.4, 12.1 Hz, 1H), 2.60 (dd, J=12.4, 7.5 Hz, 1H), 2.86 (dm, J=17.6 Hz, 1H), 2.94—3.03 (m, 1H), 3.01 (dm, J=17.6 Hz, 1H), 3.72 (s, 3H), 3.74 (s, 3H), 5.40—5.43 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=−1.05, −0.62, 13.70, 37.27, 42.31, 50.99, 52.72, 61.10, 116.20, 166.55, 172.33, 172.85; MS (20 eV) m/z (rel intensity) 386 (M^++2, 2.6), 385 (M^++1, 5.0), 384 (M^+, 17), 369 (39), 311 (75), 225 (94), 167 (35), 135 (37), 105 (30), 89 (100), 73 (63). Found: C, 53.07; H, 8.18%. Calcd for $C_{17}H_{32}O_4Si_3$: C, 53.08; H, 8.38%.

Dimethyl (*E*)-4-Methyl-3-[tris(trimethylsilyl)silylmethylene]cyclopentane-1,1-dicarboxylate (15): Bp 110—114 °C (0.40 Torr, bath temp); IR (neat) 2950, 2890, 1739, 1436, 1246, 1202, 1166, 1139, 835, 684, 621 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.18 (s, 27H), 1.08 (d, J=6.4 Hz, 3H), 1.66—1.76 (m, 1H), 2.52—2.61 (m, 2H), 2.90 (dt, J=17.2, 2.5 Hz, 1H), 3.04 (dm, J=17.2 Hz, 1H), 3.72 (s, 3H), 3.73 (s, 3H), 5.30 (q, J=2.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ= 1.13, 18.55, 40.10, 42.19 (two carbons), 52.69 (two carbons), 58.89, 110.33, 162.06, 172.35 (two carbons); MS (20 eV) m/z (rel intensity) 445 (M^++2−Me, 3.3), 444 (M^++1−Me, 6.5), 443 (M^+−Me, 16), 427 (17), 387 (M^++2−$SiMe_3$, 15), 386 (M^++1−$SiMe_3$, 33), 385 (M^+−$SiMe_3$, 100), 281 (36), 206 (10), 205 (45), 163 (11), 147 (18), 117 (20). Found: C, 52.10; H, 8.97%. Calcd for $C_{20}H_{42}O_4Si_4$: C, 52.35; H, 9.23%.

Dimethyl 3-[Tris(trimethylsilyl)silylmethylene]cyclohexane-1,1-dicarboxylate (16, Major Isomer): Bp 114—118 °C (0.47 Torr, bath temp); IR (neat) 2948, 2888, 1736, 1435, 1245, 1201, 834, 684, 620 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.15 (s, 27H), 1.63—1.74 (m, 2H), 2.04—2.09 (m, 2H), 2.13—2.19 (m, 2H), 2.78 (s, 2H), 3.69 (s, 6H), 5.26 (s, 1H); ^{13}C NMR ($CDCl_3$) δ=1.09, 24.25, 31.19, 34.43, 44.58, 52.51, 57.27, 116.45, 152.62, 171.56; MS (20 eV) m/z (rel intensity) 459 (M^++1, 2.2), 458 (M^+, 2.9), 457 (M^+−1, 5.1), 386 (M^++1−$SiMe_3$, 14), 385 (M^+−$SiMe_3$, 45), 333 (11), 332 (27), 331 (100), 263 (10), 205 (35), 163 (12), 147 (16), 121 (12). Found: C, 52.08; H, 9.29%. Calcd for $C_{20}H_{42}O_4Si_4$: C, 52.35; H, 9.23%.

Dimethyl 3-[Tris(trimethylsilyl)silylmethylene]cyclohexane-1,1-dicarboxylate (16, Minor Isomer): Bp 117—121 °C (0.35 Torr, bath temp); IR ($CDCl_3$) 2948, 1731, 1246, 837 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.19 (s, 27H), 1.54—1.62 (m, 2H), 2.03—2.08 (m, 2H), 2.23—2.29 (m, 2H), 2.69 (d, J=0.9 Hz, 2H), 3.70 (s, 6H), 5.25—5.27 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=1.28, 22.76, 30.93, 38.18, 39.31, 52.41, 55.55, 116.86, 150.91, 171.72; MS (20 eV) m/z (rel intensity) 459 (M^++1, 2.6), 458 (M^+, 4.3), 457 (M^+−1, 9.3), 443 (M^+−Me, 10), 386 (27), 385 (73), 332 (26), 331 (100), 205 (60), 163 (26), 147 (31), 131 (25), 117 (25), 73 (56). Found: C, 52.15; H, 9.39%. Calcd for $C_{20}H_{42}O_4Si_4$: C, 52.35; H, 9.23%.

Dimethyl 2-Butyl-3,3-bis(trimethylsilyl)-3-silabicyclo[3.3.0]oct-1-ene-7,7-dicarboxylate (18): Bp 111—116 °C (0.18 Torr, bath temp); IR (neat) 2950, 2890, 1737, 1435, 1273, 1245, 1199, 1168, 1152, 836 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.11 (s, 18H), 0.68 (dd, J=13.6, 9.1 Hz, 1H), 0.85—0.94 (m, 3H), 1.14 (dd, J=13.6, 7.1 Hz, 1H), 1.19—1.40 (m, 4H), 1.62 (dd, J=12.6, 12.1 Hz, 1H), 2.02—2.18 (m, 2H), 2.55 (dd, J=12.6, 7.1 Hz, 1H), 2.84 (s, 2H), 2.86—3.01 (m, 1H), 3.72 (s, 3H), 3.74 (s, 3H); ^{13}C NMR ($CDCl_3$) δ=−0.80, −0.21, 13.66, 13.96, 22.93, 31.02, 33.03, 34.38, 42.58, 50.19, 52.71, 52.77, 61.25, 132.43, 157.10, 172.54, 172.90; MS (20 eV) m/z (rel intensity 425 (M^+−Me, 5.4), 368 (M^++1−$SiMe_3$, 15), 367 (M^+−$SiMe_3$, 51), 207 (13), 191 (18), 179 (18), 163 (21), 149 (28), 133 (13), 105 (21), 89 (100). Found: C, 57.05; H, 9.38%. Calcd for $C_{21}H_{40}O_4Si_3$: C, 57.22; H, 9.15%.

Dimethyl 3-Isopropyl-4-[tris(trimethylsilyl)silylmethylene]cyclopentane-1, 1-dicarboxylate (20a): Bp 118—122 °C (0.26 Torr, bath temp); IR (neat) 2950, 2890, 1739, 1245, 1202, 1161, 834, 685, 622 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.18 (s, 27H), 0.77 (d, J=6.7 Hz, 3H), 0.94 (d, J=6.9 Hz, 3H), 1.80 (dd, J=12.7, 10.9 Hz, 1H), 1.91—2.02 (m, 1H), 2.43 (ddd, J=12.7, 7.7, 1.7 Hz, 1H), 2.57—2.67 (m, 1H), 2.82 (dt, J=16.6, 2.7 Hz, 1H), 2.97 (dm, J=16.6 Hz, 1H), 3.70 (s, 3H), 3.74 (s, 3H), 5.30—5.33 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=1.18, 16.13, 21.28, 30.00, 34.09, 43.47, 51.19, 52.61, 52.66, 58.58, 111.54, 159.66, 172.10, 172.34; MS (20 eV) m/z (rel intensity) 472 (M^++1−Me, 12), 471 (M^+−Me, 25), 456 (M^++1−OMe, 7.4), 455 (M^+−OMe, 12), 415 (M^++2−$SiMe_3$, 21), 414 (M^++1−$SiMe_3$, 40), 413 (M^+−$SiMe_3$, 100), 309 (11), 205 (27). Found: C, 53.97; H, 9.68%. Calcd for $C_{22}H_{46}O_4Si_4$: C, 54.27; H, 9.52%.

3-Isopropyl-4-[tris(trimethylsilyl)silylmethylene]-tetrahydrofuran (20b): Bp 105—109 °C (0.55 Torr, bath temp); IR (neat) 2950, 2890, 1245, 1067, 828, 685, 620 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.19 (s, 27H), 0.87 (d, J=6.8 Hz, 3H), 0.95 (d, J=6.9 Hz, 3H), 1.80—1.93 (m, 1H), 2.51—2.58 (m, 1H), 3.79 (dd, J=8.8, 4.8 Hz, 1H), 3.90 (dd, J=8.8, 7.0 Hz, 1H), 4.20 (dd, J=2.4, 1.3 Hz, 2H), 5.45 (td, J=2.4, 1.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=1.15, 18.12, 20.97, 30.63, 53.19, 70.53, 73.10, 110.24, 159.92; MS (20 eV) m/z (rel intensity) 300 (M^++1−$SiMe_3$, 4.3), 299 (M^+−$SiMe_3$, 9.6), 229 (17), 213 (20), 157 (15), 147 (47), 133 (68), 131 (26), 127 (23), 117 (24), 73 (100). Found: C, 54.75; H, 10.94%. Calcd for $C_{17}H_{40}Si_4$: C, 54.76; H, 10.81%.

Dimethyl 2-[3-Tris(trimethylsilyl)silyl-2-propenyl]malonate (27). Method D: Under argon atmosphere, a benzene (28 mL) solution of dimethyl 2-propargylmalonate (**26**) (2.38 g, 14.0 mmol), **2** (3.98 g, 16.0 mmol), and AIBN (0.230 g, 1.40 mmol) was heated at reflux for 2 h. The reaction mixture was cooled to room temperature, and concentrated in vacuo. The residual oil was purified by silica-gel column (hexane/AcOEt=10/1) to give the title compound (5.52 g, 94%, E/Z=5/4). (*E*)-isomer: Bp 99—103 °C (0.42 Torr, bath temp); IR (neat) 2948, 2890, 1757, 1741, 1437, 1245, 1222, 1151, 836, 686, 622 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.15 (s, 27H), 2.70 (ddd, J=7.6, 6.4, 1.3 Hz, 2H), 3.47 (t, J=7.7 Hz, 1H), 3.73 (s, 6H), 5.69 (dt, J=18.1, 1.3 Hz, 1H), 5.92 (dt, J=18.1, 6.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=0.70, 36.31, 51.63, 52.51, 125.71, 143.00, 169.30; MS (20 eV) m/z (rel intensity) 404 (M^++1−Me, 1.7), 403 (M^+−Me, 4.1), 347 (M^++2−$SiMe_3$, 6.9), 346 (M^++1−$SiMe_3$, 16), 345 (M^+−$SiMe_3$, 49), 307 (14), 306 (27), 305 (100), 205 (18), 189 (13). Found: C, 48.56; H, 9.23%. Calcd for $C_{17}H_{38}O_4Si_4$: C, 48.75; H, 9.14%. (*Z*)-isomer: Bp 115—120 °C (0.55 Torr, bath temp); IR (neat) 2948, 2890, 1757, 1741, 1437, 1339, 1245, 1153, 835, 686, 620 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.19 (s, 27H), 2.70 (ddd, J=7.9, 6.7, 1.6 Hz, 2H), 3.41 (t, J=7.9 Hz, 1H), 3.75 (s, 6H), 5.69 (dt, J=13.1, 1.6 Hz, 1H), 6.26 (dt, J=13.1, 6.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=1.01, 33.96, 51.49, 52.55, 124.88, 142.99, 169.31; MS (20

eV) m/z (rel intensity) 404 (M^++1−Me, 1.1), 403 (M^+−Me, 2.7), 347 (M^++2−$SiMe_3$, 12), 346 (M^++1−$SiMe_3$, 28), 345 (M^+−$SiMe_3$, 100), 306 (21), 305 (80), 205 (41), 189 (20), 147 (21), 117 (33), 73 (58). Found: C, 48.76; H, 9.39%. Calcd for $C_{17}H_{38}O_4Si_4$: C, 48.75; H, 9.14%.

Dimethyl 2-Propargyl-2-[3-tris(trimethylsilyl)silyl-2-propenyl]malonate (28). A solution of alkenylsilane **27** (5.51 g, 13.2 mmol, E/Z=5/4) in THF (15 mL) was added to a suspension of NaH (0.348 g, 15.0 mmol) in THF (20 mL) at room temperature. After stirring for 0.5 h, propargyl bromide (1.72 g, 14.5 mmol) was introduced into the reaction mixture at 0 °C. After 5 min, the mixture was warmed to room temperature and stirred for 4 h. The resulting mixture was poured into water (40 mL), and extracted with AcOEt (50 mL×2). The combined organic layer was dried over Na_2SO_4, followed by concentration and purification by silica-gel column (hexane/AcOEt=10/1) to give **28** (5.18 g, 86%, E/Z=6/5). (*E*)-isomer: Bp 113—117 °C (0.42 Torr, bath temp); IR (neat) 2948, 2890, 1741, 1437, 1292, 1245, 1204, 836, 685, 622 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.16 (s, 27H), 2.02 (t, J=2.7 Hz, 1H), 2.78 (d, J=2.7 Hz, 2H), 2.84—2.91 (m, 2H), 3.74 (s, 6H), 5.69—5.84 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=0.74, 22.63, 40.05, 52.78, 56.76, 71.39, 78.76, 128.89, 140.54, 170.15; MS (20 eV) m/z (rel intensity) 419 (M^++2−C_3H_3, 5.6), 418 (M^++1−C_3H_3, 14), 417 (M^+−C_3H_3, 21), 385 (M^++2−$SiMe_3$, 21), 384 (M^++1−$SiMe_3$, 41), 383 (M^+−$SiMe_3$, 100), 343 (38), 205 (21), 147 (26), 131 (17), 117 (14), 73 (65). Found: C, 52.29; H, 8.53%. Calcd for $C_{20}H_{40}O_4Si_4$: C, 52.58; H, 8.82%. (*Z*)-isomer: Bp 116—120 °C (0.40 Torr, bath temp); IR (neat) 2948, 1740, 1437, 1292, 1246, 1208, 1184, 835, 686, 646, 621 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.21 (s, 27H), 2.00 (t, J=2.6 Hz, 1H), 2.86 (dd, J=5.9, 2.0 Hz, 2H), 2.88 (d, J=2.6 Hz, 2H), 3.74 (s, 6H), 5.74 (dt, J=13.5, 2.0 Hz, 1H), 6.20 (dt, J=13.5, 5.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=1.14, 23.41, 36.78, 52.79, 56.70, 71.67, 78.83, 126.19, 140.26, 170.31; MS (20 eV) m/z (rel intensity) 418 (M^++1−C_3H_3, 4.4), 417 (M^+−C_3H_3, 11), 385 (M^++2−$SiMe_3$, 16), 384 (M^++1−$SiMe_3$, 37), 383 (M^+−$SiMe_3$, 100), 343 (17), 205 (22), 147 (18), 131 (13), 117 (15). Found: C, 52.47; H, 8.55%. Calcd for $C_{20}H_{40}O_4Si_4$: C, 52.58; H, 8.82%.

Dimethyl (*E*)-3-(Tributylstannyl)methylene-4-[tris(trimethylsilyl)silylmethyl]cyclopentane-1,1-dicarboxylate (29). Cyclization of enyne **28** was performed following Method D by the use of n-Bu_3SnH instead of **2**. The reaction of enyne **28** (5.16 g, 11.3 mmol) with n-Bu_3SnH (3.96 g, 13.6 mmol) gave the title compound (4.80 g, 57%): Bp 150—165 °C (0.37 Torr, bath temp); IR (neat) 2950, 2922, 2870, 2850, 1739, 1246, 1165, 835, 685, 621 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.18 (s, 27H), 0.67 (dd, J=14.5, 10.5 Hz, 1H), 0.83—1.05 (m, 15H), 1.26—1.65 (m, 13H), 1.73 (dd, J=12.3, 11.4 Hz, 1H), 2.39—2.53 (m, 1H), 2.62—2.71 (m, 1H), 2.84 (dm, J=16.7 Hz, 1H), 3.02 (dm, J=16.7 Hz, 1H), 3.72 (s, 3H), 3.73 (s, 3H), 5.66 (tm, J=31.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=1.25, 9.77, 12.25, 13.72, 27.28, 29.17, 42.30, 42.98, 44.16, 52.69 (two carbons), 57.75, 117.26, 163.21, 172.16, 172.30; Found: C, 51.32; H, 9.28%. Calcd for $C_{32}H_{68}O_4Si_4Sn$: C, 51.39; H, 9.16%.

Dimethyl (*E*)-3-(Bromomethylene)-4-[tris(trimethylsilyl)silylmethyl]cyclopentane-1,1-dicarboxylate (30). Bromine (0.88 M CH_2Cl_2 solution, 1.20 ml, 1.06 mmol) was added dropwise over 5 min to a solution of vinylstannane **29** (0.748 g, 1.00 mmol) in CH_2Cl_2 (10 mL) at −78 °C. After stirring for 25 min, the reaction mixture was warmed to 0 °C and stirred for 5 min. Aqueous $Na_2S_2O_3$ (10 wt%, 0.2 mL) was added to the mixture to destroy an excess of Br_2. After the color of Br_2 disappeared, the mixture was warmed to room temperature. The resulting mixture was treated with saturated aqueous KF (2 mL), and anhydrous KF (1.0 g) for 5 h. White precipitate was removed by filtration through anhydrous Na_2SO_4, and the filtrate was concentrated in vacuo. The crude product was purified by silica-gel column (hexane/AcOEt=10/1) to give vinyl bromide **30** (0.441 g, 82%): Bp 134—138 °C (0.28 Torr, bath temp); IR (neat) 2946, 2888, 1738, 1435, 1297, 1246, 1198, 1167, 836, 688, 622 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.18 (s, 27H), 0.76 (dd, J=14.3, 10.8 Hz, 1H), 1.29 (dd, J=14.3, 3.3 Hz, 1H), 1.83 (t, J=12.2 Hz, 1H), 2.48—2.61 (m, 1H), 2.69 (ddd, J=12.4, 6.8, 1.6 Hz, 1H), 2.88 (dt, J=18.3, 2.6 Hz, 1H), 3.17 (dm, J=18.3 Hz, 1H), 3.73 (s, 3H), 3.75 (s, 3H), 5.94 (q, J=2.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=1.20, 11.43, 40.69, 43.05, 43.44, 52.89 (two carbons), 57.26, 99.63, 151.14, 171.61, 171.72. MS (20 eV) m/z (rel intensity) 466 (M^++3−$SiMe_3$, 38), 465 (M^++2−$SiMe_3$, 100), 464 (M^++1−$SiMe_3$, 32), 463 (M^+−$SiMe_3$, 82), 205 (31), 89 (51), 73 (66). Found: C, 44.40; H, 7.61%. Calcd for $C_{20}H_{41}O_4Si_4Br$: C, 44.67; H, 7.68%.

The Reaction of 30 with TTMSS. According to Method B, a benzene (8.2 mL) solution of vinyl bromide **30** (0.441 g, 0.820 mmol) was treated with **2** (0.224 g, 0.900 mmol) in the presence of AIBN (0.10 M benzene solution, 0.82 mL×5, 0.410 mmol) to give silabicyclo product **14** (0.237 g, 75%).

Dimethyl 3-Methylene-4-[tris(trimethylsilyl)silymethyl]cyclopentane-1,1-dicarboxylate (31). Vinylstannane **29** (0.374 g, 0.500 mmol) was treated with aqueous HCl (1.0 M, 1.0 mL, 1.0 mmol) in acetonitrile (5.0 mL) at room temperature for 3 h. The reaction mixture was poured into saturated aqueous $NaHCO_3$ (30 mL), and extracted with AcOEt (30 mL×2). The organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residual oil was diluted with CH_2Cl_2 (5 mL) and treated with KF as shown in the synthesis of **30**. The resulting precipitate was filtered, then the filtrate was concentrated in vacuo. The crude product was purified by silica-gel column (hexane/AcOEt=10/1) to provide the title compound: Bp 125—129 °C (0.45 Torr, bath temp); IR (neat) 2946, 2890, 1738, 1435, 1277, 1246, 1212, 1198, 1167, 834, 685, 622 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.18 (s, 27H), 0.71 (dd, J=14.5, 10.8 Hz, 1H), 1.33 (dd, J=14.5, 3.1 Hz, 1H), 1.74 (dd, J=12.3, 11.5 Hz, 1H), 2.40—2.55 (m, 1H), 2.63 (ddd, J=12.6, 7.2, 1.2 Hz, 1H), 2.90 (dq, J=16.9, 2.2 Hz, 1H), 3.10 (dm, J=16.9 Hz, 1H), 3.72 (s, 3H), 3.73 (s, 3H), 4.85 (q, J=2.3 Hz, 1H), 4.94 (q, J=2.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=1.23, 11.88, 40.31, 41.85, 42.88, 52.74 (two carbons), 57.73, 105.80, 154.38, 172.19 (two carbons); MS (20 eV) m/z (rel intensity) 445 (M^++2−Me, 0.8), 444 (M^++1−Me, 1.8), 443 (M^+−Me, 4.7), 387 (M^++2−$SiMe_3$, 16), 386 (M^++1−$SiMe_3$, 31), 385 (M^+−$SiMe_3$, 100), 206 (11), 205 (54), 175 (12), 173 (13), 113 (17). Found: C, 52.08; H, 9.01%. Calcd for $C_{20}H_{42}O_4Si_4$: C, 52.35; H, 9.23%.

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