[2 + 1] and [2 + 2] Cycloaddition Reaction of 1-Seleno-2-silylethenes to Methylenemalonate Esters: A Novel Ring Contraction of Cyclobutane to Cyclopropane

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Reaction of (*E*)-1-(phenylseleno)-2-silylethenes **1a–c** and methylenemalonate esters **2a,b** with Lewis acids ($TiCl_4$–$^1/_2Ti(O^iPr)_4$, $BF_3{\cdot}Et_2O$, $SnCl_2$ and $ZnBr_2$) gave [2 + 2] cycloadducts in addition to [2 + 1] cycloadducts. This is a novel mode of reactivity for 1-seleno-2-silylethenes. [2 + 1] and [2 + 2] cycloaddition can be controlled by Lewis acids, the substituents on silicon, temperature, and time. A novel rearrangement of cyclobutane to cyclopropane in the presence of $ZnBr_2$ under reversible conditions was also discovered. The stereochemistry of the cyclopropane products was elucidated by NMR.

Introduction

Application of 1,2-cationic silicon migration in organic synthesis has been extensively studied.[1] To understand the factors involved in control of 1,2-silicon migration *versus* nonmigration is of synthetic and mechanistic interest. For example, Lewis acid–mediated [3 + 2] cycloaddition involving 1,2-silicon shift or [2 + 2] cycloaddition of allylsilanes to α,β-unsaturated carbonyl compounds has recently been studied in detail.[2] Reaction temperature has been shown to be a factor to control silicon migration or nonmigration in the case of reaction of allylsilane and α,β-unsaturated bicyclic lactams.[2a] We have recently reported a novel [2 + 1] cycloaddition synthesis of cyclopropanes by the combination of (*E*)-1-(phenylseleno)-2-silylethenes (**1**) and vinyl ketones in the presence of $SnCl_4$.[3] This novel [2 + 1] cyclopropanation involves a 1,2-silicon migration and has much potential in organic synthesis. Previously the electrophilic olefins used as substrates were limited to vinyl ketones. In the course of examining Lewis acid-mediated addition of 1-seleno-2-silylethenes to various α,β-unsaturated carbonyl compounds, it was found that reaction of **1** and methylenemalonate esters **2** gave [2 + 1] and [2 + 2] cycloadducts depending on Lewis acids, silicon substituents, reaction temperature, and time.

Results and Discussion

[2 + 1] and [2 + 2] Cycloaddition. Di-*tert*-butyl methylenemalonate (**2a**) is a reactive Michael acceptor and its utilization in Lewis acid mediated reactions has been reported.[4] Reaction of **1a–c** with **2a** using $TiCl_4$–$^1/_2Ti(O^iPr)_4$,[5] $BF_3{\cdot}Et_2O$, $SnCl_2$, and $ZnBr_2$ gave [2 + 1] and [2 + 2] cycloadducts in various proportions (eq 1). Table 1 summarizes the results of [2 + 1] and [2 + 2] cycloaddition of **1** and **2**. The use of $BF_3{\cdot}Et_2O$, $SnCl_2$, and $ZnBr_2$ as Lewis acid does not afford reaction at −78 °C, so temperature was increased to −48 °C to −20 °C.[6] Reaction of **1a** and **1b** in the presence of $TiCl_4$–$^1/_2Ti(O^iPr)_4$ or $BF_3{\cdot}Et_2O$ gave [2 + 1] cycloadducts **3a,b** and [2 + 2] cycloadducts **4a,b** in a 90:10–95:5 ratio in 13–48% yield along with byproducts **5** and **6** (entries 1–3 and 5–6). Thus, $TiCl_4$–$^1/_2Ti(O^iPr)_4$ and $BF_3{\cdot}Et_2O$ favor [2 + 1] cycloaddition over [2 + 2] cycloaddition. The reaction of **1a** and **1b** at −30 °C in the presence of $ZnBr_2$ gave [2 + 1] and [2 + 2] cycloadducts with low selectivity but in high yield. For **1a** no obvious change in the [2 + 1] *vs* [2 + 2] ratio was observed under the conditions examined; however, for **1b** the [2 + 1] *vs* [2 + 2] ratio changed in the range from 45:55 to 85:15 under these conditions (entries 10–12, 13–17). Reaction of (*E*)-1-(phenylseleno)-2-(triisopropylsilyl)ethene (**1c**) with $BF_3{\cdot}Et_2O$ at −30 °C gave only [2 + 2] cycloadduct **4c** in 59% yield (entry 4). Lower yields of similar product mixtures were obtained with the unstable dimethyl methylenemalonate (see entries 19 and 20).

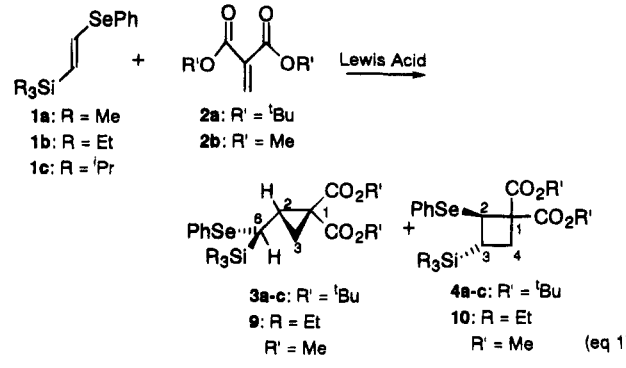

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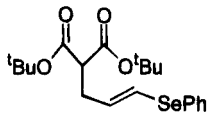
Table 1. [2 + 1] and [2 + 2] Cycloaddition of 1 and 2[a]

entry	selenoolefin	methylene malonate	Lewis Acid[b] (equiv)	T °C (time)	3:4/9:10, ratio[c]	3 + 4/9 + 10, % yield	recovered 1, % yield	byproduct (% yield)
1	1a	2a	A (1.4)	−78 (3 h)	90:10	17	41	d **6** (31)
2	1b	2a	A (1.4)	−78 (3 h)	90:10	48	27	d,e
3	1b	2a	A (1.4)	−78 (7 min)	90:10	32	34	d **6** (10)
4	1c	2a	A (1.4)	−78 (3 h)	50:50	57		
5	1a	2a	B (1.5)	−20 (3 h)	95:5	13		**5** (27)
6	1b	2a	B (1.8)	−48 (6 h)	90:10	43		
7	1c	2a	B (1.5)	−30 (4 h)	0:100	59		
8	1a	2a	C (1.5)	−30 (3 h)	85:15	20	20	d
9	1b	2a	C (1.5)	−30 (4 h)	0:100	27		**5** (13)
10	1a	2a	D (1.5)	−30 (3 h)	55:45	88		
11	1a	2a	D (1.5)	−30 (1.5 h), 10 (10 min)	55:45	94		
12	1a	2a	D (1.5)	−30 (1.5 h), 10 (30 min)	55:45	89		
13	1b	2a	D (1.5)	−30 (3 h)	45:55	93		
14	1b	2a	D (1.5)	−30 (1 h), 0 (3 h)	65:35	85		
15	1b	2a	D (1.5)	−30 (1 h), 0 (15 h)	85:15	30		**5** (12)
16	1b	2a	D (1.5)	−30 (1.5 h), 10 (10 min)	65:35	91		
17	1b	2a	D (1.5)	−30 (1.5 h), +10 (30 min)	70:30	90		
18	1c	2a	D (1.5)	−30 (1.5 h), +10 (1.5 h)	20:80	54		
19	1b	2b	D (1.5)	−30 (1 h)	89:11	33		
20	1b	2b	D (1.5)	−78 (2 h)	80:20	16		

[a] All reactions were carried out in the presence of 0.9−2.0 mmol of **1**, 1.3 equiv of **2a**, and Lewis acid in ca. 0.4 M CH_2Cl_2 solution. [b] A: $TiCl_4-{}^1/_2Ti(O^iPr)_4$. B: $BF_3{\cdot}Et_2O$. C: $SnCl_2$. D: $ZnBr_2$. [c] **3:4** ratio was determined by ^1H NMR. **9:10** ratio was determined by isolated yields. [d] A small amount of **5** was produced, but not isolated. [e] A small amount of **6** was produced, but not isolated.

Reaction of **1a** and **1b** using other strong Lewis acids such as $SnCl_4$, $AlCl_3$, and $TiCl_4$-PPh_3[7] at −78 °C gave desilylated product **5** as the major product. Reaction with **1b** using TMSOTf and $Sn(OTf)_2$ gave complex mixtures mostly consisting of desilylated products.



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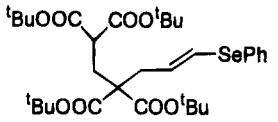

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From Table 1, three points are worth noting. First, a bulky silicon substituent (Si^iPr_3) tends to prefer cyclobutane formation. Second, $TiCl_4-{}^1/_2Ti(O^iPr)_4$ and $BF_3{\bullet}Et_2O$ tend to prefer cyclopropane formation in the case of **1a** and **1b**. Third, in the reaction of **1b** using $ZnBr_2$, cyclopropane, and cyclobutane formation is temperature and time dependent.

Ring Contraction of Cyclobutane to Cyclopropane. Since in the reaction of **1b** with **2a** and **2b** in the presence of $ZnBr_2$ a temperature and time dependency of cyclopropane and cyclobutane formation was observed, isomerization of cyclobutanes to cyclopropanes was examined. When the pure cyclobutane **4b** was treated with $ZnBr_2$ (1.5 equiv) in CH_2Cl_2 at −30 °C (1.5 h) and then +10 °C (30 min), a mixture of **3b** and **4b** (55:45) was obtained quantitatively (Table 2, entry 1). Change in the ratio of a mixture of **3b** and **4b** (90:10) under the same conditions was not detected within ^1H NMR accuracy level (entry 4). Treatment of **4b** with $ZnBr_2$ at −30 °C (1 h) and then +10 °C (1.5 h) gave a mixture of **3b:4b** (75:25) (entry 2). Longer reaction time decreased the total yield of **3b** and **4b**, and **1b** and desilylated product **5** were also produced (entry 3). Generation of **1b** is considered as a result of a retro-[2 + 2] cycloaddition process. The ratio of **3a** to **4a** increased slightly at +10 °C for 1.5 h (entry 6). When pure **4c** was treated with $ZnBr_2$ at +10 °C for 2 h, a small amount of **3c** was produced, in addition to **1c** and **2a** by retro-[2 + 2] cycloaddition (entry 7). **10** also produced **9** (24%) and **1b** (17%) along with a complex mixture (entry 8). Treatment of cyclopropane **9** gave recovered **9** (35%), a trace amount of **10**, and **1b** (12%) along with a complex mixture (entry 9). Ring contraction of cyclobutanes **4b** and **10** to cyclopropanes **3b** and **9** is apparently a favorable process under the conditions in Table 2. Such a ring contraction is novel and may well be synthetically useful. Detailed study of kinetics will help to optimize the cyclopropane

Table 2. Isomerization of Cyclobutanes 4 and 10 to Cyclopropanes 3 and 9[a]

entry	compound	T °C (time)	products	% yield
1	**4b**	−30 (1 h), 10 (30 min)[b]	**3b:4b** (55:45)	100
2	**4b**	−30 (1 h), 10 (1.5 h)[b]	**3b:4b** (75:25)	80
3	**4b**	10 (8 h)[b]	**3b:4b** (60:40)	36
			1b	10
			5	14
4	**3b:4b** (90:10)	-30 (1 h), 10 (30 min)[b]	no change	
5	**3a**	-30 (1 h), 10 (30 min)[b]	no change	
6	**3a:4a** (50:50)	10 (1.5 h)[b]	**3a:4a** (65:35)	92
7	**4c**	10 (2 h)[b]	**3c:4c** (20:80)	53
			1c	13
			2a	10
8	**10**	10 (45 min)[b]	**9**	24
			10 (trace, not isolated)	17
			1b	
9	**9**	10 (45 min)[c]	**9**	35
			10 (trace, not isolated)	
			1b	12

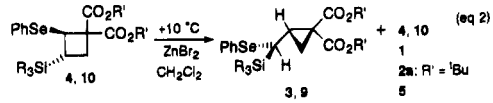
[a] All reactions were carried out in the presence of 0.07−0.2 mmol of **3/4**, **9**, or **10** and 1.5 equiv of $ZnBr_2$ in CH_2Cl_2 solution. [b] In 0.2 M CH_2Cl_2. [c] In 0.3 M CH_2Cl_2.

(5) $TiCl_4-{}^1/_2Ti(O^iPr)_4$ was prepared *in situ* by mixing $TiCl_4$ (1.4 equiv) and $Ti(O^iPr)_4$ (0.7 equiv) in CH_2Cl_2 at room temperature. Using $TiCl_2(O^iPr)_2$ (purchased from Tokyo Kasei) reaction of **1b** and **2a** did not occur at −78 °C.

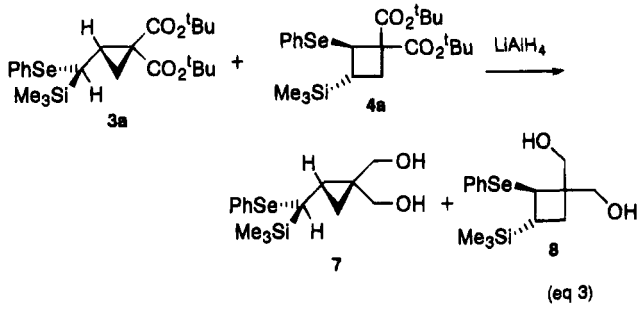
(6) All reactions in Table 1 were started at −78 °C.

(7) For use of $TiCl_4-PPh_3$, see: (a) Palazzi, C.; Colombo, L.; Gennari, C. *Tetrahedron, Lett.* **1986**, *27*, 1735. (b) Suzuki, I.; Yamamoto, Y. *J. Org. Chem.* **1993**, *58*, 4783. (c) Kadota, I.; Miura, K.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1994**, 1953.

formation and is now under way. A mixture of **3b** and **4b** (45:55) was also treated with $TiCl_4-{}^1/_2Ti(O^iPr)_4$ at −78 °C; however, it gave only desilylated product **5** in 69% yield.



Structure Assignment. Cyclopropanes **3b,c** and cyclobutanes **4b,c** can be separated by column chromatography or MPLC (SiO_2/cyclohexane−CH_2Cl_2). The structures of cyclopropanes and cyclobutanes are distinguished by NMR and IR spectra. $^1J_{CH}$ values (J = 158 Hz (C_2), 165 Hz (C_3)) in the ^{13}C NMR spectrum, which are characteristic of cyclopropanes, are evidence for structure **3b**. On the other hand, $^1J_{CH}$ values of the cyclobutane ring in **4b** are 126 (C_3), 141 (C_4), and 154 (C_2) Hz. The IR absorption of the ester carbonyl of **3a−c** appeared at 1715−1717 cm^{-1}; this is ca. 10 cm^{-1} lower field than the corresponding absorption of the cyclobutane derivatives (1725 cm^{-1} for **4b** and **4c**) due to conjugation with the cyclopropane ring. Pure **4a** was not isolated; however, the structure was confirmed by reduction of a mixture of **3a** and **4a** to the corresponding diols **7** and **8**, followed by separation of **7** and **8** and their structural assignment (eq 3). The trans stereochemistry of the phenylseleno and silyl groups in cyclobutanes **4b** and **4c** was determined by 2D-NOESY; that is, there was no NOE between H_2 and H_3 (see the numbering in eq 1).



Cyclopropanes **3a−c** and **9** are single stereoisomers. In our earlier work, the relative configuration at C_2 and C_6 of the cyclopropane products could not be determined (see the numbering in eq 1).[3] Determination of the configuration in these cyclopropanes was attempted as follows. In **3a−c**, **9**, and its derivative **7** the observed large vicinal coupling constants, $J_{2,6}$ (12.0−12.8 Hz) and steric considerations suggest that the favored dihedral angle $\angle H_2-C_2-C_6-H_6$ is close to 180°. 2D-NOESY of **3a**, **3b**, **9**, and **7** were examined. For **3a** and **3b**, because signals for the two t-Bu groups and cyclopropane-CH_2 partially overlapped, the observed NOEs did not give conclusive information. For **9** and **7**, NOEs were observed as shown in Figure 1 and 2 (all observed NOEs are in Experimental Section). In **9**, the existence of NOEs between $H_{3a,b}$ and H_{11}, H_{12} and those between H_4 and H_8, $H_{9,10}$ and the absence of NOEs between $H_{3a,b}$ and H_8, $H_{9,10}$ and those between H_4 and H_{11}, H_{12} suggest that the relative configuration is as shown in Figure 1. Similarly, NOE in **7** between H_{3a} and H_{11} and that between H_{4a} and H_8 suggest that the relative configuration is as shown in Figure 2. Thus, the stereochemistry of **9**, **7**, and **3a**, which is a precursor of **7**, in C_2 and C_6 were determined as (*R,R*) or (*S,S*).

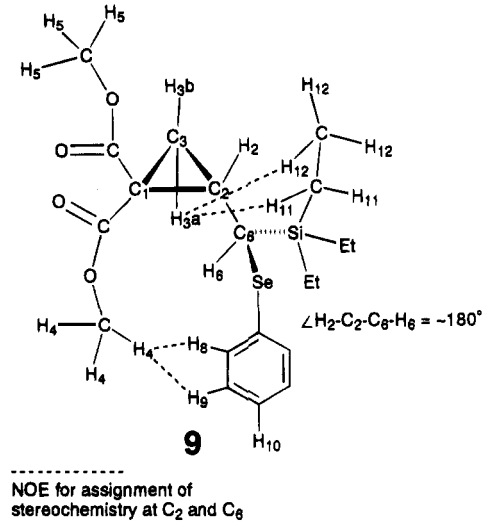


Figure 1.

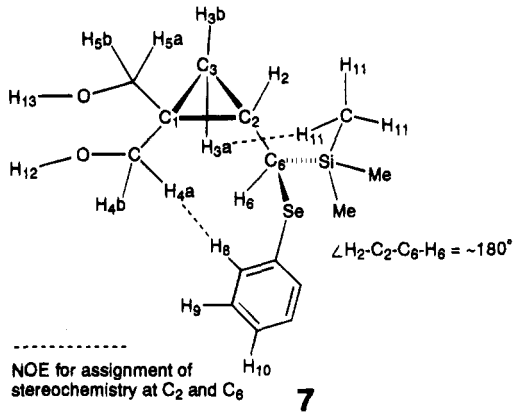
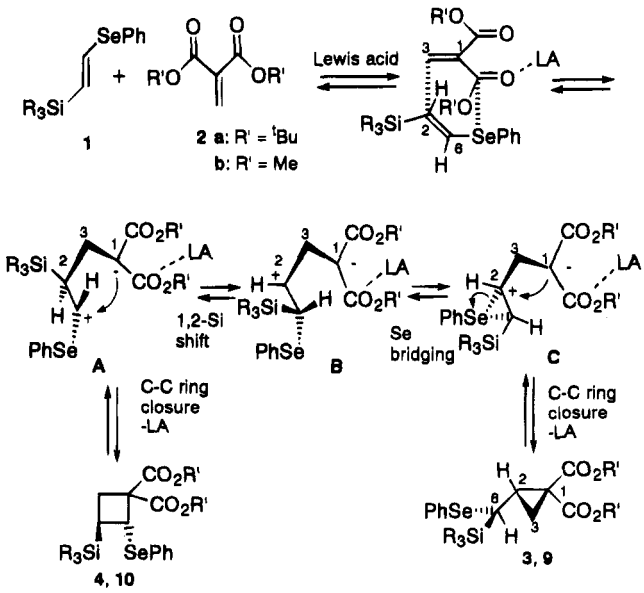


Figure 2.

Scheme 1



Reaction Mechanism. The mechanism of [2 + 1] and [2 + 2] cycloadditions is explained in a similar manner to that proposed for vinyl ketones (Scheme 1).[3a] The nucleophilic vinyl selenide **1** attacks the electrophilic olefin **2** activated by a Lewis acid to give zwitterion **A**. The initial complexation structure of **2** and a Lewis acid and the generated zwitterion **A** can be nonchelated or

chelated, depending on the Lewis acid. Ring closure of **A** gives cyclobutane **4** or **10**. Alternatively, **A** undergoes rearrangement (1,2-silicon shift) to give another β-silicon-stabilized intermediate **B**. The intermediate **B** could be transformed to the more electronically stable selenium-bridged intermediate **C**.[3a] In the reaction of **2a**, steric interaction between t-Bu groups and the Si group results in retardation of silicon migration. In the case of a weak Lewis acid such as $ZnBr_2$ under the higher temperature (~+10 °C), these processes are reversible.

The stereochemistry of **3a** and **9** in C_2 and C_6 were determined as (*R,R*) or (*S,S*) by NMR. **3a–c** and **9** were all single stereoisomers. Since it was assumed that the reactions proceed with the same stereochemical course, **3b** and **3c** also have the (*R,R*) or (*S,S*) configuration at C_2 and C_6. Thus, after synclinal stereoselective addition (due to a stabilizing secondary orbital interaction (Se···C=O)), as discussed in our previous paper,[3a] there should be minimum motion (*i.e.* dihedral angle rotation, ca. 60°) in the process leading to 1,2-silicon migration and the selenium-bridged intermediate. Finally ring closure by internal nucleophilic substitution at C_2 by C_1 in the intermediate **C** would give the observed stereoisomer.[8] In this process, single bond rotation (C_2–C_3) must be slower than cyclization. If the reaction proceeds *via* the different addition transition state such as shown in Scheme 2, which has no stabilization by Se···C=O interaction, it would finally give the opposite relative stereochemistry at C_2 and C_6, (*R,S*) or (*S,R*).

In summary, the Lewis acid-mediated cycloaddition of 1-seleno-2-silylethenes to methylenemalonate esters has been shown to give cyclopropane and cyclobutane derivatives. Generation of a four-membered ring has not been observed in the reaction of **1** and vinyl ketones. This is a novel mode of reactivity for 1-seleno-2-silylethenes. The [2 + 1] and [2 + 2] product ratio can be controlled by Lewis acid, silicon substituents, reaction temperature, and time. Also, a novel ring contraction of cyclobutane to cyclopropane was found. Further studies are underway in our laboratory to utilize the obtained cyclopropanes and cyclobutanes for synthesis of natural products.

Experimental Section

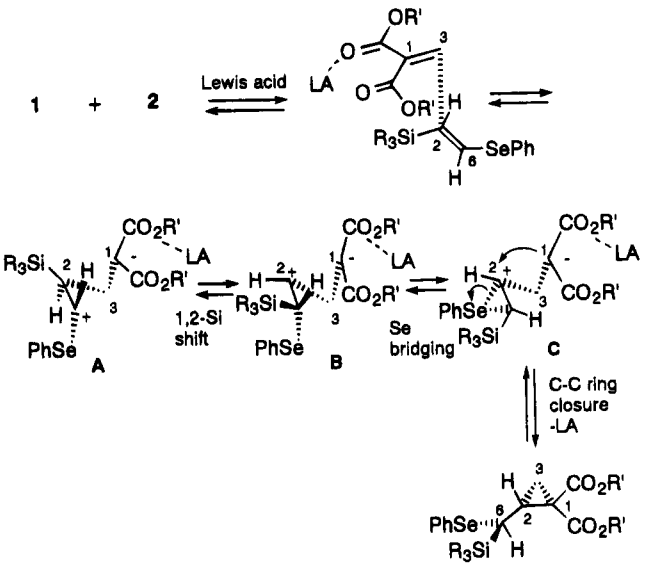
General Methods. Melting points are uncorrected. IR spectra were recorded in the FT-mode. ^1H NMR spectra were recorded in $CDCl_3$ at 200, 400, or 600 MHz. ^{13}C NMR spectra were recorded in $CDCl_3$ at 50.1 or 100.4 MHz. Chemical shifts are reported in ppm relative to Me_4Si or residual nondeuterated solvent. Mass spectra were recorded at an ionizing voltage of 70 eV by electron impact. All reactions were carried out under a nitrogen atmosphere.

A Typical Experimental Procedure Using $TiCl_4$–$^1/_2Ti(O^iPr)_4$ in Table 1 (entry 2). A typical experimental procedure in Table 1 (entries 1–4) is described for entry 2. To a solution of **1b** (333 mg, 1.12 mmol) in dichloromethane (0.5 mL), cooled to −78 °C, was added a solution of $TiCl_4$ (0.17 mL, 297 mg, 1.57 mmol) and $Ti(O^iPr)_4$ (0.23 mL, 225 mg, 0.79 mmol) in dichloromethane (2.0 mL), followed by **2a** (333 mg, 1.46 mmol). The mixture was stirred at −78 °C for 3 h. The reaction mixture was quenched by triethylamine (0.36 mL, 2.6 mmol), and then saturated aqueous $NaHCO_3$ was added to the mixture. The mixture was extracted with dichloromethane, and the organic phase was washed with saturated aqueous $NaHCO_3$ and water, dried (Na_2SO_4), and evaporated *in vacuo*. The residue was purified by column chromatography over silica gel eluting with hexane–ether (2:1) to give recovered **1b** (90 mg, 27%), a mixture of **3b** and **4b** (R_f = 0.6) (285 mg, 48%) (**3b**:**4b** = 90:10 by ^1H NMR), a mixture of recovered **2a** and **5** (93 mg) (R_f = 0.5), and a mixture containing **6** (48 mg) (R_f = 0.4).

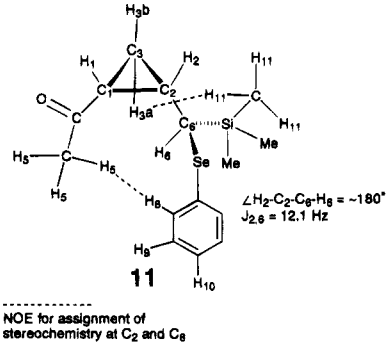
A Typical Experimental Procedure Using $ZnBr_2$ in Table 1 (entry 13). To a solution of **1b** (298 mg, 1.0 mmol) in dichloromethane (2.5 mL), cooled to −78 °C, was added $ZnBr_2$ (338 mg, 1.5 mmol), followed by **2a** (297 mg, 1.30 mmol). The mixture was allowed to warm to −30 °C and stirred for 3 h. The reaction mixture was quenched by triethylamine (0.32 mL, 2.3 mmol), and then saturated aqueous $NaHCO_3$ was added to the mixture. The mixture was extracted with dichloromethane, and the organic phase was washed with water, dried (Na_2SO_4), and evaporated *in vacuo*. The residue was purified by column chromatography over silica gel eluting with hexane–ether (2:1) to give a mixture of **3b** and **4b** (R_f = 0.6) (488 mg, 93%) (**3b**:**4b** = 45:55 by ^1H NMR). Pure **3b** and **4b** were isolated by column chromatography (silica-gel/cyclohexane–CH_2Cl_2 (1:1)) (**3b**: R_f = 0.46, **4b**: R_f = 0.50).

A Typical Experimental Procedure Using BF_3•Et_2O in Table 1 (entry 7). To a solution of **1c** (380 mg, 1.12 mmol) in dichloromethane (0.5 mL), cooled to −78 °C, was added dropwise a solution of BF_3•Et_2O (242 mg, 1.71 mmol) in dichloromethane (2.2 mL), followed by **2a** (333 mg, 1.46 mmol). The mixture was allowed to warm to −30 °C and stirred for 4 h. The reaction mixture was quenched by triethylamine (0.36 mL, 2.6 mmol), and then saturated aqueous $NaHCO_3$ was added to the mixture. The mixture was extracted with dichloromethane, and the organic phase was washed with saturated aqueous $NaHCO_3$ and water, dried (Na_2SO_4), and evaporated *in vacuo*. The residue was purified by column

Scheme 2



(8) In the previous paper, we predicted the stereochemistry at C_2 and C_6 in cyclopropane products as (*R,R*) or (*S,S*), essentially based on the mechanism addressed here in the text.[3a] However, the structure was not determined by spectral methods. We have undertaken a reexamination of the 2D-NOESY of the cyclopropyl ketone **11**, which appeared in reference 3a. NOE between H_5 and H_8 and that between H_{11} and H_{3a} are observed and a vicinal coupling constant, $J_{2,6}$ is large (12.1 Hz). The results clarified the stereochemistry of C_2 and C_6 as (*R,R*) or (*S,S*) for the cyclopropyl ketone **11** and is in good agreement with the mechanistic interpretation.



chromatography over silica gel eluting with hexane–ether (2:1) to give **4c** (R_f = 0.6) (377 mg, 59%).

Di-*tert*-butyl 2-[(phenylseleno)(trimethylsilyl)methyl]-cyclopropane-1,1-dicarboxylate (3a): R_f = 0.7 (hexane:ether = 2:1); pale yellow crystals; mp 87–88 °C (ethyl acetate); ^{1}H NMR (600 MHz, $CDCl_3$) δ −0.011 (s, 9H, Si(C*H*$_3$)$_3$), 1.43 (dd, J = 4.5, 9.1 Hz, 1H, H$_3$), 1.46 (s, 9H, C(C*H*$_3$)$_3$), 1.49 (s, 9H, C(C*H*$_3$)$_3$), 1.45–1.49 (m, 1H, H$_3$), 2.04 (ddd, J = 7.7, 9.1, 12.6 Hz, 1H, H$_2$), 2.30 (d, J = 12.6 Hz, 1H, C*H*SeSi), 7.18–7.22 (m, 3H, meta, para H of Ph), 7.58–7.60 (m, 2H, ortho H of Ph); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ −1.59 (q, J = 120 Hz, Si(*C*H$_3$)$_3$), 24.34 (t, J = 164 Hz, C$_3$), 27.26 (d, J = 125 Hz, *C*HSeSi), 28.10 (q, J = 126 Hz, C(*C*H$_3$)$_3$), 28.16 (q, J = 126 Hz, C(*C*H$_3$)$_3$), 30.06 (d, J = 157 Hz, C$_2$), 37.04 (s, C$_1$), 81.25 (s, *C*(CH$_3$)$_3$), 81.80 (s, *C*(CH$_3$)$_3$), 127.3 (d, J = 161 Hz, Ph), 128.8 (d, J = 161 Hz, Ph), 129.3 (s, Ph), 135.1 (d, J = 164 Hz, Ph), 168.0 (s, *C*O), 169.3 (s, *C*O); IR (neat) 3006, 2980, 2936, 1717, 1580, 1479, 1369, 1332, 1303, 1133, 837, 741, 692 cm^{-1}; MS (70 eV) m/z (relative intensity) 484 (30), 372 (43), 354 (28), 326 (8.7), 282 (11), 256 (33), 215 (91), 197 (100); exact mass M$^+$ 484.1511 (calcd for $C_{23}H_{36}O_4SeSi$ 484.1548). Anal. Calcd for $C_{23}H_{36}O_4SeSi$: C, 57.13; H, 7.50. Found: C, 56.64; H, 7.25. Because **3a** was crystallized from a mixture of **3a** and the oil **4a**, accurate analytical data (≤0.4%) could not be obtained probably due to retention of trace amounts of solvent or water; however, the purity was indicated by ^{1}H and ^{13}C NMR (see supporting information).

Di-*tert*-butyl 2-[(phenylseleno)(triethylsilyl)methyl]-cyclopropane-1,1-dicarboxylate (3b): (R_f = 0.6 (hexane:ether = 2:1), R_f = 0.46 (cyclohexane–CH_2Cl_2 = 1:1); colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.52–0.63 (m, 6H), 0.89 (t, J = 7.7 Hz, 9H), 1.44 (s, 9H), 1.48 (s, 9H), 1.40–1.53 (m, 2H), 2.04–2.18 (m, 1H), 2.45 (d, J = 12.5 Hz, 1H), 7.20–7.26 (m, 3H), 7.60–7.65 (m, 2H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ 3.40 (t, J = 117 Hz, *C*H$_2$CH$_3$), 7.64 (q, J = 125 Hz, CH$_2$*C*H$_3$), 24.28 (t, J = 165 Hz, C$_3$), 24.72 (d, J = 129 Hz, *C*HSeSi), 28.10 (q, J = 127 Hz, C(*C*H$_3$)$_3$), 28.16 (q, J = 127 Hz, C(*C*H$_3$)$_3$), 30.94 (d, J = 158 Hz, C$_2$), 37.36 (s, C$_1$), 81.13 (s, *C*(CH$_3$)$_3$), 81.68 (s, *C*(CH$_3$)$_3$), 127.4 (d, J = 160 Hz, Ph), 128.7 (d, J = 160 Hz, Ph), 129.3 (s, Ph), 135.4 (d, J = 164 Hz, Ph), 167.8 (s, *C*O), 169.2 (s, *C*O); IR (neat) 2978, 2958, 2878, 1715, 1479, 1369, 1332, 1303, 1174, 1133, 841, 739 cm^{-1}; MS (70 eV) m/z (relative intensity) 526 (6.5), 414 (4.3), 285 (4.3), 257 (20), 229 (93), 205 (8.7), 167 (26); exact mass M$^+$ 526.2047 (calcd for $C_{26}H_{42}O_4SeSi$ 526.2018).

Di-*tert*-butyl 2-[(phenylseleno)(triisopropylsilyl)-methyl]cyclopropane-1,1-dicarboxylate (3c): R_f = 0.6 (hexane:ether = 2:1), R_f = 0.3 (cyclohexane–CH_2Cl_2 = 1:1); colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.01–1.13 (m, 21H), 1.19–1.58 (m, 2H), 1.38 (s, 9H), 1.47 (s, 9H), 2.28 (ddd, J = 8.7, 8.7, 12.0 Hz, 1H), 2.92 (d, J = 12.0 Hz, 1H), 7.19–7.26 (m, 3H), 7.67–7.71 (m, 2H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) 12.40, 19.29, 24.16, 24.83, 28.16, 33.48, 37.54, 81.07, 81.63, 127.6, 128.7, 129.5, 135.9, 167.9, 169.3; IR (neat) 2946, 2868, 1715, 1458, 1369, 1330, 1303, 1174, 1133 cm^{-1}; MS (70 eV) m/z (relative intensity) 568 (4.7), 413 (28), 395 (6.5), 299 (12), 257 (62), 229 (100), 195 (42); exact mass M$^+$ 568.2459 (calcd for $C_{29}H_{48}O_4SeSi$ 568.2487).

Di-*tert*-butyl 2-(Phenylseleno)-3-(trimethylsilyl)cyclobutane-1,1-dicarboxylate (4a). 4a was obtained as a mixture with **3a** (R_f = 0.7 (hexane:ether = 2:1)): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.00 (s, 9H, Si(C*H*$_3$)$_3$), 1.39 (s, 9H, C(C*H*$_3$)$_3$), 1.48 (s, 9H, C(C*H*$_3$)$_3$), 1.81–2.13 (m, 2H, H$_{3,4}$), 2.76–2.92 (m, 1H, H$_4$), 4.54 (d-like, J = 10.3 Hz, 1H, H$_2$), 7.18–7.28 (m, 3H, meta, para H of Ph), 7.52–7.57 (m, 2H, ortho H of Ph).

Di-*tert*-butyl 2-(phenylseleno)-3-(triethylsilyl)cyclobutane-1,1-dicarboxylate (4b): R_f = 0.6 (hexane:ether = 2:1), R_f = 0.50 (cyclohexane–CH_2Cl_2 = 1:1); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.54 (q, J = 8.1 Hz, 6H, C*H*$_2$CH$_3$), 0.93 (t, J = 8.1 Hz, 9H, CH$_2$C*H*$_3$), 1.37 (s, 9H, C(C*H*$_3$)$_3$), 1.45 (s, 9H, C(C*H*$_3$)$_3$), 1.96–2.08 (m, 2H, H$_{3,4}$), 2.78–2.87 (m, 1H, H$_4$), 4.60 (d-like, J = 10.5 Hz, 1H, H$_2$), 7.13–7.23 (m, 3H, meta, para H of Ph), 7.51–7.54 (m, 2H, ortho H of Ph); NOEs were observed between δ 0.54 and δ 0.93, δ 0.54 and δ 1.96–2.08, δ 0.54 and δ 4.60, δ 1.96–2.08 and δ 2.78–2.87, and δ 4.60 and δ 7.51–7.54 by 2D NOESY; ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 2.12 (t, J = 116 Hz, *C*H$_2$CH$_3$), 7.49 (q, J = 123 Hz, CH$_2$*C*H$_3$), 23.06 (d, J = 126 Hz, C$_3$), 27.88 (q, J = 127 Hz, C(*C*H$_3$)$_3$), 27.96 (q, J = 127 Hz, C(*C*H$_3$)$_3$), 28.37 (t, J = 141 Hz, C$_4$), 40.93 (d, J = 154 Hz, C$_2$), 61.61 (s, C$_1$), 81.22 (s, *C*(CH$_3$)$_3$), 82.30 (s, *C*(CH$_3$)$_3$), 126.1 (dt, J = 161, 7 Hz, para C of Ph), 128.7 (dd, J = 160, 7 Hz, meta C of Ph), 131.3 (dd, J = 163, 7 Hz, ortho C of Ph), 132.9 (s, Ph), 168.6 (s, *C*O), 170.3 (s, *C*O). ^{1}H and ^{13}C assignments were determined by C–H COSY and NOESY; IR (neat) 2980, 2958, 2914, 2878, 1725, 1580, 1481, 1369, 1288, 1259, 1174, 1129, 1019, 847, 733 cm^{-1}; MS (70 eV) m/z (relative intensity) 526 (6), 453 (1), 414 (12), 396 (7), 367 (4), 257 (43), 239 (100); exact mass M$^+$ 526.2044 (calcd for $C_{26}H_{42}O_4SeSi$ 526.2018).

Di-*tert*-butyl 2-(phenylseleno)-3-(triisopropylsilyl)cyclobutane-1,1-dicarboxylate (4c): (R_f = 0.6 (hexane:ether = 2:1), R_f = 0.4 (cyclohexane–CH_2Cl_2 = 1:1)); pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05–1.11 (m, 21H, ^{i}Pr), 1.38 (s, 9H, C(C*H*$_3$)$_3$), 1.44 (s, 9H, C(C*H*$_3$)$_3$), 2.13–2.21 (m, 1H, H$_3$), 2.21–2.31 (m, 1H, H$_4$), 2.86–2.92 (m, 1H, H$_4$) 4.79 (d, J = 11.2 Hz, 1H, H$_2$), 7.13–7.23 (m, 3H, meta, para H of Ph), 7.52–7.55 (m, 2H, ortho H of Ph); NOEs were observed between δ 1.05–1.11 and δ 2.13–2.21, δ 1.05–1.11 and δ 2.21–2.31, δ 1.05–1.11 and δ 4.79, δ 2.13–2.21 and δ 2.86–2.92, δ 2.21–2.31 and δ 2.86–2.92, and δ 4.79 and δ 7.52–7.55 by 2D NOESY; ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 10.92 (d, J = 119 Hz, *C*H(CH$_3$)$_2$), 18.98 (q, J = 126 Hz, CH(*C*H$_3$)$_2$), 22.20 (d, J = 125 Hz, C$_3$), 27.83 (q, J = 127 Hz, C(*C*H$_3$)$_3$), 27.97 (q, J = 127 Hz, C(*C*H$_3$)$_3$), 29.66 (t, J = 141 Hz, C$_4$), 41.79 (d, J = 155 Hz, C$_2$), 62.09 (s, C$_1$), 81.24 (s, *C*(CH$_3$)$_3$), 82.35 (s, *C*(CH$_3$)$_3$), 126.0 (dt, J = 160, 7 Hz, para C of Ph), 128.7 (dd, J = 161, 7 Hz, meta C of Ph), 131.3 (dt, J = 164, 6 Hz, ortho C of Ph), 132.9 (s, Ph), 168.8 (s, *C*O), 170.4 (s, *C*O). ^{1}H and ^{13}C assignments were determined by C–H COSY and NOESY; IR (neat) 2944, 2868, 1725, 1580, 1369, 1288, 1259, 884, 849, 735 cm^{-1}; MS (70 eV) m/z (relative intensity) 568 (37), 495 (4.3), 456 (6.5), 413 (37), 395 (12), 299 (54), 255 (43), 229 (100); exact mass M$^+$ 568.2496 (calcd for $C_{29}H_{48}O_4SeSi$ 568.2486).

Reaction of 1a and 2a in the Presence of $SnCl_4$. To a solution of $SnCl_4$ (366 mg, 1.40 mmol) in dichloromethane (1.8 mL), cooled to −78 °C, was added **1a** (234 mg, 0.917 mmol) in dichloromethane (0.4 mL), followed by di-*tert*-butyl methylenemalonate (**2a**) (267 mg, 1.17 mmol). The mixture was stirred at −78 °C for 3 h. The reaction mixture was quenched by triethylamine (0.88 mL, 6.3 mmol) and then saturated aqueous $NaHCO_3$. The mixture was extracted with dichloromethane, and the organic phase was washed with saturated aqueous $NaHCO_3$ and water, dried (Na_2SO_4), and evaporated *in vacuo*. The residue was purified by column chromatography over silica gel eluting with hexane–ether (2:1) to give **5** (340 mg, 90%) (R_f = 0.5). **5**: colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.45 (s, 18H), 2.63 (dd, J = 7.5, 7.5 Hz, 2H), 3.24 (t, J = 7.5 Hz, 1H), 5.97 (td, J = 7.5, 15.1 Hz, 1H), 6.51 (d, J = 15.1 Hz, 1H), 7.24–7.30 (m, 3H), 7.43–7.47 (m, 2H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ 27.96, 33.33, 53.30, 81.68, 120.1, 127.1, 129.2, 130.3, 132.1, 133.8, 168.0; IR (neat) 2980, 1729, 1371, 1141, 735 cm^{-1}; MS (70 eV) m/z (relative intensity) 412 (29), 356 (34), 300 (88), 272 (28), 201 (100), 139 (60), 109 (49), 75 (32), 57 (100); exact mass M$^+$ 412.1160 (calcd for $C_{20}H_{28}O_4Se$ 412.1153).

6: R_f = 0.4 (hexane:ether = 2:1); colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.42 (s, 9H), 1.44 (s, 9H), 2.45 (d, J = 5.6 Hz, 2H), 2.57 (d, J = 7.5 Hz, 2H), 3.12 (t, J = 5.6 Hz, 1H), 5.92 (td, J = 7.5, 15.2 Hz, 1H), 6.48 (d, J = 15.2 Hz, 1H), 7.23–7.26 (m, 3H), 7.43–7.48 (m, 2H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ 27.99, 30.65, 37.80, 50.06, 57.92, 81.68, 81.92, 121.6, 127.1, 129.2, 130.3, 131.7, 132.3, 168.6, 169.7; IR (neat) 2980, 2936, 1729, 1580, 1479, 1458, 1394, 1371, 1296, 1255, 1151, 847 cm^{-1}; MS (70 eV) m/z (relative intensity) 640 (2), 528 (9), 511 (3), 472 (15), 416 (45), 259 (22), 203 (17), 176 (17), 57 (100); exact mass M$^+$ 640.2531 (calcd for $C_{32}H_{48}O_8Se$ 640.2514).

Reaction of 1b and 2b in the Presence of $ZnBr_2$ (Table 1, entry 19). To a solution of **1b** (297 mg, 1.0 mmol) in dichloromethane (2.4 mL), cooled to −78 °C, was added $ZnBr_2$ (338 mg, 1.5 mmol), followed by **2b** (141 mg, 1.30 mmol). The mixture was allowed to warm to −30 °C and stirred for 1 h. The reaction mixture was quenched by triethylamine (0.32 mL, 2.3 mmol), and then saturated aqueous $NaHCO_3$ was added

to the mixture. The mixture was extracted with dichloromethane and the organic phase was washed with water, dried (Na_2SO_4), and evaporated *in vacuo*. The residue was purified by column chromatography over silica gel eluting with hexane–ether (3:1) to give recovered **1b** (154 mg, 52%), **9** (129 mg, 29%) (R_f = 0.3), and **10** (16 mg, 4%) (R_f = 0.4). **Dimethyl 2-[(phenylseleno)(triethylsilyl)methyl]cyclopropane-1,1-dicarboxylate (9):** pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.679 (q, J = 7.9 Hz, 6H, H_{11}), 0.963 (t, J = 7.9 Hz, 9H, H_{12}), 1.60–1.64 (m, 2H, $H_{3a,b}$), 2.33 (ddd, J = 8.2, 9.2, 12.3 Hz, 1H, H_2), 2.56 (d, J = 12.3 Hz, 1H, H_6), 3.42 (s, 3H, H_4), 3.72 (s, 3H, H_5), 7.19–7.23 (m, 3H, $H_{9,10}$), 7.54–7.56 (m, 2H, H_8). (see the numbering in Figure 1); Observed NOEs were H_{11}–H_{12}, H_{11}–$H_{3a,b}$, H_{11}–H_2, H_{11}–H_6, H_{11}–H_8, H_{12}–$H_{3a,b}$, H_{12}–H_2, H_{12}–H_6, H_{12}–H_8, $H_{3a,b}$–H_2, $H_{3a,b}$–H_6, H_2–H_6, H_2–H_5, H_2–H_8, H_6–H_8, H_4–$H_{9,10}$, and H_4–H_8; ^{13}C NMR (50.1 MHz, $CDCl_3$) δ 3.35, 7.64, 25.27, 25.51, 34.65, 34.58, 52.49, 52.63, 127.4, 128.8, 129.8, 134.9, 168.8, 170.0; IR (neat) 2956, 2878, 1721, 1437, 1323, 1294, 1218, 1137, 735 cm^{-1}; MS (70 eV) m/z (relative intensity) 442 (24), 413 (9.7), 314 (4.3), 285 (32), 255 (49), 155 (17), 139 (95), 126 (30), 84 (77); exact mass M$^+$ 442.1052 (calcd for $C_{20}H_{30}O_4SeSi$ 442.1078). **Dimethyl 2-(phenylseleno)-3-(triethylsilyl)cyclobutane-1,1-dicarboxylate (10):** colorless crystals; mp 32 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.543 (q, J = 7.9 Hz, 6H), 0.934 (t, J = 7.9 Hz, 9H), 2.05–2.23 (m, 2H), 2.73–2.89 (m, 1H), 3.70 (s, 3H), 3.77 (s, 3H), 4.51 (d, J = 9.0 Hz, 1H), 7.20–7.28 (m, 3H), 7.51–7.58 (m, 2H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ 2.21, 7.58, 24.25, 28.69, 43.44, 52.34, 52.51, 61.36, 127.1, 128.9, 131.3, 133.0, 170.0, 171.4; IR (neat) 2956, 2878, 1734, 1580, 1437, 1274, 1123, 1021, 735 cm^{-1}; MS (70 eV) m/z (relative intensity) 442 (27), 413 (14), 354 (4), 285 (37), 139 (100); exact mass M$^+$ 442.1048 (calcd for $C_{20}H_{30}O_4SeSi$ 442.1078).

Rearrangement of 4b to 3b (Table 2, entry 2). To a solution of **4b** (58 mg, 0.11 mmol) in dichloromethane (0.5 mL), cooled to −78 °C, was added $ZnBr_2$ (37 mg, 0.17 mmol). The mixture was allowed to warm to −30 °C and stirred for 1 h, and then it was warmed to +10 °C and stirred for 1.5 h. The reaction mixture was quenched by triethylamine (0.03 mL, 0.22 mmol), and saturated aqueous $NaHCO_3$ was added to the mixture. The mixture was extracted with dichloromethane and the organic phase, washed with water, dried (Na_2SO_4), and evaporated to give a 75:25 mixture of **3b** and **4b** (46 mg, 80%).

Preparation of 7 and 8. $LiAlH_4$ (71 mg, 1.9 mmol) was slowly added to a solution of a mixture of **3a** and **4a** (55:45) (200 mg, 0.41 mmol) in anhydrous diethyl ether (5.3 mL) with stirring at 0 °C. The mixture was allowed to warm to room temperature and stirred for 4.5 h. Water was added to the stirred mixture with ice-cooling. The mixture was extracted with ether, and the organic phase was dried ($MgSO_4$) and evaporated *in vacuo*. Column chromatography (silica gel, hexane–ether (1:4)) of the residue gave **8** (40 mg, 29%) (R_f = 0.2) and **7** (30 mg, 22%) (R_f = 0.1). **7**: colorless crystals (mp 54 °C); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.034 (s, 9H, H_{11}), 0.324 (dd J = 5.3, 5.4 Hz, 1H, H_{3a}), 0.897 (dd, J = 5.3, 8.3 Hz, 1H, H_{3b}), 1.16 (ddd, J = 5.4, 8.3, 12.8 Hz, 1H, H_2), 2.03 (d, J = 12.8 Hz, 1H, H_6), 2.59 (bs, 2H, $H_{12,13}$), 3.51 (d, J = 11.4 Hz, H_{5a}), 3.54 (d, J = 12.4 Hz, 1H, H_{4a}), 3.68 (d, J = 11.4 Hz, 1H, H_{5b}), 3.90 (d, J = 12.4 Hz, 1H, H_{4b}), 7.24–7.29 (m, 3H, $H_{9,10}$), 7.60–7.62 (m, 2H, H_8). (see the numbering in Figure 2). Observed NOEs were H_{11}–H_{3a}, H_{11}–H_2, H_{11}–H_6, H_{11}–H_8, H_{3a}–H_{3b}, H_{3a}–H_6, H_{3a}–H_{4a}, H_{3b}–H_2, H_{3b}–H_{5a}, H_{3b}–H_{5b}, H_2–H_6, H_2–H_{5a}, H_2–H_{5b}, H_2–H_8, H_6–H_{4a}, and H_6–H_8, H_{5a}–H_{5b}, H_{4a}–H_{4b}, H_{4a}–H_8, $H_{9,10}$–H_8; ^{13}C NMR (50.1 MHz, $CDCl_3$) δ −1.65 (q, J = 120 Hz, CH_3), 19.02 (t, J = 160 Hz, cyclopropane ring carbon), 25.24 (d, J = 161 Hz, cyclopropane ring carbon), 29.86 (s, cyclopropane ring carbon), 32.28 (d, J = 129 Hz, $CHSeSi$), 64.78 (t, J = 141 Hz, CH_2OH), 69.92 (t, J = 141 Hz, CH_2OH), 128.0 (dt, J = 161, 7.3 Hz, Ph), 129.0 (s, Ph), 129.2 (dd, J = 161, 5.9 Hz, Ph), 134.8 (dt, J = 163, 5.1 Hz, Ph); IR (KBr) 3346, 2956, 1477, 1439, 1249, 1044, 1011, 839, 741, 690 cm^{-1}; MS (70 eV) m/z (relative intensity) 344 (58), 327 (9.7), 271 (11), 256 (99), 230 (24), 169 (26), 158 (47), 116 (34), 103 (54), 79 (100); exact mass M$^+$ 344.0728 (calcd for $C_{15}H_{24}O_2SeSi$ 344.0710). Anal. Calcd for $C_{15}H_{24}O_2SeSi$: C, 52.47; H, 7.04. Found: C, 52.44; H, 7.01. **8**: colorless crystals (mp. 71 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.021 (s, 9H), 1.55–1.92 (m, 4H), 2.32 (bs, 1H), 3.00 (bs, 1H), 3.65–3.84 (m, 3H), 4.22 (d, J = 12.0 Hz, 1H), 7.25–7.29 (m, 3H), 7.53–7.57 (m, 2H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) −3.14 (q, J = 119 Hz, CH_3), 25.42 (d, J = 126 Hz, cyclobutane ring carbon $CHSi$), 25.94 (t, J = 139 Hz, cyclobutane ring carbon), 44.25 (d, J = 147 Hz, cyclobutane ring carbon $CHSe$), 49.48 (s, cyclobutane ring carbon), 67.38 (t, J = 145 Hz, CH_2OH), 69.07 (t, J = 141 Hz, CH_2OH), 127.4 (dt, J = 161, 7.3 Hz, Ph), 129.3 (d, J = 160 Hz, Ph), 130.8 (s, Ph), 133.1 (d, J = 163 Hz, Ph); IR (KBr) 3320, 2930, 1578, 1439, 1251, 1054, 1019, 866, 837, 820, 735, 692 cm^{-1}; MS (70 eV) m/z (relative intensity) 344 (4), 312 (3), 256 (15), 234 (5), 186 (5), 153 (13), 123 (9), 95 (25), 84 (100); exact mass M$^+$ 344.0663 (calcd for $C_{15}H_{24}O_2SeSi$ 344.0711).

Supporting Information Available: Copies of ^{1}H and ^{13}C NMR spectra for compounds **3a–c**, **4a–c**, and **5–10** and 2D-NOESY spectra for **7**, **9**, and **11** (24 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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