Chiral Synthesis of Cyclopropanes. Stereoselective [2 + 1] Cycloaddition Reactions of 1-Seleno-2-silylethenes with Di-(−)-menthyl Ethene-1,1-dicarboxylates

Shoko Yamazaki,* Hitomi Kataoka, and Shinichi Yamabe*

Department of Chemistry, Nara University of Education, Takabatake-cho, Nara 630-8528, Japan

Received October 19, 1998

Reaction of 1-seleno-2-silylethenes **1** with the chiral electrophiles **2**, **3**, and **4** derived from (−)-menthol, in the presence of zinc halides gave the cyclopropane products **5**, **6**, and **7**, respectively, with high diastereoselectivity. The absolute configuration of **5a**, prepared by the reaction of 1-(phenylseleno)-2-(trimethylsilyl)ethene (**1a**) and di-(−)-menthyl methylenemalonate (**2**), was determined to be 2*S* by conversion to the known chiral compound **11**. The proposed mechanism, involving fixation of the (−)-menthyl group to the C═C plane by the Lewis acid in the addition step, is consistent with the experimental observations. A selenium-participating secondary orbital interaction in the synclinal addition path was elucidated by ab initio calculations and explained the observed diasteroselectivity.

Introduction

The construction of chiral cyclopropane derivatives is of continuing interest, since cyclopropane moieties are present in a large number of natural products and biologically active compounds.[1] In addition, chiral cyclopropanes are used as synthons in the synthesis of chiral carbocycles having other ring sizes by utilizing their unique structural and reactivity properties.[2,3] Numerous synthetic methods for the preparation of chiral cyclopropanes have been developed.[4] The most generally used methods are Simmons−Smith reactions[5] and metal-catalyzed decomposition of diazo compounds in the presence of alkenes.[6] However, there are relatively few methods available for asymmetric synthesis of chiral cyclopropanes involving addition to α,β-unsaturated carbonyl compounds.[7] Accordingly, there is a need for methods that would effect such an addition to α,β-unsaturated carbonyl compounds. This is because the resulting and highly substituted cyclopropanes, including carbonyl groups, are endowed with functional diversity and are potentially useful for further elaboration.

We have recently reported the development of various Lewis acid-mediated reactions of (*E*)-1-(phenylseleno)-2-silylethenes (**1**) with α,β-unsaturated carbonyl compounds to afford cyclopropane products.[8] These reactions have high stereoselectivity, and it was proposed that they involve a selenium-stabilized silicon migration and also involve a Se- - -C═O secondary orbital interaction in the first synclinal addition step. The stereochemistry adopted in the first addition step appears to be retained throughout the reaction course, leading to the high stereoselec-

(1) For reviews, see: (a) Salaün, J.; Baird, M. S. *Curr. Med. Chem.* **1995**, *2*, 511. For recent examples, see: (b) FR900848: Yoshida, M.; Ezaki, M.; Hashimoto, M.; Yamashita, M.; Shigematsu, N.; Okuhara, M.; Kohsaka, M.; Horikoshi, K. *J. Antibiot.* **1990**, *43*, 748. (c) U-106305: Kuo, M. S.; Zielinski, R. J.; Cialdella, J. I.; Marschke, C. K.; Dupuis, M. J.; Li, G. P.; Kloosterman, D. A.; Spilman, C. H.; Marshall, V. P. *J. Am. Chem. Soc.* **1995**, *117*, 10629. (d) Curacin A: Gerwick, W. H.; Proteau, P. J.; Nagle, D. G.; Hamel, E.; Blokhin, A.; Slate, D. L. *J. Org. Chem.* **1994**, *59*, 1243. (e) Solandelactones A−H: Seo, Y.; Cho, K. W.; Rho, J.-R.; Shin, J.; Kwon, B.-M.; Bok, S.-H.; Song, J. I. *Tetrahedron* **1996**, *52*, 10583. (f) Pinnatin A−E: Rodriguez, A. D.; Shi, J.-G.; Huang, S. D. *J. Org. Chem.* **1998**, *63*, 4425. (g) Callipeltoside A: Zampella, A.; D'Auria, M. V.; Minale, L.; Debitus, C.; Roussakis, C. *J. Am. Chem. Soc.* **1996**, *118*, 11085.

(2) (a) Quinkert, G.; Schwartz, U.; Stark, H.; Weber, W.-D.; Baier, H.; Adam, F.; Dürner, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1029. (b) Quinkert, G.; Schwartz, U.; Stark, H.; Weber, W.-D.; Adam, F.; Baier, H.; Frank, G.; Dürner, G. *Liebigs Ann. Chem.* **1982**, 1999. (c) Baier, H.; Dürner, G.; Quinkert, G. *Helv. Chim. Acta* **1985**, *68*, 1054. (d) Abraham, N. A. *Tetrahedron Lett.* **1974**, 1393. (e) Quinkert, G.; Schmalz, H.-G.; Dzierzynski, E. M.; Dürner, G.; Bats, J. W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 992.

(3) (a) Davies, H. M. L.; Peng, Z.-Q.; Houser, J. H. *Tetrahedron Lett.* **1994**, *35*, 8939. (b) Corey, E. J.; Grant, T. G. *Tetrahedron Lett.* **1994**, *35*, 5373. (c) Romo, D.; Romine, J. L.; Midura, W.; Meyers, A. I. *Tetrahedron* **1990**, *46*, 4951. (d) Schotten, T.; Boland, W.; Jaenicke, L. *Tetrahedron Lett.* **1986**, *27*, 2349. (e) Kajiwara, T.; Nakatomi, T.; Sasaki, Y.; Hatanaka, A. *Agric. Biol. Chem.* **1980**, *44*, 2099.

(4) For recent reviews, see (a) Salaün, J. *Chem. Rev.* **1989**, *89*, 1247. (b) Charette, A. B.; Marcoux, J.-F. *Synlett* **1995**, 1197. (c) Reissig, H.-U. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 971. (d) Doyle, M. P.; Forbes, D. C. *Chem. Rev.* **1998**, *98*, 911. (e) Doyle, M. P. *Aldrichimica Acta* **1996**, *29*, 3.

(5) (a) Charette, A. B.; Juteau, H.; Lebel, H.; Molinaro, C. *J. Am. Chem. Soc.* **1998**, *120*, 11943. (b) Charette, A. B.; Brochu, C. *J. Am. Chem. Soc.* **1995**, *117*, 11367. (c) Denmark, S. E.; O'Connor, S. P. *J. Org. Chem.* **1997**, *62*, 3390. (d) Takahashi, H.; Yoshikawa, M.; Shibasaki, M.; Ohno, M.; Imai, N.; Kobayashi, S. *Tetrahedron* **1995**, *51*, 12013. (e) Denmark, S. E.; O'Connor, S. P. *J. Org. Chem.* **1997**, 62, 584. (f) Imai, N.; Sakamoto, K.; Maeda, M.; Kouge, K.; Yoshizane, K.; Nokami, J. *Tetrahedron Lett.* **1997**, *38*, 1423. (g) Kitajima, H.; Ito, K.; Aoki, Y.; Katsuki, T. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 207.

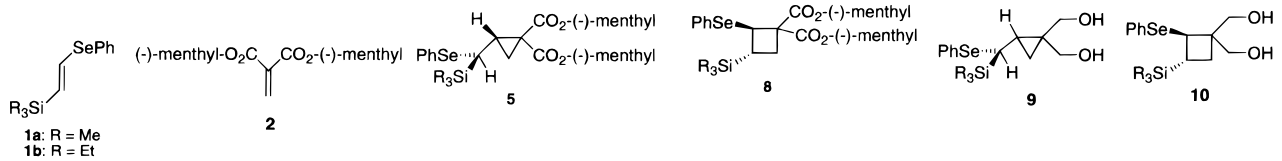
(6) (a) Müller, P.; Baud, C.; Ene, D.; Motallebi, S.; Doyle, M. P.; Brandes, B. D.; Dyatkin, A. B.; See, M. M. *Helv. Chim. Acta* **1995**, *78*, 459. (b) Denmark, S. E.; Stavenger, R. A.; Faucher, A.-M.; Edwards, J. P. *J. Org. Chem.* **1997**, *62*, 3375. (c) Davies, H. M. L.; Bruzinski, P. R.; Lake, D. H.; Kong, N.; Fall, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 6897. (d) Davies, H. M. L.; Bruzinski, P. R.; Fall, M. J. *Tetrahedron Lett.* **1996**, *37*, 4133. (e) Doyle, M. P.; Zhou, Q.-L.; Charnsangavej, C.; Longoria, M. A.; McKervey, M. A.; Garcia, C. F. *Tetrahedron Lett.* **1996**, *37*, 4129. (f) Doyle, M. P.; Austin, R. E.; Bailey, A. S.; Dwyer, M. P.; Dyatkin, A. B.; Kalinin, A. V.; Kwan, M. M. Y.; Liras, S.; Oalmann, C. J.; Pieters, R. J.; Protopopova, M. N.; Raab, C. E.; Roos, G. H.; Zhou, Q.-L.; Martin, S. F. *J. Am. Chem. Soc.* **1995**, *117*, 5763. (g) Doyle, M. P.; Peterson, C. S.; Protopopova, M. N.; Marnett, A. B.; Parker, D. L., Jr.; Ene, D.; Lynch, V. *J. Am. Chem. Soc.* **1997**, *119*, 8826. (h) Doyle, M. P.; Dyatkin, A. B.; Kalinin, A. V.; Ruppar, D. A.; Martin, S. F.; Spallar, M. R.; Liras, S. *J. Am. Chem. Soc.* **1995**, *117*, 11021.

(7) (a) Hanessian, S.; Andreotti, D.; Gomtsyan, A. *J. Am. Chem. Soc.* **1995**, *117*, 10393. (b) Pyne, S. G.; Dong, Z.; Skelton, B. W.; White, A. H. *J. Org. Chem.* **1997**, *62*, 2337.

(8) (a) Yamazaki, S.; Tanaka, M.; Yamaguchi, A.; Yamabe, S. *J. Am. Chem. Soc.* **1994**, *116*, 2356. (b) Yamazaki, S.; Tanaka, M.; Inoue, T.; Morimoto, N.; Kumagai, H. *J. Org. Chem.* **1995**, *60*, 6546. (c) Yamazaki, S.; Tanaka, M.; Yamabe, S. *J. Org. Chem.* **1996**, *61*, 4046. (d) Yamazaki, S.; Kumagai, H.; Takada, T.; Yamabe, S. *J. Org. Chem.* **1997**, *62*, 2968.

10.1021/jo9820925 CCC: $18.00
Published on Web 03/12/1999

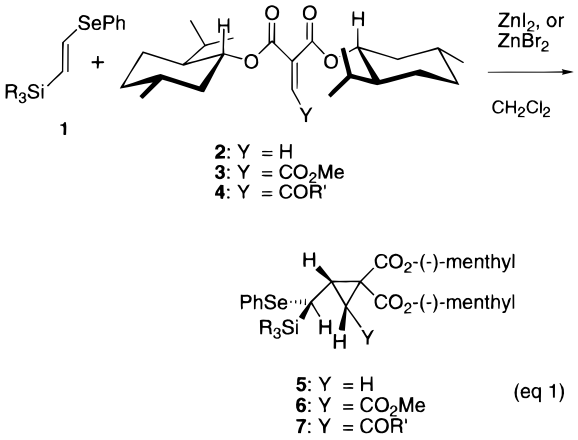
Table 1. [2 + 1] Cycloaddition Reactions of 1-Seleno-2-silylethenes 1 with Di-(−)-menthyl Methylenemalonate (2)[a]



entry	selenosilylethene	Lewis acid	reaction temp (time)	**5** + **8**, % yield	**5**:**8** ratio[b]	**9**,[c] ee%[d]	**10**,[c] ee%[d]
1	**1a**	$ZnBr_2$	−30 °C (180 min), 10 °C (10 min)	56	1.4:1	86	61
2	**1a**	ZnI_2	−30 °C (180 min), 10 °C (10 min)	92	1:1	77	78
3	**1a**	$ZnBr_2$	−30 °C (90 min), 0 °C (30 min)	95	1.9:1	80	74
4	**1a**	ZnI_2	−30 °C (90 min), 0 °C (30 min)	99	1.8:1	81	68
5	**1b**	ZnI_2	−30 °C (180 min), 10 °C (10 min)	87	1:1.5	79	84

[a] All reactions were carried out in with 1 mmol of **1**, ca. 2.6 mmol of **2**, and 1.5 mmol of ZnX_2 in CH_2Cl_2 (2 mL). [b] **5**:**8** ratio was determined by ^{1}H NMR. [c] **9** and **10** were isolated in ca. 50% total (**9** + **10**) yield. The ratio of **9**:**10** was similar to the **5**:**8** ratio determined by ^{1}H NMR. [d] ee% was determined by HPLC using a chiral column (CHIRALCEL OF).

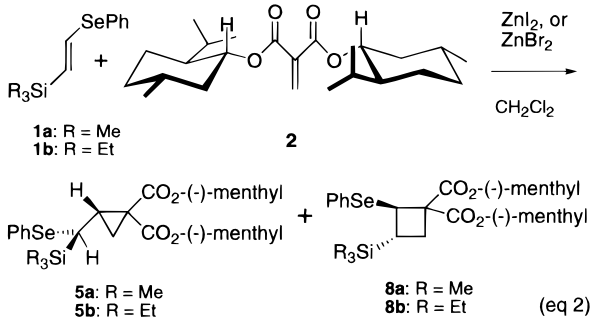
tivity . Since the first addition step is similar to that in concerted Diels−Alder reactions, the asymmetric induction methodology commonly employed in Diels−Alder reactions[9] can potentially be applied. Previously, we attempted asymmetric [2 + 1] cycloaddition reactions of **1** and vinyl ketones in the presence of a BINOL ((*R*)- or (*S*)-1,1′-binaphthol)-derived chiral titanium Lewis acid. However, the reactions only gave cyclopropanes with relatively low, although reproducible, enantioselectivity.[8c] As part of further efforts to develop this [2 + 1] cycloaddition reaction leading to efficient asymmetric cyclopropanation, we have now found and report herein that reaction of **1** with the chiral electrophiles **2**, **3**, and **4**, containing (−)-menthyl ester moieties in the presence of a Lewis acid (ZnX_2), gave cyclopropane products **5**, **6**, and **7** with high diastereoselectivity (eq 1).



In addition, we have analyzed the reaction mechanism theoretically. The selenium-participating synclinal addition was carefully examined. So far, there are no detailed reports which address the synclinal addition and secondary orbital interactions precisely in terms of transition state modeling. Since the π facial selectivity of the addition is essential for the observed high diastereoselectivity, a precise and theoretical examination of the synclinal addition has been performed as is described herein.

Results and Discussion

[2 + 1] Cycloaddition Reactions of 1-Seleno-2-silylethenes with Di-(−)-menthyl Ethene-1,1-dicarboxylates. Ethene-1,1-dicarboxylates such as methylenemalonates and 2-carbonyl-substituted ethene-1,1-dicarboxylates have been shown to have high reactivity toward (*E*)-1-(phenylseleno)-2-silylethenes (**1**) in the presence of $ZnBr_2$.[8b,d] Since highly diastereoselective Lewis acid-mediated Diels−Alder reactions of di-(−)-menthyl methylenemalonates have been reported,[10] (−)-menthyl esters **2**−**4** are attractive substrates for diastereoselective [2 + 1] cycloaddition reactions of **1** under Lewis acid conditions. These reactions were examined as described in the following discussion.



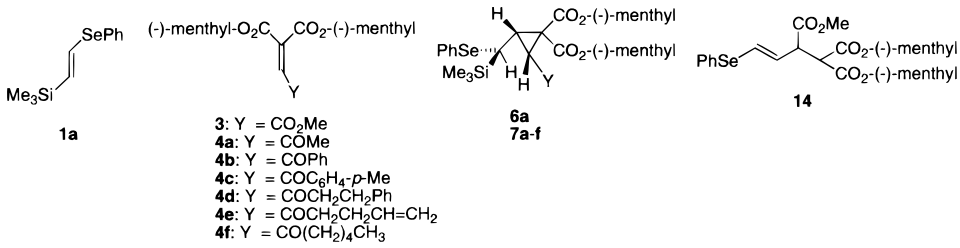
Reaction of **1a**,**b** with di-(−)-menthyl methylenemalonate (**2**) in the presence of Lewis acid gave [2 + 1] and [2 + 2] cycloadducts **5** and **8** (eq 2), similar to the reaction of the achiral substrates such as di-*tert*-butyl and dimethyl methylenemalonates. As a Lewis acid, $ZnBr_2$ was first examined since the total chemical yield was high in the case of di-*tert*-butyl malonate.[8b] The reaction leads to a high *net* yield of the cyclopropane, even though mixtures of cyclopropane and cyclobutane products resulted. ZnI_2 was also examined, and Table 1 summarizes these reactions (Table 1 containing more data is included in the Supporting Information).

To a solution of **1** in CH_2Cl_2 at −78 °C was added the Lewis acid, followed by **2** in CH_2Cl_2. Reaction temperature and time were as shown in Table 1. Quenching with triethylamine gave a mixture of **5** and **8**. The observed trends for the total yield of **5**+**8** and the ratio are as follows. Using the same reaction temperature and time in the reaction of **1a** and **2**, $ZnBr_2$ gave a slightly higher amount of cyclopropane **5** than that of the cyclobutane **8**. ZnI_2 gave a slightly higher total yield (entries 1,3 vs

(9) For reviews, see (a) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 876. (b) Masamune, S.; Choy, W.; Peterse, J. S.; Sita, L. R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1.

(10) (a) Katagiri, N.; Haneda, T.; Hayasaka, E.; Watanabe, N.; Kaneko, C. *J. Org. Chem.* **1988**, *53*, 227. (b) Katagiri, N.; Haneda, T.; Watanabe, N.; Hayasaka, E.; Kaneko, C. *Chem. Pharm. Bull.* **1988**, *36*, 3867. (c) Loncharich, R. J.; Schwartz, T. R.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 14.

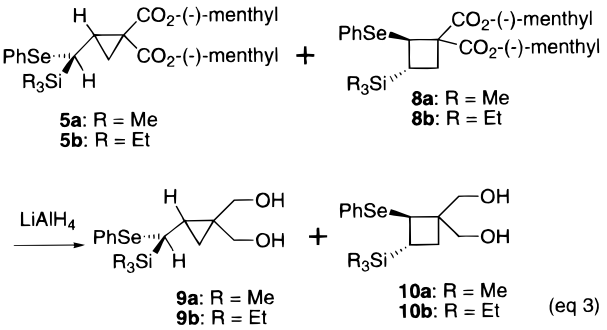
Table 2. [2 + 1] Cycloaddition Reactions of 1-Seleno-2-silylethene 1a with Di-(−)-menthyl Esters 3 and 4[a]



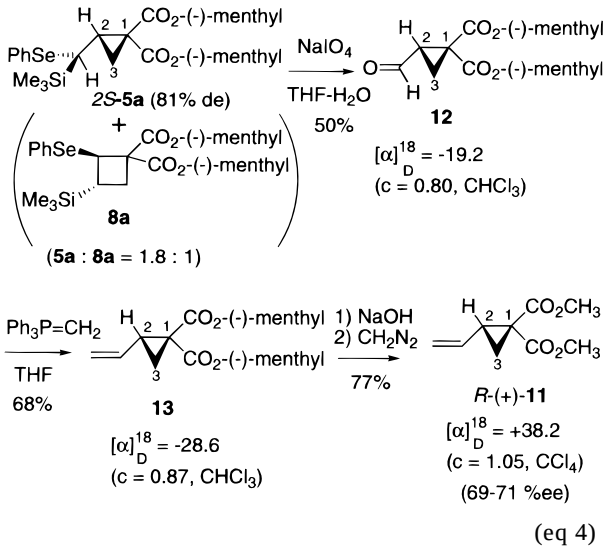
entry	dimenthyl ester	Lewis acid	reaction temp (time)	**6/7** (% yield)	**6/7** de%[b]	byproduct	recovered **1**, % yield
1	**3**	$ZnBr_2$	−30 °C (8 h)	**6a** (20)	90		62
2	**3**	ZnI_2	−30 °C (14 h)	**6a** (39)	92		60
3	**3**	$SnCl_4$	−78 °C (1 h)	**6a** (0)		**14** (86)	6
4	**4a**	ZnI_2	−30 °C (5.5 h)	**7a** (77)	ca. 95[d]		9
5	**4b**	ZnI_2	−30 °C (8 h)	**7b** (84)	ca. 95[d]		8
6	**4c**	ZnI_2	−30 °C (7 h)	**7c** (71)	ca. 95[d]		12
7	**4d**	ZnI_2	−30 °C (7 h)	**7d** (ca. 74)	ca. 95[d]		23
8	**4e**	ZnI_2	−30 °C (8 h)	**7e** (80)	ca. 95[d]		17
9	**4f**	ZnI_2	−30 °C (8 h)	**7f** (65)	ca. 95[d]		14

[a] All reactions were carried out with 1 mmol of **1a**, 1.3 mmol of **3**/**4**, and 1.5 mmol of ZnX_2 in CH_2Cl_2 (2 mL). [b] de% was determined by ^1H NMR. [c] A mixture of desilylated compounds including **14** was produced but could not be purified. [d] A trace amount of impurity was present, but the structure could not be determined as the corresponding diastereoisomer.

2,4). Higher temperature (+10 °C) reduced the total yield of **5**+**8** with $ZnBr_2$, resulting in desilylated byproducts (entry 1). Use of **1b** instead of **1a** decreased the ratio of **5** to **8**, probably because steric hindrance disturbs the silicon migration (compare entry 2 with entry 5). Cyclopropanes **5a**,**b** and cyclobutanes **8a**,**b** could not be separated by column chromatography. The cycloadducts **5** and **8** were reduced to the corresponding alcohols **9a**,**b** and **10a**,**b**, which were then readily separated (eq 3). The selectivity of each reaction was examined by measuring the ee% of **9** and **10** using chiral HPLC. In all cases, reaction of **1** with a chiral electrophile **2** gave cyclopropane products **5** with high diastereoselectivity (de 77−88%, deduced from the ee% of **9**). The cyclobutane **8** wasalso obtained with modest to high diastereoselectivity (de 61−84%, deduced from the ee% of **10**), with some excep-tions (see the Supporting Information).



The absolute configuration of **5a** was determined by conversion to the known chiral compound **11** in eq 4, a useful synthetic intermediate for steroids, prostaglandins, and jasmonates.[2] Thus, the 1.8:1 mixture of **5a** and **8a**, prepared as in entry 4, was oxidized with $NaIO_4$ in a $THF-H_2O$ solution at room temperature. The reaction mixture was purified by column chromatography to give the sila-Pummerer product, cyclopropane **12**, in 50% yield.[11] Wittig reaction of **12** with methylenetriphenylphosphorane in THF gave **13** in 68% yield. Hydrolysis and subsequent treatment with diazomethane gave (*R*)-(+)-dimethyl vinylcyclopropanedicarboxylate (**11**) in 77% yield. The enantiopurity of **11** was determined to be 69−71% ee by comparison with the reported optical rotation.[12] The absolute configuration of **5a** was also thereby confirmed to be *2S*.

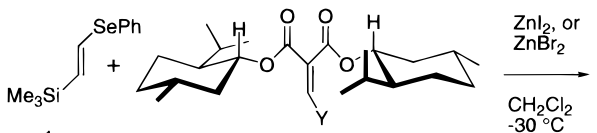


(eq 4)

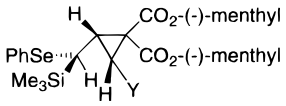
Next, reactions of **1a** with 2-carbonyl-subsituted ethene-1,1-dicarboxylates **3** and **4** were examined (eq 5 and Table 2; Table 2 containing more data is in the Supporting Information). Reactions of **1a** with the corresponding dimethyl or diethyl esters gave cyclopropanes in satisfactory yields.[8d] However, reaction of **1a** with triester olefin

(11) (a) Reich, H. J.; Shah, S. K. *J. Org. Chem.* **1977**, *42*, 1773. (b) Brook, A. G.; Anderson, D. G. *Can J. Chem.* **1968**, *46*, 2115. (c) Carey, F. A.; Hernandez, O. *J. Org. Chem.* **1973**, *38*, 2670. (d) Vedejs, E.; Mullins, M. *Tetrahedron Lett.* **1975**, 2017.

(12) (a) Danishefsky, S.; Rovnyak, G. *J. Chem. Soc., Chem. Commun.* **1972**, 821. (b) Hayashi, T.; Yamamoto, A.; Ito, Y. *Tetrahedron Lett.* **1988**, *29*, 669.



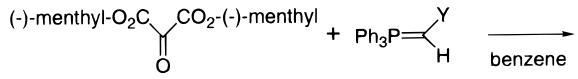
3: Y = CO_2Me
4a: Y = COMe
4b: Y = COPh
4c: Y = COC_6H_4-*p*-Me
4d: Y = $COCH_2CH_2Ph$
4e: Y = $COCH_2CH_2CH{=}CH_2$
4f: Y = $CO(CH_2)_4CH_3$



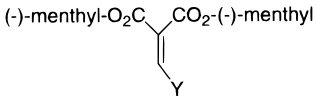
6a: Y = CO_2Me
7a: Y = COMe
7b: Y = COPh
7c: Y = COC_6H_4-*p*-Me
7d: Y = $COCH_2CH_2Ph$
7e: Y = $COCH_2CH_2CH{=}CH_2$
7f: Y = $CO(CH_2)_4CH_3$

(eq 5)

3 in the presence of $ZnBr_2$ or ZnI_2 proceeded sluggishly with low chemical yield (entries 1 and 2), probably due to steric hindrance from the menthyl group. Longer reaction time in the presence of $ZnBr_2$, higher temperature, or use of a stronger Lewis acid such as $SnCl_4$ resulted in formation of desilylated byproducts, e.g., **14** (entry 3). Reactions of di-(−)-menthyl 2-acylethene-1,1-dicarboxylates **4** with **1a** were next examined. The starting olefins **4** were conveniently prepared by reaction of di-(−)-menthyl oxomalonate (**15**) and acyl-substituted triphenylmethylenephosphoranes **16** (eq 6).[13] We found that reactions of di-(−)-menthyl 2-acylethene-1,1-dicar-



15 **16a-f**



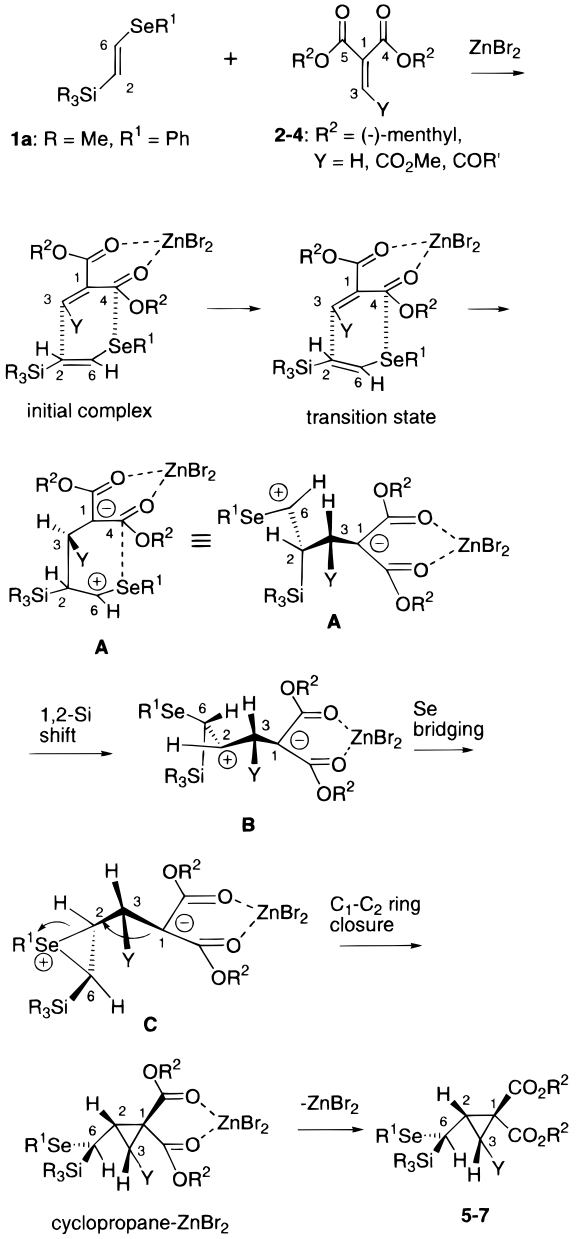
4a-f

(eq 6)

boxylates **4** with **1a** proceeded faster than those with triester **3** (entries 4−9). Thus, reaction of **4** with **1a** in the presence of ZnI_2 at −30 °C in CH_2Cl_2 for 5.5−8 h gave **7** in 62−84% yield with ca. 95% purity.[14] It should be noted that the terminal vinyl group of **4e** did not participate in the cycloaddition reaction (entry 8).

Reactions of **1a** with olefins **3** and **4** gave C_2,C_3-cis-substituted cyclopropanes **6** and **7**, respectively, and no cyclobutanes were produced, similar to reactions of **1** with the corresponding dimethyl or diethyl esters.[8d] The C_2,C_3-cis stereochemistry of **6** and **7** was detemined by a NOE cross-peak between H_2 and H_3 in 2D-NOESY.[15] The determination of configurations of **6** and **7** by conversion to other useful chiral molecules is currently under investigation in our group.

Scheme 1



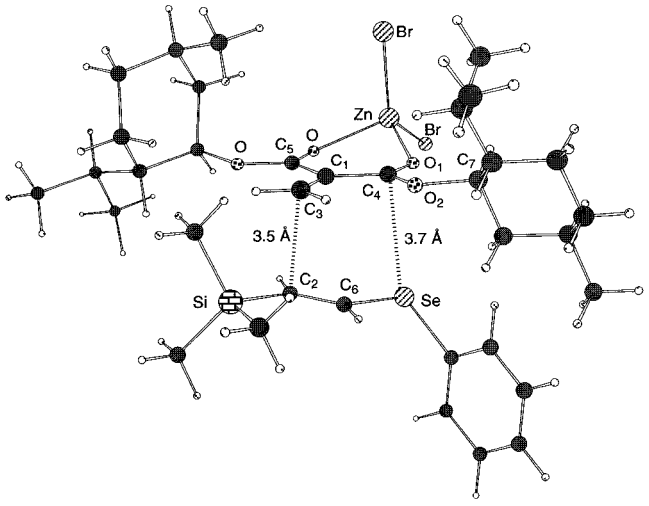
Theoretical Study of the Reaction Mechanism

To account for the diastereoselective [2 + 1] cycloaddition reaction of **1** and chiral ethene-1,1-dicarboxylates, the [2 + 1] cycloaddtion mechanism was theoretically studied and the similarity with Lewis acid promoted Diels−Alder reactions was investigated. The total reaction mechanism was proposed as shown in Scheme 1.[8] The reaction involves a Se- - -C=O secondary orbital interaction in the first synclinal addition step, and also involves a selenium-stabilized silicon migration in the

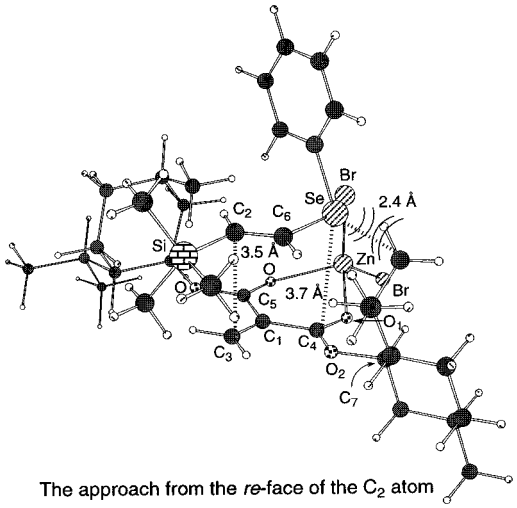
(13) **16a**−**c** were prepared from α-chloro/bromo ketones and triphenylphosphine and subsequent treatment with $NaHCO_3$. (a) Ramirez, F.; Dershowitz, S. *J. Org. Chem.* **1957**, *22*, 41. **16d**−**f** were prepared from the reaction of acetomethylenetriphenylphosphorane (**16a**), n-BuLi, and alkyl halides according to the literature procedure. (b) Taylor, J. D.; Wolf, J. F. *J. Chem. Soc., Chem. Commun.* **1972**, 876. (c) Cooke, M. P., Jr. *J. Org. Chem.* **1973**, *38*, 4082.

(14) A trace amount of impurity was present, but the structure could not be determined to be the corresponding diastereoisomer.

(15) The origin of C_2,C_3-cis selectivity of **6** and **7** probably arises from the larger LUMO coefficient of C_4 than that of C_5 in **3**−ZnX_2 or **4**−ZnX_2 complexes, which was shown for the corresponding trimethyl ester.[8d]



The approach from the *si*-face of the C_2 atom (same as Scheme 2)



The approach from the *re*-face of the C_2 atom

Figure 1. Proposed approaches of **1a** to **2**-$ZnBr_2$. For the structures of **1a** and **2**-$ZnBr_2$, RHF/3-21G* optimized bond lengths and bond angles are used. They are shown in Figure 5S of the Supporting Information. C_3---C_2 and C_4---Se distances are set to 3.5 and 3.7 Å, respectively, as an initial complex in the addition step. These distances are taken from the model system (see Figure 2S in the Supporting Information).

resulting zwitterionic intermediate. Using model calculations, we have determined the structure of the weakly interacting system composed of **1** and **2**−$ZnBr_2$ as the complex prior to the transition state.[16,17] Such weakly interacting systems are also known in Lewis-acid promoted Diels−Alder reactions.[18]

The structures of **1a** and **2**−$ZnBr_2$ were fully optimized (see Figure 1 and the Supporting Information). In the optimized structure of **2**−$ZnBr_2$ shown at the top of

Scheme 2. The π Facial Stereochemistry for the Diastereoselectivity of Cyclopropanes 5−7

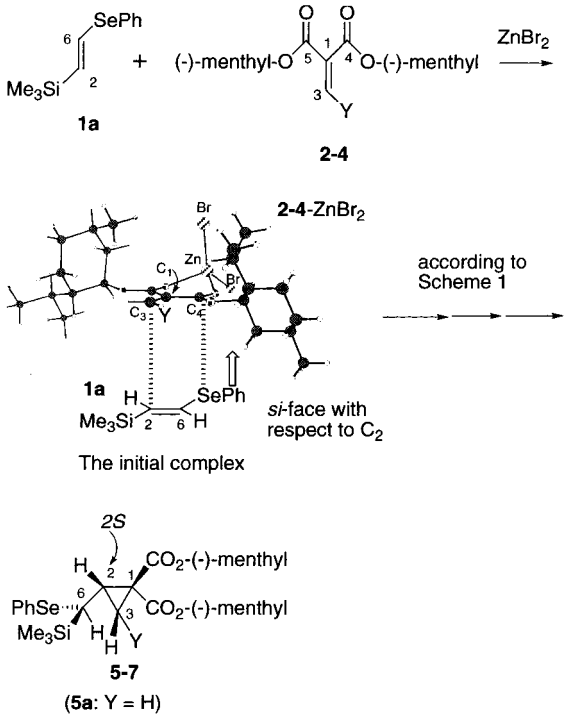


Figure 1, both menthyl groups are fixed by chelation with $ZnBr_2$. A C_2 symmetry axis exists with respect to the C_1=C_3 double bond. The ester carbonyl (C_4=O_1) is *syn*-periplanar to the O_2−C_7 bond, and the H−C_7 bond is almost *syn*-periplanar to the C_4−O_2 bond. In Figure 1, the proposed synclinal approaches of **1a** from the *si* face and *re* face of C_2 to **2**−$ZnBr_2$ are outlined, where C_4- - -Se and C_3- - -C_2 distances are set to 3.7 and 3.5 Å, respectively, as the initial complex prior to the transition state in the addition step. These distances are taken from calculated results of the model system (see the Supporting Information). Approach from the *re* face of C_2 results in steric repulsion between Se and the isopropyl carbon of the menthyl group. This proposed diastereoselection is similar to that observed in asymmetric Diels−Alder reactions involving (−)-menthyl acrylates.[3,19] The stereochemistry controlled in the first addition step seems to be retained throughout the reaction, leading to high stereoselectivity. Thus, attack from the *si*-side with respect to C_2 finally leads to (2*S*)-**5a** in the reaction of **1a** and **2** according to the mechanism shown in Scheme 1.[20] This proposed mechanism is consistent with the experimental observation of the absolute stereochemistry of the product **5a** by conversion to **11** (eq 4). Although the absolute configurations of **6** and **7** have not been determined yet, the observed high diastereoselectivity suggests the stereoselective pathway shown in Scheme 2 for the [2 + 1] cycloaddition of **1a**, and **3** and **4**.

In the case of chiral triester-substituted olefin **17** (eq 7), the Lewis acid is bidentately coordinated to two ethoxycarbonyl groups and the (−)-menthoxycarbonyl group may be not fixed in the C=C plane.[8d] As a result,

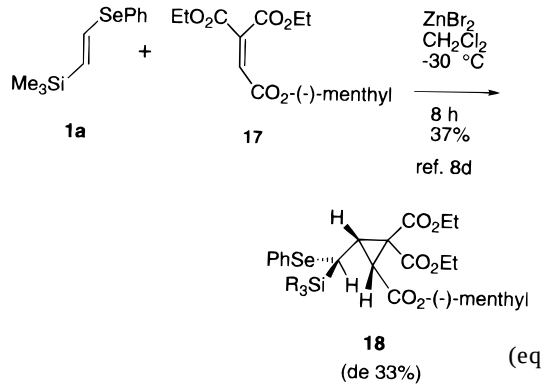
(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian *94*, *Revision B.1*, Gaussian, Inc., Pittsburgh, PA, 1995. MO calculations using Gaussian 94 were made on the CONVEX SPP1200/XA at the Information Processing Center (Nara University of Education).

(17) A detailed discussion of the ab initio calculations is presented in the Supporting Information.

(18) Yamabe, S.; Dai, T.; Minato, T. *J. Am. Chem. Soc.* **1995**, *117*, 10994.

(19) Recently, we reported the diastereoselective reaction of **1a** and (−)-menthyl 2-(dimethylphosphono)acrylate in the presence of $SnCl_4$. Yamazaki, S.; Takada, T.; Imanishi, T.; Moriguchi, Y.; Yamabe, S. *J. Org. Chem.* **1998**, *63*, 5919.

(20) The configuration of C_6 of **5a** was assumed as *S*, following the previous discussion on the relative stereochemistry of C_2−C_6.[8b]



(eq 7)

the diastereoselectivity was low (de 33%). Thus, fixation of the (−)-menthyl group by the Lewis acid in the addition step is presumed to be critical for the diastereoselective [2 + 1] cycloadditions of **1** with (−)-menthol-based chiral electrophilic olefins.

In summary, we have shown new diastereoselective cyclopropanation reactions of 1-seleno-2-silylethene **1** with di-(−)-menthyl ethene-1,1-dicarboxylates **2**−**4** in the presence of zinc halides. The absolute stereochemistry of cycloadduct **5a** was determined by conversion to the known chiral compound **11**. The stereochemical outcome of this reaction is consistent with a selective addition step in the proposed mechanism, as shown using ab initio calculations. Thus, the readily available and inexpensive (−)-menthol is a suitable chiral auxiliary in this [2 + 1] cycloaddition reaction. Further work is in progress on the utilization of these chiral highly functionalized cyclopropanes.

Experimental Section

General Methods. Melting points are uncorrected. IR spectra were recorded in the FT mode. ^{1}H NMR spectra were recorded in $CDCl_3$ at 200 or 400 MHz. ^{13}C NMR spectra were recorded in $CDCl_3$ at 50.1 or 100.6 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 EI or FAB. HPLC analysis was performed with a UV detector (detection, 254 nm light) and a flow rate of 0.5 mL/min using a CHIRALCEL OF (0.46 cm × 25 cm). Optical rotations were measured with a cylindrical 1 cm i.d. × 10 cm or 0.33 cm i.d. × 10 cm cell. All reactions were carried out under a nitrogen atmosphere.

Di-(−)-menthyl 2-(1-(Phenylseleno)-1-(trimethylsilyl)-methyl)cyclopropane-1,1-dicarboxylate (5a) and Di-(−)-menthyl 2-(Phenylseleno)-3-(trimethylsilyl)cyclobutane-1,1-dicarboxylate (8a). 2 was prepared according to the literature.[10b] **2** could not be purified from traces of remaining starting di-(−)-menthyl malonate, and the mixture was used in the reaction.

A Typical Experimental Procedure (entry 4 in Table 1). To a solution of **1a** (255 mg, 1.0 mmol) in dichloromethane (2.0 mL) cooled to −78 °C was added ZnI_2 (479 mg, 1.5 mmol) followed by a solution of **2** (1.021 g, ca. 2.6 mmol including a small amount of di-(−)-menthyl malonate) in dichloromethane (0.5 mL). The mixture was allowed to warm to −30 °C and stirred for 90 min and then at 0 °C for 30 min. The reaction mixture was quenched by triethylamine (0.36 mL, 2.37 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 hexanes−ether (9:1) to give a mixture of **5a** and **8a** (638 mg, 99%). **5a** and **8a** were obtained as a 1.8:1 mixture (R_f = 0.4 (hexane−ether = 9:1)); ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.009 (s, 9H × 0.64), 0.042 (s, 9H × 0.36), 0.602 (d, J = 6.8 Hz, 6H), 0.704−1.19 (m, 18H), 1.31−1.73 (m, 8H + 2H × 0.64), 1.93−2.25 (m, 4H + 1H × 0.64 + 2H × 0.36), 2.40 (d, J = 12.7 Hz, 1H × 0.64), 2.76 (m, 1H × 0.36), 4.35 (d, J = 10.5 Hz, 1H × 0.36), 4.68−4.88 (m, 2H), 7.27−7.31 (m, 3H), 7.61−7.67 (m, 2H); IR (neat) 2922, 2870, 1717, 1580 cm^{-1}; MS (EI) m/z 648; exact mass M$^+$ 648.3091 (calcd for $C_{35}H_{56}O_4SeSi$ 648.3113).

Di-(−)-menthyl 2-(1-(Phenylseleno)-1-(triethylsilyl)methyl)cyclopropane-1,1-dicarboxylate (5b) and Di-(−)-menthyl 2-(Phenylseleno)-3-(trimethylsilyl)cyclobutane-1,1-dicarboxylate (8b) (entry 5 in Table 1). 5b and **8b** were obtained as a 1:1.5 mixture (R_f = 0.5 (hexane−ether = 9:1)); ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.474−0.593 (m, 6H), 0.658−1.21 (m, 33H), 1.25−2.28 (m, 12H + 3H × 0.4 + 2H × 0.6), 2.50 (d, J = 12.5 Hz, 1H × 0.4), 2.75 (m, 1H × 0.6), 4.40 (d, J = 9.3 Hz, 1H × 0.6), 4.61−4.89 (m, 2H), 7.22−7.26 (m, 3H), 7.56−7.67 (m, 2H); IR (neat) 2920, 1717, 1580 cm^{-1}; MS (EI) m/z 690; exact mass M$^+$ 690.3552 (calcd for $C_{38}H_{62}O_4SeSi$ 690.3583).

Preparation of 9 and 10 (entry 4 in Table 1). $LiAlH_4$ (79 mg, 2.09 mmol) was slowly added to a solution of a mixture of **5a** and **8a** (1.8:1) (300 mg, 0.46 mmol) in anhydrous diethyl ether (5.9 mL) with stirring at 0 °C. The mixture was allowed to warm to room temperature and stirred for 4.5 h. Saturated Na_2SO_4 solution was added to the stirred mixture with ice-cooling. The mixture was extracted with ether. The aqueous layer was acidified by 1 N HCl and extracted with ether. The combined organic phase was dried ($MgSO_4$) and evaporated in vacuo. The residue was purified by column chromatography over silica gel eluting with hexanes−ether (1:4) to give **9a** (53 mg, 30%) (R_f = 0.4) and **10a** (40 mg, 23%) (R_f = 0.6).

2,2-Bis(hydroxymethyl)-1-[(phenylseleno)(trimethylsilyl)methyl]cyclopropane (9a). HPLC (hexane-^{i}PrOH = 9:1) major peak t_{R1} 38.6 min, minor peak t_{R2} 81.6 min, 81% ee. The ^{1}H NMR spectrum was in accord with the reported data.;[8b] $[\alpha]^{28.4}_D$ −9.3 (c 0.66, $CHCl_3$).

4,4-Bis(hydroxymethyl)-1-(phenylseleno)-2-(trimethylsilyl)cyclobutane (10a). HPLC (hexane-^{i}PrOH = 9:1) major peak t_{R1} 18.1 min, minor peak t_{R2} 29.1 min, 68% ee. The ^{1}H NMR spectrum was in accord with the reported data.;[8b] $[\alpha]^{24.7}_D$ +34.1 (c 1.0, $CHCl_3$).

2,2-Bis(hydroxymethyl)-1-[(phenylseleno)(triethylsilyl)-methyl]cyclopropane (9b). (R_f = 0.4 (hexane−ether = 1:4). Pale yellow oil; HPLC (hexane−^{i}PrOH = 9:1) major peak t_{R1} 30.6 min, minor peak t_{R2} 52.1 min, 79% ee; ^{1}H NMR (200 MHz, $CDCl_3$) 0.348 (dd, J = 5.4, 5.4 Hz, 1H), 0.559−0.683 (m, 6H), 0.866−0.972 (m, 10H), 1.24 (ddd, J = 12.8, 8.0, 5.4 Hz, 1H), 2.17 (d, J = 12.8 Hz, 1H), 2.50 (bs, 1H), 2.95 (bd, J = 9.0 Hz, 1H), 3.44−3.87 (m, 4H), 7.24−7.30 (m, 3H), 7.61−7.66 (m, 2H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ 3.317, 7.609, 18.79, 26.15, 29.77, 30.09, 64.49, 69.86, 128.0, 129.1, 129.3, 135.0; IR (neat) 3400, 2956, 2878, 1578 cm^{-1}; MS (EI) m/z 386; exact mass M$^+$ 386.1181 (calcd for $C_{18}H_{30}O_2SeSi$ 386.1180); $[\alpha]^{30.4}_D$ −5.5 (c 0.21, $CHCl_3$).

4,4-Bis(hydroxymethyl)-1-(phenylseleno)-2-(triethylsilyl)cyclobutane (10b). (R_f = 0.6 (hexane−ether = 1:4). Pale yellow oil; HPLC (hexane−^{i}PrOH = 9:1) major peak t_{R1} 17.9 min, minor peak t_{R2} 29.2 min, 84% ee; ^{1}H NMR (400 MHz, $CDCl_3$) 0.578 (q, J = 8.0 Hz, 6H), 0.962 (t, J = 8.0 Hz, 9H), 1.72−1.74 (m, 2H), 1.95 (ddd, J = 11.0, 9.9, 9.9 Hz, 1H), 3.64 (s, 2H), 3.81 (d, J = 11.7 Hz, 1H), 3.84 (d, J = 11.0 Hz, 1H), 4.21 (d, J = 11.7 Hz, 1H), 7.24−7.29 (m, 3H), 7.53−7.55 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 2.423, 7.642, 23.13, 26.74, 44.91, 50.28, 67.56, 69.28, 127.4, 129.4, 131.1, 133.0; IR (neat) 3380, 2950, 2876, 1578 cm^{-1}; MS (EI) m/z 386; exact mass M$^+$ 386.1175 (calcd for $C_{18}H_{30}O_2SeSi$ 386.1180); $[\alpha]^{25.3}_D$ +20.3 (c 0.54, $CHCl_3$).

Di-(−)-menthyl 2-Formylcyclopropane-1,1-dicarboxylate (12). To a solution of a mixture of **5a** and **8a** (1.8:1) (prepared as in entry 4, Table 1) (621 mg, 0.96 mmol) in THF (19.2 mL) and water (9.6 mL) was added $NaIO_4$ (1.03 g, 4.8 mmol) with vigorous stirring. The mixture was stirred for 6 h at room temperature. The reaction mixture was poured into ether and saturated aqueous $NaHCO_3$ solution and extracted with ether (×2). The combined organic layer was washed with

water, dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by column chromatography over silica gel eluting with hexanes−ether (3:1) to give **12** (208 mg, 50%). (R_f = 0.4 (hexane−ether = 3:1)). Pale yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) 0.736 (d, J = 6.8 Hz, 3H), 0.745 (d, J = 7.1 Hz, 3H), 0.819−1.18 (m, 18H), 1.21−2.12 (m, 14H), 2.75 (ddd, J = 8.7, 6.8, 4.9 Hz, 1H), 4.74 (ddd, J = 10.7, 10.7, 4.3 Hz, 1H), 4.76 (ddd, J = 10.9, 10.9, 4.2 Hz, 1H), 9.22 (d, J = 4.9 Hz, 1H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ 15.70, 16.14, 19.17, 20.87, 22.00, 22.09, 22.88, 23.20, 25.71, 26.06, 31.40, 34.15, 34.91, 37.89, 40.52, 40.66, 46.71, 47.08, 76.63, 165.5, 167.6, 196.3; IR (neat) 2960, 2872, 1727 cm^{-1}; MS (EI) m/z (relative intensity) 435 (30) $M^+ + 1$, 419 (15), 297 (100); $[\alpha]^{17.5}_D$ −19.2 (c 0.80, $CHCl_3$).

Di-(−)-menthyl 2-Vinylcyclopropane-1,1-dicarboxylate (13). A solution of n-BuLi (1.25 M in n-hexane, 0.99 mL, 1.24 mmol) was added dropwise to a stirred and ice-cold suspension of methyltriphenylphosphonium iodide (443 mg, 1.24 mmol) in THF (4.2 mL). The mixture was stirred to 0 °C for 15 min. A solution of **12** (208 mg, 0.48 mmol) in THF (1.4 mL) was added to the mixture at 0 °C. After the mixture was allowed to warm to room temperature, it was stirred for 2.5 h. Water was added, and the mixture was extracted with ether. The ether layer was separated, dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by column chromatography over silica gel eluting with hexanes−ether (9:1) to give **13** (141 mg, 68%) (R_f = 0.8 (hexane−ether = 9:1)). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) 0.707 (d, J = 6.8 Hz, 3H), 0.747 (d, J = 7.0 Hz, 3H), 0.849−0.927 (m, 14H), 0.956−1.09 (m, 4H), 1.21−1.53 (m, 6H), 1.64−1.70 (m, 4H), 1.83−1.94 (m, 2H), 2.04−2.08 (m, 2H), 2.56 (ddd, J = 7.9, 7.9, 8.2 Hz, 1H), 4.70 (ddd, J = 10.6, 10.6, 4.4 Hz, 1H), 4.72 (ddd, J = 10.6, 10.6, 4.3 Hz, 1H), 5.09 (dd, J = 10.0, 1.6 Hz, 1H), 5.29 (dd, J = 17.0, 1.6 Hz, 1H), 5.40 (ddd, J = 17.0, 10.0, 8.2 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 16.08, 16.50, 20.24, 20.83, 22.10, 22.17, 23.21, 23.65, 26.33, 30.66, 31.48, 34.37, 34.42, 36.56, 40.92, 46.98, 47.32, 75.60, 75.81, 118.0, 133.7, 167.1, 169.6; IR (neat) 2950, 2872, 1717, 1640, 984, 913 cm^{-1}; MS (EI) m/z 432; MS (FAB) m/z 433 (MH^+); $[\alpha]^{18.0}_D$ −28.6 (c 0.89, $CHCl_3$).

Dimethyl 2-Vinylcyclopropane-1,1-dicarboxylate (11). A mixture of **13** (534 mg, 1.23 mmol), NaOH (978 mg, 17.4 mmol), and a spatula of hydroquinone in H_2O (1.7 mL) and EtOH (3.4 mL) was heated for 8 h under reflux. The reaction mixture was concentrated in vacuo, and water was added. The mixture was washed with ether (×3). The water phase was saturated with $NaH_2PO_4 \cdot 2H_2O$ and concentrated hydrochloric acid was added to adjust to pH = 5 with ice-cooling. The aqueous solution was extracted with ether (×6), and the ether extracts were dried ($MgSO_4$) and concentrated in vacuo. The residue was dissolved in ether (20 mL), and the solution was treated with excess diazomethane in ether. The reaction mixture was concentrated in vacuo. The residue was purified by column chromatography over silica gel eluting with hexanes−ether (9:1) to give **11** (175 mg, 77%) (R_f = 0.4). **11**: Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) 1.59 (dd, J = 9.2, 5.0 Hz, 1H), 1.72 (dd, J = 7.6, 5.0 Hz, 1H), 2.58 (ddd, J = 9.2, 8.3, 7.6 Hz, 1H), 3.74 (s, 3H), 5.12−5.16 (m, 1H), 5.26−5.32 (m, 1H), 5.40−5.49 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 20.58, 31.42, 35.79, 52.53, 52.68, 118.6, 133.0, 167.8, 170.0; IR (neat) 3014, 2958, 1729, 1640, 990, 919 cm^{-1}; MS (EI) m/z 184; exact mass M^+ 184.0735 (calcd for $C_9H_{12}O_4$ 184.0735); $[\alpha]^{17.6}_D$ +38.2 (c 1.1, CCl_4).

1,1-Di-(−)-menthyl 2-Methyl Ethane-1,1,2-tricarboxylate (19). Sodium hydride (0.74 g, 57% dispersion in oil, 17.6 mmol, washed twice with hexane) was suspended in freshly distilled THF (35 mL). After the mixture was cooled to 0 °C, di-(−)-menthyl malonate (3.31 g, 8.69 mmol) in THF (2.3 mL) was added dropwise over 10 min. After 30 min, methyl chloroacetate (943 mg, 8.69 mmol) dissolved in THF (5.4 mL) was added dropwise, and the mixture was allowed to room temperature and stirred overnight. Water was added to the reaction, the mixture was extracted with ether, and the organic phase was dried ($MgSO_4$). The solvent was evaporated in vacuo. The residue was purified by column chromatography over silica gel eluting with hexanes−ether (19:1 to 9:1) to give the title compound (1.66 g, 42%). R_f = 0.8 (hexane−ether = 2:1); colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) 0.745 (d, J = 7.0 Hz, 3H), 0.753 (d, J = 6.8 Hz, 3H), 0.828−1.08 (m, 18H), 1.13−1.71 (m, 8H), 1.83−2.03 (m, 4H), 2.93 (d, J = 7.6 Hz, 2H), 3.69 (s, 3H), 3.81 (t, J = 7.6 Hz, 1H), 4.726 (ddd, J = 10.9, 10.9, 4.4 Hz, 1H), 4.733 (ddd, J = 10.9, 10.9, 4.3 Hz, 1H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ 15.99, 16.19, 20.78, 20.95, 22.03, 22.99, 23.29, 25.65, 26.12, 31.35, 33.10, 34.18, 40.46, 40.54, 46.79, 46.85, 48.31, 52.02, 75.82, 167.9, 168.1, 171.3; IR (neat) 2950, 2870, 1734, 1456, 1412, 996, 915, 845, 733 cm^{-1}; MS (FAB) m/z 453 (MH^+); $[\alpha]^{17.6}_D$ −59.9 (c 0.8, $CHCl_3$).

1,1-Di-(−)-menthyl 2-Methyl Ethene-1,1,2-tricarboxylate (3). A solution containing 1,1-di-(−)-menthyl 2-methyl ethane-1,1,2-tricarboxylate (**19**) (1.81 g, 4.0 mmol) in carbon tetrachloride (7.5 mL) was treated with azobis(isobutyronitrile) (3.7 mg). Bromine (918 mg, 5.75 mmol) was added to the mixture in small portions with irradiation by a 100 V−60 W lamp. The addition rate was adjusted so that hydrogen bromide was evolved at a steady rate. After the addition, stirring and irradiation was continued for 16 h. The reaction mixture was concentrated in vacuo to give crude 1,1-di-(−)-menthyl 2-methyl 1-bromoethane-1,1,2-tricarboxylate. The crude bromide (2.355 g) was dissolved in anhydrous ether (8.5 mL) and was cooled to 0 °C. Triethylamine (425 mg, 4.20 mmol) in ether (3.2 mL) was then added dropwise to the bromide solution. After the addition, the reaction mixture was stirred for 16 h at 0 °C. Water was added to the mixture, and the formed triethylamine hydrobromide salt was dissolved. The mixture was extracted with ether, and the ether extracts were dried ($MgSO_4$) and evaporated in vacuo. The residue was purified by column chromatography over silica gel eluting with hexanes−ether (4:1) to give **3** (1.63 g, 91%). **3**: R_f = 0.7 (hexane−ether = 2:1); colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) 0.74−1.15 (m, 24H), 1.32−1.88 (m, 8H), 1.99−2.26 (m, 4H), 3.78 (s, 3H), 4.86 (ddd, J = 11.2, 11.2, 4.3 Hz, 1H), 4.91 (ddd, J = 11.1, 11.1, 4.3 Hz, 1H), 6.84 (s, 1H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ 15.93, 20.75, 21.86, 21.98, 22.99, 25.42, 25.94, 31.32, 34.09, 40.11, 40.52, 46.79, 47.03, 52.19, 76.14, 76.49, 128.8, 139.4, 161.8, 163.7; IR (neat) 2950, 2868, 1730, 1653 cm^{-1}; MS (EI) m/z 450; exact mass M^+ 450.2949 (calcd for $C_{26}H_{42}O_6$ 450.2982); $[\alpha]^{19.3}_D$ −69.4 (c 1.0, $CHCl_3$).

Preparation of Olefins 4. A typical experimental procedure is described for the preparation of **4a**.

1,1-Di-(−)-menthyl 2-Acetylethene-1,1-dicarboxylate (4a). To an ice−water-cooled solution of di-(−)-menthyl oxomalonate (413 mg, 1.0 mmol) in benzene (2.0 mL) was added 1-triphenylphosphoranylidene-2-propanone (318 mg, 1.0 mmol). After stirring for 2.5 h at room temperature, benzene was evaporated and ether was added. The precipitates were removed by filtration. The filtrate was concentrated and the residue was purified by column chromatography over silica gel eluting with cyclohexane−CH_2Cl_2 (3:1) to give **4a** (410 mg, 94%). **4a**: (R_f = 0.5 (cyclohexane−CH_2Cl_2 = 3:1)). Colorless crystals; mp 70−73 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 0.762 (d, J = 6.8 Hz, 3H), 0.845 (d, J = 6.8 Hz, 3H), 0.882−1.12 (m, 18H), 1.36−1.58 (m, 4H), 1.68−1.73 (m, 4H), 1.81−1.86 (m, 1H), 2.00−2.05 (m, 2H), 2.24−2.28 (m, 1H), 2.35 (s, 3H), 4.86 (ddd, J = 10.9, 10.9, 4.5 Hz, 1H), 4.91 (ddd, J = 10.9, 10.9, 4.4 Hz, 1H), 7.09 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 16.04 (q), 16.14 (q), 20.98 (q), 21.02 (q), 22.05 (q), 22.17 (q), 23.19 (t), 23.23 (t), 25.67 (d), 26.14 (d), 30.73 (q), 31.55 (d), 34.28 (t), 34.31 (t), 40.17 (t), 40.75 (t), 47.07 (d), 47.22 (d), 76.38 (d), 76.78 (d), 135.4 (d), 136.2 (s), 162.6 (s), 164.4 (s), 196.1 (s). ^{13}C multiplicities were determined by DEPT; IR (KBr) 2962, 2872, 1736, 1698, 1630 cm^{-1}; MS (EI) m/z 434; exact mass M^+ 434.3020 (calcd for $C_{26}H_{42}O_5$ 434.3032); Anal. Calcd for $C_{26}H_{42}O_5$: C, 71.85; H, 9.74. Found: C, 71.69; H, 9.68; $[\alpha]^{33.9}_D$ −82.0 (c 0.97, $CHCl_3$).

Typical Experimental Procedure for Cycloadditions with 3 and 4 (entry 2 in Table 2). To a solution of **1a** (255 mg, 1.0 mmol) in dichloromethane (2.0 mL) cooled to −78 °C was added ZnI_2 (479 mg, 1.5 mmol) followed by a solution of **3** (586 mg, 1.3 mmol) in dichloromethane (0.5 mL). The mixture was allowed to warm to −30 °C and stirred for 14 h. The reaction mixture was quenched by triethylamine (0.36 mL, 2.37 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 cyclohexane−CH_2Cl_2 (4:1) to give **6a** (273 mg, 39%, de 92%). The de% was determined by integration of the ^1H signals at δ 2.74 (major) and δ 2.86 (minor).

1,1-Di-(−)-menthyl 2-Methyl 3-[(Phenylseleno)(trimethylsilyl)methyl]-2,3-*cis*-cyclopropane-1,1,2-tricarboxylate (6a). (R_f = 0.6 (hexane−ether = 4:1)). Pale yellow oil; ^1H NMR (200 MHz, $CDCl_3$) for the major diastereomer −0.081 (s, 9H), 0.754 (d, J = 6.8 Hz, 3H), 0.788 (d, J = 6.8 Hz, 3H), 0.837−1.11 (m, 18H), 1.32−2.14 (m, 12H), 2.20 (dd, J = 13.2, 9.5 Hz, 1H), 2.74 (d, J = 9.5 Hz, 1H), 3.19 (d, J = 13.2 Hz, 1H), 3.68 (s, 3H), 4.77 (ddd, J = 10.9, 10.9, 4.4 Hz, 2H), 7.20−7.27 (m, 3H), 7.62−7.64 (m, 2H). Selected observed NOE's were between δ 2.20 (H_3) and 2.74 (H_2) (see ^1H numbering in Scheme 1) and between δ 3.19 and 7.62−7.64.; ^{13}C NMR (50.1 MHz, $CDCl_3$) for the major diastereomer δ −1.646, 15.90, 16.14, 21.04, 21.30, 22.09, 22.21, 22.82, 23.20, 24.07, 25.39, 26.00, 31.46, 31.52, 33.59, 34.27, 36.19, 40.40, 40.49, 40.81, 47.00, 47.17, 51.96, 75.84, 76.66, 127.6, 128.7, 129.4, 135.8, 164.3, 168.5, 168.9; IR (neat) 2930, 2344, 1730, 1578 cm^{-1}; MS (EI) m/z 706; exact mass M^+ 706.3191 (calcd for $C_{37}H_{58}O_6SeSi$ 706.3168); $[\alpha]^{20.2}_D$ −108.6 (c 1.0, $CHCl_3$).

14. Yield 86% (entry 3 in Table 2). (9:1 *trans-cis* isomers) (R_f = 0.4 (hexane−ether = 4:1). Pale yellow oil; ^1H NMR (200 MHz, $CDCl_3$) for the major trans isomer) 0.736 (d, J = 6.6 Hz, 6H), 0.819−1.05 (m, 18H), 1.21−1.96 (m, 12H), 3.70 (s, 3H), 3.73−3.87 (m, 2H), 4.63−4.77 (m, 2H), 5.73 (ddd, J = 15.4, 6.5, 2.6 Hz, 1H), 6.74 (d, J = 15.4 Hz, 1H), 7.27−7.31 (m, 3H), 7.43−7.48 (m, 2H); ^{13}C NMR (50.1 MHz, $CDCl_3$) for major peaks δ 15.93, 16.11, 20.60, 20.69, 21.89, 23.05, 23.29, 25.77, 25.91, 26.06, 31.20, 31.26, 34.03, 40.28, 40.75, 46.71, 46.79, 49.65, 52.28, 53.39, 54.00, 75.52, 75.73, 125.7, 126.8, 127.5, 128.9, 129.2, 132.6, 166.8, 166.9, 171.1.; IR (neat) 2932, 2872, 1730, 1609, 1580 cm^{-1}; MS (EI) m/z 634; exact mass M^+ 634.2755 (calcd for $C_{34}H_{50}O_6Se$ 634.2773); Anal. Calcd for $C_{34}H_{50}O_6Se$: C, 64.44; H, 7.95. Found: C, 64.28; H, 8.07.

Theoretical calculations. Ab initio RHF/3-21G* calculations were performed, using the GAUSSIAN 94[16] program installed at the CONVEX SPP-1200/XA computer (Information Processing Center, Nara University of Education). Detailed data and related discussions are included in the Supporting Information.

Acknowledgment. We are grateful to Dr. K. Yamamoto (Osaka University) for measurement of mass spectral data. This work was supported by the Grant-in-Aid for Scientific Research on Priority Area No. 10125226 from the Ministry of Education, Science, Sports and Culture, of the Japanese Government.

Supporting Information Available: The detailed version of Tables 1 and 2, the product characterization data for **4b**−**f**, **6b** (which appears in the detailed version of Table 2 in the Supporting Information) and **7a**−**f**, ^1H NMR spectra for compounds **3**, **4b**,**c**, **6a**,**b**, **7a**−**c**, **7e**,**f**, **9b**, **10b**, **11**−**13**, and **20**, and results of theoretical analyses using ab initio calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

JO9820925