[2 + 1] Cycloaddition Reactions of a 1-Seleno-2-silylethene to 2-Sulfonylacrylates: Stereoselective Synthesis of Sulfone-Substituted Cyclopropanes

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Reaction of 1-(phenylseleno)-2-(trimethylsilyl)ethene **1** and methyl or ethyl 2-*p*-toluene- or benzenesulfonylacrylates **3** in the presence of $SnCl_4$ at −78 °C gave sulfone-substituted cyclopropanes **4** as single stereoisomers. The structure of one of these crystalline cyclopropane products was elucidated by X-ray crystallographic analysis. The relative stereochemistry of the cyclopropane ring carbon (C_2) and selenosilylmethyl group was determined as *R,R* and *S,S*, which is consistent with previous mechanical considerations and the NOE determination. 2-Sulfinyl acrylate **2** did not undergo this cycloaddition. The difference in reactivity of the sulfoxide **2** and sulfones **3** toward **1** was explained by comparison of LUMO levels of **2**−$SnCl_4$ and **3**−$SnCl_4$ complexes and activation energies in the synclinal addition of **1** to the complexes.

Introduction

Organosulfur compounds have attracted much attention due to their synthetic usefulness and biological interest.[1,2] Among them, sulfones and sulfoxides have been utilized for C−C bond formation as carbonyl group equivalents for many synthetic transformations.[1] In this respect, unsaturated sulfones and sulfoxides are useful Michael acceptors since they have strong electron-withdrawing properties. Lewis acid-promoted reactions of unsaturated sulfones and sulfoxides are also useful since their oxygen atoms can coordinate to Lewis acids.[3,4]

We have recently reported a novel [2 + 1] cycloaddition strategy involving reactions of (*E*)-1-(phenylseleno)-2-silylethenes with electrophilic olefins to afford cyclopropane products with high stereoselectivity in the presence of Lewis acids.[5] This new approach to cyclopropane construction is based on a selenium-stabilized 1,2-silicon migration process. As part of efforts to expand this novel [2 + 1] cycloaddition reaction to electrophilic olefins with synthetically and biologically useful substituents, we became interested in sulfur-containing substrates.

2-Sulfinylacrylates **2** and 2-sulfonylacrylates **3** were expected to have high reactivity toward 1-seleno-2-silylethene **1**. They are isoelectronic analogues of methylenemalonate esters, which have been shown to have effective reactivity toward **1**.[5b] A different class of heteroatom analogues of methylenemalonates, 2-phosphonoacrylates, have been found to be even better substrates.[5e]

The expected sulfur-substituted cyclopropane products represent potentially versatile starting materials to access biologically important compounds.[6] Herein, we report the stereoselective [2 + 1] cycloaddition of 1-seleno-2-silylethene **1** to 2-sulfonylacrylates **3** leading to the cyclopropanes **4**. These products are crystalline, and the structure of a cyclopropane product was determined by X-ray crystallographic analysis. The relative stereochemistry of the cyclopropane ring carbon (C_2) and selenosilylmethyl group, which has not been unequivocally elucidated directly so far in related cyclopropanes, was determined as *R,R* and *S,S*. On the other hand, addition did not occur in reactions between **1** and **2** (Scheme 1). The crucial difference in the reactivities of **2** and **3** was scrutinized by FMO analyses and ab initio calculations.

Results and Discussion

A. [2 + 1] Cycloaddition with 2-Sulfonylacrylates. Since Lewis acid-promoted reactions of α,β-unsaturated

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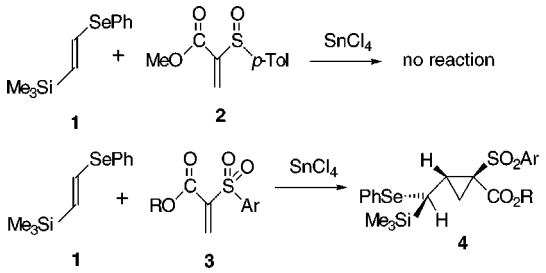
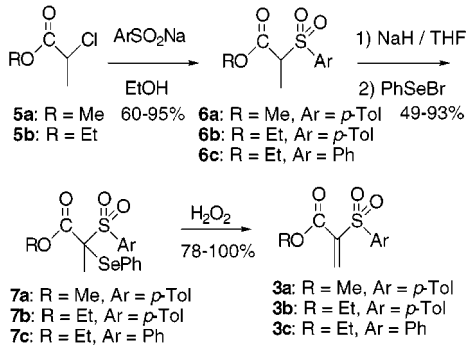
Scheme 1



Scheme 2

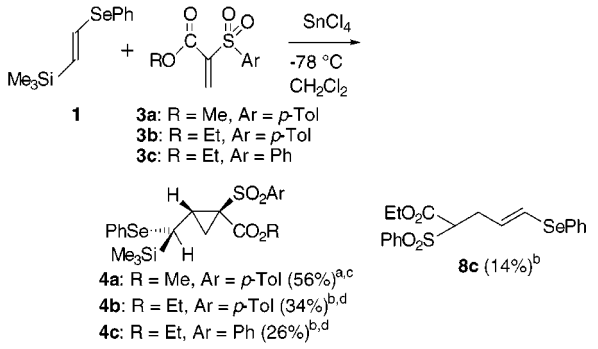


sulfoxides have received much attention recently,[3] we initially attempted reaction of a sulfoxide analogue of methylenemalonate, the 2-sulfinylacrylate **2**,[7] with **1**. However, reaction did not proceed in the presence of $SnCl_4$ and $ZnBr_2$, which are the most effective Lewis acids in this type of [2 + 1] cycloaddition reaction.[5] Next, reaction of the sulfone analogue **3** was attempted, since sulfone groups are more electron-withdrawing than sulfoxide groups, as suggested by Hammett constants and the pK_a of methyl sulfone and sulfoxide.[8] The electronic effect of the sulfone groups suggests higher reactivity of 2-sulfonylacrylates **3** toward **1**. In addition, sulfone groups often impart crystalline properties, which are useful for purification and structure determination.

2-Arylsulfonylacrylates **3** were prepared by employing known literature procedures for 2-alkylsulfonylacrylates (Scheme 2).[9] Although the difficulty of preparing pure methyl 2-(phenylsulfonyl)acrylate has been pointed out,[10] these 2-arylacrylates **3** were isolated in pure form by this procedure.[11]

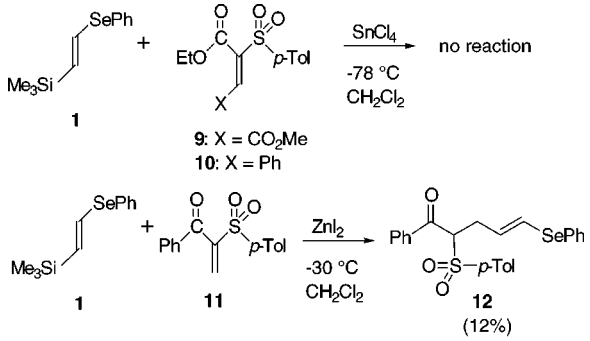
The [2 + 1] cycloaddition reactions of **1** and **3** were performed as follows (Scheme 3). Reactions of **1** (1 equiv) and 2-sulfonylacrylates **3a**−**c** (1.3 equiv) were carried out in the presence of $SnCl_4$ (1.5 equiv) in CH_2Cl_2 at −78 °C for 3 h. Quenching with triethylamine (2.6 equiv) gave [2 + 1] cycloadducts **4a**−**c** as single stereoisomeric products in 26−56% yields. The relatively low yields are

Scheme 3



[a] Isolated yield by column chromatogaphy. [b] Isolated yield by recrystallization. [c] **1** was recovered in 13% yield. [d] A small amount of **1** remained but was not isolated.

Scheme 4



probably due to the instablity of **3** and the reaction intermediates under the reaction conditions, leading to formation of complex mixtures, including desilylated products. In the case of reaction of **1** and **3c**, desilylated byproduct **8c** was isolated in 14% yield. Using $ZnBr_2$ as a Lewis acid in the reaction of **1** and **3a** resulted in decomposition of **3a**.

No reaction occurred between the donor olefin **1** and the 3-substituted (*E*)-2-sulfonylacrylates **9** and **10**[12] under these reaction conditions, indicating synthetic limitations.[13] We also attempted the reaction of **1** with α-sulfonyl-α,*β*-unsaturated ketone **11** under similar conditions ($SnCl_4$, −78 °C); however, the reaction gave a complex mixture along with recovered **1** (41%). The reaction of **1** and **11** in the presence of ZnI_2 at −30 °C for 5.5 h gave only the desilylated addition product **12** in 12% yield, and no cycloadduct was obtained (Scheme 4).

B. Structure Determination of the Cyclopropanes 4. The products **4a**−**c** in Scheme 3 are crystalline and easily purified by recrystallization. The cyclopropane skeleton of **4a** was determined by the characteristic $^1J_{CH}$ values present in the ^{13}C NMR spectrum (J = 163−169 (C_2) and 166−167 (C_3) Hz).[14] The stereochemistry in the cyclopropane rings of **4a**−**c** was readily deduced from the 2D-NOESY spectra. The NOE cross-peaks between H_1 and *o*-H of SO_2-Tol (*o*-H of SO_2Ph) and between H_2 and

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(9) Gipstein, E.; Willson, C. G.; Sachdev, H. S. *J. Org. Chem.* **1980**, *45*, 1486.

(10) (a) Snider, B. B.; Phillips, G. B. *J. Org. Chem.* **1983**, *48*, 3685. In the following references methyl 2-(phenylsulfonyl)acrylate appears; however, the preparation was not described. (b) Pearson, A. J.; Mortezaei, R. *Tetrahedron Lett.* **1989**, *30*, 5049. (c) Hirsenkon, R.; Schmidt, R. R. *Liebigs Ann. Chem.* **1990**, 883.

(11) 2-Arylsulfonylacrylates **3** were unstable to column chromatography (SiO_2).

(12) **10** was prepared according to the literature procedure. Tanikaga, R.; Tamura, T.; Nozaki, Y.; Kaji, A. *J. Chem. Soc., Chem. Commun.* **1984**, 87.

(13) Under the reaction conditions, **10** was isomerized to a ca. 1:1 mixture of *E*/*Z* isomers, by ^1H NMR of the reaction mixture. Due to instability to column chromatography, the mixture could not be isolated.

(14) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic: New York, 1972.

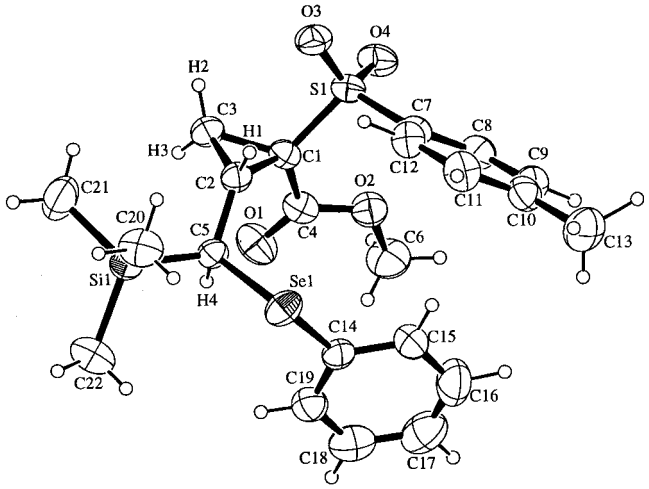
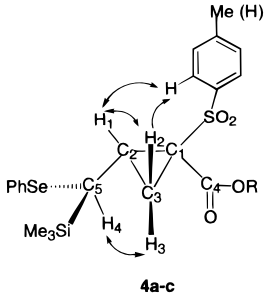


Figure 1. ORTEP drawing of **4a** (50% probability ellipsoids). Selected bond lengths (Å) and torsion angle (deg): C1−C2 = 1.548(4); C1−C3 = 1.532(4); C2−C3 = 1.497(4); C1−S1 = 1.785(3); C1−C4 = 1.495(4); C4−O1 = 1.201(3); O2−C6 = 1.444(4); S1−O3 = 1.443(2); S1−O4 = 1.437(2); S1−C7 = 1.767(3); C2−C5 = 1.510(4); C5−Se1 = 1.982(3); C5−Si1 = 1.901(3); Se1−C14 = 1.920(3); ∠H1−C2−C5−H4 = 172(2). More detailed structure data are given in the Supporting Information.

Chart 1. Observed NOE's (Atom Numbering Uses That of Figure 1)



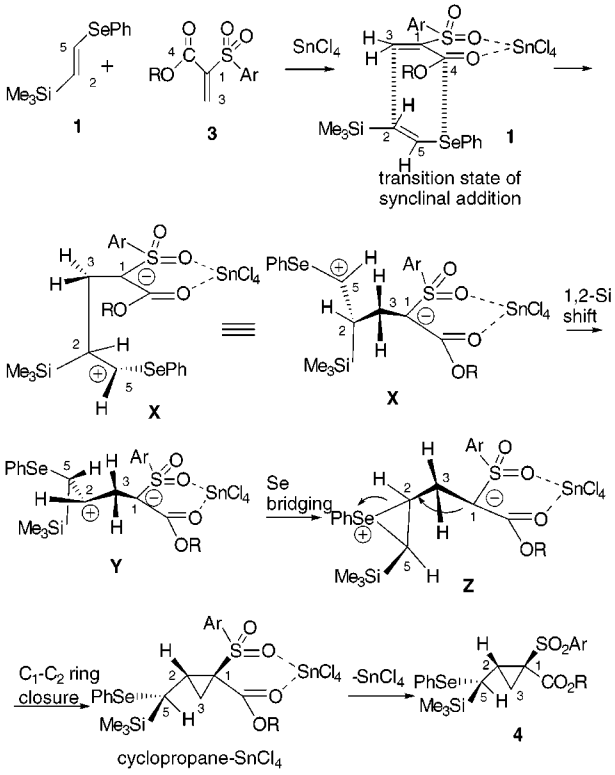
4a-c

o-H of SO_2Tol (*o*-H of SO_2Ph) indicated that the CO_2R and CH(SePh)($SiMe_3$) groups were cis (Chart 1). Finally, the structure of cyclopropane **4a** was elucidated by single-crystal X-ray analysis (Figure 1). Thus, the cis relationship of the CO_2R and CH(SePh)($SiMe_3$) groups was confirmed, and the relative stereochemistry of the cyclopropane ring carbon (C_2) and selenosilylmethyl group (C_5) in the racemic cyclopropane **4a** was determined as *R*,*R* and *S*,*S*.

In this series of novel cyclopropanation reactions of **1**, the relative stereochemistry of C_2 and the selenosilylmethyl group has hitherto been determined by mechanical considerations and by combination of the assumption that $\angle H_1-C_2-C_5-H_4$ is close to 180° and the observable NOE's in the examples reported so far.[5b,d,e] The relative stereochemistry of C_2 and C_5 confirmed by X-ray is consistent with the previous assignments of related cyclopropanes.[5] Also, the dihedral angle $\angle H_1-C_2-C_5-H_4$ observed in **4a** was found to be 172°, which is in good agreement with the above assumption.

The proposed reaction mechanism is similar to that described previously, as shown in Scheme 5.[5] Reaction involves a synclinal stereoselective addition (due to a stabilizing secondary orbital interaction, Se- - -C═O, not Se- - -SO_2Ar) and also involves a selenium-stabilized 1,2-silicon migration in the resulting zwitterionic intermediate. The stereochemistry of the original addition step is retained throughout this proposed mechanism, which finally leads to the relative stereochemistry of C_2, C_5, and C_4.

Scheme 5. Proposed reaction mechanism for cyclopropanation (The Carbon Atom Numbering Adjusts to Chart 1)



C. Theoretical Study on Reactivity of Sulfones and Sulfoxides. The difference in the electrophilic effect between the sulfone and sulfoxide groups (for example, pK_a Me_2SO_2 31.1, Me_2SO 35.1)[8b] was initially thought to be responsible for the different reactivity of **2** and **3**. However, this difference is insufficient to explain the success or failure of the cyclopropanation reaction clearly. The pronounced reactivity difference between **2** and **3** prompted us to investigate the reactive species according to our proposed mechanism (Scheme 5). The lower electrophilicity of the sulfoxide **2** compared to the sulfone **3a** toward **1** may be explained by comparison of the LUMO energy levels of **2**−$SnCl_4$ and **3a**-$SnCl_4$ complexes. Unfortunately, little is known about the chemistry and structure of sulfone-Lewis acid complexes compared to those of carbonyl-Lewis acid complexes.[15] We carried out ab initio MO calculations for structures of complexes of **2** and **3a** with $SnCl_4$ using the LANL2MB method.[16] All ab initio molecular orbital calculations were performed using the Gaussian 94 program package.[17] First, geometries of **2** and **3a** were calculated (Figure S1 in the Supporting Information). The LANL2MB-optimized S−O distances (1.439 Å) of the sulfone **3a** are in good agreement with S−O distances (1.443, 1.437 Å) of the sulfone **4a** by X-ray analysis. Chelate structures for **2**−$SnCl_4$ and

(15) Furukawa, N.; Fujiwara, H. In *The Chemistry of Sulphones and Sulphoxides*; Patai, S., Rappoport, Z., Stirling, C. J. M., Eds.; Wiley: 1988; p 541.

(16) (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270. (b) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

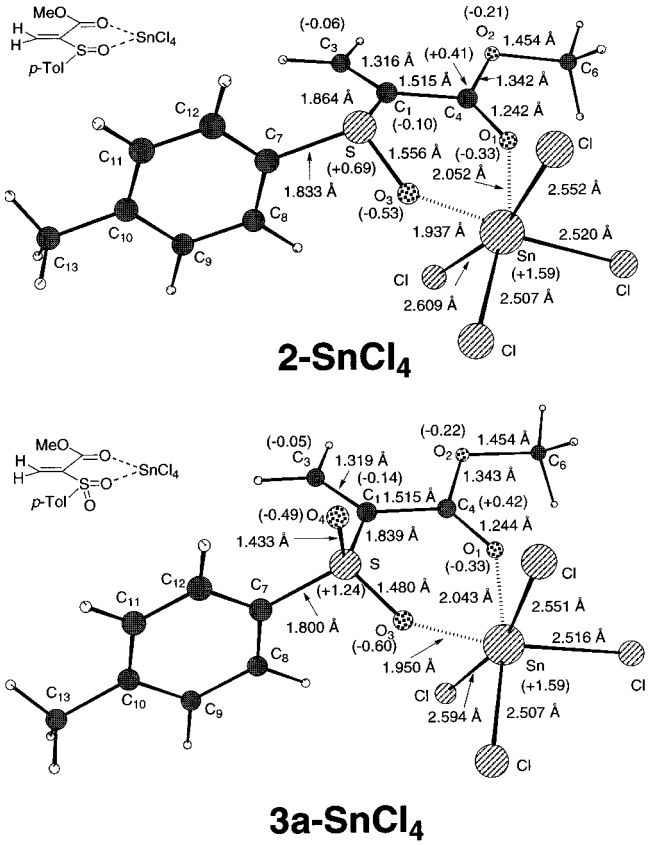
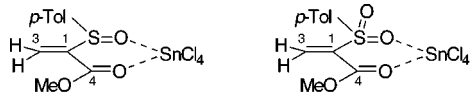


Figure 2. Ab initio RHF/LANL2MB-optimized geometries of **2**−$SnCl_4$ and **3a**−$SnCl_4$. Numbers in parentheses denote atomic net charges of STO-3G//LANL2MB.

3a−$SnCl_4$, which may be more stable than the corresponding nonchelate structures, were successfully obtained (Figure 2). Such Lewis acid-chelating properties have been suggested in Lewis acid-catalyzed reactions of β-carbonyl sulfoxides[3] and sulfones.[4]



The frontier orbital LUMOs of the complexes **2**−$SnCl_4$ and **3a**−$SnCl_4$ were calculated by STO-3G//LANL2MB. As discussed previously, the LUMO levels of electrophilic olefin−Lewis acid complexes are critical for high reactivity.[5d] The LUMO level of **3a**−$SnCl_4$ (+0.09143 au) was found to be substantially lower than that of **2**−$SnCl_4$ (+0.10019 au). Thus, the low LUMO energy level of **3a**−$2SnCl_4$ causes a small HOMO−LUMO gap between **1** and **3a**−Lewis acid complex, leading to a large charge-transfer interaction (the upward bold arrows in Figure 3) and accordingly higher reactivity. The LUMO shapes

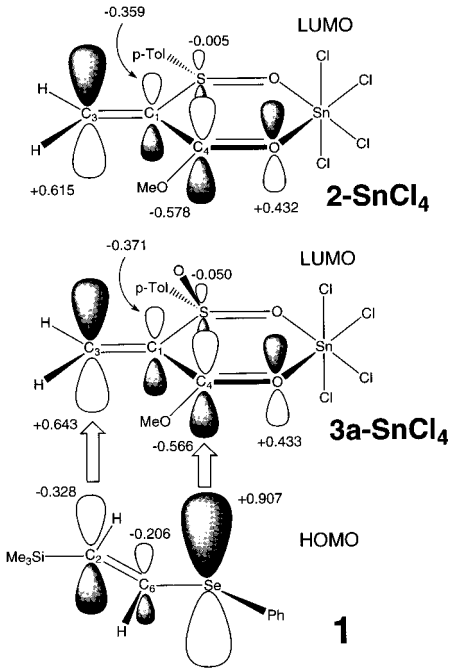


Figure 3. Frontier orbital coefficients of the LUMO of **2**−$SnCl_4$ and **3a**−$SnCl_4$ and HOMO of **1**. These coefficients are of STO-3G//LANL2MB.[16,17] Bold upward arrows show the most favorable orbital interaction leading to the synclinal-addition path in Scheme 5 and Figure 4.

of **3a**−$SnCl_4$ and **2**−$SnCl_4$ are shown in Figure 3. They indicate that the most electrophilic site in **3a**−$SnCl_4$ is the C_3 atom (+0.643) and that the coefficient of C_4 (−0.566) is larger than that of the sulfur atom (−0.050). The $SnCl_4$ coordination is found to provide the combination of the largest C_3, C_4 coefficients suitable to the synclinal orientation. Effective overlap of LUMO with the HOMO of **1** controls the orientation in the synclinal addition step, which leads to the transition-state geometries (Figure 4) and the observed stereochemistry, as discussed above (Scheme 5).

The transition states of the addition step between **3a**−$SnCl_4$ and **2**−$SnCl_4$ complexes and **1** were next calculated (Figure 4). E_a (activation energies) of addition between **2**−$SnCl_4$/**3a**−$SnCl_4$ and **1** were obtained for both top side and bottom side attack by **1**. Then, the transition states with the lower activation energies for each substrate were compared.[18] In accordance with the difference between the LUMO energies of **2**−$SnCl_4$ and **3a**−$SnCl_4$, the E_a value for **3a**−$SnCl_4$ (25.3 kcal/mol) is smaller than that for **2**−$SnCl_4$ (26.9 kcal/mol for **2**−$SnCl_4$). Comparison of both the LUMO levels of **2**−$SnCl_4$ and **3**−$SnCl_4$ complexes and the activation energies in the synclinal addition of **1** to the complexes explains the present experimental results.[19]

(17) 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).

(18) The π-facial selectivity for Lewis acid-catalyzed reactions of chiral 2-sulfinyl acrylates has been reported.[3]

(19) In addition, we have examined alternative structures for the **3a**−$SnCl_4$ complex including a double $SnCl_4$-coordinated structures[20,21] by ab initio calculations. The result shows the remarkably low activation energy of the addition step between **3a**-$2SnCl_4$ and **1**. The double $SnCl_4$ coordination to **3a** possibly gives rise to a highly enhanced reactivity in the synclinal addition. The calculation results and the discussion are presented in the Supporting Information.

(20) (a) Langford, C. H.; Langford, P. O. *Inorg. Chem.* **1962**, *1*, 184. (b) Drago, R. S.; Wayland, B.; Carlson, R. L. *J. Am. Chem. Soc.* **1963**, *85*, 3125.

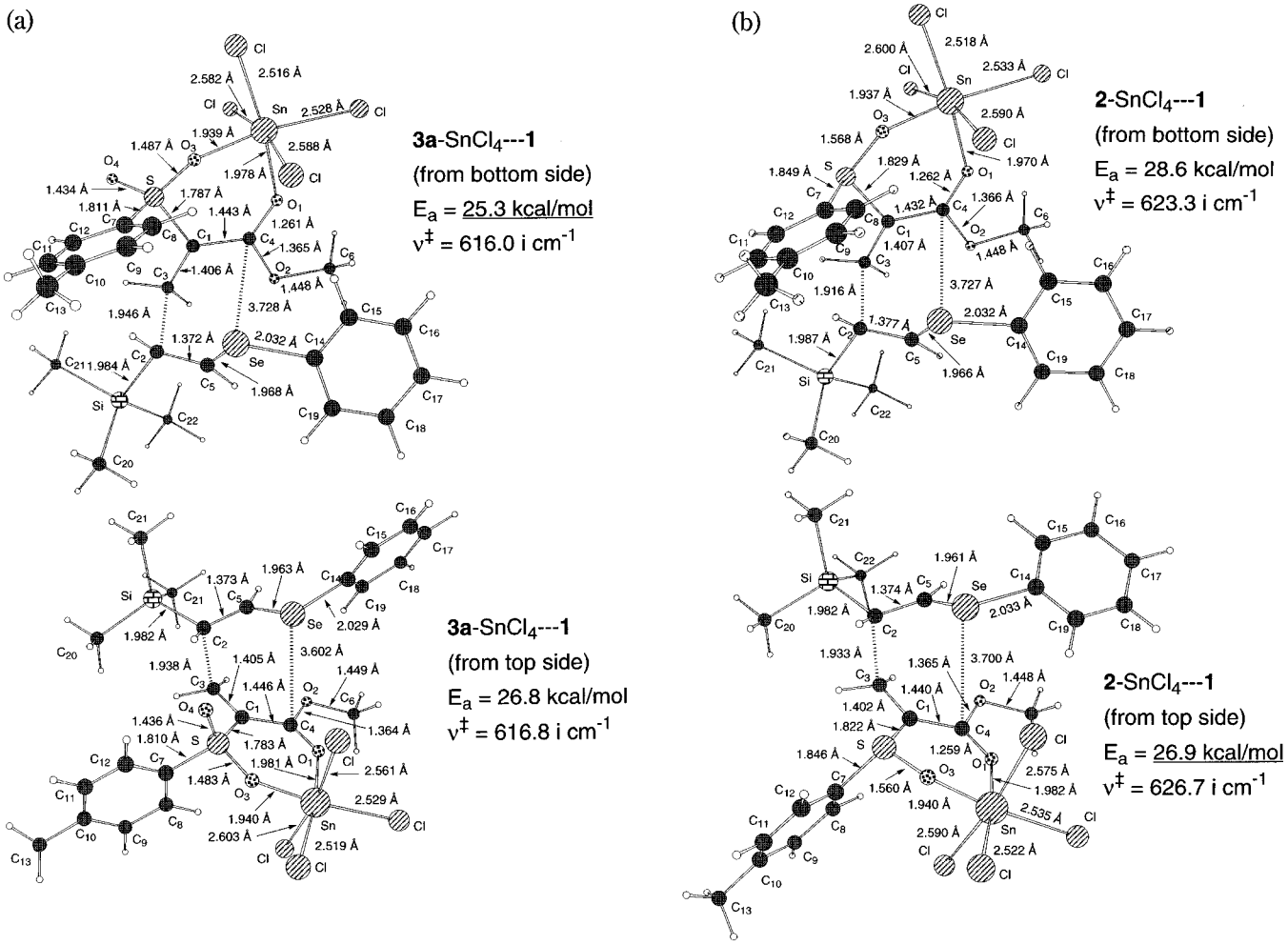


Figure 4. (a) Ab initio RHF/LANL2MB-optimized geometries of transition states (TSs) for the addition step between **3a**−$SnCl_4$ and **1**. The activation energy E_a is relative to those of reactants **3a**−$SnCl_4$ and **1**. The atom numbering follows that in Figure 1. Small white circles stand for hydrogen atoms. E_a's of addition between **3a**−$SnCl_4$ and **1** are obtained for both top side and bottom side attacks by **1**. The transition states with the lower activation energies (underlined) were compared in the text. $\nu^{\ddagger}$ denotes a sole imaginary frequency, which verifies that the obtained geometry is correctly of the saddle point. (b) Ab initio RHF/LANL2MB-optimized geometries of transition states (TSs) for the addition step between **2**−$SnCl_4$ and **1**. The activation energy E_a is relative to those of reactants **2**−$SnCl_4$ and **1**. E_a's of addition between **2**−$SnCl_4$ and **1** are obtained for both top side and bottom side attacks by **1**. The transition states with the lower activation energies (underlined) were compared in the text.

Concluding Remarks

We have shown that 1-seleno-2-silylethene **1** and 2-sulfonylacrylates **3** undergo $SnCl_4$-promoted [2 + 1] cycloaddition reactions stereoselectively. The products are crystalline, and the structure of a cyclopropane product was elucidated by X-ray crystallographic analysis for the first time in this series of [2 + 1] cycloaddition reactions. The relative stereochemistry of the cyclopropane ring carbon C_2 and selenosilylmethyl group was unambiguously determined as *R*,*R* and *S*,*S*, which is consistent with the previous assignment of the cyclopropane products. The difference in the reactivity between the sulfoxide **2** and the sulfone **3** was explained by comparison of LUMO levels of **2**−$SnCl_4$ and **3**−$SnCl_4$ complexes and activation energies in the synclinal addition of **1** to the complexes.

Although the yields in this [2 + 1] cycloaddition reaction of 2-sulfonylacrylates **3** are not high, the reasction represents a new usage of **3** in the presence of Lewis acids. We are further investigating heteroatom-based effective electrophilic olefins for the [2 + 1] cycloaddition reactions of **1**, leading to biologically interesting compounds.

Experimental Section

General Methods. Melting points are uncorrected. IR spectra were recorded in the FT-mode. ^{1}H NMR spectra were recorded at 400 MHz. ^{13}C NMR spectra were recorded at 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. All reactions were carried out under a nitrogen atmosphere.

Methyl 2-(*p*-Toluenesulfonyl)propanate (6a). A solution of *p*-toluenesulfinic acid, sodium salt hydrate (12.5 g, 50.0 mmol), methyl 2-chloropropionate (5.7 mL, 6.13 g, 50.0 mmol), and ethanol (25 mL) was refluxed for 24 h. The solution was filtered to remove sodium chloride and concentrated under reduced pressure. The residue was purified by column chromatography over silica gel eluting with CH_2Cl_2 to give **6a** (8.20 g, 68%) (R_f = 0.3): colorless crystals; mp 49−52 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.55 (d, J = 7.1 Hz, 3H), 2.46 (s, 3H), 3.70 (s, 3H), 4.07 (q, J = 7.1 Hz, 1H), 7.37 (d-like, J = 8.5 Hz, 2H), 7.75 (d-like, J = 8.5 Hz, 2H); ^{13}C NMR (100.6 MHz,

(21) For examples of chlorine-bridged tin(IV) complexes and 4−8 coordinated tin(IV) complexes, see: Harrison, R. G. In *Chemistry of Tin*; Harrison, R. G., Ed.; Blackie: Glasgow, 1989; p 9.

$CDCl_3$) δ (ppm) 12.06 (q), 21.77 (q), 53.04 (q), 65.44 (d), 129.4 (d), 129.8 (d), 133.8 (s), 145.5 (s), 166.9 (s); IR (KBr) 1742, 1601, 1317, 1139 cm^{-1}; MS (EI) *m/z* 242; exact mass M^+ 242.0620 (calcd for $C_{11}H_{14}O_4S$ 242.0613). Anal. Calcd for $C_{11}H_{14}O_4S$: C, 54.53; H, 5.82. Found: C, 54.24; H, 5.79.

Ethyl 2-(*p*-toluenesulfonyl)propanate (6b): yield 95%; R_f = 0.2 (CH_2Cl_2; colorless crystals; mp 38−40 °C (hexane−ether); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.19 (t, J = 7.1 Hz, 3H), 1.55 (d, J = 7.1 Hz, 3H), 2.46 (s, 3H), 4.02 (q, J = 7.1 Hz, 1H), 4.13 (q, J = 7.1 Hz, 2H), 7.36 (d-like, J = 8.4 Hz, 2H), 7.76 (d-like, J = 8.4 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm) 11.96 (q), 13.92 (q), 21.77 (q), 62.28 (t), 65.53 (d), 129.5 (d), 129.7 (d), 134.0 (s), 145.4 (s), 166.4 (s); IR (KBr) 1740, 1597, 1325, 1150 cm^{-1}; MS (EI) *m/z* 256; exact mass M^+ 256.0760 (calcd for $C_{12}H_{16}O_4S$ 256.0769). Anal. Calcd for $C_{12}H_{16}O_4S$: C, 56.23; H, 6.29. Found: C, 56.20; H, 6.35.

Ethyl 2-(benzenesulfonyl)propanate (6c): yield 76%; R_f = 0.3 (CH_2Cl_2); colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.17 (t, J = 7.1 Hz, 3H), 1.58 (d, J = 7.1 Hz, 3H), 4.05 (q, J = 7.1 Hz, 1H), 4.115 (q, J = 7.1 Hz, 1H), 4.117 (q, J = 7.1 Hz, 1H), 7.56−7.60 (m, 2H), 7.67−7.72 (m, 1H), 7.89−7.92 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm) 11.82 (q), 13.90 (q), 62.31 (t), 65.48 (d), 129.1 (d), 129.4 (d), 134.3 (d), 137.1 (s), 166.3 (s); IR (KBr) 1734, 1586, 1320, 1147 cm^{-1}; MS (EI) *m/z* 243 ($M^+ + 1$). Anal. Calcd for $C_{11}H_{14}O_4S$: C, 54.53; H, 5.82. Found: C, 54.26; H, 6.00.

Methyl 2-(Phenylseleno)-2-(*p*-toluenesulfonyl)propanate (7a). Sodium hydride (222 mg, 60% dispersion in oil, 5.55 mmol, washed three times with pentane) was suspended in freshly distilled THF (6.9 mL). After the mixture was cooled to −10 °C, methyl 2-(*p*-toluenesulfonyl)propanate (**6a**) (1.34 g, 5.53 mmol) in THF (2.3 mL) was added dropwise, and the mixture was cooled to −20 °C and stirred for 2 h. Phenylselenyl bromide [5.54 mmol, prepared by adding bromine (0.14 mL, 443 mg, 2.77 mmol) to a stirred solution of diphenyl diselenide (865 mg, 2.77 mmol) in THF (3.5 mL) at room temperature followed by further stirring for 10 min] was then added. After 2 h at −20 °C, the mixture was allowed to warm to room temperature. The mixture was treated with a saturated solution of NH_4Cl (0.46 mL), and THF was removed under reduced pressure. The residue was extracted with three portions of ether. The combined ether extracts were washed with brine and dried ($MgSO_4$). The solvent was evaporated in vacuo. The residue was purified by column chromatography over silica gel eluting with hexane−ether (1:1) to give **7a** (1.54 g, 70%): R_f = 0.4; colorless crystals; mp 102−105 °C; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.63 (s, 3H), 2.45 (s, 3H), 3.64 (s, 3H), 7.30−7.35 (m, 4H), 7.43 (t-like, J = 7.4 Hz, 1H), 7.71 (d-like, J = 8.2 Hz, 2H), 7.82 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm) 20.10, 21.71, 53.25, 71.08, 125.8, 129.0, 129.2, 130.2, 130.9, 132.7, 138.6, 145.4, 167.4; IR (KBr) 1740, 1597, 1299, 1137 cm^{-1}; MS (EI) *m/z* 398; exact mass M^+ 398.0161 (calcd for $C_{17}H_{18}O_4SSe$ 398.0092). Anal. Calcd for $C_{17}H_{18}O_4SSe$: C, 51.39; H, 4.57. Found: C, 51.19; H, 4.44.

Ethyl 2-(phenylseleno)-2-(*p*-toluenesulfonyl)propanate (7b): yield 93%; R_f = 0.2 (hexane/ether = 2:1); colorless crystals; mp 88−91 °C; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.20 (t, J = 7.1 Hz, 3H), 1.63 (s, 3H), 2.46 (s, 3H), 4.09 (q, J = 7.1 Hz, 2H), 7.31−7.35 (m, 4H), 7.43 (t-like, J = 7.4 Hz, 1H), 7.73 (d-like, J = 8.2 Hz, 2H), 7.84 (d, J = 8.2 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm) 13.82 (q), 20.11 (q), 21.80 (q), 62.91 (t), 71.19 (s), 126.0 (s), 129.0 (d), 129.2 (d), 130.3 (d), 131.2 (d), 132.9 (s), 138.7 (d), 145.4 (s), 167.1 (s); IR (KBr) 1736, 1595, 1300, 1139 cm^{-1}; MS (EI) *m/z* 412; exact mass M^+ 412.0208 (calcd for $C_{18}H_{20}O_4SSe$ 412.0247). Anal. Calcd for $C_{18}H_{20}O_4SSe$: C, 52.55; H, 4.90. Found: C, 52.35; H, 4.69.

Ethyl 2-(benzenesulfonyl)-2-(phenylseleno)propanate (7c): yield 66%; R_f = 0.2 (hexane/ether = 2:1); colorless crystals; mp 56−58 °C; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.17 (t, J = 7.1 Hz, 3H), 1.65 (s, 3H), 4.07 (q, J = 7.1 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.43 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.8 Hz, 2H), 7.66−7.72 (m, 3H), 7.98 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm) 13.73 (q), 20.02 (q), 62.89 (t), 71.17 (s), 125.9 (s), 128.5 (d), 129.0 (d), 130.3 (d), 131.1 (d), 134.2 (d), 135.9 (s), 138.6 (d), 166.8 (s); IR (KBr) 1738, 1305, 1145 cm^{-1}; MS (EI) *m/z* 398; exact mass M^+ 398.0108 (calcd for $C_{17}H_{18}O_4SSe$ 398.0091). Anal. Calcd for $C_{17}H_{18}O_4SSe$: C, 51.39; H, 4.57. Found: C, 51.49; H, 4.39.

Methyl 2-(*p*-Toluenesulfonyl)acrylate (3a). To a solution of **7a** (1.5 g, 3.8 mmol) in dichloromethane (7.3 mL) was added H_2O_2 (30% 2.9 mL, 25.2 mmol) in water (6 mL) at 0 °C. The reaction mixture was stirred at room temperature for 1 h. The reaction mixture was washed with saturated $NaHCO_3$ in CH_2Cl_2. The organic layer was separated and dried (Na_2SO_4). Removal of the solvent in vacuo gave **3a** (0.95 g, 100%): colorless crystals; mp 75−77 °C (hexane−ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 2.44 (s, 3H), 3.74 (s, 3H), 6.98 (s, 1H), 7.12 (s, 1H), 7.34 (d-like, J = 8.1 Hz, 2H), 7.86 (d-like, J = 8.1 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm) 21.77 (q), 52.85 (q), 129.2 (d), 129.7 (d), 136.1 (s), 137.2 (t), 143.6 (s), 145.0 (s), 161.0 (s); IR (KBr) 1729, 1597, 1321, 1154 cm^{-1}; MS (EI) *m/z* 240; exact mass M^+ 240.0447 (calcd for $C_{11}H_{12}O_4S$ 240.0456). Anal. Calcd for $C_{11}H_{12}O_4S$: C, 54.99; H, 5.03; S, 13.35. Found: C, 54.78; H, 4.98; S, 13.26.

Ethyl 2-(*p*-toluenesulfonyl)acrylate (3b): yield 78%; colorless crystals; mp 44−45 °C (hexane−ether); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.23 (t, J = 7.1 Hz, 3H), 2.44 (s, 3H), 4.19 (q, J = 7.1 Hz, 2H), 6.98 (s, 1H), 7.11 (s, 1H), 7.33 (d-like, J = 8.5 Hz, 2H), 7.85 (d-like, J = 8.5 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm) 13.95 (q), 21.76 (q), 62.28 (t), 129.1 (d), 129.6 (d), 136.2 (s), 137.1 (t), 143.8 (s), 145.0 (s), 160.5 (s); IR (KBr) 1721, 1597, 1323, 1158 cm^{-1}; MS (EI) *m/z* 254; exact mass M^+ 254.0622 (calcd for $C_{12}H_{14}O_4S$ 254.0613). Anal. Calcd for $C_{12}H_{14}O_4S$: C, 56.68; H, 5.55. Found: C, 56.71; H, 5.53.

Ethyl 2-(benzenesulfonyl)acrylate (3c): yield 89%; pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.21 (t, J = 7.1 Hz, 3H), 4.18 (q, J = 7.1 Hz, 2H), 7.02 (s, 1H), 7.14 (s, 1H), 7.52−7.57 (m, 2H), 7.64 (t-like, J = 7.4 Hz, 1H), 7.98 (d-like, J = 8.4 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm) 13.87 (q, J = 128 Hz), 62.28 (t, J = 150 Hz), 128.9 (d, J = 165 Hz), 129.0 (d, J = 165 Hz), 129.1 (s), 133.8 (d, J = 161 Hz), 137.5 (t, J = 167 Hz), 139.2 (s), 143.5 (s), 160.3 (s); IR (neat) 1729, 1615, 1323, 1162 cm^{-1}; MS (EI) *m/z* 240; exact mass M^+ 240.0451 (calcd for $C_{11}H_{12}O_4S$ 240.0456).

Methyl *r*-1-(*p*-Toluenesulfonyl)-*c*-2-[(phenylseleno)-(trimethylsilyl)methyl]-1-cyclopropanecarboxylate (4a). To a solution of **1** (255 mg, 1.0 mmol) in dichloromethane (2.4 mL) was added $SnCl_4$ (0.173 mL, 391 mg, 1.5 mmol) followed by 2-sulfonylacrylate **3a** (312 mg, 1.3 mmol) at −78 °C. The mixture was stirred at −78 °C for 3 h. The reaction mixture was quenched by triethylamine (0.32 mL, 230 mg, 2.3 mmol) and then saturated aqueous $NaHCO_3$. 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 **4a** (278 mg, 56%) (R_f = 0.3). An analytically pure sample was recrystallized from hexanes−ether: colorless crystals; mp 117−119 °C (hexanes−ether); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.146 (s, 9H, $SiMe_3$), 1.78 (dd, J = 8.4, 5.1 Hz, 1H, H_3), 2.39 (dd, J = 9.8, 5.1 Hz, 1H, H_2), 2.48 (s, 3H, C_6H_4-*p*-*Me*), 2.49 (d, J = 12.4 Hz, 1H, H_4), 2.63 (ddd, J = 12.4, 9.8, 8.4 Hz, 1H, H_1), 3.20 (s, 3H, OMe), 7.06−7.19 (m, 5H, SePh), 7.37 (d, J = 8.2 Hz, 2H, *m*-H of SO_2-Tol), 7.88 (d, J = 8.2 Hz, 2H, *o*-H of SO_2-Tol) (see numbering in Chart 1); selected NOEs in the 2D-NOESY spectra were between δ 1.78 and 2.49, δ 2.39 and 2.63, δ 2.39 and 7.88, δ 2.63 and 7.88; ^1H assignments were determined by H−H COSY and NOESY; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm) −1.894 (q, J = 120 Hz), 21.73 (qt, J = 127, 4.4 Hz), 24.61 (t, J = 166 Hz, C_3), 28.81 (d, J = 137 Hz, C_5), 36.33 (dd, J = 166, 6.5 Hz, C_2), 50.53 (s, C_1), 52.40 (q, J = 148 Hz), 127.3 (dt, J = 160, 7.4 Hz), 128.7 (dd, J = 161, 7.2 Hz), 129.2 (d, J = 162 Hz), 129.8 (d, J = 166, 5.7 Hz), 130.3 (s), 134.1 (dt, J = 163, 6.7 Hz), 137.2 (s), 144.5 (s), 166.1 (s, C_4); ^{13}C assignments were determined by HMQC and HMBC; IR (KBr) 1730, 1599, 1310, 1143 cm^{-1}; MS (EI) *m/z* 496; exact mass M^+ 496.0622 (calcd for $C_{22}H_{28}O_4SSeSi$ 496.0643). Anal. Calcd for $C_{22}H_{28}O_4SSeSi$: C, 53.32; H, 5.69. Found: C, 53.27; H, 5.58.

Ethyl *r*-1-(*p*-toluenesulfonyl)-*c*-2-[(phenylseleno)(trimethylsilyl)methyl]-1-cyclopropanecarboxylate (4b): yield

34% after purification by recrystallization from hexane−ether) (R_f = 0.3); colorless crystals; mp 89−90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.137 (s, 9H), 1.01 (t, J = 7.1 Hz, 3H), 1.79 (dd, J = 8.1, 5.0 Hz, 1H, H_3), 2.40 (dd, J = 9.6, 5.0 Hz, 1H, H_2), 2.48 (s, 3H), 2.55 (d, J = 12.5 Hz, 1H, H_4), 2.63 (ddd, J = 12.5, 9.6, 8.1 Hz, 1H, H_1), 3.44 (dq, J = 10.8, 7.2 Hz, 1H), 3.77 (dq, J = 10.8, 7.2 Hz, 1H), 7.06−7.16 (m, 3H), 7.18−7.21 (m, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.89 (d, J = 8.4 Hz, 2H); selected NOEs were between δ 1.79 and 2.55, δ 2.40 and 2.63, δ 2.40 and 7.89, δ 2.63 and 7.89; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm) −1.872 (q, J = 120 Hz), 13.66 (q, J = 127 Hz), 21.76 (qt, J = 124, 4.4 Hz), 24.52 (t, J = 166 Hz, C_3), 28.53 (d, J = 137 Hz, C_5), 36.20 (d, J = 169 Hz, C_2), 50.34 (s, C_1), 62.23 (t, J = 149 Hz), 127.2 (dt, J = 161, 7.4 Hz), 128.7 (dd, J = 161, 7.2 Hz), 129.1 (d, J = 161 Hz), 129.8 (dd, J = 166, 5.3 Hz), 130.4 (s), 133.9 (dt, J = 163, 6.9 Hz), 137.2 (t, J = 8.4 Hz), 144.5 (s), 165.7 (s, C_4); IR (KBr) 1719, 1599, 1323, 1145 cm^{-1}; MS (EI) m/z 510; exact mass M$^+$ 510.0815 (calcd for $C_{23}H_{30}O_4SSeSi$ 510.0799). Anal. Calcd for $C_{23}H_{30}O_4SSeSi$: C, 54.21; H, 5.93. Found: C, 54.16; H, 5.80.

Ethyl *r*-1-(benzenesulfonyl)-*c*-2-[(phenylseleno)(trimethylsilyl)-methyl]-1-cyclopropanecarboxylate (4c): yield 26%; R_f = 0.3 (hexane−ether = 2:1); colorless crystals; mp 108−110 °C (cyclohexane−ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.150 (s, 9H), 0.967 (t, J = 7.2 Hz, 1H), 1.81 (dd, J = 8.3, 5.1 Hz, 1H, H_3), 2.42 (dd, J = 9.8, 5.1 Hz, 1H, H_2), 2.55 (d, J = 12.5 Hz, 1H, H_4), 2.65 (ddd, J = 12.5, 9.8, 8.3 Hz, 1H, H_1), 3.39 (dq, J = 10.5, 7.3 Hz, 1H), 3.74 (dq, J = 10.5, 7.3 Hz), 7.06−7.18 (m, 5H), 7.55−7.60 (m, 2H), 7.68 (t-like, J = 7.5 Hz, 1H), 8.03 (d-like, J = 7.1 Hz, 2H). Selected NOE's were between δ 1.81 and 2.55, δ 2.42 and 2.65, δ 2.42 and 8.03, δ 2.65 and 8.03.; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm) −1.879 (q, J = 120 Hz), 13.60 (q, J = 128 Hz), 24.44 (t, J = 167 Hz, C_3), 28.57 (d, J = 136 Hz, C_5), 36.51 (d, J = 163 Hz, C_2), 50.25 (s, C_1), 62.25 (t, J = 149 Hz), 127.2 (d, J = 162 Hz), 128.5 (d, J = 161 Hz), 128.7 (d, J = 161 Hz), 129.8 (d, J = 167 Hz), 130.4 (s), 133.5 (d, J = 164 Hz), 133.8 (d, J = 164 Hz), 140.2 (s), 165.5 (s, C_4); IR (KBr) 1719, 1317, 1143 cm^{-1}; MS (EI) m/z 496; exact mass M$^+$ 496.0707 (calcd for $C_{22}H_{28}O_4SSeSi$ 496.0643). Anal. Calcd for $C_{22}H_{28}O_4SSeSi$: C, 53.32; H, 5.69. Found: C, 53.26; H, 5.51.

Ethyl (*E*)-2-(benzenesulfonyl)-5-(phenylseleno)-4-pentenoate (8c): R_f = 0.2 (hexane−ether = 2:1); colorless crystals; mp 52−54 °C (cyclohexane−ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.13 (t, J = 7.1 Hz, 3H), 2.74−2.90 (m, 2H), 3.99 (dd, J = 11.1, 4.1 Hz, 1H), 4.05−4.13 (m, 2H), 5.76 (ddd, J = 15.2, 7.7, 6.8 Hz, 1H), 6.55 (dt, J = 15.2, 1.2 Hz, 1H), 7.25−7.30 (m, 3H), 7.39−7.44 (m, 2H), 7.57 (t-like, J = 7.7 Hz, 2H), 7.69 (t-like, 7.4 Hz, 1H), 7.88 (d-like, J = 8.4 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm) 13.98 (q), 31.41 (t), 62.42 (t), 69.85 (d), 123.4 (d), 127.6 (d), 129.1 (d), 129.2 (d), 129.40 (d), 129.42 (d), 129.6 (s), 132.6 (d), 134.5 (d), 137.2 (s), 165.2 (s); IR (KBr) 1727, 1657, 1313, 1156 cm^{-1}; MS (EI) m/z 424. Anal. Calcd for $C_{19}H_{20}O_4SSe$: C, 53.90; H, 4.76. Found: C, 53.72; H, 4.63.

1-Ethyl 4-Methyl (*E*)-2-(*p*-Toluenesulfonyl)ethene-1,2-dicarboxylate (9). Prepared from 1-ethyl 4-methyl 2-(*p*-toluenesulfonyl)ethane-1,2-dicarboxylate described below, by the same procedure for **3** (phenylselenylation (45%) and oxidation (100%)) (E/Z = 9:1): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) for the major E isomer δ (ppm) 1.25 (t, J = 7.1 Hz, 3H), 2.46 (s, 3H), 3.80 (s, 3H), 4.26 (q, J = 7.1 Hz, 2H), 7.09 (s, 1H), 7.36 (bd, J = 8.1 Hz, 2H), 7.79 (bd, J = 8.1 Hz, 2H); selected NOE was between δ 7.09 (olefin-H) and 7.79 (*o*-H of *p*-tolyl); ^{13}C NMR (100.6 MHz, $CDCl_3$) for major isomer δ (ppm) 13.78 (q), 21.81 (q), 52.95 (q), 62.96 (t), 129.2 (d), 130.0 (d), 130.7 (d), 134.9 (s), 146.0 (s), 147.7 (s), 161.0 (s), 163.3 (s); IR (neat) 1734, 1636, 1330, 1156 cm^{-1}; MS (EI) m/z 312; exact mass M$^+$ 312.0667 (calcd for $C_{14}H_{16}O_6S$ 312.0668).

1-Ethyl 4-Methyl 2-(*p*-Toluenesulfonyl)ethane-1,2-dicarboxylate (Intermediate for 9). Sodium hydride (392 mg, 60% dispersion in oil, 9.80 mmol, washed three times with pentane) was suspended in freshly distilled THF (9.0 mL). After the mixture was cooled to 0 °C, ethyl 2-(*p*-toluenesulfonyl)acetate (2.16 g, 8.92 mmol) was added dropwise over 10 min. After 1 h, methyl bromoacetate (1.37 g, 8.92 mmol) was added, and the mixture was stirred for 12 h at 20 °C. The mixture was extracted with ether, and the ether extracts were washed with saturated NH_4Cl solution and saturated sodium chloride solution and dried ($MgSO_4$). The solvent was evaporated in vacuo. The residue was purified by column chromatography over silica gel eluting with ether−hexane (2:1) to give the title compound (1.84 g, 66%) (R_f = 0.4): colorless crystals; mp 63−65 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.16 (t, J = 7.1 Hz, 3H), 2.47 (s, 3H), 3.06−3.18 (m, 2H), 3.69 (s, 3H), 4.07−4.19 (m, 2H), 4.40 (dd, J = 9.7, 5.3 Hz, 1H), 7.38 (d-like, J = 8.2 Hz, 2H), 7.76 (d-like, J = 8.2 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm) 13.82 (q), 21.78 (q), 31.05 (t), 52.49 (q), 62.59 (t), 66.46 (d), 129.2 (d), 129.9 (d), 134.3 (s), 145.8 (s), 165.0 (s), 170.2 (s); IR (KBr) 1738, 1597, 1323, 1151 cm^{-1}; MS (FAB) m/z 315 (MH$^+$). Anal. Calcd for $C_{14}H_{18}O_6S$: C, 53.49; H, 5.77; S, 10.20. Found: C, 53.39; H, 5.75; S, 10.13.

1-Ethyl 4-methyl 2-(phenylseleno)-2-(*p*-toluenesulfonyl)ethane-1,2-dicarboxylate (intermediate for 9): yield 45%; R_f = 0.4 (hexane/ether = 3:1); colorless crystals; mp 108−110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.20 (t, J = 7.1 Hz, 3H), 2.46 (s, 3H), 2.68 (d, J = 17.7 Hz, 1H), 3.40 (d, J = 17.7 Hz, 1H), 3.56 (s, 3H), 4.11−4.19 (m, 2H), 7.31−7.35 (m, 4H), 7.44 (t-like, J = 7.4 Hz, 1H), 7.77−7.81 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm) 13.72 (q), 21.82 (q), 36.08 (t), 52.08 (q), 63.37 (t), 74.82 (s), 125.6 (s), 128.9 (d), 129.3 (d), 130.4 (d), 131.2 (d), 132.0 (s), 139.0 (d), 145.7 (s), 165.7 (s), 168.6 (s); IR (KBr) 1735, 1597, 1357, 1151 cm^{-1}; MS (EI) m/z 470.

Ethyl (*E*)-2-(*p*-Toluenesulfonyl)cinnamate (10). Prepared from ethyl 2-(*p*-toluenesulfonyl)acetate and benzaldehyde according to the literature procedure:[12] yield 24%; colorless crystals; mp 68 °C (hexane−ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.16 (t, J = 7.1 Hz, 3H), 2.44 (s, 3H), 4.22 (q, J = 7.1 Hz, 2H), 7.33−7.45 (m, 7H), 7.83 (d-like, J = 8.4 Hz, 2H), 7.94 (s, 1H). Selected NOE's were between δ 4.22 (OCH_2) and around 7.45 (*o*-Ph) and δ 7.83 (olefin-H) and 7.94 (*o*-H of *p*-tolyl).; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm) 13.70 (q), 21.77 (q), 62.44 (t), 128.7 (d), 128.9 (d), 129.8 (d), 129.9 (d), 131.4 (d), 131.8 (s), 135.4 (s), 137.0 (s), 143.3 (d), 144.8 (s), 163.3 (s); IR (neat) 1723, 1624, 1325, 1152 cm^{-1}; MS (EI) m/z 330; exact mass M$^+$ 330.0924 (calcd for $C_{18}H_{18}O_4S$ 330.0925). Anal. Calcd for $C_{18}H_{18}O_4S$: C, 65.43; H, 5.49. Found: C, 65.34; H, 5.42.

1-Phenyl-2-(*p*-toluenesulfonyl)-2-propen-1-one (11). Prepared by reaction of *p*-toluenesulfinic acid, sodium salt hydrate, and methyl 2-bromopropiophenone in refluxing ethanol (71%) and then the same procedure for **3** (phenylselenylation (68%) and oxidation (60%)): colorless crystals; mp 107−109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 2.45 (s, 3H), 6.27 (d, J = 0.9 Hz, 1H), 7.09 (d, J = 0.9 Hz, 1H), 7.35 (d, J = 8.1 Hz, 2H), 7.46 (t, J = 7.9 Hz, 2H), 7.61 (t-like, J = 7.5 Hz, 2H), 7.81 (d-like, J = 7.9 Hz, 2H), 7.85 (d-like, J = 8.4 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm) 21.80 (q), 128.8 (d), 129.0 (d), 129.8 (d), 130.0 (d), 132.2 (t), 134.2 (d), 136.0 (s), 136.6 (s), 145.1 (s), 149.7 (s), 190.2 (s); IR (KBr) 1663, 1595, 1321, 1141 cm^{-1}; MS (EI) m/z 286; exact mass M$^+$ 286.0662 (calcd for $C_{16}H_{14}O_3S$ 286.0664). Anal. Calcd for $C_{16}H_{14}O_3S$: C, 67.11; H,4.93. Found: C, 66.66; H, 4.83.

2-(*p*-Toluenesulfonyl)propiophenone (intermediate for 11): yield 71%, purified by recrystallization from ethyl acetate; colorless crystals; mp 97−100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.56 (d, J = 6.9 Hz, 3H), 2.44 (s, 3H), 5.15 (q, J = 6.9 Hz, 1H), 7.31 (d-like, J = 8.1 Hz, 2H), 7.48 (t-like, J = 7.7 Hz, 2H), 7.59−7.63 (m, 1H), 7.66 (d-like, J = 8.2 Hz, 2H), 7.97−8.00 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm) 13.32 (q), 21.78 (q), 65.07 (d), 128.8 (d), 129.3 (d), 129.6 (d), 129.9 (d), 133.0 (s), 134.1 (d), 136.3 (s), 145.4 (s), 192.7 (s); IR (KBr) 1678, 1315, 1151 cm^{-1}; MS (EI) m/z 288; exact mass M$^+$ 288.0761 (calcd for $C_{16}H_{16}O_3S$ 288.0820). Anal. Calcd for $C_{16}H_{16}O_3S$: C, 66.64; H, 5.59. Found: C, 66.36; H, 5.59.

2-(Phenylseleno)-2-(*p*-toluenesulfonyl)propiophenone (intermediate for 11): yield 68%, including a small amount of impurity; R_f = 0.4 (hexane−ether = 1:1); pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.62 (s, 3H), 2.42 (s,

3H), 7.27 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 7.7 Hz, 2H), 7.41 (t-like, J = 7.5 Hz, 1H), 7.45 (t-like, J = 7.7 Hz, 2H), 7.56 (t-like, J = 7.3 Hz, 1H), 7.67−7.73 (m, 4H), 8.13 (d-like, J = 7.3 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm) 21.75 (q), 22.48 (q), 76.80 (s), 126.4 (s), 128.2 (d), 129.1 (d), 129.3 (d), 129.9 (d), 130.3 (d), 130.8 (d), 132.6 (s), 132.8 (d), 136.7 (s), 138.6 (d), 145.3 (s), 194.4 (s); IR (neat) 1669, 1597, 1319, 1149 cm^{-1}; MS (EI) m/z 444; exact mass M^+ 444.0293 (calcd for $C_{22}H_{20}O_3SSe$ 444.0299).

Reaction of 1 and 11 in the Presence of ZnI_2. To a solution of **1** (222 mg, 0.87 mmol) in dichloromethane (1.7 mL) was added ZnI_2 (417 mg, 1.31 mmol), followed by a solution of 1-phenyl-2-(*p*-toluenesulfonyl)-2-propen-1-one (**11**) (239 mg, 0.87 mmol) in dichloromethane (0.35 mL) at −78 °C. The mixture was allowed to warm to −30 °C and stirred for 5.5 h. The reaction mixture was quenched by triethylamine (0.28 mL, 203 mg, 2.0 mmol) and then saturated aqueous $NaHCO_3$. 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−CH_2Cl_2 to give recovered **1** (140 mg, 63%) and **12** (47 mg, 12%) (R_f = 0.5 CH_2Cl_2). **12**: colorless crystals; mp 96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 2.43 (s, 3H), 2.80−2.94 (m, 2H), 5.12 (dd, J = 10.6, 4.0 Hz, 1H), 5.66 (dt, J = 15.1, 7.4 Hz, 1H), 6.45 (dt, J = 15.1, 1.2 Hz, 1H), 7.13−7.25 (m, 5H), 7.30 (d, J = 8.1 Hz, 2H), 7.48 (t-like, J = 7.7 Hz, 2H), 7.60−7.64 (m, 3H), 7.94 (d-like, J = 7.3 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm) 21.80 (q), 33.02 (t), 68.99 (d), 123.1 (d), 127.4 (d), 128.9 (d), 129.2 (d), 129.3 (d), 129.7 (d), 129.7 (d), 129.9 (d), 132.4 (d), 133.2 (s), 134.2 (d), 137.1 (s), 145.7 (s), 191.9 (s); IR (KBr) 1678, 1597, 1320, 1145 cm^{-1}; MS (EI) m/z 470; exact mass M^+ 470.0484 (calcd for $C_{24}H_{22}O_3SSe$ 470.0455).

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Supporting Information Available: Experimental details of X-ray structure determination for **4a** and additional results of ab initio calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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