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Reaction behavior of cyclopropylmethyl cations derived 1-phenylselenocyclopropylmethanols with acids

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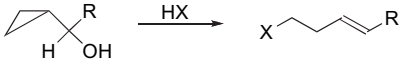
ABSTRACT

The 1-phenylselenocyclopropylmethyl cations are generated by the reaction of the corresponding cyclopropylmethanols **1** with TsOH. The reaction in methanol proceeds to afford the homoallylic ethers **2**, ring-enlargement products **3**, **4**, and ring opening products **5** depending upon the kind of substituent on the cyclopropane ring or the α-carbon. On the other hand, in the case of the absence of methanol as nucleophile, 4*H*-selenochromene derivative **7** is obtained exclusively. The oxidative elimination of the phenylselenyl group in the resulting phenylselenohomoallylic compounds **2** furnishes functionalized allene derivatives and alkyne derivatives.

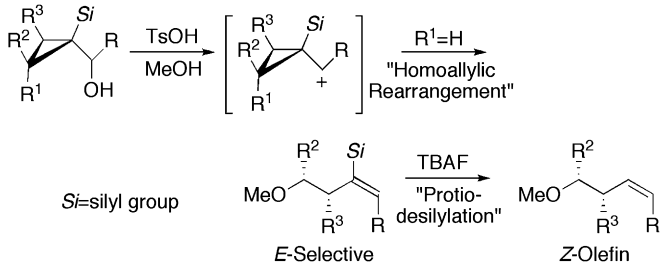
1. Introduction

The reaction of cyclopropylmethanols with acids proceed to afford the *E*-homoallyl derivatives selectively (Scheme 1).[1–4] This reaction is known as the Julia olefin synthesis that takes place



Scheme 1. Julia olefin synthesis.

through homoallylic rearrangement of cyclopropylmethyl cation intermediates. Cyclopropylmethyl cations are considered as interesting species[5,6] and have been widely employed for organic synthesis as useful intermediates.[7] In contrast, we have recently reported the simple method for the preparation of cyclopropylmethanols having a silyl group at the 1-position of the cyclopropane ring and the homoallylic rearrangement of cyclopropylmethyl cations derived from them (Scheme 2).[8] In those reactions, the silylcyclopropylmethyl cations having no substituents on the opposite side of a silyl group on a cyclopropane ring (i.e., R^1=H) reacted to give the corresponding *E*-homoallyl ethers, preferentially. Then the following protiodesilylation[9] of resulting homoallyl ethers proceeded with retention of configuration to give the corresponding *Z*-homoallyl ethers in the end. In consequence, we presented that a bulky silyl group acted as a directing group for stereoselective synthesis of the silylated homoallylic compounds, and the geometry of the alkene moiety of protiodesilylated products was the opposite to that of a Julia reaction using the corresponding cyclopropylmethanols.[1]



Scheme 2. Stereoselective construction of *Z*-homoallyl derivatives from 1-silylcyclopropylmethanols.

The above observation prompted us to explore the reaction behavior of cyclopropylmethyl cations having different functional groups at the 1-position of the cyclopropane ring. Then, we focused on the introduction of a phenylselenyl group instead of a silyl group. Organic compounds containing selenium atom are very useful materials in organic synthesis.[10] In particular, phenylselenyl groups are available for further versatile transformation.[10,11] In this paper, we describe the generation of cyclopropylmethyl cations by the reaction of 1-phenylselenocyclopropylmethanols with acid catalyst and the following rearrangement reaction behavior, including reaction mechanism. In these reactions ring-enlargement compounds, ring opening products, and 4*H*-selenochromene derivatives were yielded along with desired phenylselenohomoallylic compounds, depending upon the kind of substituent on starting cyclopropylmethanols and reaction conditions. Especially, it's

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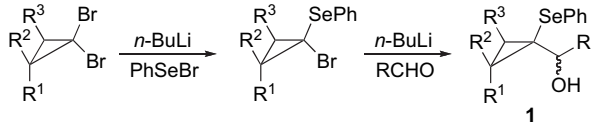
notable that 4*H*-selenochromene derivative was formed, since few reports about the preparation of 4*H*-selenochromene have been published so far.[12] Furthermore, in order to indicate the potential of phenylselenohomoallylic compounds as a synthetic intermediate, transformation of the resulting phenylselenohomoallylic compounds to functionalized allene derivatives by oxidative elimination of the phenylselenyl group is described.[11]

2. Results and discussion

2.1. Preparation of 1-phenylselenocyclopropylmethanols

The preparation of 1-phenylselenocyclopropylmethanols **1** was accomplished as follows (Scheme 3). The treatment of dibromocyclopropanes with *n*-butyllithium followed by the reaction with phenylselenyl bromide gave the corresponding phenylselenocyclopropane derivatives in high yields.[13] The resulting cyclopropane derivatives were treated with *n*-butyllithium and the subsequent reaction with aldehyde gave the desired cyclopropylmethanols **1**. The products **1a**, **1b**, and **1e–l** were yielded as a diastereomeric mixture in each case, although these mixtures were used as starting materials without separation of the diastereomers. The configurations of substituents on the cyclopropane ring of **1** were confirmed by ^{1}H NMR spectra and the NOE measurements.



1

1a R^1, R^3=Me, R^2=H, R=Ph
1b R^1, R^3=Me, R^2=H, R=*t*-Bu
1c R^1=H, R^2, R^3=Me, R=Ph
1d R^1=H, R^2, R^3=Me, R=*t*-Bu
1e R^1, R^3=H, R^2=*n*-Bu, R=Ph
1f R^1, R^3=H, R^2=*n*-Bu, R=*t*-Bu
1g R^1=Ph, R^2, R^3=H, R=Ph
1h R^1, R^3=H, R^2=Ph, R=Ph
1i R^1, R^3=H, R^2=Ph, R=Me
1j R^1, R^3=H, R^2=Ph, R=Et
1k R^1, R^3=H, R^2=Ph, R=*i*-Pr
1l R^1, R^3=H, R^2=Ph, R=*t*-Bu

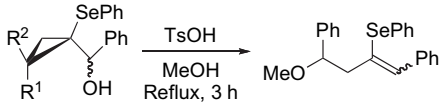
Scheme 3. Preparation of 1-phenylselenocyclopropylmethanols **1**.

2.2. Reaction of 1-phenylselenocyclopropylmethanols with acid

The 1-phenylselenocyclopropylmethanols **1a–f** having aliphatic groups on the cyclopropane ring were treated with TsOH in methanol. Incidentally, only a few reports have been published for the reaction of cyclopropylmethanols having a chalcogenyl group at the 1-position of the cyclopropane ring with acid. Trost et al. have reported that the treatment of 1-phenylthiocyclopropylmethanols with TsOH provided two different types of ring-enlargement products, phenylthiocyclobutene or cyclobutanone derivatives, depending upon the reaction conditions.[14] Similarly, it was known that the treatment of 1-phenylselenocyclopropylmethanols with Burgess reagent[15] afforded phenylselenocyclobutene derivatives.[16] On the other hand, we investigated the reaction behavior of 1-phenylselenocyclopropylmethanols with TsOH in methanol. The results are shown in Table 1. The reaction was completed in 3 h under reflux and then a mixture of the usual homoallylic rearrangement products **2** and ring-enlargement products **3** were obtained in good yields (entries 1–5). The homoallylic rearrangement products **2** were yielded as a *Z*-isomer regardless of the substituents on the cyclopropane ring and the α-carbon with the exception of the reaction of cyclopropylmethanol **1c**. The stereochemistry of olefin moiety of **2** was decided by analogy with previous results.[8] The ring-enlargement products **3** were obtained as a mixture of two types of regioisomeric cyclobutene derivatives. In addition, the cyclobutanone derivatives **4** were yielded in the reaction of cyclopropylmethanols having a phenyl group on the α-carbon (entries 1, 3, and 5). Exceptionally, the formation of homoallyl derivatives was not observed at all in the reaction using cyclopropylmethanol **1f** as a starting material (entry 6). In this reaction the cyclobutanone derivative **4f** was yielded predominantly.

The treatment of cyclopropylmethanols **1g** and **1h** having phenyl groups at the 2-position of the cyclopropane ring and α-carbon was carried out under similar conditions as above. The results are shown in Table 2. It is noteworthy that these reactions proceeded to afford 3-phenylselenohomoallylic products **2** exclusively, as a mixture of geometrical isomers with preference for *Z*-isomer, without the formation of ring expansion products, regardless of the

Table 2
Reaction of 1-phenylselenocyclopropylmethanols having phenyl groups on the cyclopropane ring and the α-carbon

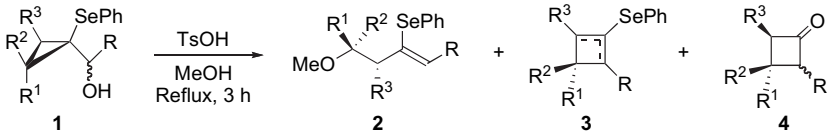


1 **2g**

Entry	Substrate	R^1	R^2	Yield[a] (%)	*E*/*Z*[b]
1	**1g**	Ph	H	57	11/89
2	**1h**	H	Ph	76	28/72

Molar ratio; cyclopropylmethanol/TsOH=1:1.2.
[a] Isolated yield.
[b] Determined by ^{1}H NMR analysis.

Table 1
Reaction of 1-phenylselenocyclopropylmethanols with TsOH in MeOH



1 **2** **3** **4**

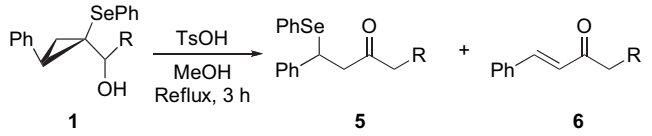
Entry	Substrate	R^1	R^2	R^3	R	Total yield[a] (%)	Ratio[b] (%)
1	**1a**	Me	H	Me	Ph	64	**2a**/**3a**/**4a**=25:41:34
2	**1b**				*t*-Bu	78	**2b**/**3b**/**4b**=27:73:—
3	**1c**	H	Me	Me	Ph	77	**2c**/**3c**/**4c**=57[c]:34:9
4	**1d**				*t*-Bu	81	**2d**/**3d**/**4d**=34:66:—
5	**1e**	H	*n*-Bu	H	Ph	67	**2e**/**3e**/**4e**=33:27:40
6	**1f**				*t*-Bu	81	**2f**/**3f**/**4f**=—:14:86

Molar ratio; cyclopropylmethanol/TsOH=1:1.2.
[a] Isolated yield.
[b] Determined by ^{1}H NMR analysis.
[c] *E*-Isomer was obtained in 8% yield.

configuration of substituents on the cyclopropane ring in starting materials **1g** and **1h**.

Additionally, the reaction of cyclopropylmethanols **1i–l** having a phenyl group at the 2-position of the cyclopropane ring and an alkyl group on the α-carbon was carried out. The results are shown in Table 3. In all cases two types of ketone derivatives, **5** derived by formal migration of the phenylselenyl group competing with the ring opening and **6** derived by elimination of the phenylselenyl group, were yielded in moderate yields as a mixture with preference for **5**, regardless of the bulkiness of the alkyl substituent on the α-carbon of starting alcohols.

Table 3
Ring opening reaction of 2-phenyl-1-phenylselenocyclopropylmethanols with TsOH

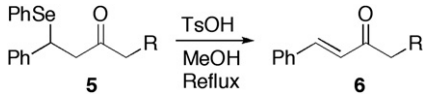


1 **5** **6**

Entry	Substrate	R	Total yield[a] (%)	Ratio[b] (%)
1	**1i**	Me	62	**5a**/**6a**=79:21
2	**1j**	Et	77	**5b**/**6b**=74:26
3	**1k**	*i*-Pr	68	**5c**/**6c**=78:22
4	**1l**	*t*-Bu	57	**5d**/**6d**=65:35

Molar ratio; cyclopropylmethanol/TsOH=1:1.2.
[a] Isolated yield.
[b] Determined by ^{1}H NMR analysis.

The treatment of the resulting β-seleno ketone derivatives **5** with TsOH in methanol under reflux gave α,β-unsaturated ketone **6** as shown in Scheme 4. Thus, it was confirmed that the formation of **6** occurred via β-elimination of selenol from **5** in acidic reaction conditions.



5 **6**

Scheme 4. Reaction of β-phenylseleno ketones with TsOH.

2.3. Mechanistic considerations

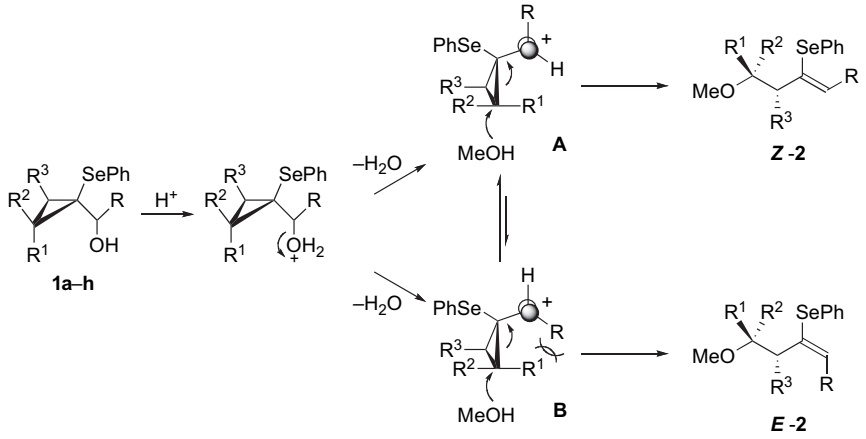
These results suggest that the reaction behavior of homoallylic rearrangement of the 1-phenylselenocyclopropylmethanols is dependent on the kind of substituents on the three-membered ring and the α-carbon. Thus, the following mechanism for the reaction was proposed (Schemes 5–7). The oxygen atom of starting alcohols was protonated by TsOH and bisected cation species[3,17] **A** and **B** are formed (Scheme 5). The nucleophilic attack of methanol to cyclopropane ring and ring opening occur nearly simultaneously, then *Z*-homoallyl derivatives are formed from bisected cation **A** and *E*-isomers are formed from cation **B**. The formation of bisected cation **A** seems to be favored compared to **B** by the less repulsion between R group and R^1 group on the three-membered ring. Thus, *Z*-homoallyl derivatives are formed preferentially. Since the attack of methanol to cation intermediate proceeds in an S_N2' manner, no epimerization is observed at all. In the case of the reaction of cyclopropylmethanols having a phenyl group at the 2-position of the cyclopropane ring, the attack of methanol to benzylic carbon occurs easily, so the homoallyl derivatives are exclusively formed.

On the other hand, in the case of the reaction using cyclopropylmethanols having alkyl groups on the cyclopropane ring, cyclobutonium cation **C** is also formed by the ring enlargement of **A** and **B**, because of the dissolution of ring strain of three-membered ring and the stabilization of the resulting carbocation with phenylselenyl group (Scheme 6). The cyclobutonium cation **C** may be formed via episelenium cation species,[18] since the reaction of cyclopropylmethanols having no phenylselenyl group did not afford four-membered ring products in our previous work.[8] The elimination of proton from **C** affords cyclobutene derivatives **3** and trace amounts of regioisomeric products **3′**. Whereas, the nucleophilic attack of methanol to **C** and the following hydrolysis gives the cyclobutanone derivatives **4**.

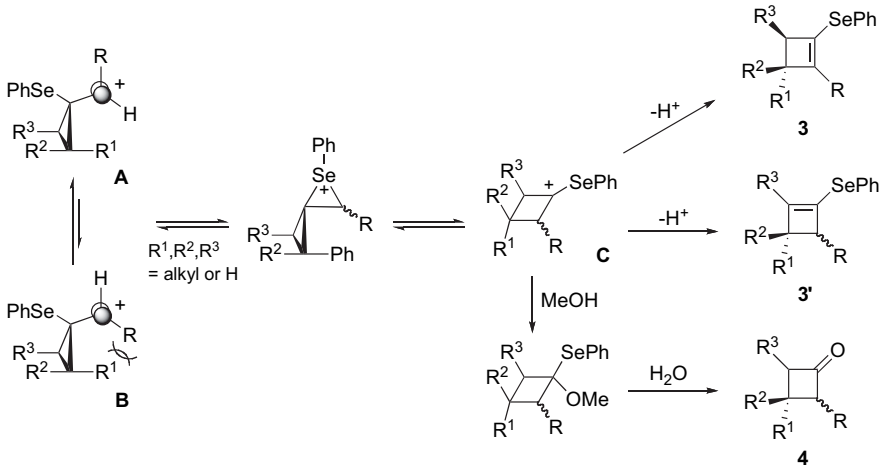
In the reaction of cyclopropylmethanols having a phenyl group at the 2-position of the cyclopropane ring and an alkyl group on the α-carbon, the cyclopropylmethyl cation is also transformed into more stable cyclobutonium cation **C** as discussed (Scheme 7). The nucleophilic attack of methanol to **C**, the elimination of phenylselenyl group, and ring opening of four-membered ring sequentially occur, then more stable benzyl cation intermediates **D** are formed. The nucleophilic attack of phenylselenyl group and the following hydrolysis gives the β-seleno ketone derivatives **5**. The formation of the α,β-unsaturated ketones **6** would be achieved by either deprotonation from cation intermediates **D** or β-elimination of selenol from **5**.

2.4. The reaction in the absence of nucleophile

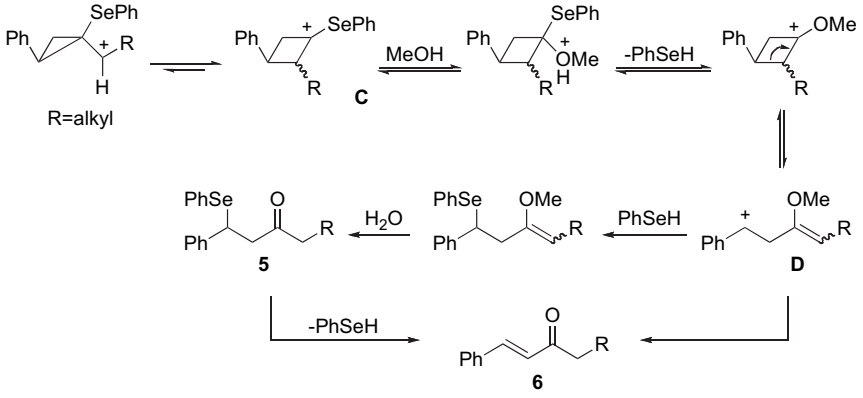
As mentioned above, in the case of the reaction using 1-phenylselenocyclopropylmethanols **1i–l** having a phenyl group at the 2-position of the cyclopropane ring and an alkyl group on the α-carbon, it became obvious that the formal migration of phenylselenyl group is caused by the nucleophilic addition of methanol to cyclobutonium cation **C**. Then we have become interested in the reaction behavior of cyclobutonium cation intermediate in the absence of nucleophile as methanol. So the reaction of compound **1l** with TsOH in acetonitrile was carried out. The reaction was



Scheme 5. Mechanism of the homoallylic rearrangement of selenocyclopropylmethanols **1a–h**.



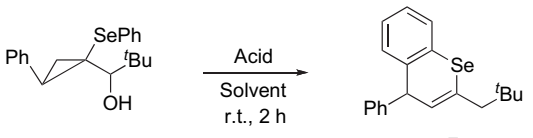
Scheme 6. Mechanism of the ring-enlargement of selenocyclopropylmethanols **1a–f**.



Scheme 7. Mechanism of the ring-enlargement of selenocyclopropylmethanols **1i–l**.

completed in 2 h at room temperature and gave the 4*H*-selenochromene derivative **7**[12] in good yield. The results are shown in Table 4. The same reactions using Lewis acid in dichloromethane were examined. The reaction with trimethylsilyl triflate as an acid afforded **7** in moderate yield (entry 2). In contrast, the treatment of **1l** with boron trifluoride diethyl etherate gave **7** in high yield (entry 3). The structure of **7** was confirmed by X-ray crystallography as depicted in Figure 1.[19]

Table 4
Reaction of 1-phenylselenocyclopropylmethanols in the absence of nucleophiles



1l **7**

Entry	Acid	Solvent	Yield[a] (%)
1	TsOH	CH_3CN	69
2	TMSOTf	CH_2Cl_2	47
3	$BF_3{\cdot}OEt_2$	CH_2Cl_2	85

Molar ratio; cyclopropylmethanol/acid=1:1.2.
[a] Isolated yield.

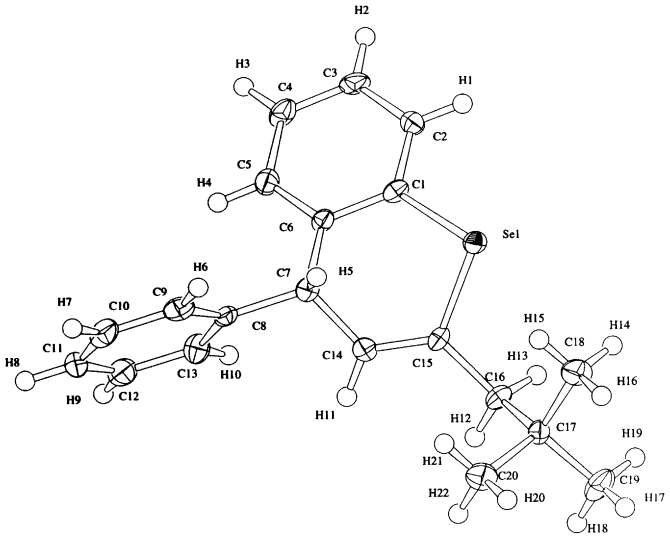
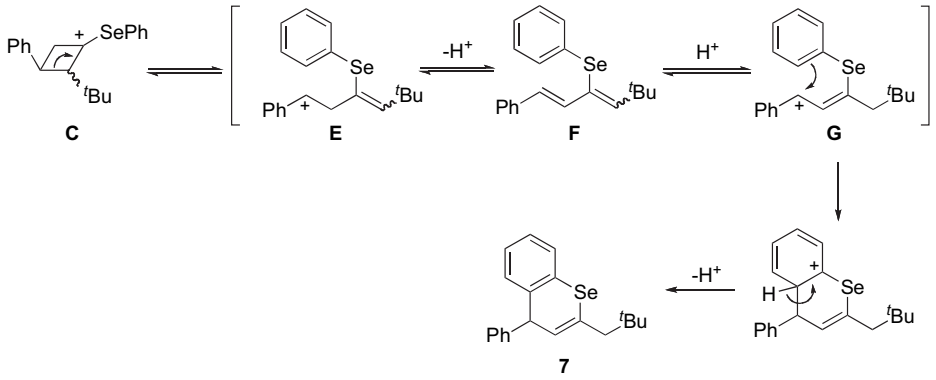


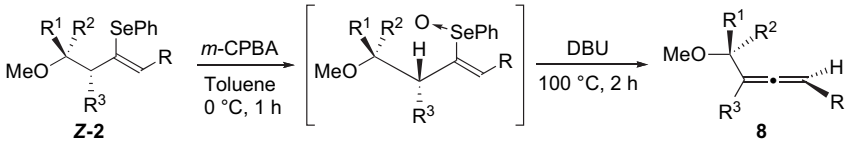
Figure 1. ORTEP view of the crystal structure of the selenochromene derivative **7**.

The structure of the product suggests that the reaction proceeds via electrophilic substitution reaction on the aromatic ring of phenylseleno group. Thus, the following mechanism for the reaction is proposed (Scheme 8). As stated previously, the cyclobutonium cation **C** is derived from the cyclopropylmethyl cation. In the absence of nucleophiles like methanol, ring opening of the cyclobutonium cation **C** proceeds to afford the benzyl cation **E**. This cation **E** is transformed into more stable benzyl allyl cation species



Scheme 8. Mechanism of the reaction in the absence of nucleophiles.

Table 5
Selenoxide elimination via oxidation of *Z*-**2**



Entry	Substrate	R^1	R^2	R^3	R′	Product	Yield[a] (%)
1	**2a**	Me	H	Me	Ph	**8a**	92
2	**2c**	H	Me	Me	Ph	**8b**	85
3	**2d**				*t*-Bu	**8c**	90

Molar ratio; **2**/*m*-CPBA/DBU=1:1.2:2.
[a] Isolated yield.

G by way of compound **F**. Finally the cation species **G** undergoes intramolecular Friedel–Crafts-type cyclization reaction to give the 4*H*-selenochromene derivative **7**.

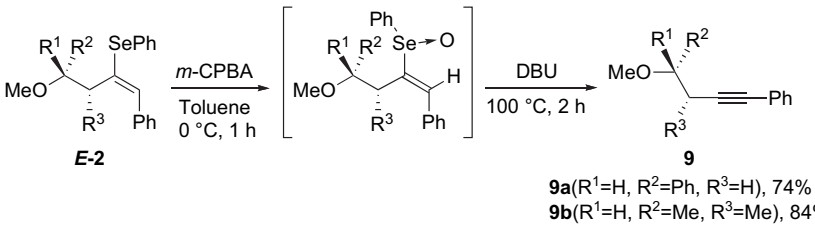
2.5. Further transformation of phenylselenyl substituted homoallylic ethers

Furthermore, in order to indicate the potential of resulting phenylselenyl substituted homoallylic derivatives **2** as a synthetic intermediate, the oxidative elimination reaction of phenylselenyl group was carried out.[20] The oxidation of (*Z*)-3-phenylselenohomoallylic compounds *Z*-**2** with *m*-CPBA in toluene at 0 °C for 1 h followed by treatment of DBU at 100 °C for 2 h gave the functionalized allene derivatives **8** as a single diastereomer in good yields via selenoxide *syn* elimination. The results are summarized in Table 5.

On the other hand, in the reaction of (*E*)-3-phenylselenohomoallylic compounds *E*-**2** under the same reaction conditions, the corresponding selenoxide eliminated with *syn*-oriented alkene proton exclusively to give alkyne derivatives **9** as shown in Scheme 9.

3. Conclusion

In summary, generation and reaction behavior of cyclopropylmethyl cations derived from 1-phenylselenocyclopropylmethanols with an acid catalyst has been described. The reaction of 1-phenylselenocyclopropylmethanols with TsOH in methanol proceeded smoothly to afford the usual homoallylic rearrangement products, ring-enlargement products, and ring opening products depending upon the kind of substituents on the cyclopropane ring or the α-carbon. On the other hand, in the absence of nucleophiles such as methanol, electrophilic substitution reaction of cation intermediate on the aromatic ring of phenylseleno group proceeded to give selenochromene derivative in good yield. In each case the reaction proceeded via cyclobutonium cation stabilized by phenylselenyl group with the exception of formation of homoallylic rearrangement. In addition, in the oxidative elimination reaction of phenylselenyl group of homoallyl derivatives, allene and alkyne derivatives were yielded from *E*-homoallyl derivatives and *Z*-isomers, respectively. Further studies to extend the scope of the reaction substrate and synthetic utility are currently under way and will be reported in due course.



Scheme 9. Selenoxide elimination via oxidation of *E*-**2**.

4. Experimental

4.1. General

IR spectra were recorded on JASCO A-202 or Shimadzu FTIR-8300 infrared spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on JEOL JNM FX-100s, EX-270 or LA-400 spectrometer. Chemical shifts of ^{1}H NMR were expressed in parts per million downfield from tetramethylsilane (TMS) with reference to internal residual $CHCl_3$ (δ=7.26) in $CDCl_3$. Chemical shifts of ^{13}C NMR were expressed in parts per million downfield from $CDCl_3$ (δ=77.0) as an internal standard. Coupling constants (J) were reported in hertz (Hz). Following abbreviations were used to designate the multiplicities: s=singlet; d=doublet; t=triplet; q=quartet; quin=quintet; sext=sextet; br=broad; m=multiplet. Mass spectra were recorded on JEOL JMS-SX102A, JMS-AM50 or Hitachi M-80 mass spectrometer. Melting points were measured on a Yanaco MP-J3 and were uncorrected. Analytical thin layer chromatography (TLC) was performed on pre-coated glass plates (Merck Kieselgel 60 F_{254}, layer thickness 0.25 mm). Visualization was accomplished with UV light (254 nm) and molybdophosphoric acid. Flash column chromatography was carried out using Fuji Silysia silica gel BW-127ZH or Kanto Chemical silica gel 60 N (40–50 μm). Preparative HPLC was performed on JAI LC-908 and LC-918 chromatograph equipped with JAIGEL-1H and -2H and JAIGEL-SIL. GC analysis was performed on a Shimadzu GC-14B equipped with a CBP1-M25-O20 column (Shimadzu, 25 m×0.22 mm, detector=FID) with a helium gas as a carrier. Unless otherwise noted, commercially available reagents were used without purification. All the solvents were distilled and stored over a drying agent. *n*-Butyllithium (1.6 M solution in hexane) was purchased from Aldrich Chemical Co., Inc. All reactions were carried out under an argon atmosphere in dried glassware.

4.2. General procedure for the preparation of 1-phenylselenocyclopropylmethanols

To a stirred solution of 1,1-dibromocyclopropane (15 mmol) in THF (160 mL) at −90 °C was added slowly a 1.6 M solution of *n*-BuLi (12.5 mL, 20 mmol) in hexane. The resulting reaction mixture was stirred at −90 °C for 0.5 h, and then phenylselenyl bromide (19.7 g, 18 mol) in THF (20 mL) was added. After stirring for 2 h, the reaction mixture was allowed to warm to ambient temperature and then poured into brine. The aqueous layer was extracted with diethyl ether for three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on a silica gel to give 1-bromo-1-phenylselenocyclopropane. This product was used for the next reaction without further purification. To a stirred solution of 1-bromo-1-phenylselenocyclopropane (15 mmol) in THF (160 mL) at −90 °C was added slowly a 1.6 M solution of *n*-BuLi (12.5 mL, 20 mmol) in hexane. The resulting reaction mixture was stirred at −90 °C for 0.5 h, and then aldehyde (18 mol) in THF (20 mL) was added. After stirring for 2 h, the reaction mixture was allowed to warm to ambient temperature and then poured into brine. The aqueous layer was extracted with diethyl ether for three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on a silica gel to give 1-phenylselenocyclopropylmethanol.

*4.2.1. (2,3-Dimethyl-1-phenylselenocyclopropyl)phenylmethanol (**1a**).* According to the typical procedure, the products yielded as a diastereomeric mixture (major isomer/minor isomer=53:47). Major isomer; a pale yellow oil, IR (neat) 3367, 3057, 3019, 2972, 1577, 1477, 1436, 1068, 1022, 734 cm^{-1}; HRMS calcd for $C_{18}H_{20}OSe$ (M^+) 332.0679, found 332.0663; ^{1}H NMR ($CDCl_3$) δ 7.54–7.17 (m, 10H), 4.49 (s, 1H), 2.73 (s, 1H), 1.37 (d, J=6.3 Hz, 3H), 1.33 (d, J=6.1 Hz, 3H), 1.05 (dq, J=6.2, 6.1 Hz, 1H), 0.80 (dq, J=6.2, 6.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 143.2, 132.9, 131.1, 128.7, 128.0, 127.3, 126.5, 125.8, 76.2, 45.2, 28.8, 28.4, 16.6, 14.1. Minor isomer; a pale yellow oil, IR (neat) 3366, 3054, 3018, 2975, 1575, 1478, 1437, 1062, 1021, 739 cm^{-1}; HRMS calcd for $C_{18}H_{20}OSe$ (M^+) 332.0679, found 332.0666; ^{1}H NMR ($CDCl_3$) δ 7.45–6.98 (m, 10H), 4.55 (s, 1H), 2.34 (s, 1H), 1.40 (d, J=5.6 Hz, 3H), 1.32 (d, J=5.9 Hz, 3H), 1.12–1.00 (m, 1H), 0.89–0.85 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 142.3, 132.1, 130.6, 128.3, 127.6, 127.1, 127.0, 126.2, 78.2, 43.5, 29.6, 28.1, 17.6, 15.5.

*4.2.2. 1-(2,3-Dimethyl-1-phenylselenocyclopropyl)-2,2-dimethylpropan-1-ol (**1b**).* According to the typical procedure, the products yielded as a diastereomeric mixture (major isomer/minor isomer=61:39). Major isomer; a pale yellow oil, IR (neat) 3360, 3055, 3021, 2979, 1575, 1478, 1435, 1065, 1021, 738 cm^{-1}; HRMS calcd for $C_{16}H_{24}OSe$ (M^+) 312.0992, found 312.0981; ^{1}H NMR ($CDCl_3$) δ 7.59–7.19 (m, 5H), 2.94 (s, 1H), 2.32 (s, 1H), 1.28 (d, J=6.1 Hz, 3H), 1.20 (d, J=6.4 Hz, 3H), 1.03 (s, 9H), 0.81 (dq, J=6.2, 6.1 Hz, 1H), 0.51 (dq, J=6.2, 6.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 133.3, 131.7, 128.8, 126.7, 81.1, 42.8, 37.6, 29.3, 28.7, 28.1, 16.5, 13.6. Minor isomer; a pale yellow oil, IR (neat) 3359, 3048, 3021, 2978, 1579, 1475, 1432, 1059, 1019, 738 cm^{-1}; HRMS calcd for $C_{16}H_{24}OSe$ (M^+) 312.0992, found 312.0983; ^{1}H NMR ($CDCl_3$) δ 7.66–7.14 (m, 5H), 3.05 (s, 1H), 1.61 (s, 1H), 1.38 (d, J=6.1 Hz, 3H), 1.22 (d, J=6.3 Hz, 3H), 1.16–1.02 (m, 1H), 1.09 (s, 9H), 0.85 (dq, J=6.2, 6.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 133.3, 131.1, 128.7, 126.3, 84.6, 39.3, 36.5, 30.1, 27.7, 24.4, 17.0, 15.8.

*4.2.3. (2,3-Dimethyl-1-phenylselenocyclopropyl)phenylmethanol (**1c**).* According to the typical procedure, the product yielded as a single isomer. A pale yellow oil, IR (neat) 3365, 3058, 3017, 2970, 1575, 1473, 1433, 1069, 1021, 738 cm^{-1}; HRMS calcd for $C_{18}H_{20}OSe$ (M^+) 332.0679, found 332.0662; ^{1}H NMR ($CDCl_3$) δ 7.48–7.18 (m, 10H), 4.77 (s, 1H), 2.69 (s, 1H), 1.27–1.19 (m, 1H), 1.19 (d, J=6.6 Hz, 3H), 1.14 (d, J=6.1 Hz, 3H), 1.03–0.92 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 140.4, 131.1, 129.0, 128.8, 127.6, 127.3, 127.0, 126.2, 77.9, 43.4, 20.3, 17.0, 11.2, 10.7.

*4.2.4. 1-(2,3-Dimethyl-1-phenylselenocyclopropyl)-2,2-dimethylpropan-1-ol (**1d**).* According to the typical procedure, the product yielded as a single isomer. A pale yellow oil, IR (neat) 3357, 3054, 3019, 2981, 1576, 1476, 1433, 1064, 1020, 739 cm^{-1}; HRMS calcd for $C_{16}H_{24}OSe$ (M^+) 312.0992, found 312.0980; ^{1}H NMR ($CDCl_3$) δ 7.68–7.13 (m, 5H), 2.67 (s, 1H), 1.61 (s, 1H), 1.31–1.23 (m, 1H), 1.19 (d, J=5.4 Hz, 3H), 1.17 (d, J=5.8 Hz, 3H), 1.12–1.05 (m, 1H), 1.07 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 130.3, 130.3, 128.7, 126.1, 90.7, 38.9, 37.6, 27.8, 23.2, 22.7, 11.7, 10.2.

*4.2.5. (2-Butyl-1-phenylselenocyclopropyl)phenylmethanol (**1e**).* According to the typical procedure, the products yielded as a diastereomeric mixture (major isomer/minor isomer=55:45). These isomers were inseparable with column chromatography on a silica gel. A pale yellow oil, IR (neat) 3360, 3055, 3022, 2973, 1574, 1473, 1432, 1061, 1018, 737 cm^{-1}; HRMS calcd for $C_{20}H_{24}OSe$ (M^+) 360.0992, found 360.0981; ^{1}H NMR ($CDCl_3$) major isomer δ 7.59–7.13 (m, 10H), 4.46 (s, 1H), 2.71 (s, 1H), 1.70–1.58 (m, 3H), 1.43–0.86 (m, 8H), 0.65–0.62 (m, 1H).

*4.2.6. 1-(2-Butyl-1-phenylselenocyclopropyl)-2,2-dimethylpropan-1-ol (**1f**).* According to the typical procedure, the products yielded as a diastereomeric mixture (major isomer/minor isomer=66:34). These isomers were inseparable with column chromatography on a silica gel. A pale yellow oil, IR (neat) 3357, 3058, 3018, 2970, 1575, 1477, 1433, 1059, 1021, 739 cm^{-1}; HRMS calcd for $C_{18}H_{28}OSe$ (M^+) 340.1305, found 340.1390; ^{1}H NMR ($CDCl_3$) major isomer δ 7.62–7.17 (m, 5H), 2.89 (s, 1H), 1.84–1.75

(m, 1H), 1.69 (s, 1H), 1.58–1.47 (m, 1H), 1.42–1.18 (m, 6H), 1.07 (s, 9H), 0.91–0.83 (m, 3H), 0.67 (dd, J=6.6, 5.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) major isomer δ 132.5, 131.0, 128.7, 126.6, 87.3, 37.6, 33.7, 31.8, 31.6, 27.7, 26.2, 22.7, 20.3, 14.1.

*4.2.7. Phenyl(2-phenyl-1-phenylselenocyclopropyl)methanol (**1g**).* According to the typical procedure, the products yielded as a diastereomeric mixture (major isomer/minor isomer=52:48). These isomers were inseparable with column chromatography on a silica gel. A pale yellow oil, IR (neat) 3358, 3055, 3020, 2968, 1577, 1475, 1432, 1061, 1024, 738 cm^{-1}; HRMS calcd for $C_{20}H_{20}OSe$ (M^+) 380.0679, found 380.0662; ^{1}H NMR ($CDCl_3$) major isomer δ 7.36–6.85 (m, 15H), 4.39 (s, 1H), 2.81 (dd, J=9.1, 7.1 Hz, 1H), 2.28 (s, 1H), 1.93 (dd, J=7.1, 6.1 Hz, 1H), 1.57 (dd, J=9.1, 6.1 Hz, 1H).

*4.2.8. Phenyl(2-phenyl-1-phenylselenocyclopropyl)methanol (**1h**).* According to the typical procedure, the products yielded as a diastereomeric mixture (major isomer/minor isomer=51:49). Major isomer; a pale yellow oil, IR (neat) 3363, 3056, 3021, 2979, 1573, 1474, 1440, 1072, 1021, 738 cm^{-1}; HRMS calcd for $C_{20}H_{20}OSe$ (M^+) 380.0679, found 380.0663; ^{1}H NMR ($CDCl_3$) δ 7.49–7.15 (m, 15H), 4.77 (s, 1H), 2.48 (dd, J=9.1, 7.1 Hz, 1H), 2.47 (s, 1H), 1.53 (dd, J=7.1, 5.3 Hz, 1H), 1.41 (dd, J=9.1, 5.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 140.0, 138.0, 133.2, 129.5, 128.9, 128.8, 127.9, 127.8, 127.7, 127.7, 127.2, 126.8, 126.5, 77.9, 40.7, 26.8, 19.7. Minor isomer; a pale yellow oil, IR (neat) 3368, 3058, 3021, 2982, 1578, 1475, 1435, 1061, 1022, 737 cm^{-1}; HRMS calcd for $C_{20}H_{20}OSe$ (M^+) 380.0679, found 380.0660; ^{1}H NMR ($CDCl_3$) δ 7.44–7.08 (m, 15H), 4.85 (s, 1H), 2.51 (dd, J=9.2, 6.9 Hz, 1H), 2.30 (s, 1H), 1.73 (dd, J=9.2, 5.9 Hz, 1H), 1.43 (dd, J=6.9, 5.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 140.9, 138.2, 133.0, 129.2, 128.9, 128.6, 128.0, 127.8, 127.6, 127.1, 126.9, 126.3, 77.6, 40.3, 28.7, 16.2.

*4.2.9. 1-(2-Phenyl-1-phenylselenocyclopropyl)ethanol (**1i**).* According to the typical procedure, the products yielded as a diastereomeric mixture (major isomer/minor isomer=57:43). Major isomer; a pale yellow oil, IR (neat) 3362, 3051, 3025, 2983, 1574, 1477, 1447, 1075, 1023, 734 cm^{-1}; HRMS calcd for $C_{17}H_{18}OSe$ (M^+) 318.0523, found 318.0510; ^{1}H NMR ($CDCl_3$) δ 7.36–7.10 (m, 10H), 3.70 (q, J=6.1 Hz, 1H), 2.45 (dd, J=9.1, 7.1 Hz, 1H), 2.11 (s, 1H), 1.59 (dd, J=9.1, 5.8 Hz, 1H), 1.51 (dd, J=7.1, 5.8 Hz, 1H), 1.38 (d, J=6.1 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 138.3, 132.6, 129.7, 128.8, 128.6, 127.6, 126.8, 126.2, 72.8, 40.1, 28.2, 21.5, 17.3. Minor isomer; a pale yellow oil, IR (neat) 3369, 3062, 3018, 2980, 1576, 1478, 1434, 1062, 1018, 733 cm^{-1}; HRMS calcd for $C_{17}H_{18}OSe$ (M^+) 318.0523, found 318.0511; ^{1}H NMR ($CDCl_3$) δ 7.46–7.14 (m, 10H), 3.48 (q, J=6.3 Hz, 1H), 2.35 (dd, J=9.1, 7.1 Hz, 1H), 2.26 (s, 1H), 1.56 (dd, J=9.1, 6.0 Hz, 1H), 1.44 (dd, J=7.1, 6.0 Hz, 1H), 1.30 (d, J=6.3 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 138.5, 132.8, 129.8, 128.8128.7, 127.6, 126.8, 126.3, 74.4, 41.7, 28.3, 21.3, 19.9.

*4.2.10. 1-(2-Phenyl-1-phenylselenocyclopropyl)propan-1-ol (**1j**).* According to the typical procedure, the products yielded as a diastereomeric mixture (major isomer/minor isomer=55:45). Major isomer; a pale yellow oil, IR (neat) 3359, 3053, 3022, 2977, 1573, 1475, 1445, 1081, 1021, 738 cm^{-1}; HRMS calcd for $C_{18}H_{20}OSe$ (M^+) 332.0679, found 332.0661; ^{1}H NMR ($CDCl_3$) δ 7.36–7.10 (m, 10H), 3.33 (dd, J=8.9, 3.3 Hz, 1H), 2.44 (dd, J=8.7, 7.3 Hz, 1H), 2.17 (s, 1H), 2.01–1.87 (m, 1H), 1.70–1.52 (m, 1H), 1.67–1.50 (m, 2H), 0.97 (t, J=7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 138.3, 132.8, 129.7, 128.8, 128.5, 127.6, 126.8, 126.1, 78.9, 39.2, 28.8, 28.1, 17.5, 10.8. Minor isomer; a pale yellow oil, IR (neat) 3366, 3061, 3025, 2973, 1574, 1479, 1431, 1057, 1019, 738 cm^{-1}; HRMS calcd for $C_{18}H_{20}OSe$ (M^+) 332.0679, found 332.0662; ^{1}H NMR ($CDCl_3$) δ 7.44–7.13 (m, 10H), 3.04 (dd, J=8.6, 4.6 Hz, 1H), 2.34 (dd, J=8.7, 7.3 Hz, 1H), 2.01 (s, 1H), 1.79–1.64 (m, 2H), 1.55 (dd, J=9.1, 6.1 Hz, 1H), 1.37 (dd, J=6.8, 6.1 Hz, 1H), 1.02 (t, J=7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 138.0, 133.1, 130.1, 128.8, 128.7, 127.6, 126.9, 126.3, 81.2, 41.4, 29.6, 29.3, 19.6, 10.8.

*4.2.11. 2-Methyl-1-(2-phenyl-1-phenylselenocyclopropyl)propan-1-ol (**1k**).* According to the typical procedure, the products yielded as a diastereomeric mixture (major isomer/minor isomer=59:41). Major isomer; a pale yellow oil, IR (neat) 3361, 3052, 3021, 2982, 1575, 1476, 1441, 1076, 1017, 734 cm^{-1}; HRMS calcd for $C_{19}H_{22}OSe$ (M^+) 346.0836, found 346.0820; ^{1}H NMR ($CDCl_3$) δ 7.35–7.09 (m, 10H), 2.93 (d, J=7.3 Hz, 1H), 2.44 (dd, J=8.9, 7.1 Hz, 1H), 2.30 (dd, J=7.1, 6.9 Hz, 1H), 1.76 (s, 1H), 1.59 (dd, J=7.1, 5.8 Hz, 1H), 1.52 (dd, J=9.0, 5.9 Hz, 1H), 1.02 (d, J=6.8 Hz, 3H), 0.82 (d, J=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 138.1, 134.2, 128.9, 128.7, 128.4, 127.4, 127.2, 126.0, 83.4, 38.5, 33.3, 28.2, 20.0, 18.2, 18.1. Minor isomer; a pale yellow oil, IR (neat) 3359, 3057, 3028, 2974, 1576, 1473, 1428, 1056, 1023, 734 cm^{-1}; HRMS calcd for $C_{19}H_{22}OSe$ (M^+) 346.0836, found 346.0821; ^{1}H NMR ($CDCl_3$) δ 7.49–7.11 (m, 10H), 2.60 (d, J=8.9 Hz, 1H), 2.37 (dd, J=8.9, 6.9 Hz, 1H), 2.07–1.94 (m, 1H), 1.86 (s, 1H), 1.49 (dd, J=9.0, 6.3 Hz, 1H), 1.28 (dd, J=6.9, 6.3 Hz, 1H), 1.08 (d, J=6.6 Hz, 3H), 0.97 (d, J=6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 137.5, 133.7, 130.0, 128.7, 128.5, 127.4, 127.0, 126.2, 86.6, 41.2, 34.7, 32.0, 19.9, 19.5, 18.8.

*4.2.12. 2,2-Dimethyl-1-(2-phenyl-1-phenylselenocyclopropyl)propan-1-ol (**1l**).* According to the typical procedure, the products yielded as a diastereomeric mixture (major isomer/minor isomer=61:39). Major isomer; a pale yellow oil, IR (neat) 3360, 3055, 3018, 2980, 1577, 1474, 1439, 1077, 1018, 739 cm^{-1}; HRMS calcd for $C_{20}H_{24}OSe$ (M^+) 360.0992, found 360.0972; ^{1}H NMR ($CDCl_3$) δ 7.28–7.02 (m, 10H), 3.13 (s, 1H), 2.49 (dd, J=9.1, 7.3 Hz, 1H), 1.76 (s, 1H), 1.62 (dd, J=9.1, 5.9 Hz, 1H), 1.52 (dd, J=7.3, 5.9 Hz, 1H), 1.13 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 138.0, 133.2, 129.8, 129.2, 128.4, 127.4, 126.9, 126.2, 86.8, 37.7, 31.5, 30.3, 27.7, 19.4. Minor isomer; a pale yellow oil, IR (neat) 3364, 3061, 3027, 2975, 1577, 1474, 1421, 1065, 1021, 739 cm^{-1}; HRMS calcd for $C_{20}H_{24}OSe$ (M^+) 360.0992, found 360.0974; ^{1}H NMR ($CDCl_3$) δ 7.52–7.05 (m, 10H), 2.76 (s, 1H), 2.52 (dd, J=9.1, 7.1 Hz, 1H), 2.18 (s, 1H), 1.44 (dd, J=9.2, 6.1 Hz, 1H), 1.25 (m, 1H), 1.12 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 137.9, 133.9, 131.0, 129.0, 128.8, 127.5, 127.2, 126.4, 88.0, 37.6, 32.4, 31.6, 28.0, 21.3.

4.3. General procedure for the reaction of 1-phenylselenocyclopropylmethanols with TsOH

To a solution of 1-phenylselenocyclopropylmethanol (1 mmol) in methanol (4 mL) was added a solution of TsOH (344 mg, 1.2 mmol) in methanol (1 mL), and the mixture was stirred for 3 h under reflux. The resulting mixture was then poured into saturated $NaHCO_3$ aq. The aqueous layer was extracted with diethyl ether for three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on a silica gel to give homoallyl ether derivative **2**, cyclobutene derivative **3**, cyclobutanone derivative **4**, β-seleno ketone derivative **5**, and α,β-unsaturated ketone **6**, respectively.

*4.3.1. 4-Methoxy-3-methyl-1-phenyl-2-phenylselenopent-1-ene (**2a**).* A pale yellow oil, IR (neat) 3059, 3029, 2956, 1578, 1476, 1432, 1104, 738 cm^{-1}; HRMS calcd for $C_{19}H_{22}OSe$ (M^+) 346.0836, found 346.0822; ^{1}H NMR ($CDCl_3$) δ 7.45–7.15 (m, 10H), 6.98 (s, 1H), 3.50 (m, 1H), 3.32 (s, 3H), 2.39 (dq, J=7.0, 6.3 Hz, 1H), 1.20 (d, J=6.9 Hz, 3H), 1.09 (d, J=6.3 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 137.9, 137.5, 133.0, 132.7, 130.1, 129.0, 128.9, 127.7, 127.0, 126.9, 79.6, 57.1, 48.5, 17.6, 16.0.

*4.3.2. 6-Methoxy-2,2,5-trimethyl-4-phenylselenohept-3-ene (**2b**).* A pale yellow oil, IR (neat) 3066, 3022, 2956, 1572, 1476, 1433, 1102, 736 cm^{-1}; HRMS calcd for $C_{17}H_{26}OSe$ (M^+) 326.1149, found

326.1136; ^{1}H NMR ($CDCl_3$) δ 7.29–7.18 (m, 5H), 6.08 (s, 1H), 3.37 (dq, J=6.1, 5.8 Hz, 1H), 3.28 (s, 3H), 2.14 (dq, J=7.3, 5.8 Hz, 1H), 1.24 (s, 9H), 1.08 (d, J=6.1 Hz, 3H), 1.02 (d, J=7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 145.6, 132.5, 132.1, 131.5, 128.8, 126.4, 79.9, 57.3, 49.0, 33.8, 30.9, 176, 16.2.

*4.3.3. 4-Methoxy-3-methyl-1-phenyl-2-phenylselenopent-1-ene (**2c**).* A pale yellow oil, IR (neat) 3057, 3026, 2952, 1577, 1475, 1436, 1101, 736 cm^{-1}; HRMS calcd for $C_{19}H_{22}OSe$ (M^+) 346.0836, found 346.0821; ^{1}H NMR (for *Z*-isomer, $CDCl_3$) δ 7.45–7.14 (m, 10H), 6.79 (s, 1H), 3.66 (dq, J=6.3 Hz, 5.4 Hz, 1H), 3.07 (s, 3H), 2.81–2.70 (m, 1H), 1.12 (d, J=7.1 Hz, 3H), 1.08 (d, J=6.3 Hz, 3H); ^{1}H NMR (for *E*-isomer, $CDCl_3$) δ 7.35–7.16 (m, 10H), 6.79 (s, 1H), 3.50–3.41 (m, 1H), 3.24 (s, 3H), 3.20–3.12 (m, 1H), 1.14 (d, J=6.1 Hz, 3H), 1.08 (d, J=6.9 Hz, 3H).

*4.3.4. 6-Methoxy-2,2,5-trimethyl-4-phenylselenohept-3-ene (**2d**).* A pale yellow oil, IR (neat) 3062, 3017, 2947, 1576, 1475, 1432, 1103, 732 cm^{-1}; HRMS calcd for $C_{17}H_{26}OSe$ (M^+) 326.1149, found 326.1134; ^{1}H NMR ($CDCl_3$) δ 7.43–7.16 (m, 5H), 6.07 (s, 1H), 3.64 (dq, J=6.4, 4.7 Hz, 1H), 3.08 (s, 3H), 2.55 (dq, J=7.1, 4.7 Hz, 1H), 1.25 (s, 9H), 0.98 (d, J=6.4 Hz, 3H), 0.94 (d, J=7.1 Hz, 3H).

*4.3.5. 4-Methoxy-1-phenyl-2-phenylselenooct-1-ene (**2e**).* A pale yellow oil, IR (neat) 3062, 3023, 2955, 1575, 1473, 1432, 1104, 739 cm^{-1}; HRMS calcd for $C_{21}H_{26}OSe$ (M^+) 374.1149, found 374.1135; ^{1}H NMR ($CDCl_3$) δ 7.52–7.18 (m, 10H), 6.95 (s, 1H), 3.41 (m, 1H), 3.14 (s, 3H), 2.61 (dd, J=14.0, 6.4 Hz, 1H), 2.32 (dd, J=14.0, 6.3 Hz, 1H), 1.46–1.15 (m, 6H), 0.88–0.83 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 137.3, 134.1, 133.3, 132.0, 128.9, 128.8, 128.7, 127.8, 127.0, 79.6, 57.0, 44.0, 33.3, 27.5, 22.8, 12.1.

*4.3.6. 4-Methoxy-1,4-diphenyl-2-phenylselenobut-1-ene (**2g**).* A pale yellow oil, IR (neat) 3063, 3025, 2945, 1576, 1477, 1433, 1101, 736 cm^{-1}; HRMS calcd for $C_{23}H_{22}OSe$ (M^+) 394.0836, found 394.0824; ^{1}H NMR (for *Z*-isomer, $CDCl_3$) δ 7.37–7.11 (m, 15H), 6.77 (s, 1H), 4.43 (dd, J=7.9, 5.6 Hz, 1H), 3.18 (s, 3H), 2.82 (dd, J=14.2, 7.9 Hz, 1H), 2.56 (dd, J=14.2, 5.6 Hz, 1H); ^{1}H NMR (for *E*-isomer, $CDCl_3$) δ 7.33–7.16 (m, 15H), 7.00 (s, 1H), 4.60 (dd, J=8.9, 4.8 Hz, 1H), 3.19 (s, 3H), 3.14 (dd, J=14.5, 8.9 Hz, 1H), 2.56 (dd, J=14.5, 4.8 Hz, 1H).

*4.3.7. trans-3,4-Dimethyl-1-phenyl-2-phenylselenocyclobut-1-ene (**3a**).* A pale yellow oil, IR (neat) 3057, 2955, 2922, 2854, 1577, 1475, 1437, 1022, 738 cm^{-1}; HRMS calcd for $C_{18}H_{18}Se$ (M^+) 314.0574, found 314.0555; ^{1}H NMR ($CDCl_3$) δ 7.58–7.18 (m, 10H), 2.77 (dq, J=6.7, 1.2 Hz, 1H), 2.47 (dq, J=6.7, 1.2 Hz, 1H), 1.32 (d, J=6.7 Hz, 3H), 0.95 (d, J=6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 148.6, 134.0, 133.3, 129.5, 128.9, 128.3, 128.4, 127.2, 127.1, 125.9, 47.5, 44.9, 17.7, 17.2.

*4.3.8. trans-3,4-Dimethyl-1-tert-butyl-2-phenylselenocyclobut-1-ene (**3b**).* A pale yellow oil, IR (neat) 3056, 2956, 2924, 2856, 1579, 1473, 1436, 1021, 739 cm^{-1}; HRMS calcd for $C_{16}H_{22}Se$ (M^+) 294.0887, found 294.0872; ^{1}H NMR ($CDCl_3$) δ 7.50–7.13 (m, 5H), 2.38 (dq, J=6.8, 1.4 Hz, 1H), 2.16 (dq, J=6.8, 1.4 Hz, 1H), 1.20 (d, J=6.8 Hz, 3H), 1.16 (s, 9H), 0.85 (d, J=6.8 Hz, 3H).

*4.3.9. trans-3-tert-Butyl-2,3-dimethyl-4-phenylselenocyclobut-1-ene (**3b′**).* A pale yellow oil, IR (neat) 3055, 2956, 2923, 2856, 1575, 1475, 1433, 1020, 739 cm^{-1}; HRMS calcd for $C_{16}H_{22}Se$ (M^+) 294.0887, found 294.0870; ^{1}H NMR ($CDCl_3$) δ 7.50–7.13 (m, 5H), 2.60–2.52 (m, 1H), 2.24–2.23 (m, 1H), 1.64 (q, J=1.2 Hz, 3H), 1.13 (d, J=8.5 Hz, 3H), 0.87 (s, 9H).

*4.3.10. cis-3,4-Dimethyl-1-phenyl-2-phenylselenocyclobut-1-ene (**3c**).* A pale yellow oil, IR (neat) 3055, 2956, 2923, 2856, 1577, 1476, 1438, 1021, 736 cm^{-1}; HRMS calcd for $C_{18}H_{18}Se$ (M^+) 314.0574, found 314.0558; ^{1}H NMR ($CDCl_3$) δ 7.58–7.09 (m, 10H), 3.40 (dq, J=7.0, 5.0 Hz, 1H), 3.06 (dq, J=7.3, 5.0 Hz, 1H), 1.17 (d, J=7.0 Hz, 3H), 0.83 (d, J=7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 149.9, 133.8, 133.6, 132.5, 128.9, 128.2, 127.7, 127.3, 127.2, 126.0, 42.1, 39.3, 13.9, 13.3.

*4.3.11. cis-3,4-Dimethyl-1-tert-butyl-2-phenylselenocyclobut-1-ene (**3d**).* A pale yellow oil, IR (neat) 3055, 2957, 2923, 2857, 1574, 1475, 1433, 1025, 739 cm^{-1}; HRMS calcd for $C_{16}H_{22}Se$ (M^+) 294.0887, found 294.0871; ^{1}H NMR ($CDCl_3$) δ 7.50–7.15 (m, 5H), 3.01 (dq, J=7.1, 4.7 Hz, 1H), 2.16 (dq, J=7.1, 4.7 Hz, 1H), 1.16 (s, 9H), 1.07 (d, J=7.1 Hz, 3H), 0.72 (d, J=7.1 Hz, 3H).

*4.3.12. 4-Butyl-1-phenyl-2-phenylselenocyclobut-1-ene (**3e**).* A pale yellow oil, IR (neat) 3050, 2958, 2920, 2856, 1575, 1474, 1432, 1021, 738 cm^{-1}; HRMS calcd for $C_{20}H_{22}Se$ (M^+) 342.0887, found 342.0871; ^{1}H NMR ($CDCl_3$) δ 7.44–7.13 (m, 5H), 3.22–3.15 (m, 1H), 2.65 (dd, J=13.5, 4.5 Hz, 1H), 2.14 (dd, J=13.5, 1.6 Hz, 1H), 1.31–1.29 (m, 5H), 0.89–0.84 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 148.8, 134.1, 134.0, 128.9, 128.2, 127.5, 126.9, 125.7, 125.6, 124.7, 41.6, 38.3, 32.8, 29.3, 22.9, 14.2.

*4.3.13. r-2-Phenyl-t-3,c-4-dimethylcyclobutanone (**4a**).* A pale yellow oil, IR (neat) 3054, 2960, 2928, 2858, 1778, 1716, 1683, 1456, 1436, 1072, 740 cm^{-1}; HRMS calcd for $C_{12}H_{14}O$ (M^+) 174.1045, found 174.1049; ^{1}H NMR ($CDCl_3$) δ 7.35–7.11 (m, 5H), 3.95 (dd, J=8.9, 2.3 Hz, 1H), 2.96–2.90 (m, 1H), 2.18–2.04 (m, 1H), 1.49 (d, J=6.4 Hz, 3H), 1.20 (d, J=7.2 Hz, 3H).

*4.3.14. 3-Butyl-2-phenylcyclobutanone (**4e**).* A colorless oil, IR (neat) 3062, 2957, 2920, 2867, 1770, 734 cm^{-1}; HRMS calcd for $C_{14}H_{18}O$ (M^+) 202.1358, found 202.1355; ^{1}H NMR ($CDCl_3$) δ 7.48–7.14 (m, 5H), 4.04 (dt, J=7.8, 2.2 Hz, 1H), 3.11 (ddd, J=11.0, 8.7, 2.3 Hz, 1H), 2.59–2.49 (m, 1H), 1.91–1.83 (m, 1H), 1.77–1.70 (m, 1H), 1.41–1.20 (m, 5H), 1.39–1.42 (m, 4H), 0.90 (t, J=7.1 Hz, 3H).

*4.3.15. 2-tert-Butyl-3-butylcyclobutanone (**4f**).* A colorless oil, IR (neat) 2955, 2916, 2855, 1780, 739 cm^{-1}; HRMS calcd for $C_{12}H_{22}O$ (M^+) 182.1671, found 182.1670; ^{1}H NMR ($CDCl_3$) δ 2.89 (ddd, J=17.6, 8.6, 2.6 Hz, 1H), 2.63 (ddd, J=9.9, 6.4, 3.3 Hz, 1H), 2.46(ddd, J=17.6, 6.4, 3.6 Hz, 1H), 2.24–2.09 (m, 1H), 1.78–1.65 (m, 1H), 1.52–1.41 (m, 1H), 1.39–1.42 (m, 4H), 0.96 (s, 9H), 0.94–0.87 (m, 3H).

*4.3.16. 1-Phenyl-1-phenylselenopentan-3-one (**5a**).* A pale yellow oil, IR (neat) 3055, 2972, 2925, 1703, 1577, 1474, 1109, 1021, 731 cm^{-1}; HRMS calcd for $C_{17}H_{18}OSe$ (M^+) 318.0523, found 318.0525; ^{1}H NMR ($CDCl_3$) δ 7.41–7.09 (m, 10H), 4.81 (dd, J=8.4, 6.6 Hz, 1H), 3.18 (dd, J=17.0, 8.4 Hz, 1H), 3.04 (dd, J=16.9, 6.6 Hz, 1H), 2.28 (m, 1H), 0.92 (t, J=7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 207.9, 141.3, 135.3, 128.7, 128.6, 128.1, 127.8, 127.3, 126.8, 48.2, 41.7, 36.5, 7.4.

*4.3.17. 1-Phenyl-1-phenylselenohexan-3-one (**5b**).* A pale yellow oil, IR (neat) 3054, 2970, 2928, 1705, 1578, 1476, 1112, 738 cm^{-1}; HRMS calcd for $C_{18}H_{20}OSe$ (M^+) 332.0679, found 332.0663; ^{1}H NMR ($CDCl_3$) δ 7.40–7.09 (m, 10H), 4.80 (dd, J=8.4, 6.4 Hz, 1H), 3.18 (dd, J=17.0, 8.4 Hz, 1H), 3.03 (dd, J=17.0, 6.4 Hz, 1H), 2.24 (dt, J=7.4, 4.1 Hz, 1H), 1.47 (m, 2H), 0.78 (t, J=7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 207.6, 141.3, 135.3, 128.7, 128.6, 128.1, 127.8, 127.3, 126.8, 48.6, 45.2, 41.7, 168, 13.5.

*4.3.18. 5-Methyl-1-phenyl-1-phenylselenohexan-3-one (**5c**).* A pale yellow oil, IR (neat) 3056, 2972, 2925, 1704, 1576, 1473, 1109, 1018, 739 cm^{-1}; HRMS calcd for $C_{19}H_{22}OSe$ (M^+) 346.0836, found 346.0823; ^{1}H NMR ($CDCl_3$) δ 7.40–7.12 (m, 10H), 4.80 (dd, J=8.4, 6.4 Hz, 1H), 3.18 (dd, J=17.0, 8.5 Hz, 1H), 3.01 (dd, J=17.0, 6.4 Hz, 1H), 2.15 (d, J=7.8 Hz, 1H), 2.15 (d, J=5.8 Hz, 1H), 2.02 (dd, J=7.7, 6.3 Hz, 1H), 0.78 (d, J=6.4 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 207.3, 141.3, 135.3, 128.7, 128.6, 128.1, 127.8, 127.3, 126.8, 51.3, 41.6, 24.2, 22.4, 22.3.

*4.3.19. 5,5-Dimethyl-1-phenyl-1-phenylselenohexan-3-one (**5d**).* A pale yellow oil, IR (neat) 3054, 2970, 2926, 1703, 1577, 1472, 1107,

1021, 738 cm^{-1}; HRMS calcd for $C_{20}H_{24}OSe$ (M^+) 360.0992, found 360.0978; ^1H NMR ($CDCl_3$) δ 7.41–7.10 (m, 10H), 4.79 (dd, J=8.4, 6.3 Hz, 1H), 3.18 (dd, J=17.3, 8.4 Hz, 1H), 3.03 (dd, J=17.2, 6.3 Hz, 1H), 2.21 (d, J=14.8 Hz, 1H), 2.14 (d, J=14.8 Hz, 1H), 0.89 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 207.3, 141.4, 135.3, 128.9, 128.7, 128.1, 127.8, 127.4, 126.8, 55.3, 50.9, 41.7, 30.9, 29.6.

4.4. General procedure for the reaction of 1-phenylselenocyclopropylmethanols with Lewis acid

To a solution of 1-phenylselenocyclopropylmethanol **1l** (1 mmol) in 5 mL of solvent was added acid (1.2 mmol), and the mixture was stirred for 2 h under reflux. The resulting mixture was then poured into saturated $NaHCO_3$ aq. The aqueous layer was extracted with diethyl ether for three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on a silica gel to give selenochromene derivative **7**.

*4.4.1. 2-Neopentyl-4-phenyl-4H-selenochromene (**7**).* A colorless solid, mp 131.2–131.4 °C, IR (neat) 3057, 2956, 1458, 1436, 1361, 1234, 1029, 740 cm^{-1}; HRMS calcd for $C_{20}H_{22}Se$ (M^+) 342.0887, found 342.0898; ^1H NMR ($CDCl_3$) δ7.52–7.46 (m, 1H), 7.38–7.23 (m, 5H), 7.13–7.07 (m, 2H), 6.86–6.81 (m, 1H), 6.14 (d, J=4.9 Hz, 1H), 4.34 (d, J=4.8 Hz, 1H), 2.46 (s, 2H), 0.96 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 142.2, 138.5, 133.3, 131.3, 128.7, 128.6, 128.5, 128.5, 128.0, 126.6, 126.5, 125.9, 52.6, 51.8, 31.7, 29.8.

4.5. General procedure for the selenoxide elimination reaction of homoallylic ether derivatives 2

To a solution of phenylselenyl substituted homoallylic derivative **2** (0.5 mmol) in toluene (5 mL) was added a solution of *m*-CPBA (104 mg, 0.6 mmol) in toluene (2 mL) at 0 °C, and the mixture was stirred for 1 h. DBU (152 mg, 1 mmol) was added to the mixture, then the resulting mixture was warmed up to 100 °C. After stirring for 2 h, the reaction mixture was cooled to 0 °C and then poured into saturated $NaHCO_3$ aq. The aqueous layer was extracted with diethyl ether for three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on a silica gel to give allene derivatives **8** and alkyne derivative **9**, respectively.

*4.5.1. 4-Methoxy-3-methyl-1-phenylpenta-1,2-diene (**8a**).* A pale yellow oil, IR (neat) 3055, 2981, 2935, 2827, 1722, 1600, 1452, 1317, 1110, 713 cm^{-1}; HRMS calcd for $C_{13}H_{16}O$ (M^+) 188.1201, found 188.1198; ^1H NMR ($CDCl_3$) δ 7.41–7.14 (m, 5H), 6.19 (dq, J=3.0, 1.0 Hz, 1H), 3.94 (dq, J=6.4, 1.0 Hz, 1H), 3.30 (s, 3H), 1.77 (d, J=3.0 Hz, 3H), 1.35 (d, J=6.4 Hz, 3H).

*4.5.2. 4-Methoxy-3-methyl-1-phenylpenta-1,2-diene (**8b**).* A pale yellow oil, IR (neat) 3045, 2979, 2936, 2826, 1719, 1599, 1451, 1319, 1108, 712 cm^{-1}; HRMS calcd for $C_{13}H_{16}O$ (M^+) 188.1201, found 188.1200; ^1H NMR ($CDCl_3$) δ 7.33–7.14 (m, 5H), 6.10 (dq, J=3.0, 1.0 Hz, 1H), 3.92 (dq, J=6.4, 1.0 Hz, 1H), 3.35 (s, 3H), 1.76 (d, J=3.0 Hz, 3H), 1.32 (d, J=6.4 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 202.7, 135.0, 128.4, 126.6, 1265, 103.8, 94.1, 78.4, 56.0, 19.5, 12.6.

*4.5.3. 6-Methoxy-2,2,5-trimethylhepta-3,4-diene (**8c**).* A pale yellow oil, IR (neat) 2980, 2924, 1719, 1112, 721 cm^{-1}; HRMS calcd for $C_{11}H_{20}O$ (M^+) 168.1514, found 168.1511; ^1H NMR ($CDCl_3$) δ 5.06 (dq, J=3.0, 1.0 Hz, 1H), 3.79 (dq, J=6.4, 1.0 Hz, 1H), 3.27 (s, 3H), 1.63 (d, J=3.0 Hz, 3H), 1.25 (d, J=6.4 Hz, 3H), 1.04 (s, 9H).

*4.5.4. 4-Methoxy-3-methyl-1-phenylpent-1-yne (**9b**).* A pale yellow oil, IR (neat) 3045, 2976, 2927, 1488, 1458, 1375, 1103, 756 cm^{-1}; HRMS calcd for $C_{13}H_{16}O$ (M^+) 188.1201, found 188.1195; ^1H NMR ($CDCl_3$) δ7.43–7.24 (m, 5H), 3.47 (dq, J=6.3, 4.5 Hz, 1H), 3.39 (s, 3H), 2.93 (dq, J=6.9, 4.5 Hz, 1H), 1.25 (d, J=6.4 Hz, 3H), 1.23 (d, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 131.5, 128.0, 127.4, 123.7, 91.8, 81.7, 79.0, 56.8, 31.1, 15.7, 15.0.

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