 

# Diphenyl Diselenide as a Useful Reagent for Intermolecular Domino Reactions of Various Unsaturated Compounds under Photoirradiation Conditions

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This paper describes full details of a series of intermolecular domino reactions mediated by diphenyl diselenide (PhSeSePh). Diphenyl diselenide, which has just the right strength of carbon radical capturing ability, can be employed as a useful mediator for intermolecular domino reactions of unsaturated compounds. Upon irradiation through Pyrex with a tungsten lamp ($h\nu > 300$ nm), a sequential addition of diphenyl diselenide to alkynes bearing an electron-withdrawing group and alkenes bearing an electron-donating group proceeds successfully to provide the corresponding intermolecular three-component coupling products in high yields. In place of alkenes, the use of isocyanides leads to the formation of the corresponding three-component coupling products of alkynes, isocyanides, and $(PhSe)_2$, selectively. Moreover, when two kinds of alkenes (i.e., electron-rich alkenes and electron-poor alkenes) are used in this photoinduced alkyne-$(PhSe)_2$ reaction system, a novel domino reaction of diphenyl diselenide with an alkyne and two kinds of alkenes, followed by 5-*exo* radical cyclization, takes place sequentially to provide the corresponding cyclic four-component coupling products in good yields.

Diphenyl diselenide has its absorption maximum in the near-UV region ($\lambda_{max} = 340$ nm, $\varepsilon_{max} = 1 \times 10^3$, see: Fig. 1), which can be assigned as an $n \rightarrow \sigma^*$ transition.[1] Therefore, irradiation with light of wavelength greater than 300 nm induces a homolytic cleavage of the selenium–selenium single bond to generate a phenylseleno radical (PhSe•) as a labile species.[2] In the absence of substrates to react, however, thus-formed PhSe• easily undergoes recombination to re-form the starting diselenides (Eq. 1). The rate constant ($k_r$) for the recombination of PhSe• is reported to be close to the diffusion-controlled rate constant ($7 \times 10^9$ $M^{-1}$ $s^{-1}$ in $CCl_4$),[3] which strongly suggests that continuous photoirradiation is required to accomplish the $(PhSe)_2$-mediated radical reactions involving PhSe• as key species.

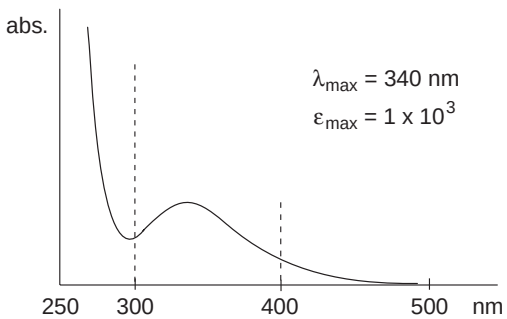
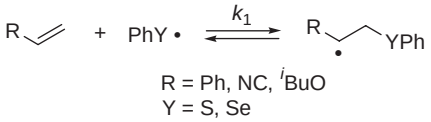



Fig. 1. UV–visible spectrum of $(PhSe)_2$.

$$\text{RSe–SeR} \underset{k_r}{\overset{h\nu}{\rightleftharpoons}} 2\ \text{RSe}\bullet \qquad (1)$$

If the photolysis of $(PhSe)_2$ is performed in the presence of carbon–carbon unsaturated compounds, phenylseleno radicals formed in situ may be trapped by unsaturated compounds. Some kinetic data are of great importance for predicting radical addition reactions of $(PhSe)_2$ to unsaturated compounds. In the case of the addition of $(PhS)_2$ to alkenes, for example, the addition rate constants ($k_1$) of PhS• to a carbon–carbon double bond are reported to be $2.0 \times 10^7$ $M^{-1}$ $s^{-1}$ for styrene, $4.6 \times 10^5$ $M^{-1}$ $s^{-1}$ for acrylonitrile, and $1.2 \times 10^5$ $M^{-1}$ $s^{-1}$ for isobutyl vinyl ether (Eq. 2).[3,4] On the other hand, the corresponding addition rate constants ($k_1$) of PhSe• are $2.2 \times 10^6$ $M^{-1}$ $s^{-1}$ for styrene, $1.4 \times 10^4$ $M^{-1}$ $s^{-1}$ for acrylonitrile, and $3.5 \times 10^4$ $M^{-1}$ $s^{-1}$ for isobutyl vinyl ether.[3,4] Accordingly, the reactivity of the phenylseleno radical toward carbon–carbon unsaturated bonds is relatively lower by the factor of about 10–50, compared with the corresponding sulfanyl radical.[3]




(2)

More importantly, the addition of PhSe• to unsaturated compounds is conceivably a reversible process, and the equi-

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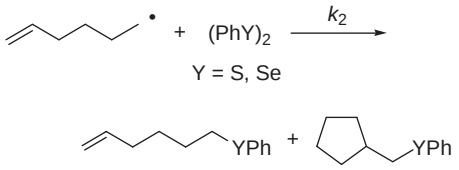
librium lies far to the left. These facts suggest that higher concentrations of the starting materials are essential for the efficient generation of carbon radical intermediates by the addition of PhSe• to unsaturated compounds.

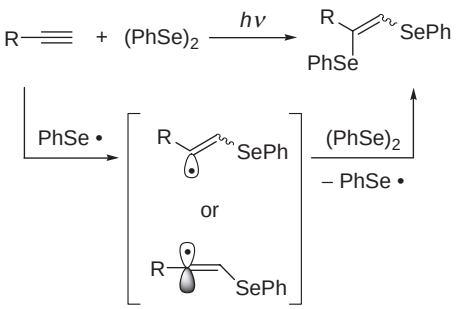
On the other hand, the rate constants ($k_2$) for the $S_H2$ reaction are estimated to be $7.6 \times 10^4$ $M^{-1}\,s^{-1}$ for $(PhS)_2$ and $1.2 \times 10^7$ $M^{-1}\,s^{-1}$ for $(PhSe)_2$ by using the free radical clock system of the 5-hexenyl radical.[5] These kinetic data indicate that $(PhSe)_2$ exhibits an excellent carbon radical capturing ability, compared with $(PhS)_2$, by a factor of approximately 160 (Eq. 3).



(3)

With these kinetic considerations in mind, the photoinduced radical addition of $(PhSe)_2$ to carbon–carbon unsaturated compounds is predicted as follows: (i) both continuous photoinitiation and higher concentrations of the starting materials are essential for the efficient radical addition of diphenyl diselenide to unsaturated compounds; (ii) the stability of carbon radical intermediates derived from PhSe• and unsaturated compounds is of great importance, especially for building up the desired intermolecular domino reactions.

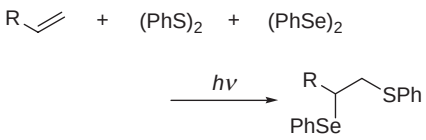
The first example of the efficient radical addition of organic diselenide to unsaturated compounds is the UV-light-irradiated addition of $(PhSe)_2$ to electron-deficient alkynes, such as dimethyl acetylenedicarboxylate (DMAD) in benzene.[6] The radical addition of $(PhSe)_2$ to a variety of alkynes and allenes has been attained upon irradiation through Pyrex with a tungsten lamp ($h\nu > 300$ nm) under higher concentrations of the starting materials (in the absence of solvent), which provides the corresponding vicinal diselenoalkenes in good yields (Eq. 4).[7]



(4)

In contrast to the radical addition of diselenides to alkenes, however, there have been no reported examples, to date, of the efficient radical addition of organic diselenides to alkenes. The difficulty in realizing the radical addition of organic diselenides to alkenes may arise from the relatively lower stability of $\beta$-selenoalkyl radical intermediates, compared with $\beta$-selenoalkenyl ones.[8] In other words, the equilibrium between the starting materials (i.e., alkenes and $(PhSe)_2$) and the $\beta$-selenoalkyl radical intermediates lies much more to the left, compared with that between the substrates (i.e., alkynes and $(PhSe)_2$) and $\beta$-selenoalkenyl radicals.

As already mentioned, the addition rate constants of PhS• to an alkenyl double bond are greater than those of PhSe• by a factor of about 10–50.[3] On the other hand, the rate constants of the $S_H2$ reaction of alkyl radicals with $(PhSe)_2$ are much greater than those with $(PhS)_2$ by a factor of ca. 160.[5] Accordingly, if the addition to alkenes is performed in the coexistence of $(PhS)_2$ and $(PhSe)_2$, the high reactivity of PhS• toward alkenes and the excellent capturing ability of $(PhSe)_2$ for carbon radicals may realize the simultaneous introduction of two different heteroatom functional groups to the double bonds. By using this $(PhS)_2$–$(PhSe)_2$ binary system, it has been found that two different chalcogeno groups can be introduced into a wide variety of unsaturated compounds successfully (Eq. 5).[8,9]

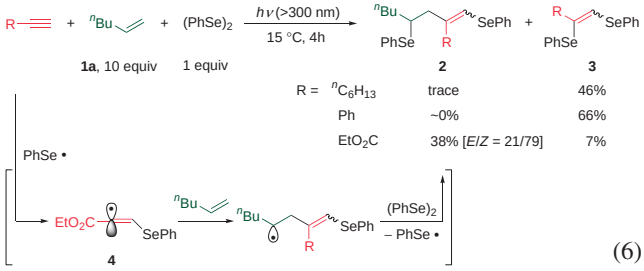


(5)

Thus, it is of great importance to consider the following points: (i) the addition rate constants of organic heteroatom radicals to unsaturated compounds, (ii) the rate constants of the $S_H2$ reaction of alkyl radicals with organic heteroatom compounds, (iii) the concentrations of the starting materials, and (iv) the stability of carbon radical intermediates. In this paper, we wish to report on full details of domino reactions of various unsaturated compounds, such as alkynes, alkenes, and isocyanides, mediated by $(PhSe)_2$, which has just the right strength of carbon radical capturing ability.[10]

## Results and Discussion

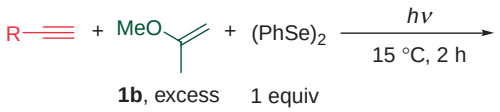
**Three-Component Coupling of $(PhSe)_2$ with Alkynes and Alkenes.** To develop highly selective three-component coupling of $(PhSe)_2$ with alkynes and alkenes, the selection and combination of alkynes and alkenes are of great importance. Thus, we initiated our work concerning this domino reaction by examining the combination of alkynes and alkenes. 1-Hexene (**1a**) was used as a standard alkene, and three types of alkynes, i.e., 1-octyne, phenylacetylene, and ethyl propiolate, were tested for the sequential addition of $(PhSe)_2$. Although 1-octyne and phenylacetylene generate vinylic $\sigma$- and $\pi$-radicals, respectively, by the addition of radical species, like seleno radicals,[11] neither 1-octyne nor phenylacetylene provided the desired alkyne–alkene coupling products (**2**), and instead, 1,2-bis(phenylseleno)-1-alkenes (**3**) were obtained as the major products (Eq. 6). On the other hand, ethyl propiolate as a representative electron-deficient alkyne, can form a relatively stable radical intermediate by the attack of radical species.[12] Thus, the domino reaction of $(PhSe)_2$ with ethyl propiolate and 1-hexene (**1a**) was examined, which took place successfully, giving the corresponding sequential addition product (**2a**, R = $EtO_2C$, $E/Z = 21/79$) in a moderate yield with good stereoselectivity. This domino reaction may proceed via the selective formation of vinylic radical (**4**) by the attack of PhSe• to the alkyne.[13] The subsequent addition of **4** to **1a** generates a homoallylic radical, which undergoes the $S_H2$ reaction with $(PhSe)_2$, leading to **2**.

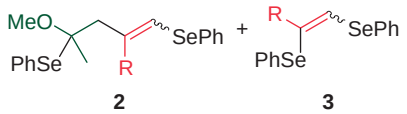



(6)

These results suggest that a combination of radicals bearing an electron-withdrawing group at the radical center and alkenes bearing an electron-donating group is a good choice for the desired domino reaction of $(PhSe)_2$ with alkynes and alkenes. This fact can be explained reasonably by molecular-orbital theory.[14] Since the level of SOMO orbital of the vinylic radical (**4**) is stabilized strongly by an electron-withdrawing group bonded to the radical center of **4**, the interactions between the SOMO of vinylic radical and HOMO of 1-hexene (**1a**) are more suitable (Scheme 1).

Accordingly, the use of alkenes bearing an electron-donating group may cause a better SOMO–HOMO interaction. Thus, we examined the domino reaction using 2-methoxypropene (**1b**), instead of **1a**, which successfully afforded the corresponding three-component coupling product (**2b**) in a good yield with high stereoselectivity (R = $EtO_2C$, 78%, $E/Z = 7/93$) (Eq. 7).



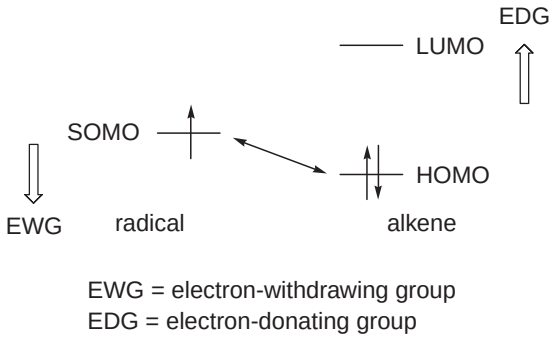

| | | |
|---|---|---|
| R = $^nC_6H_{13}$ | ~0% | 70% |
| Ph | ~0% | 55% |
| $EtO_2C$ | 78% [*E*/*Z* = 7/93] | 5% |

(7)

To clarify the influence of the concentration of the substrates on this domino reaction, the reaction was next examined by varying concentrations of the starting materials; the results are given in Table 1. When 7 equiv of **1b** was used for a reaction with ethyl propiolate and $(PhSe)_2$ in the absence of a solvent, the desired three-component coupling product (**2b**) was obtained in 60% yield successfully (Entry 1). With an increase of the amount of **1b**, the yield of **2b** increased to 78%, and the yield of the by-product (**3**) decreased to 5% (Entry 2). In the case of enol silyl ether (**1c**), again, the yield of the desired product (**2c**) increased as the amount of the alkene increased (Entries 3–5). The use of 41 equiv of **1c** improved the yield of **2c** (71%, $E/Z = 6/94$, Entry 5).

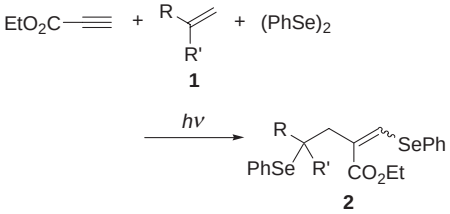
These results suggest that large excess alkenes are required in this domino reaction. In fact, the use of excess amounts of alkenes successfully attained the three-component coupling of some other alkenes, such as allyl alcohol (Entries 6 and 7) and 2,3-dihydrofuran (Entries 8 and 9). In these reactions, diphenyl diselenide was added in several portions to control the concentration of $(PhSe)_2$ in the reaction solution, because a high concentration of the $(PhSe)_2$ led to the formation of **3** as a by-product. However, the concentration of $(PhSe)_2$ can be easily monitored by the color of the solution: $(PhSe)_2$ has a yellow-orange color in an organic solvent, and therefore when the color of the reaction solution turned pale yellow, $(PhSe)_2$ should be added to the solution.

Table 2 represents the results of the sequential addition of $(PhSe)_2$ to ethyl propiolate and various alkenes. As expected, the combination of an electron-deficient alkyne and electron-rich alkenes led to good yields of the sequential addition product (**2**). In the case of butyl vinyl ether (**1f**), for example, the desired sequential addition product (**2f**) was obtained in 89% yield and the formation of vicinal diselenoalkene (**3**) was suppressed to 2–3% (Entry 1). The sequential addition products (**2d**–**2h**) were obtained as a stereoisomeric mixture with the




Scheme 1. SOMO–HOMO interaction between radicals and alkenes.

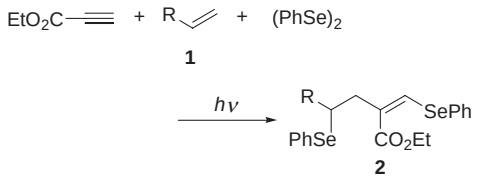
Table 1. The Influence of the Concentration of the Starting Materials on Domino Reaction[a)]




| Entry | R,R′/equiv | | | Yield/%[b)] | |
|---|---|---|---|---|---|
| | | | | **2** | **3**[c)] |
| 1 | MeO,Me | (7) | (**1b**) | 60 | 14 |
| 2 | | (14) | | 78[d)] | 5 |
| 3 | $Me_3SiO$,Me | (4) | (**1c**) | 44 | 7 |
| 4 | | (10) | | 58 | 4 |
| 5 | | (41) | | 71[d)] | —[e)] |
| 6 | $HOCH_2$,H | (2) | (**1d**) | —[e)] | 70 |
| 7 | | (20) | | 61, 55[d)] | 8 |
| 8 | **1** =  | (8) | (**1e**) | 37[d)] | 21[d)] |
| 9 | | (14) | | 57[d)] | 3 |

a) Reaction conditions: ethyl propiolate (0.16 mmol), $(PhSe)_2$ (1 equiv, added over 1.5 h in several portions), 15 °C, 2 h, *hν*: tungsten lamp (500 W, Pyrex). b) NMR yield. c) $EtO_2C$–C(SePh)=CHSePh. d) Isolated yield. e) Not detected.

Table 2. Domino Reaction of $(PhSe)_2$ with Ethyl Propiolate and Alkenes[a)]

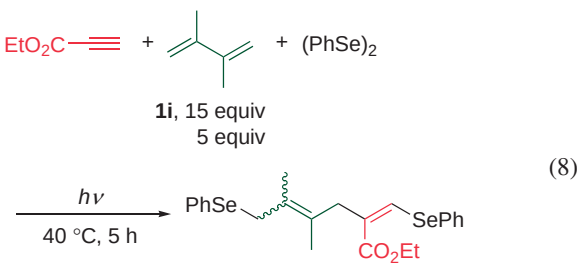



| Entry | R | | Yield/%[b)] | $E/Z$ |
|---|---|---|---|---|
| 1 | $^n$BuO | (**1f**) | 89 | 10/90 |
| 2 | **1** =  | (**1e**) | 70 | 15/85[c)] |
| 3 | $HOCH_2$ | (**1d**) | 59 | 12/88 |
| 4 | $^t$BuMe$_2$SiOCH$_2$ | (**1g**) | 36 | 9/91 |
| 5 | $(MeO)_2CH$ | (**1h**) | 57 | 8/92 |

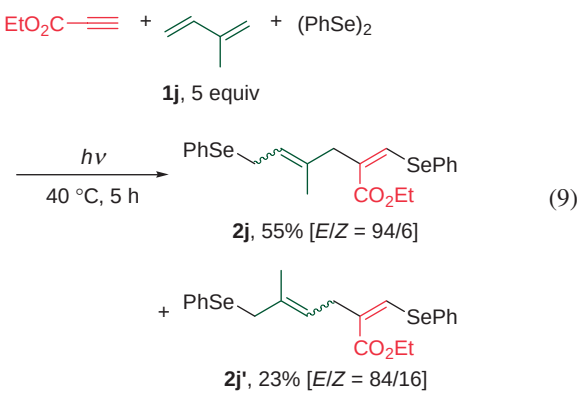
a) Reaction conditions: ethyl propiolate (0.16 mmol), alkene (15–40 equiv), $(PhSe)_2$ (1 equiv, added over 1.5 h in several portions), 15 °C, 2 h, *hν*: tungsten lamp (500 W, Pyrex). b) Isolated yield. c) The stereochemistry on the furan ring is exclusively *trans*.

*Z*-isomer predominance (Entries 1–5). With 2,3-dihydrofuran (**1e**), the stereochemistry at the furan ring of the product (**2e**) was exclusively *trans*-isomer (Entry 2). Similar conditions could be employed with allyl alcohol (**1d**) and allyl ether (**1h**), giving the corresponding three-component coupling products (**2d** and **2h**, respectively) in good yields (Entries 3 and 5).

Furthermore, the sequential alkyne–diene coupling reactions were demonstrated, as shown in Eqs. 8 and 9. In these cases, the conjugate addition the products (**2i**, **2j**, and **2j′**) were obtained selectively. The use of 5 equiv of diene was suitable for this domino reaction (three-component coupling product (**2i**): 59% yield; the $(PhSe)_2$ adduct: 20% yield), because further excess dienes caused polymerization of the dienes.




(8)



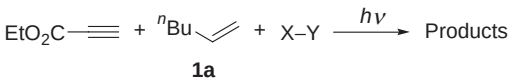

(9)

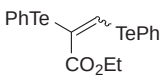
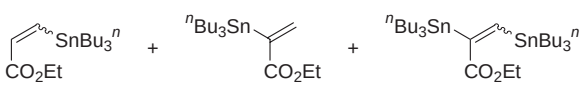
In these reactions, the use of diphenyl disulfide instead of $(PhSe)_2$, led to the formation of a complex mixture, and the desired three-component coupling products were not formed at all (Table 3). This is most probably because the lower carbon radical capturing ability of $(PhS)_2$ could not suppress polymerization.[15] On the other hand, the attempted sequential reaction by using diphenyl ditelluride resulted in the formation of only the $(PhTe)_2$ adduct to the alkyne (**3′**), probably due to both the excessive carbon radical capturing ability of $(PhTe)_2$[15] and the instability of **3′** under photoirradiation conditions.[16] Although modern free radical-based synthetic methods often utilize tin hydrides,[17] the attempted tin hydride-mediated reaction of the ethyl propiolate with **1a** under similar reaction conditions provided only the adducts of $^n$Bu$_3$SnH to the alkyne (**5**, **6**, and **7**). This observation suggests that the present domino reaction by using $(PhSe)_2$ is a kinetically well-controlled system.

The obtained sequential addition products (**2**) have two kinds of seleno groups, i.e., PhSe groups bonded to $sp^3$- and $sp^2$-carbons, and are potentially useful synthetic intermediates. The seleno group bonded to $sp^3$-carbon can be removed reductively and replaced by H (Scheme 2).[18] In addition, oxidation of the phenylseleno group can lead to alkene-formation via selenoxide *syn*-elimination.[19] On the other hand, the PhSe group bonded to $sp^2$-carbon (i.e., vinylic selenide moiety) is accepted as both carbonyl equivalents by hydrolysis[20] and vinyl-transfer reagents by transition-metal-catalyzed cross-coupling reaction.[21]

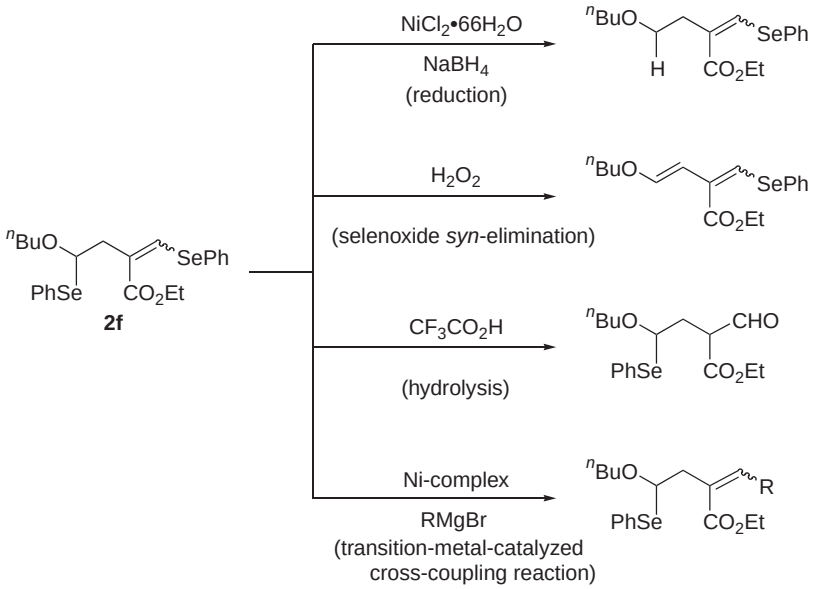
As an extension of our interest in the development of the synthetic utility of the sequential addition products, we investigated the alkylation of the sequential addition products with organocopper reagents.[22] A treatment of the coupling product (**2g**) with lithium dimethylcuprate led to chemoselective methylation, giving the corresponding alkylated product (**8g**) with retention of the stereochemistry (Table 4, Entry 1). Similarly,

Table 3. Sequential Addition Mediated by $(PhS)_2$, $(PhTe)_2$, and $^n$Bu$_3$SnH[a)]



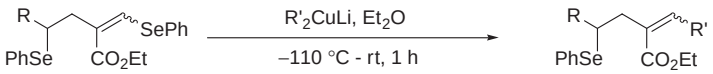

| X–Y | Products |
|---|---|
| $(PhS)_2$ | a complex mixture |
| $(PhTe)_2$ |  **3′**, 19% [$E/Z$ = 54/46] |
| $^n$Bu$_3$SnH |  **5**, 47% [$E/Z$ = 79/21] **6**, 10% **7**, 7% [$E/Z$ = 50/50] |

a) Reaction conditions: ethyl propiolate (0.16 mmol), alkene (10 equiv), X–Y (1 equiv), 15 °C, 6 h, *hν*: tungsten lamp (500 W, Pyrex).




Scheme 2. Synthetic utility of the three-component coupling products.

Table 4. Alkylation of Vinylic Seleno Groups with Organocopper Reagents[a)]



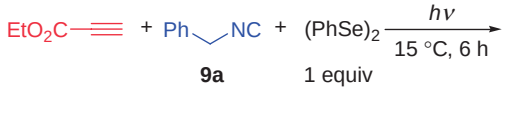

**2** **8**

| Entry | R | **2** [*E*/*Z*] | R′$_2$CuLi/equiv | Yield/%[b)] [*E*/*Z*] |
|---|---|---|---|---|
| 1 | $^t$BuMe$_2$SiOCH$_2$ | **2g** [9/91] | Me$_2$CuLi (3.0) | **8g**, 73 [8/92] |
| 2 | $^n$BuO | **2f** [10/90] | $^n$Bu$_2$CuLi (1.3) | **8f**, 84 [7/93] |
| 3 | $^n$BuO | **2f** [10/90] | $^s$Bu$_2$CuLi (1.2) | no reaction |
| 4[c)] | $^n$BuO | **2f** [10/90] | $^s$Bu$_2$CuLi (3.0) | no reaction |
| 5[d)] | $^n$BuO | **2f** [10/90] | $^s$Bu$_2$Cu(CN)Li$_2$ (5.0) | **8f′**, 58 [16/84] |
| 6[e)] | $^n$BuO | **2f** [10/90] | $^t$Bu$_2$CuLi (1.3) | no reaction |
| 7 | $^n$BuO | **2f** [10/90] | Ph$_2$CuLi (3.0) | no reaction |

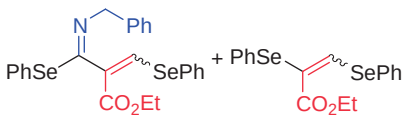
a) Reaction conditions: compound **2** (0.10 mmol). b) Isolated yield. c) Et$_2$O•BF$_3$ was added. d) THF solvent, 12 h. Et$_2$O•BF$_3$ was added. e) −78 °C–rt.

the coupling product (**2f**) underwent site-selective butylation, upon a treatment with $^n$Bu$_2$CuLi (Entry 2). Under this reaction condition, however, the introduction of secondary and tertiary alkyl groups, such as *s*-butyl and *t*-butyl groups, did not proceed at all (Entries 3, 4, and 6). The use of excess $^s$Bu$_2$Cu(CN)Li$_2$ in the presence of Et$_2$O•BF$_3$ was effective for introducing a secondary alkyl group (Entry 5).

**Three-Component Coupling of (PhSe)$_2$ with Alkynes and Isocyanides.** We next examined the (PhSe)$_2$-mediated domino reaction by the combination of alkynes and isocyanides as a useful C1-unit.[10c,23–25] Upon irradiation with a tungsten lamp (500 W) through Pyrex ($h\nu$ > 300 nm), the domino reaction of (PhSe)$_2$ with ethyl propiolate and benzyl isocyanide (**9a**) was conducted by the addition of (PhSe)$_2$ separately eight times (i.e., the total amount of (PhSe)$_2$ was 1 equiv). In this reaction, the use of excess isocyanides is essential for efficient three-component coupling. The use of 29 equiv of **9a** led to **10a** in 85% yield (Eq. 10).[26]




**9a** 1 equiv



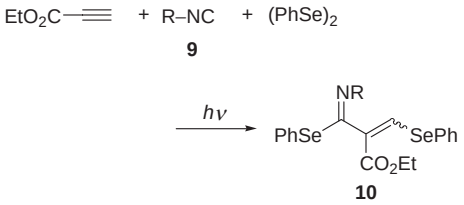

(10)

**10a** **3**

| | | |
|---|---|---|
| **9a**, 1 equiv | – | 86% |
| 15 equiv | 45% | 45% |
| 29 equiv | 85% [*E*/*Z* = 51/49] | – |

Similar conditions could be employed with cyclohexyl isocyanide (**9b**) and 2,6-xylyl isocyanide (**9c**); the desired domino reaction took place smoothly to give the corresponding three-component coupling products (**10b** and **10c**) selectively in moderate-to-good yields (Table 5, Entries 1 and 2). Isocya-

Table 5. Domino Reaction of $(PhSe)_2$ with Ethyl Propiolate and Isocyanides[a)]




| Entry | R | | Yield/%[b)] | $E/Z$ |
|---|---|---|---|---|
| 1 | $^c$C$_6$H$_{11}$ | (**9b**) | 72 | 35/65 |
| 2 | 2,6-Xylyl | (**9c**) | 59 | 52/48 |
| 3 | $(EtO)_2P(O)CH_2$ | (**9d**) | 58 | 45/55 |
| 4 | $MeO_2CCH_2$ | (**9e**) | 58 | 55/45 |
| 5 | *p*-NC-C$_6$H$_4$ | (**9f**) | 33 | —[c)] |
| 6 | $^n$Bu | (**9g**) | 18 | —[c)] |

a) Reaction conditions: ethyl propiolate (0.16 mmol), $(PhSe)_2$ (1 equiv), isocyanide (13–40 equiv), 15 °C, 6 h, *hν*: tungsten lamp (500 W, Pyrex). b) Isolated yield. c) Not determined.

nides bearing functionalities, such as $P(O)(OEt)_2$ (**9d**) and ester groups (**9e**), were tolerant toward the selective sequential addition (Entries 3 and 4). On the other hand, in the case of butyl isocyanide (**9g**), the yield of the desired three-component coupling product was lower. Moreover, a complex mixture was formed when *t*-butyl isocyanide was used for this three-component coupling reaction. This is because the imidoyl radical intermediate easily decomposed to form a *t*-butyl radical and the corresponding cyanide.[27]

A possible mechanistic pathway may include the following (see: Scheme 3): (i) upon irradiation with near-UV light, diphenyl diselenide ($\lambda_{max} = 340$ nm) undergoes homolytic dissociation to generate PhSe•, which adds to ethyl propiolate selectively, forming a $\beta$-seleno-substituted vinylic radical (**4**); (ii) **4** reacts with isocyanides to produce an imidoyl radical intermediate, which is trapped with $(PhSe)_2$, yielding the three-component coupling product (**10**) with regeneration of PhSe•.

In this reaction, another three-component coupling product that PhSe• added to **9**, and then to the alkyne (Chart 1), was not obtained at all. This is due to the less reactivity of PhSe• to **9**, and the difference in the stability between the vinylic radical intermediate and the imidoyl radical intermediate.

Next, the sequential addition of $(PhSe)_2$ to several alkynes was examined by using **9b** under identical conditions (Eq. 11). Electron-deficient terminal alkynes, such as ethyl propiolate, methyl propiolate, and 3-butyn-2-one, underwent the desired sequential reaction successfully to give the corresponding three-component coupling products (**10**) in 59, 70, and 40% yields, respectively. With inner alkyne bearing electron-withdrawing groups, such as diethyl acetylenedicarboxylate, the sequential reaction proceeded slowly, giving 18% of **10**. In contrast, when 1-octyne, phenylacetylene, and trimethylsilylacetylene were used, bisselenation of the alkyne took place in preference to the desired three-component coupling. These results suggest that electron-deficient alkynes are suitable for this sequential reaction.

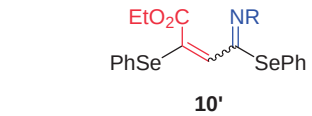
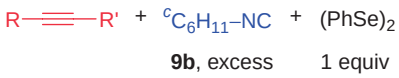
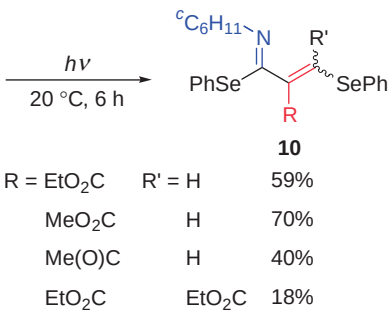



Chart 1.

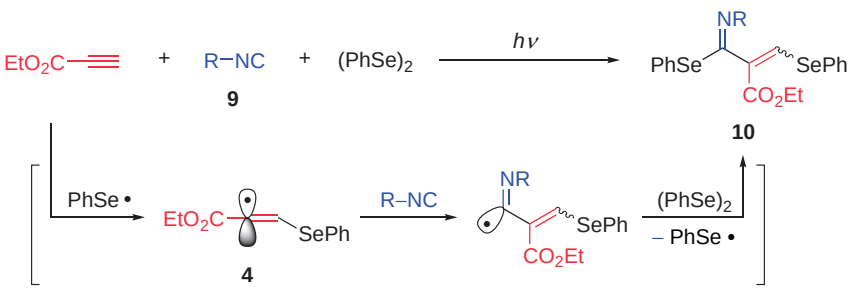


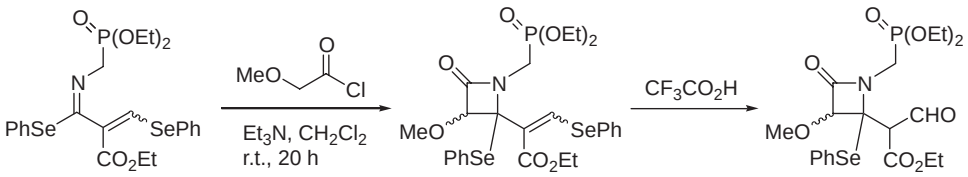

(11)

The obtained three-component coupling products, which have several hetero-functional groups, are expected to work as promising building blocks for the synthesis of useful heterocyclic compounds. For example, the reaction of the three-component coupling product (**10d**) with methoxyacetyl chloride in the presence of triethylamine successfully provided the corresponding $\beta$-lactam (**11**) in good yield through formal [2 + 2] cycloaddition, as indicated in Scheme 4. The following treatment of **11** with trifluoroacetic acid led to hydrolysis of the vinylic selenium function of **11**, giving the corresponding aldehyde (**12**) as a precursor for constructing carbapenem framework.

**Four-Component Coupling of $(PhSe)_2$ with an Alkyne and Two Types of Alkenes.** In a series of domino reactions mediated by $(PhSe)_2$, the combination of alkynes bearing an electron-withdrawing group and alkenes bearing an electron-

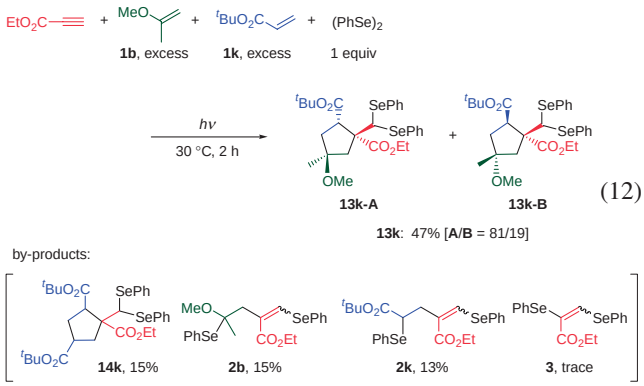



Scheme 3. A possible pathway for the domino reaction of $(PhSe)_2$ with an alkyne and an isocyanide.



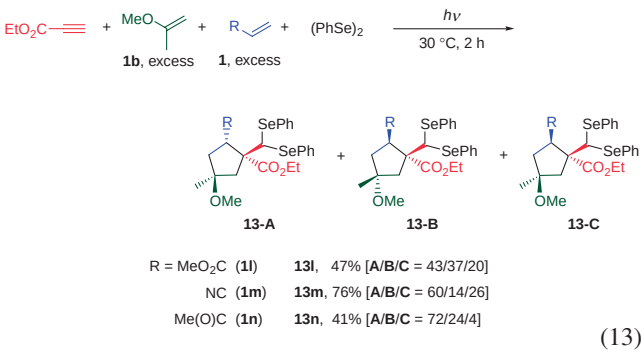

Scheme 4. Application of the three-component coupling products to $\beta$-lactam.

donating group led to an acyclic three-component coupling product (**2**). Therefore, we next examined the domino reaction in coexistence with two types of alkenes, namely, alkenes bearing electron-withdrawing and electron-donating groups. When the reaction of diphenyl diselenide with ethyl propiolate, large excess of *t*-butyl acrylate (**1k**), and 2-methoxypropene (**1b**) was performed in the absence of a solvent, a sequential addition of the diselenide to the alkyne, the electron-rich alkene, and then the electron-poor alkene followed by 5-*exo* radical cyclization took place to provide the corresponding cyclic four-component coupling product (**13k**) in a good yield with high stereoselectivity (Eq. 12).[28]




(12)

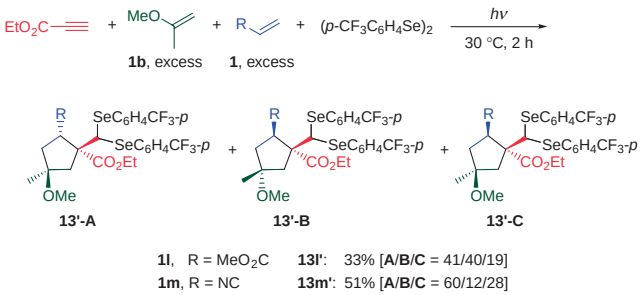
Similar conditions could be employed with methyl acrylate (**1l**), acrylonitrile (**1m**), and methyl vinyl ketone (**1n**), giving the corresponding cyclic four-component coupling products (**13l**, **13m**, and **13n**) exclusively in good yields (Eq. 13). In particular, when **1m** was employed as an alkene bearing an electron-withdrawing group, the desired four-component coupling reaction proceeded successfully to give **13m** in 76% yield.




(13)

On the other hand, when 1-octene, butyl vinyl ether, 2-propen-1-ol, or 2,3-dihydofuran was employed as the substrate alkenes, the desired four-component coupling reactions were unsuccessful. In these cases, the cyclic products consist of an alkyne, two molecules of an alkene bearing an electron-withdrawing group, and $(PhSe)_2$ were obtained (i.e., compounds **14k** mainly).

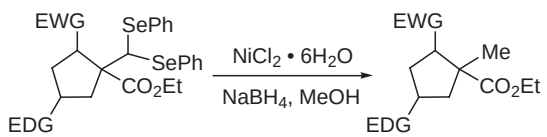
When the reactions were conducted using $(p\text{-}CF_3C_6H_4Se)_2$ in place of $(PhSe)_2$ under similar reaction conditions, the corresponding cyclic products (**13l′** and **13m′**) were formed in moderate yields with a similar ratio of the stereoisomers (Eq. 14).




(14)

The formation of **13** may be explained by the following (see: Scheme 5): (i) PhSe•, generated by irradiation with light of wavelength over 300 nm, adds to ethyl propiolate selectively, forming $\beta$-phenylseleno-substituted vinylic radical (**4**); (ii) **4** reacts with an electron-rich alkene preferentially to produce a $\alpha$-methoxy radical (**15**); (iii) **15** reacts with an electron-poor alkene and then cyclization takes place to provide the $\alpha$-seleno radical (**16**) bearing a five-membered ring, which is trapped with $(PhSe)_2$, yielding the cyclic four-component coupling product **13** with the regeneration of PhSe•.

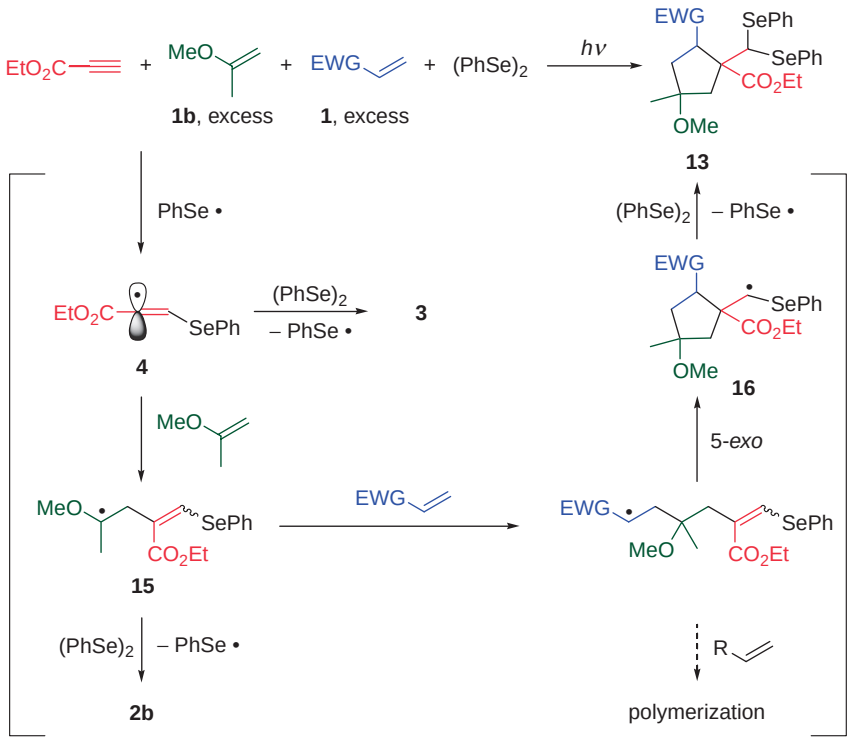
The PhSe groups of the products can be replaced by hydrogen by the use of nickel boride ($NiCl_2 \cdot 6H_2O$ and $NaBH_4$) (Eq. 15).[18]




(15)

## Conclusion

Diphenyl diselenide has been proven to be an excellent mediator for intermolecular domino reactions of unsaturated compounds. Highly selective three- and four-component coupling reactions of $(PhSe)_2$ with an alkyne and alkenes proceeded successfully, based on the appropriate carbon radical capturing ability of $(PhSe)_2$. In addition, it is of great importance to control the concentrations of the starting materials, the stability of carbon radical intermediates, and the SOMO–HOMO interaction between radical species and unsaturated compounds. The combination of electron-deficient alkynes and electron-rich al-




Scheme 5. A possible pathway of the domino reaction of $(PhSe)_2$ with an alkyne and two types of alkenes.

kenes (or isocyanides) led to three-component coupling with high regioselectivity. Moreover, the combination of alkynes and two types of alkenes (i.e., electron-deficient alkenes and electron-rich alkenes) effectively provided the corresponding cyclic four-component coupling products. These domino reactions are very useful, because carbon–carbon bond forming reactions and the introduction of heteroatom functions have been attained simultaneously.

## Experimental

**General.** Isocyanides[29] and diphenyl diselenide[30] were synthesized according to the literature. Other materials were obtained from commercial supplies and purified by distillation or recrystallization. Purification of products was performed on a recycling preparative HPLC (Japan Analytical Industry Co., Ltd., Model LC-908), equipped with JAIGEL-1H and -2H columns (GPC) using $CHCl_3$ as an eluent. $^1$H NMR spectra were recorded on Varian MERCURY 300 (300 MHz), Varian GEMINI 2000 (300 MHz), or Varian INOVA 600 (600 MHz) spectrometer using $CDCl_3$ as the solvent with $Me_4Si$ as the internal standard. $^{13}$C NMR spectra were taken on JEOL JNM-GSX-400 (100 MHz), JEOL JNM-AL-400 (100 MHz), Varian MERCURY 300 (75 MHz), Varian GEMINI 2000 (75 MHz), or Varian INOVA 600 (150 MHz) spectrometer using $CDCl_3$ as the solvent. Chemical shifts in $^1$H NMR were measured relative to $CDCl_3$ and converted to the $\delta$ ($Me_4Si$) value by using $\delta$ ($CDCl_3$) = 7.26 ppm. Chemical shifts in $^{13}$C NMR were measured relative to $CDCl_3$ and converted to the $\delta$ ($Me_4Si$) value by using $\delta$ ($CDCl_3$) = 77.0 ppm. IR spectra were determined on a Perkin Elmer Model 1600 spectrometer or JASCO FT/IR-8900 $\mu$ Fourier Transform Infrared Microsampling System. Mass spectra were obtained on a JEOL JMS-DX303 or a Varian Saturn 3. Elemental analyses were performed in the analytical section of Osaka University.

**3-(Phenylseleno)-2-[2-(phenylseleno)hexyl]acrylic Acid Ethyl Ester (2a).** In a Pyrex glass tube ($\phi$ = 10 mm, length = 75 mm) were placed ethyl propiolate (15.7 mg, 0.16 mmol) and 1-hexene (**1a**, 135 mg, 1.6 mmol) under a $N_2$ atmosphere. The mixture was irradiated with a tungsten lamp (500 W) at 15 °C for 4 h, and during the irradiation, diphenyl diselenide (49.9 mg, 0.16 mmol) was added separately several times over 1 h. After the reaction was completed, purification of the products was performed on a recycling preparative HPLC, yielding 38% of **2a** as a stereoisomeric mixture ($E/Z$ = 21/79). The stereochemistry was determined by NOE experiments between the vinylic proton and the allylic methylene proton of **2a**: Pale-yellow oil. $^1$H NMR (400 MHz, $CDCl_3$, rt): [($Z$)-isomer]: $\delta$ 0.88 (t, $J$ = 7.3 Hz, 3H, $CH_3(CH_2)_3$), 1.27 (t, $J$ = 7.1 Hz, 3H, $CH_3CH_2O_2C$), 1.35–1.69 (m, 6H, $CH_3(CH_2)_3$), 2.68 (d, $J$ = 7.3 Hz, 2H, $CH_2C{=}CH$), 3.39 (tt, $J$ = 7.3, 7.6 Hz, 1H, $CHCH_2C{=}CH$), 4.19 (q, $J$ = 7.1 Hz, 2H, $CH_3CH_2O_2C$), 7.20–7.62 (m, 10H, Ph), 7.43 (s, 1H, C=C*H*). [($E$)-isomer]: $\delta$ 0.89 (t, $J$ = 7.2 Hz, 3H, $CH_3(CH_2)_3$), 1.21–1.73 (m, 6H, $CH_3(CH_2)_3$), 1.23 (t, $J$ = 7.2 Hz, 3H, $CH_3CH_2O_2C$), 2.80 (dd, $J$ = 4.8, 7.2 Hz, 2H, $CH_2C{=}CH$), 3.55 (tt, $J$ = 4.8, 8.0 Hz, 1H, $CHCH_2C{=}CH$), 4.12 (q, $J$ = 7.2 Hz, 2H, $CH_3CH_2O_2C$), 7.22–7.60 (m, 10H, Ph), 7.99 (s, 1H, C=C*H*). $^{13}$C NMR (100 MHz, $CDCl_3$, rt): [($Z$)-isomer]: $\delta$ 14.0, 14.3, 22.4, 29.8, 34.6, 40.8, 45.4, 60.8, 126.4, 127.2, 128.0, 128.8, 129.3, 129.5, 133.3, 133.5, 134.8, 146.4, 167.1. [($E$)-isomer]: $\delta$ 14.0, 14.2, 22.4, 30.0, 35.0, 38.1, 44.6, 60.7, 127.2, 128.2, 128.8, 129.3, 133.1, 134.7, 142.6, 164.9. IR (NaCl): 3056, 2956, 2929, 2857, 1693, 1574, 1477, 1437, 1368, 1321, 1206, 1125, 1022, 737, 692 cm$^{-1}$. MS (CI): $m/z$ 497 ($M^+ + 1$, 100). Found: C, 56.00; H, 5.83%. Calcd for $C_{23}H_{28}O_2Se_2$: C, 55.88; H, 5.71%.

**2-[2-Methoxy-2-(phenylseleno)propyl]-3-(phenylseleno)-acrylic Acid Ethyl Ester (2b):** Pale-yellow oil (obtained as a stereoisomeric mixture ($E/Z$ = 7/93)). $^1$H NMR (600 MHz, $CDCl_3$, rt): [($Z$)-isomer]: $\delta$ 1.32 (t, $J$ = 7.2 Hz, 3H, $CH_3CH_2O_2C$),

1.51 (s, 3H, C$H_3$C), 2.88 (d, $J = 15.0$ Hz, 1H, C$H_2$C=CH), 3.04 (d, $J = 15.0$ Hz, 1H, C$H_2$C=CH), 3.44 (s, 3H, C$H_3$O), 4.26 (m, 2H, CH$_3$C$H_2$O$_2$C), 7.22–7.34 (m, 6H, Ph), 7.49–7.51 (m, 2H, Ph), 7.53 (s, 1H, C=C*H*), 7.57–7.59 (m, 2H, Ph). [(*E*)-isomer]: $\delta$ 1.24 (t, $J = 7.2$ Hz, 3H, C$H_3$CH$_2$O$_2$C), 1.56 (s, 3H, C$H_3$C), 3.25 (d, $J = 16.2$ Hz, 1H, C$H_2$C=CH), 3.30 (d, $J = 16.2$ Hz, 1H, C$H_2$C=CH), 3.45 (s, 3H, C$H_3$O), 4.13–4.19 (m, 2H, CH$_3$C$H_2$O$_2$C), 7.22–7.34 (m, 6H, Ph), 7.46–7.48 (m, 2H, Ph), 7.60–7.64 (m, 2H, Ph), 8.09 (s, 1H, C=C*H*). $^{13}$C NMR (150 MHz, CDCl$_3$, rt): [(*Z*)-isomer]: $\delta$ 14.4, 24.2, 43.7, 52.1, 61.0, 93.0, 123.8, 127.8, 127.9, 128.8, 129.0, 129.3, 133.2, 133.5, 136.2, 148.2, 167.7. [(*E*)-isomer]: $\delta$ 14.2, 24.5, 44.2, 51.8, 60.8, 92.9, 127.8, 127.9, 128.7, 129.3, 132.9, 133.2, 136.5, 144.8, 162.2. IR (NaCl): 3075, 2982, 2824, 1692, 1570, 1475, 1439, 1370, 1328, 1210, 1117, 1059, 1024, 911, 851, 780, 737, 693 cm$^{-1}$. MS (CI): $m/z$ 327 ($M^+ + 1 -$ PhSe, 100). Found: C, 52.59; H, 5.12%. Calcd for $C_{21}H_{24}O_3Se_2$: C, 52.29; H, 5.02%.

**3-(Phenylseleno)-2-[2-(phenylseleno)-2-(trimethylsilyloxy)-propyl]acrylic Acid Ethyl Ester (2c):** Pale-yellow oil (obtained as a stereoisomeric mixture ($E/Z = 6/94$)). $^1$H NMR (600 MHz, CDCl$_3$, rt): [(*Z*)-isomer]: $\delta$ 0.09 (s, 9H, (C$H_3$)$_3$Si), 1.27 (t, $J =$ 7.2 Hz, 3H, C$H_3$CH$_2$O$_2$C), 1.65 (s, 3H, C$H_3$C), 2.91 (d, $J =$ 14.1 Hz, 1H, C$H_2$C=CH), 3.00 (d, $J = 14.1$ Hz, 1H, C$H_2$C=CH), 4.13 (m, 2H, CH$_3$C$H_2$O$_2$C), 7.25–7.27 (m, 3H, Ph), 7.29–7.34 (m, 4H, Ph), 7.50 (s, 1H, C=C*H*), 7.59–7.62 (m, 3H, Ph). [(*E*)-isomer]: $\delta$ 0.22 (s, 9H, (C$H_3$)$_3$Si), 1.22 (t, $J = 7.2$ Hz, 3H, C$H_3$CH$_2$O$_2$C), 1.73 (s, 3H, C$H_3$C), 3.07 (d, $J = 13.2$ Hz, 1H, C$H_2$C=CH), 3.17 (d, $J = 13.2$ Hz, 1H, C$H_2$C=CH), 4.14 (dq, $J = 6.6$, 1.2 Hz, 2H, CH$_3$C$H_2$O$_2$C), 7.25–7.27 (m, 3H, Ph), 7.29–7.34 (m, 4H, Ph), 7.59–7.62 (m, 3H, Ph), 8.07 (s, 1H, C=C*H*). $^{13}$C NMR (150 MHz, CDCl$_3$, rt): [(*Z*)-isomer]: $\delta$ 2.0, 14.3, 29.2, 47.2, 60.8, 85.8, 124.0, 128.0 (2C), 128.6, 129.2, 129.6, 133.3, 133.4, 136.9, 148.3, 167.7. [(*E*)-isomer]: $\delta$ 2.3, 14.2, 29.9, 47.2, 60.7, 86.3, 124.0, 127.9, 128.1, 128.6, 129.3, 132.9, 137.0, 144.2, 166.0. IR (NaCl): 3046, 2957, 1694, 1569, 1475, 1440, 1369, 1326, 1253, 1208, 1124, 1066, 1018, 845, 742, 693 cm$^{-1}$. MS (CI): $m/z$ 313 ($M^+ + 1 -$ PhSe $-$ Me$_3$Si, 100). Found: C, 51.64; H, 5.77%. Calcd for $C_{23}H_{30}O_3Se_2Si$: C, 51.11; H, 5.60%.

**2-[3-Hydroxy-2-(phenylseleno)propyl]-3-(phenylseleno)-acrylic Acid Ethyl Ester (2d):** Pale-yellow oil (obtained as a stereoisomeric mixture ($E/Z = 12/88$)). $^1$H NMR (300 MHz, CDCl$_3$, rt): [(*Z*)-isomer]: $\delta$ 1.32 (t, $J = 7.2$ Hz, 3H, C$H_3$CH$_2$O$_2$C), 2.39 (br t, $J = 6.6$ Hz, 1H, O*H*), 2.73 (dd, $J = 7.2$, 14.6 Hz, 1H, C$H_2$C=CH), 2.76 (dd, $J = 6.6$, 14.6 Hz, 1H, C$H_2$C=CH), 3.51 (m, 1H, C*H*CH$_2$C=CH), 3.59–3.62 (m, 1H, C$H_2$OH), 3.64–3.67 (m, 1H, C$H_2$OH), 4.26 (q, $J = 7.2$ Hz, 2H, CH$_3$C$H_2$O$_2$C), 7.23–7.30 (m, 3H, Ph), 7.34–7.36 (m, 3H, Ph), 7.52–7.56 (m, 2H, Ph), 7.53 (s, 1H, C=C*H*), 7.60–7.65 (m, 2H, Ph). [(*E*)-isomer]: $\delta$ 1.25 (t, $J = 7.2$ Hz, 3H, C$H_3$CH$_2$O$_2$C), 2.39 (br t, $J =$ 6.6 Hz, 1H, O*H*), 2.82 (dd, $J = 6.6$, 14.6 Hz, 1H, C$H_2$C=CH), 2.92 (dd, $J = 7.3$, 14.6 Hz, 1H, C$H_2$C=CH), 3.46–3.51 (m, 1H, C*H*CH$_2$C=CH), 3.60–3.64 (m, 1H, C$H_2$OH), 3.69–3.72 (m, 1H, C$H_2$OH), 4.18 (q, $J = 7.2$ Hz, 2H, CH$_3$C$H_2$O$_2$C), 7.23–7.30 (m, 3H, Ph), 7.34–7.36 (m, 3H, Ph), 7.52–7.56 (m, 2H, Ph), 7.60–7.65 (m, 2H, Ph), 8.09 (s, 1H, C=C*H*). $^{13}$C NMR (150 MHz, CDCl$_3$, rt): [(*Z*)-isomer]: $\delta$ 14.3, 36.2, 48.9, 61.2, 63.6, 125.3, 127.8, 127.9, 128.1, 129.1, 129.4, 133.3, 135.1, 147.1, 167.2. [(*E*)-isomer]: $\delta$ 14.2, 33.5, 47.5, 61.2, 63.9, 125.3, 127.8, 128.4, 129.1, 129.6, 133.2, 135.1, 144.2, 158.3. IR (NaCl): 3397, 3181, 3057, 2976, 2916, 1687, 1572, 1441, 1374, 1317, 1212, 1023, 842, 743, 692 cm$^{-1}$. MS (CI): $m/z$ 471 ($M^+ + 1$, 14). Found: C, 51.38; H, 4.85%. Calcd for $C_{20}H_{22}O_3Se_2$: C, 51.30; H, 4.74%.

**3-(Phenylseleno)-2-[2-(phenylseleno)tetrahydrofuran-3-yl]-acrylic Acid Ethyl Ester (2e):** Pale-yellow oil (obtained as a stereoisomeric mixture ($E/Z = 15/85$)). $^1$H NMR (600 MHz, CDCl$_3$, rt): [(*Z*)-isomer]: $\delta$ 1.35 (t, $J = 7.2$ Hz, 3H, C$H_3$CH$_2$O$_2$C), 1.94–2.00 (m, 1H, CHOCH$_2$C$H_2$CH), 2.28–2.34 (m, 1H, CHOCH$_2$C$H_2$CH), 3.48–3.51 (m, 1H, C*H*C=CH), 4.02 (ddd, $J = 4.8$, 8.4, 16.2 Hz, 1H, CHOC$H_2$), 4.10 (dd, $J = 7.8$, 16.2 Hz, 1H, CHOC$H_2$), 4.10–4.30 (m, 2H, CH$_3$C$H_2$O$_2$C), 5.73 (d, $J =$ 3.6 Hz, 1H, PhSeC*H*O), 7.22–7.34 (m, 3H, Ph), 7.34–7.38 (m, 3H, Ph), 7.52 (s, 1H, C=C*H*), 7.57–7.63 (m, 4H, Ph). [(*E*)-isomer]: $\delta$ 1.28 (t, $J = 7.2$ Hz, 3H, C$H_3$CH$_2$O$_2$C), 2.01–2.06 (m, 1H, CHOCH$_2$C$H_2$CH), 2.16–2.24 (m, 1H, CHOCH$_2$C$H_2$CH), 3.56–3.60 (m, 1H, C*H*C=CH), 3.97 (dd, $J = 8.4$, 16.2 Hz, 1H, CHOC$H_2$), 4.17 (dd, $J = 7.2$, 14.2 Hz, 1H, CHOC$H_2$), 4.15–4.30 (m, 2H, CH$_3$C$H_2$O$_2$C), 6.25 (d, $J = 6.0$ Hz, 1H, PhSeC*H*O), 7.22–7.34 (m, 3H, Ph), 7.36–7.40 (m, 3H, Ph), 7.60–7.65 (m, 4H, Ph), 8.08 (s, 1H, C=C*H*). $^{13}$C NMR (150 MHz, CDCl$_3$, rt): [(*Z*)-isomer]: $\delta$ 14.3, 31.7, 49.7, 61.2, 67.6, 88.4, 125.1, 127.5, 127.8, 128.2, 128.9, 129.4, 133.1, 133.5, 134.2, 145.1, 166.8. [(*E*)-isomer]: $\delta$ 14.2, 27.8, 47.7, 61.1, 67.1, 90.1, 127.2, 128.1, 128.8, 129.3, 133.2, 134.6, 145.0, 165.8. IR (NaCl): 3055, 2980, 1687, 1574, 1476, 1439, 1369, 1287, 1210, 1048, 911, 738, 692 cm$^{-1}$. MS (CI): $m/z$ 481 ($M^+ + 1$, 14). Found: C, 52.70; H, 4.72%. Calcd for $C_{21}H_{22}O_3Se_2$: C, 52.51; H, 4.62%.

**2-[2-Butoxy-2-(phenylseleno)ethyl]-3-(phenylseleno)acrylic Acid Ethyl Ester (2f):** Pale-yellow oil (obtained as a stereoisomeric mixture ($E/Z = 10/90$)). $^1$H NMR (400 MHz, CDCl$_3$, rt): [(*Z*)-isomer]: $\delta$ 0.87 (t, $J = 7.2$ Hz, 3H, C$H_3$(CH$_2$)$_3$), 1.25–1.38 (m, 2H, CH$_3$C$H_2$CH$_2$CH$_2$), 1.28 (t, $J = 7.2$ Hz, 3H, C$H_3$CH$_2$O$_2$C), 1.51 (quint, $J = 6.8$ Hz, 2H, CH$_3$CH$_2$C$H_2$CH$_2$), 2.85 (dd, $J = 8.1$, 14.6 Hz, 1H, C$H_2$C=CH), 2.98 (dd, $J = 4.9$, 14.6 Hz, 1H, C$H_2$C=CH), 3.31 (dt, $J = 6.8$, 9.3 Hz, 1H, CH$_3$CH$_2$CH$_2$C$H_2$), 3.88 (dt, $J = 6.8$, 9.3 Hz, 1H, CH$_3$CH$_2$CH$_2$C$H_2$), 4.23 (q, $J = 7.2$ Hz, 2H, CH$_3$C$H_2$O$_2$C), 5.07 (dd, $J = 4.9$, 8.1 Hz, 1H, C*H*CH$_2$C=CH), 7.19–7.64 (m, 10H, Ph), 7.43 (s, 1H, C=C*H*), [(*E*)-isomer]: $\delta$ 0.89 (t, $J = 7.2$ Hz, 3H, C$H_3$(CH$_2$)$_3$), 1.23 (t, $J = 7.1$ Hz, 3H, C$H_3$CH$_2$O$_2$C), 1.25–1.38 (m, 2H, CH$_3$C$H_2$CH$_2$CH$_2$), 1.55 (quint, $J = 7.0$ Hz, 2H, CH$_3$CH$_2$C$H_2$CH$_2$), 3.01 (dd, $J = 8.1$, 14.6 Hz, 1H, C$H_2$C=CH), 3.10 (dd, $J = 4.9$, 14.6 Hz, 1H, C$H_2$C=CH), 3.31 (m, 1H, CH$_3$CH$_2$CH$_2$C$H_2$), 3.87 (m, 1H, CH$_3$CH$_2$CH$_2$C$H_2$), 4.15 (q, $J =$ 7.1 Hz, 2H, CH$_3$C$H_2$O$_2$C), 5.21 (dd, $J = 4.9$, 8.1 Hz, 1H, C*H*CH$_2$C=CH), 7.19–7.64 (m, 10H, Ph), 8.05 (s, 1H, C=C*H*). $^{13}$C NMR (100 MHz, CDCl$_3$, rt): [(*Z*)-isomer]: $\delta$ 13.8, 14.2, 19.3, 31.2, 39.7, 60.6, 69.8, 85.9, 124.3, 127.5, 128.0, 128.8, 129.2, 133.2, 135.4, 147.5, 167.0. [(*E*)-isomer]: $\delta$ 12.9, 14.2, 19.3, 31.1, 41.7, 60.8, 69.7, 86.4, 127.4, 128.0, 128.5, 129.3, 132.9, 133.2, 135.3, 143.4, 164.8. IR (NaCl): 3056, 2958, 2932, 2871, 1694, 1574, 1477, 1438, 1323, 1206, 1098, 1072, 1022, 738, 692, 670 cm$^{-1}$. MS (CI): $m/z$ 439 ($M^+ + 1$, 7). Found: C, 54.24; H, 5.66%. Calcd for $C_{23}H_{28}O_3Se_2$: C, 54.13; H, 5.53%.

**2-[3-(*t*-Butyldimethylsilyloxy)-2-(phenylseleno)propyl]-3-(phenylseleno)acrylic Acid Ethyl Ester (2g):** Pale-yellow oil (obtained as a stereoisomeric mixture ($E/Z = 9/91$)). $^1$H NMR (300 MHz, CDCl$_3$, rt): [(*Z*)-isomer]: $\delta$ $-0.06$ (s, 3H, C$H_3$), 0.01 (s, 3H, C$H_3$), 0.87 (s, 9H, (C$H_3$)$_3$C), 1.27 (t, $J = 7.2$ Hz, 3H, C$H_3$CH$_2$O$_2$C), 2.63–2.74 (m, 1H, C$H_2$C=CH), 2.95–3.07 (m, 1H, C$H_2$C=CH), 3.41–3.53 (m, 1H, C*H*CH$_2$C=CH), 3.75–3.83 (m, 1H, OC$H_2$CH), 3.83–3.93 (m, 1H, OC$H_2$CH), 4.22 (q, $J =$ 7.2 Hz, 2H, CH$_3$C$H_2$O$_2$C), 7.16–7.58 (m, 10H, Ph), 7.54 (s, 1H, C=C*H*).

**2-[3,3-Dimethoxy-2-(phenylseleno)propyl]-3-(phenylseleno)-acrylic Acid Ethyl Ester (2h):** Pale-yellow oil (obtained as a stereoisomeric mixture ($E/Z = 8/92$)). $^1$H NMR (600 MHz, $CDCl_3$, rt): [($Z$)-isomer]: $\delta$ 1.22 (t, $J = 7.2$ Hz, 3H, C$H_3$CH$_2$O$_2$C), 2.56 (dd, $J = 10.2$, 14.4 Hz, 1H, C$H_2$C=CH), 3.01 (dd, $J = 5.1$, 14.4 Hz, 1H, C$H_2$C=CH), 3.41 (s, 3H, C$H_3$O), 3.44 (s, 3H, C$H_3$O), 3.59 (m, 1H, C$H$CH$_2$C=CH), 4.11 (q, $J = 7.2$ Hz, 2H, CH$_3$C$H_2$O$_2$C), 4.45 (d, $J = 3.6$ Hz, 1H, (CH$_3$O)$_2$C$H$), 7.19–7.35 (m, 6H, Ph), 7.51 (s, 1H, C=C$H$), 7.52–7.62 (m, 4H, Ph). $^{13}$C NMR (150 MHz, $CDCl_3$, rt): [($Z$)-isomer]: $\delta$ 14.4, 35.5, 48.4, 55.6, 55.9, 60.7, 107.2, 125.6, 127.2, 127.9, 128.7, 129.2, 129.6, 133.0, 133.3, 134.7, 146.7, 166.8. IR (NaCl): 3055, 2982, 2931, 1694, 1575, 1476, 1439, 1368, 1322, 1207, 1123, 1073, 738, 693 cm$^{-1}$. MS (EI): $m/z$ 514 (M$^+$, 5). Found: C, 52.17; H, 5.50%. Calcd for $C_{22}H_{26}O_4Se_2$: C, 51.57; H, 5.11%.

**4,5-Dimethyl-6-(phenylseleno)-2-[(phenylseleno)methylene]-hex-4-enoic Acid Ethyl Ester (2i):** Pale-yellow oil (obtained as a stereoisomeric mixture (1$Z$,4$E$/1$Z$,4$Z$ = 67/33)). $^1$H NMR (400 MHz, $CDCl_3$, rt): [(1$Z$,4$E$)-isomer]: $\delta$ 1.36 (t, $J = 7.2$ Hz, 3H, C$H_3$CH$_2$O$_2$C), 1.47 (s, 3H, C$H_3$C=C), 1.79 (s, 3H, C$H_3$C=C), 3.04 (s, 2H, C$H_2$C=CH), 3.59 (s, 2H, PhSeC$H_2$), 4.29 (q, $J = 7.2$ Hz, 2H, CH$_3$C$H_2$O$_2$C), 7.19–7.60 (m, 10H, Ph), 7.26 (s, 1H, C=C$H$), [(1$Z$,4$Z$)-isomer]: $\delta$ 1.33 (t, $J = 7.2$ Hz, 3H, C$H_3$CH$_2$O$_2$C), 1.57 (s, 3H, C$H_3$C=C), 1.79 (s, 3H, C$H_3$C=C), 2.84 (s, 2H, C$H_2$C=CH), 3.62 (s, 2H, PhSeC$H_2$), 4.26 (q, $J = 7.2$ Hz, 2H, CH$_3$C$H_2$O$_2$C), 7.19–7.60 (m, 10H, Ph). 7.23 (s, 1H, C=C$H$). $^{13}$C NMR (100 MHz, $CDCl_3$, rt): [(1$Z$,4$E$)-isomer]: $\delta$ 14.4, 18.2, 18.6, 33.3, 37.7, 61.0, 125.5, 127.1, 127.6, 127.8, 128.8, 129.1, 129.3, 130.6, 132.9, 133.5, 133.6, 142.9, 167.7. [(1$Z$,4$Z$)-isomer]: $\delta$ 14.4, 18.4, 18.6, 33.1, 37.1, 60.9, 126.0, 127.2, 128.2, 128.8, 129.3, 129.4, 130.3, 133.2, 134.0, 143.3, 167.5. IR (NaCl): 3055, 2981, 2929, 1688, 1575, 1477, 1438, 1368, 1322, 1265, 1203, 1093, 1073, 1022 cm$^{-1}$. MS (CI): $m/z$ 495 (M$^+ + 1$, 10). Found: C, 55.85; H, 5.35%. Calcd for $C_{23}H_{26}O_2Se_2$: C, 56.11; H, 5.32%.

**4- and 5-Methyl-6-(phenylseleno)-2-[(phenylseleno)methylene]hex-4-enoic Acid Ethyl Esters (2j and 2j′):** Pale-yellow oil (obtained as a regio- and stereoisomeric mixture (4$E$-**2j**/4$Z$-**2j**/4$E$-**2j′**/4$Z$-**2j′** = 67/4/24/5)). $^1$H NMR (600 MHz, $CDCl_3$, rt): [4$E$-**2j**]: $\delta$ 1.33 (t, $J = 7.2$ Hz, 3H, C$H_3$CH$_2$O$_2$C), 1.45 (s, 3H, C$H_3$C=CH), 2.99 (s, 2H, C$H_2$C=CH), 3.52 (d, $J = 8.4$ Hz, 2H, PhSeC$H_2$), 4.25 (q, $J = 7.2$ Hz, 2H, CH$_3$C$H_2$O$_2$C), 5.46 (t, $J = 8.4$ Hz, 1H, CH$_2$C$H$=CCH$_2$), 7.17–7.60 (m, 10H, Ph). 7.33 (s, 1H, C=C$H$SePh), [4$E$-**2j′**]: $\delta$ 1.32 (t, $J = 7.2$ Hz, 3H, C$H_3$CH$_2$O$_2$C), 1.78 (s, 3H, C$H_3$C=CH), 2.96 (s, $J = 7.2$ Hz, 2H, C=CHC$H_2$C), 3.48 (s, 2H, PhSeC$H_2$), 4.24 (q, $J = 7.2$ Hz, 2H, CH$_3$C$H_2$O$_2$C), 5.14 (t, $J = 7.2$ Hz, 1H, C=C$H$CH$_2$), 7.17–7.60 (m, 10H, Ph), 7.33 (s, 1H, C=C$H$SePh). $^{13}$C NMR (150 MHz, $CDCl_3$, rt): [4$E$-**2j**]: $\delta$ 14.3, 15.6, 25.7, 42.4, 60.9, 126.2, 127.0, 127.9, 128.8, 129.2, 130.2, 133.1, 133.6, 136.4, 144.5, 167.4. [4$E$-**2j′**]: $\delta$ 14.3, 15.6, 32.1, 38.2, 60.9, 124.7, 126.9, 127.1, 127.9, 128.7, 129.2, 130.3, 133.1, 133.4, 133.7, 143.3, 167.2. IR (NaCl): 3058, 2979, 2924, 1692, 1572, 1474, 1438, 1370, 1322, 1274, 1212, 1105, 1071, 1024, 910, 846, 736, 693 cm$^{-1}$. MS (CI): $m/z$ 481 (M$^+ + 1$, 43). Found: C, 54.96; H, 5.04%. Calcd for $C_{22}H_{24}O_2Se_2$: C, 55.24; H, 5.06%.

**2-[2-Butoxy-2-(phenylseleno)ethyl]hept-2-enoic Acid Ethyl Ester (8f).** In 20 mL of a two-necked flask were placed copper(I) iodide (24.1 mg, 0.13 mmol) in 0.5 mL of an anhydrous ether solution at $-15$ °C under an argon atmosphere. $^n$BuLi (1.5 M in hexane, 0.3 mL) was added, and the mixture was stirred for 1 h. 2-[2-Butoxy-2-(phenylseleno)ethyl]-3-(phenylseleno)acrylic acid ethyl ester (**2f**, 50.0 mg, 0.10 mmol) in 0.5 mL of anhydrous ether solution was added dropwise to the mixture, and then the resulting solution was stirred for 1.5 h. After the reaction was completed, the resulting mixture was evaporated. Purification was performed on a recycling preparative HPLC, yielding 33.4 mg (84%) of **8f**: Pale-yellow oil (obtained as a stereoisomeric mixture ($E/Z = 7/93$)).

**2-[2-Butoxy-2-(phenylseleno)ethyl]-4-methylhex-2-enoic Acid Ethyl Ester (8f′).** In 20 mL of a two-necked flask were placed copper(I) cyanide (25.0 mg, 0.28 mmol) in 0.5 mL of anhydrous THF solution at $-20$–$-30$ °C under an argon atmosphere. $^s$BuLi (0.6 mL, 0.6 mmol) was added, and the mixture was stirred for 0.5 h. $Et_2O \cdot BF_3$ (40.0 μL, 0.31 mmol) was added after the mixture was cooled at $-78$ °C, and then **2f** (30.0 mg, 0.06 mmol) in 1.0 mL of anhydrous THF–ether mixed solution was added dropwise to the mixture. After stirring for 12 h, the resulting mixture was evaporated. Purification was performed on a recycling preparative HPLC, yielding 14.0 mg (58%) of **8f′**: Pale-yellow oil (obtained as a stereoisomeric mixture ($E/Z = 16/84$)). $^1$H NMR (600 MHz, $CDCl_3$, rt): [($Z$)-isomer]: $\delta$ 0.75–0.91 (m, 9H, C$H_3$CH$_2$CH(C$H_3$), C$H_3$(CH$_2$)$_3$), 0.89 (dd, $J = 6.6$, 13.8 Hz, 1H, C=C$H$), 1.17–1.48 (m, 6H, CH$_3$(C$H_2$)$_2$CH$_2$, CH$_3$C$H_2$CH(CH$_3$)), 1.18 (t, $J = 7.2$ Hz, 3H, C$H_3$CH$_2$O$_2$C), 2.70–2.83 (m, 2H, C$H_2$C=CH), 2.87–2.93 (m, 1H, (CH$_3$)C$H$CH$_2$CH$_3$), 3.19–3.24 (m, 1H, CH$_3$(CH$_2$)$_2$C$H_2$O), 3.74–3.79 (m, 1H, CH$_3$(CH$_2$)$_2$C$H_2$O), 4.06–4.12 (m, 2H, CH$_3$C$H_2$O$_2$C), 4.98–5.02 (m, 1H, PhSeC$H$O), 5.56 (dd, $J = 10.2$, 13.8 Hz, 1H, C=C$H$), 7.15–7.22 (m, 3H, Ph), 7.50–7.52 (m, 2H, Ph). $^{13}$C NMR (100 MHz, $CDCl_3$, rt): [($Z$)-isomer]: $\delta$ 11.8, 14.2 (2C), 19.3, 30.0, 31.2, 35.2, 43.2, 43.4, 60.0, 69.7, 87.0, 127.0, 127.3, 128.7, 128.9, 135.4, 151.3, 167.7.

**2-[3-(*t*-Butyldimethylsilyloxy)-2-(phenylseleno)propyl]but-2-enoic Acid Ethyl Ester (8g):** Pale-yellow oil (obtained as a stereoisomeric mixture ($E/Z = 8/92$)). $^1$H NMR (400 MHz, $CDCl_3$, rt): [($Z$)-isomer]: $\delta$ 0.08 (s, 3H, C$H_3$Si), 0.10 (s, 3H, C$H_3$Si), 0.96 (s, 9H, (C$H_3$)$_3$Si), 1.32 (t, $J = 7.2$ Hz, 3H, C$H_3$CH$_2$O$_2$C), 2.05 (d, $J = 7.1$ Hz, 3H, C$H_3$CH=C), 2.57–2.69 (m, 1H, C$H_2$C=CH), 2.90–3.02 (m, 1H, C$H_2$C=CH), 3.45–3.57 (m, 1H, C$H$CH$_2$C=CH), 3.77–3.97 (m, 2H, SiOC$H_2$), 4.22 (q, $J = 7.2$ Hz, 2H, CH$_3$C$H_2$O$_2$C), 6.17 (q, $J = 7.1$ Hz, 1H, C=C$H$), 7.23–7.67 (m, 5H, Ph). $^{13}$C NMR (100 MHz, $CDCl_3$, rt): [($Z$)-isomer]: $\delta$ $-5.3$ (2C), 14.4, 15.9, 18.4, 25.9 (3C), 38.0, 46.9, 60.1, 65.5, 126.9, 128.7, 130.2, 134.0, 140.0, 167.3.

**2-[(Benzylimino)(phenylseleno)methyl]-3-(phenylseleno)-acrylic Acid Ethyl Ester (10a).** In a Pyrex glass tube ($\phi = 10$ mm, length = 75 mm) were placed ethyl propiolate (15.7 mg, 0.16 mmol) and benzyl isocyanide (**9a**, 539 mg, 4.6 mmol) under a $N_2$ atmosphere. The mixture was irradiated with a tungsten lamp (500 W) at 15 °C for 6 h, and during the irradiation, diphenyl diselenide (49.9 mg, 0.16 mmol) was added separately eight times over 1 h. After the reaction was completed, purification of the products was performed on a recycling preparative HPLC, yielding 85% of **10a** as a stereoisomeric mixture ($E/Z = 51/49$). The stereochemistry was determined by NOE experiments between the vinylic proton and the benzylic methylene proton of **10a**: Yellow oil. $^1$H NMR (300 MHz, $CDCl_3$, rt): [($E$)-isomer]: $\delta$ 1.31 (t, $J = 7.1$ Hz, 3H, C$H_3$CH$_2$O$_2$C), 4.11 (q, $J = 7.1$ Hz, 2H, CH$_3$C$H_2$O$_2$C), 4.76 (s, 2H, PhC$H_2$N), 7.18–7.50 (m, 15H, Ph), 7.95 (s, 1H, C=C$H$). [($Z$)-isomer]: $\delta$ 1.19 (t, $J = 7.1$ Hz, 3H, C$H_3$CH$_2$O$_2$C), 4.00 (q, $J = 7.1$ Hz, 2H, CH$_3$C$H_2$O$_2$C), 4.71 (s, 2H, PhC$H_2$N), 7.18–7.50 (m, 15H, Ph), 7.66 (s, 1H, C=C$H$). $^{13}$C NMR (150 MHz, $CDCl_3$, rt): [($E$)-isomer]: $\delta$ 14.2, 60.0, 60.9, 133.0, 137.1, 138.5, 151.5, 159.0, 162.4. [($Z$)-isomer]: $\delta$

14.1, 59.9, 61.1, 133.5, 136.6, 138.6, 146.8, 160.0, 164.6. IR (NaCl): 3059, 3030, 2978, 2931, 2869, 2221, 2149, 1952, 1880, 1699, 1628, 1574, 1475, 1439, 1367, 1305, 1219, 1098, 1022, 911, 859, 798, 737, 693, 670, 646, 618 $cm^{-1}$. MS (CI): $m/z$ 530 ($M^+ + 1$, 52). HRMS calcd for $C_{25}H_{23}NO_2Se_2$: 530.0137, found: 530.0123.

**2-[(Cyclohexylimino)(phenylseleno)methyl]-3-(phenylseleno)acrylic Acid Ethyl Ester (10b):** Yellow oil (obtained as a stereoisomeric mixture ($E/Z = 35/65$)): $^1$H NMR (600 MHz, $CDCl_3$, rt): [(*E*)-isomer]: $\delta$ 1.23–1.95 (m, 10H, $^cC_6H_{11}$), 1.30 (t, $J = 7.0$ Hz, 3H, $CH_3CH_2O_2C$), 3.42–3.47 (m, 1H, $^cC_6H_{11}$), 4.09 (q, $J = 7.0$ Hz, 2H, $CH_3CH_2O_2C$), 7.24–7.62 (m, 10H, Ph), 7.51 (s, 1H, C=C*H*). [(*Z*)-isomer]: $\delta$ 1.15 (t, $J = 7.0$ Hz, 3H, $CH_3CH_2O_2C$), 1.23–1.95 (m, 10H, $^cC_6H_{11}$), 3.55–3.60 (m, 1H, $^cC_6H_{11}$), 3.96 (q, $J = 7.0$ Hz, 2H, $CH_3CH_2O_2C$), 7.24–7.62 (m, 10H, Ph), 7.86 (s, 1H, C=C*H*). $^{13}$C NMR (150 MHz, $CDCl_3$, rt): [(*E*)-isomer]: $\delta$ 15.2, 25.6, 32.6, 61.0, 65.5, 128.3, 128.7, 129.0, 129.3, 132.7, 133.5, 137.3, 150.9, 155.3, 164.7. [(*Z*)-isomer]: $\delta$ 14.1, 24.6, 32.9, 60.7, 66.0, 128.2, 128.8 (2C), 129.4, 131.5, 133.0, 137.0, 146.3, 154.5, 162.2. IR (NaCl): 3054, 2978, 2929, 2853, 1709, 1634, 1572, 1476, 1441, 1367, 1304, 1219, 1098, 1062, 1022, 959, 913, 864, 812, 737, 692, 646 $cm^{-1}$. MS (CI): $m/z$ 522 ($M^+ + 1$, 48). HRMS calcd for $C_{24}H_{27}NO_2Se_2$: 522.0451, found: 522.0463.

**2-[(2,6-Dimethylphenylimino)(phenylseleno)methyl]-3-(phenylseleno)acrylic Acid Ethyl Ester (10c):** Yellow oil (obtained as a stereoisomeric mixture ($E/Z = 52/48$)). $^1$H NMR (600 MHz, $CDCl_3$, rt): [(*E*)-isomer]: $\delta$ 1.34 (t, $J = 7.2$ Hz, 3H, $CH_3CH_2O_2C$), 2.39 (s, 6H, $CH_3$), 4.14 (q, $J = 7.2$ Hz, 2H, $CH_3CH_2O_2C$), 6.99–7.61 (m, 13H, Ph), 7.78 (s, 1H, C=C*H*). [(*Z*)-isomer]: $\delta$ 1.25 (t, $J = 7.1$ Hz, 3H, $CH_3CH_2O_2C$), 2.22 (s, 6H, $CH_3$), 4.07 (q, $J = 7.1$ Hz, 2H, $CH_3CH_2O_2C$), 6.99–7.61 (m, 13H, Ph), 7.99 (s, 1H, C=C*H*). $^{13}$C NMR (150 MHz, $CDCl_3$, rt): [(*E*)-isomer]: $\delta$ 14.2, 17.9, 61.3, 124.4, 126.4, 127.3, 127.8, 128.1, 128.4, 128.9, 129.4, 133.2, 136.9, 151.4, 164.3. [(*Z*)-isomer]: $\delta$ 14.3, 18.8, 61.2, 124.6, 126.6, 128.2, 128.5, 128.7, 129.2, 129.5, 129.8, 130.5, 133.0, 136.9, 146.5, 163.5. IR (NaCl): [(*E*)-isomer]: 2926, 2358, 1694, 1632, 1590, 1554, 1473, 1439, 1368, 1367, 1308, 1204, 1136, 1090, 1023, 925, 835, 766, 739, 692 $cm^{-1}$. [(*Z*)-isomer]: $\delta$ 2986, 2931, 2153, 1708, 1632, 1478, 1444, 1419, 1394, 1370, 1256, 1164, 1098, 1024, 979, 862, 722, 694 $cm^{-1}$. MS (CI): [(*E*)-isomer]: $m/z$ 544 ($M^+ + 1$, 17). HRMS calcd for $C_{26}H_{25}NO_2Se_2$: 544.0294, found: 544.0302. [(*Z*)-isomer]: $m/z$ 544 ($M^+ + 1$, 17). HRMS calcd for $C_{26}H_{25}NO_2Se_2$: 544.0294, found: 544.0297.

**2-[(Diethoxyphosphoryl)methylimino](phenylseleno)methyl-3-(phenylseleno)acrylic Acid Ethyl Ester (10d):** Yellow oil (obtained as a stereoisomeric mixture ($E/Z = 45/55$)). $^1$H NMR (600 MHz, $CDCl_3$, rt): [(*E*)-isomer]: $\delta$ 1.16 (t, $J = 7.2$ Hz, 3H, $CH_3CH_2O_2C$), 1.38 (t, $J = 7.2$ Hz, 6H, $CH_3CH_2O$), 3.98 (q, $J = 7.2$ Hz, 2H, $CH_3CH_2O_2C$), 4.12 (d, $J = 16.2$ Hz, 2H, $PCH_2N$), 4.24 (quint like, $J = 7.2$ Hz, 4H, $CH_3CH_2O$), 7.25–7.57 (m, 10H, Ph), 7.65 (s, 1H, C=C*H*). [(*Z*)-isomer]: $\delta$ 1.28 (t, $J = 7.2$ Hz, 3H, $CH_3CH_2O_2C$), 1.32 (t, $J = 7.2$ Hz, 6H, $CH_3CH_2O$), 4.05 (d, $J = 16.2$ Hz, 2H, $PCH_2N$), 4.08 (q, $J = 7.2$ Hz, 2H, $CH_3CH_2O_2C$), 4.18 (quint like, $J = 7.2$ Hz, 4H, $CH_3CH_2O$), 7.25–7.57 (m, 10H, Ph), 7.98 (s, 1H, C=C*H*). $^{13}$C NMR (75 MHz, $CDCl_3$, rt): [(*E*)-isomer]: $\delta$ 14.1, 16.4 (d, $J_{C-P} = 3.8$ Hz), 53.2 (d, $J_{C-P} = 107.6$ Hz), 60.9, 62.7 (d, $J_{C-P} = 4.7$ Hz), 126.7, 128.3, 128.9, 129.0, 129.4, 130.9, 132.9, 136.2, 152.2, 164.5. [(*Z*)-isomer]: $\delta$ 14.2, 16.5 (d, $J_{C-P} = 3.8$ Hz), 53.5 (d, $J_{C-P} = 107.6$ Hz), 61.1, 62.6 (d, $J_{C-P} = 4.7$ Hz), 126.9, 128.4, 128.9, 129.1, 129.3, 132.4, 133.4, 136.8, 147.9, 162.4. IR (NaCl): 3056, 2981, 1709, 1621, 1309, 1225, 1028, 968, 742, 692 $cm^{-1}$. MS (CI): $m/z$ 590 ($M^+ + 1$, 81). HRMS calcd for $C_{23}H_{28}NO_5PSe_2$: 590.0114, found: 590.0104. Found: C, 47.10; H, 4.89; N, 2.46%. Calcd for $C_{23}H_{28}NO_5PSe_2$: C, 47.03; H, 4.80; N, 2.38%.

**2-[(Methoxycarbonylmethylimino)(phenylseleno)methyl]-3-(phenylseleno)acrylic Acid Ethyl Ester (10e):** Yellow oil (obtained as a stereoisomeric mixture ($E/Z = 55/45$)). $^1$H NMR (300 MHz, $CDCl_3$, rt): [(*E*)-isomer]: $\delta$ 1.29 (t, $J = 7.1$ Hz, 3H, $CH_3CH_2O_2C$), 3.79 (s, 1H, $CH_3O_2C$), 4.08 (q, $J = 7.1$ Hz, 2H, $CH_3CH_2O_2C$), 4.28 (s, 2H, $CH_3O_2CCH_2N$), 7.24–7.64 (m, 10H, Ph), 7.70 (s, 1H, C=C*H*). [(*Z*)-isomer]: $\delta$ 1.17 (t, $J = 7.1$ Hz, 3H, $CH_3CH_2O_2C$), 3.82 (s, 1H, $CH_3O_2C$), 4.00 (q, $J = 7.1$ Hz, 2H, $CH_3CH_2O_2C$), 4.37 (s, 2H, $CH_3O_2CCH_2N$), 7.24–7.64 (m, 10H, Ph), 8.03 (s, 1H, C=C*H*). $^{13}$C NMR (75 MHz, $CDCl_3$, rt): [(*E*)-isomer]: $\delta$ 14.3, 52.3, 57.3, 61.2, 126.6, 128.3, 129.0, 129.2, 132.2, 133.4, 136.8, 152.2, 163.8, 169.5. [(*Z*)-isomer]: $\delta$ 14.2, 52.3, 57.2, 61.0, 128.2, 128.9, 129.0, 129.3, 130.7, 132.9, 136.1, 148.1, 164.2, 169.6. IR (NaCl): 3054, 2979, 2903, 2869, 1752, 1706, 1625, 1553, 1476, 1438, 1391, 1368, 1307, 1208, 1176, 1103, 1068, 1022, 999, 930, 857, 802, 741, 692, 670 $cm^{-1}$. MS (CI): $m/z$ 512 ($M^+ + 1$, 58). HRMS calcd for $C_{21}H_{21}NO_4Se_2$: 511.9879, found: 511.9866.

**2-[(4-Cyanophenylimino)(phenylseleno)methyl]-3-(phenylseleno)acrylic Acid Ethyl Ester (10f):** Yellow oil (obtained as a stereoisomeric mixture (64/36)). $^1$H NMR (300 MHz, $CDCl_3$, rt): [major-isomer]: $\delta$ 1.17 (t, $J = 7.2$ Hz, 3H, $CH_3CH_2O_2C$), 4.00 (q, $J = 7.2$ Hz, 2H, $CH_3CH_2O_2C$), 6.87–7.49 (m, 14H, Ph), 7.76 (s, 1H, C=C*H*). [minor-isomer]: $\delta$ 1.13 (t, $J = 7.2$ Hz, 3H, $CH_3CH_2O_2C$), 4.08 (q, $J = 7.2$ Hz, 2H, $CH_3CH_2O_2C$), 6.87–7.66 (m, 14H, Ph), 8.10 (s, 1H, C=C*H*). $^{13}$C NMR (75 MHz, $CDCl_3$, rt): [major-isomer]: $\delta$ 14.3, 61.4, 120.3, 127.2, 128.6, 128.8, 129.1, 129.3, 132.9, 133.5, 136.5, 148.8, 150.7, 163.5. [minor-isomer]: $\delta$ 14.3, 61.2, 120.2, 127.3, 129.0, 129.1, 129.3, 129.5, 132.9, 133.5, 136.8, 149.0, 150.2, 164.0. IR (NaCl): 3057, 2975, 2928, 2866, 2122, 1696, 1622, 1595, 1492, 1440, 1369, 1309, 1222, 1116, 1071, 1022, 933, 850, 741, 692, 669 $cm^{-1}$. MS (CI): $m/z$ 541 ($M^{+1} + 1$, 82). HRMS calcd for $C_{25}H_{20}N_2O_2Se_2$: 540.9934, found: 540.9928.

**2-[(Butylimino)(phenylseleno)methyl]-3-(phenylseleno)acrylic Acid Ethyl Ester (10g):** Yellow oil (obtained as a stereoisomeric mixture (51/49)). $^1$H NMR (300 MHz, $CDCl_3$, rt): [major-isomer]: $\delta$ 1.00 (t, $J = 7.5$ Hz, 3H, $CH_3(CH_2)_3$), 1.29 (t, $J = 7.1$ Hz, 3H, $CH_3CH_2O_2C$), 1.35–1.88 (m, 4H, $CH_3CH_2CH_2CH_2$), 3.56 (t, $J = 6.9$ Hz, 2H, $CH_3CH_2CH_2CH_2$), 3.97 (t, $J = 7.1$ Hz, 2H, $CH_3CH_2O_2C$), 7.22–7.63 (m, 10H, Ph), 7.90 (s, 1H, C=C*H*). [minor-isomer]: $\delta$ 0.97 (t, $J = 7.5$ Hz, 3H, $CH_3(CH_2)_3$), 1.17 (t, $J = 7.1$ Hz, 3H, $CH_3CH_2O_2C$), 1.35–1.88 (m, 4H, $CH_3CH_2CH_2CH_2$), 3.47 (t, $J = 6.9$ Hz, 2H, $CH_3CH_2CH_2CH_2$), 4.08 (t, $J = 7.1$ Hz, 2H, $CH_3CH_2O_2C$), 7.22–7.63 (m, 10H, Ph), 7.58 (s, 1H, C=C*H*). $^{13}$C NMR (75 MHz, $CDCl_3$, rt): [major-isomer]: $\delta$ 14.2, 20.9, 32.4, 56.3, 61.1, 126.9, 128.2, 128.7 (2C), 129.4, 131.5, 132.9, 136.6, 146.3, 162.2. [minor-isomer]: $\delta$ 14.0, 20.7, 32.3, 56.1, 60.9, 127.1, 128.2, 128.7, 128.9, 129.2, 132.5, 133.4, 137.1, 151.0, 164.5. IR (NaCl): 2956, 2933, 2868, 1709, 1624, 1550, 1476, 1438, 1367, 1305, 1221, 1156, 1098, 1022, 906, 871, 740, 691, 636 $cm^{-1}$. MS (CI): $m/z$ 496 ($M^{+1} + 1$, 33). HRMS calcd for $C_{22}H_{25}NO_2Se_2$: 496.0294, found: 496.0295.

**2-[(Diethoxyphosphoryl)methyl]-3-methoxy-4-oxo-2-(phenylseleno)azetidin-2-yl)-3-(phenylseleno)acrylic Acid Ethyl Ester (11).** In 20 mL of a two-necked flask were placed **10d**

(35.0 mg, 0.06 mmol) in 3 mL of anhydrous dichloromethane solution at −20 °C under an argon atmosphere. Methoxyacetyl chloride (65.0 mg, 0.60 mmol) was added, and the mixture was stirred for 1 h, further stirred at room temperature for 12 h. After the reaction was completed, the resulting mixture was evaporated. Purification was performed on a recycling preparative HPLC, yielding 33.2 mg (85%) of **11** as a stereoisomeric mixture (55/45): Yellow oil. $^1$H NMR (600 MHz, $CDCl_3$, rt): [major-isomer]: $\delta$ 1.25 (t, $J$ = 7.2 Hz, 3H, C$H_3$CH$_2$O$_2$C), 1.32 (t, $J$ = 7.2 Hz, 3H, C$H_3$CH$_2$O), 1.35 (t, $J$ = 7.2 Hz, 3H, C$H_3$CH$_2$O), 3.37 (s, 3H, C$H_3$O), 3.56 (dd, $J$ = 11.7, 15.9 Hz, 1H, PC$H_2$N), 3.65 (dd, $J$ = 12.3, 15.9 Hz, 1H, PC$H_2$N), 4.03–4.25 (m, 4H, CH$_3$C$H_2$O), 4.13–4.20 (m, 2H, CH$_3$C$H_2$O$_2$C), 4.58 (s, 1H, CH$_3$OC$H$), 7.28–7.77 (m, 10H, Ph), 7.95 (s, 1H, C=C$H$). [minor-isomer]: $\delta$ 1.20 (t, $J$ = 7.2 Hz, 3H, C$H_3$CH$_2$O), 1.24 (t, $J$ = 7.2 Hz, 3H, C$H_3$CH$_2$O), 1.39 (t, $J$ = 7.2 Hz, 3H, C$H_3$CH$_2$O$_2$C), 3.33 (s, 3H, C$H_3$O), 3.66 (dd, $J$ = 13.8, 16.2 Hz, 1H, PC$H_2$N), 3.89–4.00 (m, 2H, CH$_3$C$H_2$O), 4.02–4.12 (m, 2H, CH$_3$C$H_2$O), 4.11 (dd, $J$ = 13.8, 16.2 Hz, 1H, PC$H_2$N), 4.28–4.38 (m, 2H, CH$_3$C$H_2$O$_2$C), 4.57 (s, 1H, CH$_3$OC$H$), 7.25–7.68 (m, 10H, Ph), 8.23 (s, 1H, C=C$H$). $^{13}$C NMR (75 MHz, $CDCl_3$, rt): [major-isomer]: $\delta$ 14.0, 16.3 (d, $J_{C-P}$ = 5.7 Hz), 38.3 (d, $J_{C-P}$ = 79.0 Hz), 58.7, 62.6 (d, $J_{C-P}$ = 3.5 Hz), 86.1, 91.4, 126.0, 129.5, 133.2, 137.0, 144.1, 165.0, 165.2. [minor-isomer]: $\delta$ 14.2, 16.3 (d, $J_{C-P}$ = 5.7 Hz), 39.5 (d, $J_{C-P}$ = 79.0 Hz), 59.1, 61.5 (d, $J_{C-P}$ = 1.7 Hz), 87.7, 92.7, 123.7, 133.0, 137.6, 150.7, 165.5, 166.0. IR (NaCl): 3056, 2981, 2930, 2240, 1814, 1775, 1712, 1652, 1577, 1559, 1476, 1439, 1370, 1241, 1161, 1096, 1052, 1024, 974, 913, 787, 738, 694 cm$^{-1}$. MS (CI): $m/z$ 496 ($M^{+1}$ + 1 − PhSe, 33). Anal. Calcd for $C_{26}H_{32}NO_7PSe_2$: C, 47.36; H, 4.89; N, 2.12%. Found: C, 47.87; H, 5.26; N, 2.59%.

**2-{[(Diethoxyphosphoryl)methyl]-3-methoxy-4-oxo-2-(phenylseleno)azetidin-2-yl}-3-oxopropionic Acid Ethyl Ester (12).** In 20 mL of a two-necked flask were placed **11** (33.2 mg, 0.05 mmol) and trifluoroacetic acid (74.0 mg, 0.65 mmol) under an argon atmosphere. The mixture was stirred for 2 h. After the reaction was completed, the resulting mixture was quenched by water, and extracted with three 30 mL portions of diethyl ether. The residue was washed with saturated brine, dried ($MgSO_4$), and evaporated. Purification was performed on a recycling preparative HPLC, yielding 13.3 mg (51%) of **12**: Pale-yellow oil. $^1$H NMR (600 MHz, $CDCl_3$, rt): [major-isomer]: $\delta$ 1.32 (dt, $J$ = 3.2, 7.2 Hz, 6H, C$H_3$CH$_2$O), 1.48 (t, $J$ = 7.2 Hz, 3H, C$H_3$CH$_2$O$_2$C), 3.07 (s, 3H, C$H_3$O), 4.01–4.23 (m, 4H, CH$_3$C$H_2$O), 4.32 (dd, $J$ = 3.2, 7.2 Hz, 2H, PC$H_2$N), 4.33–4.44 (m, 2H, CH$_3$C$H_2$O$_2$C), 4.99 (s, 1H, CH$_3$OC$H$), 7.20–7.71 (m, 5H, Ph), 9.14 (s, 1H, C$H$O). $^{13}$C NMR (150 MHz, $CDCl_3$, rt): [major-isomer]: $\delta$ 14.3, 16.4 (d, $J_{C-P}$ = 3.8 Hz), 38.0 (d, $J_{C-P}$ = 152.3 Hz), 39.6, 61.4, 62.7 (d, $J_{C-P}$ = 5.7 Hz), 83.5, 128.1, 128.8, 129.9, 164.4, 167.4, 192.0.

**General Procedure for the Synthesis of the Coupling Product (13m).** In a Pyrex glass tube ($\phi$ = 10 mm, length = 75 mm) were placed ethyl propiolate (19.6 mg, 0.20 mmol), 2-methoxypropene (389 mg, 5.4 mmol), and acrylonitrile (**1m**, 106 mg, 2.0 mmol) under a $N_2$ atmosphere. The mixture was irradiated with a tungsten lamp (500 W) at 30 °C for 2 h, and during the irradiation, diphenyl diselenide (62.4 mg, 0.20 mmol) was added separately eight times over 1 h. After the reaction was completed, purification of the products was performed on a recycling preparative HPLC, yielding 77.4 mg (76%) of **13m** as a stereoisomeric mixture (60/14/26). The stereochemistry of **13m** was determined by NOE experiments.

**1-[Bis(phenylseleno)methyl]-*c*-2-*t*-butoxycarbonyl-*t*-4-methoxy-*c*-4-methylcyclopentane-γ-1-carboxylic Acid Ethyl Ester (13k-A):** Pale-yellow oil. $^1$H NMR (300 MHz, $CDCl_3$, rt): $\delta$ 1.22 (t, $J$ = 7.2 Hz, 3H, C$H_3$CH$_2$O$_2$C), 1.31 (s, 3H, C$H_3$C), 1.40 (s, 9H, (C$H_3$)$_3$CO$_2$C), 1.93 (dd, $J$ = 12.3, 13.2 Hz, 1H, CC$H_2$CH), 2.16 (ddd, $J$ = 1.8, 6.6, 13.2 Hz, 1H, CC$H_2$CH), 2.24 (dd, $J$ = 1.8, 14.4 Hz, 1H, CC$H_2$C), 2.50 (d, $J$ = 14.4 Hz, 1H, CC$H_2$C), 2.98 (s, 3H, C$H_3$O), 3.68 (dd, $J$ = 6.6, 12.3 Hz, 1H, CC$H$CH$_2$), 4.09 (q, $J$ = 6.9 Hz, 2H, CH$_3$C$H_2$O$_2$C), 4.86 (s, 1H, (PhSe)$_2$C$H$), 7.12–7.26 (m, 6H, Ph), 7.42–7.46 (m, 4H, Ph). $^{13}$C NMR (100 MHz, $CDCl_3$, rt): $\delta$ 14.1, 22.3, 28.1, 41.7, 46.4, 49.4, 53.9, 55.7, 61.5, 64.0, 80.8, 81.8, 127.5, 127.7, 128.7, 134.3, 135.0, 171.5, 172.7. IR (NaCl): 2975, 1729, 1577, 1476, 1368, 1150, 740, 692 cm$^{-1}$. MS (EI): $m/z$ 612 ($M^+$, 16). HRMS calcd for $C_{28}H_{36}O_5Se_2$: 612.0893, found: 612.0903.

**1-[Bis(phenylseleno)methyl]-*t*-2-*t*-butoxycarbonyl-*c*-4-methoxy-*t*-4-methylcyclopentane-γ-1-carboxylic Acid Ethyl Ester (13k-B):** Pale-yellow oil. $^1$H NMR (300 MHz, $CDCl_3$, rt): $\delta$ 1.27 (t, $J$ = 7.2 Hz, 3H, C$H_3$CH$_2$O$_2$C), 1.31 (s, 3H, C$H_3$C), 1.43 (s, 9H, (C$H_3$)$_3$CO$_2$C), 1.97 (dd, $J$ = 5.4, 14.1 Hz, 1H, CC$H_2$CH), 2.04 (d, $J$ = 14.1 Hz, 1H, CC$H_2$C), 2.38 (ddd, $J$ = 1.8, 8.7, 14.1 Hz, 1H, CC$H_2$CH), 2.99 (dd, $J$ = 1.8, 14.1 Hz, 1H, CC$H_2$C), 3.12 (s, 3H, C$H_3$O), 3.71 (dd, $J$ = 5.4, 8.7 Hz, 1H, CC$H$CH$_2$), 3.97–4.16 (m, 2H, CH$_3$C$H_2$O$_2$C), 5.26 (s, 1H, (PhSe)$_2$C$H$), 7.13–7.29 (m, 6H, Ph), 7.43–7.46 (m, 4H, Ph). $^{13}$C NMR (100 MHz, $CDCl_3$, rt): $\delta$ 14.2, 22.9, 28.1, 44.0, 46.8, 49.8, 50.3, 61.4, 62.9, 80.8, 81.9, 127.4, 127.8, 128.5, 128.7, 129.9, 131.8, 134.0, 135.3, 172.4, 173.2. IR (NaCl): 2974, 1719, 1578, 1476, 1368, 740, 691 cm$^{-1}$. MS (EI): $m/z$ 612 ($M^+$, 16). HRMS calcd for $C_{28}H_{36}O_5Se_2$: 612.0893, found: 612.0903.

**1-[Bis(phenylseleno)methyl]-*c*-2-methoxycarbonyl-*t*-4-methoxy-*c*-4-methylcyclopentane-γ-1-carboxylic Acid Ethyl Ester (13l-A):** $^1$H NMR (600 MHz, $CDCl_3$, rt): $\delta$ 1.10 (t, $J$ = 7.2 Hz, 3H, C$H_3$CH$_2$O$_2$C), 1.35 (s, 3H, C$H_3$C), 1.96 (dd, $J$ = 7.2, 13.2 Hz, 1H, CC$H_2$CH), 2.14 (dd, $J$ = 7.2, 13.2 Hz, 1H, CC$H_2$CH), 2.15 (d, $J$ = 15.0 Hz, 1H, CC$H_2$C), 2.60 (d, $J$ = 15.0 Hz, 1H, CC$H_2$CH), 3.09 (s, 3H, C$H_3$O), 3.55 (s, 3H, C$H_3$O$_2$C), 3.78 (dd, $J$ = 7.2, 7.2 Hz, 1H, CC$H$CH$_2$), 4.19–4.25 (m, 2H, CH$_3$C$H_2$O$_2$C), 4.90 (s, 1H, (PhSe)$_2$C$H$), 7.10–7.27 (m, 6H, Ph), 7.43–7.45 (m, 2H, Ph), 7.49–7.51 (m, 2H, Ph). IR (NaCl): 2973, 1733, 1585, 1436, 862, 797, 746, 690 cm$^{-1}$. HRMS calcd for $C_{25}H_{30}O_5Se_2$: 570.0424, found: 570.0433. Anal. Calcd for $C_{25}H_{30}O_5Se_2$: C, 52.83; H, 5.32%. Found: C, 52.72; H, 5.29%.

**1-[Bis(phenylseleno)methyl]-*t*-2-methoxycarbonyl-*c*-4-methoxy-*t*-4-methylcyclopentane-γ-1-carboxylic Acid Ethyl Ester (13l-B):** $^1$H NMR (600 MHz, $CDCl_3$, rt): $\delta$ 1.25 (s, 3H, C$H_3$C), 1.25 (t, $J$ = 7.2 Hz, 3H, C$H_3$CH$_2$O$_2$C), 1.90 (dd, $J$ = 13.2, 13.2 Hz, 1H, CC$H_2$CH), 2.01 (d, $J$ = 14.1 Hz, 1H, CC$H_2$C), 2.36 (dd, $J$ = 7.8, 13.2 Hz, 1H, CC$H_2$CH), 2.95 (d, $J$ = 14.1 Hz, 1H, CC$H_2$C), 3.08 (s, 3H, C$H_3$O), 3.54 (s, 3H, C$H_3$O$_2$C), 3.83 (dd, $J$ = 7.8, 13.2 Hz, 1H, CC$H$CH$_2$), 3.97–4.03 (m, 2H, CH$_3$C$H_2$O$_2$C), 5.16 (s, 1H, (PhSe)$_2$C$H$), 7.10–7.27 (m, 6H, Ph), 7.33–7.35 (m, 2H, Ph), 7.37–7.39 (m, 2H, Ph).

**1-[Bis(phenylseleno)methyl]-*t*-2-methoxycarbonyl-*t*-4-methoxy-*c*-4-methylcyclopentane-γ-1-carboxylic Acid Ethyl Ester (13l-C):** $^1$H NMR (600 MHz, $CDCl_3$, rt): $\delta$ 1.23 (s, 3H, C$H_3$C), 1.36 (t, $J$ = 7.2 Hz, 3H, C$H_3$CH$_2$O$_2$C), 1.85 (dd, $J$ = 7.8, 13.5 Hz, 1H, CC$H_2$CH), 2.20 (d, $J$ = 14.1 Hz, 1H, CC$H_2$C), 2.23 (dd, $J$ = 7.8, 13.5 Hz, 1H, CC$H_2$CH), 2.45 (d, $J$ = 14.1 Hz, 1H, CC$H_2$C), 2.96 (s, 3H, C$H_3$O), 3.57 (s, 3H, C$H_3$O$_2$C), 3.86 (dd, $J$ = 7.8, 7.8 Hz, 1H, CC$H$CH$_2$), 4.08–4.13 (m, 2H, CH$_3$C$H_2$O$_2$C), 5.42 (s, 1H, (PhSe)$_2$C$H$), 7.10–7.27 (m, 6H, Ph),

7.39–7.41 (m, 2H, Ph), 7.54–7.56 (m, 2H, Ph).

**1-{Bis[4-(trifluoromethyl)phenylseleno]methyl}-*c*-2-methoxycarbonyl-*t*-4-methoxy-*c*-4-methylcyclopentane-γ-1-carboxylic Acid Ethyl Ester (13l′-A):** $^1$H NMR (300 MHz, $CDCl_3$, rt): δ 1.20 (t, $J$ = 7.2 Hz, 3H, $CH_3CH_2O_2C$), 1.37 (s, 3H, $CH_3C$), 1.97 (dd, $J$ = 12.9, 12.9 Hz, 1H, $CCH_2CH$), 2.25 (d, $J$ = 14.7 Hz, 1H, $CCH_2C$), 2.32 (dd, $J$ = 6.3, 12.9 Hz, 1H, $CCH_2CH$), 2.60 (d, $J$ = 14.7 Hz, 1H, $CCH_2C$), 3.17 (s, 3H, $CH_3O$), 3.60 (s, 3H, $CH_3O_2C$), 3.77 (dd, $J$ = 6.3, 12.9 Hz, 1H, $CCHCH_2$), 4.01–4.12 (m, 2H, $CH_3CH_2O_2C$), 5.10 (s, 1H, $(p\text{-}CF_3C_6H_4Se)_2CH$), 7.16–7.61 (m, 8H, Ph). IR (NaCl): 2953, 1732, 1603, 1437, 1396, 1327, 1015, 910, 829, 735, 689 cm$^{-1}$. MS (CI): $m/z$ 706 ($M^+ + 1$, 16). Anal. Calcd for $C_{27}H_{28}O_5F_6Se_2$: C, 45.91; H, 4.28%. Found: C, 45.87; H, 4.06%.

**1-{Bis[4-(trifluoromethyl)phenylseleno]methyl}-*t*-2-methoxycarbonyl-*c*-4-methoxy-*t*-4-methylcyclopentane-γ-1-carboxylic Acid Ethyl Ester (13l′-B):** $^1$H NMR (300 MHz, $CDCl_3$, rt): δ 1.29 (s, 3H, $CH_3C$), 1.33 (t, $J$ = 7.2 Hz, 3H, $CH_3CH_2O_2C$), 1.94 (dd, $J$ = 6.6, 14.1 Hz, 1H, $CCH_2CH$), 2.08 (d, $J$ = 13.5 Hz, 1H, $CCH_2C$), 2.44 (ddd, $J$ = 2.1, 8.7, 14.1 Hz, 1H, $CCH_2CH$), 3.02 (dd, $J$ = 2.1, 13.5 Hz, 1H, $CCH_2C$), 3.10 (s, 3H, $CH_3O$), 3.64 (s, 3H, $CH_3O_2C$), 3.85 (dd, $J$ = 6.6, 8.7 Hz, 1H, $CCHCH_2$), 4.14–4.24 (m, 2H, $CH_3CH_2O_2C$), 5.45 (s, 1H, $(p\text{-}CF_3C_6H_4Se)_2CH$), 7.16–7.61 (m, 8H, Ph).

**1-{Bis[4-(trifluoromethyl)phenylseleno]methyl}-*t*-2-methoxycarbonyl-*t*-4-methoxy-*c*-4-methylcyclopentane-γ-1-carboxylic Acid Ethyl Ester (13l′-C):** $^1$H NMR (300 MHz, $CDCl_3$, rt): δ 1.27 (s, 3H, $CH_3C$), 1.39 (t, $J$ = 7.2 Hz, 3H, $CH_3CH_2O_2C$), 1.88 (dd, $J$ = 8.1, 14.4 Hz, 1H, $CCH_2CH$), 2.22–2.32 (m, 1H, $CCH_2CH$), 2.27 (d, $J$ = 13.8 Hz, 1H, $CCH_2C$), 2.52 (d, $J$ = 13.8 Hz, 1H, $CCH_2C$), 3.04 (s, 3H, $CH_3O$), 3.65 (s, 3H, $CH_3O_2C$), 3.74 (dd, $J$ = 6.3, 8.1 Hz, 1H, $CCHCH_2$), 3.97–4.15 (m, 2H, $CH_3CH_2O_2C$), 5.69 (s, 1H, $(p\text{-}CF_3C_6H_4Se)_2CH$), 7.16–7.61 (m, 8H, Ph).

**1-[Bis(phenylseleno)methyl]-*c*-2-cyano-*t*-4-methoxy-*c*-4-methylcyclopentane-γ-1-carboxylic Acid Ethyl Ester (13m-A):** $^1$H NMR (300 MHz, $CDCl_3$, rt): δ 1.29 (s, 3H, $CH_3C$), 1.34 (t, $J$ = 7.2 Hz, 3H, $CH_3CH_2O_2C$), 1.95 (dd, $J$ = 12.6, 13.2 Hz, 1H, $CCH_2CH$), 2.30 (ddd, $J$ = 2.1, 6.3, 13.2 Hz, 1H, $CCH_2CH$), 2.32 (dd, $J$ = 2.1, 14.7 Hz, 1H, $CCH_2C$), 2.42 (d, $J$ = 14.7 Hz, 1H, $CCH_2C$), 2.90 (s, 3H, $CH_3O$), 3.50 (dd, $J$ = 6.3, 12.6 Hz, 1H, $CCHCH_2$), 4.16–4.34 (m, 2H, $CH_3CH_2O_2C$), 4.58 (s, 1H, $(PhSe)_2CH$), 7.15–7.31 (m, 6H, Ph), 7.43–7.46 (m, 4H, Ph). $^{13}$C NMR (75 MHz, $CDCl_3$, rt): δ 13.9, 21.0, 38.6, 42.4, 45.6, 49.1, 54.7, 62.5, 64.6, 82.3, 119.6, 128.2, 128.3, 129.3, 134.2, 134.8, 172.2. IR (NaCl): 2977, 2245, 1718, 1578, 1478, 1439, 1369, 860, 746, 690 cm$^{-1}$. HRMS calcd for $C_{24}H_{27}NO_3Se_2$: 537.0322, found: 537.0311. Anal. Calcd for $C_{24}H_{27}NO_3Se_2$: C, 53.84; H, 5.08; N, 2.62%. Found: C, 53.50; H, 5.00; N, 2.85%.

**1-[Bis(phenylseleno)methyl]-*t*-2-cyano-*c*-4-methoxy-*t*-4-methylcyclopentane-γ-1-carboxylic Acid Ethyl Ester (13m-B):** $^1$H NMR (300 MHz, $CDCl_3$, rt): δ 1.23 (s, 3H, $CH_3C$), 1.33 (t, $J$ = 7.2 Hz, 3H, $CH_3CH_2O_2C$), 1.81 (dd, $J$ = 7.2, 14.1 Hz, 1H, $CCH_2CH$), 2.09 (d, $J$ = 14.4 Hz, 1H, $CCH_2C$), 2.41 (dd, $J$ = 1.8, 14.1 Hz, 1H, $CCH_2CH$), 2.56 (d, $J$ = 14.4 Hz, 1H, $CCH_2C$), 3.10 (s, 3H, $CH_3O$), 3.63 (dd, $J$ = 1.8, 7.2 Hz, 1H, $CCHCH_2$), 4.09–4.24 (m, 2H, $CH_3CH_2O_2C$), 4.74 (s, 1H, $(PhSe)_2CH$), 7.17–7.35 (m, 6H, Ph), 7.39–7.42 (m, 2H, Ph), 7.70–7.73 (m, 2H, Ph). $^{13}$C NMR (75 MHz, $CDCl_3$, rt): δ 14.0, 23.4, 38.8, 40.7, 43.8, 48.8, 51.3, 62.4, 63.7, 82.5, 120.0, 129.1, 129.2, 129.3, 134.8, 136.0, 171.8.

**1-[Bis(phenylseleno)methyl]-*t*-2-cyano-*t*-4-methoxy-*c*-4-methylcyclopentane-γ-1-carboxylic Acid Ethyl Ester (13m-C):** $^1$H NMR (300 MHz, $CDCl_3$, rt): δ 1.15 (t, $J$ = 7.2 Hz, 3H, $CH_3CH_2O_2C$), 1.32 (s, 3H, $CH_3C$), 1.73 (d, $J$ = 14.4 Hz, 1H, $CCH_2C$), 2.17–2.37 (m, 3H, $CCH_2CH$, $CCH_2C$), 3.10 (s, 3H, $CH_3O$), 3.70 (dd, $J$ = 5.4, 7.2 Hz, 1H, $CCHCH_2$), 3.96–4.06 (m, 2H, $CH_3CH_2O_2C$), 4.81 (s, 1H, $(PhSe)_2CH$), 7.15–7.31 (m, 6H, Ph), 7.36–7.38 (m, 2H, Ph), 7.65–7.68 (m, 2H, Ph). $^{13}$C NMR (75 MHz, $CDCl_3$, rt): δ 13.7, 21.9, 37.0 (2C), 44.3, 49.9, 51.5, 61.7, 62.9, 81.9, 120.5, 128.8, 129.0, 129.3, 135.2, 135.5, 171.0.

**1-{Bis[4-(trifluoromethyl)phenylseleno]methyl}-*c*-2-cyano-*t*-4-methoxy-*c*-4-methylcyclopentane-γ-1-carboxylic Acid Ethyl Ester (13m′-A):** $^1$H NMR (300 MHz, $CDCl_3$, rt): δ 1.33 (s, 3H, $CH_3C$), 1.38 (t, $J$ = 7.2 Hz, 3H, $CH_3CH_2O_2C$), 2.02 (dd, $J$ = 12.6, 12.6 Hz, 1H, $CCH_2CH$), 2.36–2.54 (m, 1H, $CCH_2CH$), 2.39 (dd, $J$ = 2.4, 14.7 Hz, 1H, $CCH_2C$), 2.47 (d, $J$ = 14.7 Hz, 1H, $CCH_2C$), 3.03 (s, 3H, $CH_3O$), 3.39 (dd, $J$ = 6.3, 12.6 Hz, 1H, $CCHCH_2$), 4.32 (q, $J$ = 7.2 Hz, 2H, $CH_3CH_2O_2C$), 4.75 (s, 1H, $(p\text{-}CF_3C_6H_4Se)_2CH$), 7.39–7.56 (m, 6H, Ph), 7.77 (m, 2H, Ph). $^{13}$C NMR (75 MHz, $CDCl_3$, rt): δ 13.9, 20.6, 39.1, 41.6, 47.3, 50.1, 54.2, 62.8, 64.1, 82.7, 119.4, 125.9, 134.0, 135.7, 172.1. IR (NaCl): 2982, 2245, 1732, 1603, 1470, 1448, 1327, 831, 733, 689 cm$^{-1}$. HRMS calcd for $C_{26}H_{25}F_6NO_3Se_2$: 673.0074, found: 673.0004. Anal. Calcd for $C_{26}H_{25}F_6NO_3Se_2$: C, 46.51; H, 3.75; N, 2.09%. Found: C, 46.06; H, 3.65; N, 2.19%.

**1-{Bis[4-(trifluoromethyl)phenylseleno]methyl}-*t*-2-cyano-*t*-4-methoxy-*c*-4-methylcyclopentane-γ-1-carboxylic Acid Ethyl Ester (13m′-C):** $^1$H NMR (300 MHz, $CDCl_3$, rt): δ 1.24 (t, $J$ = 7.2 Hz, 3H, $CH_3CH_2O_2C$), 1.28 (s, 3H, $CH_3C$), 1.73 (d, $J$ = 14.4 Hz, 1H, $CCH_2C$), 2.36–2.54 (m, 2H, $CCH_2CH$), 2.51 (d, $J$ = 14.1 Hz, 1H, $CCH_2C$), 3.11 (s, 3H, $CH_3O$), 3.81 (d, $J$ = 7.8 Hz, 1H, $CCHCH_2$), 4.11 (q, $J$ = 7.2 Hz, 2H, $CH_3CH_2O_2C$), 4.98 (s, 1H, $(p\text{-}CF_3C_6H_4Se)_2CH$), 7.35–7.56 (m, 8H, Ph). $^{13}$C NMR (75 MHz, $CDCl_3$, rt): δ 13.8, 22.0, 36.9, 38.9, 45.3, 49.6, 51.3, 61.7, 63.3, 81.9, 122.0, 125.8, 134.4, 135.5, 172.0.

***c*-2-Acetyl-1-[bis(phenylseleno)methyl]-*t*-4-methoxy-*c*-4-methylcyclopentane-γ-1-carboxylic Acid Ethyl Ester (13n-A):** $^1$H NMR (300 MHz, $CDCl_3$, rt): δ 1.18 (t, $J$ = 7.2 Hz, 3H, $CH_3CH_2O_2C$), 1.30 (s, 3H, $CH_3C$), 1.91 (dd, $J$ = 12.3, 12.3 Hz, 1H, $CCH_2CH$), 2.13 (ddd, $J$ = 2.1, 6.3, 12.3 Hz, 1H, $CCH_2CH$), 2.16 (s, 3H, $CH_3(O)C$), 2.31 (dd, $J$ = 2.1, 15.0 Hz, 1H, $CCH_2C$), 2.54 (d, $J$ = 15.0 Hz, 1H, $CCH_2C$), 2.97 (s, 3H, $CH_3O$), 3.86 (dd, $J$ = 6.3, 12.3 Hz, 1H, $CCHCH_2$), 3.93–4.14 (m, 2H, $CH_3CH_2O_2C$), 4.73 (s, 1H, $(PhSe)_2CH$), 7.18–7.26 (m, 6H, Ph), 7.40–7.43 (m, 4H, Ph). $^{13}$C NMR (75 MHz, $CDCl_3$, rt): δ 13.7, 21.7, 30.6, 42.1, 45.9, 49.2, 56.6, 57.1, 61.5, 64.3, 82.1, 128.2, 129.1, 134.1, 135.3, 173.0, 207.7. IR (NaCl): 2966, 1714, 1554, 1476, 1443, 1266, 738, 691 cm$^{-1}$. MS (CI): $m/z$ 553 ($M^+ + 1$, 3). HRMS calcd for $C_{25}H_{30}O_4Se_2$: 554.0474, found: 554.0479.

***t*-2-Acetyl-1-[bis(phenylseleno)methyl]-*c*-4-methoxy-*t*-4-methylcyclopentane-γ-1-carboxylic Acid Ethyl Ester (13n-B):** $^1$H NMR (300 MHz, $CDCl_3$, rt): δ 1.21 (s, 3H, $CH_3C$), 1.33 (t, $J$ = 7.2 Hz, 3H, $CH_3CH_2O_2C$), 1.77 (dd, $J$ = 6.0, 14.1 Hz, 1H, $CCH_2CH$), 2.01 (d, $J$ = 14.1 Hz, 1H, $CCH_2C$), 2.09 (s, 3H, $CH_3(O)C$), 2.34 (ddd, $J$ = 1.8, 9.0, 14.1 Hz, 1H, $CCH_2CH$), 2.98 (dd, $J$ = 1.8, 14.1 Hz, 1H, $CCH_2C$), 3.09 (s, 3H, $CH_3O$), 3.92 (dd, $J$ = 6.0, 9.0 Hz, 1H, $CCHCH_2$), 4.05–4.29 (m, 2H, $CH_3CH_2O_2C$), 5.25 (s, 1H, $(PhSe)_2CH$), 7.10–7.30 (m, 6H, Ph), 7.35–7.44 (m, 4H, Ph). $^{13}$C NMR (75 MHz, $CDCl_3$, rt): δ 14.1, 22.7, 31.4, 43.5, 47.4, 49.7, 50.1, 54.3, 61.5, 63.6, 82.1, 127.7, 128.2, 128.9, 129.0, 134.2, 135.3, 173.1, 211.0.

***t*-2-Acetyl-1-[bis(phenylseleno)methyl]-*t*-4-methoxy-*c*-4-methylcyclopentane-γ-1-carboxylic Acid Ethyl Ester (13n-C):**

$^1$H NMR (300 MHz, $CDCl_3$, rt): $\delta$ 1.23 (s, 3H, C$H_3$C), 1.39 (t, $J$ = 7.2 Hz, 3H, C$H_3$CH$_2$O$_2$C), 1.85 (dd, $J$ = 9.0, 14.4 Hz, 1H, CC$H_2$CH), 2.08 (d, $J$ = 14.4 Hz, 1H, CC$H_2$C), 2.08 (s, 3H, C$H_3$(O)C), 2.16 (d, $J$ = 14.4 Hz, 1H, CC$H_2$CH), 2.39 (d, $J$ = 14.4 Hz, 1H, CC$H_2$C), 2.94 (s, 3H, C$H_3$O), 3.52 (d, $J$ = 9.0 Hz, 1H, CC$H$CH$_2$), 4.05–4.29 (m, 2H, CH$_3$C$H_2$O$_2$C), 5.46 (s, 1H, (PhSe)$_2$C$H$), 7.10–7.28 (m, 6H, Ph), 7.35–7.44 (m, 4H, Ph). $^{13}$C NMR (75 MHz, $CDCl_3$, rt): $\delta$ 14.1, 24.4, 29.4, 42.1, 46.2, 49.5, 50.0, 57.4, 61.8, 65.5, 83.1, 127.9, 128.2, 129.1, 129.2, 134.7, 134.8, 173.6, 207.5.

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