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Palladium-catalyzed vinylselenation of allenes

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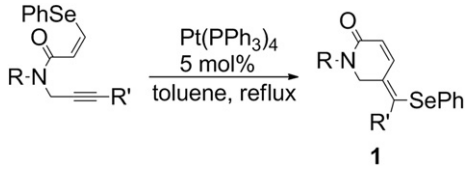
ABSTRACT

Pd(0)-catalyzed vinylselenation of allenes was found to proceed efficiently in the presence of $P(p\text{-}MeC_6H_4)_3$ as a ligand to afford the corresponding 2-selenomethyl-1,3-dienes. This reaction is highly regioselective and vinyl selenides added to the terminal double bond of the allenes exclusively to introduce the vinyl group at the inner carbon and the selenium moiety at the terminal carbon. The stereochemistry of the double bond of the vinyl selenides was perfectly retained.

1. Introduction

Simultaneous addition of carbon and heteroatom units to alkynes with the cleavage of carbon–heteroatom bond by transition metal complexes has attracted great interest in recent organic and organometallic chemistry.[1–5] This reaction proceeds in *cis*-selective manner to give multi-functionalized alkenyl heteroatom compounds. For such transformation, introduction of allyl,[1] alkynyl,[2] acyl,[3] and cyano[4] groups as carbon units has been well studied. However the introduction of vinyl group, i.e., addition of the vinyl–heteroatom bond across the triple bond, leading to 1,3-dienes was limited to the cases involving ring-expansion of three- or four-membered heterocyclic compounds, such as addition of silacyclopropenes,[5a] methylidenesiliranes,[5b] allene episulfides,[5c] and silacyclobutenes[5d] to alkynes. In these systems, ring strain of starting compounds may promote the cleavage of the vinyl–heteroatom bond by the metal catalyst.

We found that an anion stabilizing group on the β-position of acyclic vinyl sulfides and selenides enhanced oxidative addition to Pt(0) complex.[6] Based on this finding we disclosed Pt(0)-catalyzed intramolecular *cis*-vinylselenation of alkynes leading to effective construction of six-membered lactam framework **1** having a high degree of unsaturation (Scheme 1).[7]



Scheme 1. Vinylselenation of alkynes.

Allenes as well as alkynes have been shown to be versatile building blocks in organic synthesis during the past 20 years.[8] It is known that a variety of heteroatom compounds, such as organotin, -borane, -selenium species add to allenes in the presence of transition metal catalysts, where an allene double bond inserts into $R_3Sn–H$, $R_3Si–BR_2'$, and $RSe–SeR'$ bonds.[9] There are only fewer examples, however, of allene insertion into carbon–heteroatom bonds,[5a,b,10] and in these cases, vinylic heteroatom products were obtained as the major products rather than allylic compounds. We also disclosed the first example of carboselenation of allenes leading to allylic selenides **2**, where the selenol ester added to the terminal C–C double bond of the allene regioselectively to introduce the acyl moiety at the inner carbon and the SePh group at the terminal carbon (Scheme 2).[11,12]

These successful results led us to examine the reaction of vinyl selenides with allenes and found that vinylselenation of allenes took place when activated vinyl selenides were employed in the

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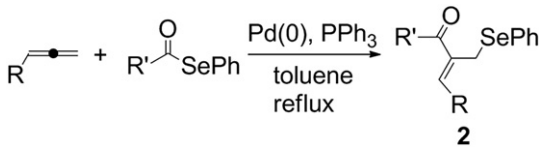
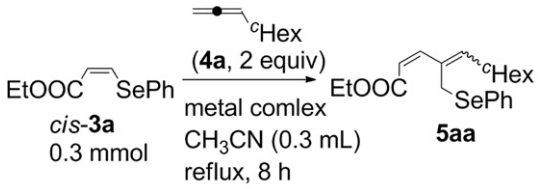


Scheme 2. Acylselenation of allenes.

presence of Pd(0) complex as a catalyst to form 1,3-diene framework.[13]

2. Results and discussion

Firstly, the reaction of *cis*-vinyl selenide **3a** having an ethoxycarbonyl group on the β-position of its vinyl moiety with cyclohexylallene **4a** was examined. Thus CH_3CN (0.3 mL) containing *cis*-**3a** (0.3 mmol), cyclohexylallene **4a** (2 equiv), and $Pt(PPh_3)_4$ (5 mol %) was heated at reflux for 8 h. As a result, only a trace amount of 1,3-diene **5aa** bearing an allyl selenide moiety was obtained.[14,15] On the contrary, when $Pd(dba)_2$ (5 mol %)–PPh_3 (10 mol %) was employed in place of $Pt(PPh_3)_4$, **5aa** was obtained in 90% NMR yield (Scheme 3, entry 1 in Table 1).[16]



metal complex	**5aa**, yield
$Pt(PPh_3)_4$ (5 mol%)	trace
$Pd(dba)_2$ (5 mol%) PPh_3 (10 mol%)	90%

Scheme 3. Vinylselenation of cyclohexylallene with vinyl selenide *cis*-**3a**.

Table 1
Phosphine ligand optimization for Pd(0)-catalyzed vinylselenation of cyclohexylallene with vinyl selenide *cis*-**3a**

Entry[a]	Phosphine	**5aa**, yield[b]	*E*/*Z*[c]
1	PPh_3	90%	17/83
2	PPh_3 (20 mol %)	77%	19/81
3	PPh_3 (50 mol %)	35%	13/87
4	P(*p*-FC_6H_4)	87%	18/82
5	P(*p*-$MeOC_6H_4$)	86%	14/86
6	P(*p*-MeC_6H_4)	94%(81%)	16/84(16/84)
7	P(*o*-$MeOC_6H_4$)	42%	6/94
8	$PMePh_2$	59%	11/89
9	P^nBu_3	13%	1/>99
10	P^cHex_3	3%	19/81

[a] Reaction conditions: *cis*-**3a** (0.3 mmol), cyclohexylallene **4a** (0.6 mmol), $Pd(dba)_2$ (5 mol %), ligand (10 mol %), CH_3CN (0.3 mL), reflux, 8 h.
[b] NMR yield (isolated yield).
[c] *E*/*Z* ratio was determined by ^1H NMR with regard to the double bond originally from the allene. Stereochemistry of vinyl selenide was retained in all entries.

Next, we carried out the reaction using other phosphines as the ligand. As can be seen from Table 1, similar results were obtained from the aromatic phosphines having either electron-donating or -withdrawing group at the *para* position (entries 1 and 4–6). The use of larger amounts of triphenyl phosphine reduced the yields of **5aa** (entries 2–3). Sterically hindered *ortho*-tolyl and aliphatic phosphines were less efficient (entries 7–10). In all entries, *Z*-isomer was obtained preferentially with the perfect retention of stereochemistry of the vinyl selenide employed.[17]

Table 2 summarizes the results obtained using several *cis*-vinyl selenides and allenes under optimized conditions. Phenylallene **4b**, 1,2-undecadiene **4c**, and benzyloxyallene **4d** afforded the expected 1,3-dienes **5ab**–**5ad** in moderate yields (entries 1–3).[18] Vinyl selenides having electron-donating and -withdrawing groups in the phenyl ring gave rise to 1,3-diene **5ba** and **5ca** in 78% and 72% yields, respectively (entries 4 and 5) indicating that aryl group on selenium exerts little effect on the yield. We then examined the effect of the substituent on the β-position of vinyl selenides and found that amide and sulfonyl groups also afforded the expected products in good yields (entries 6 and 7); however, in the case of phenyl group, almost all of **3f** was recovered and the expected 1,3-diene was not obtained probably due to the difficulty of oxidative addition of **3f** to palladium (entry 8). Interestingly selenide **3g** bearing a methoxycarbonyl group at the *ortho*-position on a phenyl ring also underwent arylselenation with **4a** to give **5ga** albeit in a moderate yield (35%) after 24 h (entry 9). Vinylthiolation of allene did proceed under similar conditions; however, the yield of the expected product was poor (15%).

To get information on the stereochemistry of this vinylselenation we run the reaction of *trans*-vinyl selenide **3a** with cyclohexylallene **4a** under similar conditions and the expected 1,3-diene **6aa** was obtained in 94% NMR yield (79% isolated yield) (Scheme 4). From the results of Table 1 and Eq. 4, the stereochemistry of the vinyl selenide was retained intact through out the reaction.

The diene products **3** include *cis*,*trans*-stereoisomers with respect to the other double bond arising from allenes. When the vinylselenation shown in entry 6 in Table 1 was stopped at 0.5 h, *E*/*Z* ratio increased to 9/91 (16% yield). The same reaction conducted at 70 °C gave only its *Z*-isomer in 26% yield as the sole detectable product by NMR. From these experiments *Z*-isomer was considered to be initially formed stereoselectively and isomerized to its *E*-isomer thermodynamically. DFT calculations by B3LYP/6-31G(d) showed *Z*-**5aa** was more stable by 0.6 kcal/mol than *E*-**5aa**.[19] These results do not conflict with the observed stereoselectivity.

A plausible reaction pathway is shown in Scheme 5. This catalytic process is initiated by oxidative addition of the *vinyl*–*Se* bond of vinyl selenide **3** to Pd(0), affording the *vinyl*–*Pd*–*Se* complex **A**. Insertion of allene into the *vinyl*–*Pd* bond via **B** generates σ-allylpalladium **C** and/or π-allylpalladium **D**, which undergoes reductive elimination to give **5**.

Finally, further transformation of the product was undertaken. Since allyl selenides are well known to lead to allyl alcohol upon treatment with oxidizing reagents, such as *m*CPBA,[20] we treated **5aa** with *m*CPBA and found that lactone **7** was produced in 82% yield probably via in situ formed allyl alcohol **8** (Scheme 6).

3. Conclusion

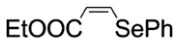
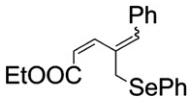
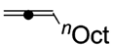
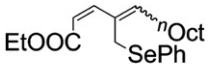
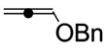
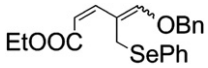
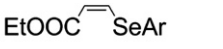
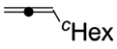
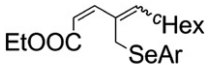
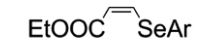
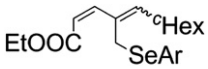
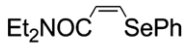
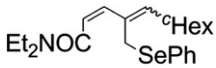
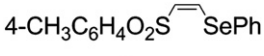
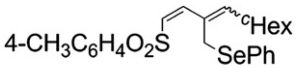
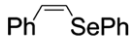
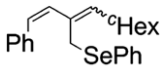
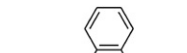
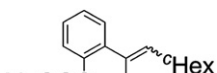
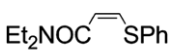
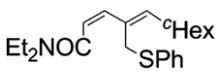
Vinyl selenides having an electron attracting group at the β-position add to the terminal double bond of allenes with excellent regioselectivity in the presence of Pd(0)-P(*p*-$MeC_6H_4)_3$ catalyst, producing functionalized 1,3-dienes having an allyl selenide moiety. This reaction was *Z*-selective with respect to the internal allene double bond and the stereochemistry of vinyl selenides were completely retained in the products. Oxidation of a product by *m*CPBA afforded a six-membered unsaturated lactone in a good yield.

4. Experimental section

4.1. Synthesis of vinyl selenide

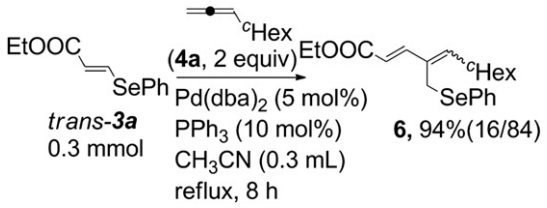
*4.1.1. (Z)-Ethyl 3-(2,6-dimethylphenylseleno)acrylate (**3b**): typical procedure A.* Into a 1000-mL flask equipped with a reflux condenser were placed di(2,6-dimehthyl)phenyl diselenide (60 mmol) and EtOH (440 mL) under N_2. After vigorous stirring and warming

Table 2
Vinylselenation of allenes

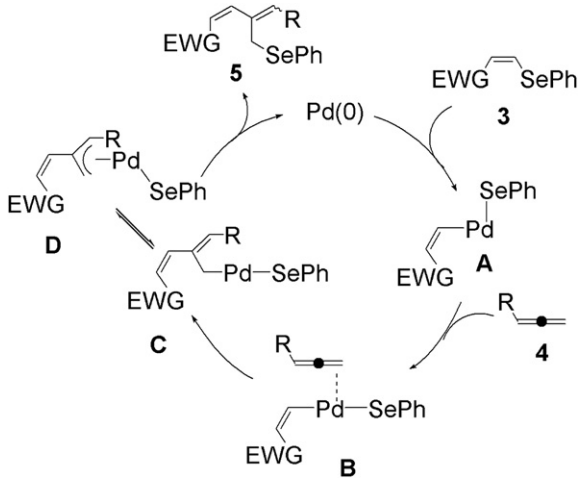
Entry[a]	Vinyl selenide	Allene	Product	Yield[b]	*E*/*Z*[c]
1[d]	 **3a**	 **4b**	 **5ab**	56%(48%)	68/32
2[e]	3a	 **4c**	 **5ac**	57%(40%)	53/47
3	3a	 **4d**	 **5ad**	61%(56%)	15/85
4	 **3b**: Ar = 2,6-$(CH_3)_2C_6H_3$	 **4a**	 **5ba**	78%(54%)	26/74
5	 **3c**: Ar = 4-$CF_3C_6H_4$	4a	 **5ca**	72%(54%)	27/73
6	 **3d**	4a	 **5da**	69%(44%)	8/92
7	 **3e**	4a	 **5ea**	70%(63%)	19/81
8	 **3f**	4a	 **5fa**	ND	ND
9[f]	 **3g**	4a	 **5ga**	35%(31%)	30/70
10	 **3h**	4a	 **5ha**	14%(5%)	0/100

[a] Reaction conditions: vinyl selenide **3** (0.3 mmol), allene **4** (0.6 mmol), $Pd(dba)_2$ (5 mol %), $P(p\text{-}MeC_6H_4)_3$ (10 mol %), CH_3CN (0.3 mL), reflux, 8 h.
[b] NMR yield (isolated yield).
[c] *E*/*Z* ratio was determined by ^1H NMR with regard to the double bond originally from the allene. Stereochemistry of vinyl selenide was retained in all entries.
[d] $Pd(PPh_3)_4$ (5 mol %), 4 h.
[e] $Pd(PPh_3)_4$ (5 mol %), 12 h.
[f] 24 h.

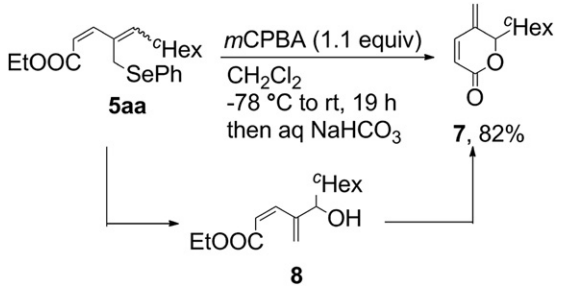
with water bath (ca. 40 °C), homogeneous red–orange solution was obtained. After cooling to room temperature, small portions of $NaBH_4$ were added successively until the solution turned slight yellow. To the solution was added ethyl propiolate (120 mmol) after gas emission ceased. Then the mixture was refluxed for 3 h under stirring (oil bath, 94 °C). EtOH was removed in vacuo and aqueous residue was obtained. Et_2O was poured into the flask and washed with satd NaCl aq. The combined organic phase was dried over



Scheme 4. Vinylselenation of cyclohexylallene with vinyl selenide *trans*-**3a**.



Scheme 5. A plausible reaction pathway.



Scheme 6. Further transformation to lactone.

anhydrous $MgSO_4$. The solvents of filtrate were removed in vacuo. Purification by silica gel column chromatography (hexane/Et_2O=7/1) afforded **3b** in 24% yield: slight-yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 1.34 (t, J=7.3 Hz, 3H), 4.28 (q, J=7.3 Hz, 2H), 6.37 (d, J=9.6 Hz, 1H), 7.12–7.21 (m, 3H), 7.38 (d, J=9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 24.6 (two peaks overlapped), 60.4, 117.0, 127.9 (two peaks overlapped), 129.1, 133.4, 142.5 (two peaks overlapped), 150.6, 167.6; NOE experiment for *Z*-isomer: irradiation for the vinylic proton doublet at δ 6.37 resulted in 12.6% enhancements of the signal at δ 7.38 (vinylic doublet).; IR (neat) 3408, 2917, 1687 (C=O), 1461, 1215, 907, 733, 650 cm^{-1}; MS (EI), m/z (%)=77 (22), 105 (98), 129 (38), 130 (27), 157 (36), 158 (29), 193 (22), 194 (50), 196 (99), 197 (23), 209 (26), 282 (50), 284 (M^+, 100). Anal. Calcd for $C_{13}H_{16}O_2Se$: C, 55.13; H, 5.69. Found: C, 55.01; H, 5.59.

*4.1.2. (Z)-Ethyl 3-(4-trifluoromethylphenylseleno)acrylate (**3c**).* 12%: white solid; mp 99.7–100.4 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.34 (t, J=7.3 Hz, 3H), 4.27 (q, J=7.3 Hz, 2H), 6.43 (d, J=9.2 Hz, 1H), 7.59 (d, J=8.2 Hz, 2H), 7.71–7.73 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 60.8, 117.7, 126.1 (two peaks overlapped), 131.2, 131.5, 133.1 (two peaks overlapped), 134.4, 147.7, 164.8; NOE experiment for *Z*-isomer: irradiation for the vinylic proton doublet at δ 6.43 resulted in 12.4% enhancements of the signal at δ 7.72 (vinylic doublet); IR (neat) 3019, 1692 (C=O), 1326, 1216, 757, 669 cm^{-1}; MS (EI), m/z (%)=145 (22), 199 (22), 225 (37), 251 (21), 279 (37), 322 (49), 324 (M^+, 100). Anal. Calcd for $C_{12}H_{11}F_3O_2Se$: C, 44.60; H, 3.43. Found: C, 44.21; H, 3.36.

*4.1.3. (Z)-N,N-Diethyl-3-phenylselenoacrylamide (**3d**).* Prepared according to the modified literature procedure.[7] 56% yield: slight-yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 1.53 (br s, 6H), 3.39 (q, J=7.1 Hz, 2H), 3.49 (q, J=7.1 Hz, 2H), 6.68 (d, J=8.8 Hz, 1H), 7.32–7.343 (m, 3H), 7.61–7.65 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.8, 15.2, 40.9, 42.2, 115.0, 127.7, 129.1, 133.2, 134.5, 147.0, 166.4; IR (neat) 2973, 1619 (C=O), 1577, 1478, 1429, 1260, 1144, 741, 693 cm^{-1}; MS (EI), m/z (%)=126 (89), 131 (36), 157 (40), 183 (23), 206 (26), 209 (48), 211 (96), 281 (50), 283 (M^+, 100); HRMS (EI) calcd for $C_{13}H_{17}NOSe$: 283.0475. Found: 283.0471.

*4.1.4. (Z)-1-(2-Phenylseleno)-vinylsulfonyl-4-methylbenzene (**3e**).* Prepared according to the modified literature procedure.[21] 57% yield: white needle crystal; mp 79.4–79.9 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 2.45 (s, 3H), 6.65 (d, J=9.6 Hz, 1H), 7.34–7.37 (m, 5H), 7.57 (d, J=8.1 Hz, 2H), 7.65 (d, J=9.6 Hz, 1H), 7.89 (d, J=8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 125.9, 127.2 (two peaks overlapped), 128.7, 129.5, 129.9 (two peaks overlapped), 131.3, 133.5 (two peaks overlapped), 138.0, 144.7, 145.2, 145.3; IR (neat) 2924, 1286, 1141, 1083, 691 cm^{-1}; MS (EI), m/z (%)=91 (42), 155 (28), 157 (56), 180 (50), 182 (100), 183 (24), 335 (36), 337 (7), 338 (M^+, 73). Anal. Calcd for $C_{15}H_{14}O_2SSe$: C, 53.41; H, 4.18. Found: C, 53.48; H, 4.13.

*4.1.5. Methyl 2-phenylselenobenzoate (**3g**).* Prepared according to the modified literature procedure.[22] 7% yield: slight-yellow solid; mp 69.5–69.8 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 3.97 (s, 3H), 6.91 (d, J=6.9 Hz, 1H), 7.14–7.72 (m, 7H), 8.05 (d, J=6.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.9, 52.3, 124.7, 127.1, 128.9, 129.0, 129.2, 129.8, 131.3, 132.6, 137.6 (two peaks overlapped), 140.5, 167.3; IR (neat) 1096, 907, 733, 650 cm^{-1}; MS (EI), m/z (%)=152 (30), 232 (36), 261 (34), 290 (49), 292 (M^+, 100). Anal. Calcd for $C_{14}H_{12}O_2Se$: C, 57.74; H, 4.15. Found: C, 57.66; H, 4.04.

*4.1.6. (Z)-N,N-Diethyl-3-phenylthioacrylamide (**3h**).* Prepared according to the modified literature procedure.[7] 82% yield: yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 1.17–1.23 (m, 6H), 3.38 (q, J=6.9 Hz, 2H), 3.48 (q, J=6.9 Hz, 2H), 6.22 (d, J=10 Hz, 1H), 7.15 (d, J=10 Hz, 1H), 7.27–7.52 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.3, 14.8, 40.6, 42.3, 112.2, 127.7, 129.1 (two peaks overlapped), 130.9 (two peaks overlapped), 138.0, 146.7, 165.8; IR (neat) 2973, 2917, 1622 (C=O), 1557, 1478, 1431, 1261, 1144, 747 cm^{-1}; MS (EI), m/z (%)=126 (45), 163 (100), 235 (M^+, 45); HRMS (EI) calcd for $C_{13}H_{17}NOS$: 235.1031. Found: 235.1029.

Vinyl selenides *cis*- and *trans*-**3a**[23] and **3f**[24] were prepared as reported.

4.2. Vinylselenation of allene

*4.2.1. 5-Cyclohexyl-4-phenylselenomethylpenta-2(Z),4-dienoate (**5aa**): typical procedure.* Into a 3-mL flask equipped with a reflux condenser were placed $Pd(dba)_2$ (0.015 mmol), P(*p*-MeC_6H_4)$_3$ (0.030 mmol) and CH_3CN (0.3 mL) at room temperature under N_2. The mixture was stirred for 10 min, added *cis*-vinyl selenide **3a** (0.3 mmol) and cyclohexylallene **4a** (0.6 mmol), and turned brown. After the mixture was refluxed for 8 h, filtered through the Celite pad with Et_2O, volatiles were removed in vacuo. After the *E*/*Z* ratio were determined by ^1H NMR (94% NMR yield, *E*/*Z*=16/84), the crude

product was purified by preparative recycling HPLC (eluted with $CHCl_3$) to afford ethyl 5-cyclohexyl-4-phenylselenomethylpenta-2(*Z*),4-dienoate (**5aa**) in 81% yield as a *E*/*Z* mixture: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89–1.70 (m, 13H), 1.94–2.02 (m, 1H), 3.82 (s, 2H, *E*), 3.98 (s, 2H, *Z*), 4.11–4.17 (q, 2H), 5.13 (d, *J*=9.6 Hz, 1H, *E*), 5.57 (d, *J*=9.6 Hz, 1H, *Z*), 5.71 (d, *J*=13 Hz, 1H, *Z*), 5.88 (d, *J*=12 Hz, 1H, *E*), 6.39 (d, *J*=13 Hz, 1H, *Z*), 6.72 (d, *J*=11 Hz, 1H, *E*), 7.23–7.26 (m, 3H), 7.46–7.48 (m, 2H, *E*), 7.52–7.55 (m, 2H, *Z*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1 (*E*), 14.2 (*Z*), 25.5 (*Z*), 25.6 (*E*), 25.7 (*Z*), 25.8 (*E*), 27.0 (*Z*), 32.3 (*E*), 32.3 (*Z*), 34.7 (*E*), 37.5 (*Z*), 37.9 (*E*), 60.2 (*E*), 60.2 (*Z*), 118.2 (*Z*), 121.3 (*E*), 127.1 (*E*), 127.3 (*Z*), 128.7 (*E*), 128.8 (*Z*), 130.3 (*E*), 131.1 (*Z*), 132.0 (*E*), 132.1 (*Z*), 134.0 (*E*), 134.2 (*Z*), 139.1 (*E*), 141.8 (*E*), 144.2 (*Z*), 145.6 (*Z*), 165.6 (*E*), 166.4 (*Z*); NOE experiment for *Z*-isomer: irradiation for the vinylic proton doublet at δ 6.39 resulted in 7.9% and 10.8% enhancements of the signal at δ 5.71 (vinylic doublet) and the signal at δ 5.57 (vinylic doublet) and irradiation of the allylic proton ($-CH_2SePh$) singlet at δ 3.98 resulted in 11.3%, 1.5%, and 3.0% enhancements of the signal at δ 1.94–2.02 (multiplet), the signal at δ 6.39 (vinylic doublet) and the signal at δ 7.52–7.55 (multiplet); NOE experiment for *E*-isomer: irradiation for the vinylic proton doublet at δ 6.72 resulted in 3.2% and 8.9% enhancements of the signal at δ 1.94–2.02 (multiplet) and the signal at δ 5.88 (vinylic doublet) and irradiation of the allylic proton ($-CH_2SePh$) singlet at δ 3.82 resulted in 7.8% and 2.2% enhancements of the signal at δ 5.13 (vinylic doublet) and the signal at δ 7.46–7.48 (multiplet); IR (neat) 2925, 2850, 1714 (C=O), 1526, 1626, 1447, 1175, 1032, 738, 691 cm^{-1}; MS (CI), *m*/*z* (%)=221 (84), 377 (52), 379 (M^++1, 100). Anal. Calcd for $C_{20}H_{26}O_2Se$: C, 63.65; H, 6.94. Found: C, 63.93; H, 6.82.

*4.2.2. Ethyl 5-phenyl-4-phenylselenomethylpenta-2(Z),4-dienoate (**5ab**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (m, 3H), 4.05 (s, 2H, *Z*), 4.14 (s, 2H, *E*), 4.12–4.81 (two q peaks overlapped, 2H), 5.87 (d, *J*=12 Hz, 1H, *E*), 5.99 (d, *J*=12 Hz, 1H, *Z*), 6.28 (s, 1H, *E*), 6.60 (d, *J*=14 Hz, 1H, *E*), 6.75 (s, 1H, *Z*), 6.76 (d, *J*=12 Hz, 1H, *Z*), 7.09–7.51 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2 (*E*), 14.3 (*Z*), 27.9 (*Z*), 35.5 (*E*), 60.4 (*E*), 60.5 (*Z*), 118.6, 120.5, 122.2, 127.1, 127.5, 128.0, 128.3, 128.6, 128.9, 129.2, 129.5, 130.1, 130.2, 132.5, 133.2, 133.3, 134.0 (two peaks overlapped), 134.5, 135.2, 135.5, 136.1, 136.3, 138.3, 140.1, 143.2, 144.0, 147.1, 166.3, 167.1, 167.2; NOE experiment for *Z*-isomer: irradiation for the vinylic proton doublet at δ 6.60 resulted in 14.5% and 8.6% enhancements of the signal at δ 5.87 (vinylic doublet) and the signal at δ 6.75 (vinylic singlet) and irradiation of the vinylic proton doublet at δ 5.87 resulted in 13.7% enhancements of the signal at δ 6.75 (vinylic singlet); NOE experiment for *E*-isomer: irradiation for the vinylic proton doublet at δ 6.28 resulted in 7.2% enhancements of the signal at δ 4.05 (allylic singlet) and irradiation of the allylic proton ($-CH_2SePh$) singlet at δ 4.05 resulted in 8.4% enhancements of the signal at δ 6.28 (vinylic singlet) and irradiation of the vinylic proton doublet at δ 5.99 resulted in 13.8% enhancements of the signal at δ 6.76 (vinylic doublet); IR (neat) 2979, 1714 (C=O), 1621, 1476, 1446, 1438, 1186, 1030, 739, 693 cm^{-1}; MS (CI), *m*/*z* (%)=215 (M^++1, 100); Anal. Calcd for $C_{20}H_{20}O_2Se$: C, 64.69; H, 5.43. Found: C, 64.63; H, 5.46.

*4.2.3. Ethyl 4-phenylselenomethyltrideca-2(Z),4-dienoate (**5ac**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86–0.90 (two t peaks overlapped, 2H), 1.19–1.31 (m, 16H), 1.87–1.91 (m, 2H), 3.83 (s, 2H, *Z*), 3.97 (s, 2H, *E*), 4.11–4.17 (two q peaks overlapped, 2H), 5.36 (t, *J*=7.3 Hz, 1H, *Z*), 5.71 (d, *J*=12 Hz, 1H, *E*), 5.77 (t, *J*=7.3 Hz, 1H, *E*), 5.90 (d, *J*=12 Hz, 1H, *Z*), 6.41 (d, *J*=13 Hz, 1H, *E*), 6.69 (d, *J*=12 Hz, 1H, *Z*), 7.23–7.54 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 14.2 (*Z*), 14.2 (*E*), 22.7, 26.9, 28.4, 29.0 (three peaks overlapped), 29.1 (*E*), 29.2, 29.4, 29.4 (*Z*), 31.9 (*E*), 34.6, 60.2 (*Z*), 60.3 (*E*), 118.2 (*E*), 121.6 (*Z*), 127.1 (*Z*), 127.3 (*E*), 128.8, 130.3 (*Z*), 130.4 (*E*), 131.9 (*Z*), 132.7 (*E*), 133.7 (*Z*), 133.9, 134.3 (*E*), 140.4, 141.8 (*Z*), 144.2 (*E*), 165.7 (*E*), 166.4 (*Z*); NOE experiment for *Z*-isomer: irradiation of the allylic proton ($-CH_2SePh$) singlet at δ 3.97 resulted in 2.6% enhancements of the signal at δ 1.87–1.91 (multiplet) and irradiation for the vinylic proton doublet at δ 6.41 resulted in 14.5% and 11.3% enhancements of the signal at δ 5.71 (vinylic doublet) and the signal at δ 5.77 (vinylic triplet); NOE experiment for *E*-isomer: irradiation of the allylic proton ($-CH_2SePh$) singlet at δ 3.83 resulted in 5.4% enhancements of the signal at δ 5.36 (vinylic triplet), irradiation of the vinylic proton triplet at δ 5.36 resulted in 1.9% and 6.0% enhancements of the signal at δ 1.87–1.91 (multiplet) and the signal at δ 3.83 (allylic singlet) and irradiation of the vinylic proton doublet at δ 6.69 resulted in 1.5% and 12.4% enhancements of the signal at δ 1.87–1.91 (multiplet) and the signal at δ 5.90 (vinylic doublet); IR (neat) 2957, 2925, 2854, 1717 (C=O), 1176, 1024 cm^{-1}; MS (CI), *m*/*z* (%)=251 (93), 407 (52), 409 (M^++1, 100); HRMS (CI) calcd for $C_{22}H_{32}O_2Se$: 408.1567. Found: 409.1642.

*4.2.4. Ethyl 5-benzyloxy-4-phenylselenomethylpenta-2(Z),4-dienoate (**5ad**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23–1.28 (t, 3H), 3.91 (s, 2H, *E*), 4.10–4.15 (q, 2H), 4.18 (s, 2H, *Z*), 4.71 (s, 2H, *E*), 4.74 (s, 2H, *Z*), 5.59 (d, *J*=13 Hz, 1H, *Z*), 5.77 (d, *J*=13 Hz, 1H, *E*), 6.04 (s, 1H, *E*), 6.12 (d, *J*=13 Hz, 1H, *Z*), 6.79 (d, *J*=13 Hz, 1H, *E*), 6.86 (s, 1H, *Z*), 7.16–7.56 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 24.1 (*Z*), 30.0 (*E*), 60.0 (*Z*), 60.1 (*E*), 72.7 (*E*), 74.9 (*Z*), 112.4 (*E*), 114.6 (*Z*), 115.3 (*Z*), 117.8 (*E*), 126.8, 127.1, 127.4 (two peaks overlapped), 128.2 (two peaks overlapped), 128.5 (two peaks overlapped), 128.6, 129.0, 129.2, 130.7, 132.0, 132.1, 133.8 (two peaks overlapped), 134.5, 134.8, 136.0, 136.2, 140.1 (*Z*), 142.1 (*E*), 150.3 (*E*), 155.3 (*Z*), 166.7; NOE experiment for *Z*-isomer: irradiation of the vinylic proton doublet at δ 6.12 resulted in 14.3% and 13.1% enhancements of the signal at δ 5.77 (vinylic doublet) and the signal at 6.86 (vinylic singlet) and irradiation for the vinylic proton singlet at δ 6.86 resulted in 17.4% and 13.0% enhancements of the signal at δ 4.74 (benzylic singlet) and the signal at δ 6.12 (vinylic doublet); NOE experiment for *E*-isomer: irradiation of the allylic proton ($-CH_2SePh$) singlet at δ 3.91 resulted in 7.2% enhancements of the signal at δ 6.04 (vinylic singlet), irradiation of the vinylic proton singlet at δ 6.04 resulted in 5.8% and 8.6% enhancements of the signal at δ 3.91 (allylic singlet) and the signal at δ 4.71 (benzylic singlet) and irradiation of the vinylic proton doublet at δ 6.79 resulted in 11.7% enhancements of the signal at δ 5.77 (vinylic doublet); IR (neat) 2980, 1722 (C=O), 1161, 1022, 737, 696 cm^{-1}; MS (CI), *m*/*z* (%)=155 (69), 245 (100), 321 (40), 403 (M^++1, 11); HRMS (CI) calcd for $C_{21}H_{22}O_3Se$: 402.0734. Found: 403.0804.

*4.2.5. Ethyl 5-cyclohexyl-4-(2,6-dimethylphenylselenomethyl)penta-2(Z),4-dienoate (**5ba**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.79–1.57 (m, 13H), 1.77–1.85 (m, 1H, *Z*), 1.94–1.96 (m, 1H, *E*), 2.52 (s, 6H, *E*), 2.56 (s, 6H, *Z*), 3.62 (s, 2H, *E*), 3.75 (s, 2H, *Z*), 4.10–4.16 (m, 2H), 4.93 (d, *J*=9.6 Hz, 1H, *E*), 5.51 (d, *J*=10 Hz, 1H, *Z*), 5.70 (d, *J*=13 Hz, 1H, *Z*), 5.84 (d, *J*=12 Hz, 1H, *E*), 6.40 (d, *J*=13 Hz, 1H, *Z*), 6.71 (d, *J*=12 Hz, 1H, *E*), 7.04–7.11 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 24.6 (two peaks overlapped), 25.8 (two peaks overlapped), 25.8, 32.2, 32.4 (two peaks overlapped), 37.7, 60.2, 117.9, 121.0, 127.4 (two peaks overlapped), 128.1, 128.4, 131.9, 143.6, 144.7, 145.2, 166.4; NOE experiment for *Z*-isomer: irradiation for the vinylic proton doublet at δ 5.51 resulted in 11.4% enhancements of the signal at δ 6.40 (vinylic doublet) and irradiation of the vinylic proton doublet at δ 6.40 resulted in 11.1% and 15.2% enhancements of the signal at δ 5.51 (vinylic doublet) and the signal at δ 5.70 (vinylic doublet); NOE experiment for *E*-isomer: irradiation for the vinylic proton doublet at δ 4.93 resulted in 5.0% enhancements of the signal at δ 3.62 (allylic singlet) and irradiation of the vinylic proton doublet at δ 6.71 resulted in 3.0% and 12.7% enhancements of the signal at δ 1.94–1.96 (multiplet) and the signal at δ 5.84 (vinylic doublet); IR (neat) 2924, 2849, 1716 (C=O), 1616, 1448, 1176, 1029, 769 cm^{-1}; MS (CI), *m*/*z* (%)=221 (83), 405 (51), 407

(M^++1, 100). Anal. Calcd for $C_{22}H_{30}O_2Se$: C, 65.17; H, 7.46. Found: C, 66.16; H, 7.37.

*4.2.6. Ethyl 5-cyclohexyl-4-(4-trifluoromethylphenylselenomethyl) penta-2(Z),4-dienoate (**5ca**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88–1.63 (m, 13H), 1.97–2.05 (m, 1H), 3.91 (s, 2H, *E*), 4.07 (s, 2H, *Z*), 4.09–4.17 (m, 2H), 5.24 (d, *J*=9.6 Hz, 1H, *E*), 5.61 (d, *J*=9.6 Hz, 1H, *Z*), 5.72 (d, *J*=13 Hz, 1H, *Z*), 5.89 (d, *J*=12 Hz, 1H, *E*), 6.37 (d, *J*=13 Hz, 1H, *Z*), 6.68 (d, *J*=12 Hz, 1H, *E*), 7.46–7.63 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 25.5 (two peaks overlapped), 25.7, 26.9, 32.3, 32.4 (two peaks overlapped), 37.7, 60.4, 118.6, 125.5, 125.6, 126.1, 130.6, 133.1, 133.5 (two peaks overlapped), 144.1, 146.5, 190.9; NOE experiment for *Z*-isomer: irradiation for the vinylic proton doublet at δ 5.61 resulted in 10.8% enhancements of the signal at δ 6.37 (vinylic doublet) and irradiation of the vinylic proton doublet at δ 6.37 resulted in 10.9% and 14.7% enhancements of the signal at δ 5.61 (vinylic doublet) and the signal at δ 5.72 (vinylic doublet); NOE experiment for *E*-isomer: irradiation for the vinylic proton doublet at δ 5.24 resulted in 5.0% enhancements of the signal at δ 3.91 (allylic singlet) and irradiation of the vinylic proton doublet at δ 6.68 resulted in 0.8% and 12.6% enhancements of the signal at δ 1.97–2.05 (multiplet) and the signal at δ 5.89 (vinylic doublet); IR (neat) 3409, 2925, 1467, 1383, 1326, 907, 733, 651 cm^{-1}; MS (CI), *m*/*z* (%)=221 (75), 444 (20), 445 (52), 447 (M^++1, 100); HRMS (CI) calcd for $C_{21}H_{25}F_3O_2Se$: 446.0972. Found: 447.1049.

*4.2.7. 5-Cyclohexyl-4-phenylselenomethyl-penta-2(Z),4-dienoic acid diethylamide (**5da**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91–1.58 (m, 16H), 1.95 (m, 1H), 3.34–3.43 (m, 4H), 3.80 (s, 2H, *E*), 3.89 (s, 2H, *Z*), 5.10 (d, *J*=9.5 Hz, 1H, *E*), 5.53 (d, *J*=9.6 Hz, 1H, *Z*), 5.83 (d, *J*=13 Hz, 1H, *Z*), 6.03 (d, *J*=13 Hz, 1H, *E*), 6.11 (d, *J*=13 Hz, 1H, *Z*), 6.47 (d, *J*=13 Hz, 1H, *E*), 7.23–7.56 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.9, 13.9, 25.6, 25.8, 26.0, 30.9, 32.5, 37.5, 39.1, 42.8, 121.3, 127.1, 128.8, 129.0, 129.2, 131.0, 132.0, 132.1, 136.0, 144.3, 167.9; NOE experiment for *Z*-isomer: irradiation of the allylic proton ($-CH_2SePh$) singlet at δ 3.89 resulted in 7.9% enhancements of the signal at δ 1.95 (multiplet), irradiation of the vinylic proton doublet at δ 5.53 resulted in 11.5% enhancements of the signal at δ 6.11 (vinylic doublet) and irradiation for the vinylic proton singlet at δ 6.11 resulted in 12.9% and 13.7% enhancements of the signal at δ 5.53 (vinylic doublet) and the signal at δ 5.83 (vinylic doublet); NOE experiment for *E*-isomer: irradiation of the vinylic proton singlet at δ 5.11 resulted in 4.9% enhancements of the signal at δ 3.80 (allylic singlet) and irradiation of the vinylic proton doublet at δ 6.03 resulted in 12.0% enhancements of the signal at δ 6.47 (vinylic doublet); IR (neat) 2924, 2849, 1628 (C=O), 1475, 1436, 1264, 738, 691 cm^{-1}; MS (CI), *m*/*z* (%)=248 (60), 250 (57), 404 (53), 406 (M^++1, 100); HRMS (CI) calcd for $C_{22}H_{31}NOSe$: 405.1571. Found: 406.1643.

*4.2.8. 1-(4-Cyclohexyl-3-phenylselenomethylbuta-1(Z),3-dienyl)sulfonyl-4-methylbenzene (**5ea**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80–1.65 (m, 10H), 1.95–2.03 (m, 1H), 2.38 (s, 3H), 3.68 (s, 2H, *Z*), 3.75 (s, 2H, *E*), 5.10 (d, *J*=9.6 Hz, 1H, *E*), 5.76 (d, *J*=9.6 Hz, 1H, *Z*), 6.26 (d, *J*=12 Hz, 1H, *Z*), 6.36 (d, *J*=12 Hz, 1H, *E*), 6.69 (d, *J*=12 Hz, 1H, *Z*), 6.80 (d, *J*=12 Hz, 1H, *E*), 7.20–7.36 (m, 5H), 7.44–7.52 (m, 2H), 7.74–7.79 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 25.6, 25.8, 27.7, 32.1, 32.3, 37.8, 127.3, 127.5, 127.6, 127.6 (two peaks overlapped), 128.9, 129.0 (two peaks overlapped), 129.6 (two peaks overlapped), 129.8, 130.1, 134.1 (two peaks overlapped), 134.1, 144.1, 144.6; NOE experiment for *Z*-isomer: irradiation for the vinylic proton doublet at δ 6.26 resulted in 14.9% enhancements of the signal at δ 6.69 (vinylic doublet) and irradiation of the vinylic proton doublet at δ 6.69 resulted in 1.7%, 3.5% and 16.0% enhancements of the signal at δ 3.68 (allylic singlet), the signal at δ 5.76 (vinylic doublet) and the signal at δ 6.26 (vinylic doublet); NOE experiment for *E*-isomer: irradiation for the vinylic proton doublet at δ 5.10 resulted in 5.9% enhancements of the signal at δ 3.75 (allylic singlet) and irradiation of the vinylic proton doublet at δ 6.80 resulted in 15.8% enhancements of the signal at δ 3.36 (vinylic doublet); IR (neat) 2925, 2851, 1313, 1146, 1086, 909, 732 cm^{-1}; MS (CI), *m*/*z* (%)=147 (23), 303 (90), 304 (20), 305 (94), 458 (20), 459 (51), 461 (M^++1, 100); HRMS (CI) calcd for $C_{24}H_{28}O_2SSe$: 460.0975. Found: 461.1056.

*4.2.9. Methyl 2-(2-cyclohexyl-1-phenylselenomethylvinyl)benzoate (**5ga**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85–1.79 (m, 10H), 2.19–2.26 (m, 1H), 3.81 (s, 3H), 3.97 (s, 2H), 5.17 (d, *J*=10 Hz, 1H, *Z*), 5.22 (d, *J*=10 Hz, 1H, *E*), 7.16–7.93 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.8 (two peaks overlapped), 25.9, 30.3, 32.9 (two peaks overlapped), 37.7, 38.0, 51.8, 126.9, 126.9, 127.1, 128.8, 128.9, 130.0, 131.2, 131.4, 131.8, 133.1, 133.5, 135.0, 138.1, 168.2; IR (neat) 2924, 2849, 1725 (C=O), 1446, 1289, 1254, 1081, 734, 690 cm^{-1}; MS (EI), *m*/*z* (%)=225 (34), 257 (100), 414 (M^+, 1). Anal. Calcd for $C_{23}H_{26}O_2Se$: C, 66.82; H, 6.34. Found: C, 66.90; H, 6.21.

*4.2.10. 5-Cyclohexyl-4-phenylthiomethylpenta-2(Z),4(Z)-dienoic acid diethylamide (**5ha**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95–1.60 (m, 16H), 2.08 (m, 1H), 3.29–3.34 (q, *J*=14 Hz, 2H), 3.36–3.41 (q, *J*=14 Hz, 2H), 3.88 (s, 2H), 5.60 (d, *J*=9.6 Hz, 1H), 5.84 (d, *J*=13 Hz, 1H), 6.12 (d, *J*=13 Hz, 1H), 7.15–7.34 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8, 13.9, 25.6, 25.8, 32.6, 32.7, 37.6, 39.1, 42.9, 53.5, 121.5, 126.3, 128.6, 128.7, 129.8, 130.3, 131.8, 135.7, 136.7, 145.1, 145.1, 168.0; IR (neat) 2925, 2850, 1619 (C=O), 1439, 1264, 1145, 749 cm^{-1}; MS (CI), *m*/*z* (%)=248 (21), 358 (M^++1, 100); HRMS (CI) calcd for $C_{22}H_{31}NOS$: 357.2126. Found: 358.2195.

*4.2.11. Ethyl 5-cyclohexyl-4-phenylselenomethylpenta-2(E),4-dienoate (**6**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93–1.74 (m, 13H), 2.01–2.05 (m, 1H), 3.61 (s, 2H, *E*), 3.72 (s, 2H, *Z*), 4.18–4.27 (q, 2H), 5.36 (d, *J*=10 Hz, 1H, *E*), 5.75 (d, *J*=10 Hz, 1H, *Z*), 5.91 (d, *J*=16 Hz, 1H, *Z*), 6.06 (d, *J*=16 Hz, 1H, *E*), 7.19–7.29 (m, 3H), 7.47–7.63 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 23.4, 25.4, 25.7, 32.2 (two peaks overlapped), 32.7, 38.0, 60.2, 116.6, 127.6, 128.9, 129.0 (two peaks overlapped), 131.3, 134.4 (two peaks overlapped), 147.1, 149.7, 167.3; NOE experiment for *Z*-isomer: irradiation for the vinylic proton doublet at δ 5.75 resulted in 7.9% enhancements of the signal at δ 7.24 (vinylic doublet) and irradiation of the allylic proton ($-CH_2SePh$) singlet at δ 3.72 resulted in 12.6% enhancements of the signal at δ 5.91 (vinylic doublet); NOE experiment for *E*-isomer: irradiation for the vinylic proton doublet at δ 5.35 resulted in 5.4% enhancements of the signal at δ 3.61 (allylic singlet) and irradiation of the vinylic proton doublet at δ 6.06 resulted in 3.2% enhancements of the signal at 3.61 (singlet); IR (neat) 2925, 2979, 2925, 2850, 1711 (C=O), 1626, 1476, 1447, 1310, 1284, 1268, 1246, 1175, 1118, 1038, 979, 739, 691 cm^{-1}; MS (CI), *m*/*z* (%)=221 (39), 377 (52), 379 (M^++1, 100). Anal. Calcd for $C_{20}H_{26}O_2Se$: C, 63.65; H, 6.94. Found: C, 63.94; H, 6.84.

*4.2.12. Transformation of **5aa** to pyran-2-one (**7**).* Into a 3-mL flask were placed **5aa** (0.2 mmol) and CH_2Cl_2 (1.5 mL) at room temperature under N_2. A solution of *m*-CPBA (0.22 mmol) in 1.1 mL of CH_2Cl_2 was added dropwise at −78 °C (acetone/CO_2) and the mixture was stirred in the same temperature for 1 h. After the mixture was stirred at room temperature for 18 h, saturated $NaHCO_3$ aq and CH_2Cl_2 were added and washed with brine, and dried over anhydrous $MgSO_4$. Evaporation of the solvent and purification by preparative recycling HPLC (eluted with $CHCl_3$) afforded 6-cyclohexyl-5-methylene-5,6-dihydropyran-2-one (**7**) in 82% yield as slight yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04–1.28 (m, 5H), 1.62–1.85 (m, 6H), 4.82 (d, *J*=5.5 Hz, 2H), 5.25 (s, 1H), 5.46 (s, 1H), 5.91 (d, *J*=10 Hz, 1H), 6.96 (d, *J*=10 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.9, 27.4, 29.1, 43.9, 75.2, 119.2 (two peaks overlapped), 137.1, 142.8, 143.6, 163.2 (two peaks overlapped); IR (neat) 2928,

2853, 1711 (C=O), 1227, 1122, 1031, 834 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{16}O_2$: 192.1150. Found: 192.1142.

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Supplementary data

Experimental details and characterization data of all new compounds. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2012.10.003. These data include MOL files and InChIKeys of the most important compounds described in this article.

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14. As for solvent, CH_3CN gave the best result. The NMR yields of **5aa** using other solvents under identical conditions were as follows: toluene (80%), benzene (75%), DMSO (74%), NMP (61%), DMA (59%), PhCN (48%), and DMF (30%).
15. As for the amount of allene, when 1 equiv of allene was employed the yield of **5aa** was diminished probably due to the oligomerization of the allene.
16. When $Ni(COD)_2$ (5 mol %)-$P(p\text{-}MeC_6H_4)_3$ (10 mol %) was employed as catalyst, the present transformation did not proceed at all.
17. The structures of the products were confirmed by NOE experiments. See Experimental section for details.
18. In entries 1 and 2, when $Pd(dba)_2$-$P(p\text{-}MeC_6H_4)_3$ was employed the products were obtained albeit in lower yields.
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