Reactions of *gem*-Aryl-Disubstituted Methylenecyclopropanes with Diaryl Diselenide in the Presence of Iodosobenzene Diacetate

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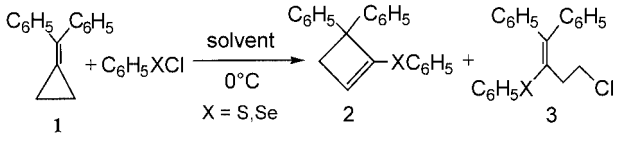
Keywords: Cyclobutyl cation / Iodosobenzene diacetate / MCPs / β-Proton elimination / Ring opening / Selenium

The reaction of *gem*-aryl-disubstituted methylenecyclopropanes **1** with diaryl diselenide produced the corresponding ring-opened products 1,2-bis(arylselanyl)-3,3-diarylcyclobut-1-ene **4** in the presence of iodosobenzene diacetate in moderate-to-good yields under mild conditions. The further transformation of **4** in the presence of MCPBA has also been examined.

Introduction

Methylenecyclopropanes (MCPs) **1** are highly strained but readily accessible molecules that serve as useful building blocks in organic synthesis. MCPs **1** undergo a variety of ring-opening reactions because the relief of ring strain provides a potent thermodynamic driving force.[1]

Transition-metal (such as Pd, Rh, Ru, and Pt)-catalyzed reactions of MCPs **1** with various reactants have attracted much attention.[2,3] In the field of Lewis acid catalyzed ring-opening reactions of MCPs **1**, we have found that the ring of MCPs **1** can be opened by alcohols and other nucleophiles in a novel manner to give the corresponding homoallylic derivatives in good yields under mild conditions.[4] Previously, we reported that the reaction of *gem*-aryl-disubstituted methylenecyclopropanes **1** with phenylsulfenyl chloride or phenylselanyl chloride gives (cyclobut-1-enylsulfanyl)benzene or (cyclobut-1-enylselanyl)benzene **2** along with ring-opened product **3** in good total yields at 0 °C in various solvents (Scheme 1).[5] In this paper we wish to report the reactions of *gem*-aryl-disubstituted methylenecyclopropanes **1** with diaryl diselenides which give 1,2-bis(arylselanyl)-3,3-diarylcyclobut-1-enes **4** in the presence of iodosobenzene diacetate [$PhI(OAc)_2$] in moderate-to-good yields under mild conditions.



Scheme 1

Results and Discussion

We examined the reaction of MCP **1a** with diphenyl diselenide in a variety of solvents in the presence of iodosobenzene diacetate at 35–40 °C.[6] The results are summarized in Table 1. It can be seen that the nature of the solvent significantly affected the reaction products. In acetonitrile, 1,2-dichloroethane (DCE), and dichloromethane (DCM), 1,2-bis(phenylselanyl)-3,3-diphenylcyclobut-1-ene **4a** was obtained as the major product in 60, 73, and 60% isolated yields, respectively, (Table 1, entries 1, 4, and 5). In THF, β-hydroxyalkyl phenyl selenide **5a**, derived from ambient water, was obtained as the major product in 43% yield along with (cyclobut-1-enylselanyl)benzene **2a** in 12% and **4a** in 10% yields (Table 1, entry 2). In toluene, **2a** was formed as the major product in 40% yield along with **4a** and **5a** in 10 and 30% yields, respectively (Table 1, entry 3). With other organic oxidants such as $PhI[OC(O)CF_3]_2$, 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), chloramines-T,[7] and $(NH_4)_2S_2O_8$[6b] under identical conditions, either no reaction occurred or **4a** was formed in low yields. Metallic oxidants such as $Cu(OAc)_2$, $Co(acac)_2$, MnO_2, and $FeCl_3$ showed no catalytic activities in this reaction. By using $[Mn(OAc)_3]\cdot 2H_2O$ and Ag_2O as oxidants, **2a** was obtained in 50 and 52% yields, respectively (Scheme 2). With ceric ammonium nitrate (CAN) as the oxidant in methanol,[8] β-methoxyalkyl phenyl selenide **6a** was exclusively formed in good yield (Scheme 2).

On the basis of the above results, **4a** was obtained in good yield with iodosobenzene diacetate as the oxidant in DCE at 35–40 °C. In order to suppress the formation of

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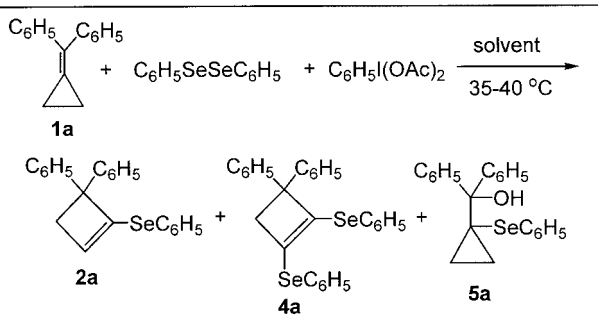
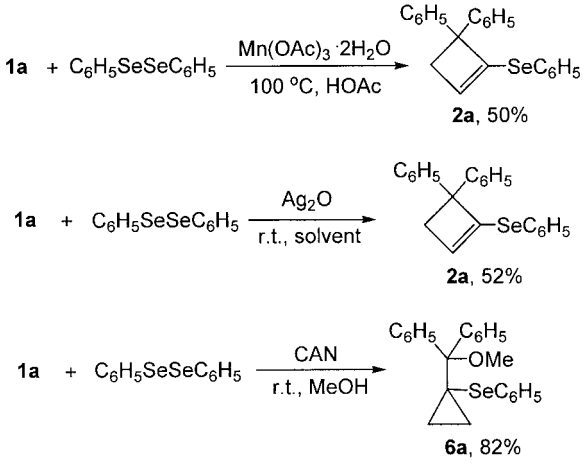
Table 1. Reaction of MCP **1a** with diphenyl diselenide in the presence of iodosobenzene diacetate in a variety of solvents



Entry	Solvent	Time/h	Yield/[%][a] 2a	Yield/[%][a] 4a	Yield/[%][a] 5a
1	MeCN	30	trace	60	trace
2	THF	70	12	10	43
3	$C_6H_5CH_3$	70	40	10	30
4	$ClCH_2CH_2Cl$	40	trace	73	trace
5	CH_2Cl_2	40	trace	60	trace

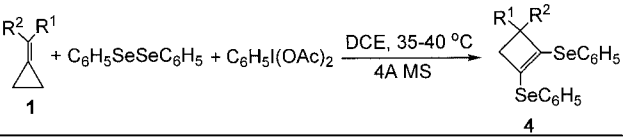
[a] Isolated yields; from **1a** (0.3 mmol, 1 equiv.), $C_6H_5SeSeC_6H_5$ (0.33 mmol, 1.1 equiv.), $C_6H_5I(OAc)_2$ (0.66 mmol, 2.2 equiv.), and 4-Å molecular sieves (300 mg).



Scheme 2

byproduct **5a**, we added 4-Å molecular sieves (300 mg for 0.3 mmol of MCPs **1**) to the reaction solution to remove the ambient moisture in the reactions of a variety of MCPs **1** with diphenyl diselenide in the presence of iodosobenzene diacetate in DCE. Therefore, we carried out this reaction by stirring MCP **1**, PhSeSePh, 4-Å molecular sieves, and DCE for 1 hour at room temperature and then iodosobenzene diacetate was added. The reaction mixture was then stirred for 20 hours at 35–40 °C. The results are summarized in Table 2; in many cases, 1,2-bis(arylselanyl)-3,3-diphenylcyclobut-1-enes **4** were obtained as the sole product in moderate-to-good yields without the formation of **5**. For MCPs **1e**–**g** bearing an electron-donating group on the benzene ring, these reactions produced the ring-opened products **7** (acetates) in 10–27% yields (Table 2, entries 5–7, and Figure 1).

Table 2. Reaction of MCPs **1** with diphenyl diselenide in the presence of iodosobenzene diacetate in DCE with 4-Å molecular sieves



Entry	R^1	R^2	1	Yield/[%][a] 4	7
1	C_6H_5	C_6H_5	**1a**	**4a**, 74	–
2	*p*-FC_6H_4	*p*-FC_6H_4	**1b**	**4b**, 78	–
3	*p*-ClC_6H_4	*p*-ClC_6H_4	**1c**	**4c**, 42	–
4	C_6H_5	o-ClC_6H_4	**1d**	**4d**, 69	–
5	*p*-MeC_6H_4	*p*-MeC_6H_4	**1e**	**4e**, 50	**7a**, 10[b]
6	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	**1f**	**4f**, 42	**7b**, 27[b]
7	C_6H_5	*p*-$MeOC_6H_4$	**1g**	**4g**, 40	**7c**, 13[b]

[a] Isolated yields; from **1** (0.3 mmol, 1 equiv.), $C_6H_5SeSeC_6H_5$ (0.33 mmol, 1.1 equiv.), $C_6H_5I(OAc)_2$ (0.66 mmol, 2.2 equiv.), and 4-Å molecular sieves (300 mg). [b] Acetates **7** were formed as byproducts (Figure 1).

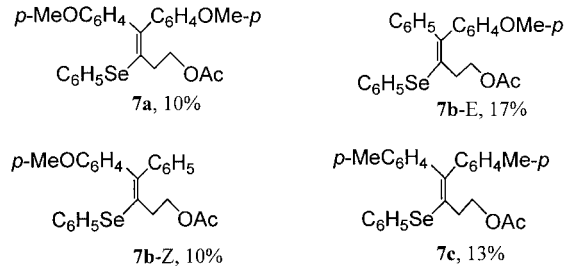


Figure 1

The structures of the reaction products were determined by ^1H and ^{13}C NMR spectroscopy and HRMS or microanalysis (see the Supporting Information). The configuration of the double bond in compound **7b** was determined by NOESY spectroscopy (see the Supporting Information). The crystal structure of the four-membered ring product **4a** was identified by X-ray diffraction and is shown in Figure 2.[9]

Since the structure of 1,2-bis(arylselanyl)-3,3-diarylcyclobut-1-enes **4** is novel for the organic chemist, we attempted to synthesize this kind of compound by using other diaryl diselenides. In the reactions of MCPs **1** with bis(*p*-methylphenyl) diselenide and bis(*p*-methoxyphenyl) diselenide[10] in the presence of iodosobenzene diacetate, the corresponding 1,2-bis(arylselanyl)-3,3-diarylcyclobut-1-enes **4** were obtained in similar yields under identical conditions. The results are summarized in Table 3. With MCP **1e**, this reac-

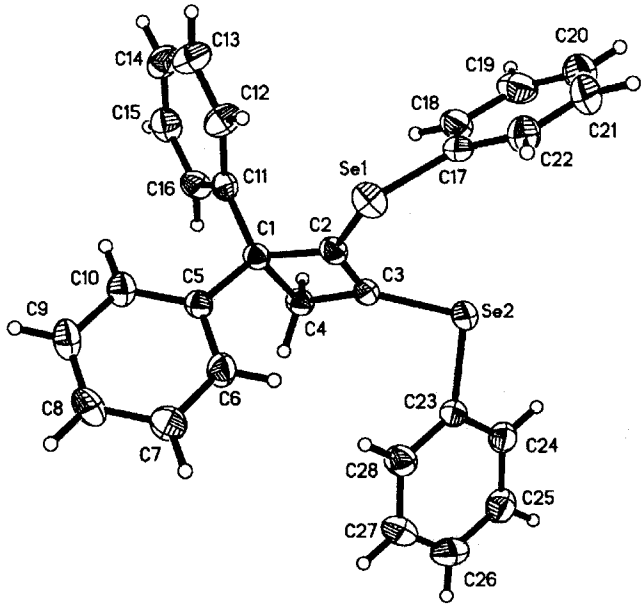
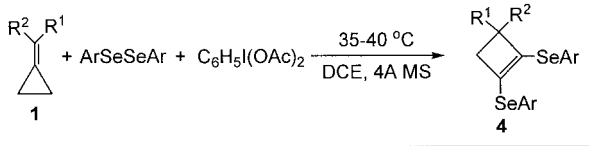


Figure 2. ORTEP drawing of **4a**

tion also produced the ring-opened acetate **7d** as a byproduct (Table 3, entry 8).

Table 3. Reaction of MCPs **1** with diaryl diselenides in the presence of iodosobenzene diacetate in DCE with 4-Å molecular sieves

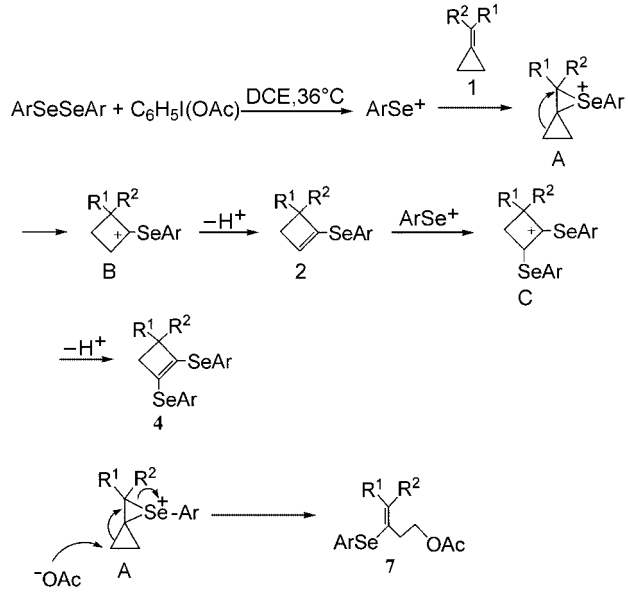


1 4

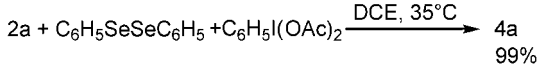
Entry	R^1	R^2	1	Ar	Yield/[%][a] 4
1	C_6H_5	C_6H_5	**1a**	*p*-MeC_6H_4	**4h**, 43
2	*p*-FC_6H_4	*p*-FC_6H_4	**1b**	*p*-MeC_6H_4	**4i**, 58
3	*o*-ClC_6H_4	C_6H_5	**1d**	*p*-MeC_6H_4	**4j**, 44
4	*p*-MeC_6H_4	*p*-MeC_6H_4	**1e**	*p*-MeC_6H_4	**4k**, 66
5	C_6H_5	C_6H_5	**1a**	*p*-$MeOC_6H_4$	**4l**, 50
6	*p*-FC_6H_4	*p*-FC_6H_4	**1b**	*p*-$MeOC_6H_4$	**4m**, 54
7	*o*-ClC_6H_4	C_6H_5	**1d**	*p*-$MeOC_6H_4$	**4n**, 37
8	*p*-MeC_6H_4	*p*-MeC_6H_4	**1e**	*p*-$MeOC_6H_4$	**4o**, 60[b]

[a] Isolated yields; from 1 (0.3 mmol), ArSeSeAr (0.33 mmol, 1.1 equiv.), $C_6H_5I(OAc)_2$ (0.66 mmol, 2.2 equiv.), and 4-Å molecular sieves (300 mg). [b] Acetate **7d** was formed as a byproduct (see Exp. Sect.).

A plausible reaction mechanism for the formation of **4** is shown in Scheme 3. The hypervalent iodine reagent [$PhI(OAc)_2$] oxidatively cleaves the Se–Se bond to generate in situ a very reactive electrophilic selenium species.[6b,11] This adds to the double bond of MCP **1** to give the cationic intermediate **A**. Rearrangement of the carbonium ion **A** gives the ring-expanded cyclobutyl cation **B** which affords product **2** by β-proton elimination.[12] Compound **2** can further react with electrophilic selenium species to produce the cationic intermediate **C** which furnishes product **4**, again by β-proton elimination (Scheme 3). At this stage, we cannot explain the formation of **7** from MCPs **1e–g**. We believe that the intermediate **A** is relatively stable owing to the electron-donating substituents on the benzene ring of MCPs **1e–g**. This long-lived species may have time to undergo nucleophilic attack by OAc^- to give the ring-opened product **7** (Scheme 3).



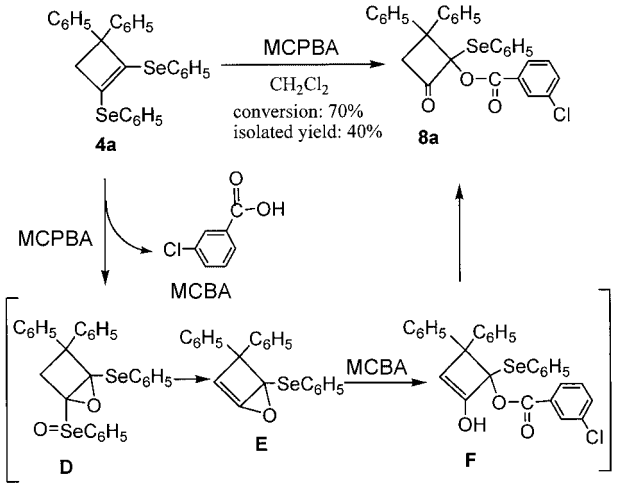
Scheme 3. A plausible reaction mechanism for the reaction of MCPs **1** with diaryl diselenides in the presence of iodosobenzene diacetate



Scheme 4

We confirmed that the reaction of **2a** with diphenyl diselenide gives **4a** in the presence of iodosobenzene diacetate in excellent yield (Scheme 4). This result clearly suggests that the reaction of **2** with the electrophilic selenium species could indeed produce cationic intermediate **C** and the product **4** under the same conditions.

Compound **4a** was further transformed on treatment with *m*-chloroperbenzoic acid (MCPBA) in DCM (Scheme 5). 4-Oxo-2,2-diphenyl-1-(phenylselanyl)cyclobutyl 3-chlorobenzoate **8a** was obtained in moderate yield. The reaction mechanism is shown in Scheme 5. The oxidation of **4a** produces intermediate **D**[13] which immediately gives intermediate **E** by selenoxide elimination. The reaction of MCBA with intermediate **E** produces enol intermediate **F** which furnishes product **8a** by isomerization.



Scheme 5

Conclusions

We have found that the reaction of *gem*-aryl-disubstituted MCPs **1** with diaryl diselenide in the presence of iodosobenzene diacetate produced the ring-opened products **4** in moderate-to-good yields under mild conditions. This process provides a novel and efficient route for the synthesis of 1,2-bis(phenylselanyl)-3,3-diphenylcyclobut-1-ene **4**. The further transformation of **4** to 4-oxo-2,2-diphenyl-1-(phenylselanyl)cyclobutyl 3-chlorobenzoate (**8**) by the use of MCPBA under mild conditions has also been disclosed. Efforts are in progress to elucidate the mechanistic details of this reaction and to disclose its scope and limitations.

Experimental Section

General Remarks: ^{1}H NMR spectra were recorded on a 300 MHz spectrometer in $CDCl_3$ using tetramethylsilane as the internal standard. Infrared spectra were measured on a Perkin–Elmer 983 spectrometer. Mass spectra were recorded on a HP-5989 instrument and HRMS on a Finnigan MA$^+$ mass spectrometer. Satisfactory CHN microanalyses were obtained using a Carlo–Erba 1106 analyzer. Melting points (uncorrected) were recorded with a Yanagimoto micro melting point apparatus. All reactions were monitored by TLC using Huanghai GF_{254} silica-gel-coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel.

General Procedure for the Reactions of MCPs 1 with Diphenyl Diselenide in the Presence of Iodosobenzene Diacetate: Under argon,a mixture of MCP **1** (0.3 mmol), PhSeSePh (0.33 mmol), and 4-Å molecular sieves (300 mg) were added to DCE (2 mL). The reaction mixture was stirred for 1 hour at room temperature and then iodosobenzene diacetate (0.66 mmol) was added and the reaction mixture was stirred for a further 20 hours at 35–40 °C. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using petroleum/ethyl acetate (300:1) as eluent to give the products.

3,3-Diphenyl-1,2-bis(phenylselanyl)cyclobut-1-ene (4a): This compound was obtained as a colorless solid (114 mg, 74%), m.p. 76–78 °C. IR (KBr): $\tilde{\nu}$ = 3056, 3021, 2965, 2952, 1945, 1871, 1800, 1577, 1559, 1492, 1475, 1438, 1201, 1067, 1021, 893, 758, 737, 691 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 3.21 (s, 2 H, CH_2), 7.27–7.15 (m, 16 H, ArH), 7.49–7.39 ppm (m, 4 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 143.94, 142.14, 135.01, 133.61, 129.09, 129.06, 128.33, 128.10, 127.36, 126.36, 61.09, 51.11 ppm. EI-MS (%): *m/z* = 518 [M]$^+$ (8.2), 361 [M – 157]$^+$ (28.2), 280 [M – 238]$^+$ (36.7), 203 [M – 315]$^+$ (100). $C_{28}H_{22}Se_2$ (516.3943): calcd. C 65.12, H 4.29; found: C 65.24, H 4.26%.

3,3-Bis(*p*-fluorophenyl)-1,2-bis(phenylselanyl)cyclobut-1-ene (4b): This compound was obtained as a white solid (129 mg, 78%), m.p. 95–97 °C. IR (KBr): $\tilde{\nu}$ = 3057, 2962, 2925, 2852, 1941, 1878, 1756, 1602, 1577, 1560, 1506, 1475, 1438, 1302, 1232, 1160, 1100, 1021, 930, 903, 830, 738, 690 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 3.17 (s, 2 H, CH_2), 6.95–6.89 (m, 4 H, ArH), 7.31–7.17 (m, 10 H, ArH), 7.52–7.37 ppm (m, 4 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 51.36, 59.91, 114.92 (d, $J_{C,F}$ = 21.2 Hz), 126.31, 127.55, 127.90, 128.26, 128.86 (d, $J_{C,F}$ = 8.3 Hz), 129.10, 129.16, 133.57, 135.07, 137.06, 139.48 (d, $J_{C,F}$ = 3.0 Hz), 142.71, 161.37 ppm (d, $J_{C,F}$ = 244.7 Hz). EI-MS (%): *m/z* = 554 [M]$^+$, 397 [M – 157]$^+$ (22.43), 316 [M – 238]$^+$ (24.67), 240 [M – 314]$^+$ (100.00), 220 [M – 334]$^+$ (19.87). HRMS (MALDI): calcd. for $C_{28}H_{21}F_2Se_2^+$ [M + 1]$^+$: 554.9936; found: 554.9944.

3,3-Bis(*p*-chlorophenyl)-1,2-bis(phenylselanyl)cyclobut-1-ene (4c): This compound was obtained as a yellow liquid (74 mg, 42%). IR (KBr): $\tilde{\nu}$ = 3056, 2924, 1952, 1893, 1577, 1558, 1489, 1475, 1438, 1397, 1203, 1093, 1014, 821, 738, 690 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 3.15 (s, 2 H, CH_2), 7.32–7.14 (m, 14 H, ArH), 7.52–7.38 ppm (m, 4 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 51.06, 60.03, 126.21, 127.62, 127.71, 128.30, 128.69, 129.14, 129.20, 132.37, 133.70, 135.10, 136.65, 141.95, 142.26, 142.90 ppm. EI-MS (%): *m/z* = 586 [M]$^+$ (8.02), 429 [M – 157]$^+$ (35.43), 349 [M – 237]$^+$ (20.92), 314 [M – 272]$^+$ (25.98), 272 [M – 314]$^+$ (46.22), 202 [M – 384]$^+$ (100.00). HRMS (MALDI): calcd. for $C_{28}H_{20}Cl_2Se_2Na^+$ [M + 23]$^+$: 608.9165; found: 608.9196.

3-(*o*-Chlorophenyl)-3-phenyl-1,2-bis(phenylselanyl)cyclobut-1-ene (4d): This compound was obtained as a yellow liquid (114 mg, 69%). IR (KBr): $\tilde{\nu}$ = 3056, 3028, 2927, 1941, 1871, 1800, 1599, 1577, 1559, 1493, 1475, 1437, 1196, 1063, 1031, 1021, 915, 892, 754, 738, 691 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 3.08 (d, *J* = 13.5 Hz, 1 H, CH_2), 3.63 (d, *J* = 13.5 Hz, 1 H, CH_2), 7.08–7.04 (m, 2 H, ArH), 7.36–7.14 (m, 14 H, ArH), 7.52–7.37 (m, 2 H, ArH), 7.80–7.77 ppm (m, 1 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 50.43, 61.12, 126.18, 126.32, 126.40, 127.45, 128.16, 128.19, 129.04 (2C), 129.18 (2C), 129.41, 130.35, 133.63, 134.09, 134.96, 138.04, 141.38, 141.51, 142.24, 142.55 ppm. EI-MS (%): *m/z* = 552 [M]$^+$ (2.98), 517 [M – 35]$^+$ (1.84), 395 [M – 157]$^+$ (7.83), 279 [M – 273]$^+$ (21.71), 238 [M – 314]$^+$ (70.29), 202 [M – 350]$^+$ (100.00). HRMS (MALDI): calcd. for $C_{28}H_{22}ClSe_2^+$ [M + 1]$^+$: 552.9735; found: 552.9748.

3,3-Bis(*p*-methylphenyl)-1,2-bis(phenylselanyl)cyclobut-1-ene (4e): This compound was obtained as a yellow liquid (82 mg, 50%). IR (KBr): $\tilde{\nu}$ = 3054, 3020, 2921, 2865, 1945, 1897, 1788, 1577, 1559, 1510, 1475, 1438, 1187, 1021, 900, 812, 737, 690 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.30 (s, 6 H, CH_3), 3.19 (s, 2 H, CH_2), 7.49–7.43 (m, 4 H, ArH), 7.67–7.15 (m, 10 H, ArH), 7.07–7.04 ppm (m, 4 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 21.00 (2C), 51.26, 60.67, 126.23, 126.75, 127.24, 128.00, 128.44, 128.77, 129.02, 129.04, 133.60, 134.94, 135.82, 137.75, 141.15, 141.49 ppm. EI-MS (%): *m/z* = 546 [M]$^+$, 426 [M – 120]$^+$ (2.86), 389 [M – 157]$^+$ (17.66), 232 [M – 314]$^+$ (85.33), 208 [M – 338]$^+$ (100.00), 193 [M – 353]$^+$ (50.68). HRMS (MALDI): calcd. for $C_{30}H_{26}Se_2Na^+$ [M + 23]$^+$: 569.0257; found: 569.0230.

3,3-Bis(*p*-methoxyphenyl)-1,2-bis(phenylselanyl)cyclobut-1-ene (4f): This compound was obtained as a yellow liquid (73 mg, 42%). IR (KBr): $\tilde{\nu}$ = 3055, 2998, 2954, 2833, 2052, 1937, 1874, 1606, 1577, 1509, 1475, 1438, 1299, 1248, 1177, 1034, 1022, 828, 738, 690 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 3.17 (s, 2 H, CH_2), 3.77 (s, 6 H, CH_3), 6.8–6.77 (m, 4 H, ArH), 7.27–7.16 (m, 10 H, ArH), 7.50–7.42 ppm (m, 4 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 51.50, 55.21 (2C), 60.09, 113.40, 113.41, 126.74, 127.31, 128.03, 128.42, 129.05, 129.07, 133.49, 134.93, 136.38, 137.96, 141.51, 157.94 ppm. EI-MS (%): *m*/*z* = 578 $[M]^+$, 421 $[M - 157]^+$ (25.42), 340 $[M - 238]^+$ (5.24), 312 $[M - 266]^+$ (6.81), 264 $[M - 314]^+$ (100.00), 249 $[M - 329]^+$ (20.89). HRMS (MALDI): calcd. for $C_{30}H_{27}O_2Se_2^+$ $[M + 1]^+$: 579.0336; found: 579.0354.

3-(*p*-Methoxyphenyl)-3-phenyl-1,2-bis(phenylselanyl)cyclobut-1-ene (4g): This compound was obtained as a white liquid (66 mg, 40%). IR (KBr): $\tilde{\nu}$ = 3055, 2957, 2928, 2833, 1945, 1878, 1797, 1606, 1577, 1509, 1475, 1438, 1298, 1248, 1179, 1033, 1022, 827, 738, 691 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 3.20 (s, 2 H, CH_2), 3.77 (s, 3 H, CH_3), 6.80–6.77 (m, 2 H, ArH), 7.27–7.17 (m, 14 H, ArH), 7.50–7.42 ppm (m, 3 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 51.31, 55.20, 60.60, 113.42, 126.30, 126.67, 127.33 (2C), 128.06, 128.08, 128.36, 128.45, 129.04, 129.07, 133.51, 134.97, 136.11, 137.66, 141.83, 144.22, 157.97 ppm. EI-MS (%): *m*/*z* = 548 $[M]^+$ (1.45), 391 $[M - 157]^+$ (26.90), 310 $[M - 238]^+$ (11.62), 234 $[M - 314]^+$ (100.00), 189 $[M - 359]^+$ (36.86). HRMS (MALDI): calcd. for $C_{29}H_{24}OSe_2Na^+$ $[M + 23]^+$: 571.0050; found: 571.0061.

Diphenyl[1-(phenylselanyl)cyclopropyl]methanol (5a): This compound was obtained as a white solid (43 mg, 40%), m.p. 94–95 °C. IR (KBr): $\tilde{\nu}$ = 3502, 3057, 3023, 1948, 1882, 1775, 1598, 1578, 1491, 1477, 1447, 1438, 1334, 1151, 1041, 1024, 756, 738, 703 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.95 (t, *J* = 6.0 Hz, 2 H, CH_2), 1.03 (t, *J* = 6.0 Hz, 2 H, CH_2), 3.58 (s, 1 H, OH), 7.31–7.22 (m, 9 H, ArH), 7.54–7.50 ppm (m, 6 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 13.96 (2C), 36.06, 82.12, 127.21, 127.32, 127.71, 127.72, 128.69, 128.96, 131.11, 133.29 ppm. EI-MS (%): *m*/*z* = 380 $[M]^+$ (14.44), 363 $[M - 17]^+$ (5.65), 198 $[M - 182]^+$ (42.77), 183 $[M - 197]^+$ (48.65), 105 $[M - 275]^+$ (100.00). HRMS (MALDI): calcd. for $C_{22}H_{20}OSeNa^+$ $[M + 23]^+$: 403.0572; found: 403.0596.

Product 6a: This compound was obtained as a white liquid (97 mg, 82%). IR (KBr): $\tilde{\nu}$ = 3056, 2978, 2938, 1948, 1897, 1819, 1578, 1490, 1477, 1444, 1405, 1264, 1221, 1190, 1158, 1073, 1034, 765, 753, 704 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.95 (dd, *J* = 4.5, 6.9 Hz, 2 H, CH_2), 1.81 (dd, *J* = 4.5, 6.9 Hz, 2 H, CH_2), 2.85 (s, 3 H, CH_3), 6.39–6.36 (m, 2 H, ArH), 7.00–6.87 (m, 3 H, ArH), 7.39–7.32 (m, 6 H, ArH), 7.66–7.63 ppm (m, 4 H, ArH). EI-MS: *m*/*z* = 394 $[M]^+$ (2.52), 281 $[M - 113]^+$ (0.58), 237 $[M - 157]^+$ (2.01), 205 $[M - 189]^+$ (11.53), 197 $[M - 197]^+$ (100.00). HRMS (MALDI): calcd. for $C_{23}H_{23}OSe^+$ $[M + 1]^+$: 395.0909; found: 395.0923.

4,4-Bis(*p*-methoxyphenyl)-3-(phenylselanyl)but-3-enyl Acetate (7a): This compound was obtained as a yellow liquid (23 mg, 10%). IR (KBr): $\tilde{\nu}$ = 3056, 2999, 2932, 2836, 2057, 1883, 1736, 1605, 1576, 1508, 1464, 1382, 1245, 1173, 1034 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.94 (s, 3 H, CH_3), 2.65 (t, *J* = 6.9 Hz, 2 H, CH_2), 3.79 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 4.15 (t, *J* = 6.9 Hz, 2 H, CH_2), 6.85–6.81 (m, 4 H, ArH), 7.13–7.10 (m, 4 H, ArH), 7.27–7.25 (m, 3 H, ArH), 7.50–7.47 ppm (m, 2 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 21.0, 33.6, 55.1, 55.2, 63.5, 113.2, 113.6, 127.3, 127.7, 129.1, 130.4, 130.5, 130.6, 133.4, 134.2, 136.1, 147.7, 158.6, 158.8, 170.8 ppm. EI-MS: *m*/*z* = 482 $[M]^+$ (3.32), 452 $[M - 30]^+$ (3.53), 341 $[M - 141]^+$ (3.22), 312 $[M - 170]^+$ (9.89), 242 $[M - 240]^+$ (26.13), 149 $[M - 333]^+$ (58.45), 135 $[M - 347]^+$ (100.00). HRMS (MALDI): calcd. for $C_{26}H_{27}O_4Se^+$ $[M + 1]^+$: 483.1069; found: 483.1061.

(*Z*)-4-Phenyl-4-(*p*-methoxyphenyl)-3-(phenylselanyl)but-3-enyl Acetate (7b-*Z*): This compound was obtained as a yellow liquid (25 mg, 10%). IR (KBr): $\tilde{\nu}$ = 3055, 3028, 2954, 2835, 2056, 1951, 1881, 1737, 1605, 1576, 1508, 1475, 1439, 1382, 1245, 1173, 1107, 1034 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.70 (s, 3 H, CH_3), 2.67 (t, *J* = 6.6 Hz, 2 H, CH_2), 3.80 (s, 3 H, OCH_3), 4.17 (t, *J* = 6.6 Hz, 2 H, CH_2), 6.87–6.84 (m, 2 H, ArH), 7.31–7.12 (m, 10 H, ArH), 7.60–7.47 ppm (m, 2 H, ArH). EI-MS: *m*/*z* = 452 $[M]^+$ (31.6), 392 $[M - 60]^+$ (19.22), 311 $[M - 141]^+$ (31.32), 235 $[M - 217]^+$ (100.00), 220 $[M - 232]^+$ (40.17), 204 $[M - 248]^+$ (38.44), 197 $[M - 255]^+$ (53.62), 178 $[M - 274]^+$ (34.70), 149 $[M - 303]^+$ (59.26). HRMS (MALDI): calcd. for $C_{25}H_{25}O_3Se^+$ $[M + 1]^+$: 453.0963; found: 453.0947.

(*E*)-4-Phenyl-4-(*p*-methoxyphenyl)-3-(phenylselanyl)but-3-enyl Acetate (7b-*E*): This compound was obtained as a yellow liquid (33 mg, 17%). IR (KBr): $\tilde{\nu}$ = 3055, 3029, 2997, 2835, 2042, 1955, 1881, 1738, 1605, 1577, 1508, 1475, 1439, 1382, 1245, 1173, 1034 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.94 (s, 3 H, CH_3), 2.63 (t, *J* = 6.6 Hz, 2 H, CH_2), 3.79 (s, 3 H, OCH_3), 4.15 (t, *J* = 6.6 Hz, 2 H, CH_2), 6.87–6.83 (m, 2 H, ArH), 7.33–7.28 (m, 10 H, ArH), 7.53–7.49 ppm (m, 2 H, ArH). EI-MS: *m*/*z* = 452 $[M]^+$ (16.54), 392 $[M - 60]^+$ (11.41), 312 $[M - 140]^+$ (27.50), 235 $[M - 217]^+$ (67.27), 220 $[M - 232]^+$ (27.17), 157 $[M - 295]^+$ (37.70), 149 $[M - 303]^+$ (100.00), 135 $[M - 317]^+$ (56.65). HRMS (MALDI): calcd. for $C_{25}H_{25}O_3Se^+$ $[M + 1]^+$: 453.0963; found: 453.0946.

4,4-Bis(*p*-methylphenyl)-3-(phenylselanyl)but-3-enyl Acetate (7c): This compound was obtained as a yellow liquid (16 mg, 13%). IR (KBr): $\tilde{\nu}$ = 3021, 2957, 2924, 2854, 1739, 1578, 1509, 1475, 1438, 1240, 1035, 1022 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.95 (s, 3 H, CH_3), 2.33 (s, 6 H, CH_3), 2.63 (t, *J* = 6.6 Hz, 2 H, CH_2), 4.15 (t, *J* = 6.6 Hz, 2 H, CH_2), 7.11–7.09 (m, 6 H, ArH), 7.28–7.26 (m, 4 H, ArH), 7.51–7.48 ppm (m, 3 H, ArH). EI-MS: *m*/*z* = 450 $[M^+, 14.83]^+$ (390 $[M - 60]^+$ (9.25), 309 $[M - 141]^+$ (13.69), 233 $[M - 217]^+$ (100.00), 218 $[M - 232]^+$ (70.17), 149 $[M - 301]^+$ (96.68), 119 $[M - 331]^+$ (51.89). HRMS (MALDI): calcd. for $C_{26}H_{27}O_2Se^+$ $[M + 1]^+$: 451.1171; found: 451.1189.

1,2-Bis(*p*-methylphenylselanyl)-3,3-diphenylcyclobut-1-ene (4h): This compound was obtained as a yellow solid (70 mg, 43%), m.p. 115 °C. IR (KBr): $\tilde{\nu}$ = 3067, 3022, 2911, 2852, 1941, 1889, 1797, 1597, 1486, 1438, 1202, 1028, 895, 758, 699 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.31 (s, 6 H, CH_3), 3.17 (s, 2 H, CH_2), 7.00–7.39 ppm (m, 18 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 21.12, 21.14, 51.05, 60.89, 122.86, 124.38, 126.22, 127.37, 127.38, 128.02, 129.80, 129.84, 133.98, 135.15, 137.36, 138.09, 141.45, 144.04 ppm. EI-MS (%): *m*/*z* = 546 $[M]^+$, 373 $[M - 173]^+$ (9.13), 342 $[M - 204]^+$ (6.81), 296 $[M - 250]^+$ (12.21), 279 $[M - 267]^+$ (11.99), 217 $[M - 329]^+$ (5.10). HRMS (MALDI/DHB): calcd. for $C_{30}H_{27}Se_2^+$ $[M + 1]^+$: 547.0438; found: 547.0431.

3,3-Bis(*p*-fluorophenyl)-1,2-bis(*p*-methylphenylselanyl)cyclobut-1-ene (4i): This compound was obtained as a yellow solid (100 mg, 58%), m.p. 80 °C. IR (KBr): $\tilde{\nu}$ = 2921, 2851, 1886, 1741, 1600, 1562, 1506, 1489, 1462, 1301, 1232, 1160, 1100, 1015, 927, 903, 830, 724 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.32 (s, 6 H, CH_3), 3.11 (s, 2 H, CH_2), 6.89–7.40 ppm (m, 16 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 21.15, 21.16, 51.39, 59.78, 114.86 (d, $J_{C,F}$ = 21.0 Hz), 122.67, 128.93 (d, $J_{C,F}$ = 8.1 Hz), 129.89, 129.90, 129.97, 132.30, 134.11, 135.25, 137.74, 138.38, 139.53 (d, $J_{C,F}$ = 2.9 Hz), 142.09, 161.40 ppm (d, $J_{C,F}$ = 243.6 Hz). EI-MS (%): *m*/*z* = 582 $[M]^+$, 448 $[M - 134]^+$ (12.65), 411 $[M - 171]^+$ (16.47), 330 [M –

252]$^+$ (34.08), 240 [M – 342]$^+$ (100.00). HRMS (MALDI/DHB): calcd. for $C_{30}H_{24}F_2Se_2Na^+$ [M + 23]$^+$: 605.0069; found: 605.0093.

3-(*o*-Chlorophenyl)-1,2-bis(*p*-methylphenylselanyl)-3-phenylcyclobut-1-ene (4j): This compound was obtained as a yellow liquid (77 mg, 44%). IR (KBr): $\tilde{\nu}$ = 3053, 3018, 2921, 2840, 1897, 1797, 1600, 1489, 1444, 1296, 1275, 1180, 884, 753, 697 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.30 (s, 6 H, CH_3), 3.03 (d, J = 13.5 Hz, 1 H, CH_2), 3.56 (d, J = 13.5 Hz, 1 H, CH_2), 6.97–7.81 ppm (m, 17 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 21.16, 29.68, 50.45, 61.02, 122.72, 126.18, 126.22, 126.38, 128.08, 128.10, 129.54, 129.82, 129.85, 129.96, 130.29, 134.08, 134.11, 135.14, 137.51, 137.93, 138.26, 141.57, 141.63, 142.12 ppm. EI-MS (%): *m*/*z* = 580 [M]$^+$ (3.32), 409 [M – 171]$^+$ (8.98), 340 [M – 240]$^+$ (8.43), 329 [M – 251]$^+$ (63.20), 293 [M – 287]$^+$ (22.52), 238 [M – 342]$^+$ (72.64), 202 [M – 378]$^+$ (100.00). HRMS (MALDI/DHB): calcd. for $C_{30}H_{25}ClSe_2Na^+$ [M + 23]$^+$: 602.9867; found: 602.9896.

3,3-Bis(*p*-methylphenyl)-1,2-bis(*p*-methylphenylselanyl)cyclobut-1-y?oas [jy[lx?>ene (4k): This compound was obtained as a yellow solid (114 mg, 66%), m.p. 129 °C. IR (KBr): $\tilde{\nu}$ = 3019, 2920, 2850, 1893, 1737, 1562, 1509, 1488, 1451, 1300, 1214, 1186, 1114, 1043, 934, 901, 803, 722 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.30 (s, 12 H, CH_3), 3.13 (s, 2 H, CH_2), 7.00–7.38 ppm (m, 16 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 20.70, 20.97, 21.00, 21.13, 21.15, 21.18, 29.70, 29.74, 51.24, 70.47, 123.07, 127.30, 128.73, 129.76, 129.81, 129.84, 133.97, 134.01, 135.14, 135.74, 137.37, 138.05, 140.30, 140.92 ppm. EI-MS (%): *m*/*z* = 574 [M]$^+$, 403 [M – 171]$^+$ (9.95), 322 [M – 252]$^+$ (19.24), 232 [M – 342]$^+$ (100.00), 215 [M – 359]$^+$ (49.50), 202 [M – 372]$^+$ (44.64). HRMS (MALDI/DHB): calcd. for $C_{32}H_{31}Se_2^+$ [M + 1]$^+$: 575.0751; found: 575.0741.

1,2-Bis(*p*-methoxyphenylselanyl)-3,3-diphenylcyclobut-1-ene (4l): This compound was obtained as a yellow liquid (87 mg, 50%). IR (KBr): $\tilde{\nu}$ = 3053, 2961, 2926, 2835, 1940, 1879, 1591, 1566, 1490, 1456, 1443, 1287, 1247, 1173, 1102, 1030, 955, 909, 824, 733, 700 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 3.13 (s, 2 H, CH_2), 3.81(s, 6 H, CH_3), 6.77–7.48 ppm (m, 18 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 51.01, 55.17, 55.20, 60.55, 114.65, 116.62, 116.64, 117.84, 126.22, 127.19, 127.60, 127.40, 127.70, 128.01, 136.50, 136.53, 136.93, 136.97, 140.27, 144.02, 159.58, 159.75 ppm. EI-MS (%): *m*/*z* = 578 [M]$^+$, 391 [M – 187]$^+$ (12.87), 374 [M – 204]$^+$ (5.69), 311 [M – 267]$^+$ (100.00), 279 [M – 299]$^+$ (8.47), 204 [M – 374]$^+$ (57.98), 187 [M – 391]$^+$ (47.22). HRMS (MALDI/DHB): calcd. for $C_{30}H_{26}O_2Se_2Na^+$ [M + 23]$^+$: 601.0156; found: 601.0163.

3,3-Bis(*p*-fluorophenyl)-1,2-bis(*p*-methoxyphenylselanyl)cyclobut-1-ene (4m): This compound was obtained as a yellow liquid (100 mg, 54%). IR (KBr): $\tilde{\nu}$ = 2926, 2844, 1885, 1863, 1845, 1590, 1571, 1505, 1453, 1287, 1239, 1169, 1102, 1028, 954, 932, 821, 725, 673 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 3.03 (s, 2 H, CH_2), 3.79 (s, 6 H, CH_3), 6.73–7.44 ppm (m, 16 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 51.39, 55.25, 55.28, 59.51, 114.71, 114.73, 114.84 (d, $J_{C,F}$ = 20.9 Hz), 116.42, 117.42, 128.95 (d, $J_{C,F}$ = 7.9 Hz), 136.62, 136.82, 137.05, 139.60 (d, $J_{C,F}$ = 3.1 Hz), 140.83, 159.72, 159.90, 161.34 ppm (d, $J_{C,F}$ = 243.8 Hz). EI-MS (%): *m*/*z* = 614 [M]$^+$, 446 [M – 168]$^+$ (12.42), 427 [M – 151]$^+$ (13.22), 347 [M – 231]$^+$ (93.76), 219 [M – 359]$^+$ (69.66), 187 [M – 391]$^+$ (100.00), 123 [M – 455]$^+$ (67.84). HRMS (MALDI/DHB): calcd. for $C_{30}H_{25}O_2Se_2F_2^+$ [M + 1]$^+$: 615.0094; found: 615.0124.

3-(*o*-Chlorophenyl)-1,2-bis(*p*-methoxyphenylselanyl)-3-phenylcyclobut-1-ene (4n): This compound was obtained as a yellow liquid (68 mg, 37%). IR (KBr): $\tilde{\nu}$ = 2925, 2836, 1964, 1879, 1638, 1591, 1572, 1490, 1460, 1288, 1248, 1173, 1102, 1030, 955, 912, 824, 755, 698 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.95 (d, J = 13.2 Hz, 1 H, CH_2), 3.48 (d, J = 13.2 Hz, 1 H, CH_2), 3.76 (s, 6 H, CH_3), 6.70–7.79 ppm (m, 17 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 29.66, 50.46, 55.21, 60.83, 114.62, 114.66, 114.78, 116.45, 117.85, 126.16, 126.19, 126.37, 128.07, 129.57, 130.25, 134.10, 136.53, 137.80, 141.16, 141.55, 141.62, 159.57, 159.84 ppm. EI-MS (%): *m*/*z* = 612 [M]$^+$, 425 [M – 187]$^+$ (6.59), 345 [M – 267]$^+$ (100.00), 238 [M – 374]$^+$ (26.19), 202 [M – 410]$^+$ (80.98), 187 [M – 425]$^+$ (81.33). HRMS (MALDI/DHB): calcd. for $C_{30}H_{25}O_2Se_2ClNa^+$ [M + 23]$^+$: 634.9766; found: 634.9795.

1,2-Bis(*p*-methoxyphenylselanyl)-3,3-bis(*p*-methylphenyl)cyclobut-1-ene (4o): This compound was obtained as a yellow liquid (108 mg, 60%). IR (KBr): $\tilde{\nu}$ = 2998, 2922, 2835, 1957, 1886, 1590, 1572, 1490, 1460, 1439, 1173, 1030, 900, 823, 717, 632 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.31 (s, 6 H, CH_3), 3.05 (s, 2 H, CH_2), 3.79 (s, 6 H, CH_3), 6.74–7.44 ppm (m, 16 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 21.00, 51.19, 55.23, 55.26, 60.24, 114.65, 116.85, 118.01, 127.34, 128.71, 135.42, 135.71, 136.53, 136.97, 137.35, 139.76, 141.29 ppm. EI-MS (%): *m*/*z* = 606 [M]$^+$, 419 [M – 187]$^+$ (24.34), 339 [M – 267]$^+$ (59.77), 232 [M – 374]$^+$ (100.00), 215 [M – 391]$^+$ (26.75), 202 [M – 404]$^+$ (23.45). HRMS (MALDI/DHB): calcd. for $C_{32}H_{30}O_2Se_2Na^+$ [M + 23]$^+$: 629.0469; found: 629.0498.

3-(*p*-Methoxphenylselanyl)-4,4-bis(*p*-methylphenyl)but-3-enyl Acetate (7d): This compound was obtained as a yellow liquid (17 mg, 5%). IR (KBr): $\tilde{\nu}$ = 3021, 2960, 2921, 2851, 1957, 1904, 1844, 1794, 1739, 1571, 1508, 1490, 1462, 1441, 1403, 1381, 1362, 1286, 1247, 1173, 1103, 1030, 945, 911, 819, 734, 596 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.30 (s, 12 H, CH_3), 3.13 (s, 2 H, CH_2), 7.00–7.38 ppm (m, 16 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 20.70, 20.97, 21.00, 21.13, 21.15, 21.18, 29.70, 29.74, 51.24, 70.47, 123.07, 127.30, 128.73, 129.76, 129.81, 129.84, 133.97, 134.01, 135.14, 135.74, 137.37, 138.05, 140.30, 140.92 ppm. EI-MS (%): *m*/*z* = 480 [M]$^+$ (21.49), 339 [M – 141]$^+$ (43.80), 247 [M – 233]$^+$ (35.69), 233 [M – 247]$^+$ (61.76), 218 [M – 262]$^+$ (100.00), 203 [M – 277]$^+$ (52.19). HRMS (MALDI/DHB): calcd. for $C_{27}H_{29}O_4Se^+$ [M + 1]$^+$: 497.1226; found: 497.1216.

4-Oxo-2,2-diphenyl-1-(phenylselanyl)cyclobutyl 3-Chlorobenzoate (8a): This compound was obtained as a white liquid (40%). IR (KBr): $\tilde{\nu}$ = 3059, 2919, 2844, 1786, 1741, 1571, 1496, 1446, 1286, 1249, 1118, 1072, 739, 697 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 3.85 (d, J = 17.4 Hz, 1 H, CH_2), 4.45 (d, J = 17.4 Hz, 1 H, CH_2), 7.1–7.08 (m, 4 H, ArH), 7.65–7.19 (m, 13 H, ArH), 8.02–7.99 ppm (m, 2 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 54.10, 55.87, 96.02, 126.18, 127.03, 127.67, 127.71, 128.04, 128.51, 128.93 (2C), 129.00, 129.55, 129.64, 130.74, 133.46, 134.38, 136.99, 140.88, 142.40, 161.74, 193.48 ppm. EI-MS (%): *m*/*z* = 532 [M]$^+$ (0.32), 375 [M – 157]$^+$ (17.36), 337 [M – 195]$^+$ (3.13), 219 [M – 313]$^+$ (13.78), 207 [M – 325]$^+$ (18.44), 180 [M – 352]$^+$ (47.42), 139 [M – 393]$^+$ (100.00). HRMS (MALDI): calcd. for $C_{29}H_{21}ClO_3SeNa^+$ [M + 23]$^+$: 555.0237; found: 555.0251.

Supporting Information Available (see also footnote on the first page of this article): The ^{1}H and ^{13}C NMR spectra of the compounds shown in Tables 1–3, Figure 1 and Schemes 2, 4, and 5.

Acknowledgments

We thank the State Key Project of Basic Research (Project 973) (No. G2000048007), the Chinese Academy of Sciences (KGCX2-210-01), Shanghai Municipal Committee of Science and Technology, and the National Natural Science Foundation of China for financial support (203900502, 20025206 and 20272069).

[1] For the synthesis of MCPs, see: a) A. Brandi, A. Goti, *Chem. Rev.* **1998**, *98*, 589–635; b) A. de Meijere (Ed.), *Methods of Organic Chemistry: Carbocyclic Three-Membered Ring Compounds(Houben-Weyl)*, Thieme, Stuttgart, **1996**, vol. E 17a–c; c) for a recent review, see: I. Nakamura, Y. Yamamoto, *Adv. Synth. Catal.* **2002**, *344*, 111–129.

[2] Three types of ring-opening reaction of MCPs have been disclosed (see ref.[4a]). For the ring opening of MCPs by type I, see: a) D. H. Camacho, I. Nakamura, S. Saito, Y. Yamamoto, *Angew. Chem. Int. Ed.* **1999**, *38*, 3365–3367; b) D. H. Camacho, I. Nakamura, S. Saito, Y. Yamamoto, *J. Org. Chem.* **2001**, *66*, 270–275; c) I. Nakamura, H. Itagaki, Y. Yamamoto, *J. Org. Chem.* **1998**, *63*, 6458–6459; d) H. Nüske, M. Notlemeyer, A. de Meijere, *Angew. Chem. Int. Ed.* **2001**, *40*, 3411–3413; e) S. Bräse, A. de Meijere, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2545–2547; f) N. Tsukada, A. Shibuya, I. Nakamura, Y. Yamamoto, *J. Am. Chem. Soc.* **1997**, *119*, 8123–8124; g) Y. Inoue, T. Hibi, H. Sataka, H. Hashimoto, *Chem. Commun.* **1979**, 982–982; h) P. Binger, A. Germer, *Chem. Ber.* **1981**, *114*, 3325–3335; h) I. Nakamura, B. H. Oh, S. Saito, Y. Yamamoto, *Angew. Chem. Int. Ed.* **2001**, *40*, 1298–1300; j) B. H. Oh, I. Nakamura, S. Saito, Y. Yamamoto, *Tetrahedron Lett.* **2001**, *42*, 6203–6205. For the ring-opening of MCPs by type II or III, see: k) A. G. Bessmertnykh, K. A. Blinov, Y. K. Grishin, N. A. Donskaya, E. V. Tveritinova, N. M. Yur'eva, I. P. Beletskaya, *J. Org. Chem.* **1997**, *62*, 6069–6076; l) M. Lautens, C. Meyer, A. Lorenz, *J. Am. Chem. Soc.* **1996**, *118*, 10676–10677; m) T. Ishiyama, S. Momota, N. Miyaura, *Synlett* **1999**, 1790–1792; n) M. Suginome, T. Matsuda, Y. Ito, *J. Am. Chem. Soc.* **2000**, *122*, 11 015–11 016; o) N. Chatani, H. Takaya, T. Hanafusa, *Tetrahedron Lett.* **1988**, *29*, 3979–3982; the metal-catalyzed cocyclization reactions of MCPs with unsaturated carbon bonds have been extensively studied, see the review: p) M. Lautens, W. Klute, W. Tam, *Chem. Rev.* **1996**, *96*, 49–92; q) T. Ohta, H. Takaya in *Comprehensive Organic Chemistry* (Eds.: B. M. Trost, I. Fleming, L. A. Paquette), Pergamon Press, Oxford, **1991**, vol. 5, pp. 1185–1196; r) P. Binger, T. Schmidt in *Methods of Organic Chemistry*, *(Houben-Weyl)* (Ed.: A. de Meijere), Thieme, Stuttgart, **1997**, vol. E 17c, pp. 2217–2294; s) P. Binger, H. M. Buch, *Top. Curr. Chem.* **1987**, *135*, 77–151.

[3] For some more recent papers related to MCPs, see: a) M. W. Nötzel, K. Rauch, T. Labahn, A. de Meijere, *Org. Lett.* **2002**, *4*, 839–841; b) D. Takauchi, K. Dsakada, *Chem. Commun.* **2002**, 646–647; c) A. de Meijere, A. Leonov, T. Heiner, M. Noltemeyer, M. T. Bes, *Eur. J. Org. Chem.* **2003**, 472–478; d) V. N. Belov, A. I. Savchenko, V. V. Sokolov, A. Straub, A. de Meijere, *Eur. J. Org. Chem.* **2003**, 551–561; e) A. de Meijere, I. D. Kuchuk, V. V. Sokolov, T. Labahn, K. Rauch, M. Es-Sayed, T. Krämer, *Eur. J. Org. Chem.* **2003**, 985–997; f) A. I. Siriwardana; I. Nakamura; Y. Yamamoto, *Tetrahedron Lett.* **2003**, *44*, 4547–4550; g) M. Shi, L.-X. Shao, B. Xu, *Org. Lett.***2003**, *5*, 579–582; h) L.-X. Shao, M. Shi, *Adv. Synth. Catal.* **2003**, *345*, 963–966; i) A. Brandi, S. Cicchi, F. M. Cordero, A. Goti, *Chem. Rev.* **2003**, *103*, 1213–1269.

[4] a) M. Shi, B. Xu, *Org. Lett*. **2002**, *4*, 2145–2148; b) M. Shi, Y. Chen, B. Xu, J. Tang, *Tetrahedron Lett*. **2002**, *43*, 8019–8024; c) G. L. N. Peron, J. Kitteringham, J. D. Kilburn, *Tetrahedron Lett*. **2000**, *41*, 1615–1618; d) G. L. N. Peron, D. Norton, J. Kitteringham, J. D. Kilburn, *Tetrahedron Lett*. **2001**, *42*, 347–349; e) L. Patient, M. B. Berry, J. D. Kilburn, *Tetrahedron Lett*. **2003**, *44*, 1015–1017; f) B. Xu, M. Shi, *Org. Lett*. **2003**, 5, 1415–1418; g) L.-X. Shao, M. Shi, *Eur.J. Org. Chem.* **2004**, 426–430; h) A. T. Bottini, L. I. Cabral, *Tetrahedron***1978**, *34*, 3187–3194; i) S. Kozhushkov, T. Spätch, T. Fiebig, B. Galland, M.-F. Ruasse, P. Xavier, Y. Apeloig, A. de Meijere, *J. Org. Chem*. **2002**, *68*, 4100–4114 and references cited therein.

[5] L. P. Liu, M. Shi, *J. Org. Chem.* **2004**, *69*, 2805–2808.

[6] It has been reported that treatment of diphenyl diselenide with iodosobenzene diacetate produces an electrophilic selenenylating agent of double bonds, see: a) M. Tingoli, M. Tiecco, L. Testaferri, A. Temperini, *Synth. Commun*. **1998**, *28*, 1769–1778; b) M. Tiecco, M. Tingoli, L. Testaferri, *Pure Appl. Chem*. **1993**, *65*, 715–722 and references cited therein; c) N. Miyoshi, Y. Takai, S. Murai, N. Sonoda, *Bull. Chem. Soc. Jpn*. **1978**, *51*, 1265–1266; d) D. Brugier, F. Outurquin, C. Paulmier, *J. Chem. Soc., Perkin Trans. 1* **2001**, 37–43.

[7] M. Kwart, A. A. Kahn, *J. Am. Chem. Soc.* **1967**, *89*, 1950–1951.

[8] Ceric ammonium nitrate (CAN) is known to be a good oxidant in methanol but is not soluble in other organic solvents, see: C. Bosman, A. D'Annibale, S. Resta, C. Trogolo, *Tetrahedron Lett.* **1994**, *35*, 6525–6528.

[9] Crystal data of **4a**: empirical formula $C_{28}H_{22}Se_2$, molecular mass 516.38,colorless, prismatic, triclinic, primitive lattice type, a = 10.5046(14), b = 10.7164(14), c = 11.8790(16) Å, α = 108.694(2), β = 111.511(2), γ = 96.036(2)°, V = 854.5(2) Å^3, space group $P\bar{1}$, Z = 2, $D_{calcd.}$ = 1.504 g/cm^3, F_{000} = 516, Rigaku AFC7R diffractometer, R = 0.0472, Rw = 0.1124. CCDC-249186 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[10] a) D. Hellwinkel, H. Stahl, *Z. Naturforsch. B* **1993**, *48,* 521–538; b) G. C. Pappalardo, *J. Organomet. Chem.* **1977**, *143*, 311–319; c) M. R. Detty, B. J. Murray, *J. Am. Chem. Soc.* **1983**, *105*, 883–890; d) P. Zhong, M.-P. Guo, *Synth. Commun.* **2001**, *31*, 1507–1510.

[11] D.-W. Chen, Z.-C. Chen, *Tetrahedron Lett*. **1994**, *35*, 7637–7638.

[12] a) B. M. Trost, M. J. Bogdanowicz, *J. Am. Chem. Soc.* **1973**, *95*, 5311–5321; b) J. K. Crandall, W. W. Conover, *J. Org. Chem.* **1978**, *43*, 3533–3535.

[13] It is conceivable that monoselenooxide **D** is formed as a result of steric hindrance.

Received September 13, 2004

