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# The reaction of mono-aryl substituted methylenecyclobutanes with diphenyl diselenide in the presence of iodosobenzene diacetate and $H_2O$

Min Jiang, Min Shi *

*State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China*

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ABSTRACT

The mono-aryl substituted methylenecyclobutanes undergo an interesting reaction with diphenyl diselenide in the presence of iodosobenzene diacetate and $H_2O$ at 40 °C in 1,2-dichloroethane to give the corresponding aryl-(1-phenylselanylcyclobutyl)methanones in moderate to good yields within 30 h. A plausible reaction mechanism has been discussed on the basis of the control and $^{18}O$-labeling experiments.



## 1. Introduction

Organoselenium compounds have become attractive synthetic targets because of their unique chemo-, regio-, and stereoselectivities in organic synthesis and their useful biological activities.[1] Furthermore, organoselenium compounds can also be used as precursor for the introduction of a wide variety of functional groups by selenoxide *syn*-elimination[2] and [2,3]-sigmatropic rearrangement,[3] thus avoiding protection group chemistry.[4] Previously, our group reported the reaction of *gem*-aryl disubstituted methylenecyclopropanes (MCPs) with diphenyl diselenide to give the corresponding 1,2-bis(arylselanyl)-3,3-diarylcyclobut-1-ene, a four-membered ring, along with a ring-opened product in the presence of iodosobenzene diacetate [$PhI(OAc)_2$] in moderate to good yields under mild conditions (Scheme 1)[5] as well as the reaction of vinylidenecyclopropanes with diphenyl diselenide catalyzed by iodosobenzene diacetate to produce the corresponding addition products in good yields.[6] In this paper, we wish to report that the mono-aryl substituted methylenecyclobutanes (MCBs)[7] can react with diphenyl diselenide in the presence of iodosobenzene diacetate and $H_2O$ at 40 °C in 1,2-dichloroethane (DCE) to give the corresponding aryl-(1-phenylselanylcyclobutyl)methanones in moderate to good yields rather than the ring-expanded or ring-opened products.

## 2. Results and discussion

At first, we investigated the reaction of mono-aryl substituted methylenecyclobutane **1a** with diphenyl diselenide in the presence of iodosobenzene diacetate and $H_2O$ to develop the optimal conditions.[8] The results of these experiments are summarized in Table 1. Using mono-aryl substituted MCB(**1a**, 1.0 equiv) with PhSeSePh (**2**, 1.0 equiv), $PhI(OAc)_2$ (**3**, 2.0 equiv), and $H_2O$ (1.0 equiv) in DCE at 40 °C, **4a** was produced in 71% yield after 30 h under ambient atmosphere (Table 1, entry 1). When the temperature was changed to room temperature (20 °C), the corresponding product **4a** was produced in trace (Table 1, entry 2). Raising the reaction temperature to 60 °C afforded **4a** in 20% yield (Table 1, entry 3). Changing the ratio of **1a**/**2**/**3**/$H_2O$ to 1:1:1:1 or 1:1.5:3:1 provided **4a** in 35% and 26% yield, respectively (Table 1, entries 4 and 5). Thus, the ratio of 1:1:2:1 for **1a**/**2**/**3**/$H_2O$ is the best one for this reaction to give **4a** in 71% yield in DCE at 40 °C (Table 1, entries 1–5). Further examination of solvent effects revealed that DCE was the best one for this transformation (Table 1, entries 9–14). In tetrahydrofuran (THF), acetonitrile ($CH_3CN$), and toluene, **4a** was obtained in 47%, 35%, and 52% yield at 40 °C after 30 h, respectively


**Scheme 1.** Reactions of *gem*-aryl disubstituted methylenecyclopropanes with diaryl diselenide in the presence of iodosobenzene diacetate.

* Corresponding author.
*E-mail address:* mshi@mail.sioc.ac.cn (M. Shi).

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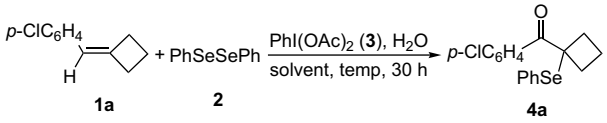
**Table 1**
Optimized reaction conditions of MCB **1a** with PhSeSePh in the presence of $PhI(OAc)_2$




1a 2 4a

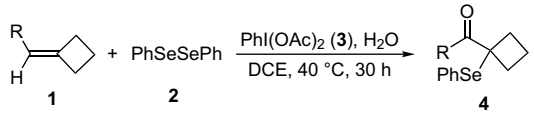
| Entry[a] | **1a**/**2**/**3**/$H_2O$ | Solvent | Temp (°C) | Yield[b] of **4a** (%) |
|---|---|---|---|---|
| *1* | *1:1:2:1* | *DCE* | *40* | *71* |
| 2 | 1:1:2:1 | DCE | rt | Trace |
| 3 | 1:1:2:1 | DCE | 60 | 20 |
| 4 | 1:1:1:1 | DCE | 40 | 35 |
| 5 | 1:1.5:3:1 | DCE | 40 | 26 |
| 6 | 1:1:2:1 | THF | 40 | 47 |
| 7 | 1:1:2:1 | Toluene | 40 | 52 |
| 8 | 1:1:2:1 | $CH_3CN$ | 40 | 35 |
| 9 | 1:1:2:1 | $CH_2Cl_2$ | 30 | 25 |
| 10 | 1:1:2:1 | $Et_2O$ | 30 | 20 |

[a] Reaction conditions: **1a** (0.3 mmol), **2** (0.3 mmol), **3** (0.6 mmol), solvent (2.0 mL), and $H_2O$ (0.3 mmol); and the reactions were carried out at various temperatures.
[b] Isolated yields.

(Table 1, entries 6–8). In dichloromethane or ether at 30 °C, **4a** was formed in only 25% and 20% yield, respectively (Table 1, entries 9 and 10).

Under these optimal reaction conditions, we next carried out the reactions of a variety of MCBs **1** with diphenyl diselenide in the presence of $H_2O$ and iodosobenzene diacetate to examine the scope and limitations. We found that the corresponding products **4** were obtained in moderate to good yields within 30 h in spite of MCBs **1** bearing electron-rich, electron-neutral, and electron-poor substituents on the benzene rings (Table 2). For mono-aryl substituted MCBs **1b**–**1f** having an electron-poor substituent at the *para* or *meta* position of benzene ring, the corresponding products **4b**–**4f** were obtained in 75%–82% yields (Table 2, entries 1–5). But for mono-aryl substituted MCB **1g** having an electron-poor substituent at the *ortho* position of benzene ring, the corresponding product **4g** was obtained in slightly lower yield (61%), presumably due to the steric reason (Table 2, entry 6). Using MCBs **1h**–**1j** bearing an electron-rich substituent on the benzene ring as the substrates afforded the corresponding products **4h**–**4j** in 62%–68% yields under the standard conditions (Table 2, entries 7–9). However, when using mono-aliphatic substituted MCB **1k** as the substrate, the reaction

**Table 2**
Reaction of MCBs **1** with PhSeSePh in the presence of $PhI(OAc)_2$ and $H_2O$



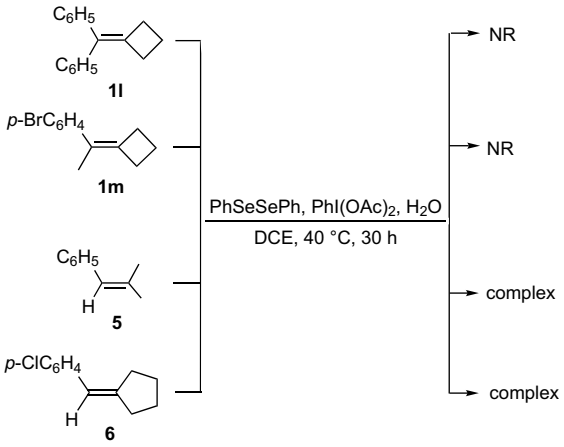

1 2 4

| Entry[a] | MCBs (R) | Yield[b] of **4** (%) |
|---|---|---|
| 1 | **1b**, (*p*-$BrC_6H_4$) | **4b**, 78 |
| 2 | **1c**, (*p*-$FC_6H_4$) | **4c**, 75 |
| 3 | **1d**, (*m*-$ClC_6H_4$) | **4d**, 78 |
| 4 | **1e**, (*m*-$BrC_6H_4$) | **4e**, 77 |
| 5 | **1f**, (*m*-$NO_2C_6H_4$) | **4f**, 82 |
| 6 | **1g**, (*o*-$ClC_6H_4$) | **4g**, 61 |
| 7 | **1h**, (*p*-$MeC_6H_4$) | **4h**, 68 |
| 8 | **1i**, (*p*-$EtC_6H_4$) | **4i**, 65 |
| 9 | **1j**, (*m*-$CH_3C_6H_4$) | **4j**, 62 |
| 10 | **1k**, ($C_4H_9$) | **4k**, - |

[a] Reaction conditions: **1** (0.3 mmol), **2** (0.3 mmol), **3** (0.6 mmol), DCE (2.0 mL), and $H_2O$ (0.3 mmol); and the reactions were carried out at 40 °C.
[b] Isolated yields.

produced complex product mixtures without the formation of **4k**, suggesting that an aromatic group is required in this transformation (Table 2, entry 10).

To further clarify the scope and limitations of this transformation, the reactions of MCBs **1l**, **1m**, alkene **5**, and methylenecyclopentane **6** with diphenyl diselenide in the presence of iodosobenzene diacetate and $H_2O$ have been also examined under identical conditions. However, we found that either none of the corresponding product was formed or complex product mixtures were obtained after 30 h under the standard conditions, indicating that the four-membered cyclobutane ring, an aromatic ring, and a hydrogen atom in MCBs are essential for this reaction (Scheme 2).

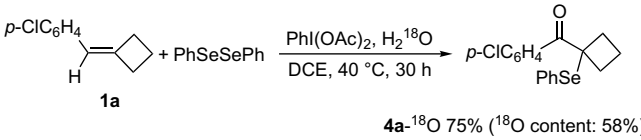



**Scheme 2.** Reaction of **1l**, **1m**, **5**, **6** with diphenyl diselenide in the presence of iodosobenzene diacetate and $H_2O$.

The structures of all these products reported in this paper were determined by $^1H$, $^{13}C$ NMR spectroscopic data, HRMS, or microanalysis. In addition, these products can be easily transformed to the corresponding cyclobutenyl methanones by oxidation.[9]

In order to clarify the reaction mechanism, $H_2^{18}O$ ($^{18}O$ content 97.7%) was used in the reaction of **1a** with diphenyl diselenide and iodosobenzene diacetate under the standard conditions. It was found that the corresponding product **4a**-$^{18}O$ was obtained in 75% yield along with 58% of $^{18}O$ content, indicating that the oxygen atom is indeed derived from water (Scheme 3). The lower $^{18}O$ content of **4a** (58%) is due to that the ambient moisture ($H_2O$) takes part into the reaction as well.

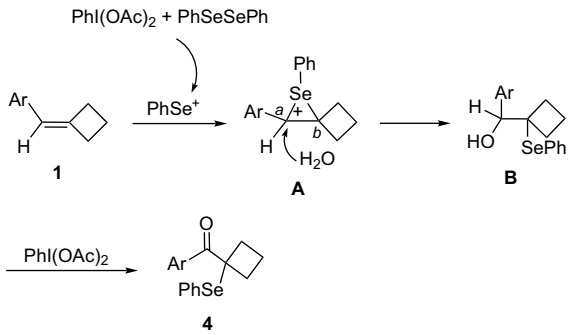
The reaction mechanism is outlined in Scheme 4 on the basis of the $^{18}O$-labeling and control experiments. Initially, the diphenyl diselenide was oxidized by iodosobenzene diacetate to generate intermediate $PhSe^+$,[10] which was added into substrate **1** to form intermediate **A**.[5,6,10] Then, alcohol **B** is formed by the nucleophilic attack of water[11] at the position a of intermediate **A**. Further oxidization of alcohol **B** by iodosobenzene diacetate[12] affords the corresponding product **4**. A hydrogen atom at position *a* can facilitate the nucleophilic attack by water as well as the subsequent oxidation by $PhI(OAc)_2$ to give a ketone. Moreover, the four-membered cyclobutane moiety and an aromatic ring in MCBs can stabilize intermediate **A**, driving the reaction forward. Therefore, the four-membered cyclobutane, an aromatic ring, and a hydrogen atom in MCBs are essential for this reaction.




1a

**4a**-$^{18}O$ 75% ($^{18}O$ content: 58%)

**Scheme 3.** Isotopic labeling experiment using $H_2^{18}O$ under the reaction conditions.




**Scheme 4.** Proposed mechanism for the reaction of MCBs with diphenyl diselenide in the presence of iodosobenzene diacetate and $H_2O$.

## 3. Conclusion

In summary, we have disclosed an interesting reaction of monoaryl substituted methylenecyclobutanes with diphenyl diselenide in the presence of iodosobenzene diacetate and $H_2O$ at 40 °C in 1,2-dichloroethane (DCE) to give the corresponding aryl-(1-phenylselanylcyclobutyl)methanone derivatives in moderate yields. A plausible reaction mechanism has been discussed on the basis of the control and $^{18}O$-labeling experiments. The particular four-membered cyclobutane ring plays a key role for this transformation. The corresponding aryl-(1-phenylselanylcyclobutyl)-methanones **4** may be useful intermediates in organic synthesis. Efforts are in progress to further elucidate the mechanistic details of this reaction and to determine its scope and limitations.

## 4. Experimental procedures

### 4.1. General methods

$^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; *J*-values are in hertz. Mass spectra were recorded by EI methods and HRMS was measured on a Finnigan $MA^+$ mass spectrometer. CHN microanalyses were recorded on a Carlo-Erba 1106 analyzer. Solvents were used without further drying up. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai $GF_{254}$ silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure.

### 4.2. General procedure

Under argon atmosphere, methylenecyclobutanes (**1**, MCBs) (0.3 mmol), PhSeSePh (**2**, 0.3 mmol), and $PhI(OAc)_2$ (**3**, 0.6 mmol) were added into an Schlenk tube. After adding 2.0 mL of dry DCE, $H_2O$ (0.3 mmol) was added rapidly via a syringe. The reaction mixture was stirred at 40 °C for 30 h. Then, the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography ($SiO_2$) to give the corresponding products **4** in moderate yields.

#### *4.2.1. (4-Chlorophenyl)(1-(phenylselanyl)cyclobutyl)-methanone (**4a**)*

A colorless oil; IR ($CH_2Cl_2$): $\nu$ 3057, 2947, 1633, 1583, 1479, 1437, 1394, 1273, 1247, 1177, 1071, 1010, 740, 691 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$, TMS): $\delta$ 1.84–1.91 (1H, m, $CH_2$), 2.31–2.51 (3H, m, $CH_2$), 2.77–2.87 (2H, m, $CH_2$), 7.22–7.27 (2H, m, ArH), 7.33–7.40 (5H, m, ArH), 7.85 (2H, d, *J*=8.7 Hz, ArH); $^{13}C$ NMR (75 MHz, $CDCl_3$, TMS): $\delta$ 16.2, 32.9, 53.2, 127.9, 128.4, 128.9, 129.0, 130.9, 132.0, 136.2, 138.8, 196.6; MS (EI) *m*/*z* (%): 350 (21.67) [$M^+$], 322 (4.74), 211 (46.04), 193 (16.01), 139 (100.00), 130 (45.49), 111 (59.40), 75 (25.35); HRMS (EI) calcd for $C_{17}H_{15}OClSe$ ($M^+$) requires: 349.9977, found: 349.9970.

#### *4.2.2. (4-Bromophenyl)(1-(phenylselanyl)cyclobutyl)-methanone (**4b**)*

A yellow oil; IR ($CH_2Cl_2$): $\nu$ 3057, 2947, 1663, 1583, 1566, 1480, 1437, 1394, 1275, 1247, 1071, 1010, 740, 691 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$, TMS): $\delta$ 1.85–1.89 (1H, m, $CH_2$), 2.31–2.51 (3H, m, $CH_2$), 2.77–2.87 (2H, m, $CH_2$), 7.22–7.27 (2H, m, ArH), 7.31–7.40 (3H, m, ArH), 7.54 (2H, d, *J*=8.4 Hz, ArH), 7.76 (2H, d, *J*=8.4 Hz, ArH); $^{13}C$ NMR (75 MHz, $CDCl_3$, TMS): $\delta$ 16.2, 32.9, 53.2, 127.6, 127.9, 128.9, 129.0, 131.1, 131.4, 132.5, 136.2, 196.8; MS (EI) *m*/*z* (%): 394 (42.68) [$M^+$], 366 (12.09), 239 (11.95), 211 (100.00), 209 (44.90), 182 (94.65), 158 (18.15), 76 (9.79); HRMS (EI) calcd for $C_{17}H_{15}OBrSe$ ($M^+$) requires: 393.9471, found: 393.9471.

#### *4.2.3. (4-Fluorophenyl)(1-(phenylselanyl)cyclobutyl)-methanone (**4c**)*

A colorless oil; IR ($CH_2Cl_2$): $\nu$ 3072, 2927, 1663, 1598, 1505, 1437, 1275, 1236, 1156, 849, 740, 691 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$, TMS): $\delta$ 1.84–1.91 (1H, m, $CH_2$), 2.32–2.51 (3H, m, $CH_2$), 2.78–2.87 (2H, m, $CH_2$), 7.07 (2H, t, *J*=9.0 Hz, ArH), 7.22–7.41 (5H, m, ArH), 7.63 (2H, dd, *J*=9.0, 5.7 Hz, ArH); $^{13}C$ NMR (75 MHz, $CDCl_3$, TMS): $\delta$ 16.1, 33.0, 53.2, 115.2 (d, $J_{C-F}$=22.0 Hz), 128.0, 128.9, 129.0, 130.0, 132.1 (d, $J_{C-F}$=8.9 Hz), 136.2, 165.1 (d, $J_{C-F}$=253.0 Hz), 196.5; MS (EI) *m*/*z* (%): 334 (17.01) [$M^+$], 306 (4.74), 211 (31.12), 209 (15.89), 177 (11.16), 130 (29.44), 123 (100.00), 77 (16.04); HRMS (EI) calcd for $C_{17}H_{15}OFSe$ ($M^+$) requires: 334.0272, found: 334.0273.

#### *4.2.4. (4-Nitrophenyl)(1-(phenylselanyl)cyclobutyl)-methanone (**4d**)*

A white solid, mp 75–77 °C; IR ($CH_2Cl_2$): $\nu$ 2964, 2932, 1682, 1606, 1417, 1252, 1222, 967, 779, 768, 744 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$, TMS): $\delta$ 1.87–1.98 (1H, m, $CH_2$), 2.39–2.59 (3H, m, $CH_2$), 2.82–2.92 (2H, m, $CH_2$), 7.22–7.27 (2H, m, ArH), 7.32–7.38 (3H, m, ArH), 7.61 (1H, t, *J*=8.1 Hz, ArH), 8.23 (1H, d, *J*=6.6 Hz, ArH), 8.33–8.37 (1H, m, ArH), 8.70 (1H, s, ArH); $^{13}C$ NMR (75 MHz, $CDCl_3$, TMS): $\delta$ 16.2, 32.6, 53.2, 124.3, 126.7, 127.6, 129.0, 129.2, 129.3, 135.0, 135.1, 136.1, 147.9, 195.2; MS (EI) *m*/*z* (%): 361 (41.63) [$M^+$], 333 (13.40), 211 (69.97), 183 (29.71), 157 (30.04), 150 (100.00), 130 (64.73), 76 (55.51). Anal. Calcd for $C_{17}H_{15}NO_3Se$: C, 56.68; N, 3.89; H, 4.20%. Found: C, 56.31; N, 3.84; H, 4.20%.

#### *4.2.5. (3-Chlorophenyl)(1-(phenylselanyl)cyclobutyl)-methanone (**4e**)*

A colorless oil; IR ($CH_2Cl_2$): $\nu$ 3064, 2948, 2853, 1666, 1569, 1475, 1437, 1420, 1278, 1244, 1206, 1022, 804, 739, 673 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$, TMS): $\delta$ 1.81–1.91 (1H, m, $CH_2$), 2.32–2.52 (3H, m, $CH_2$), 2.77–2.86 (2H, m, $CH_2$), 7.22–7.40 (6H, m, ArH), 7.46 (1H, d, *J*=8.7 Hz, ArH), 7.77 (1H, d, *J*=8.7 Hz, ArH), 7.87 (1H, s, ArH); $^{13}C$ NMR (75 MHz, $CDCl_3$, TMS): $\delta$ 16.2, 32.8, 53.2, 127.6, 127.9, 128.9, 129.1, 129.4, 129.5, 132.4, 134.4, 135.4, 136.2, 196.4; MS (EI) *m*/*z* (%): 350 (29.21) [$M^+$], 322 (6.35), 211 (71.94), 209 (35.97), 183 (18.75), 157 (18.14), 139 (100.00), 77 (39.51); HRMS (EI) calcd for $C_{17}H_{15}OClSe$ ($M^+$) requires: 349.9977, found: 349.9994.

#### *4.2.6. (3-Bromophenyl)(1-(phenylselanyl)cyclobutyl)-methanone (**4f**)*

A colorless oil; IR ($CH_2Cl_2$): $\nu$ 3056, 2948, 2860, 1662, 1572, 1477, 1438, 1276, 1248, 1182, 1021, 740, 691 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$, TMS): $\delta$ 1.82–1.92 (1H, m, $CH_2$), 2.32–2.55 (3H, m, $CH_2$), 2.77–2.84 (2H, m, $CH_2$), 7.22–7.35 (5H, m, ArH), 7.40 (1H, d, *J*=9.6 Hz, ArH), 7.63 (1H, d, *J*=9.0 Hz, ArH), 7.81 (1H, d, *J*=9.0 Hz, ArH), 8.02 (1H, s, ArH); $^{13}C$ NMR (75 MHz, $CDCl_3$, TMS): $\delta$ 16.2, 32.9, 53.2,

122.5, 127.9, 128.0, 129.0, 129.1, 129.6, 132.4, 135.3, 135.6, 136.2, 196.3; MS (EI) *m/z* (%): 394 (29.44) [$M^+$], 366 (3.76), 239 (13.35), 211 (98.19), 209 (49.75), 183 (90.98), 157 (100.00), 77 (50.50); HRMS (EI) calcd for $C_{17}H_{15}OBrSe$ ($M^+$) requires: 393.9471, found: 393.9484.

*4.2.7. (2-Chlorophenyl)(1-(phenylselanyl)cyclobutyl)-methanone (**4g**)*

A colorless oil; IR ($CH_2Cl_2$): $\nu$ 3058, 2950, 2852, 1681, 1477, 1436, 1281, 1242, 1050, 1022, 968, 898, 739, 691 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$, TMS): $\delta$ 1.88–1.96 (1H, m, $CH_2$), 2.12–2.24 (2H, m, $CH_2$), 2.34–2.43 (1H, m, $CH_2$), 2.71–2.82 (2H, m, $CH_2$), 7.21–7.44 (6H, m, ArH), 7.51 (2H, d, $J$=8.4 Hz, ArH), 7.78 (1H, d, $J$=9.0 Hz, ArH); $^{13}C$ NMR (75 MHz, $CDCl_3$, TMS): $\delta$ 16.1, 32.1, 54.4, 126.2, 128.3, 128.9, 129.0, 129.3, 130.4, 130.8, 131.5, 135.8, 137.4, 200.6; MS (EI) *m/z* (%): 350 (8.29) [$M^+$], 315 (79.95), 287 (10.50), 211 (50.30), 183 (13.88), 157 (21.35), 139 (100.00), 77 (30.72); HRMS (EI) calcd for $C_{17}H_{15}OClSe$ ($M^+$) requires: 349.9977, found: 349.9970.

*4.2.8. (p-Tolyl)(1-(phenylselanyl)cyclobutyl)methanone (**4h**)*

A colorless oil; IR ($CH_2Cl_2$): $\nu$ 3065, 2957, 2853, 1686, 1594, 1449, 1391, 1246, 1219, 1121, 775, 696 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$, TMS): $\delta$ 1.81–1.90 (1H, m, $CH_2$), 2.31–2.49 (3H, m, $CH_2$), 2.40 (3H, s, $CH_3$), 2.79–2.88 (2H, m, $CH_2$), 7.20–7.35 (5H, m, ArH), 7.41 (2H, d, $J$=7.8 Hz, ArH), 7.82 (2H, d, $J$=7.8 Hz, ArH); $^{13}C$ NMR (75 MHz, $CDCl_3$, TMS): $\delta$ 16.2, 21.6, 33.1, 53.3, 128.3, 128.81, 128.84, 128.87, 129.6, 131.1, 136.1, 143.3, 197.7; MS (EI) *m/z* (%): 330 (19.21) [$M^+$], 302 (4.74), 252 (6.19), 211 (39.99), 173 (23.83), 119 (100.00), 91 (75.29), 77 (22.51); HRMS (EI) calcd for $C_{18}H_{18}OSe$ ($M^+$) requires: 330.0523, found: 330.0517.

*4.2.9. (4-Ethylphenyl)(1-(phenylselanyl)cyclobutyl)methanone (**4i**)*

A colorless oil; IR ($CH_2Cl_2$): $\nu$ 3058, 1987, 2852, 1681, 1589, 1477, 1436, 1281, 1242, 1208, 1050, 968, 898, 739, 691 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$, TMS): $\delta$ 1.26 (3H, t, $J$=7.8 Hz, $CH_3$), 1.83–1.87 (1H, m, $CH_2$), 2.33–2.46 (3H, m, $CH_2$), 2.70 (2H, q, $J$=7.8 Hz, $CH_2$), 2.80–2.87 (2H, m, $CH_2$), 7.23–7.33 (5H, m, ArH), 7.42 (2H, d, $J$=7.2 Hz, ArH), 7.85 (2H, d, $J$=7.2 Hz, ArH); $^{13}C$ NMR (75 MHz, $CDCl_3$, TMS): $\delta$ 15.1, 16.2, 28.9, 33.1, 53.3, 127.7, 128.3, 128.8, 128.9, 129.7, 131.3, 136.2, 149.4, 197.8; MS (EI) *m/z* (%): 344 (20.76) [$M^+$], 314 (9.52), 211 (35.37), 187 (20.84), 171 (9.47), 157 (27.23), 133 (100.00), 77 (46.26); HRMS (EI) calcd for $C_{19}H_{20}OSe$ ($M^+$) requires: 344.0679, found: 344.0689.

*4.2.10. (m-Tolyl)(1-(phenylselanyl)cyclobutyl)methanone (**4j**)*

A colorless oil; IR ($CH_2Cl_2$): $\nu$ 3065, 2957, 2853, 1686, 1594, 1449, 1391, 1246, 1219, 1121, 775, 696 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$, TMS): $\delta$ 1.83–1.92 (1H, m, $CH_2$), 2.32–2.51 (3H, m, $CH_2$), 2.38 (3H, s, $CH_3$), 2.79–2.88 (2H, m, $CH_2$), 7.23–7.36 (5H, m, ArH), 7.42 (2H, d, $J$=7.8 Hz, ArH), 7.70 (2H, s, ArH); $^{13}C$ NMR (75 MHz, $CDCl_3$, TMS): $\delta$ 16.2, 21.6, 33.1, 53.3, 121.0, 128.3, 128.8, 128.9, 129.6, 131.1, 136.1, 143.3, 145.2, 197.8; MS (EI) *m/z* (%): 330 (22.39) [$M^+$], 302 (4.02), 211 (34.52), 173 (15.39), 130 (42.34), 119 (83.12), 91 (100.00), 77 (19.20); HRMS (EI) calcd for $C_{18}H_{18}OSe$ ($M^+$) requires: 330.0523, found: 330.0510.

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## Supplementary data

$^1H$ and $^{13}C$ NMR spectroscopic charts for compounds **4a**–**4j** are provided. This material is available free of charge via the Internet. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.11.052.

## References and notes

1. (a) Nogueira, C. W.; Zeni, G.; Rocha, J. B. T. *Chem. Rev.* **2004**, *104*, 6255–6286; (b) Mugesh, G.; du Mont, W. W.; Sies, H. *Chem. Rev.* **2001**, *101*, 2125–2180; (c) Parnham, M. J.; Graf, E. *Prog. Drug Res.* **1991**, *36*, 9–11; (d) Nogueira, C. W.; Quinhones, E. B.; Jung, E. A. C.; Zeni, G.; Rocha, J. B. T. *Inflamm. Res.* **2003**, *52*, 56–59.
2. (a) Huguet, J. L. *Adv. Chem. Ser.* **1967**, 345–349; (b) Sharpless, K. B.; Young, M. W.; Lauer, R. F. *Tetrahedron Lett.* **1973**, *22*, 1979–1982.
3. (a) Reich, H. J. *J. Org. Chem.* **1975**, *40*, 2570–2572; (b) Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 7154–7155.
4. (a) Nicolaou, K. C.; Petasis, N. A. *Selenium in Natural Products Synthesis*; CIS: Philadelphia, 1984; (b) Paulmier, C. *Selenium Reagents and Intermediates in Organic Synthesis*; Pergamon: Oxford, 1986; (c) Patai, S.; Rappoport, Z. *The Chemistry of Organic Selenium and Tellurium Compounds*; Wiley: New York, NY, 1986; Vol. 1; (d) Liotta, D. *Organoselenium Chemistry*; Wiley: New York, NY, 1987; (e) Krief, A.; Hevesi, L. *Organoselenium Chemistry I*; Springer: Berlin, 1988; (f) Back, T. G. *Organoselenium Chemistry: A Practical Approach*; Oxford University Press: Oxford, 1999; (g) Reich, H. J. *Acc. Chem. Res.* **1979**, *12*, 22–30; (h) Liotta, D. *Acc. Chem. Res.* **1984**, *17*, 28–34; (i) Wirth, T. *Topics in Current Chemistry*; Springer: Heidelberg, 2000; Vol. 208; (j) Mugesh, G.; Singh, H. B. *Acc. Chem. Res.* **2002**, *35*, 226–236.
5. Shi, M.; Wang, B.-Y.; Li, J. *Eur. J. Org. Chem.* **2005**, 759–765.
6. Shi, M.; Lu, J.-M. *Synlett* **2005**, 2352–2356.
7. For the synthesis of MCBs, see: Brandi, A.; Goti, A. *Chem. Rev.* **1998**, *98*, 589–636.
8. It has been reported that treatment of diphenyl diselenide with iodosobenzene diacetate produces an electrophilic selenenylating agent for double bonds. See: (a) Tingoli, M.; Tiecco, M.; Testaferri, L.; Temperini, A. *Synth. Commun.* **1998**, *28*, 1769–1772; (b) Tiecco, M.; Tingoli, M.; Testaferri, L. *Pure Appl. Chem.* **1993**, *65*, 715–722 and references cited therein; (c) Miyoshi, N.; Takai, Y.; Murai, S.; Sonoda, N. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1265–1266; (d) Brugier, D.; Outurquin, F.; Paulmier, C. *J. Chem. Soc., Perkin Trans. 1* **2001**, 37–43.
9. Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434–5449.
10. Chen, D.-W.; Chen, Z.-C. *Tetrahedron Lett.* **1994**, *41*, 7637–7638.
11. The examples of water as nucleophilic reagent: (a) Kurz, J. L.; Lu, J. Y. *J. Phys. Chem.* **1983**, *87*, 1444–1448; (b) Chi, D. Y.; Kim, D. W.; Hong, D. J.; Kim, H. S. *J. Org. Chem.* **2004**, *69*, 3186–3189.
12. The oxidation of iodobenzene diacetate: (a) Swenton, J. S.; Callinan, A.; Chen, Y.; Rohde, J. J.; Kerns, M. L.; Morrow, J. W. *J. Org. Chem.* **1996**, *61*, 1267–1274; (b) Canesi, S.; Bouchu, D.; Ciufolini, M. A. *Org. Lett.* **2005**, *7*, 175–177.