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Studies on the highly regio- and stereoselective selenohydroxylation of 1,2-allenylic sulfoxides with PhSeCl

Guangke He,[a] Chao Zhou,[a] Chunling Fu[a,*] and Shengming Ma[a,b,*]

[a]*Laboratory of Molecular Recognition and Synthesis, Department of Chemistry, Zhejiang University, 310027 Hangzhou, Zhejiang, PR China*
[b]*State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, PR China*

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Abstract—The selenohydroxylation of 1,2-allenyl sulfoxides with PhSeCl in MeCN/H_2O (10/1) afforded *E*-3-hydroxy-2-phenylseleno-1-alkenyl sulfoxides in good yields and high regio-/stereoselectivities.

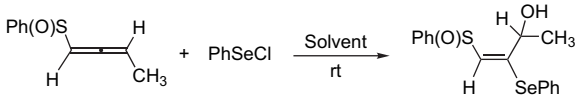
1. Introduction

Electrophilic addition of allenes is synthetically promising since two functionalities can be introduced within one preparative operation provided the issues of regio- and stereoselectivity can be addressed.[1] Recently, we have developed the halohydroxylation of sulfur-substituted allenes.[2,3] In these reactions the regioselectivity is the same by introducing the hydroxy group and halogen atom to the carbon–carbon double bond at the 2-position. However, the stereoselectivity depends on the nature of the sulfur-containing functionality providing *Z*- or *E*-isomer highly selective. In this paper, we wish to report the highly regio- and stereoselective selenohydroxylation of 1,2-allenylic sulfoxides.[3]

2. Results and discussion

The reaction of 1,2-butadienyl phenyl sulfoxide with PhSeCl in CH_2Cl_2, THF, or toluene afforded the related selenohydroxylation product **2a** in low yields (19–50%; Table 1, entries 1–3); no reaction was observed in MeCN (entry 4). Since a hydroxyl group was introduced, we proceeded to study the effect of water on this reaction. In fact, the reaction in aqueous organic solvents, such as THF, DMF, or CH_3CN all afforded **2a** in higher yields with MeCN being the best (entries 5–7). Furthermore, it was observed that the amounts of both water and PhSeCl are important for a high-yielding reaction. The optimized reaction conditions are listed in entry 11 of Table 1. The structure of **2a** was confirmed by its X-ray diffraction study (Fig. 1).[4]

Table 1. Selenohydroxylation of 1,2-butadienyl phenyl sulfoxide with PhSeCl



1a **2a**

Entry	PhSeCl (equiv)	Solvent	Temp (°C)	Time (min)	Isolated yield of **2a** (%)	dr
1	2	CH_2Cl_2[a]	10	10	32	72/28
2	2	THF	8	25	19	63/37
3	2	Toluene	8	30	50	63/37
4	2	CH_3CN	12	90	0	—
5	2	THF/H_2O=10/1	10	90	77	60/40
6	2	DMF/H_2O=10/1	10	90	81	61/39
7	2	CH_3CN/H_2O=10/1	11	10	84	60/40
8	2	CH_3CN/H_2O=20/1	11	15	66	61/39
9	1.2	CH_3CN/H_2O=10/1	15	14	78	60/40
10	2	CH_3CN/H_2O=3/1	12	240	77	59/41
11	1.5	CH_3CN/H_2O=10/1	15	14	86	60/40
12	2.5	CH_3CN/H_2O=10/1	15	6	67	60/40

[a] The reaction was conducted under N_2 atmosphere.

Then the scope of this reaction was studied with some of the most representative results being summarized in Table 2. In fact, the scope of this reaction is very broad: the reaction can proceed with the 3-monosubstituted (entries 1–8), 3,3-disubstituted (entries 9–12), 1,3-disubstituted (entry 13), and fully substituted (entry 14) 1,2-allenyl sulfoxides with the yields ranging from 48 to 93%. In all the cases, the reaction proceeded smoothly at ambient temperature to afford *E*-3-hydroxy-2-phenylseleno-1-alkenyl sulfoxides with high regio- and stereoselectivity.

* Corresponding authors. Fax: +86 21 64167510 (S.A.); e-mail: masm@mail.sioc.ac.cn

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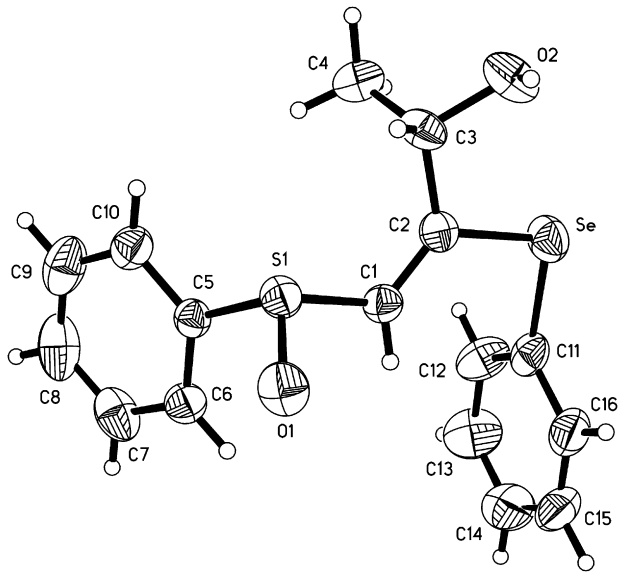
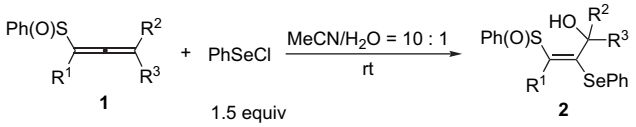


Figure 1. ORTEP representation of **2a**.

Table 2. The reaction of differently substituted 1,2-allenyl sulfoxides with PhSeCl



Entry	1			Time (min)	Isolated yield of **2** (%)	dr
	R^1	R^2	R^3			
1	H	CH_3	H	14	86 (**2a**)	60/40
2	H	H	H	10	48 (**2b**)	—
3	H	C_2H_5	H	15	76 (**2c**)	50/50
4	H	*i*-C_3H_7	H	19	80 (**2d**)	50/50
5	H	*n*-C_4H_9	H	60	85 (**2e**)	76/24
6	H	*n*-C_7H_{15}	H	18	76 (**2f**)	60/40
7	H	Ph	H	18	71 (**2g**)	65/35
8	H	Bn	H	12	80 (**2h**)	50/50
9	H	CH_3	*n*-C_3H_7	15	77 (**2i**)	69/31
10	H	C_2H_5	C_2H_5	11	85 (**2j**)	—
11	H	$(CH_2)_5$		14	89 (**2k**)	—
12	H	*n*-C_4H_9	*n*-C_4H_9	11	75 (**2l**)	—
13	*n*-C_7H_{15}	CH_3	H	21	93 (**2m**)	50/50
14	*n*-C_4H_9	CH_3	CH_3	15	51 (**2n**)	—

3. Conclusion

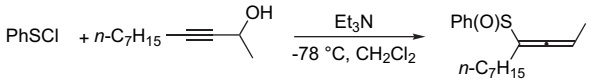
In conclusion, we have established a highly regio- and stereoselective *E*-selenohydroxylation of the relatively electron-rich carbon–carbon double bond in 1,1-allenyl sulfoxides. Due to the presence of carbon–carbon double bond, C–Se bond, and the hydroxyl group this reaction will be useful in organic synthesis. Further studies in this area are being conducted in our laboratory.

4. Experimental

4.1. Starting materials

Compounds **1a–l** and **1n** were prepared according to known procedures.[5] Compound **1m** was prepared as follows.

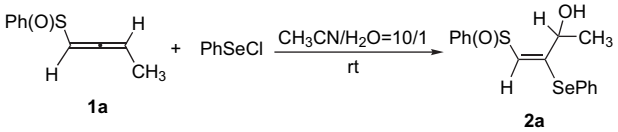
4.1.1. Undeca-2,3-dien-4-yl phenyl sulfoxide (1m).



Typical procedure:[5] a dried three-neck round-bottom flask was charged with undec-3-yn-2-ol (6.72 g, 40 mmol) and triethylamine (5.5 mL, 40 mmol) in methylene chloride (150 mL) with stirring. After the mixture was cooled to −78 °C, a solution of sulfenyl chloride (5.50 g, 38 mmol) was added dropwise. After being stirred at −78 °C for 8 min, methyl iodide (0.5 mL) was added and the reaction mixture was allowed to warm naturally to room temperature followed by quenching with water (20 mL). The organic layer was separated and the aqueous layer was extracted with methylene chloride (20× 2 mL). The combined organic extracts were washed with water and brine and dried over anhydrous Na_2SO_4. After evaporation of the solvent, chromatography on silica gel (eluent: petroleum ether/ethyl acetate=20/1) of the crude product afforded 7.82 g (75%) of **1m** as an oil. Liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63–7.58 (m, 2H), 7.57–7.42 (m, 3H), 5.72–5.60 (m, 1H), 2.25–2.12 (m, 1H), 1.82 (d, J=4.8 Hz, 2H), 1.80 (d, J=4.8 Hz, 2H), 1.40–1.23 (m, 2H), 1.23–1.10 (m, 8H), 0.85 (t, J=7.0 Hz, 3H); MS (EI, 70 eV): m/z (%) 277 (M^++1, 15.56), 276 (M^+, 75.04), 149 (100); IR (cm^{-1}): ν 2927, 2856, 1958, 1581, 1458, 1443, 1083, 1050, 749, 694. Anal. Calcd for $C_{17}H_{24}OS$: C 73.86, H 8.75. Found: C 73.96, H 8.69.

4.2. Typical procedure

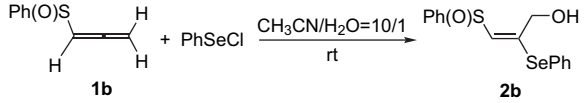
4.2.1. *E*-3-Phenylselanyl-4-phenylsulfinyl-3-buten-2-ol (*E*-2a).



To a solution of PhSeCl (57.2 mg, 0.3 mmol) in 3 mL of MeCN was added 0.4 mL of H_2O. Then a solution of **1a** (35.4 mg, 0.2 mmol) in MeCN (1 mL) was subsequently added at room temperature and the resulting mixture was stirred at room temperature for 14 min. After complete consumption of the starting material as monitored by TLC (eluent: petroleum ether/ethyl acetate=2/1), the mixture was quenched with 10 mL of H_2O, extracted with diethyl ether (3×20 mL), washed with brine, and dried over anhydrous Na_2SO_4. Filtration, evaporation, and flash chromatography on silica gel (petroleum ether/ethyl acetate=2/1) afforded *E*-**2a** (59.8 mg, 86%, dr=60/40) as a solid. Mp 152–154 °C (hexane/acetone). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58–7.50 (m, 1H), 7.50–7.39 (m, 6H), 7.37–7.28 (m, 1H), 7.28–7.22 (m, 2H), [5.64 (s, 40%), 5.60 (s, 60%), 1H], [5.43 (q, J=6.4 Hz, 60%), 5.37 (q, J=6.4 Hz, 40%), 1H], 3.89 (br s, 1H), [1.64 (d, J=6.8 Hz, 40%), 1.54 (d, J=6.8 Hz, 60%), 3H]; MS (EI, 70 eV): m/z (%) 339 (M^+(^{82}Se)−CH_3, 1.36), 338 (M^+(^{82}Se)−CH_3-H, 5.49), 337 (M^+(^{80}Se)−CH_3, 24.24), 336 (M^+(^{80}Se)−CH_3-H, 39.59), 335 (M^+(^{78}Se)−CH_3, 100), 334 (M^+(^{78}Se)−CH_3-H or M^+(^{77}Se)−CH_3, 98.04), 333 (M^+(^{77}Se)−CH_3-H or M^+(^{76}Se)−CH_3, 51.80),

332 ($M^+(^{76}Se)-CH_3$-H, 59.06), 331 ($M^+(^{74}Se)-CH_3$, 31.15), 330 ($M^+(^{74}Se)-CH_3$-H, 16.62); IR (KBr, cm^{-1}): ν 3275, 1572, 1475, 1447, 1122, 1014. Anal. Calcd for $C_{16}H_{16}O_2SSe$: C 54.70, H 4.59. Found: C 54.69, H 4.59.

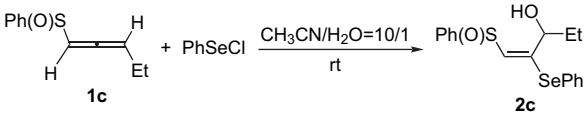
4.2.2. *E*-2-Phenylselanyl-3-phenylsulfinyl-2-propen-1-ol (*E*-2b).



1b 2b

The reaction of 48.5 mg (0.30 mmol) of **1b** and 86.1 mg (0.45 mmol) of PhSeCl in 0.6 mL of H_2O and 6 mL of CH_3CN afforded *E*-**2b** (48.3 mg, 48%) as a solid. Mp 93–95 °C (hexane/dichloromethane). ^1H NMR (400 MHz, $CDCl_3$): δ 7.57–7.51 (m, 2H), 7.51–7.42 (m, 5H), 7.38–7.22 (m, 3H), 5.83 (s, 1H), 4.84 (d, J=14.4 Hz, 1H), 4.66 (d, J=14.4 Hz, 1H), 4.29 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.7, 143.4, 136.2, 130.8, 129.9, 129.4, 129.33, 129.30, 125.9, 124.4, 62.5; MS (EI, 70 eV): *m/z* (%) 323 ($M^+(^{82}Se)-OH$, 3.62), 322 ($M^+(^{82}Se)-OH$-H, 14.49), 321 ($M^+(^{80}Se)-OH$, 16.67), 320 ($M^+(^{80}Se)-OH$-H, 50.72), 319 ($M^+(^{78}Se)-OH$, 8.70), 318 ($M^+(^{78}Se)-OH$-H or $M^+(^{77}Se)-OH$, 26.81), 317 ($M^+(^{77}Se)-OH$-H or $M^+(^{76}Se)-OH$, 8.70), 316 ($M^+(^{76}Se)-OH$-H, 8.70), 77 (100); IR (KBr, cm^{-1}): ν 3281, 1586, 1560, 1476, 1442, 1008. Anal. Calcd for $C_{15}H_{14}O_2SSe$: C 53.41, H 4.18. Found: C 53.25, H 4.09.

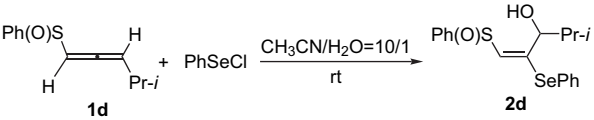
4.2.3. *E*-2-Phenylselanyl-1-phenylsulfinyl-1-penten-3-ol (*E*-2c).



1c 2c

The reaction of 38.4 mg (0.20 mmol) of **1c** and 58.2 mg (0.30 mmol) of PhSeCl in 0.4 mL of H_2O and 4 mL of CH_3CN afforded *E*-**2c** (55.2 mg, 76%, dr=50/50) as a solid. Mp 120–122 °C (hexane/dichloromethane). ^1H NMR (400 MHz, $CDCl_3$): δ 7.56–7.49 (m, 1H), 7.49–7.35 (m, 6H), 7.34–7.18 (m, 3H), 5.69 (s, 1H), 5.20–5.09 (m, 1H), [4.77 (br s, 50%), 4.12 (br s, 50%), 1H], [2.09–1.90 (m), 1.80–1.66 (m), 2H], [1.11 (t, J=7.4 Hz, 50%), 1.05 (t, J=7.4 Hz, 50%), 3H]; MS (EI, 70 eV): *m/z* (%) 353 ($M^+(^{82}Se)-CH_3$, 4.27), 352 ($M^+(^{82}Se)-CH_3$-H, 23.27), 351 ($M^+(^{80}Se)-CH_3$, 19.56), 350 ($M^+(^{80}Se)-CH_3$-H, 100), 349 ($M^+(^{78}Se)-CH_3$, 10.62), 348 ($M^+(^{78}Se)-CH_3$-H or $M^+(^{77}Se)-CH_3$, 50.76), 347 ($M^+(^{77}Se)-CH_3$-H or $M^+(^{76}Se)-CH_3$, 18.70), 346 ($M^+(^{76}Se)-CH_3$-H, 18.27), 344 ($M^+(^{74}Se)-CH_3$-H, 1.77); IR (KBr, cm^{-1}): ν 3293, 1577, 1561, 1476, 1439, 1006; Anal. Calcd for $C_{17}H_{18}O_2SSe$: C 55.89, H 4.97. Found: C 55.93, H 4.90.

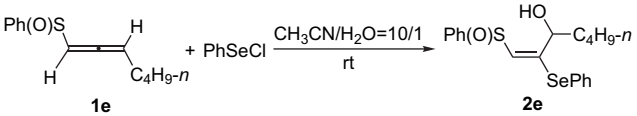
4.2.4. *E*-4-Methyl-2-phenylselanyl-1-phenylsulfinyl-1-penten-3-ol (*E*-2d).



1d 2d

The reaction of 61.7 mg (0.30 mmol) of **1d** and 87.0 mg (0.45 mmol) of PhSeCl in 0.6 mL of H_2O and 6 mL of CH_3CN afforded *E*-**2d** (90.8 mg, 80%, dr=50/50) as a solid. Mp 114.5–116.5 °C (hexane/acetone). ^1H NMR (400 MHz, $CDCl_3$): δ 7.52–7.35 (m, 7H), 7.35–7.20 (m, 3H), [5.77 (s, 50%), 5.74 (s, 50%), 1H], [4.87 (d, J=8.0 Hz, 50%), 4.82 (d, J=8.0 Hz, 50%), 1H], 3.53 (br s, 1H), 2.18–2.10 (m, 1H), 1.16 (d, J=6.4 Hz, 3H), [1.11 (d, J=6.4 Hz, 50%), 0.95 (d, J=6.4 Hz, 50%), 3H]; MS (EI, 70 eV): *m/z* (%) 367 ($M^+(^{82}Se)-CH_3$, 3.05), 366 ($M^+(^{82}Se)-CH_3$-H, 15.53), 365 ($M^+(^{80}Se)-CH_3$, 12.56), 364 ($M^+(^{80}Se)-CH_3$-H, 61.54), 363 ($M^+(^{78}Se)-CH_3$, 6.86), 362 ($M^+(^{78}Se)-CH_3$-H or $M^+(^{77}Se)-CH_3$, 32.20), 361 ($M^+(^{77}Se)-CH_3$-H or $M^+(^{76}Se)-CH_3$, 11.97), 360 ($M^+(^{76}Se)-CH_3$-H, 10.64), 359 ($M^+(^{74}Se)-CH_3$, 1.04), 358 ($M^+(^{74}Se)-CH_3$-H, 1.80), 134 (100); IR (KBr, cm^{-1}): ν 3226, 2965, 1579, 1545, 1475, 1439, 1005. Anal. Calcd for $C_{18}H_{20}O_2SSe$: C 56.99, H 5.31. Found: C 56.88, H 5.20.

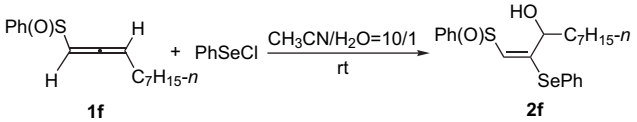
4.2.5. *E*-2-Phenylselanyl-1-phenylsulfinyl-1-hepten-3-ol (*E*-2e).



1e 2e

The reaction of 65.5 mg (0.30 mmol) of **1e** and 86.8 mg (0.45 mmol) of PhSeCl in 0.6 mL of H_2O and 6 mL of CH_3CN afforded *E*-**2e** (99.4 mg, 85%, dr=76/24) as a solid. Mp 82.5–84 °C (hexane/dichloromethane). ^1H NMR (400 MHz, $CDCl_3$): δ 7.55–7.42 (m, 7H), 7.36–7.23 (m, 3H), [5.69 (s, 24%), 5.68 (s, 76%), 1H], [5.26–5.20 (m, 76%), 5.17 (t, J=7.0 Hz, 24%), 1H], 2.06–1.88 (m, 1H), 1.80–1.61 (m, 2H), 1.61–1.46 (m, 1H), 1.46–1.32 (m, 3H), 1.00–0.90 (m, 3H); MS (EI, 70 eV): *m/z* (%) 397 ($M^+(^{82}Se)$+1, 1.18), 396 ($M^+(^{82}Se)$, 4.10), 395 ($M^+(^{80}Se)$+1, 3.90), 394 ($M^+(^{80}Se)$, 18.29), 393 ($M^+(^{78}Se)$+1, 2.53), 392 ($M^+(^{78}Se)$ or $M^+(^{77}Se)$+1, 10.26), 391 ($M^+(^{77}Se)$ or $M^+(^{76}Se)$+1, 4.15), 390 ($M^+(^{76}Se)$, 3.09), 388 ($M^+(^{74}Se)$, 0.61), 85 (100); IR (KBr, cm^{-1}): ν 3221, 2952, 2928, 1578, 1560, 1475, 1440, 1006. Anal. Calcd for $C_{19}H_{22}O_2SSe$: C 58.01, H 5.64. Found: C 57.72, H 5.51.

4.2.6. *E*-2-Phenylselanyl-1-phenylsulfinyl-1-decen-3-ol (*E*-2f).

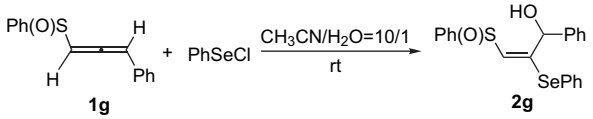


1f 2f

The reaction of 52.6 mg (0.20 mmol) of **1f** and 57.9 mg (0.30 mmol) of PhSeCl in 0.4 mL of H_2O and 4 mL of CH_3CN afforded *E*-**2f** (66.2 mg, 76%, dr=60/40) as a solid. Mp 87–89 °C (hexane/acetone). ^1H NMR (400 MHz, $CDCl_3$): δ 7.47–7.30 (m, 7H), 7.30–7.15 (m, 3H), [5.62 (s, 40%), 5.60 (s, 60%), 1H], [5.16–5.10 (m, 60%), 5.07 (t, J=6.8 Hz, 40%), 1H], 3.94 (br s, 1H), 1.93–1.80 (m, 1H), 1.66–1.17 (m, 11H), 0.84–0.75 (m, 3H); MS (EI, 70 eV): *m/z* (%) 423 ($M^+(^{82}Se)-CH_3$, 5.64), 422 ($M^+(^{82}Se)-CH_3$-H, 23.95), 421 ($M^+(^{80}Se)-CH_3$, 24.57), 420 ($M^+(^{80}Se)-CH_3$-H, 100),

419 ($M^+(^{78}Se)-CH_3$, 13.11), 418 ($M^+(^{78}Se)-CH_3$-H or $M^+(^{77}Se)-CH_3$, 51.97), 417 ($M^+(^{77}Se)-CH_3$-H or $M^+(^{76}Se)-CH_3$, 19.52), 416 ($M^+(^{76}Se)-CH_3$-H, 18.43), 415 ($M^+(^{74}Se)-CH_3$, 0.51), 414 ($M^+(^{74}Se)-CH_3$-H, 1.77); IR (KBr, cm^{-1}): ν 3293, 2923, 1636, 1560, 1446, 1006; Anal. Calcd for $C_{22}H_{28}O_2SSe$: C 60.68, H 6.48. Found: C 60.69, H 6.45.

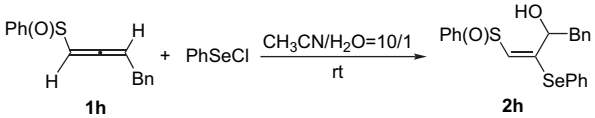
4.2.7. *E*-1-Phenyl-2-phenylselanyl-3-phenylsulfinyl-2-propen-1-ol (*E*-2g).



1g 2g

The reaction of 72.7 mg (0.30 mmol) of **1g** and 86.4 mg (0.45 mmol) of PhSeCl in 0.6 mL of H_2O and 6 mL of CH_3CN afforded *E*-**2g** (88.7 mg, 71%, dr=65/35) as a solid. Mp 144–145 °C (hexane/dichloromethane). ^1H NMR (400 MHz, $CDCl_3$): δ 7.70–7.51 (m, 3H), 7.51–7.35 (m, 7H), 7.35–7.25 (m, 2H), 7.25–7.15 (m, 2H), 7.12 (d, J=7.2 Hz, 1H), [6.36 (s, 65%), 6.33 (s, 35%), 1H], [5.85 (s, 35%), 5.73 (s, 65%), 1H], 2.49 (br s, 1H); MS (EI, 70 eV): *m/z* (%) 399 ($M^+(^{82}Se)-OH$, 2.88), 398 ($M^+(^{82}Se)-OH$-H, 5.04), 397 ($M^+(^{80}Se)-OH$, 6.47), 396 ($M^+(^{80}Se)-OH$-H, 12.95), 395 ($M^+(^{78}Se)-OH$, 3.60), 394 ($M^+(^{78}Se)-OH$-H or $M^+(^{77}Se)-OH$, 6.47), 393 ($M^+(^{77}Se)-OH$-H or $M^+(^{76}Se)-OH$, 2.88), 392 ($M^+(^{76}Se)-OH$-H, 1.80), 55 (100); IR (KBr, cm^{-1}): ν 3214, 1560, 1475, 1439, 1005. Anal. Calcd for $C_{21}H_{18}O_2SSe$: C 61.01, H 4.39. Found: C 60.93, H 4.30.

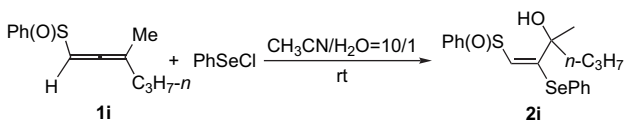
4.2.8. *E*-1-Phenyl-3-phenylselanyl-4-phenylsulfinyl-3-buten-2-ol (*E*-2h).



1h 2h

The reaction of 75.9 mg (0.30 mmol) of **1h** and 85.7 mg (0.45 mmol) of PhSeCl in 0.6 mL of H_2O and 6 mL of CH_3CN afforded *E*-**2h** (101.9 mg, 80%, dr=50/50) as a solid. Mp 130–132 °C (hexane/dichloromethane). ^1H NMR (400 MHz, $CDCl_3$): δ 7.55–7.20 (m, 14H), 6.89 (d, J=7.2 Hz, 1H), [5.68 (s, 50%), 5.64 (s, 50%), 1H], [5.53 (t, J=7.2 Hz, 50%), 5.38 (dd, J=8.8, 4.4 Hz, 50%), 1H], 3.36–3.10 (m, 2H); MS (EI, 70 eV): *m/z* (%) 415 ($M^+(^{82}Se)-CH_3$, 1.27), 414 ($M^+(^{82}Se)-CH_3$-H, 7.26), 413 ($M^+(^{80}Se)-CH_3$, 32.98), 412 ($M^+(^{80}Se)-CH_3$-H, 100), 411 ($M^+(^{78}Se)-CH_3$, 9.86); IR (KBr, cm^{-1}): ν 3338, 1578, 1475, 1438, 1027, 1007. Anal. Calcd for $C_{22}H_{20}O_2SSe$: C 61.82, H 4.72. Found: C 61.82, H 4.71.

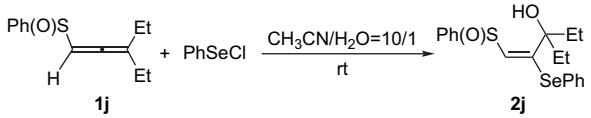
4.2.9. *E*-3-Methyl-2-phenylselanyl-1-phenylsulfinyl-1-hexen-3-ol (*E*-2i).



1i 2i

The reaction of 45.0 mg (0.20 mmol) of **1i** and 58.1 mg (0.30 mmol) of PhSeCl in 0.4 mL of H_2O and 4 mL of CH_3CN afforded *E*-**2i** (62.2 mg, 77%, dr=69/31) as a solid. Mp 117–119 °C (hexane/dichloromethane). ^1H NMR (400 MHz, $CDCl_3$): δ 7.57–7.50 (m, 2H), 7.50–7.37 (m, 5H), 7.35–7.21 (m, 3H), [5.57 (s, 31%), 5.56 (s, 69%), 1H], [4.28 (s, 69%), 3.96 (s, 31%), 1H], 1.96–1.86 (m, 1H), 1.85–1.72 (m, 1H), [1.64 (s, 71%), 1.61 (s, 29%), 3H], 1.55–1.30 (m, 2H), 0.96–0.80 (m, 3H); MS (EI, 70 eV): *m/z* (%) 381 ($M^+(^{82}Se)-CH_3$, 3.51), 380 ($M^+(^{82}Se)-CH_3$-H, 16.41), 379 ($M^+(^{80}Se)-CH_3$, 14.61), 378 ($M^+(^{80}Se)-CH_3$-H, 71.05), 377 ($M^+(^{78}Se)-CH_3$, 8.09), 376 ($M^+(^{78}Se)-CH_3$-H or $M^+(^{77}Se)-CH_3$, 35.42), 375 ($M^+(^{77}Se)-CH_3$-H or $M^+(^{76}Se)-CH_3$, 13.22), 374 ($M^+(^{76}Se)-CH_3$-H, 12.73), 373 ($M^+(^{74}Se)-CH_3$, 0.31), 372 ($M^+(^{74}Se)-CH_3$-H, 1.22), 43 (100); IR (KBr, cm^{-1}): ν 3280, 2955, 1570, 1475, 1439, 1011. Anal. Calcd for $C_{19}H_{22}O_2SSe$: C 58.01, H 5.64. Found: C 58.01, H 5.59.

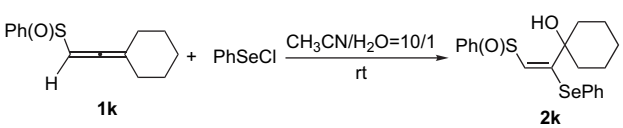
4.2.10. *E*-3-Ethyl-2-phenylselanyl-1-phenylsulfinyl-1-penten-3-ol (*E*-2j).



1j 2j

The reaction of 44.8 mg (0.20 mmol) of **1j** and 58.3 mg (0.30 mmol) of PhSeCl in 0.4 mL of H_2O and 4 mL of CH_3CN afforded *E*-**2j** (68.2 mg, 85%) as a solid. Mp 125–126 °C (hexane/dichloromethane). ^1H NMR (400 MHz, $CDCl_3$): δ 7.57–7.47 (m, 2H), 7.47–7.41 (m, 2H), 7.41–7.36 (m, 3H), 7.35–7.23 (m, 3H), 5.64 (s, 1H), 3.41 (s, 1H), 2.09–1.91 (m, 2H), 1.87–1.72 (m, 2H), 1.05 (t, J=7.3 Hz, 3H), 0.95 (t, J=7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.1, 145.6, 136.5, 131.0, 130.4, 129.8, 129.3, 128.9, 127.5, 124.7, 81.3, 35.0, 34.5, 7.7, 7.6; MS (EI, 70 eV): *m/z* (%) 381 ($M^+(^{82}Se)-CH_3$, 1.52), 380 ($M^+(^{82}Se)-CH_3$-H, 8.59), 379 ($M^+(^{80}Se)-CH_3$, 6.62), 378 ($M^+(^{80}Se)-CH_3$-H, 34.11), 377 ($M^+(^{78}Se)-CH_3$, 4.76), 376 ($M^+(^{78}Se)-CH_3$-H or $M^+(^{77}Se)-CH_3$, 18.26), 375 ($M^+(^{77}Se)-CH_3$-H or $M^+(^{76}Se)-CH_3$, 6.43), 374 ($M^+(^{76}Se)-CH_3$-H, 6.63), 373 ($M^+(^{74}Se)-CH_3$, 0.37), 372 ($M^+(^{74}Se)-CH_3$-H, 0.93), 57 (100); IR (KBr, cm^{-1}): ν 3303, 2962, 1577, 1479, 1459, 1009. Anal. Calcd for $C_{19}H_{22}O_2SSe$: C 58.01, H 5.64. Found: C 58.02, H 5.65.

4.2.11. *E*-1,1-(Pentamethylene)-2-phenylselanyl-3-phenylsulfinyl-2-propenol (*E*-2k).

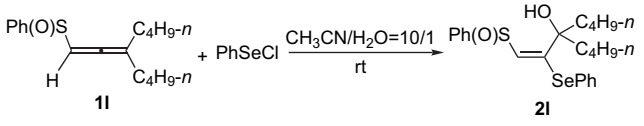


1k 2k

The reaction of 46.4 mg (0.20 mmol) of **1k** and 57.6 mg (0.30 mmol) of PhSeCl in 0.4 mL of H_2O and 4 mL of CH_3CN afforded *E*-**2k** (72.2 mg, 89%) as a solid. Mp 133–135 °C (hexane/dichloromethane). ^1H NMR (400 MHz, $CDCl_3$): δ 7.58–7.50 (m, 2H), 7.42–7.35 (m, 5H), 7.30–7.19 (m, 3H), 5.54 (s, 1H), 3.90 (s, 1H), 2.07–1.90 (m, 3H), 1.82–1.58 (m, 6H), 1.31–1.19 (m, 1H); ^{13}C NMR

(100 MHz, $CDCl_3$): δ 160.2, 145.0, 136.1, 130.4, 129.9, 129.7, 129.1, 129.0, 128.2, 124.8, 77.2, 37.7, 36.7, 24.9, 21.5, 21.3; MS (EI, 70 eV): *m/z* (%) 405 (2.14), 396 (1.25), 394 (2.21), 392 (7.87), 390 (2.54), 389 (1.32), 374 (24.08), 373 (19.54), 372 (100), 371 (14.20), 370 (43.99), 369 (14.66), 368 (21.12); IR (KBr, cm^{-1}): ν 3179, 2935, 1649, 1578, 1474, 1437, 1008. Anal. Calcd for $C_{20}H_{22}O_2SSe$: C 59.25, H 5.47. Found: C 59.12, H 5.58.

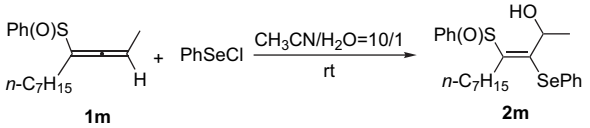
4.2.12. *E*-3-*n*-Butyl-2-phenylselanyl-1-phenylsulfinyl-hepten-3-ol (*E*-2l).



1l **2l**

The reaction of 83.4 mg (0.30 mmol) of **1l** and 87.2 mg (0.45 mmol) of PhSeCl in 0.6 mL of H_2O and 6 mL of CH_3CN afforded *E*-**2l** (102.1 mg, 75%) as a liquid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.58–7.22 (m, 10H), 5.65 (s, 1H), 3.54 (s, 1H), 2.05–1.85 (m, 2H), 1.80–1.65 (m, 2H), 1.61–1.45 (m, 1H), 1.44–1.20 (m, 7H), 0.96–0.81 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.1, 145.7, 136.4, 131.1, 130.3, 129.7, 129.1, 128.8, 127.6, 124.8, 80.8, 42.2, 41.7, 25.3, 25.0, 22.8, 22.7, 13.9; MS (EI, 70 eV): *m/z* (%) 437 ($M^+(^{82}Se)-CH_3$, 2.41), 436 ($M^+(^{82}Se)-CH_3$-H, 6.05), 435 ($M^+(^{80}Se)-CH_3$, 5.40), 434 ($M^+(^{80}Se)-CH_3$-H, 22.65), 433 ($M^+(^{78}Se)-CH_3$, 3.00), 432 ($M^+(^{78}Se)-CH_3$-H or $M^+(^{77}Se)-CH_3$, 11.71), 431 ($M^+(^{77}Se)-CH_3$-H or $M^+(^{76}Se)-CH_3$, 5.60), 430 ($M^+(^{76}Se)-CH_3$-H, 4.44), 85 (100); IR (neat, cm^{-1}): ν 3300, 2955, 2932, 1578, 1475, 1440, 1014. HRMS for $C_{23}H_{30}O_2S^{80}SeNa^+$ (M^++Na): 473.1036. Found: 473.1036.

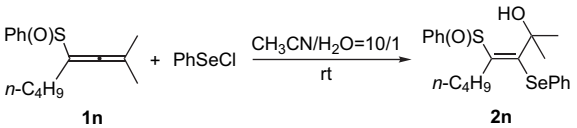
4.2.13. *E*-3-Phenylselanyl-4-phenylsulfinyl-3-undecen-2-ol (*E*-2m).



1m **2m**

The reaction of 82.5 mg (0.30 mmol) of **1m** and 85.9 mg (0.45 mmol) of PhSeCl in 0.6 mL of H_2O and 6 mL of CH_3CN afforded *E*-**2m** (125.5 mg, 93%, dr=50/50) as a liquid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.75–7.67 (m, 1H), 7.67–7.58 (m, 1H), 7.54–7.41 (m, 3H), 7.40–7.29 (m, 2H), 7.23–7.11 (m, 3H), [5.48 (q, *J*=6.4 Hz, 50%), 5.37 (q, *J*=6.4 Hz, 50%), 1H], 3.02 (br s, 1H), 2.29–2.10 (m, 2H), [1.50 (d, *J*=6.4 Hz, 50%), 1.46 (d, *J*=6.4 Hz, 50%), 3H], 1.43–0.87 (m, 10H), 0.82 (t, *J*=7.2 Hz, 3H); MS (EI, 70 eV): *m/z* (%) 327 ($M^+(^{82}Se)-PhSO$, 0.14), 326 ($M^+(^{82}Se)-PhSO$-H, 1.98), 325 ($M^+(^{80}Se)-PhSO$, 1.65), 324 ($M^+(^{80}Se)-PhSO$-H, 8.48), 323 ($M^+(^{78}Se)-PhSO$, 0.95), 322 ($M^+(^{78}Se)-PhSO$-H or $M^+(^{77}Se)-PhSO$, 5.56), 321 ($M^+(^{77}Se)-PhSO$-H or $M^+(^{76}Se)-PhSO$, 1.59), 320 ($M^+(^{76}Se)-PhSO$-H, 2.16), 318 ($M^+(^{74}Se)-PhSO$-H, 0.41), 43 (100); IR (neat, cm^{-1}): ν 3375, 2925, 2851, 1577, 1475, 1439, 1069, 1039, 1022. Anal. Calcd for $C_{23}H_{30}O_2SSe$: C 61.46, H 6.73. Found: C 61.47, H 6.68.

4.2.14. *E*-1-Methyl-3-phenylselanyl-4-phenylsulfinyl-3-octen-2-ol (*E*-2n).



1n **2n**

The reaction of 74.0 mg (0.30 mmol) of **1n** and 88.1 mg (0.45 mmol) of PhSeCl in 0.6 mL of H_2O and 6 mL of CH_3CN afforded *E*-**2n** (64.1 mg, 51%) as a solid. Mp 148–150 °C (hexane/tetrahydrofuran). ^1H NMR (400 MHz, THF-d_8): δ 8.01–7.96 (m, 2H), 8.50–7.40 (m, 3H), 7.17–7.09 (m, 5H), 5.27 (s, 1H), 2.48–2.34 (m, 2H), 1.62 (s, 3H), 1.58–1.50 (m, 1H), 1.48 (s, 3H), 1.22–1.06 (m, 2H), 1.03–0.92 (m, 1H), 0.73 (t, *J*=7.4 Hz, 3H); ^{13}C NMR (100 MHz, THF-d_8): δ 156.6, 146.9, 142.4, 133.2, 130.0, 129.7, 129.3, 128.8, 126.6, 126.0, 78.2, 34.0, 31.5, 31.3, 28.6, 23.3, 13.6; MS (EI, 70 eV): *m/z* (%) 299 ($M^+(^{82}Se)-PhSO$, 5.07), 298 ($M^+(^{80}Se)$+1-PhSO, 3.77), 297 ($M^+(^{80}Se)-PhSO$, 23.91), 296 ($M^+(^{78}Se)$+1-PhSO, 1.81), 295 ($M^+(^{78}Se)-PhSO$ or $M^+(^{77}Se)$+1-PhSO, 11.59), 294 ($M^+(^{77}Se)-PhSO$ or $M^+(^{76}Se)$ +1-PhSO, 3.77), 293 ($M^+(^{76}Se)-PhSO$, 5.07), 59 (100); IR (KBr, cm^{-1}): ν 3205, 2956, 2929, 1578, 1476, 1027, 1020. Anal. Calcd for $C_{21}H_{26}O_2SSe$: C 59.85, H 6.22. Found: C 59.89, H 6.19.

Acknowledgements

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References and notes

1. (a) *The Chemistry of Ketenes, Allenes, and Related Compounds Part 1*; Patai, S., Ed.; John Wiley and Sons: New York, NY, 1980; (b) *The Chemistry of the Allenes*; Landor, S. R., Ed.; Academic: New York, NY, 1982; Vols. 1–3; (c) *Allenes in Organic Synthesis*; Schuster, H. F., Coppola, G. M., Eds.; John Wiley and Sons: New York, NY, 1984; (d) *Modern Allene Chemistry*; Krause, N., Hashmi, A. S. K., Eds.; Wiley-VCH: Weinheim, 2004; (e) Ma, S. *Chem. Rev.* **2005**, *105*, 2829; (f) Ma, S. *Acc. Chem. Res.* **2003**, *36*, 701; (g) Sydnes, L. K. *Chem. Rev.* **2003**, *103*, 1133; (h) Leopold, H.; Volker, B. *Liebigs Ann. Chem.* **1972**, *757*, 33.
2. (a) Ma, S.; Wei, Q.; Wang, H. *Org. Lett.* **2000**, *2*, 3893; (b) Ma, S.; Ren, H.; Wei, Q. *J. Am. Chem. Soc.* **2003**, *125*, 4817.
3. (a) Fu, C.; Chen, G.; Deng, Y.; Huang, X.; Ma, S. *Chin. J. Chem.* **2004**, *22*, 990; (b) Ma, S.; Hao, X.; Huang, X. *Org. Lett.* **2003**, *5*, 1217; (c) Ma, S.; Hao, X.; Meng, X.; Huang, X. *J. Org. Chem.* **2004**, *69*, 5720; (d) Ma, S.; Hao, X.; Huang, X. *Chem. Commun.* **2003**, 1082; (e) Fu, C.; Huang, X.; Ma, S. *Tetrahedron Lett.* **2004**, *45*, 6063; (f) Fu, C.; Chen, G.; Liu, X.; Ma, S. *Tetrahedron* **2005**, *61*, 7768.

4. Crystal data of **2a**: $C_{16}H_{16}O_2SSe$, M=351.31, colorless, prismatic, monoclinic, space group $P2$ (#1), μ(Mo Kα)= 2.515 mm^{-1}, R=0.044, Rw=0.090, a=12.899 (18), b= 12.079 (17), c=10.932 (16) Å, V=1574.5(4) $Å^3$, T= 20.0 °C, Z=4; total no. of reflections measured, 3429; no. of observations ($I>2.00\sigma(I)$), 1789; no. of variables, 194.
5. Ma, S.; Wei, Q. *J. Org. Chem.* **1999**, *64*, 1026.