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Crystal Structures of β-Chalcogeno-α,β-unsaturated Chalcogenoesters: Novel Intramolecular Interaction between the Carbonyl Oxygen and the Chalcogen Atom at the β-Position

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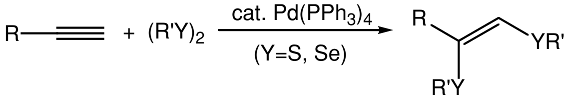
ABSTRACT: *A series of β-chalcogeno-α, β-unsaturated chalcogenoesters (***1** *and* **2***) were synthesized, and their molecular structures were investigated in detail by X-ray crystal analyses. Interestingly, intramolecular interactions between the carbonyl oxygen and the chalcogen atom at the β-position (β-S···O and β-Se···O) were observed in most cases, and intermolecular π–π interaction and hydrogen bonding were observed in the case of δ-hydroxy derivatives (***1b** *and* **2b***).* © 2011 Wiley Periodicals, Inc. Heteroatom Chem 22:579–585, 2011; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.20690

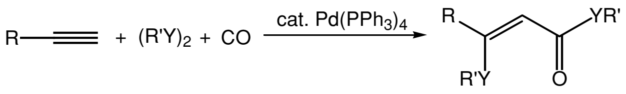
INTRODUCTION

Catalytic addition of heteroatom compounds to unsaturated bonds in the presence of transition metal complexes is becoming an increasingly powerful method for the construction of various functionalized molecules [1]. Although the numerous multifunctionalized compounds have been synthesized by multistep procedures, we have developed a series of unique methodology for simultaneous introduction of heteroatom moieties to unsaturated bonds on the basis of the transition-metal-catalyzed reactions [2]. For example, organic disulfides and diselenides add to terminal alkynes stereoselectively to give the corresponding (*Z*)-*vic*-dichalcogenoalkenes (Eq. (1)) [3a].



(1)

Furthermore, when the same catalytic reactions of dichalcogenides with alkynes are conducted under the pressurized carbon monoxide, highly selective carbonylative addition to alkynes takes place, affording the corresponding β-chalcogeno-α,β-unsaturated chalcogenoesters (**1** or **2**) with excellent regio- and stereoselectivities (Eq. (2)) [3].



1 (Y=S)
2 (Y=Se)

(2)

Dedicated to Professor Kin-ya Akiba on the occasion of his 75th birthday.

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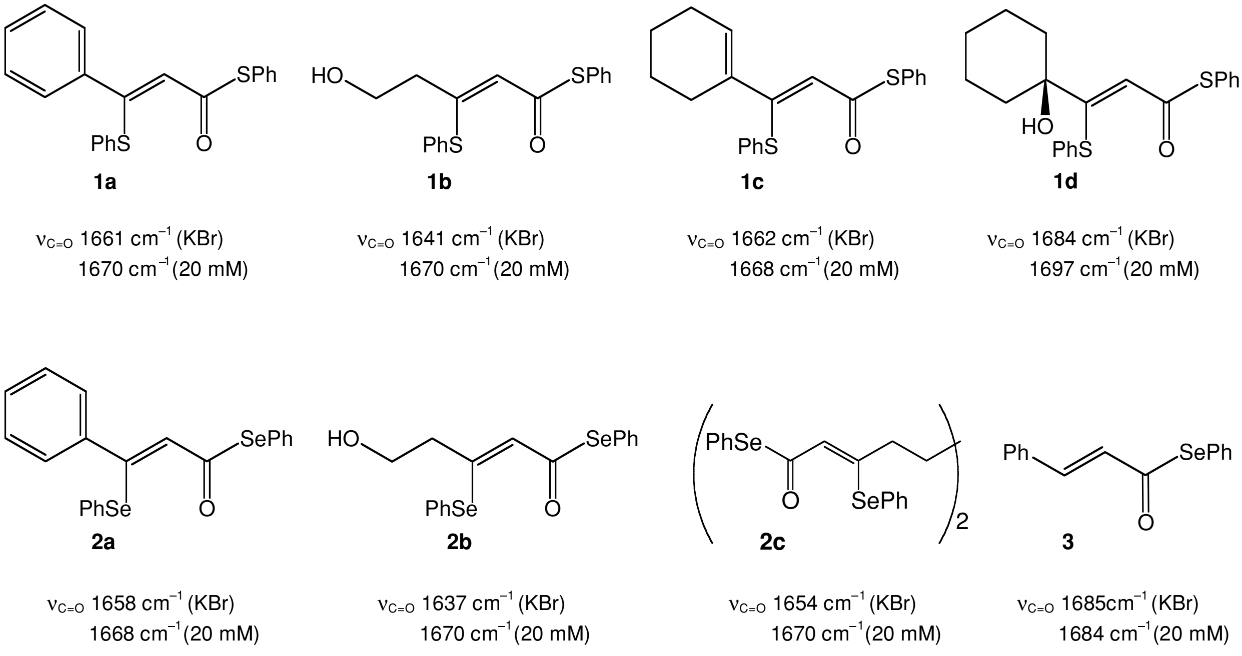
By using these highly selective methods, we have prepared a wide range of heteroatom-containing vinylic compounds so far. During these investigations, we are interested in the molecular structures of vicinally bifunctionalized alkenes, especially *cis*-isomers of β-chalcogeno-α,β-unsaturated chalcogenoesters (**1** and **2**), because interaction between heteroatoms can be investigated in detail [4]. In this paper, we report the structural properties by X-ray crystal analyses and IR spectral analyses of β-chalcogeno-α, β-unsaturated chalcogenoesters (**1** and **2**).

RESULTS AND DISCUSSION

Among the β-chalcogeno-α, β-unsaturated chalcogenoesters synthesized, we succeeded in X-ray analyses of the following seven compounds (**1a–1d** and **2a–2c**). Scheme 1 shows the chemical structures of the seven compounds and also their carbonyl wavenumbers of IR spectra in solid and in solution, comparing with that of chalcogenoester **3** [5,6].

As can be seen from Scheme 1, the carbonyl wavenumbers in solid of β-chalcogeno-α,β-unsaturated chalcogenoesters (**1** and **2**) except **1d** are lower compared with that of **3** (see, the values obtained by using the KBr method). Next, we focused on the structures of sulfur-containing compounds (**1a–1d**) and each molecular structure by X-ray analysis is shown in Fig. 1. The nonbonded distances between the O-atom of the carbonyl group and the S-atom of S—C=C moiety are 2.796, 2.830, 2.842, and 3.070 Å, respectively, and these are shorter than the sum of van der Waals radii of sulfur and oxygen (3.32 Å) (Table 1) [7]. As a result, a widespread planar arrangement was observed as torsion angles between S—C=C and C(=O)—S in **1a–1d** are 177.31°, 179.61°, 175.37°, and 178.80°, respectively. In thioesters **1a–1c**, the angles for nonbonded O··· S—$\mathrm{C_{ipso}}$ are 167.49°, 173.75°, and 165.52°, and therefore $\mathrm{C_{ipso}}$, S, and O are located approximately in line. In contrast, the angles for nonbonded O··· S-$\mathrm{C_{ipso}}$ of **1d** is 69.11°; in addition, the S···O distance of **1d** is longer than those of **1a–1c**. These results strongly suggest that, in the cases of **1a–1c**, the σ^*–n interaction between the S-atom of S—C=C moiety and the carbonyl oxygen contributes to the lower carbonyl wavenumber in IR spectra and the shorter S···O distance [8]. In the case of **1d**, however, the nonlinear relationship of $\mathrm{C_{ipso}}$, S, and O and the longer S···O distance indicate lack of such the σ^*–n interaction, resulting in the normal IR value of carbonyl wavenumber. The nonlinear relationship of $\mathrm{C_{ipso}}$, S, and O may be due to the bulkiness of 1-hydroxycyclohexyl group and the CH–π interaction between the phenyl group and cyclohexyl group.

Figure 2 indicates the results of the X-ray analyses of the corresponding selenoesters **2**. The selenoesters (**2a–2c**) show almost the same structures as those of the thioesters **1a–1c**. The torsion angles



SCHEME 1 IR spectra of carbonyl group of chalcogenoesters (**1–3**) in solid and in solution.

TABLE 1 Selected Distances and Angles for **1a–1d**

Product	*1a*	*1b*	*1c*	*1d*
S····O distance (Å)	2.796	2.830	2.842	3.070
Torsion angle between S—C=C and C(=O)—S (°)	177.31	179.61	175.37	178.80
Angle for nonbonded O···S—C_{ipso} (°)	167.49	173.75	165.52	69.11

The sum of van der Waals radii (S···O): 3.32 Å.

TABLE 2 Selected Distances and Angles for **2a–2c**

Product	*2a*	*2b*	*2c*
Se···O distance (Å)	2.791	2.801	2.735
Torsion angle between Se—C=C and C(=O)—Se (°)	176.64	178.80	167.31
Angle for nonbonded O···Se—C_{ipso} (°)	168.20	174.97	171.43

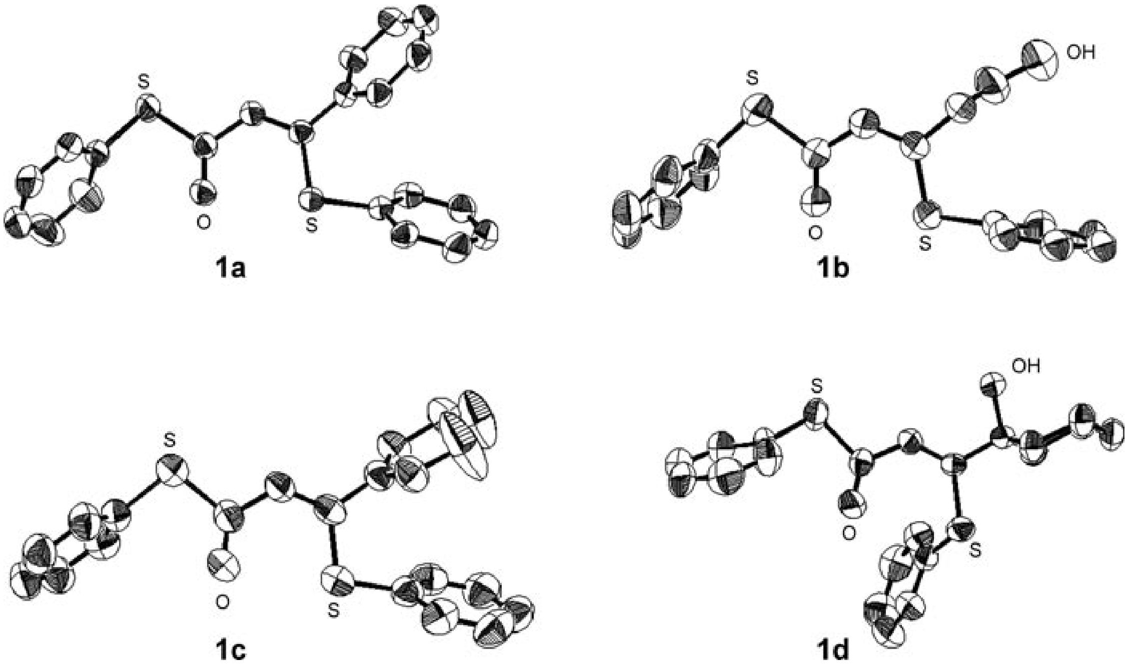
The sum of van der Waals radii (Se···O): 3.42 Å.

between Se—C=C and C(=O)—Se indicate the planarity of Se—C=C—C(=O)—Se unit (Table 2). The angles for nonbonded O···Se—C_{ipso} indicate that C_{ipso}, Se, and O are located approximately on line. These results and the lower carbonyl wavenumbers strongly suggest the σ^*–n interaction between the Se-atom of Se—C=C moiety and the carbonyl oxygen.

Considering that the van der Waals radius of Se···O (3.42 Å) is longer than that of S···O (3.32 Å), the σ^*–n interaction selenoesters **2** is somewhat stronger, compared with thioesters **1a–1c** [9].

Next, we examined to clarify the packing structures of thioesters **1** and selenoesters **2**. In the packing structures of **1a, 1c, 1d, 2a**, and **2c**, significant intermolecular interactions were not observed. In the cases of **1b** and **2b**, however, remarkable π–π stacking interactions and hydrogen bondings were observed (Fig. 3). The phenyl rings of SPh or SePh groups take part to form intermolecular π–π stacking (3.53 Å; **1b,** 3.55 Å; **2b**), and hydroxy groups are available for participating in intermolecular hydrogen bonding with carbonyl groups (2.77 Å; **1b,** 2.87 Å; **2b**). Interestingly, the packing structures of **1b** and **2b** are almost the same despite of different atoms, i.e., S and Se.

Scheme 1 also indicates the IR values in solution of the carbonyl group of chalcogenoesters **1–3**. By comparing the values in solution with those in solid, an increase in ca. 10 cm^{-1} was observed in the cases of **1a, 1c, 2a**, and **2c**. On the other hand, the increase in ca. 30 cm^{-1} was observed in the cases of **1b** and **2b**, which suggests the strong hydrogen bonding is present in solid state. In all cases that the σ^*–n interaction is observed (**1a–1c** and **2a–2c**), the wavenumbers of carbonyl groups in solution are lower than that of β-chalcogeno-unsubstituted **3**.



1a **1b** **1c** **1d**

FIGURE 1 Molecular structures of **1a–1d**.

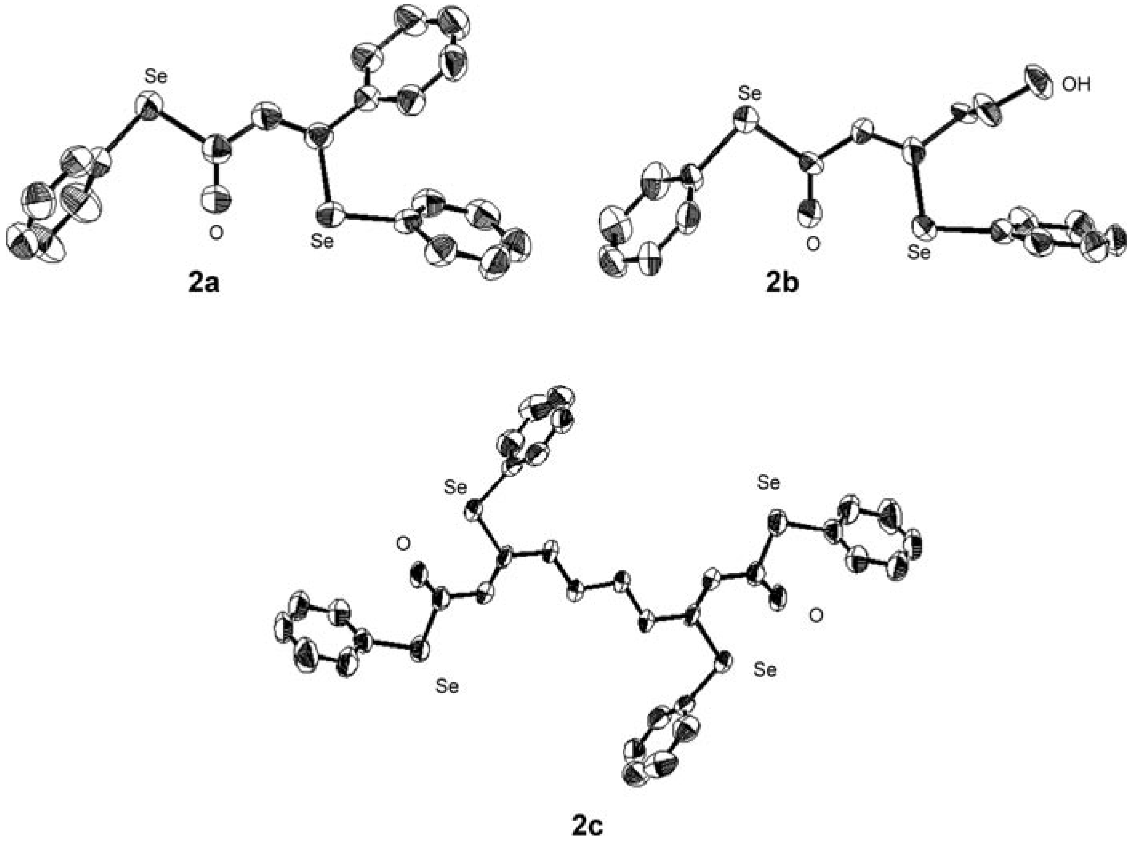


FIGURE 2 Molecular structures of **2a–2c**.

CONCLUSIONS

Details of the X-ray analyses and IR spectral analyses of β-chalcogeno-α,β-unsaturated chalcogenoesters (**1** and **2**) have been revealed. Interestingly, the σ^*–n interaction between the chalcogen atom bonded directly to vinyl and the carbonyl oxygen has been observed, based on the linear relationship of C_{ipso}, S (Se), and O and the shorter S (Se)···O distance [10]. The σ^*–n interaction effects the decrease in IR values of carbonyl groups. In pharmaceutical [11] or materials science [12], molecular structure and packing structure in crystal play important roles to realize each functionality, and therefore, we believe that this study will make great contributions and store-rich knowledge in the scientific fields.

EXPERIMENTAL

General

^{1}H NMR spectra were recorded on JNM-GSX 270 (270 MHz; JEOL Ltd., Tokyo, Japan) spectrometers using $CDCl_3$ as the solvent with Me_4Si as the internal standard. ^{13}C NMR spectra were taken on JNM-GSX 270 (68 MHz; JEOL Ltd.) spectrometers using $CDCl_3$ as the solvent. The purification of the products was carried out by medium-pressure liquid chromatography (MPLC; silica gel, 25–40 μm, length 310 mm, i.d. 25 mm) and preparative TLC (PTLC) on B-5F silica gel (Wako Ltd., Osaka, Japan).

According to the reported procedure [3a], to a two-necked 5 mL reaction vessel equipped with a magnetic stirring bar, $Pd(PPh_3)_4$ (24 mg, 0.02 mmol), toluene (2.0 mL), alkynes (1.0 mmol), and diphenyl disulfide or diphenyl diselenide (1.0 mmol) were added. The mixture was heated at 80°C for 19 h under the pressure of carbon monoxide (1–60 atm). The reaction mixture was filtered through Celite and purified by MPLC and PTLC to give the objective substances. Recrystallization for X-ray analyses was carried out from solutions of **1a** (ethyl acetate), **1b** (diethyl ether), **1c** (ethyl acetate), **1d** (*n*-hexane), **2a** (ethyl acetate), **2b** (benzene), and **2c** (benzene).

IR Measurements

Infrared spectra were determined on a Perkin Elmer Model 1600 spectrometer (PerkinElmer Japan Co., Ltd., Yokohama, Japan) or FT/IR-8900 μ Fourier Transform Infrared Microsampling System (JASCO

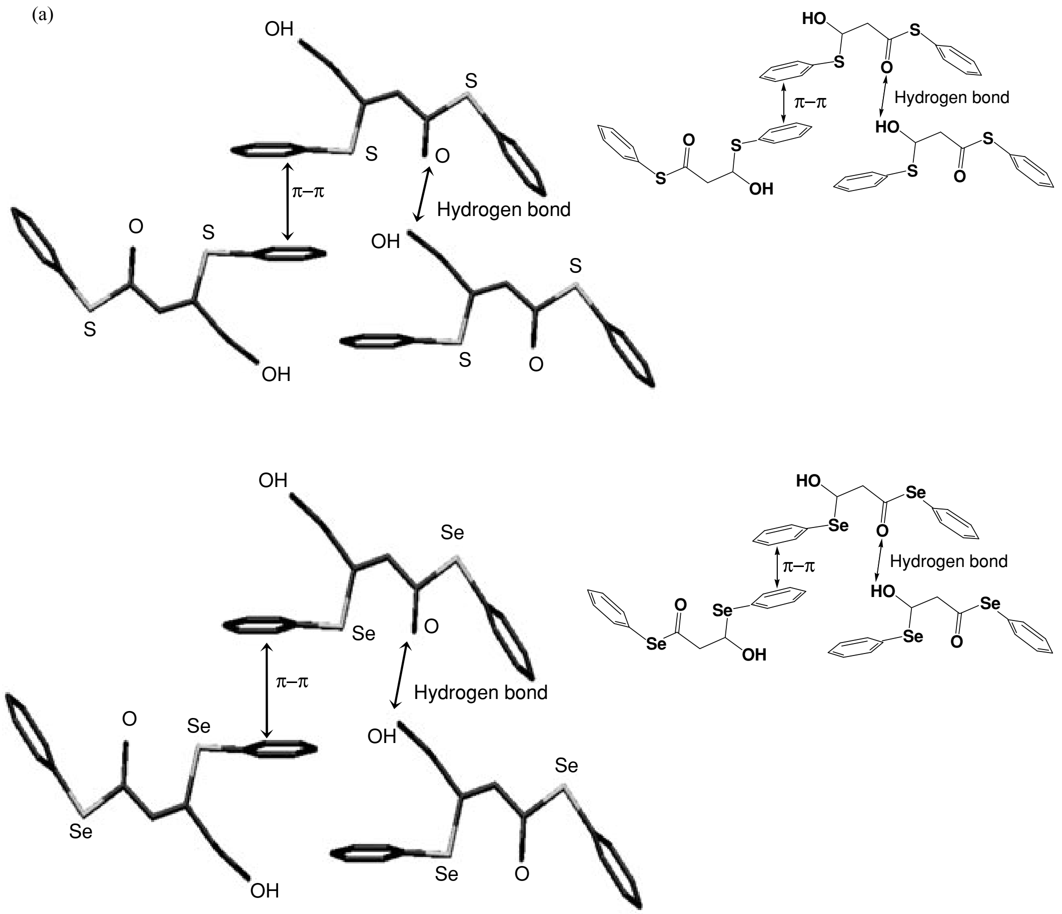


FIGURE 3 Packing structures of **1b** (a) and **2b** (b).

Inc., Tokyo, Japan). The carbonyl wavenumbers were measured in the transmittance scale mode for 20 mM solution or KBr pellet.

X-Ray Structure Determination

X-ray crystallographic measurements were carried out on a RAXIS-RAPID diffractometer (RIGAKU Corp., Tokyo, Japan) with Mo Kα radiation. The structure was solved by direct methods. All hydrogen atoms were located in different Fourier maps, but for consistency they were included in the final refinement in idealized positions. Final refinement was carried out by full-matrix least squares procedures.

(Z)-1,3-Bis(phenylthio)-3-phenyl-2-propen-1-one (**1a**)

mp 135–139°C (a yellow solid); ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.45 (s, 1 H), 7.03–7.13 (m, 10 H), 7.43–7.44 (m, 3 H), 7.52–7.53 (m, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 121.02, 127.83, 128.01, 128.11, 128.43, 128.66, 128.93, 129.14, 129.32, 132.06, 134.17, 134.67, 137.74, 158.63, 185.19; IR (KBr) 3059, 1661, 1537, 1078, 949, 791, 752, 705, 690, 671, 588 cm^{-1}; mass spectrum (CI), m/z 349 (M^+ +1, 100). Anal. Calcd for $C_{21}H_{16}OS_2$: C, 72.38; H, 4.62; S, 18.40. Found C, 72.37; H, 4.61; S, 18.32.

(Z)-1,3-Bis(phenylthio)-5-hydroxy-2-penten-1-one (**1b**)

mp 110–112°C (a white solid); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.46 (t, $J = 5.4$ Hz, 1 H), 2.41 (t, $J = 6.4$ Hz, 2 H), 3.58, (q, J (average) = 5.9 Hz, 2 H), 6.35 (s, 1 H), 7.34–7.55 (m, 10 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 39.20, 60.95, 118.64, 127.93, 129.05, 129.23, 129.27, 129.69, 130.07, 134.60, 135.62, 157.15, 185.16; IR (KBr) 3531, 2872, 1641, 1537, 1476, 1439, 1111, 1073, 1046, 842, 748, 706 cm^{-1}; mass spectrum (CI),

TABLE 3 Crystal Data

	1a	*1b*	*1c*	*1d*	*2a*	*2b*	*2c*
Empirical formula	$C_{21}H_{16}OS_2$	$C_{17}H_{16}O_2S_2$	$C_{21}H_{20}OS_2$	$C_{21}H_{22}O_2S_2$	$C_{21}H_{16}OSe_2$	$C_{17}H_{16}O_2Se_2$	$C_{34}H_{30}O_2Se_4$
Formula weight	348.48	316.43	352.51	370.52	436.23	410.23	786.45
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	P-1	$P2_1/c$	$P2_1/c$	$P2_1/c$	P-1	P-1
a (Å)	13.2163(8)	7.5762(8)	11.097(2)	11.2792(8)	13.4125(10)	7.5865(8)	8.0549(10)
b (Å)	10.7102(6)	8.0860(10)	6.8867(12)	10.5264(7)	10.8288(8)	8.3999(8)	9.8707(15)
c (Å)	13.4857(10)	13.4902(14)	24.871(4)	32.362(2)	13.6220(10)	13.3219(12)	10.2129(11)
α (°)	90	81.774(4)	90	90	90	103.137(3)	98.561(4)
β (°)	108.1074(18)	86.605(3)	97.668(4)	91.5709(19)	108.698(3)	93.777(3)	92.772(3)
γ (°)	90	80.579(4)	90	90	90	95.747(3)	93.959(5)
V (Å^3)	1814.3(2)	806.35(16)	1883.8(6)	3840.9(4)	1874.1(2)	819.13(13)	799.62(18)
Z	4	2	4	8	4	2	1
D_{calc}	1.276	1.303	1.243	1.281	1.546	1.663	1.633
θ Range (°)	3.1–27.4	3.1–27.4	3.1–27.5	3.1–27.4	3.0–27.4	3.0–27.4	3.1–27.4
Crystal size (mm)	0.50 × 0.30 × 0.30	0.60 × 0.60 × 0.40	0.40 × 0.30 × 0.30	0.30 × 0.30 × 0.30	0.30 × 0.30 × 0.30	0.30 × 0.30 × 0.30	0.30 × 0.30 × 0.30
R_1	0.0469	0.0947	0.0737	0.1203	0.0706	0.1176	0.0816
wR_2	0.0560	0.1252	0.0888	0.1234	0.0737	0.1510	0.0891
Goodness of fit	1.038	0.949	1.339	1.219	1.151	1.010	1.081

m/z 317 (M$^+$ + 1, 100). Anal. Calcd for $C_{17}H_{16}O_2S_2$: C, 64.53; H, 5.10; S, 20.26. Found C, 64.46; H, 5.09; S, 20.12.

(Z)-1,3-Bis(phenylthio)-3-(1-cyclohexenyl)-2-propene-1-one (**1c**)

mp 95.5–96.5°C (light yellow crystal); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.08–1.14 (m, 2H), 1.26–1.29 (m, 2H), 1.78 (m, 2H), 1.87–1.90 (m, 2H), 5.76 (m, 1H), 6.29 (s, 1H), 7.24–7.30 (m, 3H), 7.35–7.43 (m, 4H), 7.44–7.50 (m, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.33, 21.88, 25.11, 28.89, 118.05, 128.31, 129.02, 129.15, 130.93, 132.51, 134.59, 134.63, 136.28, 161.92, 185.44; IR (KBr) 2934, 1662, 1542, 1474, 1438, 1184, 1039, 904, 748, 690, 616, 606, 528 cm^{-1}; mass spectrum (CI), *m/z* 353 (M$^+$ + 1, 50). Anal. Calcd for $C_{21}H_{20}OS_2$: C, 71.55; H, 5.72; S, 18.19. Found C, 71.59; H, 5.63; S, 18.09.

(Z)-1,3-Bis(phenylthio)-3-(1-hydroxy-cyclohexyl)-2-propene-1-one (**1d**)

mp 86°C–87°C (yellow crystal) ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.23 (m, 1H), 1.53–1.77 (m, 7H), 1.88–1.97 (m, 2H), 2.21 (s, 1H), 6.92 (s, 1H), 7.04–7.08 (m, 2H), 7.15–7.33 (m, 8H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.58, 25.11, 35.76, 76.11, 125.97, 126.58, 127.71, 128.92, 128.96, 129.13, 129.79, 134.33, 135.36, 158.01, 186.51; IR (KBr) 3427, 3057, 2924, 1684, 1567, 1478, 1439, 1098, 1039, 1020, 883, 844, 735, 686, 581 cm^{-1}; mass spectrum (CI) *m/z* 371 (M$^+$ + 1, 8). Anal. Calcd for $C_{21}H_{22}O_2S_2$: C, 68.07; H, 5.98; S, 17.31. Found C, 67.98; H, 5.97; S, 17.24.

(Z)- 1,3-Bis(phenylseleno)-3-phenyl-2-propen-l-one (**2a**)

mp 135°C–141°C (yellow crystal); ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.80 (s, 1 H), 6.95–7.08 (m, 8 H), 7.19 (d, 2 H, $J = 6.8$ Hz), 7.40–7.42 (m, 3 H), 7.60–7.62 (m, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 124.73, 126.66, 127.57, 128.09, 128.33, 128.45, 128.67, 128.93, 129.05, 129.37, 135.79, 136.05, 138.58, 159.57, 187.77; IR (KBr) 3057, 1658, 1531, 1486, 1476, 1437, 1227, 1042, 935, 760, 744, 696 cm^{-1}; mass spectrum (CI), *m/z* 439 (M$^+$ + 1, 56). Anal. Calcd for $C_{21}H_{16}OSe_2$: C, 57.03; H, 3.64. Found C, 57.19; H, 3.64.

(Z)-1,3-Bis(phenylseleno)-5-hydroxy-2-penten-1-one (**2b**)

mp 83–84°C (yellow solid); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.63 (br, 1 H), 2.41 (t, $J = 6.7$ Hz, 2 H), 3.52, (t, $J = 6.3$ Hz, 2 H), 6.75 (s, 1 H), 7.33–7.48 (m, 10 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 29.92, 61.33, 115.17, 129.08, 129.50, 129.54, 129.72, 130.25, 135.93, 136.78, 137.35, 137.59, 157.82, 187.97; IR (KBr) 3554, 1637, 1521, 1473, 1438, 1103, 1068, 1037, 1020, 999, 823, 800, 740, 686 cm^{-1}; HRMS (FAB): Calcd for $C_{17}H_{17}O_2Se_2$, 412.9559: Found 412.9563.

(2Z, 8Z)-1,3,8,10-Tetrakis(phenylseleno)-2,8-decadien-1,10-dione (**2c**)

mp 114–115°C (yellow solid); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.02 (br s, 4H), 1.91 (br s, 4H), 6.52 (s, 2H), 7.30–7.43 (m, 12H), 7.54–7.60 (m, 8H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 28.74, 37.00, 122.33, 126.59, 127.12, 129.23, 129.31, 129.43, 135.76, 137.19, 161.75, 187.46; IR (KBr) 3056, 2953, 1654, 1541, 1477, 1438, 1093, 1070, 1020, 819, 793, 738, 685, 540, 489 cm^{-1}; mass spectrum (CI), *m/z* 791 (M^++1, 6); Anal. Calcd for $C_{34}H_{30}O_2Se_4$: C, 51.93; H, 3.84. Found C, 52.05; H, 3.82.

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