The First Example of the 1-Chalcogene-Substituted Formylolefination of the Ketones and Aldehydes Using 1-Lithio-2-ethoxyvinyl Chalcogenides

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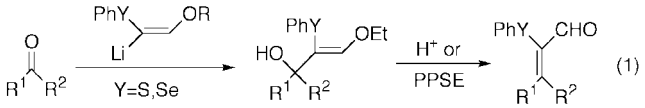
The α-chalcogene-substituted formylolefinations of ketones and aldehydes proceeded using 1-lithio-2-ethoxyvinyl chalcogenides/PPSE or TMSOTf to produce the α-chalcogenoformylolefinated products **4a**−**l** in high yields. Tandem-formylolefination provided the (2*Z*,4*Z*)-2,4-bis(chalcogeno)pent-2,4-dienals **5d**,**h**,**i** and (2*Z*,4*Z*,6*Z*)-2,4,6-tris(phenylthio)hept-2,4,6-trienal derivatives **7d** and **8d**, respectively.

The direct conversion of aldehydes and ketones into α,β-unsaturated aldehydes can occur via the two-carbon homologation of the carbonyl compounds.[1] Many formylolefinations of the carbonyl group have already been reported; imine anions (metaloenamines)[2] and their Wittig-type reagents,[3] especially, are conveniently used as the representative method for the formylolefination of various carbonyl compounds.

On the other hand, vinyl chalcogenides are potentially versatile intermediates in synthetic organic chemistry.[4] Their hydrolysis afforded the ketones,[5] the reactions with the organometallic reagents provided the formations of the regioselective trisubstituted alkenes,[6] and recently, other transformations have been actively investigated.[7] There is a convenient synthetic method for the α-chalcogene-substituted olefination using Wittig-type reagents;[8a] however, the α-chalcogene-substituted formylolefinations of the carbonyl compounds have not been reported, because their formyl or imine-substituted Wittig-type reagents are difficult to prepare.[8b] We incidentally found a convenient method for the synthesis of the 2-alkoxyvinyl chalcogenide,[9] which could be used as a substitute for the Wittig-type reagents. If a new method for α-chalcogenoformylolefination is to be developed, it would generate considerable interest from a synthetic point of view due to the presence of a versatile formyl group at the α-center of the chalcogenide. Therefore, we planned the retrosynthesis for the α-chalcogenoformylolefinations as shown in eq 1. If the α-lithiation of β-alkoxyvinyl



(1)

chalcogenides and their reactions with aldehydes and ketones occurs, the titled α-chalcogenoformylolefination would be accomplished via the successive dehydration or the acid-promoted isomerization. Previously, we reported that the polyphosphoric acid trimethylsilyl ester (PPSE)

(1) Martin, S. F. *Synthesis* **1979**, 633−665.
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(7) Other transformation of the vinyl chalcogenides: Diels−Alder cycloaddition: Reich, H. J.; Kelly, M. J.; Olson, R. E.; Holtan, R. C. *Tetrahedron* **1983**, *39*, 949−960. Allene formation: Back, T. G.; Krishina, M. V.; Muralidharan, K. R. *J. Org. Chem.* **1989**, *54*, 4146−4153. Back, T. G.; Dyck, B. P. *Tetrahedron Lett.* **992**, *33*, 4725−4726. Komatsu, N.; Murakami, Y.; Nishibayashi, Y.; Sugita, T.; Uemura, S. *J. Org. Chem.* **1993**, *58*, 3697−3702. Nishibayashi, Y.; Singh, D. J.; Fukuzawa, S.; Uemura, S. *J. Org. Chem.* **1995**, *60*, 4114−4120. Lerouge, P.; Paulmier, C. *Bull. Soc. Chim. Fr.* **1985**, 1225−1229. [2 + 2]-, [2 + 1]-, and [2 + 3]-cycloadditions: De Cock, Ch.; Piettre, S.; Lahousse, F.; Janouseki, Z.; Merenyi, R.; Viehe, H. G. *Tetrahedron* **1985**, *41*, 4183−4193. Yamazaki, S.; Hama, M.; Yamabe, S. *Tetrahedron Lett.* **1990**, *31*, 2917−2920. Yamazaki, S.; Mizuno, W.; Yamabe, S. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1555−1560. Yamazaki, S.; Fujitsuka, H.; Yamabe, S. *J. Org. Chem.* **1992**, *57*, 5610−5619. Yamazaki, S.; Katoh, S.; Yamabe, S. *J. Org. Chem.* **1992**, *57*, 4−6. Yamazaki, S.; Tanaka, M.; Yamaguchi, A.; Yamabe, S. *J. Am. Chem. Soc.* **1994**, *116*, 2356−2365. Yamazaki, S.; Tanaka, M.; Inoue, T.; Morimoto, N.; Kumagai, H. *J. Org. Chem.* **1995**, *60*, 6546−6551. Yamazaki, S.; Tanaka, M.; Yamabe, S. *J. Org. Chem.* **1996**, *61*, 4046−4050. Yamazaki, S.; Kumagai, H.; Takada, T.; Yamabe, S. *J. Org. Chem.* **1997**, *62*, 2968−2974. Yamazaki, S.; Imanishi, T.; Moriguchi, Y.; Takada, T. *Tetrahedron Lett.* **1997**, *38*, 6397−6400. Terada, M.; Matsukawa, S.; Mikami, K. *J. Chem. Soc., Chem. Commun.* **1993**, 327−328.
(8) (a)Comasseto, J. V. *J. Organomet. Chem.* **1983**, *253*, 131−181. Comasseto, J. V.; Petragnani, N. P. *J. Organomet. Chem.* **1978**, *152*, 295−304. Coutrot, P.; Grison, C.; Youssefi-Tabrizi, M. *Synthesis* **1987**, 169−170. Shin, W. S.; Lee, K.; Oh, D. Y. *Tetrahedron Lett.* **1992**, *33*, 5375−5376. (b)Huang, Z. Z.; Huang, X.; Huang, Y. Z. *Tetrahedron Lett.* **1995**, *36*, 425−426. Huang, Z. Z.; Huang, X.; Huang, Y. Z. *J. Organomet. Chem.* **1995**, *490*, C23−C26. Huang, Z. Z.; Huang, X.; Huang, Y. Z. *J. Chem. Soc., Perkin. Trans. 1* **1995**, 95−96. Huang, Z. Z.; Huang, X.; Huang, Y. Z. *J. Chem. Res., Synop.* **1995**, 206−207. Robinson, C. N.; Shaffer, A. A. *J. Org. Chem.* **1993**, *58*, 3563−3567.
(9) The sulfur analogues have been obtained in 30% yield (*E*/*Z* = 70:30) according to the literature: Duhamel, L.; Duhamel, P.; Ancel, J.-E. *Tetrahedron Lett.* **1994**, *35*, 1209−1210. However, we originally prepared it (quantitative *Z* only) from the 2-(phenylthio)acetaldehyde diethyl acetal/LDA at −70 °C. The 2-ethoxyvinyl selenide (Mannafov, T. G.; Islyamova, E. V. *Zh. Org. Khim.* **1988**, *24*, 1945−1948) was also prepared from the corresponding acetal by the same method described above (quantitative *Z* only).

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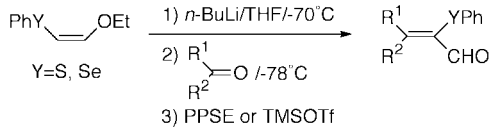
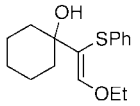
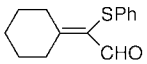
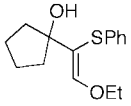
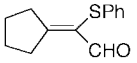
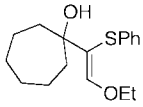
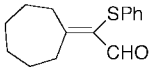
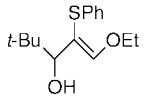
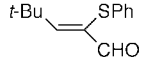
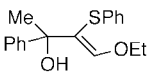
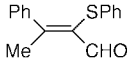
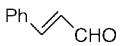
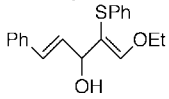
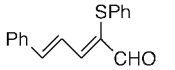
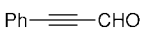
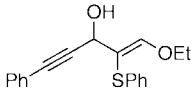
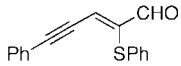
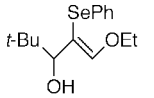
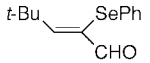
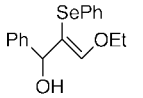
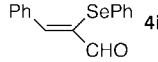
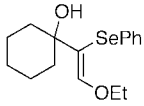
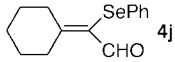
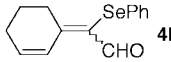
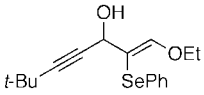
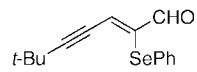
Table 1. 1-Chalcogenoformylolefination Reactions of Ketones or Aldehydes



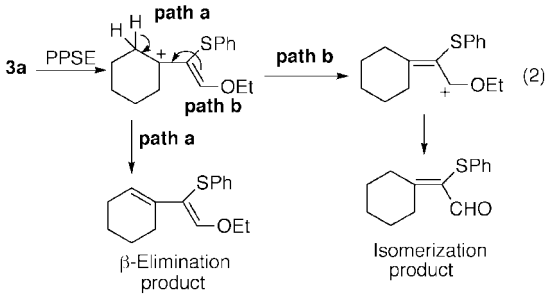
Entry	Ketones or Aldehydes	Allyl Alcohol (%yield)	Conditions	Product (%yield)
1		 **3a** (quant.)	A/83 °C	 **4a** (75)
2		 **3b** (48)	A/83 °C	 **4b** (74)
3		 **3c** (41)	A/83 °C	 **4c** (88)
4	*t*-BuCHO	 **3d** (81)	A/83 °C	 **4d** (88)
5		 **3e** (58)	A/83 °C	 **4e** (46)
6		 **3f** (56)	A/rt	 **4f** (97)
7		 **3g** (52)	A/83 °C	 **4g** (97)
8	*t*-BuCHO	 **3h** (79)	B/-78 °C	 **4h** (94)
9	PhCHO	 **3i** (quant.)	B/-78 °C	 **4i** (94)
10		 **3j** (67)	B/-78 °C	 **4j** (64)
11		—	B/-78 °C	 **4k** (63)[a]
12	*t*-Bu—≡—CHO	 **3l** (57)	B/-78 °C	 **4l** (73)

[a] *E*/*Z* = 1:1 overall yield from the cyclohexenone. Condition A: PPSE/$ClCH_2CH_2Cl$. Condition B: TMSOTf/CH_2Cl_2.

was effective for the dehydration of prop-2-ynyl alcohols.[10] We expected that this mild dehydration route could be supplemented for the dehydration of the allyl alcohols as shown in eq 1. We now wish to describe in this report the initial studies of a convenient synthetic route for the α-chalcogenoformylolefination of aldehydes and ketones and their application to the syntheses of polyvinyl chalcogenides using the tandem-homologations.

A typical procedure is represented by the cyclohexanol **3a**, which was obtained from the reaction of the hitherto unknown α-lithio 2-ethoxyvinyl sulfide,[9] which was easily generated from PhSCH=CHOEt/*n*-BuLi at −70 °C, and cyclohexanone. The alcohol **3a** was treated with PPSE according to our previous report to give [(phenylthio-)formylmethylene]cyclohexane (**4a**) in 75% yield (Table 1, entry 1). The structure of **4a** was determined by its IR, MS, and NMR spectra. Previously, we reported that the reactions of the γ-sulfur-substituted prop-2-ynylated cycloalkanols exclusively gave the 1-alkynylcycloalkenes;[10b] however, the dehydration of the allyl alcohol **3a** by PPSE (eq 2) produced the formylolefinated product **4a** (via path b), not the cyclohexenes (via path a). Other cycloalkanols, **3b** and **3c**, also gave the formylolefinated products, **4b** and **4c**, in good yields (Table 1, entries 2 and 3). The

(10) (a)Yoshimatsu, M.; Shimizu, H.; Kataoka, T. *J. Chem. Soc., Chem. Commun.* **1994**, 2107−2108. (b) Yoshimatsu, M. Naito, M.; Kawahigashi, M.; Shimizu, H.; Kataoka, T. *J. Org. Chem.* **1995**, *60*, 4798−4802. (c)Yoshimatsu, M.; Fuseya, T. *Chem. Pharm. Bull.* **1996**, *44*, 1954−1957.



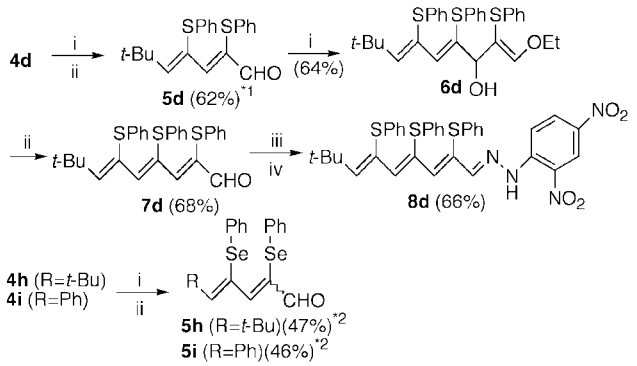
tert-butylprop-2-enol **3d** stereoselectively afforded (*Z*)-4,4-dimethyl-2-(phenylthio)-2-butenal (**4d**) (Table 1, entry 4). Acetophenone also gave the (*Z*)-acrolein derivative (**4e**) (Table 1, entry 5). Cinnamaldehyde provided 1,4-pentadien-3-ol **3f**, which gave the (2*Z*,4*E*)-penta-2,4-dienal (**4f**) at room temperature (Table 1, entry 6). The acetylenic derivative **3g** also gave the 1-formyl enyne sulfide **4g** (Table 1, entry 7). The stereochemistry of the products **4d**−**g** were determined as *Z* on the basis of the NOE experiments.

We next examined the α-(phenylseleno)-substituted formylolefination of the ketones and the aldehydes. The alcohols **3h**−**l** could be prepared by the same method as that of the sulfur analogues; however, the dehydrations of these alcohols by PPSE were not effective with the selenium moieties. On the basis of the results with other acids, the dehydration of the alcohols was found to proceed using *O*-trimethylsilyl trifluoromethanesulfonate (TMSOTf). The treatment of **3h** with TMSOTf afforded the selenium-substituted prop-2-enal **4h** in high yield (Table 1, entry 8). The cyclohexanol **3j** also gave **4j**. The reaction of cyclohexenone could not give the pure alcohol; however, the successive treatment with TMSOTf gave the dienal **4k** in 63% overall yield from the cyclohexenone (Table 1, entry 11). The acetylenic aldehyde stereoselectively yielded the enynal **4l** (Table 1, entry 12).

This methodology may potentially serve as a powerful procedure for the α-chalcogene-substituted formylolefination of various ketones and aldehydes. Therefore, we next examined the tandem-homologation method of the aldehyde as shown in Scheme 1. The bis-homologation of *tert*-butyl aldehyde proceeded using PhSCH=CHOEt/PPSE or TMSOTf, and (2*Z*,4*Z*)-6,6-dimethyl-2,4-bis(phenylthio)hepta-2,4-dienal (**5d**) was obtained in high yield. The trienal **7d** was also obtained via **6d** by the subsequent nucleophilic addition to the aldehyde **5d**. Finally, the formyl groups of the aldehydes **7d** converted to the 2,4-dinitrophenyl hydrazone **8d**. The stereochemistries of the products **5d**,**h**,**i**, **7d**, and **8d** were determined by NOE and NOESY experiments to be all *Z*.

Furthermore, the polyvinyl chalcogenides would be interesting with respect to the following aspects: (i) the interactions between the chalcogene atoms on the polyene unit[12] and (ii) the biological activities.[13] We are now also examining a method to synthesize a new dication of the dienes or a trication of the triene, which were obtained from our tandem formylolefinations of the aldehydes. These results will be reported elsewhere.

Scheme 1[a]



[a] Reagents: (i) PhYCH=CHOEt/*n*-BuLi; (ii) PPSE or TMSOTf; (iii) $ArNHNH_2$/TsOH. *1, overall yield from *t*-BuCHO. *2, overall yield from **4h**,**i**.

Experimental Section[14]

Synthesis of 2-Ethoxyvinyl Phenyl Selenide. A THF (20 mL) solution of 2-(phenylseleno)propynal diethyl acetal (13.7 g, 50.0 mmol) was added dropwise to a THF (100 mL) solution of LDA (prepared from diisopropylamine (10.1 g, 0.10 mol) at −72 °C. The reaction mixture was stirred for 10 min and then poured into water (150 mL). The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluted with hexane. 2-Ethoxyvinyl phenyl selenide (11.3 g, 99%) was obtained as a yellow oil.

2-Ethoxyvinyl phenyl selenide:[9] IR (film, cm^{-1}) 1160 (ether); ^1H NMR (400 MHz, $CDCl_3$) δ 1.33 (3H, t, J = 7 Hz), 3.90 (2H, q, J = 7 Hz), 5.63 (1H, d, J = 12 Hz), 6.90 (1H, d, J = 12 Hz), 7.14−7.28 (3H, m), 7.37−7.49 (2H, m); MS *m*/*z* 228 (M^+). Anal. Calcd for $C_{10}H_{12}OSe$: C, 52.87; H, 5.32. Found: C, 52.91; H, 5.33.

Reaction of 2-Ethoxyvinyl Phenyl Sulfide with Cyclohexanone. Typical Procedure. Under an Ar atmosphere, BuLi (4.40 mL, 6.66 mmol) was added to a THF (9 mL) solution of 2-ethoxyvinyl phenyl sulfide (1.00 g, 5.55 mmol) at −70 °C. After the mixture was stirred for 5 min, a THF (5 mL) solution of cyclohexanone (0.47 g, 5.55 mmol) was added dropwise to the mixture. The entire mixture was poured into water (100 mL), and the organic layer was separated. The aqueous layer was then extracted with ether. The organic layer and the extracts were combined and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel, eluting with AcOEt/hexane (1:20). (*Z*)-1-[2-Ethoxy-1-(phenylthio)ethenyl]-1-cyclohexanol (**3a**) (1.22 g, 59%) was obtained as a yellow oil.

(*Z*)-1-[2-Ethoxy-1-(phenylthio)ethenyl]-1-cyclohexanol (3a): IR (film, cm^{-1}) 3600−3400 (OH); ^1H NMR (400 MHz, $CDCl_3$) δ 1.36 (3H, t, J = 7 Hz), 1.38−1.79 (10H, m), 3.40 (1H, s), 4.01 (2H, q, J = 7 Hz), 6.66 (1H, s), 7.09−7.13 (1H, m), 7.23−7.27 (2H, m), 7.30−7.33 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.37 (q), 21.74 (t × 2), 25.48 (t), 36.36 (t × 2), 69.77 (t), 75.18 (s), 116.58 (s), 125.23 (d), 126.41 (d × 2), 128.73 (d × 2), 139.51 (s), 154.17 (d); MS *m*/*z* 278 (M^+). Anal. Calcd for $C_{16}H_{22}O_2S$: C, 69.03; H, 7.96. Found: C, 69.27; H, 8.37.

(*Z*)-1-[2-Ethoxy-1-(phenylthio)ethenyl]-1-cyclopentanol (3b): IR (film, cm^{-1}) 3600−3400 (OH); ^1H NMR (400 MHz, $CDCl_3$) δ 1.36 (3H, t, J = 7 Hz), 1.57−1.92 (8H, m), 3.39 (1H,

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s), 4.02 (2H, q, J = 7 Hz), 6.70 (1H, s), 7.09−7.13 (1H, m), 7.23−7.31 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.35 (q), 23.22 (t × 2), 39.52 (t × 2), 69.65 (t), 84.24 (s), 114.16 (s), 125.12 (d), 126.14 (d × 2), 128.74 (d × 2), 139.42 (s), 154.29 (d); MS m/z 218 (M^+ − EtOH). Anal. Calcd for $C_{15}H_{20}O_2S$: C, 68.15; H, 7.62. Found: C, 68.42; H, 7.56.

(*Z*)-1-[2-Ethoxy-1-(phenylthio)ethenyl]-1-cycloheptanol (3c): IR (film, cm^{-1}) 3600−3400 (OH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (3H, t, J = 7 Hz), 1.39−2.04 (12H, m), 3.49 (1H, s), 4.00 (2H, q, J = 7 Hz), 6.63 (1H, s), 7.09−7.13 (1H, m), 7.23−7.30 (2H, m), 7.30−7.35 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.35 (q), 22.28 (t × 2), 29.31 (t × 2), 40.72 (t × 2), 69.70 (t), 78.54 (s), 117.73 (s), 125.23 (d), 126.35 (d × 2), 128.73 (d × 2), 139.55 (s), 153.77 (d); high-resolution mass calcd for $C_{17}H_{24}O_2S$ m/z 292.1498, found 292.1505.

(*Z*)-1-Ethoxy-4,4-dimethyl-2-(phenylthio)-1-penten-3-ol (3d): IR (film, cm^{-1}) 3600−3400 (OH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (9H, s), 1.31 (3H, t, J = 7 Hz), 2.78 (1H, brd, J = 10 Hz), 3.96 (2H, q, J = 7 Hz), 4.20 (1H, brd, J = 10 Hz), 6.72 (1H, s), 7.09−7.13 (1H, m), 7.24−7.37 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.36 (q), 26.34 (q × 3), 37.56 (s), 69.38 (t), 78.21 (d), 109.44 (s), 125.15 (d), 126.03 (d × 2), 128.88 (d × 2), 139.62 (s), 155.66 (d); MS m/z 266 (M^+). Anal. Calcd for $C_{15}H_{22}O_2S$: C, 67.63; H, 8.32. Found: C, 67.57; H, 8.32.

(*Z*)-1-Ethoxy-3-phenyl-2-(phenylthio)-1-buten-3-ol (3e): IR (film, cm^{-1}) 3600−3400 (OH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17 (3H, t, J = 7 Hz), 1.68 (3H, s), 3.83−3.95 (2H, m), 4.06 (1H, s), 6.73 (1H, s), 7.09−7.35 (8H, m), 7.42−7.46 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.19 (q), 26.11 (s), 29.41 (q), 69.73 (t), 115.79 (s), 124.84 (dx2), 125.41 (d), 126.52 (d), 126.63 (d × 2), 127.67 (d × 2), 128.76 (d × 2), 139.12 (s), 148.54 (s), 154.96 (d); MS m/z 300 (M^+). Anal. Calcd for $C_{18}H_{20}O_2S$: C, 71.97; H, 6.71. Found: C, 71.74; H, 6.91.

(1*Z*,4*E*)-1-Ethoxy-5-phenyl-2-(phenylthio)penta-1,4-dien-3-ol (3f): IR (film, cm^{-1}) 3600−3400 (OH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (3H, t, J = 7 Hz), 2.68 (1H, d, J = 8 Hz), 4.03 (2H, dq, J = 7, 1 Hz), 5.26 (1H, brt, J = 7 Hz), 6.16 (1H, dd, J = 6, 16 Hz), 6.54 (1H, d, J = 16 Hz), 6.72 (1H, s), 7.10−7.28 (8H, m), 7.31−7.36 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.38 (q), 69.62 (t), 70.83 (d), 110.70 (s), 125.66 (d), 126.50 (d × 2), 127.13 (d × 2), 127.38 (d), 128.34 (d × 2), 128.84 (d × 2), 129.72 (d), 130.08 (d), 136.89 (s), 138.04 (s), 154.73 (d); MS m/z 312 (small M^+).

***(Z)*-1-Ethoxy-5-phenyl-2-(phenylthio)pent-1-en-4-yn-3-ol (3g):** IR (film, cm^{-1}) 3600−3400 (OH), 2220 (acetylene); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (3H, t, J = 7 Hz), 2.82 (1H, d, J = 9 Hz), 4.03−4.12 (2H, m), 5.65 (1H, d, J = 10 Hz), 6.77 (1H, s), 7.09−7.33 (8H, m), 7.40−7.43 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.35 (q), 60.20 (d), 69.84 (t), 84.78 (s), 88.47 (s), 108.66 (s), 122.56 (s), 125.53 (d), 126.82 (d × 2), 127.96 (d × 2), 128.20 (d), 128.75 (d × 2), 131.71 (d × 2), 138.09 (s), 155.99 (d); high-resolution mass calcd for $C_{19}H_{18}O_2S$ m/z 310.1028, found 310.1019.

(*Z*)-1-Ethoxy-4,4-dimethyl-2-(phenylseleno)pent-1-en-3-ol (3h): IR (film, cm^{-1}) 3600−3400 (OH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (9H, s), 1.29 (3H, t, J = 7 Hz), 2.59 (1H, brd, J = 10 Hz), 3.92 (2H, q, J = 7 Hz), 4.32 (1H, brd, J = 10 Hz), 6.76 (1H, s), 7.14−7.27 (3H, m), 7.43−7.48 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.37 (q), 26.30 (q × 3), 37.41 (s), 68.99 (t), 79.92 (d), 108.57 (s), 125.97 (d), 128.85 (d × 2), 129.08 (d × 2), 134.30 (s), 155.67 (d); MS m/z 314 (M^+). Anal. Calcd for $C_{15}H_{22}O_2Se$: C, 57.51; H, 7.08. Found: C, 57.46; H, 7.09.

(*Z*)-1-Ethoxy-3-phenyl-2-(phenylseleno)prop-1-en-3-ol (3i): IR (film, cm^{-1}) 3600−3400 (OH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (3H, t, J = 7 Hz), 2.83 (1H, d, J = 8 Hz), 3.99−4.04 (2H, m), 5.87 (1H, d, J = 8 Hz), 6.77 (1H, s), 7.11−7.27 (5H, m), 7.31−7.38 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.39 (q), 69.27 (t), 70.91 (d), 111.21 (s), 125.79 (d × 2), 126.18 (d), 127.04 (d), 127.96 (d × 2), 128.34 (d), 128.88 (d × 2), 129.59 (d × 2), 132.46 (s), 142.92 (s), 154.47 (d); high-resolution mass calcd for $C_{17}H_{18}O_2Se_2$ m/z 334.0472, found 334.0468.

(*Z*)-1-[2-Ethoxy-1-(phenylseleno)ethenyl]-1-cyclohexanol (3j): IR (film, cm^{-1}) 3600−3400 (OH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.12−1.88 (10H, m), 2.34 (3H, t, J = 7 Hz), 3.42 (1H, s), 3.98 (2H, q, J = 7 Hz), 6.73 (1H, s), 7.16−7.18 (1H, m), 7.22−7.27 (2H, m), 7.44−7.46 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.34 (q), 21.84 (t × 2), 25.46 (t), 37.04 (t × 2), 69.44 (t), 75.23 (s), 118.30 (s), 126.03 (d), 128.96 (d × 2), 129.26 (d × 2), 133.81 (s), 153.53 (d); MS m/z 326 (small M^+).

(*Z*)-1-Ethoxy-6,6-dimethyl-2-(phenylseleno)hept-1-en-6-yn-3-ol (3l): IR (film, cm^{-1}) 3600−3400 (OH), 2210 (acetylene); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02 (9H, s), 1.33 (3H, t, J = 7 Hz), 2.47 (1H, brd, J = 9 Hz), 3.96−4.03 (2H, m), 5.52 (1H, brd, J = 9 Hz), 6.71 (1H, s), 7.13−7.26 (3H, m), 7.46−7.49 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.31 (q), 27.19 (s), 30.54 (q × 3), 59.83 (d), 69.32 (t), 78.10 (s), 93.64 (s), 108.24 (s), 125.89 (d), 128.88 (d × 2), 129.01 (d × 2), 133.37 (s), 155.59 (d); MS m/z 338 (M^+). Anal. Calcd for $C_{17}H_{22}O_2Se$: C, 60.53; H, 6.57. Found: C, 61.12; H, 6.67.

Preparation of α-(Phenylthio)prop-2-enal 4a−g by PPSE. Typical Procedure (Method A). PPSE was prepared according to our previous method, and the experimental procedure was very similar to that reported in the literature.[10b]

[(Phenylthio)formylmethylene]cyclohexane (4a): IR (film, cm^{-1}) 1680 (CO); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.66−1.72 (4H, m), 1.77−1.80 (2H, m), 2.80−2.83 (2H, m), 2.92−2.95 (2H, m), 7.11−7.24 (5H, m), 10.00 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.14 (t), 28.53 (t), 28.83 (t), 31.75 (t), 35.91 (t), 125.58 (d), 127.02 (s), 127.42 (d × 2), 128.86 (d × 2), 136.35 (s), 172.79 (s), 188.09 (d); high-resolution mass calcd for $C_{14}H_{16}OS$ m/z 232.0922, found 232.0937.

[(Phenylthio)formylmethylene]cyclopentane (4b): IR (film, cm^{-1}) 1680 (CO); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.70−1.77 (2H, m), 1.85−1.92 (2H, m), 2.74−2.78 (2H, m), 2.98−3.02 (2H, m), 7.10−7.25 (5H, m), 9.80 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.57 (t), 26.99 (t), 33.47 (t), 37.00 (t), 124.57 (s), 125.69 (d), 126.54 (s), 127.40 (d × 2), 128.93 (d × 2), 135.83 (s), 189.31 (d); high-resolution mass calcd for $C_{13}H_{14}OS$ m/z 218.0765, found 218.0757.

[(Phenylthio)formylmethylene]cycloheptane (4c): IR (film, cm^{-1}) 1680 (CO); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.50−1.59 (4H, m), 1.60−1.72 (2H, m), 1.75−1.81 (2H, m), 2.85−2.88 (2H, m), 2.98−3.01 (2H, m), 7.08−7.23 (5H, m), 9.90 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.20 (t), 27.58 (t), 28.16 (t), 28.45 (t), 32.72 (t), 37.22 (t), 125.47 (d), 127.14 (d × 2), 128.60 (s), 128.80 (d × 2), 136.18 (s), 174.32 (s), 188.76 (d); high-resolution mass calcd for $C_{15}H_{18}OS$ m/z 246.1078, found 246.1086.

(*Z*)-4,4-Dimethyl-2-(phenylthio)pent-2-enal (4d): IR (film, cm^{-1}) 1680 (CO); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (9H, s), 7.15−7.26 (5H, m), 7.26 (1H, s), 9.32 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.73 (q × 3), 34.88 (s), 126.14 (d), 128.27 (d × 2), 128.97 (d × 2), 134.22 (s), 134.58 (s), 168.87 (d), 191.02 (d); MS m/z 220 (M^+). Anal. Calcd for $C_{13}H_{16}OS$: C, 70.87; H, 7.32. Found: C, 70.76; H, 7.32.

(*Z*)-3-Phenyl-2-(phenylthio)but-2-enal (4e): IR (film, cm^{-1}) 1680 (CO); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.62 (3H, s), 7.15−7.32 (8H, m), 7.41−7.45 (2H, m), 9.48 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.23 (q), 126.03 (d), 128.17 (d × 2), 128.45 (d × 2), 128.55 (d × 2), 128.96 (d × 2), 129.44 (d), 133.48 (s), 135.32 (s), 139.20 (s), 167.86 (s), 188.87 (d); MS m/z 254 (M^+). Anal. Calcd for $C_{16}H_{14}OS$: C, 75.56; H, 5.55. Found: C, 75.48; H, 5.56.

(2*Z*,4*E*)-5-Phenyl-2-(phenylthio)pent-2,4-dienal (4f): IR (film, cm^{-1}) 1680 (CO); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14−7.38 (9H, m), 7.49−7.67 (4H, m), 9.52 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.21 (d), 126.43 (d), 127.87 (d × 2), 128.67 (d × 2), 128.87 (d × 2), 129.04 (d × 2), 130.02 (d), 133.14 (s), 134.55 (s), 135.56 (s), 144.86 (d), 153.00 (d), 190.10 (d); MS m/z 266 (M^+). Anal. Calcd for $C_{17}H_{14}OS$: C, 76.66; H, 5.30. Found: C, 76.48; H, 5.42.

(*Z*)-5-Phenyl-2-(phenylthio)pent-2-en-4-ynal (4g): IR (film, cm^{-1}) 2200 (acetylene), 1680 (CO); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (1H, s), 7.23−7.45 (10H, m), 9.46 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 86.05 (s), 110.17 (s), 121.95 (s),

127.54 (d), 127.80 (d), 128.42 (d × 2), 129.11 (d × 2), 129.80 (d), 131.06 (d × 2), 131.58 (s), 132.13 (d × 2), 143.78 (s), 189.08 (d); MS *m*/*z* 264 (M^+). Anal. Calcd for $C_{17}H_{12}OS$: C, 77.24; H, 4.58. Found: C, 77.26; H, 4.73.

Preparation of 2-(Chalcogeno)prop-2-enal 4h−l by TMSOTf (Method B). TMSOTf (9.40 mL, 48.5 mmol) was added dropwise to a CH_2Cl_2 (80 mL) solution of (*Z*)-1-ethoxy-4,4-dimethyl-2-(phenylseleno)pent-1-en-3-ol (**3h**) (7.60 g, 24.3 mmol). The mixture was stirred for 10 min and poured into saturated $NaHCO_3$ (200 mL). The organic layer was separated, and the aqueous layer was extracted with $CHCl_3$. The workup procedure afforded (*Z*)-4,4-dimethyl-2-(phenylseleno-)pent-2-enal (**4h**) (6.34 g, 98%) as a yellow oil.

(*Z*)-4,4-Dimethyl-2-(phenylseleno)pent-2-enal (4h): IR (film, cm^{-1}) 1680 (CO); ^1H NMR (400 MHz, $CDCl_3$) δ 1.37 (9H, s), 7.20−7.24 (3H, m), 7.35−7.38 (2H, m), 7.36 (1H, s), 9.23 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.96 (q × 3), 35.35 (s), 126.92 (d), 129.18 (d × 2), 131.05 (s), 131.43 (d × 2), 132.49 (s), 170.02 (d), 191.64 (d); MS *m*/*z* 268 (M^+). Anal. Calcd for $C_{13}H_{16}OSe$: C, 58.43; H, 6.04. Found: C, 58.34; H, 6.01.

(*Z*)-3-Phenyl-2-(phenylseleno)pent-2-enal (4i): IR (film, cm^{-1}) 1660 (CO); ^1H NMR (400 MHz, $CDCl_3$) δ 7.17−7.20 (3H, m), 7.35−7.43 (5H, m), 7.82−7.86 (2H, m), 7.99 (1H, brs), 9.48 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.23 (d), 128.44 (d × 2), 129.18 (d × 2), 130.84 (d), 131.03 (d × 2), 131.88 (d × 2), 132.27 (s), 134.16 (s × 2), 152.43 (d), 191.33 (d); MS *m*/*z* 288 (M^+). Anal. Calcd for $C_{15}H_{12}OSe$: C, 62.73; H, 4.21. Found: C, 62.48; H, 4.22.

[(Phenylseleno)formylmethylene]cyclohexane (4j): IR (film, cm^{-1}) 1690 (CO); ^1H NMR (400 MHz, $CDCl_3$) δ 1.62−1.68 (4H, m), 1.70−1.77 (2H, m), 2.81−2.84 (2H, m), 2.90−2.93 (2H, m), 7.15−7.27 (3H, m), 7.32−7.35 (2H, m), 9.95 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.27 (t), 28.55 (t), 28.95 (t), 32.32 (t), 38.76 (t), 126.48 (d), 129.14 (d × 2), 130.72 (d × 2), 131.49 (s), 154.35 (s), 172.13 (s), 188.29 (d); MS *m*/*z* 280 (small M^+).

(*E*)- and (*Z*)-1-[(Phenylseleno)formylmethylene]-2-cyclohexene (4k): IR (film, cm^{-1}) 1680 (CO); ^1H NMR (400 MHz, $CDCl_3$) δ 1.79−1.87 (m), 2.17−2.28 (m), 2.29−2.35 (m), 2.79−2.83 (m), 3.07−3.10 (m), 6.38−6.41 (m), 6.42−6.49 (m), 7.13−7.35 (m), 9.96 (s), 10.00 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.21 (t), 22.31 (t), 26.36 (t), 26.40 (t), 28.31 (t), 33.23 (t), 124.46 (d), 126.49 (d), 126.61 (d), 127.09 (s), 128.00 (s), 129.14 (d × 2), 129.24 (d × 2), 130.59 (d × 2), 130.65 (d × 2), 130.78 (d), 131.54 (s), 141.00 (d), 143.02 (d), 150.00 (s), 158.97 (s), 188.91 (d), 189.70 (d); MS *m*/*z* 278 (M^+). Anal. Calcd for $C_{14}H_{14}OSe$: C, 60.66; H, 5.09. Found: C, 60.42; H, 5.22.

(*Z*)-6,6-Dimethyl-2-(phenylseleno)hept-2-en-4-yne (4l): IR (film, cm^{-1}) 2200 (acetylene), 1690 (CO); ^1H NMR (400 MHz, $CDCl_3$) δ 1.20 (9H, s), 7.05 (1H, s), 7.24−7.26 (3H, m), 7.46−7.49 (2H, m), 9.37 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.00 (s), 30.22 (q × 3), 77.34 (s), 121.70 (s), 127.49 (d × 2), 128.45 (s), 129.11 (d × 2), 133.06 (d × 2), 141.71 (s), 190.27 (d); MS *m*/*z* 292 (small M^+). Anal. Calcd for $C_{15}H_{16}OSe$: C, 61.86; H, 5.54. Found: C, 61.90; H, 5.58.

(1*Z*,4*Z*)-1-Ethoxy-6,6-dimethyl-2,4-bis(phenylthio)hepta-1,4-dien-3-ol: IR (film, cm^{-1}) 3600−3400 (OH); ^1H NMR (400 MHz, $CDCl_3$) δ 1.04 (9H, s), 1.17 (3H, t, *J* = 7 Hz), 2.78 (1H, brd, *J* = 8 Hz), 3.82−3.89 (2H, m), 5.08 (1H, brd, *J* = 8 Hz), 6.39 (1H, s), 6.71 (1H, s), 7.06−7.11 (2H, m), 7.18−7.32 (8H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.10 (q), 30.27 (q × 3), 33.32 (s), 69.20 (t), 71.11 (d), 109.22 (s), 125.11 (d), 125.31 (d), 126.48 (d × 2), 127.73 (d × 2), 128.56 (d × 2), 128.64 (d × 2), 129.64 (s), 136.88 (s), 138.51 (s), 148.21 (d), 156.95 (d); high-resolution mass calcd for $C_{23}H_{28}O_2S_2$ 400.1531, found *m*/*z* 400.1539.

(2*Z*,4*Z*)-6,6-Dimethyl-2,4-bis(phenylthio)hepta-2,4-dienal (5d): IR (film, cm^{-1}) 1700 (CO); ^1H NMR (400 MHz, $CDCl_3$) δ 1.35 (9H, s), 6.40 (1H, s), 7.07−7.11 (2H, m), 7.17−7.37 (8H, m), 7.26 (1H, s), 9.19 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.40 (q × 3), 34.89 (s), 125.88 (s), 126.50 (d), 126.82 (d), 128.93 (d × 2), 129.13 (d × 2), 129.36 (d × 2), 129.41 (d × 2), 133.99 (s), 135.27 (s), 136.25 (s), 152.10 (d), 157.66 (d), 189.29 (d); MS *m*/*z* 354 (M^+). Anal. Calcd for $C_{21}H_{22}OS_2$: C, 71.15; H, 6.25. Found: C, 70.99; H, 6.36.

(1*Z*,4*Z*,6*Z*)-1-Ethoxy-8,8-dimethyl-2,4,6-tris(phenylthio)nona-1,4,6-trien-3-ol (6d): IR (film, cm^{-1}) 3600−3400 (OH); ^1H NMR (400 MHz, $CDCl_3$) δ 1.11 (3H, t, *J* = 7 Hz), 1.20 (9H, s), 2.05 (1H, brs), 3.79 (2H, q, *J* = 7 Hz), 5.07 (1H, s), 5.60 (1H, s), 6.51 (1H, s), 6.66 (1H, s), 7.07−7.27 (15H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.03 (q), 30.42 (q × 3), 34.07 (s), 69.22 (t), 69.56 (d), 109.12 (s), 125.15 (s), 125.59 (d), 125.63 (d), 126.05 (d), 126.82 (d × 2), 128.52 (d × 2), 128.61 (d × 2), 128.71 (d × 2), 129.34 (d × 2), 129.76 (d × 2), 135.27 (s), 135.30 (s), 135.48 (d), 136.18 (s), 138.18 (s), 152.84 (d), 156.61 (d); MS *m*/*z* 534 (M^+). Anal. Calcd for $C_{31}H_{34}O_2S_3$: C, 69.62; H, 6.41. Found: C, 69.10; H, 6.48.

(2*Z*,4*Z*,6*Z*)-8,8-Dimethyl-2,4,6-tris(phenylthio)nona-2,4,6-trienal (7d): IR (film, cm^{-1}) 1700 (CO); ^1H NMR (400 MHz, $CDCl_3$) δ 1.36 (9H, s), 6.19 (1H, s), 6.60 (1H, s), 7.07 (1H, s), 7.13−7.40 (15H, m), 9.03 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.26 (q × 3), 35.24 (s), 127.09 (d), 127.36 (d), 127.62 (s), 127.94 (d), 129.50 (d × 2), 129.55 (d × 2), 129.62 (d × 2), 130.02 (d × 2), 130.94 (s), 131.00 (d × 2), 131.46 (d × 2), 134.54 (s), 135.13 (s), 135.98 (s), 136.72 (s), 143.24 (d), 149.53 (d), 154.17 (d), 189.95 (d); high-resolution mass calcd for $C_{29}H_{28}OS_3$ 488.1302, found *m*/*z* 488.1294.

Synthesis of (2*Z*,4*Z*,6*Z*)-8,8-Dimethyl-2,4,6-tris(phenylthio)nona-2,4,6-trienal 2,4-Dinitrophenyl Hydrazone (8d). A benzene (100 mL) solution of (2*Z*,4*Z*,6*Z*)-8,8-dimethyl-2,4,6-tris(phenylthio)nona-2,4,6-trienal (**7d**) (2.90 g, 5.94 mmol), 2,4-dinitrophenyl hydrazine (2.83 g, 14.3 mmol), and TsOH (0.23 g, 1.20 mmol) was heated under reflux for 10 min. The mixture was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with AcOEt−hexane (1:20) to give the title compound **8d** (2.63 g, 66%) as an orange powder: IR (film, cm^{-1}) 3300 (NH), 1740 (C═N), 1620, 840 (NO_2); ^1H NMR (400 MHz, $CDCl_3$) δ 1.37 (9H, s), 6.21 (1H, d, *J* = 1 Hz), 6.49 (1H, d, *J* = 1 Hz), 6.64 (1H, d, *J* = 1 Hz), 6.82−7.45 (1H, m), 7.99−8.04 (17H, m), 8.95 (1H, brs), 10.83 (1H, brs); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.57 (q × 3), 34.41 (s), 116.71 (d), 122.99 (d), 126.20 (d), 126.29 (d), 127.12 (d), 128.48 (d × 2), 128.74 (d × 2), 128.85 (d × 2), 129.16 (d × 2), 129.20 (d), 130.42 (d × 2), 130.65 (s), 131.03 (d × 2), 131.41 (s), 132.39 (s), 134.63 (s), 135.24 (s), 135.34 (s), 138.25 (s), 140.64 (d), 142.56 (d), 144.24 (s), 146.96 (d), 152.50 (d), 171.10 (s); MS *m*/*z* 501 (M^+ − dinitrophenyl). Anal. Calcd for $C_{35}H_{32}N_4O_4S_3$: C, 62.81; H, 4.82; N, 8.38. Found: C, 62.81; H, 4.95; N, 8.14.

(1*Z*,4*Z*)-1-Ethoxy-6,6-dimethyl-2,4-bis(phenylseleno-)hepta-1,4-dien-3-ol: IR (film, cm^{-1}) 3600−3200 (OH); ^1H NMR (400 MHz, $CDCl_3$) δ 1.08 (9H, s), 1.21 (3H, t, *J* = 7 Hz), 2.69 (1H, d, *J* = 8 Hz), 3.86−3.92 (2H, m), 5.12 (1H, d, *J* = 8 Hz), 6.46 (1H, s), 6.74 (1H, s), 7.15−7.19 (6H, m), 7.39−7.44 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.28 (q), 30.64 (q × 3), 33.82 (s), 69.05 (t), 73.05 (d), 109.32 (s), 125.98 (d), 126.12 (d), 128.60 (s), 128.88 (d × 2), 129.00 (d × 2), 129.31 (d × 2), 130.55 (d × 2), 132.47 (s), 133.27 (s), 147.68 (d), 156.51 (d); MS *m*/*z* 496 (M^+). Anal. Calcd for $C_{23}H_{28}O_2Se_2$: C, 55.88; H, 5.71. Found: C, 55.74; H, 5.71.

(1*Z*,4*Z*)-1-Ethoxy-5-phenyl-2,4-bis(phenylseleno)penta-1,4-dien-3-ol: IR (film, cm^{-1}) 3600−3200 (OH); ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (3H, t, *J* = 7 Hz), 2.89 (1H, d, *J* = 8 Hz), 3.92−3.96 (2H, m), 5.36 (1H, dt, *J* = 8 and 1 Hz), 6.82 (1H, brs), 7.13−7.26 (9H, m), 7.33−7.37 (4H, m), 7.45−7.47 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.33 (q), 69.25 (d), 73.15 (t), 126.41 (d), 126.45 (d), 127.54 (d), 127.65 (d × 3), 127.98 (s), 128.87 (d × 2), 129.05 (d × 3), 129.38 (d × 2), 129.96 (d), 131.22 (s), 131.44 (d), 132.73 (s), 133.63 (s), 135.42 (d), 136.65 (s), 156.36 (d); MS *m*/*z* 516 (M^+). Anal. Calcd for $C_{25}H_{24}O_2Se_2$: C, 58.38; H, 4.70. Found: C, 58.29; H, 4.90.

(2*Z*,4*Z*)- and (2*E*,4*Z*)-6,6-Dimethyl-2,4-bis(phenylseleno)hept-2,4-dienal (5h): 2*Z*/2*E* = 3:1; IR (film, cm^{-1}) 1720, 1680 (CO); ^1H NMR (400 MHz, $CDCl_3$) δ 1.11 (s), 1.36 (s), 6.22 (s), 6.28 (brs), 7.16−7.28 (m), 7.36−7.38 (m), 7.41 (brs), 7.45−7.47 (m), 7.52−7.54 (m), 7.78 (brs), 9.09 (s), 9.25 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.05 (q), 30.58 (q), 35.20 (s), 36.35 (s), 123.82 (s), 127.23 (d), 127.43 (d), 127.52 (d), 127.62 (d), 129.00 (d), 129.13 (d), 129.27 (d), 129.34 (d), 129.72 (s), 129.95 (s), 131.91 (d), 132.93 (d), 133.03 (d), 135.03 (s), 136.07 (s), 151.06

(d), 152.92 (d), 154.79 (d), 154.83 (d), 189.62 (d), 189.81 (d); high-resolution mass calcd for $C_{21}H_{22}OSe_2$ 450.0001, found *m*/*z* 450.0019.

(2*Z*,4*Z*)- and (2*E*,4*Z*)-5-Phenyl-2,4-bis(phenylseleno-)pent-2,4-dienal (5i): 2*Z*/2*E* = 3:1; IR (film, cm^{-1}) 1700 (CO); ^1H NMR (400 MHz, $CDCl_3$) δ 7.10−7.42 (m), 7.59 (brs), 7.60−7.63 (m), 9.15 (s), 9.22 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 128.15 (d), 128.39 (s), 128.62 (d), 128.74 (d), 129.04 (d), 129.28 (d), 129.70 (d), 129.75 (d), 129.83 (d), 129.90 (s), 130.11 (d), 130.14 (d), 130.39 (d), 130.45 (s), 133.04 (d), 133.63 (d), 134.22 (d), 134.69 (d), 134.75 (s), 136.08 (s), 136.09 (s), 136.10 (s), 136.37 (s), 136.76 (s), 137.09 (s), 141.04 (d), 142.35 (d), 148.94 (d), 154.13 (d), 190.56 (d), 190.66 (d); MS *m*/*z* 393 (M^+ − Ph).

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Supporting Information Available: NMR characterization data for all compounds complete with peak assignments (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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