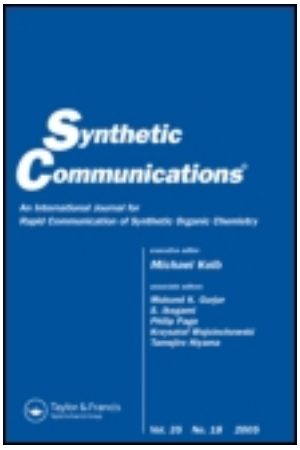

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A Novel Radical-Based Synthesis of Valerolactones

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A NOVEL RADICAL-BASED SYNTHESIS OF VALEROLACTONES

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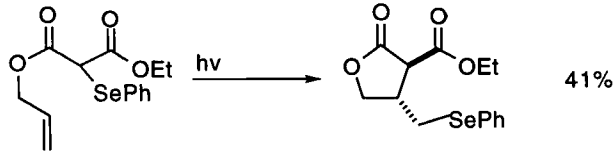
Abstract: The photolytic radical addition of phenylselenomalonates to allylic alcohols, followed by acid-catalyzed cyclization yields valerolactones incorporating a phenylseleno substituent.

Several years ago, we described the radical addition reactions of diethyl 2-phenylselenopropanedioate to a variety of alkenes.[1] These constituted the first examples of radical carbon-carbon bond formation proceeding via phenyl selenide transfer. Since this discovery, there have been numerous further examples of phenyl selenide transfer addition reactions, which have served to gain a better mechanistic understanding of the process, as well as illustrate its synthetic utility.[2]

A particularly interesting reaction which we have demonstrated involves the radical cyclization of a malonate ester derivative, leading to a highly substituted butyrolactone, as shown in Eq. 1.[2a] This reaction proceeded through the expected *5-exo* mode of cyclization, generating a butyrolactone product. Given the ubiquitous nature of the lactone functionality in synthetic intermediates and important natural products, we felt that the development of complementary methodology leading to lactones possessing six-membered rings would be of value.

Eq. 1.



We had hoped to achieve this goal through a reaction sequence involving

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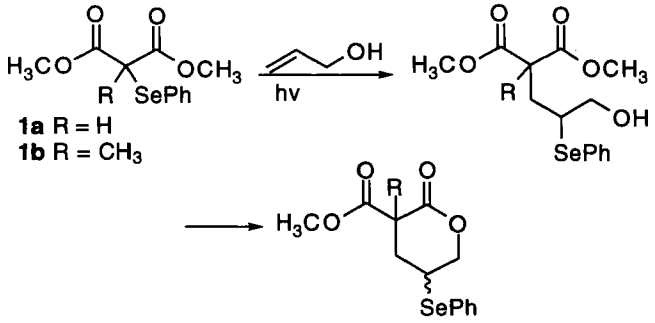
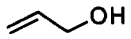
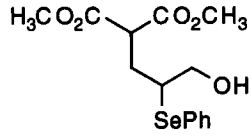
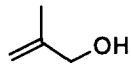
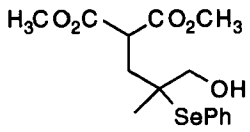
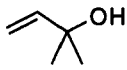
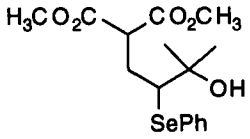
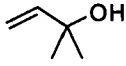
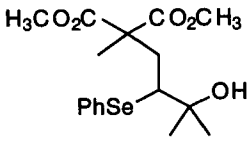
radical addition of a phenylselenomalonate to an allylic alcohol to generate a hydroxyester, followed by ionic cyclization to yield a valerolactone, as shown in Eq. 2. In this sequence, the size of the ring formed in the cyclization step would be established in the initial radical addition step where the radical should add cleanly to the olefinic terminus. While a similar sequence, involving well-established H-transfer radical addition methodology was reported some time ago,[3] we felt that our proposed methodology could be useful, given the variety of subsequent reactions which the incorporated phenylseleno group might be expected to undergo.[4]

Eq. 2



We chose the simple diesters dimethyl 2-phenylselenopropanedioate[1b] (**1a**) and dimethyl 2-methyl-2-phenylselenopropanedioate[2f,5] (**1b**) as our organoselenide radical precursors, given their ease of preparation. In the reactions of **1a**, as well as one of the reactions using **1b**, the desired addition products were obtained after overnight photolyses of a benzene solution of the phenylselenomalonate and allylic alcohol. These successful examples are summarized in Table I. It was unneccessary to protect the hydroxyl group in the course of these radical transformations, in sharp contrast to most ionic carbon-carbon bond forming reactions, in which this functionality is labile. We were, however, concerned that the intermediate malonate radicals, which we had hoped would add to the olefinic funtionality of the allylic alcohol, might simply abstract an allylic hydrogen, leading to a diminished yield of addition product. While small quantities of malonate esters in which a hydrogen atom was substituted for the phenylseleno functionality were obseerved in the crude reaction mixtures, the satisfactory yields of addition products obtained indicated that this hydrogen-abstraction process was not a dominant reaction pathway.

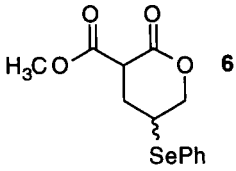
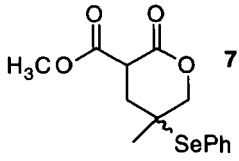
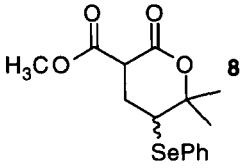
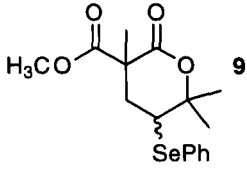
Table I.

Selenide	Alcohol	Product		Yield
1a			**2**	77%
1a			**3**	68%
1a			**4**	59%
1b			**5**	65%

The subsequent cyclization, leading to the desired lactone products was found to proceed most readily by heating a THF solution of the requisite alcohol (ie: **2** - **5**) to reflux in the presence of catalytic 10-camphorsulfonic acid. All of these cyclizations, which are summarized in Table II, proceeded to completion overnight, except for the case of **9**, where steric factors probably led to the longer reaction time of 36 h. As expected, a roughly 1:1 mixture of diastereomers was obtained in all cases, as shown by the presence of two sets of peaks of equal intensity in each NMR spectrum. Thus, we were unable to discern which peaks were associated with which stereoisomer. The stereoisomeric products in Table II were characterized as a mixture, given our inability to isolate the individual stereoisomeric components.

Simple radical addition products were not observed in the photolyses of **1b** with two of the allylic alcohols studied. Instead, upon the presumed formation of the hydroxyester, it underwent cyclization *in situ* to generate the diastereomeric

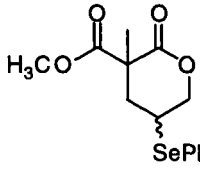
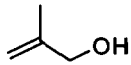
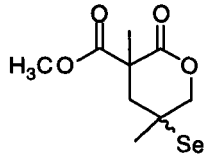
Table II.

Alcohol	Lactone	Yield
2	 **6**	84%
3	 **7**	74%
4	 **8**	61%
5	 **9**	41%

mixture of lactones, as shown in Table III. The products obtained from the radical addition of **1b** were apparently more reactive towards cyclization than in the case of **1a**, possibly arising from the inability of the **1b** adducts to form an enol tautomer, which might be expected to diminish the rate of cyclization. In the case of lactone **10**, we were able to generate a sample enriched in one of the two components, which allowed us to assign most spectral lines to individual components. In the case of lactone **11**, we were able to separate and characterize both diastereomers.

In summary, we have demonstrated that phenylselenomalonates will add effectively to unprotected allylic alcohols. The hyroxyesters thus obtained can, in a few cases undergo cyclization *in situ* to form valerolactones. In other cases, however, valerolactones could only be generated effectively upon acid-catalyzed intramolecular transesterification of the hydroxyesters.

Table III.

Selenide	Alcohol	Product	Yield
1b		 **10**	68%
1b		 **11**	73%

EXPERIMENTAL

General: Infrared spectra were obtained on a Perkin-Elmer 1600 FT-IR. NMR Spectra were obtained in $CDCl_3$ on a General-Electric GN-300 Omega Spectrometer. Mass spectra were obtained on a Hewlett-Packard 5970 Mass Selective Detector (EI, 70 eV) interfaced to a Hewlett Packard 5890 gas chromatograph equipped with a 25-m HP-1 methyl silicone capillary column. Elemental analyses were performed by Atlantic Microlabs of Norcross, GA. In cases where inseparable diastereomeric mixtures were obtained, the products were characterized as a mixture. Photolyses were performed in screw-cap Pyrex test tubes suspended in a beaker of water, approximately 6 in from a 450-W Hanovia lamp. The temperature of the reaction was maintained at about 30 °C under these conditions. Integrations for proton NMR spectra of 1:1 diastereomeric mixtures are listed in 0.5 - H increments, where a resolved signal for an individual proton from only one of the diastereomers is given a value of 0.5. All radical reaction mixtures were deoxygenated by bubbling Ar through the sample for 15 min prior to photolysis. Benzene and THF were freshly distilled from K/benzophenone under Ar. Reagent-grade hexane and ethyl acetate were distilled prior to use. Medium-pressure liquid chromatography (MPLC) was carried out on Merck grade 9385 230-400 mesh silica gel.

Dimethyl 2-(3-Hydroxy-2-phenylselenopropyl) Propanedioate (2). A mixture of **1a** (193 mg, 0.67 mmol) and allyl alcohol (116 mg, 2 mmol) were

dissolved in 2 mL of benzene and photolyzed for 18 h. Purification by MPLC (hexane, followed by 65% hexane, 35% EtOAc, v/v) gave pure **2** (178 mg, 77% yield) as a clear, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) ∂ 7.6 (m, 2H), 7.3 (m, 3H), 3.95 (dd, J = 5.7, 9.7 Hz, 1H) 3.75 (s, 3H) 3.70 (s, 3H), 3.62 (dd, J = 6.5, 9.7 Hz, 1H), 3.20 (m, 1H), 2.33 (ddd, J = 5.8, 11.6, 17.3 Hz, 1H) 2.30 (bs, 1H), 2.10 (ddd, J = 5.8, 11.6, 17.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) ∂ 169.6, 169.4, 135.7, 129.3, 128.4, 126.6, 64.5, 52.8, 52.7, 50.0, 47.8, 30.7; IR (neat) 3517, 1737 cm^{-1}; Anal. Calcd. for $C_{14}H_{18}O_5Se$: C, 48.70; H, 5.25; Found: C, 48.87; H, 5.33.

Dimethyl 2-(3-Hydroxy-2-methyl-2-phenylselenopropyl) Propanedioate (3). A mixture of **1a** (198 mg, 0.69 mmol) and 2-methyl-2-propen-1-ol (299 mg, 4.1 mmol) were dissolved in 2 mL of benzene and photolyzed for 19 h. Purification by MPLC (hexane, followed by 25% EtOAc, 75% hexane, v/v) yielded **3** as a yellow oil (169 mg, 68%): ^{1}H NMR ∂ 7.60 (m, 2H), 7.30 (m, 3H), 3.90 (t, J = 6.1 Hz, 1H), 3.74 (s, 6H), 3.30 (s, 2H), 2.60 (bs, 1H), 2.3-2.1 (m, 2H), 1.2 (s, 3H); ^{13}C NMR ∂ 170.3, 170.1, 138.2, 129.1, 129.0, 125.2, 68.1, 53.5, 52.9, 52.8, 48.7, 35.8, 23.2; IR (neat) 3442, 1735 cm^{-1}; Anal. Calcd. for $C_{15}H_{20}O_5Se$: C, 50.15; H, 5.61; Found: C, 50.08; H, 5.57.

Dimethyl 2-(3-Hydroxy-3-methyl-2-phenylselenobutyl) Propanedioate (4). A mixture of **1a** (192 mg, 0.667 mmol) and 3-buten-2-ol (183 mg, 2.12 mmol) were dissolved in 2 mL of benzene and photolyzed for 16 h. Purification by MPLC (hexane, followed by 30% EtOAc, 70% hexane, v/v) gave **4** as a yellow oil (148 mg, 59%): ^{1}H NMR ∂ 7.50 (m, 2H), 7.20 (m, 3H), 3.95 (dd, J=11.2, 3.4 Hz, 1H), 3.65 (s, 3H), 3.45 (s, 3H), 3.00 (dd, J = 2.7, 12.9 Hz, 1H), 2.65 (bs, 1H), 2.45 (m, 1H), 1.95 (m, 1H), 1.30 (s, 3H), 1.20 (s, 3H); ^{13}C NMR ∂ 169.8, 169.4, 133.8, 130.5, 129.3, 127.6, 72.8, 62.5, 52.8, 52.4, 51.0, 32.2, 27.0, 26.8; IR (neat) 3516, 1738 cm^{-1}; Anal. Calcd. for $C_{16}H_{22}O_5Se$: C, 51.48; H, 5.94; Found: C, 51.45; H, 5.93.

Dimethyl 2-(3-Hydroxy-3-methyl-2-phenylselenobutyl)-2-methyl Propanedioate (5). A mixture of **1b** (202 mg, 0.66 mmol) and 2-methyl-3-buten-2-ol (144 mg, 1.67 mmol) were dissolved in 2 mL of benzene and photolyzed for 17 h. Purification by MPLC (hexane, followed by 65% hexane, 35% EtOAc, v/v) gave **5** (166 mg, 65% yield) as a clear, colorless oil. ^{1}H NMR ∂ 7.70 (m, 2H), 7.40 (m, 3H) 3.85 (s, 3H), 3.80 (s, 3H), 3.36, (dd, J = 1.3, 10.2 Hz, 1H), 2.75 (bs, 1H), 2.61 (dd, J = 1.3, 15.3 Hz, 1H), 2.33 (dd, J = 10.2,

15.3 Hz, 1H), 1.60 (s, 3H), 1.44 (s, 3H), 1.36 (s, 3H); ^{13}C NMR ∂ 172.5, 172.4, 132.7, 131.4, 129.2, 127.1, 73.7, 55.4, 52.9, 52.6, 52.5, 37.1, 27.3, 25.9, 20.4; IR (neat) 3511, 1731 cm^{-1}; Anal. Calcd. for $C_{17}H_{24}O_5Se$: C, 52.72; H, 6.25; Found: C, 52.85; H, 6.23.

2-Methoxycarbonyl-4-phenylseleno-5-pentanolide (6) A 48-mg (0.14-mmol) portion of **2** and 6.5 mg (.028 mmol) of 10-camphorsulfonic acid were dissolved in 5 ml of THF and heated to reflux for 18 h. The mixture was eluted through a 1-in pad of basic alumina with ether, and solvents were removed by rotary evaporation. Purification by MPLC (hexane, followed by 20% EtOAc, 80% hexane, v/v)) yielded the two diastereomers of **6** (37 mg, 84%) as a clear, colorless oil, homogeneous by tlc. ^1H NMR ∂ 7.55 (m, 2H), 7.30 (m, 3H), 4.85 (m, 0.5H), 4.58 (m, 0.5H), 3.81 (s, 1.5H), 3.80 (s, 1.5H), 3.65 (m, 1H), 3.36 (dd, J = 5.1, 12.5 Hz, 0.5H), 3.28 (dd, J = 4.4, 13.2 Hz), 3.05 (m, 1H), 2.80 (m, 0.5H), 2.68 (m, 0.5H), 2.44 (m, 0.5H), 2.23 (m, 0.5H); ^{13}C NMR ∂ 168.0 (2 peaks), 133.5, 133.4, 131.8, 131.6, 129.4 (2 peaks), 127.9, 127.8, 78.6, 78.2, 53.2, 53.1, 47.2, 46.7, 31.9 (2 peaks), 31.4, 31.2; IR (neat) 1738, 1780 cm^{-1}; MS 256 (M^+ - CO_2CH_3) Anal. Calcd. for $C_{13}H_{14}O_4Se$: C, 49.85; H, 4.51; Found: C, 49.82; H, 4.50.

2-Methoxycarbonyl-4-methyl-4-phenylseleno-5-pentanolide (7). A 74-mg (0.21-mmol) portion of **3** and 9 mg (0.04 mmol) of 10-camphorsulfonic acid were dissolved in 5 mL of THF and heated to reflux for 16 h. The mixture was eluted through a 1-in pad of basic alumina with ether, and solvents were removed by rotary evaporation. Purification by MPLC (hexane, followed by 25% EtOAc, 75% hexane, v/v) yielded the two diastereomers of **7** as a pale-yellow oil (50 mg, 74%): ^1H NMR ∂ 7.60 (m, 2H), 7.30 (m, 3H), 3.85 (m, 1H), 3.84 (s, 1.5H), 3.83 (s, 1.5H), 3.3 (s, 1H), 3.2 (s, 1H), 2.75 (dd, J = 13.2, 9.8 Hz, 0.5H), 2.5 (d, J = 9.3 Hz, 1H), 2.35 (dd, J = 13.2, 9.8 Hz,0.5H), 1.60 (s, 1.5H), 1.50 (s, 1.5H); ^{13}C NMR ∂ 170.8, 170.5, 168.2, 168.0, 133.4, 133.0, 129.8, 129.7, 129.4, 129.3, 127.7, 127.6, 85.5, 85.4, 53.2, 53.1, 47.9, 47.1, 39.3, 38.9, 36.4, 35.9, 27.6, 26.0; IR (neat) 1774, 1736 cm^{-1}; MS *m/z* 328 M^+), 171 (M^+ - SePh), 157 (SePh) 125; Anal. Calcd. for $C_{13}H_{16}O_4Se$: C, 51.39; H, 4.93; found: C, 51.39; H, 5.10.

5,5-Dimethyl-2-methoxycarbonyl-4-phenylseleno-5-pentanolide (8). A 39-mg (0.10 - mmol) portion of **4** and 4.2 mg (0.018 mmol) of 10-camphorsulfonic acid were dissolved in 5 mL of THF and heated to reflux for 12 h.

The mixture was eluted through a 1-in pad of basic alumina with ether, and solvents were removed by rotary evaporation. Purification by MPLC (hexane, followed by 25% EtOAc, 75% hexane, v/v) yielded the two diastereomers of **8** as a pale yellow oil (22 mg, 61%): ^{1}H NMR ∂ 7.60 (m, 2H), 7.30 (m, 2H), 4.55 (dd, J = 14.4, 7.1 Hz, 0.5H), 4.35 (dd, J = 9.8, 6.8 Hz, 0.5H), 3.84 (s, 1.5H), 3.82 (s, 1.5H), 3.65 (m, 1H), 2.6 (m, 2H), 1.46 (s, 1.5H), 1.43 (s, 1.5H), 1.41 (s, 1.5H), 1.36 (s, 1.5H); IR (neat) 1780, 1739 cm^{-1}; Anal. Calcd. for $C_{15}H_{18}O_4Se$: C, 52.79; H, 5.32; found: C, 52.95; H, 5.51.

2-Methoxycarbonyl-2,5,5-trimethyl-4-phenylseleno-5-pentanolide (9). A 79-mg portion of **5** (0.2 mmol) and 10 mg of 10-camphorsulfonic acid (0.04 mmol) were dissolved in 5 mL of THF and heated to reflux for 36 h. The mixture was eluted through a 1-in pad of basic alumina with ether, and solvents were removed by rotary evaporation. MPLC (hexane, followed by 25% EtOAc, 75% hexane, v/v) gave **9** (29 mg, 41%) as a clear, colorless oil, homogeneous by tlc. ^{1}H NMR ∂ 7.62 (m, 2H), 7.40 (m, 3H), 4.40 (m, 2H), 3.81 (s, 1.5H), 3.77, (s, 1.5H), 2.90 (m, 1H), 2.28 (dd, J = 13.6, 6.8 Hz, 0.5H), 2.12 (dd, J = 13.6, 9.8 Hz, 0.5H), 1.57 (s, 1.5H), 1.55, (s, 1.5H), 1.46, (s, 1.5H), 1.42 (s, 1.5H), 1.40, (s, 1.5H), 1.38, (s, 1.5H); ^{13}C NMR ∂ 174.7, 171.0, 170.9, 138.3 (2 peaks), 129.2 (2 peaks), 129.0, 128.9, 126.0 (2 peaks) 84.2, 83.9, 53.2, 53.1, 52.0, 51.7, 46.6, 46.4, 37.8, 37.0, 27.0, 26.9, 23.9, 23.1, 20.7, 20.2; IR (neat) 1771, 1742 cm^{-1}; MS *m/z* 356 (M^+) 199 (M^+ - SePh), 139. Anal. Calcd. for $C_{16}H_{20}O_4Se$: C, 54.09; H, 5.67; Found: C, 54.15; H, 5.75.

2-Methoxycarbonyl-2-methyl-4-phenylseleno-5-pentanolide (10). Selenide **1b** (202 mg, 0.66 mmol) and allyl alcohol (116 mg, 2.00 mmol) were dissolved in 2 ml of benzene and photolyzed for 16 h. Purification by MPLC (hexane, followed by 70% hexane, 30% EtOAc, v/v) gave 146 mg of **10** (68%) as a clear, colorless oil, homogeneous by tlc. Partial resolution of the two diastereomeric components was performed by MPLC (75% hexane, 25% EtOAc, v/v) yielding several fractions which were enriched in one of the components, allowing for assignment of most spectral lines to either the major or minor component of this mixture. ^{1}H NMR ∂ 7.60 (m, 2H), 7.35 (m, 3H), 4.50 (ddd, J = 2.0, 5.4, 11.7 Hz, 1H, minor), 4.40 (ddd, J = 2.0, 5.4, 11.7 Hz, 1H, major), 4.25 (t, J = 11.7 Hz, 1H, minor), 4.24 (t, J = 11.7 Hz, 1H, major), 3.77 (s, 3H, minor), 3.76 (s, 3H, major), 3.55 (m, 1H), 2.74, (ddd, J = 2.5, 4.4, 14.2 Hz, 1H, minor), 2.56 (dd, J = 10.7, 14.2 Hz, 1H, major), 2.22 (ddd, j = 2.0, 6.8,

14.2 Hz, 1H, major), 1.78 (dd J = 12.2, 14.2 Hz, 1H, minor), 1.54 (s, 3H, major), 1.52 (s, 3H, minor); ^{13}C NMR major isomer ∂ 171.8, 170.1, 135.4, 129.5, 128.8, 126.3, 72.3, 53.3, 50.8, 37.7, 32.2, 23.3; minor isomer ∂ 171.9, 169.3, 135.7, 129.5, 128.9, 125.6, 73.4, 53.3, 51.4, 38.9, 32.3, 23.4; IR (neat) 1738 cm^{-1}; MS *m/z* 328 (M^+) 171 (M^+ - SePh); Anal. Calcd. for $C_{14}H_{16}O_4Se$: C, 51.39; H, 4.93; Found: C, 51.32; H, 4.94.

2-Methoxycarbonyl-2,4-dimethyl-4-phenylseleno-5-pentanolide (11). Selenide **1b** (201 mg, 0.66 mmol) and 2-methyl-2-propen-1-ol (144 mg, 2.00 mmol) were dissolved in 2 mL of benzene and photolyzed for 23 h. MPLC (hexane, followed by 70% hexane, 30% EtOAc, v/v) gave 165 mg of **11** (73%) as a clear, colorless oil, homogeneous by tlc. Two isomeric products were observed in a 1:1 ratio upon GC/MS of this product. Purification by MPLC (80% hexane, 20% EtOAc, v/v) generated small samples of each of the purified diastereomers suitable for individual characterization. Less polar diastereomer: ^1H NMR ∂ 7.60 (m, 2H), 7.40 (m, 3H), 4.40 (d, J = 11.7 Hz, 1H), 4.05, (d, J = 11.7 Hz, 1H), 3.71 (s, 3H), 2.87 (d, J = 15.6 Hz, 1H), 1.80 (d, J = 15.6 Hz), 1.49 (s, 3H), 1.44 (s, 3H); ^{13}C NMR ∂ 172.0, 170.7, 138.3, 129.5, 129.2, 125.7, 75.6, 53.3, 49.5, 44.3, 39.9, 27.0, 24.4; IR (neat) 1737 cm^{-1}; MS *m/z* 342 (M^+) 171, 111; Anal. Calcd. for $C_{15}H_{18}O_4Se$: C, 52.79; H, 5.32; Found: C, 52.90; H, 5.35. More polar diastereomer: ^1H NMR ∂ 7.60 (m, 2H), 7.40 (m, 3H), 3.95 (s, 2H), 3.76 (s, 3H), 2.75 (d, J = 15.6 Hz, 1H), 1.80 (d, J = 15.6 Hz, 1H) 1.53 (s, 3H), 1.46 (s, 3H); ^{13}C NMR ∂ 172.4, 170.3, 138.3, 129.6, 129.1, 125.9, 73.8, 53.4, 49.1, 44.2, 42.8, 26.4, 24.4; IR (neat) 1737 cm^{-1}; MS *m/z* 342 (M^+) 171, 111; Anal. Calcd. for $C_{15}H_{18}O_4Se$: C, 52.79; H, 5.32; Found: C, 52.84; H, 5.31.

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5. Our synthesis of **1b** was adapted from a procedure for the analogous ethyl diester described in ref 2f, substituting dimethyl methylmalonate for diethyl methylmalonate.

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