Electrophilic Intereaction of 2, 3-allenoates with PhSeCl.

An Unexpected Highly Stereoselective Synthesis of

3-Phenylseleno-4-oxo-2(*E*)-alkenoates

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(1) Preparation of 2-Methyl-4-oxo-3-phenylselanyloct-2(*E*)-enoic acid ethyl ester

(2a). Typical procedure.

To a solution of PhSeCl (79.3 mg, 0.41 mmol) in 5 mL of MeCN was added Li₂CO₃ (45.0 mg, 0.61 mmol). Then **1a** (35.6 mg, 0.20 mmol) and 1 mL of MeCN were subsequently added. After being stirred at room temperature for 1 h, the reaction was complete as monitored by TLC and the mixture was filtered through a short column of silica gel to afford the crude product, which analyzed by 400 MHz ¹H NMR measurement. The crude product was then purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 40:1) to afford **2a** (53.1 mg, 77%) and **3a** (3.2 mg, 4%). **2a**: liquid, ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, *J* = 8.0 Hz, 2 H), 7.39-7.27 (m, 3 H), 4.13 (q, *J* = 7.0 Hz, 2 H), 2.32 (t, *J* = 7.4 Hz, 2 H), 2.06 (s, 3 H), 1.22 (t, *J* = 7.0 Hz, 3 H), 1.22-1.13 (m, 2 H), 1.10-0.99 (m, 2 H), 0.73 (t, *J* = 7.4 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 201.9, 164.7, 150.1, 136.6, 129.33, 129.30, 125.3, 124.2, 61.3, 42.0, 24.6, 21.9, 17.2, 13.9, 13.8; MS (70 eV, EI) *m/z* (%): 356 (M⁺(⁸²Se), 5.72), 355 (M⁺(⁸⁰Se)+1, 7.13), 354 (M⁺(⁸⁰Se), 28.85), 352 (M⁺(⁷⁸Se), 16.29), 351 (M⁺(⁷⁷Se), 9.26), 350 (M⁺(⁷⁶Se), 7.31), 41 (100); IR ν (cm⁻¹): 2958, 2932, 1704, 1591, 1477, 1465, 1439, 1366, 1270, 1156, 1133, 1022; HRMS calcd for C₁₇H₂₂O₃⁸⁰SeNa⁺ (M⁺+Na): 377.0638. Found: 377.0620.

(2) 4-Oxo-3-phenylselanyl-2-propyloct-2(*E*)-enoic acid ethyl ester (2b)

The reaction of 41.2 mg (0.20 mmol) of **1b**, 77.4 mg (0.40 mmol) of PhSeCl, and 44.3 mg (0.60 mmol) of Li₂CO₃ in 6 mL of MeCN afforded 51.2 mg (68%) of **2b**: liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, *J* = 8.0 Hz, 2 H), 7.37-7.26 (m, 3 H), 4.13 (q, *J* = 7.1 Hz, 2 H), 2.53 (t, *J* = 7.6 Hz, 2 H), 2.36 (t, *J* = 7.6 Hz, 2 H), 1.61-1.50 (m, 2 H), 1.22 (t, *J* = 7.1 Hz, 3 H), 1.23-1.15 (m, 2 H), 1.12-1.01 (m, 2 H), 0.99 (t, *J* = 7.4 Hz, 3 H), 0.74 (t, *J* = 7.0 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 201.7, 165.1, 148.8, 136.2, 130.8, 129.3, 129.1, 125.7, 61.2, 41.9, 34.2, 24.8, 21.9, 21.5, 13.9, 13.8, 13.7; MS (70 eV, EI) *m/z* (%): 384 (M⁺(⁸²Se), 5.61), 383 (M⁺(⁸⁰Se)+1, 7.41), 382 (M⁺(⁸⁰Se), 28.09), 381 (M⁺(⁷⁸Se)+1, 4.31), 380 (M⁺(⁷⁸Se), 14.60), 379 (M⁺(⁷⁷Se) or M⁺(⁷⁶Se)+1, 7.12), 378 (M⁺(⁷⁶Se), 5.32), 41 (100); IR ν (cm⁻¹): 2962, 2931, 2871, 1756, 1708, 1578, 1477, 1464, 1439, 1281, 1223, 1155, 1021; HRMS calcd for C₁₉H₂₆O₃⁸⁰SeNa⁺ (M⁺+Na): 405.0952. Found: 405.0932.

(3) 2-Benzyl-4-oxo-3-phenylselenanyloct-2(*E*)-enoic acid ethyl ester (**2c**)

The reaction of 51.1 mg (0.20 mmol) of **1c**, 77.8 mg (0.41 mmol) of PhSeCl, and 43.5 mg (0.59 mmol) of Li₂CO₃ in 6 mL of MeCN afforded 57.3 mg (67%) of **2c**: liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.49 (d, *J* = 7.6 Hz, 2 H), 7.35-7.15 (m, 8 H), 4.04 (q, *J* = 7.2 Hz, 2 H), 3.89 (s, 2 H), 2.35 (d, *J* = 7.6 Hz, 2 H), 1.23-1.13 (m, 2 H),

1.10 (t, $J = 7.2$ Hz, 3 H), 1.08-0.97 (m, 2 H), 0.70 (t, $J = 7.4$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.5, 164.6, 151.5, 137.9, 136.5, 129.38, 129.32, 128.49, 128.42, 128.3, 126.4, 125.3, 61.3, 42.0, 37.6, 24.7, 21.9, 13.7; MS (70 eV, EI) m/z (%): 433 ($\text{M}^+(\text{}^{82}\text{Se})+1$, 7.06), 432 ($\text{M}^+(\text{}^{82}\text{Se})$, 9.84), 431 ($\text{M}^+(\text{}^{80}\text{Se})+1$, 33.09), 430 ($\text{M}^+(\text{}^{80}\text{Se})$, 17.49), 429 ($\text{M}^+(\text{}^{78}\text{Se})+1$, 22.64), 428 ($\text{M}^+(\text{}^{78}\text{Se})$ or $\text{M}^+(\text{}^{77}\text{Se})+1$, 13.93), 427 ($\text{M}^+(\text{}^{77}\text{Se})$ or $\text{M}^+(\text{}^{76}\text{Se})+1$, 11.68), 426 ($\text{M}^+(\text{}^{76}\text{Se})$, 4.21), 57 (100); IR ν (cm^{-1}): 2958, 2932, 2871, 1706, 1577, 1494, 1477, 1453, 1439, 1270, 1201, 1021; HRMS calcd for $\text{C}_{23}\text{H}_{26}\text{O}_3\text{}^{80}\text{SeNa}^+$ (M^++Na): 453.0954. Found: 453.0932.

(4) 2-Methyl-4-oxo-3-phenylselanylundec-2(*E*)-enoic acid ethyl ester (2d)

The reaction of 45.4 mg (0.20 mmol) of **1d**, 78.9 mg (0.41 mmol) of PhSeCl, and 44.3 mg (0.60 mmol) of Li_2CO_3 in 6 mL of MeCN afforded 53.5 mg (67%) of **2d**: liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.53 (d, $J = 7.2$ Hz, 2 H), 7.38-7.27 (m, 3 H), 4.13 (q, $J = 7.2$ Hz, 2 H), 2.32 (t, $J = 7.8$ Hz, 2 H), 2.07 (s, 3 H), 1.23 (t, $J = 7.2$ Hz, 3 H), 1.26-1.06 (m, 8 H), 1.04-0.95 (m, 2 H), 0.85 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.8, 164.8, 149.9, 136.5, 129.3, 125.5, 124.5, 61.2, 42.3, 31.6, 28.9, 28.7, 22.52, 22.49, 17.2, 14.0, 13.9; MS (70 eV, EI) m/z (%): 398 ($\text{M}^+(\text{}^{82}\text{Se})$, 4.29), 397 ($\text{M}^+(\text{}^{80}\text{Se})+1$, 7.05), 396 ($\text{M}^+(\text{}^{80}\text{Se})$, 17.30), 395 ($\text{M}^+(\text{}^{78}\text{Se})+1$, 4.71), 394 ($\text{M}^+(\text{}^{78}\text{Se})$ or $\text{M}^+(\text{}^{77}\text{Se})+1$, 9.93), 393 ($\text{M}^+(\text{}^{77}\text{Se})$ or $\text{M}^+(\text{}^{76}\text{Se})+1$, 4.37), 392 ($\text{M}^+(\text{}^{76}\text{Se})$, 3.85), 193 (100); IR ν (cm^{-1}): 2955, 2928, 2855, 1706, 1591, 1578, 1477, 1465, 1439, 1270, 1153,

1022; HRMS calcd for $C_{20}H_{28}O_3^{80}SeNa^+$ ($M^+ + Na$): 419.1109. Found: 419.1091.

(5) 4-Oxo-3-phenylselanyl-2-propylundec-2(E)-enoic acid ethyl ester (2e)

The reaction of 49.8 mg (0.20 mmol) of **1e**, 78.5 mg (0.41 mmol) of PhSeCl, and 44.0 mg (0.59 mmol) of Li_2CO_3 in 6 mL of MeCN afforded 52.3 mg (63%) of **2e**: liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, $J = 8.0$ Hz, 2 H), 7.37-7.26 (m, 3 H), 4.13 (q, $J = 7.1$ Hz, 2 H), 2.53 (t, $J = 7.8$ Hz, 2 H), 2.36 (t, $J = 7.6$ Hz, 2 H), 1.61-1.51 (m, 2 H), 1.22 (t, $J = 7.1$ Hz, 3 H), 1.27-1.07 (m, 8 H), 0.99 (t, $J = 7.4$ Hz, 3 H), 1.05-0.95 (m, 2 H), 0.85 (t, $J = 7.0$ Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.8, 165.1, 148.7, 136.2, 131.0, 129.3, 129.1, 125.8, 61.2, 42.2, 34.3, 31.6, 28.9, 28.8, 22.7, 22.5, 21.5, 14.04, 13.98, 13.9; MS (70 eV, EI) m/z (%): 427 ($M^+ (^{82}Se)+1$, 3.80), 426 ($M^+ (^{82}Se)$, 5.88), 425 ($M^+ (^{80}Se)+1$, 20.35), 424 ($M^+ (^{80}Se)$, 11.43), 423 ($M^+ (^{78}Se)+1$, 14.02), 422 ($M^+ (^{78}Se)$ or $M^+ (^{77}Se)+1$, 8.87), 421 ($M^+ (^{77}Se)$ or $M^+ (^{76}Se)+1$, 6.89), 420 ($M^+ (^{76}Se)$, 2.93), 43 (100); IR ν (cm^{-1}): 2958, 2928, 1757, 1707, 1578, 1477, 1463, 1439, 1277, 1222, 1153, 1021; HRMS calcd for $C_{22}H_{32}O_3^{80}SeNa^+$ ($M^+ + Na$): 447.1423. Found: 447.1406.

(6) 2-Methyl-4-oxo-4-phenyl-3-phenylselanylbuto-2(E)-enoic acid ethyl ester (2f)

The reaction of 40.0 mg (0.20 mmol) of **1f**, 77.1 mg (0.40 mmol) of PhSeCl, and 42.7 mg (0.58 mmol) of Li₂CO₃ in 6 mL of MeCN afforded 56.6 mg (77%) of **2f**: liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, *J* = 7.6 Hz, 2 H), 7.42 (t, *J* = 7.2 Hz, 1 H), 7.33-7.24 (m, 4 H), 7.18 (t, *J* = 7.2 Hz, 1 H), 7.04 (t, *J* = 7.6 Hz, 2 H), 3.93 (q, *J* = 7.2 Hz, 2 H), 2.20 (s, 3 H), 0.90 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 192.0, 164.2, 148.8, 137.5, 135.9, 132.8, 129.2, 128.7, 128.6, 128.1, 124.6, 124.3, 61.2, 16.9, 13.4; MS (70 eV, EI) *m/z* (%): 377 (M⁺(⁸²Se)+1, 0.86), 376 (M⁺(⁸²Se), 3.55), 375 (M⁺(⁸⁰Se)+1, 4.13), 374 (M⁺(⁸⁰Se), 17.43), 373 (M⁺(⁷⁸Se)+1, 2.74), 372 (M⁺(⁷⁸Se), 8.24), 371 (M⁺(⁷⁷Se) or M⁺(⁷⁶Se)+1, 3.37), 370 (M⁺(⁷⁶Se), 3.56), 105 (100); IR ν (cm⁻¹): 3059, 2982, 2935, 1708, 1668, 1596, 1580, 1476, 1449, 1439, 1366, 1270, 1176, 1144, 1021; HRMS calcd for C₁₉H₁₈O₃⁸⁰SeNa⁺ (M⁺+Na): 397.0326. Found: 397.0311.

(7) 4-Oxo-4-phenyl-3-phenylselanyl-2-propylbut-2(*E*)-enoic acid ethyl ester (2g)

The reaction of 46.8 mg (0.20 mmol) of **1g**, 114.0 mg (0.60 mmol) of PhSeCl, and 43.7 mg (0.59 mmol) of Li₂CO₃ in 6 mL of MeCN afforded 67.0 mg (82%) of **2g**: liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, *J* = 9.6 Hz, 2 H), 7.43 (t, *J* = 9.6 Hz, 1 H), 7.28 (t, *J* = 10.8 Hz, 4 H), 7.19 (t, *J* = 10.0 Hz, 1 H), 7.05 (t, *J* = 10.0 Hz, 2 H), 3.93 (t, *J* = 9.8 Hz, 2 H), 2.66 (t, *J* = 10.2 Hz, 2 H), 1.79-1.64 (m, 2 H), 1.09 (t, *J* = 9.8 Hz, 3 H), 0.90 (t, *J* = 9.4 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 191.8, 164.3, 148.1,

137.4, 135.9, 132.7, 130.4, 129.2, 128.7, 128.6, 128.1, 124.4, 61.1, 33.9, 21.4, 14.2, 13.3; MS (70 eV, EI) m/z (%): 404 ($M^+(^{82}\text{Se})$, 1.35), 403 ($M^+(^{80}\text{Se})+1$, 1.38), 402 ($M^+(^{80}\text{Se})$, 5.88), 401 ($M^+(^{78}\text{Se})+1$, 1.03), 400 ($M^+(^{78}\text{Se})$ or $M^+(^{77}\text{Se})+1$, 3.15), 399 ($M^+(^{77}\text{Se})$ or $M^+(^{76}\text{Se})+1$, 1.26), 398 ($M^+(^{76}\text{Se})$, 1.24), 105 (100); IR ν (cm^{-1}): 2961, 2871, 1707, 1671, 1596, 1581, 1449, 1439, 1280, 1243, 1220, 1146, 1021; HRMS calcd for $\text{C}_{21}\text{H}_{22}\text{O}_3^{80}\text{SeNa}^+$ ($M^++\text{Na}$): 425.0640. Found: 425.0624.

(8) 2-Benzyl-4-oxo-4-phenyl-3-phenylselanylbut-2(E)-enoic acid ethyl ester (2h)

The reaction of 54.2 mg (0.19 mmol) of **1h**, 78.0 mg (0.41 mmol) of PhSeCl, and 45.7 mg (0.62 mmol) of Li_2CO_3 in 6 mL of MeCN afforded 67.3 mg (77%) of **2h**: liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.62 (d, $J = 6.8$ Hz, 2 H), 7.44 (t, $J = 6.6$ Hz, 3 H), 7.38 (t, $J = 7.6$ Hz, 2 H), 7.33-7.25 (m, 5 H), 7.22 (t, $J = 7.4$ Hz, 1 H), 7.07 (t, $J = 7.6$ Hz, 2 H), 4.08 (s, 2 H), 3.93 (q, $J = 7.2$ Hz, 2 H), 0.88 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.5, 164.1, 150.3, 138.1, 137.4, 136.0, 132.7, 129.3, 128.9, 128.8, 128.7, 128.62, 128.56, 128.1, 126.5, 124.4, 61.3, 37.5, 13.3; MS (70 eV, EI) m/z (%): 453 ($M^+(^{82}\text{Se})+1$, 3.78), 452 ($M^+(^{82}\text{Se})$, 7.36), 451 ($M^+(^{80}\text{Se})+1$, 16.83), 450 ($M^+(^{80}\text{Se})$, 26.36), 449 ($M^+(^{78}\text{Se})+1$, 11.69), 448 ($M^+(^{78}\text{Se})$ or $M^+(^{77}\text{Se})+1$, 15.50), 447 ($M^+(^{77}\text{Se})$ or $M^+(^{76}\text{Se})+1$, 8.02), 446 ($M^+(^{76}\text{Se})$, 5.74), 105 (100); IR ν (cm^{-1}): 3060, 2981, 1707, 1670, 1596, 1450, 1270, 1022; HRMS calcd for $\text{C}_{25}\text{H}_{22}\text{O}_3^{80}\text{SeNa}^+$ ($M^++\text{Na}$): 473.0642. Found: 473.0618.

(9) 4-(4'-Bromophenyl)-2-methyl-4-oxo-3-phenylselanylbut-2(E)-enoic acid ethyl ester (2i)

The reaction of 56.1 mg (0.20 mmol) of **1i**, 78.0 mg (0.41 mmol) of PhSeCl, and 44.7 mg (0.60 mmol) of Li₂CO₃ in 6 mL of MeCN afforded 56.5 mg (63%) of **2i**: solid. m.p. 70-71 °C (hexane). ¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, *J* = 8.4 Hz, 2 H), 7.35 (d, *J* = 8.4 Hz, 2 H), 7.20 (d, *J* = 8.0 Hz, 2 H), 7.15 (t, *J* = 7.6 Hz, 1 H) 7.00 (t, *J* = 7.6 Hz, 2 H), 3.89 (q, *J* = 7.1 Hz, 2 H), 2.12 (s, 3 H), 0.89 (t, *J* = 7.1 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 191.0, 164.2, 148.2, 137.5, 134.9, 131.4, 130.1, 129.4, 128.9, 127.8, 125.1, 124.1, 61.3, 16.9, 13.5; MS (70 eV, EI) *m/z* (%): 456 (M⁺(⁸²Se, ⁸¹Br), 5.53), 455 (M⁺(⁸⁰Se, ⁸¹Br)+1 or M⁺(⁸²Se, ⁷⁹Br)+1, 6.65), 454 (M⁺(⁸⁰Se, ⁸¹Br) or M⁺(⁸²Se, ⁷⁹Br), 32.61), 453 (M⁺(⁸⁰Se, ⁷⁹Br)+1 or M⁺(⁷⁸Se, ⁸¹Br)+1, 8.45), 452 (M⁺(⁸⁰Se, ⁷⁹Br) or M⁺(⁷⁸Se, ⁸¹Br) or M⁺(⁷⁷Se, ⁸¹Br)+1, 41.11), 451 (M⁺(⁷⁷Se, ⁸¹Br) or M⁺(⁷⁸Se, ⁷⁹Br)+1 or M⁺(⁷⁶Se, ⁸¹Br)+1, 8.04), 450 (M⁺(⁷⁸Se, ⁷⁹Br) or M⁺(⁷⁶Se, ⁸¹Br) or M⁺(⁷⁷Se, ⁷⁹Br)+1, 18.45), 449 (M⁺(⁷⁷Se, ⁷⁹Br) or M⁺(⁷⁶Se, ⁷⁹Br)+1 or M⁺(⁷⁴Se, ⁸¹Br)+1, 5.37), 448 (M⁺(⁷⁶Se, ⁷⁹Br) or M⁺(⁷⁴Se, ⁸¹Br), 5.59), 446 (M⁺(⁷⁴Se, ⁷⁹Br), 0.52), 183 (100); IR ν (cm⁻¹): 2980, 1704, 1668, 1586, 1478, 1439, 1272, 1247, 1173, 1145, 1021, 1010; Anal. calcd for C₁₉H₁₇BrO₃Se: C 50.47, H 3.79. Found: C 50.48, H 3.79.

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

(10) 4-(4'-Bromophenyl)-4-oxo-3-phenylselanyl-2-propylbut-2(*E*)-enoic acid ethyl ester (2j**)**

The reaction of 60.6 mg (0.20 mmol) of **1j**, 115.9 mg (0.61 mmol) of PhSeCl, and 44.7 mg (0.60 mmol) of Li₂CO₃ in 6 mL of MeCN afforded 80.3 mg (85%) of **2j**: liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, *J* = 9.0 Hz, 2 H), 7.42 (d, *J* = 9.0 Hz, 2 H), 7.26 (d, *J* = 7.6 Hz, 2 H), 7.21 (t, *J* = 7.4 Hz, 1 H), 7.07 (t, *J* = 7.8 Hz, 2 H), 3.96 (q, *J* = 7.3 Hz, 2 H), 2.64 (t, *J* = 8.0 Hz, 2 H), 1.76-1.64 (m, 2 H), 1.08 (t, *J* = 7.3 Hz, 3 H), 0.95 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 190.9, 164.3, 147.5, 137.4, 134.9, 131.5, 130.8, 130.1, 129.4, 128.9, 127.7, 124.3, 61.2, 33.9, 21.4, 14.2, 13.5; MS (70 eV, EI) *m/z* (%): 484 (M⁺(⁸²Se, ⁸¹Br), 4.93), 483 (M⁺(⁸⁰Se, ⁸¹Br)+1 or

$M^+ (^{82}\text{Se}, ^{79}\text{Br})+1$, 5.75), 482 ($M^+ (^{80}\text{Se}, ^{81}\text{Br})$ or $M^+ (^{82}\text{Se}, ^{79}\text{Br})$, 26.48), 481 ($M^+ (^{80}\text{Se}, ^{79}\text{Br})+1$ or $M^+ (^{78}\text{Se}, ^{81}\text{Br})+1$, 7.85), 480 ($M^+ (^{80}\text{Se}, ^{79}\text{Br})$ or $M^+ (^{78}\text{Se}, ^{81}\text{Br})$ or $M^+ (^{77}\text{Se}, ^{81}\text{Br})+1$, 34.11), 479 ($M^+ (^{77}\text{Se}, ^{81}\text{Br})$ or $M^+ (^{78}\text{Se}, ^{79}\text{Br})+1$ or $M^+ (^{76}\text{Se}, ^{81}\text{Br})+1$, 7.14), 478 ($M^+ (^{78}\text{Se}, ^{79}\text{Br})$ or $M^+ (^{76}\text{Se}, ^{81}\text{Br})$ or $M^+ (^{77}\text{Se}, ^{79}\text{Br})+1$, 16.18), 477 ($M^+ (^{77}\text{Se}, ^{79}\text{Br})$ or $M^+ (^{76}\text{Se}, ^{79}\text{Br})+1$ or $M^+ (^{74}\text{Se}, ^{81}\text{Br})+1$, 4.64), 476 ($M^+ (^{76}\text{Se}, ^{79}\text{Br})$ or $M^+ (^{74}\text{Se}, ^{81}\text{Br})$, 4.54), 474 ($M^+ (^{74}\text{Se}, ^{79}\text{Br})$, 0.35), 183 (100); IR ν (cm^{-1}): 2960, 2931, 2871, 1705, 1673, 1586, 1281, 1247, 1219, 1010; HRMS calcd for $\text{C}_{21}\text{H}_{21}^{79}\text{BrO}_3^{80}\text{SeNa}^+$ ($M^++\text{Na}$): 502.9738. Found: 502.9724.

(11) 2-Methyl-4-(naphthalen-1'-yl)-4-oxo-3-phenylselanylbuto-2(E)-enoic ethyl ester (2k)

The reaction of 51.3 mg (0.20 mmol) of **1k**, 114.3 mg (0.60 mmol) of PhSeCl, and 41.3 mg (0.56 mmol) of Li_2CO_3 in 6 mL of MeCN afforded 80.4 mg (93%) of **2k**: liquid. ^1H NMR (400 MHz, CDCl_3) δ 8.63 (d, $J = 8.4$ Hz, 1 H), 8.02 (d, $J = 7.2$ Hz, 1 H), 7.92 (d, $J = 8.4$ Hz, 1 H), 7.76 (d, $J = 8.0$ Hz, 1 H), 7.44-7.36 (m, 3 H), 7.26 (d, $J = 7.6$ Hz, 2 H), 6.97 (t, $J = 7.4$ Hz, 1 H), 6.87 (t, $J = 7.8$ Hz, 2 H), 3.91 (q, $J = 7.1$ Hz, 2 H), 2.27 (s, 3 H), 0.83 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3) δ 193.6, 164.8, 149.5, 137.2, 134.0, 133.6, 132.6, 131.5, 130.6, 128.9, 128.6, 128.0, 127.9, 126.02, 125.99, 125.5, 124.6, 123.9, 61.1, 17.4, 13.4; MS (70 eV, EI) m/z (%): 427

($M^+(^{82}\text{Se})+1$, 5.15), 426 ($M^+(^{82}\text{Se})$, 21.16), 425 ($M^+(^{80}\text{Se})+1$, 2.94), 424 ($M^+(^{80}\text{Se})$, 10.79), 423 ($M^+(^{78}\text{Se})+1$, 4.33), 421 ($M^+(^{77}\text{Se})$ or $M^+(^{76}\text{Se})+1$, 3.62), 155 (100); IR ν (cm^{-1}): 3056, 2982, 1705, 1662, 1592, 1508, 1439, 1271, 1233, 1146, 1021; HRMS calcd for $\text{C}_{23}\text{H}_{20}\text{O}_3^{80}\text{SeNa}^+$ ($M^++\text{Na}$): 447.0484. Found: 447.0462.

(12) 4-(Naphthalen-1'-yl)-4-oxo-3-phenylselanyl-2-propylbut-2(E)-enoic acid ethyl ester (2I)

The reaction of 57.3 mg (0.20 mmol) of **1I**, 115.2 mg (0.60 mmol) of PhSeCl, and 44.6 mg (0.60 mmol) of Li_2CO_3 in 6 mL of MeCN afforded 82.4 mg (89%) of **2I**: liquid. ^1H NMR (400 MHz, CDCl_3) δ 8.50 (d, $J = 8.4$ Hz, 1 H), 8.01 (d, $J = 7.2$ Hz, 1 H), 7.92 (d, $J = 8.4$ Hz, 1 H), 7.76 (d, $J = 8.4$ Hz, 1 H), 7.46-7.34 (m, 3 H), 7.24 (d, $J = 7.6$ Hz, 2 H), 7.00 (t, $J = 7.2$ Hz, 1 H), 6.89 (t, $J = 7.6$ Hz, 2 H), 3.91 (q, $J = 7.2$ Hz, 2 H), 2.73 (t, $J = 7.8$ Hz, 2 H), 1.81-1.69 (m, 2 H), 1.12 (t, $J = 7.2$ Hz, 3 H), 0.84 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 193.6, 165.1, 148.2, 137.0, 133.7, 133.6, 132.3, 131.8, 130.7, 128.8, 128.7, 127.9, 127.8, 126.02, 125.96, 124.9, 123.9, 61.0, 34.6, 21.4, 14.1, 13.4; MS (EI) m/z (%): 455 ($M^+(^{82}\text{Se})+1$, 1.81), 454 ($M^+(^{82}\text{Se})$, 7.82), 453 ($M^+(^{80}\text{Se})+1$, 0.94), 452 ($M^+(^{80}\text{Se})$, 3.72), 451 ($M^+(^{78}\text{Se})+1$, 1.50), 450 ($M^+(^{78}\text{Se})$ or $M^+(^{77}\text{Se})+1$, 1.74), 155 (100); IR ν (cm^{-1}): 2960, 2871, 1706, 1664, 1590, 1575, 1275, 1234, 1219, 1146, 1021; HRMS calcd for $\text{C}_{25}\text{H}_{24}\text{O}_3^{80}\text{SeNa}^+$ ($M^++\text{Na}$):

475.0798. Found: 475.0776.

(13) 3-Methyl-4-phenylselanyl-1-oxa-spiro[4.5]dec-3-en-2-one (3m)^[1]

The reaction of 38.1 mg (0.20 mmol) of **1m**, 77.6 mg (0.41 mmol) of PhSeCl, and 44.6 mg (0.60 mmol) of Li₂CO₃ in 6 mL of MeCN afforded 55.4 mg (88%) of **3m**: liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.41 (d, *J* = 8.0 Hz, 2 H), 7.30-7.20 (m, 3 H), 1.79-1.59 (m, 7 H), 1.47 (s, 3 H), 1.46 (d, *J* = 9.6 Hz, 2 H), 1.15-1.06 (m, 1 H). This compound was identified by comparison with the authentic sample prepared in this group.^[1]

[1] Chen, G.; Fu, C. Ma, S. *Tetrahedron* **2006**, 62, 4444.

2a

2b

2d

2e

2g

2h

2i

2j

2k