

Terms & Conditions

Electronic Supporting Information files are available without a subscription to ACS Web Editions. The American Chemical Society holds a copyright ownership interest in any copyrightable Supporting Information. Files available from the ACS website may be downloaded for personal use only. Users are not otherwise permitted to reproduce, republish, redistribute, or sell any Supporting Information from the ACS website, either in whole or in part, in either machine-readable form or any other form without permission from the American Chemical Society. For permission to reproduce, republish and redistribute this material, requesters must process their own requests via the RightsLink permission system. Information about how to use the RightsLink permission system can be found at <http://pubs.acs.org/page/copyright/permissions.html>



ACS Publications

MOST TRUSTED. MOST CITED. MOST READ.

Copyright © 1996 American Chemical Society

General Cyclization Procedures

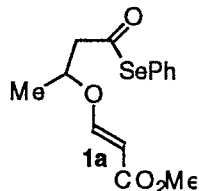
Method A: The acyl selenide **1a** (0.609 g, 1.86 mmol, azeotroped with anhyd. benzene) was dissolved in anhydrous benzene (166 ml), protected from moisture by a drying tube packed with Drierite. Triphenyltin hydride (0.783 g, 2.23 mmol, 1.2 eq) was added in anhydrous benzene (20 ml) followed by triethylborane (2.0 ml, 2.0 mmol, 1.05 eq of a 1M solution in hexanes) and the mixture heated at reflux for 2 hours. The reaction mixture was cooled to ambient temperature and the solvent removed *in vacuo* to afford a crude oil. Purification by flash chromatography on silica gel (eluting with 1:4, 1:1, 7:3 Ethyl Acetate/Hexane) furnished the 2,5-disubstituted tetrahydrofuran-3-one **2a/3a** (0.31 g, 97%) as a colorless oil in a 10 : 1 mixture of diastereoisomers.

Method B: The acyl selenide **1d** (0.391 g, 1.14 mmol, azeotroped with anhyd. benzene) was dissolved in anhydrous benzene (52 ml). AIBN (0.02 g, 0.122 mmol) was added, and the mixture heated to reflux. Tributyltin hydride (0.48 ml, 1.71 mmol) was added in 5 ml anhydrous benzene *via* syringe pump (1.7 ml/hr). After the addition, the reaction stirred at reflux overnight. The reaction mixture was allowed to cool to ambient temperature and the solvent removed *in vacuo* to afford a crude oil. Purification by flash chromatography on silica gel (eluting with 1:9, 1:4 Diethyl Ether/Hexane) furnished the 2,6-disubstituted tetrahydropyran-3-ones **2d/3d** (0.2 g, 94%), as a colorless oil in a 3.5 : 1 mixture of diastereoisomers.

Method C: The acyl selenide **1d** (0.354 g, 1.034 mmol, azeotroped with anhyd. benzene) was dissolved in anhydrous benzene (207 ml) and stirred under an atmosphere of dry air using a drying tube packed with Drierite. Triethylborane (1.24 ml, 1.24 mmol, 1.2 eq of a 1M solution in hexanes) was added, followed by tris(trimethylsilyl)silane (0.48 ml, 1.55 mmol, 1.5 eq), and the mixture stirred at room temperature for 5 hours. The solvent was removed *in vacuo* to afford a crude oil, which was purified by flash chromatography on silica gel (eluting with 1:9, 1:4, 3:7 Ethyl Acetate/ Hexane) to furnish the 2,6-disubstituted tetrahydropyran-3-ones **2d/3d** (0.182 g, 94%) as a colorless oil in a 5.7 : 1 mixture of diastereoisomers.

Method D: The acyl selenide **1d** (0.344 g, 1.006 mmol, azeotroped with anhyd. toluene) was dissolved in anhydrous toluene (200 ml) and cooled with stirring to -20 °C (using a cryocool to maintain the temperature) under an atmosphere of dry air using a drying tube packed with Drierite. Triethylborane (1.21 ml, 1.21 mmol, 1.2 eq of a 1M solution in hexanes) was added, followed by tris(trimethylsilyl)silane (0.47 ml, 1.51 mmol, 1.5 eq), and the mixture stirred at for 22 hours. The reaction was allowed to warm to ambient temperature and the solvent was removed *in vacuo* to afford a crude oil. The crude oil was purified by flash chromatography on

silica gel (eluting with 1:9, 1:4, 3:7 Ethyl Acetate/ Hexane) to furnish the *2,6-disubstituted tetrahydropyran-3-ones 2d/3d* (0.175 g, 94%) as a colorless oil in a 7.1 : 1 mixture of diastereoisomers.



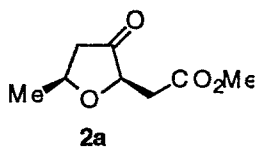
IR (neat) 3064 (w), 3020 (s), 2977 (m), 2904 (w), 1701 (s), 1580 (w) cm^{-1} .

^1H NMR (250 MHz, CDCl_3) δ 7.50-7.31 (6H, m), 5.26 (1H, d, $J = 12.4$ Hz), 4.59-4.46 (1H, m), 3.67 (3H, s), 3.10 (1H, A of ABX, $J_{AB} = 16.0$ Hz, $J_{AX} = 7.2$ Hz), 2.84 (1H, B of ABX, $J_{AB} = 16.0$ Hz, $J_{BX} = 5.4$ Hz) 1.33 (3H, d, $J = 6.2$ Hz).

^{13}C NMR (62.5 MHz, CDCl_3) δ 196.64 (e), 167.51 (e), 160.76 (o), 135.32 (o), 129.04 (o), 128.74 (o), 125.58 (e), 97.42 (o), 74.70 (o), 52.58 (e), 50.61 (o), 19.42 (o).

m/z (EI) 297 (7), 172 (17), 171 (100), 160 (4), 159 (20), 158 (24), 157 (82), 156 (16), 154 (22), 153 (21), 143 (23), 129 (94), 111 (15), 101 (99), 85 (24), 77 (50), 70 (98), 59 (66).

HRMS (EI) calcd for $\text{C}_{14}\text{H}_{18}\text{O}_4^{80}\text{Se}$ 330.0370 found 330.0340.



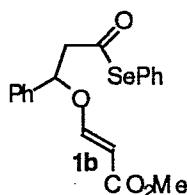
IR (neat) 2975 (s), 2956 (s), 2932 (s), 2873 (m), 1762 (s), 1740 (s) cm^{-1} .

^1H NMR (400 MHz, C_6D_6) δ 3.79-3.77 (1H, m), 3.72-3.59 (1H, m), 3.28 (3H, s), 2.71 (1H, A of ABX, $J_{AB} = 16.7$ Hz, $J_{AX} = 4.2$ Hz), 2.61 (1H, B of ABX, $J_{AB} = 16.7$ Hz, $J_{BX} = 5.6$ Hz), 1.99 (2H, d, $J = 8.1$ Hz), 1.11 (3H, d, $J = 6.0$ Hz).

^{13}C NMR (62.5 MHz, CDCl_3) δ 213.78 (e), 169.20 (e), 76.60 (o), 71.08 (o), 50.52 (o), 42.59 (e), 34.51 (e), 19.66 (o).

m/z (EI) 173 (9), 172 (56), 141 (42), 140 (27), 112 (74), 103 (62), 101 (10), 99 (51), 86 (17), 84 (24), 74 (25), 71 (100), 61 (57), 59 (44).

HRMS (EI) calcd for $\text{C}_8\text{H}_{12}\text{O}_4$ 172.0736 found 172.0747.



IR (neat) 3016 (w), 2922 (w), 1710 (s), 1644 (m), 1626 (m) cm^{-1} .

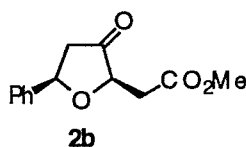
6 2253-3

^1H NMR (250 MHz, CDCl_3) δ 7.49-7.27 (11H, m), 5.37 (1H, dd, $J = 8.8$ Hz, $J = 4.1$ Hz), 5.22 (1H, d, $J = 12.5$ Hz), 3.61 (3H, s), 3.36 (1H, A of ABX, $J_{AB} = 16.2$ Hz, $J_{AX} = 9.0$ Hz), 3.01 (1H, B of ABX, $J_{AB} = 16.2$ Hz, $J_{BX} = 4.1$ Hz).

^{13}C NMR (62.5 MHz, CDCl_3) δ 196.16 (e), 167.17 (e), 160.45 (o), 137.75 (e), 135.32 (o), 129.06 (o), 128.74 (o), 128.59 (o), 128.42 (o), 125.66 (o), 125.55 (e), 98.64 (o), 79.22 (o), 53.79 (e), 50.57 (o).

m/z (EI) 289 (4), 261 (4), 191 (36), 157 (24), 132 (13), 131 (100), 121 (11), 104 (22), 103 (17), 86 (45), 84 (64), 78 (13), 77 (21).

HRMS (EI) calcd for $\text{C}_{19}\text{H}_{18}\text{O}_4^{80}\text{Se}$ 390.0370 found 390.0390.



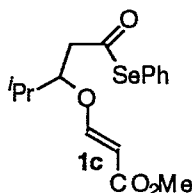
IR (neat) 3024 (m), 3015 (m), 2955 (w), 2852 (w), 1761 (s), 1738 (s) cm^{-1} .

^1H NMR (400 MHz, CDCl_3) δ 7.41-7.28 (5H, m), 5.12 (1H, dd, $J = 10.7$ Hz, $J = 6.2$ Hz), 4.13 (1H, t, $J = 4.6$ Hz), 3.68 (3H, s), 2.93 (1H, A of ABX, $J_{AB} = 17.1$ Hz, $J_{AX} = 4.3$ Hz), 2.86 (1H, B of ABX, $J_{AB} = 17.1$ Hz, $J_{BX} = 4.8$ Hz), 2.81 (1H, A of ABX, $J_{AB} = 18.0$ Hz, $J_{AX} = 6.3$ Hz), 2.71 (1H, B of ABX, $J_{AB} = 18.0$ Hz, $J_{BX} = 10.7$ Hz).

^{13}C NMR (62.5 MHz, CDCl_3) δ 213.86 (e), 170.13 (e), 139.81 (e), 128.45 (o), 128.19 (o), 126.15 (o), 77.63 (o), 77.57 (o), 51.73 (o), 44.37 (e), 35.40 (e).

m/z (EI) 235 (5), 234 (35), 133 (16), 105 (57), 104 (100), 103 (29), 78 (24), 77 (27).

HRMS (EI) calcd for $\text{C}_{13}\text{H}_{14}\text{O}_4$ 234.0892 found 234.0907.



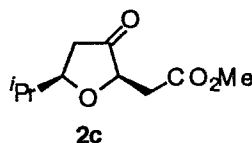
IR (neat) 3017 (m), 2968 (m), 1707 (s), 1641 (s), 1621 (m) cm^{-1} .

^1H NMR (250 MHz, CDCl_3) δ 7.50-7.34 (6H, m), 5.28 (1H, d, $J = 12.3$ Hz), 4.25-4.18 (1H, m), 3.67 (3H, s), 3.02 (1H, A of ABX, $J_{AB} = 16.1$ Hz, $J_{AX} = 8.2$ Hz), 2.85 (1H, B of ABX, $J_{AB} = 16.1$ Hz, $J_{BX} = 4.0$ Hz), 1.94-1.88 (1H, m), 0.92 (6H, dd, $J = 6.8$ Hz, $J = 1.8$ Hz).

^{13}C NMR (62.5 MHz, CDCl_3) δ 197.63 (e), 168.06 (e), 162.51 (o), 135.66 (o), 129.35 (o), 129.05 (o), 125.94 (e), 97.52 (o), 84.23 (o), 50.91 (o), 48.78 (e), 31.95 (o), 17.77 (o), 17.31 (o),

m/z (EI) 357 (1), 199 (53), 171 (59), 167 (11), 157 (39), 155 (20), 139 (55), 103 (14), 101 (21), 97 (100), 91 (11), 77 (16), 70 (12), 69 (74), 59 (12).

HRMS (EI) calcd for $C_{16}H_{21}O_4^{80}Se$ 357.0605 found 357.0611.



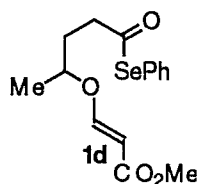
IR (neat) 3026 (m), 2961 (m), 2930 (w), 2875 (w), 1760 (s), 1740 (s) cm^{-1} .

1H NMR (400 MHz, C_6D_6) δ 3.78 (1H, t, $J = 4.7$ Hz), 3.36-3.31 (1H, m), 3.27 (3H, s), 2.71 (1H, A of ABX, $J_{AB} = 16.7$ Hz, $J_{AX} = 4.4$ Hz), 2.62 (1H, B of ABX, $J_{AB} = 16.7$ Hz, $J_{BX} = 5.1$ Hz), 2.17 (1H, A of ABX, $J_{AB} = 17.6$ Hz, $J_{AX} = 10.9$ Hz), 1.96 (1H, B of ABX, $J_{AB} = 17.6$ Hz, $J_{BX} = 5.7$ Hz), 1.7 (1H, octet, $J = 6.8$ Hz), 0.93 (3H, d, $J = 6.7$ Hz), 0.71 (3H, d, $J = 6.8$ Hz).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ 214.95 (e), 170.27 (e), 81.21 (o), 77.59 (o), 51.75 (o), 39.83 (e), 35.70 (e), 32.68 (o), 18.38 (o), 17.71 (o).

m/z (EI) 201 (4), 200 (29), 169 (15), 168 (11), 140 (30), 125 (52), 103 (12), 97 (19), 71 (14), 70 (100), 69 (7), 56 (12), 55 (68).

HRMS (EI) calcd for $C_{10}H_{16}O_4$ 200.1049 found 200.1053.



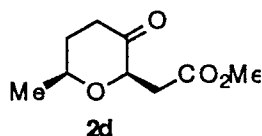
IR ($CHCl_3$) 3020 (s), 2981 (w), 2952 (m), 1709 (s), 1642 (s), 1622 (s) cm^{-1} .

1H NMR (250 MHz, $CDCl_3$) δ 7.50-7.44 (3H, m), 7.38-7.34 (3H, m), 5.24 (1H, d, $J = 12.4$ Hz), 4.17-4.03 (1H, m), 3.68 (3H, s), 2.82-2.75 (2H, m), 1.98-1.90 (2H, m), 1.26 (3H, d, $J = 6.3$ Hz).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ 199.37 (e), 168.03 (e), 161.31 (o), 135.59 (o), 129.21 (o), 128.83 (o), 126.04 (e), 97.31 (o), 77.70 (o), 50.85 (o), 42.79 (e), 31.15 (e), 19.71 (o).

m/z (CI) 360 (50), 343 (42), 311 (37), 284 (7), 265 (8), 255 (11), 241 (100), 230 (28), 185 (45), 169 (14), 157 (87), 141 (10), 125 (19).

HRMS (CI) calcd for $C_{15}H_{19}O_4^{80}Se$ 343.0449 found 343.0444.



IR ($CHCl_3$) 3025 (m), 3016 (m), 2978 (w), 2954 (w), 2856 (w), 1727 (s) cm^{-1} .

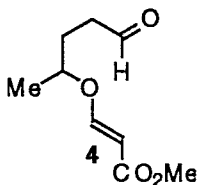
1H NMR (400 MHz, $CDCl_3$) δ 4.19-4.16 (1H, m), 3.87-3.79 (1H, m), 3.54 (3H, s), 2.71 (1H, A of ABX, $J_{AB} = 16.6$ Hz, $J_{AX} = 5.3$ Hz), 2.47 (1H, B of ABX, $J_{AB} = 16.6$ Hz, $J_{BX} = 6.5$ Hz), 2.47-2.37 (2H, m), 1.99-1.92 (1H, m), 1.79-1.68 (1H, m), 1.12 (3H, d, $J = 6.2$ Hz).

672253-5

^{13}C NMR (100 MHz, CDCl_3) δ 206.77 (e), 170.98 (e), 78.65 (o), 72.46 (o), 51.44 (o), 37.13 (e), 34.80 (e), 33.23 (e), 20.79 (o).

m/z (EI) 186, (20), 155 (25), 154 (28), 126 (30), 116 (10), 103 (10), 85 (20), 71 (27), 61 (12), 59 (10), 56 (100).

HRMS (EI) calcd for $\text{C}_9\text{H}_{14}\text{O}_4$ 186.0892 found 186.0879.



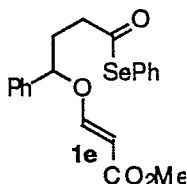
IR (CHCl_3) 3020 (s), 2987 (w), 2952 (w), 2832 (w), 2733 (w), 1724 (s), 1703 (s), 1642 (s), 1622 (s) cm^{-1} .

^1H NMR (250 MHz, CDCl_3) δ 9.76 (1H, s), 7.47 (1H, d, $J = 12.4$ Hz), 5.23 (1H, d, $J = 12.4$ Hz), 4.09 (1H, sextet, $J = 6.2$ Hz), 3.67 (3H, s), 2.55 (2H, t, $J = 7.2$ Hz), 1.94-1.85 (2H, m), 1.27 (3H, d, $J = 6.2$ Hz).

^{13}C NMR (62.5 MHz, CDCl_3) δ 200.88 (o), 168.06 (e), 161.33 (o), 97.21 (o), 78.14 (o), 50.81 (o), 39.33 (e), 28.21 (e), 19.71 (o).

m/z (EI) 103 (8), 102 (7), 85 (100), 71 (32), 67 (25), 57 (34), 55 (18).

HRMS (EI) calcd for $\text{C}_9\text{H}_{14}\text{O}_4$ 186.0892 found 186.0895.



IR (CHCl_3) 3065 (w), 3022 (m), 2952 (w), 1707 (s), 1644 (s), 1625 (s) cm^{-1} .

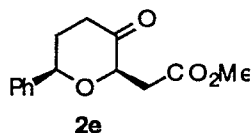
^1H NMR (250 MHz, CDCl_3) δ 7.50-7.20 (11H, m), 5.21 (1H, d, $J = 12.6$ Hz), 4.95-4.90 (1H, dd, $J = 7.8$ Hz, 5.4 Hz), 3.62 (3H, s), 2.90-2.69 (2H, m), 2.31-2.08 (2H, m).

^{13}C NMR (62.5 MHz, CDCl_3) δ 199.05 (e), 167.51 (e), 160.90 (o), 138.82 (e), 135.50 (o), 129.12 (o), 128.73 (o), 128.62 (o), 128.25 (o), 125.96 (e), 125.75 (o), 98.41 (o), 82.36 (o), 50.70 (o), 42.78 (e), 32.36 (e).

m/z (EI) 304 (1), 247 (36), 157 (14), 145 (73), 118 (14), 117 (100), 115 (15), 104 (22), 103 (59), 91 (20), 77 (13), 57 (13).

HRMS (EI) calcd for $\text{C}_{20}\text{H}_{21}\text{O}_4^{80}\text{Se}$ 405.0605 found 405.0615.

622536



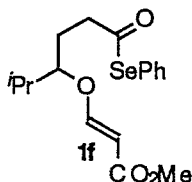
IR (CHCl₃) 3023 (m), 3015 (m), 2955 (m), 2855 (w), 1731 (s) cm⁻¹.

¹H NMR (250 MHz, CDCl₃) δ 7.54-7.22 (5H, m), 4.83 (1H, dd, J = 10.8 Hz, J = 2.7 Hz), 4.47 (1H, t, J = 5.8 Hz), 3.63 (3H, s), 2.92 (1H, A of ABX, J_{AB} = 16.6 Hz, J_{AX} = 5.4 Hz), 2.78-2.61 (2H, m), 2.72 (1H, B of ABX, J_{AB} = 16.6 Hz, J_{BX} = 6.0 Hz), 2.31-2.11 (2H, m).

¹³C NMR (100 MHz, CDCl₃) δ 206.16 (e), 170.85 (e), 140.74 (e), 128.14 (o), 127.54 (o), 125.50 (o), 79.16 (o), 77.85 (o), 51.52 (o), 37.48 (e), 34.96 (e), 33.60 (e).

m/z (EI) 249 (1), 248 (7), 146 (7), 117 (19), 105 (11), 104 (100), 77 (6), 55 (4).

HRMS (EI) calcd for C₁₄H₁₆O₄ 248.1049 found 248.1031.



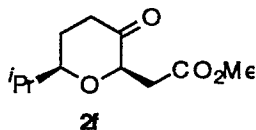
IR (CHCl₃) 3022 (s), 3017 (s), 2968 (m), 2879 (w), 1708 (s), 1639 (s), 1620 (s) cm⁻¹.

¹H NMR (250 MHz, CDCl₃) δ 7.50-7.28 (6H, m), 5.26 (1H, d, J = 12.3 Hz), 3.73-3.66 (1H, m), 3.68 (3H, s), 2.86-2.65 (2H, m), 2.04-1.78 (3H, m), 0.90 (3H, d, J = 6.8 Hz), 0.89 (3H, d, J = 6.8 Hz).

¹³C NMR (62.50 MHz, CDCl₃) δ 199.53 (e), 168.13 (e), 162.87 (o), 135.59 (o), 129.18 (o), 128.80 (o), 126.04 (e), 96.88 (o), 87.69 (o), 50.80 (o), 43.03 (e), 31.72 (o), 26.22 (e), 17.58 (o).

m/z (FAB) 371 (7), 339 (15), 269 (45), 267 (24), 243 (10), 213 (44), 185 (9), 153 (12), 111 (100), 103 (51), 83 (64), 69 (61).

HRMS (FAB) calcd for C₁₇H₂₃O₄⁸⁰Se 371.0762 found 371.0740.



IR (CHCl₃) 3024 (m), 3016 (m), 2962 (s), 2876 (m), 1729 (s) cm⁻¹.

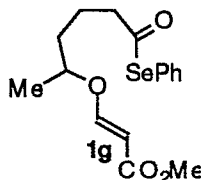
¹H NMR (400 MHz, CDCl₃) δ 4.23-4.20 (1H, m), 3.63 (3H, s), 3.42-3.38 (1H, m), 2.80 (1H, A of ABX, J_{AB} = 16.3 Hz, J_{AX} = 5.1 Hz), 2.59-2.37 (3H, m), 2.07-2.02 (1H, m), 1.88-1.78 (1H, m), 1.68 (1H, octet, J = 6.8 Hz), 0.90 (3H, d, J = 6.8 Hz), 0.87 (3H, d, J = 6.8 Hz).

¹³C NMR (100 MHz, CDCl₃) δ 206.98 (e), 170.83 (e), 81.12 (o), 78.97 (o), 51.23 (o), 37.07 (e), 34.78 (e), 32.27 (o), 28.41 (e), 18.09 (o), 18.06 (o).

672253-7

m/z (EI) 215 (3), 214 (22), 183 (10), 145 (12), 139 (33), 111 (15), 103 (16), 97 (15), 84 (37), 69 (34), 56 (100), 43 (26).

HRMS (EI) calcd for $C_{11}H_{18}O_4$ 214.1205 found 214.1200.



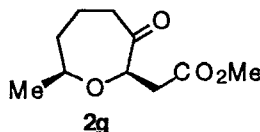
IR (neat) 3016 (m), 2952 (w), 1708 (s), 1641 (s), 1620 (s) cm^{-1} .

1H NMR (250 MHz, $CDCl_3$) δ 7.51-7.45 (3H, m), 7.41-7.33 (3H, m), 5.22 (1H, d, $J = 12.5$ Hz), 4.08-3.96 (1H, m), 3.67 (3H, s), 2.71 (2H, t, $J = 6.9$ Hz), 1.82-1.55 (4H, m), 1.25 (3H, d, $J = 6.3$ Hz).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ 199.36 (e), 167.95 (e), 161.46 (o), 135.43 (o), 129.02 (o), 128.58 (o), 126.06 (e), 96.76 (o), 78.69 (o), 50.63 (o), 46.56 (e), 34.77 (e), 20.68 (e), 19.52 (o).

m/z (CI) 357 (5), 325 (16), 257 (14), 255 (100), 199 (16), 171 (65), 139 (37), 115 (22).

HRMS (CI) calcd for $C_{16}H_{21}O_4^{80}Se$ 357.0605 found 357.0577.



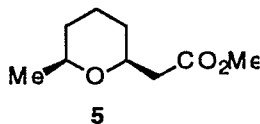
IR (neat) 3024 (s), 3017 (m), 2976 (m), 2935 (m), 2868 (w), 1737 (s), 1711 (s) cm^{-1} .

1H NMR (400 MHz, $CDCl_3$) δ 4.04 (1H, dd, $J = 8.4, 4.0$ Hz), 3.51 (3H, s), 3.47-3.33 (1H, m), 2.74-2.65 (1H, m), 2.59 (1H, A of ABX, $J_{AB} = 16.1$ Hz, $J_{AX} = 4.0$ Hz), 2.45 (1H, B of ABX, $J_{AB} = 16.1$ Hz, $J_{BX} = 8.4$ Hz), 2.29 (1H, B of ABX, $J_{AB} = 13.9$ Hz, $J_{BX} = 6.9$ Hz), 1.85-1.66 (2H, m), 1.58-1.37 (2H, m), 1.05 (3H, d, $J = 6.2$ Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 214.52 (e), 170.89 (e), 82.32 (o), 81.20 (o), 51.49 (o), 41.84 (e), 38.10 (e), 37.64 (e), 23.04 (o), 22.43 (e).

m/z (EI) 200 (19), 169 (12), 129 (11), 116 (13), 103 (24), 99 (19), 98 (40), 84 (100), 80 (10), 71 (30), 70 (29), 69 (21), 61 (14), 55 (31).

HRMS (EI) calcd for $C_{10}H_{16}O_4$ 200.1049 found 200.1050.



IR ($CHCl_3$) 3022 (m), 3002 (m), 2974 (m), 2937 (s), 2864 (m), 1732 (s) cm^{-1} .

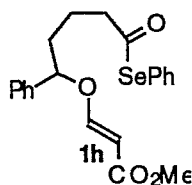
6722536

^1H NMR (250 MHz, CDCl_3) δ 3.80-3.70 (1H, m), 3.48-3.39 (1H, m), 3.66 (3H, s), 2.55 (1H, A of ABX, $J_{AB} = 15.1$ Hz, $J_{AX} = 7.4$ Hz), 2.37 (1H, B of ABX, $J_{AB} = 15.1$ Hz, $J_{BX} = 6.0$ Hz), 1.82-1.74 (1H, m), 1.63-1.42 (3H, m), 1.26-1.06 (2H, m), 1.13 (3H, d, $J = 6.2$ Hz).

^{13}C NMR (100 MHz, CDCl_3) δ 171.90 (e), 74.17 (o), 74.00 (o), 51.50 (o), 41.48 (e), 32.84 (e), 30.90 (e), 23.39 (e), 22.03 (o).

m/z (EI) 172 (6), 30 (30), 129 (55), 116 (94), 113 (13), 112 (17), 100 (37), 99 (79), 97 (23), 81 (46), 74 (59), 59 (47), 55 (68), 41 (100).

HRMS (EI) calcd for $\text{C}_9\text{H}_{16}\text{O}_3$ 172.1100 found 172.1102.



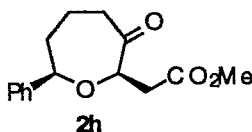
IR (CHCl_3) 3024 (m), 3017 (s), 2929 (w), 1709 (s), 1643 (s), 1623 (m) cm^{-1} .

^1H NMR (250 MHz, CDCl_3) δ 7.49-7.44 (3H, m), 7.37-7.17 (8H, m), 5.19 (1H, d, $J = 12.5$ Hz), 4.84-4.79 (1H, m), 3.61 (3H, s), 2.73-2.68 (2H, m), 1.99-1.64 (4H, m).

^{13}C NMR (100 MHz, CDCl_3) δ 199.81 (e), 167.98 (e), 161.37 (o), 139.53 (e), 135.68 (o), 129.28 (o), 128.87 (o), 128.74 (o), 128.30 (o), 126.16 (e), 125.96 (o), 98.25 (o), 83.89 (o), 50.97 (o), 46.71 (e), 36.42 (e), 21.20 (e).

m/z (FAB) 419 (1), 317 (24), 315 (13), 159 (55), 131 (20), 118 (10), 117 (100), 105 (11), 103 (27), 91 (26), 71 (10), 69 (16), 57 (20).

HRMS (FAB) calcd for $\text{C}_{21}\text{H}_{23}\text{O}_4^{80}\text{Se}$ 419.0762 found 419.0775.



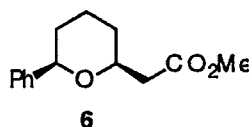
IR (CHCl_3) 3182 (s), 3008 (s), 2941 (w), 2865 (w), 1738 (s), 1713 (s) cm^{-1} .

^1H NMR (400 MHz, CDCl_3) δ 7.44-7.16 (5H, m), 4.41 (1H, d, $J = 11.0$ Hz), 4.31 (1H, dd, $J = 7.9$ Hz, 4.3 Hz), 3.54 (3H, s), 2.93 (1H, dt, $J = 13.3$ Hz, $J = 2.1$), 2.77 (1H, A of ABX, $J_{AB} = 16.0$ Hz, $J_{AX} = 4.2$ Hz), 2.66 (1H, B of ABX, $J_{AB} = 16.0$ Hz, $J_{BX} = 8.0$ Hz), 2.48 (1H, dd, $J = 13.7$ Hz, 6.1 Hz), 2.11-2.08 (1H, m), 2.00-1.96 (1H, m), 1.88-1.78 (1H, m), 1.71-1.61 (1H, m).

^{13}C NMR (100 MHz, CDCl_3) δ 214.90 (e), 171.44 (e), 143.06 (e), 128.66 (o), 127.78 (o), 125.88 (o), 86.66 (o), 83.56 (o), 52.26 (o), 42.56 (e), 38.88 (e), 38.49 (e), 23.32 (e).

m/z (EI) 244 (2), 231 (9), 160 (77), 142 (8), 132 (20), 117 (34), 104 (100), 91 (29), 78 (16), 65 (9).

HRMS (EI) calcd for $\text{C}_{15}\text{H}_{18}\text{O}_4$ 262.1205 found 262.1216.



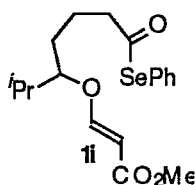
IR (CHCl₃) 3066 (w), 3020 (s), 2942 (s), 2863 (m), 1734 (s) cm⁻¹.

¹H NMR (250 MHz, CDCl₃) δ 7.34-7.13 (5H, m), 4.37 (1H, dd, J = 11.2 Hz, J = 2.2 Hz), 3.99-3.89 (1H, m), 3.64 (3H, s), 2.64 (1H, A of ABX, J_{AB} = 15.1 Hz, J_{AX} = 7.1 Hz), 2.45 (1H, B of ABX, J_{AB} = 15.1 Hz, J_{BX} = 6.1 Hz), 1.96-1.59 (4H, m) 1.53-1.21 (2H, m).

¹³C NMR (100 MHz, CDCl₃) δ 171.70 (e), 142.98 (e), 128.07 (o), 127.04 (o), 125.62 (o), 79.49 (o), 74.59 (o), 51.47 (o), 41.41 (e), 33.04 (e), 30.80 (e), 23.66 (e).

m/z (EI) 235 (11), 234 (61), 216 (31), 202 (14), 184 (10), 174 (34), 161 (46), 133 (75), 120 (33), 105 (100), 91 (35), 77 (36), 59 (21).

HRMS (EI) calcd for C₁₄H₁₈O₃ 234.1256 found 234.1257.



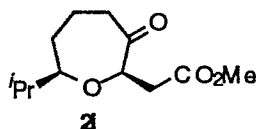
IR (CHCl₃) 3019 (s), 2966 (m), 2877 (w), 1706 (s), 1638 (s), 1619 (s) cm⁻¹.

¹H NMR (250 MHz, CDCl₃) δ 7.50-7.45 (3H, m), 7.37-7.35 (3H, m), 5.24 (1H, d, J = 12.3 Hz), 3.67 (3H, s), 3.65-3.59 (1H, m), 2.70 (2H, t, J = 6.8 Hz), 1.92-1.52 (5H, m), 0.89 (3H, d, J = 6.8 Hz), 0.88 (3H, d, J = 6.8 Hz).

¹³C NMR (100 MHz, CDCl₃) δ 198.53 (e), 167.43 (e), 162.67 (o), 135.04 (o), 128.62 (o), 128.14 (o), 125.80 (e), 95.89 (o), 88.28 (o), 50.08 (o), 46.24 (e), 30.93 (o), 29.36 (e), 20.52 (e), 17.37 (o), 16.92 (o).

m/z (FAB) 385 (5), 353 (11), 283 (22), 227 (11), 157 (5), 125 (100), 103 (65), 97 (38), 83 (25), 69 (17).

HRMS (FAB) calcd for C₁₈H₂₅O₄⁸⁰Se 385.0918 found 385.0916.



IR (CHCl₃) 3026 (m), 2956 (m), 2871 (m), 1737 (s), 1712 (s) cm⁻¹.

¹H NMR (400 MHz, CDCl₃) δ 4.02 (1H, dd, J = 8.9 Hz, J = 3.7 Hz), 3.52 (3H, s), 2.93-2.89 (1H, m), 2.73-2.66 (1H, m), 2.58 (1H, A of ABX, J_{AB} = 15.6 Hz, J_{AX} = 3.7 Hz), 2.43 (1H, B of ABX,

62253-10

$J_{AB} = 15.6$ Hz, $J_{BX} = 8.9$ Hz), 2.28 (1H, dd, $J = 13.5$ Hz, $J = 6.7$ Hz), 1.86-1.81 (1H, m), 1.75-1.72 (1H, m), 1.55-1.34 (3H, m), 0.74 (3H, d, $J = 6.8$ Hz), .73 (3H, d, $J = 6.9$ Hz).

^{13}C NMR (100 MHz, CDCl_3) δ 214.57 (e), 170.74 (e), 89.77 (o), 82.89 (o), 51.38 (o), 41.65 (e), 37.51 (e), 33.60 (o), 33.47 (e), 22.69 (e), 18.91 (o), 17.50 (o).

m/z (CI) 228 (18), 197 (6), 157 (23), 125 (13), 103 (9), 98 (14), 82 (100), 69 (45), 55 (54).

HRMS (EI) calcd for $\text{C}_{12}\text{H}_{20}\text{O}_4$ 228.1362 found 228.1369.