

Studies on the Synthesis of Tedanolide. 2. Stereoselective Synthesis of a Protected C(1)-C(12) Fragment

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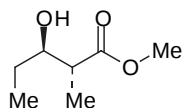
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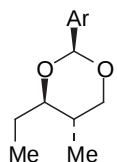
SUPPORTING INFORMATION

Tabulated spectroscopic data for new compounds (8 pages)

Methyl (2R, 3R)-3-hydroxy-2-methylpentanoate (12). This intermediate is a



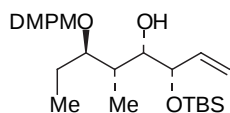
known compound:¹ $[\alpha]_D^{23.6} = -12.1^\circ$ ($c = 1.06$, CHCl_3); 3.71 (s, 3H), 3.67-3.55 (m, 1H), 2.56 (app. q, $J = 7.1$ Hz, 1H), 2.55 (s, 1H) 1.58 (m, 1H), 1.45 (m, 1H), 1.21 (d, $J = 7.3$ Hz, 3H), 0.98 (t, $J = 7.4$ Hz 3H).



(2S,3R,1'S)-1,3-O-[1'-(3,4-Dimethoxyphenyl)methylidene]-2-methylpentane (13). $[\alpha]_D^{25}$

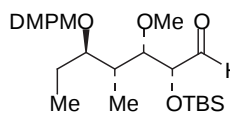
$= +32.2^\circ$ ($c = 1.70$, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 7.06-7.03 (m, 2H), 6.84 (d, $J = 8.3$ Hz, 1H), 5.44 (s, 1H), 4.08 (dd, $J = 4.8, 11.2$ Hz, 1H), 3.90 (s, 3H), 3.86 (s, 3H), 3.47 (dd, $J = 11.2, 11.2$ Hz, 1H), 3.34 ddd, $J = 2.8, 8.1, 9.8$ Hz, 1H), 1.86 (m, 1H), 1.78 (m, 1H),

1.54 (m, 1H), 1.02 (t, $J = 7.45$ Hz, 3H), 0.77 (d, $J = 6.6$ Hz, 3H); ^{13}C (125 MHz, CDCl_3) δ 149.1, 148., 131.69, 118.5, 110.6, 108.9, 100.9, 84.2, 72.9, 55.7, 33.3, 25.4, 12.3, 9.4; IR (thin film, cm^{-1}) 2960, 2931, 2876, 2836, 1736, 1611, 1596, 1519, 1463, 1264, 1235, 1162, 1113, 1029, 963, 760; HRMS (CI with ammonia) m/z Calcd for $\text{C}_{15}\text{H}_{23}\text{O}_4$ ($\text{M}+\text{H}$)⁺ 266.1518, found 266.1512.



(3S,4S,5S,6R)-6-[(3,4-Dimethoxybenzyl)oxy]-4-Methoxy-5-Methyl-3-[(tert-Butyldimethylsilyl)oxy]oct-1-ene (16). $[\alpha]_D^{25} = -6.4^\circ$ ($c = 1.08$, CHCl_3); ^1H

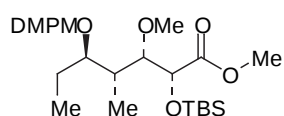
NMR (500 MHz, CDCl_3) δ 6.93-6.80 (m, 3H), 5.80 (m, 1H), 5.24-5.14 (m, 2H), 4.50 (A of AB, $J_{AB} = 11.2$ Hz, 1H), 4.45 (B of AB, $J_{AB} = 11.2$ Hz, 1H), 4.03 (app. t, $J = 7.7$ Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.52 (dt, $J = 2.0, 7.8$ Hz, 1H), 3.40 (m, 1H), 2.62 (d, $J = 2.2$ Hz, 1H), 1.80-1.70 (m, 2H), 1.54-1.49 (m, 1H), 0.91 (t, $J = 7.3$ Hz, 3H), 0.90 (s, 9H), 0.88 (d, $J = 7.1$ Hz, 3H), 0.09 (s, 3H), 0.05 (s, 3H); ^{13}C (125 MHz, CDCl_3) δ 148.9, 148.4, 138.2, 131.7, 120.1, 117.1, 111.2, 110.8, 82.6, 77.0, 73.6, 72.1, 55.9, 55.7, 36.1, 25.9, 23.6, 18.2, 9.7, 9.1, -4.0, -4.8; IR (thin film, cm^{-1}) 3561, 2956, 2932, 2857, 1517, 1464, 1262, 1156, 1139, 1073, 1031, 936, 836, 778; HRMS (FAB in NBA) m/z Calcd for $\text{C}_{25}\text{H}_{44}\text{O}_5\text{SiNa}$ ($\text{M}+\text{Na}$)⁺ 461.2700, found 461.2699.



(2R,3S,4S,5R)-5-[(3,4-Dimethoxybenzyl)oxy]-3-Methoxy-4-Methyl-2-[(tert-Butyldimethylsilyl)oxy]heptanal (17). $[\alpha]_D^{25} = -11.8^\circ$ ($c = 2.30$, CHCl_3); ^1H

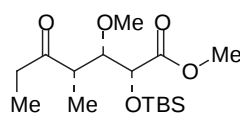
NMR (500 MHz, CDCl_3) δ 9.67 (d, $J = 1.7$ Hz, 1H), 6.90-6.82 (m, 3H), 4.44 (A of AB, $J_{AB} = 11.2$ Hz, 1H), 4.36 (B of AB, $J_{AB} = 11.2$ Hz, 1H), 4.14 (dd, $J = 2.0, 6.1$ Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.68 (dd, $J = 3.2, 6.1$ Hz, 1H), 3.41 (s, 3H), 3.34 (m, 1H), 1.95 (ddq, $J = 3.2, 7.1, 7.1$

Hz, 1H), 1.68 (ddq, $J = 3.7, 7.3, 7.3$ Hz, 1H), 1.49 (ddq, $J = 5.9, 7.3, 7.3$ Hz, 1H), 0.91 (s, 9H), 0.90 (t, $J = 7.3$, 3H), 0.88 (d, 7.1, 3H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C (125 MHz, CDCl_3) δ 202.9, 148.9, 18.4, 131.4, 120.1, 111.1, 110.8, 81.9, 80.8, 79.6, 70.7, 60.3, 55.9, 55.7, 36.5, 25.8, 22.1, 18.2, 10.5, 8.43, -4.7, -5.0; IR (thin film, cm^{-1}) 2954, 2933, 2857, 1734, 1608, 1593, 1517, 1464, 1419, 1388, 1361, 1331, 1262, 1239, 1191, 1157, 1139, 1090, 1031, 953, 938, 893, 838, 808, 780; HRMS (FAB in NBA) m/z Calcd for $\text{C}_{24}\text{H}_{42}\text{O}_6\text{Si}$ ($\text{M}+\text{Na}$) $^+$ 477.2649, found 477.2625.

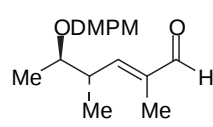


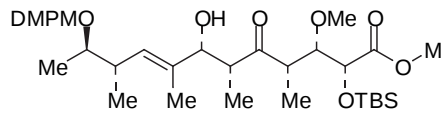
Methyl (2R,3S,4S,5R)-5-[(3,4-Dimethoxybenzyl)oxy]-3-Methoxy-4-Methyl-2-[(*tert*-Butyldimethylsilyl)oxy]heptanoate (18a). $[\alpha]_{\text{D}}^{25} = +8.8^\circ$ ($c = 1.80$, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 6.95-6.80 (m, 3H), 4.45 (A of AB, $J_{\text{AB}} = 11.2$ Hz, 1H), 4.37 (B of AB $J_{\text{AB}} = 11.2$ Hz, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.71 (s, 3H), 3.70 (m, 1H), 3.42 (s, 3H), 3.35 (m, 3H), 1.82 (ddq, $J = 2.9, 7.3, 7.3$ Hz, 1H), 1.67 (ddq, $J = 3.6, 7.3, 7.3$ Hz, 1H), 1.50 (ddq, $J = 6.1, 7.3, 7.3$ Hz, 1H), 0.92-0.88 (m, 15H), 0.07 (s, 6H); ^{13}C (125 MHz, CDCl_3) δ

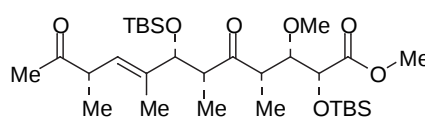
172.6, 148.9, 148.3, 131.6, 120.0, 111.1, 110.8, 82.5, 81.2, 75.7, 70.5, 60.8, 55.9, 55.8, 51.7, 36.8, 25.7, 22.3, 18.3, 10.2, 8.6, -5.1, -5.2; IR (thin film, cm^{-1}) 2950, 2934, 2857, 1753, 1736, 1607, 1593, 1517, 1464, 1419, 1389, 1362, 1262, 1239, 1191, 1156, 1137, 1031, 956, 838, 807, 779; HRMS (FAB in NBA) m/z Calcd for $\text{C}_{25}\text{H}_{44}\text{O}_7\text{SiNa}$ ($\text{M}+\text{Na}$) $^+$ 507.2754, found 507.2762. *Anal.* Calcd for $\text{C}_{25}\text{H}_{44}\text{O}_7\text{Si}$: C, 61.95; H, 9.15. Found: C, 61.82; H, 9.20.



Methyl (2R,3S,4S)-3-Methoxy-4-Methyl-2-[(*tert*-Butyldimethylsilyl)oxy]-5-oxoheptanoate (7a). $[\alpha]_{405}^{25} = -15.5^\circ$ ($c = 2.16$, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 4.36 (d, $J = 4.9$ Hz, 1H), 3.80 (dd, $J = 4.9, 7.6$ Hz, 1H), 3.73 (s, 3H), 3.41 (s, 3H), 2.88 (dq, $J = 7.1, 7.6$ Hz, 1H), 2.62-2.48 (m, 2H), 1.15 (d, $J = 7.1$ Hz, 3H), 1.02 (t, $J = 7.3$, 3H), 0.88 (s, 9H), 0.05 (s, 3H), 0.00 (s, 3H); ^{13}C (125 MHz, CDCl_3) δ 212.7, 172.3, 82.4, 73.5, 59.8, 51.8, 46.3, 34.7, 25.7, 18.3, 13.2, 7.5, -5.1, -5.4; IR (thin film, cm^{-1}) 2952, 2934, 2897, 2858, 1754, 1714, 1462, 1437, 1413, 1362, 1280, 1256, 1204, 1148, 1094, 1022, 970, 905, 839, 780, 668; HRMS (CI with ammonia) m/z Calcd for $\text{C}_{16}\text{H}_{33}\text{O}_5\text{Si}$ ($\text{M}+\text{H}$) $^+$ 333.2097, found 333.2094.

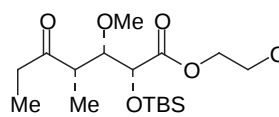

(2E,4S,5R)-5-(3,4-Dimethoxybenzyloxy)-2,4-Dimethyl-Hexenal (8). $[\alpha]_D^{24.8} = +13.7^\circ$ ($c = 2.53$, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 9.40 (s, 1H), 6.85-6.80 (m, 3H), 6.43 (dq, $J = 1.2, 9.9$ Hz, 1H), 4.54 and 4.36 (AB system, $J_{AB} = 11.5$ Hz, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 3.49 (dq, $J = 5.3, 6.4$ Hz, 1H), 2.82 (m, 1H), 1.74 (d, $J = 1.2$ Hz, 1H), 1.16 (d, $J = 6.4$ Hz, 3H), 1.08 (d, $J = 6.8$ Hz, 3H); ^{13}C (125 MHz, CDCl_3) δ 195.8, 157.3, 149.2, 148.8, 139.4, 131.3, 120.4, 111.2, 111.0, 77.6, 71.0, 56.2, 56.0, 39.7, 17.5, 16.3; IR (thin film, cm^{-1}) 2969, 2933, 2872, 2835, 2709, 1686, 1640, 1608, 1593, 1516, 1464, 1419, 1375, 1328, 1265, 1238, 1157, 1137, 1103, 1069, 1029, 935, 855, 807, 765, 741, 697, 676; HRMS (DCI with ammonia) m/z Calcd for $\text{C}_{17}\text{H}_{28}\text{O}_4\text{N}$ ($\text{M}+\text{NH}_4$) $^+$ 310.2025, found 310.2032. *Anal.* Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_4$: C, 69.84; H, 8.27. Found: C, 69.78; H, 8.36.


Methyl (2R,3S,4S,6R,7R,8E,10S,11R)-11-[(3,4-Dimethoxybenzyl)oxy]-7-Hydroxy-3-Methoxy-5-Oxo-2-[(tert-Butyldimethylsilyl)oxy]-4,6,8,10-Tetramethyldodec-8-enoate (21). ^1H NMR (500 MHz, CDCl_3) δ 6.92 (d, $J = 1.9$ Hz, 1H), 6.85 (dd, $J = 1.9, 8.1$ Hz, 1H), 6.81 (d, $J = 8.1$ Hz, 1H), 5.25 (d, $J = 9.3$ Hz, 1H), 4.48 (A of AB, $J_{AB} = 11.7$ Hz, 1H), 4.39 (B of AB, $J_{AB} = 11.7$ Hz, 1H), 4.21 (d, $J = 5.6$ Hz, 1H), 4.16 (d, $J = 7.6$ Hz, 1H), 3.91 (dd, $J = 2.9, 5.6$ Hz, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.70 (s, 3H), 3.38 (s, 3H), 3.32 (dq, $J = 4.2, 6.1$ Hz, 1H), 2.95 (dq, $J = 7.1, 7.6$ Hz, 1H), 2.65 (dq, $J = 2.9, 7.3$ Hz, 1H), 2.57 (ddq, $J = 4.2, 6.8, 9.3$ Hz, 1H), 1.55 (d, $J = 1.2$ Hz, 3H), 1.18 (d, $J = 7.3$ Hz, 3H), 1.12 (d, $J = 7.1$ Hz, 3H), 1.04 (d, $J = 6.1$ Hz, 3H), 0.94 (d, $J = 6.8$ Hz, 3H), 0.90 (s, 9H), 0.86 (s, 9H), 0.07 (s, 3H), 0.05 (s, 3H), 0.02 (s, 3H), -0.04 (s, 3H); ^{13}C (500 MHz, CDCl_3) δ 217.4, 172.1, 148.9, 148.3, 132.9, 131.8, 128.5, 119.9, 111.0, 110.7, 82.4, 77.8, 73.7, 73.6, 70.4, 60.2, 55.9, 55.8, 52.0, 46.7, 45.7, 37.0, 25.7, 18.4, 16.2, 15.8, 14.2, 12.5, 9.2, -5.0, -5.1; IR (thin film, cm^{-1}) 3390, 2932, 2887, 2855, 1820, 1755, 1723, 1622, 1516, 1463, 1455, 1377, 1257, 1167, 1140, 1101, 1052, 1022, 981, 939, 915, 839, 781, 668; HRMS (ionization) m/z Calcd for $\text{C}_{39}\text{H}_{70}\text{O}_9\text{Si}_2\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 738.4558, found 738.4558. *Anal.* Calcd for $\text{C}_{39}\text{H}_{70}\text{O}_9\text{Si}_2$: C, 63.37; H, 9.55. Found: C, 63.50; H, 9.48.


Methyl (2R,3S,4S,6R,7R,8E,10S)-5,11-Bisoxo-2,7-Bis[(tert-Butyldimethylsilyl)oxy]-3-Methoxy-4,6,8,10-Tetramethyldodec-8-enoate (6a). $[\alpha]_{589}^{23.4} = +64.5^\circ$ ($c = 1.10$, CHCl_3); ^1H NMR (500

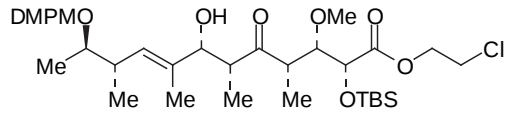
(d, $J = 2.0$ Hz, 1H), 6.88 (dd, $J = 2.0, 8.1$ Hz, 1H), 6.82 (d, $J = 8.1$ Hz, 1H), 4.47 and 4.36 (AB system, $J_{AB} = 11.7$ Hz, 1H), 4.38-4.31 (m, 3H), 3.90 (s, 3H), 3.87 (s, 3H), 3.76 (dd, $J = 2.7, 6.6$ Hz, 1H), 3.43 (s, 3H), 3.35 (m, 1H), 1.82 (ddq, $J = 2.7, 2.7, 7.1$ Hz, 1H), 1.71 (m, 1H), 1.50 (m, 1H), 0.91-0.88 (m, 15H), 0.83 (s, 6H); ^{13}C (125 MHz, CDCl_3) δ 171.8, 148.9, 148.3, 131.6, 119.9, 111.1, 110.8, 82.3, 81.0, 75.7, 70.5, 64.3, 60.9, 55.9, 55.8, 41.2, 36.8, 25.7, 22.1, 18.2, 10.2, 8.3, -5.1, -5.2; IR (thin film, cm^{-1}) 2957, 2934, 2857, 1753, 1608, 1593, 1517, 1465, 1420, 1389, 1362, 1331, 1303, 1263, 1156, 1140, 1119, 1030, 958, 940, 893, 861, 838, 809, 780, 667; HRMS (FAB in NBA) m/z Calcd for $\text{C}_{26}\text{H}_{45}\text{ClO}_7\text{SiNa}$ ($\text{M}+\text{Na}$) $^+$ 555.2521, found 555.2540.

2' - C h l o r o e t h y l (2*R*,3*S*,4*S*)-3-Methoxy-4-Methyl-2-[(*tert*-Butyldimethylsilyl)oxy]-5-oxoheptanoate (7b).



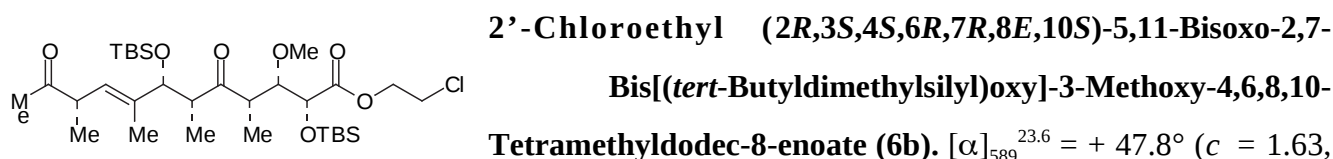
$[\alpha]_{\text{D}}^{25} = -1.2^\circ$ ($c = 2.00$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 4.45-4.43 (m, 3H), 3.84 (dd, $J = 4.8, 7.3$ Hz, 1H), 3.71 (t, $J = 5.7$ Hz, 1H), 3.43 (s, 3H), 2.91 (dq, $J = 7.0, 7.3$ Hz, 1H), 2.56 (m, 2H), 1.16 (d, $J = 7.0$ Hz, 3H), 1.03 (t, $J = 7.3$, 3H), 0.89 (s, 9H), 0.07 (s, 3H), 0.01 (s, 3H); ^{13}C (125 MHz, CDCl_3) δ 212.6, 171.5, 82.2, 73.5, 64.4, 59.7, 46.1, 41.3, 34.7, 25.7, 18.3, 13.3, 7.5, -5.1, -5.4; IR (thin film, cm^{-1}) 2933, 2887, 2858, 1757, 1714, 1472, 1462, 1412, 1363, 1303, 1254, 1186, 1145, 1093, 1022, 970, 897, 839, 781, 668; HRMS (CI with ammonia) m/z Calcd for $\text{C}_{17}\text{H}_{35}\text{ClO}_5\text{Si}$ ($\text{M}+\text{H}$) $^+$ 381.1864, found 381.1857.

2'-Chloroethyl (2*R*, 3*S*,4*S*,6*R*,7*R*,8*E*,10*S*,11*R*)-11-[(3,4-Dimethoxybenzyl)oxy]-7-Hydroxy-3-Methoxy-5-Oxo-2-[(*tert*-Butyldimethylsilyl)oxy]-4,6,8,10-Tetramethyldodec-8-enoate (22).

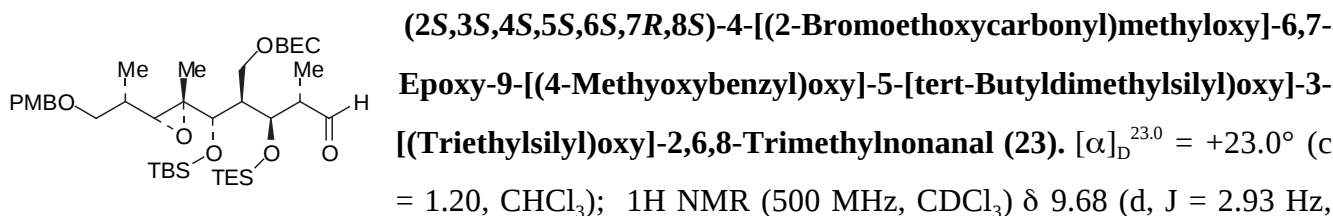


$[\alpha]_{589}^{23.6} = +10.0^\circ$ ($c = 1.56$, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 6.91 (d, $J = 1.7$ Hz, 1H), 6.86 (dd, $J = 1.7, 8.1$ Hz, 1H), 6.80 (d, $J = 8.1$ Hz, 1H), 5.48 (ap dp, $J = 1.5, 9.5$ Hz, 1H), 4.50 (A of AB, $J_{AB} = 11.7$ Hz, 1H), 4.42 (B of AB $J_{AB} = 11.7$ Hz, 1H), 4.41-4.38 (m, 4H), 3.88 (s, 3H), 3.86 (s, 3H), 3.77 (ap t, $J = 5.9$ Hz, 1H), 3.71 (d, $J = 4.6$ Hz, 1H), 3.69 (dd, $J = 0.5, 5.1$ Hz, 1H), 3.45 (s, 3H), 3.39 (dq, $J = 5.1, 6.3$ Hz, 1H), 3.11 (d, $J = 2.4$ Hz, 1H), 3.03-2.95 (m, 2H), 2.66 (ddq, $J = 5.1, 6.3, 9.5$ Hz, 1H), 1.57 (d, $J = 1.0$ Hz, 3H), 1.16 (d, $J = 7.1$ Hz, 3H), 1.12 (d, $J = 6.3$ Hz, 3H), 1.02 (d, $J = 7.3$ Hz, 3H), 0.97 (d, $J = 6.8$ Hz, 3H), 0.89 (s, 9H), 0.10 (s, 3H), 0.07 (s, 3H); ^{13}C (125 MHz, CDCl_3) δ 213.1, 171.3, 148.8, 148.3, 132.8, 131.7, 128.5, 119.9, 110.9, 110.7, 82.1, 77.7, 73.7, 73.6, 70.4, 64.5,

60.1, 55.9, 55.7, 46.6, 45.6, 41.3, 37.0, 25.7, 18.4, 16.1, 15.8, 14.1, 12.5, 9.2, -5.0, -5.2; IR (thin film, cm^{-1}) 3516, 2959, 2933, 2858, 1753, 1707, 1607, 1594, 1516, 1464, 1419, 1372, 1262, 1156, 1138, 1101, 1030, 1007, 839, 808, 781, 668; HRMS (FAB in NBA) m/z Calcd for $\text{C}_{34}\text{H}_{57}\text{ClO}_9\text{SiNa}$ ($\text{M}+\text{Na}$)⁺ 695.3358, found 695.3361. *Anal.* Calcd for $\text{C}_{34}\text{H}_{57}\text{ClO}_9\text{Si}$: C, 60.65; H, 8.53. Found: C, 60.36; H, 8.47.

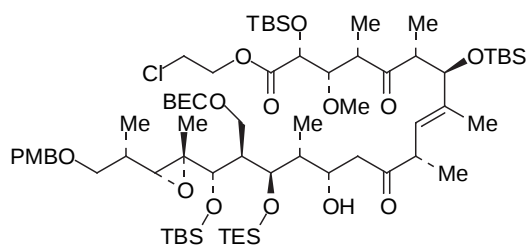


CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 5.27 (dp, $J = 9.5$ Hz, 1H), 4.43-4.32 (m, 2H), 4.26 (d, $J = 5.6$ Hz, 1H), 4.23 (d, $J = 7.6$ Hz, 1H), 3.89 (dd, $J = 3.2, 5.4$ Hz, 1H), 3.70 (t, $J = 5.6$ Hz, 2H), 3.37 (s, 3H), 3.28 (dq, $J = 7.1, 9.5$ Hz, 1H), 2.91 (dq, $J = 6.8, 7.6$ Hz, 1H), 2.69 (dq, $J = 3.2, 7.3$ Hz, 1H), 2.06 (s, 3H), 1.62 (d, $J = 1.5$ Hz, 3H), 1.17 (d, $J = 7.3$ Hz, 3H), 1.13 (d, $J = 7.1$ Hz, 3H), 1.12 (d, $J = 6.8$ Hz, 3H), 0.90 (s, 9H), 0.86 (s, 9H), 0.09 (s, 3H), 0.07 (s, 3H), 0.03 (s, 3H), -0.05 (s, 3H); ^{13}C (125 MHz, CDCl_3) δ 213.5, 209.4, 171.4, 138.3, 127.0, 80.2, 78.6, 74.9, 64.5, 48.6, 47.0, 46.8, 41.3, 27.5, 25.8, 25.7, 18.3, 18.1, 16.3, 13.7, 12.2, 10.8, -4.5, -5.0, -5.3; IR (thin film, cm^{-1}) 2957, 2932, 2887, 2857, 1756, 1716, 1472, 1463, 1389, 1361, 1304, 1253, 1153, 1102, 995, 939, 905, 877, 838, 778, 670; HRMS (FAB in NBA) m/z Calcd for $\text{C}_{31}\text{H}_{59}\text{ClO}_7\text{Si}_2\text{Na}$ ($\text{M}+\text{Na}$)⁺ 657.3386, found 657.3396. *Anal.* Calcd for $\text{C}_{31}\text{H}_{59}\text{ClO}_7\text{Si}_2$: C, 58.60; H, 9.39. Found: C, 58.57; H, 9.30.



1H), 7.20 (m, 2H), 6.86 (m, 2H), 4.42-4.33 (m, 5H), 4.27 (dd, $J = 2.3, 7.1$ Hz, 1H), 4.18 (dd, $J = 4.1, 11.2$ Hz, 1H), 3.81 (s, 3H), 3.49 (t, $J = 6.1$ Hz, 2H), 3.44 (A of ABX, $J_{\text{AB}} = 9.3$ Hz, $J_{\text{AX}} = 4.6$ Hz, 1H), 3.35 (A of ABX, $J_{\text{AB}} = 9.3$ Hz, $J_{\text{BX}} = 7.6$ Hz, 1H), 3.10 (d, $J = 9.8$ Hz, 1H), 2.77 (ddq, $J = 2.9, 6.8, 7.1$ Hz, 1H), 2.53 (d, $J = 8.8$ Hz, 1H), 2.02 (m, 1H), 1.78 (dddq $J = 4.6, 7.1, 7.6, 8.8$ Hz, 1H), 1.28 (s, 3H), 1.07 (d, $J = 6.8$ Hz, 3H), 1.04 (d, $J = 1.0$ Hz, 3H), 0.93-0.90 (m, 18H), 0.59 (m, 6H), 0.19 (s, 3H), 0.12 (s, 3H); ^{13}C (125 MHz, CDCl_3) δ 204.7, 159.0, 154.5, 130.3, 129.0, 113.6, 78.2, 72.7, 72.4,

66.7, 65.1, 64.8, 63.0, 55.2, 52.3, 45.4, 39.4, 33.3, 28.1, 26.1, 18.4, 14.9, 11.8, 11.4, 6.9, -3.7, -5.4; IR (thin film, cm⁻¹) 2956, 2935, 2878, 2857, 2735, 2708, 1749, 1731, 1613, 1586, 1514, 1462, 1390, 1360, 1250, 1173, 1080, 1039, 1005, 961, 937, 901, 837, 779, 743, 670, 637; HRMS (FAB in NBA) *m/z* Calcd for C₃₆H₆₃BrO₉Si₂Na (M+Na)⁺ 797.3292, found 797.3266



2'-Chloroethyl (2*R*,3*S*,4*S*,6*R*,7*R*,8*E*,10*S*,13*S*,14*R*,15*R*,16*S*,17*S*,18*S*,19*R*,20*S*) - 5,11-Bisoxo-16-[(2-Bromoethoxycarbonyl)methoxy] -18,19-Epoxy-21-[(4-Methoxybenzyl)oxy] -3-Methoxy-4,6,8,10,14,18,20-Heptamethyl-13-Hydroxy-15- [(Triethylsilyl)oxy]-2,7,17-

Tris[(*tert*-Butyldimethylsilyl)oxy] henicos-8-enoate (9b). [α]_D^{25.0} = 40.3° (c = 1.40, CHCl₃); ¹H NMR (500 MHz, , CDCl₃) δ 7.20 (m, 2H), 6.86 (m, 2H), 5.38 (d, J = 9.8 Hz, 1H), 4.43-4.29 (m, 10H), 4.14 (dd, J = 4.4, 11.5 Hz, 1H), 4.06 (dd, J = 1.6, 7.1 Hz, 1H), 3.85 (dd, J = 4.2, 5.6 Hz, 1H), 3.80 (s, 3H), 3.70 (t, J = 6.1 Hz, 2H), 3.48 (t, J = 6.1 Hz, 2H), 3.42 (dd, J = 4.9, 9.3 Hz, 1H), 3.39 (s, 3H), 3.37-3.31 (m, 2H), 3.10 (d, J = 10.0 Hz, 1H), 2.89-2.80 (m, 3H), 2.67 (dd, J = 9.3, 17.1 Hz, 1H), 2.57 (d, J = 8.5 Hz, 1H), 2.37 (dd, J = 3.2, 17.1 Hz, 1H), 2.14 (m, 1H), 1.77 (m, 1H), 1.62 (d, J = 1.2 Hz, 3H), 1.59 (m, 1H), 1.30 (s, 3H), 1.13 (overlap d, J = 7.1 Hz, 3H), 1.13 (overlap d, J = 7.4 Hz, 3H), 1.08 (d, J = 6.8 Hz, 3H), 0.94-0.86 (m, 39H), 0.61 (m, 6H), 0.18 (s, 3H), 0.12 (s, 3H), 0.09 (s, 3H), 0.07 (s, 3H), 0.02 (s, 3H), -0.04 (s, 3H); ¹³C (125 MHz, CDCl₃) δ 213.0, 211.8, 171.4, 159.0, 154.5, 138.2, 130.4, 129.1, 126.2, 113.6, 80.9, 79.0, 77.4, 74.5, 73.8, 72.6, 72.3, 66.6, 65.8, 65.4, 64.5, 63.1, 60.1, 55.2, 49.0, 46.2, 46.0, 45.7, 45.0, 42.9, 41.2, 39.4, 33.2, 32.1, 28.3, 26.0, 25.8, 25.7, 22.6, 18.4, 18.1, 16.4, 15.0, 13.0, 12.5, 11.9, 11.1, 9.8, 7.1, 5.4, 3.7, -4.4, -5.0, -5.2, -5.3; IR (thin film, cm⁻¹) 3541, 2955, 2932, 2882, 2857, 1749, 1708, 1613, 1514, 1462, 1387, 1361, 1250, 1078, 1005, 938, 902, 838, 778, 741, 670; HRMS (FAB in NBA w/Na⁺) *m/z* Calcd for C₆₇H₁₂₂ClBrO₁₆Si₄Na (M+Na)⁺ 1433.7, found 1433.7.

References Cited in the Supporting Information:

- (1) Meyers, A. I.; Yamamoto, Y. *Tetrahedron* **1984**, *40*, 2309.