Total Synthesis of (+)-Thiazinotrienomycin E

Supporting Information

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Benzoate 8. Yellow oil: IR ($CHCl_3$) 3100 (w), 3040 (w), 2960 (w), 1700 (s), 1610 (s), 1550 (s), 1350 (s), 1310 (s), 1270 (s), 1155 (s), 1080 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.75 (d, J = 7.7 Hz, 1 H), 4.09 (s, 3 H), 4.04 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 156.6, 156.5, 154.4, 138.6, 132.0, 124.9, 120.9, 120.8, 64.0, 53.9.

Anal. Calcd for $C_9H_7FN_2O_7$: C, 39.42; H, 2.55; N, 10.27. Found: C, 39.80; H, 2.76; N, 9.93.

Aniline 9. Yellow powder: IR ($CHCl_3$) 3400 (w), 3200 (w), 3000 (w), 1730 (m), 1680 (s), 1620 (m), 1480 (m), 1435 (m), 1365 (m), 1260 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.64 (s, 1 H), 6.39 (s, 1 H), 3.99 (s, 3 H), 3.82 (s, 3 H), 3.33 (s, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7, 166.3, 141.7, 139.7, 133.5, 126.7, 107.6, 106.0, 61.3, 52.6, 30.5; high resolution mass spectrum (CI, NH_3) m/z 286.0868 [$(M+NH_4)^+$; calcd for $C_{11}H_{16}N_3O_4S$: 286.0862].

Sulfone 10. Yellow oil: IR ($CHCl_3$) 3500 (m), 3300 (m), 3000 (s), 2900 (m), 1770 (m), 1720 (w), 1670 (m), 1600 (w), 1450 (w), 1340 (m), 1240 (m), 1175 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.84 (m, 2 H), 7.73 (br s, 1 H), 7.65 (m, 1 H), 7.53 (m, 2 H), 7.44 (m, 5 H), 7.01 (s, 1 H), 5.25 (s, 2 H), 4.64 (s, 2 H), 3.75 (s, 3 H), 3.19 (s, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 153.0, 144.8, 139.1, 135.5, 134.0, 133.8, 130.9, 129.1, 128.8, 128.67, 128.65, 128.5, 120.9, 117.4, 108.9, 67.7, 61.8, 56.2, 30.5; high resolution mass spectrum (ES, Na) m/z 521.0811 [$(M+Na)^+$; calcd for $C_{24}H_{22}N_2O_6S_2Na$: 521.0817].

Anal. Calcd for $C_{24}H_{22}N_2O_6S_2$: C, 57.82; H, 4.45; N, 5.62. Found: C, 57.43; H, 4.17; N, 5.37.

TBS Aniline 3. Light yellow oil: IR ($CHCl_3$) 3400 (m), 2940 (s), 2880 (m), 1680 (s), 1600 (m), 1470 (s), 1350 (m), 1320 (w), 1260 (s), 1140 (m), 1090 (m), 940 (s) cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 7.64 (m, 2 H), 6.94-6.82 (m, 3 H), 6.76 (s, 1 H), 4.74 (s, 2H), 3.50 (s, 1 H), 2.82 (s, 2 H), 0.98 (s, 9 H), 0.87 (s, 9 H), 0.27 (s, 6 H), -0.03 (s 6 H); ^{13}C NMR (125 MHz, C_6D_6) δ 168.0, 139.6, 139.2, 132.7, 132.6, 129.1, 128.2, 128.0, 118.9, 109.5, 105.1, 57.2, 30.7, 26.4, 25.5, 18.4, 18.1, -3.9, -4.6; high resolution mass spectrum (ES, Na) m/z 579.2220 [$(M+H)^+$; calcd for $C_{27}H_{43}N_2O_4S_2(Si)_2$: 579.2202].

Vinyl Stannane (+)-12. Colorless oil: $[\alpha]_D^{23}$ +17.7° (*c* 1.20, $CHCl_3$); IR ($CHCl_3$) 3500 (br s), 2960 (s), 2930 (s), 2880 (m), 2860 (m), 1600 (w), 1450 (m), 1100 (m), 1070 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.12 (d *J* = 19.1 Hz, 1 H), 5.80 (dd, *J* = 19.1, 7.2 Hz, 1 H), 3.72 (m, 3 H), 3.21 (s, 3 H), 2.53 (dd, *J* = 6.3, 4.5 Hz, 1 H), 1.75 (m, 2 H), 1.48 (m, 6 H), 1.24 (m, 6 H), 0.95 (m, 15 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.8, 131.9, 85.5, 60.9, 56.2, 37.7, 29.1, 27.2, 13.7, 9.5; high resolution mass spectrum (CI, NH_3) *m/z* 349.1192 [$(M-C_4H_9)^+$; calcd for $C_{14}H_{29}O_2Sn$: 349.1189].

Anal. Calcd for $C_{18}H_{38}O_2Sn$: C, 53.33; H, 9.38. Found: C, 53.44; H, 9.45.

Vinyl Iodide (+)-13. Colorless oil: $[\alpha]_D^{23}$ +10.4° (*c* 0.95, $CHCl_3$); IR ($CHCl_3$) 3005 (s), 2960 (s), 2930 (s), 2860 (s), 1601 (s), 1470 (m), 1250 (s), 1210 (s), 1100 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.42 (dd, *J* = 14.5, 7.8 Hz, 1 H), 6.24 (d, *J* = 14.5, 1 H), 3.73-3.68 (m, 2 H), 3.64-3.59 (m, 1 H), 3.23 (s, 3 H), 1.78-1.72 (m, 1 H), 1.68-1.62 (m, 1 H), 0.87 (s, 9 H), 0.03 (s 3 H), 0.02 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 80.7, 77.9, 58.8, 56.7, 37.9, 25.9, 18.3, -5.36, -5.40; high resolution mass spectrum (CI, NH_3) *m/z* 357.0746 [$(M+H)^+$; calcd for $C_{12}H_{26}IO_2Si$: 357.0746].

Aldehyde (-)-5. Yellow oil: $[\alpha]_D^{23}$ -11.0° (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) 3002 (s), 2950 (s), 2930 (s), 2860 (s), 2820 (m), 1675 (s), 1640 (s), 1460 (m), 1250 (s), 1205 (s), 1160 (m), 1100 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.52 (d, *J* = 8.2 Hz, 1 H), 7.04 (dd, *J* = 15.3, 11.0 Hz, 1 H), 6.44 (dd, *J* = 15.3, 11.0 Hz, 1 H), 6.10 (m, 2 H), 3.96 (m, 1 H), 3.73-3.68 (m, 1 H), 3.64-3.59 (m, 1 H), 3.27 (s, 3 H), 1.82-1.71 (m, 2 H), 0.91 (s, 9 H), 0.025 (s 3 H), 0.018 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.6, 151.1, 145.5, 131.8, 129.1, 78.1, 58.9, 57.0, 38.3, 25.9, 18.3; high resolution mass spectrum (CI, NH_3) *m/z* 285.2250 [$(M+H)^+$; calcd for $C_{15}H_{29}O_3Si$: 285.2245].

Aldehyde (+)-16. Colorless oil: $[\alpha]_D^{23}$ +11.7° (*c* 0.6, $CHCl_3$); IR (Plate) 2960 (s), 2920 (s), 2850 (s), 1725 (s), 1470 (m), 1460 (m), 1250 (s), 1100 (s); ^1H NMR (500 MHz, $CDCl_3$) δ 9.72 (d, *J* = 2.2 Hz, 1 H), 4.13 (dt, *J* = 4.8, 7.1 Hz, 1 H), 3.72-3.68 (m, 2 H), 2.50-2.43 (m, 1 H), 1.80-1.64 (m, 2 H), 1.09 (d, *J* = 7.1 Hz, 3 H), 0.90 (s, 9 H), 0.12 (s, 9 H), 0.05 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.5, 70.4, 59.0, 51.7,

37.8, 25.9, 18.1, 10.4, 0.2, -5.5; high resolution mass spectrum (ES, Na) *m/z* 341.1954 [(M+Na)$^+$; calcd for $C_{15}H_{34}O_3(Si)_2Na$: 341.1944].

Alcohol (+)-18. Colorless oil: $[\alpha]_D^{23}$ +10.8° (*c* 0.5, $CHCl_3$); IR ($CHCl_3$) 3490 (m), 3065 (m), 3010 (m), 3000 (s), 2955 (s), 2900 (s), 2847 (s), 1675 (m), 1600 (m), 1470 (m), 1420 (m); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68-7.62 (m, 4 H), 7.42-7.37 (m, 6 H), 6.03 (t, *J* = 5.6 Hz, 1 H), 4.58-4.47 (m, 2 H), 3.92 (m, 1 H), 3.83 (m, 1 H), 3.76 (m, 1 H), 3.37 (d, *J* = 4.1 Hz, 1 H), 2.95 (m, 1 H), 1.98 (s, 3 H), 1.68-1.54 (m, 2 H), 1.05 (s, 9 H), 0.96 (d, *J* = 7.1 Hz, 3 H), 0.90 (s, 9 H), 0.08 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.0, 142.9, 135.5, 133.68, 133.65, 133.60, 129.5, 127.64, 127.59, 72.7, 63.0, 61.8, 48.0, 35.8, 26.8, 25.8, 20.6, 19.1, 16.9, 13.0, -5.6; high resolution mass spectrum (ES, Na) *m/z* 577.3143 [(M+Na)$^+$; calcd for $C_{32}H_{50}O_4(Si)_2Na$: 577.3145].

Anal. Calcd for $C_{32}H_{50}O_4(Si)_2$: C, 69.31; H, 9.03. Found: C, 69.70; H, 9.24.

Alcohol (+)-20. Colorless oil: $[\alpha]_D^{23}$ +11.2° (*c* 0.9, $CHCl_3$); IR ($CHCl_3$) 3510 (s), 2990 (s), 2930 (m), 1715 (s), 1480 (m), 1452 (m), 1380 (s), 1281 (s), 1205 (s), 1160 (s), 1120 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.40-5.38 (m, 1 H), 4.72-4.56 (m, 3 H), 3.79-3.70 (m, 2 H), 3.50 (dt, *J* = 9.1, 2.9 Hz, 1 H), 2.52 (br s, 1 H), 1.83-1.62 (m, 3 H), 1.70 (s, 3 H), 1.36 (s, 3 H), 1.32 (s, 3 H), 1.17 (s, 9 H), 0.80 (d, *J* = 6.7 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.5, 138.2, 121.3, 101.0, 75.0, 70.5, 61.6, 61.0, 40.8, 38.7, 36.2, 27.2, 24.6, 24.0, 21.1, 12.2; high resolution mass spectrum (ES, Na) *m/z* 351.2146 [(M+Na)$^+$; calcd for $C_{18}H_{32}O_5Na$: 351.2147].

Sulfone (+)-22. Colorless oil: $[\alpha]_D^{23}$ +5.4° (*c* 1.15, $CHCl_3$); IR ($CHCl_3$) 3005 (s), 2980 (s), 1720 (s), 1450 (m), 1380 (m), 1340 (s), 1150 (s) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (m, 2 H), 7.62-7.51 (m, 3 H), 5.34 (t, *J* = 6.7 Hz, 1 H), 4.74-4.70 (m, 1 H), 4.63 (d, *J* = 5.6 Hz, 1 H), 4.59-4.56 (m, 1 H), 4.01-3.90 (m, 1 H), 3.80-3.72 (m, 1 H), 3.46-3.41 (m, 1 H), 2.30-2.21 (m, 1 H), 2.12-2.03 (m, 1 H), 1.82-1.76 (m, 1 H), 1.68 (s, 3 H), 1.31 (s, 6 H), 1.16 (s, 9 H), 0.83 (d, *J* = 6.7 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.4, 153.5, 137.8, 133.1, 131.5, 129.7, 125.1, 121.6, 101.2, 72.6, 70.4, 61.0, 53.2, 40.8, 38.7, 27.2, 26.9,

24.4, 24.0, 21.1, 12.2; high resolution mass spectrum (ES, Na) *m/z* 543.2265 [$(M+Na)^+$; calcd for $C_{25}H_{36}N_4O_6SNa$: 543.2253].

Chloride (+)-4. A solution of (+)-**22** (1.9 g, 3.65 mmol) in THF (20 mL) at -78 °C was treated with KHMDS (0.5 M in toluene, 9.5 mL, 4.75 mmol). The resultant yellow solution was stirred for 20 min. before (-)-**5** (1.1 g, 3.84 mmol) in THF (10 mL) was introduced via cannular. The mixture was then stirred for 1 h, the -78 °C bath was removed, and the mixture stirred at ambient temperature for an additional 1 h. The mixture was then added to brine (100 mL) and extracted with ether (3 x 100 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (hexanes/ethyl acetate, 20:1) provided the corresponding triene (1.8 g, 85% yield) as a colorless oil.

A solution of the above triene (1.74 g, 3.01 mmol) in CH_2Cl_2 (20 mL) at -78 °C was treated with DIBAL (1 M in hexane, 6.02 mL, 6.02 mmol). The mixture was stirred for 10 minutes, quenched with methanol (5 mL), diluted with ether (150 mL) and then stirred vigorously with a saturated Rochelle salt solution (200 mL) until two clear layers appeared. After separation, the aqueous phase was extracted with ether (3 x 150 mL), the combined organic phases dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (hexanes/ethyl acetate, 3:1) afforded the corresponding alcohol (1.38 g, 93% yield) as a colorless oil.

A solution of the above alcohol (185 mg, 0.374 mmol) in DMF (4 mL) was treated with 2,6-lutidine (0.175 mL, 1.5 mmol), LiCl (63.6 mg, 1.5 mmol) and mesyl chloride (0.058 mL, 0.75 mmol). The mixture was stirred at room temperature for 1 h and then added to brine and saturated $NaHCO_3$ (25 mL each). The resultant mixture was next extracted with ether (3 x 50 mL), the combined organic phases dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (hexanes/ethyl acetate, 20:1) afforded (+)-**4** (150 mg, 78% yield) as a colorless oil: $[\alpha]_D^{23}$ +2.9° (*c* 0.75, $CHCl_3$); IR ($CHCl_3$) 3001 (s), 2940 (s), 2880 (m), 1470 (m), 1380 (s), 1210 (s), 1100 (s), 1000 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.22-6.08 (m, 4 H), 5.82-5.76 (m, 1 H), 5.52-5.37 (m, 2 H), 4.65 (d, *J* = 5.6 Hz, 1 H), 4.22-4.17 (m, 2 H), 3.81-3.70 (m, 2 H), 3.67-3.55 (m, 1 H), 3.38-3.31 (m, 1 H), 3.22 (s, 3 H), 2.35-2.27 (m, 2 H), 1.90-1.81 (m, 2 H), 1.70-1.59 (m, 1 H), 1.68 (s, 3 H), 1.31 (s, 6 H), 0.87 (s, 9 H), 0.80 (d, *J* = 6.7 Hz, 3 H), 0.020 (s, 3 H), 0.014 (s, 3 H); ^{13}C

NMR (125 MHz, $CDCl_3$) δ 139.0, 133.5, 133.0, 132.6, 132.3, 131.2, 130.4, 122.8, 100.9, 78.8, 74.5, 70.9, 59.3, 56.2, 41.1, 40.2, 38.9, 37.6, 26.0, 24.7, 23.9, 21.4, 17.6, 12.6, -5.33, -5.35; high resolution mass spectrum (CI, NH_3) *m/z* 530.3427 [$(M+NH_4)^+$; calcd for $C_{28}H_{53}ClNO_4Si$: 530.3432].

MOM Ether (+)-24. White amorphous solid: $[\alpha]_D^{23}$ +12.6° (*c* 0.50, $CHCl_3$); IR ($CHCl_3$) 3680 (m), 3400 (m), 3010 (s), 2960 (s), 2940 (s), 1730 (s), 1680 (s), 1600 (s), 1515 (s), 1440 (m), 1380 (m), 1220 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 2 H), 7.61 (s, 1 H), 6.23-6.07 (m, 4 H), 5.98-5.92 (m, 1 H), 5.80-5.70 (m, 1 H), 5.57-5.49 (m, 1 H), 5.33 (d, *J* = 17.8 Hz, 1 H), 5.24 (m, 2 H), 4.93 (s, 2 H), 4.68 (m, 3 H), 3.80-3.68 (m, 2 H), 3.65-3.57 (m, 1 H), 3.60 (s, 3 H), 3.38-3.30 (m, 1 H), 3.34 (s, 2 H), 3.21 (s, 3 H), 2.72 (t, *J* = 7.1 Hz, 2 H), 2.34-2.10 (m, 4 H), 1.81-1.77 (m, 1 H), 1.74-1.62 (m, 2 H), 1.68 (s, 3 H), 1.30 (s, 3 H), 1.29 (s, 3 H), 0.87 (s, 9 H), 0.74 (d, *J* = 7.0 Hz, 3 H), 0.029 (s, 3 H), 0.023 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.6, 153.2, 142.1, 135.3, 133.8, 133.7, 133.4, 133.1, 132.6, 132.4, 132.3, 132.0, 131.6, 131.0, 124.7, 118.0, 114.2, 106.4, 101.0, 100.6, 78.8, 74.5, 69.3, 65.9, 59.4, 57.6, 56.2, 40.8, 38.8, 37.8, 30.1, 29.2, 27.8, 26.0, 24.7, 24.0, 20.8, 18.3, 12.7, -5.32, -5.34; high resolution mass spectrum (ES, Na) *m/z* 837.4184 [$(M+Na)^+$; calcd for $C_{43}H_{66}N_2O_9SSiNa$: 837.4156].

Acid (+)-25. Colorless oil: $[\alpha]_D^{23}$ +26.5° (*c* 0.40, $CHCl_3$); IR ($CHCl_3$) 3500 (br s), 2920 (s), 2840 (s), 1760 (m), 1740 (s), 1605 (s), 1505 (s), 1460 (m), 1370 (m), 1245 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.92 (s, 1 H), 8.05 (overlapping s, 1H), 7.82 (s, 1 H), 6.42 (dd, *J* = 14.9, 10.1 Hz, 1 H), 6.23 (dd, *J* = 15.6, 11.2 Hz, 1 H), 6.15-5.38 (complex series of m, 6 H), 5.30 (m, 2 H), 5.06-4.81 (complex series of m, 2 H), 4.72 (m, 3 H), 4.17 (m, 1 H), 3.67 (overlapping s, 3 H), 3.51-3.32 (m, 3 H), 3.22-3.18 (m, 3 H), 2.88-2.77 (m, 2 H), 2.60-2.50 (m, 2 H), 2.38-2.10 (m, 3 H), 1.92-1.81 (m, 1 H), 1.73 (overlapping s, 3 H), 1.80-1.70 (m, 1 H), 1.40 (overlapping s, 6 H), 0.80 (overlapping d, *J* = 7.1 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.6, 166.1, 153.7, 141.8, 136.3, 135.6, 134.4, 133.9, 133.6, 132.5, 132.4, 132.1, 131.6, 131.0, 130.7, 129.5, 123.7, 118.6, 118.1, 114.8, 107.3, 106.9, 101.0, 100.5, 78.8, 73.3, 69.2, 66.2, 66.0, 57.6, 57.5, 56.1, 40.5, 38.6, 36.3, 30.6, 29.3, 29.1, 28.6, 24.9, 24.1, 24.0, 20.74, 20.67, 12.7, 12.5; high resolution mass spectrum (ES, Na) *m/z* 737.3082 [$(M+Na)^+$; calcd for $C_{37}H_{50}N_2O_{10}SNa$: 737.3084].

(+)-Thiazinotrienomycinol (2). A solution of (+)-**25** (8 mg, 0.0112 mmol) in THF (2 mL) was treated with dimedone (16 mg, 0.112 mmol) and tetrakis(triphenylphosphine)palladium(0) (13mg, 0.0112 mmol). The resultant yellow solution was stirred for 1 h at room temperature and then concentrated in vacuo. Flash chromatography (ethyl acetate/hexanes, 1:1; CH_2Cl_2/MeOH, 20:1 to 1:1) afforded the corresponding unstable amino acid as a yellow solid. The acid was used immediately in the following step.

A solution of the above amino acid in THF-toluene (2:3, 5 mL) was treated with TEA (0.02 mL, 0.143 mmol). The resultant yellow solution was then added over a 2 h period via a syringe pump to a suspension of 2-chloro-1-methylpyridinium iodide (30 mg, 0.117 mmol) and TEA (0.03 mL, 0.215 mmol) in toluene (5 mL). After addition, the mixture was stirred for an additional 1 h. The resultant solid was then removed by filtration and the yellow filtrate concentrated in vacuo. Flash chromatography (ethyl acetate/hexanes, 3:1) provided the corresponding macrolactam (4.2 mg, 61% yield for two steps) as a yellow glass.

A solution of the above macrolactam (4.2 mg, 0.00686 mmol) in methanol (2 mL) was treated with camphorsulfonic acid (3 crystals). The mixture was stirred for 15 minutes and then quenched with TEA (3 drops). After concentration to dryness, the residue was dissolved in ethyl acetate (5 mL), added to silica gel (ca. 0.2 g) and concentrated in vacuo. Flash chromatography (ethyl acetate) provided (+)-**2** (4 mg, 90% yield) as a white glass: $[\alpha]_D^{23}$ +16.1° (*c* 0.13, $CHCl_3$); IR ($CHCl_3$) 3390 (w), 2980 (m), 2940 (m), 2920 (s), 2850 (m), 1670 (s), 1610 (m), 1517 (s), 1372 (m), 1350 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.41 (s, 1 H), 7.90 (s, 1 H), 7.52 (s, 1 H), 6.17-5.90 (m, 4 H), 5.73 (m, 1 H), 5.58 (dd, *J* = 15.2, 7.3 Hz, 1 H), 5.24 (t, *J* = 5.6 Hz, 1 H), 4.97 (d, *J* = 5.8 Hz, 1 H), 4.82 (m, 1 H), 4.81 (d, *J* = 5.8 Hz, 1 H), 4.14 (m, 1 H), 3.78 (m, 1 H), 3.62 (s, 3 H), 3.31 (overlapping s, 5 H), 2.86 (m, 2 H), 2.60 (dt, *J* = 12.4, 4.4 Hz, 1 H), 2.55 (m, 1 H), 2.36 (m, 2 H), 2.11-1.90 (m, 4 H), 1.82 (s, 3 H), 1.84-1.72 (m, 1 H), 0.95 (d, *J* = 7.1 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.0, 150.4, 141.9, 139.6, 138.4, 132.1, 133.7, 133.2, 132.7, 132.6, 131.4, 130.5, 130.3, 129.2, 124.6, 107.3, 100.7, 96.1, 73.4, 70.1, 57.6, 56.6, 39.3, 29.9, 29.7, 29.5, 29.3, 20.3, 14.1, 11.0; high resolution mass spectrum (ES, Na) *m/z* 595.2442 [$(M+Na)^+$; calcd for $C_{30}H_{40}N_2O_7SNa$: 595.2454].

(+)-Thiazinotrienomycin E (1). White powder: $[\alpha]_D^{23}$ +195° (*c* 0.035, CH_3OH); ^1H NMR (500 MHz, d_5-pyridine) δ 11.82 (s, 1 H), 10.83 (s, 1 H), 9.74 (br s, 1 H), 9.10 (d, *J* = 6.1 Hz, 1 H), 7.63 (s, 1 H), 6.56 (dd, *J* = 15.6, 10.1 Hz, 1 H), 6.37 (dd, *J* = 15.0, 10.0 Hz, 1 H), 6.32 (dd, *J* = 15.0, 10.0 Hz, 1 H), 6.20 (dd, *J* = 15.3, 10.1 Hz, 1 H), 5.95 (m, 1 H), 5.75 (dd, *J* = 15.6, 8.9 Hz, 1 H), 5.56 (t, *J* = 4.6, 1 H), 5.41 (m, 1 H), 5.34 (m, 1 H), 5.23 (br s, 1 H), 4.78 (m, 1 H), 4.45 (m, 1 H), 3.60 (d, *J* = 14.6 Hz, 1 H), 3.54 (d, *J* = 14.6 Hz, 1 H), 3.27 (s, 3 H), 3.16 (dd, *J* = 12.2, 4.3 Hz, 1 H), 3.18-3.06 (m, 2 H), 2.95 (m, 1 H), 2.84-2.27 (m, 6 H), 2.03 (s, 3 H), 2.05-1.70 (m, 4 H), 1.58 (d, *J* = 7.3 Hz, 3 H), 1.55-1.17 (m, 6 H), 0.94 (d, *J* = 6.7 Hz, 3 H); ^{13}C NMR (125 MHz, d_5-pyridine) δ 176.9, 173.1, 170.4, 165.9, 143.9, 140.6, 135.2, 134.8, 133.7, 131.6, 131.5, 130.8, 129.9, 129.6, 126.9, 124.2, 117.8, 109.4, 80.8, 75.4, 68.3, 56.2, 49.6, 44.4, 43.7, 39.0, 33.5, 30.7, 30.1, 29.8, 29.2, 27.3, 26.2, 26.1, 26.0, 21.2, 17.3, 10.3; high resolution mass spectrum (ES, Na) *m/z* 732.3293 [$(M+Na)^+$; calcd for $C_{38}H_{51}N_3O_8SNa$: 732.3295]