Supporting Information

for

Angew. Chem. Int. Ed. Z52423

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69451 Weinheim, Germany
Total Synthesis of Microsclerodermin E

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Experimental
$\gamma$-Hydroxyl sulphone 3. To a solution of methyl phenyl sulphone (150 mg, 0.96 mmol) in dry THF (4 mL) stirred under argon at -78 °C, n-butyllithium in hexane (1.6 M, 0.6 mL, 0.96 mmol) was added. The mixture was stirred at -78 °C for 30 min, whereupon it was added BF$_3$Et$_2$O (0.12 mL, 0.96 mmol), followed by a solution of 2 (196 mg, 0.80 mmol) in THF (2 mL). After 1 h at -78 °C, the mixture was allowed to warm to r.t. during 1.5 h, then aq. NH$_4$Cl was added and extracted with EtOAc. The organic phase was dried over Na$_2$SO$_4$ and evaporated and the residue was purified by flash chromatography on silica to give 3 (270 mg, 84%) as a white solid. [$\alpha$]$_D^{25}$ = -9.9 (c 0.8, CHCl$_3$); IR (film) 3550, 3479, 2990, 2932, 2881, 1446, 1370, 1216, 1152, 1068, 841 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J$ = 7.2 Hz, 2H), 7.67 (t, $J$ = 7.2 Hz, 1H), 7.59 (t, $J$ = 7.2 Hz, 2H), 4.15 (dd, $J$ = 8.1, 5.7 Hz, 1H), 4.03-3.93 (m, 2H), 3.86-3.75 (m, 3H), 3.45 (m, 1H), 3.23 (m, 1H), 2.32 (d, $J$ = 9.3 Hz, 1H), 2.02 (m, 1H), 1.39 (s, 6H), 1.37 (s, 3H), 1.34 (s, 3H); EI-MS m/z 385 (M – CH$_3$)$^+$, 327, 299, 281, 267, 241; Anal. Calcd. for C$_{19}$H$_{28}$O$_7$S requires C: 56.98, H: 7.05, found C: 56.94, H: 7.06.

Acetonide 4a. A solution of 3 (8.5 g, 20.5 mmol) in THF (50 mL) and 1 N HCl (50 mL) was stirred for 5 h at 60 °C. The mixture was evaporated in vacuo to afford white solid. To the suspension of the residue in 2,2-dimethoxypropane (40 mL) and acetone (70 mL) was added TsOH (1.0 g, 5.3 mmol). The mixture was stirred overnight at room temperature, and then neutralized with solid Na$_2$CO$_3$ and filtered. The clear filtrate was evaporated in vacuo and the residue was subjected to flash chromatography on silica to give 4a (5.7 g, 67%) as a colorless oil. [$\alpha$]$_D^{25}$ = -21.5 (c 1.1, CHCl$_3$); IR (film) 3541, 3508, 3480, 2992, 2937, 1452, 1372, 1308, 1145, 1068, 880 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J$ = 7.2 Hz, 2H), 7.68 (t, $J$ = 7.2 Hz, 1H), 7.60 (t, $J$ = 7.2 Hz, 2H), 4.13 (m, 1H), 3.99 (m, 3H), 3.86 (m, 2H), 3.36 (m, 1H), 3.23 (m, 1H), 2.28 (d, $J$ = 8.1 Hz, 1H), 2.12 (m, 1H), 1.98 (m, 1H), 1.39 (s, 6H), 1.36 (s, 3H), 1.35 (s, 3H); EI-MS m/z 385 (M – CH$_3$)$^+$, 327, 309, 267, 241, 211, 143, 125, 101; Anal. Calcd. for C$_{19}$H$_{28}$O$_7$S requires C: 56.98, H: 7.05, found C: 56.94, H: 6.81.
Azide 5a. A solution of 4a (5.73 g, 14.3 mol) in dry CH$_2$Cl$_2$ (50 mL) was treated with Et$_3$N (2.6 mL, 18.6 mmol) and MsCl (1.3 mL, 17.3 mmol) successively at 0 °C. The mixture was stirred for 5 h and partitioned between CH$_2$Cl$_2$ (20 mL) and water (50 mL). The aqueous layer was further extracted with dichloromethane and the organic extracts were combined, dried over Na$_2$SO$_4$, evaporated in vacuo, and purified by flash chromatography on silica to give 4b (6.61 g, 97%).

NaN$_3$ (8.0 g, 0.12 mol) was added to a solution of 4b (6.61 g, 13.8 mmol) in DMF (50 mL). The mixture was stirred for 24 h at 120 °C, evaporated in vacuo, and partitioned between water (60 mL) and EtOAc (80 mL). The aqueous layer was separated, and extracted with EtOAc. The organic layers were combined, washed with brine, dried over Na$_2$SO$_4$, evaporated in vacuo, and purified by flash chromatography on silica to give 5a (4.86 g, 83%) as a colorless oil. $[\alpha]_D^{25}$ = -36.3 (c 2.2, CHCl$_3$); IR (film) 2989, 2937, 2114, 1448, 1373, 1309, 1258, 1216, 1152, 1068, 865 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J$ = 7.2 Hz, 2H), 7.68 (m, 1H), 7.59 (m, 2H), 4.21 (t, $J$ = 6.1 Hz, 1H), 4.08 (dd, $J$ = 8.7, 6.5 Hz, 1H), 4.00 (m, 1H), 3.90 (dd, $J$ = 8.7, 6.6 Hz, 1H), 3.57 (t, $J$ = 7.6 Hz, 1H), 3.39-3.22 (m, 3H), 2.30-2.22 (m, 1H), 1.97-1.89 (m, 1H), 1.44 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H), 1.31 (s, 3H); EI-MS m/z 410 (M – CH$_3$)$^+$, 382, 352, 269, 211, 101; Anal. Calcd. for C$_{19}$H$_{27}$N$_3$O$_6$S requires C: 53.63, H: 6.40, N: 9.88, found C: 53.50, H: 6.45, N: 10.09.

Amide 5b. A suspension of 10% Pd/C (300 mg) in a solution of 5a (4.86 g, 11.4 mmol) in methanol (50 mL) was stirred under H$_2$ (30 atm) at room temperature for 24 h. The mixture was filtered, and the filtrate was evaporated in vacuo. The residue was purified by flash chromatography on silica to give the free amine 2.83 g.
A solution of the above amine (2.83 g, 6.85 mmol) in dry CH₂Cl₂ (30 mL) was treated with pyridine (0.68 mL, 8.5 mmol) and trifluoroacetic anhydride (1.1 mL, 7.8 mmol) successively at 0 °C. The mixture was stirred for 2 h and partitioned between CH₂Cl₂ (20 mL) and water (30 mL). The aqueous layer was further extracted with dichloromethane and the organic extracts were combined, dried over Na₂SO₄, evaporated in vacuo, and purified by flash chromatography on silica to give 5b (3.51 g, 62%) as a white solid. [α]₀D₂⁵ = -25.8 (c 1.3, CHCl₃); IR (KBr) 3402, 2999, 2984, 2962, 2883, 1718, 1544, 1309, 1212, 1171, 1073 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.91 (d, J = 8.0 Hz, 2H), 7.67 (t, J = 7.5 Hz, 1H), 7.57 (t, J = 7.5 Hz, 2H), 6.64 (d, J = 9.6 Hz, 1H), 4.52 (t, J = 6.8 Hz, 1H), 4.12-4.05 (m, 2H), 3.97 (td, J = 8.0, 2.8 Hz, 1H), 3.75 (dd, J = 8.6, 7.3 Hz, 1H), 3.55 (dd, J = 8.8, 6.5 Hz, 1H), 3.35-3.29 (m, 1H), 3.20-3.14 (m, 1H), 2.04 (m, 2H), 1.45 (s, 3H), 1.36 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 158.0, 157.5, 138.8, 133.8, 129.3, 127.8, 109.8, 109.6, 79.1, 77.0, 73.1, 66.1, 52.74, 52.71, 27.1, 26.9, 26.7, 25.9, 24.4; El-MS m/z 480 (M – CH₃)+, 422, 380, 362, 336, 269, 211; Anal. Calcd. for C₂₁H₂₈NO₇F₃S requires C: 50.90, H: 5.70, N: 2.83, found C: 50.99, H: 5.55, N: 2.84.

**Julia olefination of 5b.** To a solution of 5b (5.15 g, 10.4 mmol) in dry THF (70 mL) stirred under argon at -78 °C, n-butyllithium in hexane (1.6 M, 14.3 mL, 22.9 mmol) was added. The mixture was stirred at -78 °C for 2 h, whereupon it was added a solution of 6 (4.03 g, 22.9 mmol) in THF (20 mL). After 20 min at -78 °C, aq. NH₄Cl (30 mL) was added and extracted with EtOAc. The organic phase was dried over Na₂SO₄, evaporated in vacuo and the residue was purified by flash chromatography on silica to give crude coupling product (6.96 g, 100%).

A solution of the above product (6.96 g, 10.4 mol) in dry CH₂Cl₂ (100 mL) was treated with Et₃N (3.6 mL, 26.0 mmol), DMAP (65 mg, 0.53 mmol) and PhCOCl (2.4 mL, 20.8 mmol) successively at room temperature. The mixture was stirred for 24 h and partitioned between CH₂Cl₂ (50 mL) and water (100 mL). The aqueous layer was further extracted with dichloromethane and the organic extracts were combined, washed with brine, dried over Na₂SO₄, evaporated in vacuo, and purified by flash chromatography on silica to
give acylation product (8.06 g, 100%).

A suspension of Na(Hg) (20.0 g, 52 mmol) in a solution of the above product (8.06 g, 10.4 mmol) in 120 mL of EtOAc/MeOH (1:2) was stirred at -20 °C for 4 h. The reaction was filtered through a plug of Celite, the plug was washed with EtOAc, and the filtrates were combined and evaporated in vacuo. The residue was partitioned between EtOAc (100 mL) and water (70 mL). The aqueous layer was further extracted with EtOAc and the organic extracts were combined, washed with brine, dried over Na₂SO₄, evaporated in vacuo, and purified by flash chromatography on silica to give 7 (4.26 g, 80%) as a pale yellow solid. [α]D⁰²⁵ = -37.8 (c 1.1, CHCl₃); IR (KBr) 3359, 1716, 1606, 1546, 1510 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.30 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.5 Hz, 2H), 6.66-6.54 (m, 2H), 6.43 (d, J = 15.7 Hz, 1H), 6.22 (dd, J = 15.3, 10.3 Hz, 1H), 5.75-5.70 (m, 1H), 4.57 (t, J = 6.8 Hz, 1H), 4.13-4.00 (m, 5H), 3.81 (m, 1H), 3.56 (dd, J = 8.0, 6.7 Hz, 1H), 2.40 (m, 2H), 1.46-1.33 (m, 15H); ¹³C NMR (75 MHz, CDCl₃) δ 158.5, 133.8, 133.4, 131.7, 131.2, 129.9, 127.7, 127.6, 127.4, 126.4, 124.7, 121.4, 114.5, 109.8, 109.5, 78.9, 78.8, 73.2, 66.2, 63.4, 52.9, 37.5, 32.3, 27.3, 26.0, 24.5, 14.8; EI-MS m/z 513 (M⁺), 498, 440, 414, 340, 282, 268; HRMS Calcd. for C₂₆H₃₄F₃NO₆Na (M + Na)⁺ requires 536.22359, found 536.22304.

Amide 8a. PPTs (1.51 g, 6.00 mmol) was added to a solution of 7 (2.05 g, 4.00 mmol) in dry methanol (20 mL). The mixture was stirred at 45 °C for 10 h, allowed to cool and neutralized with aqueous NaHCO₃. The methanol was removed in vacuo and the
residue was extracted with EtOAc and the organic extracts were combined, washed with brine, dried over Na₂SO₄, evaporated in vacuo, and purified by flash chromatography on silica to give the diol (1.27g, 87%), along with the recovered 7 (476 mg). [α]D²⁵ = -24.6 (c 1.2, CHCl₃); IR (film) 3411, 2986, 2935, 1718, 1608, 1512, 1245, 1214, 1176, 1049 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.31 (d, J = 8.7 Hz, 2H), 7.01 (d, J = 15.6 Hz, 1H), 6.84 (d, J = 8.7 Hz, 2H), 6.63 (dd, J = 15.6, 10.2 Hz, 1H), 6.45 (d, J = 15.6 Hz, 1H), 6.27 (dd, J = 15.4, 10.6 Hz, 1H), 5.75 (m, 1H), 4.24-3.90 (m, 6H), 3.57 (m, 2H), 3.02 (s, 1H), 2.46 (m, 2H), 2.08 (s, 1H), 1.45-1.34 (m, 15H); ESI-MS m/z 496 (M + Na)+, 474 (M + H)+; HRMS Calcd. for C₂₃H₃₀F₃NO₆Na (M + Na)+ requires 496.19174, found 496.19312.

A solution of the above diol (1.27 g, 2.68 mmol) in dry DMF (10 mL) was treated with imidazole (200 mg, 2.95 mmol) and TBSCl (408 mg, 2.70 mmol) at 0°C. The mixture was stirred overnight and evaporated in vacuo. The residue was partitioned between EtOAc (20 mL) and water (20 mL). The organic layer was washed with brine, dried over Na₂SO₄, evaporated in vacuo, and purified by flash chromatography on silica to give silyl ether (1.44 g, 91%). [α]D²⁵ = -30.3 (c 1.1, CHCl₃); IR (film) 3416, 1728, 1605, 1511, 1252, 1174 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.30 (d, J = 8.7 Hz, 2H), 7.02 (d, J = 9.2 Hz, 1H), 6.84 (d, J = 8.7 Hz, 2H), 6.62 (dd, J = 15.6, 10.5 Hz, 1H), 6.43 (d, J = 15.6 Hz, 1H), 6.22 (dd, J = 15.3, 10.5 Hz, 1H), 5.76 (m, 1H), 4.20-3.92 (m, 9H), 3.55 (d, J = 7.0 Hz, 2H), 2.95 (d, J = 3.0 Hz, 1H), 2.44 (m, 2H), 1.43 (s, 6H), 1.26 (t, J = 7.1 Hz, 3H), 0.88 (s, 9H), 0.06 (s, 6H); ESI-MS m/z 610 (M + Na)+, 605 (M + NH₄)+, 588 (M + H)+; HRMS Calcd. for C₂₉H₄₄F₃NO₆SiNa (M + Na)+ requires 610.27822, found 610.27864.

A solution of the above silyl ether (1.44 g, 2.45 mmol) in dry CH₂Cl₂ (15 mL) was treated with DIEA (0.98 mL, 5.64 mmol) and MOMCl (0.37 mL, 4.90 mmol) successively. The mixture was stirred overnight at room temperature and diluted with water (10 mL). The organic layer was separated, washed with brine, dried over Na₂SO₄, evaporated in vacuo, and purified by flash chromatography on silica to give the MOM ether (1.54 g, 99%). [α]D²⁵ = -15.8 (c 1.1, CHCl₃); IR (film) 2687, 1730, 1512, 1251, 1173, 1035, 838, 779 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.30 (d, J = 8.4 Hz, 2H), 6.84 (d, J = 8.4 Hz, 2H), 6.65 (d, J = 9.9 Hz, 1H), 6.62 (dd, J = 15.6, 10.2 Hz, 1H), 6.42 (d, J = 15.6 Hz, 1H), 6.19 (dd, J = 15.3, 10.2 Hz, 1H), 5.76 (m, 1H), 4.74 (m, 2H), 4.36 (m, 1H), 4.15 (m, 2H), 4.05 (q, J = 7.0 Hz, 2H), 3.76 (m, 1H), 3.68 (dd, J = 9.9, 5.7 Hz, 1H), 3.39 (s, 3H), 3.37 (m, 1H), 2.37 (m, 2H), 1.42 (s, 9H), 0.88 (s, 9H), 0.04 (s, 6H); ESI-MS m/z 654 (M + Na)+, 649 (M + NH₄)+, 632 (M + H)+; HRMS Calcd. for C₃₁H₄₄F₃NO₇SiNa (M + Na)+ requires 654.30444, found 654.3044.
To a solution of the above ether (804 mg, 1.27 mmol) in THF (5 mL) was added a solution of TBAF in THF (1.0 M, 1.5 mL, 1.50 mmol). The reaction was stirred for 2 h and partitioned between EtOAc (10 mL) and water (10 mL). The organic layer was dried over Na$_2$SO$_4$, evaporated in vacuo, and purified by flash chromatography on silica to give 8a (656 mg, 100%) as a pale yellow solid. [$\alpha$]$_{D}^{25}$ = -9.4 (c 1.05, CHCl$_3$); IR (film) 3504, 3300, 1702, 1510, 1252, 1180 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.32 (d, $J$ = 8.7 Hz, 2H), 6.86 (d, $J$ = 8.7 Hz, 2H), 6.64 (dd, $J$ = 15.3, 10.3 Hz, 1H), 6.61 (d, $J$ = 10.5 Hz, 1H), 6.45 (d, $J$ = 15.3 Hz, 1H), 6.22 (dd, $J$ = 15.3, 10.2 Hz, 1H), 5.73 (m, 1H), 4.77 (m, 2H), 4.20 (t, $J$ = 9.3 Hz, 1H), 4.09 (m, 2H), 3.84 (q, $J$ = 6.9 Hz, 2H), 3.78 (dd, $J$ = 9.0, 6.9 Hz, 1H), 3.64 (m, 1H), 3.55 (m, 1H), 3.44 (s, 3H), 2.84 (m, 1H), 2.41 (m, 2H), 1.44 (t, $J$ = 6.9 Hz, 3H), 1.43 (s, 6H); EI-MS $m/z$ 517 (M$^+$), 272, 240, 210, 187; HRMS Calcd. for C$_{25}$H$_{34}$F$_3$NO$_7$Na (M + Na$^+$) requires 540.21851, found 540.21796.

**Amine 8b.** NaBH$_4$ (73 mg, 1.93 mmol) was added to a solution of 8a (333 mg, 0.64 mmol) in dry ethanol (3 mL). The mixture was stirred for 6 h and diluted with water (1 mL). The ethanol was removed in vacuo and the residue was partitioned between EtOAc (10 mL) and water (5 mL). The aqueous layer was further extracted with EtOAc. The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, evaporated in vacuo to give 8b (270 mg, 100%) without further purification.
**Dipeptide 11a.** NaOH (287 mg, 7.20 mmol) was added in one portion to a stirred solution of the ester 10 (981 mg, 3.60 mmol) in CH₂OH/H₂O (4 : 1) (10 mL) at room temperature. The solution was stirred overnight and then acidified to pH 6 with 1 N HCl. After methanol was removed in vacuo, the residue was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, evaporated in vacuo to give crude acid.

A solution of the above acid in dry CH₂Cl₂ (10 mL) was treated with HOSu (538 mg, 4.7 mmol) and EDCI (760 mg, 4.0 mmol) at room temperature. The mixture was stirred overnight and evaporated in vacuo. The residue was partitioned between EtOAc (10 mL) and water (10 mL). The organic layer was washed with brine, dried over Na₂SO₄, evaporated in vacuo, and purified by flash chromatography on silica to give activated ester (1.27 g, 99%). [α]D²⁵ = -7.3 (c 2.4, CHCl₃); IR (KBr) 2931, 2859, 2107, 1787, 1742, 1203, 1067, 838, 779 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 4.33 (m, 1H), 3.48 (dd, J = 12.8, 4.5 Hz, 1H), 3.35 (dd, J = 12.8, 5.0 Hz, 1H), 2.90 (m, 2H), 2.87 (s, 4H), 0.93 (s, 9H), 0.17 (s, 6H). ESI-MS m/z 379 (M + Na)⁺, 374 (M + NH₄)⁺, 357 (M + H)⁺; HRMS Calcd. for C₁₄H₂₄N₄O₅SiNa (M + Na)⁺ requires 379.14082, found 379.14242.

A solution of the above activated ester (252 mg, 0.71 mmol) and 8b (270 mg, 0.64 mmol) in ethyl acetate was added solid NaHCO₃ (108 mg, 1.29 mmol) and then refluxed for 6 h. The mixture was allowed to cool, evaporated in vacuo and the residue was purified by flash chromatography on silica to give 11a (415 mg, 96%) as a pale yellow oil. [α]D²⁵ = -8.0 (c 0.6, CHCl₃); IR (film) 3347, 2105, 1655, 1606, 1511, 1252, 1101 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.31 (d, J = 8.7 Hz, 1H), 6.84 (d, J = 8.7 Hz, 1H), 6.64 (dd, J = 15.6, 10.3 Hz, 1H), 6.44 (d, J = 15.6 Hz, 1H), 6.24 (dd, J = 15.3, 10.3 Hz, 1H), 6.10 (d, J = 9.8 Hz, 1H), 5.78 (m, 1H), 4.75 (d, J = 6.7 Hz, 1H), 4.67 (d, J = 6.7 Hz, 1H), 4.25 (m, 2H), 4.07 (m, 4H), 3.70 (m, 2H), 3.38 (m, 3H), 3.28 (m, 1H), 2.59-2.41 (m, 4H), 1.41 (t, J = 7.0 Hz, 3H), 1.40 (s, 6H), 0.92 (s, 9H), 0.15 (s, 3H), 0.13 (s, 3H); ESI-MS m/z 685 (M + Na)⁺, 663 (M + H)⁺; HRMS Calcd. for C₃₃H₅₄N₄O₈SiNa (M + Na)⁺ requires 685.36031, found 685.36048.
Activated ester 11b. To a solution of 11a (2.00 g, 3.02 mmol) in dry CH₂Cl₂ (20 mL) was added Dess-Martin reagent (1.50 g, 3.56 mmol) at 0 °C. The mixture was stirred for 2 h before diluted with saturated Na₂S₂O₃ (10 mL). The organic layer was washed with 5% NaHCO₃ (5 mL) and brine, dried over Na₂SO₄, evaporated in vacuo and purified by flash chromatography on silica to give the aldehyde, which was dissolved in 1-butyl alcohol (15 mL) and water (6 mL). After the resultant solution was added resorcinol (664 mg, 6.04 mmol), NaH₂PO₄ (1.88 g, 12.08 mmol) and sodium chlorite (80%, 510 mg, 4.53 mmol) at 0 °C, it was stirred for 2 h and then partitioned between EtOAc (50 mL) and water (20 mL). The aqueous layer was further extracted with EtOAc and the combined organic layers were washed with brine, dried (Na₂SO₄), evaporated in vacuo and purified by flash chromatography on silica to give the acid (1.51 g, 74%).

A solution of the resulting acid (1.51 g, 2.23 mmol) in dry CH₂Cl₂ (10 mL) was treated with HOSu (308 mg, 2.68 mmol) and EDCI (470 mg, 2.45 mmol) at room temperature. The mixture was stirred overnight and evaporated in vacuo. The residue was partitioned between EtOAc (20 mL) and water (20 mL). The organic layer was washed with brine, dried over Na₂SO₄, evaporated in vacuo, and purified by flash chromatography on silica to give 11b (1.47 g, 85%) as a pale yellow solid. [α]D²⁵ = -16.8 (c 1.1, CHCl₃); IR (KBr) 3342, 2931, 2858, 2106, 1744, 1682, 1511, 1251, 1205, 1046, 780 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.30 (d, J = 8.4 Hz, 2H), 6.91 (d, J = 9.9 Hz, 1H), 6.84 (d, J = 8.4 Hz, 2H), 6.62 (dd, J = 15.9, 10.8 Hz, 1H), 6.41 (dd, J = 15.9 Hz, 1H), 6.22 (dd, J = 14.7, 10.8 Hz, 1H), 5.75 (m, 1H), 5.05 (s, 1H), 4.77 (m, 3H), 4.28 (m, 1H), 4.14 (m, 1H), 4.03 (q, J = 6.9 Hz, 2H), 3.69 (dd, J = 9.6, 6.9 Hz, 1H), 3.42 (s, 3H), 3.35 (m, 2H), 2.82 (s, 4H), 2.60 (dd, J = 16.2, 6.0 Hz, 1H), 2.44 (m, 1H), 2.41 (m, 1H), 2.29 (m, 1H), 1.45 (s, 3H), 1.41 (s, 3H), 1.40 (t, J = 6.9 Hz, 3H), 0.95 (s, 9H), 0.18 (s, 3H), 0.14 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 169.5, 168.3, 166.6, 158.4, 133.5, 130.8, 130.0, 128.2, 127.7, 127.4, 126.7, 114.6, 109.2, 96.6, 79.1, 78.1, 72.1, 68.5, 63.4, 56.6, 56.5, 55.5, 53.6, 41.1, 37.3, 27.4, 27.1, 25.7, 25.5, 17.9, 14.8, -4.8, -5.0; ESI-MS m/z 796 (M + Na)⁺, 774 (M + H)⁺; HRMS Calcd. for C₃₇H₅₅N₅O₁₁SiNa (M + Na)⁺ requires 796.35596 found 796.35368.

Keto ester 15. To a solution of trimethylsilyl ethyl acetate (918 mg, 5.74 mmol) in dry THF (3 mL) stirred under argon at -78 °C, LDA in THF (1.0 M, 5.74 mL, 5.74 mmol)
was added. The mixture was stirred at -78 °C for 1 h, whereupon it was added a solution of 14 (1.00 g, 2.87 mmol) in THF (5 mL). After 30 min at -78 °C, the mixture was added HOAc (0.5 mL, 8.61 mmol) and allowed to warm to rt. The mixture was partitioned between EtOAc (20 mL) and water (20 mL). The organic phase was dried over Na₂SO₄ and evaporated and the residue was purified by flash chromatography on silica to give 15 (1.06 g, 80%) as a colorless oil. [α]D²⁵ = +35.9 (c 1.7, CHCl₃); IR (film) 3367, 2956, 1719, 1500, 1251, 1168, 1053, 981, 861, 838, 753 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.36 (s, 5H), 5.67 (d, J = 9.0 Hz, 1H), 5.14 (s, 2H), 4.61 (m, 1H), 4.23 (m, 2H), 3.62 (s, 2H), 3.08 (dd, J = 17.4, 5.4 Hz, 1H), 2.83 (dd, J = 17.4, 4.8 Hz, 1H), 1.45 (s, 9H), 1.03 (m, 2H), 0.06 (s, 9H); EI-MS m/z 466 (M + H)+, 428, 410, 382, 338, 322, 278, 222, 178, 91, 57.

Pyrrolidinone 16. A suspension of 10% Pd/C (150 mg) in a solution of 15 (1.91 g, 4.12 mmol) in EtOAc (20 mL) was stirred under H₂ (1 atm) at room temperature for 3 h. The mixture was filtered, and the filtrate was evaporated in vacuo to give the crude acid, which was dissolved in dry THF (15 mL). To this solution NMM (0.56 mL, 5.08 mmol) and ClCO₂iBu (0.61 mL, 4.66 mmol) were added at 0 °C under argon. After 30 min, the mixture was added aqueous ammonia (5 mL) and stirred for another 30 min before diluted with 10 mL of water. The aqueous layer was extracted with ether and the combined organic layers were washed with brine, dried over Na₂SO₄ and evaporated in vacuo. The resulting hydroxypyrrolidinone was then dissolved in dry CH₂Cl₂ (15 mL) and treated with Et₃N (1.5 mL, 10.58 mmol) and MsCl (0.40 mL, 5.08 mmol) at 0 °C. The mixture was stirred for 4 h and then diluted with water (10 mL). The organic layer was washed with brine, dried over Na₂SO₄, evaporated in vacuo, and purified by flash chromatography on silica to give 16 (1.18 g, 81%) as a white solid. [α]D²⁵ = +58.9 (c 1.05, CHCl₃); IR (KBr) 3409, 3272, 2956, 1750, 1684, 1545, 1265, 1217, 1170, 1064, 867 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 9.76 (s, 1H), 5.19 (s, 1H), 4.98 (m, 2H), 4.23 (t, J = 8.7 Hz, 2H), 2.94 (dd, J = 21.0, 7.5 Hz, 1H), 2.42 (dd, J = 21.0, 4.8 Hz, 1H), 1.48 (s, 9H), 1.02 (t, J = 8.7 Hz, 2H), 0.07 (s, 9H); EI-MS m/z 356 (M⁺), 300, 272, 257, 228, 213, 195, 183, 139, 73; Anal. Calcd. for C₁₆H₃₀N₂O₅Si (M + H₂O) requires C: 51.31, H: 8.07, N: 7.48, found C: 51.27, H: 8.09, N: 7.39; HRMS Calcd. for C₁₆H₂₈N₂O₅Si requires 356.17675 found 356.17358.
**Activated ester 17.** To a solution of 16 (201 mg, 0.56 mmol) and TsOH (215 mg, 1.13 mmol) in THF (0.5 mL) was added TBAF in THF (1 M, 3.4 mL, 3.4 mmol) at room temperature. The mixture was stirred for 24 h and evaporated in vacuo. The residue was purified by flash chromatography on silica to give the crude acid (119 mg, 82%) as a white solid. This acid (119 mg, 0.46 mmol) was dissolved in dry CH$_2$Cl$_2$ (3 mL) and treated with C$_6$F$_5$OH (93 mg, 0.51 mmol) and EDCI (98 mg, 0.51 mmol). The mixture was stirred overnight and evaporated in vacuo. The residue was purified by flash chromatography on silica to give 17 (175 mg, 89%) as a white solid. IR (KBr) 3381, 3342, 3252, 2984, 1693, 1663, 1523, 1174, 1122, 1008, 994 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 9.54 (s, 1H), 5.51 (s, 1H), 5.06 (m, 2H), 3.01 (dd, $J$ = 17.4, 7.8 Hz, 1H), 2.51 (dd, $J$ = 17.4, 5.7 Hz, 1H), 1.49 (s, 9H); ESI-MS $m/z$ 445 (M + Na)$^+$; Anal. Calcd. for C$_{17}$H$_{15}$F$_5$N$_2$O$_5$ requires C: 48.35, H: 3.58, N: 6.63, found C: 48.02, H: 3.44, N: 6.38.

**Amino ester 19.** A solution of 18 (21.2 g, 53.3 mmol) in dry THF (150 mL) stirred under argon at -78°C was treated with Et$_3$N (8.9 mL, 64.0 mmol) and t-BuOCl (7.7 mL, 64.0 mmol). After stirred for 1 h, the mixture was added TMSCN (10.6 mL, 80.0 mmol), followed by BF$_3$Et$_2$O (10.1 mL, 80 mmol). The reaction was allowed to warm to rt, stirred overnight and then diluted with 5% NaHCO$_3$ (100 mL). The aqueous layer was extracted with EtOAc, and the combined organic layers were washed with brine, dried (Na$_2$SO$_4$), evaporated in vacuo, and purified by flash chromatography on silica to give 19 (20.0 g, 89%) as a pale yellow oil. $[\alpha]_D^{25}$ = +157.1 (c 0.7, CHCl$_3$); IR (film) 3326, 3030, 2223, 1733, 1495, 1454, 1245, 1173, 745, 699 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.47 (s, 1H), 7.38-7.20 (m, 12H), 6.96 (d, $J$ = 3.1 Hz, 2H), 4.00 (d, $J$ = 13.7 Hz, 2H), 3.85 (dd, $J$ = 8.8, 6.1 Hz, 1H), 3.74 (s, 3H), 3.57 (d, $J$ = 13.7 Hz, 2H), 3.51 (dd, $J$ = 14.2, 8.8 Hz, 1H), 3.23 (dd, $J$ = 14.2, 6.1 Hz, 1H); EI-MS $m/z$ 424 (M + H)$^+$, 364 (M – CO$_2$Me)$^+$, 268, 181, 155, 91.
Diester 20. To a solution of 19 (2.15 g, 5.1 mmol) in methanol (30 mL) was added 6 N KOH (10 mL). The solution was heated to reflux for 24 h, allowed to cool and then acidified to pH 3 with 6 N HCl. The methanol was evaporated in vacuo, and the residue was extracted with CHCl₃. The combined organic layers were dried (Na₂SO₄), evaporated in vacuo to give the dicarboxylic acid, which was dissolved in dry DMF (20 mL). To this solution were added KHCO₃ (1.8 g, 18.0 mmol) and CH₃I (2.6 g, 18.0 mmol). The mixture was stirred overnight and then evaporated in vacuo. The residue was partitioned between EtOAc (50 mL) and water (50 mL). The organic layer was washed with brine, dried over Na₂SO₄, evaporated in vacuo and purified by flash chromatography on silica to give 20 (1.65 g, 71%) as a white solid. [α]D²⁵ = +121.6 (c 1.2, CHCl₃); IR (KBr) 3344, 2951, 1727, 1684, 1456, 1257, 740, 698 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 8.76 (s, 1H), 7.41-7.30 (m, 3H), 7.14-6.95 (m, 1H), 4.02 (d, J = 14.0 Hz, 2H), 3.95 (dd, J = 8.9, 6.6 Hz, 1H), 3.71 (s, 3H), 3.64 (dd, J = 14.0, 6.6 Hz, 1H); EI-MS m/z 456 (M⁺), 397, 306, 268, 181, 156, 128, 91; Anal. Calcd. for C₂₈H₂₈N₂O₄ requires C: 73.66, H: 6.18, N: 6.14, found C: 73.98, H: 5.99, N: 6.08.

Tripeptide 21. A suspension of Pd(OH)₂ (100 mg) in a solution of 20 (850 mg, 1.86 mmol) in methanol (10 mL) was stirred under H₂ (40 atm) at room temperature for 24 h. The mixture was filtered, and the filtrate was evaporated in vacuo. The residue was purified by flash chromatography on silica to give the free amine (361 mg, 70%).

A solution of the above amine (361 mg, 1.31 mmol) and Boc-N-Me-Gly-OH (297 mg, 1.57 mmol) in 5.0 mL of dry CH₂Cl₂ was treated with DIEA (0.46 mL, 2.62 mmol),
HOBt (212 mg, 1.57 mmol), and EDCI (301 mg, 1.57 mmol) at 0 °C. The mixture was stirred for overnight at r.t. and evaporated in vacuo. The residue was partitioned between EtOAc (10 mL) and water (10 mL). The organic layer was washed with brine, dried over Na₂SO₄, evaporated in vacuo and purified by flash chromatography on silica to give the dipeptide (564 mg, 96%) as a colorless solid. [α]D²⁵ = -21.6 (c 1.0, CHCl₃); IR (KBr) 3335, 2954, 1745, 1702, 1549, 1450, 1251, 1151, 1099 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 8.90 (s, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.36 (m, 2H), 7.19 (t, J = 8.1 Hz, 1H), 7.07 (br s, 1H), 4.81 (m, 1H), 4.01 (s, 3H), 3.81 (m, 1H), 3.69 (s, 3H), 3.61 (m, 3H), 2.78 (s, 3H), 1.40 (s, 9H); EI-MS m/z 447 (M⁺), 374, 347, 304, 288, 259; HRMS Calcd. for C₂₂H₂₉N₃O₇Na (M + Na)⁺ requires 470.19032, found 470.18977.

A solution of the above dipeptide (1.40 g, 3.13 mmol) in methanol (16 mL) was treated with 1 N LiOH (4.1 mL, 4.1 mmol) at 0 °C. The mixture was stirred overnight, and acidified to pH 5 with 1 N HCl. The methanol was removed in vacuo and the residue was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, evaporated in vacuo to give the crude acid, which was dissolved in 20 mL of dry CH₂Cl₂. To this solution were added H-Gly-OTMSE (657 mg, 3.75 mmol), DIEA (1.1 mL, 6.26 mmol), HOBt (506 mg, 3.75 mmol), and EDCI (720 mg, 3.75 mmol) at 0 °C, respectively. The mixture was stirred for overnight at r.t. and evaporated in vacuo. The residue was partitioned between EtOAc (30 mL) and water (20 mL). The organic layer was washed with brine, dried over Na₂SO₄, evaporated in vacuo and purified by flash chromatography on silica to give 21 (1.63 g, 88%) as a colorless solid. [α]D²⁵ = +14.0 (c 0.8, CHCl₃); IR (KBr) 3327, 3062, 2955, 1700, 1656, 1545, 1251, 1178, 1151 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 9.13 (s, 1H), 7.66 (d, J = 7.5 Hz, 1H), 7.28 (m, 2H), 7.09 (t, J = 7.5 Hz, 1H), 7.06 (s, 1H), 6.88 (s, 1H), 4.77 (dd, J = 14.7, 7.5 Hz, 1H), 4.10 (t, J = 8.4 Hz, 2H), 3.98 (s, 3H), 3.87 (m, 2H), 3.84 (d, J = 16.5 Hz, 1H), 3.66 (d, J = 16.5 Hz, 1H), 3.52 (m, 2H), 2.76 (s, 3H), 1.42 (s, 9H), 0.93 (t, J = 8.4 Hz, 2H), 0.00 (s, 9H); ESI-MS m/z 613 (M + Na)⁺, 591 (M + H)⁺; HRMS Calcd. for C₂₈H₄₂N₄O₈SiNa (M + Na)⁺ requires 613.26641, found 613.26521.
Tetrapeptide 22. A solution of 21 (200 mg, 0.34 mmol) in dry CH₂Cl₂ (2.5 mL) was treated with CF₃CO₂H (0.5 mL) at 0 °C. The mixture was stirred for 2.5 h and then evaporated in vacuo to give the amine salt, which was dissolved in 2 mL of dry DMF. To this solution were added 17 (156 mg, 0.37 mmol) and NaHCO₃ (143 mg, 1.70 mmol). The reaction mixture was stirred for 10 h at 40 °C, evaporated in vacuo, and purified by flash chromatography on silica to give 22 (199 mg, 81%) as a white solid. [α]D²⁵ = +28.6 (c 0.9, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 10.47 (s, 1H), 9.40 (s, 1H), 7.71 (t, J = 7.8 Hz, 1H), 7.33 (m, 2H), 7.14 (t, J = 5.4 Hz, 1H), 6.98 (s, 1H), 6.82 (s, 1H), 5.37 (s, 1H), 5.20 (d, J = 9.0 Hz, 1H), 4.93 (m, 1H), 4.71 (m, 1H), 4.22 (m, 2H), 4.01 (s, 3H), 3.96 (m, 2H), 3.87 (m, 1H), 3.64 (m, 2H), 3.55 (m, 1H), 2.89 (m, 3H), 2.70 (m, 1H), 2.37 (m, 1H), 1.48 (s, 9H), 1.00 (m, 2H), 0.06 (s, 9H); ESI-MS m/z 767 (M + K)⁺, 751 (M + Na)⁺, 729 (M + H)⁺; HRMS Calcd. for C₃₄H₄₈N₆O₁₀SiNa (M + Na)⁺ requires 751.31245, found 751.30934.

Coupling tetrapeptide 22 with dipeptide 11b. A solution of 22 (180 mg, 0.25 mmol) in dry CH₂Cl₂ (3.0 mL) was treated with CF₃CO₂H (0.6 mL) at 0 °C. The mixture was stirred for 2.5 h and then evaporated in vacuo at 0 °C to give the amine salt, which was dissolved in 4 mL of dry CH₃CN. To this solution were added 11b (160 mg, 0.21 mmol) and NaHCO₃ (83 mg, 0.99 mmol). The reaction mixture was stirred for 10 h at 70 °C, evaporated in vacuo, and purified by flash chromatography on silica to give 23 (224 mg, 84%) as a pale yellow solid. ¹H NMR (300 MHz, CDCl₃) δ 10.58 (s, 1H), 9.40 (s, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.49 (m, 1H), 7.40-7.24 (m, 4H), 7.12 (m, 3H), 6.94 (m, 1H), 6.84 (m, 2H), 6.57 (m, 1H), 6.39 (m, 1H), 6.23 (m, 1H), 5.72 (m, 1H), 5.43 (s, 1H), 5.17 (m, 1H), 4.50 (s, 1H), 4.36 (s, 1H), 4.13 (s, 1H), 3.93 (s, 1H), 3.69 (s, 1H), 3.57 (s, 1H), 3.54 (s, 1H), 2.88 (s, 1H), 2.72 (s, 1H), 2.59 (s, 1H), 2.49 (s, 1H), 2.45 (s, 1H), 2.38 (s, 1H), 2.13 (s, 1H), 1.90 (s, 1H), 1.48 (s, 9H), 1.00 (s, 9H), 0.05 (s, 9H).
5.04 (m, 1H), 4.85-4.65 (m, 4H), 4.51 (m, 1H), 4.28-4.20 (m, 3H), 4.17-3.93 (m, 9H), 3.76-3.57 (m, 3H), 3.42 (s, 3H), 3.29 (m, 2H), 2.89 (s, 3H), 2.52 (m, 2H), 2.38 (m, 3H), 2.02 (m, 1H), 1.45-1.37 (m, 9H), 1.03 (m, 2H), 0.95 (m, 9H), 0.18-0.05 (m, 15H);

ESI-MS m/z 1287 (M + H)$^+$, 1305 (M + NH$_4$)$^+$, 1309 (M + Na)$^+$; HRMS Calcd. for C$_{62}$H$_{90}$N$_{10}$O$_{16}$Si$_{2}$Na (M + Na)$^+$ requires 1309.59670, found 1309.59451.

**Lactam 24.** A solution of 23 (200 mg, 0.156 mmol) in THF (1.0 mL) was treated with TsOH (59 mg, 0.312 mmol) and TBAF in THF (1 M, 0.94 mL) at room temperature. The mixture was stirred for 24 h, diluted with CHCl$_3$ (10 mL) and washed with water. The organic phase was dried over Na$_2$SO$_4$ and evaporated in vacuo. The resultant acid was dissolved in THF (3 mL) and treated with Me$_3$P in THF (1 M, 1.6 mL, 1.6 mmol) under argon. After 2 h, water (100 µL) was added and the mixture was stirred overnight, and evaporated in vacuo. Toluene (2 mL) was added to the residue and evaporated in vacuo to remove the remaining water. The residue was dissolved in dry DMF (100 mL), cooled at 0°C and treated with NaHCO$_3$ (131 mg, 1.56 mmol) and DPPA (215 mg, 0.78 mmol) under argon. The mixture was stirred for 3 days at 0°C, allowed to warm to rt and stirred for 10 days. The solvent was evaporated in vacuo, and the residue was partitioned between EtOAc (10 mL) and water (5 mL). The organic phase was washed with brine, dried over Na$_2$SO$_4$, evaporated in vacuo, and purified by flash chromatography on silica to give 24 (63.2 mg, 40%) as a colorless solid and its isomer (15.1 mg, 9%). 24: [α]$_D^{25}$ = -73.2 (c 1.6, CHCl$_3$); $^1$H NMR (300 MHz, CDCl$_3$) δ 10.33 (s, 1H), 9.01 (s, 1H), 8.72 (s, 1H), 7.92 (m, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.56 (m, 2H), 7.41 (m, 2H), 7.30 (d, J = 6.9 Hz, 2H), 7.16 (m, 2H), 6.82 (d, J = 6.9 Hz, 2H), 6.60 (dd, J = 15.9, 10.8 Hz, 1H), 6.39 (d, J = 15.9 Hz, 1H), 6.22 (dd, J = 15.6, 10.8 Hz, 1H), 5.74 (m, 1H), 5.48 (s, 1H), 5.45 (m, 1H), 4.99 (m, 1H), 4.71 (m,
3H), 4.55 (s, 1H), 4.44 (m, 1H), 4.33 (dd, J = 17.1, 8.4 Hz, 1H), 4.13 (m, 3H), 4.02 (s, 3H), 3.99 (m, 3H), 3.66 (m, 3H), 3.40 (m, 1H), 3.30 (s, 3H), 2.83 (m, 2H), 2.42 (m, 3H), 2.21 (m, 3H), 1.44 (s, 3H), 1.40 (s, 3H), 1.27 (t, J = 7.2 Hz, 3H); 13C NMR (75 MHz, CDCl3) δ 174.8, 172.0, 171.3, 170.9, 169.7, 163.8, 158.3, 156.9, 135.9, 133.5, 130.7, 129.9, 129.3, 128.4, 127.4, 127.3, 126.7, 123.5, 121.0, 120.7, 119.9, 114.5, 112.0, 109.3, 97.0, 89.6, 79.7, 77.6, 77.4, 76.6, 67.8, 63.4, 60.4, 57.7, 56.6, 52.6, 45.9, 42.4, 40.9, 39.3, 34.8, 29.6, 27.4, 27.1, 21.0, 14.8, 14.1; ESI-MS m/z 1051 (M + Na)+, 1067 (M + K)+; HRMS Calcd. for C51H64N8O15Na (M + Na)+ requires 1051.43834, found 1051.43396.

**Microsclerodermin E 1.** A solution of 24 (15.7 mg, 15.3 µmol) in methanol/THF (2 : 3, 0.5 mL) was treated with aqueous LiOH (1 M, 92 µL, 92 µmol) at 0 °C. The mixture was stirred for 5 h, acidified with 1 N HCl, and evaporated in vacuo. A suspension of Amberlyst-15 (100 mg) in a solution of the resulting acid in methanol/THF (4 : 1, 2.5 mL) was heated to 70 °C and stirred for 24 h. The mixture was filtered and the resin was washed with methanol. The combined filtrates was evaporated in vacuo, and the residue was purified by flash chromatography on silica eluting with methanol/CHCl3 (1 : 2) to give 1 (8.7 mg, 61%) as a white solid. [α]D 25 = -22.7 (c 0.4, 1 : 1 MeOH/0.1 N NH4HCO3 (aq); lit. reported: [α]D 25 = -24 (c 0.4, 1 : 1 MeOH/0.1N NH4HCO3 (aq)); 1H NMR (300 MHz, DMF-d7 with trace of TFA) δ 11.58 (s, 1H), 10.60 (s, 1H), 8.88 (d, J = 4.8 Hz, 1H), 8.62 (d, J = 8.7 Hz, 1H), 8.49 (t, J = 6.2 Hz, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.59 (br, 1H), 7.54 (d, J = 8.1 Hz, 1H), 7.40 (d, J = 8.7 Hz, 2H), 7.35 (m, 1H), 7.31 (t, J = 7.8 Hz, 1H), 7.16 (t, J = 7.8 Hz, 1H), 6.91 (d, J = 8.7 Hz, 2H), 6.73 (dd, J = 15.9, 10.8 Hz, 1H), 6.45 (d, J = 15.9 Hz, 1H), 6.24 (dd, J = 15.0, 10.8 Hz, 1H), 5.83 (m, 1H), 5.45 (s, 1H), 5.42 (m, 1H), 4.68 (s, 1H), 4.64 (d, J = 15.9 Hz, 1H), 4.33 (m, 1H), 4.27 (m, 1H), 4.05 (q, J = 5.7 Hz, 2H), 3.95 (br, 1H), 3.73 (m, 1H), 3.68 (m, 2H), 3.61 (m, 2H), 3.47 (d, J = 15.9 Hz, 1H), 3.45 (m, 2H), 3.07 (s, 3H), 2.91 (m, 2H), 2.59 (dd, J = 18.9, 4.8 Hz, 1H), 2.48 (d, J = 13.5 Hz, 1H), 2.39 (m, 2H), 2.21 (m, 1H), 1.35 (t, J = 5.7 Hz, 3H); negative ESI-MS m/z 929 (M – H).
16

17