Supporting Information

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69451 Weinheim, Germany
Enantioselective Synthesis of Oasomycin A, Part III. Fragment Assembly and Confirmation of Structure

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**General Information and Materials**

All reactions were carried out under an atmosphere of nitrogen in flame- or oven-dried glassware with magnetic stirring, unless otherwise noted. Air-sensitive reagents and solutions were transferred via syringe or cannula and were introduced to the apparatus through rubber septa. Reactions were cooled via external cooling baths: ice water (0 °C), dry ice-acetone (–78 °C), ice-acetone (–10 °C), methanol-liquid nitrogen (–95 °C), or Neslab immersion cooler (–20 → –80 °C). Heating was accomplished by heating mantle or silicon oil bath using a temperature controller. Analytical thin layer chromatography (TLC) was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and exposure to aqueous ceric ammonium molybdate (CAM) solution or anisaldehyde followed by heating. Flash chromatography was performed using EM silica gel 60 (230-240 mesh). Solvents for extraction and chromatography were HPLC grade.

When necessary, solvents and reagents were dried prior to use. Reagents were purified prior to use following the guidelines of Perrin and Armarego.\(^1\) Tetrahydrofuran (THF), dichloromethane (CH\(_2\)Cl\(_2\)), toluene and diethyl ether (Et\(_2\)O) were filtered through a column of activated alumina under an argon atmosphere. Methanol (MeOH) was distilled from magnesium methoxide. Benzene, acetonitrile, 2,6-lutidine, pyridine, \(N,N\)-disopropylethylamine, \(N,N\)-dimethylethylamine, triethylamine, diisopropylamine and chlorotrimethylsilane were distilled from calcium hydride. Optical rotations were measured on a Jasco DIP-0181 digital polarimeter with a sodium lamp and reported as follows: [\(\alpha\)]\(_D\) \(^25\) (c g/100 ml, solvent). Infrared spectra were recorded on a Perkin Elmer model 1600 FT-IR spectrometer. Mass spectra were obtained on a JEOL AX-505 or SX-102 high resolution magnetic sector mass spectrometer by the Harvard University Mass Spectrometry Laboratory. Electrospray mass spectra were obtained using a LCT mass spectrometer (Micromass Instruments, Beverly, MA). Exact mass measurements were obtained by internal calibration with an appropriate lock mass compound. \(^1\)H NMR spectra were recorded on Varian Inova-600 (600 MHz), Inova-500 (500 MHz) or Mercury-400 (400 MHz) spectrometers. Chemical shifts (\(\delta\)) are reported from tetramethylsilane with the solvent resonance as the internal standard (CDCl\(_3\): \(\delta\) 7.26, C\(_6\)D\(_6\): \(\delta\) 7.15, CD\(_3\)OD: \(\delta\) 4.78, 3.22). Data are reported as follows: chemical shift (\(\delta\)), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, appt = apparent, br = broad, m = multiplet), coupling constants (Hz), integration, and assignment. \(^13\)C NMR spectra were recorded on Varian INOVA-500 (125 MHz) or Mercury-400 (100 MHz) spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal standard (CDCl\(_3\): \(\delta\) 77.0, C\(_6\)D\(_6\): \(\delta\) 128.0, CD\(_3\)OD: \(\delta\) 49.0). Unless noted otherwise, the reported \(^1\)H NMR signals were assigned using standard 2D NMR techniques or by a direct comparison to the \(^1\)H NMR spectra of corresponding starting materials.
(3a). Sulfone 1 (147 mg, 0.203 mmol), was azeotroped with benzene (2 × 10 mL), dissolved in 1,2-dimethoxyethane (4.2 mL) and cooled to –46 °C. The solution of KHMDS (0.436 M, 0.458 mL, 0.200 mmol) in toluene was added dropwise over 3 min period. The obtained yellow solution was stirred for 10 minutes, and the pre-cooled to –46 °C solution of aldehyde 2 (152 mg, 0.163 mmol) was canulated over 3 minute period. The reaction mixture was stirred for 25 minutes and then warmed to room temperature, and stirred for additional 30 minutes during which the solution decolorized and formed a white precipitate. The solution of NH₄Cl(sat.) (5 mL) was added, and the obtained slurry was partitioned between diethyl ether (5 mL) and water (5 mL). The aqueous phase was then washed with diethyl ether (5 mL), and the combined organic phase was washed with brine (10 mL), dried (MgSO₄), filtered and concentrated under reduced pressure to afford a colorless oil. Subjection of this material to flash chromatography (silica, 9% → 15% v/v diethyl ether/pentanes elution) afforded, after concentration of the appropriate fractions (Rf 0.6, 18 % v/v ethyl acetate/hexanes), the title compound 3a (135 mg, 57% yield) as a 7:1 mixture of Δ¹² olefin isomers: [α]D²⁵ = +9.0 (c = 6.30, CHCl₃); IR (film) 2957, 2929, 2897, 2857, 1721, 1616, 1514, 1426, 1388, 1360, 1250, 1074, 1015 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.25 (d, J = 8.5 Hz, 2H, PMPH), 6.86 (d, J = 8.8 Hz, 2H, PMPH), 6.76 (td, J = 7.3, 1.3 Hz, 1H, C₃H), 5.80 (ddt, J = 14.0, 10.2, 7.0 Hz, 1H, C₂₇H), 5.49–5.43 (m, 2H, C₁₃H), 5.42–5.33 (m, 3H, C₁₂H, C₁₆H, C₂₁H), 5.09 (d, J = 15.0 Hz, 1H, C₂₈H), 5.05 (d, J = 10.0 Hz, 1H, C₂₈H), 4.57 (d, JAB = 10.5 Hz, 1H, PMPCHH), 4.35 (d, JAB = 10.7 Hz, 1H, PMPCHH), 4.30 (d, J = 8.8 Hz, 1H, C₂₂H), 3.99 (d, J = 8.8 Hz, 1H, C₂₃H), 3.89–3.86 (m, 3H, C₉H, C₁₃H, C₁₉H), 3.80 (s, 3H, PMPOCH₃), 3.75 (s, 3H, CO₂CH₃), 3.69 (m, 1H, C₂₅H), 3.46 (d, J = 8.8 Hz, 1H, C₇H), 2.38 (dt, J = 13.8, 5.6 Hz, 2H, C₂₆H), 2.32–2.24 (m, 2H, C₁₈H, C₂₀H), 2.24–2.13 (m, 4H, C₄H, C₄H, C₁₁H, C₁₄H), 1.89 (dt, J = 15.8, 6.2 Hz, 1H, C₁₁H), 1.85 (s, 3H, C₂CH₃), 1.80 (m, 1H, C₈H), 1.60 (m, 1H, C₆H), 1.57 (s, 3H, C₂₀CH₃), 1.54 (m, 1H, C₂₄H), 1.49 (m, 2H, C₁₀H, C₂₄H), 1.36 (m, 3H, C₃H, C₃H, C₁₀H), 0.98 (t, J = 7.9 Hz, 9H, Si(CH₂CH₃)₃), 0.93 (d, J = 7.0 Hz, 3H, C₁₄CH₃), 0.90 (s, 9H, (CH₃)₃CSi), 0.89 (s, 9H, (CH₃)₃CSi), 0.89 (s, 9H, (CH₃)₃CSi), 0.88 (s, 9H, (CH₃)₂CSi), 0.87 (s, 9H, (CH₃)₂CSi), 0.91–0.87 (m, 3H, C₁₈CH₃), 0.85 (d, J = 7.0 Hz, 3H, C₆CH₃), 0.76 (d, J = 7.0 Hz, 3H, C₅CH₃), 0.61 (q, J = 7.9 Hz, 6H, Si(CH₂CH₃)₃), 0.15 (s, 3H, SiCH₃), 0.053 (s, 3H, SiCH₃), 0.041 (s, 3H, SiCH₃), 0.033 (s, 3H, SiCH₃), 0.033 (s, 3H, SiCH₃), 0.011 (s, 3H, SiCH₃), 0.011 (s,
3H, SiCH$_3$), 0.004 (s, 3H, SiCH$_3$), –0.18 (s, 3H, SiCH$_3$), –0.032 (s, 3H, SiCH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.7, 159.0, 142.5, 136.5, 134.5, 134.4, 132.8, 131.4, 131.1, 129.8, 129.0, 127.5, 126.5, 117.2, 113.7, 80.7, 78.1, 77.8, 75.4, 74.8, 74.2, 72.4, 70.3, 55.2, 51.7, 43.4, 43.4, 42.5, 39.1, 38.5, 36.1, 33.4, 31.2, 29.9, 27.0, 26.2, 26.0, 26.0, 25.9, 18.4, 18.3, 18.2, 18.2, 18.1, 15.4, 14.9, 14.3, 12.9, 12.4, 10.2, 7.2, 5.7, –3.2, –3.8, –4.2, –4.3, –4.4, –4.6, –4.7, –4.9, –5.1; LRMS (ESI): Exact mass calcd for C$_{79}$H$_{152}$O$_{16}$Si$_6$ [M+NH$_4$]$^+$: 1447.0, and [M+Na]$^+$: 1452.0. Found: 1447.0, 1452.0.

Compound 3a (245 mg, 0.172 mmol), was dissolved in THF/H$_2$O mixture (10:1, 3.8 mL) and PdCl$_2$ (40 mg, 0.226 mmol) followed by Cu(OAc)$_2$ (70 mg, 0.350 mmol) was added. The obtained brown suspension was stirred for 4 hours, and then diluted with ethyl acetate (10 mL) and pH 7 buffer (10 mL). The organic phase was washed with NH$_4$Cl(sat.) (5 mL), and the combine aqueous phase was re-extracted with ethyl acetate (5 mL). The combined organic phase was then washed with brine (10 mL), dried (MgSO$_4$), filtered and concentrated under reduced pressure to afford a yellow oil. Subjection of this material to flash chromatography (silica, 17% → 20% v/v ethyl acetate/hexanes elution) afforded, after concentration of the appropriate fractions (R$_f$ 0.5, 25 % v/v ethyl acetate/hexanes), the title compound 8 (ca. 187 mg, 75% yield) contaminated with ca. 8% of an inseparable byproduct. 8: [α]$^D_{25} = +2.1$ (c 4.65, CHCl$_3$); IR (film) 2958, 2926, 2894, 2852, 1722, 1713, 1470, 1383, 1357, 1251, 1097, 1066, 1013 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$) δ 7.21 (d, $J = 8.5$ Hz, 2H, PMPH), 6.85 (d, $J = 8.2$ Hz, 2H, PMPH), 6.76 (t, $J = 7.1$ Hz, 1H, C$_3$H), 5.51–5.34 (m, 5H, C$_2$H, C$_3$H, C$_6$H, C$_7$H, C$_{12}$H), 4.46 (d, $J_{AB} = 10.8$ Hz, 1H, PMPCHH), 4.42 (d, $J_{AB} = 10.8$ Hz, 1H, PMPCHH), 4.33 (d, $J = 8.8$ Hz, 1H, C$_2$H), 4.14 (m, 1H, C$_{25}$H), 3.95 (d, $J = 7.9$ Hz, 1H, C$_{23}$H), 3.91–3.83 (m, 3H, C$_9$H, C$_{15}$H, C$_{19}$H), 3.79 (s, 3H, COOCH$_3$), 3.73 (s, 3H, PMPOCH$_3$), 3.46 (d, $J = 8.9$ Hz, 1H, C$_7$H), 2.77 (dd, $J = 15.5$, 5.6 Hz, 1H, C$_{26}$H), 2.52 (dd, $J = 15.5$, 6.4 Hz, 1H, C$_{26}$H), 2.28 (m, 1H, C$_{18}$H), 2.20–2.13 (m, 2H, C$_1$H, C$_{14}$H), 2.16 (dt, $J = 13.2$, 6.4 Hz, 2H, C$_4$H$_2$), 2.13 (s, 3H, C$_{28}$H$_3$), 1.88 (m, 1H, C$_{11}$H), 1.84 (s, 3H, C$_2$CH$_3$), 1.80 (m, 1H, C$_8$H), 1.60–1.55 (m, 2H, C$_8$H, C$_{10}$H), 1.58 (s, 3H, C$_{20}$CH$_3$), 1.54 (m, 1H, C$_{24}$H), 1.47 (tt, $J = 7.8$, 6.0 Hz, 1H, C$_{24}$H), 1.36 (m, 3H, C$_5$H, C$_{21}$H, C$_{25}$H), 0.98 (t, $J = 7.9$ Hz, 9H, Si(CH$_2$CH$_3$)$_3$), 0.92 (s, 9H, (CH$_3$)$_3$C$, 0.92$ (s, 9H, (CH$_3$)$_3$C$)), 0.89 (s, 9H, (CH$_3$)$_3$C$)), 0.88 (s, 9H, (CH$_3$)$_3$C$)), 0.87 (s, 9H, (CH$_3$)$_3$C$)), 0.92–0.87 (m, 6H, CHCH$_3$, CHCH$_3$), 0.85 (d, $J = 7.0$ Hz, 3H, CHCH$_3$), 0.77 (d, $J = 7.0$ Hz, 3H,
C₈(CH₃), 0.61 (q, J = 7.9 Hz, 6H, Si(CH₂CH₃)₃), 0.15 (s, 3H, SiCH₃), 0.092 (s, 3H, SiCH₃), 0.046 (s, 3H, SiCH₃), 0.046 (s, 3H, SiCH₃), 0.040 (s, 3H, SiCH₃), 0.017 (s, 3H, SiCH₃), 0.017 (s, 3H, SiCH₃), 0.017 (s, 3H, SiCH₃), -0.012 (s, 3H, SiCH₃), -0.029 (s, 3H, SiCH₃); ¹³C NMR (100 MHz, CDCl₃) δ 206.7, 168.7, 159.1, 142.5, 136.9, 134.3, 132.8, 131.4, 130.7, 129.9, 129.1, 129.0, 127.5, 126.4, 113.8, 113.7, 80.6, 78.0, 77.8, 74.6, 74.1, 72.6, 72.4, 70.9, 55.2, 51.7, 51.7, 49.5, 43.4, 39.5, 36.1, 31.2, 30.9, 29.9, 27.0, 26.3, 26.1, 26.0, 26.0, 25.9, 18.4, 18.3, 18.2, 18.1, 15.3, 14.9, 14.4, 12.9, 12.4, 10.2, 7.2, 5.7, -3.2, -3.8, -4.2, -4.3, -4.4, -4.6, -4.7, -4.9, -5.0, -5.1; LRMS (ESI): Exact mass calcd for C₇₉H₁₅₂O₁₁Si₆ [M+NH₄]⁺: 1463.0. Found: 1462.8.

(2E,6S,7R,8S,9S,12E,14S,15S,16E,18S,19R,20E,22S,23R,25R,29S,30S,31R,32R,33S,37S,38E,41S,42R)-methyl 9,15,19,22,23,33,35,37-octakis(tert-butylidimethylsilyloxy)-29-hydroxy-25,31-bis(4-methoxybenzoyloxy)-2,6,8,14,18,20,30,32-octamethyl-27-oxo-42-((R)-5-oxo-tetrahydrofuran-2-yl)-7-(triethylsilyloxy)-41-(trimethylsilyloxy)tritetaconta-2,12,16,20,38-pentae noate (10). Ketone 8 (250 mg, 0.173 mmol), was azeotroped with benzene (2×5 mL), and dissolved in diethyl ether (0.5 mL). The obtained solution was cooled to -78 °C, and DIPEA (43 μL, 0.261 mmol) followed by Bu₃BOTf (1.74 M in ether, 100 μL, 0.174 mmol) was added. The yellowish solution was stirred for 40 min, and pre-cooled to -78 °C aldehyde 9 (120 mg, 0.126 mmol, azeotroped with 3×2 mL benzene) dissolved in diethyl ether (0.5 mL then 0.3 mL rinse) was canulated over 5 min period. After 4 h at -78 °C, the solution was warmed to 0 °C, and treated with MeOH/pH 7 buffer (1 mL, 5:1 v/v solution) followed by MeOH/H₂O₂ (30% aqueous solution) (1 mL, 2:1 v/v solution). The obtained solution was then stirred for 1 h, diluted with ethyl acetate (5 mL) and water (5 mL), and the separated organic phase was washed with brine (10 mL), dried (MgSO₄), filtered and concentrated under reduced pressure to afford a yellow oil. Subjection of this material to flash chromatography (silica, 25% v/v ethyl acetate/hexanes elution) afforded, after concentration of the appropriate fractions (Rₜ 0.2, 25 % v/v ethyl acetate/hexanes), the title compound 10 (ca. 235 mg, 78% yield) together with (ca. 11 mg, 5%) of an inseparable byproduct. Starting ketone 8 (25 mgs, 10%) was also recovered. 10: [α]D²⁵ = -18.6 (c = 4.50, CHCl₃); IR (film) νmax 3535, 2957, 2935, 2890, 2857, 1779, 1712, 1612, 1512, 1462, 1362, 1245, 1068 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.27 (d, J = 9.3 Hz, 2H, PMPH), 7.16 (d, J = 8.5 Hz, 2H, PMPH), 6.83 (d, J = 8.5 Hz, 2H, PMPH), 6.79 (d, J = 8.5 Hz, 2H, PMPH), 6.75 (t, J = 6.9 Hz, 1H, C₃H), 5.55–5.43 (m, 3H, C₁₃H, C₁₇H, C₃₀H), 5.41–5.34 (m, 4H, C₁₂H, C₁₀H, C₂₁H, C₃₈H), 4.74 (d, JAB = 11.4 Hz,
1H, PMPCHH), 4.63 (d, J<sub>AB</sub> = 11.6 Hz, 1H, PMPCHH), 4.52 (dd, J = 15.8, 7.0 Hz, 1H, C<sub>32</sub>H), 4.41 (d, J<sub>AB</sub> = 11.1 Hz, 1H, PMPCHH), 4.39 (d, J<sub>AB</sub> = 11.1 Hz, 1H, PMPCHH), 4.34 (d, J = 8.8 Hz, 1H, C<sub>22</sub>H), 4.29 (t, J = 8.0 Hz, 1H, C<sub>37</sub>H), 4.14–4.10 (m, 2H, C<sub>25</sub>H, C<sub>33</sub>H), 4.03 (d, J = 9.7 Hz, 1H, C<sub>23</sub>H), 3.91–3.81 (m, 5H, C<sub>9</sub>H, C<sub>13</sub>H, C<sub>19</sub>H, C<sub>30</sub>H, C<sub>31</sub>H), 3.85–3.78 (m, 3H, C<sub>29</sub>H, C<sub>32</sub>H, C<sub>41</sub>H), 3.77 (s, 3H, COOC<sub>3</sub>), 3.76 (s, 3H, PMPOCH<sub>3</sub>), 3.74 (s, 3H, PMPOCH<sub>3</sub>), 3.45 (d, J = 9.1 Hz, 1H, C<sub>7</sub>H), 3.29 (d, J = 3.2 Hz, 1H, OH), 2.74 (dd, J = 15.5, 7.0 Hz, 1H, C<sub>26</sub>H), 2.70 (dd, J = 18.2, 1.0 Hz, 1H, C<sub>28</sub>H), 2.51–2.48 (m, 2H, C<sub>43</sub>H), 2.47 (dd, J = 15.8, 5.0 Hz, 1H, C<sub>26</sub>H), 2.44 (dd, J = 17.9, 9.5 Hz, 1H, C<sub>28</sub>H), 2.28 (m, 1H, C<sub>18</sub>H), 2.24–2.12 (m, 7H, C<sub>4</sub>H, C<sub>4</sub>H, C<sub>11</sub>H, C<sub>14</sub>H, C<sub>40</sub>H, C<sub>40</sub>H, C<sub>44</sub>H), 2.00 (dq, J = 11.4, 6.7 Hz, 1H, C<sub>42</sub>H), 1.96–1.85 (m, 3H, C<sub>11</sub>H, C<sub>32</sub>H, C<sub>44</sub>H), 1.84 (s, 3H, C<sub>2</sub>CH<sub>3</sub>), 1.80 (m, 1H, C<sub>8</sub>H), 1.70 (m, 1H, C<sub>36</sub>H), 1.62–1.55 (m, 6H, C<sub>6</sub>H, C<sub>8</sub>H, C<sub>10</sub>H, C<sub>24</sub>H, C<sub>30</sub>H, C<sub>32</sub>H, C<sub>34</sub>H), 1.58 (s, 3H, C<sub>20</sub>CH<sub>3</sub>), 1.47 (tt, J = 13.5, 6.7 Hz, 1H, C<sub>24</sub>H), 1.35 (m, 3H, C<sub>5</sub>H, C<sub>5</sub>H, C<sub>10</sub>H), 1.25 (t, J = 10.5 Hz, 1H, C<sub>36</sub>H), 0.97 (t, J = 7.9 Hz, 9H, Si(CH<sub>2</sub>CH<sub>3</sub>)), 0.92 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>Si), 0.90 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>Si), 0.89 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>Si), 0.88 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>Si), 0.87 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>Si), 0.87 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>Si), 0.76 (d, J = 7.0 Hz, 3H, CHCH<sub>3</sub>), 0.74 (d, J = 7.0 Hz, 3H, CHCH<sub>3</sub>), 0.74 (d, J = 7.0 Hz, 3H, CHCH<sub>3</sub>), 0.74 (d, J = 7.0 Hz, 3H, CHCH<sub>3</sub>), 0.60 (q, J = 7.9 Hz, 6H, Si(CH<sub>2</sub>CH<sub>3</sub>)), 0.14 (s, 3H, SiCH<sub>3</sub>), 0.095 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 0.084 (s, 3H, SiCH<sub>3</sub>), 0.078 (s, 3H, SiCH<sub>3</sub>), 0.074 (s, 3H, SiCH<sub>3</sub>), 0.062 (s, 3H, SiCH<sub>3</sub>), 0.055 (s, 3H, SiCH<sub>3</sub>), 0.038 (s, 3H, SiCH<sub>3</sub>), 0.031 (s, 3H, SiCH<sub>3</sub>), 0.016 (s, 3H, SiCH<sub>3</sub>), 0.006 (s, 3H, SiCH<sub>3</sub>), 0.006 (s, 3H, SiCH<sub>3</sub>), 0.006 (s, 3H, SiCH<sub>3</sub>), −0.010 (s, 3H, SiCH<sub>3</sub>), −0.023 (s, 3H, SiCH<sub>3</sub>), −0.042 (s, 3H, SiCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 210.9, 177.2, 168.7, 159.1, 158.5, 142.5, 137.2, 137.0, 134.4, 132.7, 132.2, 131.3, 130.6, 129.9, 129.0, 128.1, 127.5, 126.3, 113.7, 113.5, 94.4, 81.4, 80.3, 77.9, 77.8, 77.9, 74.5, 74.0, 73.7, 73.4, 72.6, 72.3, 71.1, 70.8, 69.1, 68.8, 66.6, 55.2, 55.2, 51.7, 49.7, 48.6, 46.0, 44.1, 43.4, 43.4, 42.4, 42.2, 40.3, 39.2, 39.0, 36.2, 36.1, 33.4, 31.2, 29.9, 29.0, 27.0, 26.2, 26.1, 26.0, 26.0, 26.0, 25.9, 25.9, 25.6, 18.4, 18.3, 18.2, 18.2, 18.1, 15.1, 15.0, 14.6, 13.0, 12.4, 10.2, 9.9, 9.5, 8.9, 7.2, 5.7, 0.43, −3.0, −3.1, −3.3, −3.8, −4.2, −4.2, −4.3, −4.3, −4.4, −4.4, −4.5, −4.7, −4.9, −5.0; LRMS (ESI): Exact mass calcd for C<sub>129</sub>H<sub>246</sub>O<sub>20</sub>Si<sub>10</sub> [M+NH<sub>4</sub>]<sup>+</sup>: 2413.6. Found: 2413.2.

furan-2-yl)-7-(triethylsilyloxy)tritetacontra-2,12,16,20,38-pentaenoate (11a). Ketone 10 (103 mg, 42.8 μmol), was azeotroped with benzene (2 × 5 mL), dissolved in methylene chloride (1.5 mL), and cooled to –78 °C. The solution of Zn(BH₄)₂ in ether (0.145 M, 0.98 mL, 0.142 mmol) was then added. The mixture was warmed to –30 °C and stirred for 23 h. The solution was then treated with NH₄Cl (sat.) (2 mL), warmed to room temperature and extracted with ethyl acetate (5 mL). The separated organic phase was washed with brine (5 mL), dried (MgSO₄), filtered and concentrated under reduced pressure to afford a colorless oil. The oil was redissolved in CH₂Cl₂/MeOH mixture (1:1 v/v, 2.4 mL). The solution was cooled to 0 °C, and PPTS (1.19 mg, 4.7 μmol) was then added. The reaction mixture was stirred for 1 h, treated with triethylamine (ca. 0.1 mL), and concentrated. Subjection of the obtained material to flash chromatography (silica, 25% → 33% v/v ethyl acetate/hexanes elution) afforded, after concentration of the appropriate fractions (Rf 0.2, 25 % v/v ethyl acetate/hexanes), the title compound 11a (ca. 87 mg, 84% yield) together with (ca. 7 mg, 7%) of an inseparable impurity. 11a: [α]₅D²⁵ = −6.9 (c = 8.7, CHCl₃); IR (film) 3496, 2956, 2930, 2857, 1773, 1720, 1654, 1616, 1560, 1515, 1472, 1463, 1388, 1362, 1251, 1073 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.25 (d, J = 8.5 Hz, 2H, PMPH), 7.21 (d, J = 8.5 Hz, 2H, 2H, PMPH), 6.85 (d, J = 8.5 Hz, 2H, 2H, PMPH), 6.84 (d, J = 8.5 Hz, 2H, PMPH), 6.75 (td, J = 6.9, 1.2 Hz, 1H, C₂H), 5.52–5.47 (m, 3H, 3H, C₁₃H, C₁₇H, C₃₉H), 5.45 (dd, J = 15.6, 7.2 Hz, 1H, C₂₁H), 5.41–5.35 (m, 3H, C₁₂H, C₁₆H, C₃₈H), 4.78 (d, Jₐb = 11.7 Hz, 1H, PMPCH₃H), 4.63 (ddd, J = 13.5, 9.1, 6.7 Hz, 1H, C₄₃H), 4.59 (d, Jₐb = 11.7 Hz, 1H, PMPCH₃H), 4.56 (d, Jₐb = 10.5 Hz, 1H, PMPCH₃H), 4.38 (d, J = 8.5 Hz, 1H, C₂₂H), 4.37 (d, Jₐb = 10.5 Hz, 1H, PMPCH₃H), 4.30 (ddd, J = 9.1, 6.7, 2.3 Hz, 1H, C₃₇H), 4.15 (t, J = 10.2 Hz, 1H, C₂₅H), 4.09 (dd, J = 12.6, 7.2 Hz, 1H, C₃₃H), 3.99 (d, J = 10.0 Hz, 1H, C₂₃H), 3.90–3.84 (m, 4H, C₉H, C₁₃H, C₁₉H, C₃₁H), 3.84 (m, 1H, C₃₅H), 3.83–3.79 (s, 2H, C₂₇H, C₂₉H), 3.79 (s, 3H, OCH₃), 3.78 (s, 3H, OCH₃), 3.74 (s, 3H, OCH₃), 3.63 (ddd, J = 8.8, 6.2, 2.9 Hz, 1H, C₄₁H), 3.45 (d, J = 9.1 Hz, 1H, C₁₉H), 2.53 (d, J = 10.5 Hz, 1H, C₄₅H), 2.52 (d, J = 10.0 Hz, 1H, C₄₅H), 2.31 (dq, J = 15.2, 6.4 Hz, 1H, C₁₈H), 2.29–2.24 (m, 3H, C₄₀H C₄₀H, C₄₄H), 2.23–2.14 (m, 3H, C₄₄H, C₁₁H, C₁₁H), 2.10 (ddd, J = 16.4, 14.4, 8.8 Hz, 1H, C₁₄H), 2.02 (ddd, J = 13.8, 7.0 Hz, 1H, C₄₂H), 1.97 (ddd, J = 20.0, 9.7, 3.1 Hz, 1H, C₃₄H), 1.93–1.80 (m, 3H, C₁₁H, C₂₈H, C₄₄H), 1.84 (s, 3H, C₂₃H₃), 1.80 (ddd, J = 8.8, 7.0, 3.8, 1H, C₈H), 1.73–1.67 (m, 3H, C₆H, C₂₆H, C₃₆H), 1.64–1.56 (m, 4H, C₁₀H C₂₄H, C₂₈H, C₃₄H), 1.56 (s, 3H, C₂₀CH₃), 1.55 (dd, J = 9.4, 2.0 Hz, 1H, C₂₆H), 1.52 (m, 1H, C₂₄H), 1.40–1.32 (m, 3H, C₃H, C₃H, C₁₀H), 1.27–1.25 (m, 3H, C₃₉H, C₃₂H, C₃₈H), 0.96 (t, J = 7.9 Hz, 9H, Si(CH₂CH₂CH₃)₃), 0.90 (d, J = 7.4 Hz, 3H, CHCH₃), 0.89 (s, 9H, (CH₃)₃CSi), 0.89 (s, 9H, (CH₃)₃CSi), 0.88 (s, 9H, (CH₃)₃CSi), 0.88 (s, 9H, (CH₃)₃CSi), 0.89–0.84 (m, 3H, CHCH₃), 0.84 (d, J = 6.2 Hz, 3H, CHCH₃), 0.83 (d, J = 7.6 Hz, 3H, CHCH₃), 0.80 (d, J = 7.4 Hz, 3H, CHCH₃), 0.77 (d, J = 7.0 Hz, 3H, CHCH₃), 0.76 (d, J = 6.7 Hz, 3H, CHCH₃), 0.60 (q, J = 7.9 Hz, 6H, Si(CH₂CH₂CH₃), 0.14 (s, 3H, SiCH₃), 0.079 (s, 3H, SiCH₃), 0.079 (s, 3H, SiCH₃), 0.064 (s, 3H, SiCH₃), 0.057 (s, 3H, SiCH₃), 0.045 (s, 3H, SiCH₃), 0.040 (s, 3H, SiCH₃), 0.037 (s, 3H, SiCH₃), 0.030 (s, 3H, SiCH₃), 0.028
(s, 3H, SiCH₃), 0.015 (s, 3H, SiCH₃), 0.004 (s, 3H, SiCH₃), 0.000 (s, 3H, SiCH₃), −0.007 (s, 3H, SiCH₃), −0.029 (s, 3H, SiCH₃), −0.067 (s, 3H, SiCH₃); ¹³C NMR (100 MHz, CDCl₃) δ 177.0, 168.7, 159.3, 158.5, 142.5, 139.1, 137.1, 134.5, 132.8, 132.2, 132.2, 131.3, 130.1, 129.9, 129.3, 128.0, 127.5, 125.4, 113.8, 113.6, 81.8, 80.2, 78.0, 77.8, 74.7, 74.6, 74.0, 72.4, 72.1, 70.7, 70.6, 70.5, 68.8, 66.8, 55.2, 55.2, 51.7, 46.0, 44.0, 43.4, 43.4, 42.3, 41.8, 41.1, 39.0, 37.1, 36.1, 34.7, 33.4, 31.6, 31.2, 29.9, 29.7, 28.8, 27.0, 26.3, 26.2, 26.0, 26.0, 25.9, 25.9, 25.9, 25.3, 25.1, 22.6, 20.7, 18.3, 18.3, 18.3, 18.2, 18.2, 18.1, 18.1, 18.1, 18.1, 15.1, 14.9, 14.7, 14.1, 13.0, 12.4, 10.3, 10.2, 9.0, 7.2, 5.7, −3.1, −3.2, −3.2, −3.4, −3.8, −4.0, −4.2, −4.2, −4.3, −4.3, −4.4, −4.5, −4.7, −4.9, −5.0; LRMS (ESI): Exact mass calcd for C₁₂₆H₂₄₀O₂₀Si₉ [M+NH₄]^+: 2343.6. Found: 2343.9.

(2E,6S,7R,8S,9S,12E,14S,15S,16E,18S,19R,20E,22S,23R,25S)-methyl 9,15,19,22,23-pentakis(tert-butylidimethylsilyloxy)-26-((4S,6S)-2,2-dimethyl-6-((2S,3R,4R,5R,7S,9S,13S,14S,E)-5,7,9-tris(tert-butylidimethylsilyloxy)-13-hydroxy-3-(4-methoxybenzyl)-4-methyl-14-((R)-5-oxo-tetrahydrofuran-2-yl)pentadec-10-en-2-yl)-1,3-dioxan-4-yl)-25-(4-methoxybenzyl)oxy)-2,6,8,14,18,20-hexamethyl-7-(triethylsilyloxy)hexacosa-2,12,16,20-tetraenoate (11). Triol 11a (102 mg, 43.8 μmol), was dissolved in 2,2-dimethoxypropane (2.1 mL), and PPTS (1.73 mg, 6.9 μL) was added. The solution was stirred for 45 minutes, treated with triethylamine, and concentrated under reduced pressure to afford a yellow oil. Subjection of the obtained crude material to flash chromatography (silica, 30 % v/v ethyl acetate/hexanes elution) afforded, after concentration of the appropriate fractions (Rᵣ 0.2, 25 % v/v ethyl acetate/hexanes), the title compound 11 (ca. 94 mg, 91% yield) together with (ca. 9 mg, 8%) of an inseparable impurity. 11: [α]D²⁵ = −9.1 (c = 6.5, CHCl₃); IR (film) 3486, 2956, 2930, 1780, 1720, 1613, 1585, 1513, 1463, 1385, 1357, 1246, 1179, 1074 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.25 (d, J = 8.5 Hz, 2H, PMPH), 7.21 (d, J = 8.2 Hz, 2H, PMPH), 6.85 (d, J = 8.5 Hz, 2H, PMPH), 6.84 (d, J = 8.5 Hz, 2H, PMPH), 6.75 (t, J = 7.0 Hz, 1H, C₃H), 5.56–5.43 (m, 4H, C₁₃H, C₁₇H, C₂₁H, C₃₉H), 5.40–5.33 (m, 3H, C₁₂H, C₁₆H, C₃₈H), 4.64 (d, JAB = 10.5 Hz, 1H, PMPCHH), 4.64–4.62 (m, 1H, C₄₅H), 4.58 (d, JAB = 11.4 Hz, 1H, PMPCHH), 4.47 (d, JAB = 10.5 Hz, 1H, PMPCHH), 4.41 (d, JAB = 10.5 Hz, 1H, PMPCHH), 4.31 (t, J = 8.8 Hz, 1H, C₃H), 4.33–4.28 (m, 1H, C₂₂H), 4.06 (m, 1H, C₂₃H), 4.06 (dd, J = 10.2, 3.8 Hz, 1H, C₃₃H), 4.01–3.95 (m, 3H, C₂₅H, C₂₇H, C₃₃H), 3.86 (m, 3H, C₉H, C₁₃H, C₁₉H), 3.80 (s, 3H, OCH₃), 3.78 (s, 3H, OCH₃), 3.74 (s, 3H, OCH₃), 3.80–3.78 (m, 2H, C₂₉H, C₃₅H), 3.63 (tt, J = 8.0, 1.8 Hz, 1H, C₄₁H), 3.45 (d, J = 10.1 Hz, 1H, C₇H), 2.53 (d, J = 10.2 Hz, 1H, C₄₅H), 2.52 (d, J = 10.1 Hz, 1H, C₄₅H), 2.31 (dq, J = 14.1, 6.7 Hz, 1H,
C_{18}H, 2.27 (dt, J = 12.6, 6.4 Hz, 2H, C_{11}H, C_{44}H), 2.20 (appt dq, J = 14.1, 6.7 Hz, 1H, C_{4}H), 2.27–2.16 (m, 4H, C_{4}H, C_{4}H, C_{40}H, C_{40}H), 2.11 (appt dd, J = 7.3, 6.8, 1H, C_{42}H), 1.97–1.89 (m, 4H, C_{11}H, C_{44}H, C_{44}H, C_{44}H), 1.84 (s, 3H, C_{2}CH_{3}), 1.80 (m, 1H, C_{8}H), 1.69 (dd, J = 13.5, 8.8 Hz, 1H, C_{36}H), 1.65–1.53 (m, 6H, C_{6}H, C_{24}H, C_{24}H, C_{24}H, C_{30}H, C_{32}H), 1.58 (s, 3H, C_{20}CH_{3}), 1.47–1.42 (m, 5H, C_{5}H, C_{5}H, C_{10}H C_{26}H, C_{28}H), 1.42–1.39 (m, 1H, C_{24}H), 1.39 (s, 3H, OC(CH_{3}CH_{3})O), 1.38 (s, 3H, OC(CH_{3}CH_{3})O), 1.25–1.21 (m, 2H, C_{10}H, C_{36}H), 0.96 (t, J = 7.2 Hz, 9H, Si(CH_{2}CH_{3})_{3}), 0.91 (s, 9H, (CH_{3})_{3}CSi), 0.90 (s, 9H, (CH_{3})_{3}CSi), 0.89 (s, 9H, (CH_{3})_{3}CSi), 0.88 (s, 9H, (CH_{3})_{3}CSi), 0.88 (s, 9H, (CH_{3})_{3}CSi), 0.88 (s, 9H, (CH_{3})_{3}CSi), 0.84 (s, 9H, (CH_{3})_{3}CSi), 0.81–0.84 (m, 12H, CHCH_{3}, CHCH_{3}, CHCH_{3}, CHCH_{3}), 0.78 (d, J = 7.8 Hz, 3H, CHCH_{3}), 0.76 (d, J = 8.4 Hz, 3H, CHCH_{3}), 0.73 (d, J = 7.2 Hz, 3H, CHCH_{3}), 0.60 (q, J = 7.8 Hz, 6H, Si(CH_{2}CH_{3})_{3}), 0.14 (s, 3H, SiCH_{3}), 0.084 (s, 3H, SiCH_{3}), 0.075 (s, 3H, SiCH_{3}), 0.075 (s, 3H, SiCH_{3}), 0.062 (s, 3H, SiCH_{3}), 0.05 (s, 3H, SiCH_{3}), 0.041 (s, 3H, SiCH_{3}), 0.035 (s, 3H, SiCH_{3}), 0.028 (s, 3H, SiCH_{3}), 0.021 (s, 3H, SiCH_{3}), 0.008 (s, 3H, SiCH_{3}), 0.004 (s, 3H, SiCH_{3}), 0.002 (s, 3H, SiCH_{3}), 0.000 (s, 3H, SiCH_{3}), –0.026 (s, 3H, SiCH_{3}), –0.038 (s, 3H, SiCH_{3}).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 177.0, 168.7, 159.0, 158.5, 142.5, 139.2, 136.7, 134.5, 132.7, 132.4, 131.3, 131.2, 129.3, 129.0, 128.0, 128.0, 127.5, 125.3, 113.8, 113.6, 98.3, 81.8, 80.5, 78.0, 77.8, 77.3, 74.9, 73.9, 73.4, 72.4, 72.2, 72.1, 71.1, 70.5, 69.7, 69.0, 66.7, 65.8, 55.2, 55.2, 51.7, 46.0, 44.0, 43.4, 43.4, 42.3, 41.6, 40.1, 38.9, 37.1, 36.1, 34.7, 33.4, 31.6, 31.2, 30.3, 29.9, 29.7, 28.9, 27.0, 26.3, 26.2, 26.0, 26.0, 26.0, 25.9 25.3, 25.1, 22.7, 20.2, 18.4, 18.4, 18.4, 18.3, 18.2, 18.2, 18.1, 18.1, 15.2, 15.0, 14.5, 14.1, 13.0, 12.4, 10.3, 10.2, 8.9, 8.4, 7.2, 5.7, –2.8, –3.2, –3.3, –3.3, –3.3, –3.8, –4.1, –4.2, –4.2, –4.2, –4.3, –4.4, –4.4, –4.5, –4.7, –4.9, –5.1; LRMS (ESI): Exact mass calcd for C$_{129}$H$_{244}$O$_{26}$Si$_{9}$ requires [M+NH$_4$]$^+$: 2384.6. Found: 2384.9.

(2E,6S,7R,8S,9S,12E,14S,15S,16
9,15,19,22,23-pentakis(tert-
butyldimethylsilyloxy)-26-
((4S,6S)-2,2-dimethyl-6-
((2S,3R,4R,5R,7S,9S,13S,14S,5)-5,7,9-tris(tert-
butyldimethylsilyloxy)-13-hydroxy-3-(4-methoxybenzyl-
ol)-4-methyl-14-((R)-5-oxo-tetrahydrofuran-2-yl)pentadec-10-en-2-yl)-1,3-dioxan-4-yl)-25-(4-methoxy-
benzylxyloxy)-2,6,8,14,18,20-hexamethyl-7-(triethlyslyloxy)hexacosa-2,12,16,20-tetraenoic acid (12).
oil was redissolved in chloroform (2 mL), and cooled to 0 °C. TFA (20 µL, 0.27 µmol) was added, and the obtained solution was stirred for 1.5 hours. The mixture was concentrated under reduced pressure, and subjection of the obtained crude material to flash chromatography (silica, 30 → 50 % v/v ethyl acetate/hexanes elution) afforded, after concentration of the appropriate fractions (Rf 0.3, 25 % v/v ethyl acetate/hexanes), the title compound 12 (ca. 103 mg, 80% yield) together with (ca. 10 mg, 11%) of an inseparable impurity. 12: [α]_D^{25} = −12.2 (c = 1.35, CHCl₃); ¹H NMR (600 MHz, CDCl₃) δ 7.25 (d, J = 8.6 Hz, 2H, PMPH), 7.21 (d, J = 8.3 Hz, 2H, PMPH), 6.88 (t, J = 7.0 Hz, 1H, C₃H), 6.86 (d, J = 8.8 Hz, 2H, PMPH), 6.84 (d, J = 8.8 Hz, 2H, PMPH), 5.54–5.3 (m, 7H, C₁₂H, C₁₂H, C₁₆H, C₁₇H, C₂₁H, C₃₈H, C₃₉H), 4.62 (d, J = 10.3 Hz, 1H, PMPCHH), 4.64–4.62 (m, 1H, C₄₀H), 4.57 (d, J = 11.7 Hz, 1H, PMPCHH), 4.48 (d, J = 10.7 Hz, 1H, PMPCHH), 4.41 (d, J = 10.3 Hz, 1H, PMPCHH). 4.31 (d, J = 8.8 Hz, 1H, C₃₇H), 4.33–4.28 (m, 1H, C₂₂H), 4.06 (dd, J = 10.7, 4.9 Hz, 1H, C₂₅H), 4.01 (d, J = 9.8 Hz, 1H, C₃₃H), 4.01–3.95 (m, 2H, C₂₇H, C₂₉H), 3.95 (d, J = 9.8 Hz, 1H, C₂₃H), 3.88–3.80 (m, 3H, C₃H, C₁₃H, C₁₀H), 3.80 (s, 3H, OCH₃), 3.78 (s, 3H, OCH₃), 3.80–3.78 (m, 1H, C₃₅H), 3.74 (t, J = 8.4 Hz, 1H, C₃₁H), 3.63 (tt, J = 6.3, 2.4 Hz, 1H, C₄₄H), 3.45 (d, J = 8.8 Hz, 1H, C₇H), 2.54 (d, J = 9.3 Hz, 1H, C₄₅H), 2.52 (d, J = 10.2 Hz, 1H, C₄₅H), 2.31 (m, 1H, C₁₈H), 2.28 (t, J = 5.9 Hz, 2H, C₄₀H), 2.25 (t, J = 6.3 Hz, 1H, C₄₀H). 2.28–2.15 (m, 5H, C₄₄H, C₄₄H, C₁₁H, C₁₄H, C₄₄H), 2.09–1.98 (m, 3H, C₄₂H, C₃₄H, C₄₄H), 1.94–1.89 (m, 2H, C₁₁H, C₃₄H), 1.84 (s, 3H, C₂₇H), 1.80 (m, 1H, C₈H), 1.69 (dd, J = 13.5, 8.8 Hz, 1H, C₃₆H), 1.65–1.53 (m, 6H, C₈H, C₂₄H, C₂₈H, C₂₈H, C₃₀H, C₃₂H), 1.58 (s, 3H, C₂₀CH₃), 1.47–1.42 (m, 5H, C₅H, C₅H, C₁₀H C₂₆H, C₂₈H), 1.42–1.39 (m, 1H, C₂₄H), 1.39 (s, 3H, OC(CH₃CH₃)O), 1.38 (s, 3H, OC(CH₃CH₃)O), 1.25–1.21 (m, 2H, C₁₀H, C₃₆H), 0.96 (t, J = 7.2 Hz, 9H, Si(CH₂CH₃)₃), 0.94 (s, 9H, (CH₃)₃CSi), 0.93 (s, 9H, (CH₃)₃CSi), 0.93 (s, 9H, (CH₃)₃CSi), 0.92 (s, 9H, (CH₃)₃CSi), 0.92 (s, 9H, (CH₃)₃CSi), 0.91 (s, 9H, (CH₃)₃CSi), 0.91 (s, 9H, (CH₃)₃CSi), 0.90 (s, 9H, (CH₃)₃CSi), 0.91–0.84 (m, 12H, CHCH₃, CHCH₃, CHCH₃, CHCH₃, CHCH₃), 0.81 (d, J = 6.7 Hz, 3H, CHCH₃), 0.79 (d, J = 7.0 Hz, 3H, CHCH₃), 0.77 (d, J = 7.9 Hz, 3H, CHCH₃), 0.63 (q, J = 7.8 Hz, 6H, Si(CH₂CH₃)₃), 0.11 (s, 3H, SiCH₃), 0.040 (s, 3H, SiCH₃), 0.040 (s, 3H, SiCH₃), 0.035 (s, 3H, SiCH₃), 0.035 (s, 3H, SiCH₃), 0.035 (s, 3H, SiCH₃), 0.029 (s, 3H, SiCH₃), 0.016 (s, 3H, SiCH₃), 0.007 (s, 3H, SiCH₃), 0.001 (s, 3H, SiCH₃), −0.005 (s, 3H, SiCH₃), −0.013 (s, 3H, SiCH₃), −0.031 (s, 3H, SiCH₃), −0.037 (s, 3H, SiCH₃), −0.059 (s, 3H, SiCH₃), −0.073 (s, 3H, SiCH₃); ¹³C NMR (125 MHz, CDCl₃) δ 177.1, 172.6, 159.0, 158.5, 144.9, 139.2, 136.7, 134.5, 132.7, 132.4, 131.3, 131.2, 129.9, 129.3, 129.0, 127.7, 127.0, 125.3, 113.8, 113.6, 98.3, 81.8, 80.5, 78.1, 77.8, 77.2, 74.9, 74.7, 72.4, 72.3, 72.2, 71.1, 70.5, 70.0, 69.0, 66.7, 65.9, 60.4, 55.3, 55.2, 46.0, 44.0, 43.4, 43.3, 41.6, 38.9, 37.1, 36.1, 33.4, 31.2, 30.3, 29.9, 29.7, 29.7, 28.9, 27.3, 26.3, 26.2, 26.1, 26.1, 26.0, 26.0, 26.0, 25.1, 21.1, 20.2, 18.5, 18.4, 18.4, 18.3, 18.2, 18.1, 18.1, 15.2, 15.0, 14.5, 14.2, 12.9, 12.0, 10.3, 10.2, 8.9, 8.5, 7.2, 5.8, −2.8, −3.2, −3.2, −3.3, −3.7, −4.1, −4.2, −4.2, −4.3, −4.3, −4.4, −4.5, −4.7, −4.9, −5.0. IR (film) 3442, 2960, 2938, 1774, 1721, 1685, 1552, 1511, 1467, 1362, 1248, 1171, 1072, 1007 cm⁻¹.

tetrahydrofuran-2-yl)ethen-21-(triethylsilyloxy)-14,42,44-trioxa-bicyclo[39.3.1]pentatetraconta-10,-16,26,30,34-penta-en-15-one (13a). Seco acid 12 (22.1 mg, 9.4 µmol), was azeotroped with benzene (2 x 3 mL), dissolved in THF (0.94 mL), and DIPEA (67.0 µL, 406 µmol) followed by 2,4,6-trichlorobenzoyl chloride (25 µL, 160 µmol) was added. The solution was stirred for 2.5 hours, and then the solvent was evaporated with a stream of nitrogen, and the residue was redissolved in toluene (5 mL). The obtained solution was added to solution of DMAP (104 mg, 852 µmol) in toluene (9 mL) via a syringe pump over 2 h period. The residue of the mixture was then re-dissolved in toluene (1 mL) and then added to the solution of DMAP over 1 h period. The obtained white cloudy solution was stirred for additional 7 hours, and then treated with 0.1 M HCl (2 mL). The resulting mixture was diluted with water (3 mL) and extracted with ethyl acetate (3 x 3 mL), dried (MgSO4), filtered and concentrated under reduced pressure to afford a colorless oil. Subjection of the obtained crude material to flash chromatography (silica, 20 → 30 % v/v ethyl acetate/hexanes elution) afforded, after concentration of the appropriate fractions (Rf 0.3, 25 % v/v ethyl acetate/hexanes), the mixture of the deconjugated product 13b (ca. 3.9 mg, 18%) and the title compound 13a (ca. 12.6 mg, 58% yield). 13a: [α]D25 = -3.8 (c = 2.9, CHCl3); IR (film) 2946, 2926, 2885, 2854, 1787, 1711, 1609, 1513, 1467, 1249, 1171, 1072 cm⁻¹; 1H NMR (600 MHz, CDCl3) δ 7.23 (d, J = 9.1 Hz, 2H, PMPH), 7.20 (d, J = 8.9 Hz, 2H, PMPH), 6.84 (d, J = 8.5 Hz, 2H, PMPH), 6.82 (d, J = 8.8 Hz, 2H, PMPH), 6.76 (t, J = 6.6 Hz, 1H, C3H), 5.56–5.30 (m, 7H, C12H, C13H, C16H, C17H, C21H, C38H, C39H), 5.10 (q, J = 6.0 Hz, 1H, C41H), 4.58 (d, JAB = 11.1 Hz, 1H, PMPCHH), 4.56 (d, JAB = 12.0 Hz, 1H, PMPCHH), 4.53 (d, JAB = 10.5 Hz, 1H, PMPCHH), 4.45 (dd, J = 8.8, 6.7 Hz, 1H, C43H), 4.36 (d, JAB = 10.5 Hz, 1H, PMPCHH), 4.26 (d, J = 10.0 Hz, 1H, C22H), 4.24 (m, 1H, C37H), 4.08 (dd, J = 10.5, 4.4 Hz, 1H, C25H), 4.07 (m, 1H, C23H), 4.09 (m, 1H, C26H, C33H, C38H), 3.91 (dd, J = 7.0, 3.8 Hz, 1H, C13H), 3.88–3.82 (m, 4H, C9H, C19H, C27H, C29H), 3.79 (s, 3H, PMPOCH3), 3.78 (s, 3H, PMPOCH3), 3.72 (t, J = 9.8 Hz, 1H, C3H), 3.40 (d, J = 9.1 Hz, 1H, C7H), 2.51 (d, J = 10.0 Hz, 1H, C45H), 2.50 (d, J = 10.0 Hz, 1H, C45H), 2.34–2.28 (m, 3H, C40H2, C42H), 2.27 (dt, J = 12.6, 6.3 Hz, 1H, C44H), 2.26 (m, 1H, C18H), 2.26–2.07 (m, 2H, C4H, C4H), 1.96 (dd, J = 12.0, 9.0 Hz, 1H, C44H), 1.90–1.86 (m, 3H, C1H2, C14H), 1.81 (s, 3H, C2CH3), 1.80 (m, 1H, C8H), 1.74–1.70 (m, 1H, C36H), 1.69–1.53 (m, 6H, C6H, C26H, C28H, C30H, C32H, C34H, C38H), 1.56 (s, 3H, C20CH3), 1.48 (m, 1H, C10H), 1.39 (s, 3H, OC(CH3CH3)O), 1.37 (s, 3H, OC(CH3CH3)O), 1.39–1.21 (m, 7H, C3H, C5H, C10H, C24H,
Subjection of the obtained crude material to flash chromatography (RP-C₈ silica, 60 → 100 % v/v methanol/water elution) afforded, after concentration of the appropriate fractions (Rf 0.6, 20 % v/v water/methanol), fully deprotected and monosilylated oasomycin A. Resubmission of the monosilylated oasomycin A derivative to the deprotection conditions described above followed by a HPLC
purification of the combined crude samples (Eclipse XDB-C18 column, gradient: TFA (0.1% in H2O/MeOH 60 → 98% MeOH, 3 → 20 min, λ = 210 nm, Tt = 15.7 min) afforded synthetic oasomycin A (6.5 mg, 60%).

$\text{H}\text{T}\text{S}\text{O}\text{T}\text{B}\text{S}$

(1S,2R,3R,4R,5R,7S,9S,10E,13S,16E,20S,21R,22S,23S,26E,28S,29S,30E,32S,33R,34E,36S,37R,39S,41S)-5,7,9,23,29,33,36,37-octakis(tert-butyldimethylsilyloxy)-3,39-dihydroxy-2,4,16,20,22,28,32,34,43,43-decamethyl-13-((R)-1-((R)-5-oxo-tetrahydrofuran-2-yl)ethyl)-21-(triethyilsilyloxy)-14,42,44-trioxa-bicyclo[39.3.1]pentatetraconta-10,16,26,30,34-pentaen-15-one (14). $^1$H NMR (600 MHz, CDCl$_3$) δ 6.76 (t, J = 7.0 Hz, 1H, C$_3$H), 5.58–5.51 (m, 2H, C$_3$H, C$_3$H), 5.45 (dt, J = 15.8, 7.9 Hz, 2H, C$_{12}$H, C$_{16}$H), 5.36 (dd, J = 15.2, 7.1 Hz, 2H, C$_{13}$H, C$_{17}$H), 5.31 (d, J = 8.5 Hz, 1H, C$_{21}$H), 5.02 (q, J = 6.5 Hz, 1H, C$_{44}$H), 4.50 (dt, J = 8.8, 6.4 Hz, 1H, C$_{43}$H), 4.39 (d, J = 7.9 Hz, 1H, C$_{22}$H), 4.27–4.08 (m, 2H), 4.11 (m, 1H), 4.01–3.87 (m, 5H), 3.81 (dd, J = 13.5, 5.3 Hz, 1H), 3.86–3.78 (m, 2H), 3.43 (d, J = 9.4 Hz, 1H, C$_7$H), 2.51 (d, J = 9.4 Hz, 1H, C$_{45}$H), 2.49 (d, J = 9.7 Hz, 1H, C$_{45}$H), 2.38 (t, J = 6.7 Hz, 1H, C$_{46}$H), 2.34–2.28 (m, 2H, C$_{44}$H, C$_{44}$H), 2.27 (dt, J = 12.6, 6.3 Hz, 2H), 2.22 (d, J = 6.6 Hz, 1H), 2.19 (d, J = 6.6 Hz, 1H), 2.35 (m, 1H), 2.32 (appd dd, J = 13.8, 6.9 Hz, 1H), 2.3–2.26 (m, 1H), 2.18 (t, J$_{AB}$ = 6.3 Hz, 1H), 2.15 (t, J$_{AB}$ = 6.4 Hz, 1H), 2.21–2.06 (m, 2H), 1.95 (m, 1H), 1.82 (s, 3H, C$_2$CH$_3$), 1.80 (m, 1H), 1.58 (s, 3H, C$_{20}$CH$_3$), 1.75–1.53 (m, 6H), 1.42 (s, 3H, OC(CH$_3$CH$_3$))O, 1.41 (m, 1H), 1.33 (s, 3H, OC(CH$_3$CH$_3$)O), 1.43–1.19 (m, 8H), 0.97 (t, J = 7.9 Hz, 9H, Si(Ch$_3$Ch$_3$)), 0.94 (d, J = 7.4 Hz, 3H, CHCH$_3$), 0.92 (d, J = 7.0 Hz, 3H, CHCH$_3$), 0.90 (s, 9H, CH$_3$)CSi, 0.90 (s, 9H, (CH$_3$)$_2$CSi), 0.89 (s, 9H, (CH$_3$)$_3$CSi), 0.89 (s, 9H, (CH$_3$)$_3$CSi), 0.88 (s, 9H, (CH$_3$)$_3$CSi), 0.87 (s, 9H, (CH$_3$)$_3$CSi), 0.87 (s, 9H, (CH$_3$)$_3$CSi), 0.85 (s, 9H, (CH$_3$)$_3$CSi), 0.83 (d, J = 6.7 Hz, 3H, CHCH$_3$), 0.80 (d, J = 7.0 Hz, 3H, CHCH$_3$), 0.78 (d, J = 6.4 Hz, 3H, CHCH$_3$), 0.75 (d, J = 7.0 Hz, 3H, CHCH$_3$), 0.70 (d, J = 7.0 Hz, 3H, CHCH$_3$), 0.61 (q, J = 7.6 Hz, 6H, Si(Ch$_2$Ch$_3$)), 0.14 (s, 3H, SiCh$_3$), 0.11 (s, 3H, SiCh$_3$), 0.094 (s, 3H, SiCh$_3$), 0.077 (s, 3H, SiCh$_3$), 0.074 (s, 3H, SiCh$_3$), 0.067 (s, 3H, SiCh$_3$), 0.067 (s, 3H, SiCh$_3$), 0.063 (s, 3H, SiCh$_3$), 0.054 (s, 3H, SiCh$_3$), 0.042 (s, 3H, SiCh$_3$), 0.034 (s, 3H, SiCh$_3$), 0.027 (s, 3H, SiCh$_3$), 0.021 (s, 3H, SiCh$_3$), 0.006 (s, 3H, SiCh$_3$), −0.019 (s, 3H, SiCh$_3$), −0.019 (s, 3H, SiCh$_3$). LRMS (MALDI, 2,5-dihydroxybenzoic acid): Exact mass calcd for C$_{112}$H$_{224}$O$_{17}$Si$_9$ requires [M+Na]$^+$: 2117.4, [M+K]$^+$: 2133.4. Found: 2117.1, 2133.0.

Synthetic oasomycin A.$^{[3]}$ [α]$_D^{25}$ = −8.8 (c = 1.5, MeOH); $^1$H NMR (600 MHz, CD$_3$OD) δ 6.72 (td, J
Data for natural oasomycin A.\[^{[3]}\] \(^1\)H NMR (600 MHz, CD$_3$OD) δ 6.72 (td, \(J = 7.3, 1.0\) Hz, 1H, C$_3$H), 5.57–5.48 (m, 2H, C$_{30}$H, C$_{38}$H), 5.43–5.35 (m, 4H, C$_{12}$H, C$_{13}$H, C$_{17}$H, C$_{16}$H), 5.32 (d, \(J = 8.8\) Hz, 1H, C$_{21}$H), 5.02 (ddd, \(J = 9.1, 6.1, 3.5\) Hz, 1H, C$_{41}$H), 4.44 (q, \(J = 7.6\) Hz, 1H, C$_{43}$H), 4.19 (dd, \(J = 8.8, 3.5\) Hz, 1H, C$_{22}$H), 4.19 (m, 1H, C$_3$H), 4.08 (d, \(J = 10.0\) Hz, 1H, C$_{33}$H), 3.99 (m, 2H, C$_{25}$H, C$_{27}$H), 3.94 (d, \(J = 9.4, 1.8\) Hz, 1H, C$_{23}$H), 3.79 (q, \(J = 5.3\) Hz, 1H, C$_{13}$H), 3.75 (appt dt, \(J = 9.1, 2.6\) 1H, C$_3$H), 3.74–3.72 (m, 2H, C$_9$H, C$_{20}$H), 3.58 (d, \(J = 8.9\) Hz, 1H, C$_{19}$H), 3.31 (dd, \(J = 9.9, 1.8\) Hz, 1H, C$_7$H), 2.50 (dt, \(J = 17.9, 10.0\) Hz, 1H, C$_4$H), 2.41 (td, \(J = 9.4, 2.9\) Hz, 1H, C$_{45}$H), 2.36 (appt dt, \(J = 13.2, 3.2\) 1H, C$_{40}$H), 2.31 (appt dt, \(J = 14.8, 8.5\) Hz, 1H, C$_{46}$H), 2.24 (appt dq, \(J = 12.7, 6.7\) Hz, 1H, C$_{18}$H), 2.20–2.14 (m, 5H, C$_4$H, C$_4$H, C$_{11}$H, C$_{12}$H, C$_{44}$H), 2.12 (appt dt, \(J = 12.8, 7.2\) Hz, 1H, C$_{14}$H), 1.98 (m, 1H, C$_{11}$H), 1.91 (m, 1H, C$_{4a}$H), 1.77 (s, 3H, C$_2$-Me), 1.67 (m, 1H, C$_8$H), 1.64 (m, 1H, C$_{28}$H), 1.60–1.53 (m, 7H, C$_6$H, C$_{28}$H, C$_{30}$H, C$_{32}$H, C$_{34}$H, C$_{39}$H), 1.57 (s, 3H, C$_{20}$Me), 1.53–1.41 (m, 6H, C$_5$H, C$_{10}$H, C$_{26}$H, C$_{28}$H, C$_{36}$H, C$_{38}$H), 1.39 (t, \(J = 6.3\) Hz, 2H, C$_{2a}$H, C$_{24}$H), 1.41–1.29 (m, 2H, C$_3$H, C$_{16}$H), 1.02 (d, \(J = 6.4\) Hz, 3H, C$_{18}$-Me), 0.88 (d, \(J = 7.0\) Hz, 3H, C$_{14}$-Me), 0.87 (d, \(J = 7.0\) Hz, 3H, C$_{42}$-Me), 0.86 (d, \(J = 6.7\) Hz, 3H, C$_{32}$-Me), 0.80 (d, \(J = 6.7\) Hz, 3H, C$_6$-Me), 0.71 (d, \(J = 7.3\) Hz, 3H, C$_{30}$-Me), 0.69 (d, \(J = 7.0\) Hz, 3H, C$_8$-Me); $^{13}$C NMR (125 MHz, CD$_3$OD) δ 179.71 (C$_{46}$), 169.07 (C$_1$), 144.48 (C$_3$), 141.25 (C$_{20}$), 138.38 (C$_{38}$), 134.60 (C$_{13}$ or C$_{17}$), 133.91 (C$_{13}$ or C$_{17}$), 131.94 (C$_{12}$ or C$_{16}$), 131.59 (C$_{12}$ or C$_{16}$), 128.72 (C$_2$), 127.69 (C$_{21}$), 125.54 (C$_{39}$), 83.60 (C$_9$), 83.03 (C$_{43}$), 77.56 (C$_7$), 76.68 (C$_{15}$), 75.29 (C$_{29}$), 75.08 (C$_{41}$), 74.68 (C$_5$), 73.56 (C$_{23}$), 72.68 (C$_3$), 72.61 (C$_{22}$), 70.19 (C$_{33}$), 69.65 (C$_{37}$), 69.13 (C$_{27}$), 66.45 (C$_{35}$), 66.09 (C$_{25}$), 46.34 (C$_{36}$), 46.28 (C$_{26}$), 44.04 (C$_{14}$), 43.17 (C$_{28}$), 42.84 (C$_{34}$), 42.52 (C$_5$), 41.72 (C$_{24}$), 41.72 (C$_{42}$), 41.28 (C$_{32}$), 41.06 (C$_{18}$), 40.81 (C$_{30}$), 35.90 (C$_6$), 34.38 (C$_{40}$), 34.38 (C$_5$), 34.47 (C$_{10}$), 30.36 (C$_{11}$), 29.54 (C$_{45}$), 27.60 (C$_4$), 26.42 (C$_{44}$), 17.73 (C$_{18}$-CH$_3$), 16.07 (C$_{14}$-CH$_3$), 12.66 (C$_6$-CH$_3$), 12.52 (C$_2$-CH$_3$), 12.00 (C$_{20}$-CH$_3$), 11.97 (C$_8$-CH$_3$), 11.49 (C$_{32}$-CH$_3$), 10.26 (C$_{42}$-CH$_3$), 10.10 (C$_{30}$-CH$_3$). HRMS (TOF ES$^+$): Exact mass calcd for C$_{52}$H$_{94}$O$_{17}$ [M+Na$^+$]: 1049.639. Found: 1049.648.
C_{2a}H), 1.41–1.29 (m, 2H, C_{3}H, C_{10}H), 1.02 (d, J = 6.7 Hz, 3H, C_{18}-Me), 0.88 (d, J = 7.4 Hz, 3H, C_{14}-Me), 0.87 (d, J = 7.0 Hz, 3H, C_{42}-Me), 0.86 (d, J = 6.7 Hz, 3H, C_{32}-Me), 0.80 (d, J = 6.7 Hz, 3H, C_{6}-Me), 0.71 (d, J = 7.3 Hz, 3H, C_{30}-Me), 0.69 (d, J = 7.4 Hz, 3H, C_{8}-Me); ^{13}C NMR (125 MHz, CD_{3}OD) δ 179.69 (C_{46}), 169.05 (C_{1}), 144.46 (C_{3}), 141.24 (C_{20}), 138.39 (C_{38}), 134.58 (C_{13} or C_{17}), 133.92 (C_{13} or C_{17}), 131.94 (C_{12} or C_{16}), 131.58 (C_{12} or C_{16}), 128.71 (C_{2}), 127.70 (C_{21}), 125.52 (C_{39}), 83.60 (C_{19}), 83.01 (C_{43}), 77.56 (C_{7}), 76.67 (C_{15}), 75.28 (C_{29}), 75.07 (C_{41}), 74.69 (C_{9}), 73.54 (C_{23}), 72.67 (C_{31}), 72.61 (C_{22}), 70.15 (C_{33}), 69.64 (C_{37}), 69.12 (C_{27}), 66.44 (C_{35}), 66.07 (C_{25}), 46.33 (C_{36}), 46.29 (C_{26}), 44.03 (C_{14}), 43.15 (C_{28}), 42.82 (C_{34}), 42.54 (C_{8}), 41.70 (C_{24}), 41.70 (C_{42}), 41.28 (C_{32}), 41.07 (C_{18}), 40.81 (C_{30}), 35.90 (C_{6}), 34.38 (C_{40}), 34.38 (C_{5}), 34.47 (C_{10}), 30.37 (C_{11}), 29.54 (C_{45}), 27.60 (C_{4}), 26.40 (C_{44}), 17.74 (C_{18}-CH_{3}), 16.05 (C_{14}-CH_{3}), 12.67 (C_{6}-CH_{3}), 12.51 (C_{2}-CH_{3}), 12.00 (C_{20}-CH_{3}), 11.97 (C_{8}-CH_{3}), 11.47 (C_{32}-CH_{3}), 10.26 (C_{42}-CH_{3}), 10.09 (C_{30}-CH_{3}).

Reported data for natural oasomycin A.^[4] [α]D^{25} = −13.1 (c = 0.122, MeOH); ^{1}H NMR (500 MHz, [D6] DMSO) δ 6.69 (C_{3}H), 5.48 (C_{38}H), 5.48 (C_{39}H), 5.40 (C_{12}H), 5.39 (C_{17}H), 5.39 (C_{13}H), 5.34 (C_{16}H), 5.26 (C_{21}H), 5.00 (C_{41}H), 4.48 (C_{43}H), 4.14 (C_{37}H), 4.06 (C_{34}H), 4.05 (C_{22}H), 3.90 (C_{27}H), 3.90 (C_{23}H), 3.82 (C_{35}H), 3.74 (C_{15}H), 3.74 (C_{23}H), 3.68 (C_{31}H), 3.69 (C_{3}H), 3.62 (C_{29}H), 3.50 (C_{19}H), 3.25 (C_{7}H), 2.54 (C_{45}H), 2.54 (C_{45}H), 2.32 (C_{40}H), 2.18 (C_{18}H), 2.16 (C_{44}H), 2.16 (C_{44}H), 2.14 (C_{42}H), 2.08 (C_{14}H), 1.90 (C_{11}H), 1.88 (C_{4}H), 1.58 (C_{3}H), 1.54 (C_{5}H), 1.52 (C_{29}H), 1.52 (C_{6}H), 1.50 (C_{10}H), 1.46 (C_{30}H), 1.42 (C_{24}H), 1.42 (C_{34}H), 1.40 (C_{26}H), 1.34 (C_{36}H), 1.26 (C_{32}H), 1.26 (C_{3}H), 1.20 (C_{10}H), 1.11 (C_{34}H); ^{13}C NMR (125.7 MHz, [D6] DMSO) δ 176.7 (C_{46}), 166.4 (C_{1}), 142.5 (C_{3}), 138.2 (C_{38}), 138.1 (C_{20}), 132.7 (C_{17}), 132.5 (C_{13}), 130.9 (C_{16}), 129.5 (C_{12}), 126.9 (C_{21}), 126.8 (C_{2}), 122.4 (C_{39}), 81.0 (C_{19}), 80.4 (C_{43}), 74.6 (C_{7}), 74.3 (C_{15}), 73.0 (C_{41}), 72.8 (C_{29}), 72.0 (C_{9}), 70.9 (C_{22}), 70.8 (C_{23}), 70.8 (C_{31}), 66.8 (C_{33}), 66.8 (C_{37}), 66.7 (C_{27}), 63.8 (C_{35}), 63.7 (C_{25}), 45.7 (C_{36}), 45.6 (C_{26}), 42.2 (C_{28}), 42.2 (C_{34}), 42.2 (C_{14}), 41.4 (C_{8}), 40.4 (C_{24}), 40.1 (C_{32}), 39.9 (C_{42}), 39.5 (C_{30}), 39.2 (C_{18}), 34.3 (C_{6}), 32.9 (C_{5}), 32.4 (C_{40}), 32.0 (C_{10}), 28.9 (C_{11}), 28.2 (C_{45}), 24.8 (C_{44}), 26.0 (C_{4}), 16.8 (C_{18}-CH_{3}), 15.2 (C_{14}-CH_{3}), 12.2 (C_{6}-CH_{3}), 12.1 (C_{2}-CH_{3}), 11.5 (C_{20}-CH_{3}), 11.1 (C_{8}-CH_{3}), 10.5 (C_{32}-CH_{3}), 9.6 (C_{42}-CH_{3}), 9.4 (C_{30}-CH_{3}). HRMS (FAB): Exact mass calcd for [M+Na]^{+}: 1049.6389, [M+K]^{+}: 1065.6. Found: 1049.6389, 1065.6.
References and Notes:


[2] Refer to p. 30 of this supporting information.

[3] $^1$H and $^{13}$C NMR signals of natural and synthetic oasomycins A in CD$_3$OD were assigned based on the corresponding HSQC and COSY 2D correlation methods as well as using the isolation paper assignments (Reference [3]).

$^1$H NMR, CDCl$_3$, 600 MHz
$^{13}$C NMR, CDCl$_3$, 100 MHz

Chemical Shift (ppm)

Intensity

$^{13}$C NMR, CDCl$_3$, 100 MHz

MeMe
OTESOTBS
MeMe
OTBS
TBSO
Me
Me
OTBS
OPMB
OMe
O
O

1
288
$^1$H NMR, CDCl$_3$, 600 MHz
$^{13}$C NMR, CDCl$_3$, 100 MHz
STANDARD PROTON PARAMETERS

Data Collected on: mrsun-inova600
Archive directory: /export/home/1669/vn SYS/data
Sample directory:

File: PROTON
Pulse Sequence: z2pul
Solvent: CDCl3
Temp. 22.8 °C / 295.1 K
Relax. delay 1.000 sec
Pulse 90.0 degrees
Acq. time 3.424 sec
Width 0.126.5 Hz
6 repetitions

OBSERVE H2, 699.776464 MHz
DATA PROCESSING
Resol. enhancement 8.1 Hz
2T size 89888
Total time 6 min

[Chemical structure diagram]
$^{13}$C NMR, CDCl$_3$, 125 MHz
$^1$H NMR, CDCl$_3$, 600 MHz

[Chemical Spectrum Diagram]

Chemical Shift (ppm)

- 13a
- 13b

Normalized Intensity

$1H$ NMR, CDCl$_3$, 600 MHz
Chemical Shift (ppm)

$^{13}$C NMR, CDCl$_3$, 125 MHz

13a

13b

R

Normalized Intensity

220 200 180 160 140 120 100 80 60 40 20 0
Natural Oasomycin A, CD$_3$OD, 600 MHz

Synthetic Oasomycin A, CD$_3$OD, 600 MHz

Chemical Shift (ppm)
Natural Oasomycin A, 9mg/mL, 10 µL injection
Synthetic Oasomycin A, 7 mg/mL, 10 µL injection
Mixed Injection: Synthetic Oasomycin A, 7 mg/mL, 5 µL injection
Natural Oasomycin A, 9 mg/mL, 5 µL injection
TLC comparison of synthetic and natural samples of oasomycin A (Merck ready-to-use-plates, RP-8 F254S 0.25 mm thickness; methanol/water = 4:1, visualization with CAN).