Supporting Information Available

I) Experimental Section

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I) Experimental Section

Experimental Data for Compounds

General Procedures. All reactions were carried out under a nitrogen or argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Dry tetrahydrofuran (THF), pentane, diethyl ether (Et₂O), 1,2-dimethoxyethane (DME), 1,4-dioxane, methylene chloride (CH₂Cl₂), toluene and triethylamine (Et₃N) were obtained by passing commercially available pre-dried, oxygen-free formulations through activated alumina columns. Methanol (MeOH), benzene and dimethyl sulfoxide (DMSO) were purchased in anhydrous form and used without further purification. Water, ethyl acetate (EtOAc), diethyl ether (Et₂O), methylene chloride (CH₂Cl₂), acetone and hexanes were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Yields refer to chromatographically and spectroscopically (¹H NMR) homogeneous materials, unless otherwise stated. Reactions were monitored by thin-
layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and an ethanolic solution of ammonium molybdate, anisaldehyde, and heat as developing agents. E. Merck silica gel (60, particle size 0.040–0.063 mm) was used for flash column chromatography. NMR spectra were recorded on a Bruker AV-400 instrument and calibrated using residual undeuterated solvent as an internal reference. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, pent = pentet, hex = hexet, br = broad. IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer with diamond ATR accessory. Melting points (m.p.) are uncorrected, and recorded on a Buchi B-540 melting point apparatus. High-resolution mass spectra (HRMS) were recorded on an Agilent ESI TOF (time of flight) mass spectrometer at 3500 V emitter voltage.

Benzyl ester 11: To a stirred solution of 9\(^1\) (33.42 g, 100.0 mmol) in DMF (150 mL) at room temperature were added K\(_2\)CO\(_3\) (27.64 g, 200.0 mmol) followed by BnBr (14.25 ml, 120.0 mmol). The resulting mixture was stirred for 0.5 h before it was quenched with H\(_2\)O (150 mL). The mixture was extracted with Et\(_2\)O (3 × 200 mL). The combined organic layers were dried (Na\(_2\)SO\(_4\)) and concentrated in vacuo. Flash column chromatography (silica gel, hexanes:EtOAc 4:1) afforded benzyl ester 11 (38.16 g, 90%) as a yellow amorphous solid. 11: \(R_f = 0.32\) (hexanes:EtOAc 2:1); \([\alpha]_{D}^{20} = +3.5\) (c = 1.0, CHCl\(_3\)); IR (film) \(\nu_{\text{max}}\) 3348, 3103, 2969, 2891, 2757, 1741, 1711, 1612, 1573, 1491, 1358, 1246, 1138, 1031, 846, 758, 721 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.27\) (d, \(J = 20.7\) Hz,
1 H), 7.31–7.23 (m, 3 H), 7.21–7.14 (m, 2 H), 7.10 (dd, \( J = 8.0, 2.6 \) Hz, 1 H), 7.00–
6.93 (m, 1 H), 6.70 (s, 1 H), 6.57 (d, \( J = 7.7 \) Hz, 1 H), 5.03 (q, \( J = 12.1 \) Hz, 3 H), 4.65
(s, 1 H), 3.87 (s, 3 H), 3.27–3.13 (m, 2 H), 1.37 ppm (s, 9 H); \(^{13}\)C NMR (100 MHz, 
CDCl\( _3 \)): \( \delta = 172.2, 155.3, 146.2, 135.4, 129.1, 128.5 \) (2C), 128.4 (2C), 128.3, 126.7, 
122.5, 120.1, 111.6, 110.3, 101.9, 79.8, 67.1, 55.3, 54.4, 28.3 (3C), 28.1 ppm; HRMS
(ESI): calcd for C\(_{24}H_{29}N_2O_5^+\) [M + H\(^+\)] 425.2071, found 425.2074.

**Indoline 12**: To a stirred solution of benzyl ester 11 (21.20 g, 50.0 mmol) in AcOH
(100 mL) at 0 °C was added NaBH\(_3\)CN (6.20 g, 100.0 mmol). The resulting mixture was stirred at room temperature for 24 h
before it was concentrated in vacuo and quenched with NaHCO\(_3\)
(100 mL, sat. aq.). The aqueous layer was extracted with EtOAc (3 × 100 mL). The
combined organic layers were dried (Na\(_2\)SO\(_4\)) and concentrated in vacuo. Flash column
chromatography (silica gel, CH\(_2\)Cl\(_2\):EtOAc 20:1) afforded indoline 12 (17.89 g, 84%,
ca. 1.2:1 mixture of diastereomers by \(^1\)H NMR) as a colorless oil.

**12a**: \( R_f = 0.25 \) (hexanes:EtOAc 3:1); [\( \alpha \)]\(_{D}^{20} = -31.8 \) (c = 0.5, CHCl\(_3\)); IR (film) \( \nu_{\text{max}} \) 3326,
3084, 2971, 2856, 2713, 1739, 1713, 1610, 1582, 1501, 1366, 1238, 1140, 1027, 851,
760, 723 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.34 \) (s, 5 H), 6.74–6.63 (m, 3 H), 
5.22–5.06 (m, 3 H), 4.45 (td, \( J = 9.2, 4.5 \) Hz, 1 H), 3.81 (s, 3 H), 3.77 (d, \( J = 8.5 \) Hz, 1
H), 3.45–3.36 (m, 1 H), 3.36–3.26 (m, 1 H), 2.07 (td, \( J = 10.4, 9.7, 4.3 \) Hz, 2 H), 1.45
ppm (s, 9 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 172.7, 155.5, 145.5, 140.2, 135.2, 132.7,
128.6 (3C), 128.4, 128.3, 119.3, 116.1, 109.7, 80.1, 67.2, 55.3, 53.5, 52.2, 39.4, 37.4,
28.3 ppm (3C); HRMS (ESI): calcd for C\(_{24}H_{31}N_2O_5^+\) [M + H\(^+\)] 427.2227, found
12b: $R_f = 0.20$ (hexanes:EtOAc 3:1); $[\alpha]_{D}^{20} = +28.1$ ($c = 0.4$, CHCl$_3$); IR (film) $\nu_{\text{max}}$ 3332, 3092, 2969, 2857, 2721, 1735, 1721, 1611, 1583, 1505, 1370, 1240, 1142, 1030, 853, 764, 726 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.34 (s, 5 H), 6.82–6.64 (m, 3 H), 5.16 (d, $J = 2.8$ Hz, 3 H), 4.54–4.41 (m, 1 H), 3.81 (s, 3 H), 3.71 (t, $J = 8.7$ Hz, 1 H), 3.44–3.34 (m, 1 H), 3.23 (dd, $J = 8.8$, 7.0 Hz, 1 H), 2.37–2.25 (m, 1 H), 1.87 (m, $J = 14.0$, 8.2 Hz, 1 H), 1.45 ppm (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 172.6, 155.2, 145.5, 140.1, 135.2, 132.6, 128.6 (3C), 128.4, 128.3, 119.4, 116.5, 109.7, 80.1, 67.1, 55.3, 53.9, 52.5, 39.6, 37.3, 28.3 ppm (3C); HRMS (ESI): calcd for C$_{24}$H$_{31}$N$_2$O$_5$+$ [M + H$^+$] 427.2227, found 427.2232.

Indoline ester 8: To a stirred solution of indoline 12 (4.05 g, 9.5 mmol) in CH$_2$Cl$_2$ (15 mL) at room temperature were added Et$_3$N (2.65 mL, 19.0 mmol) followed by a solution of acyl chloride 10$^2$ (4.20 g, 19.0 mmol) in CH$_2$Cl$_2$ (10 mL). The resulting mixture was stirred for 1 h before it was quenched with NH$_4$Cl (20 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH$_2$Cl$_2$ (3 $\times$ 20 mL). The combined organic layers were washed with brine (30 mL), dried (Na$_2$SO$_4$) and concentrated in vacuo. Flash column chromatography (silica gel, hexanes:EtOAc 3:1) afforded indoline ester 8 (5.12 g, 88%, ca. 1.2:1 mixture of diastereomers by $^1$H NMR) as a colorless oil.

8a: $R_f = 0.25$ (hexanes:EtOAc 2:1); $[\alpha]_{D}^{20} = -31.3$ ($c = 0.7$, CHCl$_3$); IR (film) $\nu_{\text{max}}$ 3357, 3105, 2967, 2867, 2769, 1741, 1703, 1651, 1523, 1483, 1358, 1246, 1158, 1031, 864,
δ-Lactamindole 7: To a solution of indoline ester 8 (6.12 g, 10.0 mmol) in AcOH (100 mL) were added CAN (550 mg, 1.0 mmol) and NaOAc (1.64 g, 20.0 mmol). The reaction vessel was exposed to air through a CaCl₂ tube. The resulting mixture was
stirred at 110 °C for 12 h before it was cooled down to room temperature and concentrated *in vacuo*. The residue was diluted with H₂O (100 mL), neutralized with NaHCO₃ (200 mL, sat. aq.) and extracted with EtOAc (3 × 200 mL). The combined organic layers were washed with brine (400 mL), dried (Na₂SO₄) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 1:1) afforded δ-lactamindole 7 (5.05g, 83%) as a white amorphous solid. 7: *R*ᵣ = 0.35 (hexanes:EtOAc 1:1); [α]ᵣ⁰ = −8.6 (c = 0.7, CHCl₃); IR (film) νₘₚₐₓ 3413, 3095, 2967, 1744, 1709, 1513, 1458, 1362, 1246, 1172, 1047, 1010, 918, 761, 721 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.37–7.20 (m, 7 H), 6.95–6.90 (m, 1 H), 5.51 (d, *J* = 6.8 Hz, 1 H), 5.13 (s, 2 H), 4.75 (dd, *J* = 11.2, 5.4 Hz, 1 H), 3.97 (s, 3 H), 3.80 (s, 3 H), 3.73 (s, 3 H), 3.09 (dd, *J* = 14.9, 5.6 Hz, 1 H), 2.97–2.82 (m, 3 H), 2.79–2.63 (m, 2 H), 1.34 ppm (s, 9 H); ¹³C NMR (100 MHz, CDCl₃): δ = 172.4, 169.4, 169.2, 165.1, 155.3, 149.1, 135.5, 133.3, 131.8, 128.4 (2C), 128.2, 128.1 (2C), 125.6, 124.3, 117.2, 112.1, 109.3, 79.7, 67.1, 56.5, 55.9, 53.9, 53.6, 52.9, 31.1, 29.4, 28.2 (3C), 27.1 ppm; HRMS (ESI): calcd for C₃₂H₃₇N₂O₁₀⁺ [M + H⁺] 609.2443, found 609.2450.

**Monoester 13:** To a stirred solution of δ-lactamindole 7 (1.82 g, 3.0 mmol) in DMSO (20 mL) were added LiCl (1.26 g, 30 mmol) and H₂O (0.54 mL, 30.0 mmol). The resulting mixture was stirred at 65 °C for 8 h before it was quenched with ice water (40 mL, sat. aq.) and extracted with Et₂O (3 × 50 mL). The combined organic
layers were dried (Na$_2$SO$_4$) and concentrated *in vacuo*. Flash column chromatography (silica gel, CH$_2$Cl$_2$:Et$_2$O 20:1) afforded monoesters 13a and 13b (1.35 g, 82% ca. 1:1 mixture of diastereomers by $^1$H NMR) as a colorless oil.

**13a:** $R_f = 0.20$ (CH$_2$Cl$_2$:Et$_2$O 20:1); $[\alpha]_D^{20} = -21.8$ (c = 2.0, CHCl$_3$); IR (film) $\nu_{\text{max}}$ 3412, 3358, 3096, 2976, 1705, 1523, 1462, 1298, 1230, 1168, 1048, 986, 753, 714 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.30 (s, 3 H), 7.22 (d, $J$ = 7.8 Hz, 1 H), 7.20–7.06 (m, 3 H), 6.89 (d, $J$ = 8.0 Hz, 1 H), 5.09 (dd, $J$ = 21.1, 8.5 Hz, 2 H), 4.97 (d, $J$ = 12.1 Hz, 1 H), 4.68–4.56 (m, 1 H), 4.11 (s, 1 H), 3.97 (s, 3 H), 3.67 (s, 3 H), 3.29–3.11 (m, 2 H), 3.07–2.92 (m, 1 H), 2.76 (d, $J$ = 17.0 Hz, 1 H), 2.44 (d, $J$ = 12.6 Hz, 1 H), 2.13 (s, 1 H), 1.40 ppm (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 171.8, 171.3, 166.4, 155.1, 149.1, 134.9, 134.2, 133.3, 128.5 (3C), 128.4, 128.1, 125.2, 124.5, 114.4, 111.7, 109.1, 80.1, 67.3, 56.7, 53.6, 52.6, 37.9, 31.7, 28.2 (3C), 27.3, 24.5 ppm; HRMS (ESI): calcd for C$_{30}$H$_{35}$N$_2$O$_8^+$ [M + H$^+$] 551.2388, found 551.2384.

**13b:** $R_f = 0.20$ (CH$_2$Cl$_2$:Et$_2$O 20:1); $[\alpha]_D^{20} = +6.0$ (c = 1.2, CHCl$_3$); IR (film) $\nu_{\text{max}}$ 3400, 3365, 3090, 2976, 1701, 1515, 1456, 1370, 1250, 1168, 1071, 978, 748, 710 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.34–7.27 (m, 3 H), 7.24 (d, $J$ = 7.9 Hz, 1 H), 7.13 (dd, $J$ = 10.1, 5.8 Hz, 3 H), 6.90 (d, $J$ = 7.9 Hz, 1 H), 5.23 (d, $J$ = 7.1 Hz, 1 H), 5.05 (d, $J$ = 3.2 Hz, 2 H), 4.72 (d, $J$ = 7.1 Hz, 1 H), 4.09 (s, 1 H), 3.98 (s, 3 H), 3.68 (s, 3 H), 3.24–2.93 (m, 3 H), 2.82–2.70 (m, 1 H), 2.45 (ddt, $J$ = 13.5, 5.3, 2.6 Hz, 1 H), 2.13–1.98 (m, 1 H), 1.38 ppm (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 172.1, 171.3, 166.3, 155.1, 149.2, 135.1, 134.1, 132.9, 128.5 (3C), 128.3, 127.9, 125.3, 124.5, 114.1, 111.4, 109.1, 80.1, 67.1, 56.7, 53.1, 52.7, 37.8, 31.7, 28.2(3C), 27.6, 24.1 ppm; HRMS (ESI): calcd
for C$_{30}$H$_{35}$N$_{2}$O$_{8}$ [M + H$^+$] 551.2388, found 551.2392.

**Pyrrroloindole 6':** To a stirred solution of monoesters 13a and 13b (5.50 g, 10.0 mmol) in acetone (100 mL) at 0 °C was added NaHCO$_3$ (100 mL, sat. aq.). The resulting mixture was stirred for 0.5 h before it was added oxone (12.28 g, 20.0 mmol). The reaction mixture was stirred at 0 °C for an additional 2 h before it was diluted with H$_2$O (100 mL). The aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 200 mL). The combined organic layers were washed with brine (300 mL), dried (Na$_2$SO$_4$) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 1:3) afforded pyrrroloindole 6' (3.86 g, 68%) as a white amorphous solid. 6': $R_f = 0.23$ (hexanes:EtOAc 3:1); [α]$_D^{20} = +8.0$ (c = 1.0, MeOH); IR (film) $\nu_{\text{max}}$ 3412, 3368, 2984, 2924, 2877, 1701, 1680, 1634, 1596, 1370, 1243, 1160,1041, 912, 758, 724 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.32$ (q, $J = 7.2$ Hz, 5 H), 7.19 (t, $J = 7.8$ Hz, 1 H), 7.04 (d, $J = 7.4$ Hz, 1 H), 6.94 (d, $J = 6.6$ Hz, 1 H), 5.16 (d, $J = 12.0$ Hz, 1 H), 5.02 (d, $J = 12.3$ Hz, 1 H), 4.24 (s, 1 H), 3.76 (s, 6 H), 3.61 (s, 1 H), 3.37 (dd, $J = 13.8$, 3.4 Hz, 1 H), 3.23 (s, 1 H), 2.97 (s, 1 H), 2.69 (dd, $J = 12.4$, 7.4 Hz, 1 H), 2.59–2.31 (m, 2 H), 2.10–1.87 (m, 1 H), 1.33 ppm (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 171.1$, 167.9, 161.4, 158.7, 151.5, 135.5, 135.2, 135.1, 129.9, 128.5 (3C), 128.4, 128.2, 127.6, 115.7, 88.3, 86.9, 82.1, 66.7, 58.2, 53.1, 45.7, 30.9, 29.7, 29.3, 27.9 (3C), 20.1 ppm; HRMS (ESI): calcd for C$_{30}$H$_{35}$N$_{2}$O$_{8}$ [M + H$^+$] 567.2337, found 567.2335.

**Silyl ether 15:** To a stirred solution of pyrrroloindole 6' (1.13 g, 2.0 mmol) in CH$_2$Cl$_2$...
(20 mL) at room temperature were added DMAP (2.44 g, 20.0 mmol) and TESOTf (1.35 mL, 6.0 mmol). The resulting mixture was stirred for 1 h before it was quenched with NaHCO₃ (35 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 20 mL). The combined organic layers were washed with brine (40 mL), dried (Na₂SO₄) and concentrated in vacuo. Flash column chromatography (silica gel, hexanes:EtOAc 3:1) afforded silyl ether 15 (1.16 g, 85%) as a colorless oil. 15: Rf = 0.40 (hexanes:EtOAc 3:1); [α]D²⁰ = −12.0 (c = 0.5, CHCl₃); IR (film) νmax 3551, 3434, 2957, 2861, 2334, 1746, 1671, 1483, 1236, 1138, 1021, 760, 723 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.31 (s, 5 H), 7.17 (t, J = 7.9 Hz, 1 H), 6.95 (dd, J = 26.9, 7.5 Hz, 2 H), 5.24–4.99 (m, 2 H), 3.88–3.65 (m, 6 H), 3.64–3.36 (m, 2 H), 3.22–2.75 (m, 2 H), 2.69–2.54 (m, 2 H), 2.34 (ddd, J = 18.6, 11.8, 6.9 Hz, 1 H), 2.04–1.91 (m, 1 H), 1.46 (s, 6 H), 1.17 (s, 3 H), 0.82 (t, J = 7.9 Hz, 9 H), 0.56–0.40 ppm (m, 6 H); ¹³C NMR (100 MHz, CDCl₃): δ = 170.7, 170.2, 168.1, 153.7, 152.3, 136.2, 135.8, 130.3, 128.4, 128.1, 127.3, 126.9, 116.8, 115.7, 115.2, 114.1, 89.4, 86.6, 82.1, 66.6, 58.7, 55.7, 52.2, 44.3, 34.8, 30.7, 28.1 (3C), 21.4, 6.7 (3C), 6.1 ppm (3C); HRMS (ESI): calcd for C₃₆H₄₉N₂O₉Si⁺ [M + H⁺] 681.3202, found 681.3208.

Acid 16: To a stirred solution of silyl ether 15 (0.68 g, 1.0 mmol) in CH₂Cl₂ (20 mL) was added Pd/C (10 % wt/wt, 0.07 g) and bubbled with H₂ over 3 h before it was filtered through a short pad of celite. The filtrate was concentrated in vacuo. Flash column chromatography (silica gel, CH₂Cl₂:MeOH 20:1) afforded acid 16 (0.51 g, 86%) as a
colorless oil. 16: $R_f = 0.50$ (CH$_2$Cl$_2$:MeOH 20:1); $[\alpha]_{D}^{20} = +42.7$ ($c = 0.8$, CHCl$_3$); IR (film) $\nu_{\text{max}}$ 3584, 3431, 2974, 2852, 2371, 1746, 1710, 1681, 1463, 1326, 1249, 1123, 1034, 923, 749, 721 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.20$ (t, $J = 7.8$ Hz, 1 H), 7.04–6.95 (m, 2 H), 3.79 (d, $J = 6.1$ Hz, 6 H), 3.53 (s, 1 H), 3.35 (s, 1 H), 2.92 (s, 2 H), 2.71 (dd, $J = 12.3$, 6.5 Hz, 1 H), 2.58–2.14 (m, 2 H), 2.02 (s, 1 H), 1.34 (s, 9 H), 0.81 (t, $J = 7.9$ Hz, 9 H), 0.45 ppm (q, $J = 7.9$ Hz, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 172.9, 171.8, 167.6, 152.0 (2C), 130.6, 127.2 (3C), 115.8, 89.7, 86.4, 83.0, 60.9, 56.5, 54.6, 52.9, 44.1, 31.3, 27.7 (3C), 22.8, 6.6 (3C), 6.00 ppm (3C); HRMS (ESI): calcd for C$_{29}$H$_{43}$N$_2$O$_9$Si$^+$ [$M + H^+$] 591.2732, found 591.2734.

Acetate 17: To a stirred solution of acid 16 (0.59 g, 1.0 mmol) in CH$_2$Cl$_2$ (10 mL) at room temperature were added iodine (0.16 g, 0.5 mmol) followed by PhI(OAc)$_2$ (0.62 g, 2.0 mmol). The resulting mixture was stirred for 3 h before it was quenched with NaHCO$_3$ (20 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 10 mL). The combined organic layers were washed with brine (20 mL), dried (Na$_2$SO$_4$) and concentrated in vacuo. Flash column chromatography (silica gel, hexanes:EtOAc 3:1) afforded acetate 17 (0.50 g, 83%) as a colorless oil. 17: $R_f = 0.42$ (hexanes:EtOAc 3:1); $[\alpha]_{D}^{20} = +36.0$ ($c = 1.0$, CHCl$_3$); IR (film) $\nu_{\text{max}}$ 3572, 3428, 2965, 2849, 2342, 1736, 1669, 1453, 1232, 1140, 1051, 756, 719 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.18–7.10 (m, 1 H), 7.00 (d, $J = 7.9$ Hz, 1 H), 6.95 (d, $J = 7.5$ Hz, 1 H), 6.08 (d, $J = 5.3$ Hz, 1 H), 3.82 (s, 3 H), 3.73 (s, 3 H), 3.50–3.40 (m, 1 H), 3.01 (s, 2 H), 2.55–2.37 (m, 3 H), 2.05–1.93 (m, 1 H), 1.57 (s, 3
H), 1.36 (s, 9 H), 0.81 (t, J = 7.9 Hz, 9 H), 0.46 ppm (q, J = 7.9 Hz, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 171.9, 169.7, 168.3, 167.6, 152.5, 152.1, 136.7, 131.1, 126.1, 117.2, 114.2, 89.7, 85.8, 81.6, 57.1, 52.1, 43.2, 30.9, 29.7, 28.1 (3C), 23.1, 20.6, 6.6 (3C), 6.1 ppm (3C); HRMS (ESI): calcd for C$_{30}$H$_{45}$N$_2$O$_9$Si$^+$ [M + H$^+$] 605.2889, found 605.2885.

**Pyrroloindole 18**: To a stirred solution of acid 16 (1.18 g, 2.0 mmol) in CH$_2$Cl$_2$ (20 mL) at room temperature were added iodine (0.32 g, 1.0 mmol) followed by PhI(OAc)$_2$ (1.23 g, 4.0 mmol). The resulting mixture was stirred for 3 h before it was added NaBH$_3$CN (1.24 g, 20.0 mmol). The resulting mixture was stirred for further 1 h before it was quenched with NaHCO$_3$ (20 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 30 mL). The combined organic layers were dried (Na$_2$SO$_4$) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 3:1) afforded pyrroloindole 18 (0.95 g, 76%) as a yellow oil. 18: 

$^{1}$H NMR (400 MHz, CDCl$_3$): δ = 7.15 (t, J = 7.9 Hz, 1 H), 6.95 (dd, J = 14.9, 7.9 Hz, 2 H), 3.86 (s, 2 H), 3.73 (s, 3 H), 3.49–3.36 (m, 1 H), 3.21 (t, J = 10.1 Hz, 2 H), 2.99–2.65 (m, 3 H), 2.34 (dq, J = 43.1, 11.3 Hz, 3 H), 2.02–1.90 (m, 1 H), 1.38 (d, J = 48.1 Hz, 9 H), 0.82 (t, J = 7.9 Hz, 9 H), 0.47 ppm (d, J = 7.9 Hz, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 171.9, 167.8, 153.7, 152.2, 136.5, 130.7, 126.8, 115.4, 114.4, 88.4, 87.2, 81.0, 55.9, 52.1, 44.9, 43.3, 30.9, 30.3, 28.1 (3C), 22.4, 6.7 (3C), 6.1 ppm (3C); HRMS (ESI):
Alternatively, pyrroloindole 18 can also be obtained from acetate 17 through the following procedure:

To a stirred solution of acetate 17 (121 mg, 0.2 mmol) in CH$_2$Cl$_2$ (5 mL) at room temperature was added NaBH$_3$CN (124 mg, 2.0 mmol). The resulting mixture was stirred for 1 h before it was quenched with NaHCO$_3$ (5 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 10 mL). The combined organic layers were dried (Na$_2$SO$_4$) and concentrated in vacuo. Flash column chromatography (silica gel, hexanes:EtOAc 3:1) afforded pyrroloindole 18 (97 mg, 90%) as a yellow oil.

**Synthesis of pyrroloindole 18 through reductive decarboxylation of Barton ester:**

To a stirred solution of acid 16 (59 mg, 0.10 mmol) in THF (5 mL) at room temperature were added Et$_3$N (56 μL, 0.40 mmol), DMAP (6 mg, 0.05 mmol) and HOTT$_3$ (56 mg, 0.15 mmol). The resulting mixture was stirred in the dark for 2 h before it was added t-dodecanethiol (41 mg, 0.20 mmol). The resulting mixture was stirred at 65 ºC for further 12 h before it was cooled to room temperature and diluted with H$_2$O (10 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with Et$_2$O (3 × 10 mL). The combined organic layers were dried (Na$_2$SO$_4$) and concentrated in vacuo. Flash column chromatography (silica gel, hexanes:EtOAc 3:1) afforded pyrroloindole 18 (23 mg, 43%) as a yellow oil.

**Synthesis of pyrroloindole 18 through reductive decarboxylation of selenoester:**

To a stirred solution of acid 16 (59 mg, 0.10 mmol) in CH$_2$Cl$_2$ (5 mL) at 0 ºC were...
added PhSeSePh (47 mg, 0.15 mmol) and \( n\)-Bu\(_3\)P (76 \( \mu\)L, 0.30 mmol). The resulting mixture was stirred at room temperature for 12 h before it was diluted with EtOAc (5 mL) and washed with H\(_2\)O (5 mL). The organic layer was dried (Na\(_2\)SO\(_4\)) and concentrated \textit{in vacuo}. Flash column chromatography (silica gel, hexanes:EtOAc 5:1) afforded crude selenoester (68 mg, 83\%) as a yellow solid, which was subjected immediately into the next step.

To a stirred solution of the selenoester (crude, obtained above) in benzene (8 mL) were added AIBN (8 mg, 0.05 mmol) and (TMS)\(_3\)SiH (138 \( \mu\)L, 0.40 mmol). The resulting mixture was stirred at 80 °C for 24 h before it was cooled to room temperature and concentrated \textit{in vacuo}. Flash column chromatography (silica gel, hexanes:EtOAc 3:1) afforded pyrroloindole 18 (29 mg, 54\%) as a yellow oil.

\textbf{Amine 19:} To a stirred solution of pyrroloindole 18 (1.09 g, 2.0 mmol) in CH\(_2\)Cl\(_2\) (9 mL) at 0 °C was added CF\(_3\)CO\(_2\)H (3 ml). The resulting mixture was stirred at room temperature for 1 h before it was quenched with NaHCO\(_3\) (20 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH\(_2\)Cl\(_2\) (3 \( \times \) 20 mL). The combined organic layers were washed with brine (40 mL), dried (Na\(_2\)SO\(_4\)) and concentrated \textit{in vacuo}. Flash column chromatography (silica gel, hexanes:EtOAc 1:1) afforded amine 19 (0.80 g, 90\%) as a colorless oil. 19: \( R_f = 0.33 \) (hexanes:EtOAc 1:2); [\( \alpha \)]\(_{50}^0\) = +28.0 (\( c = 0.8, \text{CHCl}_3\)); IR (film) \( \nu_{\text{max}} \) 3572, 3423, 2974, 2812, 2364, 1738, 1668, 1474, 1239, 1126, 1031, 986, 768, 724 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.17 \) (t, \( J = 7.9 \) Hz, 1 H), 7.01–6.97 (m, 1 H), 6.94 (d, \( J = 7.9 \) Hz, 1 H), 3.88 (s, 3 H), 3.73 (s, 3 H), 3.10 (s, 3 H), 3.10
(dd, J = 13.1, 2.8 Hz, 1 H), 2.91 (t, J = 9.1 Hz, 1 H), 2.83 (ddd, J = 17.8, 6.6, 1.4 Hz, 1 H), 2.50–2.15 (m, 6 H), 2.08 (ddd, J = 4.9, 2.8, 1.4 Hz, 1 H), 0.82 (t, J = 7.9 Hz, 9 H), 0.45 ppm (m, J = 8.4, 4.4 Hz, 6 H); 13C NMR (100 MHz, CDCl3): δ = 173.1, 167.1, 151.3, 136.9, 130.9, 126.5, 116.1, 113.8, 92.1, 88.3, 56.1, 51.7, 44.6, 43.8, 37.2, 32.1, 21.6, 6.7 (3C), 6.1 ppm (3C); HRMS (ESI): calcd for C23H35N2O5Si+ [M + H+] 447.2310, found 447.2312.

Vinyl bromide 21: To a stirred solution of amine 19 (580 mg, 1.3 mmol) in MeCN (10 mL) were added allyl iodide 20 (642 mg, 2.6 mmol) and K2CO3 (542 mg, 3.9 mmol). The resulting mixture was stirred at 50 °C for 12 h before it was cooled to room temperature and filtered through a short pad of celite. The filtrate was diluted with EtOAc (15 mL) and washed with brine (15 mL). The organic layer was dried (Na2SO4) and concentrated in vacuo. Flash column chromatography (silica gel, hexanes:EtOAc 3:1) afforded vinyl bromide 21 (623 mg, 85%) as a colorless oil. 21: Rf = 0.40 (hexanes:EtOAc 3:1); [α]20D = +64.5 (c = 1.0, CHCl3); IR (film) νmax 2972, 2874, 2831, 2370, 1729, 1667, 1478, 1379, 1253, 1166, 1017, 775, 735 cm−1; 1H NMR (400 MHz, CDCl3): δ = 7.20 (s, 1 H), 7.00–6.94 (m, 2 H), 5.87 (d, J = 1.4 Hz, 1 H), 5.46–5.41 (m, 1 H), 3.93 (d, J = 15.5 Hz, 4 H), 3.72 (s, 3 H), 3.72 (t, J = 8.2 Hz, 1 H), 2.88 (ddd, J = 17.7, 6.1, 2.2 Hz, 1 H), 2.73 (d, J = 16.8 Hz, 1 H), 2.53–2.36 (m, 2 H), 2.35–2.23 (m, 2 H), 2.11–2.02 (m, 1 H), 1.78 (ddd, J = 11.2, 8.5, 6.4 Hz, 1 H), 0.82 (t, 9 H), 0.48 ppm (m, 6 H); 13C NMR (100 MHz, CDCl3): δ = 171.6, 168.4, 151.5, 137.5, 131.2, 130.7, 127.1, 116.9, 115.6, 114.1, 92.2, 87.7, 59.9, 56.3,
51.5, 50.8, 45.9, 34.1, 31.5, 20.6, 6.7 (3C), 6.1 ppm (3C); HRMS (ESI): calcd for C_{26}H_{38}BrN_{2}O_{5}Si^{+} [M + H^{+}] 565.1728, found 565.1730.

**Enone ent-5 and Amine 22:** To a stirred solution of vinyl bromide 21 (620 mg, 1.1 mmol) in THF (10 mL) at –78 °C was added LiHMDS (1.0 M in THF, 1.65 mL, 1.65 mmol). The resulting mixture was stirred for 0.5 h before it was added a solution of PhSeCl (316 mg, 1.65 mmol) in THF (10 mL). The resulting mixture was stirred at –78 °C for further 0.5 h before it was diluted with EtOAc (15 mL) and quenched with NaHCO_{3} (10 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (20 mL), dried (Na_{2}SO_{4}) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 5:1) afforded crude selenide (750 mg, 95%), which was subjected immediately into the next step.

To a stirred solution of the selenide (crude, obtained above) in THF (10 mL) at room temperature was added H_{2}O_{2} (30% wt/wt in H_{2}O, 0.34 mL, 3.0 mmol). The resulting mixture was stirred for 0.5 h before it was diluted with Et_{2}O (5 mL) and quenched with Na_{2}S_{2}O_{3} (10 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with Et_{2}O (3 × 10 mL). The combined organic layers were washed with brine (20 mL), dried (Na_{2}SO_{4}) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 5:1) afforded enone *ent-5* (56 mg, 10%) as a colorless oil, along with amine 22 (365 mg, 65%) as a colorless oil.
**ent-5:** $R_f = 0.32$ (hexanes:EtOAc 5:1); $[\alpha]_D^{20} = +45.6 \ (c = 1.0, \ CHCl_3)$; IR (film) $\nu_{\text{max}}$ 2971, 2868, 2816, 2371, 1735, 1671, 1476, 1379, 1238, 1173, 1133, 1015, 741, 713 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.20 \ (t, J = 7.9 \text{ Hz}, 1 \text{ H}), 7.05–6.95 \ (m, 2 \text{ H}), 6.81 \ (dd, J = 10.1, 2.1 \text{ Hz}, 1 \text{ H}), 6.12 \ (dd, J = 10.1, 3.2 \text{ Hz}, 1 \text{ H}), 5.45 \ (s, 1 \text{ H}), 5.35 \ (s, 1 \text{ H}), 4.39–4.34 \ (m, 1 \text{ H}), 3.93 \ (s, 3 \text{ H}), 3.78 \ (s, 3 \text{ H}), 3.75–3.65 \ (m, 1 \text{ H}), 3.13 \ (d, J = 15.5 \text{ Hz}, 1 \text{ H}), 2.85 \ (t, J = 8.0 \text{ Hz}, 1 \text{ H}), 2.68–2.57 \ (m, 1 \text{ H}), 2.23 \ (dd, J = 11.6, 5.5 \text{ Hz}, 1 \text{ H}), 1.88–1.78 \ (m, 1 \text{ H}), 0.82 \ (t, J = 7.9 \text{ Hz}, 9 \text{ H}), 0.54–0.42 \text{ ppm} \ (m, 6 \text{ H});$ $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 169.7, 160.6, 150.8, 137.8, 136.8, 130.5, 129.8, 126.9, 123.3, 117.9, 115.9, 114.4, 90.8, 88.5, 57.9, 56.4, 52.1, 49.1, 46.5, 35.7, 6.7 \ (3 \text{ C}), 6.2 \text{ ppm} \ (3 \text{ C});$ HRMS (ESI): calcd for C$_{26}$H$_{36}$BrN$_2$O$_5$Si$^+$ [M + H$^+$] 563.1571, found 563.1575.

**22:** $R_f = 0.22$ (hexanes:EtOAc 2:1); $[\alpha]_D^{20} = -31.2 \ (c = 1.0, \ CHCl_3)$; IR (film) $\nu_{\text{max}}$ 3351, 2968, 2874, 2843, 2372, 1671, 1552, 1485, 1248, 1099, 1033, 964, 768, 732 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.72 \ (d, J = 9.6 \text{ Hz}, 1 \text{ H}), 7.32 \ (t, J = 7.9 \text{ Hz}, 1 \text{ H}), 7.08 \ (dd, J = 7.9, 3.6 \text{ Hz}, 2 \text{ H}), 6.56 \ (d, J = 9.6 \text{ Hz}, 1 \text{ H}), 5.54 \ (d, J = 1.3 \text{ Hz}, 1 \text{ H}), 5.38 \ (d, J = 1.6 \text{ Hz}, 1 \text{ H}), 3.99 \ (s, 3 \text{ H}), 3.88 \ (s, 3 \text{ H}), 3.30–3.20 \ (m, 1 \text{ H}), 3.17 \ (s, 2 \text{ H}), 2.42–2.32 \ (m, 1 \text{ H}), 2.08 \ (t, J = 7.4 \text{ Hz}, 2 \text{ H}), 0.72 \ (t, J = 7.9 \text{ Hz}, 9 \text{ H}), 0.20 \text{ ppm} \ (q, J = 8.0 \text{ Hz}, 6 \text{ H});$ $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 164.4, 159.3, 158.1, 149.3, 138.3, 138.7, 132.9, 128.4, 127.6, 120.9, 117.3, 116.1, 115.8, 109.3, 83.2, 57.1, 56.8, 52.1, 42.5, 41.5, 6.6 \ (3 \text{ C}), 5.5 \text{ ppm} \ (3 \text{ C});$ HRMS (ESI): calcd for C$_{26}$H$_{36}$BrN$_2$O$_5$Si$^+$ [M + H$^+$] 563.1571, found 563.1573.

**Tetracycle C16-epi-ent-4:** To a stirred solution of amine 22 (303 mg, 0.54 mmol) in toluene (10 mL) at $-78 \degree \text{C}$ were added $n$-Bu$_3$SnH (0.17 mL, 0.64 mmol) and Et$_3$B (57
μL, 0.54 mmol). The resulting mixture was stirred for 0.5 h before it was warmed to 0 °C and stirred for an additional 2 h. The solvent was removed, and flash column chromatography (silica gel, hexanes:EtOAc 1:1) afforded tetracycle C16-epi-ent-4 (183 mg, 70%) as a white amorphous solid. C16-epi-ent-4: Rf = 0.23 (hexanes:EtOAc 3:1); [α]D
20 = +126.5 (c = 1.0, CHCl3); IR (film) νmax 2971, 2868, 2822, 2361, 1741, 1683, 1485, 1395, 1237, 1135, 1012, 761, 729 cm⁻¹; ¹H NMR (400 MHz, CDCl3): δ = 7.13 (t, J = 7.9 Hz, 1 H), 6.99 (d, J = 7.5 Hz, 1 H), 6.91 (d, J = 8.2 Hz, 1 H), 4.82 (d, J = 10.7 Hz, 2 H), 3.87 (s, 3 H), 3.66 (s, 4 H), 3.36 (d, J = 13.1 Hz, 1 H), 3.25–3.19 (m, 1 H), 2.98–2.88 (m, 2 H), 2.79 (d, J = 1.7 Hz, 1 H), 2.73–2.62 (m, 2 H), 2.22–2.13 (m, 1 H), 2.09 (dd, J = 10.6, 4.3 Hz, 1 H), 0.82 (t, J = 7.9 Hz, 9 H), 0.47 ppm (q, J = 7.8 Hz, 6 H); ¹³C NMR (100 MHz, CDCl3): δ = 169.7, 166.6, 149.8, 143.3, 136.6, 130.7, 126.1, 116.6, 114.3, 111.1, 89.9, 89.2, 56.3, 51.3, 49.01, 48.5, 47.5, 40.5, 40.2, 40.1, 6.8 (3C), 6.3 ppm (3C); HRMS (ESI): calcd for C26H37N2O5Si+ [M + H+] 485.2466, found 485.2467.

Alternatively, tetracycle C16-epi-ent-4 can also be obtained from enone ent-5 through the following procedure:

To a stirred solution of enone ent-5 (264 mg, 0.47 mmol) and AIBN (77 mg, 0.47 mmol) in benzene (5 mL) at 80 °C were added n-Bu3SnH (253 μL, 0.94 mmol). The resulting mixture was stirred for 0.5 h before it was cooled to room temperature and concentrated in vacuo. Flash column chromatography (silica gel, hexanes:EtOAc 1:1) afforded tetracycle C16-epi-ent-4 (186 mg, 82%) as a white amorphous solid.
**Alcohol 24**: To a stirred solution of tetracycle C16-epi-ent-4 (126 mg, 0.26 mmol) and Rh(PPh₃)₃Cl (120 mg, 0.13 mmol) in THF (5 mL) at 0 °C was added catecholborane (140 μL, 1.32 mmol). The resulting mixture was warmed to room temperature and stirred for 2 h before it was added NaOH (3 M aq., 0.43 mL, 1.3 mmol) and H₂O₂ (30% wt/wt in H₂O, 0.15 mL, 1.3 mmol). The resulting mixture was stirred for 1 h before it was quenched with NaHCO₃ (5 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried (Na₂SO₄) and concentrated in vacuo. Flash column chromatography (silica gel, EtOAc) afforded alcohol 24 (109 mg, 84%) as a white amorphous solid. **24**: Rᵣ = 0.40 (EtOAc); [α]ᵣ²⁰⁺ = +95.3 (c = 1.2, CHCl₃); IR (film) νmax 2970, 2858, 2831, 2358, 1736, 1679, 1474, 1386, 1246, 1138, 1017, 971, 758, 732 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.17–7.11 (m, 1 H), 6.99 (dd, J = 7.5, 0.9 Hz, 1 H), 6.92 (dd, J = 8.2, 0.6 Hz, 1 H), 3.90 (s, 3 H), 3.70 (s, 3 H), 3.64–3.56 (m, 1 H), 3.17 (dd, J = 11.9, 4.4 Hz, 1 H), 2.97 (dd, J = 18.1, 8.0 Hz, 1 H), 2.89–2.81 (m, 3 H), 2.81–2.74 (m, 1 H), 2.66 (dd, J = 9.7, 8.3 Hz, 2 H), 2.17–2.06 (m, 2 H), 1.80 (s, 2 H), 1.62 (s, 1 H), 0.82 (t, J = 7.9 Hz, 9 H), 0.51–0.42 ppm (m, 6 H); ¹³C NMR (100 MHz, CDCl₃): δ = 171.2, 166.8, 149.7, 136.9, 130.5, 126.1, 116.5, 114.2, 90.3, 89.1, 64.7, 56.3, 51.4, 49.4, 45.4, 44.0, 42.9, 42.1, 39.6, 33.1, 6.8 (3C), 6.3 ppm (3C); HRMS (ESI): calcd for C₂₆H₃₉N₂O₆Si⁺ [M + H⁺] 503.2572, found 503.2576.

**Aldehyde 25**: To a stirred solution of alcohol 24 (50 mg, 0.1 mmol) in CH₂Cl₂ (5 mL) at room temperature were added NaHCO₃ (50 mg, 0.6 mmol) and Dess–Martin
periodinane (46 mg, 0.11 mmol). The resulting mixture was stirred for 0.5 h before it was diluted with CH$_2$Cl$_2$ (10 mL) and quenched with Na$_2$S$_2$O$_3$ (5 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 10 mL). The combined organic layers were dried (Na$_2$SO$_4$) and concentrated *in vacuo*. Flash column chromatography (silica gel, EtOAc) afforded aldehyde **25** (44 mg, 88%) as a white amorphous solid. **25**: $R_f = 0.65$ (EtOAc); $[\alpha]_D^{20} = +112.4$ (c = 0.7, CHCl$_3$); IR (film) $\nu_{max}$ 2983, 2976, 2820, 2353, 1730, 1661, 1468, 1429, 1386, 1249, 1178, 1024, 754, 714 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 9.62 (s, 1 H), 7.15 (t, $J = 7.9$ Hz, 1 H), 7.01–6.96 (m, 1 H), 6.93 (d, $J = 8.1$ Hz, 1 H), 3.90 (s, 3 H), 3.64 (s, 3 H), 3.41–3.30 (m, 3 H), 3.00 (ddd, $J =$ 14.8, 13.1, 7.6 Hz, 2 H), 2.75–2.59 (m, 3 H), 2.20–2.02 (m, 3 H), 0.81 (t, $J =$ 7.9 Hz, 9 H), 0.54–0.41 ppm (m, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta =$ 203.1, 170.1, 166.3, 149.7, 136.4, 130.5, 126.2, 116.6, 114.2, 89.6, 89.1, 56.2, 51.5, 51.2, 49.2, 44.7, 42.2, 40.2, 39.9, 31.5, 6.3 ppm (3C); HRMS (ESI): calcd for C$_{26}$H$_{37}$N$_2$O$_6$Si$^+$ [M + H$^+$] 501.2415, found 501.2417.

**Aldehyde 27**: To a stirred solution of aldehyde **25** (80 mg, 0.16 mmol) in MeCN (5 mL) at room temperature was added HF·py (0.73 mL, 8.0 mmol). The resulting mixture was stirred for 12 h before it was quenched with NaHCO$_3$ (20 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (5 mL), dried (Na$_2$SO$_4$) and concentrated *in vacuo*. Flash column chromatography (silica gel,
CH$_2$Cl$_2$:MeOH 10:1) afforded aldehyde 27 (53 mg, 86%) as a white amorphous solid.

27: $R_f = 0.59$ (CH$_2$Cl$_2$:MeOH 10:1); $[\alpha]^0_{D} = +25.6$ ($c = 0.8$, CHCl$_3$); IR (film) $\nu_{\text{max}}$ 3391, 3306, 2983, 2835, 2348, 1809, 1732, 1652, 1482, 1424, 1393, 1271, 1168, 1130, 1021, 924, 756, 720 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.72$ (s, 1 H), 7.19 (t, $J = 7.8$ Hz, 1 H), 7.08–7.04 (m, 1 H), 6.92 (d, $J = 8.0$ Hz, 1 H), 5.21 (s, 1 H), 3.89 (s, 3 H), 3.87 (s, 3 H), 3.47–3.41 (m, 1 H), 3.18–3.09 (m, 2 H), 3.07–2.98 (m, 2 H), 2.78–2.54 (m, 3 H), 2.45–2.34 (m, 1 H), 2.12–1.99 (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 201.4, 171.8, 166.2, 149.2, 136.2, 129.8, 126.9, 115.9, 113.9, 89.1, 88.7, 56.2, 53.1, 49.4, 48.2, 47.7, 42.6, 40.6, 34.8, 29.3 ppm; HRMS (ESI): calcd for C$_{20}$H$_{23}$N$_2$O$_6^+$ [M + H$^+$] 387.1551, found 387.1554.

Aldehyde 26: To a stirred solution of aldehyde 25 (100 mg, 0.2 mmol) in MeCN (5 mL) at room temperature were added HF-py (0.91 mL, 10.0 mmol). The resulting mixture was stirred for 6 h before it was quenched with NaHCO$_3$ (20 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (5 mL), dried (Na$_2$SO$_4$) and concentrated in vacuo. Flash column chromatography (silica gel, CH$_2$Cl$_2$:MeOH 10:1) afforded both aldehydes 26 (41 mg, 53%) and 27 (29 mg, 38%) as white amorphous solids.

26: $R_f = 0.62$ (CH$_2$Cl$_2$:MeOH 10:1); $[\alpha]^0_{D} = +108.3$ ($c = 0.5$, CHCl$_3$); IR (film) $\nu_{\text{max}}$ 3389, 3301, 2969, 2835, 2349, 1816, 1723, 1648, 1469, 1441, 1362, 1264, 1157, 1138, 1028, 931, 744, 718 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.62$ (s, 1 H), 7.21 (t, $J = 7.8$ Hz, 1 H), 7.06 (dd, $J = 7.5$, 0.8 Hz, 1 H), 6.94 (d, $J = 7.8$ Hz, 1 H), 6.92 (s, 1 H), 7.19 (t, $J = 7.8$ Hz, 1 H), 7.08–7.04 (m, 1 H), 6.92 (d, $J = 8.0$ Hz, 1 H), 5.21 (s, 1 H), 3.89 (s, 3 H), 3.87 (s, 3 H), 3.47–3.41 (m, 1 H), 3.18–3.09 (m, 2 H), 3.07–2.98 (m, 2 H), 2.78–2.54 (m, 3 H), 2.45–2.34 (m, 1 H), 2.12–1.99 (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 201.4, 171.8, 166.2, 149.2, 136.2, 129.8, 126.9, 115.9, 113.9, 89.1, 88.7, 56.2, 53.1, 49.4, 48.2, 47.7, 42.6, 40.6, 34.8, 29.3 ppm; HRMS (ESI): calcd for C$_{20}$H$_{23}$N$_2$O$_6^+$ [M + H$^+$] 387.1551, found 387.1554.
8.1 Hz, 1 H), 5.07 (s, 1 H), 3.91 (s, 3 H), 3.73 (s, 3 H), 3.45 (d, \( J = 12.0 \) Hz, 1 H), 3.37 (dd, \( J = 6.8, 5.3 \) Hz, 1 H), 3.15 (dd, \( J = 12.0, 4.8 \) Hz, 1 H), 2.95 (d, \( J = 2.0 \) Hz, 1 H), 2.83 (dd, \( J = 8.5, 6.4 \) Hz, 1 H), 2.79–2.67 (m, 2 H), 2.40 (d, \( J = 6.5 \) Hz, 1 H), 2.24 (d, \( J = 4.8 \) Hz, 1 H), 2.13–1.96 ppm (m, 2 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta = 200.7, 171.5, 166.2, 149.3, 136.6, 129.7, 127.1, 116.1, 113.8, 88.6, 88.4, 56.2, 52.3, 51.3, 48.5, 46.7, 41.2, 40.6, 40.1, 30.3 \) ppm; HRMS (ESI): calcd for C\(_{20}\)H\(_{23}\)N\(_2\)O\(_6\) \([\text{M} + \text{H}^+]\) 387.1551, found 387.1552.

\((-\text{Asmaphorzaine E (ent-3) and C19-epi-ent-3): To a stirred solution of aldehyde 27 (40 mg, 0.10 mmol) in THF (2 mL) at \(-78 \) °C was added MeMgBr (3.0 M in Et\(_2\)O, 0.17 mL, 0.52 mmol). The resulting mixture was stirred for 0.5 h before it was quenched with NaHCO\(_3\) (10 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (4 × 5 mL). The combined organic layers were washed with brine (5 mL), dried (Na\(_2\)SO\(_4\)) and concentrated in vacuo to afford the crude alcohol (38 mg, 90%, ca. 3:1 mixture of inseparable diastereomers by \(^1\)H NMR) as a colorless oil, which was used directly in the next step.}

\(-\text{Asmaphorzaine E (ent-3)}\) \hspace{1cm} \text{C19-epi-ent-3} \hspace{1cm} \text{(+)-Asmaphorzaine E (ent-3)} \hspace{1cm} \text{C19-epi-ent-3}

\(\text{(+)-asmaphorzaine E (ent-3)}\) \hspace{1cm} \text{C19-epi-ent-3} \hspace{1cm} \text{(+)-asmaphorzaine E (ent-3)} \hspace{1cm} \text{C19-epi-ent-3} \hspace{1cm} \text{(+)-asmaphorzaine E (ent-3)} \hspace{1cm} \text{C19-epi-ent-3}

\(-\text{Asmaphorzaine E (ent-3) and C19-epi-ent-3): To a stirred solution of aldehyde 27 (40 mg, 0.10 mmol) in THF (2 mL) at \(-78 \) °C was added MeMgBr (3.0 M in Et\(_2\)O, 0.17 mL, 0.52 mmol). The resulting mixture was stirred for 0.5 h before it was quenched with NaHCO\(_3\) (10 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (4 × 5 mL). The combined organic layers were washed with brine (5 mL), dried (Na\(_2\)SO\(_4\)) and concentrated in vacuo to afford the crude alcohol (38 mg, 90%, ca. 3:1 mixture of inseparable diastereomers by \(^1\)H NMR) as a colorless oil, which was used directly in the next step.}

To a stirred solution of the alcohol (crude, obtained above) in toluene (2 mL) at 90 °C was added DBU (74 \( \mu \)L, 0.52 mmol). The resulting mixture was stirred for 16 h before it was diluted with EtOAc (10 mL) and quenched with NaHCO\(_3\) (10 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried (Na\(_2\)SO\(_4\)) and concentrated in vacuo.
Flash column chromatography (silica gel, EtOAc) afforded (+)-asmaphorzaine E (ent-3) (26 mg, 68%) as a white solid, along with C19-epi-ent-3 (8 mg, 20%) as a white solid. ent-3: \( R_f = 0.12 \) (EtOAc); m.p. 257–259 °C (EtOAc/hexanes); \([\alpha]_D^{20} = +35.8 \) (c = 0.4, MeOH); Lit. \([\alpha]_D^{20} = +26 \) (c = 0.1, MeOH);\(^4\) IR (film) \( \nu_{\text{max}} \) 3383, 2985, 2808, 1588, 1462, 1437, 1382, 1317, 1206, 1021, 910, 756, 712 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CD\(_3\)OD): \( \delta = 7.22 \) (t, \( J = 7.8 \) Hz, 1 H), 7.04 (d, \( J = 7.7 \) Hz, 1 H), 7.00 (d, \( J = 8.2 \) Hz, 1 H), 3.85 (s, 3 H), 3.69 (dq, \( J = 9.5, 6.1 \) Hz, 1 H), 3.60 (s, 3 H), 3.06 (d, \( J = 2.8 \) Hz, 1 H), 3.04–2.97 (m, 1 H), 2.85 (dd, \( J = 11.6, 4.9 \) Hz, 1 H), 2.78 (d, \( J = 18.8 \) Hz, 1 H), 2.74 (dd, \( J = 8.7, 6.5 \) Hz, 1 H), 2.61 (dd, \( J = 11.6, 11.5 \) Hz, 1 H), 2.37 (dd, \( J = 18.8, 8.5 \) Hz, 1 H), 2.27–2.19 (m, 1 H), 2.09–2.00 (m, 1 H), 1.94 (dd, \( J = 11.2, 3.8 \) Hz, 1 H), 1.90–1.84 (m, 1 H), 1.24 ppm (d, \( J = 6.1 \) Hz, 3 H); \(^{13}\)C NMR (125 MHz, CD\(_3\)OD): \( \delta = 173.7, 171.5, 150.8, 138.7, 131.7, 128.0, 117.1, 115.2, 89.2, 88.8, 66.7, 56.7, 52.2, 49.6, 48.9, 48.7, 45.9, 43.3, 32.3, 31.8, 22.3 ppm; HRMS (ESI): calcd for C\(_{21}\)H\(_{27}\)N\(_2\)O\(_6\)\(^+\) [M + H\(^+\)] 403.1864, found 403.1864.

C19-epi-ent-3: \( R_f = 0.10 \) (EtOAc); m.p. 236–238 °C; \([\alpha]_D^{20} = +52.8 \) (c = 0.5, MeOH); IR (film) \( \nu_{\text{max}} \) 3386, 2954, 2821, 1583, 1452, 1421, 1401, 1322, 1208, 1122, 1032, 910, 754, 716 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CD\(_3\)OD): \( \delta = 7.26–7.19 \) (m, 1 H), 7.03 (ddd, \( J = 13.6, 7.9, 0.9 \) Hz, 2 H), 3.86 (s, 3 H), 3.74–3.67 (m, 1 H), 3.60 (s, 3 H), 3.23 (dd, \( J = 11.9, 4.8 \) Hz, 1 H), 3.11–3.05 (m, 1 H), 2.79–2.64 (m, 4 H), 2.37 (dd, \( J = 18.7, 8.5 \) Hz, 1 H), 2.24 (td, \( J = 11.0, 6.4 \) Hz, 1 H), 2.06 (ddd, \( J = 10.8, 8.8, 4.0 \) Hz, 1 H), 1.94 (dd, \( J = 11.3, 3.8 \) Hz, 1 H), 1.91–1.81 (m, 1 H), 1.24 ppm (d, \( J = 6.3 \) Hz, 3 H); \(^{13}\)C NMR (100 MHz, CD\(_3\)OD): \( \delta = 173.5, 171.1, 150.7, 138.6, 131.6, 128.0, 117.0, 115.2, 89.3, 88.8,
68.5, 56.6, 52.2, 49.7, 48.8, 48.6, 46.1, 43.3, 33.8, 31.6, 21.8 ppm; HRMS (ESI): calcd for C_{21}H_{27}N_{2}O_{6}^[M + H^+] 403.1864, found 403.1863.
Table 1. $^1$H NMR Spectroscopic (CD$_3$OD, 25 °C) Comparison of Synthetic and Natural (+)-Alsmaphorazine E (ent-3)$^4$

\[
\begin{array}{llll}
\text{No.} & \text{Natural}$^4$ & & \text{Synthetic} \\
& \delta^1$H [ppm, mult, $J$ (Hz)] & & \delta^1$H [ppm, mult, $J$ (Hz)] \\
2 & & & \\
3 & & & \\
5a & 2.75 (dd, $J = 8.7$, 6.5 Hz) & 2.74 (dd, $J = 8.7$, 6.5 Hz) & \\
5b & 2.04 (m) & 2.09–2.00 (m) & \\
6a & 2.23 (m) & 2.27–2.19 (m) & \\
6b & 1.93 (dd, $J = 11.5$, 3.8 Hz) & 1.93 (dd, $J = 11.2$, 3.8 Hz) & \\
7 & & & \\
8 & & & \\
9 & 7.03 (d, $J = 7.7$ Hz) & 7.04 (d, $J = 7.7$ Hz) & \\
10 & 7.22 (dd, $J = 8.0$, 7.7 Hz) & 7.22 (dd, $J = 7.8$, 7.8 Hz) & \\
11 & 7.00 (d, $J = 8.0$ Hz) & 7.00 (d, $J = 8.2$ Hz) & \\
12 & & & \\
13 & & & \\
14a & 2.76 (d, $J = 18.8$ Hz) & 2.78 (d, $J = 18.8$ Hz) & \\
14b & 2.37 (dd, $J = 18.8$, 8.5 Hz) & 2.37 (dd, $J = 18.8$, 8.5 Hz) & \\
15 & 3.00 (m) & 3.04–2.97 (m) & \\
16 & 3.05 (d, $J = 2.8$ Hz) & 3.05 (d, $J = 2.8$ Hz) & \\
18 & 1.24 (d, $J = 6.1$ Hz) & 1.24 (d, $J = 6.1$ Hz) & \\
19 & 3.68 (dq, $J = 9.5$, 6.1 Hz) & 3.69 (dq, $J = 9.5$, 6.1 Hz) & \\
20 & 1.88 (m) & 1.90–1.84 (m) & \\
21a & 2.85 (dd, $J = 11.5$, 3.8 Hz) & 2.85 (dd, $J = 11.6$, 4.9 Hz) & \\
21b & 2.61 (dd, $J = 11.6$, 11.5 Hz) & 2.61 (dd, $J = 11.6$, 11.5 Hz) & \\
22 & & & \\
23 & 3.60 (s) & 3.60 (s) & \\
24 & 3.85 (s) & 3.85 (s) & \\
\end{array}
\]
Table 2. $^{13}$C NMR Spectroscopic (CD$_3$OD, 25 °C) Comparison of Synthetic and Natural (+)-alsmaphorazine E (ent-3)$^4$

<table>
<thead>
<tr>
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<th>Synthetic $\delta^{13}$C (ppm)</th>
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II) Abbreviations

AIBN 2,2’-azobis(2-methylpropionitrile)
CAN cerium ammonium nitrate
DBU 1,8-diazabicyclo[5.4.0]undec-7-ene
DMAP N,N-Dimethylpyridin-4-amine
DMF N,N-Dimethylformamide
HOTT S-(1-oxido-2-pyridinyl) 1,1,3,3-tetramethylthiouronium hexafluorophosphate
LiHMDS lithium bis(trimethylsilyl)amide
py pyridine
TESOTf triethylsilyltrifluoromethanesulfonate

III) References


IV) $^1$H and $^{13}$C NMR Spectra of Compounds

$^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$)
**1H NMR spectrum (400 MHz, CDCl₃)**

**13C NMR spectrum (100 MHz, CDCl₃)**
$^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$)
$^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$)
$^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$)
$^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$)
\[f_1(p_{\text{Me}})\]

\(0\) \(10\) \(20\) \(30\) \(40\) \(50\) \(60\) \(70\) \(80\) \(90\) \(110\) \(130\) \(150\) \(170\) \(190\) \(210\)

**\(\text{H NMR spectrum (400 MHz, CDCl}_3\)**

(crude, ca. 1:1 mixture of diastereomers)

\[\text{S33}\]

\[f_1(p_{\text{Me}})\]

\(0\) \(10\) \(20\) \(30\) \(40\) \(50\) \(60\) \(70\) \(80\) \(90\) \(110\) \(130\) \(150\) \(170\) \(190\) \(210\)

**\(\text{C NMR spectrum (100 MHz, CDCl}_3\)**

(crude, ca. 1:1 mixture of diastereomers)

\[\text{S33}\]
13C NMR spectrum (100 MHz, CDCl3)
$^{1}$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$)
\[1^H\text{ NMR spectrum (400 MHz, CDCl}_3)\]

\[13^C\text{ NMR spectrum (100 MHz, CDCl}_3)\]
1H NMR spectrum (400 MHz, CDCl₃)

13C NMR spectrum (100 MHz, CDCl₃)
$^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$)
$^{1}$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$)
$^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$)
$^1$H NMR spectrum (400 MHz, CDCl$_3$)

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

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$^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$)
$^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$)
$^{13}$C NMR spectrum (100 MHz, CDCl$_3$)
$^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$)
$^{1}$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$)
$^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$)
$^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$)
$^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$)
(+)-asmaphorzaine E (ent-3)

$^1$H NMR spectrum (400 MHz, CD$_3$OD)

$^{13}$C NMR spectrum (125 MHz, CD$_3$OD)
$^1$H NMR spectrum (400 MHz, CD$_3$OD)

$^{13}$C NMR spectrum (100 MHz, CD$_3$OD)