Supporting Information

Total Synthesis of (–)-Depyranoversicolamide B

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General methods:

All commercially available reagents were used without further purification. All solvents were dried and distilled before use; THF were distilled from sodium/benzophenone ketyl; DCM and DMF were distilled from calcium hydride. Chromatography was conducted by using 200-300 mesh silica gel. All new compounds gave satisfactory spectroscopic analyses (\(^1\)H NMR, \(^{13}\)C NMR, HRMS). NMR spectra were recorded on 400 MHz NMR or 600 MHz NMR spectrometer. HRMS spectra were obtained by the ESI method.

[Chemical structure image]

Synthesis of N2-Boc pyrroloindoline

Pyrroloindoline 20 (15.0 g, 52.4 mmol) in dichloromethane (500 mL) was reacted with di-tert-butyl-dicarbonate (45.80 g, 209.6 mmol) at room temperature for 24 h. The reaction mixture was then quenched by addition of saturated NaHCO\(_3\) and extracted with DCM (500 mL × 3). The combined organic layers were washed with saturated NaHCO\(_3\) solution (100 mL) and brine (100 mL), dried over Na\(_2\)SO\(_4\), filtered, and concentrated in vacuum. The residue was purified by silica gel flash chromatography (EtOAc/petroleum 1:10 ) to give N2-Boc pyrroloindoline as a pair of inseparable amide rotamers A and B (18.86 g, 90%) as white solids. [\(\alpha\)]\(^{20}\)\(_D\) = \(-301.9\) (c 0.4, CH\(_2\)Cl\(_2\)). \(^1\)H NMR (400 MHz, CDCl\(_3\); a mixture of rotamer A and B in 1:4 ratio) \(\delta\) 7.17-7.08 (rotamer A and B; m, 2H), 6.75-6.71 (rotamer A and B; m, 1H), 6.60 (rotamer A and B; d, \(J = 8.0\) Hz, 1H), 5.41 (rotamer A; s, 1H), 5.35 (rotamer B; s, 1H), 5.07 (rotamer A and B; dd, \(J = 25.6, 11.2\) Hz, 2H), 3.94 (rotamer A and B; t, \(J = 8.0\) Hz, 1H), 3.72 (rotamer B; s, 3H), 3.71 (rotamer A; s, 3H), 2.43-2.34 (rotamer A and B; m, 2H), 1.36 (rotamer A and B; s, 9H), 1.06 (rotamer B; s, 3H), 1.05 (rotamer A; s, 3H), 1.00 (rotamer B; s, 3H), 0.98 (rotamer A; s, 3H) ppm. \(^{13}\)C NMR (100 MHz,
CDCl₃; a mixture of rotamer A and B in a 1:4 ratio) rotamer B: δ 173.4, 153.7, 149.8, 143.9, 130.1, 128.6, 124.9, 118.7, 113.9, 109.1, 80.8, 78.4, 67.1, 59.3, 52.1, 41.0, 36.4, 28.5, 22.9, 22.3 ppm. rotamer A: δ 173.4, 153.7, 149.8, 143.9, 130.1, 128.6, 124.9, 118.2, 113.9, 109.3, 80.8, 79.1, 61.7, 59.3, 51.9, 41.0, 37.1, 28.1, 22.3 ppm. HRESIMS m/z 409.2103 [M+Na]+ (calcd for C₂₂H₃₀N₂O₄Na 409.2115); IR (neat): ν = 2977, 1753, 1693, 1607, 1394, 1365, 1172, 734 cm⁻¹.

(3aR)-1-tert-buty 2-methyl 8-methyl-2a-(2-methylbut-3-en-2-yl)-3,3a,8,8a-tetrahydro-pyrrolo[2,3-b]indole-1,2(2H)-dicarboxylate 21

To a solution of N2-Boc pyrroloindoline (2.1 g, 5.4 mmol) in 10% acetic acid (7.0 mL) in acetonitrile (63.0 mL), sodium cyanoborohydride (1.02 g, 16.3 mmol) and formaldehyde (37 % aqueous solution, 63 mL) was added. The reaction mixture was stirred at room temperature for 30 min and then quenched by addition of saturated NaHCO₃. The mixture was extracted with EtOAc (50 mL × 3). The combined organic phases were dried over Na₂SO₄, filtered, and concentrated in vacuum. The residue was purified by silica gel flash chromatography (EtOAc/petroleum 1:10) to afford 21 (1.85 g, 85%) as a white solid. [α]²⁰ₒ = -256.6 (c 0.5, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.15-7.11 (m, 1H), 7.03 (d, J = 7.6 Hz, 1H), 6.67-6.64 (m, 1H), 6.38 (d, J = 7.2 Hz, 1H), 5.88 (dd, J = 17.2, 11.2 Hz, 1H), 5.35 (s, 1H), 5.16-4.99 (m, 2H), 3.99-3.95 (m, 1H), 3.70 (s, 3H), 3.07-3.01 (m, 3H), 2.35 (d, J = 8.4 Hz, 2H), 1.37 (s, 9H), 1.00 (s, 3H), 0.93 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 173.3, 153.7, 151.4, 143.9, 130.2, 128.8, 124.4, 116.8, 113.7, 106.3, 85.0, 80.3, 61.3, 59.5, 51.8, 40.9, 37.6, 34.9, 28.0, 27.3, 23.1, 22.0 ppm. HRESIMS m/z 400.2362 [M]⁺ (calcd for C₂₃H₃₂N₂O₄ 400.2372). IR (neat): ν = 2977, 1753, 1704, 1605, 1495, 1394, 1169, 738 cm⁻¹.
Methyl 2-((tert-butoxycarbonyl)amino)-3-((R)-1-methyl-3-(2-methylbut-3-en-2-yl)indolin-3-yl)propanoate 24

To a solution of 21 (3.2 g, 8.0 mmol) in THF (125 mL) was added NaBH$_3$CN (5.0 g, 80.0 mmol) at $-60^\circ$C. After stirred for 10 min, a solution of TiCl$_4$ (3.2 mL) in DCM (200 mL) was added dropwise. The reaction mixture was warmed up to $-30^\circ$C, stirred for additional 24 h, and then quenched by addition of saturated NaHCO$_3$. The residue was extracted with EtOAc (100 mL × 3), and then combined organic layers were washed with saturated NaHCO$_3$ solution (100 mL) and brine (100 mL), dried over Na$_2$SO$_4$, filtered, and concentrated in vacuum. The residue was purified by silica gel flash chromatography (EtOAc/petroleum 1:10 ) to afford 24 (2.57 g, 80%) as a white solid. $[\alpha]^{20}_D = +0.6$ (c 0.6, CH$_2$Cl$_2$). $^1$H NMR (400 MHz, CDCl$_3$) 7.06 (t, $J$ = 8.0 Hz, 1H ), 6.98 (d, $J$ = 7.6 Hz, 1H), 6.59 (t, $J$ = 6.8 Hz, 1H ), 6.39 (d, $J$ = 8.0 Hz, 1H), 5.96 (dd, $J$ = 17.2,10.8 Hz, 1H), 5.04 (dd, $J$ = 17.2, 10.8 Hz, 2H), 4.99 (s, 1H),  4.06 (s, 1H), 3.45 (d, $J$ = 9.6 Hz, 1H), 3.38 (s, 3H), 3.29 (d, $J$ = 10.4 Hz, 1H), 2.73 (s, 3H), 2.39 (dd, $J$ = 14.4, 6.0 Hz, 1H), 1.87 (dd, $J$ = 14.0, 6.8 Hz, 1H), 1.41 (s, 9H), 1.01 (s, 3H), 0.98 (s, 3H) ppm. $^{13}$C NMR (150 MHz, CDCl$_3$) δ 173.7, 154.7, 153.9, 144.8, 130.2, 128.1, 125.5, 116.4, 113.2, 106.6, 60.9, 52.3, 52.0, 51.6, 43.4, 37.3, 35.3, 30.9, 28.2, 22.6, 22.4 ppm. HRESIMS m/z 425.2416 [M+Na]$^+$ (calcd for C$_{23}$H$_{34}$N$_2$ Na O$_4$ 425.2418). IR (neat): v = 2928, 2857, 1718, 1604, 1499, 1366, 1168, 799 cm$^{-1}$.

Methyl 2-amino-3-((R)-1-methyl-3-(2-methylbut-3-en-2-yl)indolin-3-yl)propanoate
To a solution of 24 (3.0 g, 7.4 mmol) in DCM (100 mL), 10% TFA (20 mL) in DCM (80 mL) was added dropwise at 0 °C. The reaction mixture was warmed up to room temperature and stirred for additional 2 h. After completion of the reaction, it was quenched by addition of saturated NaHCO₃ at 0 °C and extracted with DCM (100 mL × 3). The combined organic layers were washed with saturated NaHCO₃ solution (100 mL) and brine (100 mL), dried over Na₂SO₄, filtered, and concentrated in vacuum. The residue was purified by silica gel flash chromatography (EtOAc/petroleum 1:10 to 1:1) to afford C3-isoprenylated indoline (2.1 g, 93%) as a white solid. [α]²⁰D = +11.6 (c 0.4, CH₂Cl₂).¹H NMR (400 MHz, CDCl₃) 7.07 (t, J = 7.6 Hz, 1H), 7.01 (d, J = 7.2 Hz, 1H), 6.59 (t, J = 7.6 Hz, 1H), 6.41 (d, J = 8.0 Hz, 1H), 5.96 (dd, J = 17.2, 10.8 Hz, 1H), 5.04 (dd, J = 11.2, 10.0 Hz, 2H), 3.54 (d, J = 10.0 Hz, 1H), 3.47 (s, 3H), 3.42 (d, J = 10.4 Hz, 1H), 2.74 (s, 3H), 2.44 (dd, J = 14.0, 4.8 Hz, 1H), 1.71 (dd, J = 14.0, 6.8 Hz, 1H), 1.87 (dd, J = 14.0, 6.8 Hz, 1H), 1.03 (s, 3H), 1.00 (s, 3H) ppm.¹³C NMR (150 MHz, CDCl₃) δ 176.8, 154.1, 145.1, 130.8, 128.0, 125.7, 116.3, 112.9, 106.6, 61.5, 52.8, 52.5, 51.8, 43.7, 39.7, 35.4, 22.7, 22.5 ppm. HRESIMS m/z 303.2073 [M+H]+ (calcd for C₁₈H₂₇N₂O₂ 303.2067); IR (neat): ν = 3611, 3289, 2966, 1681, 1262, 1144, 1019, 801 cm⁻¹.

(9H-fluoren-9-yl)methyl 2-(((1-methoxy-3-((R)-1-methyl-3-(2-methylbut-3-en-2-yl)indolin-3-yl)-1-oxopropan-2-yl)carbamoyl)pyrrolidine-1-carboxylate 26

Under N₂, C3-isoprenylated indoline (2.0 g, 6.6 mmol) and HATU (3.0 g, 7.9 mmol) was stirred in dry acetonitrile (100 mL) at 0 °C. After stirring for five minutes, triethylamine (1.8 mL, 13.2 mmol) was added slowly to the mixture and reacted at 0 °C for another five minutes when Fmoc-L-proline 25 (4.5 g, 13.2 mmol) was introduced to the mixture by syringe. The mixture was warmed up to room temperature and stirred for additional 2 h. After completion of the reaction, it was quenched by addition of H₂O at 0 °C and extracted with EtOAc (100 mL × 3).
combined organic phases were dried over Na₂SO₄, filtered, and concentrated in vacuum. The residue was purified by silica gel flash chromatography (EtOAc/petroleum 1:3) to afford 26 (3.7 g, 90%) as a white solid. [α]²⁰₀ = -60.7 (c 0.8, CH₂Cl₂). ^1H NMR (400 MHz, CDCl₃) 7.76 (s, 2H), 7.59-7.52 (m, 2H), 7.40-7.26 (m, 4H), 7.07-6.97 (m, 3H), 6.58 (t, J = 8.0 Hz, 1H), 6.37-6.35 (m, 1H), 5.89-5.85 (m, 1H), 4.95 (t, J = 10.4 Hz, 2H), 4.42-4.26 (m, 5H), 3.52 (s, 2H), 3.38 (s, 3H), 3.33 (d, J = 10.0 Hz, 1H), 3.19 (d, J = 10.4 Hz, 1H), 2.70-2.63 (m, 3H), 2.43-2.26 (m, 2H), 1.98-1.88 (m, 4H), 0.96 (s, 3H), 0.91 (s, 3H) ppm. ^13C NMR (150 MHz, CDCl₃) δ 172.8, 170.6, 155.9, 153.9, 144.6, 143.7, 141.2, 130.3, 128.2, 127.6, 127.0, 125.3, 124.9, 119.9, 116.4, 113.0, 106.6, 67.6, 60.5, 60.2, 52.3, 52.0, 50.4, 47.1, 46.8, 43.2, 38.4, 36.9, 35.2, 28.0, 24.5, 22.5, 22.3 ppm. HRESIMS m/z 622.3281 [M+H]^+ (calcd for C₃₈H₄₄N₆O₆ 622.3278); IR (neat): ν = 2951, 1744, 1695, 1451, 1419, 1355, 1201, 1121, 742 cm⁻¹.

3-(((R)-1-methyl-3-(2-methylbut-3-en-2-yl)indolin-3-yl)methyl)hexahydropyrrolo[1,2-a]pyrazine-1,4-dione 27

To a solution of 26 (3.7 g, 6.0 mmol) in dry THF (100 mL) was added 2-piperidinol (1.2 g, 12.0 mmol) in one portion. After stirring at 0 °C for five minutes, a solution of piperidine (15 mL) in THF (85 mL) was added slowly to the mixture. The mixture was warmed up to room temperature and stirred for additional 24 h. After completion of the reaction, it was quenched by addition of saturated NH₄Cl at 0 °C and extracted with EtOAc (100 mL × 3). The combined organic phases were dried over Na₂SO₄, filtered, and concentrated in vacuum. The residue was purified by silica gel flash chromatography (EtOAc/petroleum 1:10 to 1:2) to afford 27 (1.8 g, 85%) as a yellow oil. [α]²⁰₀ = -60.9 (c 0.7, CH₂Cl₂). ^1H NMR (600 MHz, CDCl₃) 7.20 (d, J = 7.8 Hz, 1H), 7.14 (t, J = 7.8 Hz, 1H), 6.71 (t, J = 7.2 Hz, 1H), 6.55 (d, J = 8.4 Hz, 1H), 6.00-
5.97 (m, 1H), 5.08 (t, J = 9.6 Hz, 2H), 3.87 (t, J = 7.2 Hz, 1H), 3.58-3.56 (m, 1H), 3.45-3.41 (m, 3H), 3.21 (d, J = 15.6 Hz, 1H), 3.12 (d, J = 10.2 Hz, 1H), 2.80 (s, 3H), 2.28-2.26 (m, 1H), 1.97-1.94 (m, 2H), 1.81-1.77 (m, 2H), 1.12 (s, 3H), 1.11 (s, 3H) ppm. ^13C NMR (150 MHz, CDCl$_3$) δ 169.6, 165.6, 152.8, 145.0, 131.3, 128.4, 125.2, 118.8, 113.4, 108.7, 64.1, 58.7, 54.5, 52.2, 45.4, 43.3, 37.6, 35.7, 28.5, 23.5, 23.1, 22.2 ppm. HRESIMS m/z 390.2157 [M+Na]$^+$ (calcd for C$_{22}$H$_{29}$N$_3$NaO$_2$ 390.2153); IR (KBr) v$_{max}$ 3609, 2971, 1680, 1419, 749 cm$^{-1}$.

1-methoxy-3-(((R)-1-methyl-3-(2-methylbut-3-en-2-yl)indolin-3-yl)methyl)-6,7,8,8a-tetrahydropyrrolo[1,2-a]pyrazin-4(3H)-one 28

27 (500 mg, 1.4 mmol), CsCO$_3$ (2.9 g, 8.9 mmol), and 4Å molecular sieves (150 mg) were mixed and stirred in dry DCM (50 mL), when trimethyloxonium tetrafluoroborate (2.0 g, 14.0 mmol) was introduced by syringe and stirred at 0 °C under nitrogen. The mixture was warmed up to room temperature and stirred for additional 3h. After completion of the reaction, it was quenched by addition of saturated NaCl and extracted with DCM (50 mL × 3). The combined organic phases were dried over Na$_2$SO$_4$, filtered, and concentrated in vacuum. The residue was purified by silica gel flash chromatography (EtOAc/petroleum 1:5) to afford 28 (389.3 mg, 75%) as a yellow oil. [α]$^2$_D = −126.4 (c 0.3, CH$_2$Cl$_2$). ^1H NMR (600 MHz, CDCl$_3$) 7.07-7.03 (m, 2H), 6.56 (t, J = 7.2 Hz, 1H ), 6.33 (d, J = 7.8 Hz, 1H ), 6.01 (dd, J = 17.4, 10.8 Hz, 1H), 5.02 (t, J = 10.8 Hz, 2H), 4.00 (d, J = 9.6 Hz, 1H), 3.83 (s, 1H), 3.63 (s, 3H), 3.59-3.58 (m, 1H), 3.51 (dd, J = 20.4, 9.6 Hz, 1H), 3.42 (d, J = 9.6 Hz, 1H), 3.37 (t, J = 9.6 Hz, 1H), 3.13 (d, J = 15.0 Hz, 1H), 2.69 (s, 3H), 2.18-2.16 (m, 1H), 1.95 (s, 1H), 1.79-1.75 (m, 2H), 1.07 (s, 3H), 1.03 (s, 3H) ppm. ^13C NMR (150 MHz, CDCl$_3$) δ 169.0, 160.8, 154.5, 145.5, 131.6, 127.6, 126.0, 116.0, 112.3, 105.6, 60.5, 58.1, 56.4, 53.4, 44.5, 43.7, 35.2, 34.4, 31.8, 29.6, 28.7, 22.6, 22.4 ppm.
HRESIMS $m/z$ 382.2495 [M+H]$^+$ (calcd for C$_{23}$H$_{32}$N$_3$O$_2$ 382.2494). IR (neat): $\nu$ = 3626, 2943, 1673, 1603, 1499, 1433, 1258, 750 cm$^{-1}$.

(8a$\alpha$)-1-methoxy-3-((($R$)-1-methyl-3-(2-methylbut-3-en-2-yl)indolin-3-yl)methyl)-8a-(phenylthio)-6,7,8,8a-tetrahydropyrrolo[1,2-a]pyrazin-4(3H)-one 29

LDA (1.5 M solution in tetrahydrofuran, 15.7 mmol) was added slowly to a solution of 28 (1.0 g, 2.6 mmol) in anhydrous THF (50 mL) at $-78$ $^\circ$C. After stirring for 30 min, diphenyl disulfide (3.4 g, 15.7 mmol) was added and the mixture was stirred for another 30 min at the same temperature. The reaction mixture was then quenched by addition of saturated NH$_4$Cl and extracted with EtOAc (50 mL $\times$ 3). The combined organic layers were washed with saturated NaHCO$_3$ solution (50 mL) and brine (50 mL), dried over Na$_2$SO$_4$, filtered, and concentrated in vacuum. The residue was purified by silica gel flash chromatography (EtOAc/petroleum 1:20) to give 29 (0.8 g, 63%) as a yellow oil. [$\alpha$]$^\text{20}$D = $-289.5$ ($c$ 0.4, CH$_2$Cl$_2$). $^1$H NMR (600 MHz, CDCl$_3$) 7.13-7.08 (m, 3H), 6.99 (t, $J$ = 7.2 Hz, 1H), 6.93-6.89 (m, 3H), 6.60 (t, $J$ = 7.2 Hz, 1H), 6.40 (d, $J$ = 7.2 Hz, 1H), 5.89 (dd, $J$ = 17.4, 10.8 Hz, 1H), 4.94 (dd, $J$ = 22.2, 10.8 Hz, 2H), 3.84-3.79 (m, 1H), 3.66 (d, $J$ = 9.6 Hz, 1H), 3.59 (s, 3H), 3.29 (d, $J$ = 10.2 Hz, 1H), 2.76 (d, $J$ = 15.0Hz, 1H), 2.69 (m, 3H), 2.28-2.19 (m, 4H), 2.02-1.97 (m, 1H), 1.43 (dd, $J$ = 14.4, 9.6Hz, 1H), 0.95 (s, 3H), 0.90 (s, 3H) ppm. $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 170.5, 156.4, 154.5, 145.5, 137.0, 131.2, 130.3, 129.2, 128.4, 127.6, 126.0, 116.3, 112.2, 105.9, 74.1, 60.1, 57.1, 53.4, 53.1, 43.8, 43.5, 36.2, 35.6, 35.5, 22.5, 22.2, 20.3 ppm. HRESIMS $m/z$ 490.2528 [M+H]$^+$ (calcd for C$_{29}$H$_{36}$N$_3$O$_2$S 490.2536); IR (neat): $\nu$ = 3479, 2919, 1680, 1604, 1440, 1421, 1302, 749 cm$^{-1}$. 
(3R)-3-(((8aS)-1-methoxy-4-oxo-8a-(phenylthio)-3,4,6,7,8,8a-hexahydropyrrolo[1,2-a]pyrazin-3-yl)methyl)-3-(2-methylbut-3-en-2-yl)indoline-1-carbaldehyde 30

To a stirred solution of 29 (200 mg, 0.4 mmol) in DCM (20 mL) was added potassium permanganate (194 mg, 1.2 mmol) and stirred at 0 °C. The mixture was warmed up to room temperature and stirred for additional 20 h. After completion of the reaction, it was quenched by saturated NaHSO₃ and extracted with DCM (20 mL × 3). The combined organic phases were dried over Na₂SO₄, filtered, and concentrated in vacuum. The residue was purified by silica gel flash chromatography (EtOAc/petroleum 1:2) to give a mixture of two amide rotamer 30a and 30b (113.1 mg, 55%, 1:4) as a yellow oil. [α]²⁰D = −265.2 (c 0.2, CH₂Cl₂). ¹H NMR (600 MHz, CDCl₃; a mixture of rotamers 30a and 30b) δ 8.90 (rotamer a; s, 1H), 8.92 (rotamer b; s, 1H), 8.15 (rotamer b; d, J = 12.0 Hz, 1H), 7.33-7.26 (rotamers a and b; m, 1H), 7.27 (rotamers a and b; d, J = 7.8 Hz, 1H), 7.19 (rotamers a and b; d, J = 7.8 Hz, 1H), 7.08-7.05 (rotamers a and b; m, 1H), 7.08 (rotamers a and b; t, J = 7.2 Hz, 1H), 6.88 (rotamers a and b; t, J = 7.2 Hz, 1H), 5.71 (rotamers a and b; dd, J = 16.2, 10.8 Hz, 1H), 5.01-4.91 (rotamers a and b; m, 2H), 4.48 (rotamer b; d, J = 11.4 Hz, 1H), 4.13 (rotamer a; d, J = 12.6 Hz, 1H), 4.02 (rotamer a; d, J = 13.2 Hz, 1H), 3.95 (rotamer b; d, J = 6.8 Hz, 1H), 3.82-3.79 (rotamers a and b; m, 1H), 2.83-2.20 (rotamers a and b; m, 3H), 2.07-1.99 (rotamers a and b; m, 1H), 1.55 (rotamers a and b; dd, d, J = 13.8, 9.6 Hz, 1H), 0.92 (rotamers a and b; s, 3H), 0.89 (rotamers a and b; s, 3H) ppm. ¹³C NMR (150 MHz, CDCl₃; all signals for the amide rotamers are listed) δ 169.7, 159.0, 157.2, 156.8, 143.9, 143.6, 142.5, 137.1, 137.0, 134.2, 129.9, 129.3, 128.4, 128.2, 127.3, 126.1, 123.8, 123.5, 116.1, 113.8, 74.0, 56.8, 53.4, 53.1, 52.7, 52.6, 50.8, 43.8, 36.0, 35.1, 22.2, 21.8, 20.2 ppm. HRESIMS m/z 526.2140 [M+Na]⁺ (calcd for
C₂₀H₃₃N₅O₃NS 526.2157); IR (neat): ν = 2938, 1794, 1671, 1484, 1385, 1238, 1118, 1039, 898, 753 cm⁻¹.

31 (51.4 mg, 25%) as a yellow oil. [α]²⁰ᵣ = -198.8 (c 0.4, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) 7.28 (d, J = 8.4 Hz, 2H), 7.20 (t, J = 7.6 Hz, 1H), 7.08 (t, J = 7.6 Hz, 2H), 6.77 (t, J = 7.2 Hz, 1H), 6.71 (d, J = 8.0 Hz, 1H), 5.86 (dd, J = 17.6, 10.8 Hz, 1H), 5.37 (s, 1H), 5.06-4.97 (m, 3H), 3.73-3.68 (m, 1H), 3.48 (s, 0.5H), 3.10 (s, 0.5H), 2.43-2.36 (m, 3H), 2.20-2.00 (m, 4H), 1.00 (s, 3H), 0.91 (s, 3H) ppm. ¹³C NMR (150 MHz, CDCl₃) δ 171.0, 166.8, 164.9, 149.9, 143.4, 137.3, 130.0, 129.2, 128.8, 128.6, 124.9, 118.5, 114.2, 108.9, 74.4, 76.2, 61.2, 60.2, 59.2, 44.9, 40.4, 43.5, 36.1, 35.5, 22.5, 22.6, 22.2, 20.9 ppm. HRESIMS m/z 482.1878 [M+Na-CH₂Cl₂]⁺ (calcd for C₂₇H₂₉N₃O₂S 482.1878); IR (neat): ν = 3508, 2661, 1415, 753, 693 cm⁻¹.

(3R)-3-(((1-methoxy-4-oxo-3,4,6,7-tetrahydropyrrolo[1,2-a]pyrazin-3-yl)methyl)-3-(2-methylbut-3-en-2-yl)indoline-1-carbaldehyde 18

Monoperoxyphthalic acid magnesium salt hexahydrate (MMPP) (704 mg, 1.4 mmol) and silica gel (54-75um) (3.0 g) in 2.25 mL H₂O was vigorously stirred for 5 minutes. The freshly prepared mixture was then added to a solution of 30a and 30b (180 mg, 0.36 mmol) in DCM (18 mL) in one portion and stirred for another 30 minutes. After completion of the reaction, it was quenched by addition of saturated NaHSO₃ and extracted with DCM (20 mL x 3). The combined organic phases were dried over Na₂SO₄, filtered, and concentrated in vacuum. The residue was purified by silica gel flash chromatography (EtOAc/petroleum 1:2) to give a mixture of diene 18a and 18b (109.7 mg, 78%) as a white solid. [α]²⁰ᵣ = -265.2 (c 0.2, CH₂Cl₂). ¹H NMR (600 MHz, CDCl₃; a mixture of rotamer a and b in a 1:4 ratio) δ 8.88 (rotamer a; s, 1H),
8.44 (rotamer b; s, 1H), 8.08 (rotamer a; d, J = 7.8 Hz, 1H), 7.43-7.40 (rotamers a and b; m, 1H), 7.21 (rotamers a and b; d, J = 7.2 Hz, 1H), 7.09 (rotamers a and b; tt, J = 7.2 Hz, 1H), 5.82 (rotamers a and b; dd, J = 17.2, 10.8 Hz, 1H), 5.51 (rotamers a and b; s, 1H), 5.05 (rotamers a and b; dd, J = 17.2, 10.8 Hz, 1H), 4.73 (rotamer b; d, J = 8.4 Hz, 1H), 4.53 (rotamer a; d, J = 8.4 Hz, 1H), 4.13 (rotamer a; d, J = 8.4 Hz, 1H), 4.08 (rotamer b; d, J = 6.8 Hz, 1H), 3.94-3.81 (rotamers a and b; m, 3H), 3.64-3.62 (rotamers a and b; m, 3H), 2.95-2.92 (rotamers a and b; m, 1H), 2.71-2.69 (rotamers a and b; m, 2H), 1.82 (rotamers a and b; s, 3H), 1.02 (rotamers a and b; s, 3H), 1.00 (rotamers a and b; s, 3H) ppm. 

$^{13}$C NMR (150 MHz, CDCl$_3$; all signals for the amide rotamers are listed) δ 166.7, 159.1, 157.0, 150.8, 143.7, 142.8, 134.1, 129.6, 128.1, 127.6, 126.4, 123.9, 123.5, 116.2, 114.1, 111.0, 108.7, 60.5, 53.1, 53.0, 52.9, 52.1, 44.4, 44.0, 38.4, 27.8, 22.4, 22.0 ppm. HRESIMS m/z 416.1950 [M+Na]$^+$ (calcd for C$_{23}$H$_{27}$N$_3$O$_3$Na 416.1949). IR (neat): ν = 3613, 2924, 2855, 1681, 1626, 1261, 1019, 801 cm$^{-1}$.

To a solution of diene 18a and 18b (175 mg, 0.405 mmol) in MeOH (28 mL) at 0 ºC was added 20% aqueous KOH (7 mL). The reaction mixture was slowly warmed to room temperature over 1 hour and stirred for another 5 hours. After completion of the reaction, it was quenched by addition of H$_2$O at 0 ºC and extracted with EtOAc (30 mL × 3). The combined organic phases were dried over Na$_2$SO$_4$, filtered, and concentrated in vacuum. The residue was purified by silica gel flash chromatography (EtOAc/petroleum 1:2) to give a mixture of two amide rotamer 19a and 19b (148.7
mg, 85%) in 1:4 ratio as a white solid. [α]_{D}^{20} = −92.4 (c 0.2, CH₂Cl₂); {^1}H NMR (600 MHz, CDCl₃; a mixture of rotamers a and b in a 1:4 ratio) δ 8.80 (rotamer a; s, 1H), 8.43 (rotamer a; s, 1H), 7.19 (rotamer b; d, J = 7.8 Hz, 1H), 8.06 (rotamer b; d, J = 7.8 Hz, 1H), 7.43 (rotamer b; d, J = 7.2 Hz, 1H), 7.28-7.23 (rotamers a and b; m, 1H), 7.19 (rotamer a; d, J = 7.8 Hz, 1H), 7.13-7.11 (rotamers a and b; m, 1H), 4.64 (rotamer a; d, J = 12.6 Hz, 1H), 4.38 (rotamer b; d, J = 11.4 Hz, 1H), 3.79 (rotamers a and b; s, 3H), 3.54 (rotamer a; d, J = 12.0 Hz, 2H), 3.41-3.36 (rotamers a and b; m, 2H), 2.99 (rotamers a and b; t, J = 15.6 Hz, 1H), 2.87 (rotamers a and b; t, J = 15.6 Hz, 1H), 2.59-2.56 (rotamers a and b; m, 1H), 2.49-2.46 (rotamers a and b; m, 1H), 2.04-2.00 (v; m, 1H), 1.98-1.88 (rotamers a and b; m, 2H), 1.85-1.81 (rotamers a and b; m, 1H), 1.50-1.45 (rotamers a and b; m, 1H), 0.73 (rotamer b; s, 3H), 0.72 (rotamer a; s, 3H), 0.69 (rotamer b; s, 3H), 0.68 (rotamer a; s, 3H) ppm. {^{13}}C NMR (150 MHz, CDCl₃; all signals for the amide rotamers are listed) δ 172.3, 170.8, 158.3, 156.8, 141.2, 134.6, 128.2, 127.2, 125.9, 124.0, 123.7, 116.6, 109.7, 72.4, 67.3, 59.8, 59.0, 57.3, 54.3, 54.1, 53.6, 46.8, 46.7, 43.1, 41.8, 41.6, 30.5, 30.4, 29.6, 28.8, 25.1, 21.5, 21.0, 19.8, 19.6 ppm. HRESIMS m/z 416.1950 [M+Na]^+ (calcd for C_{23}H_{27}N_{3}O_{3}Na 416.1949); IR (neat): ν = 3600, 2947, 1679, 1590, 1489, 1362 cm\(^{-1}\).

(3'R,5aS,8aR,9aR)-8,8-dimethyl-5,10-dioxo-1,2,3,5,6,8,8a,9-octahydrospiro[5a,9a-(epiminomethano)cyclopenta[f]indolizine-7,3'-indoline]-1'-carbaldehyde 33

To a solution of rotamers 19a and 19b (100 mg, 0.254 mmol) in THF (5 mL) at 0 °C was added 0.1N HCl (5 mL). The reaction mixture was slowly warmed to room temperature and stirred for another 20 minutes. After completion of the reaction, it was then quenched by addition of NaHCO₃ at 0 °C and extracted with EtOAc (10 mL × 3). The combined organic phases were dried over Na₂SO₄, filtered, and
concentrated in vacuum. The residue was purified by silica gel flash chromatography (EtOAc/petroleum 1:2) to give a mixture of two amide rotamers 33a and 33b (91.6 mg, 95%) in 1:4 ratio as a white solid. \([\alpha]^{20}_D = -91.2 \text{ (c 0.1, CH}_2\text{Cl}_2)\). \(^1\)H NMR (600 MHz, CDCl\(_3\): a mixture of rotamer a and b in a 1:4 ratio) \(\delta 8.82 \text{ (rotamer a; s, 1H), 8.45 (rotamer b; s, 1H), 0.08 (rotamer b; d, } J = 7.8 \text{ Hz, 1H), 7.96 (rotamer b; s, 1H), 7.80 (rotamer a; s, 1H), 7.42 (rotamers a and b; d, } J = 7.8 \text{ Hz, 1H), 7.32-7.28 (rotamers a and b; m, 1H), 7.20 (rotamers a and b; d, } J = 7.8 \text{ Hz, 1H), 7.15-7.12 (rotamers a and b; m, 1H), 4.64 (rotamer a; d, } J = 12.6 \text{ Hz, 1H), 4.37 (rotamer b; d, } J = 11.4 \text{Hz, 1H), 3.83 (rotamer a; d, } J = 10.8 \text{ Hz, 1H), 3.52 (rotamer a; d, } J = 12.6 \text{ Hz, 1H), 3.50-3.43 (rotamers a and b; m, 2H), 2.92 (rotamers a and b; t, } J = 15.0 \text{ Hz,1H), 2.80-2.74 (rotamers a and b; m, 1H), 2.51-2.41(rotamers a and b; m, 2H), 2.09-2.00 (rotamers a and b; m, 2H), 1.99-1.96 (rotamers a and b; m, 1H), 1.96-1.86 (rotamers a and b; m, 1H), 1.80-1.75 (rotamers a and b; m, 1H), 0.83 (rotamer a; s, 3H), 0.80 (rotamer b; s, 3H); 0.79 (rotamer b; s, 3H), 0.74 (rotamer a; s, 3H) ppm. \(^{13}\)C NMR (150 MHz, CDCl\(_3\): all signals for the amide rotamers are listed) \(\delta 173.8, 169.7, 158.2, 156.8, 141.1, 133.4, 128.6, 126.8, 125.6, 124.2, 123.9, 116.8, 110.0, 68.9, 66.7, 59.6, 58.9, 58.7, 53.3, 52.8, 46.8, 43.8, 38.6, 38.4, 29.0, 28.9, 24.9, 21.7, 21.3, 19.3; 19.1 ppm. HRESIMS m/z 402.1794 [M+Na]\(^+\) (calcd for C\(_{22}\)H\(_{25}\)N\(_3\)O\(_3\)Na 402.1798); IR (neat): \(\nu = 3646, 2955, 1675, 1589, 1493, 1370, 760 \text{ cm}^{-1}\).

(3'R,5aS,8aR,9aR)-8,8-dimethyl-2,3,6,8,8a,9-hexahydrospiro[5a,9a-(epiminomethano)cyclopenta[f]indolizine-7,3'-indoline]-5,10(1H)-dione 34

To a solution of 33a and 33b (100 mg, 0.405 mmol) in MeOH (10 mL) at 0 °C was added 20% aqueous NaOH (2.5 mL). The reaction mixture was heated to 75°C and stirred for 4 hours. After completion of the reaction, it was cooled to room temperature and quenched by cold water at 0 °C and extracted with EtOAc (15 mL ×
The combined organic phases were dried over Na$_2$SO$_4$, filtered, and concentrated in vacuum. The residue was purified by silica gel flash chromatography (EtOAc/petroleum 1:2) to afford 34 (72.2 mg, 78%) as a white solid. [$\alpha$]$^{20\text{D}}$ = $-12.0$ (c 0.2, CH$_2$Cl$_2$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.11-7.07 (m, 2H), 6.76 (t, $J$ = 7.2 Hz, 1H), 6.68 (d, $J$ = 8.0 Hz, 1H), 5.84 (s, 1H), 3.79 (d, $J$ = 10.0 Hz, 1H), 3.47-3.40 (m, 3H), 2.89 (d, $J$ = 15.6 Hz, 1H), 2.78-2.72 (m, 1H), 2.44 (t, $J$ = 8.4 Hz, 1H), 2.20 (d, $J$ = 15.6 Hz, 1H), 2.06-1.99 (m, 2H), 1.97-1.94 (m, 1H), 1.91-1.67 (m, 2H), 0.93 (s, 3H), 0.87 (s, 3H) ppm. $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 173.2, 170.2, 152.1, 129.9, 128.2, 125.6, 118.0, 110.0, 69.0, 66.8, 59.9, 53.1, 46.4, 43.8, 40.6, 31.9, 25.0, 22.6, 22.2, 19.6, 14.1 ppm. HRESIMS m/z 352.2025 [M+H]$^+$ (calcd for C$_{21}$H$_{26}$N$_3$O$_2$ 325.2029).

IR (neat): $\nu$ = 3521, 2917, 2849, 1651, 1261, 1018, 799 cm$^{-1}$.

Synthesis of (–)-Depyranoversicolamide B (12)

To a solution of 34 (20 mg, 0.057 mmol) in DCM (2 mL) was added MnO$_2$ (99 mg, 1.14 mmol). The reaction mixture was stirred for 2 hours and then filtered and concentrated in vacuum. The residue was dissolved in a mixture of MeCN (1 mL) and H$_2$O (0.5 mL) and added with NaOClO$_2$ (10.4 mg, 0.114 mmol) and NaH$_2$PO$_4$ (18.0 mg, 0.114 mmol). The reaction mixture was stirred at room temperature for 3 hours. After completion of the reaction, it was quenched by addition of Na$_2$S$_2$O$_3$ at 0 °C and extracted with EtOAc (5 mL × 3). The combined organic phases were dried over Na$_2$SO$_4$, filtered, and concentrated in vacuum. The residue was purified by silica gel flash chromatography (EtOAc/petroleum 1:1) to afford (–)-depyranoversicolamide B (12) (10.4 mg, 50%) as a white solid. [$\alpha$]$^{20\text{D}}$ = $-12.60$ (c 0.1, CH$_2$Cl$_2$). $^1$H NMR (600 MHz, CD$_3$OD: (CD$_3$)$_2$SO = 6:1) $\delta$ 7.43-7.40 (m, 1H), 7.25 (t, $J$ = 7.8 Hz, 1H), 7.04 (t, $J$ = 7.2 Hz, 1H), 6.89 (d, $J$ = 7.2 Hz, 1H), 3.46-3.43 (m, 1H), 3.41-3.39 (m, 1H), 3.03
(dd, $J = 15.6, 3.6$ Hz, 1H), 2.67-2.62 (m, 1H), 2.20 (dt, $J = 15.0, 3.0$ Hz, 1H), 2.12-2.07 (m, 1H), 2.05-1.89 (m, 3H), 1.78 (dd, $J = 13.2, 7.2$ Hz, 1H), 1.10 (s, 3H), 0.81 (s, 3H) ppm. $^{13}$C NMR (150 MHz, CD$_3$OD: (CD$_3$)$_2$SO = 6:1) δ 184.3, 178.3, 171.9, 143.6, 130.9, 129.6, 127.4, 122.6, 110.5, 70.7, 69.1, 64.3, 52.1, 49.3, 44.9, 35.2, 29.8, 29.3, 25.8, 23.5, 21.1 ppm. HRESIMS $m/z$ 388.1637 [M+Na]$^+$ (calcd for C$_{21}$H$_{23}$N$_3$NaO$_3$ 388.1641). IR (neat): ν = 3613, 3290, 1699, 1572, 694 cm$^{-1}$

2D NMR spectrum data of (–)-depyranoversicolamide B (12)

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<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>49.3</td>
<td>-</td>
<td>-</td>
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<td>21.1</td>
<td>1.10 s</td>
<td>C3, C10, C19, C22, C24</td>
<td>-</td>
</tr>
<tr>
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<td>23.5</td>
<td>0.81 s</td>
<td>C3, C10, C19, C22, C23</td>
<td>-</td>
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</table>
$^1$H NMR spectrum of compound N2-Boc pyrroloindoline
$^{13}$C NMR spectrum of compound N2-Boc pyrroloindoline
$^1$H NMR spectrum of compound 21
$^{13}$C NMR spectrum of compound 21
$^1$H NMR spectrum of compound 24
$^{13}$C NMR spectrum of compound 24
DEPT spectrum of compound 24
gCOSY spectrum of compound 24
gHMBC spectrum of compound 24
gHMOC spectrum of compound 24
$\text{C3-isoprenylated indoline}$

$^1\text{H NMR spectrum of C3-isoprenylated indoline}$
C3-isoprenylated indoline

$\text{C3-isoprenylated indoline}$

$^{13}\text{C}$ NMR spectrum of C3-isoprenylated indoline
$^1$H NMR spectrum of compound 26
$^{13}$C NMR spectrum of compound 26
$^{1}H$ NMR spectrum of compound 27
$^{13}$C NMR spectrum of compound 27
DEPT spectrum of compound 27
gCOSY spectrum of compound 27
gHMBC spectrum of compound 27
gHMOC spectrum of compound 27
$^1$H NMR spectrum of compound 28
$^{13}$C NMR spectrum of compound 28
$^1$H NMR spectrum of compound 29
$^{13}$C NMR spectrum of compound 29
DEPT spectrum of compound 29
gCOSY spectrum of compound 29
gHMBC spectrum of compound 29
gHMQD spectrum of compound 29
NOEDS spectrum of compound 29 (1)

NOEDS spectrum of compound 29 (2)
NOEDS spectrum of compound 29 (3)

NOEDS spectrum of compound 29 (4)
$^1$H NMR spectrum of compound 30
$^{13}$C NMR spectrum of compound 30
$^1$H NMR spectrum of compound 31
$^{13}$C NMR spectrum of compound 31
$^1$H NMR spectrum of compound 18
$^{13}$C NMR spectrum of compound 18
$^{1}$H NMR spectrum of compound 19
\(\text{19a and 19b} \quad \text{rotamers: a:b = 4:1}\)

\(13^C\) NMR spectrum of compound 19
DEPT spectrum of compound 19

19a and 19b
rotamers: a/b = 4:1
gCOSY spectrum of compound 19

19a and 19b rotamers: a/b = 4:1
gHMBC spectrum of compound 19
gHMQC spectrum of compound 19
NOEDS spectrum of compound 19 (1)

NOEDS spectrum of compound 19 (2)
irradiation at H-4 at 7.42 ppm
noe H-5 at 7.12 ppm
noe H-c at 2.86 ppm
noe H-23 at 0.72 ppm

NOEDS spectrum of compound 19 (3)

irradiation at H-d at 3.02 ppm
noe H-b at 3.55 ppm
noe H-c at 2.86 ppm

NOEDS spectrum of compound 19 (4)
H NMR spectrum of compound 33
$^{13}$C NMR spectrum of compound 33
NOEDS spectrum of compound 33 (1)

irradiation at H-4 at 7.42 ppm
noe H-5 at 7.13 ppm

irradiation at H-13 at 7.82 ppm
noe H-c at 2.47 ppm

NOEDS spectrum of compound 33 (2)

noe H-c at 0.83 ppm
noe H-23 at 0.83 ppm
NOEDS spectrum of compound 33 (3)

NOEDS spectrum of compound 33 (4)
$^1$H NMR spectrum of compound 34
$^{13}$C NMR spectrum of compound 34
H NMR spectrum of (–)-depyranoversicolamide B (12)
C NMR spectrum of (–)-depyranoversicolamide B (12)
DEPT spectrum of (–)-depyranoversicolamide B (12)
HSQC spectrum of (-)-depyranoversicolamide B (12)
HSQC spectrum of (−)-depyranoversicolamide B (12)
HMBC spectrum of (–)-depyranoversicolamide B (12)
HMBC spectrum of (−)-depyranoversicolamide B (12)
COSY spectrum of (-)-depyranoversicolamide B (12)
COSY spectrum of (-)-depyranoversicolamide B (12)