Supporting Information Ⅰ

Total Synthesis of (±)-Communesin F

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General methods.
All commercially available reagents were used without further purification. All solvents were dried and distilled before use; THF and Et₂O were distilled from sodium/benzophenone ketyl; dichloromethane was distilled from calcium hydride; methanol was distilled from Mg/I₂; CHCl₃ was distilled from P₂O₅. Chromatography was conducted by using 200-300 mesh silica gel. All new compounds gave satisfactory spectroscopic analyses (IR, ¹H NMR, ¹³C NMR, HRMS, NOEDs). IR spectra were recorded on a FT IR spectrometer. NMR spectra were recorded on 400/200 MHz NMR spectrometers. HRMS spectra were obtained by the FAB method. Microwave reaction was carried out in MCL-2 microwave reactor (200 mA).

Methyl 2-(1H-4-bromoindol-3-yl)-2-oxoacetate 26
Oxalyl chloride (65.0 g, 0.52 mol) was added dropwise to a solution of 4-bromoindole (50.0 g, 0.26 mol) in ether (200 mL) at 0 °C. The solution was warmed to room temperature and stirred for 24 h. The resulting suspension was filtered and the filter cake was washed thoroughly with cold ether. The filter cake was dried under vacuum to give the oxoacetyl chloride (48.0 g) as a yellow solid, which was used without further purification. A suspension of the above oxoacetyl chloride (48.0 g, 0.17 mol) in ether (200 mL) was treated with methanol (34.0 mL) at 0 °C and stirred for 2 h. The resulting suspension was filtered. The filter cake was washed with water and cold ether, and dried under vacuum to give methyl 2-(1H-4-bromoindol-3-yl)-2-oxoacetate 26 (45.0 g, 62.4 %, two steps) as a yellow solid. Mp: 165－168 °C. ¹H NMR (CDCl₃) δ 3.96 (s, 3H), 1.96 (s, 3H), 7.16 (t, J = 7.8 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 7.6, 0.8 Hz, 1H), 8.27 (d, J = 3.2 Hz, 1H), 9.05 (broad s, 1H)ppm; ¹³C NMR (CDCl₃) δ 53.0, 111.0, 115.0, 115.3, 125.2, 126.7, 128.3, 136.2, 137.8, 164.0, 190.4ppm; IR (KBr) 3218, 1730, 1655, 1500, 1413, 1254, 1139, 1105 cm⁻¹.
A solution of methyl 2-(1H-4-bromoindol-3-yl)-2-oxoacetate (50.0 g, 0.18 mol) in THF (200 mL) was added dropwise to a suspension of LiAlH₄ (20.5 g, 0.54 mol) in THF (100 mL) at 0 °C over a period of 1 h. The reaction was refluxed for 4 h, then cooled to 0 °C, and quenched with water. The suspension was filtered and the filter cake was washed thoroughly with EtOAc. The combined filtrate was extracted with EtOAc (3 × 200 mL). The combined organic phases were washed with sat. NaCl solution (3 × 200 mL), dried over sodium sulfate and concentrated. The residue was recrystallized from EtOAc to give 2-(1H-4-bromoindol-3-yl)ethanol 27 (37.1 g, 87 %) as a white solid. Mp: 101 – 103 °C. ¹H NMR (CDCl₃) δ 3.28 (dt, J = 6.4, 0.8 Hz, 2H), 3.97 (t, J = 6.4 Hz, 2H), 7.00 (t, J = 7.8 Hz, 1H), 7.10 (dd, J = 2.8 Hz, 1H), 7.27 (dd, J = 7.6, 0.8 Hz, 1H), 7.29 (dd, J = 7.6, 0.8 Hz, 1H), 8.22 (broad s, 1H) ppm; ¹³C NMR (CDCl₃) δ 29.5, 63.6, 110.6, 113.0, 114.3, 122.9, 124.1, 124.5, 125.4, 137.8 ppm; IR (KBr) 3373, 2852, 1563, 1479, 1426, 1363, 1336, 1187, 1030, 914, 771 cm⁻¹.

To a solution of 2-(1H-4-bromoindol-3-yl)ethanol (80.0 g, 0.33 mol) in CH₂Cl₂ (250 mL) was added Et₃N (67.6 g, 0.67 mol) and DMAP (8.2 g, 0.07 mol). The resulting solution was added dropwise a solution of chlorotriethylsilane (45.6 g, 0.30 mol) in CH₂Cl₂ (50 mL) over a period of 30 minutes at 0 °C. After stirring for 3 h at room temperature, the resulting mixture was washed with water, dried over sodium
sulfate, and concentrated. The residue was dissolved in dry CH₂Cl₂ (50 mL). Sodium hydroxide (53.6 g, 1.33 mmol), Bu₄NHSO₄ (9.5 g, 0.03 mol), MeI (57.0 g, 0.40 mmol) were added sequentially to above solution. The mixture was warmed to 35 °C and stirred for 24 h. The suspension was filtered and the filtrate was concentrated. The residue was dissolved in THF (200 mL) and Bu₄NF (13.7 g, 0.07 mol) was added in. The resulting solution was stirred for 4 h at room temperature, and then diluted with water (200 mL), extracted with EtOAc (3 × 200 mL). The combined organic phases were washed with sat. NaCl solution (3 × 200 mL), dried over sodium sulfate and concentrated. The crude material was purified by chromatography (EtOAc) to give 7 (74.5 g, 88 %) as a white solid. Mp: 58–60 °C. ¹H NMR (CDCl₃) δ 3.23 (t, J = 6.6 Hz, 2H), 3.69 (s, 3H), 3.92 (t, J = 6.4 Hz, 2H), 6.94 (s, 1H), 7.01 (t, J = 7.8 Hz, 1H), 7.20 (dd, J = 8.2, 0.6 Hz, 1H), 7.24 (dd, J = 7.6, 0.8 Hz, 1H)ppm; ¹³C NMR (CDCl₃) δ 29.1, 32.6, 63.5, 108.5, 111.3, 114.1, 122.1, 123.2, 125.5, 129.1, 138.2ppm; HRMS (M+H⁺) calcd for C₁₁H₁₃Br₁N₁O₁ 254.0175, found 254.0171; IR (KBr) 3267, 1549, 1478, 1418, 1319, 1070, 1045, 773 cm⁻¹.

Ester 19a

A solution of acid 8¹ (4.53 g, 22 mmol) in thionyl chloride (20 mL) was warmed to 60 °C with stirring for 4 h and was then concentrated under reduced pressure. The residue was dissolved in CH₂Cl₂ (100 mL). Under N₂, the solution was added dropwise to a solution of 7 (5.00 g, 20 mmol) and Et₃N (4.04 g, 40 mmol) in CH₂Cl₂ at 0 °C over a period of 1 h. The resulting solution was stirred for another 5 h until complete consumption of the starting material 7. The mixture was then washed with water (3 × 50 mL), dried over sodium sulfate and concentrated. The crude material was then purified by chromatography (EtOAc/petroleum 1:5) to afford ester 19a (8.04...
g, 95 %) as a white solid. Mp: 106—109 °C. ¹H NMR (CDCl₃) δ 3.48 (t, J = 7.0 Hz, 2H), 3.71 (s, 3H), 4.67 (t, J = 7.2 Hz, 2H), 6.96 (s, 1H), 7.03 (t, J = 8.0 Hz, 1H), 7.17 (dd, J = 8.0, 0.4 Hz, 1H), 7.24 (m, 3H), 7.61 (dt, J = 7.8, 1.6 Hz, 1H), 7.84 (dd, J = 7.6 1.6 Hz, 1H) ppm; ¹³C NMR (CDCl₃) δ 25.1, 32.9, 67.3, 108.7, 110.3, 114.1, 118.9, 122.4, 123.6, 125.1, 125.3, 125.6, 129.4, 131.3, 135.3, 138.3, 141.0, 164.2, 185.8 ppm; HRMS (M+Na⁺) calcd for C₁₉H₁₅Br₁N₄Na₁O₃ 449.0220, found 449.0218; IR (KBr) 2940, 2137, 1731, 1665, 1591, 1459, 1321, 1258, 1190, 1141, 1070, 995, 738 cm⁻¹.

Hydrazone 19b

To a solution of 19a (20.0 g, 46.8 mmol) in CHCl₃ (100 mL) was added TsOH (0.4 g, 2.3 mmol) and TsNHNH₂ (10.5 g, 56.5 mmol). The resulting solution was refluxed with a dean-stark trap for 5 h. After cooling to room temperature, the suspension was filtered and the filtrate was concentrated. The residue was recrystallized from EtOAc to give 19b (23.7 g, 85 %) as a white solid. Mp: 134—136 °C. ¹H NMR (CDCl₃) δ 2.41 (s, 3H), 3.28 (t, J = 6.8 Hz, 2H), 3.65 (s, 3H), 4.49 (t, J = 6.6 Hz, 2H), 6.60 (s, 1H), 7.00-7.04 (m, 2H), 7.16 (dt, J = 7.6, 1.6 Hz, 1H), 7.21 (dd, J = 6.0, 1.2 Hz, 1H), 7.22 (dd, J = 5.2, 0.8 Hz, 1H), 7.27-7.33 (m, 3H), 7.42 (dt, J = 7.8, 1.6 Hz, 1H), 7.80-7.85 (m, 2H) ppm; ¹³C NMR (CDCl₃) δ 21.5, 24.8, 32.8, 67.2, 108.7, 110.2, 114.0, 117.8, 122.4, 123.5, 124.7, 125.4, 126.7, 127.8, 129.2, 129.6, 130.4, 130.8, 135.5, 136.6, 138.2, 139.0, 144.3, 161.6 ppm; HRMS (M+Na⁺) calcd for C₂₆H₂₃Br₁N₆Na₁O₄S₁ 617.0577, found 617.0592; IR (KBr) 3250, 2947, 2128, 1692, 1597, 1551, 1485, 1452, 1368, 1300, 1234, 1169, 1119, 1086, 995 cm⁻¹.
Diazo 1

To a solution of 19b (30.0 g, 50.5 mmol) in CH₂Cl₂ (200 mL) was added DBU (11.5 g, 75.7 mmol). The reaction mixture was stirred at room temperature for 12 h. After concentration, the crude material was purified by chromatography (EtOAc/petroleum 1:15) to afford 1 as a yellow oil (18.8 g, 85 %). ^1H NMR (CDCl₃) δ 3.40 (t, J = 6.8 Hz, 2H), 3.75 (s, 3H), 4.54 (t, J = 6.8 Hz, 2H), 6.92 (s, 1H), 7.04 (t, J = 7.8 Hz, 1H), 7.15-7.19 (m, 2H), 7.23-7.28 (m, 2H), 7.34 (dt, J = 7.8, 1.6 Hz, 1H), 7.52 (d, J = 8.0 Hz 1H) ppm; ^13C NMR (CDCl₃) δ 25.6, 32.9, 66.1, 108.7, 111.0, 114.3, 116.7, 118.5, 122.4, 123.5, 125.1, 125.7, 129.0, 129.3, 130.0, 130.4, 131.3, 137.1, 138.3, 165.6 ppm; HRMS (M+Na⁺) calcd for C₁₉H₁₅Br₁N₆Na₁O₂ 461.0332, found 461.0315; IR (KBr) 2929, 2130, 2090, 1691, 1493, 1341, 1283, 1230, 1159, 1022, 748 cm⁻¹.

Cyclopropane compound 9

Under N₂, a solution of diazo 1 (1.000 g, 2.3 mmol) in 20 mL of dry CH₂Cl₂ was added via an injector into a solution of CuOTf—benzene complex (5 mg) in 25 mL of dry CH₂Cl₂ at room temperature. The solution was stirred for 1 h and then concentrated under reduced pressure. The residue was purified by chromatography (EtOAc/petroleum 1:3) to afford compound 9 (0.823 g, 88 %) as a mixture of two diastereoisomers in a 1.6:1 ratio. ^1H NMR (CDCl₃) δ 2.46-2.48 (m, minor, 1H), 2.49-2.52 (m, major, 1H), 3.09 (s, minor, 3H), 3.20 (s, major, 3H), 3.53-3.62 (m, minor, 1H), 3.71-3.81 (m, major, 1H), 4.26-4.35 (m, minor + major, 2H), 4.47-4.52 (m, minor, 1H), 4.56-4.61 (m, major, 1H), 4.61 (s, major, 1H), 4.75 (s, minor, 1H), 4.80 (s, minor, 1H), 4.80 (s, major, 1H).
6.03 (dd, \( J = 5.8, 3.4 \text{ Hz}, 1\text{H}, \text{minor} \)), 6.07 (dd, \( J = 7.2, 1.6 \text{ Hz}, 1\text{H}, \text{major} \)), 6.72-6.77 (m, \( \text{minor + major}, 2\text{H} \)), 6.79-6.85 (m, \( \text{minor + major}, 4\text{H} \)), 6.90-6.94 (m, \( \text{minor + major}, 2\text{H} \)), 7.03-7.15 (m, \( \text{minor + major}, 4\text{H} \)) ppm; HRMS (M+Na\(^+\)) calcd for C\(_{19}\)H\(_{15}\)Br\(_1\)N\(_4\)Na\(_1\)O\(_2\) 433.0271, found 433.0273; IR (KBr) 2927, 2130, 2100, 1707, 1601, 1492, 1479, 1306, 1187, 1083, 762 cm\(^{-1}\).

(-)-Pentacyclic lactone 2

To a solution of 9 (4.00 g, 9.8 mmol) in a mixture of THF and H\(_2\)O (50 mL, 50:1) was added PBu\(_3\) (2.17 g, 10.7 mmol) at 0 \(^\circ\)C. After stirring at 0 \(^\circ\)C for 0.5 h, the reaction was quenched with water (50 mL), extracted with CH\(_2\)Cl\(_2\) (3 \( \times \) 100 mL), dried over sodium sulfate and concentrated under reduced pressure. The residue was recrystallized from EtOAc to give single diastereomeric isomer 2 (3.11 g, 83 \%) as a white solid. Mp: 201-203 \(^\circ\)C. \(^1\)H NMR (CDCl\(_3\)) \( \delta \) 2.32-2.36 (m, 1H), 2.37-2.43 (m, 1H), 2.90 (s, 3H), 3.89 (s, 1H), 4.38 (broad s, 1H), 4.54 (dt, \( J = 12.0, 4.8 \text{ Hz}, 1\text{H} \)), 4.74-4.80 (m, 1H), 4.81 (s, 3H), 6.23(d, \( J = 7.6 \text{ Hz}, 1\text{H} \)), 6.44 (d, \( J = 7.6 \text{ Hz}, 1\text{H} \)), 6.62 (d, \( J = 8.0 \text{ Hz}, 1\text{H} \)), 6.73 (t, \( J = 7.6 \text{ Hz}, 1\text{H} \)), 6.80 (t, \( J = 7.8 \text{ Hz}, 1\text{H} \)), 6.91 (t, \( J = 7.4 \text{ Hz}, 1\text{H} \)), 8.16 (d, \( J = 7.6 \text{ Hz}, 1\text{H} \)) ppm; NOE: correlation between protons at 3.89 ppm and at 4.81ppm was observed; \(^{13}\)C NMR (CDCl\(_3\)) \( \delta \) 30.5, 34.2, 42.3, 52.6, 66.1, 85.0, 105.5, 113.7, 118.6, 119.1, 121.4, 122.9, 126.7, 127.1, 129.1, 130.1, 144.5, 152.5, 169.5ppm. HRMS (M+Na\(^+\)) calcd for C\(_{19}\)H\(_{17}\)Br\(_1\)N\(_2\)Na\(_1\)O\(_2\) 407.0366, found 407.0376; IR (KBr) 3361, 2914, 1717, 1606, 1593, 1488, 1263, 1233, 1182, 1117, 1016, 981, 763 cm\(^{-1}\).
(±)-Pentacyclic lactone 11

To a solution of 2 (0.500 g, 1.3 mmol) in CH₂Cl₂ (20 mL) was added DMAP (0.230 g, 1.9 mmol), ClCOOMe (1.200 g, 13.0 mmol) at room temperature. The solution was stirred for 12 h. The reaction was washed with water (50 mL × 3), dried over sodium sulfate and concentrated. The residue was washed with small amount of CH₂Cl₂ and filtered to give 20 (0.350 g, 70 %) as a white solid. Mp: 280—282 °C. The filtrate was concentrated and the residue was purified by chromatography (EtOAc/petroleum 1:3) to afford 20 (0.025 g, 5 %) and 11 (0.127 g, 22 %) as a white solid.

Compound 11: ¹H NMR (CDCl₃) δ 2.15-2.21 (m, 1H), 2.79 (s, 3H), 3.13-3.21 (m, 1H), 3.79 (s, 3H), 4.70-4.76 (m, 2H), 4.81 (s, 1H), 6.04 (d, J = 7.6 Hz, 1H), 6.18 (s, 1H), 6.64 (d, J = 7.6 Hz, 1H), 6.79 (t, J = 8.0 Hz, 1H), 7.06-7.10 (m, 1H), 7.17-7.28 (m, 3H)ppm; NOE: correlation between protons at 6.18ppm and 4.81 ppm was not observed; ¹³C NMR (CDCl₃) δ 29.8, 31.7, 45.5, 53.5, 55.4, 65.5, 81.6, 103.7, 118.2, 121.5, 125.9, 126.3, 126.6, 128.4, 129.4, 130.6, 131.1, 135.6, 152.0, 170.3ppm; HRMS (M+Na⁺) calcd for C₂₁H₁₉Br₁N₂Na₁O₄ 465.0420, found 465.0398. IR (KBr) 3459, 2925, 1740, 1703, 1597, 1488, 1440, 1331, 1254, 1015, 765cm⁻¹.

Compound 20: ¹H NMR (CDCl₃) δ 1.99 (dt, J = 14.8, 3.2 Hz, 1H), 2.75 (s, 3H), 3.32-3.40 (m, 1H), 4.54 (s, 1H), 4.55-4.60 (m, 1H), 4.62 (broad s, 1H), 4.68 (td, J = 11.6, 3.6 Hz, 1H), 4.72 (s, 1H), 6.14 (d, J = 8.0 Hz, 1H), 6.67 (d, J = 7.6 Hz, 1H), 6.71 (d, J = 8.0 Hz, 1H), 6.79-6.86 (m, 2H), 7.08 (td, J = 8.0, 0.8 Hz, 1H), 7.14 (d, J = 7.6 Hz, 1H)ppm; ¹³C NMR (CDCl₃) δ 30.3, 31.6, 45.6, 51.7, 64.6, 82.7, 104.6, 116.5, 118.3, 121.3, 122.1, 124.5, 127.8, 128.6, 129.6, 130.3, 141.4, 152.3, 171.6ppm. HRMS (M+Na⁺) calcd for C₁₉H₁₇Br₁N₂Na₁O₂ 407.0366, found 407.0382; IR (KBr) 3343, 2918, 1721, 1596, 1492, 1476, 1259, 1196, 1065cm⁻¹.
Conversion of 20 to 11

To a solution of 20 (9.98 g, 2.6 mmol) in CHCl₃ (150 mL) was added DMAP (4.70 g, 39 mmol) and ClCOOMe (24.4 g, 260 mmol) at room temperature. The mixture was stirred at room temperature for 12 h. The reaction was washed with water (3 × 50 mL), dried over sodium sulfate and concentrated. The residue was purified by chromatography (EtOAc/petroleum 1:3) to afford 11 (11.21 g, 97%) as a white solid.

Conversion of compound 2 to 10

To a solution of 2 (0.505 g, 1.3 mmol) in CHCl₃ (20 mL) was added DMAP (0.230 g, 1.9 mmol) and ClCOOMe (1.207 g, 12.8 mmol) at room temperature. The solution was stirred for 12 h at room temperature and then washed with water (3 × 50 mL), dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by chromatography (EtOAc/petroleum 1:3) to afford compound 10 (0.543 g, 93%) as a white solid. ¹H NMR (CDCl₃) δ 2.40-2.47 (m, 1H), 2.51-2.58 (m, 1H), 2.94 (s, 3H), 3.76 (s, 3H), 3.78 (s, 1H), 4.56-4.61 (m, 1H), 4.76-4.82 (m, 1H), 5.93 (broad s, 1H), 6.15 (d, J = 8.0 Hz, 1H), 6.55 (d, J = 8.0 Hz 1H), 6.75 (t, J = 8.0 Hz, 1H), 7.07-7.11 (broad m, 3H), 8.25 (d, J = 6.8 Hz, 1H)ppm; NOE: peak at 5.93ppm versus peak at 3.78ppm; ¹³C NMR (CDCl₃) δ 30.7, 34.2, 42.4, 53.4, 56.2, 66.2, 85.3, 104.6, 116.4, 122.5, 125.5, 125.8, 126.3, 126.9, 128.0, 129.3, 130.3, 137.4, 153.9, 156.1,
169.2ppm.

\[ \text{Conversion of compound 2 to 20} \]

To a solution of 2 (0.384 g, 1.0 mmol) in CH\(_2\)Cl\(_2\) (20 mL) was added DMAP (0.182 g, 1.5 mmol). The solution was stirred for 6 h at room temperature and then washed with water (3 \(\times\) 50 mL), dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by chromatography (EtOAc/petroleum 1:3) to afford compound 20 (0.380 g, 99\%) as a white solid.

\[ \text{Conversion of compound 10 to 11} \]

Compound 10 was quantitatively converted to 11 by using the same procedure for the conversion of 2 to 20.

\[ \text{(±)-Allylic lactone 3} \]

Under N\(_2\), to a solution of compound 11 or 12 (1.000 g, 2.3 mmol) in DMF (30 mL) was added NaH (0.230 g, 60\% dispersion in mineral oil, 5.7 mmol) at 0 °C. After
stirring at this temperature for 30 min, allyl bromide (0.414 g, 3.5 mmol) was added. The reaction mixture was stirred at room temperature for 1 h, and then warmed to 65 °C for 3 h. After cooling to room temperature, the reaction mixture was quenched with water and extracted with EtOAc (3 × 60 mL). The combined organic phases were washed with brine, dried over sodium sulfate, and concentrated in vacuum. The residue was purified by flash column chromatography (EtOAc/petroleum 1:4) to give 3 (0.920 g, 84 %) as a white solid. Mp: 257−258 °C. \(^1\)H NMR (CDCl\(_3\)) δ 2.08 (dd, \(J = 14.2, 2.6\) Hz, 1H), 2.77 (dd, \(J = 14.0, 6.0\) Hz, 1H), 2.84 (t, \(J = 7.4\) Hz, 1H), 2.91 (dd, \(J = 14.4, 2.8\) Hz, 1H), 2.97 (s, 3H), 3.75 (s, 3H), 4.52 (m, 1H), 4.78 (dt, \(J = 13.0, 3.2\) Hz, 1H), 4.77-4.91 (m, 2H), 5.66 (m, 1H), 5.76 (s, 1H), 6.25 (dd, \(J = 7.6, 0.4\) Hz, 1H), 6.56 (d, \(J = 8.0\) Hz, 1H), 6.77 (t, \(J = 8.0\) Hz, 1H), 6.99-7.03 (m, 3H), 8.33-8.36 (m, 1H); NOE 5.75 (2.77-2.96)ppm; \(^13\)C NMR (CDCl\(_3\))δ 30.5, 31.2, 40.2, 49.6, 53.3, 58.6, 66.7, 83.2, 105.7, 117.9, 118.5, 123.7, 124.7, 126.1, 126.8, 127.6, 129.6 130.0, 131.1, 132.7, 137.4, 152.6, 155.8, 170.2ppm; HRMS (M+Na\(^+\)) calcd for C\(_{24}\)H\(_{23}\)Br\(_1\)N\(_2\)Na\(_1\)O\(_4\) 505.0733, found 505.0750; IR (KBr) 2924, 1728, 1695, 1595, 1448, 1331, 1241, 1172, 1126 cm\(^{-1}\).

**Isolation of (±)-ketene acetal 12**

Ketene acetal 12 could be detected during the reaction, and was obtained by quenching the reaction with water before the reaction was completed, followed by flash chromatography (EtOAc/petroleum 1:4) as a white foam. \(^1\)H NMR (CDCl\(_3\)) δ 2.06 (d, \(J = 12.0\) Hz, 1H), 2.96 (s, 3H), 3.08 (dt, \(J = 13.6, 5.6\) Hz, 1H), 3.50 (m, 1H), 3.68 (s, 3H), 3.98 (dd, \(J = 12.2, 4.6\) Hz, 1H), 4.54 (dd, \(J = 12.0, 5.2\) Hz, 1H), 4.82-4.88 (m, 1H), 5.05 (d, \(J = 10.4\) Hz, 1H), 5.12 (d, \(J = 17.2\) Hz, 1H), 5.65-5.73 (m, 1H), 5.76 (s, 1H), 6.24 (d, \(J = 7.6\) Hz, 1H ), 6.54 (d, \(J = 8.0\) Hz, 1H), 6.78 (t, \(J = 7.8\) Hz, 1H), 7.02 (broad s, 1H), 7.06 (t, \(J = 7.4\) Hz, 1H), 7.14 (broad t, \(J = 7.2\) Hz, H), 8.32 (d, \(J = 8.0\) Hz, 1H)ppm; \(^13\)C NMR (CDCl\(_3\)) δ 30.6, 31.0, 53.2, 59.8, 66.6, 67.2, 75.4, 82.5, 105.6, 116.1, 118.5, 122.8, 124.7, 126.9, 127.5, 128.7, 128.8 129.2, 130.3, 133.7, 138.6, 153.3, 156.2, 164.3ppm; HRMS (M+H\(^+\)) calcd for C\(_{24}\)H\(_{24}\)Br\(_1\)N\(_2\)O\(_4\) 483.0914, found 483.0931. IR (KBr) 3446, 2953, 1728, 1695, 1596, 1568, 1485, 1439, 1329, 1016, 766, 733cm\(^{-1}\).
(±)-Aldehyde 13

To a solution of 3 (2.050 g, 4.3 mmol) in a mixture of acetone (100 mL) and H₂O (10 mL) was added OsO₄ (11 mg) and NMO (0.600 g, 4.9 mmol) at room temperature. The mixture was stirred for 12 h and then concentrated under reduced pressure. The residue was diluted with water, and extracted with CH₂Cl₂ (3 × 60 mL). The combined organic phases were dried over Na₂SO₄, concentrated and purified by flash chromatography (EtOAc/petroleum 1:3) to give a mixture of diastereomeric diols.

The diols was dissolved in a mixture of THF and H₂O (50 mL, 10:1) at room temperature. To the solution, NaIO₄ (1.310 g, 6.3 mmol) was added. After stirring for 12 h, the reaction mixture was diluted with water (60 mL) and extracted with EtOAc (3 × 60 mL). The combined organic phases were washed with brine, dried over sodium sulfate, and concentrated in vacuum to give a residue. The residue was purified by flash chromatography (EtOAc/petroleum 1:4) to afford aldehyde 13 (1.967 g, 95 %) as a white solid. Mp: 275−277 °C. ¹H NMR (CDCl₃) δ 2.15 (dd, J = 14.0, 2.4 Hz, 1H), 2.65 (td, J = 14.0, 5.6 Hz, 1H), 2.82 (dd, J = 16.4, 6.0 Hz, 1H), 2.96 (s, 3H), 3.03 (dd, J = 16.0, 2.8 Hz, 1H), 4.57 (dd, J = 12.4, 4.8 Hz, 1H), 4.77-4.84 (m, 1H), 5.67 (s, 1H), 6.28 (d, J = 8.0 Hz, 1H), 6.58 (d, J = 7.6 Hz, 1H), 6.80 (t, J = 8.0 Hz, 1H), 7.05-7.10 (m, 3H), 8.41-8.43 (m, 1H), 9.49 (t, J = 2.4 Hz, 1H) ppm; NOE: correlations among peaks at 5.67ppm, 2.66ppm and 2.83ppm were observed; ¹³C NMR (CDCl₃) δ 29.6, 30.4, 31.2, 46.8, 53.6, 58.4, 67.1, 83.1, 105.9, 118.4, 123.8, 125.0, 126.7, 127.5, 127.8, 128.3, 129.5, 130.4, 137.5, 152.7, 155.6, 171.1, 198.2 ppm; HRMS (M+Na⁺) calcd for C₂₃H₂₁Br₁N₂Na₁O₅ 507.0526, found 507.0545; IR (KBr) 3425, 1722, 1689, 1595, 1485, 1447, 1330, 1243, 1045 cm⁻¹.
(±)-Oxime 21
To a solution of 13 (1.903 g, 3.9 mmol) in a mixture of THF and H$_2$O (50 mL, 25:1) was added NH$_2$OH-HCl (0.297 g, 4.3 mmol) and Na$_2$CO$_3$ (0.240 g, 2.2 mmol) at room temperature. The mixture was stirred for 1 h, diluted with water, and extracted with EtOAc (3 × 60 mL). The combined organic phases were washed with brine, dried over sodium sulfate, and concentrated in vacuum to give oxime 21 as a white solid (2.008 g, trans/cis 1.6:1, 100 %), which was used without further purification. $^1$H NMR (CDCl$_3$) δ 2.09-2.15 (m, major+minor, 2H), 2.69-2.82 (m, major+minor, 2H), 2.90-3.05 (m, major+minor, 2H), 2.96 (s, 6H), 3.10-3.15 (dd, $J = 12.0$, 4.0 Hz, major 1H), 3.33 (dd, $J = 17.6$, 4.8 Hz, minor 1H), 3.66 (s, major 3H), 3.73 (s, minor 3H), 4.51-4.57 (m, major+minor, 2H), 4.73-4.82 (m, major+minor, 2H), 5.74 (s, minor 1H), 5.78 (s, major 1H), 6.26 (d, $J = 7.6$ Hz major+minor, 2H), 6.57 (d, $J = 8.0$ Hz, major+minor, 2H), 6.76-6.82 (m, major+minor, 6H), 7.03-7.05 (m, major+minor, 3H), 7.24 (t, $J = 6.2$ Hz, minor 1H), 7.41 (broad s, minor 1H), 8.05 (broad s, major 1H), 8.33-8.36 (m, minor 1H), 8.40-8.42 (m, major 1H) ppm; HRMS (M+Na$^+$) calcd for C$_{23}$H$_{22}$Br$_3$Na$_3$O$_5$ 522.0635, found 522.0639. IR (KBr) 3443, 2924, 1728, 1681, 1595, 1568, 1337, 1258, 1123, 1024, 769 cm$^{-1}$.

(±)-Amine 22
To a solution of oxime 21 (2.008 g, 4.0 mmol) in MeOH (100 mL) was added Raney-Ni (1.0 g, freshly prepared, W-2 form, stored in ethanol) at room temperature. The mixture was hydrogenated at 40 °C under 1 atm of H$_2$ pressure for 3 h. The reaction mixture was filtered to remove the catalyst and the solution was concentrated. The residue was purified by flash chromatography (CH$_2$Cl$_2$/MeOH 10:1) to give aldehyde 13 (0.402 g, 22 %) and amine 22 (1.305 g, 67 % yield, 86% yield based on recovered 13) as a white solid. Mp: 201–203 °C. $^1$H NMR (DMSO-d$_6$) δ 1.92-1.98
(m, 2H), 2.09-2.17 (m, 2H), 2.50-2.56 (m, 1H), 2.82-2.91 (m, 1H), 2.91 (s, 3H), 3.70 (s, 3H), 4.50 (d, $J = 8.8$ Hz, 2H), 5.71 (s, 1H), 6.41 (d, $J = 7.6$ Hz, 1H), 6.52 (d, $J = 7.6$ Hz, 1H), 6.80 (t, $J = 7.8$ Hz, 1H), 6.96-7.04 (m, 3H), 8.18 (dd, $J = 7.0$, 1.4 Hz, 1H) ppm; $^{13}$C NMR (DMSO-$d_6$) $\delta$ 30.0, 31.2, 47.8, 53.6, 59.0, 66.8, 83.0, 106.3, 117.8, 123.1, 124.3, 126.6, 126.9, 129.4, 130.5, 131.5, 137.8, 153.1, 155.2, 170.5 ppm. HRMS (M+H$^+$) calcd for C$_{23}$H$_{25}$Br$_1$N$_3$O$_4$ 486.1023, found 486.1009; IR (KBr) 3525, 2957, 2922, 1708, 1571, 1483, 1440, 1326, 1182, 1128, 736 cm$^{-1}$.

$\textbf{(+\text{)-Lactam 14}}$

Under N$_2$, amine 22 (1.019 g, 2.1 mmol) was added to a solution of sodium (97 mg, 4.2 mmol) dissolved in methanol (25 mL) at room temperature. The reaction mixture was heated to 70 °C and stirred for 12 h. After cooling to room temperature, the reaction mixture was diluted with water (50 mL), extracted with CH$_2$Cl$_2$ (3 × 60 mL). The combined organic phases were washed with brine, dried over sodium sulfate, and concentrated in vacuum. The residue was purified by flash chromatography (CH$_2$Cl$_2$/acetone 4:1) to give lactam 14 (0.98 g, 98 %) as white solid. Mp: 244−246 °C. $^1$H NMR (CDCl$_3$) $\delta$ 1.88-1.96 (m, 1H), 2.32-2.39 (m, 1H), 2.49 (s, 3H), 3.00 (dd, $J = 14.0$, 7.2 Hz, 1H), 3.14-3.21 (m, 1H), 3.33 (t, $J = 9.6$ Hz, 1H), 3.54 (dd, $J = 16.6$, 9.4 Hz, 1H), 3.68 (broad s, 2H), 3.87 (s, 3H), 5.99 (d, $J = 8.0$ Hz, 1H), 6.25 (broad s, 1H), 6.39 (s, 1H), 6.69 (d, $J = 7.6$ Hz, 1H), 6.80 (t, $J = 8.0$ Hz, 1H), 7.06 (t, $J = 8.2$ Hz, 1H), 7.20 (t, $J = 7.2$ Hz, 1H), 7.46 (d, $J = 7.6$ Hz, 1H) ppm; $^{13}$C NMR (CDCl$_3$) $\delta$ 30.9, 35.1, 35.6, 40.2, 52.2, 53.3, 60.4, 60.8, 83.1, 104.4, 122.3, 123.3, 124.9, 126.0, 126.5, 126.8, 130.3, 136.3, 138.5, 152.8, 155.4, 174.6 ppm; HRMS (M+Na$^+$) calcd for C$_{23}$H$_{24}$Br$_1$N$_3$Na$_1$O$_4$ 508.0842, found 508.0835; IR (KBr) 3472, 2926, 1712, 1596, 1564, 1446, 1332, 1286, 755 cm$^{-1}$.
(±)-Aldehyde 23

To a solution of 14 (50.0 mg, 0.10 mmol) in CH$_2$Cl$_2$ (5 mL) was added the Dess-Martin reagent (55.0 mg, 0.13 mmol) at room temperature. After stirring for 5 min, the reaction was quenched with sat. Na$_2$S$_2$O$_4$ solution. The mixture was extracted with CH$_2$Cl$_2$ (3 × 10 mL), dried over Na$_2$SO$_4$ and concentrated in vacuum. The residue was purified by flash chromatography (CH$_2$Cl$_2$/EtOAc 2:1) to give aldehyde 23 (48.0 mg, 93%) as a white solid. Mp: 128 - 130 °C. $^1$H NMR (CDCl$_3$) δ 1.92-2.00 (m, 1H), 2.52 (s, 3H), 2.82 (dd, $J$ = 14.4, 6.8 Hz, 1H), 3.16-3.23 (m, 1H), 3.35 (t, $J$ = 9.6 Hz, 1H), 3.57 (dd, $J$ = 16.6, 9.4 Hz, 1H), 3.04-3.08 (broad d, $J$ = 16.0 Hz, 1H), 3.37 (t, $J$ = 9.8 Hz, 1H), 3.47-3.54 (m, 1H), 3.87 (s, 3H), 4.24 (d, $J$ = 14.8 Hz, 1H), 6.04 (d, $J$ = 7.6 Hz, 1H), 6.25 (broad s, 1H), 6.67 (d, $J$ = 8.0 Hz, 1H), 6.82 (t, $J$ = 7.6 Hz, 1H), 7.08 (dt, $J$ = 7.6, 1.2 Hz, 1H), 7.23 (dt, $J$ = 7.6, 1.2 Hz, 1H), 7.32 (broad s, 1H), 7.47 (d, $J$ = 7.6 Hz, 1H), 7.68 (s, 1H), 9.74 (t, $J$ = 1.6 Hz, 1H) ppm; $^{13}$C NMR (CDCl$_3$) δ 31.0, 35.6, 40.3, 45.7, 52.2, 53.3, 58.5, 83.9, 104.7, 122.2, 122.3, 124.8, 125.0, 126.0, 126.4, 127.0, 130.7, 136.3, 137.8, 152.9, 174.7, 200.0 ppm; HRMS (M+Na$^+$) calcd for C$_{23}$H$_{22}$Br$_1$N$_3$Na$_1$O$_4$ 506.0686, found 506.0699; IR (KBr) 3416, 3210, 2902, 1705, 1594, 1568, 1442, 1394, 1331, 1284, 1059, 762 cm$^{-1}$.
(±)-Amine 24

To a solution of aldehyde 23 (2.003 g, 4.1 mmol) in a mixture of THF and H₂O (50 mL, 25:1) was added NH₂OH-HCl (0.342 g, 4.9 mmol) and Na₂CO₃ (0.270 g, 2.5 mmol) at room temperature. The mixture was stirred for 1 h, and then diluted with water (50 mL), extracted with EtOAc (3 × 60 mL). The combined organic phases were washed with brine, dried over sodium sulfate, and concentrated in vacuum to give oxime as a white solid (2.003 g, 97 %), which was used without purification. To a solution of above oxime (2.003 g, 4.0 mmol) in MeOH (100 mL) at room temperature was added Raney-Ni (1.00 g, freshly prepared, W-2 form, stored in ethanol). The mixture was hydrogenated at 50 °C under 1 atm of H₂ pressure for 2 h. The reaction mixture was filtered to remove the catalyst and the solution was concentrated to give amine 24 as white solid (2.085 g), which was used without further purification. An analytic sample of 24 was obtained by flash chromatography (CH₂Cl₂/MeOH 5:1). Mp: 142–145 °C. ¹H NMR (CDCl₃) δ 1.85-1.93 (m, 1H), 2.02 (broad s, 2H), 2.14-2.21 (m, 1H), 2.48 (s, 3H), 2.61 (dt, J = 11.6, 4.4 Hz, 1H), 2.70 (dt, J = 11.2, 4.0 Hz, 1H), 2.97 (dd, J = 14.0, 7.2 Hz, 1H), 3.06 (dt, J = 12.0, 4.8 Hz, 1H), 3.29 (t, J = 9.4 Hz, 1H), 3.54 (dd, J = 17.0, 9.4 Hz, 1H ), 3.86 (s, 3H), 5.97 (d, J = 7.6 Hz, 1H), 6.06 (broad s, 1H), 6.67 (d, J = 8.0 Hz, 1H), 6.78 (t, J = 8.0 Hz, 1H), 6.87 (broad s, 1H), 7.05 (t, J = 8.2 Hz, 1H), 7.19 (t, J = 7.0 Hz, 1H), 7.24 (broad s, 1H), 7.45 (d, J = 8.0 Hz, 1H); δ ppm; ¹³C NMR (CDCl₃) δ 30.8, 35.6, 36.2, 39.5, 40.2, 52.3, 53.2, 60.8, 82.8, 104.3, 122.2, 123.3, 124.8, 125.1, 125.9, 126.4, 126.7, 130.1, 136.2, 138.6, 152.6, 155.4, 174.7; HRMS (M+H⁺) calcd for C₂₃H₂₆Br₁N₄O₃ 485.1183, found 485.1196.

(±)-Pentacyclic lactam 15

Under N₂, to a solution of crude 24 (2.005 g, 4.1 mmol) in dried CH₂Cl₂ (50 mL) was added Na₂CO₃ (0.870 g, 8.2 mmol) and (Boc)₂O (0.903 g, 4.1 mmol) at room temperature. After stirring for 24 h, the reaction mixture was filtered and the filtrate was concentrated. The residue was purified by flash chromatography (EtOAc/petroleum 1:1) to give 15 (1.307 g, 54 % from 23) as a white foam. ¹H NMR (CDCl₃) δ 1.45 (s, 9H), 1.87-1.96 (m, 1H), 2.24-2.27 (broad d, 1H), 2.50 (s, 3H), 2.94 (dd, J =
14.2, 7.0 Hz, 1H), 3.04 (broad s, 1H), 3.31 (t, $J = 9.6$ Hz, 1H), 3.50 (dd, $J = 16.8$, 5.2 Hz, 1H), 3.88 (s, 3H), 4.64 (broad s, 1H), 5.98 (d, $J = 7.6$ Hz, 1H), 6.10 (broad s, 1H), 6.38 (s, 1H), 6.68 (d, $J = 7.6$ Hz, 1H), 6.78 (t, $J = 7.8$ Hz, 1H), 7.05 (t, $J = 8.2$ Hz, 1H), 7.20 (t, $J = 7.6$ Hz, 1H), 7.45 (d, $J = 7.6$ Hz, 1H) ppm; $^{13}$C NMR (CDCl$_3$) $\delta$ 28.4, 30.7, 32.8, 35.4, 38.3, 40.4, 52.4, 53.2, 60.8, 79.2, 82.7, 104.3, 122.3, 123.3, 124.5, 124.8, 125.9, 126.4, 126.8, 130.3, 136.3, 138.5, 152.7, 155.2, 155.7, 174.9 ppm; HRMS (M+Na$^+$) calcd for C$_{28}$H$_{33}$Br$_1$N$_4$Na$_1$O$_5$ 607.1527, found 607.1491; IR (KBr) 3446, 2923, 1700, 1650, 1597, 1457, 1377, 1334, 1285, 1169, 756 cm$^{-1}$.

![Chemical structure of lactam 4](image)

(±)-Pentacyclic lactam 4

To a solution of lactam 15 (100.0 mg, 0.17 mmol) in 2-methylbut-3-en-2-ol (1 mL) was added Pd(OAc)$_2$ (20 mg, 0.09 mmol), P(o-Tol)$_3$ (104 mg, 0.34 mmol) and Et$_3$N (34 mg, 0.34 mmol). The mixture was irradiated under microwave (200 mA) for two h ($6 \times 20$ min) and then concentrated under reduced pressure. The residue was purified by flash chromatography (EtOAc) to give 4 (68.7 mg, 68 %, 86% yield based on recovered 15) as a white solid and 15 (21 mg, 21 %). Mp: 192—194 °C. $^1$H NMR (CDCl$_3$) $\delta$ 1.38 (s, 3H), 1.41 (s, 9H), 1.43 (s, 3H), 1.90-2.01 (m, 1H), 2.04 (s, 1H), 2.04-2.18 (m, 1H), 2.50 (s, 3H), 2.63-2.69 (m, 1H), 2.92-3.00 (m, 2H), 3.15-3.16 (m, 1H), 3.32 (t, $J = 9.6$ Hz, 1H), 3.51 (dd, $J = 17.0$, 9.6 Hz, 1H), 3.85 (s, 3H), 4.80 (broad s, 1H), 5.93 (s, 1H), 5.94 (d, $J = 7.2$ Hz, 1H), 6.17 (broad s, 1H), 6.20 (d, $J = 15.6$ Hz, 1H), 6.79 (d, $J = 8.0$ Hz, 1H), 6.93 (t, $J = 7.8$ Hz, 1H), 6.96 (d, $J = 17.6$ Hz, 1H), 7.03 (t, $J = 8.4$ Hz, 1H), 7.18 (dt, $J = 7.6$, 1.2 Hz, 1H), 7.23 (broad s, 1H), 7.44 (d, $J = 7.6$ Hz, 1H) ppm; $^{13}$C NMR (CDCl$_3$) $\delta$ 28.4, 28.9, 30.2, 31.2, 35.5, 38.3, 40.0, 52.6, 53.2, 59.9, 60.4, 79.8, 83.7, 104.1, 114.7, 123.4, 124.7, 125.0, 125.9, 126.5, 126.7, 129.1, 136.4, 137.3, 138.6, 150.8, 155.8, 174.8 ppm; HRMS (M+Na$^+$) calcd for
C_{33}H_{42}N_{4}Na_{1}O_{6} \ 613.2997, \ found \ 613.3021; \ IR (KBr) \ 3369, \ 2971, \ 1698, \ 1580, \ 1493, \ 1443, \ 1396, \ 1367, \ 1335, \ 1284, \ 1166, \ 757 \ cm^{-1}.

(\pm)-Hexacyclic lactam 17 and diene 16

To a solution of 4 (200.0 mg, 0.34 mmol) in CHCl$_3$ (20 mL) was added PPTS (4.3 mg, 0.02 mmol) at room temperature. The reaction mixture was stirred for 1 h, then diluted with CHCl$_3$ (40 mL), and washed with water (3 × 30 mL). The organic phases were dried over sodium sulfate and concentrated. The crude material was purified by chromatography (petroleum/acetone 5:1) to afford lactam 17 (128 mg, 66%) as a white solid and diene 16 (50.4 mg, 26%) as a white solid.

**Lactam 17:** Mp: 244−246 °C; $^1$H NMR (CDCl$_3$) $\delta$ 1.51 (broad s, 9H), 1.77 (s, 3H), 1.87 (broad s, 3H), 1.96-1.99 (m, 1H), 2.16 (d, $J$ = 13.2 Hz, 1H), 2.50 (broad s, 3H), 2.94 (m, 1H), 3.03-3.16 (m, 3H), 3.51 (broad s, 1H), 3.85 (s, 3H), 3.93 (broad s, 1H), 5.10 (s, 1H), 5.60 (broad d, $J$ = 72 Hz, 1H), 5.92 (broad s, 2H), 6.02 (broad s, 1H), 6.32 (broad s, 1H), 6.91 (t, $J$ = 8.0 Hz 1H), 6.99 (dt, $J$ = 7.6, 1.2 Hz, 1H), 7.18 (t, $J$ = 7.0 Hz, 1H), 7.25 (broad s, 1H), 7.38 (broad d, $J$ = 4.4 Hz, 1Hp; $^{13}$C NMR (CDCl$_3$) $\delta$ 18.9, 25.6, 28.6, 30.8, 36.1, 39.2, 41.0, 52.3, 53.1, 59.7, 60.4, 61.3, 79.6, 90.0, 103.2, 117.0, 124.2, 124.9, 125.5, 126.1, 126.7, 128.8, 136.8, 139.4, 141.0, 150.6, 155.1, 171.1 ppm; HRMS (M+Na$^+$) calcd for C$_{33}$H$_{40}$N$_{4}$Na$_{1}$O$_{5}$ 595.2891, found 595.2912; IR (KBr) 3448, 1700, 1392, 1333, 1284 cm$^{-1}$.

(±)-Diene 16: Mp: 185−187 °C; $^1$H NMR (CDCl$_3$) $\delta$ 1.42 (s, 9H), 1.96 (broad s, 1H), 2.43 (broad s, 1H), 2.55 (broad s, 1H), 2.55 (s, 3H), 2.89 (broad s, 1H), 2.96-3.02 (m, 2H), 3.28 (t, $J$ = 9.6 Hz, 1H), 3.44 (dd, $J$ = 17.2, 8.4 Hz, 1H), 3.87 (broad s, 3H), 4.45 (t, $J$ = 5.8 Hz, 1H), 4.89 (s, 1H), 4.99 (s, 1H), 5.92 (d, $J$ = 7.6 Hz, 1H), 6.06 (s, 1H), 6.63 (d, $J$ = 16.0 Hz, 1H), 6.78 (d, $J$ = 8.4 Hz, 1H), 6.79 (d, $J$ = 13.6 Hz, 1H), 6.91 (t,
$J = 7.8$ Hz, 1H), 7.03 (t, $J = 8.2$ Hz, 1H), 7.20 (t, $J = 7.2$ Hz, 1H), 7.33 (broad s, 1H), 7.53 (d, $J = 7.6$ Hz, 1H) ppm; $^{13}$C NMR (CDCl$_3$) $\delta$ 19.2, 28.4, 30.7, 35.1, 35.3, 37.9, 40.0, 52.6, 53.2, 61.5, 79.2, 83.6, 104.0, 114.6, 116.8, 123.4, 125.1, 125.6, 126.3, 126.8, 128.2, 129.2, 131.7, 136.6, 137.2, 138.3, 142.2, 151.2, 155.5, 175.6 ppm; HRMS (M+Na$^+$) calcd for C$_{33}$H$_{40}$N$_4$Na$_2$O$_5$ 595.2891, found 595.2871; IR (KBr) 3392, 1699, 1603, 1492, 1443, 1396, 1366, 1334, 1285, 1169 cm$^{-1}$.

(±)-Hexacyclic imidate 25

Under N$_2$, diethylisopropylamine (20.0 mg, 0.16 mmol) and triethyloxonium tetrafluoroborate (160 uL, freshly prepared, 1.0 M in CH$_2$Cl$_2$, 0.16 mmol) were added sequentially to a solution of compound 17 (30.0 mg, 0.05 mmol) in CH$_2$Cl$_2$ (3 mL) at 0 °C. The reaction mixture was allowed to stir at room temperature for 2 h. The reaction was then quenched with water. The mixture was then extracted with CH$_2$Cl$_2$ (3 × 5 mL). The combined organic phases were dried over sodium sulfate and concentrated. The residue was purified by chromatography (petroleum/acetone 5:1) to afford the imidate 25 (30.0 mg, 95 %) as a white solid. Mp: 81−82 °C. $^1$H NMR (CDCl$_3$) $\delta$ 1.02 (broad s, 3H), 1.50 (broad s, 9H), 1.63-1.73 (m, 1H), 1.75 (s, 3H), 1.85 (s, 3H), 2.24 (m, 1H), 2.38 (s, 3H), 2.77 (broad s, 1H), 2.85-2.92 (m, 1H), 3.23 (broad s, 1H), 3.34 (broad, 1H), 3.66-3.72 (m, 1H), 3.85 (s, 1H), 4.03 (broad s, 2H), 4.36 (broad s, 1H), 5.21 (broad s, 1H), 5.71 (s, 1H), 5.98 (d, $J = 6.4$ Hz, 1H), 6.31 (broad s, 1H), 6.79 (d, $J = 7.2$ Hz, 1H), 6.92 (t, $J = 7.6$ Hz, 1H), 6.99 (dt, $J = 7.6, 1.2$ Hz, 1H), 7.19 (dt, $J = 7.6, 1.2$ Hz, 1H), 7.29 (broad d, $J = 7.2$ Hz, 1H) ppm; $^{13}$C NMR (CDCl$_3$) $\delta$ 13.9, 18.8, 25.8, 28.5, 29.7, 31.5, 38.2, 39.4, 50.9, 53.1, 57.7, 58.5, 58.9, 64.0, 80.2, 88.8, 103.9, 117.2, 124.4, 124.7, 125.0, 125.2, 126.4, 128.2, 136.2, 140.4, 141.1, 150.5, 155.1,
155.8, 169.1 ppm; HRMS (M+H+) calcd for C_{35}H_{45}N_{4}O_{5} 601.3384, found 601.3382; IR (KBr) 3446, 2929, 1711, 1649, 1442, 1395, 1368, 1331, 1166, 1049 cm\(^{-1}\).

(±)-Heptacyclic amidine 6a

To a solution of imidate 25 (150.0 mg, 0.25 mmol) in CH\(_2\)Cl\(_2\) (27 mL) was added TFA (1.430 g, 12.50 mmol) dropwise at 0 °C. After stirring at room temperature for 30 min, the reaction was quenched with sat. NaHCO\(_3\) solution. The mixture was extracted with CH\(_2\)Cl\(_2\) (3 × 30 mL). The combined organic phases were dried over (Na\(_2\)SO\(_4\)) and concentrated under reduced pressure at a temperature below 30 ºC to give crude 5. The crude 5 was dissolved in a mixture of CH\(_2\)Cl\(_2\) and MeOH (10 mL, 1:1) and silica gel (1.0 g) was added. The reaction mixture was stirred at 50 °C for 12 h. The suspension was filtered and the filtrate was concentrated. The residue was purified by flash chromatography (petroleum/acetone 2:1) to give amidine 6a (92.0 mg, 81 %) as a white solid. Mp: 163–164 °C. \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 1.74 (d, \(J = 1.2\) Hz, 3H), 1.80 (d, \(J = 1.2\) Hz, 3H), 1.88 (d, \(J = 14.8\) Hz, 1H), 2.08 (t, \(J = 9.8\) Hz, 1H), 2.22-2.30 (m, 1H), 2.82-2.90 (m, 1H), 2.94 (s, 3H), 3.25 (dd, \(J = 13.8, 7.8\) Hz, 1H), 3.37 (m, 1H), 3.74 (s, 3H), 3.74-3.79 (m, 1H), 3.86 (dd, \(J = 18.5, 7.6\) Hz, 1H), 4.83 (d, \(J = 8.8\) Hz, 1H), 5.37 (dt, \(J = 9.2, 1.2\) Hz, 1H), 5.84 (s, 1H), 6.08 (dd, \(J = 16.8, 7.6\) Hz, 1H), 6.82 (t, \(J = 8.0\) Hz, 1H), 6.94 (t, \(J = 7.4\) Hz, 1H), 7.03-7.11 (m, 2H) ppm; \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 18.6, 25.7, 27.0, 29.7, 30.5, 38.6, 45.5, 53.2, 54.8, 55.4, 60.1, 80.2, 104.3, 117.0, 122.1, 123.9, 125.2, 127.0, 127.3, 128.6, 130.0, 134.3, 136.7, 136.9, 137.3, 149.5, 158.2, 179.8 ppm; HRMS (M+H\(^+\)) calcd for C\(_{28}\)H\(_{31}\)N\(_4\)O\(_2\) 455.2442, found 455.2456; IR (KBr) 3399, 2931, 1709, 1636, 1596, 1485, 1441, 1370, 1333, 1203, 1124, 752 cm\(^{-1}\).
(±)-Unprotected heptacyclic amidine 6b

To a solution of amidine 6a (20.0 mg, 0.04 mmol) in a mixture of MeOH and H₂O (1.1 mL, 10:1) was added KOH (100.0 mg, 1.79 mmol) at room temperature. The resulting mixture was heated to 100 °C and stirred for 24 h. After cooling to room temperature, AcOH (110 ul) and sat. NaHCO₃ solution was added sequentially to adjust the pH value to 8—9. The solution was extracted with CH₂Cl₂, dried over Na₂SO₄ and concentrated. The residue was purified by flash chromatography (petroleum/EtOAc 1:1.5) to afford the aminal 6b (11.5 mg, 65 %) as a white solid. Mp: 90—93 °C. ¹H NMR (CDCl₃) δ 1.72 (d, J = 0.8 Hz, 3H), 1.82 (s, 3H), 1.97-2.02 (m, 1H), 2.11 (dd, J = 11.8, 4.6 Hz, 1H), 2.18-2.25 (m, 1H), 2.85-2.94 (m, 1H), 2.94 (s, 3H), 3.27-3.35 (m, 2H), 3.73-3.81 (m, 1H), 3.87 (dd, J = 15.0, 7.8 Hz, 1H), 4.44 (broad s, 1H), 4.70 (s, 1H), 4.87 (d, J = 9.2 Hz, 1H), 5.38 (d, J = 8.8 Hz, 1H), 6.16 (d, J = 8.0 Hz, 1H), 6.22 (d, J = 7.6 Hz, 1H), 6.46 (d, J = 7.6 Hz, 1H), 6.58 (t, J = 7.4 Hz, 1H), 6.88 (t, J = 7.8 Hz, 1H), 6.89 (dt, J = 7.6, 1.2 Hz, 1H), 6.99 (dd, J = 7.2, 0.8 Hz, 1H) ppm; ¹³C NMR (CDCl₃) δ 18.5, 25.7, 26.3, 29.3, 30.4, 38.4, 45.9, 52.3, 53.8, 60.0, 79.7, 105.3, 114.6, 117.5, 118.1, 122.2, 124.1, 127.3, 128.3, 128.7, 131.6, 133.8, 136.6, 144.4, 149.0, 180.6 ppm; HRMS (M+H⁺) calcd for C₂₆H₂₉N₄ 397.2387, found 397.2402; IR (KBr) 3286, 2925, 1638, 1605, 1485, 1464, 1375, 1258, 1229 cm⁻¹.
(±)-Communesin F

To a solution of amidine 6b (25.0 mg, 0.06 mmol) in a mixture of AcOH and Ac₂O (2 mL, 1:1) was added NaBH₄ (192.0 mg, 5.05 mmol) at 0 °C. After stirring at 0 °C for 10 min, sat. NaHCO₃ solution was added to adjust the pH value to 8–9. The resulting solution was extracted with CH₂Cl₂, dried over Na₂SO₄ and concentrated. The residue was purified by flash chromatography (petroleum/EtOAc 1:1.5) to afford (±)-communesin F (20.3 mg, 73 %) as an inseparable mixture of two amide rotamer isomers. The ¹H NMR and ¹³C NMR spectra of the synthetic (±)-communesin F were fully consistent with that of the natural (-)-communesin F provided by Prof. H. Hayashi.² The ratio of two rotamers varied in different solvents, for example, a 2.6:1 ratio in CDCl₃ and a 5.1:1 ratio in DMSO-d₆. Ether protonation of the mixture with 5% trifluoroacetic acid in CDCl₃ provided one stable rotamer.

Cis rotamer of the synthetic (±)-communesin F: ¹H NMR (CDCl₃) δ 1.79 (d, J = 0.8 Hz, 3H), 1.85 (d, J = 0.8 Hz, 3H), 1.96 (dd, J = 13.2, 7.6 Hz, 1H), 2.20-2.24 (m, 1H), 2.26-2.33 (m, 1H), 2.41 (s, 3H), 2.70-2.78 (m, 1H), 2.82 (s, 3H), 2.99-3.07 (m, 1H), 3.10-3.18 (m, 1H), 3.34 (dd, J = 15.4, 9.2 Hz, 1H), 3.85 (dd, J = 11.6, 9.2 Hz, 1H), 4.60 (broad s, 1H), 4.67 (s, 1H), 5.05 (d, J = 8.8 Hz, 1H), 5.11 (s, 1H), 5.22 (broad d, J = 8.8 Hz, 1H), 5.86 (d, J = 7.6 Hz, 1H), 6.08 (d, J = 7.6 Hz, 1H), 6.66-6.73 (m, 3H), 6.82 (t, J = 7.6 Hz, 1H), 7.00 (td, J = 7.4, 2.0 Hz, 1H) ppm; ¹³C NMR (CDCl₃) δ 18.4, 22.6, 26.0, 29.6, 30.9, 36.3, 37.8, 44.2, 51.2, 51.8, 64.4, 79.6, 82.6, 100.8, 114.7, 117.0, 120.6, 123.2, 124.6, 127.3, 128.4, 131.3, 132.7, 136.0, 140.6, 142.7, 150.1, 171.6 ppm; HRMS (M+H⁺) calcd for C₂₈H₃₅N₄O₁ 441.2649, found 441.2667; IR (KBr) 2927, 1631, 1605, 1480, 1439, 1389, 1317, 1281, 1156, 1084, 887 cm⁻¹.

Trans rotamer of the synthetic (±)-communesin F: ¹H NMR (CDCl₃) δ 1.75 (s, 3H), 1.97 (s, 3H), 2.05 (m, 1H), 2.11 (s, 3H), 2.21 (m, 1H), 2.30 (m, 1H), 2.80 (s, 3H), 2.92 (m, 1H), 3.12 (m, 1H), 3.20 (m, 1H), 3.41 (m, 1H), 3.68 (broad s, 1H), 4.63 (s, 1H), 5.22 (d, J = 8.4 Hz, 1H), 5.36 (d, J = 8.4 Hz, 1H), 5.48 (s, 1H), 5.86 (d, J = 8.0 Hz, 1H), 6.14 (d, J = 8.0 Hz, 1H), 6.67-6.84 (m, 3H), 6.82 (m, 1H), 7.00 (m, 1H) ppm. ¹³C NMR (CDCl₃) δ 18.4, 23.0, 26.0, 29.9, 32.5, 36.7, 38.1, 46.0, 49.9, 51.2, 64.4, 78.1, 83.0, 100.8, 115.4, 117.0, 120.8, 123.5, 124.7, 127.2, 128.2, 131.5, 132.9, 137.9,
141.5, 142.9, 150.1, 170.7ppm.

**Trifluoroacetic acid salts of the synthetic (±)-communesin F:** $^1$H NMR (5% CF$_3$COOH in CDCl$_3$) $\delta$ 1.86 (s, 3H), 2.06 (s, 3H), 2.20 (s, 3H), 2.26 (dd, $J$ = 13.6, 7.2 Hz, 1H), 2.40 (dd, $J$ = 22.0, 9.6 Hz, 1H), 2.59 (t, $J$ = 11.4 Hz, 1H), 2.82 (s, 3H), 2.99 (dd, $J$ = 17.6, 9.6 Hz, 1H), 3.26 (dd, $J$ = 17.6, 9.6 Hz, 1H), 3.74 (t, $J$ = 12.6 Hz, 1H), 4.04 (t, $J$ = 8.8 Hz, 1H), 4.09-4.15 (m, 1H), 4.76 (s, 1H), 5.13 (d, $J$ = 9.2 Hz, 1H), 5.74 (s, 1H), 5.90 (d, $J$ = 9.2 Hz, 1H), 5.97 (d, $J$ = 8.0 Hz, 1H), 6.15 (d, $J$ = 7.6 Hz, 1H), 6.52 (d, $J$ = 7.6 Hz, 1H), 6.77 (t, $J$ = 7.6 Hz, 1H), 6.80 (d, $J$ = 7.6 Hz, 1H), 6.93 (t, $J$ = 7.8 Hz, 1H), 7.10 (t, $J$ = 7.6 Hz, 1H) ppm. $^{13}$C NMR (5% CF$_3$COOH in CDCl$_3$) $\delta$ 18.8, 21.6, 26.0, 29.6, 31.9, 33.4, 38.8, 46.4, 50.5, 50.5, 66.4, 79.7, 82.3, 102.7, 114.8, 117.1, 118.2, 121.5, 122.4, 128.5, 128.5, 129.7, 129.9, 130.7, 142.1, 147.5, 150.3, 173.2ppm.

$^1$H NMR spectrum of the synthetic (±)-communesin F in DMSO-d$_6$ at 25 ºC: $^1$H NMR (DMSO-d$_6$, 25 ºC) $\delta$ 1.71 (s, 3H, minor), 1.75 (s, 3H, major), 1.80 (s, 3H, major), 1.99 (s, 3H, minor), 2.04 (m, 1H, major), 2.29 (s, 3H, major), 2.28 (m, 1H, major), 2.69 (m, 1H, major), 2.75 (s, 3H, minor), 2.76 (s, 3H, major), 3.02 (m, 1H, major), 3.18 (m, 1H, major), 3.64 (broad s, 1H, major), 3.68 (m, 1H, minor), 4.58 (s, 1H, minor), 4.61 (s, 1H, major), 5.02 (d, $J$ = 8.0 Hz, 1H, minor), 5.07 (d, $J$ = 9.2 Hz, 1H, minor), 5.13 (s, 1H, major), 5.17 (s, 1H, minor), 5.22 (d, $J$ = 8.8 Hz, 1H, major), 5.82 (d, $J$ = 8.0 Hz, 1H), 5.97 (d, $J$ = 7.6 Hz, 1H), 6.24 (s, 1H), 6.61 (t, $J$ = 7.2 Hz, 1H), 6.68-6.72 (t, $J$ = 8.0 Hz, 1H), 6.79-6.81 (d, $J$ = 8.0 Hz, 1H), 6.92-6.96 (t, $J$ = 7.6 Hz, 1H) ppm.

$^1$H NMR spectrum of the synthetic (±)-communesin F in DMSO-d$_6$ at 115 ºC: $^1$H NMR (DMSO-d$_6$, 115 ºC) $\delta$ 1.77 (s, 3H), 1.83 (s, 3H), 2.07 (m, 1H), 2.23 (s, 3H), 2.30 (m, 1H), 2.79 (s, 3H), 3.22 (broad s, 1H), 3.70 (broad s, 1H), 4.63 (s, 1H), 5.06 (d, $J$ = 8.4 Hz, 1H), 5.18 (broad s, 1H), 5.20 (d, $J$ = 9.6 Hz, 1H), 5.82 (d, $J$ = 7.6 Hz, 1H), 5.98 (d, $J$ = 8.0 Hz, 1H), 6.11 (s, 1H), 6.64 (m, 2H), 6.71 (t, $J$ = 7.8 Hz, 1H), 6.80 (d, $J$ = 7.6 Hz, 1H), 6.93 (t, $J$ = 7.6 Hz, 1H) ppm. The partially truncated, compiled $^1$H NMR spectra of (±)-communesin F at variable temperature (25 ºC to 115 ºC) in
DMSO-d$_6$ were put on page 17 in supporting information II, which spectra indicated that the trans rotamer gradually changed to the cis rotamer with the temperature raised.

The assignments of the $^1$H NMR and $^{13}$C NMR spectra of cis rotamer, trans rotamer, and the trifluoroacetic acid salts of (±)-communesin F in CDCl$_3$ were summarized in tables I and II.

**Table I, $^1$H NMR data comparison of the synthetic (±)-communesin F with the natural communesin F**

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Table II. $^{13}$C NMR data comparison of the synthetic (±)-communesin F with the natural communesin F

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References:
2-(1H-4-bromoindol-3-yl)-2-oxoacetate
Irradiation δ 5.927 ppm

NOE δ 3.781 ppm
no NOE δ 4.810 ppm

irradiation δ 6.176

NOE δ 2.177 ppm
21 trans/cis=1.6:1