Supporting Information

An efficient one-pot decarboxylative aromatization of tetrahydro-β-carbolines by using N-chlorosuccinimide: Total synthesis of norharmane, harmane and eudistomins

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**Experimental Section**

**General information**

Unless otherwise stated, all the starting materials and other reagents of the best grade were commercially available and were used without further purification. TLC was performed on 0.25 mm silica gel 60-F254 plates. Spots were visualized by UV light. All the melting points were taken by Electrothermal apparatus and the values are uncorrected. $^1$H and $^{13}$C NMR spectra were recorded on 300 MHz, 400 MHz and 500 MHz NMR instruments using tetramethylsilane as the internal standard. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane. Spin multiplicities are described as s (singlet), bs (broad singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), or m (multiplet). Coupling constants are reported in hertz (Hz). HRMS analyses were acquired on single quadruple and carried out using the ESI techniques at 70 eV. Wherever required column chromatography was performed using silica gel of 60–120 mm with hexane, ethyl acetate and methanol as eluents.

**Pictet-Spengler reaction and decarboxylative aromatization of L-tryptophan.**

![Scheme S1: Synthesis of β-carboline (2a-t) using NCS.](image)

**General Procedure**

To a stirred solution of L-tryptophan (1, 1 mmol) in acetic acid was added aldehyde (1.1 mmol), stirred at 80 °C for 1 h and the acetic acid was removed under reduced pressure and dried well. This residue was taken in DMF, added TEA (3 mmol) and solution of NCS (2.1 mmol) in DMF. Then the reaction mixture was stirred for 30 min at room temperature. After completion of the reaction (monitored by TLC), the reaction mixture was quenched with water, extracted with ethyl acetate and washed with saturated Na$_2$CO$_3$ solution. The combined organic layers were washed with water, brine solution, dried over sodium sulfate, filtered and concentrated under reduced pressure. The residue obtained was purified by column chromatography by using ethyl acetate and hexane to afford the desired β-carboline (2a-t).

**9H-Pyrido[3,4-b]indole (norharmane, 2a).**

Yellow solid: 80% yield; mp: 195–198 °C (ref. 1: 195–197 °C); $^1$H NMR (300 MHz, CDCl$_3$) δ: 9.16 (bs, 1H), 8.94 (s, 1H), 8.47 (d, $J = 4.9$ Hz, 1H), 8.14 (d, $J = 7.9$ Hz, 1H), 7.98 (d, $J = 4.9$ Hz, 1H), 7.58–7.51 (m, 2H), 7.30 (t, $J = 7.7$ Hz, 1H); $^{13}$C NMR (125 MHz, DMSO–$d_6$) δ: 140.4, 137.9, 135.8, 133.9, 128.0, 127.3, 121.6, 120.5, 119.1, 114.5, 111.8; MS (ESI): m/z 169 [M + H]$^+$; HRMS (ESI): calcd for C$_{11}$H$_8$N$_2$: m/z 169.0760 [M + H]$^+$; found: 169.0757.

**1-Methyl-9H-pyrido[3,4-b]indole (harmane, 2b).**

Off white solid: 82% yield; mp: 230–233 °C (ref. 2: 235–236 °C); $^1$H NMR (300 MHz, CDCl$_3$ + DMSO–$d_6$) δ: 10.77 (bs, 1H), 8.30 (d, $J = 4.7$ Hz, 1H), 8.10 (d, $J = 7.5$ Hz, 1H), 7.81 (d, $J = 4.7$ Hz, 1H), 7.63–7.48 (m, 2H), 7.23 (t, $J = 6.9$ Hz, 1H), 2.86 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$ + DMSO–$d_6$) δ: 141.6, 140.2, 136.3, 134.3, 127.3, 126.9, 120.1, 118.8, 112.1, 111.5, 20.0; MS (ESI): m/z 183 [M + H]$^+$; HRMS (ESI): calcd for C$_{12}$H$_{10}$N$_2$: m/z 183.0916 [M + H]$^+$; found: 183.0916.

**1-Propyl-9H-pyrido[3,4-b]indole (2c).**

Brown colour solid: 78% yield; mp: 170–175 °C (ref. 3: 218–220 °C); $^1$H NMR (300 MHz, DMSO–$d_6$) δ: 11.05 (bs, 1H), 8.30 (d, $J = 5.3$ Hz, 1H), 8.09 (d, $J = 7.7$ Hz, 1H), 7.80 (d, $J = 5.3$ Hz, 1H), 7.58 (d, $J = 8.1$ Hz, 1H), 7.50 (t, $J = 7.5$ Hz, 1H), 7.22 (t, $J = 7.5$ Hz, 1H), 3.14 (t, $J = 7.5$ Hz, 2H), 1.92 (q, $J = 7.5$, 15.1 Hz, 2H), 1.05 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, DMSO–$d_6$) δ: 145.6, 140.2, 137.3, 134.0, 127.6, 126.9, 121.5, 120.9, 119.0, 112.4, 111.7, 35.3, 21.3, 13.8; MS (ESI): m/z 211 [M + H]$^+$; HRMS (ESI): calcd for C$_{13}$H$_{12}$N$_2$: m/z 211.1229 [M + H]$^+$; found: 211.1216.

**1-(4-Methoxybenzyl)-9H-pyrido[3,4-b]indole (2d)**
Yellow solid: 90% yield; mp: 142–144 °C; ¹H NMR (300 MHz, DMSO−d₆) δ: 11.67 (s, 1H), 8.26 (d, J = 5.3 Hz, 1H), 8.21 (d, J = 7.7 Hz, 1H), 7.96 (d, J = 5.1 Hz, 1H), 7.62 (d, J = 8.1 Hz, 1H), 7.54 (t, J = 7.2 Hz, 1H), 7.31 (d, J = 8.7 Hz, 2H), 7.23 (t, J = 7.7 Hz, 1H), 6.82 (d, J = 8.5 Hz, 2H), 4.38 (s, 2H), 3.67 (s, 3H); ¹³C NMR (100 MHz, DMSO−d₆) δ: 157.5, 144.7, 140.3, 137.6, 133.8, 131.1, 129.6, 127.9, 127.6, 121.6, 120.9, 119.2, 113.6, 112.8, 111.8, 54.8, 38.4; MS (ESI): m/z 289 [M + H]⁺; HRMS (ESI): calcd for C₁₉H₁₉ONO₂ m/z 289.1335 [M + H]⁺; found: 289.1328.

1-Phenyl-9H-pyrido[3,4-b]indole (2e).²

Yellow solid: 85% yield; mp: 241–244 °C (ref. 2: 241–242 °C); ¹H NMR (300 MHz, DMSO−d₆) δ: 11.52 (bs, 1H), 8.47 (d, J = 5.2 Hz, 1H), 8.26 (d, J = 7.7 Hz, 1H), 8.13 (d, J = 5.3 Hz, 1H), 8.03 (d, J = 7.0 Hz, 2H), 7.67−7.49 (m, 5H), 7.26 (t, J = 7.5 Hz, 1H); ¹³C NMR (75 MHz, DMSO−d₆) δ: 142.1, 141.0, 138.3, 138.3, 132.9, 129.0, 128.6, 128.4, 128.3, 128.0, 121.5, 120.7, 119.4, 113.8, 112.3; MS (ESI): m/z 245 [M + H]⁺; HRMS (ESI): calcd for C₁₉H₁₇ONO₂ m/z 245.1073 [M + H]⁺; found: 245.1074.

1-(p-Tolyl)-9H-pyrido[3,4-b]indole (2f).³

White solid: 88% yield; mp: 192–195 °C (ref. 4: 190.3–191.6 °C); ¹H NMR (300 MHz, CDCl₃ + DMSO−d₆) δ: 11.23 (bs, 1H), 8.38 (d, J = 5.1 Hz, 1H), 8.11 (d, J = 7.9 Hz, 2H), 7.89 (t, J = 5.4 Hz, 3H), 7.59 (d, J = 8.2 Hz, 1H), 7.45 (t, J = 7.3 Hz, 1H), 7.34 (d, J = 7.9 Hz, 2H), 7.19 (t, J = 7.3 Hz, 1H), 2.41 (s, 3H); ¹³C NMR (75 MHz, CDCl₃ + DMSO−d₆) δ: 142.2, 140.8, 137.8, 137.5, 135.4, 132.8, 128.8, 127.9, 127.5, 120.8, 120.6, 118.9, 112.9, 112.0, 20.6; MS (ESI): m/z 259 [M + H]⁺; HRMS (ESI): calcd for C₁₃H₁₃N₂O₂ m/z 259.1229 [M + H]⁺; found: 259.1219.

1-(2-Methoxyphenyl)-9H-pyrido[3,4-b]indole (2g).⁴

White solid: 93% yield; mp: 157–160 °C (ref. 5: 172–174 °C); ¹H NMR (500 MHz, CDCl₃) δ: 8.58 (bs, 1H), 8.55 (d, J = 5.2 Hz, 1H), 8.17 (d, J = 7.9 Hz, 1H), 7.93−7.90 (m, 3H), 7.55 (t, J = 7.1 Hz, 1H), 7.51 (t, J = 8.1 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.11 (d, J = 8.6 Hz, 2H), 3.90 (s, 3H); ¹³C NMR (75 MHz, CDCl₃ + DMSO−d₆) δ: 158.7, 141.5, 140.2, 137.2, 132.2, 130.1, 128.7, 128.2, 126.8, 120.1, 118.3, 113.0, 111.9, 111.3, 54.2; MS (ESI): m/z 275 [M + H]⁺; HRMS (ESI): calcd for C₁₃H₁₃ONO₂ m/z 275.1178 [M + H]⁺; found: 275.1166.

1-(3,4,5-Trimethoxyphenyl)-9H-pyrido[3,4-b]indole (2h).⁵

White solid: 92% yield; mp: 169−172 °C (ref. 6: 167−169 °C); ¹H NMR (500 MHz, CDCl₃) δ: 8.77 (bs, 1H), 8.55 (d, J = 5.1 Hz, 1H), 8.16 (d, J = 7.9 Hz, 1H), 7.94 (d, J = 5.1 Hz, 1H), 7.60−7.52 (m, 2H), 7.33 (t, J = 7.5 Hz, 1H), 7.13 (s, 1H), 3.92 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ: 153.5, 143.0, 140.5, 139.0, 138.2, 134.0, 133.4, 129.8, 128.4, 121.8, 121.7, 120.1, 113.7, 111.6, 105.2, 60.8, 56.1; MS (ESI): m/z 335 [M + H]⁺; HRMS (ESI): calcd for C₁₉H₁₅ONO₂ m/z 335.1390 [M + H]⁺; found: 335.1391.

2-Methoxy-4-(9H-pyrido[3,4-b]indol-1-yl)phenol (2i).⁶

White solid: 83% yield; mp: 262–264 °C (ref. 7: 260–262 °C); ¹H NMR (300 MHz, CDCl₃ + DMSO−d₆) δ: 11.17 (s, 0.8H), 8.98 (s, 0.8H), 8.35 (d, J = 5.1 Hz, 1H), 8.07 (d, J = 7.9 Hz, 2H), 7.87−7.83 (m, 1H), 7.58 (d, J = 8.1 Hz, 1H), 7.51 (d, J = 1.7 Hz, 0.8H), 7.46−7.40 (m, 2H), 7.17 (d, J = 7.7 Hz, 1H), 6.98 (d, J = 8.1 Hz, 1H), 3.92 (s, 2.5H), peaks at 11.29, 9.22, 7.54 and 3.96 are due to 20% minor rotamers; ¹³C NMR (75 MHz, CDCl₃ + DMSO−d₆) δ: 147.4, 146.9, 142.5, 140.8, 137.6, 132.6, 129.5, 128.6, 127.4, 120.9, 120.7, 118.9, 115.2, 112.5, 111.2, 111.8, 55.2; MS (ESI): m/z 291 [M + H]⁺; HRMS (ESI): calcd for C₁₉H₁₅O₂N₂ m/z 291.1128 [M + H]⁺; found: 291.1115.

3-(9H-Pyrido[3,4-b]indol-1-yl)phenol (2j).⁷
Cream colour solid: 78% yield; mp: 213–216 °C (ref. 5: 215–216 °C); 1H NMR (300 MHz, CDCl₃ + DMSO–d₆) δ: 10.79 (s, 1H), 9.14 (bs, 1H), 8.38 (d, J = 5.1 Hz, 1H), 7.85 (d, J = 7.7 Hz, 1H), 7.54 (d, J = 5.1 Hz, 1H), 7.61 (d, J = 3.0 Hz, 1H), 7.47–7.37 (m, 3H), 7.30 (t, J = 7.7 Hz, 1H), 7.17 (t, J = 7.4 Hz, 1H), 6.87 (d, J = 7.2 Hz, 1H); 13C NMR (75 MHz, CDCl₃ + DMSO–d₆) δ: 156.9, 142.1, 140.4, 139.0, 137.4, 132.6, 128.9, 128.6, 127.1, 120.4, 118.6, 115.0, 114.8, 112.6, 111.5; MS (ESI): m/z 261 [M + H]⁺; HRMS (ESI): calcd for C₁₇H₁₇ON₂ m/z 261.1022 [M + H]⁺; found: 261.1019.

1-(4-Chlorophenyl)-9H-pyrido[3,4-b]indole (2k).

Light yellow solid: 80% yield; mp: 200–265 °C (ref. 4: 203–205 °C); 1H NMR (300 MHz, CDCl₃ + DMSO–d₆) δ: 11.42 (s, 1H), 8.39 (d, J = 5.3 Hz, 1H), 8.13 (d, J = 7.7 Hz, 1H), 8.00 (s, 1H), 7.99 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 8.3 Hz, 1H), 7.55 (d, J = 8.5 Hz, 2H), 7.48 (t, J = 7.2 Hz, 1H), 7.21 (t, J = 7.7 Hz, 1H); 13C NMR (125 MHz, CDCl₃ + DMSO–d₆) δ: 141.1, 140.7, 137.8, 136.7, 133.4, 132.9, 129.8, 129.4, 128.4, 127.9, 121.1, 120.6, 119.3, 113.7, 112.1; MS (ESI): m/z 279 [M + H]⁺; HRMS (ESI): calcd for C₁₇H₁₆ClN₂ m/z 279.0689 [M + H]⁺; found: 279.0942.

4-(9H-Pyrido)[3,4-b]indol-1-yl)benzonitrile (2m).

Yellow solid: 79% yield; mp: 243–246 °C (ref. 5: 244–246 °C); 1H NMR (300 MHz, CDCl₃ + DMSO–d₆) δ: 10.82 (bs, 1H), 8.31 (d, J = 5.3 Hz, 1H), 8.17 (d, J = 8.9 Hz, 2H), 8.06 (d, J = 8.9 Hz, 2H), 7.92 (d, J = 7.9 Hz, 1H), 7.79 (d, J = 5.1 Hz, 1H), 7.40 (d, J = 8.1 Hz, 1H), 7.32 (t, J = 7.7 Hz, 1H), 7.06 (t, J = 7.0 Hz, 1H); 13C NMR (75 MHz, CDCl₃ + DMSO–d₆) δ: 146.8, 144.5, 141.0, 139.2, 138.2, 133.3, 129.9, 129.0, 128.0, 123.2, 120.9, 120.5, 119.4, 114.4, 111.9; MS (ESI): m/z 290 [M + H]⁺; HRMS (ESI): calcd for C₁₈H₁₇N₂O₂ m/z 290.0924 [M + H]⁺; found: 290.0927.

1-(Naphthalen-1-yl)-9H-pyrido[3,4-b]indole (2p).

Off white solid: 94% yield; mp: 177–180 °C (ref. 5: 178–180 °C); 1H NMR (300 MHz, CDCl₃ + DMSO–d₆) δ: 10.80 (bs, 1H), 8.46 (d, J = 5.3 Hz, 1H), 8.12 (d, J = 7.9 Hz, 1H), 8.00 (d, J = 5.5 Hz, 1H), 7.95 (d, J = 5.5 Hz, 1H), 7.84–7.79 (m, 3H), 7.54 (d, J = 7.9 Hz, 1H), 7.47–7.42 (m, 3H), 7.30 (t, J = 7.7 Hz, 1H), 7.17 (t, J = 7.4 Hz, 1H), 6.87 (d, J = 7.2 Hz, 1H); 13C NMR (75 MHz, CDCl₃ + DMSO–d₆) δ: 156.9, 142.1, 140.4, 139.0, 137.4, 132.6, 128.9, 128.6, 127.1, 120.4, 118.6, 115.0, 114.8, 112.6, 111.5; MS (ESI): m/z 261 [M + H]⁺; HRMS (ESI): calcd for C₁₈H₁₇O₂N₂ m/z 289.0971 [M + H]⁺; found: 289.0973.
1H), 7.72–7.67 (m, 2H), 7.62 (d, J = 7.5 Hz, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.45–7.40 (m, 2H), 7.34 (t, J = 8.1 Hz, 1H), 7.21–7.15 (m, 1H); 13C NMR (75 MHz, CDCl3 + DMSO-d6) δ: 141.3, 139.7, 136.4, 134.3, 133.4, 132.3, 130.0, 127.4, 127.2, 126.7, 126.6, 126.0, 124.8, 124.5, 124.3, 124.0, 119.9, 119.5, 117.9, 112.3, 110.8; MS (ESI): m/z 295 [M + H]+; HRMS (ESI): calcld for C18H12N2O m/z 295.1229 [M+H]+; found: 295.1232.

1-(Phenanthren-9-yl)-9H-pyrido[3,4-b]indole (2q).

White solid: 95% yield; mp: 230–235 °C; 1H NMR (300 MHz, CDCl3 + DMSO-d6) δ: 11.51 (bs, 1H), 8.88 (t, J = 8.6 Hz, 2H), 8.52 (d, J = 5.3 Hz, 1H), 8.22 (d, J = 7.9 Hz, 1H), 7.95 (d, J = 5.5 Hz, 1H), 8.13 (d, J = 5.3 Hz, 1H), 8.04 (s, 1H), 8.03 (d, J = 5.5 Hz, 1H), 7.78–7.64 (m, 4H), 7.53–7.42 (m, 3H), 7.26–7.19 (m, 1H); 13C NMR (125 MHz, CDCl3 + DMSO-d6) δ: 142.4, 140.9, 137.6, 137.5, 134.8, 133.8, 130.9, 130.3, 128.9, 128.7, 128.2, 127.9, 127.2, 126.8, 126.6, 126.6, 126.3, 122.8, 122.4, 121.3, 120.7, 119.2, 113.8, 112.0; MS (ESI): m/z 345 [M + H]+; HRMS (ESI): calcld for C23H17N2O m/z 345.1386 [M + H]+; found: 345.1369.

1-(Pyridin-3-yl)-9H-pyrido[3,4-b]indole (2r).

Creamish solid: 88% yield; mp: 130–135 °C; 1H NMR (300 MHz, CDCl3 + DMSO-d6) δ: 11.45 (bs, 1H), 8.41 (d, J = 5.1 Hz, 1H), 8.17 (d, J = 6.7 Hz, 1H), 8.01 (d, J = 5.1 Hz, 1H), 7.71 (dd, J = 1.7, 8.5 Hz, 1H), 7.62 (d, J = 8.3 Hz, 1H), 7.59–7.53 (m, 1H), 7.50 (t, J = 7.9 Hz, 1H), 7.33 (dd, J = 8.3, 11.1 Hz, 1H), 7.22 (t, J = 7.2 Hz, 1H), 3.98 (s, 3H); 13C NMR (125 MHz, CDCl3 + DMSO-d6) δ: 152.7 and 150.7 (d, J = 8.3, 11.1 Hz, 1H), 147.1 (d, J = 10.9 Hz), 141.2, 141.0, 137.7 (d, J = 17.2 Hz), 134.8 (d, J = 2.7 Hz), 132.8, 129.1, 127.9, 127.8, 121.1, 120.6, 119.2, 115.6 (dd, J = 3.6, 17.2 Hz), 113.6, 113.5, 112.2, 55.7; MS (ESI): m/z 293 [M + H]+; HRMS (ESI): calcld for C18H12NO2F m/z 293.1084 [M + H]+; found: 293.1066.

1-(4-Fluoro-3-methoxyphenyl)-9H-pyrido[3,4-b]indole (2s).

Light yellow solid: 85% yield; mp: 150–153 °C; 1H NMR (400 MHz, DMSO-d6) δ: 8.51 (d, J = 5.1 Hz, 1H), 8.30 (d, J = 7.9 Hz, 1H), 8.25 (d, J = 8.1 Hz, 2H), 8.20 (d, J = 5.2 Hz, 1H), 7.97 (d, J = 8.2 Hz, 2H), 7.65 (d, J = 1H), 7.58 (t, J = 5.8 Hz, 1H), 7.29 (t, J = 6.7 Hz, 1H); 13C NMR (125 MHz, DMSO-d6) δ: 142.2, 141.1, 140.3, 138.4, 133.1, 129.5, 129.1, 128.7, 128.4, 128.3, 125.4, 121.6, 120.6, 119.6, 114.6, 112.3; MS (ESI): m/z 313 [M + H]+.

Synthesis of Eudistomin I (6)

1-(Pyrrolidin-2-yl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole-3-carboxylic acid dihydrochloride (5)

A stirred solution of L-tryptophan (1.0 g, 4.90 mmol) and N-boc-L-prolinal (0.975 g, 4.90 mmol) in glacial acetic acid was heated at 80 °C for 2 h. After cooling to rt, the acetic acid was removed, the residue was taken in 1,4-dioxane (10 mL) and was added 2N HCl in 1,4-dioxane (5 mL) at 0 °C. The resulting reaction mixture was stirred at room temperature for 4 h. After total consumption of the starting material (monitored by TLC), the reaction mixture was concentrated under reduced pressure and dried well. The crude product was triturated in acetone, the resulted solid filtered and dried to afford the dihydrochloride salt 5 as white solid (1.57 g, 90% yield). mp: 238–240 °C; 1H NMR (300 MHz, DMSO-d6) δ: 11.61 (s, 0.2H), 11.47 (s, 0.8H), 10.36 (bs, 0.3H), 9.98 (bs, 0.8H), 9.61 (bs, 1H), 7.53 (d, J = 7.9 Hz, 1H), 7.39 (d, J = 8.1 Hz, 1H), 7.16 (t, J = 7.3 Hz, 1H), 7.04 (t, J = 7.1 Hz, 1H), 5.44–5.24 (m, 1H), 4.74–4.63 (m, 1H), 4.61–4.51 (m, 1H), 4.30–4.15 (m, 1H), 3.46–3.27 (m, 3H), 3.09–2.97 (m, 2H), 2.55–2.44 (m, 1H), 2.09–1.98 (m, 1H), 1.85–1.64 (m, 1H), 1.57–1.47 (m, 1H), 1.30–1.10 (m, 1H). MS (ESI): m/z 346 [M+H]+; HRMS (ESI): calcld for C23H26N2O5HCl m/z 363.1724 [M + H]+; found: 363.1726.
1-(3,4-Dihydro-2H-pyrrol-5-yl)-9H-pyrido[3,4-b]indol-1-yl)ethanone (or) Eudistomin T (9)

To a stirred solution of dihydrochloride salt 5 (500 mg, 1.39 mmol) in DMF (4 mL) was added TEA (0.97 mL, 6.98 mmol), cooled to 0 °C and added a solution of NCS (0.575 mg, 4.32 mmol) in DMF (5 mL) and the reaction mixture was allowed to stir at room temperature 30 min. After the completion of starting material (monitored by TLC) reaction mixture was diluted with water and extracted with ethyl acetate (2x50 mL), washed with water (50 mL), brine (50 mL), dried over sodium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography using 20% ethyl acetate in 'n-hexane to afford the eudistomin T (6, 288 mg, 70% yield) as a light yellow solid, mp: 151–154 °C (ref. 8: 153–155 °C); 1H NMR (500 MHz, CDCl₃) δ: 10.85 (s, 1H), 8.50 (d, J = 5.1 Hz, 1H), 7.61–7.53 (m, 2H), 7.32–7.28 (m, 1H), 4.30–4.26 (m, 2H), 3.37–3.31 (m, 2H), 2.14–2.05 (m, 2H); 13C NMR (125 MHz, CDCl₃) δ: 176.8, 140.8, 138.2, 135.8, 135.4, 129.5, 128.5, 121.8, 121.2, 120.1, 116.1, 111.9, 62.2, 34.9, 21.9; MS (ESI): m/z 286 [M + H]+; HRMS (ESI): calcd for C₂₅H₂₄N₂O₂S; found: 286.1545.

6-Bromo-9H-pyrido[3,4-b]indole (or) Eudistomin N (7)

To a mixture of 0.1 N H₂SO₄ (1.5 mL) and 37% formaldehyde (0.8 mL) was added L-tryptophan (0.5 g, 2.4 mmol) with stirring. After being stirred for 4 h at room temperature, the resulted white solid was collected by filtration and dried well.

The solid material was taken in DMF (7 mL), added TEA (0.61 mL, 7.34 mmol), cooled to 0 °C and added solution of NCS (0.69 g, 5.14 mmol) in DMF. The reaction mixture was stirred for 30 min at room temperature, diluted with water (50 mL), extracted with ethyl acetate (2x50 mL) and washed with water (50 mL). The combined extracts were dried over sodium sulfate, filtered, concentrated in vacuo and the crude product was purified by silica gel column chromatography using ethyl acetate:n-hexane (1:1) to afford norharmarine (2a, 0.33 g, 80% yield). To the stirred solution of 2a in acetic acid (10 mL) was added NBS (0.38 g, 2.16 mmol) and stirred for 5 h at room temperature. The solvent most removed in vacuo and neutralized with saturated Na₂HCO₃ solution and extracted with ethyl acetate (2x30 mL) and washed with water (30 mL). The combined extracts were dried over sodium sulfate, filtered, concentrated in vacuo and the crude product was purified by silica gel column chromatography using ethyl acetate:n-hexane (1:1) to afford eudistomin N (7, 0.43 g, 89% yield) as creamish solid, mp: 265–270 °C (ref. 8: 265–268 °C); 1H NMR (300 MHz, CDCl₃) δ: 11.09 (bs, 1H), 8.84 (s, 1H), 8.31 (d, J = 5.3 Hz, 1H), 8.16 (S, 1H), 7.83 (d, J = 5.1 Hz, 1H), 7.51 (dd, J = 1.7, 8.6 Hz, 1H), 7.38 (d, J = 8.7 Hz, 1H); 13C NMR (125 MHz, CDCl₃) δ: 139.1, 137.6, 136.0, 133.7, 130.2, 126.8, 123.6, 122.2, 114.0, 113.1, 111.3; MS (ESI): m/z 247 [M]+ and 249 [M + 2H]+; HRMS (ESI): calcd for C₁₅H₁₄NO₂Br m/z 246.9865 [M + H]+; found: 246.9855.

**Synthesis of eudistomin T (9)**

tert-Butyl 2-phenyl-1-(9H-pyrido[3,4-b]indol-1-yl)ethylcarbamate (8)

A stirred solution of L-tryptophan (1.0 g, 4.90 mmol) and N-boc-L-alaninal (1.22 g, 4.90 mmol) in glacial acetic acid was heated at 80 °C for 2 h. After cooling to rt, the acetic acid was removed, the residue was taken DMF (7 mL), added TEA (2.0 mL, 14.70 mmol), cooled to 0 °C and added solution of NCS (1.37 g, 10.29 mmol) in DMF. The reaction mixture was stirred for 30 min at room temperature, diluted with water (70 mL), extracted with ethyl acetate (2x70 mL) and washed with water (100 mL). The combined extracts were dried over sodium sulfate, filtered, concentrated in vacuo and the crude product was purified by silica gel column chromatography using ethyl acetate:n-hexane (1:1) to afford compound 8 (1.51 g, 80% yield) as white solid, Mp: 236–240 °C (ref. 9: 230–232 °C); 1H NMR (400 MHz, DMSO-d₆) δ: 8.29 (d, J = 5.1 Hz, 1H), 8.21 (d, J = 7.8 Hz, 1H), 8.01 (d, J = 5.1 Hz, 1H), 7.62 (d, J = 8.1 Hz, 1H), 7.55 (t, J = 7.4 Hz, 1H), 7.32–7.1 (m, 7H), 5.50 (q, J = 6.9, 13.8 Hz, 0.8H), 3.21–3.09 (m, 2H), 1.28 (s, 8H), peaks at 5.32 and 0.99 are due to the 20% minor rotamer; 13C NMR (100 MHz, DMSO-d₆) δ: 155.1, 145.1, 140.3, 138.1, 137.1, 137.0, 132.6, 129.3, 127.9, 127.8, 125.9, 121.6, 121.5, 120.7, 119.2, 113.5, 111.8, 77.8, 53.1, 28.0; MS (ESI): m/z 388 [M + H]+; HRMS (ESI): calcd for C₂₅H₂₄O₂N₃ m/z 388.2019 [M + H]+; found: 388.2020.

2-Phenyl-1-(9H-pyrido[3,4-b]indol-1-yl)ethanone (or) Eudistomin T (9)

A stirred solution of 1-(3,4-Dihydro-2H-pyrrol-5-yl)-9H-pyrido[3,4-b]indol-1-yl)ethanone (or) Eudistomin T (9)
To a stirred solution of boc product 8 (0.3 g, 1.04 mmol) in 1,4-dioxiane (20 mL) was added 2 N HCl in 1,4-dioxane solution (1 mL) at 0°C and stirred for 3 h. After consumption of the starting material (monitored by TLC), the solvent was removed in vacuo and dried. The crude product was dissolved in methanol (10 mL) and added sodium carbonate (4 g), followed by aq. NaCl (1 mL, 5.9 % w/w) over a period of 15 mins. After being stirred for 1 h at room temperature, reaction mixture was diluted with 1 N HCl solution (30 mL), extracted with DCM (2x30 mL), washed with saturated sodium bicarbonate solution (30 mL) and water (50 mL). The combined organic phases were dried over sodium sulfate, filtered and evaporated in vacuo. The crude product was purified by column chromatography using ethyl acetate and n-hexane (3:7) to afford eudistomin T (9) as yellow solid (0.19 g, 88% yield). Mp: 163–165°C (ref. 9: 155–157°C); 1H NMR (400 MHz, CDCl3) δ: 10.26 (bs, 1H), 8.59 (d, J = 4.9 Hz, 1H), 8.15 (d, J = 5.5 Hz, 1H), 8.14 (d, J = 8.9 Hz, 1H), 7.61–7.56 (m, 1H), 7.51 (d, J = 8.2 Hz, 1H), 7.43–7.40 (m, 2H), 7.37–7.30 (m, 3H), 7.29–7.24 (m, 1H), 4.74 (s, 2H); 13C NMR (100 MHz, CDCl3) δ: 202.3, 141.0, 138.2, 135.9, 134.9, 131.6, 130.0, 129.2, 128.4, 126.7, 121.8, 120.7, 120.5, 119.2, 111.9, 43.9; MS (ESI): m/z 287 [M + H]+; HRMS (ESI): calcld for C15H12ON2 m/z 287.1178 [M + H]+; found: 287.1175.

Synthesis of 1-(1H-indol-3-yl)-9H-pyrido[3,4-b]indole (or) Eudistomin U (10)

A stirred solution of L-tryptophan methyl ester hydrochloride (0.50 g, 2.45 mmol) and indole-3-carbaldehyde (0.35 g, 2.45 mmol) in glacial acetic acid (5 mL) was heated at 80 °C for 2 h. After cooling to rt, the solvent most was removed in vacuo, the residue was taken in DMF (5 mL), added TEA (1.02 mL, 7.35 mmol), cooled to 0 °C and added solution of NCS (0.69 g, 5.14 mmol) in DMF (5 mL). The reaction mixture was stirred for 30 min at room temperature, diluted with water (30 mL), extracted with ethyl acetate (2x50 mL) and washed with water (50 mL). The combined extracts were dried over sodium sulfate, filtered, evaporated in vacuo and the crude product was purified by silica gel column chromatography using ethyl acetate/methanol (9:1) to afford eudistomin U (10, 0.59 g, 85% yield) as light yellow solid. Mp: 230–235 °C (ref. 10: 235–236 °C); 1H NMR (500 MHz, DMSO−d6) δ: 11.72 (s, 1H), 11.31 (s, 1H), 8.55 (d, J = 7.9 Hz, 1H), 8.4 (d, J = 5.1 Hz, 1H), 8.30 (d, J = 2.7 Hz, 1H), 8.23 (d, J = 7.9 Hz, 1H), 7.95 (d, J = 5.1 Hz, 1H), 7.69 (d, J = 8.1 Hz, 1H), 7.56–7.50 (m, 2H), 7.25 (t, J = 7.3 Hz, 1H), 7.21 (t, J = 7.0 Hz, 1H), 7.14 (t, J = 7.9 Hz, 1H); 13C NMR (100 MHz, DMSO−d6) δ: 140.6, 140.3, 137.8, 136.4, 131.9, 128.0, 127.6, 126.1, 125.9, 122.2, 121.9, 121.3, 121.1, 119.7, 119.3, 113.1, 112.3, 111.5, 111.4; MS (ESI): m/z 284 [M + H]+; HRMS (ESI): calcld for C15H15N2O m/z 284.1182 [M + H]+; found: 284.1185.

Pictet-Spengler reaction and aromatization of tetrahydro-β-carboline esters.

![Scheme S2: Synthesis of methyl-β-carbolinecarboxylates (4a-h)](image)

General Procedure

To a stirred solution of L-tryptophan methyl ester hydrochloride (3, 1 mmol) in ethanol was added aldehyde (1 mmol), stirred at 80 °C for 4 h and the ethanol was evaporated in vacuo and dried well. This residue was directly taken in DMF, added TEA (2.5 mmol) and NCS (2.1 mmol) in DMF (5 mL). After consumption of the starting material (monitored by TLC), the solvent was removed in vacuo and the residue was taken in DMF, added solution of NCS (0.69 g, 5.14 mmol) in DMF (5 mL). The reaction mixture was stirred for 30 min at room temperature, diluted with water (30 mL), extracted with ethyl acetate (2x50 mL) and washed with water (50 mL). The combined extracts were dried over sodium sulfate, filtered, evaporated in vacuo and the crude product was purified by silica gel column chromatography using ethyl acetate/methanol (9:1) to afford eudistomin U (10, 0.59 g, 85% yield) as light yellow solid. Mp: 230–235 °C (ref. 10: 235–236 °C); 1H NMR (500 MHz, DMSO−d6) δ: 11.72 (s, 1H), 11.31 (s, 1H), 8.55 (d, J = 7.9 Hz, 1H), 8.4 (d, J = 5.1 Hz, 1H), 8.30 (d, J = 2.7 Hz, 1H), 8.23 (d, J = 7.9 Hz, 1H), 7.95 (d, J = 5.1 Hz, 1H), 7.69 (d, J = 8.1 Hz, 1H), 7.56–7.50 (m, 2H), 7.25 (t, J = 7.3 Hz, 1H), 7.21 (t, J = 7.0 Hz, 1H), 7.14 (t, J = 7.9 Hz, 1H); 13C NMR (100 MHz, DMSO−d6) δ: 140.6, 140.3, 137.8, 136.4, 131.9, 128.0, 127.6, 126.1, 125.9, 122.2, 121.9, 121.3, 121.1, 119.7, 119.3, 113.1, 112.3, 111.5, 111.4; MS (ESI): m/z 284 [M + H]+; HRMS (ESI): calcld for C15H15N2O m/z 284.1182 [M + H]+; found: 284.1185.

**Methyl 1-phenethyl-9H-pyrido[3,4-b]indole-3-carboxylate (4a).**

Brown solid: 81% yield; mp: 165–170 °C; 1H NMR (300 MHz, CDCl3) δ: 8.77 (s, 1H), 8.30 (bs, 1H), 8.13 (d, J = 7.9 Hz, 1H), 7.52 (t, J = 8.2 Hz, 1H), 7.37 (d, J = 8.2 Hz, 1H), 7.30 (t, J = 7.1 Hz, 1H), 7.21–7.15 (m, 3H), 7.12 (d, J = 7.9 Hz, 2H), 4.05 (s, 3H), 3.47 (t, J = 7.3 Hz, 2H), 3.18 (t, J = 7.7 Hz, 2H); 13C NMR (100 MHz, DMSO−d6) δ: 166.1, 144.8, 141.5, 140.6, 135.9, 135.6, 128.4, 128.3, 128.1, 127.1, 125.8, 121.9, 121.2, 120.6, 116.0, 112.2, 51.8, 35.1, 33.5; MS (ESI): m/z 331 [M + H]+; HRMS (ESI): calcld for C21H19O2N2 m/z 331.1441 [M + H]+; found: 331.1428.

**Methyl 1-(3,4,5-trimethoxyphenyl)-9H-pyrido[3,4-b]indole-3-carboxylate (4b).**

![image](image)
Methyl 1-(naphthalen-1-yl)-9H-pyrido[3,4-b]indole-3-carboxylate (4c).

**Off white solid: 94% yield; mp: 226–229 °C (ref. 11: 229–230 °C); **^1^H NMR (300 MHz, CDCl\(_3\) + DMSO\(-d_6\)) δ: 8.79 (s, 1H), 8.22 (d, J = 7.9 Hz, 1H), 7.64 (d, J = 8.3 Hz, 1H), 7.51 (t, J = 7.2 Hz, 1H), 7.26 (t, J = 7.2 Hz, 1H), 7.17 (s, 2H), 3.93 (s, 3H), 3.92 (s, 6H), 3.79 (s, 3H); ^1^C NMR (CDCl\(_3\), 75 MHz) δ: 165.8, 152.7, 142.2, 141.2, 137.8, 136.2, 134.5, 132.9, 128.7, 128.0, 121.1, 120.9, 119.9, 116.1, 112.4, 105.5, 59.9, 55.5, 51.6; MS (ESI): m/z 393 [M + H]^+; HRMS (ESI): calcd for C\(_{23}\)H\(_{20}\)O\(_2\)N\(_2\) m/z 393.1445 [M + H]^+; found: 393.1432.

Methyl 1-(4-chlorophenyl)-9H-pyrido[3,4-b]indole-3-carboxylate (4d).¹²

**Yellow solid: 92% yield; mp: 268–272 °C (ref. 12: 270 °C); **^1^H NMR (300 MHz, CDCl\(_3\) + DMSO\(-d_6\)) δ (ppm): 8.81 (s, 1H), 8.23 (d, J = 7.7 Hz, 1H), 8.01 (d, J = 8.3 Hz, 1H), 7.64 (d, J = 8.3 Hz, 1H), 7.59–7.51 (m, 3H), 7.27 (t, J = 7.2 Hz, 1H), 6.92 (d, J = 7.4 Hz, 1H), 3.93 (s, 3H); ^1^C NMR (100 MHz, DMSO\(-d_6\)) δ (ppm): 165.8, 141.4, 140.6, 136.5, 136.2, 134.4, 133.6, 130.3, 129.3, 128.7, 125.4, 121.9, 120.4, 116.8, 112.6, 51.9; MS (ESI): m/z 337 [M + H]^+; HRMS (ESI): calcd for C\(_{19}\)H\(_{13}\)ClO\(_2\)N\(_2\) m/z 337.0738 [M + H]^+; found: 337.0729.

Methyl 1-(phenanthren-9-yl)-9H-pyrido[3,4-b]indole-3-carboxylate (4e).⁹

**White solid: 96% yield; mp: 290–295 °C; **^1^H NMR (300 MHz, CDCl\(_3\) + DMSO\(-d_6\)) δ (ppm): 11.56 (s, 1H), 8.98 (s, 1H), 8.89 (t, J = 8.7 Hz, 2H), 8.34 (d, J = 7.9 Hz, 1H), 8.03 (d, J = 6.6 Hz, 2H), 7.80–7.60 (m, 4H), 7.52–7.45 (m, 3H), 7.29 (t, J = 7.9 Hz, 1H), 3.92 (s, 3H); ^1^C NMR (152 MHz, DMSO\(-d_6\) + CDCl\(_3\)) δ: 165.9, 142.3, 141.2, 136.4, 136.2, 133.2, 130.8, 130.2, 130.1, 130.0, 128.9, 128.4, 128.3, 127.2, 126.7, 126.6, 126.1, 122.8, 122.5, 121.5, 121.0, 120.0, 116.8, 112.3, 51.8; MS (ESI): m/z 403 [M + H]^+; HRMS (ESI): calcd for C\(_{22}\)H\(_{15}\)O\(_2\)N\(_2\) m/z 403.1441 [M + H]^+; found: 403.1427.

Methyl 1-(4-fluoro-3-methoxyphenyl)-9H-pyrido[3,4-b]indole-3-carboxylate (4f).

**Off white solid: 94% yield; mp: 215–220 °C; **^1^H NMR (300 MHz, DMSO\(-d_6\)) δ: 8.94 (s, 1H), 8.44 (d, J = 7.9 Hz, 1H), 7.73–7.66 (m, 2H), 7.61 (t, J = 7.2 Hz, 1H), 7.55–7.43 (m, 2H), 7.34 (t, J = 7.4 Hz, 1H), 3.99 (s, 3H), 3.93 (s, 3H); ^1^C NMR (75 MHz, DMSO\(-d_6\)) δ: 165.8, 152.8 and 150.9 (d, J = 246.1 Hz), 147.1 (d, J = 10.9 Hz), 141.3 (d, J = 3.6 Hz), 136.4, 134.5, 134.2 (d, J = 3.6 Hz), 129.0, 128.6, 121.9, 121.1 (d, J = 7.2 Hz), 121.0, 120.3, 116.7, 116.1, 116.0, 114.0 (1.8 Hz), 112.6, 55.9, 51.9; MS (ESI): m/z 351 [M + H]^+; HRMS (ESI): calcd for C\(_{20}\)H\(_{16}\)O\(_2\)N\(_2\) F m/z 351.1139 [M + H]^+; found: 351.1128.

Methyl 1-(4-(trifluoromethyl)phenyl)-9H-pyrido[3,4-b]indole-3-carboxylate (4g).⁵

**White solid: 91% yield; mp: 303–306°C (ref. 5: 306–310 °C); **^1^H NMR (300 MHz, DMSO\(-d_6\)) δ: 8.80 (s, 1H), 8.13 (t, J = 7.4 Hz, 3H), 7.75 (d, J = 8.3 Hz, 2H), 7.60 (d, J = 8.1 Hz, 1H), 7.50 (t, J = 7.7 Hz, 1H), 7.26 (t, J = 7.5 Hz, 1H), 3.95 (s, 3H); ^1^C NMR (75 MHz, DMSO\(-d_6\)) δ: 165.4, 141.4, 141.2, 140.2, 136.6, 134.6, 129.4, 129.3, 129.2, 129.2, 128.5, 125.3 (q, J = 3.8, 7.7 Hz), 121.7, 120.9, 120.3, 116.9, 112.5, 51.8; MS (ESI): m/z 371 [M + H]^+; HRMS (ESI): calcd for C\(_{20}\)H\(_{14}\)F\(_3\)N\(_2\)F\(_2\) m/z 371.1001 [M + H]^+; found: 371.0993.

Methyl 1-(1-((cet)-butoxycarbonyl)amino)-2-phenylethyl)-9H-pyrido[3,4-b]indole-3-carboxylate (4b)
White solid: 88% yield; mp: 147–150 °C; $^1$H NMR (400 MHz, DMSO–d$_6$) δ: 12.01 (bs, 1H), 8.85 (s, 1H), 8.38 (d, $J$ = 7.8 Hz, 1H), 7.69 (d, $J$ = 8.2 Hz, 1H), 7.62 (t, $J$ = 7.2 Hz, 1H), 7.37–7.26 (m, 4H), 7.22 (t, $J$ = 7.2 Hz, 2H), 7.14 (d, $J$ = 7.2 Hz, 1H), 5.52 (q, $J$ = 7.2, 14.7 Hz, 1H), 3.94 (s, 3H), 3.22 (d, $J$ = 7.1 Hz, 2H), 1.30 and 0.96 (s, 8H and s, 1H); $^{13}$C NMR (100 MHz, DMSO–d$_6$) δ: 165.8, 155.1, 145.2, 140.7, 137.9, 135.7, 134.5, 129.4, 128.5, 127.9, 127.7, 126.0, 121.9, 120.9, 120.2, 116.7, 112.2, 78.0, 53.6, 51.9, 40.0, 28.0; MS (ESI): m/z 446 [M + H]$^+$; HRMS (ESI): calcd for C$_{26}$H$_{28}$O$_4$N$_3$ m/z 446.2074 [M + H]$^+$; found: 446.2063.

1-(4-Methoxyphenyl)-4,9-dihydro-3$^H$-pyrido[3,4-b]indole (14).

Creamish solid: 85% yield; mp: 185–188 °C (ref. 13: 196−197 °C); $^1$H NMR (300 MHz, DMSO–d$_6$) δ: 7.78 (d, $J$ = 7.6 Hz, 1H), 7.46–7.39 (m, 1H), 7.34–7.28 (m, 2H), 6.76 (d, $J$ = 8.8 Hz, 2H), 6.29 (d, $J$ = 8.8 Hz, 2H), 4.67–4.55 (m, 1H), 4.51–4.39 (m, 1H), 3.52 (s, 3H), 2.94 (m, 1H), 2.31–2.21 (m, 1H); $^{13}$C NMR (75 MHz, DMSO–d$_6$) δ: 174.1, 167.5, 160.1, 153.5, 143.8, 128.6, 128.5, 127.7, 125.3, 122.6, 121.9, 113.1, 72.5, 59.8, 54.6, 36.9; MS (ESI): m/z 277 [M + H]$^+$.

1-(4-Nitrophenyl)-4,9-dihydro-3$^H$-pyrido[3,4-b]indole (15)

Yellow solid: 82% yield; mp: 218–220 °C (ref. 14: 220−222 °C); $^1$H NMR (300 MHz, DMSO–d$_6$ + CDCl$_3$) δ: 11.04 (s, 1H), 8.30 (d, $J$ = 8.7 Hz, 2H), 7.99 (d, $J$ = 8.7 Hz, 2H), 7.55 (d, $J$ = 7.9 Hz, 1H), 7.38 (d, $J$ = 8.1 Hz, 1H), 7.17 (t, $J$ = 7.5 Hz, 1H), 7.04 (t, $J$ = 7.5 Hz, 1H), 3.96 (t, $J$ = 7.9 Hz, 2H), 2.89 (t, $J$ = 8.3 Hz, 2H); $^{13}$C NMR (75 MHz, DMSO–d$_6$ + CDCl$_3$) δ: 155.8, 146.4, 141.6, 135.5, 127.6, 125.3, 123.0, 122.3, 121.6, 118.0, 117.8, 115.3, 110.9, 47.1, 17.3; MS (ESI): m/z 292 [M + H]$^+$.

References
9H-Pyrido[3,4-b]indole (norharmane, 2a)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, DMSO–d$_6$)
1-Methyl-9H-pyrido[3,4-b]indole (harmane, 2b)

$^1$H NMR (300 MHz, CDCl$_3$ + DMSO–d$_6$)

$^{13}$C NMR (75 MHz, CDCl$_3$ + DMSO–d$_6$)
1-Propyl-9H-pyrido[3,4-b]indole (2c)

$^1$H NMR (300 MHz, DMSO–$d_6$)

$^{13}$C NMR (100 MHz, DMSO–$d_6$)
1-(4-Methoxybenzyl)-9H-pyrido[3,4-b]indole (2d)

$^1$H NMR (300 MHz, DMSO-$d_6$)

$^{13}$C NMR (100 MHz, DMSO-$d_6$)
1-Phenyl-9H-pyrido[3,4-b]indole (2e)

$^1$H NMR (300 MHz, DMSO-$d_6$)

$^{13}$C NMR (75 MHz, DMSO-$d_6$)
1-(p-Tolyl)-9H-pyrido[3,4-b]indole (2f)

$^1$H NMR (300 MHz, CDCl$_3$ + DMSO-d$_6$)

$^{13}$C NMR (75 MHz, CDCl$_3$ + DMSO-d$_6$)
1-(2-Methoxyphenyl)-9H-pyrido[3,4-b]indole (2g)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$ + DMSO–d$_6$)
1-(3,4,5-Trimethoxyphenyl)-9H-pyrido[3,4-b]indole (2h)

$^1$H NMR (500 MHz, CDCl$_3$)

13C NMR (CDCl$_3$, 75 MHz)
2-Methoxy-4-(9H-pyrido[3,4-b]indol-1-yl)phenol (2i)

$^1$H NMR (300 MHz, CDCl$_3$ + DMSO-$d_6$)

$^{13}$C NMR (75 MHz, CDCl$_3$ + DMSO-$d_6$)
3-(9H-Pyrido[3,4-b]indol-1-yl)phenol (2j)

NMR (300 MHz, CDCl$_3$ + DMSO-$d_6$)

$^{13}$C NMR (75 MHz, CDCl$_3$ + DMSO-$d_6$)
1-(4-Chlorophenyl)-9H-pyrido[3,4-b]indole (2k)

$^1$H NMR (300 MHz, CDCl$_3$ + DMSO-$d_6$)

$^{13}$C NMR (125 MHz, CDCl$_3$ + DMSO-$d_6$)
1-(4-Fluorophenyl)-9H-pyrido[3,4-b]indole (2l)

$^1$H NMR (300 MHz, CDCl$_3$ + DMSO-$d_6$)

$^{13}$C NMR (75 MHz, CDCl$_3$ + DMSO-$d_6$)
4-(9H-Pyrido[3,4-b]indol-1-yl)benzonitrile (2m)

$^1$H NMR (300 MHz, CDCl$_3$ + DMSO-$d_6$)

$^{13}$C NMR (75 MHz, CDCl$_3$ + DMSO-$d_6$)
1-(4-Nitrophenyl)-9H-pyrido[3,4-b]indole (2n)

$^1$H NMR (300 MHz, CDCl$_3$ + DMSO−$d_6$)

$^{13}$C NMR (75 MHz, CDCl$_3$ + DMSO−$d_6$)
1-(Benzo[d][1,3]dioxol-5-yl)-9H-pyrido[3,4-b]indole (2o)

$^1$H NMR (300 MHz, CDCl$_3$ + DMSO–d$_6$)

$^{13}$C NMR (75 MHz, CDCl$_3$ + DMSO–d$_6$)
1-(Naphthalen-1-yl)-9H-pyrido[3,4-b]indole (2p)

$^1$H NMR (300 MHz, CDCl$_3$ + DMSO−$d_6$)

$^{13}$C NMR (75 MHz, CDCl$_3$ + DMSO−$d_6$)
1-(Phenanthren-9-yl)-9H-pyrido[3,4-b]indole (2q)

$^1$H NMR (300 MHz, CDCl$_3$ + DMSO–d$_6$)

$^{13}$C NMR (125 MHz, CDCl$_3$ + DMSO–d$_6$)
1-(Pyridin-3-yl)-9H-pyrido[3,4-b]indole (2r)

$^1$H NMR (300 MHz, CDCl$_3$ + DMSO–$d_6$)

$^{13}$C NMR (75 MHz, DMSO–$d_6$)
1-(4-Fluoro-3-methoxyphenyl)-9H-pyrido[3,4-b]indole (2s)

$^1$H NMR (300 MHz, CDCl$_3$ + DMSO–d$_6$)

$^{13}$C NMR (125 MHz, CDCl$_3$ + DMSO–d$_6$)
1-(4-(trifluoromethyl)phenyl)-9H-pyrido[3,4-b]indole (2t)

$^1$H NMR (400 MHz, DMSO–d$_6$)

$^{13}$C NMR (125 MHz, DMSO–d$_6$)
1-(Pyrrolidin-2-yl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole-3-carboxylic acid dihydrochloride (5)

$^1$H NMR (300 MHz, DMSO-$d_6$)

$^{13}$C NMR (75 MHz, DMSO-$d_6$)
1-(3,4-Dihydro-2H-pyrrol-5-yl)-9H-pyrrido[3,4-b]indole (or) eudistomin I (6)

$^1$H NMR (500 MHz, CDCl$_3$)

$^3$C NMR (125 MHz, CDCl$_3$)
6-Bromo-9H-pyrido[3,4-b]indole (or) Eudistomin N (7)

$^1$H NMR (300 MHz, CDCl$_3$ + DMSO-$d_6$)

$^{13}$C NMR (125 MHz, CDCl$_3$ + DMSO-$d_6$)
tert-Butyl 2-phenyl-1-[(9H-pyrido[3,4-b]indol-1-yl)ethylcarbamate (8)

$^1$H NMR (400 MHz, DMSO-$d_6$)

$^{13}$C NMR (100 MHz, DMSO-$d_6$)
2-Phenyl-1-(9H-pyrido[3,4-b]indol-1-yl)ethanone (or) Eudistomin T (9)

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

$^{13}$C NMR (100 MHz, CDCl$_3$)
Synthesis of 1-(1H-indol-3-yl)-9H-pyrido[3,4-b]indole (or) Eudistomin U (10)

$^1$H NMR (500 MHz, DMSO–$d_6$)

$^{13}$C NMR (100 MHz, DMSO–$d_6$)
Methyl 1-phenethyl-9H-pyrido[3,4-b]indole-3-carboxylate (4a)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, DMSO–$d_6$)
Methyl 1-(3,4,5-trimethoxyphenyl)-9H-pyrido[3,4-b]indole-3-carboxylate (4b)

$^1$H NMR (300 MHz, CDCl$_3$ + DMSO-$d_6$)

$^{13}$C NMR (CDCl$_3$, 75 MHz)
Methyl 1-(naphthalen-1-yl)-9H-pyrido[3,4-b]indole-3-carboxylate (4c)

$^1$H NMR (300 MHz, DMSO–d$_6$)

$^{13}$C NMR (125 MHz, DMSO–d$_6$)
Methyl 1-(4-chlorophenyl)-9H-pyrido[3,4-b]indole-3-carboxylate (4d)

$^1$H NMR (300 MHz, CDCl$_3$ + DMSO–d$_6$)

$^{13}$C NMR (100 MHz, DMSO–d$_6$)
Methyl 1-(phenanthren-9-yl)-9H-pyrido[3,4-b]indole-3-carboxylate (4e)

$^1$H NMR (300 MHz, DMSO-$d_6$ + CDCl$_3$)

$^{13}$C NMR (125 MHz, DMSO-$d_6$ + CDCl$_3$)
Methyl 1-(4-fluoro-3-methoxyphenyl)-9H-pyrido[3,4-b]indole-3-carboxylate (4f)

$^1$H NMR (300 MHz, DMSO-$d_6$)

$^{13}$C NMR (725 MHz, DMSO-$d_6$)
Methyl 1-(4-(trifluoromethyl)phenyl)-9H-pyrido[3,4-b]indole-3-carboxylate (4g)

$^1$H NMR (300 MHz, DMSO–$d_6$)

$^{13}$C NMR (75 MHz, DMSO–$d_6$)
Methyl 1-((tert-butoxycarbonyl)amino)-2-phenylethyl)-9H-pyrido[3,4-b]indole-3-carboxylate (4h)

$^1$H NMR (400 MHz, DMSO-$d_6$)

$^{13}$C NMR (100 MHz, DMSO-$d_6$)
1-(4-Methoxyphenyl)-4,9-dihydro-3H-pyrido[3,4-b]indole (15)

$^1$H NMR (300 MHz, DMSO–$d_6$)

$^{13}$C NMR (75 MHz, DMSO–$d_6$)
1-(4-Nitrophenyl)-4,9-dihydro-3H-pyrido[3,4-b]indole (16)

$^1$H NMR (300 MHz, DMSO-$d_6$ + CDCl$_3$)

$^{13}$C NMR (75 MHz, DMSO-$d_6$ + CDCl$_3$)