Electronic Supplementary Information:

Racemic and diastereoselective construction of indole alkaloids under solvent- and catalyst-free microwave assisted Pictet-Spengler condensation

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Contents

1. General information ........................................................................................................................................1
2. General Procedure for Pictet-Spengler using solvent-free microwave conditions. ..................2
3. Characterization of compounds....................................................................................................................3
4. X-ray diffraction data for 7 and 14.................................................................................................................9
5. NMR Spectra...............................................................................................................................................14
1. General information

$^1$H NMR and $^{13}$C NMR were recorded at room temperature on a Bruker™ DPX 300 at 300 and 100 MHz, respectively. Chemical shifts are in parts per million (ppm). The assignments were made using one dimensional (1D) $^1$H and $^{13}$C spectra or two-dimensional (2D) HSQC and COSY spectra. Mass spectra were recorded with a LCMS-MS triple-quadrupole system (Varian 1200ws). HPLC analysis were performed using a C18 TSK-GEL Super ODS 2 µm particle size column, dimensions 50 * 4.6 mm with a gradient starting from 100% H$_2$O / 0.1% formic acid and reaching 20% H$_2$O /80% CH$_3$CN / 0.08% formic acid within 10 min at a flow rate of 1 mL/min. Melting points were determined on a Büchi B-540 apparatus and are uncorrected. Reactions were performed using a Discover™ microwave from CEM™. All commercial reagents and solvents were used without further purification. Specific rotations were measured on a Jasco™ DIP-370 polarimeter using a 10 cm cell.

Crystal data were collected with a Bruker™ Smart Apex-II CCD diffractometer using graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å) at 298 K. Cell parameters were retrieved using APEX2$^1$ software and refined with SAINT$^2$ on all observed reflections. Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS$^3$. The structure was solved by charge flipping methods using SUPERFLIP$^4$ program and refined by full-matrix least-squares methods on F using CRYSTALS software$^5$. All non-hydrogen atomic positions were located in difference Fourier maps and refined anisotropically. The hydrogen atoms were placed in their geometrically generated positions. Colorless crystals were isolated in rectangular shape at room temperature.

2. General Procedure for Pictet-Spengler using solvent-free microwave conditions.

The tryptamine derivative (0.5 mmol, 1eq.) and the ketoacid (0.5 mmol, 1 eq.) were mixed in a capped 10-mL microwave-vessel. The mixture was heated at 180 °C for 2 min (average effective ramp time =1 min). The power was set at 100 W and the pressure was set at 15 bar (average effective pressure = 3 bar). After completion of the reaction, the crude product was dissolved in DCM/MeOH : 90/10 (10 mL). The organic layer was washed with NaHCO₃ sat. (5mL), and dried over MgSO₄. Solvent was removed under reduced pressure. In some cases, the product was purified by simple precipitation in MeOH. If required flash chromatography (95/5: EtOAc/MeOH) was used for purification. In all cases, the resulting products were isolated in total purity, as determined by LC-MS and afforded analytically pure products in excellent yields as a white solid. In general, the reaction is very clean.
3. Characterization of compounds.

(11b-Methyl-1,2,5,6,11,11b-hexahydro-indolizino[8,7-b]indol-3-one (6a):
Synthesized from levulinic acid and tryptamine

![Chemical Structure]

Yield (109 mg, 91%); off-white solid; mp= 260–262 °C; Purity: 100% ; \(^1\)H
NMR (300 MHz, DMSO) \(\delta\) 11.22 (br s, 1H, NH), 7.36 (d, J = 7.8 Hz, 1H),
7.31 (d, J = 7.8 Hz, 1H), 7.06 (dd, J = 7.2, 1.2 Hz, 1H) , 6.95 (dd, J = 7.2, 1.2
Hz, 1H), 4.19 (dd, J = 13.2, 5.4 Hz, 1H), 3.04 (dt, J = 19.8, 4.8 Hz, 1H), 2.73-
2.53 (m, 3H), 2.33-2.18 (m, 2H), 2.04 (t, J = 9.9 Hz, 1H), 1.54 (s, 3H); \(^1\)C
NMR (75 MHz, DMSO) \(\delta\) 172.38 (Cq), 139.44 (Cq), 136.40 (Cq), 126.70
(Cq), 121.40, 118.99, 118.40, 111.63, 105.00 (Cq), 59.39 (Cq), 34.73, 33.09,
30.55, 25.39, 21.37; rt(LCMS) = 2.40 min; HRMS-ESI (m/z): [M+H]^+ calcd
241.13354; found 241.13292 (\(\Delta = 2.8\) ppm).

8-Chloro-11b-methyl-1,2,5,6,11,11b-hexahydro-indolizino[8,7-b]indol-3-one (6b):
Synthesized from levulinic acid and 5-chloro tryptamine

![Chemical Structure]

Yield (130 mg, 95%); off-white solid; mp= 227-229 °C; Purity: 100%; \(^1\)H
NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.95 (br s, 1H, NH), 7.43 (d, J = 1.8 Hz, 1H), 7.25
(t, J = 8.4 Hz, 1H), 7.11(dd, J = 8.4, 1.8 Hz, 1H), 4.49 (dt, J = 12.6, 2.1 Hz,
1H), 3.16-3.06 (m, 1H), 2.81-2.63 (m, 3H), 2.52-2.43 (m, 1H), 2.37-2.29 (m,
1H), 2.25-2.18 (m, 1H), 1.62 (s, 3H); \(^1\)C NMR (300 MHz, CDCl\(_3\)) \(\delta\) 173.07
(Cq), 139.44 (Cq), 134.67 (Cq), 127.91 (Cq), 125.43 (Cq), 122.34, 118.17,
112.17, 106.46 (Cq), 59.75 (Cq), 35.06, 32.81, 30.62, 25.47, 21.22; rt(LCMS)
= 2.70 min; HRMS-ESI (m/z): [M+H]^+ calcd 275.09457; found 275.09389 (\(\Delta
= 2.5\) ppm).

9-Chloro-11b-methyl-1,2,5,6,11,11b-hexahydro-indolizino[8,7-b]indol-3-one (6c):
Synthesized from levulinic acid and 4-chloro tryptamine

![Chemical Structure]

Yield (127 mg, 93%); white crystals; mp= 220-222 °C; Purity: 100%; \(^1\)H
NMR (300 MHz, CDCl\(_3\)) \(\delta\) 9.66 (br s, 1H, NH), 7.36 (d, J = 4.5 Hz, 1H), 7.31
(s, 1H), 7.07 (d, J = 8.4 Hz, 1H), 4.49 (dd, J = 12.3, 3.9 Hz, 1H), 3.20-3.07
(m,1H), 2.87-2.64 (m,3H), 2.51-2.31 (m,2H), 2.25-2.15 (m,1H), 1.63 (s,3H);
\(^1\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 172.71 (Cq), 138.20 (Cq), 136.17 (Cq),
126.89 (Cq), 124.72, 119.49, 118.71, 110.64, 105.64 (Cq), 59.37 (Cq), 34.53,
32.11, 30.30, 24.66, 20.62; rt(LCMS) = 2.70 min; HRMS-ESI (m/z): [M+H]^+
calcd 275.09457; found 275.09370 (\(\Delta = 2.4\) ppm).

8,11b-Dimethyl-1,2,5,6,11,11b-hexahydro-indolizino[8,7-b]indol-3-one (6d):
Synthesized from levulinic acid and 5-methyl tryptamine

![Chemical Structure]
8-Methoxy-11b-methyl-1,2,5,6,11,11b-hexahydro-indolizino[8,7-b]indol-3-one (6e):
Synthesized from levulinic acid and 5-methoxy tryptamine

Yield (130 mg, 94%); off-white solid; mp= 199-201 °C; Purity: 100%; 1H NMR (300 MHz, CDCl3) δ 7.81 (br s, 1H, NH), 7.24 (d, J = 9 Hz, 1H), 6.93 (d, J = 2.4 Hz, 1H), 6.85 (dd, J = 9, 2.4 Hz, 1H), 4.48 (dd, J = 12.6, 4.2 Hz, 1H), 3.86 (s, 3H), 3.15-3.03 (m, 1H), 2.86-2.75 (m, 2H), 2.71-2.62 (m, 1H), 2.52-2.43 (m, 1H), 2.32-2.23 (m, 2H), 1.60 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 167.96 (Cq), 163.35 (Cq), 135.23 (Cq), 133.20 (Cq), 132.38 (Cq), 128.99, 128.44, 128.19, 127.60, 127.29 (Cq), 62.44, 58.25 (Cq), 47.92, 45.77, 29.47, 22.36; rt(LCMS) = 2.75 min; HRMS-ESI (m/z): [M+H]+ calcld 271.13683; found 271.13619 (Δ = 2.8 ppm).

9-Fluoro-11b-methyl-1,2,5,6,11,11b-hexahydro-indolizino[8,7-b]indol-3-one (6f):
Synthesized from levulinic acid and 4-fluoro tryptamine

Yield (120 mg, 93%); off-white solid; mp= 196-198 °C; Purity: 100%; 1H NMR (300 MHz, CDCl3) δ 8.96 (br s, 1H, NH), 7.37 (dd, J = 8.7, 5.1 Hz, 1H), 7.02 (dd, J = 9.6, 2.4 Hz, 1H), 6.87 (dd, J = 9.6, 5.1, 2.4 Hz, 1H), 4.46 (dd, J = 12.3, 3.9 Hz, 1H), 3.17-3.03 (m, 1H), 2.84-2.78 (m, 2H), 2.77-2.67 (m, 1H), 2.52-2.44 (m, 1H), 2.33-2.32 (m, 1H), 2.30-2.22 (m, 1H), 1.62 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 172.89 (Cq), 159.80 (d, J = 235.5 Hz, 1Cq), 136.27 (d, J = 12.2 Hz, 1Cq), 135.99 (d, J = 3.8 Hz, 1Cq), 123.16 (Cq), 118.96 (d, J = 9.8 Hz, 1C), 108.05 (d, J = 24 Hz, 1C), 106.36 (Cq), 97.48 (d, J = 25.5 Hz, 1C), 59.56 (Cq), 34.88, 32.62, 30.63, 25.21, 21.06; rt(LCMS) = 2.53 min; HRMS-ESI (m/z): [M+H]+ calcld 259.12335; found 259.12335 (Δ = 2.8 ppm).

12b-Methyl-2,3,6,7,12,12b-hexahydro-1H-indol[2,3-a]quinolizin-4-one (7):
Synthesized from 4-acetylbutyric acid and tryptamine

Yield (116 mg, 92%); off-white solid; mp = 257 -259 °C; Purity: 100%; 1H NMR (300 MHz, CDCl3) δ 9.91 (br s, 1H, NH), 7.57 (d, J = 7.8 Hz, 1H), 7.43 (d, J = 7.8 Hz, 1H), 7.25 (td, J = 7.8, 1.2 Hz, 1H), 7.15 (td, J = 7.8, 1.2 Hz, 1H), 5.22 (dd, J = 12.3, 3.6 Hz, 1H), 3.13 (dt, J = 19.5, 4.8 Hz, 1H), 2.97-2.80 (m, 2H), 2.79-2.70 (m, 1H), 2.69-2.43 (m, 2H), 1.99-1.83 (m, 3H), 1.76 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 169.88 (Cq), 139.03 (Cq), 136.53 (Cq), 126.63 (Cq), 121.78, 119.37, 118.32, 111.35, 107.10 (Cq), 57.26 (Cq), 36.86, 35.31, 32.28, 25.85, 21.48, 16.76; rt(LCMS) = 2.46 min; HRMS-ESI (m/z): [M+H]+ calcld 255.14919; found 255.14857 (Δ = 2.4 ppm).
11b-Phenyl-1,2,5,6,11,11b-hexahydro-indolizino[8,7-b]indol-3-one (8):
Synthesized from 3-benzoylpropanic acid and tryptamine

Yield (136 mg, 90%); off-white crystals; mp= 262-264 °C; Purity: 100%;

\[\text{iH NMR (300 MHz, DMSO) } \delta 11.43 (br s, 1H, NH), 7.42-7.28 (m, 7H), 7.12 (td, J = 7.2, 1.2 Hz, 1H), 6.99 (td, J = 7.2, 1.2 Hz, 1H), 4.26-4.17 (m, 1H), 2.85-2.61 (m, 4H), 2.52 (dd, J = 10.2, 1.8 Hz, 1H), 2.49 (dd, J = 10.2, 1.8 Hz, 1H), 2.41-2.32 (m, 1H); \text{[13C NMR (75MHz, DMSO) } \delta 173.60 (Cq), 144.36 (Cq), 136.65 (Cq), 136.44 (Cq), 129.05, 128.00, 126.51 (Cq), 126.32, 121.90, 119.25, 118.59, 111.80, 107.23 (Cq), 65.30 (Cq), 35.41, 34.10, 30.71, 20.77; rt(LCMS) = 2.77 min; \text{HRMS-ESI (m/z): } [\text{M+H}]^+ \text{ calcld 303.14919; found 303.14837 (Δ = 2.7 ppm).}

2,3,3a,4,8,13-hexahydro-7H-cyclopenta[1,8a]indolizino[8,7-b]indol-5(1H)-one (9):
Synthesized from 2-oxocyclopentanecetic acid (rac) and tryptamine

Yield (128 mg, 96%); off-white solid; mp= 237-239 °C; Purity: 100%;

\[\text{iH NMR (300 MHz, DMSO) } \delta 111.00 (br s, 1H, NH), 7.33 (t, J = 7.8 Hz, 2H), 7.06 (td, J = 7.2, 1.2 Hz, 1H), 6.96 (td, J = 7.2, 1.2 Hz, 1H), 4.26-4.19 (m, 1H), 3.09-2.99 (m, 1H), 2.86-2.78 (m, 1H), 2.66-2.60 (m, 3H), 2.24-2.06 (m,3H), 1.84-1.75 (m, 2H), 1.67-1.57 (m, 2H); \text{[13C NMR (75 MHz, DMSO) } \delta 173.79 (Cq), 138.03 (Cq), 136.74 (Cq), 126.74 (Cq), 121.49, 119.03, 118.18, 111.61, 106.65 (Cq), 70.80 (Cq), 41.14, 39.17, 38.63, 36.52, 34.80, 24.68, 20.92 ; rt(LCMS) = 2.60 min; \text{HRMS-ESI (m/z): } [\text{M+H}]^+ \text{ calcld 267.14919; found 267.14834 (Δ = 3.2 ppm).}

1,2,3,4,5,9,14-octahydro-6H,8H-pyrido[3,4-b:2,1-i'] diindol-6-one (10):
Synthesized from 2-oxocyclohexanacetic acid (rac) and tryptamine

Yield (133 mg, 95%); off-white solid; mp= 256-258 °C; Purity: 100%;

\[\text{iH NMR (300 MHz, CDCl3) } \delta 9.22 (br s, 1H, NH), 7.54 (d, J = 7.8 Hz, 1H), 7.45 (d, J = 7.8 Hz, 1H), 7.27-7.15 (m, 2H), 4.52 (dd, J = 12.9, 6.0 Hz, 1H), 3.19 (dt, J =18.6, 6.0 Hz, 1H), 3.01-2.81 (m, 2H), 2.59-2.43 (m, 3H), 2.28-2.24 (m, 1H), 2.16-2.05 (m, 1H), 1.88-1.59 (m, 6H); \text{[13C NMR (75 MHz, CDCl3) } \delta 173.52 (Cq), 138.13 (Cq), 136.13 (Cq), 126.57 (Cq), 125.00, 119.67, 118.38, 111.34, 106.73 (Cq), 60.72 (Cq), 37.95, 35.88, 34.94, 34.23, 25.98, 21.69, 21.16, 20.55; rt(LCMS) = 2.73 min; \text{HRMS-ESI (m/z): } [\text{M+H}]^+ \text{ calcld 281.16433; found 281.16433 (Δ = 1.8 ppm).}
5,6,11b,12-Tetrahydro-6a,12-diaza-indeno[1,2-a]fluoren-7-one (11):  
Synthesized from 2-formylbenzoic acid and tryptamine

Yield (130 mg, 95%); off-white solid; mp= 261-263 °C; Purity: 100%; ¹H NMR (300 MHz, DMSO) δ 11.37 (br s, 1H, NH), 8.31 (dd, J = 7.8, 0.6 Hz, 1H), 7.77-7.68 (m, 2H), 7.54 (t, J = 7.5 Hz, 1H), 7.41 (d, J = 8.7 Hz, 2H), 7.12 (td, J = 7.5, 1.2 Hz, 1H), 6.99 (td, J = 7.5, 1.2 Hz, 1H), 6.04 (s, 1H), 4.60 (dd, J = 13.2, 5.4 Hz, 1H, 3.45-3.31(m, 1H), 2.86-2.69 (m, 2H); ¹³C NMR (75MHz, DMSO) δ 167.64 (Cq), 144.12 (Cq), 136.92 (Cq), 132.34, 132.17 (Cq), 131.36 (Cq), 129.09, 126.63 (Cq), 124.25, 123.61, 122.01, 119.35, 118.62, 111.75, 107.63 (Cq), 57.12, 38.18, 21.87; rt(LCMS) = 2.70 min; HRMS-ESI (m/z): [M+H]⁺ calcd 275.11789; found 275.11681 (Δ = 1.1 ppm).

11b-Methyl-5,6,11b,12-tetrahydro-6a,12-diaza-indeno[1,2-a]fluoren-7-one (12):  
Synthesized from 2-acetylbenzoic acid and tryptamine

Yield (139 mg, 97%); off-white solid; mp= 253-255 °C; Purity: 100%; ¹H NMR (300 MHz, DMSO) δ 11.37 (br s, 1H, NH), 8.33 (d, J = 7.8 Hz, 1H), 7.72 (t, J = 7.8 Hz, 2H), 7.51 (t, J = 7.8 Hz, 1H), 7.38 (d, J = 7.8 Hz, 2H), 7.09 (t, J = 7.8 Hz, 1H), 6.97 (t, J = 7.8 Hz, 1H), 4.53 (dd, J = 13.2, 5.1 Hz, 1H), 3.44-3.34 (m, 1H), 2.82-2.63 (m, 2H), 1.85 (s, 3H); ¹³C NMR (75MHz, DMSO) δ 167.68 (Cq), 149.80 (Cq), 136.65 (Cq), 135.63 (Cq), 132.68, 130.73 (Cq), 129.06, 126.45 (Cq), 123.64, 123.24, 122.07, 119.36, 118.79, 111.68, 106.81 (Cq), 62.49 (Cq), 35.90, 26.35, 21.93; rt(LCMS) = 2.77 min; HRMS-ESI (m/z): [M+H]⁺ calcd 289.13354; found 289.13246 (Δ = 1.1 ppm).

(5S,11bS)-5-Hydroxymethyl-11b-methyl-1,2,5,6,11,11b-hexahydro-indolizino[8,7-b]indol-3-one (13):  
Synthesized from levulinic acid and L-tryptophanol

Yield (124 mg, 92%); off-white solid; mp= 224-226 °C; [α]D = -1.8 ° (c 0.6, CH2Cl2); Purity: 100%; ¹H NMR (300 MHz, CDCl3) δ 8.81 (br s, 1H, NH), 7.48 (d, J = 7.5 Hz, 1H), 7.31 (d, J = 7.8 Hz, 1H), 7.19 (dd, J = 7.8, 1.5 Hz, 1H), 7.16 (dd, J = 7.8, 1.5 Hz, 1H), 4.28-4.14 (m, 1H), 3.70 (br s, 1H, OH), 3.06-2.89 (m, 1H), 2.83-2.61 (m, 2H), 2.54-2.36 (m, 2H), 2.32-2.10 (m, 3H), 1.66 (s, 3H); ¹³C NMR (75 MHz, CDCl3) δ 174.86 (Cq), 137.35 (Cq), 136.40 (Cq), 126.53 (Cq), 122.21, 119.70, 118.46, 111.17, 106.81 (Cq), 62.84, 62.36 (Cq), 55.51, 32.69, 31.39, 25.36, 24.29; rt(LCMS) = 2.23 min; HRMS-ESI (m/z): [M+H]⁺ calcd 271.14410; found 271.14380 (Δ = 1.1 ppm).
(3aS,7S,13bS)-7-(Hydroxymethyl)-2,3,3a,4,7,8-hexahydro-1H-cyclopenta[1,8a]indolizino[8,7-b]indol-5(13H)-one (14):
Synthesized from 2-oxocyclopentanecarboxylic acid (rac) and L-tryptophanol

Yield (140 mg, 95%); white crystals; mp= 144-146 °C; [α]D = -87 ° (c 0.5, CH2Cl2); Purity 100 %; δH (300 MHz, CDCl3) 11.01 (br s, 1H, NH), 7.37 (d, J = 7.8 Hz, 1H, C(16)H), 7.31 (d, J = 7.8 Hz, 1H, C(13)H), 7.06 (dd, J = 7.2, 3 Hz, 1H, C(9)H), 5.05 (dd, J = 7.5, 5.1 Hz, 1H, C(9)H), 4.14-3.99 (m, 2H, C(9)H, C(10)H), 3.55-3.47 (m, 1H, C(8)H), 3.35 (br s, 1H, OH), 2.89-2.68 (m, 3H, C(5)H, C(6)H, C(10)H), 2.57 (dd, J = 18, 10.8 Hz, 1H, C(2)H), 2.27-2.07 (m, 3H, C(2)H, C(6)H, C(3)H), 1.88-1.58 (m, 3H, C(3)H, C(4)H), 0.58 (5H, CDCl3) 24.0 (C(3)), 24.9 (C(4)), 34.8 (C(2)), 38.9 (C(6)), 39.5 (C(10)), 41.3 (C(5)), 56.6 (C(8)), 62.2 (C(9)), 73.9 (C(11)), 107.8 (C(11)), 111.6 (C(13)), 118.1 (C(16)), 119.1 (C(14)), 121.5 (C(15)), 126.7 (C(12)), 136.8 (C(19)), 138.1 (C(17)), 176.0 (C(7)); rt(LCMS) = 2.37 min; HRMS-ESI (m/z): [M+H]+ calcd 297.15975; found 297.15880 (Δ = 3.2 ppm).

(4aS,8S,14bS)-8-(Hydroxymethyl)-1,2,3,4,4a,5,8,9-octahydropyrido[3,4-b:2,1-i']diindol-6(14H)-one (15):
Synthesized from 2-oxocyclohexanecarboxylic acid (rac) and L-tryptophanol

Yield (147 mg, 95%); off-white solid; mp= 233-235 °C; [α]D = -105 ° (c 0.6, CH2Cl2); Purity: 100%; 1H NMR (300 MHz, DMSO) δ 10.91 (br s, 1H, NH), 7.35 (t, J = 7.5 Hz, 2H), 7.05 (dt, J = 7.5, 0.9 Hz, 1H), 6.96 (t, J = 7.5 Hz, 1H), 4.97 (t, J = 6 Hz, 1H), 4.08-3.99 (m, 1H), 3.96 (br s, 1H, OH), 3.62-3.53 (m, 1H), 2.86-2.66 (m, 2H), 2.59-2.48 (m, 1H), 2.10 (d, J = 6.6 Hz, 2H), 2.01-1.87 (m, 3H), 1.64-1.45 (m, 5H); 13C NMR (75 MHz, DMSO) δ 178.03 (Cq), 139.32 (Cq), 136.49 (Cq), 126.74 (Cq), 121.46, 119.10, 118.21, 111.82, 107.29 (Cq), 64.17, 62.61 (Cq), 54.34, 37.70, 36.46, 33.69, 27.65, 23.47, 22.40, 21.25; rt(LCMS) = 2.63 min; HRMS-ESI (m/z): [M+H]+ calcd 311.17540; found 311.17476 (Δ = 2.1 ppm).

(6S,11bS)-6-Hydroxymethyl-5,6,11b,12-tetrahydro-6a,12-diaza-indeno[1,2-a]fluoren-7-one (16):
Synthesized from 2-formylbenzoic acid and L-tryptophanol

Yield (145 mg, 96%); white crystals; mp= 276-279 °C; [α]D = -67 ° (c 0.6, CH2Cl2); Purity: 100%; 1H NMR (300 MHz, DMSO) δ 11.28 (br s, 1H, NH), 8.28 (d, J = 7.5 Hz, 1H), 7.71 (t, J = 7.5 Hz, 2H), 7.53 (t, J = 7.5 Hz, 1H), 7.40 (dd, J = 12.6, 7.8 Hz, 2H), 7.09 (t, J = 7.8 Hz, 1H), 7.53 (t, J = 7.2 Hz, 1H), 6.10 (s, 1H), 5.18 (t, J = 6.6 Hz, 1H), 4.35-4.28 (m, 1H), 4.27 (br s, 1H, OH), 3.91-3.82 (m, 1H), 2.97-2.76 (m, 2H); 13C NMR (75 MHz, DMSO) δ 168.27 (Cq), 143.84 (Cq), 137.04 (Cq), 132.67 (Cq), 132.51, 131.89 (Cq), 129.6 (Cq), 126.58, 124.08, 123.53, 122.00, 119.42, 118.60, 111.80, 108.56 (Cq), 61.93, 59.83, 58.89, 25.30; rt(LCMS) = 2.77 min; HRMS-ESI (m/z): [M+H]+ calcd 305.12845; found 305.12731 (Δ = 1.1 ppm).
(6S,11bS)-6-Hydroxymethyl-11b-methyl-5,6,11b,12-tetrahydro-6a,12-diaza-indeno[1,2-a]fluoren-7-one (17):
Synthesized from 2-acetylbenzoic acid and L-tryptophanol

Yield (149 mg, 94%); white crystals; m.p= 250-252 °C; [α]D = -83 ° (c 0.5, CH2Cl2); Purity: 100%; 1H NMR (300 MHz, DMSO) δ 11.33 (br s, 1H, NH), 8.32 (d, J = 7.5 Hz, 1H), 7.71 (d, J = 7.5 Hz, 2H), 7.50 (t, J = 7.2 Hz, 1H), 7.40 (t, J = 7.2 Hz, 2H), 7.09 (t, J = 7.2 Hz, 1H), 6.98 (t, J = 7.2 Hz, 1H), 5.23 (t, J = 6.6 Hz, 1H), 4.43-4.31 (m, 1H), 4.29 (br s, 1H, OH), 3.92-3.82 (m, 1H), 3.01-2.72 (m, 2H), 1.89 (s, 3H); 13C NMR (75 MHz, DMSO) δ 168.83 (Cq), 149.61 (Cq), 136.80 (Cq), 136.17 (Cq), 132.88, 131.07 (Cq), 129.12, 126.41 (Cq), 123.56, 123.18, 122.08, 119.44, 118.79, 111.72, 107.82 (Cq), 64.96, 62.34 (Cq), 55.87, 50.97, 25.29; rt(LCMS) = 2.72 min; HRMS-ESI (m/z): [M+H]+ calcd 319.14410; found 319.14296 (Δ = 1.1 ppm).

(4aR,8R,14bR)-8-(Hydroxymethyl)-1,2,3,4,4a,5,8,9-octahydropyrido[3,4-b:2,1-i’]diindol-6(14H)-one (18):
Synthesized from 2-oxocyclohexanacetic acid (rac) and D-tryptophanol

Yield (144 mg, 93%); off-white solid; m.p= 247-249 °C; [α]D = +107 ° (c 0.6, CH2Cl2); Purity: 100%; 1H NMR (300 MHz, DMSO) δ 10.91 (br s, 1H, NH), 7.36 (t, J = 7.5 Hz, 2H), 7.06 (t, J = 7.5 Hz, 1H), 6.96 (t, J = 7.5 Hz, 1H), 4.99 (t, J = 5.7 Hz, 1H), 4.12-3.99 (m, 1H), 3.96 (br s, 1H, OH), 3.63-3.51 (m, 1H), 2.87-2.65 (m, 2H), 2.58-2.47 (m, 1H), 2.11 (d, J = 6.3 Hz, 2H), 1.83-1.76 (m, 3H), 1.66-1.38 (m, 5H); 13C NMR (75 MHz, DMSO) δ 178.00 (Cq), 139.30 (Cq), 136.52 (Cq), 126.75 (Cq), 121.47, 119.11, 118.22, 111.83, 107.29 (Cq), 64.17, 62.62 (Cq), 54.36, 37.68, 36.48, 33.69, 27.62, 23.48, 22.38, 21.26; rt(LCMS) = 2.66 min; HRMS-ESI (m/z): [M+H]+ calcd 311.17540; found 311.17476 (Δ = 2.1 ppm).
4. X-ray diffraction data for 7 and 14 and CCDC codes.

12b-Methyl-2,3,6,7,12,12b-hexahydro-1H-indolo[2,3-a]quinolizin-4-one (7):

CCDC 856036
Unit cell parameters: a 8.715(4) b 11.090(4) c 13.771(7) beta 90.303(6)
space group P21/c

![Methyl-2,3,6,7,12,12b-hexahydro-1H-indolo[2,3-a]quinolizin-4-one (7)](image)

(1R,5S,11bR)-5-Hydroxymethyl-1,11b-cyclohexyl-1,2,5,6,11,11b-hexahydro-
indolizino[8,7-b]indol-3-one (14):

CCDC 749287
Unit cell parameters:
a 8.4078(8) b 8.3744(8) c 11.4399(10) beta 98.698(4) space group P21

![5-Hydroxymethyl-1,11b-cyclohexyl-1,2,5,6,11,11b-hexahydro-
indolizino[8,7-b]indol-3-one (14)](image)
Basic crystal data for the product 7

CCDC 856036 contains the supplementary crystallographic data for the product 7. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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**Datablock: 1**

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The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level. Click on the hyperlinks for more details of the test.
Basic crystal data for the product 14

CCDC 749287 contains the supplementary crystallographic data for the product 14. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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### Datablock: 1

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The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level.

Click on the hyperlinks for more details of the test.
5. NMR Spectra

(6a): $^1$H NMR (300 MHz, DMSO)

(6a): $^{13}$C NMR (75 MHz, DMSO)
(6b): \(^1\)H NMR (300 MHz, CDCl\(_3\))

(6b): \(^{13}\)C NMR (75 MHz, CDCl\(_3\))
(6c): $^1$H NMR (300 MHz, CDCl$_3$)

(6c): $^{13}$C NMR (75 MHz, CDCl$_3$)
(6d): $^1$H NMR (300 MHz, CDCl$_3$)

(6d): $^{13}$C NMR (75 MHz, CDCl$_3$)
(6e): $^1$H NMR (300 MHz, CDCl$_3$)

(6e): $^{13}$C NMR (75 MHz, CDCl$_3$)
(6f): $^1$H NMR (300 MHz, CDCl$_3$)
(7): $^1$H NMR (300 MHz, CDCl$_3$)

(7): $^{13}$C NMR (75 MHz, CDCl$_3$)
(8): $^1$H NMR (300 MHz, DMSO)

(8): $^{13}$C NMR (75 MHz, DMSO)
(9): $^1$H NMR (300 MHz, DMSO)

(9): $^{13}$C NMR (75 MHz, DMSO)
(10): $^1$H NMR (300 MHz, CDCl$_3$)

(10): $^{13}$C NMR (75 MHz, CDCl$_3$)
(11): $^1$H NMR (300 MHz, DMSO)

(11): $^{13}$C NMR (75 MHz, DMSO)
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(12): $^{13}$C NMR (75 MHz, DMSO)
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(13): $^{13}$C NMR (75 MHz, CDCl$_3$)
(14): $^1$H NMR (300MHz, DMSO)

(14): $^{13}$C NMR (75 MHz, DMSO)
(15): $^1$H NMR (300 MHz, DMSO)

(15): $^{13}$C NMR (75 MHz, DMSO)
(16): $^1$H NMR (300 MHz, DMSO)

(16): $^{13}$C NMR (75 MHz, DMSO)
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(17): $^{13}$C NMR (75 MHz, DMSO)
(18): $^1$H NMR (300 MHz, DMSO)

(18): $^{13}$C NMR (75 MHz, DMSO)