Electronic Supplementary Information

Syntheses of Tetrahydro-*β*-Carbolines via Tandem Hydformylation / Pictet-Spengler Reaction, Scope and Limitations

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Materials

All solvents were dried and purified before use by the usual procedures. Rh(acac)(CO)2 was purchased. Cyclopentene, cyclohexene, cycloheptene, cyclooctene, tryptamine and tryptophan were purchased and used as received. Metallylic amines and alcohols were synthesized by the reaction of the corresponding metallylic amines or alcohols with the corresponding acid chlorides in the presence of triethylamine and DMAP.

General methods

^{1}H-NMR and ^{13}C-NMR spectra were measured on a Bruker Advance DRX400 spectrometer or a Bruker Advance DRX 500 spectrometer using $CDCl_3$ or DMSO-D6 as solvents with $CHCl_3$ or DMSO as internal standards. Chemical shifts (δ) are given in parts per million (ppm) and coupling constants are given in Hertz (Hz).The proton spectra are reported as follows δ/ppm (multiplicity, number of protons, coupling constant *J*/Hz). Two dimensional (COSY, HSQC, HMBC) were used were appropriate to aid the assignments in ^{1}H and ^{13}C spectra. IR spectra were measured on a Nicolet Impact 400D FT-IR spectrometer. IR spectra were recorded as films on NACl or KBr plates or for solids pressed with KBr. The peak intensities are defined as very strong (vs), strong (s), middle (m) or weak (w). Melting points were determined on a Büchi B-540 melting point apparatus, and are uncorrected. Column chromatography was carried out on 70–230 mesh silica gel (Macherey– Nagel; silicagel 60) using Cyclohexane/EA or CH_2Cl_2/MeOH as eluents. High resolution mass analyses were performed on a Jeol JMS-SX 102A.

General procedure for tandem Hydroformylation/Pictet-Spengler reaction under aprotic conditions

In a thick walled sample vial containing PTFE septum (S)-tryptophanmethylester (1 equiv.), olefin (1 equiv.) and $Rh(acac)(CO)_2$ (0.01 equiv.) were dissolved in dry solvent (8 mL). The vial was placed in a pressure vessel, flushed with argon and pressurized with 50 bar CO and 10 bar H_2. The reaction mixture was stirred for 3 days at designated temperature. Volatiles were removed under reduced pressure and the crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexan/ethylacetat) to give the desired product.

The general procedure was followed with (S)-tryptophanmethylester (218 mg, 1 mmol), cyclopenten (68 mg, 1 mmol) and $Rh(acac)(CO)_2$ (3.6 mg, 0.01 mmol) in 8 ml of DCM under 50 bar CO and 10 bar H_2 at 80 °C for 72 h (Table 1, entry 7). The crude reaction mixture was purified by flash column chromatography on silica gel (Cyclohexan/Ethylacetat = 6/1) to give 113 mg (38 %) of **2a**, 119 mg (40 %) of **3a**, 3 mg (1 %) of **4a**, 19 mg (5 %) of **5a** and. 9 mg, (3 %) of **6a;**

(1S,3S)-methyl 1-cyclopentyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole-3-carboxylate, (Table 1, Entry 7), (2a). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.97 (s, 1H), 7.48 (d, 1H, *J* = 7.6Hz), 7.30 (d, 1H, *J* = 7.9 Hz), 7.12 (dt, 2H, *J* = 7.0 Hz, *J* = 20.1 Hz), 4.10 (d, 1H, *J* = 6.4 Hz), 3.81 (s, 3H), 3.74 (dd, 1H, *J* = 4.1Hz, *J* = 11.2 Hz), 3.12 (ddd, 1H, *J* = 1.5 Hz, *J* = 4.0 Hz, *J* = 14.9 Hz), 2.86-2.76 (m, 1H), 2.28 (q, 1H, *J* = 8.0 Hz), 2.02-1.93 (m, 1H), 1.80-1.36 (m, 8H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 173.7, 135.8, 135.6, 126.9, 121.5, 119.4, 117.8, 110.7, 108.4, 56.7, 56.4, 52.1, 44.3, 29.2, 28.5, 25.9, 25.4; HRMS: m/z (ESI) calc for $C_{18}H_{23}N_2O_2$ ($M+H^+$) 299.17540, found 299.17489; IR(film): ν [cm^{-1}] = 3402 (s), 3060 (w), 2955 (s), 2863 (s), 1740 (vs), 1457 (s), 1359 (m), 1181 (m), 741 (m).

(1R,3S)-methyl 1-cyclopentyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole-3-carboxylate, (Table 1, Entry 7), (3a). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.86 (s, 1H), 7.48 (d, 1H, *J* = 7.6 Hz), 7.28 (d, 1H, *J* = 7.8 Hz), 7.12 (dt, 2H, *J* = 6.7 Hz, *J* = 14.7 Hz), 4.06-3.98 (m, 2H), 3.73 (s, 3H), 3.11 (dd, 1H, *J* = 5.1 Hz, *J* = 15.3 Hz), 2.99 (dd, 1H, *J* = 7.3 Hz, *J* = 15.2 Hz), 2.36 (bs, 1H), 2.21 (dd, 1H, *J* = 9.1 Hz, *J* = 17.2 Hz), 1.94-1.80 (m, 2H), 1.78-1.36 (m, 6H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 174.3, 135.7, 135.4, 126.9, 121.5, 119.2, 117.9, 110.6, 107.1, 55.1, 52.7, 52.0, 45.2, 30.2, 29.9, 25.6, 24.9, 24.7; HRMS: m/z (ESI) calc for $C_{18}H_{23}N_2O_2$ ($M+H^+$) 299.17540, found 299.17489; IR(film): ν [cm^{-1}] = 3395 (m), 3054 (w), 2995 (s), 1727 (vs), 1444 (s), 1319 (m), 1260 (m), 1221 (m), 1010 (m), 741 (s).

(S)-methyl 2-(cyclopentylmethylamino)-3-(1H-indol-3-yl)propanoate, (Table 1, Entry 7), (4a). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 8.71 (s, 1H), 7.62 (d, 1H, *J* = 7.8 Hz), 7.29 (d, 1H, *J* = 8.0 Hz), 7.14 (dt, 2H, *J* = 7.1 Hz, *J* = 14.7 Hz), 6.96 (s, 1H), 3.67 (t, 1H, *J* = 6.8 Hz), 3.64 (s, 3H), 3.17 (qd, 2H, *J* = 6.7 Hz, *J* = 14.3 Hz), 2.50 (ddd, 2H, *J* = 7.3 Hz, *J* = 10.9 Hz, *J* = 17.8 Hz), 1.96 (dt, 1H, *J* = 7.6 Hz, *J* = 15.1 Hz), 1.76 (bs, 1H), 1.74-1.62 (m, 2H), 1.58-1.42 (m, 4H), 1.14-1.00 (m, 2H). ^{13}C-NMR ($CDCl_3$, 100 MHz) 175.4, 136.1, 127.2, 122.9, 121.7, 119.1, 118.4, 111.1, 110.6, 62.3, 53.9, 51.5, 39.8, 30.6, 30.5, 29.1, 25.1. HRMS: m/z (ESI) calc for $C_{18}H_{24}N_2O_2$ ($M+H^+$) 301.19105, found 301.19067. IR (film): ν [cm^{-1}] = 3152 (m), 2942 (m), 2916 (m), 2863 (m), 2364 (w), 1740 (vs)1457 (s), 1431 (s), 1325 (s), 1221 (m), 1135 (m), 735 (s).

(S)-methyl 2-(bis(cyclopentylmethyl)amino)-3-(1H-indol-3-yl)propanoate, (Table 1, Entry 7), (5a). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 8.00 (s, 1H), 7.57 (d, 1H, *J* = 7.7 Hz), 7.32 (d, 1H, *J* = 7.9 Hz), 7.13 (dt, 2H, *J* = 7.1 Hz, *J* = 23.4 Hz), 7.00 (s, 1H), 3.74 (dd, 1H, *J* = 4.4 Hz, *J* = 9.7 Hz), 3.57 (s, 3H), 3.26 (dd, 1H, *J* = 10.0 Hz, *J* = 14.1 Hz), 2.92 (dd, 1H, *J* = 3.8 Hz, *J* = 14.1 Hz), 2.52-2.34 (m, 4H), 2.09-1.97 (m, 2H), 1.72-1.42 (m, 12 H), 1.36-1.18 (m, 2H), 1.15-1.04 (m, 2H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 173.2, 136.1, 127.5, 122.7, 121.8, 119.2, 118.5, 112.7, 111.1, 63.3, 56.7, 50.7, 38.2, 30.8, 30.7, 25.5, 25.1, 25.1; HRMS: m/z (ESI) calc for $C_{24}H_{35}N_2O_2$ ($M+H^+$) 383.26931, found

383.26895. IR(film): ν [cm^{-1}] = 3415 (m), 2948 (s), 2856 (s), 1733 (vs), 1457 (s), 1339 (w), 1162 (m), 735 (s).

(1R,3S)-methyl 1-cyclopentyl-2-(cyclopentylmethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole-3-carboxylate, (Table 1, Entry 7), (6a). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.82 (s, 1H), 7.54 (d, 1H, *J* = 7.7 Hz), 7.32 (d, 1H, *J* = 8.0 Hz), 7.15 (dt, 2H, *J* = 7.0 Hz, *J* = 14.9 Hz), 4.05 (dd, 1H, *J* = 4.6 Hz, *J* = 11.5 Hz), 3.80 (s, 3H), 3.50 (d, 1H, *J* = 9.5 Hz), 3.11 (dd, 1H, *J* = 11.6 Hz, *J* = 15.8 Hz), 2.82 (dd, 1H, *J* = 4.6 Hz, *J* = 15.9 Hz), 2.44 (dd, 1H, *J* = 4.0 Hz, *J* = 12.7 Hz), 2.25-2.02 (m, 4H), 1.96-1.20 (m, 14H), 1.01-0.84(m, 1H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 173.8, 135.8, 135.3, 126.9, 121.5, 119.4, 118.1, 110.6, 107.5, 62.0, 57.1, 53.8, 51.7, 45.5, 38.1, 31.7, 31.1, 30.7, 30.4, 25.5, 25.3, 24.9, 24.3, 19.5; HRMS: m/z (ESI) calc for $C_{24}H_{32}N_2O_2$ ($M+H^+$) 381.25366, found 381.25362; IR(film): ν [cm^{-1}] = 3395 (m), 2935 (s), 2870 (s), 1740 (vs), 1575 (m), 1451 (s), 1260 (w), 1083 (w), 748 (s).

The general procedure was followed with (S)-tryptophanmethylester (218 mg, 1 mmol), cyclohexen (82 mg, 1 mmol) and $Rh(acac)(CO)_2$ (3.6 mg, 0.01 mmol) in 10 ml of DCM under 50 bar CO and 10 bar H_2 at 100 °C for 72 h (Table 1, Entry 9). The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexan/ethylacetat = 6/1) to give 87 mg (28 %) of **2b**, 109 mg (35 %) of **3b**, 3 mg (1 %) of **4b**, 45 mg (11 %) of **5b**, 21 mg (5.1 %) of **6b,** and 15 mg (4.8 %) of **7b.**

(1S,3S)-methyl 1-cyclohexyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole-3-carboxylate, (Table 1, Entry 9), (2b). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.92 (s, 1H), 7.47 (d, 1H, *J* = 7.6 Hz), 7.31 (d, 1H, *J* = 7.9 Hz), 7.12 (dt, 2H, *J* = 7.1 Hz, *J* = 14.6 Hz), 4.14 (d, 1H, *J* = 1.6 Hz), 3.81 (s, 1H), 3.73 (dd, 1H, *J* = 4.0 Hz, *J* = 11.1 Hz), 3.10 (ddd, 1H, *J* = 1.3 Hz, *J* = 3.6 Hz, *J* = 14.6 Hz), 2.82-2.73 (m, 1H), 2.42 (bs, 1H), 1.88-1.64 (m, 6H), 1.50-1.10 (m, 5H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 173.8, 135.9, 134.7, 127.1,

121.5, 119.4, 117.8, 110.7, 108.9, 57.6, 56.4, 52.1, 42.3, 29.7, 26.8, 26.5, 26.3, 25.9. Analytical data fits with literature.[1]

(1R,3S)-methyl 1-cyclohexyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole-3-carboxylate, (Table 1, Entry 9), (3b). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.81 (s, 1H), 7.50 (d, 1H, *J* = 7.6 Hz), 7.31 (d, 1H, *J* = 7.9 Hz), 7.13 (dt, 2H, *J* = 6.7 Hz, *J* = 14.9 Hz), 4.06 (d, 1H, *J* = 5.0 Hz), 4.02 (dd, 1H, *J* = 5.6 Hz, *J* = 6.6 Hz), 3.73 (s, 3H), 3.05 (qd, 2H, *J* = 6.5 Hz, *J* = 15.7 Hz, *J* = 44.4 Hz), 2.21 (bs, 1H), 1.85-1.62 (m, 6H), 1.36-1.12 (m, 5H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 174.5, 135.7, 134.5, 127.0, 121.5, 119.3, 117.9, 110.6, 107.7, 55.2, 53.3, 52.0, 43.1, 30.2, 28.4, 26.5, 26.4, 26.3, 24.9. Analytical data fits with literature.[1]

(S)-methyl 2-(cyclohexylmethylamino)-3-(1H-indol-3-yl)propanoate, (Table 1, Entry 9), (4b). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 1H-NMR (400 MHz), 8.80 (s, 1H), 7.62 (d, 1H, *J* = 7.8 Hz), 7.28 (d, 1H, *J* = 8.0 Hz), 7.15 (dt, 2H, *J* = 7.1 Hz, *J* = 22.7 Hz), 6.95 (d, 1H, *J* = 1.2 Hz), 3.67 (t, 1H, *J* = 6.7 Hz), 3.64 (s, 3H), 3.19 (qd, 2H, *J* = 6.7 Hz, *J* = 14.4 Hz), 2.41 (ddd, 2H, *J* = 6.8 Hz, *J* = 11.3 Hz, *J* = 17.7 Hz), 1.85 (bs, 1H), 1.72-1.59 (m, 5H, *J* = 8.9Hz), 1.47-1.34 (m, 1H),1.24-1.04 (m, 3H), 0.89-0.76 (m, 2H). ^{13}C-NMR ($CDCl_3$, 100 MHz) 175.4, 136.0, 127.1, 122.9, 121.6, 118.9, 118.4, 111.1, 110.4, 62.1, 54.7, 51.5, 37.7, 31.01, 30.9, 29.0, 26.3, 25.7, 25.6. HRMS: m/z (ESI) calc for $C_{19}H_{27}N_2O_2$ ($M+H^+$) 315.20670, found 315.20630. IR(film): ν [cm^{-1}] = 3421 (s), 2843 (s), 2843 (s), 1746 (vs), 1444 (vs), 1354 (m), 1267 (m), 1214 (m), 1010 (m), 748 (s).

(S)-methyl 2-(bis(cyclohexylmethyl)amino)-3-(1H-indol-3-yl)propanoate, (Table 1, Entry 9), (5b). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 8.01 (s, 1H), 7.57 (d, 1H, *J* = 7.7 Hz), 7.32 (d, 1H, *J* = 8.0 Hz), 7.14 (dt, 2H, *J* = 7.0 Hz, *J* = 22.0 Hz), 6.97 (d, 1H, *J* = 1.9 Hz), 3.69 (dd, 1H, *J* = 4.2 Hz, *J* = 10.1 Hz), 3.57 (s, 3H), 3.26 (dd, 1H, *J* = 10.1 Hz, *J* = 14.1 Hz), 2.92 (dd, 1H, *J* = 4.0 Hz, *J* = 14.1 Hz), 2.40 (dd, 2H, *J* = 9.1 Hz, *J* = 12.9 Hz), 2.28 (dd, 2H, *J* = 5.2 Hz, *J* = 12.9 Hz), 1.92 (d, 2H, *J* = 12.7 Hz), 1.75-1.61 (m, 8H), 1.43-

[1] Ungemach, F; Soerens, D.; Weber, R.; DiPierro, M.;Campos, O.; Mokry, P.; Cook, J. M. *J. Am. Chem. Soc,* **1980***, 102,* 6976.

1.33(m, 2H), 1.28-1.09 (m, 6H), 0.90-0.75 (m, 4H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 173.2, 136.2, 127.4, 122.6, 121.7, 119.2, 118.4, 112.7, 111.1, 63.4, 58.5, 50.7, 36.2, 31.6, 26.9, 26.2, 26.1, 25.6. HRMS: m/z (ESI) calc for $C_{26}H_{39}N_2O_2$ ($M+H^+$) 411.30061, found 411.30012. IR (film): ν [cm^{-1}] = 3415 (m), 2935 (vs), 2850 (vs), 1740 (vs), 1451 (s), 1352 (w), 1221 (w), 741 (s).

(1R,3S)-methyl 1-cyclohexyl-2-(cyclohexylmethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole-3-carboxylate, (Table 1, Entry 9), (6b). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.73 (s, 1H), 7.52 (d, 1H, *J* = 7.6 Hz), 7.30 (d, 1H, *J* = 7.9 Hz), 7.12 (td, 2H, *J* = 7.1 Hz, *J* = 22.1 Hz), 4.00 (dd, 1H, *J* = 4.8 Hz, *J* = 10.5 Hz), 3.74 (s, 3H), 3.39 (d, 1H, *J* = 8.5 Hz), 3.09 (dd, 1H, *J* = 10.6 Hz, *J* = 15.8 Hz), 2.82 (dd, 1H, *J* = 4.8 Hz, *J* = 15.9 Hz), 2.36 (d, 1H, *J* = 12.8Hz), 2.26-2.12 (m, 3H), 1.94-1.60 (m, 9H), 1.40-1.00 (m, 9H), 0.83-0.70 (m, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 173.8, 135.7, 134.5, 126.9, 121.4, 119.3, 118.0, 110.5, 107.8, 63.2, 57.2, 55.9, 51.7, 42.0, 36.6, 31.6, 31.4, 30.9, 30.7, 26.9, 26.8, 26.5, 26.4, 26.3, 26.2, 26.1, 20.1. HRMS: m/z (ESI) calc for $C_{26}H_{37}N_2O_2$ ($M+H^+$) 409.28496, found 409.28483. IR(film): ν [cm^{-1}] = 3454 (w), 2916 (s), 2850 (s), 1740 (vs), 1451 (s), 1260 (m), 1076 (m), 741 (vs).

(S)-methyl 2-(cyclohexylmethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole-3-carboxylate, (Table 1, Entry 9), (7b). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.76 (s, 1H), 7.45 (d, 1H, *J* = 7.4 Hz), 7.26 (d, 1H, *J* = 7.8 Hz), 7.09 (tt, 2H, *J* = 6.7 Hz, *J* = 13.6 Hz), 4.13 (d, 1H, *J* = 15.1 Hz), 3.90 (d, 1H, *J* = 15.1 Hz), 3.84 (dd, 1H, *J* = 4.1 Hz, *J* = 5.9 Hz), 3.62 (s, 3H), 3.12 (qd, 2H, *J* = 4.9 Hz, *J* = 15.5 Hz), 2.57 (ddd, 2H, *J* = 7.1 Hz, *J* = 12.8 Hz, *J* = 20.7 Hz), 1.87 (d, 1H, *J* = 12.7 Hz), 1.76-1.60 (m, 4H), 1.59-1.47 (m, 1H), 1.30-1.11 (m, 3H), 0.94-0.80 (m, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 173.5, 136.0, 131.9, 127.1, 121.3, 119.2, 117.8, 110.6, 106.2, 61.3, 60.3, 51.4, 46.8, 36.2, 31.6, 26.8, 26.1, 26.0, 23.7; HRMS: m/z (ESI) calc for $C_{20}H_{27}N_2O_2$ ($M+H^+$) 327.20670, found 327.20631; IR (film): ν [cm^{-1}] = 3395 (s), 2935 (s), 2837 (s), 1733 (vs), 1628 (w), 1451 (s), 1155 (m), 1010 (m), 741 (s).

The general procedure was followed with (S)-tryptophanmethylester (218 mg, 1 mmol), cycloheptene (97 mg, 1 mmol) and $Rh(acac)(CO)_2$ (3.6 mg, 0.01 mmol) in 10 ml of DCM under 50 bar CO and 10 bar H_2 at 80 °C for 72 h (Table 1, Entry 10). The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexan/ethylacetat = 10/1) to give 101 mg (31 %) of **2c**, 130 mg (40 %) of **3c** and 72 mg (22 %) of 4**c.**

(1S,3S)-methyl 1-cycloheptyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole-3-carboxylate, (Table 1, Entry 10), (2c). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.88 (s, 1H) ppm 7.47 (d, 1H, *J* = 7.6 Hz), 7.32 (d, 1H, *J* = 7.8 Hz), 7.12 (dt, 2H, *J* = 7.2 Hz, *J* = 21.0 Hz), 4.19 (s, 1H), 3.81 (s, 3H), 3.72 (dd, 1H, *J* = 4.0 Hz, *J* = 11.1 Hz), 3.10 (dd, 1H, *J* = 2.5 Hz, *J* = 14.8 Hz), 2.82-2.72 (m, 1H), 2.05-1.96 (m, 2H), 1.83-1.71 (m, 2H), 1.70-1.28 (m, 12H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 173.8, 135.9, 135.1, 127.2, 121.6, 119.4, 117.8, 1.7, 109.3, 59.2, 56.4, 52.1, 43.3, 31.6, 28.7, 28.1, 27.8, 27.5, 27.5, 25.9. HRMS: m/z (ESI) calc for $C_{20}H_{27}N_2O_2$ ($M+H^+$) 327.20670, found 327.20607. IR(film): ν [cm^{-1}] = 3375 (m), 3054 (w), 2922 (s), 1733 (vs), 1464 (s), 1325 (m), 1260 (m), 1214 (m), 754 (m).

(1R,3S)-methyl 1-cycloheptyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole-3-carboxylate, (Table 1, Entry 10), (3c). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.76 (s, 1H), 7.48 (d, 1H, *J* = 7.5 Hz), 7.29 (d, 1H, *J* = 7.8 Hz), 7.11 (dt, 2H, *J* = 7.1 Hz, *J* = 20.0 Hz), 4.28 (s, 1H), 4.02 (t, 1H, *J* = 5.0 Hz), 3.65 (s, 3H), 3.15-3.06 (m, 2H), 2.01-1.92 (m, 2H), 1.91-1.71 (m, 2H), 1.70-1.23 (m, 12H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 174.7, 135.8, 134.4, 127.1, 121.6, 121.5, 119.5, 119.3, 117.9, 117.9, 110.7, 110.6, 108.0, 55.6, 53.9, 51.9, 44.7, 31.8, 29.2, 28.2, 27.8, 27.6, 27.3, 24.2. HRMS: m/z (ESI) calc for $C_{20}H_{27}N_2O_2$ ($M+H^+$) 327.20670, found 327.20618. IR(film): ν [cm^{-1}] = 3389 (m), 2929 (s), 2850 (s), 1733 (vs9, 1621 (w), 1451 (s), 1339 (m), 1267 (s), 1214 (s), 1017 (w), 735 (s).

(S)-methyl 2-(cycloheptylmethylamino)-3-(1H-indol-3-yl)propanoate, (Table 1, Entry 10), (4c). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 8.27 (s, 1H), 7.60 (d, 1H, *J* = 7.8

Hz), 7.31 (d, 1H, *J* = 8.0 Hz), 7.13 (dt, 1H, *J* = 7.2 Hz, J = 25.8 Hz), 7.00 (d, 1H, *J* = 1.5 Hz), 3.61 (s, 3H), 3.59 (t, 1H, *J* = 6.7 Hz), 3.13 (qd, 2H, *J* = 6.7 Hz, *J* = 14.4 Hz), 2.36 (ddd, 2H, *J* = 6.8 Hz, *J* = 11.2 Hz, *J* = 43.8 Hz), 1.75-1.20 (m, 12H), 1.07 (dd, 2H, *J* = 10.2 Hz, *J* = 21.4 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 175.6, 136.1, 127.4, 122.7, 121.9, 119.3, 118.7, 111.2, 111.1, 62.3, 55.2, 51.6, 39.5, 32.5, 32.3, 29.2, 28.4, 28.4, 26.4, 26.4; HRMS: m/z (ESI) calc for $C_{20}H_{29}N_2O_2$ ($M+H^+$) 329.22235, found 329.22250. IR(film): ν [cm^{-1}] = 3408 (m), 2922 (s), 2843 (s), 1733 (vs), 1457 (s), 1352 (m), 1267 (m), 1241 (m), 741 (s).

(S)-methyl 2-(cyclooctylmethylamino)-3-(1H-indol-3-yl)propanoate, (Table 1, Entry 11), (4d). The general procedure was followed with (S)-tryptophan methylester (218 mg, 1 mmol), cyclooctene (110 mg, 1 mmol) and $Rh(acac)(CO)_2$ (3.6 mg, 0.01 mmol) in 10 ml of DCM under 50 bar CO and 10 bar H_2 at 80 °C for 72 h (Table 1, entry 11). The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexan/ethylacetat = 10/1) to give 147 mg (43 %) of title compound as brownish oil. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 8.29 (s, 1H), 7.60 (d, 1H, J=7.8Hz), 7.31 (d, 1H, J=8.0Hz), 7.13 (dt, 2H, J=7.1Hz, J=26.3Hz), 7.01 (d, 1H, J=1.8Hz), 3.61 (s, 3H), 3.58 (d, 1H, J=6.7Hz), 3.13 (qd, 2H, J=6.7Hz, J=14.4Hz), 2.40 (dd, 1H, J=7.1Hz, J=11.2Hz), 2.27 (dd, 1H, J=6.4Hz, J=11.1Hz), 2.05-1.80 (m, 2H), 1.65-1.27 (m, 12H), 1.22-1.09 (m, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 175.5, 136.1, 127.3, 122.8, 121.9, 119.3, 118.7, 111.2, 111.1, 62.3, 55.6, 51.6, 37.5, 30.8, 30.5, 29.2, 26.9, 26.3, 25.5, 25.3; HRMS: m/z (ESI) calc for $C_{21}H_{31}N_2O_2$ ($M+H^+$) 343.23801, found 343. 23755; IR(film): ν [cm^{-1}] = 3402 (m), 2922 (s), 2850 (s), 2364 (w), 1733 (vs), 1451 (s), 1345 (m), 1194 (m), 1010 (w), 748 (s).

The general procedure was followed with (S)-Tryptophanmethylester (218 mg, 1 mmol), 1,1´diphenylethylene (180 mg, 1 mmol) and $Rh(acac)(CO)_2$ (3.6 mg, 0.01 mmol) in 8 ml of DCM. The crude reaction mixture was purified by flash column chromatography on silica gel (Cyclohexan/Ethylacetat = 10/1) to give 275 mg (67 %) of mixture of diastereoisomers **2e+3e**, and 72 mg (17 %) of **4e**.

1-(2,2-Diphenyl-ethyl)-2,3,4,9-tetrahydro-1H-b-carboline-3-carboxylic acid methyl ester (mixture of *cis* and *trans*), (Table 1, Entry 12), (2e+3e). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.56 (bs, 1H), 7.46 (bs, 1H), 7.44 (d, 2H, *J* = 7.7 Hz), 7.38-7.02 (m, 26H), 4.42-4.34 (m, 2H), 4.08-4.00 (m, 2H), 3.91 (dd, 1H, *J* = 4.9 Hz, *J* = 9.1 Hz), 3.78 (s, 3H), 3.73 (s, 3H), 3.63 (dd, 1H, *J* = 4.2 Hz, *J* = 11.1 Hz), 3.06 (dd, 2H, *J* = 4.5 Hz, *J* = 15.3 Hz), 2.84-2.66 (m, 3H), 2.47-2.41 (m, 2H), 2.35 (ddd, 1H, *J* = 4.7 Hz, *J* = 9.0 Hz, *J* = 13.7 Hz), 1.82 (bs, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm174.1, 173.6, 144.6, 144.5, 144.3, 143.6, 135.9, 135.7, 135.5, 135.3, 128.9, 128.8, 128.6, 128.5, 128.2, 127.7, 127.6, 127.1, 126.9, 126.7, 126.6, 126.3, 121.8, 119.6, 119.5, 117.9, 110.7, 110.7, 108.2, 107.2, 56.4, 52.1, 52.0, 51.9, 51.1, 48.6, 47.8, 47.4, 41.4, 41.3, 25.9, 25.6; HRMS: m/z (ESI) calc for $C_{27}H_{27}N_2O_2$ ($M+H^+$) 411.20670, found 411.20654; IR(film): ν [cm^{-1}] = 3054 (m), 2916 (m), 2850 (m), 1950 (w), 1815 (w), 1733 (vs), 1680 (s) 1490 (s), 1425 (s), 1345 (m), 1260 (vs), 1010 (m), 754 (s), 708 (s).

(S)-methyl 2-(3,3-diphenylpropylamino)-3-(1H-indol-3-yl)propanoate, (Table 1, Entry 12), (4e). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 8.31 (s, 1H), 7.64 (d, 1H, *J* = 7.8 Hz), 7.33 (d, 1H, *J* = 8.0 Hz), 7.27-7.12 (m, 10H), 7.09 (d, 2H, *J* = 7.1 Hz), 6.96 (d, 1H, *J* = 1.9 Hz), 3.91 (t, 1H, *J* = 7.8 Hz), 3.61 (s, 3H), 3.59 (d, 1H, *J* = 7.4 Hz), 3.15 (qd, 2H, *J* = 6.6Hz, *J* = 14.3 Hz, *J* = 21.6 Hz), 2.63 (dt, 1H, *J* = 7.0 Hz, *J* = 11.5 Hz), 2.42 (dt, 1H, *J* = 7.1 Hz, *J* = 11.5 Hz), 2.18 (qd, 2H, *J* = 2.8 Hz, *J* = 7.5 Hz, *J* = 14.2 Hz), 1.77 (bs, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 175.2, 144.5, 144.4, 136.1, 128.3, 127.7, 127.6, 127.3, 126.0, 125.9, 122.8, 121.9, 119.3, 118.6, 111.2, 110.9, 61.9, 51.6, 48.4, 46.2, 35.5, 29.2; HRMS: m/z (ESI) calc for $C_{27}H_{29}N_2O_2$ ($M+H^+$) 413.22235, found 413.22155; IR(film): ν [cm^{-1}] = 3421 (s), 3054 (w), 2916 (m), 2850 (m), 1950 (w), 1884 (w), 1800 (w), 1733 (vs), 1490 (s), 1451 (s), 1345 (m), 1260 (m), 1010 (m), 754 (s), 702 (s).

The general procedure was followed with (S)-Tryptophanmethylester (218 mg, 1 mmol), *trans*-stilbene (180 mg, 1 mmol) and $Rh(acac)(CO)_2$ (3.6 mg, 0.01 mmol) in 8 ml of DCM. The crude reaction mixture was purified by flash column chromatography on silica gel (Cyclohexan/Ethylacetat = 10/1) to give 138 mg (34 %) of **2f** and 136 mg (33 %) **3f**, and 169 mg (41 %) of **4f**.

(1S,3S)-methyl 2,3,4,9-tetrahydro-1-((S)-1,2-diphenylethyl)-1H-pyrido[3,4-b]indole-3-carboxylate, (Table 1, Entry 13), (2f). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.66 (bs, 1H), 7.46 (d, 1H, *J* = 6.5 Hz), 7.35-6.95 (m, 11H), 6.88 (d, 2H, *J* = 6.7 Hz), 4.54 (d, 1H, *J* = 7.3 Hz), 3.83 (s, 3H), 3.76 (dd, 1H, *J* = 3.9 Hz, *J* = 11.2 Hz), 3.35 (dd, 1H, *J* = 3.3 Hz, *J* = 13.5 Hz), 3.25-3.05 (m, 3H), 2.92-2.82 (m, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 173.6, 141.3, 139.8, 135.5, 134.3, 129.0, 128.9, 128.8, 127.9, 127.4, 126.6, 125.7, 121.8, 119.4, 117.9, 110.8, 109.4, 57.7, 56.5, 53.0, 52.2, 37.6, 25.9; HRMS: m/z (ESI) calc for $C_{27}H_{27}N_2O_2$ ($M+H^+$) 411.20670, found 411.20665; IR(film): ν [cm^{-1}] = 3415 (m), 2922 (s), 2843 (s), 1700 (vs), 1654 (vs), 1457 (s), 1352 (m), 1260 (vs), 1037 (m), 754 (s).

(1R,3S)-methyl 2,3,4,9-tetrahydro-1-((R)-1,2-diphenylethyl)-1H-pyrido[3,4-b]indole-3-carboxylate, (Table 1, Entry 13), (3f). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.55 (s, 1H), 7.43 (d, 1H, J=8.0Hz), 7.40-7.0 (m, 11H), 6.93 (d, 2H, J=6.8Hz), 4.47 (d, 1H, J=9.2Hz), 4.02 (dd, 1H, J=5.1Hz, J=8.3Hz), 3.76 (s, 3H), 3.54 (dd, 1H, J=3.5Hz, J=13.6Hz), 3.19 (td, 1H, J=3.7Hz, J=10.2Hz), 3.13 (dd, 1H, J=4.9Hz, J=15.4Hz), 3.04-2.90 (m, 2H), 2.11 (bs, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 174.3, 142.1, 140.3, 135.6, 134.5, 129.2, 129.0, 128.9, 128.1, 127.3, 126.6, 125.8, 121.8, 119.3, 118.0, 110.7, 108.1, 55.9, 53.1, 52.5, 52.3, 39.1, 25.7; HRMS: m/z (ESI) calc for $C_{27}H_{27}N_2O_2$ ($M+H^+$) 411.20670, found 411.20676; IR(film): ν [cm^{-1}] = 3435 (m), 2922 (s), 2847 (s), 1720 (vs), 1624 (vs), 1457 (s), 1352 (m), 1267 (vs), 1024 (w), 728 (s).

(S)-methyl 2-(2,3-diphenylpropylamino)-3-(1H-indol-3-yl)propanoate, (Table 1, Entry 13), (4f). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 8.04, 7.97 (2s, 1H), 7.54 (t, 1H, *J* = 6.9 Hz), 7.28 (dd, 1H, *J* = 4.2 Hz, *J* = 8.0 Hz), 7.22-7.06 (m, 8H), 7.03 (d, 1H, *J* = 6.9 Hz), 6.98 (t, 1H, *J* = 6.7 Hz), 6.89 (d, 1H, *J* = 6.5 Hz), 6.82, 6.72 (2d, 1H, *J* = 1.7 Hz), 3.62-3.50 (m, 4H), 3.13 (dd, 0.5H, *J* = 5.4 Hz, *J* = 14.4 Hz), 3.08-2.70 (m, 6H), 2.64 (dd, 0.5H, *J* = 7.9 Hz, *J* = 10.9 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 175.0, 174.9, 142.8, 142.5, 140.0, 139.9, 136.1, 136.0, 129.0, 128.9, 128.3, 128.2, 128.0, 127.9, 127.7, 127.7, 127.3, 127.1, 126.4, 126.3, 125.8, 125.7, 122.8, 122.6, 122.0, 121.9, 119.3, 118.6, 118.6, 111.1, 111.1, 111.0, 110.9, 77.3, 77.0, 76.7, 62.1, 62.0, 52.9, 52.3, 51.7, 51.6, 47.7, 47.6,

41.2, 40.6, 29.2, 28.7; HRMS: m/z (ESI) calc for $C_{27}H_{29}N_2O_2$ ($M+H^+$) 413.22235, found 413.22195; IR(film): ν [cm^{-1}] = 3428 (m), 3034 (m), 2922 (m), 2850 (m), 2370 (w), 1937 (w), 1733 (vs9, 1464 (s9, 1208 (m), 741 (s) , 659 (s).

General procedure for tandem Hydroformylation/Pictet-Spengler reaction under protic conditions

In a thick walled sample vial containing PTFE septum Tryptamine (1 equiv.), olefin (1 equiv.), $Rh(acac)(CO)_2$ (0.01 equiv.), and Bronsted acid (1 equiv) were dissolved in dry solvent (8 mL). The vial was placed in a pressure vessel , flushed with argon and pressurized with 50 bar CO and 10 bar H_2. The reaction mixture was stirred for 3 days at 80 °C or 110 °C. Reaction was quenched with ammonia solution (30% in water) and the aqueous phase was extracted with 4x10 mL DCM. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (DCM/MeOH) to give the desired product.

1-Cyclopentyl-2, 3, 4, 9-tetrahydro-1H-b-carboline, (Table 2, Entry 1), (10a). The general procedure was followed with tryptamine (160 mg, 1 mmol), cyclopenten (68 mg, 1 mmol), $Rh(acac)(CO)_2$ (3.6 mg, 0.01 mmol) and camphor sulphonicacid (218 mg, 1 mmol) in 8 ml of DCM. The crude reaction mixture was purified by flash column chromatography on silica gel (DCM/MeOH/triethylamine = 20/1/0.1) to give (156 mg, 65 % yield) of the title compound as yellowish oil; ^{1}H-NMR ($CDCl_3$, 500 MHz) δ ppm 7.99 (s, 1H), 7.50 (d, 1H, *J* = 7.7 Hz), 7.32 (d, 1H, *J* = 7.9 Hz), 7.14 (dt, 2H, *J* = 7.3 Hz, *J* = 26.4 Hz), 3.93 (d, 1H, *J* = 7.4 Hz), 3.37 (dt, 1H, *J* = 4.7 Hz, *J* = 12.5 Hz), 3.06-3.00 (m, 1H), 2.82-2.72 (m, 2H), 2.41 (bs, 1H), 2.27 (q, 1H, *J* = 7.4 Hz), 2.00-1.92 (m, 1H), 1.84 (dtd, 1H, *J* = 3.7 Hz, *J* = 7.6 Hz, *J* = 11.5 Hz), 1.79-1.50 (m, 6H), 1.38 (ddd, 1H, *J* = 8.6 Hz, *J* = 12.4 Hz, *J* = 17.7 Hz); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ ppm 135.9, 135.5, 127.2, 121.4, 119.2, 117.9, 110.6, 109.1, 56.9, 44.4, 42.3, 29.8, 29.3, 25.8, 25.2, 22.5; HRMS: m/z (FAB) calc for $C_{16}H_{21}N_2$ ($M+H^+$) 241.1699, found 241.1686; IR(film): ν [cm^{-1}] =

3421 (m), 3224 (m), 3047 (m), 2955 (m), 2581 (w), 2475 (w), 1667 (m), 1464 (s), 1418 (s), 1300 (s), 1254 (s), 1004 (m), 741 (vs).

1-Cyclohexyl-2,3,4,9-tetrahydro-1H-b-carboline, (Table 2, Entry 2), (10b). The general procedure was followed with tryptamine (160 mg, 1 mmol), cyclohexen (82 mg, 1 mmol), $Rh(acac)(CO)_2$ (3.6 mg, 0.01 mmol) and camphor sulphonicacid (218 mg, 1 mmol) in 8 ml of DCM at 110 °C for 72 h. The crude reaction mixture was purified by flash column chromatography on silica gel (DCM/MeOH/triethylamine = 20/1/0.1) to give (117 mg, 46 % yield) of the title compound as brown oil; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.81 (s, 1H), 7.39 (d, 1H, *J* = 7.6 Hz), 7.22 (d, 1H, *J* = 7.8 Hz), 7.02 (dt, 2H, *J* = 7.1 Hz, *J* = 14.9 Hz), 3.89 (s, 1H), 3.27 (dt, 1H, *J* = 4.3 Hz, *J* = 12.5 Hz), 2.92-2.83 (m, 1H), 2.70-2.56 (m, 2H), 1.80-1.00 (m, 11H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 135.5, 135.2, 127.5, 121.3, 119.2, 117.9, 110.6, 109.9, 57.7, 43.0, 42.2, 30.2, 27.5, 26.9, 26.8, 26.5, 26.4, 22.7. Analytical data fits with literature.[2]

1-Cycloheptyl-2,3,4,9-tetrahydro-1H-b-carboline, (Table 2, Entry 3), (10c). The general procedure was followed with tryptamine (160 mg, 1 mmol), cyclohepten (96 mg, 1 mmol), $Rh(acac)(CO)_2$ (3.6 mg, 0.01 mmol) and camphor sulphonicacid (218 mg, 1 mmol) in 8 ml of DCM. The crude reaction mixture was purified by flash column chromatography on silica gel (DCM/MeOH/triethylamine = 20/1/0.1) to give (182 mg, 68 % yield) of the title compound as brown oil; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.89 (s, 1H), 7.48 (d, 1H, *J* = 7.6 Hz), 7.31 (d, 1H, *J* = 7.9 Hz), 7.12 (dt, 2H, *J* = 7.3 Hz, *J* = 25.2 Hz), 4.10 (s, 1H), 3.40 (ddd, 1H, *J* = 1.8 Hz, *J* = 4.5 Hz, *J* = 12.0 Hz), 2.94 (ddd, 1H, *J* = 5.0 Hz, *J* = 10.1 Hz, *J* = 12.5 Hz), 2.80-2.64 (m, 2H), 2.16 (bs, 1H), 2.02-1.93 (m, 1H), 1.84-1.28 (m, 12H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 135.6, 135.3, 127.5, 121.3, 119.2, 117.9, 110.6, 110.3, 59.3, 43.6, 43.3, 32.0, 28.7, 28.2, 27.7, 27.5, 22.6; HRMS: m/z (FAB) calc for $C_{18}H_{25}N_2$ ($M+H^+$) 269.2012, found 269.1997; IR(film): ν [cm^{-1}] = 3415 (m), 3283(m), 2935 (m), 2364 (w), 1917 (w), 1674 (s), 1608 (s), 1464 (s), 1319 (m), 1201 (m), 991 (m), 748 (s).

[2] Gremmen, C.; Willemse, B.; Wanner, M. J.; Koomen, G. J.; *Org. Lett.* **2000**; 1955 - 1958.

1-Cyclooctyl-2,3,4,9-tetrahydro-1H-b-carboline, (Table 2, Entry 4), (10d). The general procedure was followed with tryptamine (160 mg, 1 mmol), cycloocten (110 mg, 1 mmol), $Rh(acac)(CO)_2$ (3.6 mg, 0.01 mmol) and camphor sulphonicacid (218 mg, 1 mmol) in 8 ml of DCM. The crude reaction mixture was purified by flash column chromatography on silica gel (DCM/MeOH/triethylamine = 20/1/0.1) to give (166 mg, 59 % yield) of the title compound as brown oil; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 8.04 (s, 1H) ppm 7.51 (d, 1H, *J* = 7.6 Hz), 7.33 (d, 1H, *J* = 7.8 Hz), 7.15 (dt, 2H, *J* = 6.9 Hz, *J* = 20.2 Hz), 4.08 (s, 1H), 3.42 (ddd, 1H, *J* = 2.0 Hz, *J* = 4.5 Hz, *J* = 12.0 Hz), 2.95 (ddd, 1H, *J* = 5.0 Hz, *J* = 10.0 Hz, *J* = 12.5 Hz), 2.83-2.68 (m, 2H), 2.24-2.02 (m, 1H), 1.86-1.30 (m, 14H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 135.6, 135.3, 127.4, 121.2, 119.1, 117.8, 110.6, 110.4, 60.1, 43.5, 41.2, 31.7, 27.9, 27.4, 26.6, 25.6, 25.5, 22.6; HRMS: m/z (FAB) calc for $C_{19}H_{25}N_2$ ($M\text{-}H^+$) 281.2023, found 281.1996; IR(film): ν [cm^{-1}] = 3408 (m), 3237 (m), 3040 (m), 2916 (s), 2856 (s), 2686 (w), 2357 (w), 1924 (w), 1621 (s), 1464 (s), 1326 (m), 1260 (m), 741 (s).

1-(2,2-Diphenyl-ethyl)-2,3,4,9-tetrahydro-1H-b-carboline, (Table 2, Entry 5), (10e). The general procedure was followed with tryptamine (160 mg, 1 mmol), 1,1´diphenylethen (180 mg, 1 mmol), $Rh(acac)(CO)_2$ (3.6 mg, 0.01 mmol) and camphor sulphonic acid (218 mg, 1 mmol) in 8 ml of DCM. The crude reaction mixture was purified by flash column chromatography on silica gel (DCM/MeOH/triethylamine = 10/1/0.1) to give (229 mg, 64 % yield) of the title compound as white solid; Mp:142-144 °C; ^{1}H-NMR (DMSO D6, 400 MHz) δ ppm 10.78 (s, 1H), 7.53 (d, 2H, *J* = 7.3 Hz), 7.37-7.30 (m, 6H), 7.26 (t, 2H, *J* = 7.7 Hz), 7.19 (t, 1H, *J* = 7.4 Hz), 7.13 (t, 1H, *J* = 7.3 Hz), 7.02 (t, 1H, *J* = 8.0 Hz), 6.93 (t, 1H, *J* = 7.4 Hz), 4.51 (dd, 1H, *J* = 3.3 Hz, *J* = 12.0 Hz), 3.68 (d, 1H, *J* = 10.7 Hz), 3.41 (bs, 1H), 3.12 (dt, 1H, *J* = 4.8 Hz, *J* = 12.6 Hz), 3.00-2.93 (m, 1H), 2.76 (ddd, 1H, *J* = 5.0 Hz, *J* = 7.4 Hz, *J* = 12.6 Hz), 2.62-2.49 (m, 2H), 2.03-1.94 (m, 1H); ^{13}C-NMR (DMSO D6, 100 MHz) δ ppm 146.1, 143.7, 137.3, 135.5, 128.3, 128.2, 128.1, 127.3, 127.1, 126.0, 125.7, 120.2, 118.0, 117.2, 110.7, 107.2, 49.7, 46.4, 41.4, 39.5, 22.4; HRMS: m/z (FAB) calc for $C_{25}H_{25}N_2$ ($M\text{+}H^+$) 353.2012, found 353.2032; IR(film): ν [cm^{-1}] = 3375 (m), 2929 (m), 2909 (m), 1602 (w), 1490 (s), 1464 (m), 1345 (m), 1313 (w), 1120 (s), 1010 (m), 741 (vs).

2,3,4,9-tetrahydro-1-(1,2-diphenylethyl)-1H-pyrido[3,4-b]indole, (Table 2, Entry 6), (10f). The general procedure was followed with tryptamine (160 mg, 1 mmol), *trans*-1,2 diphenylethylen (180 mg, 1 mmol), $Rh(acac)(CO)_2$ (3.6 mg, 0.01 mmol) and camphor sulphonicacid (218 mg, 1 mmol) in 8 ml of DCM. The crude reaction mixture was purified by flash column chromatography on silica gel (DCM/MeOH/triethylamine = 20/1/0.1) to give (173 mg, 49 % yield) of the title compound as white solid; Mp: 128-129 °C; ^{1}H-NMR (DMSO D6, 400 MHz) δ ppm 10.87 (s, 1H), 7.28-7.15 (m, 8H), 7.08 (t, 1H, *J* = 7.0 Hz), 7.01 (t, 2H, *J* = 7.4 Hz), 6.98-6.90 (m, 2H), 6.83 (t, 1H, *J* = 7.3 Hz), 4.16 (s, 1H), 3.75 (dt, 1H, *J* = 3.1 Hz, *J* = 7. 8Hz), 3.30-3.22 (m, 1H), 3.15 (dd, 1H, *J* = 8.5 Hz, J = 13.7 Hz), 2.86 (dt, 1H, *J* = 4.5 Hz, *J* = 11.8 Hz), 2.68 (ddd, 1H, *J* = 4.6 Hz, *J* = 7.9 Hz, *J* = 12.3Hz), 2.41-2.33 (m, 1H), 2.30-2.20 (m, 1H); ^{13}C-NMR (DMSO D6, 100 MHz) δ ppm 140.8, 140.7, 135.6, 135.5, 129.1, 128.9, 127.9, 127.3, 126.9, 125.8, 125.7, 120.1, 117.9, 117.2, 110.7, 108.4, 55.3, 48.7, 42.1, 38.1, 22.3; HRMS: m/z (FAB) calc for $C_{25}H_{25}N_2$ ($M+H^+$) 353.2012, found 353.2011; IR(film): ν [cm^{-1}] = 3421 (m), 3290 (w), 3054 (m), 2962 (s), 2922 (s), 2344 (w9, 1871 (w), 1700 (m), 1602 (m), 1541 (vs), 1267 (m), 1102 (m), 1004 (m), 740 (vs).

N-Ethyl-4-methyl-N-[2-methyl-3-(2,3,4,9-tetrahydro-1H-b-carbolin-1-yl)-propyl]-benzene sulfonamide, (Table 2, Entry 7), (10g). The general procedure was followed with tryptamine (160 mg, 1 mmol), N-Ethyl-4-methyl-N-(2-methyl-allyl)-benzenesulfonamide (253 mg, 1 mmol), $Rh(acac)(CO)_2$ (3.6 mg, 0.01 mmol) and camphor sulphonicacid (218 mg, 1 mmol) in 8 ml of DCM. The crude reaction mixture was purified by flash column chromatography on silica gel (DCM/MeOH/triethylamine = 9/1/0.1) to give (315 mg, 74 % yield) of the title compound as yellowish oil. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 8.37 (s, 1H), 7.66 (d, 2H, *J* = 8.1 Hz), 7.45 (d, 1H, *J* = 7.6 Hz), 7.32 (d, 1H, *J* = 7.9 Hz), 7.24 (d, 2H, *J* = 8.0 Hz), 7.09 (dt, 2H, *J* = 7.1 Hz, *J* = 14.6 Hz), 4.16 (d, 1H, *J* = 5.2 Hz), 3.31-3.12 (m, 4H), 3.00 (td, 1H, *J* = 6.3 Hz, *J* = 12.9 Hz), 2.83 (dd, 1H, *J* = 7.2 Hz, *J* = 13.7 Hz), 2.73-2.67 (m, 2H), 2.37 (s, 3H), 2.24-2.15 (m, 1H), 1.94 (bs, 1H), 1.81 (ddd, 1H, *J* = 4.4 Hz, *J* = 9.3 Hz, *J* = 13.8 Hz), 1.64-1.59 (m, 1H), 1.01 (dd, 6H, *J* = 6.9 Hz, *J* = 16.4 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 143.2, 136.9,

136.3, 135.7, 129.6, 127.4, 127.1, 121.4, 119.2, 117.9, 110.9, 108.8, 53.8, 49.9, 43.3, 42.1, 39.1, 28.8, 22.8, 21.4, 18.0, 13.4; HRMS: m/z (FAB) calc for $C_{24}H_{32}N_3O_2S$ ($M+H^+$) 426.2215, found 426.2224; IR(film): ν [cm^{-1}] = 3380 (s), 2925 (s),1610 (w), 1448 (vs), 1132 (vs), 1080 (m), 745 (s).

2-[2-Methyl-3-(2,3,4,9-tetrahydro-1H-b-carbolin-1-yl)-propyl]-isoindole-1,3-dione, (Table 2, Entry 8), (10h). The general procedure was followed with tryptamine (160 mg, 1 mmol), 2-(2-Methyl-allyl)-isoindole-1,3-dione (201 mg, 1 mmol), $Rh(acac)(CO)_2$ (3.6 mg, 0.01 mmol) and camphor sulphonicacid (218 mg, 1 mmol) in 8 ml of DCM. The crude reaction mixture was purified by flash column chromatography on silica gel (DCM/MeOH/triethylamine = 9/1/0.1) to give (307 mg, 82 % yield) of the title compound as yellow solid. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ ppm 8.99, 8.64 (2s, 1H), 7.86 (dq, 2H, *J* = 3.0 Hz, *J* = 5.4 Hz, *J* = 13.0 Hz), 7.71 (ddd, 2H, *J* = 3.0 Hz, *J* = 5.5 Hz, *J* = 8.4 Hz), 7.47 (d, 1H, *J* = 7.7 Hz), 7.39 (dd, 1H, *J* = 8.0 Hz, *J* = 12.6 Hz), 7.15 (ddd, 1H, *J* = 1.5 Hz, *J* = 3.2 Hz, *J* = 9.2 Hz), 7.08 (t, 1H, *J* = 7.4 Hz), 4.25, 4.20 (dd, *J* = 3.0 Hz, *J* = 9.0 Hz; t, *J* = 7.4 Hz, 1H), 3.77 (d, 1H, *J* = 5.2 Hz), 3.71 (dd, 1H, *J* = 5.6 Hz, *J* = 13.7 Hz), 3.58 (dd, 1H, *J* = 8.8 Hz, *J* = 13.7 Hz), 3.30-3.26 (m, 1H), 3.09-3.01 (m, 1H), 2.72 (t, 2H, *J* = 5.7 Hz), 2.40-2.31 (m, 1H), 2.12 (bs, 1H), 1.85-1.70, 1.60-1.54 (2m, 1H), 1.01 (d, 3H, *J* = 6.8 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 169.3, 168.7, 136.4, 135.8, 135.7, 133.9, 131.8, 127.2, 123.2, 121.3, 121.2, 119.0, 117.8, 110.9, 110.8, 108.6, 50.3, 49.4, 43.6, 42.4, 41.4, 41.3, 40.2, 40.1, 30.5, 29.6, 22.7, 19.3, 18.2; HRMS: m/z (ESI) calc for $C_{23}H_{24}N_2O_3$ ($M+H^+$) 374.18630, found 374.18575; IR(film): ν [cm^{-1}] = 3395(s), 3054 (m), 2942 (s), 1772 (vs), 1713 (vs), 1621 (w), 1470 (s), 1267 (m), 1043 (vs), 748 (vs).

1-(3-Benzyloxy-2-methyl-propyl)-2,3,4,9-tetrahydro-1H-b-carboline, (Table 2, Entry 9), (10i). The general procedure was followed with tryptamine (160 mg, 1 mmol), (2-Methyl-allyloxymethyl)-benzene (162 mg, 1 mmol), $Rh(acac)(CO)_2$ (3.6 mg, 0.01 mmol) and camphor sulphonicacid (218 mg, 1 mmol) in 8 ml of DCM. The crude reaction mixture was purified by flash column chromatography on silica gel (DCM/MeOH/triethylamine = 10/1/0.1) to give (171 mg, 51 % yield) of the title

compound as yellow oil; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 8.64 (s, 1H), 7.45 (d, 1H, *J* = 7.4 Hz), 7.37-7.26 (m, 5H), 7.12-7.02 (m, 1H), 4.53 (d, 1H, *J* = 1.1 Hz) ppm 4.25 (t, 1H, *J* = 6.9 Hz), 3.48 (dd, 1H, *J* = 4.1 Hz, *J* = 9.0 Hz), 3.39 (t, 1H, *J* = 8.7 Hz), 3.32-3.25 (m, 1H), 3.09-3.01 (m, 1H), 2.75-2.60 (m, 3H), 2.17-2.08 (m, 1H), 1.82 (td, 2H, *J* = 3.1 Hz, *J* = 6.8 Hz), 0.97 (d, 3H, *J* = 6.8 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 137.8, 136.2, 135.4, 128.5, 127.8, 127.3, 121.2, 118.9, 117.8, 110.7, 108.1, 76.8, 73.4, 50.1, 41.2, 40.6, 30.3, 22.5, 17.9; HRMS: m/z (FAB) calc for $C_{22}H_{27}N_2O$ ($M+H^+$) 335.2118, found 335.2095; IR(film): ν [cm^{-1}] = 3336 (m), 3054 (w), 2870 (m),1713 (m), 1621 (m), 1451 (m), 1109 (s), 735 (s).

2,3,4,9-tetrahydro-1-isobutyl-1H-pyrido[3,4-b]indole, (11) This compound was obtained as a byproduct in the syntheses of the **10 g and 10h**, in the yields of 8% and 12% respectively.^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.89 (s, 1H), 7.49 (d, 1H, *J* = 7.5 Hz), 7.27 (d, 1H, *J* = 7.8 Hz), 7.12 (ddd, 2H, *J* = 7.1 Hz, *J* = 14.2 Hz, *J* = 14.8 Hz), 4.10 (dd, 1H, *J* = 6.1 Hz, *J* = 7.7 Hz), 3.34 (dt, 1H, *J* = 4.6 Hz, *J* = 12.7 Hz), 3.02 (ddd, 1H, *J* = 4.5 Hz, *J* = 7.9 Hz, *J* = 14.8 Hz), 2.80-2.68 (m, 2H), 2.05-1.90 (m, 1H), 1.73 (bs, 1H), 1.64-1.54 (m, 2H), 1.01 (dd, 6H, *J* = 6.6 Hz, *J* = 12.1 Hz), ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 136.7, 135.5, 127.5, 121.3, 119.2, 117.9, 110.6, 108.6, 50.4, 44.3, 42.4, 24.5, 23.8, 22.7, 21.6.Analytical data fits with literature.[3]

[3] Yamada, H.; Kawate, T.; Matsumizu, M.; Nishida, A.; Yamaguchi, K.; Nakagawa, M. *J. Org. Chem.* **1998**, 6348