Investigations into the Regioselectivity of Fischer Indole and Friedländer Quinoline Syntheses with Octahydroisobenzofuran and Octahydroisoindole Derivatives

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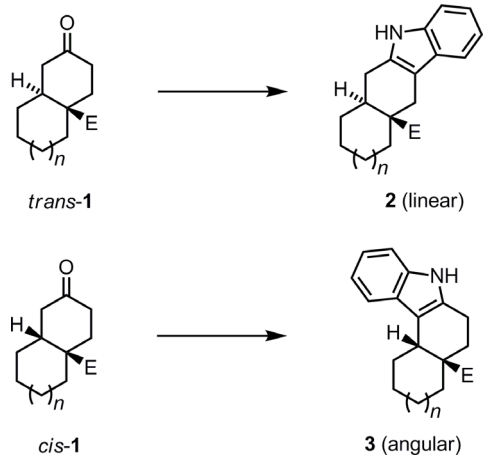
A Fischer indole synthesis with a *cis*-configurated octahydroisobenzofuran-6-one yielded exclusively a furo[3,4-*c*]carbazole derivative as the product of a regioselective angular annulation reaction. A Friedländer quinoline synthesis from the same substrate gave a mixture of angular and linear annulation products, *i. e.* furo[3,4-*a*]acridine and furo[3,4-*b*]acridine derivatives. When submitting a mixture of *cis*- and *trans*-octahydroisoindole derivatives to Fischer and Friedländer syntheses, the *trans*-starting material gave regioselectively linear annulation products, *i. e.* pyrrolo[3,4-*b*]carbazole and pyrrolo[3,4-*b*]acridine derivatives. In contrast, the respective *cis*-configurated isoindole gave mixtures of angular and linear annulation products. The constitutions and relative configurations of nine new indole and quinoline derivatives were established by 2D NMR experiments and X-ray single-crystal investigations.

Key words: Indoles, Quinolines, Isoindoles, Isobenzofurans, Carbazoles, Acridines, N-Heterocycles

Introduction

Indole [1 – 3] and quinoline [4, 5] derivatives are among the privileged structural motifs in medicinal chemistry. The to date still most efficient access to these heterocycles are the Fischer [6] and the Friedländer [7] syntheses both starting from ketones. Two regioisomeric products can be formed, when unsymmetrical ketones are submitted to these annulation procedures. We had recently investigated bicyclic ketones **1** regarding this regioselectivity. In the case of indole formation with phenyl hydrazine, highly regioselective annulation was observed [8 – 10], which was dependent on the relative configuration of starting materials (Scheme 1): ketones *trans*-**1** gave exclusively linear annulation products **2**, whereas diastereoisomeric *cis*-**1** yielded only the angular compounds **3**. When submitting the ketones *cis*- and *trans*-**1** to a Friedländer quinoline synthesis with *ortho*-aminobenzaldehyde, a less pronounced regioselectivity was observed [11, 12].



Scheme 1. Linear *versus* angular indole annulation of bicyclic ketones **1**. E = CO_2Et or CO_2Me; n = 0, 1, 2.

Very recently, we have developed an access to the enantiopure hexahydroisobenzofuran **6a** and the hexahydroisoindole derivative **6b** by a sequence of copper-catalyzed asymmetric Michael addition with L-valine diethylamide as chiral auxiliary [13] and aldol condensation [14] (Scheme 2). Compounds **6a** and **6b** were obtained with $>$ 99 % and 97 % *ee*, respectively.

Subject of the present study was an investigation into the regioselectivity of Fischer indole and Friedländer quinoline synthesis starting from an octahydroisobenzofuran **8a** and an octahydroisoindole

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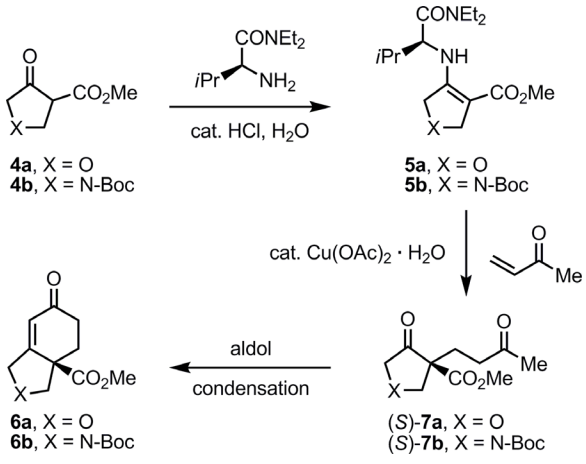
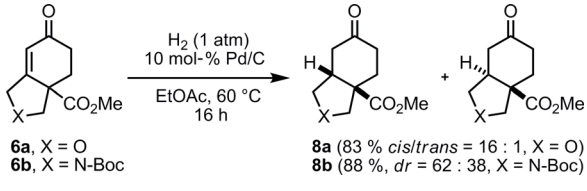


Scheme 2. Synthesis of enantiopure hexahydroisobenzofuran **6a** and -isoindole derivatives **6b** [14].

derivative **8b**, *i. e.* the hydrogenation products of enones **6a** and **6b**. Starting materials herein are used as racemates. Particular focus of the study was on the dependence of angular *versus* linear annulation from the relative *cis*- or *trans*-configuration of the hydrogenation products **8a** and **8b**.

Results and Discussion

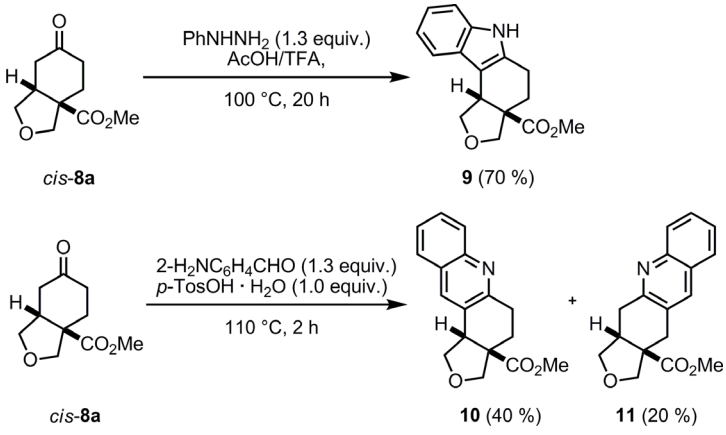
Enones **6a** and **6b** were prepared in the racemic series according to the literature procedure [14]. Hydrogenation of both substrates proceeded smoothly at ambient pressure, but elevated temperature (Scheme 3). Isobenzofuran derivative **8a** was obtained in 83 % yield as a mixture of two diastereoisomers with a high ratio of 16 : 1 (by NMR and GLC analysis), which could not be separated. This mixture was used in subsequent transformations, which revealed that the major diastereoisomer had *cis*-configuration (*vide infra*). Isoindole **8b** was obtained in 88 % yield and also as an inseparable mixture of diastereoisomers with moderate *dr* = 62 : 38. In this case, the relative configuration (*cis* or *trans*) could not be assigned.



Scheme 3. Hydrogenation of enones **6a** and **6b**.

Fischer indolization of compound **8a** with phenyl hydrazine was performed in a mixture of trifluoroacetic acid (TFA) and acetic acid (AcOH) at 100 °C in a tightly closed reaction flask (Scheme 4). After workup and chromatography, compound **9** was obtained as a single regio- and diastereoisomer with 70 % yield. The structure of this compound was established by NMR, with all proton and carbon resonances assigned by 2D experiments (HMBC, HMQC, H,H-COSY). The ABX system of 10c-H and the two 1-H protons was indicative of the angular constitution. Moreover, the two 3-H protons appeared as a characteristic AB system, and both 4-H and 5-H as an ABXY system. An X-ray single-crystal structure determination of this compound confirmed the angular constitution and moreover established the relative *cis*-configuration of both fused aliphatic rings (Fig. 1). The exclusive formation of an angular annulation product from a *cis*-configurated starting material is in perfect accordance with earlier observations with carbocyclic substrates [9].

In order to obtain quinoline derivatives, ketone *cis*-**8a** was converted into quinoline derivatives with freshly prepared *ortho*-aminobenzaldehyde and



Scheme 4. Fischer indole and Friedländer quinoline syntheses starting from octahydroisobenzofuran **8a**.

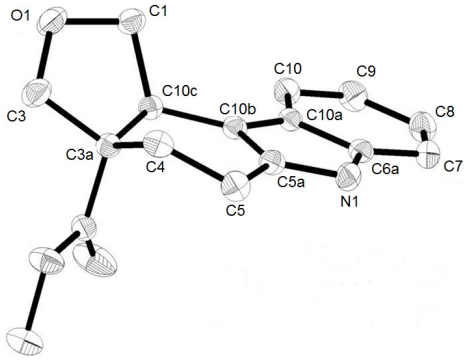


Fig. 1. ORTEP representation of the molecular structure of compound **9** in the solid state showing angular constitution and *cis*-configuration.

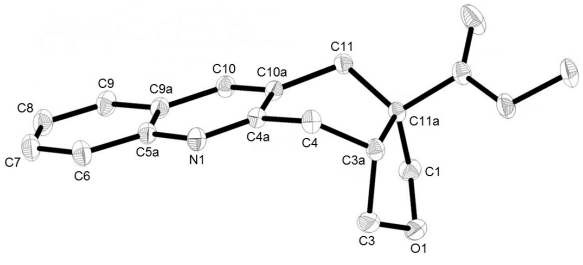
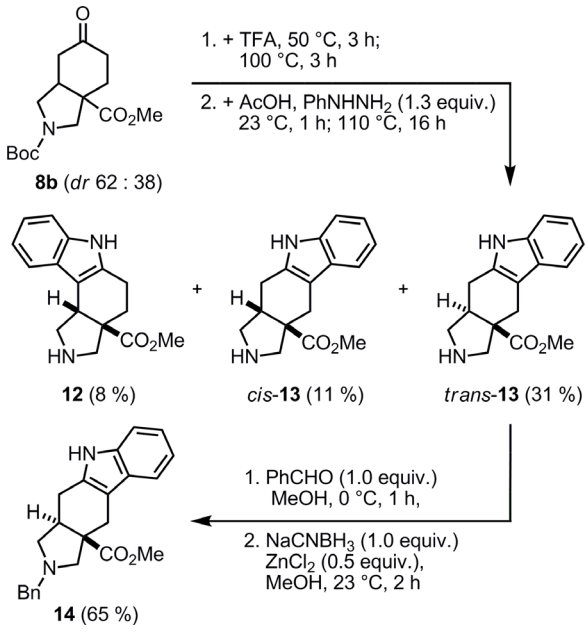


Fig. 2. ORTEP representation of the molecular structure of compound **11** in the solid state showing linear constitution and *cis*-configuration.

p-TosOH as acidic additive without use of a solvent, at elevated temperature in a tightly closed reaction flask (Scheme 4). After workup, the two annulation products **10** and **11** were obtained in 2 : 1 ratio and 60 % overall yield, and were separated by chromatography. The angular constitution of compound **10** was elucidated by comparison of its ^{1}H NMR spectra with those of compound **9**, where the same ABX, AB and ABXY spin systems were observed. The linear constitution of regioisomer **11** was already indicated by a characteristic AB system of both 11-H protons in the proton NMR spectrum. Moreover, it was unequivocally proved by an X-ray single-crystal structure determination (Fig. 2). Apart from the constitution, again a relative *cis*-configuration was observed. Lower regioselectivity of this Friedländer quinoline formation is again in accordance with earlier observations at carbocyclic systems [11].

A Fischer indolization could be conveniently achieved in a mixture of TFA and AcOH. A *tert*-butyl carbamate protective group would however be cleaved during such reaction conditions under formation of isobutene, which could undergo Friedel-



Scheme 5. Fischer indole synthesis starting from octahydroisoindole **8b**.

Crafts alkylations of the aromatic rings [10]. For this reason, we cleaved the Boc group of compound **8b** by heating it with TFA prior to its conversion with phenylhydrazine (Scheme 5). Starting material **8b** was submitted to this procedure as a mixture of diastereoisomers. After workup, the three products **12**, *cis*-**13** and *trans*-**13** were obtained in 8 %, 11 % and 31 % yield, respectively, and could be separated by chromatography. The constitution of all three products was unequivocally established by NMR spectroscopy. Spin systems in the proton NMR spectra of the angular (**12**) and linear (*cis*- and *trans*-**13**) compounds are similar to those of the isobenzofurans **9** – **11**. The relative configuration of the angular compound **12** was elucidated by NOE experiments: irradiation of 10c-H (δ = 3.87 ppm) indicated clearly its *syn*-relationship to the ester methyl group (δ = 3.68 ppm). Regarding the relative configuration of compound **13**, NOE experiments were not fruitful, since the 3a-H protons were in both cases overlapping with other signals. Anyhow, a crystalline derivative of the major isomer *trans*-**13** was obtained by reductive amination with benzaldehyde and a zinc-modified cyanoborohydride according to a literature procedure [15] furnishing the *N*-benzyl amine **14** (65 % yield, Scheme 5), which was submitted to X-ray single-crystal structure determination. Its ORTEP re-

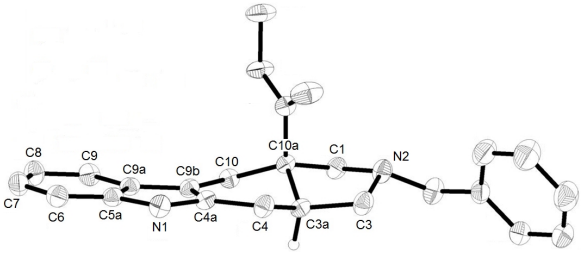


Fig. 3. ORTEP representation of the molecular structure of compound **14** in the solid state showing linear constitution and *trans*-configuration.

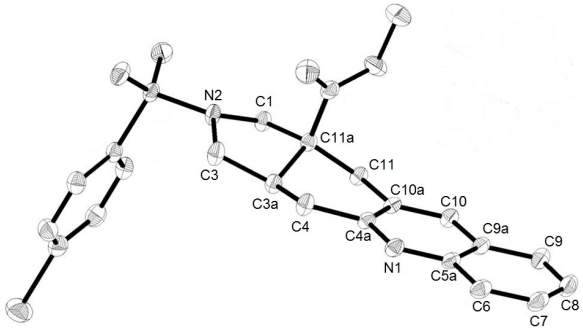
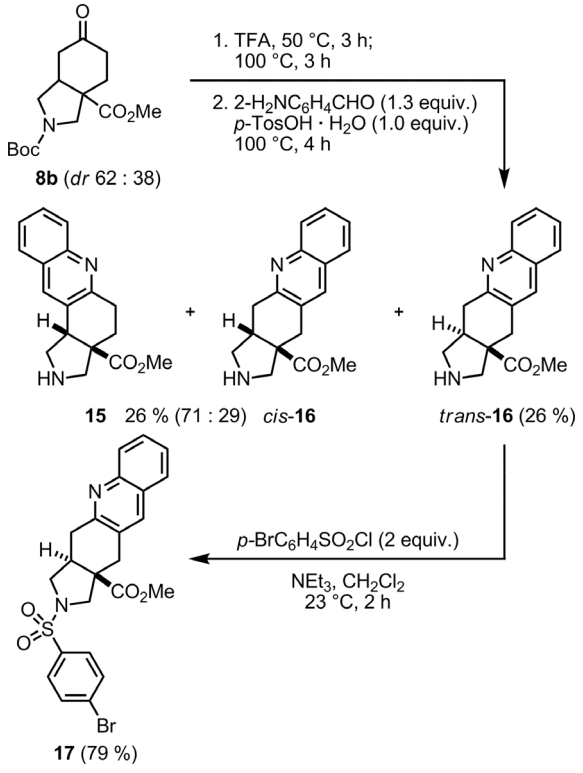


Fig. 4. ORTEP representation of the molecular structure of compound **17** in the solid state showing linear constitution and *trans*-configuration.

presentation (Fig. 3) shows, beside the linear constitution, the relative *trans*-configuration. It can therefore be concluded that the other linear isomer of **13** must be *cis*-configurated. Whereas the exclusive formation of the linear annulation product *trans*-**13** from the *trans*-configurated starting material **8b** is in perfect accordance with earlier observations with carbocyclic substrates [9], the regioselectivity starting from *cis*-**8b** is low.

In order to prearrange the Friedländer quinoline synthesis, the Boc group was again cleaved from isoindole **8b** by using TFA. The respective mixture of *cis*- and *trans*-diastereoisomers was then treated with *ortho*-aminobenzaldehyde in the presence of TosOH to yield a mixture of three quinolines (Scheme 6). Only compound *trans*-**16** was separable by chromatography and obtained as a pure material (26 % yield). Apart from spectroscopic evidence, its constitution and configuration was enlightened by preparation of a crystalline derivative **17** by sulfonamide formation. Single-crystal X-ray structure determination of compound **17** revealed the material to be linear and *trans*-configurated (Fig. 4). The two other quinoline derivatives were obtained from the annulation reaction as an inseparable mixture (26 % yield, ratio 71 : 29). We presume the major of the two components to be the angular *cis*-isomer **15** by comparison of its ^{13}C chemical shifts with those of compound **10**: δ = 29.01 *vs.* 28.14 (CH_2; C-5), 30.35 *vs.* 28.72 (CH_2; C-4) and 45.96 *vs.* 45.08 (CH; C-11b) ppm. In the same manner, the minor component of the mixture was assigned to be linear *cis*-**16** by comparing its ^{13}C resonances whith those of compound **11**: δ = 34.58 *vs.* 34.83 (CH_2; C-4 or C-11), 34.97 *vs.* 34.98 (CH_2; C-11 or C-4) and 43.20 *vs.* 42.88 (CH; C-3a) ppm. The ^{13}C chemical shift analogy is further evidenced by comparing furo- with the pyrrolo[3,4-*c*]carbazoles **9** and **12**, which are both angular and *cis*-configurated: δ = 20.30 *vs.* 20.17 (CH_2; C-5), 27.75 *vs.* 28.14 (CH_2; C-4) and 39.91 *vs.* 40.86 (CH; C-10c) ppm. In summary, the regioselectivities of Fischer and Friedländer syntheses with isoindole **8b** gave the same features: *trans*-**8b** gave exclusively linear products *trans*-**13** and *trans*-**16**, whereas starting material *cis*-**8b** gave both, angular and linear products **12**, **15** and *cis*-**13**, *cis*-**16**.



Scheme 6. Friedländer quinoline synthesis starting from octahydroisoindole **8b**.

Experimental Section

General

Preparative column chromatography was carried out using Merck SiO_2 (0.035 – 0.070 mm, type 60 A) with hexane, ethyl acetate (EtOAc), or *tert*-butylmethylether (MTBE) as eluents. TLC was performed on Merck SiO_2 F_{254} plates on aluminum sheets. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance DRX 500 instrument. Multiplicities of carbon signals were determined with DEPT experiments. Assignments of proton and carbon resonances were made with H,H-COSY, HMBC, HMQC, and NOE experiments. MS and HRMS spectra were obtained with a Finnigan MAT 95 (EI and CI) and a Waters Q-TOF Premier (ESI, positive mode) spectrometer. IR spectra were recorded on a Bruker Tensor 27 spectrometer equipped with a "GoldenGate" diamond ATR unit. Compounds **6a** and **6b** were prepared according to literature procedures [14]. *ortho*-Aminobenzaldehyde was always freshly prepared by reduction of *ortho*-nitrobenzaldehyde with iron powder as reported previously [16]. All other starting materials were commercially available.

*Methyl cis-6-oxo-1,3,3a,4,5,6,7,7a-octahydroisobenzofuran-3a-carboxylate (**8a**)*

A degassed suspension of enone **6a** (18.9 mmol, 3.70 g) and Pd/C (0.94 mmol, 1.0 g, 10 % w/w Pd) in EtOAc (60 mL) was stirred for 15 h at 60 °C under an atmosphere of H_2 (1 bar). After cooling the reaction mixture to ambient temperature, it was filtered through SiO_2 and the residue rinsed with EtOAc (60 mL). The filtrate was evaporated and the crude material purified by chromatography (SiO_2, hexane-EtOAc = 1 : 1, R_f = 0.23) to give **8a** (3.12 g, 15.7 mmol, 83 %) as a colorless oil, being a mixture of *cis*/*trans*-diastereoisomers (ratio 16 : 1 according to ^1H NMR and ^{13}C NMR). – IR (ATR): ν = 2953 (w), 2867 (w), 1713 (s), 1434 (w), 1347 (w), 1284 (m), 1211 (m), 1121 (m), 1066 (m), 1043 (m), 1009 (m), 937 (m) cm^{-1}. – ^1H NMR (500 MHz, $CDCl_3$), *cis*-isomer: δ = 2.03 – 2.09 (m, 1 H), 2.34 – 2.44 (m, 4 H), 2.61 (dd, J = 15.9 Hz, J = 6.4 Hz, 1 H), 3.12 (quint, J = 6.7 Hz, 1 H), 3.57 (dd, J = 8.8 Hz, J = 6.4 Hz, 1 H), 3.77 (s, 3 H), 3.81 (d, J = 9.1 Hz, 1 H), 4.05 (t, J = 8.2 Hz, 1 H), 4.08 (d, J = 9.1 Hz, 1 H) ppm; *trans*-isomer: δ = 1.69 (td, J = 12.9 Hz, J = 5.7 Hz, 1 H), 2.42 – 2.48 (m, 3 H), 2.89 (t, J = 15.1 Hz, 1 H), 3.74 (s, 3 H), 3.81 – 3.87 (m, 1 H), 3.91 (t, J = 7.6 Hz, 1 H), 4.22 (d, J = 8.5 Hz, 1 H) ppm; all other resonances are hidden by those of the *cis*-isomer. – $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$), *cis*-isomer: δ = 28.50 (CH_2), 36.20 (CH_2), 40.42 (CH_2), 41.17 (CH), 51.78 (C), 52.66 (CH_3), 73.98 (CH_2), 76.84 (CH_2), 175.00 (C), 210.44 (C) ppm; *trans*-isomer: δ = 29.26 (CH_2), 37.76 (CH_2), 39.08 (CH_2), 47.44 (CH), 52.12 (C), 52.38 (CH_3), 69.31 (CH_2), 75.36 (CH_2), 173.46 (C), 208.45 (C) ppm. – MS (CI, isobutane), m/z (%) = 199 (100) $[M+H]^+$, 181 (17), 167 (7). – HRMS (CI, isobutane): m/z = 199.0968 (calcd. 199.0970 for $C_{10}H_{15}O_4$, $[M+H]^+$). – $C_{10}H_{14}O_4$ (198.22).

*2-tert-Butyl-3a-methyl 6-oxooctahydroisoindole-2,3a-dicarboxylate (**8b**)*

A degassed suspension of enone **6b** (10 mmol, 3.0 g) and Pd/C (1.0 mmol, 1.1 g, 10 % w/w Pd) in EtOAc (60 mL) was stirred for 15 h at 60 °C under an atmosphere of H_2 (1 bar). After cooling to ambient temperature, the reaction mixture was filtered through SiO_2 and the residue rinsed with EtOAc (60 mL). The filtrate was evaporated and the crude material purified by chromatography (SiO_2, hexane-EtOAc = 1 : 1, R_f = 0.37) to give **8b** (2.63 g, 8.77 mmol, 88 %) as a yellow, viscous oil, being a mixture of two diastereoisomers (ratio 62 : 38 according to GLC), causing doubled signal sets in the NMR spectra (integral ratio 0.6 H : 1 H in ^1H NMR, resulting in a total proton integral of 36.8 H). – IR (ATR): ν = 2976 (w), 2833 (w), 1693 (s), 1480 (w), 1456 (w), 1399 (s), 1367 (m), 1339 (w), 1291 (w), 1259 (m), 1206 (m), 1168 (s), 1152 (s), 1092 (m), 1014 (w), 973 (w) cm^{-1}. – ^1H NMR (500 MHz, $[D_6]$DMSO, 80 °C): δ = 1.36 (m, 9 H), 1.36 (s, 5.4 H), 1.74 – 1.81 (m, 0.6 H), 1.87 – 1.93 (m, 1 H), 2.16 – 2.20 (m, 2 H), 2.22 – 2.26 (m, 1 H), 2.29 – 2.35 (m, 1.8 H), 2.35 – 2.39 (m, 1 H), 2.45 (quint, J = 1.8 Hz, 1 H), 2.53 – 2.58 (m, 1.6 H), 2.90 (dd, J = 10.4 Hz, J = 8.7 Hz, 1 H), 2.94 – 3.04 (m, 1.8 H), 3.12 – 3.16 (m, 0.6 H), 3.34 – 3.40 (m, 1.6 H), 3.52 (dd, J = 10.5 Hz, J = 7.7 Hz, 1 H), 3.57 (d, J = 11.0 Hz, 1 H), 3.65 (s, 1.8 H), 3.69 (s, 3 H), 3.76 (d, J = 10.9 Hz, 0.6 H) ppm. – $^{13}C\{^1H\}$ NMR (125 MHz, $[D_6]$DMSO, 80 °C), major isomer: δ = 27.66 (3 CH_3), 28.14 (CH_2), 36.18 (CH_2), 39.01 (CH_2), 48.70 (C), 49.32 (CH_2), 51.38 (CH), 51.77 (CH_3), 53.44 (CH_2), 78.31 (C), 153.04 (C), 173.38 (C), 208.11 (C) ppm; minor isomer: δ = 27.70 (3 CH_3), 28.70 (CH_2), 36.72 (CH_2), 39.06 (CH_2), 47.94 (C), 49.32 (CH_2), 51.38 (CH), 51.77 (CH_3), 53.44 (CH_2), 78.07 (C), 153.12 (C), 173.39 (C), 206.97 (C) ppm. – MS (EI, 70 eV), m/z (%) = 297 (0.5) $[M]^+$, 242 (8), 240 (20), 224 (11), 196 (20), 138 (20), 57 (100). – HRMS (CI, isobutane): m/z = 298.1656 (calcd. 298.1654 for $C_{15}H_{24}NO_5$, $[M+H]^+$). – $C_{15}H_{23}NO_5$ (297.35).

*Methyl cis-1,3,3a,4,5,10c-hexahydrofuro[3,4-c]carbazole-3a-carboxylate (**9**)*

A solution of ketone **8a** (240 mg, 1.21 mmol) and phenylhydrazine (170 mg, 1.57 mmol) in a mixture of AcOH (4 mL) and TFA (1 mL) was stirred in a tightly closed reaction flask for 20 h at 100 °C. After cooling to ambient temperature, the mixture was adjusted to pH = 10 with 50 % aqueous KOH solution (*ca.* 2 mL) and then extracted with CH_2Cl_2 (3 × 70 mL). The combined organic layers were dried ($MgSO_4$), filtered and evaporated. The residue was submitted to column chromatography (SiO_2, hexane-EtOAc = 1 : 1, R_f = 0.41) to yield the indole derivative **9** (230 mg,

0.848 mmol, 70 %) as a yellow solid. – M. p. 132 °C. – IR (ATR): ν = 3415 (s), 3048 (w), 3010 (w), 2952 (w), 2903 (w), 2863 (w), 1724 (s), 1455 (m), 1434 (m), 1331 (m), 1253 (s), 1235 (m), 1201 (s), 1166 (s), 1045 (s), 913 (m), 750 (s) cm^{-1}. – ^1H NMR (500 MHz, $CDCl_3$): δ = 2.06 – 2.14 (m, 1 H; 4-H), 2.38 (dt, J = 13.5 Hz, J = 4.8 Hz, 1 H; 4-H), 2.65 (dt, J = 16.6 Hz, J = 4.9 Hz, 1 H; 5-H), 2.76 – 2.82 (m, 1 H; 5-H), 3.72 (s, 3 H; Me), 3.77 (t, J = 7.9 Hz, 1 H; 1-H), 3.85 (d, J = 8.8 Hz, 1 H; 3-H), 4.10 (t, J = 7.8 Hz, 1 H; 10c-H), 4.26 (d, J = 8.8 Hz, 1 H; 3-H), 4.55 (t, J = 8.0 Hz, 1 H; 1-H), 7.10 – 7.15 (m, 2 H; 9-H, 8-H), 7.20 (d, J = 7.7 Hz, 1 H; 7-H), 7.43 (d, J = 7.5 Hz, 1 H; 8-H), 8.12 (br s, 1 H; NH) ppm. – $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 20.30 (CH_2; C 5), 27.75 (CH_2; C 4), 39.91 (CH; C 10c), 52.21 (CH_3; Me), 52.77 (C; C 3a), 73.97 (CH_2; C 1), 75.81 (CH_2; C 3), 108.18 (C; C 10b), 110.61 (CH; C 7), 117.57 (CH; C 10), 119.23 (CH; C 8), 121.25 (CH; C 9), 127.10 (C; C 10a), 132.99 (C; C 5a), 135.87 (C; C 6a), 175.17 (C; C 3a) ppm. – MS (EI, 70 eV), m/z (%) = 271 (91) $[M]^+$, 240 (46), 212 (25), 182 (100), 167 (28), 143 (13), 130 (8). – HRMS (EI, 70 eV): m/z = 271.1202 (calcd. 271.1208 for $C_{16}H_{17}NO_3$, $[M]^+$). – $C_{16}H_{17}NO_3$ (271.31).

*Friedländer quinoline synthesis from ketone **8a***

A mixture of ketone **8a** (240 mg, 1.21 mmol), freshly prepared 2-aminobenzaldehyde (230 mg, 1.57 mmol) and *p*-TosOH·H_2O (230 mg, 1.21 mmol) was heated for 2 h at 110 °C. After cooling to ambient temperature, the mixture was dissolved in CH_2Cl_2 (20 mL), the resulting solution was washed with saturated $NaHCO_3$ solution (10 mL) and brine (10 mL). The organic layer was dried ($MgSO_4$), filtered and evaporated. The residue was submitted to chromatography (SiO_2, hexane-EtOAc = 1 : 1) to yield the angular quinoline **10** (140 mg, 0.494 mmol, 40 %) as a yellow oil in the first fraction (R_f = 0.54). A second fraction (R_f = 0.46) contained the linear quinoline **11** (70 mg, 0.25 mmol, 20 %) as a colorless solid.

*Methyl cis-1,3,3a,4,5,11b-hexahydrofuro[3,4-a]acridine-3a-carboxylate (**10**)*

IR (ATR): ν = 3056 (w), 2951 (w), 2863 (w), 1724 (vs), 1621 (w), 1602 (w), 1564 (w), 1492 (m), 1433 (m), 1422 (m), 1251 (m), 1198 (m), 1172 (m), 1106 (w), 1062 (s), 941 (m), 792 (m), 752 (s) cm^{-1}. – ^1H NMR (500 MHz, $CDCl_3$): δ = 2.11 – 2.17 (m, 1 H; 5-H), 2.27 – 2.34 (m, 1 H; 5-H), 3.00 – 3.06 (m, 1 H; 4-H), 3.12 – 3.17 (m, 1 H; 4-H), 3.58 (dd, J = 9.1 Hz, J = 8.5 Hz, 1 H; 1-H), 3.70 (s, 3 H; Me), 3.90 (d, J = 9.2 Hz, 1 H; 3-H), 4.14 (dd, J = 9.1 Hz, J = 8.5 Hz, 1 H; 11b-H), 4.31 (d, J = 9.2 Hz, 1 H; 3-H), 4.40 (t, J = 8.5 Hz, 1 H; 1-H), 7.42 – 7.45 (m, 1 H), 7.60 – 7.63 (m, 1 H), 7.69 (d, J = 8.1 Hz, 1 H), 7.85 (s, 1 H), 7.97 (d, J = 8.5 Hz, 1 H) ppm. – $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 28.14 (CH_2; C 5), 28.72 (CH_2; C 4), 45.08 (CH; C 11b), 52.26 (C; C 3a), 52.41 (CH_3; OMe), 75.35 (CH_2; C 1), 77.05 (CH_2; C 3), 125.87 (CH; C 8), 126.89 (CH; C 7), 127.17 (C; C 10a), 128.30 (CH; C 10), 128.41 (C; C 11a), 129.08 (CH; C 9), 135.06 (CH; C 11), 146.54 (C; C 6a) 157.34 (C; C 5a), 175.00 (C; C 3a) ppm. – MS (EI, 70 eV), m/z (%) = 283 (19) $[M]^+$, 265 (18), 252 (72), 194 (100), 180 (17). – HRMS (EI, 70 eV): m/z = 283.1201 (calcd. 283.1208 for $C_{17}H_{17}NO_3$, $[M]^+$). – $C_{17}H_{17}NO_3$ (283.32).

*Methyl cis-1,3,3a,4,11,11a-hexahydrofuro[3,4-b]acridine-11a-carboxylate (**11**)*

M. p. 88 °C. – IR (ATR): ν = 3055 (w), 2997 (w), 2839 (w), 2361 (w), 1738 (s), 1720 (vs), 1496 (w), 1435 (m), 1368 (m), 1231 (m), 1199 (m), 1110 (m), 1065 (m), 933 (m), 874 (m), 757 (s) cm^{-1}. – ^1H NMR (500 MHz, $CDCl_3$): δ = 2.95 – 3.03 (m, 2 H; 11-H, 4-H), 3.24 – 3.30 (m, 2 H), 3.35 (d, J = 14.7 Hz, 1 H; 11-H), 3.39 (dd, J = 8.8 Hz, J = 6.0 Hz, 1 H), 3.52 (d, J = 9.3 Hz, 1 H; 1-H), 3.72 (s, 3 H), 4.16 (dd, J = 8.3 Hz, J = 7.2 Hz, 1 H), 4.21 (d, J = 9.3 Hz, 1 H; 1-H), 7.49 – 7.52 (m, 1 H), 7.65 – 7.68 (m, 1 H), 7.76 (d, J = 8.1 Hz, 1 H), 7.88 (s, 1 H), 8.04 (d, J = 8.4 Hz, 1 H) ppm. – $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 34.83 (CH_2; C 4 or C 11), 34.98 (CH_2; C 11 or C 4), 42.88 (CH; C 3a), 52.63 (CH_3), 54.46 (C), 74.41 (CH_2), 76.82 (CH_2), 126.03 (CH), 127.23 (CH), 127.76 (C), 128.58 (CH), 128.96 (CH), 134.13 (CH), 147.13 (2 C), 159.11 (C), 175.87 (C) ppm. – MS (EI, 70 eV), m/z (%) = 283 (90) $[M]^+$, 252 (100), 238 (24), 223 (37), 206 (25), 194 (92), 180 (21), 167 (15). – HRMS (EI, 70 eV): m/z = 283.1200 (calcd. 283.1208 for $C_{17}H_{17}NO_3$, $[M]^+$). – $C_{17}H_{17}NO_3$(283.32).

*Fischer indole synthesis from ketone **8b***

TFA (1.5 mL) was added at 0 °C (ice-water bath) to carbamate **8b** (280 mg, 0.942 mmol, *dr* = 62 : 38). The resulting mixture was stirred for 3 h at 50 °C and then for 3 h at 100 °C. After cooling to ambient temperature, AcOH (4.5 mL) and phenylhydrazine (129 mg, 1.22 mmol) were added, and the mixture was stirred in a tightly closed reaction flask for 1 h at ambient temperature and then for 16 h at 110 °C. After cooling to ambient temperature, CH_2Cl_2 (15 mL) was added, and the mixture was extracted with H_2O (3 × 15 mL). The combined aqueous extracts were adjusted with 50 % aqueous KOH solution (*ca.* 5 mL) to pH = 10. The resulting suspension was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried ($MgSO_4$), filtered and evaporated. The residue was chromatographed on SiO_2 (MTBE-MeOH = 1 : 1, +3 vol-% NEt_3) to give three fractions: The first fraction (R_f = 0.50) contained the linear indole derivative *cis*-**13** (30 mg, 0.11 mmol, 11 %) as an orange-brown solid. Secondly, the angular indole **12** (R_f = 0.45, 20 mg, 0.073 mmol, 8 %) was obtained as a red-brown solid. Finally, the linear indole derivative *trans*-**13** (R_f = 0.31, 80 mg, 0.30 mmol, 31 %) was eluted as an orange solid.

*Methyl cis-1,2,3,3a,4,5,6,10c-octahydropyrrolo[3,4-c]carbazole-3a-carboxylate (**12**)*

M. p. 170 – 175 °C. – IR (ATR): ν = 3376 (w), 3204 (w), 2948 (m), 2741 (w), 1722 (s), 1619 (m), 1454 (m), 1454 (s), 1374 (m), 1331 (m), 1259 (s), 1231 (s), 1200 (s), 1169 (s), 1095 (m), 1011 (w), 907 (w), 738 (vs) cm^{-1}. – ^1H NMR (500 MHz, $CDCl_3$): δ = 1.94 – 2.00 (m, 1 H; 4-H), 2.29 (dt, J = 13.5 Hz, J = 5.5 Hz, 1 H; 4-H), 2.66 (dt, J = 16.6 Hz, J = 5.5 Hz, 1 H; 5-H), 2.75 – 2.81 (m, 1 H; 5-H), 2.94 (dd, J = 11.2 Hz, J = 7.3 Hz, 1 H; 1-H), 3.00 (d, J = 12.1 Hz, 1 H; 3-H), 3.48 (d, J = 12.1 Hz, 1 H; 3-H), 3.62 – 3.67 (m, 1 H; 1-H), 3.68 (s, 3 H; Me), 3.87 (t, J = 7.2 Hz, 1 H; 10c-H), 4.58 (br s, 1 H), 7.04 – 7.07 (m, 1 H), 7.09 – 7.12 (m, 1 H), 7.26 (d, J = 7.9 Hz, 1 H), 7.39 (d, J = 7.7 Hz, 1 H), 8.41 (br s, 1 H) ppm. – $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 20.17 (CH_2; C 5), 28.14 (CH_2; C 4), 40.86 (CH; C 10c), 52.39 (CH_3; OMe), 52.40 (CH_2; C 1), 52.59 (C; C 3a), 55.11 (CH_2; C 3), 108.37 (C), 110.83 (CH), 117.73 (CH), 119.36 (CH), 121.42 (CH), 126.89 (C), 133.40 (C), 136.07 (C), 175.96 (C) ppm. – MS (ESI), m/z (%) = 271 (100) $[M+H]^+$, 236 (4), 215 (6). – HRMS (ESI): m/z = 271.1446 (calcd. 271.1447 for $C_{16}H_{19}N_2O_2$, $[M+H]^+$). – $C_{16}H_{18}N_2O_2$ (270.33).

Methyl cis-1,2,3,3a,4,5,10,10a-octahydropyrrolo[3,4-*b*]*-carbazole-10a-carboxylate (cis-**13**)*

M. p. 190 – 200 °C (decomp.). – IR (ATR): ν = 3396 (w), 3233 (w), 3058 (w), 2953 (m), 2925 (m), 2724 (w), 1725 (s), 1598 (m), 1455 (m), 1434 (m), 1330 (m), 1236 (m), 1202 (s), 1102 (m), 1096 (m), 909 (m), 729 (vs) cm^{-1}. – ^1H NMR (500 MHz, $CDCl_3$): δ = 2.60 (d, J = 15.6 Hz, 1 H), 2.79 (t, J = 9.9 Hz, 1 H), 2.87 (d, J = 16.3 Hz, 1 H), 3.00 – 3.09 (m, 3 H), 3.25 – 3.28 (m, 1 H), 3.32 (d, J = 16.3 Hz, 1 H), 3.40 (d, J = 10.9 Hz, 1 H), 3.66 (s, 3 H), 4.19 (br s, 1 H), 7.05 – 7.08 (m, 1 H), 7.10 – 7.13 (m, 1 H), 7.26 (d, J = 7.8 Hz, 1 H), 7.43 (d, J = 7.6 Hz, 1 H), 8.22 (br s, 1 H) ppm. – $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 21.94 (CH_2), 25.08 (CH_2), 39.97 (CH), 50.63 (CH_2), 51.37 (C), 52.38 (CH_3), 55.34 (CH_2), 106.04 (C), 110.61 (CH), 117.67 (CH), 119.21 (CH), 121.34 (CH), 127.21 (C), 131.01 (C), 136.32 (C), 175.42 (C) ppm. – MS (ESI), m/z (%) = 271 (100) $[M+H]^+$, 267 (6), 236 (7), 253 (9), 237 (7). – HRMS (ESI): m/z = 271.1443 (calcd. 271.1447 for $C_{16}H_{19}N_2O_2$, $[M+H]^+$). – $C_{16}H_{18}N_2O_2$ (270.33).

*Methyl trans-1,2,3,3a,4,5,10,10a-octahydropyrrolo[3,4-b]-carbazole-10a-carboxylate (trans-**13**)*

M. p. 180 – 190 °C (decomp.). – IR (ATR): ν = 3364 (w), 3337 (w), 2948 (m), 2930 (m), 2874 (m), 2872 (m), 2844 (m), 1714 (s), 1560 (w), 1458 (m), 1428 (m), 1355 (m), 1315 (m), 1288 (m), 1208 (s), 1177 (s), 1091 (m), 849 (m), 743 (s) cm^{-1}. – ^1H NMR (500 MHz, CD_3OD): δ = 2.47 – 2.53 (m, 1 H), 2.56 (d, J = 15.2 Hz, 1 H), 2.91 – 2.95 (m, 1 H), 2.98 – 3.05 (m, 2 H), 3.27 – 3.31 (m, 2 H), 3.44 (d, J = 11.3 Hz, 1 H), 3.52 (d, J = 8.5 Hz, 1 H), 3.57 (s, 3 H), 6.98 – 7.00 (m, 1 H), 7.04 – 7.07 (m, 1 H), 7.27 (d, J = 8.0 Hz, 1 H), 7.38 (d, J = 7.8 Hz, 1 H) ppm; NH protons are not detected. – $^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD): δ = 24.55 (CH_2), 30.22 (CH_2), 46.94 (CH), 49.45 (CH_2), 52.35 (CH_3), 54.94 (C), 56.01 (CH_2), 109.41 (C), 111.68 (CH), 118.27 (CH), 119.59 (CH), 121.84 (CH), 128.51 (C), 135.23 (C), 138.44 (C), 176.17 (C) ppm. – MS (ESI), m/z (%) = 271 (100) $[M+H]^+$, 239 (2). – HRMS (ESI): m/z = 271.1451 (calcd. 271.1447 for $C_{16}H_{19}N_2O_2$, $[M+H]^+$). – $C_{16}H_{18}N_2O_2$ (270.33).

*Methyl trans-2-benzyl-1,2,3,3a,4,5,10,10a-octahydro-pyrrolo[3,4-b]carbazole-10a-carboxylate (**14**)*

Benzaldehyde (16 mg, 0.15 mmol) was added at 0 °C (ice-water bath) to a solution of the amine *trans*-**13** (40 mg, 0.15 mmol) in MeOH (0.2 mL). The mixture was stirred for 1 h at 0 °C, then a solution of $ZnCl_2$ (10 mg, 0.075 mmol) and sodium cyanoborohydride (9.0 mg, 0.15 mmol) in MeOH (0.2 mL) was added. The resulting mixture was stirred for 2 h at ambient temperature, then diluted with H_2O (5 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were dried ($MgSO_4$), filtered and evaporated. The residue was chromatographed (SiO_2, MTBE, R_f = 0.28) to yield **14** (35 mg, 0.097 mmol, 65 %) as a colorless solid. – M. p. 190 °C (decomp). – IR (ATR): ν = 3363 (m), 3050 (w), 3030 (w), 2921 (w), 2898 (w), 2846 (m), 2782 (m), 1718 (s), 1583 (w), 1492 (w), 1453 (m), 1427 (m), 1350 (m), 1297 (m), 1211 (s), 1189 (s), 1170 (s), 1096 (m), 987 (m), 733 (vs), 695 (s) cm^{-1}. – ^1H NMR (500 MHz, $CDCl_3$): δ = 2.45 – 2.53 (m, 1 H), 2.56 (d, J = 14.9 Hz, 1 H), 2.73 (dd, J = 15.6 Hz, J = 5.1 Hz, 1 H), 2.89 – 2.94 (m, 2 H), 3.18 – 3.25 (m, 2 H), 3.24 (d, J = 9.6 Hz, 1 H), 3.44 (d, J = 15.2 Hz, 1 H), 3.54 (s, 3 H), 3.75 (d, J = 13.4 Hz, 1 H), 3.80 (d, J = 13.4 Hz, 1 H), 6.98 – 7.05 (m, 2 H), 7.15 – 7.19 (m, 2 H), 7.23 – 7.29 (m, 4 H), 7.36 (d, J = 7.7 Hz, 1 H), 7.76 (br s, 1 H) ppm. – $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 23.94 (CH_2), 29.38 (CH_2), 44.34 (CH_3), 51.63 (CH), 51.69 (C), 55.14 (CH_2), 60.48 (CH_2), 62.69 (CH_2), 108.97 (C), 110.49 (CH), 117.70 (CH), 119.10 (CH), 121.19 (CH), 126.83 (CH), 127.36 (C), 128.23 (2 CH), 128.47 (2 CH), 134.13 (C), 136.35 (C), 139.53 (C), 175.31 (C) ppm. – MS (ESI), m/z (%) = 361 (100) $[M+H]^+$, 449 (5), 333 (12), 305 (9), 289 (23), 245 (20), 217 (66). – HRMS (ESI): m/z = 361.1915 (calcd. 361.1916 for $C_{23}H_{25}N_2O_2$, $[M+H]^+$). – $C_{23}H_{24}N_2O_2$ (360.45).

*Friedländer quinoline synthesis from ketone **8b***

TFA (1 mL) was added at 0 °C (ice-water bath) to the carbamate **8b** (200 mg, 0.677 mmol, dr = 62 : 38). The resulting

mixture was stirred for 3 h at 50 °C and then for 3 h at 100 °C. After cooling to ambient temperature, the volatiles were evaporated in high vacuum, and *p*-TosOH·H_2O (129 mg, 0.677 mmol) and freshly prepared 2-aminobenzaldehyde (107 mg, 0.88 mmol) were added to the residue. The mixture was stirred for 4 h at 100 °C, then cooled to ambient temperature and dissolved in CH_2Cl_2 (50 mL). The solution was extracted with hydrochloric acid (1.5 mol L^{-1}, 3 × 50 mL). The combined aqueous extracts were adjusted with 50 % aqueous KOH (*ca.* 25 mL) to pH = 10 and then extracted with CH_2Cl_2 (3 × 100 mL). The combined organic extracts were dried ($MgSO_4$), filtered and evaporated. Chromatography (SiO_2, MTBE-MeOH = 1 : 1, +3 vol-% NEt_3) of the residue gave two fractions: The first fraction (R_f = 0.45) contained an unseparable mixture of the angular and linear quinoline derivatives **15** and *cis*-**16** (ratio 71 : 29, 50 mg, 0.18 mmol, 26 %) as an orange-yellow oil. The second fraction (R_f = 0.15) contained compound *trans*-**16** (50 mg, 0.18 mmol, 26 %) as a yellow solid.

*Methyl trans-2,3,3a,4,11,11a-hexahydro-1H-pyrrolo[3,4-b]-acridine-11a-carboxylate (trans-**16**)*

M. p. 145 – 147 °C. – IR (ATR): ν = 3374 (br w), 3043 (w), 2954 (w), 2869 (w), 1721 (s), 1620 (m), 1600 (m), 1577 (m), 1489 (m), 1455 (m), 1430 (m), 1412 (s), 1335 (m), 1303 (w), 1224 (s), 1194 (s), 1103 (m), 1014 (m), 971 (w), 753 (s) cm^{-1}. – ^1H NMR (500 MHz, $CDCl_3$): δ = 2.55 – 2.63 (m, 1 H), 2.91 (d, J = 15.9 Hz, 1 H), 2.96 – 3.02 (m, 2 H), 3.21 (dd, J = 11.3 Hz, J = 10.0 Hz, 1 H), 3.35 – 3.40 (m, 2 H), 3.54 (s, 3 H), 3.57 (d, J = 11.3 Hz, 1 H), 3.62 (d, J = 16.0 Hz, 1 H), 5.17 (br s, 1 H), 7.43 – 7.46 (m, 1 H), 7.60 – 7.63 (m, 1 H), 7.71 (d, J = 8.0 Hz, 1 H), 7.88 (s, 1 H), 7.96 (d, J = 8.5 Hz, 1 H) ppm. – $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 33.73 (CH_2), 37.09 (CH_2), 45.91 (CH), 48.84 (CH_2), 51.97 (C), 52.05 (CH_3), 55.76 (CH_2), 126.05 (CH), 127.01 (CH), 127.02 (C), 128.40 (CH), 129.00 (C), 129.01 (CH), 135.74 (CH), 146.61 (C), 157.18 (C), 174.16 (C) ppm. – MS (CI, isobutane), m/z (%) = 283 (100) $[M+H]^+$. – HRMS (ESI): m/z = 283.1452 (calcd. 283.1447 for $C_{17}H_{19}N_2O_2$, $[M+H]^+$). – $C_{17}H_{18}N_2O_2$ (282.34).

*Mixture of compounds **15** and cis-**16***

Doubled signal sets in the NMR spectra are observed (integral ratio 0.4 H : 1 H in ^1H NMR, resulting in a total proton integral of 25.2 H). – IR (ATR): ν = 3303 (br w), 3056 (w), 2950 (w), 2868 (w), 1721 (vs), 1621 (w), 1601 (w), 1565 (w), 1492 (w), 1432 (m), 1421 (m), 1250 (s), 1194 (s), 1169 (m), 1066 (m), 909 (m), 792 (m), 752 (s), 729 (s) cm^{-1}. – ^1H NMR (500 MHz, $CDCl_3$): δ = 2.06 – 2.11 (m, 1 H), 2.29 – 2.33 (m, 1 H), 2.47 (dd, J = 11.2 Hz, J = 8.4 Hz, 0.4 H), 2.67 (d, J = 12.1 Hz, 0.4 H), 2.85 (t, J = 10.7 Hz, 1 H), 2.92 (d, J = 15.0 Hz, 0.4 H), 2.94 – 3.19 (m, 4.2 H), 3.31 – 3.34 (m, 0.4 H), 3.42 – 3.45 (m, 0.4 H), 3.57 (d, J = 12.0 Hz, 0.4 H), 3.67 – 3.75 (m, 6.2 H), 4.00 (t, J = 9.0 Hz, 1 H), 4.58 (br s, 1 H), 4.77 (br s, 0.4 H), 7.44 – 7.49 (m, 1.4 H), 7.62 – 7.65 (m, 1.4 H), 7.70 – 7.74 (m, 1.4 H), 7.84 (s, 0.4 H), 7.89 (s, 1 H), 7.96 – 8.00 (m, 1.4 H) ppm. – $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$), major isomer **15**: δ = 29.01 (CH_2; C 5), 30.35 (CH_2; C 4), 45.96 (CH; C 11b), 51.86 (C), 52.63 (CH_3), 55.16 (CH_2), 56.98 (CH_2), 126.03 (CH), 127.05 (CH), 127.23 (C), 128.31 (CH), 128.77 (C), 129.27 (CH), 135.72 (CH), 146.56 (C), 157.60 (C), 175.82 (C) ppm; minor isomer *cis*-**16**: δ = 34.58 (CH_2; C 4 or C 11), 34.97 (CH_2; C 11 or C 4), 43.20 (CH; C 3a), 52.69 (CH_3), 53.20 (CH_2), 53.51 (C), 56.71 (CH_2), 126.10 (CH), 127.20 (CH), 127.69 (C), 128.49 (CH), 128.64 (C), 129.03 (CH), 134.46 (CH), 147.05 (C), 158.71 (C), 176.33 (C) ppm. – MS (ESI), m/z (%) = 283 (100) $[M+H]^+$. – HRMS (ESI): m/z = 283.1447 (calcd. 283.1447 for $C_{17}H_{19}N_2O_2$, $[M+H]^+$). – $C_{17}H_{18}N_2O_2$ (282.34).

*Methyl trans-2-(4-bromophenylsulfonyl)-2,3,3a,4,11,11a-hexahydro-1H-pyrrolo[3,4-b]acridine-11a-carboxylate (**17**)*

para-Bromobenzenesulfonylchloride (90 mg, 0.35 mmol) was added at 0 °C (ice-water bath) to a solution of the amine *trans*-**16** (50 mg, 0.18 mmol) and NEt_3 (35 mg, 0.35 mmol) in CH_2Cl_2 (0.8 mL). The mixture was stirred for 2 h at ambient temperature, subsequently diluted with H_2O (1 mL) and extracted with CH_2Cl_2 (3 × 3 mL). The layers were separated and the combined organic layers dried ($MgSO_4$), filtered and evaporated. The residue was submitted to chromatography (SiO_2, MTBE, R_f = 0.36) to yield the title compound **17** (70 mg, 0.14 mmol, 79 %) as a colorless solid. – M. p. 220 °C (decomp.). – IR (ATR): ν = 3081 (w), 3039 (w), 2947 (w), 2925 (w), 2885 (w), 2852 (w), 1729 (s), 1571 (w), 1491 (m), 1460 (m), 1384 (m), 1366 (m), 1342 (s), 1214 (s), 1164 (vs), 1090 (s), 1061 (s), 1004 (m), 821 (m), 777 (s), 757 (s), 735 (s), 616 (vs) cm^{-1}. – ^1H NMR (500 MHz, $CDCl_3$): δ = 2.55 – 2.62 (m, 1 H), 2.92 (d, J = 15.8 Hz, 1 H), 3.09 (dd, J = 17.3 Hz, J = 13.5 Hz, 1 H), 3.25 (s, 3 H), 3.33 (dd, J = 17.4 Hz, J = 5.3 Hz, 1 H), 3.39 (d, J = 10.5 Hz, 1 H), 3.45 (dd, J = 11.2 Hz, J = 8.7 Hz, 1 H), 3.58 (d, J = 15.9 Hz, 1 H), 3.84 (t, J = 8.0 Hz, 1 H), 3.89 (d, J = 10.4 Hz, 1 H), 7.45 – 7.48 (m, 1 H), 7.62 – 7.65 (m, 1 H), 7.68 – 7.75 (m, 5 H), 7.88 (br s, 1 H), 7.96 – 7.97 (m, 1 H) ppm. – $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 32.46 (CH_2), 37.16 (CH_2), 43.92 (CH), 50.77 (C), 50.83 (CH_2), 52.08 (CH_3), 55.57 (CH_2), 126.33 (CH), 126.86 (C), 127.02 (CH), 127.55 (C), 127.60 (C), 128.14 (CH), 128.84 (CH), 129.39 (CH), 132.29 (2 CH), 136.23 (CH), 136.84 (2 CH), 146.44 (C), 155.69 (C), 172.46 (C) ppm. – MS (EI, 70 eV), m/z (%) = 500 (0.5) $[M]^+$, 281 (100), 238 (10), 221 (27), 192 (10). – HRMS (EI, 70 eV): m/z = 500.0400 (calcd. 500.0405 for $C_{23}H_{21}BrN_2O_4S$, $[M]^+$). – $C_{23}H_{21}BrN_2O_4S$ (501.39).

Table 1. Crystal structure data for compounds **9**, **11**, **14** and **17**.

	9	**11**	**14**	**17**
Formula	$C_{16}H_{17}NO_3$	$C_{17}H_{17}NO_3$	$C_{23}H_{24}N_2O_2$	$C_{23}H_{21}BrN_2O_4S \cdot CH_2Cl_2$
M_r	271.31	283.32	362.04	586.31
Crystal size, mm^3	$0.28 \times 0.24 \times 0.11$	$0.47 \times 0.28 \times 0.12$	$0.33 \times 0.25 \times 0.05$	$0.63 \times 0.18 \times 0.07$
Crystal system	orthorhombic	monoclinic	triclinic	monoclinic
Space group	*Pbca*	$P2_1$	$P\bar{1}$	$P2_1/n$
a, Å	13.4190(3)	9.3325(4)	6.7195(10)	11.6939(2)
b, Å	9.9061(2)	6.5750(3)	9.9363(2)	9.1180(2)
c, Å	19.8155(4)	11.2834(4)	14.2175(3)	22.6997(4)
α, deg	90	90	88.4180(10)	90
β, deg	90	96.998(2)	79.1770(10)	98.9080(10)
γ, deg	90	90	84.5160(10)	90
V, Å^3	2638.07(10)	687.20(5)	928.03(3)	2391.16(8)
Z	8	2	2	4
D_{calcd}, g cm^{-3}	1.37	1.37	1.30	1.63
μ (MoK_α), cm^{-1}	0.7	0.7	0.7	0.7
F(000), e	1152	300	384	1192
hkl range	$-17 \le h \le 18$	$-15 \le h \le 15$	$-9 \le h \le 9$	$-17 \le h \le 17$
	$-13 \le k \le 13$	$-10 \le k \le 9$	$-11 \le k \le 13$	$-13 \le k \le 10$
	$-7 \le l \le 27$	$-18 \le l \le 18$	$-20 \le l \le 20$	$-34 \le l \le 34$
$((\sin\theta)/\lambda)_{max}$, Å^{-1}	1.371	0.615	1.375	1.286
Refl. measured	49915	13298	24271	69921
Refl. unique / R_{int}	3858 / 0.0320	5369 / 0.0197	5424 / 0.0363	8630 / 0.0374
Param. refined	195	191	254	308
$R(F)$ / $wR(F^2)$[a] (all refl.)	0.0538 / 0.1174	0.0430 / 0.0984	0.0638 / 0.1221	0.0602 / 0.1094
GoF (F^2)[b]	1.038	1.038	1.028	1.030
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	0.405 / −0.198	0.445 / −0.202	0.387 / −0.260	0.750 / −0.733

[a] $R1 = ||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$; [b] $\mathrm{GoF} = [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

Crystal structure determination

Intensity data for the single-crystal structure determinations were collected on a Bruker Apex II CCD diffractometer at 153(2) K with MoK_α radiation (graphite monochromator, λ = 71.07 pm). The structures were solved by Direct Methods and refined by full-matrix least-squares methods with SHELXS-97 [17] and SHELX-93 [18], respectively. Non-hydrogen atoms were refined with anisotropic displacement parameters. All H atoms were placed in calculated positions and refined using a riding model. Crystallographic data can be found in Table 1.

CCDC 846587 (**11**), 846588 (**9**), 846589 (**14**) and 846590 (**17**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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