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Substituted Pyrrolo[3,4-*a*]carbazoles from Reactions between 3-(1-Methoxyvinyl)indoles and Maleimides

Michaela Bleile and **Hans-Hartwig Otto***

Department of Pharmaceutical/Medicinal Chemistry, Institute of Pharmacy, University of Greifswald, D-17487 Greifswald

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Summary. 5-Methylenolether derivatives of pyrrolo[3,4-*a*]carbazoles were obtained from cycloadditions between 3-(1-methoxyvinyl)-1-tosylindole and N-substituted maleimides. They were transformed into the hydroxy derivatives by treatment with H_2SO_4, selectively reduced to the ether by H_2/Pd–C, and in the imide moiety by L-Selectride®. From the analogous *BOC* protected indole derivative the parent α,β-unsaturated ketones were obtained, which were transformed into hydroxyimino compounds, and which could be deprotected by heating to the melting point. Deprotection of the tosyl derivatives was not successful. The imide part of the molecule was hydrolyzed using methanolic NaOH. The stereochemistry of all products was elucidated mainly by spectroscopic methods, and compared with results of calculations.

Keywords. 3-Vinylindole; Pyrrolo[3,4-*a*]carbazole; Maleimide; Cycloaddition.

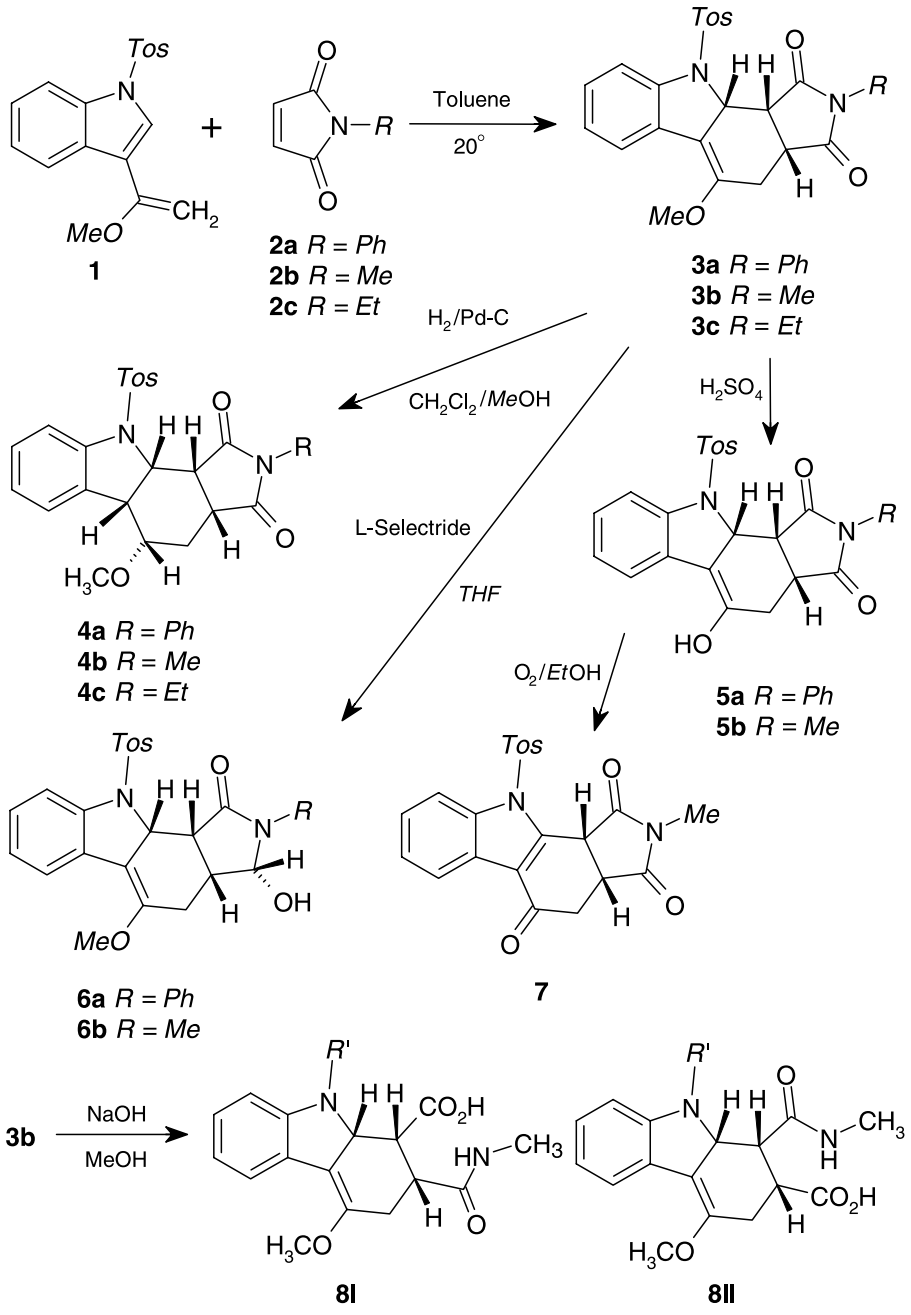
Introduction

Carbazole and other annelated indole derivatives form the basic structure of many valuable, and highly potent drugs like camptothecine and its derivatives topotecane and irinotecane used as inhibitors of the enzyme topoisomerase I against different types of cancer, or like vincamine used in the therapy of *Alzheimer* disease [1]. Many synthesis procedures in this area start with the cycloaddition of appropriate dienes to substituted 2- or 3-vinylindoles [2]. We have described reactions of maleimides and related systems with cyclopentadiene and with 1-(1-siloxyvinyl) naphthalene [3], and in a preceding paper we have reported about unusual reactions between maleimides and silylated indole derivatives [4]. Here we report about the synthesis of pyrrolo[3,4-*a*]carbazole derivatives by cycloadditions between maleimides and 3-(1-methoxyvinyl)indole derivatives.

* Corresponding author. E-mail: ottohh@pharmazie.uni-greifswald.de

Results and Discussion

The indole derivative **1** was prepared from 3-acetyl-1-tosylindole by reaction with trimethyl orthoformiate *via* the ketal 3-(α,α-dimethoxyethyl)-1-tosylindole by elimination of *Me*OH with $KHSO_4$ at 100°C with yields up to 95%. It was obtained as an unstable compound which easily polymerized. Therefore, we had to use it immediately for reactions with **2a**, **2b**, and **2c**, which were done by stirring a



Scheme 1

solution of **1** and the maleimide in toluene at room temperature. After standard work-up we obtained the crystalline pyrrolo[3,4-*a*]carbazole derivatives **3a**, **3b**, and **3c** (Scheme 1). IR spectra of these compounds were characterized by the strong carbonyl bands at 1779 and 1709 cm^{-1} (**3b**) caused by the carbonyl groups in positions 1 and 3. The structure was established using $^1H,^1H$- and $^1H,^{13}C$–COSY spectra and N*O*E experiments. The following coupling constants were found in the ^1H NMR spectra (**3c**): $J_{3a\text{-}H/4\text{-}HA} = 6.6$ Hz, $J_{3a\text{-}H/4\text{-}HB} = 1.7$ Hz, $J_{3a\text{-}H/10b\text{-}H} = 8.7$ Hz, and $J_{10a\text{-}H/10b\text{-}H} = 7.1$ Hz. A calculation of the torsion angles (MM2, SYBYL [5]) resulted in $\varphi(3a\text{-}H/4\text{-}H_A) = -59.3°$, $\varphi(3a\text{-}H/4\text{-}H_B) = 57.0°$, $\varphi(3a\text{-}H/10b\text{-}H) = 8.5°$, and $\varphi(10a\text{-}H/10b\text{-}H) = 48.6°$. These values demonstrate the *cis* addition (3a-H/10b-H), and the *endo* (*cis*) orientation of 10b-H and 10a-H. N*O*E experiments showed that 3a-H, 10b-H, and 10a-H were orientated to the same side of the molecule, which agreed with the calculated distances 10a-H – 10b-H = 2.47 Å, 10aH – 4-H_A = 2.57 Å, 3a-H – 4-H_A = 2.54 Å, and 3a-H – 4-H_B = 2.47 Å. The calculated data agreed with the data obtained by NMR experiments, and thereby we propose a structure as given in Fig. 1. Spectral data of **3a** and **3b** showed no significant differences, thus, they should have analogue structures.

The double bond between C-5 and C-5a of **3a**, **3b**, and **3c** was hydrogenated with H_2/Pd–C at room temperature yielding **4a**, **4b**, and **4c** with yields of 60–75%. This hydrogenation occurred stereoselectively as a *cis* addition whereby 5-H and 5a-H were *cis* orientated. The structure agreed with the following data. Positive N*O*Es were observed (**4a**) between 5a-H and 5-H, 5a-H and 10a-H, 3a-H and 10b-H, 10b-H and 10a-H, and 5-H and 4-H_B. In the ^1H NMR spectrum of **4b** the following characteristic coupling constants were found: $J_{5\text{-}H/5a\text{-}H} = 5.1$ Hz, $J_{5a\text{-}H/10a\text{-}H} = 11$ Hz, $J_{10a\text{-}H/10b\text{-}H} = 7.8$ Hz, and $J_{10b\text{-}H/3a\text{-}H} = 9.7$ Hz. Finally, the calculated structure fitted to that one deduced from the NMR data. In contrast to the reduction with H_2/Pd–C the reduction using L-Selectride® in *THF* at −78°C

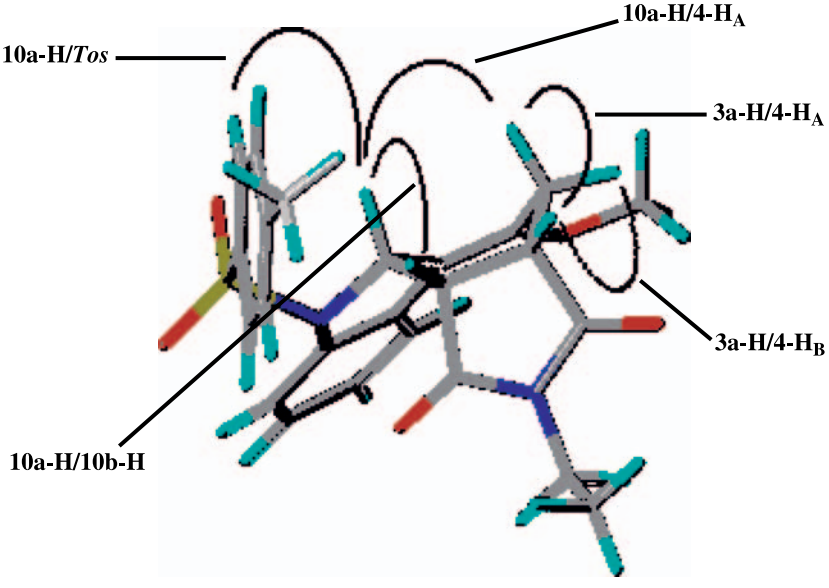
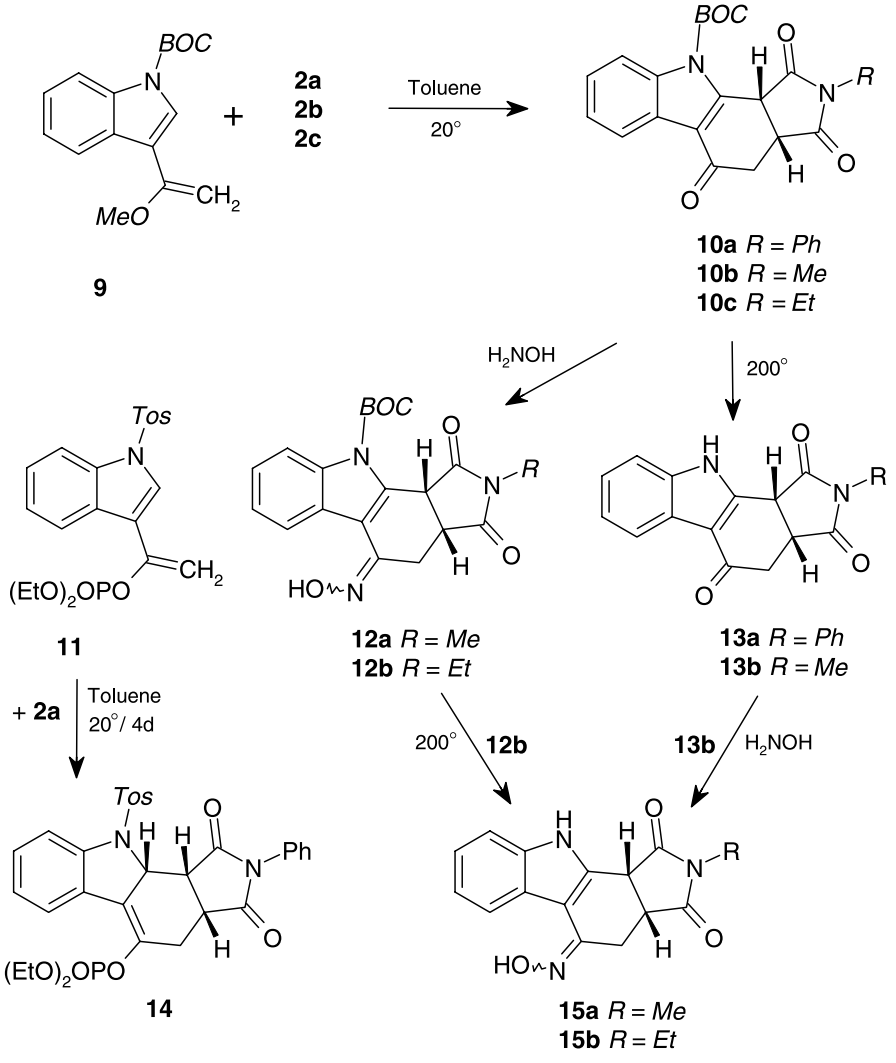


Fig. 1. Calculated structure of **3c** with observed N*O*Es

attacked the carbonyl group at position 3, and we isolated **6a** and **6b** with yields up to 85%.

The IR spectra of **6a** and **6b** showed significant differences when compared with the spectra of **3a** and **3b**. Instead of the two carbonyl bands of the imide moiety we found one amide band at 1684 cm^{-1} and an H–O-band at 3440 cm^{-1}. In the ^{13}C NMR spectrum (**6b**) only one carbonyl C was observed at 170 ppm. Comparing the ^{1}H NMR spectra we found significant shifts of the signal of 3a-H and 4-H_A from 3.20/3.29 ppm (**3b**) to 2.45 ppm (**6b**), whereas the resonance signals of 10a-H and 10b-H showed only small differences. In N*O*E experiments, irradiation at 5.56 ppm (H–O) caused positive effects at the signals of 3-H, 3a-H, and 4-H_B. Thus, they support that the reduction had occurred at C-3, and that the hydroxyl group in **6a** and **6b** is orientated to the down side.

Cleavage of the enol ether was successful when **3a** and **3b** were treated with H_2SO_4 yielding the enols **5a** and **5b**, and by refluxing of **5b** in *Et*OH, the α,β-



Scheme 2

unsaturated ketone **7** was obtained with ~70% yield. Finally, when we tried to deprotect the indole nitrogen by cleavage of the sulfonamide bond by heating of **3b** with a mixture of *Me*OH and aq. NaOH (20%) [6] we isolated a mixture of the two isomeric compounds **8I** and **8II** which we did not separate.

A different behavior was observed when we reacted the *BOC*-protected indole derivative **9** with the maleimides **2a**, **2b**, and **2c** in toluene at room temperature (Scheme 2). After usual work-up, the crystalline α,β-unsaturated ketone derivatives **10a**, **10b**, and **10c** were isolated with poor yields ($\leq$35%). The structure was comparable with that of **7**, as could be deduced from the spectroscopic data, and the carbonyl group at C-5 was reacted with H_2NOH yielding the oxime derivatives **12a** and **12b** with high yields. Finally, the *BOC* group was deleted thermally by heating of **10a** and **10b** to the melting point yielding the deprotected pyrrolocarbazole derivatives **13a** and **13b**. The crystalline oxime **15a** was obtained from **13b** by reaction with H_2NOH (72%), whereas the analogous derivative **15b** was prepared by thermal elimination of the *BOC* group from **12b** with 90% yield. As could be seen from IR and NMR data, during these reactions the stereochemistry of the ring system was not modified.

Finally, we compared the reactivity of the *O*-phosphorylated *N*-tosyl protected indole diene **11**, prepared from 3-acetyl-1-tosylindole by reaction with *n-Bu*Li and $Cl(EtO)_2PO$ at $-78°C$, with that of **1** and **9** in the reaction with **2a** (Scheme 2). We isolated the adduct **14** after a reaction time of 4 d at room temperature with a yield of 25%, and stopped further experiments. The general structure and stereochemistry of **14** did not differ from that of **3a**.

Experimental

Melting points: Mel-Temp II apparatus (uncorrected); IR spectra (KBr): Perkin-Elmer IR 841; NMR spectra: ^1H: Varian T 60 (60 MHz), Bruker WP 80 (80 MHz), room temperature (27°C), internal *TMS*, Varian Unity 300 (300 MHz), room temperature (27°C), ^{13}C: Varian Unity 300 (75.43 MHz), room temperature (27°C), related to δ ($CDCl_3$) = 77.00 ppm; all NMR values from spectra in $CDCl_3$, if not otherwise noted; MS spectra: Finnigan MAT 312, MAT 44 S, EI, 70 eV; elemental analyses: Pharm. Inst. or Chemisches Laboratorium, University of Freiburg or Pharmazeutisches Institut, University of Greifswald, Perkin Elmer Analyzer 2400; the results agreed with the calculated values within experimental error. Column chromatography (CC): silica gel 60 Merck 7734. TLC = thin layer chromatography (pre-coated silica gel plates 60 F_{254}, Merck 5549). Lithium diisopropylamide (*LDA*) was freshly prepared by mixing of equimolar amounts of diisopropylamine in *THF* and *n*-butyl lithium (*Bu*Li, 1.6 *M* solution in *n*-hexane) at $-78°C$. Solvents were purified/dried according to literature procedures. Abbreviations: *Ac*O*Et* = ethyl acetate; *ar* = aromatic; *Tos* = *p*-tosyl. The following compounds were prepared according to lit. procedures: 3-Acetyl-1-tosylindole [7], 3-acetyl-1-(2,2-dimethylpropanoyl)indole [8], 3-acetyl-1-(*tert*-butoxycarbonyl)indole [9].

3-(α,α-Dimethoxyethyl)-1-tosylindole (**1a**, $C_{19}H_{21}NO_4S$)

3-Acetyl-1-tosylindole (6.24 g, 20 mmol), 10–12 cm^3 $HC(OMe)_3$, and 1 cm^3 $MeSO_3H$ were suspended at 0°C in 40 cm^3 *Me*OH, and stirred for 14 h (TLC control). Then, the mixture was neutralized by a methanolic solution of NaOH (50%), and poured into 20 cm^3 ice-H_2O. After extraction with 3×100 cm^3 Et_2O, the combined organic layers were washed with 150 cm^3 H_2O, dried ($MgSO_4$), and evaporated. Yield 6.7 g (93%); colorless crystals; mp 85°C (*Me*OH); IR: $\bar{\nu}$ = 2829 (O*Me*), 1123 (COC), 1369, 1180 (SO_2) cm^{-1}; ^1H NMR (60 MHz): δ = 1.60 (s, *Me*), 2.30 (s, *Me*), 3.15 (s, 2 O*Me*), 7.00–8.00 (m, 9 *ar* H) ppm.

3-(α-Methoxyvinyl)-1-tosylindole (**1**, $C_{18}H_{17}NO_3S$)
A mixture of 6.7 g **1a** (18.6 mmol) and 100 mg $KHSO_4$ was heated to 100°C at 14×133 Pa. After cooling to room temperature 100 cm^3 of xylene were added, and after stirring for 5 min and filtration, the solvent was evaporated *in vacuo*. Yield 5.7 g (93%, not purified); IR (Film): $\bar{\nu} = 3052$ (=CH_2), 2833 (O*Me*), 1656, 1643 (=CH_2), 1372, 1175 (SO_2) cm^{-1}; ^1H NMR (60 MHz): $\delta = 2.30$ (s, *Me*), 3.15 (s, O*Me*), 4.35, 4.45 (=CH_2), 7.00–8.00 (m, 9 *ar* H) ppm; MS: m/z (%) = 327 (25) [M^+], 359 (10). The product was immediately used for further reactions.

5-Methoxy-2-phenyl-10-tosyl-4,10,10a,10b-tetrahydro-3aH-pyrrolo[3,4-a]carbazole-1,3-dione (**3a**, $C_{28}H_{24}N_2O_5S$)
From **1** (4.3 g, 13 mmol) and 2.25 g **2a** (13 mmol) in 100 cm^3 of toluene with stirring for 16 h and evaporation of the solvent *in vacuo*. Yield 2.25 g (24%); colorless crystals; mp 194°C (*Ac*O*Et*); IR: $\bar{\nu} = 2825$ (*Me*O), 1711 (CO), 1680 (=C–OSi), 1361, 1170 (SO_2) cm^{-1}; ^1H NMR (300 MHz): $\delta = 2.28$ (ddd, $J_{4A/10a} = 2$ Hz, $J_{4A/3a} = 6.6$ Hz, $J_{4A/4B} = 16.1$ Hz, 4-H_A), 2.34 (s, *Me*), 3.37 (dd, $J_{4B/3a} = 2$ Hz, $J_{4B/4A} = 15.9$ Hz, 4-H_B), 3.37 (m, 3a-H), 3.63 (s, *Me*O), 4.1 (dd, $J_{10b/10a} = 6.8$ Hz, $J_{10b/3a} = 8.8$ Hz, 10b-H), 4.66 (dd, $J_{10a/4A} = 2$ Hz, $J_{10a/10b} = 6.8$ Hz, 10a-H), 6.92–7.75 (m, 13 *ar* H) ppm.

5-Methoxy-2-methyl-10-tosyl-4,10,10a,10b-tetrahydro-3aH-pyrrolo[3,4-a]carbazole-1,3-dione (**3b**, $C_{23}H_{22}N_2O_5S$)
From **1** (4.3 g, 13 mmol) and 1.44 g **2b** (13 mmol) as described for **3a**, stirring for 72 h at room temperature. Yield 1.6 g (28%); colorless crystals; mp 205°C (*Ac*O*Et*); IR: $\bar{\nu} = 2943$ (CH), 2848 (*Me*O), 1779, 1709 (CO), 1596, 1492 (*ar* C–C), 1459, 1435, 1382 (CH), 1360, 1166 (SO_2) cm^{-1}; ^1H NMR (300 MHz): $\delta = 2.22$ (ddd, $J_{4A/10a} = 2.2$ Hz, $J_{4A/3a} = 6.6$ Hz, $J_{4A/4B} = 15.6$ Hz, 4-H_A), 2.34 (s, *Me*), 2.84 (s, N*Me*), 3.2 (ddd, $J_{3a/4B} = 1.7$ Hz, $J_{3a/4A} = 6.6$ Hz, $J_{3a/10b} = 8.7$ Hz, 3a-H), 3.29 (dd, $J_{4B/3a} = 1.7$ Hz, $J_{4B/4A} = 15.9$ Hz, 4-H_B), 3.63 (s, *Me*O), 3.85 (dd, $J_{10b/10a} = 7.1$ Hz, $J_{10b/3a} = 8.8$ Hz, 10b-H), 4.59 (dd, $J_{10a/4A} = 2.2$ Hz, $J_{10a/10b} = 7.1$ Hz, 10a-H), 6.94 (ddd, $J_{7/9} = 1.2$ Hz, $J_{7/6} = 7.6$ Hz, $J_{7/8} = 7.6$ Hz, 7-H), 7.12 (ddd, $J_{8/6} = 1.2$ Hz, $J_{8/7} = 7.6$ Hz, $J_{8/9} = 7.8$ Hz, 8-H), 7.21 (d, $J = 7.8$ Hz, 2 *ar* H), 7.48 (dd, $J_{9/7} = 1.2$ Hz, $J_{9/8} = 7.6$ Hz, 9-H), 7.61 (dd, $J_{6/8} = 0.7$ Hz, $J_{6/7} = 7.3$ Hz, 6-H), 7.75 (dd, $J = 1.7$ Hz, $J = 6.6$ Hz, 2 *ar* H) ppm.

2-Ethyl-5-methoxy-10-tosyl-4,10,10a,10b-tetrahydro-3aH-pyrrolo[3,4-a]carbazole-1,3-dione (**3c**, $C_{24}H_{24}N_2O_5S$)
From **1** (4.3 g, 13 mmol) and 1.7 g **2c** (13 mmol) as described for **3a**, but reflux for 2 d, and stirring for 3 d at room temperature. Yield 1.4 g (24%); colorless crystals; mp 200°C (*Ac*O*Et*); IR: $\bar{\nu} = 2940$, 2845 (CH), 1770, 1696 (CO), 1595 (*ar* C–C), 1455, 1404 (CH), 1360, 1165 (SO_2) cm^{-1}; ^1H NMR (300 MHz): $\delta = 0.86$ (t, $J = 7.1$ Hz, *Me*), 2.18 (ddd, $J_{4A/10a} = 2.2$ Hz, $J_{4A/3a} = 6.6$ Hz, $J_{4A/4B} = 15.9$ Hz, 4-H_A), 2.32 (s, *Me*), 3.16 (ddd, $J_{3a/4B} = 2$ Hz, $J_{3a/4A} = 6.6$ Hz, $J_{3a/10b} = 8.6$ Hz, 3a-H), 3.27 (dd, $J_{4B/3a} = 2$ Hz, $J_{4B/4A} = 15.9$ Hz, 4-H_B), 3.37 (dq, $J = 1.7$ Hz, $J = 7.1$ Hz, CH_2), 3.65 (s, *Me*O), 3.9 (dd, $J_{10b/10a} = 6.8$ Hz, $J_{10b/3a} = 8.6$ Hz, 10b-H), 4.56 (dd, $J_{10a/4A} = 2$ Hz, $J_{10a/10b} = 6.8$ Hz, 10a-H), 6.91 (dd*d*, $J_{7/9} = 1$ Hz, $J_{7/6} = 7.6$ Hz, $J_{7/8} = 7.6$ Hz, 7-H), 7.09 (ddd, $J_{8/6} = 1.5$ Hz, $J_{8/7} = 7.6$ Hz, $J_{8/9} = 7.8$ Hz, 8-H), 7.18 (*d*, $J = 8.1$ Hz, 2 *ar* H), 7.44 (dd, $J_{9/7} = 1$ Hz, $J_{9/8} = 7.6$ Hz, 9-H), 7.59 (*d*, $J_{6/7} = 8.1$ Hz, 6-H), 7.73 (dd, $J = 1.7$ Hz, $J = 8.3$ Hz, 2 *ar* H) ppm.

5-Methoxy-2-phenyl-10-tosyl-4,5,5a,10,10a,10b-hexahydro-3aH-pyrrolo[3,4-a]carbazole-1,3-dione (**4a**, $C_{28}H_{26}N_2O_5S$)
Pd–C (10%, 0.4 g) was added to a soln. of 1.0 g **3a** (2 mmol) in a mixture of 40 cm^3 CH_2Cl_2 and 40 cm^3 *Me*OH. The mixture was hydrogenated for 12 h at room temperature, the catalyst was separated, the solvent was removed *in vacuo*, a 1:1 mixture of cyclohexane and *Ac*O*Et* was added to the residue, and the insoluble part was separated and washed with the mixture of solvents until no impurities could be detected in the solvent (TLC control). Yield 660 mg (66%); colorless crystals; mp 274°C; IR: $\bar{\nu} = 1710$

(CO), 1597, 1499, 1479 (*ar* C–C), 1351, 1163 (SO_2), 1114, 1090 (C–O–C) cm^{-1}; ^1H NMR (300 MHz): $\delta = 1.73$ (ddd, $J_{4A/5} = 0.7$ Hz, $J_{4A/3a} = 8.5$ Hz, $J_{4A/4B} = 14.7$ Hz, 4-H_A), 2.71 (ddd, $J_{4B/3a} = 1$ Hz, $J_{4B/5} = 4.4$ Hz, $J_{4B/4A} = 14.9$ Hz, 4-H_B), 2.35 (s, *Me*), 3.14 (s, *Me*O), 3.22 (ddd, $J_{3a/4B} = 1$ Hz, $J_{3a/4A} = 8.5$ Hz, $J_{3a/10b} = 10.0$ Hz, 3a-H), 3.45 (dd, $J_{5a/5} = 6.1$ Hz, $J_{5a/10a} = 11$ Hz, 5a-H), 3.74 (dd, $J_{10b/3a} = 10.0$ Hz, $J_{10b/10a} = 7.8$ Hz, 10b-H), 3.90 (dd, $J_{5/5a} = 5.1$ Hz, $J_{5/4B} = 5.1$ Hz, 5-H), 4.68 (dd, $J_{10a/10b} = 7.8$ Hz, $J_{10a/5a} = 11$ Hz, 10a-H), 6.91–7.67 (m, 13 *ar* H) ppm.

5-Methoxy-2-methyl-10-tosyl-4,5,5a,10,10a,10b-hexahydro-3aH-pyrrolo[3,4-a]carbazole-1,3-dione (**4b**, $C_{23}H_{24}N_2O_5S$)

From **3b** (1.0 g, 2.3 mmol) as described for **4a**. Yield 720 mg (72%); colorless crystals; mp 240°C; IR: $\bar{\nu} = 2851$ (*Me*), 1701 (CO), 1597 (*ar* C–C), 1346, 1163 (SO_2), 1111, 1090 (C–O–C), 835, 815 (*ar*) cm^{-1}; ^1H NMR (300 MHz): $\delta = 1.67$ (dd, $J_{4A/3a} = 7.8$ Hz, $J_{4A/4B} = 14.2$ Hz, 4-H_A), 2.38 (s, *Me*), 2.66 (dd, $J_{4B/5} = 4.6$ Hz, $J_{4B/4A} = 14.2$ Hz, 4-H_B), 2.82 (s, N*Me*), 3.08 (s, *Me*O), 3.06–3.12 (m, 3a-H), 3.42 (dd, $J_{5a/5} = 6.1$ Hz, $J_{5a/10a} = 11$ Hz, 5a-H), 3.60 (dd, $J_{10b/3a} = 9.7$ Hz, $J_{10b/10a} = 7.8$ Hz, 10b-H), 3.85 (dd, $J_{5/5a} = 5.1$ Hz, $J_{5/4B} = 5.1$ Hz, 5-H), 4.62 (dd, $J_{10a/10b} = 7.8$ Hz, $J_{10a/5a} = 11$ Hz, 10a-H), 6.89 (d, $J_{6/7} = 7.3$ Hz, 6-H), 7.01 (ddd, $J_{7/9} = 1$ Hz, $J_{7/6} = 7.5$ Hz, $J_{7/8} = 7.5$ Hz, 7-H), 7.21 (*d*, $J = 8.1$ Hz, 2 *ar* H), 7.26 (dd, $J_{8/9} = 7.6$ Hz, $J_{8/7} = 7.2$ Hz, 8-H), 7.66 (*d*, $J = 8.3$ Hz, 2 *ar* H), 7.71 (*d*, $J_{9/8} = 8.1$ Hz, 9-H) ppm.

5-Methoxy-2-ethyl-10-tosyl-4,5,5a,10,10a,10b-hexahydro-3aH-pyrrolo[3,4-a]carbazole-1,3-dione (**4c**, $C_{24}H_{26}N_2O_5S$)

From **3c** (1.0 g, 2.2 mmol) as described for **4a**. Yield 650 mg (65%); colorless crystals; mp 221–223°C; IR: $\bar{\nu} = 1697$ (CO), 1599 (*ar* C–C), 1352, 1167 (SO_2), 1090 (C–O–C), 837, 815 (*ar*) cm^{-1}; ^1H NMR (300 MHz): $\delta = 1.0$ (t, $J = 7.1$ Hz, *Me*), 1.61 (ddd, $J_{4A/10a} = 0.9$ Hz, $J_{4A/3a} = 8.3$ Hz, $J_{4A/4B} = 14.7$ Hz, 4-H_A), 2.33 (s, *Me*), 2.59 (ddd, $J_{4B/3a} = 1.3$ Hz, $J_{4B/5} = 4.7$ Hz, $J_{4B/4A} = 14.7$ Hz, 4-H_B), 3.00 (ddd, $J_{3a/4B} = 1.3$ Hz, $J_{3a/4A} = 9$ Hz, $J_{3a/10b} = 9$ Hz, 3a-H), 3.05 (s, *Me*O), 3.34 (dq, $J = 1.8$ Hz, $J = 7.1$ Hz, CH_2), 3.37 (m, 5a-H), 3.52 (dd, $J_{10b/3a} = 9.8$ Hz, $J_{10b/10a} = 8.1$ Hz, 10b-H), 3.80 (dd, $J_{5/5a} = 4.9$ Hz, $J_{5/4B} = 4.8$ Hz, 5-H), 4.57 (dd, $J_{10a/5a} = 10.9$ Hz, $J_{10a/10b} = 7.9$ Hz, 10a-H), 6.85 (d, $J_{6/7} = 7.5$ Hz, 6-H), 6.96 (ddd, $J_{7/9} = 1.1$ Hz, $J_{7/6} = 7.5$ Hz, $J_{7/8} = 7.5$ Hz, 7-H), 7.16 (dd, $J = 0.6$ Hz, $J = 8.6$ Hz, 2 *ar* H), 7.20 (dd, $J_{8/7} = 7.5$ Hz, $J_{8/9} = 7.5$ Hz, 8-H), 7.60 (d, $J = 8.4$ Hz, 2 *ar* H), 7.66 (*d*, $J_{9/8} = 8.1$ Hz, 9-H) ppm.

5-Hydroxy-2-phenyl-10-tosyl-4,10,10a,10b-tetrahydro-3aH-pyrrolo[3,4-a]carbazole-1,3-dione (**5a**, $C_{27}H_{22}N_2O_5S$)

Compound **3a** (500 mg, 1 mmol) was suspended in a mixture of 20 cm^3 dil. H_2SO_4 (98 g · dm^{-3}) and 10 cm^3 conc. H_2SO_4, the mixture was refluxed until the reaction was completed (TCL control), and after cooling to room temperature the precipitate was separated and washed with H_2O until H_2O reacted neutral. Yield 3–5 mg; ^1H NMR (300 MHz): $\delta = 2.31$ (s, *Me*), 2.62 (dd, $J_{4A/4B} = 15.8$ Hz, $J_{4A/3a} = 7.7$ Hz, 4-H_A), 2.88 (d, $J_{4B/4A} = 15.8$ Hz, 4-H_B), 3.42 (dd, $J_{3a/10b} = 7.1$ Hz, $J_{3a/4A} = 7.1$ Hz, 3a-H), 3.92 (dd, $J_{10b/10a} = 6.8$ Hz, $J_{10b/3a} = 8.7$ Hz, 10b-H), 4.85 (dd, $J_{10a/4A} = 1.5$ Hz, $J_{10a/10b} = 6.8$ Hz, 10a-H), 6.9–8.0 (m, 13 *ar* H), 9.8 (*b*s, H–O) ppm.

5-Hydroxy-2-methyl-10-tosyl-4,10,10a,10b-tetrahydro-3aH-pyrrolo[3,4-a]carbazole-1,3-dione (**5b**, $C_{22}H_{20}N_2O_5S$)

From **3b** (400 mg, 0.9 mmol) as described for **5a**. Yield 140 mg (40%); colorless crystals; mp 245°C; IR: $\bar{\nu} = 3432$ (OH), 1777, 1702 (CO), 1595 (*ar* C–C), 1361, 1166 (SO_2) cm^{-1}; ^1H NMR (300 MHz): $\delta = 2.32$ (s, *Me*), 2.53 (ddd, $J_{4A/10a} = 2$ Hz, $J_{4A/3a} = 7.3$ Hz, $J_{4A/4B} = 15.6$ Hz, 4-H_A), 2.72 (s, N*Me*), 2.95 (dd, $J_{4B/3a} = 1.5$ Hz, $J_{4B/4A} = 15.8$ Hz, 4-H_B), 3.27 (ddd, $J_{3a/4B} = 1.5$ Hz, $J_{3a/4A} = 7.6$ Hz, $J_{3a/10b} = 7.8$ Hz, 3a-H), 3.88 (dd, $J_{10b/3a} = 8.8$ Hz, $J_{10b/10a} = 6.6$ Hz, 10b-H), 4.78 (dd, $J_{10a/4A} = 2$ Hz, $J_{10a/10b} = 6.6$ Hz, 10a-H), 6.89 (ddd, $J_{7/9} = 1$ Hz, $J_{7/6} = 7.6$ Hz, $J_{7/8} = 7.6$ Hz, 7-H), 7.03 (ddd,

$J_{8/6} = 1.2$ Hz, $J_{8/7} = 8.1$ Hz, $J_{8/9} = 8.1$ Hz, 8-H), 7.31 (d, $J = 8.1$ Hz, 2 *ar* H), 7.38 (d, $J_{6/7} = 6.6$ Hz, 6-H), 7.54 (d, $J_{9/8} = 8.1$ Hz, 9-H), 7.77 (dd, $J = 1.7$, 8.3 Hz, 2 *ar* H), 9.60 (*b*s, H–O) ppm; MS (CI(Isobutane), 170 eV: m/z (%) = 425 (100) [M^+].

3-Hydroxy-5-methoxy-2-phenyl-10-tosyl-3,3a,4,10,10a,10b-hexahydropyrrolo[3,4-a]carbazole-1-one (**6a**, $C_{28}H_{26}N_2O_5S$)

Under a N_2 atmosphere, 1.8 cm^3 of a L-Selectride® soln. (1.8 mmol) were added at −78°C to a soln. of 500 mg **3a** (1 mmol) in *THF*, and the mixture was stirred for 1 h. Then 1.5 cm^3 *Me*OH were added, and stirring was continued for 10 min. The mixture was allowed to warm to room temperature, 1.5 cm^3 H_2O and 3 g Na_2SO_4 were added, after 30 min the mixture was filtered, the residue was washed with Et_2O, and the combined org. layers were evaporated *in vacuo*. Yield 210 mg (42%); colorless crystals; mp 170–172°C (*Et*OH); IR: $\bar{\nu} = 3435$ (OH), 1685 (CO), 1597 (*ar* C), 1359, 1167 (SO_2), 1110, 1091 (C–O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$/*DMSO*-d_6 1/1): $\delta = 1.98$ (s, *Me*), 2.06 (ddd, $J_{4A/10a} = 2.2$ Hz, $J_{4A/3a} = 8.5$ Hz, $J_{4A/4B} = 16.4$ Hz, 4-H_A), 2.29 (d, $J_{4B/4A} = 16.4$ Hz, 4-H_B), 2.39 (dd, $J_{3a/4A} = 8.3$ Hz, $J_{3a/10b} = 8.3$ Hz, 3a-H), 3.22 (s, *Me*O), 3.72 (dd, $J_{10b/3a} = 8.3$ Hz, $J_{10b/10a} = 5.1$ Hz, 10b-H), 4,13 (dd, $J_{10a/4A} = 1.7$ Hz, $J_{10a/10b} = 4.6$ Hz, 10a-H), 4.77 (d, $J_{3/OH} = 8.1$ Hz, 3-H), 5.99 (d, $J_{OH/3} = 8.3$ Hz, H–O), 6.52–7.36 (m, 13 *ar* H) ppm.

3-Hydroxy-5-methoxy-2-methyl-10-tosyl-3,3a,4,10,10a,10b-hexahydropyrrolo[3,4-a]carbazole-1-one (**6b**, $C_{23}H_{24}N_2O_5S$)

From **3b** (1.0 g, 2.3 mmol) and 4.1 cm^3 of a L-Selectride® soln. as described for **6a**. Yield 850 mg (83%); colorless crystals; mp 164–166°C (*Et*OH); IR: $\bar{\nu} = 3440$ (OH), 1684 (CO), 1596 (*ar* C), 1356, 1167 (SO_2), 1109, 1090 (C–O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$/*DMSO*-d_6 5/1): $\delta = 2.06$ (ddd, $J_{4A/10a} = 2.4$ Hz, $J_{4A/3a} = 8.3$ Hz, $J_{4A/4B} = 16.6$ Hz, 4-H_A), 2.16 (s, *Me*), 2.5 (m, 3a-H, 4-H_B, N*Me*), 3.45 (s, *Me*O), 3.64 (dd, $J_{10b/3a} = 8.9$ Hz, $J_{10b/10a} = 5.6$ Hz, 10b-H), 4,23 (dd, $J_{10a/4A} = 2.4$ Hz, $J_{10a/10b} = 5.6$ Hz, 10a-H), 4.34 (dd, $J_{3/OH} = 8.2$ Hz, $J = 1$ Hz, 3-H), 5.56 (*d*, $J_{OH/3} = 8.3$ Hz, H–O), 6.72 (ddd, $J_{7/6} = 7.6$ Hz, $J_{7/8} = 7.6$ Hz, $J_{7/9} = 1$ Hz, 7-H), 6.89 (ddd, $J_{8/7} = 7.6$ Hz, $J_{8/9} = 7.6$ Hz, $J_{8/6} = 1.2$ Hz, 8-H), 7.02 (dd, $J = 7.8$ Hz, $J = 0.7$ Hz, 2 *ar* H), 7.27 (*d*, $J_{9/8} = 7.3$ Hz, 9-H), 7.35 (*d*, $J_{6/7} = 8.1$ Hz, 6-H), 7.53 (dd, $J = 6.6$ Hz, $J = 1.7$ Hz, 2 *ar* H).

2-Methyl-10-tosyl-3a,4,10,10b-tetrahydropyrrolo[3,4-a]carbazole-1,3,5-trione (**7**, $C_{22}H_{18}N_2O_5S$)

Compound **5b** (120 mg, 0.28 mmol) was refluxed in *Et*OH for 30 min. Yield 85 mg (71%); colorless crystals; mp 236–239°C; IR: $\bar{\nu} = 1779$, 1709, 1678 (CO), 1595 (*ar* C–C), 1379, 1171 (SO_2), 813 (*ar*) cm^{-1}; ^{1}H NMR (300 MHz): $\delta = 2.4$ (s, *Me*), 2.81 (dd, $J_{4A/4B} = 17.2$ Hz, $J_{4A/3a} = 9.0$ Hz, 4-H_A), 3.07 (dd, $J_{4B/4A} = 17.2$ Hz, $J_{4B/3a} = 8.1$ Hz, 4-H_B), 3.08 (s, N*Me*), 3.79 (ddd, $J_{3a/4A} = 8.8$ Hz, $J_{3a/4B} = 8.4$ Hz, $J_{3a/10b} = 8.4$ Hz, 3a-H), 5.39 (d, $J_{10b/3a} = 7.8$ Hz, 10b-H), 7.3 (m, 7-H, 8-H, 2 *ar* H), 7.73 (m, 1 *ar* H), 8.05 (d, $J = 8.5$ Hz, 2 *ar* H), 8.22 (m, 1 *ar* H) ppm.

3-(α,α-Dimethoxyethyl)-1-(tert-butoxycarbonyl)indole (**9a**, $C_{17}H_{23}NO_4$)

From 3-acetyl-1-(*tert*-butoxycarbonyl)indole (5.18 g, 20 mmol) as described for **1a**. Yield 5.75 g (94%); mp 108–110°C (*Me*OH); IR: $\bar{\nu} = 3049$ (*ar* CH), 2990 (CH), 2827 (O*Me*), 1730 (CO), 1610 (*ar* C–C), 1430 (*Me*), 1248, 1211 (CMe_3) cm^{-1}; ^{1}H NMR (60 MHz): $\delta = 1.70$ (s, *Me*, CMe_3), 3.20 (s, 2 O*Me*), 7.10–8.40 (m, 5 *ar* H) ppm.

3-(α-Methoxyvinyl)-1-(tert-butoxycarbonyl)indole (**9**, $C_{16}H_{19}NO_3$)

From **9a** (6.1 g, 20 mmol) as described for **1**. Yield 4.9 g (90%, not purified); IR (Film): $\bar{\nu} = 2980$ (CH), 1737 (CO), 1606 (*ar* C–C), 1245 (C(Me)$_3$) cm^{-1}; ^{1}H NMR (60 MHz): $\delta = 1.70$ (s, CMe_3), 3.20 (s, O*Me*), 4.40, 4.70 (=CH_2), 7.00–8.30 (m, 5 *ar* H) ppm. The product was immediately used for further reactions.

10-(tert-Butoxycarbonyl)-2-phenyl-3a,4,10,10b-tetrahydropyrrolo[3,4-a]carbazole-1,3,5-trione (**10a**, $C_{25}H_{22}N_2O_5$)
From **9** (4.9 g, 18 mmol) and 1.73 g **2a** (10 mmol) in toluene with stirring for 5 d at room temperature, and evaporation of the solvent *in vacuo*. Yield 1.51 g (35%); colorless crystals; mp 190°C (*Ac*O*Et*); IR: $\bar{\nu} = 2986$ (CH), 1756, 1722, 1661 (CO), 1596 (*ar* C–C), 1455, 1371, 1208 (*Me*) cm^{-1}; ^1H NMR (300 MHz): $\delta = 1.75$ (s, C*Me*$_3$), 3.08 (d, $J_{4/3a} = 7.6$ Hz, 4-H_A, 4-H_B), 3.89 (dt, $J_{3a/10b} = 8.4$ Hz, $J_{3a/4} = 7.6$ Hz, 3a-H), 5.52 (d, $J_{10b/3a} = 8.5$ Hz, 10b-H), 7.20–8.30 (m, 9 *ar* H) ppm.

10-(tert-Butoxycarbonyl)-2-methyl-3a,4,10,10b-terahydropyrrolo[3,4-a]carbazole-1,3,5-trione (**10b**, $C_{20}H_{20}N_2O_5$)
From **9** (4.9 g, 18 mmol) and 1.1 g **2b** (10 mmol) as described for **10a**. Yield 1.2 g (33%); colorless crystals; mp 176°C (*Ac*O*Et*); IR: $\bar{\nu} = 2982$ (CH), 1745, 1697, 1666 (CO), 1454, 1375 (*Me*) cm^{-1}; ^1H NMR (300 MHz): $\delta = 1.80$ (s, C*Me*$_3$), 2.98 (s, N*Me*), 2.99 (*d*, $J_{4A/3a} = 8.1$ Hz, 4-H_A), 3.01 (*d*, $J_{4B/3a} = 5.6$ Hz, 4-H_B), 3.70 (ddd, $J_{3a/4B} = 6.1$ Hz, $J_{3a/4A} = 8.3$ Hz, $J_{3a/10b} = 8.3$ Hz, 3a-H), 5.32 (d, $J_{10b/3a} = 8.3$ Hz, 10b-H), 7.7–8.25 (m, 4 *ar* H) ppm.

10-(tert-Butoxycarbonyl)-2-ethyl-3a,4,10,10b-tetrahydropyrrolo[3,4-a]carbazole-1,3,7-trione (**10c**, $C_{21}H_{22}N_2O_5$)
From **9** (4.9 g, 18 mmol) and 1.3 g **2c** (10 mmol) as described for **10a**. Yield 0.76 g (20%); colorless crystals; mp 169°C (*Ac*O*Et*); IR: $\bar{\nu} = 2986$ (CH), 1752, 1707, 1664 (CO), 1453, 1372 (*Me*) cm^{-1}; ^1H NMR (300 MHz): $\delta = 1.15$ (t, $J = 7.3$ Hz, *Me*), 1.8 (s, C*Me*$_3$), 2.98 (*d*, $J_{4/3a} = 7.7$ Hz, 4-H_A, 4-H_B), 3.56 (q, $J = 7.3$ Hz, CH_2), 3.70 (dt, $J_{3a/4} = 7.6$ Hz, $J_{3a/10b} = 8.1$ Hz, 3a-H), 5.31 (*d*, $J_{10b/3a} = 8.5$ Hz, 10b-H), 7.34–8.25 (m, 4 *ar* H) ppm.

3-(α-Diethylphosphoryloxyvinyl)-1-tosylindole (**11**, $C_{21}H_{24}NO_6S$)
At −78°C 3.12 g **1a** (10 mmol) in 20 cm^3 *THF* were added to a soln. of 15 mmol *LDA* in 20 cm^3 *THF*, and after 10 min stirring 2.9 cm^3 of diethyl chlorophosphate (20 mmol) were added in one portion. After warming to room temperature (*ca.* 2 h) 50 cm^3 of *n*-pentane were added, the organic layer was separated, the aqueous layer was extracted with Et_2O, the combined organic layers were washed with 100 cm^3 satd. $NaHCO_3$ solution, dried ($MgSO_4$), and evaporated *in vacuo*: Yield 3 g (67%, not purified). The product was immediately used for further reactions.

5-Hydroxyimino-2-methyl-10-(tert-butoxycarbonyl)-3a,4,10,10b-tetrahydropyrrolo[3,4-a]carbazole-1,3-dione (**12a**, $C_{20}H_{21}N_3O_5$)
A mixture of 5.0 g *Ac*ONa (60 mmol) and 4.2 g $H_2NOH \times HCl$ (60 mmol) in 50 cm^3 *Et*OH was refluxed for some min, filtered, 0.2 g **10b** (0.54 mmol) were added to the filtrate, which was then refluxed for 3 h. After evaporation of the solvent *in vacuo*, 20 cm^3 *Et*OH were added to the residue, and H_2O was added until milkiness. Yield 160 mg (78%); colorless crystals; mp 185°C (*Et*OH); IR: $\bar{\nu} = 3435$ (OH), 2983 (CH), 1745, 1703 (CO), 1629 (C=N), 1435, 1370, 1208 (*Me*) cm^{-1}; ^1H NMR (300 MHz): $\delta = 1.80$ (s, C*Me*$_3$), 2.93 (dd, $J_{4A/3} = 7.3$ Hz, $J_{4A/4B} = 16.4$ Hz, 4-H_A), 2.97 (s, N*Me*), 3.56 (m, 3a-H), 3.63 (dd, $J_{4B/3a} = 4.9$ Hz, $J_{4B/4A} = 16.1$ Hz, 4-H_B), 5.22 (d, $J_{10b/103a} = 8.3$ Hz, 10b-H), 7.27 (dd, 1 *ar* H), 7.35 (dd, 1 *ar* H), 7.42 (s, 1 H–O), 8.08 (*d*, 2 *ar* H) ppm.

2-Ethyl-5-hydroxyimino-10-(tert-butoxycarbonyl)-3a,4,10,10b-tetrahydropyrrolo[3,4-a]carbazole-1,3-dione (**12b**, $C_{21}H_{23}N_3O_5$)
From 250 mg **10c** (0.65 mmol) as described for **12a**. Yield 197 mg (77%); colorless crystals; mp 176°C (*Et*OH); IR: $\bar{\nu} = 3439$ (OH), 2982 (CH), 1742, 1709 (CO), 1624 (C=N), 1456, 1371, 1223 (*Me*) cm^{-1}; ^1H NMR (300 MHz): $\delta = 1.13$ (t, $J = 7.3$ Hz, *Me*), 1.85 (s, C*Me*$_3$), 3.06 (dd, $J_{4A/3a} = 7.8$ Hz, $J_{4A/4B} = 16.6$ Hz, 4-H_A), 3.41 (dd, $J_{4B/3a} = 5.9$ Hz, $J_{4B/4A} = 16.6$ Hz, 4-H_B), 3.51 (ddd, $J_{3a/4B} =$

5.6 Hz, $J_{3a/4A} = 8.1$ Hz, $J_{3a/10b} = 8.1$ Hz, 3a-H), 3.53 (q, $J = 7.3$ Hz, CH_2), 5.19 (*d*, $J_{10b/3a} = 8.3$ Hz, 10b-H), 7.27 (ddd, 1 *ar* H), 7.35 (ddd, 1 *ar* H), 7.41 (s, H–O), 8.10 (m, 2 *ar* H) ppm.

2-Phenyl-3a,4,10,10b-tetrahydropyrrolo[3,4-a]carbazole-1,3,5-trione (**13a**) [10]
Compound **10a** (0.3 g, 0.7 mmol) was heated until melting. Yield 0.21 g (90%); colorless crystals; mp 275°C (Ref. [10] 275–280°C); IR: $\bar{\nu} = 3408$ (NH), 1712, 1629 (CO) cm^{-1}; ^1H NMR (300 MHz, acetone-d_6): $\delta = 2.96$ (dd, $J_{4A/3a} = 8.5$ Hz, $J_{4A/4B} = 17.3$ Hz, 4-H_A), 3.15 (dd, $J_{4B/3a} = 3.7$ Hz, $J_{4B/4A} = 17.3$ Hz, 4-H_B), 4.15 (ddd, $J_{3a/4B} = 3.7$ Hz, $J_{3a/4A} = 8.3$ Hz, $J_{3a/10b} = 8.3$ Hz, 3a-H), 4.82 (*d*, $J_{10b/3a} = 8.3$ Hz, 10b-H), 7.19–8.16 (m, 9 *ar* H), 11.1 (*b*s, H–N) ppm.

2-Methyl-3a,4,10,10b-tetrahydropyrrolo[3,4-a]carbazole-1,3,5-trione (**13b**, $C_{15}H_{12}N_2O_3$) [4]
From 260 mg **10b** (0.7 mmol) as described for **13a**. Yield 0.24 g (90%); colorless crystals; mp 282°C (*Me*OH); IR: $\bar{\nu} = 3227$ (NH), 1779, 1703, 1626 (CO) cm^{-1}; ^1H NMR (300 MHz): $\delta = 2.59$ (dd, $J_{4A/3a} = 8.8$ Hz, $J_{4A/4B} = 17.6$ Hz, 4-H_A), 2.68 (s, N*Me*), 2.88 (dd, $J_{4B/3a} = 2.7$ Hz, $J_{4B/4A} = 17.3$ Hz, 4-H_B), 3.45 (ddd, $J_{3a/4B} = 2.7$ Hz, $J_{3a/4A} = 8.6$ Hz, $J_{3a/10b} = 8.6$ Hz, 3a-H), 4.19 (d, $J_{10b/3a} = 8.3$ Hz, 10b-H), 6.93 (m, 2 *ar* H), 7.22 (m, 1 *ar* H), 7.84 (m, 1 *ar* H), 11.4 (bs, H–N) ppm.

5-(Diethylphosphoryloxy)-2-phenyl-10-tosyl-4,10,10a,10b-tetrahydro-3aH-pyrrolo[3,4-a]carbazole-1,3-dione (**14**, $C_{31}H_{31}N_2O_8PS$)
From 3.0 g **11** (6.7 mmol) and 1.73 g **2a** (10 mmol) as described for **10a**, purification CC (*Ac*O*Et*/cyclohexane 4/1). Yield 1.6 g (25%); colorless crystals; mp 204°C; IR: $\bar{\nu} = 1716$ (C=C), 1359, 1170 (SO_2), 1271 (P=O) cm^{-1}; ^1H NMR (300 MHz): $\delta = 1.25$ (m, 2 *Me*), 2.36 (s, *Me*), 2.65 (dddd, $J_{4A/10a} = 2.4$ Hz, $J_{4A/3a} = 7.8$ Hz, $J_{4A/4B} = 16.9$ Hz, $J_{4A/P} = 2.4$ Hz, 4-H_A), 3.35 (ddd, $J_{3a/4A} = 7.8$ Hz, $J_{3a/10b} = 8.9$ Hz, $J_{3a/P} = 1.5$ Hz, 3a-H), 3.37 (*d*, $J_{4B/4A} = 15.1$ Hz, 4-H_B), 4.13 (m, 2 CH_2), 4.17 (dd, $J_{10b/3a} = 8.9$ Hz, $J_{10b/10a} = 6.6$ Hz, 10b-H), 4.61 (ddd, $J_{10a/10b} = 6.6$ Hz, $J_{10a/4A} = 2.3$ Hz, $J_{10a/P} = 4.3$ Hz, 10a-H), 6.96–7.77 (m, 13 *ar* H) ppm. HREIMS: m/z = calcd 622.154444; found 622.153876 (0.9 ppm).

5-Hydroxyimino-2-methyl-3a,4,10,10b-tetrahydropyrrolo[3,4-a]carbazole-1,3-dione (**15a**, $C_{15}H_{13}N_3O_3$)
From 200 mg **13b** (0.75 mmol) as described for **12a**. Yield 153 mg (72%); mp 252–255°C (dec, *Et*OH); IR: $\bar{\nu} = 3366$ (OH, NH), 1778, 1696 (CO), 1620 (C=N) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$/*DMSO*-d_6): $\delta = 2.29$ (dd, $J_{4A/3} = 8.3$ Hz, $J_{4A/4B} = 17.3$ Hz, 4-H_A), 2.53 (s, N*Me*), 3.22 (ddd, $J_{3a/4B} = 2.9$ Hz, $J_{3a/4A} = 8.2$ Hz, $J_{3a/10b} = 8.2$ Hz, 3a-H), 3.48 (dd, $J_{4B/3a} = 2.9$ Hz, $J_{4B/4A} = 17.4$ Hz, 4-H_B), 3.95 (d, $J_{10b/3a} = 8.1$ Hz, 10b-H), 6.68 (dd, $J = 7.5$, 7.5 Hz, 7(8)-H), 6.77 (dd, $J = 7.3$, 7.3 Hz, 8(7)-H), 7.05 (*d*, $J = 7.8$ Hz, 9-H), 7.62 (*d*, $J = 7.9$ Hz, 6-H), 9.9 (s, H–O), 10.6 (s, NH) ppm.

2-Ethyl-5-hydroxyimino-3a,4,10,10b-tetrahydropyrrolo[3,4-a]carbazole-1,3-dione (**15b**, $C_{16}H_{15}N_3O_3$)
From 200 mg **12b** (0.5 mmol) as described for **12a**. Yield 134 mg (90%); mp 225–227°C; IR: $\bar{\nu} = 3439$ (OH), 2982 (CH), 1742, 1709 (CO), 1624 (C=N), 1456, 1371, 1223 (*Me*) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$/*DMSO*-d_6): $\delta = 0.88$ (t, $J = 7.1$ Hz, *Me*), 2.55 (dd, $J_{4A/3a} = 8.4$ Hz, $J_{4A/4B} = 17.4$ Hz, 4-H_A), 3.27 (q, $J = 7.1$ Hz, CH_2), 3.33 (ddd, $J_{3a/4} = 3.1$ Hz, $J_{3a/4A} = 8.2$ Hz, $J_{3a/10b} = 8.3$ Hz, 3a-H), 3.61 (dd, $J_{4B/3a} = 3.1$ Hz, $J_{4B/4A} = 17.4$ Hz, 4-H_B), 4.07 (d, $J_{10b/3a} = 8.2$ Hz, 10b-H), 6.87 (ddd, $J = 1.1$, 7.1, 7.1 Hz, 7(8)-H), 6.96 (ddd, $J = 1.3$, 7.1, 7.1 Hz, (8)7-H), 7.22 (dd, $J = 1.1$, 8.1 Hz, 9-H), 7.83 (dd, $J = 0.6$, 7.8 Hz, 6-H), 9.85 (s, H–O), 10.30 (s, NH) ppm.

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