General Methods for Chemical Synthesis:

Materials: Unless otherwise noted, reagents were purchased from Acros Chimica, Fluka, Sigma, Aldrich and used without further purification. LC-MS was performed on the 1100 series from Hewlett-Packard with a VP 50/10 Nucleosil C18PPN-column (Macherey-Nagel) and a Finnigan LCQ ESI-Spectrometer with a gradient: 90/10 (v/v) H_2O/Acetonitril (0.1% trifluoroacetic acid) to 10/90 (v/v) in 30 min, flow 1 ml/min. Preparative HPLC was conducted by using Pro Star 215/Varian HPLC with a VP 250/21 Nucleosil C18PPN-column (Macherey-Nagel) and a gradient: 90/10 (v/v) H_2O/Acetonitril (0.1% trifluoroacetic acid) to 10/90 (v/v) in 30 min, flow 20 ml/min. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Mercury 400 (400 MHz ^{1}H-, 100,6 MHz ^{13}C-NMR). ^{1}H NMR spectra are tabulated in the following order: chemical shifts calculated with reference to solvent standards based on tetramethylsilane, multiplicity (s, singulet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constants in Hz, and number of protons. 70 eV- electronionisation (EI) high-resolution mass spectra (HR-MS) were recorded on Finnigan MAT MS 70 spectrometer.

General procedure for the carbodiimide-mediated preparation of polymer-bound phenylhydrazides: To a suspension of the acid-functionalized support **11** in methylene chloride (10 ml/g resin) *N*,*N*-diisopropylcarbodiimide (3 equiv.), 1-hydroxybenzotriazole (3 equiv.), triethylamine (3 equiv.) and phenylhydrazine (3 equiv.) were added. The mixture was shaken for 18 h at room temperature and filtered. The resin was washed with methylene chloride, DMF, DMF/water (1:1), DMF, methanol, methylene chloride and cyclohexane (2 times each) and dried to constant weight in vacuo.

General procedure for the preparation of polymer-bound phenylhydrazines:

To a suspension of the polymer-bound phenylhydrazide **13** 80 mg (0.05 mmol) in 300 µl THF 250 µl of a 1M BH_3/THF-solution (0.250 mmol, 5 eq.) were added under argon atmosphere. The reaction mixture was heated at 60°C, shaken over night and filtered. The resin was washed with 5 ml DMF, DMF/water (1:1), DMF, methanol and methylene chloride (2 times each) and dried to constant weight in vacuo.

General procedure for the Fischer-indole-rearrangement on the solid support :

To a suspension of 80 mg (0.05 mmol) of the polymer-bound phenylhydrazine **14** in 1 ml methylene chloride ketone **15** (3 eq.) and 3 ml TFA were added under argon atmosphere. The reaction mixture was heated at 80°C, was shaken for 1-3 days and filtered. The resin was washed with 5 ml methylene chloride, methylene chloride /methanol (1:1), methylene

chloride and methanol (2 times each), the filtrate was evaporated and the residue was dried in vacuo. The product was isolated by prep. HPLC.

6,7,8,9-Tetrahydro-5*H*-carbazole-3-sulfonic acid: colorless oil; 41%; ^{1}H-NMR (400 MHz, CD_3OD): δ = 7.90 (s, 1 H, arom. CH), 7.52 (d, ^3J = 8.6 Hz, 1 H, arom. CH), 7.27 (d, ^3J = 8.6 Hz, 1 H, arom. CH), 2.71 (m, 4 H, CH_2), 1.89 (m, 4 H, CH_2); MS (ESI): 252.05 $[M+H]^+$; $C_{12}H_{13}NO_3S$ (251.06 g/mol).

6-Bromo-2,3,4,9-tetrahydro-carbazol-1-one: colorless oil; 7%; ^{1}H-NMR (400 MHz, CD_3OD): δ = 8.28 (d, ^3J = 8,0 Hz, 1 H, arom. CH), 7.75 (dd, ^3J = 8,0 Hz, ^4J = 5,0 Hz, 1 H, arom. CH), 7.56 (s, 1 H, arom. CH), 2.43 (m, 2 H, CH_2), 2.39 (m, 2 H, CH_2), 1.85-1.80 (m, 2 H, CH_2); GCMS, m/z (rel Int. %): 265 (100); 263 (100) $[M^+]$, 236 (31), 221 (10), 207 (55), 154 (8), 128 (20), 115 (4), 101 (5), 78 (3); $C_{12}H_{10}BrNO$ (262.99 g/mol).

6-Bromo-1-methyl-2,3,4,9-tetrahydro-1*H*-carbazole: colorless oil; 7%; ^{1}H-NMR (400 MHz, CD_3OD): δ = 8.28 (d, ^3J = 8.0 Hz, 1 H, arom. CH), 7.75 (dd, ^3J = 8.0 Hz, ^4J = 5.0 Hz, 1H, arom. CH), 7.56 (s, 1 H, arom. CH), 2.91 (m, 1 H, CH), 2.43 (m, 2 H, CH_2), 1.56 (m, 2 H, CH_2), 1.52 (m, 2 H, CH_2), 1.81 (m, 3 H, CH_3); GCMS, m/z (rel Int. %): 265 (83); 263 (85) $[M^+]$, 248 (100), 235 (41), 221 (10), 208 (5), 184 (8), 168 (35), 154 (20), 128 (5), 115 (4); $C_{13}H_{14}BrN$ (263.03 g/mol).

6,8-Difluoro-2,3,4,9-tetrahydro-1*H*-carbazole: colorless oil; 9%; ^{1}H-NMR (400 MHz, CD_3OD): δ = 6.95 (dd, ^3J (HF) = 9.0 Hz, ^4J (HH) = 2.0 Hz, 1 H, arom. CH), 6.63 (ddd, ^3J (HF) = 9.0 Hz, ^4J (HH) = 2.0 Hz, 1 H, arom. CH), 2.75 (t, ^3J = 6.0 Hz, 2 H, CH_2), 2.60 (t, ^3J = 6.0 Hz, 2 H, CH_2), 1.92-1.85 (m, 4 H, CH_2); MS (ESI): 208.05 $[M+H]^+$; $C_{12}H_{11}F_2N$ (207.09 g/mol).

1-(5-Bromo-1*H*-indol-2-yl)-ethanone: colorless oil; 39%; ^{1}H-NMR (400 MHz, CD_3OD): δ = 7.83 (s, 1 H, arom. CH), 7.40 (dd, ^3J = 8.0 Hz, ^4J = 5.0 Hz, 1 H, arom. CH), 7.28 (d, ^3J = 8.0 Hz, 1 H, arom. CH), 7.10 (s, 1 H, arom. CH), 2.59 (m, 3 H, CH_3); MS (ESI): 238.1, 240.1 $[M+H]^+$; GCMS, m/z (rel Int. %): 239 (100); 237 (100) $[M^+]$, 222 (89), 194 (25), 167 (31), 143 (8), 114 (10), 88 (15), 62 (5), 43 (8); $C_{10}H_8BrNO$ (236.98 g/mol).

6-Bromo-2,3,4,9-tetrahydro-1*H*-carbazole: colorless oil; 33%; ^{1}H-NMR (400 MHz, CD_3OD): 7.56 (s, 1 H, arom. CH), 7.18 (dd, ^3J = 8.6 Hz, ^4J = 5.0 Hz, 1 H, arom. CH), 7.13 (d, ^3J = 8.6 Hz, 1 H, arom. CH), 2.72 (t, ^3J = 5.5 Hz, 2 H, CH_2), 2.65 (t, ^3J = 5.5 Hz, 2 H, CH_2), 1.93-1.84 (m, 4 H, 2 CH_2); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ = 135.8 (C_q), 135.7 (C_q), 129.9 (C_q), 123.9 (arom. CH), 120.7 (arom. CH), 112.6 (C_q), 111.9 (arom. CH), 110.3 (C_q), 23.4 (CH_2), 23.3 (CH_2), 23.2 (CH_2), 20.9 (CH_2); GCMS, m/z (rel Int. %): 251 (55); 249 (50) $[M^+]$, 221 (100), 168 (31), 142 (15), 115 (20), 83 (4); $C_{12}H_{12}BrN$ (249.02 g/mol).

6-Trifluoromethyl-2,3,4,9-tetrahydro-1*H*-carbazole: colorless oil; 6%; ^{1}H-NMR (400 MHz, CD_3OD): δ = 7.38 (d, ^3J = 8.0 Hz, 1 H, arom. CH), 7.11 (s, 1 H, arom. CH), 6.95 (dd, ^3J = 8.0 Hz, ^4J = 5.0 Hz, 1 H, arom. CH), 2.77 (t, ^3J = 5.5 Hz, 2 H, CH_2), 2.68 (t, ^3J = 5.4 Hz, 2 H), 1.98-1.89 (m, 4 H, 2 CH_2); GCMS, m/z (rel Int. %): 239 (35) [M^+], 211 (100), 198 (5), 167 (5), 131 (4), 115 (4); $C_{13}H_{12}F_3N$ (239.09 g/mol).

5-Bromo-3-ethyl-2-methyl-1*H*-indole: colorless oil; 12%; ^{1}H-NMR (400 MHz, CD_3OD): δ = 7.61 (s, 1 H, arom. CH), 7.16 (dd, ^3J = 8.6 Hz, ^4J = 5.0 Hz, 1 H, arom. CH), 7.11 (d, ^3J = 8.6 Hz, 1 H, arom. CH), 2.65 (q, ^3J = 7.6 Hz, 2 H, CH_2), 2.36 (s, 3 H, CH_3), 1.20 (t, ^3J = 7.6 Hz, 3 H, CH_3); MS (ESI): 238.1, 239.9 $[M+H]^+$; GCMS, m/z (rel Int. %): 239 (45); 237 (43) [M^+], 222 (100), 157 (10), 143 (25), 115 (15), 79 (5); $C_{11}H_{12}BrN$ (237.02 g/mol).

6-Methyl-2,3,4,9-tetrahydro-1*H*-carbazole: colorless oil; 14%; ^{1}H-NMR (400 MHz, CD_3OD): δ = 7.23 (s, 1 H, arom. CH), 7.15 (d, ^3J = 8.2 Hz, 1 H, arom. CH), 6.92 (d, ^3J = 8.2 Hz, 1 H, arom. CH), 2.70 (t, ^3J = 5.5 Hz, 2 H, CH_2), 2.43 (s, 3 H, CH_3), 2.68 (t, ^3J = 5.4 Hz, 2 H, CH_2), 1.91 (m, 4 H, 2 CH_2); GCMS, m/z (rel Int. %): 185 (65) [M^+], 157 (100), 128 (5), 115 (5), 91 (3), 77 (3); $C_{13}H_{15}N$ (185.12 g/mol).

2-Bromo-6,7,8,9,10,11-hexahydro-5*H*-cycloocta[β]indole: colorless oil; 7%; ^{1}H-NMR (400 MHz, CD_3OD): δ = 7.59 (s, 1 H, arom. CH), 7.16-7.14 (m, 2 H, arom. CH), 2.82 (m, 4 H, 2 CH_2), 1.71 (m, 4 H, 2 CH_2), 1.44 (m, 4 H, 2 CH_2); MS (ESI): 278.07, 280.10 $[M+H]^+$; GCMS, m/z (rel Int. %): 279 (100); 277 (98) [M^+], 249 (50), 234 (63), 223 (75), 208 (20), 198 (15), 168 (35), 154 (51), 142 (20), 129 (15), 115 (30), 102 (4); $C_{14}H_{16}BrN$ (277.05 g/mol).

6-Bromo-3-tert-butyl-2,3,4,9-tetrahydro-1*H*-carbazole: colorless oil; 24%; ^{1}H-NMR (400 MHz, CD_3OD): δ = 7.58 (s, 1 H, arom. CH), 7.17 (dd, ^3J = 10.1 Hz, ^4J = 1.8 Hz, 1 H, arom. CH), 7.12 (d, ^3J = 8.4 Hz, 1 H, arom. CH), 2.79-2.75 (m, 2 H, CH_2), 2.38-2.32 (m, 1 H, CH), 2.11-2.00 (m, 2 H, CH_2), 1.53-1.50 (m, 2 H, CH_2), 0.99 (s, 9 H, 3 CH_3); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ = 135.8 (C_q), 131.9 (C_q), 130.0 (C_q), 123.8 (arom. CH), 120.6 (arom. CH), 112.6 (C_q), 111.9 (arom. CH), 110.7 (C_q), 45.5 (CH), 32.8 (CH_2), 27.8 (3 CH_3), 24.8 (CH_2), 24.3 (CH_2), 22.3 (CH_2); GCMS, m/z (rel Int. %): 307 (55); 305 (55) [M^+], 248 (10), 221 (100), 168 (27), 142 (15), 115 (13), 83 (4), 57 (5), 41 (5); $C_{16}H_{20}BrN$ (305.08 g/mol).