Tandem Hydroformylation / Fischer Indole Synthesis:

A Novel Approach to Indoles

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Supporting Information

General Experimental Details: The procedure we employed to purify THF, DMF, toluene, and dioxane has been described¹; other general experimental details also have been described.²

***N*-Benzhydrylidene-*N'*-(4-chloro-phenyl)-hydrazine (5d)**

5.8g (33mmol) 4-chloro-phenylhydrazine hydrochloride, 5.9g (33mmol) benzophenone and 1ml sulphuric acid are diluted in 50ml ethanol and stirred at 80°C. The mixture is cooled down and the product is filtrated to yield 5.1g (51%) *N*-benzhydrylidene-*N'*-(4-chloro-phenyl)-hydrazine (**5d**). ¹H-NMR: (CDCl₃, 400MHz) [ppm] = 7.03 (d, 2H, J = 8.3 Hz, 2xCH_{Ar}), 7.22 (d, 2H, J = 8.3 Hz, 2xCH_{Ar}), 7.32-7.37 (5H, 5xCH_{Ar}), 7.55-7.62 (6H, 6xCH_{Ar}), NH not observed. ¹³C-NMR: (CDCl₃, 100MHz) [ppm] = 114.0 (2xCH_{Ar}), 124.5 (C_q), 126.5 (3xCH_{Ar}), 128.2 (3xCH_{Ar}), 129.1 (3xCH_{Ar}), 129.4 (2xCH_{Ar}), 129.7 (2xCH_{Ar}), 132.5 (C_q), 138.1 (C_q), 143.2 (C_q), 145.0 (C_q). NMR data fits with literature.³

¹ Perrin, D.D.; Armarego, W.L.F.; *Purification of laboratory chemicals*; 3rd ed.; Butterworth Heinemann Ltd., Oxford, **1988**.

² Roggenbuck, R.; Schmidt, A.; Eilbracht, P.; *Org Lett.*, **2**, **2002**, 289-291.

³ Wagaw, S.; Yang, B.H.; Buchwald, S.; *J. Amer. Chem. Soc.*, **121**, **44**, **1999**, 10251-10263.

***N*-Benzhydrylidene-*N'*-phenyl-hydrazine (5e)**

19.9g (184mmol) phenylhydrazine, 33.5g (184mmol) benzophenone and 1.7g (9mmol) *p*-toluenesulfonic acid monohydrate are diluted in 500ml ethanol and stirred at 80°C. The mixture is cooled down and the product is filtrated to yield 42.4g (85%) *N*-benzhydrylidene-*N'*-phenyl-hydrazine (**5e**). ¹H-NMR: (CDCl₃, 400MHz) [ppm] = 6.88 (dd, 1H, J = 7.3 Hz, CH_{Ar}), 7.10-7.12 (2H, 2xCH_{Ar}), 7.24-7.37 (7H, 7xCH_{Ar}), 7.52-7.64 (5H, 5xCH_{Ar}). ¹³C-NMR: (CDCl₃, 100MHz) [ppm] = 112.9 (2xCH_{Ar}), 120.0 (CH_{Ar}), 126.4 (2xCH_{Ar}), 128.0 (CH_{Ar}), 128.1 (2xCH_{Ar}), 129.1 (2xCH_{Ar}), 129.2 (3xCH_{Ar}), 129.6 (2xCH_{Ar}), 132.7 (C_q), 138.3 (C_q), 144.1 (C_q), 144.5 (C_q). NMR data fits with literature.⁴

***N*-Benzhydrylidene-*N'*-*o*-tolyl-hydrazine (5f)**

0.07g (0.2mmol) Pd(OAc)₂, 0.19g (0.3mmol) *R/S*-BINAP and 4.4g (22mmol) benzophenonhydrazone are diluted in 35ml anhydrous toluene. This mixture is stirred at 100°C for 5 minutes and added to a solution of 3.5g (20mmol) 1-bromo-2-methyl-benzene and 2.7g (28mmol) sodium *t*-butylat in 5ml anhydrous toluene. After stirring over night at 100°C the mixture is poured into 10ml of ether and is filtrated over silica. The solvent is evaporated and the residue is purified by flash chromatography to yield 4.9g (84%) *N*-benzhydrylidene-*N'*-*o*-tolyl-hydrazine(**5f**). ¹H-NMR: (CDCl₃, 500MHz) [ppm] = 1.93 (s, 3H, CH₃), 6.87 (m, 1H, CH_{Ar}), 7.09 (m, 1H, CH_{Ar}), 7.32 (m, 1H, CH_{Ar}), 7.37-7.45 (5H, 5xCH_{Ar}), 7.59-7.61 (2H, 2xCH_{Ar}), 7.65-7.66 (2H, CH_{Ar}), 7.73 (m, 1H, CH_{Ar}), 7.80 (m, 1H, CH_{Ar}), NH not observed. ¹³C-NMR: (CDCl₃, 125MHz) [ppm] = 16.4 (CH₃), 112.4 (CH_{Ar}), 119.5 (CH_{Ar}), 120.2 (C_q), 126.4 (3xCH_{Ar}), 127.2 (CH_{Ar}), 128.0 (CH_{Ar}), 128.2 (2xCH_{Ar}), 128.8 (CH_{Ar}), 129.2 (CH_{Ar}), 129.7 (CH_{Ar}), 130.2 (2xCH_{Ar}), 132.9 (C_q), 138.2 (C_q), 142.3 (C_q), 145.1 (C_q). NMR data fits with literature.⁵

***N*-Benzhydrylidene-*N'*-(4-bromo-phenyl)-hydrazine (5g)**

0.02g (0.07mmol) Pd(OAc)₂, 0.09g (0.14mmol) *R/S*-BINAP and 3.1g (16mmol) benzophenonhydrazone are diluted in 35ml anhydrous toluene. This mixture is stirred at 100°C for 5 minutes and added to a solution of 4.0g (14mmol) 1-Bromo-4-iodo-benzene and 1.9g (20mmol) sodium *t*-butylat in 5ml anhydrous toluene. After stirring over night at 100°C the mixture is poured into 10ml of ether and is filtrated over silica. The solvent is evaporated and the residue is purified by flash chromatography to yield 3.6g (71%) *N*-benzhydrylidene-

⁴ Drew, M.G.B.; Willey, G.R.; *J. Chem. Soc., Perkin Trans.2*; **1986**, 215-220.

N'-(4-bromo-phenyl)-hydrazine (**5g**). ¹H-NMR: (CDCl₃, 500MHz) [ppm] = 6.95 (d, 2H, J = 8.2 CH_{Ar}) ; 7.28-7.32 (7H, 7xCH_{Ar}), 7.50-7.59 (6H, CH_{Ar}, NH). ¹³C-NMR: (CDCl₃, 125MHz) [ppm] = 111.7 (C_q), 114.5 (2xCH_{Ar}), 126.5 (CH_{Ar}), 128.2 (CH_{Ar}), 129.0 (3xCH_{Ar}), 129.3 (CH_{Ar}), 129.7 (3xCH_{Ar}), 131.9 (3xCH_{Ar}), 132.5 (C_q), 138.1 (C_q), 143.6 (C_q), 145.0 (C_q). NMR data fits with literature.³

***N*-Benzhydrylidene-*N'*-(2-chloro-phenyl)-hydrazine (**5h**)**

2.9g (33mmol) 2-chloro-phenylhydrazine hydrochloride, 5.9g (33mmol) benzophenone and 1ml sulphuric acid are diluted in 25ml ethanol and stirred at 80°C. The mixture is cooled down and the product is filtrated to yield 3.5g (71%) *N*-benzhydrylidene-*N'*-(2-chloro-phenyl)-hydrazine (**5h**). ¹H-NMR: (CDCl₃, 500MHz) [ppm] = 6.80 (m, 1H, CH_{Ar}), 7.23 (m, 1H, CH_{Ar}), 7.29 (m, 1H, CH_{Ar}), 7.36-7.41 (5H, CH_{Ar}), 7.56 (m, 1H, CH_{Ar}), 7.61-7.64 (m, 2H, CH_{Ar}), 7.66-7.68 (m, 2H, CH_{Ar}), 7.78-7.80 (m, 1H, CH_{Ar}), 8.11 (s, 1H, NH). ¹³C-NMR: (CDCl₃, 125MHz) [ppm] = 113.4 (CH_{Ar}), 117.4 (C_q), 119.9 (CH_{Ar}), 126.7 (3xCH_{Ar}), 127.9 (CH_{Ar}), 128.2 (3xCH_{Ar}), 128.4 (CH_{Ar}), 128.8 (2xCH_{Ar}), 129.0 (CH_{Ar}), 129.7 (CH_{Ar}), 132.6 (C_q), 138. (C_q), 140.5 (C_q), 146.6 (C_q). IR: $\tilde{\nu}$ [cm⁻¹] = 3325 (m), 3047 (m), 3032 (m), 1597 (s), 1550 (s), 1500 (vs), 1492 (vs), 1252 (vs), 1074 (vs). MS (EI, 70eV): m/z (%) = 306 (M⁺, 100), 180 (71), 165 (5), 77 (47), 51 (11). Elementary analysis found C 74.30%, H 4.55%, N 9.00%, C₁₉H₁₅ClN₂ requires C 74.38%, H 4.93%, N 9.13%.

3-(1-Phenyl-ethyl)-indole (8a**)**

0.60g (5.1mmol) methylstyrene, 0.58g (5.3mmol) phenylhydrazine, 10 mg (0.5mol%) [Rh(cod)Cl]₂ and 0.95g (5.0mmol) *p*-toluenesulfonic acid are diluted in 30 ml anhydrous dioxane, filled in an autoclave and pressurized with 50bar CO and 20bar H₂. After stirring for 2 days at 120°C the mixture is filtered over alumina. The solvent is evaporated and the residue is purified by flash chromatography on silica to yield 0.74g (67%) of 3-(1-phenyl-ethyl)-indole (**8a**). ¹H-NMR: (DMSO-d₆, 400 MHz) [ppm] = 1.63 (d, J = 7.0 Hz, 3H, CH-CH₃), 4.31 (q, J = 7.0 Hz, 1H, CH-CH₃), 6.83 (dd, J = 7.0 Hz, J = 7.8 Hz 1H, CH_{Ar}), 7.03 (dd, J = 7.0 Hz, J = 7.8 Hz, 1H, CH_{Ar}), 7.13 (dd, J = 7.3 Hz, J = 7.3 Hz, 1H, CH_{Ar}), 7.25-7.45 (7H, 7 CH_{Ar}), 10.86 (bs, 1H, NH). ¹³C-NMR: (DMSO-d₆, 100 MHz) [ppm] = 22.7 (CH-CH₃), 36.6 (CH-CH₃), 111.7 (CH_{Ar}), 118.4 (CH_{Ar}), 119.2 (CH_{Ar}), 119.8 (C_q), 121.2 (CH_{Ar}), 122.0 (CH_{Ar}), 126.0 (CH_{Ar}), 126.7 (C_q), 127.5 (2 CH_{Ar}), 128.5 (2 CH_{Ar}), 136.9 (C_q), 147.6 (C_q).

³ Hartwig, J.F.; *Angew. Chem. Int. Ed. Engl.*; 37, 15, **1998**, 2090-2093.

GC-MS (EI, 70 eV): m/z (%) = 221 (M^+ , 52), 207 (40), 206 (100), 179 (22), 77 (15). IR: $\tilde{\nu}$ [cm^{-1}] = 3398 (vs), 2966 (m), 2852 (w), 1599 (w), 1452 (s), 1101 (s), 746 (vs). Elementary analysis found C 86.44 %, H 6.90 %, N 6.34 %, $\text{C}_{16}\text{H}_{15}\text{N}$ requires C 86.84 %, H 6.83 %, N 6.33 %.

3-Benzhydrylindole (8b)

0.90g (5.0mmol) 1,1-diphenylethylene, 0.54g (5.0mmol) phenylhydrazine, 10 mg (0.5mol%) $[\text{Rh}(\text{cod})\text{Cl}]_2$ and 0.95g (5.0mmol) *p*-toluenesulfonic acid are diluted in 30 ml anhydrous dioxane, filled in an autoclave and pressurized with 50bar CO and 20bar H_2 . After stirring for 2 days at 120°C the mixture is filtered over alumina. The solvent is evaporated and the residue is purified by flash chromatography on silica to yield 0.55g (59%) of 3-(1-phenylethyl)-indole (**8b**). $^1\text{H-NMR}$: (CDCl_3 , 400 MHz) [ppm] = 5.66 (s, 1H, $\text{CH}(\text{Ph})_2$), 6.53 (s, 1H, CH_{Ar}), 7.10-7.35 (14H, 14 CH_{Ar}), 7.91 (bs, 1H, *NH*). $^{13}\text{C-NMR}$: (CDCl_3 , 100 MHz) [ppm] = 48.8 ($\text{CH}(\text{Ph})_2$), 111.0 (CH_{Ar}), 119.3 (CH_{Ar}), 119.9 (CH_{Ar}), 119.9 (C_q), 122.1 (CH_{Ar}), 124.0 (CH_{Ar}), 126.2 (2 CH_{Ar}), 127.0 (C_q), 128.2 (4 CH_{Ar}), 129.0 (4 CH_{Ar}), 136.7 (C_q), 143.9 (2 C_q). GC-MS (EI, 70 eV): m/z (%) = 283 (M^+ , 97), 207 (46), 206 (100), 179 (16), 167 (11), 77 (10). IR: $\tilde{\nu}$ [cm^{-1}] = 3394 (vs), 3023 (m), 1597 (m), 1492 (s), 1454 (s), 1124 (m), 1093 (m), 1006 (m), 747 (vs), 698 (vs). HRMS found M^+ , 283.1382, $\text{C}_{21}\text{H}_{17}\text{N}$ requires M^+ , 283.1361.

Ethyl methallyl ether (9b)

51.20g (1.28mol) NaOH and 2.96g (0.01mol) BnNEt_3Cl are diluted in 50ml water. A mixture of 12.90g (0.28mol) ethanol and 22.64g (0.25mol) methallylic chloride are poured into the solution. The reaction mixture is refluxed for 4h. The organic layer is washed three times with water. The solvent is evaporated and the product is purified by distillation ($p=15\text{mbar}$, $T=37\text{-}40^\circ\text{C}$) to yield 11.42g (46%) ethyl methallyl ether (**9b**). $^1\text{H-NMR}$: (CDCl_3 , 200 MHz) [ppm] = 1.21 (t, $J = 7.1$ Hz, 3H, CH_3), 1.74 (s, 3H, $\text{CH}_2\text{-CH}_3$), 3.46 (q, $J = 7.1$ Hz, 2H, $\text{CH}_2\text{-CH}_3$), 3.87 (s, 2H, CH_2), 4.91 (d, $J = 15.4$ Hz, 2H, $=\text{CH}_2$). $^{13}\text{C-NMR}$: (CDCl_3 , 100 MHz) [ppm] = 15.0 (CH_3), 19.3 (CH_3), 65.3 (CH_2), 74.4 (CH_2), 111.6 ($=\text{CH}_2$), 142.4 (C_q). NMR data fits with literature.⁶

⁶ Schlegel, G.; Schaefer, H.J.; *Chem.Ber.*, 117, 4, **1984**, 1400-1423.

Benzyl methallyl ether (9c)

5.4g (50mmol) benzyl alcohol, 0.3g (1mmol) BrNEt₄, 5.4g (68mmol) aqueous NaOH (50 weight%) and 15ml toluene are mixed for 30min at room temperature. 4.5g (50mmol) methallylic chloride are poured into the solution and the reaction mixture is heated at 70°C for 2h. The organic layer is separated and washed with water. The solvent is evaporated and the product is cleaned by flash chromatography on silica to yield 5.0g (63%) of benzyl methallyl ether (**9c**). ¹H-NMR: (CDCl₃, 400 MHz) [ppm] = 1.76 (s, 3H, CH₃), 3.93 (s, 2H, CH₂), 4.49 (s, 2H, CH₂), 4.92 (s, 1H, CHH=), 5.00 (s, 1H, CHH=), 7.23-7.36 (5H, 5 CH_{Ar}). ¹³C-NMR: (CDCl₃, 100 MHz) [ppm] = 19.5 (CH₃), 71.8 (CH₂), 74.1 (CH₂), 112.3 (=CH₂), 127.5 (CH_{Ar}), 127.6 (2 CH_{Ar}), 128.3 (2 CH_{Ar}), 138.4 (C_q), 142.2 (C_q). NMR data fits with literature.⁷

Benzoic acid methallyl ester (9d)

7.8g (55mmol) benzoyl chloride are diluted in 50ml of THF and cooled to 0°C. 3.6g (50mmol) methallylic alcohol and 5.6g (55mmol) triethylamine are poured into the solution. The reaction mixture is stirred for 2h at 0°C and for 24h at room temperature. 70ml ethylacetate are poured into the solution and the mixture is washed with aqueous HCl-, NaHCO₃- and NaCl-solution. The solvent is evaporated and the product is by column chromatography on silica to give 6.4g (72%) of benzoic acid methallyl ester (**9d**). ¹H-NMR: (CDCl₃, 400 MHz) [ppm] = 1.84 (s, 3H, CH₃), 4.75 (s, 2H, CH₂), 4.99 (s, 1H, CHH=), 5.08 (s, 1H, CHH=), 7.41-7.46 (2H, 2 CH_{Ar}), 7.55 (dd, J = 7.3 Hz, J = 7.5 Hz, 1H, CH_{Ar}), 8.07-8.09 (2H, 2 CH_{Ar}). ¹³C-NMR: (CDCl₃, 100 MHz) [ppm] = 19.6 (CH₃), 68.1 (CH₂-O), 112.9 (=CH₂), 128.4 (2 CH_{Ar}), 129.6 (2 CH_{Ar}), 130.2 (C_q), 133.0 (CH_{Ar}), 140.0 (C_q), 166.2 (C_q). NMR data fits with literature.⁸

3-(2-Hydroxy-1-methyl-ethyl)-indole (10a)

0.22g (3.1mmol) methallylic alcohol, 0.33g (3.1mmol) phenylhydrazine, 4mg (0.5mol%) Rh(acac)CO₂ and 0.58g (3.0mmol) *p*-toluenesulfonic acid are diluted in 7ml anhydrous dioxane, filled in an autoclave and pressurized with 50bar CO and 20bar H₂. After stirring for 2 days at 100°C the mixture is washed with an aqueous ammonia solution. The solvent is evaporated and the residue is purified by flash chromatography on silica to yield 0.15g (28%)

⁷ Tietze, L.F.; Goerlitzer, J.; *Synthesis*, 6, **1998**, 873-878.

⁸ Takeda, K.; Tsuboyama, K.; Takayanagi, H.; Ogura, H.; *Synthesis*, 6, **1987**, 560-562.

of 3-(2-hydroxy-1-methyl-ethyl)-indole (**10a**). $^1\text{H-NMR}$: (CDCl_3 , 500 MHz) [ppm] = 1.42 (d, $J = 7.0$ Hz, 3H, CH_3), 1.99 (bs, 1H, OH), 3.30 (m, 1H, CH), 3.81 (dd, $J = 6.2$ Hz, $J = 10.5$ Hz, 1H, CHH-OH), 3.85 (dd, $J = 6.2$ Hz, $J = 10.5$ Hz, 1H, CHH-OH), 6.98 (s, 1H, CH_{Ar}), 7.17 (dd, $J = 7.7$ Hz, $J = 7.7$ Hz, 1H, CH_{Ar}), 7.24 (dd, $J = 7.7$ Hz, $J = 7.7$ Hz, 1H, CH_{Ar}), 7.35 (d, $J = 7.7$ Hz, 1H, CH_{Ar}), 7.69 (d, $J = 7.7$ Hz, 1H, CH_{Ar}), 8.31 (bs, 1H, NH). $^{13}\text{C-NMR}$: (CDCl_3 , 125 MHz) [ppm] = 17.2 (CH_3), 33.8 (CH), 67.7 ($\text{CH}_2\text{-OH}$), 111.3 (CH_{Ar}), 117.6 (C_q), 119.1 (CH_{Ar}), 119.2 (CH_{Ar}), 121.3 (CH_{Ar}), 122.0 (CH_{Ar}), 126.6 (C_q), 136.5 (C_q). GC-MS (EI, 70 eV): m/z (%) = 175 (M^+ , 30), 144 (100), 117 (13). IR: $\tilde{\nu}$ [cm^{-1}] = 3543 (m), 3411 (vs), 3056 (m), 2961 (s), 1602 (m), 1456 (vs), 1028 (s), 743 (vs). HRMS found $[\text{M}+\text{H}]^+$, 176.1082, $\text{C}_{11}\text{H}_{13}\text{NO}$ requires $[\text{M}+\text{H}]^+$, 176.1076.

3-(2-Ethoxy-1-methyl-ethyl)-indole (**10b**)

0.30g (3.0mmol) ethyl methallyl ether, 0.32g (3.0mmol) phenylhydrazine, 4mg (0.5mol%) $\text{Rh}(\text{acac})\text{CO}_2$ and 0.57g (3.0mmol) *p*-toluenesulfonic acid are diluted in 7ml anhydrous dioxane, filled in an autoclave and pressurized with 50bar CO and 20bar H_2 . After stirring for 2 days at 100°C the mixture is washed with an aqueous ammonia solution. The solvent is evaporated and the residue is purified by flash chromatography on silica to yield 0.15g (25%) of 3-(2-ethoxy-1-methyl-ethyl)-indole (**10b**). $^1\text{H-NMR}$: (CDCl_3 , 400 MHz) [ppm] = 1.21 (t, $J = 7.0$ Hz, 3H, $\text{CH}_2\text{-CH}_3$), 1.41 (d, $J = 6.8$ Hz, 3H, CH-CH_3), 3.36 (m, 1H, CH-CH_3), 3.46 (dd, $J = 8.5$ Hz, $J = 9.3$ Hz, 1H, O-CHH-CH), 3.50-3.60 (2H, $\text{O-CH}_2\text{-CH}_3$), 3.76 (dd, $J = 5.0$ Hz, $J = 9.3$ Hz, 1H, O-CHH-CH), 6.96 (s, 1H, CH_{Ar}), 7.10 (d, $J = 8.0$ Hz, 1H, CH_{Ar}), 7.17 (d, $J = 8.0$ Hz, 1H, CH_{Ar}), 7.35 (d, $J = 8.0$ Hz, 1H, CH_{Ar}), 7.67 (d, $J = 8.0$ Hz, 1H, CH_{Ar}), 8.05 (bs, 1H, NH). $^{13}\text{C-NMR}$: (CDCl_3 , 100 MHz) [ppm] = 15.2 (CH_3), 18.1 (CH_3), 31.3 (CH-CH_3), 66.3 ($\text{CH}_2\text{-O}$), 76.1 ($\text{CH}_2\text{-O}$), 111.1 (CH_{Ar}), 119.0 (CH_{Ar}), 119.0 (C_q), 119.1 (CH_{Ar}), 120.5 (CH_{Ar}), 121.8 (CH_{Ar}), 126.8 (C_q), 136.3 (C_q). GC-MS (EI, 70 eV): m/z (%) = 203 (M^+ , 21), 145 (20), 144 (100), 117 (12), 77 (5), 57 (5). IR: $\tilde{\nu}$ [cm^{-1}] = 3417 (m), 2973 (m), 2870 (m), 1601 (m), 1457 (m), 1105 (s), 1011 (w), 742 (s). HRMS found M^+ , 203.1294, $\text{C}_{13}\text{H}_{17}\text{NO}$ requires M^+ , 230.1310.

3-(2-Benzoyloxy-1-methyl-ethyl)-indole (**10c**)

0.49g (3.0mmol) benzyl methallyl ether, 0.33g (3.1mmol) phenylhydrazine, 4mg (0.5mol%) $\text{Rh}(\text{acac})\text{CO}_2$ and 0.59g (3.1mmol) *p*-toluenesulfonic acid are diluted in 7ml anhydrous dioxane, filled in an autoclave and pressurized with 50bar CO and 20bar H_2 . After stirring for 2 days at 100°C the mixture is washed with an aqueous ammonia solution. The solvent is

evaporated and the residue is purified by flash chromatography on silica to yield 0.18g (23%) of 3-(2-benzyloxy-1-methyl-ethyl)-indole (**10c**). $^1\text{H-NMR}$: (CDCl_3 , 400 MHz) [ppm] = 1.47 (d, J = 6.8 Hz, 3H, CH_3), 3.45 (m, 1H, CH), 3.57 (dd, J = 5.0 Hz, J = 9.0 Hz, 1H, CHH-OBn), 3.84 (dd, J = 9.0 Hz, J = 9.0 Hz, 1H, CHH-OBn), 4.59 (d, J = 12.0 Hz, 2H, $\text{O-CH}_2\text{-Ph}$), 6.99 (s, 1H, CH_{Ar}), 7.13 (dd, J = 7.8 Hz, J = 7.8 Hz, 1H, CH_{Ar}), 7.19 (dd, J = 7.8 Hz, J = 7.8 Hz, 1H, CH_{Ar}), 7.34-7.37 (6H, 6 CH_{Ar}), 7.65 (d, J = 7.8 Hz, 1H, CH_{Ar}), 7.99 (bs, 1H, NH). $^{13}\text{C-NMR}$: (CDCl_3 , 100 MHz): [ppm] = 18.1 (CH_3), 31.4 (CH), 73.0 ($\text{CH}_2\text{-O}$), 75.7 ($\text{CH}_2\text{-O}$), 111.1 (CH_{Ar}), 119.0 (C_q), 119.1 (CH_{Ar}), 119.2 (CH_{Ar}), 120.6 (CH_{Ar}), 121.9 (CH_{Ar}), 126.8 (C_q), 127.4 (CH_{Ar}), 127.6 (2 CH_{Ar}), 128.3 (2 CH_{Ar}), 136.3 (C_q), 138.6 (C_q). MS (EI, 70 eV): m/z (%) = 266 (M^+ , 16), 173 (100), 144 (74), 135 (91), 130 (28), 84 (57), 77 (49). IR: $\tilde{\nu}$ [cm^{-1}] = 3420 (vs), 3060 (m), 2961 (s), 2867 (s), 1619 (m), 1455 (s), 1375 (m), 1094 (s), 909 (m), 743 (vs). HRMS found M^+ , 265.1466, $\text{C}_{18}\text{H}_{19}\text{NO}$ requires M^+ , 265.1467.

3-(2-Benzoyloxy-1-methyl-ethyl)-indole (**10d**)

0.53g (3.0mmol) benzoic acid methyl ester, 0.33g (3.1mmol) phenylhydrazine, 4mg (0.5mol%) $\text{Rh}(\text{acac})\text{CO}_2$ and 0.57g (3.0mmol) *p*-toluenesulfonic acid are diluted in 7ml anhydrous dioxane, filled in an autoclave and pressurized with 50bar CO and 20bar H_2 . After stirring for 2 days at 100°C the mixture is washed with an aqueous ammonia solution. The solvent is evaporated and the residue is purified by flash chromatography on silica to yield 0.48g (57%) of 3-(2-benzoyloxy-1-methyl-ethyl)-indole (**10d**). $^1\text{H-NMR}$: (CDCl_3 , 400 MHz) [ppm] = 1.57 (d, J = 7.0 Hz, 3H, CH_3), 3.65 (m, 1H, CH), 4.45 (dd, J = 6.3 Hz, J = 10.5 Hz, 1H, CHH-OBz), 4.76 (dd, J = 6.3 Hz, J = 10.5 Hz, 1H, CHH-OBz), 7.07 (s, 1H, CH_{Ar}), 7.22 (dd, J = 6.5 Hz, J = 7.5 Hz, 1H, CH_{Ar}), 7.27 (dd, J = 6.5 Hz, J = 7.5 Hz, 1H, CH_{Ar}), 7.39 (d, J = 8.0 Hz, 1H, CH_{Ar}), 7.47-7.51 (2H, 2 CH_{Ar}), 7.61 (dd, J = 6.5 Hz, J = 7.5 Hz, 1H, CH_{Ar}), 7.83 (d, J = 7.5 Hz, 1H, CH_{Ar}), 8.10-8.16 (2H, 2 CH_{Ar}) 8.28 (bs, 1H, NH). $^{13}\text{C-NMR}$: (CDCl_3 , 100 MHz) [ppm] = 17.8 (CH_3), 30.5 (CH), 69.8 ($\text{CH}_2\text{-O}$), 111.2 (CH_{Ar}), 117.7 (C_q), 119.0 (CH_{Ar}), 119.2 (CH_{Ar}), 120.7 (CH_{Ar}), 121.9 (CH_{Ar}), 126.6 (C_q), 128.3 (2 CH_{Ar}), 129.5 (2 CH_{Ar}), 130.3 (C_q), 132.9 (CH_{Ar}), 136.3 (C_q), 166.8 (C_q). MS (EI, 70 eV): m/z (%) = 279 (M^+ , 6), 157 (100), 144 (95), 143 (32), 115 (22), 105 (43), 77 (48). IR: $\tilde{\nu}$ [cm^{-1}] = 3345 (s), 3056 (w), 2965 (m), 1708 (vs), 1600 (s), 1460 (s), 1288 (vs), 745 (vs). HRMS found M^+ , 279.1264, $\text{C}_{18}\text{H}_{17}\text{NO}$ requires M^+ , 279.1259.

Methallylic phthalimide (**11**)

44.1g (300mmol) potassium phthalimide and 5ml methyltrioctylammoniumchloride are diluted in 160ml anhydrous DMF. 29.9g (330mmol) methallylic chloride is added dropwise. The mixture is stirred at room temperature over night and then poured into 150ml of water. The solid is filtrated and washed with water. The crude product is purified by recrystallization from hexane to yield 59.9g (99%) methallylic phthalimide (**11**). ¹H-NMR: (CDCl₃, 400MHz) [ppm] = 1.77 (s, 3H, CH₃), 4.21 (s, 2H, NCH₂), 4.80 (s, 1H, CH₂), 4.88 (s, 1H, CH₂), 7.71-7.73 (2H, CH_{Ar}), 7.84-7.86 (2H, CH_{Ar}). ¹³C-NMR: (CDCl₃, 100MHz) [ppm] = 20.4 (CH₃), 43.2 (NCH₂), 111.9 (CH₂), 123.3 (2xCH_{Ar}), 132.0 (2xC_q), 134.0 (2xC_q), 139.3 (C_q), 167.7 (2xC_q). NMR data fits with literature⁹

2-{2-[1-(Toluene-4-sulfonyl)-1H-indol-3-yl]-propyl}-isoindole-1,3-dione (**12a**)

0.66g (3.3mmol) methallylic phthalimide, 0.36g (3.3mmol) phenylhydrazine, 0.016g (1 mol%) Rh(acac)(CO)₂ and 0.63g (3.3mmol) *p*-toluenesulfonic acid monohydrate are dissolved in 12g anhydrous toluene, filled in an autoclave and pressurized with 10bar H₂ and 10bar CO. After stirring for 2days at 120°C the mixture is poured into a suspension of 100mg tetrabutylammoniumhydrogensulfate in 15 ml toluene and 10g 50wt% NaOH. 0.69g (3.6mmol) tosylchloride in 15ml toluene are dropped to the mixture during 10 minutes. After stirring for 1 hour the layers are separated and the organic layer is extracted 3 times with ethylacetate. The solvent is evaporated and the residue is purified by flash chromatography on silica to yield 0.91g (60%) of 2-{2-[1-(toluene-4-sulfonyl)-1H-indol-3-yl]-propyl}-isoindole-1,3-dione (**12a**). ¹H-NMR: (CDCl₃, 400MHz) [ppm] = 1.24 (d, 3H, J = 7.0 Hz, CHCH₃), 2.16 (s, 3H, CH₃), 3.43 (m, 1H, CH₃CH), 3.64 (dd, 1H, J = 8.9 Hz, J = 13.8 Hz, CHH), 3.88 (dd, 1H, J = 6.1 Hz, J = 13.8 Hz, CHH), 7.03 (d, 1H, J = 8.3 Hz, CH_{Ar}), 7.09- 7.22 (2H, 2xCH_{Ar}), 7.38 (s, 1H, NCH_{Ar}), 7.56 – 7.68 (8H, 8xCH_{Ar}), 7.84 (d, 1H, J = 8.3 Hz, CH_{Ar}). ¹³C-NMR: (CDCl₃, 100MHz) [ppm] = 17.7 (CHCH₃), 21.3 (C_qCH₃), 29.9 (CHCH₃), 43.4 (NCH₂), 113.5 (CH_{Ar}), 119.7 (CH_{Ar}), 122.2 (2xCH_{Ar}), 123.0 (2xCH_{Ar}), 124.6 (CH_{Ar}), 124.7 (C_q), 126.6 (2xCH_{Ar}), 127.7 (CH_{Ar}), 129.6 (2xCH_{Ar}), 130.0 (C_q), 131.7 (C_q), 133.8 (2xCH_{Ar}), 135.0 (2xC_q), 144.6 (C_q), 168.2 (2xNCO), C_q not observed. IR: $\tilde{\nu}$ [cm⁻¹] = 2966 (s), 2933 (s), 1770 (vs), 1718 (vs), 1398 (vs), 1184 (vs), 1132 (vs), 717 (vs), 671 (vs). MS (EI, 70eV): m/z (%) = 458 (M⁺, 22), 298 (100), 200 (25), 160 (51), 155 (60), 106 (31), 91 (91). HRMS found

⁹ Stille, J.K., Becker, Y.; *J. Org.Chem.*; 45, 11, **1980**, 2139-2145.

M⁺, 458.1314, C₂₆H₂₂N₂O₄S requires M⁺, 458.1300. Elementary analysis found C 67.30%, H 4.60%, N 5.90%, C₂₆H₂₂N₂O₄S requires C 68.11%, H 4.84%, N 6.11%.

2-{2-[5-Chloro-1-(toluene-4-sulfonyl)-1H-indol-3-yl]-propyl}-isoindole-1,3-dione (12b)

1.30g (6.5mmol) methallylic phthalimide, 0.92g (6.5mmol) 4-chloro-phenylhydrazine, 0.032g (1 mol%) [Rh(cod)Cl]₂ and 1.23g (6.5mmol) *p*-toluenesulfonic acid monohydrate are dissolved in 10.5g anhydrous THF, filled in an autoclave and pressurized with 10bar H₂ and 10bar CO. After stirring for 3 days at 100°C the mixture is poured into 50ml ethyl acetate and is washed with 20ml water. The organic layer is separated and dried over MgSO₄ and the solvent is evaporated to get 2.47g crude product. 1.31g crude product together with 100mg tetrabutylammoniumhydrogensulfate are dissolved in 16ml toluene and 10g 50wt% NaOH. 0.68g (3.5mmol) tosylchloride in 15ml toluene are dropped to the mixture during 10 minutes. After stirring for 1 hour the layers are separated and the organic layer is extracted 3 times with ethylacetate. The solvent is evaporated and the residue is purified by flash chromatography on silica to yield 0.82g (53%) of 2-{2-[5-chloro-1-(toluene-4-sulfonyl)-1H-indol-3-yl]-propyl}-isoindole-1,3-dione (**12b**). ¹H-NMR: (CDCl₃, 500MHz) [ppm] = 1.37 (d, 3H, J = 7.0 Hz, CHCH₃), 2.35 (s, 3H, C_{Ar}CH₃), 3.52 (m, 1H, CHCH₃), 3.78 (dd, 1H, J = 8.6 Hz, J = 13.6 Hz, CHH), 3.98 (dd, 1H, J = 6.4 Hz, J = 13.6 Hz, CHH), 7.21 (d, 1H, J = 8.2 Hz, CH_{Ar}), 7.26 (d, 1H, J = 8.7 Hz, CH_{Ar}), 7.52 (s, 1H, CH_{Ar}), 7.69 (s, 1H, CH_{Ar}), 7.73-7.75 (4H, 4xCH_{Ar}), 7.83- 7.88 (4H, 4xCH_{Ar}). ¹³C-NMR: (CDCl₃, 125MHz) [ppm] = 17.9 (CHCH₃), 21.5 (C_qCH₃), 29.9 (CH₃CH), 43.5 (NCH₂), 114.7 (CH_{Ar}), 119.5 (CH_{Ar}), 123.3 (2xCH_{Ar}), 124.3 (C_q), 125.0 (CH_{Ar}), 126.7 (2xCH_{Ar}), 129.0 (CH_{Ar}), 129.1 (C_q), 129.9 (2xCH_{Ar}), 131.4 (C_q), 131.8 (C_q), 133.5 (C_q), 134.0 (2xCH_{Ar}), 145.0 (2xC_q), 168.3 (2xC_q), C_q not observed.

2-{2-[5-*t*-Butyl-1-(toluene-4-sulfonyl)-1H-indol-3-yl]-propyl}-isoindole-1,3-dione (12c)

0.27g (1.3mmol) methallylic phthalimide, 0.22g (1.3mmol) 4-*t*-butyl-phenylhydrazine, 0.014g (1 mol%) Rh(acac)(CO)₂ and 247 (1.3mmol) *p*-toluenesulfonic acid monohydrate are dissolved in 5g anhydrous toluene, filled in an autoclave and pressurized with 10bar H₂ and 10bar CO. After stirring for 2days at 120°C the mixture is poured into a suspension of 100mg tetrabutylammoniumhydrogensulfate in 15 ml toluene and 10g 50wt% NaOH. 0.27g (1.4mmol) tosylchloride in 15ml toluene are dropped to the mixture during 10 minutes. After stirring for 1 hour the layers are separated and the organic layer is extracted 3 times with ethylacetate. The solvent is evaporated and the residue is purified by flash chromatography on silica to yield 0.32g (48%) of 2-{2-[5-*t*-butyl-1-(toluene-4-sulfonyl)-1H-indol-3-yl]-propyl}-

isoindole-1,3-dione (**12c**). $^1\text{H-NMR}$: (CDCl_3 , 400MHz) [ppm] = 1.20 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.26 (d, 3H, $J = 6.8$ Hz, CHCH_3), 2.15 (s, 3H, C_qCH_3), 3.44 (m, 1H, CHCH_3), 3.64 (dd, 1H, $J = 8.5$ Hz, $J = 13.5$ Hz, CHH), 3.86 (dd, 1H, $J = 6.2$ Hz, $J = 13.5$ Hz, CHH), 7.03 (d, 2H, $J = 8.6$ Hz, $2\times\text{CH}_{\text{Ar}}$), 7.23 (d, 1H, $J = 8.8$ Hz, CH_{Ar}), 7.54 (s, 1H, CH_{Ar}), 7.53-7.55 (2H, $2\times\text{CH}_{\text{Ar}}$), 7.62-7.67 (4H, CH_{Ar}), 7.66 (d, 2H, $J = 8.6$ Hz, $2\times\text{CH}_{\text{Ar}}$). $^{13}\text{C-NMR}$: (CDCl_3 , 100MHz) [ppm] = 17.7 (CHCH_3), 21.3 (C_qCH_3), 26.7 ($\text{C}_q(\text{CH}_3)_3$), 29.7 (CHCH_3), 31.5 ($\text{C}_q(\text{CH}_3)_3$), 43.6 (NCH_2), 112.9 (CH_{Ar}), 115.6 (CH_{Ar}), 122.1 (CH_{Ar}), 122.6 (CH_{Ar}), 123.0 ($2\times\text{CH}_{\text{Ar}}$), 124.9 (C_q), 126.6 ($2\times\text{CH}_{\text{Ar}}$), 129.6 ($2\times\text{CH}_{\text{Ar}}$), 129.9 (C_q), 131.7 ($2\times\text{C}_q$), 133.0 (C_q), 133.8 ($2\times\text{CH}_{\text{Ar}}$), 135.2 (C_q), 144.4 (C_q), 146.1 (C_q), 168.5 ($2\times\text{NCO}$). IR: $\tilde{\nu}$ [cm^{-1}] = 2962 (s), 2870 (m), 1772 (s), 1713 (vs), 1398 (vs), 1398 (vs), 1369 (vs), 1173 (vs). HRMS found M^+ , 514.1946, $\text{C}_{30}\text{H}_{30}\text{N}_2\text{O}_4$ requires M^+ , 514.1926. Elementary analysis found C 69.10%, H 5.7%, N 5.4%, $\text{C}_{30}\text{H}_{30}\text{N}_2\text{O}_4$ requires C 70.02%, H 5.88%, N 5.44%.

2-[2-(5-Chloro-1H-indol-3-yl)-propyl]-isoindole-1,3-dione (**12d**)

0.92g (4.6mmol) methallylic phthalimide, 1.40g (4.6mmol) *N*-benzhydrylidene-*N'*-(4-chlorophenyl)-hydrazine (**5d**), 0.022g (1 mol%) $[\text{Rh}(\text{cod})\text{Cl}]_2$ and 0.87g (4.6mmol) *p*-toluenesulfonic acid monohydrate are dissolved in 12g anhydrous THF, filled in an autoclave and pressurized with 10bar H_2 and 10bar CO. After stirring for 3days at 100°C the mixture is filtrated through a pad alumina and the solvent is evaporated to get 3.0g crude product. 1.4g crude product are purified by flash chromatography on silica to yield 0.58g (78%) of 2-[2-(5-chloro-1H-indol-3-yl)-propyl]-isoindole-1,3-dione (**12d**). $^1\text{H-NMR}$: (CDCl_3 , 400MHz) [ppm] = 1.41 (d, 3H, $J = 7.0$ Hz, CHCH_3), 3.63 (m, 1H, CHCH_3), 3.8 (dd, 1H, $J = 8.3$ Hz, $J = 13.6$ Hz, CHH), 4.00 (dd, 1H, $J = 6.8$ Hz, $J = 13.6$ Hz, CHH), 7.09 (d, 1H $J = 8.2$ Hz, CH_{Ar}), 7.14 (s, 1H CH_{Ar}), 7.24 (m, 1H, CH_{Ar}), 7.69-7.72 (3H, $3\times\text{CH}_{\text{Ar}}$), 7.81-7.83 (2H, $2\times\text{CH}_{\text{Ar}}$), 8.31 (bs, 1H, NH). $^{13}\text{C-NMR}$: (CDCl_3 , 100MHz) [ppm] = 18.4 (CHCH_3), 29.9 (CHCH_3), 44.5 (NCH_2), 112.12 (CH_{Ar}), 118.24 (C_q), 118.5 (CH_{Ar}), 122.0 (CH_{Ar}), 122.2 (CH_{Ar}), 123.1 ($2\times\text{CH}_{\text{Ar}}$), 125.0 (C_q), 128.0 (C_q), 131.8 (C_q), 133.9 ($2\times\text{CH}_{\text{Ar}}$), 134.5 ($2\times\text{C}_q$), 168.6 ($2\times\text{NCO}$). IR: $\tilde{\nu}$ [cm^{-1}] = 3383 (m), 2964 (w), 2360 (w), 1765 (s), 1705 (vs), 1466 (s), 1429 (s), 1398 (vs), 1032 (s), 717 (s). HRMS found M^+ , 338.0802, $\text{C}_{19}\text{H}_{15}\text{N}_2\text{O}_2\text{Cl}$ requires M^+ , 338.0822. Elementary analysis found C 66.90%, H 4.35%, N 8.10%, $\text{C}_{19}\text{H}_{15}\text{N}_2\text{O}_2\text{Cl}$ requires C 67.36%, H 4.46%, N 8.27%.

2-[2-(1H-Indol-3-yl)-propyl]-isoindole-1,3-dione (**12e**)

1.32g (6.6mmol) methallylic phthalimide, 1.79g (6.6mmol) *N*-Benzhydrylidene-*N'*-phenylhydrazine (**5e**), 0.032g (1 mol%) [Rh(cod)Cl]₂ and 1.25g (6.6mmol) *p*-toluenesulfonic acid monohydrate are dissolved in 11g anhydrous THF, filled in an autoclave and pressurized with 10bar H₂ and 10bar CO. After stirring for 3 days at 100°C the mixture is filtrated through a pad alumina and the solvent is evaporated to get 3.16g crude product. 1.06g crude product are purified by flash chromatography on silica to yield 0.51g (76%) of 2-[2-(1H-indol-3-yl)-propyl]-isoindole-1,3-dione (**12e**). ¹H-NMR: (CDCl₃, 400MHz) [ppm] = 1.44 (d, 3H, J = 7.0 Hz, CHCH₃), 3.73 (m, 1H, CHCH₃), 3.87 (dd, 1H, J = 9.0 Hz, J = 13.3 Hz, CH₂), 4.09 (dd, 1H, J = 6.3 Hz, J = 13.3 Hz, CH₂), 7.13-7.24 (3H, 3xCH_{Ar}), 7.37 (d, 1H, J = 8.0 Hz, CH_{Ar}), 7.70-7.87 (5H, 5xCH_{Ar}), 8.31 (s, 1H, NH). ¹³C-NMR: (CDCl₃, 100MHz) [ppm] = 18.4 (CHCH₃), 30.0 (CHCH₃), 44.5 (NCH₂), 111.1 (CH_{Ar}), 118.3 (C_q), 119.1 (CH_{Ar}), 119.2 (CH_{Ar}), 120.6 (CH_{Ar}), 121.9 (2xCH_{Ar}), 123.0 (2xCH_{Ar}), 126.7 (C_q), 131.9 (C_q), 133.8 (CH_{Ar}), 136.2 (2xC_q), 168.6 (2xNC=O). IR: $\tilde{\nu}$ [cm⁻¹] = 3406 (s), 2962 (m), 2931 (m), 1770 (vs), 1712 (vs), 1398 (vs), 1034 (s), 714 (vs). HRMS found M⁺, 304.1219, C₁₉H₁₆N₂O₂ requires M⁺, 304.1212.

2-[2-(7-Methyl-1H-indol-3-yl)-propyl]-isoindole-1,3-dione (**12f**)

0.95g (4.7mmol) methallylic phthalimide, 1.35g (4.7mmol) *N*-benzhydrylidene-*N'*-*o*-tolylhydrazine (**5f**), 0.023g (1 mol%) [Rh(cod)Cl]₂ and 0.90g (4.7mmol) *p*-toluenesulfonic acid monohydrate are dissolved in 11g anhydrous THF, filled in an autoclave and pressurized with 10bar H₂ and 50bar CO. After stirring for 3 days at 100°C the mixture is filtrated through a pad alumina and the solvent is evaporated to get 2.51g crude product. The residue is purified by flash chromatography on silica to yield 0.72g (48%) of 2-[2-(7-Methyl-1H-indol-3-yl)-propyl]-isoindole-1,3-dione (**12f**). ¹H-NMR: (CDCl₃, 400MHz) [ppm] = 1.38 (d, 3H, J = 7.0 Hz, CHCH₃), 2.45 (s, 3H, C_qCH₃), 3.68 (m, 1H, CHCH₃), 3.81 (dd, 1H, J = 8.9 Hz, J = 13.7 Hz, CHH), 4.05 (dd, 1H, J = 6.4 Hz, J = 13.7 Hz, CHH), 6.96-7.11 (3H, 3xCH_{Ar}), 7.66-7.82 (5H, 5xCH_{Ar}), 8.07 (bs, 1H, NH). ¹³C-NMR: (CDCl₃, 100MHz) [ppm] = 16.5 (C_qCH₃), 18.5 (CHCH₃), 30.2 (CHCH₃), 44.5 (NCH₂), 116.9 (CH_{Ar}), 118.9 (C_q), 119.6 (CH_{Ar}), 120.2 (CH_{Ar}), 120.3 (C_q), 122.5 (CH_{Ar}), 123.1 (2xCH_{Ar}), 126.3 (C_q), 132.0 (C_q), 133.8 (2xCH_{Ar}), 135.8 (2xC_q), 168.6 (2xC_q). IR: $\tilde{\nu}$ [cm⁻¹] = 3402 (s), 1770 (s), 1716 (vs), 1466 (s), 1458 (s), 1433 (s), 1398 (vs), 1034 (s), 714 (vs). HRMS found M⁺, 318.1395, C₂₀H₁₈N₂O₂ require M⁺, 318.1368. Elementary analysis found C 75.30%, H 5.80%, N 8.20%, C₂₀H₁₈N₂O₂ requires C 75.45%, H 5.70%, N 8.80%.

2-[2-(5-Bromo-1H-indol-3-yl)-propyl]-isoindole-1,3-dione (**12g**)

0.79g (3.9mmol) methallylic phthalimide, 1.38g (3.9mmol) *N*-benzhydrylidene-*N'*-(4-bromophenyl)-hydrazine (**5g**), 0.019g (1 mol%) [Rh(cod)Cl]₂ and 0.74g (3.9mmol) *p*-toluenesulfonic acid monohydrate are dissolved in 11g anhydrous THF, filled in an autoclave and pressurized with 10bar H₂ and 50bar CO. After stirring for 3 days at 100°C the mixture is filtrated through a pad alumina and the solvent is evaporated to get 2.31g crude product. The residue is purified by flash chromatography on silica to yield 0.74g (50%) of 2-[2-(5-bromo-1H-indol-3-yl)-propyl]-isoindole-1,3-dione (**12g**). ¹H-NMR: (CDCl₃, 400MHz) [ppm] = 1.36 (d, 3H, J = 6.9 Hz, CHCH₃), 3.58 (m, 1H, CHCH₃), 3.79 (dd, 1H, J = 8.7 Hz, J = 13.8 Hz, CHH), 3.94 (dd, 1H, J = 6.2 Hz, J = 13.8 Hz, CHH), 7.08-7.16 (3H, 3xCH_{Ar}), 7.65-7.81 (5H, 5xCH_{Ar}), 8.27 (s, 1H, NH_{Ar}). ¹³C-NMR: (CDCl₃, 100MHz) [ppm] = 18.4 (CHCH₃), 29.8 (CHCH₃), 44.5 (NCH₂), 112.6 (CH_{Ar}), 112.6 (C_q), 118.2 (C_q), 121.6 (CH_{Ar}), 121.8 (CH_{Ar}), 123.14 (2xCH_{Ar}), 124.8 (CH_{Ar}), 128.6 (C_q), 131.8 (C_q), 133.9 (2xCH_{Ar}), 134.8 (2xC_q), 168.5 (2xC_q). IR: $\tilde{\nu}$ [cm⁻¹] = 3377 (s), 1770 (s), 1716 (vs), 1466 (s), 1433 (s), 1398 (vs), 1354 (s), 1034 (s), 795 (s), 715 (vs). HRMS found M⁺, 382.0280, C₁₉H₁₅BrN₂O₂ requires M, 382.0317. Elementary analysis found C 59.75%, H 3.95%, N 7.35%, C₁₉H₁₅BrN₂O₂ requires C 59.55%, H 3.95%, N 7.31%.

2-[2-(7-Chloro-1H-indol-3-yl)-propyl]-isoindole-1,3-dione (**12h**)

0.93g (4.6mmol) methallylic phthalimide, 1.41g (4.6mmol) *N*-benzhydrylidene-*N'*-(2-chlorophenyl)-hydrazine (**5h**), 0.023g (1 mol%) [Rh(cod)Cl]₂ and 0.87g (4.6mmol) *p*-toluenesulfonic acid monohydrate are dissolved in 11g anhydrous THF, filled in an autoclave and pressurized with 10bar H₂ and 10bar CO. After stirring for 3 days at 100°C the mixture is filtrated through a pad alumina and the solvent is evaporated to get 3.3g crude product. 0.83g crude product are purified by flash chromatography on silica to yield 0.21g (42%) of 2-[2-(7-chloro-1H-indol-3-yl)-propyl]-isoindole-1,3-dione (**12h**). ¹H-NMR: (CDCl₃, 400MHz) [ppm] = 1.38 (d, 3H, J = 7.0 Hz, CHCH₃), 3.63 (m, 1H, CHCH₃), 3.80 (dd, 1H, J = 8.8 Hz, J = 13.8 Hz, CH₂), 4.00 (dd, 1H, J = 6.5 Hz, J = 13.8 Hz, CH₂), 7.00 (dd, 1H J = 7.8 Hz, CH_{Ar}), 7.15 (s, 1H CH_{Ar}), 7.65-7.70 (4H, 4xCH_{Ar}), 7.78-7.82 (2H, 2xCH_{Ar}), 8.38 (bs, 1H, NH). ¹³C-NMR: (CDCl₃, 100MHz) [ppm] = 18.4 (CHCH₃), 30.2 (CHCH₃), 44.4 (NCH₂), 116.5 (C_q), 117.8 (CH_{Ar}), 119.5 (C_q), 120.1 (CH_{Ar}), 121.3 (2xCH_{Ar}), 123.1 (2xCH_{Ar}), 128.3 (C_q), 131.9. (2xC_q), 133.5 (C_q), 133.9 (2xCH_{Ar}), 168.6 (2xNCO). IR: $\tilde{\nu}$ [cm⁻¹] = 3381(m), 1765 (m), 1705 (vs), 1398 (m), 1032 (m), 893 (m), 717 (m). HRMS found M⁺, 338.0844, C₁₉H₁₅ClN₂O₂

requires M, 338.0822. Elementary analysis found C 67.43%, H 4.07%, N 8.10%, C₁₉H₁₅ClN₂O₂ requires C 67.36%, H 4.46%, N 8.27%.

3-(1-Phenyl-ethyl)-5-chloro-indole (**13**)

0.36g (3.0mmol) methylstyrene, 0.42g (2.9mmol) *p*-chloro-phenylhydrazine or 0.92g (3.0mmol) *N*-benzhydrylidene-*N'*-(4-chloro-phenyl)-hydrazine (**5d**), 4mg (0.5mol%) Rh(acac)CO₂ and 0.58g (3.0mmol) *p*-toluenesulfonic acid are diluted in 7ml anhydrous dioxane, filled in an autoclave and pressurized with 50bar CO and 20bar H₂. After stirring for 3 days at 100°C the mixture is washed with an aqueous ammonia solution. The solvent is evaporated and the residue is purified by flash chromatography on silica to yield 0.14g (18%) 3-(1-phenyl-ethyl)-5-chloro-indol (**13**) for the hydrazine and 0.52g (68%) for the hydrazone. ¹H-NMR: (CDCl₃, 500 MHz) [ppm] = 1.69 (d, J = 7.2 Hz, 3H, CH-CH₃), 4.31 (q, J = 7.2 Hz, 1H, CH-CH₃), 7.04 (s, 1H, CH_{Ar}), 7.10 (d, J = 6.7 Hz, 1H, CH_{Ar}), 7.18-7.30 (6H, 6 CH_{Ar}), 7.33 (s, 1H, CH_{Ar}), 8.00 (bs, 1H, NH). ¹³C-NMR: (CDCl₃, 125 MHz) [ppm] = 22.4 (CH-CH₃), 36.8 (CH-CH₃), 112.0 (CH_{Ar}), 119.1 (CH_{Ar}), 121.3 (C_q), 122.3 (CH_{Ar}), 122.4 (CH_{Ar}), 124.9 (C_q), 126.1 (CH_{Ar}), 127.3 (2 CH_{Ar}), 128.4 (2 CH_{Ar}), 134.9 (C_q), 146.3 (C_q), C_q not observed. MS (EI, 70 eV): m/z (%) = 255 (M⁺, 41), 240 (100), 204 (15), 105 (13), 77 (8). IR: $\tilde{\nu}$ [cm⁻¹] = 3421 (m), 3060 (w), 2964 (m), 1656 (s), 1452 (s), 1279 (s), 701 (vs). HRMS found M⁺, 255.0810, C₁₆H₁₄NCl requires M⁺, 255.0815.

Allyl benzyl ether (**14b**)

5.40g (50mmol) benzyl alcohol, 0.30g (1mmol) BrNEt₄, 5.60g (70mmol) aqueous NaOH (50 weight%) and 15ml toluene are mixed for 30min at room temperature. 6.20g (51mmol) allylbromid are poured into the solution and the reaction mixture is heated at 70°C for 2h. The organic layer is separated and washed with water. The solvent is evaporated and the product is cleaned by flash chromatography on silica to yield 4.79g (65%) of allyl benzyl ether (**14b**). ¹H-NMR: (CDCl₃, 500 MHz) [ppm] = 4.06 (d, J = 5.7 Hz, 2H, CH₂), 4.54 (s, 2H, CH₂), 5.23 (d, J = 10.2 Hz, 1H, CHH=), 5.34 (d, J = 17.2 Hz, 1H, CHH=), 5.99 (m, 1H, CH=), 7.29-7.38 (5H, 5 CH_{Ar}). ¹³C-NMR: (125 MHz, CDCl₃) [ppm] = 71.1 (CH₂), 72.1 (CH₂), 117.1 (CH₂=), 127.6 (CH_{Ar}), 127.7 (2 CH_{Ar}), 128.4 (2 CH_{Ar}), 134.7 (CH=), 138.3 (C_q). NMR data fits with literature.¹⁰

¹⁰ Westwell, A.D.; Williams, J.M.; *Tetrahedron*, 53, 38, **1997**, 13063-13078.

Benzoic acid allyl ester (**14c**)

7.73g (55mmol) benzoyl chloride are diluted in 50ml of THF and cooled to 0°C. 2.90g (50mmol) allylic alcohol and 5.60g (55mmol) triethylamine are poured into the solution. The reaction mixture is stirred for 2h at 0°C and for 24h at room temperature. 70ml ethylacetate are poured into the solution and the mixture is washed with aqueous HCl-, NaHCO₃- and NaCl-solution. The solvent is evaporated and the product is by column chromatography on silica to give 6.62g (82%) of benzoic acid allyl ester (**14c**). ¹H-NMR: (CDCl₃, 400 MHz) [ppm] = 4.83 (d, J = 5.8 Hz, 2H, CH₂), 5.29 (d, J = 10.5 Hz, 1H, CHH=), 5.42 (d, J = 17.1 Hz, 1H, CHH=), 6.05 (m, 1H, CH=), 7.42-7.60 (3H, 3 CH_{Ar}), 8.05-8.10 (2H, 2 CH_{Ar}). ¹³C-NMR: (CDCl₃, 100 MHz) [ppm] = 65.5 (CH₂), 118.2 (CH₂=), 128.3 (3 CH_{Ar}), 129.6 (2 CH_{Ar}), 132.9 (CH=), 166.2 (C_q). NMR data fits with literature.¹¹

Allylic phthalimide (**14d**)

10.2 g (54 mmol) potassium phthalimide and 1ml methyltrioctylammoniumchloride are diluted in 50ml anhydrous DMF. 6.5 g (54mmol) allylbromide is added dropwise. The mixture is stirred at room temperature over night and then poured into 50ml of water. The solid is filtrated and washed with water. The crude product is purified by recrystallization from hexane to yield 7.2g (72%) allylic phthalimide (**14d**). ¹H-NMR: (CDCl₃, 500MHz) [ppm] = 4.23 (d, 2H, J = 5.5 Hz, NCH₂), 5.16 (dd, 2H, J = 10.2 Hz, J = 17.2 Hz, CHCH₂), 5.82 (ddt, 1H, J = 5.5 Hz, J = 10.2 Hz, J = 17.7 Hz, CHCH₂), 7.66-7.67 (2H, CH_{Ar}), 7.78-7.80 (2H, CH_{Ar}). ¹³C-NMR: (CDCl₃, 125MHz) [ppm] = 39.9 (NCH₂), 117.5 (CHCH₂), 123.1 (2xCH_{Ar}), 131.4 (CHCH₂), 131.9 (2xC_q), 133.8 (2xCH_{Ar}), 167.7 (2xC_q). NMR data fits with literature¹²

3-(2-Hydroxy-ethyl)-indole (**15a**)

0.18g (3.1mmol) allylic alcohol, 0.33g (3.1mmol) phenylhydrazine, 4mg (0.5mol%) Rh(acac)CO₂, 47 mg (2.0mol%) BIPHEPHOS and 0.58g (3.0mmol) *p*-toluenesulfonic acid are diluted in 7ml anhydrous dioxane, filled in an autoclave and pressurized with 10bar CO and 10bar H₂. After stirring for 6h at 60°C and 37h at 100°C the mixture is washed with an aqueous ammonia solution. The solvent is evaporated and the residue is purified by flash

¹¹ Schmidt, B.; Wildemann, H.; *J. Chem. Soc., Perkin Trans. I*, 8, **2002**, 1050-1060.

¹² Bower, J.F.; Jumnah, R.; Williams, A.C.; Williams, J.M.J.; *J. Chem. Soc., Perkin Trans. I*; 9, **1997**, 1411-1420.

chromatography on silica to yield 0.08g (17%) of 3-(2-hydroxy-ethyl)-indole (**15a**). ¹H-NMR: (CDCl₃, 500 MHz) [ppm] = 1.77 (bs, 1H, OH), 3.04 (dd, J = 6.5 Hz, J = 6.5 Hz, 2H, CH₂-CH₂-OH), 3.90 (dd, J = 6.5 Hz, J = 6.5 Hz, 2H, CH₂-CH₂-OH), 7.03 (s, 1H, CH_{Ar}), 7.15 (dd, J = 7.5 Hz, J = 8.0 Hz, 1H, CH_{Ar}), 7.21 (dd, J = 7.5 Hz, J = 8.0 Hz, 1H, CH_{Ar}), 7.34 (d, J = 8.0 Hz, 1H, CH_{Ar}), 7.63 (d, J = 7.5 Hz, 1H, CH_{Ar}), 8.19 (bs, 1H, NH). ¹³C-NMR: (CDCl₃, 125 MHz) [ppm] = 28.7 (CH₂-CH₂-OH), 62.5 (CH₂-CH₂-OH), 111.2 (CH_{Ar}), 112.1 (C_q), 118.7 (CH_{Ar}), 119.4 (CH_{Ar}), 122.1 (CH_{Ar}), 122.5 (CH_{Ar}), 127.4 (C_q), 136.4 (C_q). NMR data fits with literature.¹³

3-(2-Benzoyloxy-ethyl)-indole (**15b**)

0.44g (3.0mmol) benzyl allyl ether, 0.33g (3.1mmol) phenylhydrazine, 4mg (0.5mol%) Rh(acac)CO₂, 47 mg (2.0mol%) BIPHEPHOS and 0.58g (3.0mmol) *p*-toluenesulfonic acid are diluted in 7ml anhydrous dioxane, filled in an autoclave and pressurized with 10bar CO and 10bar H₂. After stirring for 6h at 60°C and 37h at 100°C the mixture is washed with an aqueous ammonia solution. The solvent is evaporated and the residue is purified by flash chromatography on silica to yield 0.15g (20%) of 3-(2-benzyloxy-ethyl)-indole (**15b**). ¹H-NMR: (CDCl₃, 400 MHz) [ppm] = 3.14 (t, J = 7.2 Hz, 2H, CH₂-CH₂-OBn), 3.81 (t, J = 7.2 Hz, 2H, CH₂-CH₂-OBn), 4.60 (s, 2H, O-CH₂Ph), 7.04 (s, 1H, CH_{Ar}), 7.14 (dd, J = 8.0 Hz, J = 8.0 Hz, 1H, CH_{Ar}), 7.21 (dd, J = 8.0 Hz, J = 8.0 Hz, 1H, CH_{Ar}), 7.30-7.39 (6H, 6 CH_{Ar}), 7.63 (d, J = 8.0 Hz, 1H, CH_{Ar}), 8.01 (bs, 1H, NH). ¹³C-NMR: (CDCl₃, 100 MHz) [ppm] = 25.8 (CH₂-CH₂-OBn), 70.6 (CH₂-O), 73.0 (CH₂-O), 111.1 (CH_{Ar}), 113.0 (C_q), 118.8 (CH_{Ar}), 119.2 (CH_{Ar}), 121.9 (CH_{Ar}), 122.0 (CH_{Ar}), 125.0 (C_q), 127.5 (CH_{Ar}), 127.7 (2 CH_{Ar}), 128.4 (2 CH_{Ar}), 136.1 (C_q), 138.5 (C_q). MS (EI, 70 eV): m/z (%) = 251 (M⁺, 100), 92 (68), 77 (12). IR: $\tilde{\nu}$ [cm⁻¹] = 3417 (m), 3058 (w), 2858 (m), 1455 (s), 1099 (s), 741 (vs). HRMS found M⁺, 251.1302, C₁₇H₁₇NO requires M⁺, 251.1310.

3-(2-Benzoyloxy-ethyl)-indole (**15c**)

0.48g (3.0mmol) benzoic acid allyl ester, 0.33g (3.1mmol) phenylhydrazine, 4mg (0.5mol%) Rh(acac)CO₂, 47 mg (2.0mol%) BIPHEPHOS and 0.58g (3.0mmol) *p*-toluenesulfonic acid are diluted in 7ml anhydrous dioxane, filled in an autoclave and pressurized with 10bar CO and 10bar H₂. After stirring for 6h at 60°C and 37h at 100°C the mixture is washed with an aqueous ammonia solution. The solvent is evaporated and the residue is purified by flash

¹³ Sugawara, F.; Strobel, G.A.; *Phytochemistry*, 26, 5, **1987**, 1349-1351.

chromatography on silica to yield 0.10g (13%) of 3-(2-benzoyloxy-ethyl)-indole (**15c**). ¹H-NMR: (CDCl₃, 500 MHz) [ppm] = 3.28 (t, J = 7.2 Hz, 2H, CH₂-CH₂-OBz), 4.64 (t, J = 7.2 Hz, 2H, CH₂-CH₂-OBz), 7.09 (s, 1H, CH_{Ar}), 7.18 (dd, J = 7.5 Hz, J = 7.5 Hz, 1H, CH_{Ar}), 7.24 (dd, J = 7.5 Hz, J = 7.5 Hz, 1H, CH_{Ar}), 7.38 (d, J = 7.5 Hz, 1H, CH_{Ar}), 7.44-7.49 (2H, 2 CH_{Ar}), 7.58 (dd, J = 7.5 Hz, J = 7.5 Hz, 1H, CH_{Ar}), 7.72 (d, J = 7.5 Hz, 1H, CH_{Ar}), 8.07-8.11 (2H, 2 CH_{Ar}), 8.14 (bs, 1H, NH). ¹³C-NMR: (CDCl₃, 125 MHz) [ppm] = 24.8 (CH₂-CH₂-OBz), 65.1 (CH₂-CH₂-OBz), 111.2 (CH_{Ar}), 112.0 (C_q), 118.7 (CH_{Ar}), 119.4 (CH_{Ar}), 122.0 (CH_{Ar}), 122.1 (CH_{Ar}), 127.4 (C_q), 128.3 (2 CH_{Ar}), 129.6 (2 CH_{Ar}), 130.4 (C_q), 132.9 (CH_{Ar}), 136.2 (C_q), 166.7 (C_q). MS (EI, 70 eV): m/z (%) = 265 (M⁺, 40), 144 (100), 130 (25), 77 (65). IR: $\tilde{\nu}$ [cm⁻¹] = 3412 (m), 3061 (w), 2960 (w), 1709 (vs), 1456 (m), 1275 (vs), 1118 (s), 910 (vs), 732 (vs). HR-MS found M⁺, 265.1113, C₁₇H₁₅NO requires M⁺, 265.1103.

2-[2-(1H-Indol-3-yl)-ethyl]-isoindole-1,3-dione (**15d**)

0.16g (0.9mmol) allylic phthalimide (**14d**), 0.24g (0.9mmol) *N*-benzhydrylidene-*N'*-phenylhydrazine (**5e**), 0.002g (1 mol%) Rh(acac)(CO)₂, 0.05g (10mol%) XANTHPHOS and 0.16g (0.9mmol) *p*-toluenesulfonic acid monohydrate are dissolved in 1.3g anhydrous THF, filled in an autoclave and pressurized with 10bar H₂ and 10bar CO. After stirring for 18h at 60°C and additional 50h at 100°C the mixture is filtrated through a pad alumina and the solvent is evaporated to get 0.29g crude product. The residue is purified by flash chromatography on silica to yield 0.12g (46%) of 2-[2-(1H-Indol-3-yl)-ethyl]-isoindole-1,3-dione (**15d**) ¹H-NMR: (CDCl₃, 400MHz) [ppm] = 3.20 (t, 2H, J = 7.0 Hz, CH₂), 4.05 (t, 2H, J = 7.0 Hz, CH₂), 7.10 (s, 1H, CH_{Ar}), 7.16 (dd, 1H, J = 7.9 Hz, CH_{Ar}), 7.22 (dd, 1H, J = 7.9 Hz, CH_{Ar}), 7.37 (d, 1H, J = 7.9 Hz, CH_{Ar}), 7.72-7.73 (2H, 2xCH_{Ar}), 7.77 (d, 1H, J = 7.9 Hz, CH_{Ar}), 7.85-7.87 (2H, 2xCH_{Ar}), 8.24 (s, 1H, NH). ¹³C-NMR: (CDCl₃, 100MHz) [ppm] = 24.4 (CH₂), 38.4 (CH₂), 111.1 (CH_{Ar}), 112.2 (C_q), 118.7 (CH_{Ar}), 119.4 (CH_{Ar}), 122.0 (CH_{Ar}), 123.1 (2xCH_{Ar}), 127.3 (C_q), 128.3 (CH_{Ar}), 132.1 (2xC_q), 133.8 (2xCH_{Ar}), 136.1 (C_q), 168.3 (2xC_q). NMR data fits with literature.¹⁴

¹⁴ de Silva, S.; *Can. J. Chem.*; 56, **1978**, 1621.