SUPPORTING INFORMATION

One-Pot Homolytic Aromatic Substitution/HWE-Olefinations under Microwave Conditions for the Formation of a Small Oxindole Library

*Antje Teichert,[a] Katja Jantos,[a] Klaus Harms,[a] and Armido Studer[a,b]**
[a]Fachbereich Chemie, Philipps-Universität Marburg, 35032 Marburg, Germany. [b]Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, Corrensstrasse 40, 48149 Münster, Germany.

General. ^{1}H and ^{13}C-NMR spectra were recorded on a Bruker ARX 300 and ARX 200. Chemical shifts δ in ppm rel. to $SiMe_4$ as an internal standard. TLC: Merck silica gel 60 F_{254} plates; detection with UV or dipping into a soln. of $KMnO_4$ (6.0 g), $NaHCO_3$ (20.0 g) and H_2O (800 mL) or a soln. of $Ce(SO_4)_2 \cdot H_2O$ (10.0 g), phosphormolybdic acid hydrate (25.0 g), conc. H_2SO_4 (60 mL) and H_2O (940 mL), followed by heating. FC: Merck or Fluka silica gel 60 (40 – 63 μm) at *ca*. 0.4 bar. IR spectra were recorded on an IR 750 (*Nicolet Magna*) or a IFS-200 (*Bruker*). MS: Recorded on a VG Tribid, Varian CH7 (EI); IonSpec Ultima, Finnigan MAT TSQ 700 or a Finnigan MAT 95S (ESI) in m/z (% of basis peak). Melting points: Büchi Kofler apparatus; uncorrected. Microwave assisted heating was performed in an MLS-Ethos 1600 Microwave System (*MLS*). Solvents were purified by standard methods. Compounds sensitive to air and moisture were handled under argon using *Schlenk* techniques.

(Diethoxyphosphoryl)acetic acid

According to *Patel et al.*[1] ethyl (diethoxyphosphoryl)acetate (4.40 mL, 22.3 mmol) was added dropwise to 1 M NaOH (22.5 mL). After stirring for 3 h at RT, EtOH was partially evaporated and the reaction mixture was treated with 2 N HCl (until pH 1). The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* to yield (diethoxyphosphoryl)acetic acid (3.36 g, 77%) as a greenish oil. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 10.79 (*s*, 1 H, OH); 4.27-4.12 (*m*, 4 H, OCH_2); 2.97 (*d*, *J* = 21.7, 2 H, PCH_2); 1.34 (*t*, *J* = 7.0, 6 H, CH_3). The acid was used for the subsequent reaction without further purification.

(Diethoxyphosphoryl)acetic acid chloride 4

According to *Fryxell et al.*[2] (diethoxyphosphoryl)acetic acid (2.00 g, 10.20 mmol) was added dropwise to thionyl chloride (3.20 mL, 43.63 mmol). After stirring for 4 h at RT, the excess thionyl chloride was evaporated to give **4** (2.10 g, 96%).^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.23 (*dq*, J_1 = 7.1, J_2 = 1.3, 4 H, OCH_2); 3.50 (*d*, J = 21.2, 2 H, PCH_2); 1.38 (*t*, J = 7.1, 6 H, CH_3). The compound was used without further purification.

***p*-Methoxy-*N*-methylaniline**

According to *Barluenga et al.*[3,4] *p*-anisidin (1.00 g, 8.12 mmol) was added to a suspension of NaOMe (2.18 g, 40.6 mmol) in MeOH (12 mL). The resulting brown solution was poured into a suspension of paraformaldehyde (340 mg, 11.36 mmol) in MeOH (8 mL). The reaction mixture was stirred for 5 h at RT and then $NaBH_4$ (306 mg, 8.12 mmol) was added. The solution was heated to reflux for 1.75 h. After evaporating part of the solvent, the reaction mixture was treated with 1 M KOH. After extraction with MTBE, the organic layer was dried over $MgSO_4$. Evaporation of the solvent *in vacuo* and purification by FC (pentane/Et_2O 1:2) afforded *p*-methoxy-*N*-methylaniline (887 mg, 80%). The spectroscopic data are in agreement with the literature values.[3,4]

***m*-Methoxy-*N*-methylaniline**

According to *Barluenga et al.*[3,4] *m*-anisidine (1.00 g, 8.12 mmol) was added to a suspension of NaOMe (2.18 g, 40.6 mmol) in MeOH (12 mL). The resulting brown solution was poured into a suspension of paraformaldehyde (340 mg, 11.36 mmol) in MeOH (8 mL). The solution was stirred for 5 h at RT and then $NaBH_4$ (306 mg, 8.12 mmol) was added. The solution was heated to reflux for 1.75 h. After evaporating part of the solvent, the reaction mixture was treated with 1 M KOH. After extraction with MTBE, the organic layer was dried over $MgSO_4$. Evaporation of the solvent and purification by FC (pentane/Et_2O 1:2) afforded *m*-methoxy-*N*-methylaniline (949 mg, 85%) as a brown oil. The spectroscopic data are in agreement with the literature values.[3,4]

***o*-Methoxy-*N*-methylaniline**

According to *Barluenga et al.*[3,4] *o*-anisidine (1.00 g, 8.12 mmol) was added to a suspension of NaOMe (2.18 g, 40.6 mmol) in MeOH (12 mL). The resulting brown solution was poured into a suspension of paraformaldehyde (340 mg, 11.36 mmol) in MeOH (8 mL). The solution

was stirred for 5 h at RT and then $NaBH_4$ (306 mg, 8.12 mmol) was added. The solution was heated to reflux for 1.75 h. After evaporating part of the solvent, the reaction mixture was treated with 1 M KOH. After extraction with MTBE, the organic layer was dried over $MgSO_4$. Evaporation of the solvent and purification by FC (pentane/Et_2O 1:2) afforded *o*-methoxy-*N*-methylaniline (327 mg, 29%) as a yellow oil. The spectroscopic data are in agreement with the literature values.[3,4]

_p_-Methoxy-_N_-tosylaniline

NEt_3 (0.62 mL, 4.46 mmol), DMAP (tip of spatula) and tosyl chloride (850 mg, 4.46 mmol) were added to a solution of *p*-anisidine (500 mg, 4.06 mmol) in CH_2Cl_2 (20 mL). After stirring for 3 h at RT the reaction mixture was treated with 1 M NaOH. After separation of the layers the organic phase was washed with brine and dried over $MgSO_4$. Evaporation of the solvent gave *p*-methoxy-*N*-tosylaniline (1.13 g, 99%). ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 7.45 (*d*, *J* = 8.3, 2 H, CH); 7.22 (*d*, *J* = 8.5, 2 H, CH); 6.98-6.91 (*m*, 2 H, CH); 6.81-6.74 *(m*, 2 H, CH); 3.76 (*s*, 3 H, OCH_3); 2.40 (*s*, 3 H, CH_3). The tosylamide was used without further purification.

Synthesis of phosphonamides: General Procedure 1 (GP 1)

According to *Khan et al.*[5] a soln. of NEt_3 and the aniline derivative in CH_2Cl_2 was added to a soln. of **4** in CH_2Cl_2 at 0 °C. After stirring for 16 h at 0 °C, the reaction mixture was treated with sat. aq. NH_4Cl soln. and extracted with methyl(*t*-butyl)ether (MTBE). The organic layer was dried over $MgSO_4$. Removal of the solvent *in vacuo* and purification by FC afforded the corresponding phosphonamides **5a**-**g**.

[(Methyl-phenyl-carbamoyl)-methyl]-phosphonic acid diethyl ester 5a

According to GP 1 a soln. of NEt_3 (1.00 mL, 9.32 mmol) and *N*-methylaniline (1.28 mL, 9.32 mmol) in CH_2Cl_2 (10 mL) were added to **4** (2.00 g, 9.32 mmol) in CH_2Cl_2 (30 mL) at 0 °C. Purification by FC (pentane/MTBE 4:1 then acetone): **5a** (1.60 g, 60%). IR (film): 3474*br*, 2982*s*, 1656*s*, 1595*m*, 1497*m*, 1422*w*, 1375*m*, 1256*s*, 1026*s*, 966*m*, 777*m*, 516*br*. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.45-7.26 (*m*, 5H, CH); 4.14 (*qd*, $J_1 = J_2$ = 7.1, 4 H, CH_2); 3.29 (*s*, 3H, CH_3); 2.82 (*d*, *J* = 21.7, 2 H, CH_2); 1.31 (*t*, *J* = 7.1, 6 H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): 164.8 (*d*, J_{CP} = 5.6, C), 143.8 (C), 129.7 (CH), 128.0 (CH), 127.4 (CH), 62.3 (*d*, J_{CP}

= 6.2, OCH_2), 37.5 (NCH_3), 33.1 (*d*, J_{CP} = 138.0, CH_2), 16.3 (*d,* J_{CP} = 6.7, CH_3), 16.2 (CH_3). MS (EI): 285 (20, $[M]^+$), 137 (100, *N*-methylaniline). HRMS (EI) calcd for $C_{13}H_{20}NO_4P$ ($[M]^+$): 285.1130. Found: 285.1132.

{[(4-Methoxy-phenyl)-methyl-carbamoyl]-methyl}-phosphonic acid diethyl ester 5b

According to GP 1 a soln. of NEt_3 (0.87 mL, 6.34 mmol) and *p*-methoxy-*N*-methylaniline (870 mg, 6.34 mmol) in CH_2Cl_2 (10 mL) were added to **4** (1.36 g, 6.34 mmol) in CH_2Cl_2 (25 mL) at 0 °C. Purification by FC (pentane/acetone 1:1): **5b** (1.47 g, 74%). IR (film): 3500*br*, 2982*s*, 1656*s*, 1513*s*, 1375*s*, 1300*s*, 1250*s*, 1109*m*, 1027*s*, 968*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 7.18 (*d*, *J* = 9.0, 2 H, CH); 6.90 (*d*, *J* = 9.0, 2 H, CH); 4.20-4.04 (*m*, 4 H, OCH_2); 3.81 (*s*, 3 H, OCH_3); 3.23 (*s*, 3 H, NCH_3); 2.79 (*d*, *J* = 21.5, 2 H, CH_2); 1.32-1.23 (*m*, 6 H, CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$): 163.6 (*d*, J_{CP} = 5.3, C), 159.0 (C), 136.5 (C), 128.5 (CH), 114.8 (CH), 62.3 (*d,* J_{CP} = 6.1, CH_2), 55.4 (CH_3), 37.7 (CH_3), 32.9 (*d*, J_{CP} = 137.0, CH_2), 16.3 (*d,* J_{CP} = 6.6, CH_3). MS (EI): 315 (17, $[M]^+$), 137 (100, *p*-methoxy-*N*-methylaniline). HRMS (EI) calcd for $C_{14}H_{22}NO_5P$ ($[M]^+$): 315.1236. Found: 315.1225.

{[(3-Methoxy-phenyl)-methyl-carbamoyl]-methyl}-phosphonic acid diethyl ester 5c

According to GP 1 a soln. of NEt_3 (0.80 mL, 5.83 mmol) and *m*-methoxy-*N*-methylaniline (800 mg, 5.83 mmol) in CH_2Cl_2 (10 mL) were added to **4** (1.25 g, 5.83 mmol) in CH_2Cl_2 (20 mL) at 0 °C. Purification by FC (pentane/acetone 1:1): **5c** (1.03 g, 56%). IR (film): 3477*br*, 2838*s*, 1659*s*, 1601*s*, 1490*s*, 1372*s*, 1254*s*, 1109*m*, 1028*s*, 966*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.32-7.28 (*m*, 1 H, CH); 6.91-6.85 (*m*, 3 H, CH); 4.15 (*qd*, J_1 = J_2 = 7.3, 4 H, OCH_2); 3.84 (*s*, 3 H, OCH_3); 3.28 (*d*, *J* = 1.0, 3 H, NCH_3); 2.84 (*d*, *J* = 21.7, 2 H, CH_2); 1.32 (*t*, *J* = 7.1, 6 H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): 164.8 (C), 160.6 (C), 145.0 (C), 130.4 (CH), 119.4 (CH), 114.0 (CH), 113.2 (CH), 62.3 (*d,* J_{CP} = 6.2, CH_2), 55.4 (CH_3), 37.5 (CH_3), 33.7 (*d*, J_{CP} = 137.0, CH_2), 16.3 (*d,* J_{CP} = 6.7, CH_3). MS (EI): 315 (20, $[M]^+$), 137 (100, *m*-methoxy-*N*-methylaniline). HRMS (EI) calcd for $C_{14}H_{22}NO_5P$ ($[M]^+$): 315.1236. Found: 315.1233.

{[(2-Methoxy-phenyl)-methyl-carbamoyl]-methyl}-phosphonic acid diethyl ester 5d

According to GP 1 a soln. of NEt_3 (0.33 mL, 2.33 mmol) and *o*-methoxy-*N*-methylaniline (320 mg, 2.33 mmol) in CH_2Cl_2 (4 mL) were added to **4** (0.50 g, 2.33 mmol) in CH_2Cl_2 (8

mL) at 0 °C. Purification by FC (pentane/acetone 1:1): **5d** (331 mg, 45%). IR (film): 3473*br*, 2841*s*, 1660*s*, 1597*m*, 1502*s*, 1375*s*, 1257*s*, 1102*m*, 1027*s*, 967*m*, 761*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.34-7.27 (*m*, 2 H, CH); 7.02-6.95 (*m*, 2 H, CH); 4.12 (*m*, 4 H, OCH_2); 3.84 (*s*, 3 H, OCH_3); 3.20 (*d*, *J* = 1.0, 3 H, NCH_3); 2.82 (*dd*, J_1 = 15.2, J_2 = 20.3, 1 H, CH_2); 2.72 (*dd*, J_1 = 15.2, J_2 = 20.3, 1 H, CH_2); 1.30 (*dt*, J_1 = 7.1, J_2 = 9.3, 6 H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): 165.8 (C), 154.7 (C), 132.0 (C), 129.7 (CH), 129.4 (CH), 121.1 (CH), 111.8 (CH), 62.4 (*d*, J_{CP} = 6.5, CH_2), 62.1 (*d*, J_{CP} = 6.1, CH_2), 55.5 (CH_3), 36.3 (CH_3), 32.7 (*d*, J_{CP} = 139.0, CH_2), 16.3 (*d,* J_{CP} = 6.6, CH_3). MS (EI): 315 (17, $[M]^+$), 137 (100, *o*-methoxy-*N*-methylaniline), 122 (63). HRMS (EI) calcd for $C_{14}H_{22}NO_5P$ ($[M]^+$): 315.1236. Found: 315.1227.

{2-[4-Methoxy-phenyl-(toluene-4-sulfonyl)-amino]-2-oxo-ethyl}-phosphonic acid diethyl ester 5e

According to GP 1 a soln. of NEt_3 (0.64 mL, 4.66 mmol) and *p*-methoxy-*N*-tosylanilide (1.20 g, 4.00 mmol) in CH_2Cl_2 (5 mL) were added to **4** (1.00 g, 4.66 mmol) in CH_2Cl_2 (15 mL) at 0 °C. Purification by FC (pentane/acetone 1:1): **5e** (741 mg, 41%). IR (film): 2983*w*, 1703*s*, 1602*m*, 1507*s*, 1361*s*, 1252*s*, 1171*s*, 1025*s*, 972*m*, 641*m*, 564*s*, 547*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.92 (*d*, *J* = 8.6, 2 H, CH); 7.33 (*d*, *J* = 8.0, 2 H, CH); 7.25 (*d*, *J* = 8.8, 2 H, CH); 6.97 (*d*, *J* = 6.8, 2 H, CH); 4.08-3.98 (*m*, 4 H, OCH_2); 3.86 (*s*, 3 H, OCH_3); 2.80 (*d*, *J* = 21.7, 2 H, CH_2); 2.45 (*s*, 3 H, CH_3); 1.25 (*t*, *J* = 7.1, 6 H, $OCH_2C\underline{H}_3$). ^{13}C-NMR (75 MHz, $CDCl_3$): 165.1 (C), 160.8 (C), 144.9 (C), 135.7 (C), 131.4 (CH), 129.3 (CH), 128.5 (C), 115.0 (CH), 62.8 (*d,* J_{CP} = 6.7, CH_2), 55.5 (OCH_3), 35.5 (*d*, J_{CP} = 134.0, CH_2), 21.6 (CH_3), 16.3 (*d,* J_{CP} = 9.9, CH_3). MS (ESI): 478 (100, $[M+Na]^+$), 398 (20), 323 (24). HRMS (ESI) calcd for $C_{20}H_{26}NNaO_7PS$ ($[M+Na]^+$): 478.1066. Found: 478.1066.

[(Benzyl-phenyl-carbamoyl)-methyl]-phosphonic acid diethyl ester 5f

According to GP 1 a soln. of NEt_3 (0.75 mL, 5.46 mmol) and *N*-phenylbenzylamine (1.00 g, 5.46 mmol) in CH_2Cl_2 (5 mL) were added to **4** (1.17 g, 5.46 mmol) in CH_2Cl_2 (20 mL) at 0 °C. Purification by FC (pentane/acetone 1:1): **5f** (828 mg, 42%) was obtained as a brown oil. IR (film): 3475*s*, 3031*m*, 1657*s*, 1595*s*, 1496*s*, 1410*m*, 1389*m*, 1256*s*, 1027*s*, 967*s*, 778*m*, 701*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 7.32-7.05 (*m*, 10 H, CH); 4.92 (*s*, 2 H, NCH_2); 4.15 (*qd*, J_1 = J_2 = 7.2, 4 H, OCH_2); 2.84 (*d*, *J* = 21.9, 2 H, CH_2); 1.31 (*t*, *J* = 7.2, 6 H, CH_3). ^{13}C-

NMR (75 MHz, $CDCl_3$): 164.9 (*d*, J_{CP} = 5.6, C), 142.1 (C), 137.0 (C), 129.6 (CH), 128.7 (CH), 128.6 (CH), 128.3 (CH), 128.3 (CH), 127.4 (CH), 62.4 (*d,* J_{CP} = 6.2, CH_2), 53.2 (CH_2), 33.5 (*d*, J_{CP} = 136.0, CH_2), 16.3 (*d,* J_{CP} = 6.2, CH_3). MS (EI): 361 (4, $[M]^+$), 182 (100, *N*-phenylbenzylamine), 91 (31). HRMS (EI) calcd for $C_{19}H_{24}NO_4P$ ($[M]^+$): 361.1443. Found: 301.1440.

[(4-Methoxy-phenylcarbamoyl)-methyl]-phosphonic acid diethyl ester 5g

According to GP 1 a soln. of NEt_3 (1.28 mL, 9.32 mmol) and *p*-methoxy-*N*-methylaniline (1.14 g, 9.32 mmol) in CH_2Cl_2 (10 mL) were added to **4** (2.00 g, 9.32 mmol) in CH_2Cl_2 (40 mL) at 0 °C. Purification by FC (pentane/acetone 1:1): **5g** (1.87 g, 66%). M.p. 79 °C. IR (KBr): 3273*m*, 2987*m*, 1688*s*, 1607*m*, 1554*m*, 1513*s*, 1250*s*, 1226*s*, 1029*s*, 953*m*, 880*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.70 (*s*, 1 H, NH); 7.43 (*d*, *J* = 9.0, 2 H, CH); 6.84 (*d*, *J* = 9.0, 2 H, CH); 4.23-4.13 (*m*, 4 H, OCH_2); 3.79 (*s*, 3 H, OCH_3); 2.99 (*d*, *J* = 20.5, 2 H, CH_2); 1.36 (*t*, *J* = 7.1, 6 H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): 161.9 (C), 156.3 (C), 131.1 (C), 121.5 (CH), 114.0 (CH), 63.0 (*d,* J_{CP} = 6.7, CH_2), 55.4 (OCH_3), 36.0 (*d*, J_{CP} = 129.0, CH_2), 16.3 (*d,* J_{CP} = 6.2, CH_3). MS (EI): 301 (32, $[M]^+$), 123 (100). HRMS (EI) calcd for $C_{13}H_{20}NO_5P$ ($[M]^+$): 301.1079. Found: 301.1079.

Synthesis of alkoxyamines: General Procedure 2 (GP 2)

A soln. of diisopropylamine (DIPA) in 1,2-dimethoxyethane (DME) was treated with BuLi at –60 °C. After stirring for 20 min. at –60 °C the phosphonamide was added and stirring was continued for 30 min. at –60 °C. 2,2,6,6-Tetramethylpiperidin-1-oxyl radical (TEMPO) and subsequently anhydrous $CuCl_2$ were added. The resulting mixture was stirred for 1 h at –60 °C and was then allowed to warm to 0 °C and was stirred for another 3 h at this temperature. The reaction mixture was treated with sat. aq. NH_4Cl soln. and extracted with MTBE (three times). The organic layers were combined and dried over $MgSO_4$. Evaporation of the solvent *in vacuo* and purification of by FC afforded the alkoxyamines **6a-g**.

[(Methyl-phenyl-carbamoyl)-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-methyl]-phosphonic acid diethyl ester 6a

According to GP 2 TEMPO (358 mg, 2.29 mmol) and $CuCl_2$ (1.67 g, 12.48 mmol) were added to a soln. of DIPA (0.32 mL, 2.29 mmol), BuLi (1.21 mL, 1.89 M in hexane, 2.29

mmol) and **5a** (594 mg, 2.08 mmol) in DME (20 mL). After purification by FC (EtOAc) **6a** (685 mg, 75%) was obtained as yellow crystals. M.p. 98 – 104 °C. IR (KBr): 2972*s*, 2935*s*, 1662*s*, 1595*w*, 1496*m*, 1390*m*, 1252*s*, 1033*s*, 972*m*, 540*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 7.42-7.32 (*m*, 5 H, CH); 4.94 (*d*, *J* = 17.7, 1 H, PCH); 4.31-4.15 (*m*, 4 H, OCH_2); 3.30 (*s*, 3 H, NCH_3); 1.47-1.09 (*m*, 24 H, CH_3, CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): 130.1 (C), 129.4 (CH), 128.2 (CH), 127.8 (C), 63.0 (*d*, J_{CP} = 55.0, CH), 61.3 (CH_2), 59.5 (C), 40.7 (CH_2), 37.7 (CH_3), 33.12 (CH_3), 31.6 (CH_3), 20.2 (CH_3), 20.0 (CH_3), 17.0 (CH_2). MS (ESI): 463 (55, $[M+Na]^+$), 307 (100). HRMS (ESI) calcd for $C_{22}H_{37}N_2NaO_6P$ ($[M+Na]^+$): 463.2338. Found: 463.2344.

{[(4-Methoxy-phenyl)-methyl-carbamoyl]-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-methyl}-phosphonic acid diethyl ester 6b

According to GP 2 TEMPO (791 mg, 5.06 mmol) and $CuCl_2$ (3.71 g, 27.60 mmol) were added to a soln. of DIPA (0.71 mL, 5.06 mmol), BuLi (2.67 mL, 1.89 M in hexane, 5.06 mmol) and **5b** (1.45 g, 4.60 mmol) in DME (30 mL). After purification by FC (EtOAc) **6b** (1.72 mg, 81%) was obtained as a brown oil. IR (film): 3479*br*, 2975*s*, 2932*s*, 1665*s*, 1512*s*, 1466*w*, 1380*m*, 1249*s*, 1013*s*, 974*m*, 540*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 7.28 (*d*, *J* = 9.0, 2 H, CH); 6.91 (*d*, *J* = 9.0, 2 H, CH); 4.95 (*d*, *J* = 18.0, 1 H, PCH); 4.27-4.10 (*m*, 4 H, OCH_2); 3.83 (*s*, 3 H, OCH_3); 3.26 (*s*, 3 H, NCH_3); 1.47-1.10 (*m*, 24 H, CH_3, CH_2). ^{13}C-NMR (50 MHz, $CDCl_3$): 167.5 (C), 158.9 (C), 136.2 (C), 129.2 (CH), 114.4 (CH), 78.5 (*d*, J_{CP} = 155.0, CH), 63.4 (*d,* J_{CP} = 9.2, CH_2), 62.6 (C), 62.5 (C), 55.5 (CH_3), 40.9 (CH_2), 40.6 (CH_2), 38.0 (CH_3), 33.1 (CH_3), 31.6 (CH_3), 20.1 (CH_3), 20.1 (CH_3), 16.9 (CH_2). MS (ESI): 493 (30, $[M+Na]^+$), 337 (100), 280 (85), 233 (38), 201 (85). HRMS (ESI) calcd for $C_{23}H_{39}N_2NaO_6P$ ($[M+Na]^+$): 493.2443. Found: 493.2436.

{[(3-Methoxy-phenyl)-methyl-carbamoyl]-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-methyl}-phosphonic acid diethyl ester 6c

According to GP 2 TEMPO (436 mg, 2.79 mmol) and $CuCl_2$ (2.05 g, 15.24 mmol) were added to a soln. of DIPA (0.40 mL, 2.79 mmol), BuLi (1.47 mL, 1.89 M in hexane, 2.79 mmol) and **5c** (800 mg, 2.54 mmol) in DME (18 mL). After purification by FC (EtOAc/ pentane 4:1) **6c** (1.06 g, 89%) was obtained as a red oil. IR (film): 3480*br*, 2976*s*, 2932*s*, 1669*s*, 1601*s*, 1489*m*, 1380*m*, 1257*s*, 1030*s*, 975*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.33-7.28 (*m*, 1 H, CH); 6.97-6.85 (*m*, 3 H, CH); 4.99 (*d*, *J* = 18.1, 1 H, PCH); 4.37-4.11 (*m*, 4 H, OCH_2); 3.84 (*s*, 3 H, OCH_3); 3.29 (*d*, *J* = 1.0, 3 H, NCH_3); 1.53- 1.10 (*m*, 24 H, CH_3, CH_2).

^{13}C-NMR (75 MHz, $CDCl_3$): 167.3 (C), 160.3 (C), 144.6 (C), 130.0 (CH), 120.2 (CH), 113.9 (CH), 113.8 (CH), 78.0 (*d*, J_{CP} = 152.0, CH), 63.3 (*d*, J_{CP} = 6.2, CH_2), 63.0 (*d*, J_{CP} = 6.2, CH_2), 61.4 (C), 59.5 (C), 55.5 (CH_3), 41.0 (CH_2), 40.7 (CH_2), 37.5 (CH_3), 33.3 (CH_3), 31.7 (CH_3), 20.2 (CH_3), 19.7 (CH_3), 17.0 (CH_2), 16.4 (*d*, J_{CP} = 8.4, CH_3). MS (ESI): 493 (85, $[M+Na]^+$), 337 (100), 156 (35). HRMS (ESI) calcd for $C_{23}H_{39}N_2NaO_6P$ ($[M+Na]^+$): 493.2443. Found: 493.2445.

{[(2-Methoxy-phenyl)-methyl-carbamoyl]-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-methyl}-phosphonic acid diethyl ester 6d

According to GP 2 TEMPO (158 mg, 1.01 mmol) and $CuCl_2$ (750 mg, 5.52 mmol) were added to a soln. of DIPA (0.15 mL, 1.01 mmol), BuLi (0.53 mL, 1.89 M in hexane, 1.01 mmol) and **5d** (290 mg, 0.92 mmol) in DME (10 mL). After purification by FC (EtOAc/ pentane 4:1) **6d** (302 mg, 70%, *isomer ratio* 1:1.7) was obtained as a mixture of isomers. *Both isomers*: IR (film): 2979*s*, 2940*s*, 1667*s*, 1502*s*, 1382*m*, 1254*s*, 1047*m*, 1026*s*, 969*m*, 704*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 7.35-7.28 (*m*, 2 H, CH); 7.02-6.91 (*m*, 2 H, CH); 4.92, 4.82 (*d*, *J* = 20.8, 1 H, PCH); 4.28-4.15 (*m*, 4 H, OCH_2); 3.88, 3.85 (*2 s*, 3 H, OCH_3); 3.21 (*2 s*, 3 H, NCH_3); 1.43-1.06 (*m*, 24 H, CH_3, CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): 155.3 (C), 130.7 (CH), 130.3 (CH), 129.4 (CH), 129.2 (CH), 120.7 (CH), 120.3 (CH), 111.7 (CH), 111.4 (CH), 79.0 (CH), 78.6 (CH), 63.6 (*d*, J_{CP} = 6.7, CH_2), 62.4 (*d*, J_{CP} = 6.7, CH_2), 61.6 (C), 61.1 (C), 55.3 (CH_3), 40.8 (CH_2), 40.6 (CH_2), 36.6 (CH_3), 35.9 (CH_3), 32.8 (CH_3), 32.6 (CH_3), 32.2 (CH_3), 31.3 (CH_3), 20.4 (CH_3), 20.2 (CH_3), 19.7 (CH_3), 17.0 (CH_2), 16.4 (CH_3), 16.3 (CH_3). MS (EI): 470 (6, $[M]^+$), 314 (6), 156 (100), 69 (27). HRMS (EI) calcd for $C_{23}H_{39}N_2O_6P$ ($[M]^+$): 470.2546. Found: 470.2545.

[2-(4-Methoxy-phenyl)-(toluene-4-sulfonyl)-amino)-2-oxo-1-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl]-phosphonic acid diethyl ester 6e

According to GP 2 TEMPO (257 mg, 1.64 mmol) and $CuCl_2$ (1.60 g, 11.95 mmol) were added to a soln. of DIPA (0.24 mL, 1.64 mmol), BuLi (0.87 mL, 1.89 M in hexane, 1.64 mmol) and **5e** (680 mg, 1.50 mmol) in DME (25 mL). After purification by FC (1. FC EtOAc, 2. FC pentane/acetone 2:1) **6e** (694 mg, 76%) was obtained as a yellow oil. IR (film): 2934*w*, 1711*s*, 1604*w*, 1508*s*, 1365*s*, 1250*s*, 1173*s*, 1054*s*, 1025*s*, 667*m*, 568*s*, 550*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 7.97 (*d*, *J* = 8.3, 2 H, CH); 7.31 (*d*, *J* = 8.3, 4 H, CH); 6.97 (*d*, *J* =9.0, 2 H, CH); 4.82 (*d*, *J* = 20.0, 1 H, PCH); 4.25-4.02 (*m*, 4 H, OCH_2); 3.86 (*s*, 3 H, OCH_3); 2.44 (*s*, 3

H, CH_3); 1.35-0.76 (*m*, 24 H, CH_3, CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): 168.0 (C), 160.6 (C), 144.6 (C), 136.0 (C), 132.1 (CH), 129.5 (CH), 129.1 (CH), 128.2 (C), 114.7 (CH), 81.3 (*d*, J_{CP} = 150.5, CH), 63.7 (CH_2), 63.3 (OCH_2), 61.6 (C), 55.6 (CH_3), 40.9 (CH_2), 40.7 (CH_2), 33.7 (CH_3), 31.7 (CH_3), 21.6 (CH_3), 20.1 (CH_3), 16.9 (CH_2), 16.3 (CH_2). MS (ESI): 633 (15, $[M+Na]^+$), 477 (25), 331 (50), 299 (100). HRMS (ESI) calcd for $C_{29}H_{43}N_2NaO_8PS$ ($[M+Na]^+$): 633.2375. Found: 633.2382.

[(Benzyl-phenyl-carbamoyl]-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-methyl]-phosphonic acid diethyl ester 6f

According to GP 2 TEMPO (380 mg, 2.22 mmol) and $CuCl_2$ (1.81 g, 13.29 mmol) were added to a soln. of DIPA (0.36 mL, 2.44 mmol), BuLi (1.28 mL, 1.89 M in hexane, 2.44 mmol) and **5f** (800 mg, 2.22 mmol) in DME (24 mL). After purification by FC (EtOAc/ pentane 4:1) **6f** (1.05 g, 92%) was obtained as a yellow oil. IR (film): 2976*s*, 2931*s*, 1667*s*, 1496*s*, 1396*m*, 1256*s*, 1026*s*, 973*m*, 700*s*, 536*m*.. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.34-7.15 (*m*, 10 H, CH); 5.03 (*d*, *J* = 14.3, 1 H, NCH_2); 4.89 (*d*, *J* = 18.2, 1 H, PCH); 4.81 (*d*, *J* = 13.9, 1 H, NCH_2); 4.39-4.12 (*m*, 4 H, OCH_2); 1.45-1.10 (*m*, 24 H, CH_3, CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.1 (C), 141.5 (C), 136.6 (C), 129.3 (CH), 129.1 (CH), 129.0 (CH), 128.0 (CH), 127.9 (CH), 127.2 (CH), 78.4 (CH), 63.0 (*d*, J_{CP} = 6.2, CH_2), 62.7 (*d*, J_{CP} = 5.6, CH_2), 61.2 (C), 59.3 (C), 53.3 (CH_2), 40.8 (CH_2), 40.6 (CH_2), 33.5 (CH_3), 31.5 (CH_3), 20.1 (CH_3), 19.8 (CH_3), 16.9 (CH_2), 16.3 (CH_3), 16.3 (CH_3). MS (ESI): 743 (60), 560 (20), 539 (100, $[M+Na]^+$), 383 (80), 156 (50). HRMS (ESI) calcd for $C_{28}H_{41}N_2NaO_5P$ ($[M+Na]^+$): 539.2651. Found: 539.2654.

[(4-Methoxy-phenylcarbamoyl)-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-methyl]-phosphonic acid diethyl ester 6g

According to GP 2 TEMPO (284 mg, 1.82 mmol) and $CuCl_2$ (1.78 g, 13.28 mmol) were added to a soln. of DIPA (0.50 mL, 3.49 mmol), BuLi (2.14 mL, 1.63 M in hexane, 3.49 mmol) and **5g** (500 mg, 1.66 mmol) in DME (15 mL). After purification by FC (EtOAc) **6g** (403 mg, 53%) was obtained as yellow crystals. M.p. 115–119 °C. IR (KBr): 3259*m*, 2983*m*, 2937*m*, 1680*s*, 1551*m*, 1511*s*, 1234*m*, 1063*s*, 1037*s*, 834*m*, 549*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 8.21 (*s*, 1 H, NH); 7.44 (*d*, *J* = 7.0, 2 H, CH); 6.84 (*d*, *J* = 7.0, 2 H, CH); 4.74 (*d*, *J* = 17.0, 1 H, PCH); 4.32-4.13 (*m*, 4 H, OCH_2); 3.79 (*s*, 3 H, OCH_3); 1.47-1.18 (*m*, 24 H, CH_3, CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): 165.3 (C), 156.5 (C), 130.5 (C), 121.2 (CH), 114.2

(CH), 85.2 (*d*, J_{CP} = 146.0, CH) 63.4 (*d*, J_{CP} = 6.7, CH_2), 63.2 (*d*, J_{CP} = 7.3, CH_2), 55.4 (CH_3), 40.8 (CH_2), 16.9 (CH_2), 16.4 (CH_3). MS (ESI): 479 (100, $[M+Na]^+$), 323 (75). HRMS (ESI) calcd for $C_{22}H_{37}N_2NaO_6P$ ($[M+Na]^+$): 479.2287. Found: 479.2282

(1-Methyl-2-oxo-2,3-dihydro-1*H*-indol-3-yl)-phosphonic acid diethyl ester 7

Phosphonate **6a** (56 mg, 0.13 mmol) was dissolved under Ar in DMF (5 mL). In a sealed tube the soln. was heated to 180 °C for 2 min using microwave irradiation. Evaporation of the solvent and purification by FC (EtOAc) afforded **7** (29 mg, 81%) as an oil. IR (film): 3500*br*, 2980*s*, 1717*s*, 1559*s*, 1539*s*, 1473*s*, 1377*s*, 1185*m*, 1021*s*, 960*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 7.48-7.33 (*m*, 4 H, CH); 4.44 *(d*, *J* = 13.6, 2 H, PCH); 4.41-4.26 (*m*, 2 H, OCH_2); 4.24-4.11 (*m*, 2 H, OCH_2); 3.33 (*s*, 3 H, NCH_3); 1.38 (*td*, J_1 = 6.8, J_1 = 0.8, 3 H, CH_3); 1.29 (*t*, *J* = 6.8, 3 H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.8 (C), 159.1 (C), 136.4 (C), 129.4 (CH), 114.6 (CH), 62.8 (CH_2), 62.7 (CH_2), 55.7 (CH), 33.4 (CH_3), 20.3 (CH_3), 20.1 (CH_3). MS (EI): 283 (87, $[M]^+$), 255 (38), 227 (79), 157 (TEMPOH). HRMS (EI) calcd for $C_{13}H_{18}NO_4P$ ($[M]^+$): 283.0973. Found: 283.0960.

Homolytic Aromatic Substitution with Subsequent *Horner-Wadsworth-Emmons*-Olefination: General Prodcedure 3 (GP 3)

The alkoxyamine was dissolved under Ar in DMF (5 mL). In a sealed tube the soln. was heated to 180 °C for 2 min using microwave irradiation. The reaction mixture was then allowed to cool to room temperature and KO*t*-Bu and the aldehyde (10-20 equiv) were added. The reaction mixture was then heated to 180 °C for 6 min using microwave irradiation. The reaction mixture was treated with sat. Na_2SO_3 soln. and the aqueous layer was extracted with CH_2Cl_2 (three times). The organic layer was dried over $MgSO_4$. Removal of the solvent *in vacuo* and FC afforded the 2-oxindole derivatives.

3-Benzylidene-1-methyl-1,3-dihydro-indol-2-one 8a

According to GP 3 with **6a** (217 mg, 0.49 mmol) in DMF (5 mL) and KO*t*-Bu (66 mg, 0.59 mmol) and benzaldehyde (0.53 g, 4.9 mmol). After purification by FC (pentane/MTBE 4:1) **8a** (87 mg, 75%) was obtained as a mixture of isomers (*cis*:*trans* = 1:3.4) which were separated. *cis-Isomer*: M.p. 106 °C. IR (KBr): 1688*s*, 1618*w*, 1604*m*, 1491*m*, 1469*s*, 1389*m*, 1090*s*, 1040*m*, 752*s*, 708*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.29 (*d*, *J* = 7.8, 2 H, CH); 7.51

(*s*, 1 H, CH=C); 7.49 (*d*, 1 H, CH); 7.46-7.31 (*m*, 3 H, CH); 7.26 (*dd*, J_1= J_2 = 7.6, 1.0, 1 H, CH); 7.05 (*dd*, J_1 = J_2 = 7.6, 1 H, CH); 6.80 (*d*, *J* = 7.8, 1 H, CH); 3.26 (*s*, 3 H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): 165.1 (C), 141.4 (C), 136.0 (CH), 132.8 (C), 130.9 (CH), 129.4 (CH), 128.3 (CH), 127.2 (CH), 125.1 (C), 123.4 (C), 120.8 (CH) 118.0 (CH), 106.9 (CH), 24.9 (CH_3). MS (EI): 235 (100, $[M]^+$). HRMS (EI) calcd for $C_{16}H_{13}NO$ ($[M]^+$): 235.0997. Found: 235.0998.

trans-Isomer: ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.85 (*s*, 1 H, CH=C); 7.66-7.46 (*m*, 3 H, CH); 7.43-7.24 (*m*, 4 H, CH); 6.90-6.81 (*m*, 2 H, CH); 3.28 (*s*, 3 H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): 168.2 (C), 144.0 (C), 136.9 (CH), 134.8 (C), 129.5 (CH), 129.2 (CH), 129.0 (CH), 128.4 (CH), 127.0 (C), 122.5 (CH), 121.5 (CH), 120.9 (C), 107.9 (CH), 25.9 (CH_3).

1-Methyl-3-(4-trifluoromethyl-benzylidene)-1,3-dihydro-indol-2-one 8b

According to GP 3 with **6a** (189 mg, 0.43 mmol) in DMF (5 mL) and KO*t*-Bu (58 mg, 0.52 mmol) and *α,α,α*-trifluorotolylaldehyde (0.75 g, 4.3 mmol). After purification by FC (pentane/MTBE 4:1) **8b** (113 mg, 87%) was obtained as a mixture of isomers (*cis*:*trans* = 1:1.9) which were separated. *cis-Isomer*: M.p. 131 °C. IR (KBr): 3452*br*, 2963*w*, 1687*s*, 1322*s*, 1176*m*, 1109*s*, 1067*m*, 1040*m*, 1018*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 8.32 (*d*, *J* = 8.3, 2 H, CH); 7.68 (*d*, *J* = 7.0, 2 H, CH); 7.54 (*d*, *J* = 7.0, 1 H, CH); 7.53 (*s*, 1 H, CH=C); 7.30 (*dd*, J_1= J_2 = 7.5, 1 H, CH); 7.09 (*dd*, J_1= J_2 = 7.5, 1 H, CH); 6.84 (*d*, *J* = 7.7, 1 H, CH); 3.27 (*s*, 3 H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): 165.8 (C), 142.8 (C), 137.0 (C), 134.4 (CH), 131.7 (CH), 131.1 (C), 130.7 (CH), 128.3 (C), 125.0 (CH), 123.7 (C), 122.0 (CH), 119.3 (CH), 108.1 (CH), 26.0 (CH_3). MS (EI): 303 (100, $[M]^+$). HRMS (EI) calcd for $C_{17}H_{12}F_3NO$ ($[M]^+$): 303.0871. Found: 303.0875.

trans-Isomer: ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 7.82 (*s*, 1 H, CH=C); 7.74 (*br, s*, 3 H, CH); 7.42 (*d*, *J* = 7.5, 1 H, CH); 7.33 (*dd*, J_1 = 6.74, J_2 = 1.0, 2 H, CH); 6.94-6.83 (*m*, 2 H, CH); 3.30 (*s*, 3 H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.9 (C), 144.6 (C), 138.7 (C), 134.6 (CH), 130.5 (C), 130.4 (CH), 129.3 (CH), 128.9 (C), 125.6 (CH), 122.8 (CH), 121.9 (CH), 120.6 (C) 108.4 (CH), 24.9 (CH_3).

1-Methyl-3-(4-nitro-benzylidene)-1,3-dihydro-indol-2-one 8c

According to GP 3 with **6a** (78 mg, 0.18 mmol) in DMF (5 mL) and KO*t*-Bu (24 mg, 0.21 mmol) and 4-nitrobenzaldehyde (0.27 g, 1.8 mmol). After purification by FC (pentane/MTBE 4:1) **8c** (22 mg, 44%) was obtained as a mixture of isomers (*cis*:*trans* = 1:1.4) which were separated. *cis-Isomer*: M.p. 189 °C. IR (KBr): 2963*w*, 1677*s*, 1605*m*, 1588*m*, 1517*m*, 1469*m*, 1337*s*, 1263*m*, 1090*m*, 906*m*, 816*w*, 744*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 8.37 (*d*, *J* = 13.5, 2 H, CH); 8.25 (*d*, *J* = 13.5, 2 H, CH); 7.55 (*d*, *J* = 13.5, 1 H, CH); 7.53 (*s*, 1 H, CH=C); 7.36 (*dd*, $J_1 = J_2$ = 11.3, 1 H, CH); 7.10 (*dd*, $J_1 = J_2$ = 11.3, 1 H, CH); 6.85 (*d*, *J* = 12.4, 1 H, CH); 3.28 (*s*, 3 H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): 165.7 (C), 148.0 (C), 143.1 (C), 139.9 (C), 133.0 (CH), 132.2 (CH), 130.4 (C), 130.3 (CH), 129.7 (C), 123.5 (CH), 122.3 (CH), 119.4 (CH), 108.3 (CH), 26.0 (CH_3). MS (EI): 280 (100, $[M]^+$), 158 (21). HRMS (EI) calcd for $C_{16}H_{12}N_2O_3$ ($[M]^+$): 280.0848. Found: 280.0857.

trans-Isomer: ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 8.34 (*d*, *J* = 9.0, 1 H, CH); 7.81-7.77 (*m*, 2 H, CH, CH=C); 7.46-7.29 (*m*, 4 H, CH); 6.94-6.84 (*m*, 2 H, CH); 3.30 (*s*, 3 H, NCH_3).

3-(4-Bromo-benzylidene)-1-methyl-1,3-dihydro-indol-2-one 8d

According to GP 3 with **6a** (202 mg, 0.46 mmol) in DMF (5 mL) and KO*t*-Bu (62 mg, 0.55 mmol) and 4-bromobenzaldehyde (1.27 g, 6.9 mmol). After purification by FC (pentane/MTBE 4:1) **8d** (55 mg, 38%) was obtained as a mixture of isomers (*cis*:*trans* = 1:2.4) which were separated. *cis-Isomer*: M.p. 146 °C. IR (KBr): 3439*br*, 2826*w*, 1686*s*, 1605*s*, 1489*m*, 1469*m*, 1338*m*, 1091*m*, 743*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.18 (*d*, *J* = 8.5, 2 H, CH); 7.57-7.49 (*m*, 3 H, CH); 7.42 (*s*, 1 H, CH=C); 7.33-7.26 (*m*, 1 H, CH); 7.06 (*ddd*, $J_1 = J_2$ = 7.6, J_3 = 1.0, 1 H, CH); 6.81 (*d*, *J* = 7.8, 1 H, CH); 3.26 (*s*, 3 H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.0 (C), 142.4 (C), 135.4 (CH), 133.4 (CH), 132.7 (CH), 129.4 (CH), 126.7 (C), 125.6 (C), 124.9 (C), 124.1 (C), 121.9 (CH), 119.0 (CH), 108.0 (CH), 25.9 (CH_3). MS (EI): 303 (100, $[M]^+$). HRMS (EI) calcd for $C_{16}H_{12}{}^{81}BrNO$ ($[M]^+$): 315.0083. Found: 315.0084.

trans-Isomer: ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.74 (*s*, 1 H, CH=C); 7.61-7.45 (*m*, 4 H, CH); 7.31-7.23 (*m*, 2 H, CH); 6.89 (*ddd*, $J_1 = J_2$ = 7.8, J_3 = 1.0, 1 H, CH); 6.83 (*d*, *J* = 7.8, 1 H, CH); 3.27 (*s*, 3 H, NCH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): 168.1 (C), 144.3 (C), 135.3 (CH), 133.8 (C), 131.8 (CH), 130.7 (CH), 130.0 (CH), 127.7 (C), 124.2 (C), 123.5 (CH), 121.7 (CH), 120.7 (C), 108.2 (CH), 26.1 (CH_3).

1-Methyl-3-(4-methyl-benzylidene)-1,3-dihydro-indol-2-one 8e

According to GP 3 with **6a** (207 mg, 0.47 mmol) in DMF (5 mL) and KO*t*-Bu (63 mg, 0.56 mmol) and *p*-tolylaldehyde (1.12 g, 9.4 mmol). After purification by FC (pentane/MTBE 4:1) **8e** (50 mg, 43%) was obtained as a mixture of isomers (*cis*:*trans* = 1:2.3) which were separated. *cis-Isomer*: M.p. 134 °C. IR (KBr): 1677*s*, 1626*w*, 1606*m*, 1470*w*, 1385*w*, 1337*w*, 1089*m*, 1042*m*, 736*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.23 (*d*, *J* = 8.0, 2 H, CH); 7.50 (*d*, *J* = 5.1, 1 H, CH); 7.49 (*s*, 1 H, CH=C); 7.28-7.23 (*m*, 3 H, CH); 7.03 (*dd*, $J_1 = J_2$ = 7.6, 1 H, CH); 6.79 (*d*, *J* = 7.8, 1 H, CH); 3.26 (*s*, 3 H, NCH_3); 2.40 (*s*, 3 H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.1 (C), 142.1 (C), 141.1 (C), 137.2 (CH), 132.1 (CH), 129.4 (C), 129.0 (CH), 128.4 (CH), 125.0 (C), 124.5 (C), 121.7 (CH), 118.7 (CH), 107.7 (CH), 25.9 (CH_3), 21.6 (CH_3). MS (EI): 249 (100, $[M]^+$), 248 (43), 158 (30). HRMS (EI) calcd for $C_{17}H_{15}NO$ ($[M]^+$): 249.1154. Found: 249.1158.

trans-Isomer: ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.82 (*s*, 1 H, CH=C); 7.69 (*d*, *J* = 7.6, 1 H, CH); 7.60 (*d*, *J* = 7.8, 2 H, CH); 7.27-7.22 (*m*, 3 H, CH); 6.88 (*dd*, $J_1 = J_2$ = 7.6, 1 H, CH); 6.78 (*d*, *J* = 7.8, 1 H, CH); 3.26 (*s*, 3 H, NCH_3); 2.41 (*s*, 3 H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): 168.2 (C), 143.8 (C), 139.5 (C), 137.0 (CH), 131.7 (C), 129.1 (CH), 128.9 (CH), 128.8 (CH), 126.1 (C), 122.3 (CH), 121.3 (CH), 120.9 (C), 107.7 (CH), 25.7 (CH_3), 21.2 (CH_3).

3-(4-Methoxy-benzylidene)-1-methyl-1,3-dihydro-indol-2-one 8f

According to GP 3 with **6a** (177 mg, 0.40 mmol) in DMF (5 mL) and KO*t*-Bu (54 mg, 0.48 mmol) and anisaldehyde (0.98 mL, 8.0 mmol). After purification by FC (pentane/MTBE 4:1) **8f** (55 mg, 52%) was obtained as a mixture of isomers (*cis*:*trans* = 1:1.9) which were separated. *cis-Isomer*: IR (film): 3436*br*, 1699*s*, 1601*s*, 1512*s*, 1469*s*, 1380*m*, 1252*s*, 1175*s*, 1099*s*, 1030*s,* 834*s,* 777*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 8.40 (*d*, *J* = 9.0, 2 H, CH); 7.52 (*d*, *J* = 1.0, 1 H, CH); 7.48 (*s*, 1 H, CH=C); 7.26 (*ddd*, $J_1 = J_2$ = 7.7, J_3 = 1.0, 1 H, CH); 7.03-6.94 (*m*, 3 H, CH); 6.79 (*d*, *J* = 8.0, 1 H, CH); 3.87 (*s*, 3 H, OCH_3); 3.28 (*s*, 3 H, NCH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): 161.6 (C), 141.9 (C), 137.0 (CH), 134.4 (CH), 131.4 (C), 128.1 (CH), 127.1 (C), 124.9 (C), 123.6 (C), 121.6 (CH), 118.4 (CH), 113.8 (CH), 107.7 (CH), 55.4 (CH_3), 25.9 (CH_3). MS (EI): 265 (100, $[M]^+$), 222 (15), 165 (25). HRMS (EI) calcd for $C_{17}H_{15}NO_2$ ($[M]^+$): 265.1103. Found: 265.1104.

trans-Isomer: ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.80 (*s*, 1 H, CH=C); 7.75 (*d*, *J* = 7.1, 1 H, CH); 7.64 (*d*, *J* = 8.8, 2 H, CH); 7.30-7.23 (*m*, 1 H, CH); 7.05-6.82 (*m*, 4 H, CH); 3.87 (*s*, 3 H, OCH_3); 3.28 (*s*, 3 H, NCH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): 168.9 (C), 160.8 (C), 144.0 (C), 137.4 (CH), 132.2 (CH), 129.3 (CH), 127.3 (C), 125.4 (C), 122.4 (CH), 121.7 (CH), 121.4 (C), 114.0 (CH), 108.1 (CH), 55.2 (CH_3), 26.1 (CH_3).

3-(2-Bromo-benzylidene)-1-methyl-1,3-dihydro-indol-2-one 8g

According to GP 3 with **6a** (158 mg, 0.36 mmol) in DMF (5 mL) and KO*t*-Bu (48 mg, 0.43 mmol) and 2-bromobenzaldehyde (0.62 mL, 5.4 mmol) were added. After purification by FC (pentane/MTBE 4:1) **8g** (65 mg, 58%) was obtained as a mixture of isomers (*cis*:*trans* = 1:3.6) which were separated. *cis-Isomer*: ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 8.28 (*dd*, J_1 = 7.8, J_2 = 1.5, 1 H, CH); 7.75 (*s*, 1 H, CH=C); 7.65-7.04 (*m*, 6 H, CH); 7.74 (*d*, *J* = 7.8, 1 H, CH); 3.23 (*s*, 3 H, CH_3).

trans-Isomer: IR (film): 1702*s*, 1607*s*, 1468*s*, 1378*s*, 1336*s*, 1256*m*, 1099*s*, 1026*m*, 734*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 7.81 (*s*, 1 H, CH=C); 7.73-7.64 (*m*, 2 H, CH); 7.43-7.23 (*m*, 4 H, CH); 6.83-6.79 (*m*, 2 H, CH); 3.28 (*s*, 3 H, NCH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.8 (C), 144.4 (C), 135.6 (C), 135.4 (CH), 133.1 (CH), 130.9 (CH), 130.2 (CH), 130.0 (CH), 128.5 (C), 127.1 (CH), 124.0 (C), 122.8 (CH), 121.7 (CH), 120.8 (C), 107.9 (CH), 26.6 (CH_3). MS (EI): 315 (3, $[M]^+$), 234 (100), 219 (14). HRMS (EI) calcd for $C_{16}H_{12}{}^{81}BrNO$ ($[M]^+$): 315.0083. Found: 315.0090.

1-Methyl-3-(2-methyl-benzylidene)-1,3-dihydro-indol-2-one 8h

According to GP 3 with **6a** (129 mg, 0.29 mmol) in DMF (5 mL) and KO*t*-Bu (39 mg, 0.35 mmol) and *o*-tolylaldehyde (0.51 mL, 4.4 mmol). After purification by FC (pentane/MTBE 4:1) **8h** (28 mg, 38%) was obtained as a mixture of isomers (*cis*:*trans* = 1:6) which were separated. *cis-Isomer*: ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.07 (*d*, *J* = 6.3, 1 H, CH); 7.75 (*s*, 1 H, CH=C); 7.54 (*d*, *J* = 7.6, 1 H, CH); 7.33-7.22 (*m*, 4 H, CH); 7.06 (*dd*, $J_1 = J_2$ = 7.6, 1 H, CH); 6.82 (*d*, *J* = 7.8, 1 H, CH); 3.23 (*s*, 3 H, NCH_3); 2.41 (*s*, 3 H, CH_3).

trans-Isomer: IR (Film): 1710*s*, 1605*s*, 1467*s*, 1376*m*, 1336*w*, 774*s*, 752*s*, 735*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.92 (*s*, 1 H, CH=C); 7.55 (*d*, *J* = 7.6, 1 H, CH); 7.34-7.22 (*m*, 5 H, CH); 6.85-6.80 (*m*, 2 H, CH); 3.29 (*s*, 3 H, NCH_3); 2.35 (*s*, 3 H, CH_3). ^{13}C-NMR (75 MHz,

$CDCl_3$): 168.0 (C), 143.9 (C), 137.1 (C), 136.1 (CH), 134.1 (C), 130.3 (CH), 129.4 (CH), 129.1 (CH), 128.3 (CH), 127.7 (C), 125.5 (CH), 122.7 (CH), 121.6 (CH), 121.1 (C), 107.8 (CH), 25.9 (CH_3), 19.7 (CH_3). MS (EI): 249 (80, $[M]^+$), 232 (100), 205 (22), 124 (20). HRMS (EI) calcd for $C_{17}H_{15}NO$ ($[M]^+$): 249.1154. Found: 249.1152.

1-Methyl-3-pyridin-4-ylmethylene-1,3-dihydro-indol-2-one 9

According to GP 3 with **6a** (195 mg, 0.44 mmol) in DMF (5 mL) and KO*t*-Bu (60 mg, 0.53 mmol) and 4-pyridincarboxaldehyde (0.74 mL, 7.8 mmol). After purification by FC (pentane/MTBE 4:1) **9** (50 mg, 48%) was obtained as a mixture of isomers (*cis*:*trans* = 1:2.3), which could not be separated. *Both isomers*: IR (Film): 2930*w*, 1706*s*, 1607*s*, 1488*m*, 1469*s*, 1414*m*, 1379*m*, 1338*m*, 1125*m*, 1102*m*, 742*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 8.72 (*d*, *J* = 6.8, 2 H, CH); 8.00 (*dd*, J_1 = 4.5, J_2 = 1.5, 1 H, CH); 7.54 (*s*, 1 H, CH=C); 7.51-7.29 (*m*, 3 H, CH); 6.92-6.79 (*m*, 2 H, CH); 3.28, 3.24 (*2 s*, 3 H, NCH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.6 (C), 150.3 (CH), 149.9 (CH), 144.7 (C), 143.0 (C), 142.9 (C), 140.5 (C), 132.8 (CH), 132.6 (CH), 130.9 (CH), 130.1 (CH), 124.6 (CH), 123.0 (CH), 122.9 (CH), 122.1 (CH), 121.9 (CH), 119.6 (CH), 108.4 (CH), 108.1 (CH), 26.1 (CH_3), 25.8 (CH_3). MS (EI): 236 (100, $[M]^+$), 207 (12), 158 (74), 118 (55), 77 (10), 51 (13). HRMS (EI) calcd for $C_{15}H_{12}N_2O$ ($[M]^+$): 236.0950. Found: 236.0950.

3-Benzylidene-5-methoxy-1-methyl-1,3-dihydro-indol-2-one 10

According to GP 3 with **6b** (213 mg, 0.45 mmol) in DMF (5 mL) and KO*t*-Bu (61 mg, 0.54 mmol) and benzaldehyde (0.69 mL, 6.8 mmol). After purification by FC (pentane/MTBE 4:1) **10** (78 mg, 65%) was obtained as a mixture of isomers (*cis*:*trans* = 1:3.1) which were separated. *cis-Isomer*: IR (film): 3070*w*, 2942*w*, 2833*w*, 1694*s*, 1652*m*, 1593*m*, 1512*m*, 1439*m*, 1383*s*, 1345*m*, 1284*s*, 1230*m*, 1098*m*, 1042*s,* 760*s*, 455*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.23 (*d*, *J* = 7.6, 2 H, CH); 7.43 (*s*, 1 H, CH=C); 7.38-7.36 (*m*, 3 H, CH); 7.05 (*d*, *J* = 2.4, 1 H, CH); 6.77 (*dd*, J_1 = 8.3, J_2 = 2.5, 1 H, CH); 6.64 (*d*, *J* = 7.8, 1 H, CH); 3.78 (*s*, 3 H, OCH_3); 3.18 (*s*, 3 H, NCH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.0 (C), 155.7 (C), 137.1 (CH), 136.5 (C), 133.8 (C), 130.4 (CH), 129.2 (CH), 128.2 (CH), 127.0 (C), 125.3 (C), 114.0 (CH), 108.2 (CH), 105.9 (CH), 56.0 (CH_3), 25.9 (CH_3). MS (EI): 303 (100, $[M]^+$). HRMS (EI) calcd for $C_{17}H_{15}NO_2$ ($[M]^+$): 265.1103. Found: 265.1099.

trans-Isomer: ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.10 (*s*, 1 H, CH=C); 7.56-7.55 (*m*, 2 H, CH); 7.43-7.35 (*m*, 3 H, CH); 7.16 (*d*, *J* = 2.4, 1 H, CH); 6.83 (*dd*, J_1= 8.5, J_2 = 2.7, 1 H, CH); 6.64 (*d*, *J* = 8.3, 1 H, CH); 3.61 (*s*, 3 H, OCH_3); 3.19 (*s*, 3 H, NCH_3).

3-Benzylidene-7-methoxy-1-methyl-1,3-dihydro-indol-2-one 11

According to GP 3 with **6d** (151 mg, 0.32 mmol) in DMF (5 mL) and KO*t*-Bu (43 mg, 0.39 mmol) and benzaldehyde (0.48 mL, 4.8 mmol). After purification by FC (pentane/MTBE 4:1) **11** (36 mg, 42%) was obtained as a mixture of isomers (*cis*:*trans* = 1:2.6) which were separated. *cis-Isomer*: ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 8.29 (*m*, 2 H, CH); 7.52 (*s*, 1 H, CH=C); 7.45-7.40 (*m*, 3 H, CH); 7.18 (*dd*, J_1 = 7.1, J_2 = 1.5, 1 H, CH); 6.98 (*dd*, J_1 = 12.4, J_1 = 11.3, 1 H, CH); 6.84 (*dd*, J_1 = 12.4, J_2 = 1.5, 1 H, CH); 3.86 (*s*, 3 H, OCH_3); 3.55 (*s*, 3 H, NCH_3).

trans-Isomer: IR (film): 1702*s*, 1608*m*, 1459*m*, 1446*m*, 1331*m*, 1254*s*, 1126*s*, 1071*s*, 1049*s*, 694*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 7.85 (*s*, 1 H, CH=C); 7.64-7.59 (*m*, 2 H, CH); 7.50-7.39 (*m*, 3 H, CH); 7.22 (*d*, *J* = 1.8, 1 H, CH); 6.87-6.74 (*m*, 2 H, CH); 3.85 (*s*, 3 H, OCH_3); 3.56 (*s*, 3 H, NCH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): 168.7 (C), 145.5 (C), 137.4 (CH), 135.1 (C), 129.4 (CH), 129.2 (CH), 128.6 (CH), 127.6 (C), 126.8 (C), 122.6 (C), 122.1 (CH), 115.9 (CH), 113.9 (CH), 56.1 (CH_3), 29.6 (CH_3). MS (EI): 265 (100, $[M]^+$), 222 (19), 152 (21), 77 (12). HRMS (EI) calcd for $C_{17}H_{15}NO_2$ ($[M]^+$): 265.1103. Found: 265.1109.

3-Benzylidene-4-methoxy-1-methyl-1,3-dihydro-indol-2-one 12a and 3-Benzylidene-6-methoxy-1-methyl-1,3-dihydro-indol-2-one 12b

According to GP 3 with **6c** (216 mg, 0.46 mmol) in DMF (5 mL) and KO*t*-Bu (62 mg, 0.55 mmol) and benzaldehyde (0.80 mL, 8.0 mmol). After purification by FC (pentane/MTBE 4:1) **12a** and **12b** (106 mg, 87%, ratio 1.4:1) were obtained (the regioisomers were separated). **12a** was obtained as a mixture of isomers (*cis*:*trans* = 5:1). **12a**: *cis-Isomer*: M.p. 125 °C. IR (KBr): 2931*m*, 1692*s*, 1608*s*, 1473*s*, 1451*m*, 1264*s*, 1068*s*, 750*s*, 689*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.13 (*s*, 1 H, CH=C); 8.12 (*m*, 2 H, CH); 7.42-7.34 (*m*, 3 H, CH); 7.22 (*d*, *J* = 8.0, 1 H, CH); 6.66 (*d*, *J* = 8.6, 1 H, CH); 6.49 (*d*, *J* = 7.1, 1 H, CH); 3.99 (*s*, 3 H, OCH_3); 3.25 (*s*, 3 H, NCH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): 156.0 (C), 143.8 (C), 141.4 (CH), 134.9 (C), 131.5 (CH), 130.6 (C), 129.6 (CH), 129.5 (CH), 127.9 (CH), 126.5 (C), 126.9 (C), 105.3 (CH),

101.2 (CH), 55.5 (CH_3), 26.0 (CH_3). MS (EI): 265 (100, $[M]^+$), 222 (20), 188 (45), 165 (32), 102 (15), 91 (28). HRMS (EI) calcd for $C_{17}H_{15}NO_2$ ($[M]^+$): 265.1103. Found: 265.1093.

trans-Isomer: ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.95 (*s*, 1 H, CH=C); 7.38-7.25 (*m*, 6 H, CH); 6.66-6.51 (*m*, 2 H, CH); 3.45 (*s*, 3 H, OCH_3); 3.25 (*s*, 3 H, NCH_3).

12b: Tentatively assigned as *cis-Isomer*: IR (film): 2935*m*, 1708*s*, 1620*s*, 1505*m*, 1466*s*, 1382*s*, 1259*s*, 1229*s*, 1107*s*, 1057*m*, 700*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.70 (*s*, 1 H, CH=C); 7.63 (*d*, *J* = 8.3, 2 H, CH); 7.56 (*d*, *J* = 9.0, 1 H, CH); 7.48-7.41 (*m*, 3 H, CH); 6.40-6.37 (*m*, 2 H, CH); 3.83 (*s*, 3 H, OCH_3); 3.26 (*s*, 3 H, NCH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): 161.5 (C), 146.0 (C), 135.4 (C), 134.1 (CH), 131.5 (C), 129.2 (CH), 129.1 (CH), 128.5 (CH), 127.8 (C), 126.8 (C), 123.9 (CH), 105.8 (CH), 95.8 (CH), 55.5 (CH_3), 26.1 (CH_3). MS (EI): 265 (100, $[M]^+$), 222 (17), 142 (24), 131 (30), 77 (16). HRMS (EI) calcd for $C_{17}H_{15}NO_2$ ($[M]^+$): 265.1103. Found: 265.1098.

3-Benzyl-4-methoxy-1-methyl-1,3-dihydro-indol-2-one 13a

12a (41 mg, 0.16 mmol) was dissolved in MeOH (4 mL), then Pd/C (10 %) was added. After stirring for 18 h under an H_2–atmosphere at normal pressure, the reaction mixture was filtered. Removal of the solvents afforded **13a** (26 mg, 62%) as a white solid. IR (KBr): 2931*m*, 1710*s*, 1608*s*, 1474*s*, 1455*m*, 1318*m*, 1262*s*, 1061*s*, 751*s*, 702*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.27 (*s*, 1 H, CH); 7.15 (*dd*, $J_1 = J_2$ = 8.3, 1 H, CH); 7.06-7.05 (*m*, 2 H, CH); 6.97-6.95 (*m*, 2 H, CH); 6.59 (*d*, *J* = 8.6, 1 H, CH); 6.27 (*d*, *J* = 7.8, 1 H, CH); 3.91 (*s*, 3 H, OCH_3); 3.80 (*m*, 1 H, CHC(=O)); 3.47 (*dd*, J_1 = 13.4, J_2 = 5.3, 1 H, CH_2); 3.37 (*dd*, J_1 = 13.2, J_2 = 4.4, 1H, CH_2); 2.99 (*s*, 3 H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): 177.3 (C), 155.9 (C), 145.6 (C), 137.4 (C), 129.4 (CH), 127.6 (CH), 126.1 (CH), 114.0 (C), 105.8 (CH), 101.2 (CH), 96.0 (CH), 55.3 (CH_3), 46.2 (CH), 34.2 (CH_2), 26.1 (CH_3). MS (EI): 267 (41, $[M]^+$), 176 (100), 133 (23), 105 (11), 91 (34), 65 (20). HRMS (EI) calcd for $C_{17}H_{17}NO_2$ ($[M]^+$): 267.1259. Found: 267.1267.

3-Benzyl-6-methoxy-1-methyl-1,3-dihydro-indol-2-one 13b

12b (43 mg, 0.16 mmol) was dissolved in MeOH (4 mL), then Pd/C (10 %) was added. After stirring for 18 h under an H_2–atmosphere at normal pressure, the reaction mixture was filtered. Removal of the solvents afforded **13b** (34 mg, 78%) as an oil.

IR (film): 3437*br*, 1712*s*, 1626*s*, 1600*m*, 1506*m*, 1455*m*, 1378*s*, 1259*m*, 1230*m*, 910*s*, 700*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.29-7.15 (*m*, 5 H, CH); 6.57 (*d*, *J* = 8.0, 1 H, CH); 6.39 (*dxd*, J_1 = 12.7, J_2 = 2.5, 1 H, CH); 6.34 (*d*, *J* = 2.2, 1 H, CH); 3.78 (*s*, 3 H, OCH_3); 3.65 (*dxd*, J_1= 9.8, J_2 = 4.4, 1 H, CH_2); 3.46 (*dxd*, J_1= 13.7, J_2 = 4.4, 1 H, CH_2); 3.13 (*s*, 3 H, NCH_3); 2.80 (*dxd*, J_1= 13.4, J_2 = 9.5, 1H, CHC(=O)). ^{13}C- NMR (75 MHz, $CDCl_3$): 177.7 (C), 160.1 (C), 145.5 (C), 138.1 (C), 129.4 (CH), 128.4 (CH), 126.5 (CH), 125.1 (CH), 120.3 (C), 105.8 (CH), 96.0 (CH), 55.4 (CH_3), 46.5 (CH), 37.1 (CH_2), 26.1 (CH_3). MS (EI): 267 (15, $[M]^+$), 176 (100), 133 (10), 91 (22), 65 (8). HRMS (EI) calcd for $C_{17}H_{17}NO_2$ ($[M]^+$): 267.1259. Found: 267.1262.

1-Benzyl-3-benzylidene-1,3-dihydro-indol-2-one 14

According to GP 3 with **6f** (146 mg, 0.28 mmol) in DMF (5 mL) and KO*t*-Bu (38 mg, 0.34 mmol) and benzaldehyde (0.42 mL, 4.2 mmol). After purification by FC (pentane/MTBE 4:1) **14** (31 mg, 35%) was obtained as a mixture of isomers (*cis*:*trans* = 1:4.2) which were separated. *cis-Isomer*: ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 8.32 (*m*, 2 H, CH); 7.61-7.04 (*m*, 12 H, CH); 6.73 (*d*, *J* = 7.7, 1 H, CH); 5.00 (*s*, 2 H, NCH_2).

trans-Isomer: IR (film): 3399*w*, 1705*s*, 1607*s*, 1481*m*, 1467*s*, 1384*s*, 1352*s*, 1179*s*, 778*m*, 748*s*, 698*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.94 (s, 1 H, CH=C); 7.67-7.62 (*m*, 2 H, CH); 7.49-7.42 (*m*, 3 H, CH); 7.34-7.25 (*m*, 6 H, CH); 7.16-7.11 (*m*, 1 H, CH); 6.84 (*ddd*, $J_1 = J_2$ = 7.6, J_3 = 1.3, 1 H, CH); 6.72 (*d*, *J* = 7.8, 1 H, CH); 5.01 (*s*, 2 H, NCH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): 168.5 (C), 143.4 (C), 137.5 (CH), 136.0 (C), 135.0 (C), 129.7 (CH), 129.5 (CH), 129.3 (CH), 128.7 (CH), 128.6 (CH), 128.3 (C), 127.5 (CH), 127.3 (CH), 122.8 (CH), 121.8 (CH), 121.3 (C), 109.5 (CH), 44.2 (CH_2). MS (EI): 311 (34, $[M]^+$), 165 (16), 91 (100). HRMS (EI) calcd for $C_{22}H_{17}NO$ ($[M]^+$): 311.1310. Found: 311.1313.

Literature

[1] D. V. Patel, R. J. Schmidt, S. A. Biller, E. M. Gordon, S. S. Robinson and V. Manne, *J. Med. Chem.* **1995**, *38*, 2906.

[2] J. C. Birnbaum, B. Busche, Y. Lin, W. J. Shaw and G. E. Fryxell, *Chem. Commun.* **2002**, 1374.

[3] J. Berluenga, A. M. Bayón and G. Asensio, *Chem. Commun.* **1983**, 1109.

[4] J. Berluenga, A. M. Bayón and G. Asensio, *Chem. Commun.* **1984**, 1334.

[5] S. R. Khan, A. Mhaka, R. Pili and J. T. Isaacs, *Bioor. Med. Chem. Let.* **2001**, *11*, 451.