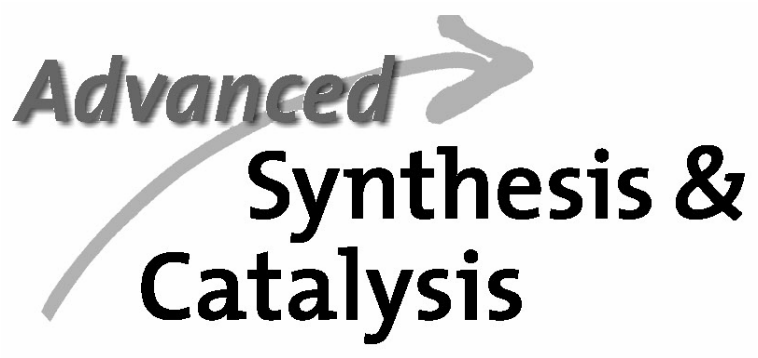

Supporting Information

Auto-Tandem Catalysis: Synthesis of Substituted 11*H*-indolo[3,2-*c*]quinolines via Pd-catalyzed Intermolecular C-N and Intramolecular C-C Bond Formation.

Caroline Meyers, Geert Rombouts, Kristof T.J. Loones, Alberto Coelho and Bert U.W. Maes*.

Department of Chemistry, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium

Phone: (+32) 32653205, Fax: (+32) 32653233, e-mail: bert.maes@ua.ac.be

Supporting information

General Remarks:

All melting points were determined on a Büchi apparatus and are uncorrected. The ^{1}H- and ^{13}C NMR spectra were recorded on a Bruker spectrometer Avance II 400 in the solvent indicated with TMS as the internal standard. All coupling constants are given in Hz and chemical shifts are given in ppm. For mass spectrometric analysis, samples were dissolved in CH_3OH containing 0.1% formic acid and diluted to a concentration of approximately 10^{-5} mol/L. Injections (1 µL) were directed to the mass spectrometer at a flow rate of 5 µL/min (CH_3OH and 0.1% formic acid), using a CapLC HPLC system (Waters-Micromass). Accurate mass data were acquired on a Q-TOF 2 mass spectrometer (Waters-Micromass) equipped with a standard electrospray ionisation (ESI) interface. Cone voltage (approx. 35 V) and capillary voltage (approx. 3.3 kV) were optimized on one compound and used for all others. For the determination of the accurate mass of the molecular ion $[M+H]^+$, a solution of polyethylene glycol 300 in CH_3OH/H_2O with 1 mmol ammonium acetate, was added just before the mass spectrometer (at a rate of 1 µL/min) to the mobile phase. The calculated masses of PEG $[M+H]^+$ and $[M+NH_4]^+$ ions were used as internal calibrant (lock mass). $Pd_2(dba)_3$ (Acros), P-(*t*-Bu_3) solution in toluene (Aldrich), 4-chloroquinoline (Aldrich), K_3PO_4 (Aldrich) as well as the anilines were obtained form commercial sources and used without further purification. Flash column chromatography was performed on Kieselgel 60 (ROCC SI 1721, 40-60 µm).

Ethyl 4-(quinolin-4-ylamino)benzoate (7a):

The general procedure was followed using ethyl 4-aminobenzoate (**6a**) (2.4 mmol, 0.396 g) as aniline. Eluent: EtOAc (500 mL), EtOAc/MeOH (85/15); yield: 0.556 g (95%); white solid; mp: 202°C; ^{1}H-NMR (400 MHz, $CDCl_3$): 8.61 (d, *J* = 5.3 Hz, 1H, H-2), 8.13-8.04 (m, 4H, H-5, H-8, H-3′, H-5′), 7.72 (dd, *J* = 8.3, 6.9 Hz, 1H, H-6 or H-7), 7.54 (dd, *J* = 8.1, 6.9 Hz, 1H, H-6 or H-7), 7.35 (d, *J* = 8.7 Hz, 2H, H-2′ and H-6′), 7.19 (d, *J* = 5.3 Hz, 1H, H-3), 6.89 (s, 1H, NH), 4.40 (q, *J* = 7.1 Hz, 2H, CH_2), 1.42 (t, *J* = 7.1 Hz, 3H, CH_3); ^{13}C-NMR (100 MHz, $CDCl_3$): 166.0, 149.6, 148.1, 146.7, 144.5, 131.4, 130.1, 129.1, 126.1, 125.6, 120.5, 120.3, 119.9, 104.3, 60.9, 14.4; HRMS (ESI) for $C_{18}H_{17}N_2O_2$ $[M+H]^+$ calcd 293.1290, found 293.1302.

Ethyl 2-(quinolin-4-ylamino)benzoate (7b):

The general procedure was followed using ethyl 2-aminobenzoate (**6b**) (2.4 mmol, 0.396 g) as aniline. Eluent: EtOAc; yield: 0.471 g (81%); white solid; mp: 91°C; ^{1}H-NMR (400 MHz, $CDCl_3$): 10.47 (s, 1H, NH), 8.71 (d, *J* = 5.2 Hz, 1H, H-2), 8.16 (d, *J* = 8.4 Hz, 1H, H-8 or H-5), 8.09 (d, *J* = 8.2 Hz, 1H, H-3′), 8.07 (d, *J* = 8.4 Hz, 1H, H-5 or H-8), 7.71 (dd, *J* = 8.4, 6.9 Hz, 1H, H-6 or H-7), 7.67 (d, *J* = 8.4 Hz, 1H, H-6′), 7.57 (dd, *J* = 8.4, 6.9 Hz, 1H, H-7 or H-6), 7.49 (dd, *J* = 8.2, 7.4 Hz, 1H, H-5′), 7.42 (d, *J* = 5.2 Hz, 1H, H-3), 6.98 (dd, *J* = 7.9, 7.1 Hz, 1H, H-4′), 4.41 (q, *J* = 7.1 Hz, 2H, CH_2), 1.43 (t, *J* = 7.1 Hz, 3H, CH_3); ^{13}C-NMR (100 MHz, $CDCl_3$): 168.5, 150.4, 149.2, 145.4, 144.4, 134.0, 131.9, 129.8, 129.7, 126.2, 121.8, 120.9, 120.6, 117.5, 116.1, 105.4, 61.3, 14.3; HRMS (ESI) for $C_{18}H_{17}N_2O_2$ $[M+H]^+$ calcd 293.1290, found 293.1292.

4-(Quinolin-4-ylamino)benzonitrile (7c):

The general procedure was followed using 4-aminobenzonitrile (**6c**) (2.4 mmol, 0.288 g) as aniline. Eluent: EtOAc; yield: 0.422 g (86%); white solid; mp: 206°C; ^{1}H-NMR (400 MHz, [D_6] DMSO): 9.39 (s, 1H, NH), 8.64 (d, *J* = 5.1 Hz, 1H, H-2), 8.30 (d, *J* = 8.1 Hz, 1H, H-8 or H-5), 7.96 (d, *J* = 8.3 Hz, 1H, H-5 or H-8), 7.76 (d, *J* = 8.6 Hz, 2H, H-3′ and H-5′), 7.75 (m, 1H, H-6 or H-7), 7.59 (dd, *J* = 8.3, 6.9 Hz, 1H, H-7 or H-6), 7.45 (d, *J* = 8.6 Hz, 2H, H-2′ and H-6′), 7.30 (d, *J* = 5.1 Hz, 1H, H-3); ^{13}C-NMR (100 MHz, [D_6] DMSO): 150.7, 149.1, 146.3, 145.1, 133.6, 129.6, 129.3, 125.3, 122.3, 121.0, 119.3, 118.9, 105.9, 102.8; HRMS (ESI) for $C_{16}H_{12}N_3$ $[M+H]^+$ calcd 246.1031, found 246.1030.

***N*-(4-Fluorophenyl)quinolin-4-amine (7d):**

The general procedure was followed using 4-fluoroaniline (**6d**) (2.4 mmol, 0.266 g) as aniline. Eluent: EtOAc; yield: 0.419 g (88%); white solid; mp: 192°C; ^{1}H-NMR (400 MHz, $CDCl_3$): 8.51 (d, J_{H-H} = 5.2 Hz, 1H, H-2), 8.05 (d, J_{H-H} = 8.2 Hz, 1H, H-8 or H-5), 8.01 (d, J_{H-H} = 8.5 Hz, 1H, H-5 or H-8), 7.68 (dd, J_{H-H} = 8.4, 6.9 Hz, 1H, H-7 or H-6), 7.50 (dd, J_{H-H} = 8.3, 6.9 Hz, 1H, H-7 or H-6), 7.23 (dd, J_{H-H} = 8.5 Hz, $^{4}J_{H-F}$ = 4.4 Hz, 2H, H-2′ and H-6′), 7.11 (t, J_{H-H} and $^{3}J_{H-F}$ = 8.6 Hz, 2H, H-3′ and H-5′), 6.77 (d, J_{H-H} = 5.2 Hz, 1H, H-3); 6.62 (s, 1H, NH); ^{13}C-NMR (100 MHz, $CDCl_3$): 160.2 (d, $^{1}J_{C-F}$ = 244.9 Hz), 150.4, 148.5, 148.4, 135.6 (d, $^{4}J_{C-F}$ = 5.9 Hz), 129.7, 129.6, 125.6, 125.5 (d, $^{3}J_{C-F}$ = 10.0 Hz), 119.8, 119.3, 116.7 (d, $^{2}J_{C-F}$ = 22.7 Hz), 101.6; HRMS (ESI) for $C_{15}H_{12}N_2F$ $[M+H]^+$ calcd 239.0985, found 239.0979.

***N*-(4-*tert*-Butylphenyl)quinolin-4-amine (7e):**

The general procedure was followed using $Pd_2(dba)_3$ (0.05 mmol, 0.046 g), P(*t*-Bu)$_3$ (0.20 mmol, 0.5 mL of 0.4 M solution in toluene) and 4-*tert*-butylaniline (**6e**) (2.4 mmol, 0.358 g) as aniline. Eluent: Heptane/EtOAc (1/1) (500 mL), Heptane/EtOAc (1/4); yield: 0.536 g (97%) white solid; mp: 221°C; ^{1}H-NMR (400 MHz, $CDCl_3$): 8.48 (d, *J* = 5.4 Hz, 1H, H-2), 8.06 (d, *J* = 8.1 Hz, 1H, H-5 or H-8), 8.04 (d, *J* = 8.0 Hz, 1H, H-8 or H-5), 7.67 (dd, *J* = 8.4, 7.2 Hz, 1H, H-6 or H-7), 7.49 (dd, *J* = 8.1, 7.2 Hz, 1H, H-6 or H-7), 7.43 (d, *J* = 8.3 Hz, 2H, H-2′ and H-6′ or H-3′ and H-5′); 7.26 (d, *J* = 8.3 Hz, 2H, H-2′ and H-6′ or H-3′ and H-5′), 7.15 (br s, 1H, NH), 6.92 (d, *J* = 5.4 Hz, 1H, H-3); ^{13}C-NMR (100 MHz, $CDCl_3$): 149.7, 148.7, 148.3, 147.8, 136.7, 129.8, 129.0, 126.6, 125.4, 123.0, 120.1, 119.3, 101.6, 34.5, 31.4; HRMS (ESI) for $C_{19}H_{21}N_2$ $[M+H]^+$ calcd 277.1705, found 277.1703.

***N*-(4-Methoxyphenyl)quinolin-4-amine (7f):**

The general procedure was followed using $Pd_2(dba)_3$ (0.05 mmol, 0.046 g), P(*t*-Bu)$_3$ (0.20 mmol, 0.5 mL of 0.4 M solution in toluene), *p*-anisidine (**6f**) (2.4 mmol, 0.295 g) as aniline. Eluent: EtOAc/MeOH (85/15); yield: 0.411 g (80%); yellow solid; mp: 171°C; ^{1}H-NMR (400 MHz, $CDCl_3$): 8.52 (d, *J* = 5.3 Hz, 1H, H-2), 8.0 (d, *J* = 7.9 Hz, 1H, H-5 or H-8), 7.91 (d, *J* = 7.9 Hz, 1H, H-5 or H-8), 7.68 (dd, *J* = 8.4, 6.9 Hz, 1H, H-6 or H-7), 7.50 (dd, *J* = 8.4, 6.9 Hz, 1H, H-7 or H-6), 7.26 (d, *J* = 8.8 Hz, 2H, H-2′ and H-6′ or H-3′ and H-5′), 6.98 (d, *J* = 8.8 Hz, 2H, H-2′ and H-6′ or H-3′ and H-5′), 6.71 (d, *J* = 5.2 Hz, 1H, H-3), 6.55 (1H, s, 1H, NH), 3.86 (3H, s, CH_3); ^{13}C-NMR (100 MHz, $CDCl_3$): 157.5, 150.4, 149.3, 148.5, 132.2, 129.6, 129.4,

126.1, 125.1, 119.8, 119.1, 115.0, 101.1, 55.5; HRMS (ESI) for $C_{16}H_{15}N_2O$ $[M+H]^+$ calcd 251.1184, found 251.1193.

11*H*-Indolo[3,2-*c*]quinoline (4a):

The general procedure was followed using 2-chloroaniline (**2a**) (2.4 mmol, 0.306 g) as aniline. Filtration through a pad of Celite: CH_2Cl_2 (360 mL). Eluent: a gradient going from EtOAc to EtOAc/MeOH (96/4) was used; yield: 0.360 g (82%); the characterization data were identical with those previously reported in the literature.[4]

8-Fluoro-11*H*-indolo[3,2-*c*]quinoline (4b):

The general procedure was followed using 2-chloro-4-fluoroaniline (**2b**) (2.4 mmol, 0.349 g) as aniline. Filtration through a pad of Celite: CH_2Cl_2/MeOH (5/1) (600 mL). Eluent: EtOAc/Heptane (1/2) (300 mL), EtOAc (300 mL) then EtOAc/MeOH (98:2). The 8-fluoro-11*H*-indolo[3,2-*c*]quinoline obtained was subsequently washed with 25 mL Et_2O.; yield: 0.260 g (55%); mp: 376-377°C; ^{1}H-NMR (400 MHz, [D_6] DMSO): 12.76 (s, 1H), 9.59 (s, 1H), 8.51 (dd, *J* = 7.9, 1.1 Hz, 1H), 8.15 (br td, *J* = 9.5, 2.6 Hz, 2H), 7.73 (m, 3H), 7.34 (td, *J* = 9.2, 2.6 Hz, 1H); MS (ESI): 217; HRMS (ESI) for $C_{15}H_{10}N_2F$ $[M+H]^+$ calcd 237.0828 , found 237.0820.

10-Fluoro-11*H*-indolo[3,2-*c*]quinoline (4c):

The general procedure was followed using 2-chloro-6-fluoroaniline (**2c**) (2.4 mmol, 0.349 g) as aniline. Filtration through a pad of Celite: CH_2Cl_2/MeOH (4/1) (500 mL). Eluent: EtOAc/Heptane (1/3) (400 mL), EtOAc (300 mL), EtOAc/MeOH (98:2). The 10-fluoro-11*H*-indolo[3,2-*c*]quinoline obtained was subsequently washed with 25 mL Et_2O.; yield: 0.380 g (80%); mp: 343-344°C; ^{1}H-NMR (400 MHz, [D_6] DMSO): 13.06 (s, 1H), 9.61 (s, 1H), 8.70 (dd, *J* = 7.6, 0.8 Hz, 1H), 8.16 (d, *J* = 8.2 Hz, 2H), 7.78 (br ddd, *J* = 8.3, 7.0, 1.4 Hz, 2H), 7.71 (m, 2H); MS (ESI): 190, 217; HRMS (ESI) for $C_{15}H_{10}N_2F$ $[M+H]^+$ calcd 237.0828, found 237.0826.

Methyl 11*H*-indolo[3,2-*c*]quinoline-8-carboxylate (4d):

The general procedure was followed using methyl 4-amino-3-chlorobenzoate (**2d**) (2.4 mmol, 0.448 g) as aniline. Filtration through a pad of Celite: CH_2Cl_2/MeOH (7/1) (800 mL). Eluent:

EtOAc (300 mL), EtOAc/MeOH (97:3) (1500 mL), EtOAc/MeOH (95:5). The methyl 11*H*-indolo[3,2-*c*]quinoline-8-carboxylate obtained was subsequently washed with 25 mL Et_2O.; yield: 0.280 g (50%); mp: 309-310°C; ^{1}H-NMR (400 MHz, [D_6] DMSO): 13.06 (s, 1H), 9.73 (s, 1H), 9.01 (d, *J* = 1.3 Hz, 1H), 8.53 (dd, *J* = 8.2 Hz, 1.1 Hz, 1H), 8.16 (d, *J* = 7.8 Hz, 1H), 8.11 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.80 (br d, *J* = 8.4 Hz, 2H), 7.74 (m, 2H), 3.93 (s, 3H); MS (ESI): 190, 218; HRMS (ESI) for $C_{17}H_{13}N_2O_2$ $[M+H]^+$ calcd 277.0977, found 277.0989.

11*H*-Indolo[3,2-*c*]quinoline-8-carbonitrile (4e):

The general procedure was followed using $Pd_2(dba)_3$ (0.07 mmol, 0.064 g), P(*t*-Bu)$_3$ (0.28 mmol, 0.28 mL) and methyl 4-amino-3-chlorobenzonitrile (**2e**) (2.4 mmol, 0.366 g) as aniline. Filtration through a pad of Celite: CH_2Cl_2/MeOH (4/1) (500 mL). Eluent: EtOAc/MeOH (98:2).; yield: 0.194 g (80%); mp: 397-398°C; ^{1}H-NMR (400 MHz, [D_6] DMSO): 13.22 (s, 1H), 9.69 (s, 1H), 8.92 (s, 1H), 8.54 (dd, *J* = 7.9, 1.0 Hz, 1H), 8,18 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 1.0, 2H), 7.81 (ddd, *J* = 8.4, 7.0, 1.5 Hz, 1H), 7.75 (m, 1H); HRMS (ESI) for $C_{16}H_{10}N_3$ $[M+H]^+$ calcd 244.0875, found 244.0882.

8-*tert*-Butyl-11*H*-indolo[3,2-*c*]quinoline (4f):

The general procedure was followed using 4-*t*-butyl-2-chloroaniline (**2f**) (2.4 mmol, 0.440 g) as aniline. Filtration through a pad of Celite: CH_2Cl_2/MeOH (4/1) (500 mL). Eluent: EtOAc/Heptane (1/3) (400 mL), EtOAc (300 mL), EtOAc/MeOH (98:2). The 8-*tert*-butyl-11*H*-indolo[3,2-*c*]quinoline obtained was subsequently washed with 25 mL Et_2O.; yield: 0.420 g (76%); mp: 347-348°C; ^{1}H-NMR (400 MHz, [D_6] DMSO): 12.56 (s, 1H), 9.61 (s, 1H), 8.50 (dd, *J* = 8.0, 1.8 Hz, 1H), 8.33 (d, *J* = 1.7 Hz, 1H), 8.12 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.73 (br td, *J* = 8.4, 1.5 Hz, 1H),7.67 (br td, *J* = 8.2, 1.3 Hz, 1H), 7.63 (d, *J* = 8.6 Hz, 1H), 7.57 (dd, *J* = 8.6, 1.9 Hz, 1H); MS (ESI): 259; HRMS (ESI) for $C_{19}H_{19}N_2$ $[M+H]^+$ calcd 275.1548, found 275.1556.

8-Methoxy-11*H*-indolo[3,2-*c*]quinoline (4g):

The general procedure was followed using 2-chloro-*p*-anisidine (**2g**) (2.4 mmol, 0.378 g) as aniline. Filtration through a pad of Celite: CH_2Cl_2/MeOH (5/1) (600 mL). Eluent: EtOAc/Heptane (1/3) (400 mL), EtOAc (300 mL), EtOAc/MeOH (98:2). The 8-methoxy-11*H*-indolo[3,2-*c*]quinoline obtained was subsequently washed with 25 mL Et_2O.; yield: 0.260 g (52%); mp: 327-328°C; ^{1}H-NMR (400 MHz, [D_6] DMSO): 12.64 (s, 1H), 9.51 (s,

1H), 8.48 (dd, *J* = 7.6, 1.7 Hz, 1H), 8.18 (d, *J* = 8.6 Hz, 1H), 8,11 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.70 (br td, *J* = 7.0, 1.6 Hz, 2H,), 7.66 (br td, *J* = 7.0, 1.3 Hz, 1H), 7.18 (d, *J* = 2.2 Hz, 1H), 6.97 (dd, *J* = 8.5, 2.2 Hz, 1H), 4,10 (s, 1H); HRMS (ESI) for $C_{16}H_{13}N_2O$ $[M+H]^+$ calcd 249.1028, found 249.1017.

8-Fluoro-5-methyl-5*H*-indolo[3,2-*c*]quinoline (5b):

The general procedure was followed using BTF as solvent. ^{1}H-NMR (400 MHz, [D_6] DMSO): 9.42 (s, 1H, H-6), 8.75 (dd, J_{H-H} = 8.0, 1.2 Hz, 1H, H-1), 8.08 (d, J_{H-H} = 8.6 Hz, 1H, H-4), 7.90 (dd, J_{H-F} = 9.2, J_{H-H} = 2.6 Hz, 1H, H-7), 7.87 (ddd, J_{H-H} = 8.6, 7.1, ~1.5 Hz, 1H, H-3), 7.77 (dd, J_{H-F} = 4.7, J_{H-H} = ~9.1 Hz 1H, H-10), 7.74 (m, 1H, H-2), 7.29 (br td, *J* = ~9.5, 2.6 Hz, 1H, H-9), 4.27 (s, 3H, NCH_3); ^{13}C-NMR (100 MHz, [D_6] DMSO): 157.5 (d, $^1J_{C-F}$ = 234.5 Hz), 152.0, 148.9, 139.8, 135.5, 129.8, 125.9, 125.6 (d, $^3J_{C-F}$ = 10.7 Hz), 123.9, 120.5, 118.5 (d, $^3J_{C-F}$ = 9.4 Hz), 117.9, 115.7 (d, $^4J_{C-F}$ = 4.4 Hz), 113.4 (d, $^2J_{C-F}$ = 24.8 Hz), 105.4 (d, $^2J_{C-F}$ = 24.3 Hz), 42.6; MS (ESI): 236; HRMS (ESI) for $C_{16}H_{12}N_2F$ $[M+H]^+$ calcd 251.0985, found 251.0979.

10-Fluoro-5-methyl-5*H*-indolo[3,2-*c*]quinoline (5c):

^{1}H-NMR (400 MHz, [D_6] DMSO): 9.49 (s, 1H, H-6), 8.82 (dd, J_{H-H} = 8.0, 1.5 Hz, 1H, H-1), 8.11 (d, J_{H-H} = 8.6 Hz, 1H, H-4), 7.95 (m, 1H, H-7), 7.89 (ddd, J_{H-H} = 8.6, 7.0, 1.6 Hz, 1H, H-3), 7.76 (br td, J_{H-H} = ~7.9 , 0.8 Hz 1H, H-2), 7.23 (m, 2H, H-8 and H-9), 4.31 (s, 3H, NCH_3); ^{13}C-NMR (100 MHz, [D_6] DMSO): 153.0 (d, $^1J_{C-F}$ = 247.7 Hz), 151.9, 139.9, 135.6, 129.8, 129.0 (d, $^3J_{C-F}$ = 6.9 Hz), 125.8, 124.0, 120.9, 120,3 (d, $^3J_{C-F}$ = 6.4 Hz), 117.8, 115.9, 115.8 (d, $^2J_{C-F}$ = 18.3 Hz), 115.7 (d, $^4J_{C-F}$ = 3.3 Hz), 110.7 (d, $^2J_{C-F}$ = 17.7 Hz), 42.5; MS (ESI): 231, 236; HRMS (ESI) for $C_{16}H_{12}N_2F$ $[M+H]^+$ calcd 251.0985, found 251.0981.

Methyl 5-methyl-5*H*-indolo[3,2-*c*]quinoline-8-carboxylate (5d):

^{1}H-NMR (400 MHz, [D_6] DMSO): 9.59 (s, 1H, H-6), 8.82 (d, *J* = 1.4 Hz, 1H, H-7), 8.80 (dd, *J* = 8.0, 1.2 Hz, 1H, H-1), 8.10 (d, *J* = 8.6 Hz, 1H, H-4), 8.04 (dd, *J* = 8.5, 1.7 Hz, 1H, H-9), 7.89 (ddd, *J* = 8.5, 7.1, 1.4 Hz, 1H, H-3), 7.82 (d, *J* = 8.5 Hz, 1H, H-10), 7.77 (t, *J* = 7.3 Hz, 1H, H-2), 4.29 (s, 3H, NCH_3) 3.90 (s, 3H, OCH_3); ^{13}C-NMR (100 MHz, [D_6] DMSO): 167.1, 157.3, 154.8, 139.5, 135.7, 129.9, 126.3, 125.7, 125.3, 124.0, 121.7, 121.0, 120.4, 117.9, 117.8, 116.1, 51.6, 42.5; MS (ESI): 232; HRMS (ESI) for $C_{18}H_{15}N_2O_2$ $[M+H]^+$ calcd 291.1134, found 291.1141.

5-Methyl-5*H*-indolo[3,2-*c*]quinoline-8-carbonitrile (5e):

^{1}H-NMR (400 MHz, [D_6] DMSO): 9.51 (s, 1H, H-6), 8.80 (dd, *J* = 8.0, 1.4 Hz, 1H, H-1), 8.57 (d, *J* = 1.2 Hz, 1H, H-7), 8.12 (d, *J* = 8.7 Hz, 1H, H-4), 7.91 (ddd, *J* = 8.6, 7.0, 1.6 Hz, 1H, H-3), 7.89 (dd, *J* = 8.4, 0.4 Hz, 1H, H-10), 7.77 (m, 1H, H-2), 7.74 (d, *J* = 8.4, 1.7 Hz, 1H, H-9), 4.29 (s, 3H, NCH_3); ^{13}C-NMR (100 MHz, [D_6] DMSO): 156.7, 155.1, 140.1, 135.7, 130.1, 128.1, 126.0, 125.8, 124.5, 124.1, 121.1, 120.9, 119.2, 118.0, 115.2, 100.5, 42.8; MS (ESI): 190, 243; HRMS (ESI) for $C_{17}H_{12}N_3$ $[M+H]^+$ calcd 258.1031, found 258.1036.

8-*tert*-Butyl-5-methyl-5*H*-indolo[3,2-*c*]quinoline (5f):

^{1}H-NMR (400 MHz, [D_6] DMSO): 9.55 (s, 1H, H-6), 8.79 (dd, *J* = 8.1, 1.3 Hz, 1H, H-1), 8.21 (d, *J* = 1.6 Hz, 1H, H-7), 8.12 (d, *J* = 8.6 Hz, 1H, H-4), 7.89 (ddd, *J* = 8.6, 7.1, 1.5 Hz, 1H, H-3), 7.76 (m, 1H, H-2), 7.73 (dd, *J* = 8.5, 0.3 Hz, 1H, H-10), 7.58 (dd, *J* = 8.5, 2 Hz, 1H, H-9), 4.31 (s, 3H, NCH_3) 1.43 (s, 9H, *t*Bu); ^{13}C-NMR (100 MHz, [D_6] DMSO): 150.2, 148.9, 143.2, 139.3, 135.5, 129.8, 125.7, 124.4, 124.0, 123.9, 119.8, 117.9, 116.4, 115.9, 115.8, 42.5, 34.5, 31.8; MS (ESI): 273; HRMS (ESI) for $C_{20}H_{21}N_2$ $[M+H]^+$ calcd 289.1705, found 289.1697.

8-Methoxy-5-methyl-5*H*-indolo[3,2-*c*]quinoline (5g):

^{1}H-NMR (400 MHz, [D_6] DMSO): 9.19 (s, 1H, H-6), 8.73 (dd, *J* = 8.0, 1.4 Hz, 1H, H-1), 8.00 (d, *J* = 8.6 Hz, 1H, H-4), 7.96 (d, *J* = 8.4 Hz, 1H, H-10), 7.80 (ddd, *J* = 8.6, 7.1, 1.5 Hz, 1H, H-3), 7.67 (m, 1H, H-2), 7.31 (d, *J* = 2.2 Hz, 1H, H-7), 6.89 (dd, *J* = 8.4, 2.3 Hz, 1H, H-9), 4.23 (s, 3H, NCH_3) 3.87 (s, 9H, OCH_3); ^{13}C-NMR (100 MHz, [D_6] DMSO): 158.7, 154.8, 152.4, 137.1, 135.1, 129.2, 125.1, 123.8, 120.1, 118.5, 117.4, 116.2, 109.2, 101.1, 55.2, 42.2; MS (ESI): 220, 248; HRMS (ESI) for $C_{17}H_{15}N_2O$ $[M+H]^+$ calcd 263.1184, found 263.1182.