Supplementary materials

8-quinolinyl trifluoromethanesulfonate 1b

To a pyridine solution of 8-hydroxyquinoline (0.29g, 2mmol) trifluoromethanesulfonic anhydride (2.4 mmol) was added dropwise at 0°C. The solution was stirred at 0°C for 5 min and warmed to 25°C with stirring for 24h. The resulting mixture was poured into cold water and extracted with ethyl acetate. The organic layer was then washed sequentially with 1N aqueous hydrochloric acid solution, and water, dried over $MgSO_4$, and concentrated to yield **1b** (0.5g, 92%) as an orange solid which was used without purification. NMR data according to Li and al.[12]

8-quinolinyl methanesulfonate 1c

To a dichloromethane solution of 8-hydroxyquinoline (0.29g, 2mmol) triéthylamine (3 mmol) and methanesulfonic chloride (2.4 mmol) were added at 0°C. The solution was stirring at 0°C for 5 min and warmed to 25°C with stirring for 3h. The resulting mixture was poured into water and extracted with dichloromethane. The dichloromethane extract was then washed with water, dried over $MgSO_4$ and concentrated to give **1c** (0.38g, 85 %) as brown oil which was used without purification.

Palladium catalyzed coupling reaction with Cacchi's conditions.

2.4 mmol of bromoquinoline, 7.2 mmol of acrolein (or diethyl acetal acrolein), 3.6 mmol of K_2CO_3, 2.4 mmol of n-Bu_4NOAc, 2.4 mmol of KCl and 5mol% of $Pd(OAc)_2$ were introduced in a pressure tube under argon. 10 mL of DMF previously deaerated was added and the mixture was deaerated by an argon flow for 5 min. The reactor was then placed in a pre-heated oil bath at 90°C for 24 h under vigorous stirring and then cooled to room temperature before the reaction mixture was analyzed by GC.

3-Quinolin-8-yl-propenal 2

At completion of the reaction, the mixture was diluted with water (150 mL) and the resulting mixture was extracted with CH_2Cl_2 (4 x 20 mL). The combined organic layers were washed

three times with H_2O (acrolein) or HCl 0.1N (diethylacetal acrolein), then brine (15 mL), dried over $MgSO_4$ and evaporated. The residue was then purified by flash chromatography on silica gel. Orange solid. mp 125°C. ν_{max}(KBr)/cm^{-1} 1663 and 1118; δ_H (250 MHz; $CDCl_3$) 6.90 (1 H, dd, *J* 7.9 and 16.2, HC=C*H*-CHO), 7.42 (1 H, dd, *J* 8.3 and 4.2, C(3)H); 7.52 (1 H, t, *J* 7.7, C(6)H); 7.85 (1 H, d, *J* 8.2, C(5)H); 7.97 (1 H, d, *J* 7.3, C(7)H); 8.13 (1 H, d, *J* 8.3, C(4)H); 8.83 (1 H, d, *J* 16.2, *H*C=CH-CHO); 8.90 (1 H, d, *J* 4.2, C(2)H) and 9.79 (1 H, d, *J* 7.9 C*H*O); δ_C (62.9 MHz; $CDCl_3$) 194.32 (*C*HO); 150.25 (*C*H=CH-CHO); 148.64 (C^2-C_9H_7N); 145.58 (C^{10}- C_9H_6N); 136.31 (C^4- C_9H_6N); 132.08 (C^8- C_9H_6N); 130.85 (CH=*C*H-CHO); 129.85 (C^5- C_9H_6N); 128.30 (C^9- C_9H_6N); 127.79 (C^7- C_9H_6N); 126.15 (C^6- C_9H_6N); 121.66 (C^3- C_9H_6N); m/z (CI) 184.0765 (M + H^+ $C_{12}H_{10}NO$ requires 184.0762) 184 (MH^+, 100%), 85 (17)

Palladium catalyzed coupling reaction with palladacycle catalyst.

2.4 mmol of bromoquinoline, 7.2 mmol of acrolein (or diethyl acetal acrolein), 3.6 mmol of NaOAc and 1mol% of Hermann's palladacycle were introduced in a pressure tube under argon. 8 mL of NMP previously deaerated was added and the mixture was deaerated by an argon flow for 5 min. The reactor was then placed in a pre-heated oil bath at 140°C for 24 h under vigorous stirring and then cooled to room temperature before the reaction mixture was analyzed by GC.

5*H*-Pyrido[3,2,1-ij]quinolin-3-one 3

At completion of the reaction, the mixture was diluted with water (150 mL) and the resulting mixture was extracted with CH_2Cl_2 (4 x 20 mL). The combined organic layers were washed three times with H_2O, then brine, dried over $MgSO_4$ and evaporated. The residue was then purified by flash chromatography on silica gel. The structure of the 5*H*-pyrido[3,2,1-ij]quinolin-3-one **3** was assigned according to NMR data and GC/MS analysis: yellow solid. m.p: 127 °C. ν_{max}(KBr)/cm^{-1} 1640, 1576, 1132; δ_H (250 MHz; $CDCl_3$) 4.78 (2 H, m, CH_2N). 5.94 (1 H, dt, *J* 10.2 and 3.6, C(3)H); 6.43 (1 H, dt, *J* 10.2 and 2.2, C(4)H); 6.62 (1 H, d, *J* 9.5, HC=C*H*-CO); 6.98-7.26 (3H, m, C(5)H, C(6)H, C(7)H); 7.57 (1H, d, *J* 9.5, *H*C=CH-CO); δ_C (62.9 MHz; $CDCl_3$) 161.71 (*C*ON); 138.80 (H*C*=CH-CON); 131.89(C^{10}-C_9H_7N); 127.28 (C^9-C_9H_7N); 126.99 (C^8-C_9H_7N); 125.56 (C^7-C_9H_7N); 125.35 (C^5-C_9H_7N); 123.96 (C^6-C_9H_7N); 123.14 (C^3-C_9H_7N); 122.33 (C^4-C_9H_7N); 121.18 (HC=*C*H-CON); 45.44 (C^2-C_9H_7N); m/z (CI) 184.0762 (M + H^+ $C_{12}H_{10}NO$ requires 184.0762) 184 (MH^+, 100%), 170 (9), 114 (21).

3-Quinolin-8-yl-propionic acid ethyl ester 5

Using same work-up as for **3** except that the combined organic layers were washed three times with HCl 0.2 N. Yellow solid. m.p.: 133 °C. ν_{max}(KBr)/cm^{-1} 1728, 1168; δ_H (250 MHz; $CDCl_3$) 1.04 (3 H, t, *J* 7.2, $COOCH_2CH_3$); 2.71 (2 H, t, *J* 7.7, $CH_2CH_2CO_2$);. 3.44 (2 H, t, *J* 7.7, $CH_2CH_2CO_2$); 3.96 (2 H, q, *J* 7.2, $COOCH_2CH_3$); 7.67- 8.07 (8 H, m, aromatics); ^{13}C NMR: 173.23 (CO_2Et); 151.04 (C^2-C_9H_6N); 149.20 (C^{10}-C_9H_6N); 136.44 (C^4-C_9H_6N); 136.15 (C^8-C_9H_6N); 132.98 (C^7-C_9H_6N); 129.34 (C^9-C_9H_6N); 127.69 (C^6-C_9H_6N); 126.81 (C^5-C_9H_6N); 121.76 (C^3-C_9H_6N); 60.12 ($COOCH_2CH_3$); 35.07 ($CH_2COOC_2H_5$); 27.29 (CH_2CH_2); 14.17 (CH_2CH_3). m/z (CI) 230.1182 ($M + H^+$ $C_{14}H_{15}NO_2$ requires 230.1181) 230 (MH^+, 100%), 184 (73), 79 (12).