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Supporting Information For One-pot synthesis of quinolines via Co(III)-catalyzed C–H activation/carbonylation/cyclization of anilines

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General Methods and Materials

AgNTf₂ and HOTf were purchased from Energy Chemical and used without further purification. The cobalt catalyst Cp*Co(CO)I₂ was synthesized according to previously described methods.¹ Other chemicals were purchased from commercial suppliers, further dried and purified if necessary. The water used was re-distillated and ion-free. ¹H and ¹³C NMR spectra were achieved on a Bruker AVANCE 400 MHz spectrometer (¹H 400 MHz; ¹³C 100 MHz) in CDCl₃. Abbreviations for data quoted are s-singlet; brs-broad singlet; d-doublet; t-triplet; dd-doublet of doublets; m-multiplet. High-resolution mass spectra were measured on a Waters Micromass GCT facility. Thin-layer chromatographies were done on pre-coated silica gel 60F254 plates (Merck). Silica gel 60H (200-300 mesh) manufactured by Qingdao Haiyang Chemical Group Co. (China) was used for general chromatography.

General catalytic procedure for the synthesis of quinolines



A reaction kettle (25 mL) was charged with amine **1** (0.5 mmol, 1 equiv.), acetophenone **2** (0.5 mmol, 1.2 equiv.), $[Cp*Co(CO)I_2]$ (12.0 mg, 5.0 mol%), AgNTf₂ (20 mg, 10.0 mol%), (HCHO)_n (1.25 mol, 2.5 equiv.), CH₃OH (2 mL), then the HOTf (0. 5 mmol) was added. The mixture was stirred at 120 °C for 8 hours under an atmosphere of air. The mixture was quenched by sat. aq. NaHCO₃, and diluted with 20 mL dichloromethane and washed with 10 mL H₂O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over Na₂SO₄. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 10 : 1) to afford quinoline products. All other compounds are synthesized in a similar manner, with the yields listed in the main text calculated from the isolated, pure products.

Control experiments



A reaction kettle (25 mL) was charged with *p*-tolylamine **1m** (0.5 mmol, 1 equiv), Methyl 4-aminobenzoate **1p** (0.5 mmol, 1 equiv), acetophenone **2** (0.5 mmol, 1.0 equiv), [Cp*Co(CO)I₂] (12.0 mg, 5.0 mol %), AgNTf₂ (20 mg, 10.0 mol%), (HCHO)_n (1.25 mol), CH₃OH (2 mL), then the HOTf (0. 5 mmol) was added. The mixture was stirred at 120 °C for 8 hours under an atmosphere of air. The mixture was quenched by sat. aq. NaHCO₃, and diluted with 20 mL dichloromethane and washed with 10 mL H₂O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over Na₂SO₄. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 10 : 1) to yield product **3m** (27.4 mg, 25%) and **3p** (22.4 mg, 17%).



A reaction kettle (25 mL) was charged with 2-styrylphenylamine (0.5 mmol, 1 equiv), [Cp*Co(CO)I₂] (12.0 mg, 5.0 mol %), AgNTf₂ (20 mg, 10.0 mol %), (HCHO)_n (1.25 mol), CH₃OH (2 mL), then the HOTf (0. 5 mmol) was added. The mixture was stirred at 120 °C for 8 hours under an atmosphere of air. The mixture was quenched by sat. aq. NaHCO₃, and diluted with 20 mL dichloromethane and washed with 10 mL H₂O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over Na₂SO₄. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 10 : 1) to yield product 5 (23.6 mg, 23%).

3-Phenylquinoline (**5**): ¹**H NMR** (400 MHz, CDCl₃) δ ppm: 9.19 (s, 1H), 8.30 (s, 1H), 8.15 - 8.13 (d, J = 8.4 Hz, 1H), 7.89 - 7.87 (d, J = 8 Hz, 1H), 7.74 - 7.71 (m, 3H), 7.60 - 7.51 (m, 3H), 7.46 - 7.42 (m, 1H); ¹³**C NMR** (100 MHz, CDCl₃) δ ppm: 149.9, 147.3, 137.9, 133.8, 133.2, 129.4, 129.2, 129.2, 128.10, 128.0, 127.4, 127.0; **HRMS** (**ESI-TOF**) m/z calcd for C₁₅H₁₂N [M + H]⁺ 206.0964, found 206.0966.



A reaction kettle (25 mL) was charged with 9*H*-Carbazole (0.5 mmol, 1 equiv.), 1-*p*-tolylethanone (0.6 mmol, 1.2 equiv.), [Cp*Co(CO)I₂] (12.0 mg, 5.0 mol%), AgNTf₂ (20 mg, 10.0 mol%), CH₃OH (2 mL), then the HOTf (0. 5 mmol) was added. The mixture was stirred at 120 °C for 8 hours under an atmosphere of air. The mixture was quenched by sat. aq. NaHCO₃, and diluted with 20 mL dichloromethane and washed with 10 mL H₂O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over Na₂SO₄. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 20 : 1) to yield product **6** (59.0 mg, 42%).

4-*p***-Tolyl-pyrrolo[3,2,1-jk]carbazole (6): ¹H NMR** (400 MHz, CDCl₃) δ ppm: 8.27 (d, *J* = 8.8 Hz, 2H), 7.73 - 7.77 (m, 4H), 7.39 - 7.42 (m, 4H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.52 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 148.8, 147.5, 128.2, 132.9, 130.4, 129.9, 129.6, 129.2, 127.0, 125.5, 125.3, 21.4; **HRMS (ESI-TOF)** m/z calcd for C₂₁H₁₆N [M + H]⁺ 282.1283, found 282.1286.



A reaction kettle (25 mL) was charged with 2-styrylphenylamine (0.5 mmol, 1 equiv), [Cp*Co(CO)I₂] (12.0 mg, 5.0 mol %), AgNTf₂ (20 mg, 10.0 mol %), CH₃OH (2 mL), then the HOTf (0. 5 mmol) was added. The reaction was sealed with a rubber septum and a CO atmosphere was injected in the flask with a balloon and a needle. The mixture was stirred at 120 °C for 8 hours under an atmosphere of CO. The mixture was quenched by sat. aq. NaHCO₃, and diluted with 20 mL dichloromethane and washed with 10 mL H₂O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over Na₂SO₄. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 10 : 1) to yield product **5** (14.4 mg, 14%).



A reaction kettle (25 mL) was charged with *N*-phenylformamide (0.5 mmol, 1 equiv), acetophenone **2** (0.5 mmol, 1.2 equiv), $[Cp*CoI_2(CO)]$ (12.0 mg, 5.0 mol %), AgNTf₂ (20 mg, 10.0 mol%), CH₃OH (2 mL), then the HOTf (0. 5 mmol) was added. The mixture was stirred at 120 °C for 8 hours under an atmosphere of air. When the reaction finished, no product 3a was obtained.



A reaction kettle (25 mL) was charged with *p*-tolylamine **1m** (0.5 mmol, 1 equiv), [Cp*Co(CO)I₂] (12.0 mg, 5.0 mol %), AgNTf₂ (20 mg, 10.0 mol%), CD₃OD (2 mL), then the DOTf (0. 5 mmol) was added. The mixture was stirred at 120 °C for 2 hours under an atmosphere of air. The mixture was quenched by sat. aq. NaHCO₃, and diluted with 20 mL dichloromethane and washed with 10 mL H₂O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over Na₂SO₄. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 20 : 1) to yield product.



Characterization data for products



4-Phenylquinoline (3a): Obtained as a yellow liquid (64.9 mg, 63% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.93 (d, J = 4.0 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H), 7.68 - 7.72 (t, 1H), 7.45 - 7.52 (m, 6H), 7.31 (d, J = 4.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 150.0, 148.6, 148.4, 137.9, 129.7, 129.4, 129.2, 128.5, 128.3, 126.7, 126.5, 125.8, 121.2; HRMS (ESI-TOF) m/z calcd for C₁₅H₁₂N [M + H] ⁺ 206.0970, found 209.0976.



8-Methyl-4-phenylquinoline (3b): Obtained as a white solid (71.2 mg, 65% yield);
¹H NMR (400 MHz, CDCl₃) δ ppm: 8.97 (d, J = 4.4 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H),
7.57 (d, J = 6.8 Hz, 1H), 7.45 - 7.53 (m, 5H), 7.35 - 7.39 (t, 1H), 7.32 (d, J = 4.4 Hz,
1H), 2.87 (s, 3H);
¹³C NMR (100 MHz, CDCl₃) δ ppm: 148.7, 147.7, 138.4, 137.3,
129.54, 129.49, 128.4, 128.2, 126.7, 126.2, 123.9, 120.1, 18.6; HRMS (ESI-TOF)
m/z calcd for C₁₆H₁₄N [M + H] ⁺ 220.1126, found 220.1128.



8-tert-Butyl-4-phenylquinoline (**3c**): Obtained as a yellow liquid (80.9 mg, 62% yield); **¹H NMR** (400 MHz, CDCl₃) δ ppm: 8.93 (d, *J* = 4.0 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.40 - 7.50 (m, 5H), 7.34 - 7.38 (t, 1H), 7.24 (d, *J* = 4.0 Hz, 1H), 1.72 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 148.6, 148.3, 147.8, 146.7, 139.0, 129.6, 128.4, 128.0, 127.7, 125.9, 124.6, 120.5, 36.7, 31.1; **HRMS (ESI-TOF)** m/z calcd for C₁₉H₂₀N [M + H] ⁺ 262.1596, found 262.1602.



8-Fluoro-4-phenylquinoline (3d): Obtained as yellow liquid (56.9 mg, 51% yield); ¹**H** NMR (400 MHz, CDCl₃) δ ppm: 8.98 (d, J = 4.0 Hz, 1H), 7.68 - 7.70 (t, 1H), 7.45 - 7.54 (m, 5H), 7.38 - 7.52 (m, 3H); ¹³**C** NMR (100 MHz, CDCl₃) δ ppm: 159.4, 156.9, 149.9, 148.3 (d, J = 2.8 Hz), 138.9 (d, J = 11.3 Hz), 137.5, 129.3, 128.5, 128.4 (d, J = 1.5 Hz), 126.1 (d, J = 8.2 Hz), 122.1, 121.5 (d, J = 4.7 Hz), 113.2 (d, J = 18.9 Hz); **HRMS (ESI-TOF)** m/z calcd for C₁₅H₁₁FN [M + H] ⁺ 224.0876, found 224.0878.



8-Bromo-4-phenylquinoline (**3e**): Obtained as a white solid (76.4 mg, 54% yield); ¹**H NMR** (400 MHz, CDCl₃) *δ* ppm: 9.05 (d, *J* = 4.4 Hz, 1H), 8.04 (d, *J* = 7.2 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.44 - 7.53 (m, 5H), 7.37 (d, *J* = 4.4 Hz, 1H), 7.28 - 7.32 (t, 1H); ¹³**C NMR** (100 MHz, CDCl₃) *δ* ppm: 150.5, 149.0, 145.5, 137.4, 133.0, 129.4, 128.52, 128.50, 128.1, 126.7, 125.8, 125.1, 122.1; **HRMS** (**ESI-TOF**) m/z calcd for C₁₅H₁₅BrN [M + H] ⁺ 284.0075, found 284.0079.



7-Methyl-4-phenylquinoline (**3f**): Obtained as a white solid (78.8 mg, 72% yield); ¹**H NMR** (400 MHz, CDCl₃) δ ppm: 8.85 (d, *J* = 4.0 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.57 - 7.61 (t, 1H), 7.42 - 7.43 (m, 3H), 7.27 - 7.32 (m, 3H), 7.20 (d, *J* = 8.4 Hz, 1H), 2.01 (s, 3H); ¹³**C NMR** (100 MHz, CDCl₃) δ ppm: 149.7, 148.9, 148.6, 142.4, 135.6, 129.8, 128.9, 128.7, 127.9, 127.7, 126.2, 123.4, 24.4; **HRMS** (**ESI-TOF**) m/z calcd for C₁₆H₁₄N [M + H] ⁺ 220.1126, found 220.1128.



7-Methoxy-4-phenylquinoline (3g): Obtained as a white solid (83.4 mg, 71% yield);
¹H NMR (400 MHz, CDCl₃) δ ppm: 8.78 (d, J = 4.4 Hz, 1H), 8.07 (d, J = 9.2 Hz, 1H),
7.46 - 7.53 (m, 5H), 7.35 - 7.38 (m, 1H), 7.25 (d, J = 4.4 Hz, 1H), 7.18 (d, J = 2.0 Hz,
1H), 3.76 (s, 3H);
¹³C NMR (100 MHz, CDCl₃) δ ppm: 157.8, 147.4, 147.0, 144.7,
138.2, 131.2, 129.2, 128.6, 128.2, 127.6, 121.62, 121.55, 103.6, 55.3; HRMS
(ESI-TOF) m/z calcd for C₁₆H₁₄NO [M + H]⁺ 236.1075, found 236.1079.



7-Chloro-4-phenylquinoline (3h): Obtained as a white solid (80.1 mg, 67% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.93 (d, *J* = 4.4 Hz, 1H), 8.17 (d, *J* = 1.2 Hz, 1H), 7.85 (d, *J* = 9.2 Hz, 1H), 7.42 - 7.55 (m, 6H), 7.33 (d, *J* = 4.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 151.0, 149.1, 148.6, 137.5, 135.2, 129.4, 128.70, 128.67, 127.6, 127.3, 125.2, 121.4; HRMS (ESI-TOF) m/z calcd for C₁₅H₁₁NCl [M + H]⁺ 240.0580, found 240.0584.



7-trifluoromethyl-4-phenylquinoline (3i): Obtained as a white solid (65.5 mg, 48% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.93 (d, *J* = 4.4 Hz, 1H), 8.17 (d, *J* = 1.2 Hz, 1H), 7.85 (d, *J* = 9.2 Hz, 1H), 7.42 - 7.55 (m, 6H), 7.33 (d, *J* = 4.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 151.3, 148.6, 147.8, 137.2, 130.9, 129.5, 128.9, 128.8, 128.4, 127.7 (q, *J* = 8.6 Hz), 127.3, 122.9, 122.2 (q, *J* = 6.2 Hz); HRMS (ESI-TOF) m/z calcd for C₁₆H₁₁NF₃ [M + H]⁺ 274.0844, found 274.0847.



6-Fluoro-4-phenylquinoline (3j): Obtained as a white solid (68.0 mg, 61% yield); ¹**H NMR** (400 MHz, CDCl₃) δ ppm: 8.88 (d, *J* = 4.4 Hz, 1H), 8.16 (dd, *J* = 8.8, 5.6 Hz, 1H), 7.43 - 7.52 (m, 7H), 7.30 (d, *J* = 4.4 Hz, 1H); ¹³**C NMR** (100 MHz, CDCl₃) δ ppm: 161.7, 159.2, 149.0 (d, *J* = 2.6 Hz), 147.8 (d, *J* = 5.6 Hz), 145.6, 137.3, 132.2 (d, *J* = 9.1 Hz), 129.1, 128.6, 128.5, 127.4 (d, *J* = 9.5 Hz), 121.6, 119.4 (d, *J* = 25.6 Hz), 109.0 (d, *J* = 22.9 Hz); **HRMS (ESI-TOF)** m/z calcd for C₁₅H₁₁FN [M + H] ⁺ 224.0876, found 224.0878.



6-Chloro-4-phenylquinoline (3k): Obtained as a white solid (76.5 mg, 64% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.90 (d, J = 4.0 Hz, 1H), 8.09 (d, J = 8.8 Hz, 1H), 7.87 (s, 1H), 7.63 (d, J = 8.8 Hz, 1H), 7.44 - 7.52 (m, 5H), 7.31 - 7.32 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 150.0, 147.6, 147.0, 137.2, 132.5, 131.4, 130.1, 129.3, 128.7, 128.6, 127.3, 124.5, 121.9; HRMS (ESI-TOF) m/z calcd for C₁₅H₁₁NCl [M + H]⁺ 240.0580, found 240.0584.



6-Bromo-4-phenylquinoline (**3l**): Obtained as a white solid (94.8 mg, 67% yield); ¹**H NMR** (400 MHz, CDCl₃) *δ* ppm: 8.92 (d, *J* = 3.6 Hz, 1H), 8.03 (d, *J* = 10.4 Hz, 2H), 7.76 (d, *J* = 9.2 Hz, 1H), 7.45 - 7.52 (m, 5H), 7.31 - 7.32 (m, 1H); ¹³**C NMR** (100 MHz, CDCl₃) *δ* ppm: 150.1, 147.5, 147.2, 137.1, 132.7, 131.5, 129.3, 128.7, 128.6, 127.9, 127.8, 121.9, 120.8; **HRMS** (**ESI-TOF**) m/z calcd for C₁₅H₁₅BrN [M + H] ⁺ 284.0075, found 284.0079.



6-Methyl-4-phenylquinoline (3m): Obtained as a white solid (85.4 mg, 78% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.86 (d, *J* = 4.4 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.66 (s, 1H), 7.48 - 7.56 (m, 6H), 7.27 (d, *J* = 4.4 Hz, 1H), 2.46 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 149.1, 147.8, 147.3, 138.3, 136.5, 131.6, 129.59, 129.53, 128.6, 128.3, 126.7, 124.6, 121.4, 21.8; HRMS (ESI-TOF) m/z calcd for C₁₆H₁₄N [M + H]⁺ 220.1126, found 220.1128.



6-trifluoromethyl-4-phenylquinoline (3n): Obtained as a yellow liquid (73.7 mg, 54% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 9.03 (d, J = 4.4 Hz, 1H), 8.25 - 8.30 (m, 2H), 7.89 (d, J = 4.4 Hz, 1H), 7.48 - 7.57 (m, 5H), 7.42 (d, J = 4.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 152.0, 149.7, 149.5, 137.0, 131.2, 129.4, 129.0, 128.9, 128.3 (q, J = 52.3 Hz), 125.9, 125.0 (q, J = 5.5 Hz), 123.9 (q, J = 8.9 Hz), 122.4; HRMS (ESI-TOF) m/z calcd for C₁₆H₁₁NF₃ [M + H] ⁺ 274.0844, found 274.0849.



6-Methylsulfanyl-4-phenylquinoline (30): Obtained as a white solid (76.6 mg, 61% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.84 (d, J = 4.4 Hz, 1H), 8.06 (d, J = 8.8 Hz, 1H), 7.66 (d, J = 1.2 Hz, 1H), 7.60 (dd, J = 8.8, 1.6 Hz, 1H), 7.48 - 7.54 (m, 5H), 7.29 (d, J = 4.4 Hz, 1H), 2.44 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 149.1, 147.1, 147.0, 137.9, 137.5, 130.1, 129.4, 128.73, 128.67, 128.5, 127.1, 121.9, 121.1, 15.7; HRMS (ESI-TOF) m/z calcd for C₁₆H₁₄NS [M + H] ⁺ 252.0847, found 252.0852.



4-Phenylquinoline-6-carboxylic acid methyl ester (3p): Obtained as a yellow liquid (57.9 mg, 44% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.79 (d, J = 4.4 Hz, 1H), 8.18 (s, 1H), 7.49 - 7.56 (m, 5H), 7.27 (d, J = 4.4 Hz, 1H), 7.22 (s, 1H), 3.83 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 153.5, 148.6, 147.0, 144.5, 138.0, 130.7, 129.2, 128.8, 128.6, 127.5, 126.4, 121.8, 104.2, 56.2; HRMS (ESI-TOF) m/z calcd for C₁₆H₁₄NO₂ [M + H] ⁺ 264.1025, found 264.1032.



6,8-Dimethyl-4-phenylquinoline (3q): Obtained as a white solid (103.7 mg, 89% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.90 (d, J = 4.4 Hz, 1H), 7.48 - 7.54 (m, 6H), 7.43 (s, 1H), 7.28 (d, J = 4.4 Hz, 1H), 2.83 (s, 3H), 2.42 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 147.9, 147.8, 146.4, 138.7, 137.0, 136.0, 131.9, 129.6, 128.5, 128.1, 126.8, 122.6, 121.3, 21.8, 18.5; HRMS (ESI-TOF) m/z calcd for C₁₇H₁₆N [M + H] ⁺ 234.1283, found 234.1286.



7-Chloro-6-methoxy-4-phenylquinoline (**3r**): Obtained as a white solid (96.8 mg, 72% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 9.01 (d, J = 4.0 Hz, 1H), 8.69 (s, 1H), 8.30 (d, J = 8.8 Hz, 1H), 8.20 (d, J = 8.8 Hz, 1H), 7.50 - 7.57 (m, 5H), 7.39 (d, J = 4.4 Hz, 1H), 3.92 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 166.7, 152.0, 150.6, 149.9, 137.3, 130.2, 129.6, 129.1, 128.8, 128.7, 128.2, 126.0, 122.1, 52.4; HRMS (ESI-TOF) m/z calcd for C₁₆H₁₃CINO [M + H] ⁺ 270.0686, found 270.0694.



4-Phenyl-benzo[h]quinoline (3s): Obtained as a white solid (75.2 mg, 59% yield); ¹**H NMR** (400 MHz, CDCl₃) δ ppm: 9.01 (d, *J* = 4.0 Hz, 1H), 8.69 (s, 1H), 8.30 (d, *J* = 8.8 Hz, 1H), 8.20 (d, *J* = 8.8 Hz, 1H), 7.50 - 7.57 (m, 5H), 7.39 (d, *J* = 4.4 Hz, 1H), 3.92 (s, 3H); ¹³**C NMR** (100 MHz, CDCl₃) δ ppm: 166.7, 152.0, 150.6, 149.9, 137.3, 130.2, 129.6, 129.1, 128.8, 128.7, 128.2, 126.0, 122.1, 52.4; **HRMS (ESI-TOF)** m/z calcd for C₁₉H₁₄N [M + H] ⁺ 256.1126, found 256.1129.



6-piperidin-1-yl-4-Phenylquinoline (**3t**): Obtained as a white solid (87.8 mg, 61% yield); ¹**H NMR** (400 MHz, CDCl₃) δ ppm: 8.69 (d, J = 4.4 Hz, 1H), 8.01 (d, J = 9.2 Hz, 1H), 7.45 - 7.51 (m, 6H), 7.19 (d, J = 4.4 Hz, 1H), 7.13 (d, J = 2.0 Hz, 1H), 3.13 - 3.15 (m, 4H), 1.63 - 1.70 (m, 4H), 1.51 - 1.57 (m, 2H); ¹³**C NMR** (100 MHz, CDCl₃) δ ppm: 150.3, 146.8, 146.6, 144.1, 138.7, 130.3, 129.4, 128.6, 128.2, 127.8, 122.9, 121.6, 107.3, 50.5, 25.7, 24.2; **HRMS** (**ESI-TOF**) m/z calcd for C₂₀H₂₁N₂ [M + H]⁺ 289.1705, found 289.1707.



6-Morpholin-4-yl-4-phenyl-quinoline (**3u**): Obtained as a yellow solid (92.8 mg, 64% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.64 (d, J = 4.4 Hz, 1H), 7.96 (d, J = 9.2 Hz, 1H), 7.36 - 7.45 (m, 6H), 7.13 (d, J = 4.4 Hz, 1H), 7.05 (d, J = 2.0 Hz, 1H), 3.73 - 3.75 (m, 4H), 3.04 - 3.06 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 149.4, 147.3, 146.9, 144.4, 138.5, 130.6, 129.3, 128.7, 128.3, 127.7, 121.8, 121.6, 107.1, 66.8, 49.2; HRMS (ESI-TOF) m/z calcd for C₁₉H₁₉N₂O [M + H]⁺ 291.1497, found 291.1502.



4-(4-Chloro-phenyl)-6,8-dimethyl-quinoline (4a): Obtained as a yellow solid (108.1 mg, 81% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.86 (d, J = 4.4 Hz, 1H), 7.35 - 7.46 (m, 6H), 7.19 (d, J = 4.4 Hz, 1H), 2.81 (s, 3H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 147.8, 146.6, 146.4, 137.2, 137.1, 136.3, 134.4, 132.0, 130.9, 128.7, 126.5, 122.3, 121.2, 21.8, 18.5; HRMS (ESI-TOF) m/z calcd for C₁₇H₁₅ClN [M + H] ⁺ 268.0893, found 268.0899.



4-(4-Bromo-phenyl)-6,8-dimethyl-quinoline (4b): Obtained as a yellow solid (127.5 mg, 82% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.88 (d, *J* = 4.4 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.42 (s, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 4.4 Hz, 1H), 2.82 (s,

3H), 2.42 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 147.8, 146.6, 146.4, 137.6, 137.2, 136.3, 132.0, 131.7, 131.2, 126.5, 122.5, 122.2, 121.2, 21.8, 18.5; **HRMS** (**ESI-TOF**) m/z calcd for C₁₇H₁₅BrN [M + H] ⁺ 312.0388, found 312.0393.



4-(4-Iodo-phenyl)-6,8-dimethyl-quinoline (4c): Obtained as a yellow solid (124.4 mg, 78% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.87 (d, J = 4.4 Hz, 1H), 7.82 (d, J = 8.0 Hz, 2H), 7.41 (s, 2H), 7.17 - 7.20 (t, 3H), 2.81 (s, 3H), 2.40 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 147.8, 146.6, 146.4, 137.6, 137.2, 136.3, 132.0, 131.7, 131.2, 126.5, 122.5, 122.2, 121.2, 21.8, 18.5; HRMS (ESI-TOF) m/z calcd for C₁₇H₁₅IN [M + H] ⁺ 360.0249, found 360.0251.



6,8-Dimethyl-4-(4-trifluoromethyl-phenyl)-quinoline (4d): Obtained as a yellow solid (103.8 mg, 69% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.91 (d, *J* = 4.4 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.44 (s, 1H), 7.38 (s, 1H), 7.25 (d, *J* = 4.0 Hz, 1H), 2.83 (s, 3H), 2.42 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 147.7, 146.4, 146.3, 142.4, 137.3, 136.6, 132.2, 130.2 (d, *J* = 32.3 Hz), 129.9, 126.3, 125.5 (d, *J* = 7.4 Hz), 122.1, 121.1, 21.8, 18.5; HRMS (ESI-TOF) m/z calcd for C₁₈H₁₅F₃N [M + H]⁺ 302.1157, found 302.1163.



[4-(6,8-Dimethyl-quinolin-4-yl)-phenyl]-dimethyl-amine (4e): Obtained as a yellow solid (115.9 mg, 84% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.84 (d, J= 4.4 Hz, 1H), 7.66 (s, 1H), 7.37 - 7.39 (m, 3H), 7.23 (d, J= 4.4 Hz, 1H), 6.81 (d, J= 8.8 Hz, 2H), 3.00 (s, 3H), 2.82 (s, 3H), 2.40 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 150.4, 148.3, 147.9, 146.6, 136.8, 135.5, 131.7, 130.6, 127.1, 126.3, 123.1, 121.1, 112.1, 40.4, 21.8, 18.7; HRMS (ESI-TOF) m/z calcd for C₁₉H₂₁N₂ [M + H]⁺ 277.1705, found 277.1712.



4-(2-Fluoro-phenyl)-6,8-dimethyl-quinoline (4f): Obtained as a yellow solid (90.4 mg, 72% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.92 (d, J = 4.4 Hz, 1H), 7.42 - 7.47 (m, 2H), 7.36 (t, 1H), 7.21 - 7.30 (m, 4H), 2.83 (s, 3H), 2.40 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 160.9, 158.5, 147.7, 146.2, 142.0, 137.0, 136.3, 132.1, 131.7 (d, J = 3.2 Hz), 130.3 (d, J = 7.9 Hz), 127.0, 126.1 (d, J = 16.0 Hz), 124.2 (d, J = 3.6 Hz), 122.3 (d, J = 39.6 Hz), 116.0 (d, J = 21.7 Hz), 21.8, 18.4; **HRMS** (ESI-TOF) m/z calcd for C₁₇H₁₅FN [M + H] + 252.1189, found 252.1191.



6,8-Dimethyl-4-*o***-tolyl-quinoline (4g):** Obtained as a yellow solid (107.4 mg, 87% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.90 (d, J = 4.4 Hz, 1H), 7.29 - 7.40 (m, 4H), 7.18 - 7.20 (m, 2H), 7.07 (s, 1H), 2.84 (s, 3H), 2.37 (s, 3H), 2.03 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 147.91, 147.86, 146.2, 138.2, 136.9, 136.09, 136.06, 132.0, 130.1, 129.6, 128.2, 127.3, 125.7, 122.7, 121.4, 21.7, 20.0, 18.4; HRMS (ESI-TOF) m/z calcd for C₁₈H₁₈N [M + H]⁺ 248.1439, found 248.1442.



4-(3-Fluoro-phenyl)-6,8-dimethyl-quinoline (4h): Obtained as a yellow solid (85.3 mg, 68% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.90 (d, J = 4.4 Hz, 1H), 7.44 - 7.51 (m, 3H), 7.24 - 7.26 (m, 2H), 7.16 - 7.20 (t, 2H), 2.83 (s, 3H), 2.42 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 163.9, 161.5, 147.8, 146.5 (d, J = 13.3 Hz), 140.8 (d, J = 7.6 Hz), 137.1, 136.4, 132.0, 130.0 (d, J = 8.3 Hz), 126.5, 125.3 (d, J = 2.9 Hz), 122.3, 121.1, 116.7 (d, J = 21.9 Hz), 115.1 (d, J = 20.9 Hz), 21.8, 18.4; **HRMS** (ESI-TOF) m/z calcd for C₁₇H₁₅FN [M + H] ⁺ 252.1189, found 252.1191.



6,8-Dimethyl-4-*m***-tolyl-quinoline** (**4i**): Obtained as a yellow solid (108.7 mg, 88% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.88 (d, J = 4.4 Hz, 1H), 7.50 (s, 1H), 7.38 - 7.42 (m, 2H), 7.25 - 7.29 (m, 4H), 2.83 (s, 3H), 2.45 (s, 3H), 2.41 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 148.1, 147.8, 146.4, 138.7, 138.2, 136.9, 135.9, 131.8, 130.2, 128.9, 128.3, 126.9, 126.7, 122.7, 121.2, 21.8, 21.5, 18.5; HRMS (ESI-TOF) m/z calcd for C₁₈H₁₈N [M + H]⁺ 248.1439, found 248.1442.



6,8-Dimethyl-2,3-dihydro-1H-cyclopenta[c]quinoline (**4j**): Obtained as a yellow solid (70.9 mg, 72% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.78 (s, 1H), 7.40 (s, 1H), 7.34 (s, 1H), 3.20 - 3.24 (t, 2H), 3.10 - 3.14 (t, 2H), 2.78 (s, 3H), 2.49 (s, 3H), 2.22 - 2.30 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 149.3, 145.6, 144.7, 137.0, 136.4, 135.8, 130.8, 126.1, 121.1, 31.4, 31.1, 24.5, 21.7, 18.6; HRMS (ESI-TOF) m/z calcd for C₁₄H₁₆N [M + H] ⁺ 198.1283, found 198.1286.



2,4-Dimethyl-7,8,9,10-tetrahydro-phenanthridine (**4k**): Obtained as a yellow solid (84.4 mg, 80% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.55 (s, 1H), 7.49 (s, 1H), 7.29 (s, 1H), 3.00 - 3.03 (t, 2H), 2.82 - 2.85 (t, 2H), 2.75 (s, 3H), 2.47 (s, 3H), 1.80 - 1.94 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 150.3, 144.0, 140.6, 137.0, 135.5, 130.5, 129.2, 127.5, 119.6, 27.2, 25.1, 22.6, 22.4, 21.9, 18.4; HRMS (ESI-TOF) m/z calcd for C₁₅H₁₈N [M + H] ⁺ 212.1439, found 212.1444.



2,4-Dimethyl-8,9,10,11-tetrahydro-7H-cyclohepta[c]quinoline (**4l**): Obtained as a yellow liquid (76.5 mg, 68% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.61 (s, 1H), 7.70 (s, 1H), 7.31 (s, 1H), 3.16 - 3.19 (t, 2H), 2.92 - 2.95 (t, 2H), 2.77 (s, 3H), 2.48 (s, 3H), 1.87 - 1.93 (m, 2H), 1.65 - 1.68 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 149.4, 147.5, 145.1, 137.1, 135.3, 135.2, 130.6, 126.6, 120.1, 33.2, 32.5, 28.1, 27.5,

26.4, 22.0, 18.6; **HRMS (ESI-TOF)** m/z calcd for $C_{16}H_{20}N [M + H]^+$ 226.1596, found 226.1604.



4-Furan-2-yl-6,8-dimethyl-quinoline (4m): Obtained as a yellow solid (84.7 mg, 76% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.85 (d, J = 4.4 Hz, 1H), 8.04 (s, 1H), 7.64 (s, 1H), 7.53 (d, J = 4.4 Hz, 1H), 7.39 (s, 1H), 6.89 (d, J = 2.4 Hz, 1H), 6.57 - 6.59 (m, 1H), 2.79 (s, 3H), 2.48 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 151.5, 147.8, 146.8, 143.6, 137.1, 136.4, 135.2, 131.9, 124.6, 122.2, 118.7, 111.9, 111.8, 22.0, 18.7; HRMS (ESI-TOF) m/z calcd for C₁₅H₁₄NO [M + H]⁺ 224.1075, found 224.1077.



6,8-Dimethyl-4-thiophen-2-yl-quinoline (4n): Obtained as a yellow liquid (88.4 mg, 74% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.84 (d, J = 4.4 Hz, 1H), 7.87 (s, 1H), 7.46 (d, J = 5.2 Hz, 1H), 7.41 (s, 1H), 7.36 (d, J = 4.4 Hz, 1H), 7.31 - 7.32 (m, 1H), 7.17 - 7.19 (m, 1H), 2.81 (s, 3H), 2.44 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 147.7, 146.6, 140.2, 139.5, 137.1, 136.5, 132.1, 128.4, 127.7, 126.9, 126.5, 122.4, 121.8, 21.9, 18.6; **HRMS (ESI-TOF)** m/z calcd for C₁₅H₁₄NS [M + H] ⁺ 240.0847, found 240.0849.



6,8-Dimethyl-4-pyridin-3-yl-quinoline (**4o**): Obtained as a yellow liquid (63.2 mg, 54% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.93 (d, J = 4.4 Hz, 1H), 8.73 - 8.75 (m, 2H), 7.82 (d, J = 7.6 Hz, 1H), 7.46 - 7.49 (m, 2H), 7.40 (s, 1H), 7.27 - 7.29 (m, 1H), 2.84 (s, 3H), 2.43 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 150.0, 149.5, 147.8, 146.4, 144.1, 137.3, 136.9, 136.7, 134.5, 132.2, 126.5, 123.3, 121.9, 121.5, 21.8, 18.5; **HRMS (ESI-TOF)** m/z calcd for C₁₆H₁₅N₂ [M + H] ⁺ 235.1235, found 235.1239.



4-(1H-Indol-3-yl)-6,8-dimethyl-quinoline (4p): Obtained as a yellow solid (121.0 mg, 89% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.90 (d, *J* = 4.0 Hz, 1H), 8.88 (s, 1H), 7.79 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.44 - 7.51 (t, 4H), 7.27 - 7.31 (t, 1H), 7.15 - 7.19 (t, 1H), 2.86 (s, 3H), 2.40 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 148.0, 146.6, 141.5, 136.8, 136.3, 135.6, 131.9, 127.6, 127.0, 124.4, 123.2, 122.8, 121.8, 120.6, 120.1, 114.6, 111.5, 21.8, 18.7; HRMS (ESI-TOF) m/z calcd for C₁₉H₁₇N₂ [M + H] ⁺ 273.1392, found 273.1397.



6,8-Dimethyl-4-naphthalen-2-yl-quinoline (4q): Obtained as a yellow solid (111.7 mg, 79% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.92 (d, J = 4.4 Hz, 1H), 7.89 -

7.97 (m, 4H), 7.52 - 7.59 (m, 4H), 7.42 (s, 1H), 7.35 (d, J = 4.4 Hz, 1H), 2.85 (s, 3H), 2.38 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 147.93, 147.85, 146.5, 137.1, 136.3, 136.2, 133.3, 133.0, 131.9, 128.6, 128.3, 128.0, 127.8, 127.6, 127.0, 126.62, 126.58, 122.8, 121.6, 21.8, 18.6; **HRMS (ESI-TOF)** m/z calcd for C₂₁H₁₈N [M + H]⁺ 284.1439, found 284.1442.



6,8-Dimethyl-4-naphthalen-1-yl-quinoline (4r): Obtained as a yellow solid (100.5 mg, 71% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.97 (d, J = 4.0 Hz, 1H), 7.94 - 7.99 (t, 2H), 7.57 - 7.61 (t, 1H), 7.47 - 7.51 (t, 1H), 7.41 - 7.45 (t, 2H), 7.29 - 7.36 (m, 3H), 7.03 (s, 1H), 2.87 (s, 3H), 2.26 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 147.8, 146.7, 146.2, 136.9, 136.3, 136.1, 133.5, 132.1, 132.0, 128.5, 128.3, 128.1, 127.3, 126.4, 126.1, 125.3, 123.1, 122.5, 21.7, 18.5; HRMS (ESI-TOF) m/z calcd for C₂₁H₁₈N [M + H] ⁺ 284.1439, found 284.1442.



2,4,8-Trimethyl-7,8-dihydro-benzo[k]phenanthridine (**4s**): Obtained as a yellow liquid (114.7 mg, 84% yield); ¹**H NMR** (400 MHz, CDCl₃) δ ppm: 8.76 (s, 1H), 8.12 (s, 1H), 7.98 - 8.00 (t, 1H), 7.38 - 7.41 (m, 4H), 2.98 - 3.05 (m, 2H), 2.82 (s, 3H), 2.66 - 2.73 (m, 2H), 2.50 (s, 3H), 1.27 (d, J = 6.4 Hz, 3H); ¹³**C NMR** (100 MHz, CDCl₃) δ ppm: 148.5, 146.7, 144.6, 138.4, 137.2, 135.9, 131.9, 130.7, 129.5, 129.1, 128.8, 126.2, 126.1, 124.4, 122.3, 34.3, 32.7, 22.0, 18.8, 18.4; **HRMS (ESI-TOF)** m/z calcd for C₂₀H₂₀N [M + H] ⁺ 274.1596, found 274.1603.



6,8-Dimethyl-3,4-diphenylquinoline (4t): Obtained as a yellow solid (112.8 mg, 73% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.96 (s, 1H), 7.40 (s, 1H), 7.27 - 7.32 (m, 4H), 7.14 - 7.21 (m, 7H), 2.86 (s, 3H), 2.37 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 149.6, 145.3, 145.1, 138.6, 136.9, 136.7, 136.3, 132.9, 131.7, 130.6, 130.2, 128.1, 128.0, 127.5, 127.2, 126.9, 123.4, 21.9, 18.4; HRMS (ESI-TOF) m/z calcd for C₂₃H₂₀N [M + H] ⁺ 310.1596, found 310.1602.



6,8-Dimethyl-4-styrylquinoline (4u): Obtained as a yellow solid (117.8 mg, 91% yield); ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.83 (d, J = 4.4 Hz, 1H), 7.75 - 7.79 (m, 2H), 7.60 (d, J = 7.2 Hz, 2H), 7.51 (d, J = 4.4 Hz, 1H), 7.39 - 7.43 (m, 3H), 7.31 - 7.35 (t, 1H), 7.25 (d, J = 16.4 Hz, 1H), 2.79 (s, 3H), 2.51 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 148.1, 146.4, 142.4, 137.2, 136.8, 135.9, 134.5, 131.9, 128.9, 128.6, 127.1, 126.4, 123.7, 120.4, 117.0, 21.9, 18.6; HRMS (ESI-TOF) m/z calcd for C₁₉H₁₈N [M + H] ⁺ 260.1439, found 260.1443.

References:

(1) (a) W. Li, L. Weng, and G. Jin, *Inorg. Chem. Commun.*, 2004, **7**, 1174; (b) B. Sun,

T. Yoshino, S. Matsunaga and M. Kanai, Adv. Synth. Catal., 2014, 356, 1491.

Copies of ¹H and ¹³C NMR spectra of products



















27







28



29



3g

30









32





33



34











3m









p





41

3r



3s

42











4b













4f







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4j

54

















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0











4r















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