Supporting Information

Easy Access to Novel Substituted 6-Aminoimidazo[1,2-*a*]pyridines using Palladium- and Copper-Catalyzed Aminations

Cécile Enguehard,[†] Hassan Allouchi,[‡] Alain Gueiffier^{†,} and Stephen L. Buchwald,[§]*

[†]EA 3247, Laboratoire de Chimie Thérapeutique, [‡]Laboratoire de Chimie Physique, UFR des Sciences Pharmaceutiques, 31 Avenue Monge, 37200 Tours, France [§]Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139

gueiffier@univ-tours.fr

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General considerations: Unless otherwise noted, all chemicals were used as received. 5-Bromopyridin-2-amine, α -bromo-4-fluoroacetophenone, 5-iodopyridin-2-amine, tris(dibenzylideneacetone)dipalladium (0) and *rac*-BINAP were purchased from commercial sources. CuI (Strem, 98%, powdered form) and Potassium Phosphate (Fluka, free flowing powder) were used as received. Sodium *tert*-butylate was purchased from Aldrich and stored in a vacuum atmospheres glovebox under nitrogen. Small amounts were removed from the glovebox as needed, stored in a dessicator for less than two weeks and weighed in the air. Toluene was purchased from J.T. Baker in CYCLE-TAINER® solvent delivery kegs, was vigorously purged with argon for 2h, and further purified by passing through two packed columns of neutral alumina and copper (II) oxide under argon pressure. All new compounds were fully characterized by ^1H , ^{13}C and two-dimensional NMR experiments, and elemental analysis. NMR spectra were run at 200 or 300 MHz (^1H) and 50 or 75 MHz (^{13}C) in CDCl_3 with chemical shifts reported relative to residual deuterated solvent peaks. Possible inversion of two values in the ^{13}C -NMR spectra is expressed by an asterisk. Mp were determined in a capillary apparatus and are uncorrected.

6-Iodo-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine 1a:

A mixture of 10 g (45.5 mmol) of 2-amino-5-iodopyridine and 10 g (46.1 mmol) of α -bromo-4-fluoroacetophenone in 100 mL of ethanol was refluxed for 5 hours. After cooling, the precipitate was filtered off, washed with ethanol and suspended in water. The suspension was made alkaline with sodium carbonate and extracted with dichloromethane. After drying over calcium chloride, the organic layers were evaporated to dryness to give 11 g of **1a**. The filtrate was evaporated to dryness, suspended in water and made basic with sodium carbonate. The aqueous layer was extracted with dichloromethane. After drying over calcium chloride,

the organic layers were evaporated to dryness. The residue was chromatographed on neutral alumina eluting with dichloromethane to give 12.9 g (84% yield) of **1a**.

mp 177°C; ¹H NMR (200 MHz, CDCl₃) δ 8.33 (d, 1H, *J* = 1.5 Hz, H-5), 7.89 (dd, 2H, *J* = 8.7-5.4 Hz, F-Ph-2,6), 7.70 (s, 1H, H-3), 7.41 (d, 1H, *J* = 9.4 Hz, H-8), 7.32 (dd, 1H, *J* = 9.4-1.5 Hz, H-7), 7.14 (t, 2H, *J* = 8.7 Hz, F-Ph-2,6); ¹³C NMR (50 MHz) δ 163.2 (*J* = 245.5 Hz, F-Ph-4), 145.7 (C-8a*), 144.6 (C-2*), 133.1 (C-7), 130.8 (C-5), 129.8 (*J* = 3 Hz, F-Ph-1), 128.2 (*J* = 8 Hz, F-Ph-2,6), 188.8 (C-8), 116.2 (*J* = 21.5 Hz, F-Ph-3,5), 107.9 (C-3), 75.6 (C-6); Anal. Calcd for C₁₃H₈FIN₂: C, 46.18; H, 2.38. Found: C, 48.89; H, 2.43.

General procedure for Cu-catalyzed aminations: Method A

6-Iodo-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine **1a** (338 mg, 1 mmol), copper (I) iodide (9.5 mg, 0.05 mmol or 29 mg, 0.15 mmol) and potassium phosphate (425 mg, 2 mmol) were added to a screw-capped test tube. The tube was evacuated and back filled with argon. Ethylene glycol (111 μL, 2 mmol), amine (1.1 mmol) and 2-propanol (1 mL) were added successively by syringe at room temperature. The tube was sealed with a teflon-lined cap and the reaction mixture was heated at 85 or 112°C for 20 or 48 h. After cooling to room temperature, the suspension was diluted with dichloromethane (15 mL) and was filtered through Celite®. The solvent was removed with the aid of a rotary evaporator to give a brown residue which was purified by column chromatography on silica gel, eluting with dichloromethane and then a mixture of CH₂Cl₂/MeOH=99.5/0.5 to give pure product.

General procedure for Pd-catalyzed aminations: Method B

6-Bromo-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine^{2b} **1b** (291 mg, 1 mmol), tris(dibenzylideneacetone)dipalladium (9.2 mg, 0.01 mmol), *rac*-BINAP (19 mg, 0.03 mmol) and sodium *tert*-butylate (135 mg, 1.4 mmol) were added to a screw-capped test tube. The tube was evacuated and back filled with argon. Amine (1.1 mmol) and toluene (2 mL) were added successively by syringe at room temperature. The tube was sealed with a teflon-lined

cap and the reaction mixture was heated at 85 or 112°C for 20 h. After cooling to room temperature, the suspension was diluted with dichloromethane (15 mL) and filtered through Celite®. The solvent was removed with the aid of a rotary evaporator to give a brown residue which was purified by column chromatography on silica gel, eluting with dichloromethane and then CH₂Cl₂/MeOH=99.5/0.5 to give pure product.

6-benzylamino-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine 2:

Method A: The general procedure was followed using compound **1a** (338 mg, 1 mmol), copper (I) iodide (29 mg, 0.15 mmol), K₃PO₄ (425 mg, 2 mmol), ethylene glycol (111 µL, 2 mmol), benzylamine (120 µL, 1.1 mmol) and 2-propanol (1 mL) at 85°C for 20 h. Column chromatography afforded compound **2** (270 mg, 85% yield) as a grey solid.

Method B: The general procedure was followed using compound **1b** (291 mg, 1 mmol), Pd₂(dba)₃ (9.2 mg, 0.01 mmol), *rac*-BINAP (19 mg, 0.03 mmol), sodium *tert*-butylate (135 mg, 1.4 mmol), benzylamine (120 µL, 1.1 mmol) and toluene (2 mL) at 112°C. Column chromatography afforded compound **2** (185 mg, 58% yield) as a grey solid.

mp 159°C; ¹H NMR (200 MHz, CDCl₃) δ 7.89 (dd, 2H, *J* = 8.8-5.4 Hz, F-Ph-2,6), 7.66 (s, 1H, H-3), 7.47 (bs, 1H, *J* = 9.6 Hz, H-8), 7.40 (m, 5H, Bn), 7.30 (m, 1H, H-5), 7.13 (t, 2H, *J* = 8.8 Hz, F-Ph-3,5), 6.80 (dd, 1H, *J* = 9.6-2.2 Hz, H-7), 4.30 (d, 1H, *J* = 4.8 Hz, CH₂), 3.90 (bs, 1H, NH); ¹³C NMR (50 MHz) δ 163.0 (*J* = 245 Hz, F-Ph-4), 144.4 (C-2*), 142.7 (C-8a*), 138.5 (Bn-1*), 136.8 (C-6*), 130.8 (*J* = 3 Hz, F-Ph-1), 129.3 (Bn-3,5), 128.1 (Bn-4), 127.9 (Bn-2,6), 127.7 (*J* = 8 Hz, F-Ph-2,6), 120.4 (C-7), 117.9 (C-8), 116.0 (*J* = 21 Hz, F-Ph-3,5), 108.9 (C-3), 105.7 (C-5), 49.3 (CH₂); Anal. Calcd for C₂₀H₁₆FN₃: C, 75.69; H, 5.08. Found: C, 75.02; H, 5.16.

6-(*N*-morpholino)-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine 3:

Method A: The general procedure was followed using compound **1a** (338 mg, 1 mmol), copper (I) iodide (29 mg, 0.15 mmol), K₃PO₄ (425 mg, 2 mmol), ethylene glycol (111 µL, 2

mmol), morpholine (96 μ L, 1.1 mmol) and 2-propranol (1 mL) at 85°C for 48 h. Column chromatography afforded compound **3** (215 mg, 72% yield) as a white solid.

Method B: The general procedure was followed using compound **1b** (291 mg, 1 mmol), Pd₂(dba)₃ (9.2 mg, 0.01 mmol), *rac*-BINAP (19 mg, 0.03 Mmol), sodium *tert*-butylate (135 mg, 1.4 mmol), morpholine (96 μ L, 1.1 mmol) and toluene (2 mL) at 112°C. Column chromatography afforded compound **3** (206 mg, 69% yield) as a white solid.

mp 199°C; ¹H NMR (200 MHz, CDCl₃) δ 7.92 (dd, 2H, *J* = 8.9-5.4 Hz, F-Ph-2,6), 7.76 (s, 1H, H-3), 7.57 (s, 1H, H-5), 7.56 (d, 1H, *J* = 9.9 Hz, H-8), 7.15 (t, 2H, *J* = 8.9 Hz, F-Ph-3,5), 7.09 (dd, 1H, *J* = 9.9-2.2 Hz, H-7), 3.93 (m, 4H, morpholine), 3.10 (m, 4H, morpholine); ¹³C NMR (50 MHz) δ 162.9 (*J* = 246 Hz, Ph-4), 145.0 (C-2*), 143.2 (C-8a*), 140.4 (C-6), 130.6 (*J* = 3.5 Hz, Ph-1), 127.8 (*J* = 8 Hz, Ph-2,6), 121.6 (C-7), 117.8 (C-8), 116.0 (*J* = 21.6 Hz, Ph-3,5), 111.5 (C-5), 109.0 (C-3), 67.1 (morpholine), 51.0 (morpholine); Anal. Calcd for C₁₇H₁₆FN₃O: C, 68.67; H, 5.42. Found: C, 68.51; H, 5.50.

6-(*n*-hexylamino)-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine 4:

Method A: The general procedure was followed using compound **1a** (338 mg, 1 mmol), copper (I) iodide (29 mg, 0.15 mmol), K₃PO₄ (425 mg, 2 mmol), ethylene glycol (111 μ L, 2 mmol), *n*-hexylamine (145 μ L, 1.1 mmol) and 2-propranol (1 mL) at 85°C for 48 h. Column chromatography afforded compound **4** (235 mg, 76% yield) as a brown solid.

Method B: The general procedure was followed using compound **1b** (291 mg, 1 mmol), Pd₂(dba)₃ (9.2 mg, 0.01 mmol), *rac*-BINAP (19 mg, 0.03 mmol), sodium *tert*-butylate (135 mg, 1.4 mmol), *n*-hexylamine (145 μ L, 1.1 mmol) and toluene (2 mL) at 112°C. Column chromatography afforded compound **4** (220 mg, 71% yield) as a brown solid.

Mp 108°C; ¹H NMR (300 MHz, CDCl₃) δ 7.83 (dd, 2H, *J* = 8.7-5.4 Hz, F-Ph-2,6), 7.58 (s, 1H, H-3), 7.35 (d, 1H, *J* = 9.6 Hz, H-8), 7.17 (m, 1H, H-5), 7.05 (t, 2H, *J* = 8.7 Hz, F-Ph-3,5), 6.65 (dd, 1H, *J* = 9.6-2.4 Hz, H-7), 2.91 (m, 2H, CH₂), 1.58 (m, 2H, CH₂), 1.33 (m, 6H,

3CH₂), 0.88 (m, 3H, CH₃); ¹³C NMR (75 MHz) δ 162.5 (*J* = 246 Hz, F-Ph-4), 143.9 (C-2*), 142.5 (C-8a*), 137.1 (C-6), 130.8 (*J* = 3.3 Hz, F-Ph-1), 127.4 (*J* = 8.1 Hz, F-Ph-2,6), 120.4 (C-7), 117.4 (C-8), 115.7 (*J* = 21.5 Hz, F-Ph-3,5), 108.5 (C-3), 104.8 (C-5), 44.7 (CH₂), 31.8 (CH₂), 29.3 (CH₂), 27.1 (CH₂), 22.8 (CH₂), 14.3 (CH₃); Anal. Calcd for C₁₉H₂₂FN₃: C, 73.31; H, 7.07. Found: C, 73.65; H, 6.93.

6-cyclohexylamino-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine 5:

Method A: The general procedure was followed using compound **1a** (338 mg, 1 mmol), copper (I) iodide (29 mg, 0.15 mmol), K₃PO₄ (425 mg, 2 mmol), ethylene glycol (111 μL, 2 mmol), cyclohexylamine (126 μL, 1.1 mmol) and 2-propanol (1 mL) at 85°C for 48 h. Column chromatography afforded compound **5** (223 mg, 72% yield) as a grey solid.

Method B: The general procedure was followed using compound **1b** (291 mg, 1 mmol), Pd₂(dba)₃ (9.2 mg, 0.01 mmol), *rac*-BINAP (19 mg, 0.03 mmol), sodium *tert*-butylate (135 mg, 1.4 mmol), cyclohexylamine (126 μL, 1.1 mmol) and toluene (2 mL) at 112°C. Column chromatography afforded compound **5** (215 mg, 70% yield) as a grey solid.

Mp 154°C; ¹H NMR (200 MHz, CDCl₃) δ 7.90 (dd, 2H, *J* = 8.6-5.4 Hz, F-Ph-2,6), 7.70 (s, 1H, H-3), 7.45 (bd, 1H, *J* = 9.3 Hz, H-8), 7.36 (d, 1H, *J* = 1.9 Hz, H-5), 7.13 (t, 2H, *J* = 8.6 Hz, F-Ph-3,5), 7.73 (dd, 1H, *J* = 9.3-1.9 Hz, H-7), 3.14 (m, 1H, Cy), 2.12 (m, 2H, Cy), 1.80 (m, 4H, Cy), 1.35 (m, 4H, Cy); ¹³C NMR (50 MHz) δ 162.8 (*J* = 246 Hz, F-Ph-4), 144.4 (C-2), 142.7 (C-8a), 135.8 (C-6), 130.9 (*J* = 3 Hz, F-Ph-1), 127.7 (*J* = 8 Hz, F-Ph-2,6), 120.9 (C-7), 117.9 (C-8), 115.9 (*J* = 21.6 Hz, Ph-3,5), 108.5 (C-3), 106.0 (C-5), 53.1 (Cy-1), 33.5 (Cy-2,6), 26.3 (Cy-4), 25.3 (Cy-3,5); Anal. Calcd for C₁₉H₂₀FN₃: C, 73.76; H, 6.52. Found: C, 73.93; H, 6.49.

2-(4-fluorophenyl)-6-(pyrrolidin-1-yl)imidazo[1,2-*a*]pyridine 6:

Method A: The general procedure was followed using compound **1a** (338 mg, 1 mmol), copper (I) iodide (29 mg, 0.15 mmol), K₃PO₄ (425 mg, 2 mmol), ethylene glycol (111 μL, 2

mmol), pyrrolidine (92 μ L, 1.1 mmol) and 2-propranol (1 mL) at 85°C for 20 h. Column chromatography afforded compound **6** (235 mg, 84% yield) as a white solid.

Method B: The general procedure was followed using compound **1b** (291 mg, 1 mmol), Pd₂(dba)₃ (9.2 mg, 0.01 mmol), *rac*-BINAP (19 mg, 0.03 mmol), sodium *tert*-butylate (135 mg, 1.4 mmol), pyrrolidine (92 μ L, 1.1 mmol) and toluene (2 mL) at 112°C. Column chromatography afforded compound **6** (240 mg, 85% yield) as a white solid.

mp 196°C; ¹H NMR (300 MHz, CDCl₃) δ 7.87 (dd, 2H, *J* = 8.7-5.7 Hz, F-Ph-2,6), 7.65 (s, 1H, H-3), 7.46 (d, 1H, *J* = 9.6 Hz, H-8), 7.19 (d, 1H, *J* = 2.1 Hz, H-5), 7.08 (t, 2H, *J* = 8.7 Hz, F-Ph-3,5), 6.88 (dd, 1H, *J* = 9.6-2.1 Hz, H-7), 3.22 (m, 4H, pyrrolidine), 2.02 (m, 4H, pyrrolidine); ¹³C NMR (75 MHz) δ 162.6 (*J* = 246 Hz, F-Ph-4), 144.1 (C-2*), 142.0 (C-8a*), 137.5 (C-6), 130.9 (*J* = 3.5 Hz, F-Ph-1), 127.4 (*J* = 8.1 Hz, F-Ph-2,6), 118.0 (C-7), 117.2 (C-8*), 115.7 (*J* = 21.5 Hz, F-Ph-3,5), 108.1 (C-3), 104.9 (C-5), 48.4 (pyrrolidine), 25.4 (pyrrolidine); Anal. Calcd for C₁₇H₁₆FN₃: C, 72.60; H, 5.69. Found: C, 72.69; H, 5.71.

2-(4-fluorophenyl)-6-(4-ethylpiperazin-1-yl)imidazo[1,2-*a*]pyridine 7:

Method A: The general procedure was followed using compound **1a** (338 mg, 1 mmol), copper (I) iodide (29 mg, 0.15 mmol), K₃PO₄ (425 mg, 2 mmol), ethylene glycol (111 μ L, 2 mmol), *N*-ethylpiperazine (140 μ L, 1.1 mmol) and 2-propranol (1 mL) at 85°C for 48 h. Column chromatography afforded compound **7** (222 mg, 69% yield) as a grey solid.

Method B: The general procedure was followed using compound **1b** (291 mg, 1 mmol), Pd₂(dba)₃ (9.2 mg, 0.01 mmol), *rac*-BINAP (19 mg, 0.03 mmol), sodium *tert*-butylate (135 mg, 1.4 mmol), *N*-ethylpiperazine (140 μ L, 1.1 mmol) and toluene (2 mL) at 112°C. Column chromatography afforded compound **7** (217 mg, 67% yield) as a grey solid.

mp 209°C; ¹H NMR (200 MHz, CDCl₃) δ 7.90 (dd, 2H, *J* = 8.8-5.4 Hz, F-Ph-2,6), 7.75 (s, 1H, H-3), 7.55 (m, 1H, H-5), 7.52 (d, 1H, *J* = 9.7 Hz, H-8), 7.13 (t, 2H, *J* = 8.7 Hz, F-Ph-3,5), 7.10 (d, 1H, *J* = 9.7 Hz, H-7), 3.15 (m, 4H, piperazine), 2.68 (m, 4H, piperazine), 2.54 (q, 2H,

$J = 7.2$ Hz, CH₂), 1.17 (t, 3H, $J = 7.2$ Hz, CH₃); ¹³C NMR (50 MHz) δ 162.9 ($J = 245$ Hz, F-Ph-4), 145.0 (C-2*), 143.2 (C-8a*), 140.5 (C-6), 130.7 ($J = 3$ Hz, F-Ph-1), 127.8 ($J = 8$ Hz, F-Ph-2,6), 122.1 (C-7), 117.6 (C-8), 116.0 ($J = 21.5$ Hz, F-Ph-3,5), 111.5 (C-5), 109.0 (C-3), 53.0 (piperazine), 52.7 (CH₂), 50.8 (piperazine), 12.4 (CH₃); Anal. Calcd for C₁₉H₂₁FN₄: C, 70.35; H, 6.52. Found: C, 70.55; H, 6.70.

2-(4-fluorophenyl)-6-(piperidin-1-yl)imidazo[1,2-*a*]pyridine 8:

Method A: The general procedure was followed using compound **1a** (338 mg, 1 mmol), copper (I) iodide (29 mg, 0.15 mmol), K₃PO₄ (425 mg, 2 mmol), ethylene glycol (111 μ L, 2 mmol), piperidine (109 μ L, 1.1 mmol) and 2-propanol (1 mL) at 85°C for 48 h. Column chromatography afforded compound **8** (205 mg, 70% yield) as a grey solid.

mp 209°C; ¹H NMR (300 MHz, CDCl₃) δ 7.86 (dd, 2H, $J = 8.9$ -5.4 Hz, F-Ph-2,6), 7.66 (s, 1H, H-3), 7.48 (s, 1H, H-5), 7.46 (d, 1H, $J = 9.6$ Hz, H-8), 7.08 (t, 2H, $J = 8.9$ Hz, F-Ph-3,5), 7.05 (dd, 1H, $J = 9.6$ -2.4 Hz, H-7), 2.99 (m, 4H, piperidine), 1.74 (m, 4H, piperidine), 1.58 (m, 2H, piperidine); ¹³C NMR (75 MHz) δ 162.59 ($J = 248$ Hz, F-Ph-4), 144.53 (C-2), 142.90 (C-8a), 141.16 (C-6), 130.55 ($J = 2.9$ Hz, F-Ph-1), 127.48 ($J = 8.1$ Hz, Ph-2,6), 122.76 (C-7), 177.11 (C-8), 155.69 ($J = 21.6$ Hz, F-Ph-3,5), 111.44 (C-5), 108.63 (C-3), 52.02 (piperidine), 25.99 (piperidine), 24.08 (piperidine); Anal. Calcd for C₁₈H₁₈FN₃: C, 73.22; H, 6.10. Found: C, 73.57; H, 6.03.

6-(*N*-anilino)-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine 9:

Method B: The general procedure was followed using compound **1b** (291 mg, 1 mmol), Pd₂(dba)₃ (9.2 mg, 0.01 mmol), *rac*-BINAP (19 mg, 0.03 mol), sodium *tert*-butylate (135 mg, 1.4 mmol), aniline (100 μ L, 1.1 mmol) and toluene (2 mL) at 112°C. Column chromatography afforded compound **9** (247 mg, 82% yield) as a white solid.

mp 173°C; ¹H NMR (200 MHz, CDCl₃) δ 7.97 (m, 1H, H-5), 7.93 (dd, 2H, $J = 8.9$ -5.5 Hz, F-Ph-2,6), 7.73 (s, 1H, H-3), 7.58 (bd, 1H, $J = 9.5$ Hz, H-8), 7.31 (m, 2H, Ph-3,5), 7.15 (t, 2H,

$J = 8.9$ Hz, F-Ph-3,5), 7.09 (dd, 1H, $J = 9.5$ -2.1 Hz, H-7), 6.98 (m, 3H, Ph-2,4,6), 5.62 (bs, 1H, NH); ^{13}C NMR (50 MHz) δ 163.0 ($J = 247$ Hz, F-Ph-4), 145.4 (C-2*), 144.4 (C-8a*), 143.9 (Ph-1), 131.1 (C-6), 130.5 ($J = 3$ Hz, F-Ph-1), 130.0 (Ph-3,5), 127.9 ($J = 8$ Hz, F-Ph-2,6), 123.8 (C-7), 121.4 (Ph-4), 117.9 (C-8), 117.2 (Ph-2,6), 116.1 ($J = 21.6$ Hz, F-Ph-3,5), 115.9 (C-5), 108.8 (C-3); Anal. Calcd for $\text{C}_{19}\text{H}_{14}\text{FN}_3$: C, 75.23; H, 4.65. Found: C, 75.46; H, 4.71.

6-(*N*-methylanilino)-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine 10:

Method B: The general procedure was followed using compound **1b** (291 mg, 1 mmol), $\text{Pd}_2(\text{dba})_3$ (9.2 mg, 0.01 mmol), *rac*-BINAP (19 mg, 0.03 mol), sodium *tert*-butylate (135 mg, 1.4 mmol), *N*-methylaniline (119 μL , 1.1 mmol) and toluene (2 mL) at 112°C. Column chromatography afforded compound **10** (175 mg, 55% yield) as a grey solid.

mp 128°C; ^1H NMR (200 MHz, CDCl_3) δ 7.94 (dd, 2H, $J = 8.5$ -5.4 Hz, F-Ph-2,6), 7.90 (dd, 1H, $J = 2.2$ -0.7 Hz, H-5), 7.79 (s, 1H, H-3), 7.57 (dd, 1H, $J = 9.7$ -0.7 Hz, H-8), 7.32 (m, 2H, Ph-3,5), 7.16 (t, 2H, $J = 8.5$ Hz, F-Ph-3,5), 7.06 (dd, 1H, $J = 9.7$ -2.2 Hz, H-7), 7.00 (m, 3H, Ph-2,4,6), 3.35 (s, 3H, CH_3); ^{13}C NMR (50 MHz) δ 163.0 ($J = 245$ Hz, F-Ph-4), 149.2 (Ph-1), 145.5 (C-2*), 143.9 (C-8a*), 137.2 (C-6), 130.5 ($J = 3$ Hz, F-Ph-1), 129.8 (Ph-3,5), 127.9 ($J = 8$ Hz, F-Ph-2,6), 125.1 (C-7), 121.4 (Ph-4), 118.9 (Ph-2,6), 118.8 (C-5), 117.9 (C-8), 116.1 ($J = 21.5$ Hz, F-Ph-3,5), 109.0 (C-3), 41.3 (CH_3); Anal. Calcd for $\text{C}_{20}\text{H}_{16}\text{FN}_3$: C, 75.69; H, 5.08. Found: C, 75.83; H, 5.06.

Crystal structure for compound 10

The structure of the anilino compound **10** was confirmed by X-ray analysis (Tables 1-5, Scheme 1).

Table S1. Crystal data and structure refinement for compound **10**.

Empirical formula	C ₂₀ H ₁₆ F N ₃
Formula weight	317.36 g
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
space group	Pbca
Unit cell dimensions	a = 8.6865(2) Å b = 30.2155(4) Å c = 12.4800(4) Å
Volume	3275.59(14) Å ³
Z	8
Calculated density	1.287 g/cm ³
Absorption coefficient	0.086 mm ⁻¹
F(000)	1328
Max. theta for data collection	25 °
Reflections collected / unique	10561 / 2577 [R(int) = 0.0322]
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2527 / 0 / 218
Goodness-of-fit on F ²	0.972
Final R indices [I>2σ(I)]	R1 = 0.0570, wR2 = 0.1231
R indices (all data)	R1 = 0.1498, wR2 = 0.1534
Extinction coefficient	0.0030(8)
diff. density max.	0.248 (e. Å ⁻³)
diff. density min.	-0.169 (e. Å ⁻³)

Table S2. Final coordinates and equivalent isotropic displacement parameters of the non-hydrogen atoms for compound **10**.

Atom	x	y	z	U(eq) [Å ²]
N1	0.0625(3)	0.27932(9)	0.90366(17)	0.0528(10)
N4	0.0383(3)	0.24693(9)	0.74349(16)	0.0463(10)
N9	-0.1652(3)	0.15143(10)	0.63112(17)	0.0651(11)
C2	0.1454(3)	0.30268(11)	0.8285(2)	0.0498(11)
C3	0.1311(3)	0.28296(11)	0.7302(2)	0.0523(13)
C5	-0.0126(3)	0.21575(11)	0.6709(2)	0.0536(13)
C6	-0.1056(3)	0.18316(11)	0.7047(2)	0.0504(11)
C7	-0.1491(3)	0.18077(11)	0.8141(2)	0.0553(14)
C8	-0.0976(3)	0.21119(11)	0.8850(2)	0.0568(13)
C8A	-0.0014(3)	0.24586(11)	0.8502(2)	0.0469(13)
C10	-0.1283(4)	0.10690(13)	0.6395(2)	0.0600(14)
C11	-0.1911(4)	0.07644(17)	0.5682(3)	0.0833(19)
C12	-0.1551(6)	0.03286(18)	0.5753(4)	0.106(2)
C13	-0.0580(6)	0.01709(15)	0.6527(4)	0.120(3)
C14	0.0081(5)	0.04706(17)	0.7224(3)	0.102(2)
C15	-0.0254(4)	0.09118(14)	0.7157(2)	0.0743(16)
C16	-0.2439(3)	0.16888(13)	0.5364(2)	0.0705(13)
C17	0.2278(3)	0.34343(11)	0.8555(2)	0.0511(11)
C18	0.3434(4)	0.36002(13)	0.7895(2)	0.0680(14)
C19	0.4207(4)	0.39833(14)	0.8145(3)	0.0807(17)
C20	0.3832(5)	0.42015(14)	0.9067(3)	0.0743(17)
C21	0.2694(5)	0.40559(14)	0.9727(3)	0.0760(16)
C22	0.1926(4)	0.36715(12)	0.9472(2)	0.0603(14)
F23	0.4603(3)	0.45732(8)	0.93239(18)	0.1114(11)

U(eq) = 1/3 of the trace of the orthogonalized U Tensor.

Table S3. Hydrogen atom positions and isotropic displacement parameters for compound **10**.

Atom	x	y	z	U(iso) [$\text{\AA}^2$]
H3	0.17610	0.29230	0.66650	0.0620
H5	0.01710	0.21730	0.59950	0.0640
H7	-0.21340	0.15810	0.83720	0.0670
H8	-0.12570	0.20920	0.95670	0.0680
H11	-0.25840	0.08610	0.51510	0.1000
H12	-0.19760	0.01320	0.52630	0.1270
H13	-0.03700	-0.01300	0.65820	0.1440
H14	0.07620	0.03710	0.77460	0.1220
H15	0.02130	0.11090	0.76280	0.0890
H16A	-0.27950	0.14470	0.49290	0.1060
H16B	-0.17370	0.18680	0.49570	0.1060
H16C	-0.33010	0.18650	0.55840	0.1060
H18	0.36890	0.34480	0.72720	0.0810
H19	0.49700	0.40920	0.76940	0.0970
H21	0.24380	0.42140	1.03420	0.0910
H22	0.11550	0.35690	0.99250	0.0720

Table S4. Bond distances (Å) for compound **10**.

N1-C2	1.377(4)	F23-C20	1.346(5)
N1-C8A	1.332(4)	C18-C19	1.374(6)
N4-C3	1.365(4)	C19-C20	1.366(5)
N4-C5	1.380(4)	C20-C21	1.360(6)
N4-C8A	1.376(3)	C21-C22	1.377(6)
N9-C6	1.425(4)	C3-H3	0.9297
N9-C10	1.387(5)	C5-H5	0.9288
N9-C16	1.464(4)	C7-H7	0.9297
C2-C3	1.369(4)	C8-H8	0.9295
C2-C17	1.464(4)	C11-H11	0.9306
C5-C6	1.342(4)	C12-H12	0.9290
C6-C7	1.418(4)	C13-H13	0.9298
C7-C8	1.352(4)	C14-H14	0.9300
C8-C8A	1.409(4)	C15-H15	0.9301
C10-C11	1.392(6)	C16-H16A	0.9613
C10-C15	1.389(4)	C16-H16B	0.9607
C11-C12	1.356(7)	C16-H16C	0.9589
C12-C13	1.368(7)	C18-H18	0.9301
C13-C14	1.381(7)	C19-H19	0.9295
C14-C15	1.367(7)	C21-H21	0.9310
C17-C18	1.392(4)	C22-H22	0.9296
C17-C22	1.385(4)		

Table S5. Bond angles (°) for compound **10**.

C2-N1-C8A	105.4(2)	C2-C17-C18	121.3(3)
C3-N4-C5	130.9(2)	C2-C17-C22	121.2(3)
C3-N4-C8A	106.5(2)	C18-C17-C22	117.5(3)
C5-N4-C8A	122.6(3)	C17-C18-C19	121.4(3)
C6-N9-C10	121.3(2)	C18-C19-C20	118.8(3)
C6-N9-C16	116.6(3)	F23-C20-C19	119.0(4)
C10-N9-C16	121.2(3)	F23-C20-C21	119.2(3)
N1-C2-C3	109.9(3)	C19-C20-C21	121.8(4)
N1-C2-C17	122.0(2)	C20-C21-C22	119.0(4)
C3-C2-C17	128.1(3)	C17-C22-C21	121.4(3)
N4-C3-C2	107.0(2)	N4-C3-H3	126.47
N4-C5-C6	119.2(2)	C2-C3-H3	126.57
N9-C6-C5	120.7(2)	N4-C5-H5	120.43
N9-C6-C7	119.3(3)	C6-C5-H5	120.39
C5-C6-C7	120.0(3)	C6-C7-H7	119.74
C6-C7-C8	120.5(3)	C8-C7-H7	119.79
C7-C8-C8A	120.0(2)	C7-C8-H8	119.95
N1-C8A-N4	111.2(3)	C8A-C8-H8	120.05
N1-C8A-C8	131.1(2)	C10-C11-H11	119.61
N4-C8A-C8	117.7(3)	C12-C11-H11	119.73
N9-C10-C11	120.2(3)	C11-C12-H12	119.09
N9-C10-C15	122.1(3)	C13-C12-H12	119.15
C11-C10-C15	117.6(4)	C12-C13-H13	120.91
C10-C11-C12	120.7(4)	C14-C13-H13	120.88
C11-C12-C13	121.8(5)	C13-C14-H14	119.58
C12-C13-C14	118.2(4)	C15-C14-H14	119.59
C13-C14-C15	120.8(4)	C10-C15-H15	119.63

C10-C15-C14	120.8(3)	C14-C15-H15	119.55
N9-C16-H16A	109.42	C19-C18-H18	119.34
N9-C16-H16B	109.48	C18-C19-H19	120.57
N9-C16-H16C	109.48	C20-C19-H19	120.65
H16A-C16-H16B	109.51	C20-C21-H21	120.46
H16A-C16-H16C	109.42	C22-C21-H21	120.51
H16B-C16-H16C	109.52	C17-C22-H22	119.30
C17-C18-H18	119.23	C21-C22-H22	119.32

Figure S1. Ellipsoïd representation of the non-hydrogen atoms and atomic labelling of **10** (X-Ray numbering).