Supporting Information

Ipso- or *cine*-substitutions of 6-haloimidazo[1,2-*a*]pyridine derivatives with different azoles depending on the reaction conditions.

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General considerations: *Trans-N,N'*-dimethyl-1,2-diaminocyclohexane^{9b}, 6-bromo-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine^{4a} and 6-iodo-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine^{4b} were prepared according to a literature procedure. All materials were weighed in the air. ¹H and ¹³C NMR were recorded using the residual non-deuteriated solvent as an internal standard. Possible inversion of two values in the NMR spectra is expressed by an asterisk.

General procedure for Cu-catalyzed arylations: Method A. A screw-cap test tube was charged with 6-halogeno-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine **1a-b** (1.00 mmol), base (2.10 mmol), copper (I) iodide (9.5 mg, 0.050 mmol) and azole (1.00 mmol). A teflon septum was attached and the tube was evacuated and back filled with argon, the evacuated/backfilled sequence was repeated an additional time. Ligand (0.15 mmol) and solvent (1 mL) were added by syringe under argon. The screw-cap test tube was sealed with a cap and the reaction mixture was stirred magnetically at 112°C (oil bath) for 24 h. After cooling, the suspension was diluted with dichloromethane (25 mL) and filtered through celite. The filtrate was concentrated and the residue chromatographed to afford pure product.

***N*-[2-(4-fluorophenyl)imidazo[1,2-*a*]pyridin-6-yl]indole **2**.** Using the general procedure A, 6-bromo-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine **1a** (291 mg, 1.00 mmol) was coupled with indole (117.2 mg, 1.00 mmol) in the presence of copper (I) iodide (9.5 mg, 0.050 mmol), potassium phosphate (446 mg, 2.10 mmol) and *trans-N,N'*-dimethyl-1,2-cyclohexanediamine (23.6 µL, 21.3 mg, 0.15 mmol) in toluene (1 mL). The crude product was purified by chromatography on silica gel eluting with ether. Further concentration and chromatography on neutral alumina, eluting with dichloromethane gave 231 mg of **2** (72% yield) as white plates. Mp: 225-227°C. ¹H NMR (300 MHz, CDCl₃): δ 8.29 (m, 1H, H-5), 7.96 (dd, 2H, *J* = 8.7-5.7 Hz, F-Ph-2,6), 7.87 (s, 1H, H-3), 7.75 (d, 1H, *J* = 9.5 Hz, H-8), 7.72 (m, 1H, Ind-4), 7.47 (bd, 1H, *J* = 8.1 Hz, Ind-7), 7.37 (dd, 1H, *J* = 9.5-2.4 Hz, H-7), 7.30 (d, 1H, *J* = 3.3 Hz, Ind-2), 7.25 (m, 2H, Ind-5,6), 7.16 (t, 2H, *J* = 8.7 Hz, F-Ph-3,5), 6.74 (dd, 1H,

$J = 3.3\text{-}0.9$ Hz, Ind-3). ^{13}C NMR (75 MHz, CDCl_3): δ 163.0 ($J = 246$ Hz, F-Ph-4), 146.4 (C-2*), 144.5 (C-8a*), 136.6 (Ind-7a), 129.8 ($J = 3$ Hz, F-Ph-1), 129.3 (C-6), 128.2 (Ind-2), 128.0 ($J = 8.2$ Hz, F-Ph-2,6), 127.7 (Ind-3a), 124.1 (C-7), 123.0 (Ind-5), 121.6 (Ind-4*), 121.6 (C-5*), 121.0 (Ind-6), 118.1 (C-8), 116.0 ($J = 21.6$ Hz, F-Ph-3,5), 110.2 (Ind-7), 108.9 (C-3), 104.5 (Ind-3). Anal. Calcd for $\text{C}_{21}\text{H}_{14}\text{FN}_3$: C, 77.78; H, 4.32. Found: C, 77.52; H, 4.44.

Using the general procedure A, 6-bromo-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine **1a** (291 mg, 1.00 mmol) was coupled with indole (117.2 mg, 1.00 mmol) in the presence of copper (I) iodide (9.5 mg, 0.050 mmol), potassium phosphate (446 mg, 2.10 mmol) and *N,N'*-dimethyl-1,2-ethylenediamine (16.0 μL , 13.2 mg, 0.15 mmol) in toluene (1 mL). The crude product was chromatographed on neutral alumina, eluting with dichloromethane to give 228 mg of **2** (70% yield) as white plates.

Using the general procedure A, 6-iodo-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine **1b** (338 mg, 1.00 mmol) was coupled with indole (117.2 mg, 1.00 mmol) in the presence of copper (I) iodide (9.5 mg, 0.050 mmol), potassium phosphate (446 mg, 2.10 mmol) and *trans-N,N'*-dimethyl-1,2-cyclohexanediamine (23.6 μL , 21.3 mg, 0.15 mmol) in toluene (1 mL). The crude product was chromatographed on silica gel, eluting with dichloromethane to give 241 mg of **2** (74% yield) as white plates.

***N*-[2-(4-fluorophenyl)imidazo[1,2-*a*]pyridin-6-yl]-7-azaindole 3.** Using the general procedure A, 6-bromo-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine **1a** (291 mg, 1.00 mmol) was coupled with 7-azaindole (118 mg, 1.00 mmol) in the presence of copper (I) iodide (9.5 mg, 0.050 mmol), potassium phosphate (446 mg, 2.10 mmol) and *trans-N,N'*-dimethyl-1,2-cyclohexanediamine (23.6 μL , 21.3 mg, 0.15 mmol) in toluene (1 mL). The crude product was chromatographed on silica gel, eluting with ether to give 308 mg of **3** (94% yield) as white plates. Mp: 150-152°C. ^1H NMR (300 MHz, CDCl_3): δ 8.83 (m, 1H, H-5), 8.39 (dd, 1H, $J = 4.7\text{-}1.5$ Hz, Het-6), 8.00 (dd, 1H, $J = 7.8\text{-}1.5$ Hz, Het-4), 7.93 (dd, 2H, $J = 8.9\text{-}5.4$ Hz,

F-Ph-2,6), 7.88 (s, 1H, H-3), 7.72 (d, 1H, $J = 9.6$ Hz, H-8), 7.49 (d, 1H, $J = 3.5$ Hz, Het-2), 7.47 (dd, 1H, $J = 9.6$ -2.1 Hz, H-7), 7.18 (dd, 1H, $J = 7.8$ -4.7 Hz, Het-5), 7.13 (t, 2H, $J = 8.9$ Hz, F-Ph-3,5), 6.68 (d, 1H, $J = 3.5$ Hz, Het-3). ^{13}C NMR (75 MHz, CDCl_3): δ 162.9 ($J = 247$ Hz, F-Ph-4), 147.7 (C-8a*), 145.9 (C-2*), 144.1 (Het-7a), 143.8 (Het-6), 130.0 ($J = 3.2$ Hz, F-Ph-1), 129.5 (Het-4), 127.8 ($J = 8.1$ Hz, F-Ph-2,6), 127.3 (Het-2), 126.1 (C-6), 122.6 (C-7), 121.6 (Het-3a), 121.0 (C-5), 117.6 (C-8), 117.3 (Het-5), 115.8 ($J = 21.6$ Hz, F-Ph-3,5), 109.0 (C-3), 102.6 (Het-3). Anal. Calcd for $\text{C}_{20}\text{H}_{13}\text{FN}_4$: C, 73.17; H, 3.96. Found: C, 72.91; H, 3.92.

***N*-1-[2-(4-fluorophenyl)imidazo[1,2-*a*]pyridin-6-yl]indazole 4a** and ***N*-2-[2-(4-fluorophenyl)imidazo[1,2-*a*]pyridin-6-yl]indazole 4b**. Using the general procedure A, 6-bromo-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine **1a** (291 mg, 1.00 mmol) was coupled with indazole (118 mg, 1.00 mmol) in the presence of potassium phosphate (446 mg, 2.10 mmol), copper (I) iodide (9.5 mg, 0.050 mmol) and *trans*-*N,N'*-dimethyl-1,2-cyclohexanediamine (23.6 μL , 21.3 mg, 0.15 mmol) in toluene (1 mL). The crude product was chromatographed on silica gel, eluting with dichloromethane and then with dichloromethane-methanol (99.5/0.5 v/v) to give 171 mg of **4a** and **4b** (52% yield). The separation of the two regioisomers was achieved on silica gel, eluting with ethyl acetate-pentane (20/80 v/v) to give **4a** as white plates. Mp: 210-212°C. ^1H NMR (300 MHz, CDCl_3): δ 8.52 (m, 1H, H-5), 8.24 (d, 1H, $J = 0.9$ Hz, Het-3), 7.95 (dd, 2H, $J = 9$ -5.4 Hz, F-Ph-2,6), 7.90 (s, 1H, H-3), 7.85 (dt, $J = 8.1$ -0.9 Hz, Het-4), 7.77 (d, 1H, $J = 9.6$ Hz, H-8), 7.68 (m, 1H, Het-7), 7.62 (dd, 1H, $J = 9.6$ -2.1 Hz, H-7), 7.49 (m, 1H, Het-6), 7.28 (m, 1H, Het-5), 7.15 (t, 2H, $J = 9$ Hz, F-Ph-3,5). ^{13}C NMR (75 MHz, CDCl_3): δ 163.0 ($J = 247.5$ Hz, F-Ph-4), 146.5 (C-2*), 144.5 (C-8a*), 139.4 (Het-7a), 136.2 (Het-3), 129.8 ($J = 3$ Hz, F-Ph-1), 128.5 (C-6), 128.0 ($J = 8.1$ Hz, F-Ph-2,6), 127.8 (Het-6), 125.4 (Het-3a), 122.1 (Het-5,C-7), 121.8 (Het-4), 120.3 (C-5), 117.9 (C-8), 115.9 ($J = 21.9$ Hz, F-Ph-3,5), 109.9 (Het-7), 109.0 (C-3). Anal. Calcd for $\text{C}_{20}\text{H}_{13}\text{FN}_4$: C, 73.17; H, 3.96. Found: C, 73.32; H, 3.99. Further elution gave **4b** as white plates. Mp: 223-225°C. ^1H

NMR (500 MHz, CDCl₃): δ 8.93 (d, 1H, J = 1.8 Hz, H-5), 8.41 (s, 1H, Het-3), 7.96 (dd, 2H, J = 9-5.5 Hz, F-Ph-2,6), 7.94 (s, 1H, H-3), 7.82 (d, 1H, J = 9.5 Hz, H-8), 7.78 (d, 1H, J = 9 Hz, Het-4), 7.74 (d, 1H, J = 8.5 Hz, Het-7), 7.70 (dd, 1H, J = 9.5-1.8 Hz, H-7), 7.38 (m, 1H, Het-6), 7.16 (t, 2H, J = 9 Hz, F-Ph-3,5), 7.15 (m, 1H, Het-5). ¹³C NMR (75 MHz, CDCl₃): δ 163.2, 150.1, 146.6, 144.5, 129.5, 129.4, 128.1, 127.7, 123.2, 123.1, 121.0, 120.6, 119.5, 119.0, 117.9, 117.8, 116.1, 109.4. Anal. Calcd for C₂₀H₁₃FN₄: C, 73.17; H, 3.96. Found: C, 72.93; H, 3.87.

Using the general procedure A, 6-iodo-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine **1b** (338 mg, 1.00 mmol) was coupled with indazole (118 mg, 1.00 mmol) in the presence of copper (I) iodide (9.5 mg, 0.050 mmol), potassium phosphate (446 mg, 2.10 mmol) and *trans*-*N,N'*-dimethyl-1,2-cyclohexanediamine (23.6 μ L, 21.3 mg, 0.15 mmol) in toluene (1 mL). The crude product was chromatographed on silica gel, eluting with dichloromethane and then with dichloromethane-methanol (99.5/0.5 v/v) to give 281 mg of **4a** and **4b** (86% yield) in a 97/3 ratio.

N-[2-(4-fluorophenyl)imidazo[1,2-*a*]pyridin-6-yl]pyrazole **5**. Using the general procedure A, 6-iodo-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine **1b** (338 mg, 1.00 mmol) was coupled with pyrazole (68.1 mg, 1.00 mmol) in the presence of copper (I) iodide (9.5 mg, 0.050 mmol), potassium phosphate (446 mg, 2.10 mmol) and *trans*-*N,N'*-dimethyl-1,2-cyclohexanediamine (23.6 μ L, 21.3 mg, 0.15 mmol) in toluene (1 mL). The crude product was chromatographed on neutral alumina, eluting with dichloromethane to give 220 mg of **5** (79% yield) as white plates. Mp: 219-221°C. ¹H NMR (300 MHz, CDCl₃): δ 8.64 (m, 1H, H-5), 7.94 (dd, 2H, J = 8.9-5.4 Hz, F-Ph-2,6), 7.89 (d, 1H, J = 2.6 Hz, Pyr-5*), 7.88 (s, 1H, H-3), 7.76 (d, 1H, J = 1.6 Hz, Pyr-3*), 7.70 (d, 1H, J = 9.6 Hz, H-8), 7.51 (dd, 1H, J = 9.6- 2.1 Hz, H-7), 7.14 (t, 2H, J = 8.9 Hz, F-Ph-3,5), 6.53 (dd, 1H, J = 2.6-1.6 Hz, Pyr-4). ¹³C NMR (75 MHz, CDCl₃): δ 163.0 (J = 247 Hz, F-Ph-4), 146.4 (C-2*), 144.3 (C-8a*), 141.7 (Het-5*),

129.7 ($J = 3$ Hz, F-Ph-1), 129.0 (C-6), 127.9 ($J = 8.4$ Hz, F-Ph-2,6), 127.4 (Het-3*), 118.9 (C-7), 117.8 (C-8), 117.1 (C-5), 115.9 ($J = 21.9$ Hz, F-Ph-3,5), 109.1 (C-3), 108.3 (Het-4). Anal. Calcd for $C_{16}H_{11}FN_4$: C, 69.06; H, 3.96. Found: C, 69.15; H, 3.92.

***N*-[2-(4-fluorophenyl)imidazo[1,2-*a*]pyridin-6-yl]pyrrole 6.** Using the general procedure A, 6-iodo-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine **1b** (338 mg, 1.00 mmol) was coupled with pyrrole (69.4 μ L, 67.09 mg, 1.00 mmol) in the presence of copper (I) iodide (9.5 mg, 0.050 mmol), potassium phosphate (446 mg, 2.10 mmol) and *trans*-*N,N'*-dimethyl-1,2-cyclohexanediamine (23.6 μ L, 21.3 mg, 0.15 mmol) in toluene (1 mL). The crude product was chromatographed on silica gel, eluting with dichloromethane to give 210 mg of **6** (76% yield) as white plates. Mp: 152-154°C. 1H NMR (300 MHz, $CDCl_3$): δ 8.20 (m, 1H, H-5), 7.93 (dd, 2H, $J = 8.6$ -5.4 Hz, F-Ph-2,6), 7.85 (s, 1H, H-3), 7.68 (d, 1H, $J = 9.5$ Hz, H-8), 7.33 (dd, 1H, $J = 9.5$ -1.6 Hz, H-7), 7.14 (t, 2H, $J = 8.6$ Hz, F-Ph-3,5), 7.02 (m, 2H, Pyr-2,5), 6.40 (m, 2H, Pyr-3,4). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.0 ($J = 246$ Hz, F-Ph-4), 146.2 (C-2*), 144.3 (C-8a*), 129.8 ($J = 3.3$ Hz, F-Ph-1), 129.5 (C-6), 127.8 ($J = 8$ Hz, F-Ph-2,6), 121.5 (C-7), 120.1 (Pyr-2,5), 118.0 (C-5*), 117.7 (C-8*), 115.9 ($J = 21.4$ Hz, F-Ph-3,5), 111.1 (Pyr-3,4), 108.8 (C-3). Anal. Calcd for $C_{17}H_{12}FN_3$: C, 75.28; H, 4.43. Found: C, 75.42; H, 4.37.

***N*-[2-(4-fluorophenyl)imidazo[1,2-*a*]pyridin-6-yl]imidazole 7.** Using the general procedure A, 6-iodo-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine **1b** (338 mg, 1.00 mmol) was coupled with imidazole (68 mg, 1.00 mmol) in the presence of copper (I) iodide (9.5 mg, 0.050 mmol), potassium phosphate (446 mg, 2.10 mmol) and *trans*-*N,N'*-dimethyl-1,2-cyclohexanediamine (23.6 μ L, 21.3 mg, 0.15 mmol) in toluene (1 mL). The crude product was chromatographed on silica gel, eluting with dichloromethane-methanol (99/1 v/v) to give 153 mg of **7** (55% yield) as white plates. Mp: 156-158°C. 1H NMR (300 MHz, $CDCl_3$): δ 8.28 (d, 1H, $J = 2.1$ Hz, H-5), 7.93 (dd, 2H, $J = 8.4$ -5.4 Hz, F-Ph-2,6), 7.90 (s, 1H, H-3), 7.82 (br.s., 1H, Im-2), 7.73 (d, 1H, $J = 9.3$ Hz, H-8), 7.27 (dd, 1H, $J = 9.3$ -2.1 Hz, H-7), 7.27

(m, 2H, Im-4,5), 7.15 (t, 2H, J = 8.4 Hz, F-Ph-3,5). ^{13}C NMR (75 MHz, CDCl_3): δ 163.4, 147.1, 144.7, 136.6, 131.2, 129.7, 128.3, 126.1, 121.7, 119.6, 119.5, 118.7, 116.3, 109.4. MS : 279 $[\text{M}+\text{H}]^+$. Anal. Calcd for $\text{C}_{16}\text{H}_{11}\text{FN}_4$: C, 69.06; H, 3.96. Found: C, 69.17; H, 3.98.

***N*-[2-(4-fluorophenyl)imidazo[1,2-*a*]pyridin-6-yl]imidazole 7 and *N*-[2-(4-fluorophenyl)imidazo[1,2-*a*]pyridin-5-yl]imidazole 11.** Using the general procedure A, 6-bromo-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine **1a** (291 mg, 1.00 mmol) was coupled with imidazole (68 mg, 1.00 mmol) in the presence of copper (I) iodide (9.5 mg, 0.050 mmol), cesium carbonate (684 mg, 2.10 mmol) and *trans*-*N,N'*-dimethyl-1,2-cyclohexanediamine (23.6 μL , 21.3 mg, 0.15 mmol) in *N,N*-dimethylformamide (1 mL). After filtration through celite, the organic layer was washed with water (5 x 25 ml), dried over magnesium sulfate and concentrated. The residue was chromatographed on silica gel, eluting with dichloromethane and then dichloromethane-methanol (99/1 v/v) to give 102 mg of **11** (37% yield) as white plates. Mp 218-220°C. ^1H NMR (300 MHz, CDCl_3): δ 7.89 (dd, 2H, J = 9-5.4 Hz, F-Ph-2,6), 7.89 (m, 1H, Het-2), 7.74 (dt, 1H, J = 9-1 Hz, H-8), 7.57 (s, 1H, H-3), 7.40 (m, 1H, Het-4*), 7.38 (m, 1H, Het-5*), 7.31 (dd, 1H, J = 9-7.2 Hz, H-7), 7.12 (t, 2H, J = 9 Hz, F-Ph-3,5), 6.86 (dd, 1H, J = 7.2-1 Hz, H-6). ^{13}C NMR (75 MHz, CDCl_3): δ 163.1, 146.8, 146.2, 137.4, 131.3, 130.0, 129.3, 128.1, 124.6, 119.3, 117.9, 115.9, 109.4, 104.7. Anal. Calcd for $\text{C}_{16}\text{H}_{11}\text{FN}_4$: C, 69.06; H, 3.96. Found: C, 69.17; H, 3.99. Further elution gave 86 mg (31% yield) of **7** as white plates.

***N*-[2-(4-fluorophenyl)imidazo[1,2-*a*]pyridin-6-yl]-1,2,4-triazole 8.** Using the general procedure A, 6-iodo-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine **1a** (338 mg, 1.00 mmol) was coupled with 1,2,4-triazole (69.1 mg, 1.00 mmol) in the presence of copper (I) iodide (9.5 mg, 0.05 mmol), cesium carbonate (684 mg, 2.10 mmol) and *trans*-*N,N'*-dimethyl-1,2-cyclohexanediamine (23.6 μL , 21.3 mg, 0.15 mmol) in *N,N*-dimethylformamide (1 mL). After filtration through celite, the organic layer was washed with water (5 x 25 ml), dried over

magnesium sulfate and concentrated. The residue was chromatographed on silica gel, eluting with dichloromethane and then with dichloromethane/methanol (99/1 v/v) to give 125 mg of **8** (45% yield) as white plates. Mp: 250-252°C. ¹H NMR (300 MHz, CDCl₃): δ 8.68 (d, 1H, *J* = 2.1 Hz, H-5), 8.57 (s, 1H, triazole), 8.16 (s, 1H, triazole), 7.95 (dd, 2H, *J* = 8.7-5.4 Hz, F-Ph-2,6), 7.94 (s, 1H, H-3), 7.77 (d, 1H, *J* = 9.6 Hz, H-8), 7.49 (dd, 1H, *J* = 9.6-2.1 Hz, H-7), 7.16 (t, 2H, *J* = 8.7 Hz, F-Ph-3,5). ¹³C NMR (75 MHz, DMSO-d₆): δ 162.7, 153.3, 145.6, 144.3, 130.7, 128.3, 125.8, 119.7, 119.5, 117.9, 116.4, 111.1. Anal. Calcd for C₁₅H₁₀FN₅: C, 64.52; H, 3.58. Found: C, 64.40; H, 3.47.

***N*-1-[2-(4-fluorophenyl)imidazo[1,2-*a*]pyridin-6-yl]-1,2,3-triazole 9a** and ***N*-2-[2-(4-fluorophenyl)imidazo[1,2-*a*]pyridin-6-yl]-1,2,3-triazole 9b**. Using the general procedure A, 6-iodo-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine **1b** (338 mg, 1.00 mmol) was coupled with 1,2,3-triazole (69.1 mg, 1.00 mmol) in the presence of copper (I) iodide (9.5 mg, 0.050 mmol), potassium phosphate (446 mg, 2.10 mmol) and *trans*-*N,N'*-dimethyl-1,2-cyclohexanediamine (23.6 μL, 21.3 mg, 0.15 mmol) in *N,N*-dimethylformamide (1 mL). After filtration through celite, the organic layer was washed with water (5 x 25 ml), dried over magnesium sulfate and concentrated. The residue was chromatographed on silica gel. Elution with dichloromethane-methanol (99.5/0.5 v/v) gave the *N*-2 derivative **9b** (92 mg, 33%) as white plates. Mp : 225-227°C. ¹H NMR (300 MHz, CDCl₃): δ 8.92 (m, 1H, H-5), 8.01 (dd, 1H, *J* = 9-2.4 Hz, H-7), 7.94 (dd, 2H, *J* = 8.7-5.4 Hz, F-Ph-2,6), 7.91 (bs, 1H, H-3), 7.85 (bs, 2H, triazole), 7.73 (bd, 1H, *J* = 9.6 Hz, H-8), 7.15 (t, 2H, *J* = 8.7 Hz, F-Ph-3,5). ¹³C NMR (75 MHz, CDCl₃): δ 163.1, 146.6, 144.7, 136.1, 129.7, 129.2, 128.0, 118.5, 117.8, 116.8, 116.0, 109.3. Anal. Calcd for C₁₅H₁₀FN₅: C, 64.52; H, 3.58. Found: C, 64.38; H, 3.57. Further elution with dichloromethane-methanol (99 : 1 v/v) gave the *N*-1 derivative **9a** (73 mg, 26%) as white plates. Mp : 247-249°C. ¹H NMR (300 MHz, DMSO-d₆): δ 9.30 (m, 1H, H-5), 8.85 (d, 1H, *J* = 0.9 Hz, triazole), 8.54 (s, 1H, H-3), 8.05 (dd, 2H, *J* = 9-5.4 Hz, F-Ph-2,6), 8.04 (d,

1H, $J = 1.2$ Hz, H-7), 7.83 (m, 2H, H-8, triazole), 7.31 (t, 2H, $J = 9$ Hz, F-Ph-3,5). ^{13}C NMR (75 MHz, CDCl_3): δ 162.1, 144.6, 143.7, 134.5, 129.6, 127.8, 125.2, 124.1, 119.9, 119.8, 117.1, 115.8, 110.6. Anal. Calcd for $\text{C}_{15}\text{H}_{10}\text{FN}_5$: C, 64.52; H, 3.58. Found: C, 64.66; H, 3.62.

***N*-[2-(4-fluorophenyl)imidazo[1,2-*a*]pyridin-6-yl]benzimidazole 10** and ***N*-[2-(4-fluorophenyl)imidazo[1,2-*a*]pyridin-5-yl]benzimidazole 12**. Using the general procedure A, 6-bromo-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine **1a** (291 mg, 1.00 mmol) was coupled with benzimidazole (118.1 mg, 1.00 mmol) in the presence of copper (I) iodide (9.5 mg, 0.050 mmol), cesium carbonate (684 mg, 2.10 mmol) and *trans*-*N,N'*-dimethyl-1,2-cyclohexanediamine (23.6 μL , 21.3 mg, 0.15 mmol) in *N,N*-dimethylformamide (1 mL). After filtration through celite, the organic layer was washed with water (5 x 25 mL), dried over magnesium sulfate and concentrated. The residue was chromatographed on silica gel, eluting with dichloromethane and then with dichloromethane-methanol (99.5/0.5 v/v) to give 69 mg of **12** (21% yield) as white plates. Mp: 185-187°C. ^1H NMR (300 MHz, CDCl_3): δ 8.18 (s, 1H, Het-2), 7.97 (bd, 1H, $J = 8.1$ Hz, Het-7), 7.81 (dd, 2H, $J = 9$ -5.1 Hz, F-Ph-2,6), 7.79 (bd, 1H, $J = 9.3$ Hz, H-8), 7.43 (m, 1H, Het-6*), 7.38 (s, 1H, H-3), 7.36 (dd, 1H, $J = 9.3$ -7.2 Hz, H-7), 7.34 (m, 1H, Het-5*), 7.15 (m, 1H, Het-4), 7.05 (t, 2H, $J = 9$ Hz, F-Ph-3,5), 6.96 (dd, 1H, $J = 7.2$ -1.2 Hz, H-6). ^{13}C NMR (75 MHz, CDCl_3): δ 163.1, 146.8, 146.1, 143.7, 142.1, 133.1, 129.3, 128.1, 125.0, 124.6, 124.1, 121.5, 118.2, 115.9, 110.8, 110.8, 105.5. Anal. Calcd for $\text{C}_{20}\text{H}_{13}\text{FN}_4$: C, 73.17; H, 3.96. Found: C, 73.30; H, 3.98. Further elution gave 39 mg of **10** (12%) as white plates. Mp: 226-228°C. ^1H NMR (300 MHz, CDCl_3): δ 8.34 (m, 1H, H-5), 8.08 (s, 1H, Het-2), 7.94 (dd, 2H, $J = 8.7$ -5.4 Hz, F-Ph-2,6), 7.91 (s, 1H, H-3), 7.89 (m, 1H, Het-7), 7.78 (bd, 1H, $J = 9.6$ Hz, H-8), 7.46 (m, 1H, Het-4), 7.37 (m, 2H, Het-5,6), 7.32 (dd, 1H, $J = 9.6$ -2.1 Hz, H-7), 7.15 (t, 2H, $J = 8.7$ Hz, F-Ph-3,5). ^{13}C NMR (125 MHz, CDCl_3): δ 163.6, 147.5, 145.1, 144.5, 134.9, 130.0, 128.6, 124.9, 124.8, 124.0, 123.4, 122.3, 121.6,

119.2, 116.6, 110.7, 109.6. Anal. Calcd for C₂₀H₁₃FN₄: C, 73.17; H, 3.96. Found: C, 73.04; H, 3.89.

General procedure for *cine*-substitutions: Method B. A screw-cap test tube was charged with 6-bromo-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine **1a** (291 mg, 1.00 mmol), cesium carbonate (684 mg, 2.10 mmol) and azole (1.00 mmol). A teflon septum was attached and the tube was evacuated and back filled with argon, the evacuated/backfield sequence was repeated an additional time. *N,N*-dimethylformamide (1 mL) was added by syringe under argon. The screw-cap test tube was sealed with a cap and the reaction mixture was stirred magnetically at 112°C (oil bath) for 24 h. After cooling, the suspension was diluted with dichloromethane (25 mL) and filtered through celite. The filtrate was washed with water (4 x 50 mL), dried over magnesium sulfate and concentrated under vacuo. The crude product was chromatographed to afford pure product.

***N*-[2-(4-fluorophenyl)imidazo[1,2-*a*]pyridin-5-yl]imidazole **11**.** Using the general procedure B, 6-bromo-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine **1a** (291 mg, 1.00 mmol) was coupled with imidazole (68 mg, 1.00 mmol). The crude product was chromatographed on silica gel, eluting with dichloromethane and then with dichloromethane-methanol (99.5/0.5 then 99/1 v/v) to give 162 mg of **11** (58% yield) as white plates.

***N*-[2-(4-fluorophenyl)imidazo[1,2-*a*]pyridin-5-yl]imidazole **11** and *N*-[2-(4-imidazol-1-ylphenyl)imidazo[1,2-*a*]pyridin-5-yl]imidazole **17**.** Using the general procedure B, 6-bromo-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine **1a** (291 mg, 1.00 mmol) was coupled with imidazole (68 mg, 1.00 mmol) at 140°C. The residue was chromatographed on silica gel, eluting with dichloromethane and then with dichloromethane-methanol (99.5/0.5 then 99/1 v/v) to give 103 mg of **11** (37% yield) as white plates. Further elution with dichloromethane-methanol (95/5 v/v) gave 64 mg of **17** (20% yield) as pale brown plates. Mp: 247°C. ¹H NMR (400 MHz, CDCl₃): δ 8.06 (d, 2H, *J* = 8.5 Hz, Ph-2,6), 7.96 (bs, 1H, Het-2'), 7.93 (bs, 1H,

Het-2), 7.79 (d, 1H, $J = 9.1$ Hz, H-8), 7.68 (s, 1H, H-3), 7.49 (d, 2H, $J = 8.5$ Hz, Ph-3,5), 7.44 (bs, 1H, Het-5*), 7.41 (bs, 1H, Het-4*), 7.36 (m, 2H, H-7, Het-4'*), 7.26 (bs, 1H, Het-5'), 6.91 (d, 1H, $J = 7.4$ Hz, H-6). ^{13}C NMR (100 MHz, CDCl_3): δ 147.3, 146.0, 137.7, 137.6, 135.8, 132.8, 131.7, 130.7, 130.4, 128.1, 125.2, 122.1, 119.6, 118.5, 118.4, 109.9, 105.5. MS : $326[\text{M}]^+$. Anal. Calcd for $\text{C}_{19}\text{H}_{14}\text{N}_6$: C, 69.94 ; H, 4.29. Found: C, 70.06 ; H, 4.20.

***N*-[2-(4-fluorophenyl)imidazo[1,2-*a*]pyridin-5-yl]pyrazole 13.** Using the general procedure B, 6-bromo-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine **1a** (291 mg, 1.00 mmol) was coupled with pyrazole (68 mg, 1.00 mmol). The crude product was chromatographed on silica gel, eluting with dichloromethane and then with dichloromethane-methanol (99.5/0.5 then 99/1 v/v) to give 165 mg of **13** (59% yield) as white plates. Mp: 95-97°C. ^1H NMR (300 MHz, CDCl_3): δ 8.17 (s, 1H, H-3), 7.92 (dd, 2H, $J = 9-5.4$ Hz, F-Ph-2,6), 7.91 (d, 1H, $J = 2.1$ Hz, Het-3*), 7.87 (d, 1H, $J = 2.4$ Hz, Het-5*), 7.69 (dt, 1H, $J = 9-0.9$ Hz, H-8), 7.27 (dd, 1H, $J = 9-7.2$ Hz, H-7), 7.09 (t, 2H, $J = 9$ Hz, F-Ph-3,5), 6.83 (dd, 1H, $J = 7.2-0.9$ Hz, H-6), 6.58 (dd, 2H, $J = 2.4-2.1$ Hz, Het-4). ^{13}C NMR (75 MHz, CDCl_3): δ 163.0, 146.8, 145.3, 142.9, 133.2, 131.2, 129.8, 128.1, 124.6, 116.8, 115.8, 108.2, 106.7. Anal. Calcd for $\text{C}_{20}\text{H}_{13}\text{FN}_4$: C, 73.17; H, 3.96. Found: C, 73.02; H, 3.90.

***N*-[2-(4-fluorophenyl)imidazo[1,2-*a*]pyridin-5-yl]pyrrole 14.** Using the general procedure B, 6-bromo-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine **1a** (291 mg, 1.00 mmol) was coupled with pyrrole (69.4 μL , 67 mg, 1.00 mmol). The crude product was chromatographed on silica gel, eluting with ethyl acetate-pentane (50/50 v/v) to give 111 mg of **14** (40% yield) as white plates. Mp: 156-158°C. ^1H NMR (300 MHz, CDCl_3): δ 7.88 (dd, 2H, $J = 8.7-5.4$ Hz, F-Ph-2,6), 7.71 (s, 1H, H-3), 7.63 (bd, 1H, $J = 9$ Hz, H-8), 7.25 (dd, 1H, $J = 9-7.2$ Hz, H-7), 7.09 (t, 2H, $J = 8.7$ Hz, F-Ph-3,5), 7.06 (t, 2H, $J = 2.4$ Hz, Het-2,5), 6.74 (dd, 1H, $J = 7.2-0.9$ Hz, H-6), 6.47 (t, 2H, $J = 2.4$ Hz, Het-3,4). ^{13}C NMR (75 MHz, CDCl_3): δ 163.1 ($J = 246$ Hz, F-Ph-4), 147.1 (C-2*), 145.6 (C-8a*), 134.0 (C-5), 129.8 ($J = 3$ Hz, F-

Ph-1), 128.1 ($J = 8$ Hz, F-Ph-2,6), 125.1 (C-7), 121.4 (Het-2,5), 116.4 (C-8), 115.9 ($J = 21.7$ Hz, F-Ph-3,5), 111.5 (Het-3,4), 108.2 (C-6), 105.2 (C-3). Anal. Calcd for $C_{20}H_{13}FN_4$: C, 73.17; H, 3.96. Found: C, 72.91; H, 4.02.

***N*-[2-(4-fluorophenyl)imidazo[1,2-*a*]pyridin-5-yl]indole 15.** Using the general procedure B, 6-bromo-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine **1a** (291 mg, 1.00 mmol) was coupled with indole (117.2 mg, 1.00 mmol). The residue was chromatographed on silica gel, eluting with ethyl acetate-pentane (50/50 v/v) to give 171 mg of **15** (52% yield) as white plates. Mp: 133-135°C. 1H NMR (300 MHz, $CDCl_3$): δ 7.82 (dd, 2H, $J = 9-5.4$ Hz, F-Ph-2,6), 7.77 (m, 1H, Ind-4), 7.74 (d, 1H, $J = 9$ Hz, H-8), 7.42 (s, 1H, H-3), 7.35 (d, 1H, $J = 3.3$ Hz, Ind-2), 7.32 (dd, 1H, $J = 9-7.2$ Hz, H-7), 7.24 (m, 2H, Het-7,6*), 7.07 (m, 1H, Het-5*), 7.05 (t, 2H, $J = 9$ Hz, F-Ph-3,5), 6.89 (dd, 1H, $J = 7.2-0.9$ Hz, H-6), 6.84 (dd, 1H, $J = 3.3-0.6$ Hz, Het-3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.1, 147.1, 145.6, 136.2, 132.4, 129.8, 129.2, 128.1, 127.5, 125.0, 123.7, 121.9, 117.0, 115.9, 110.9, 110.4, 106.1, 105.8. Anal. Calcd for $C_{21}H_{14}FN_3$: C, 77.78; H, 4.32. Found: C, 77.61; H, 4.27.

***N*-[2-(4-fluorophenyl)imidazo[1,2-*a*]pyridin-5-yl]-7-azaindole 16.** Using the procedure B, 6-bromo-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine **1a** (291 mg, 1.00 mmol) was coupled with 7-azaindole (118 mg, 1.00 mmol). The crude product was chromatographed on silica gel, eluting with dichloromethane and then with dichloromethane-methanol (99:1 v/v) to give 180 mg of **16** (55% yield) as white plates. Mp: 205-207°C. 1H NMR (300 MHz, $CDCl_3$): δ 8.34 (dd, 1H, $J = 4.8-1.5$ Hz, Het-6), 8.08 (dd, 1H, $J = 7.8-1.5$ Hz, Het-4), 7.85 (dd, 2H, $J = 8.7-5.4$ Hz, F-Ph-2,6), 7.83 (bd, 1H, $J = 9$ Hz, H-8), 7.47 (d, 1H, $J = 3.4$ Hz, Het-2), 7.43 (s, 1H, H-3), 7.40 (dd, 1H, $J = 9-7.2$ Hz, H-7), 7.27 (dd, 1H, $J = 7.8-4.8$ Hz, Het-5), 7.07 (t, 2H, $J = 8.7$ Hz, F-Ph-3,5), 7.01 (dd, 1H, $J = 7.2-0.9$ Hz, H-6), 6.83 (d, 1H, $J = 3.4$ Hz, Het-3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.9, 148.0, 146.3, 144.6, 144.2, 131.2, 130.0, 128.9, 128.1, 127.8,

125.6, 121.1, 118.0, 116.7, 115.8, 115.6, 106.1, 104.3. Anal. Calcd for $C_{20}H_{13}FN_4$: C, 73.17; H, 3.96. Found: C, 73.01; H, 4.04.

2-(6-Chloropyridin-2-ylamino)-1-(4-fluorophenyl)ethanone 18. A mixture of 6-chloro-2-aminopyridine (0.5 g, 3.9 mmol) and *p*-fluorophenacyl bromide (0.93 g, 4.3 mmol) was refluxed in ethanol for 17 h. After cooling the solvent was removed under vacuum and the residue taken up in water and basified with sodium carbonate. The solution was extracted with dichloromethane, the organic layer dried over calcium chloride and evaporated to dryness. The residue was chromatographed on silica gel, eluting with dichloromethane to give 103 mg of **18** (10% yield) as white plates. Mp: 141-143°C. 1H NMR (200 MHz, $CDCl_3$): δ 8.14 (dd, 1H, $J = 9-5.3$ Hz, F-Ph-2,6), 7.40 (dd, 1H, $J = 8.2-7.5$ Hz, Pyr-4), 7.23 (t, 2H, $J = 8.4$ Hz, F-Ph-3,5), 6.66 (dd, 1H, $J = 7.5-0.6$ Hz, Pyr-5*), 6.49 (dd, 1H, $J = 8.2-0.6$ Hz, Pyr-3*), 5.65 (br.s., 1H, NH), 4.89 (d, 2H, $J = 4.3$ Hz, CH_2). Anal. Calcd for $C_{13}H_{10}ClFN_2O$: C, 58.98 ; H, 3.78. Found: C, 59.12 ; H, 3.67.

Crystal structure for compound 7

The structure of the imidazolyl compound **7** was confirmed by X-ray analysis (Tables 1-5, Figure 1).

Table S1. Crystal data and details of the structure determination for **7**.

Crystal Data	
Formula	C ₁₆ H ₁₁ F N ₄ , H ₂ O
Formula Weight	296.30
Crystal System	Triclinic
Space group	P-1 (No. 2)
a, b, c [Å]	7.247(8), 14.078(6), 14.564(7)
alpha, beta, gamma [°]	110.59(3), 90.06(8), 93.60(7)
V [Å ³]	1387.8(18)
Z	4
D(calc) [g.cm ⁻³]	1.418
Absorption coefficient μ (MoKa) [mm ⁻¹]	0.102
F(000)	616
Crystal Size [mm]	0.10 x 0.20 x 0.45
Data Collection	
Temperature (K)	296
Radiation [Å]	MoK α [0.71069]
Theta Max [°]	25
Dataset	0 : 8 ; -16 : 16 ; -17 : 17
Tot., Uniq. Data, R(int)	5269, 4852, 0.075
Observed data [I > 2 σ (I)]	2868
Refinement	
Refinement method	Full-matrix least-squares on F ²
Nref, Npar	4852, 409
Final R indices [I > 2 σ (I)]	R = 0.0519, wR2 = 0.1261
R indices (all data)	R = 0.1139, wR2 = 0.1458
Goodness-of-fit on F ²	1.090
weight	w = 1/[σ^2 (F _o ²)+(0.0586P) ² +0.1972P]

	where $P=(F_o^2+2F_c^2)/3$
Min. and Max. Resd. Dens. [$e^- \cdot \text{\AA}^{-3}$]	-0.205, 0.154

Table S2. Final coordinates and equivalent isotropic displacement parameters of the non-hydrogen atoms for **7**.

Atom	x	y	z	U(eq) [$\text{\AA}^2$]
F1_1	0.6708(3)	0.09244(14)	0.34318(15)	0.0857(9)
N1_1	0.5849(3)	0.54889(18)	0.35874(17)	0.0508(9)
N4_1	0.7163(3)	0.67557(17)	0.48607(16)	0.0445(8)
N9_1	0.7664(4)	0.95293(18)	0.56902(19)	0.0546(10)
N12_1	0.8503(4)	1.1160(2)	0.6076(2)	0.0727(11)
C2_1	0.6733(4)	0.5100(2)	0.4203(2)	0.0443(10)
C3_1	0.7531(4)	0.5867(2)	0.4989(2)	0.0483(11)
C5_1	0.7675(4)	0.7742(2)	0.5421(2)	0.0481(10)
C6_1	0.7147(4)	0.8495(2)	0.5115(2)	0.0482(10)
C7_1	0.6071(4)	0.8257(2)	0.4248(2)	0.0542(12)
C8_1	0.5559(4)	0.7279(2)	0.3708(2)	0.0535(11)
C8A_1	0.6130(4)	0.6492(2)	0.3998(2)	0.0456(10)
C10_1	0.8052(7)	0.9918(3)	0.6669(3)	0.095(2)
C11_1	0.8555(7)	1.0899(3)	0.6881(3)	0.0975(19)
C13_1	0.7981(5)	1.0315(2)	0.5373(3)	0.0622(12)
C1'_1	0.6736(4)	0.3999(2)	0.3992(2)	0.0451(10)
C2'_1	0.7603(4)	0.3624(2)	0.4631(2)	0.0520(11)
C3'_1	0.7614(4)	0.2586(2)	0.4438(2)	0.0552(11)
C4'_1	0.6734(5)	0.1940(2)	0.3610(2)	0.0564(11)
C5'_1	0.5834(5)	0.2270(2)	0.2962(2)	0.0643(14)
C6'_1	0.5850(4)	0.3303(2)	0.3155(2)	0.0569(11)
F2_2	0.5159(4)	0.98195(15)	0.09082(17)	0.1023(10)
N3_2	0.7977(3)	0.46329(17)	0.08560(16)	0.0451(8)
N5_2	0.7343(3)	0.51651(18)	-0.03802(17)	0.0486(9)
N7_2	0.9457(3)	0.23263(18)	0.11539(18)	0.0520(9)

N9_2	1.0866(4)	0.1763(2)	0.2189(2)	0.0703(12)
C14_2	0.8481(4)	0.3964(2)	0.1297(2)	0.0488(10)
C15_2	0.7593(4)	0.5632(2)	0.1271(2)	0.0498(10)
C21_2	0.9907(6)	0.0979(3)	0.1496(3)	0.0746(16)
C24_2	0.8854(4)	0.3017(2)	0.0711(2)	0.0457(10)
C25_2	0.8694(4)	0.2716(2)	-0.0316(2)	0.0531(11)
C26_2	0.8175(4)	0.3375(2)	-0.0747(2)	0.0525(11)
C27_2	0.6733(4)	0.6966(2)	0.0582(2)	0.0473(10)
C28_2	0.5736(5)	0.8882(2)	0.0786(3)	0.0674(16)
C29_2	0.7812(4)	0.4373(2)	-0.0155(2)	0.0456(10)
C30_2	0.6807(5)	0.7741(2)	0.1491(2)	0.0677(14)
C32_2	0.6192(4)	0.7193(2)	-0.0226(2)	0.0558(11)
C33_2	0.7208(4)	0.5944(2)	0.0504(2)	0.0454(10)
C36_2	1.0566(5)	0.2563(3)	0.1963(2)	0.0608(12)
C37_2	0.9038(5)	0.1299(2)	0.0852(3)	0.0658(12)
C40_2	0.5697(5)	0.8163(3)	-0.0120(3)	0.0662(12)
C41_2	0.6302(6)	0.8699(3)	0.1600(3)	0.0761(14)
O1_3	0.2475(3)	0.50297(19)	0.24286(18)	0.0686(9)
O2_3	0.0141(4)	0.6682(2)	0.3229(2)	0.0857(11)

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

Table S3. Hydrogen atom positions and isotropic displacement parameters for **7**.

Atom	x	y	z	U(iso) [Å ²]
H19_1	0.81920	0.58010	0.55090	0.0580
H5_1	0.83690	0.78950	0.59990	0.0580
H7_1	0.57100	0.87770	0.40450	0.0650
H8_1	0.48270	0.71280	0.31430	0.0640
H10_1	0.79820	0.95680	0.71050	0.1140
H11_1	0.88990	1.13480	0.75060	0.1170
H13_1	0.78410	1.02580	0.47200	0.0740
H2'_1	0.81890	0.40760	0.51980	0.0620
H3'_1	0.82090	0.23400	0.48660	0.0660
H5'_1	0.52270	0.18090	0.24060	0.0770
H6'_1	0.52580	0.35380	0.27180	0.0680
H14_2	0.85620	0.41580	0.19760	0.0590
H15_2	0.75930	0.60200	0.19360	0.0600
H21_2	0.98570	0.03080	0.14690	0.0890
H25_2	0.89460	0.20580	-0.07050	0.0640
H26_2	0.80610	0.31690	-0.14260	0.0630
H30_2	0.72070	0.76100	0.20390	0.0810
H32_2	0.61590	0.66900	-0.08460	0.0670
H36_2	1.10570	0.32170	0.23170	0.0730
H37_2	0.83030	0.09030	0.03130	0.0790
H40_2	0.53460	0.83150	-0.06640	0.0790
H41_2	0.63440	0.92110	0.22150	0.0910
H1A_3	0.268(5)	0.494(3)	0.175(3)	0.0820
H1B_3	0.351(5)	0.511(3)	0.273(3)	0.0820
H2A_3	0.069(6)	0.739(3)	0.348(3)	0.1030
H2B_3	0.088(6)	0.621(3)	0.302(3)	0.1030

Table S4. Bond distances (Angstrom) for **7**.

F1_1-C4'_1	1.359(4)	C5_1-C6_1	1.361(4)
F2_2-C28_2	1.361(4)	C6_1-C7_1	1.408(4)
O1_3-H1B_3	0.85(4)	C7_1-C8_1	1.351(4)
O1_3-H1A_3	0.96(4)	C8_1-C8A_1	1.401(4)
O2_3-H2A_3	0.99(5)	C10_1-C11_1	1.331(7)
O2_3-H2B_3	0.85(4)	C1'_1-C2'_1	1.388(4)
N1_1-C2_1	1.379(4)	C1'_1-C6'_1	1.392(4)
N1_1-C8A_1	1.328(4)	C2'_1-C3'_1	1.388(4)
N4_1-C8A_1	1.383(4)	C3'_1-C4'_1	1.357(4)
N4_1-C5_1	1.367(4)	C4'_1-C5'_1	1.370(5)
N4_1-C3_1	1.370(4)	C5'_1-C6'_1	1.380(4)
N9_1-C13_1	1.348(5)	C3_1-H19_1	0.9306
N9_1-C6_1	1.427(4)	C5_1-H5_1	0.9306
N9_1-C10_1	1.357(5)	C7_1-H7_1	0.9316
N12_1-C11_1	1.347(5)	C8_1-H8_1	0.9304
N12_1-C13_1	1.301(5)	C10_1-H10_1	0.9304
N3_2-C29_2	1.390(4)	C11_1-H11_1	0.9302
N3_2-C14_2	1.379(4)	C13_1-H13_1	0.9307
N3_2-C15_2	1.368(4)	C2'_1-H2'_1	0.9289
N5_2-C29_2	1.331(4)	C3'_1-H3'_1	0.9298
N5_2-C33_2	1.375(4)	C5'_1-H5'_1	0.9296
N7_2-C24_2	1.431(4)	C6'_1-H6'_1	0.9295
N7_2-C37_2	1.369(5)	C14_2-C24_2	1.351(4)
N7_2-C36_2	1.354(4)	C15_2-C33_2	1.371(4)
N9_2-C36_2	1.310(5)	C21_2-C37_2	1.346(6)
N9_2-C21_2	1.356(5)	C24_2-C25_2	1.406(4)
C2_1-C1'_1	1.470(5)	C25_2-C26_2	1.360(4)

C2_1-C3_1	1.364(4)	C26_2-C29_2	1.408(4)
C27_2-C32_2	1.386(4)	C21_2-H21_2	0.9299
C27_2-C33_2	1.466(5)	C25_2-H25_2	0.9299
C27_2-C30_2	1.387(4)	C26_2-H26_2	0.9295
C28_2-C40_2	1.350(6)	C30_2-H30_2	0.9299
C28_2-C41_2	1.366(6)	C32_2-H32_2	0.9303
C30_2-C41_2	1.375(6)	C36_2-H36_2	0.9299
C32_2-C40_2	1.389(6)	C37_2-H37_2	0.9299
C14_2-H14_2	0.9294	C40_2-H40_2	0.9294
C15_2-H15_2	0.9297	C41_2-H41_2	0.9305

Table S5. Bond angles (°) for **7**.

H1A_3-O1_3-H1B_3	109(3)	N4_1-C8A_1-C8_1	117.8(3)
H2A_3-O2_3-H2B_3	117(4)	N1_1-C8A_1-C8_1	131.3(3)
C2_1-N1_1-C8A_1	105.4(2)	N1_1-C8A_1-N4_1	110.9(3)
C3_1-N4_1-C8A_1	106.9(2)	N9_1-C10_1-C11_1	106.4(4)
C3_1-N4_1-C5_1	130.3(2)	N12_1-C11_1-C10_1	111.5(4)
C5_1-N4_1-C8A_1	122.8(3)	N9_1-C13_1-N12_1	112.9(3)
C10_1-N9_1-C13_1	105.3(3)	C2'_1-C1'_1-C6'_1	118.0(3)
C6_1-N9_1-C13_1	127.6(3)	C2_1-C1'_1-C2'_1	120.8(3)
C6_1-N9_1-C10_1	127.0(3)	C2_1-C1'_1-C6'_1	121.2(3)
C11_1-N12_1-C13_1	104.0(3)	C1'_1-C2'_1-C3'_1	121.2(3)
C14_2-N3_2-C15_2	129.7(2)	C2'_1-C3'_1-C4'_1	118.4(3)
C14_2-N3_2-C29_2	123.2(3)	C3'_1-C4'_1-C5'_1	122.8(3)
C15_2-N3_2-C29_2	107.2(2)	F1_1-C4'_1-C3'_1	118.4(3)
C29_2-N5_2-C33_2	105.4(2)	F1_1-C4'_1-C5'_1	118.8(3)
C24_2-N7_2-C37_2	127.4(3)	C4'_1-C5'_1-C6'_1	118.4(3)
C24_2-N7_2-C36_2	126.5(3)	C1'_1-C6'_1-C5'_1	121.2(3)
C36_2-N7_2-C37_2	106.1(3)	C2_1-C3_1-H19_1	126.96
C21_2-N9_2-C36_2	104.8(3)	N4_1-C3_1-H19_1	126.79
N1_1-C2_1-C3_1	110.6(3)	C6_1-C5_1-H5_1	120.73
N1_1-C2_1-C1'_1	121.7(3)	N4_1-C5_1-H5_1	120.73
C3_1-C2_1-C1'_1	127.7(3)	C6_1-C7_1-H7_1	119.81
N4_1-C3_1-C2_1	106.3(3)	C8_1-C7_1-H7_1	119.77
N4_1-C5_1-C6_1	118.5(3)	C7_1-C8_1-H8_1	119.97
N9_1-C6_1-C5_1	119.4(3)	C8A_1-C8_1-H8_1	119.98
N9_1-C6_1-C7_1	120.3(3)	C11_1-C10_1-H10_1	126.83
C5_1-C6_1-C7_1	120.3(3)	N9_1-C10_1-H10_1	126.81
C6_1-C7_1-C8_1	120.4(3)	N12_1-C11_1-H11_1	124.24

C7_1-C8_1-C8A_1	120.1(3)	C10_1-C11_1-H11_1	124.29
N12_1-C13_1-H13_1	123.64	C27_2-C32_2-C40_2	120.7(3)
N9_1 -C13_1-H13_1	123.50	C15_2-C33_2-C27_2	126.1(3)
C3'_1-C2'_1-H2'_1	119.38	N5_2-C33_2-C27_2	122.9(3)
C1'_1-C2'_1-H2'_1	119.38	N5_2-C33_2-C15_2	111.0(3)
C2'_1-C3'_1-H3'_1	120.77	N7_2-C36_2-N9_2	112.1(3)
C4'_1-C3'_1-H3'_1	120.87	N7_2-C37_2-C21_2	105.9(3)
C4'_1-C5'_1-H5'_1	120.78	C28_2-C40_2-C32_2	118.9(4)
C6'_1-C5'_1-H5'_1	120.83	C28_2-C41_2-C30_2	118.5(4)
C5'_1-C6'_1-H6'_1	119.37	C24_2-C14_2-H14_2	121.00
C1'_1-C6'_1-H6'_1	119.43	N3_2-C14_2-H14_2	121.11
N3_2-C14_2-C24_2	117.9(3)	C33_2-C15_2-H15_2	127.02
N3_2-C15_2-C33_2	105.8(3)	N3_2-C15_2-H15_2	127.15
N9_2-C21_2-C37_2	111.1(4)	N9_2-C21_2-H21_2	124.44
C14_2-C24_2-C25_2	121.0(3)	C37_2-C21_2-H21_2	124.43
N7_2-C24_2-C25_2	120.2(3)	C24_2-C25_2-H25_2	119.57
N7_2-C24_2-C14_2	118.7(3)	C26_2-C25_2-H25_2	119.61
C24_2-C25_2-C26_2	120.8(3)	C25_2-C26_2-H26_2	120.36
C25_2-C26_2-C29_2	119.4(3)	C29_2-C26_2-H26_2	120.27
C30_2-C27_2-C33_2	119.7(3)	C41_2-C30_2-H30_2	119.26
C30_2-C27_2-C32_2	118.0(3)	C27_2-C30_2-H30_2	119.29
C32_2-C27_2-C33_2	122.3(3)	C27_2-C32_2-H32_2	119.60
F2_2-C28_2-C41_2	118.1(4)	C40_2-C32_2-H32_2	119.68
C40_2-C28_2-C41_2	122.3(4)	N7_2-C36_2-H36_2	123.97
F2_2-C28_2-C40_2	119.6(4)	N9_2-C36_2-H36_2	123.93
N5_2-C29_2-C26_2	131.7(3)	C21_2-C37_2-H37_2	127.00
N3_2-C29_2-N5_2	110.6(3)	N7_2-C37_2-H37_2	127.11
N3_2-C29_2-C26_2	117.7(3)	C28_2-C40_2-H40_2	120.51

C27_2-C30_2-C41_2	121.4(3)	C32_2-C40_2-H40_2	120.55
C30_2-C41_2-H41_2	120.67	C28_2-C41_2-H41_2	120.79

Figure S1. Ellipsoid representation of the non-hydrogen atoms and atomic labelling of **7** (X-Ray numbering).