Supporting Information

Selective Synthesis of Pyridyl Pyridones and Oxydipyridines by Transition-Metal-Free Hydroxylation and Arylation of 2-Fluoropyridine Derivatives

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The X-ray crystallographic structures for **2k**. ORTEP representation with 50% probability thermal ellipsoids. Solvent and hydrogen are omitted for clarity. Solvent and hydrogen are omitted for clarity. Crystal data have been deposited to CCDC, number 1918627.

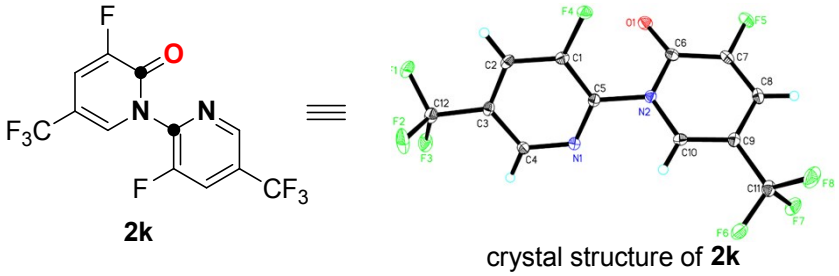


Table 1. Crystal Data and Structure Refinement for 2k

Identification code	**2k**
Empirical formula	$C_{12}H_4F_8N_2O$
Formula weight	344.17
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	I2/a
a/Å	14.0204(10)
b/Å	7.9073(5)
c/Å	22.6326(16)
α/	90
β/	103.220(7)
γ/	90
Volume/Å^3	2442.6(3)
Z	8
ρ_{calc}g/cm^3	1.872
μ/mm^{-1}	0.204

F(000)	1360.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/	5.474 to 49.99
Index ranges	-14 ≤ h ≤ 16, -8 ≤ k ≤ 9, -26 ≤ l ≤ 23
Reflections collected	4381
Independent reflections	2121 [R_{int} = 0.0235, R_{sigma} = 0.0361]
Data/restraints/parameters	2121/0/208
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0360, wR_2 = 0.0855
Final R indexes [all data]	R_1 = 0.0443, wR_2 = 0.0912
Largest diff. peak/hole / e Å^{-3}	0.25/-0.21

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2k.

Atom	*x*	*y*	*z*	U(eq)
F4	5684.0(7)	3636.7(13)	8360.4(5)	23.1(3)
F6	3017.7(8)	3720.5(15)	5653.6(5)	31.6(3)
F5	7008.2(8)	6302.2(15)	6766.1(5)	31.4(3)
F7	3850.0(8)	5302.5(15)	5182.0(5)	31.2(3)
F3	2652.6(8)	7404.9(16)	9220.8(5)	33.9(3)
F1	3786.1(8)	5945.6(17)	9795.3(5)	36.4(3)
F8	4266.8(9)	2722.0(16)	5364.3(5)	38.7(3)
F2	2478.7(9)	4735.4(17)	9291.2(6)	41.9(4)
O1	6260.5(9)	6371.8(17)	7772.3(6)	23.4(3)
N2	4831.9(10)	5147.2(19)	7245.6(6)	16.2(3)
N1	3577.7(10)	6137(2)	7691.2(7)	18.4(4)
C1	4872.8(12)	4575(2)	8318.4(8)	17.2(4)

C9	4570.3(13)	4609(2)	6191.4(8)	18.2(4)
C6	5786.2(13)	5784(2)	7296.5(8)	18.1(4)
C10	4236.4(13)	4626(2)	6704.2(8)	17.3(4)
C3	3611.0(13)	5673(2)	8739.0(8)	17.7(4)
C5	4415.8(12)	5290(2)	7766.4(8)	16.6(4)
C4	3172.2(13)	6301(2)	8167.2(8)	18.5(4)
C2	4480.8(13)	4780(2)	8816.8(8)	19.5(4)
C8	5543.3(14)	5156(2)	6202.6(8)	22.0(4)
C7	6101.0(13)	5696(2)	6732.7(9)	20.9(4)
C11	3922.7(14)	4088(3)	5603.7(8)	23.0(5)
C12	3129.5(14)	5938(3)	9261.2(8)	23.5(5)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 2k

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F4	20.7(6)	24.7(6)	22.5(6)	0.4(5)	2.2(4)	7.7(5)
F6	28.2(6)	45.8(8)	19.5(6)	-1.1(5)	2.4(5)	-11.4(6)
F5	16.9(6)	44.8(8)	35.1(7)	-0.3(6)	11.1(5)	-4.0(5)
F7	39.4(7)	35.6(7)	17.5(6)	9.2(5)	4.5(5)	-1.3(6)
F3	42.5(7)	35.5(8)	27.6(7)	-2.9(5)	15.8(5)	10.7(6)
F1	37.5(7)	57.2(9)	13.7(6)	-2.3(6)	4.3(5)	5.3(6)
F8	51.4(8)	34.9(8)	26.3(6)	-12.2(6)	1.6(5)	11.4(6)
F2	54.4(8)	43.6(8)	37.2(7)	-8.0(6)	30.3(6)	-21.2(7)
O1	19.0(7)	25.1(8)	25.4(8)	-5.5(6)	3.5(6)	-2.9(6)
N2	16.9(7)	17.1(8)	14.8(8)	0.7(7)	3.8(6)	-0.9(7)
N1	17.8(8)	21.3(9)	16.5(8)	0.7(7)	4.4(6)	0.4(7)
C1	18.3(9)	13.8(10)	18.2(9)	-1.2(8)	1.7(7)	2.0(8)

C9	22.2(9)	15.7(10)	17.1(10)	1.0(8)	5.6(7)	2.6(8)
C6	17.6(9)	13.7(10)	22.9(10)	0.6(8)	4.2(8)	2.5(8)
C10	15.8(9)	16.3(10)	18.7(9)	1.5(8)	1.6(7)	-0.1(8)
C3	22.5(9)	16.8(10)	14.2(9)	-2.0(8)	4.9(7)	-5.5(8)
C5	17.9(9)	16.5(10)	15.7(9)	-1.4(8)	4.3(7)	-3.7(8)
C4	16.5(9)	20.5(10)	18.9(9)	-0.8(8)	5.0(7)	-0.5(8)
C2	22.9(10)	19.6(10)	13.9(9)	0.0(8)	0.1(7)	-4.5(9)
C8	25.0(10)	22.8(11)	21.5(10)	0.2(9)	11.8(8)	2.5(9)
C7	15.4(9)	20.5(11)	28.9(11)	1.7(9)	9.2(8)	1.3(8)
C11	28.2(11)	22.0(11)	19.7(10)	1.8(9)	7.4(8)	3.9(9)
C12	26.9(10)	24.5(11)	19.3(10)	-1.1(9)	6.1(8)	-3.6(10)

Table 4 Bond Lengths for 2k.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F4	C1	1.343(2)	N1	C5	1.329(2)
F6	C11	1.331(2)	N1	C4	1.334(2)
F5	C7	1.345(2)	C1	C5	1.387(2)
F7	C11	1.341(2)	C1	C2	1.373(3)
F3	C12	1.332(2)	C9	C10	1.347(2)
F1	C12	1.342(2)	C9	C8	1.426(3)
F8	C11	1.346(2)	C9	C11	1.487(3)
F2	C12	1.330(2)	C6	C7	1.444(3)
O1	C6	1.221(2)	C3	C4	1.391(3)
N2	C6	1.410(2)	C3	C2	1.385(3)
N2	C10	1.379(2)	C3	C12	1.504(3)
N2	C5	1.434(2)	C8	C7	1.343(3)

Table 5 Bond Angles for 2k.

Atom	Atom	Atom	Angle/	Atom	Atom	Atom	Angle/
C6	N2	C5	117.50(14)	C1	C5	N2	121.14(16)
C10	N2	C6	123.37(15)	N1	C4	C3	122.48(17)
C10	N2	C5	118.46(14)	C1	C2	C3	117.52(16)
C5	N1	C4	118.22(15)	C7	C8	C9	118.13(17)
F4	C1	C5	119.88(16)	F5	C7	C6	114.16(16)
F4	C1	C2	119.92(15)	F5	C7	C8	120.89(17)
C2	C1	C5	120.17(17)	C8	C7	C6	124.85(17)
C10	C9	C8	120.08(16)	F6	C11	F7	107.32(15)
C10	C9	C11	120.80(17)	F6	C11	F8	107.17(16)
C8	C9	C11	119.07(16)	F6	C11	C9	112.54(15)
O1	C6	N2	121.56(17)	F7	C11	F8	105.30(15)
O1	C6	C7	125.66(17)	F7	C11	C9	111.69(16)
N2	C6	C7	112.75(15)	F8	C11	C9	112.37(15)
C9	C10	N2	120.64(16)	F3	C12	F1	106.74(16)
C4	C3	C12	119.93(16)	F3	C12	C3	112.08(16)
C2	C3	C4	119.29(17)	F1	C12	C3	111.72(15)
C2	C3	C12	120.76(16)	F2	C12	F3	106.65(16)
N1	C5	N2	116.63(15)	F2	C12	F1	107.14(16)
N1	C5	C1	122.24(17)	F2	C12	C3	112.15(16)

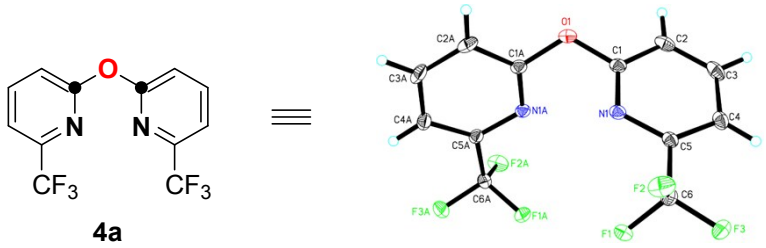
Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2k.

Atom	*x*	*y*	*z*	U(eq)

H10	3598.07	4282.43	6692.92	21
H4	2573.7	6855.02	8114.68	22
H2	4787.76	4335.66	9192.72	23
H8	5785.02	5138.84	5852.71	26

F. X-ray Crystallographic Data of 4a

The X-ray crystallographic structures for **4a**. ORTEP representation with 50% probability thermal ellipsoids. Solvent and hydrogen are omitted for clarity. Solvent and hydrogen are omitted for clarity. Crystal data have been deposited to CCDC, number 1918628.



4a crystal structure of **4a**

Table 7. Crystal Data and Structure Refinement for 4a

Identification code	**4a**
Empirical formula	$C_{12}H_6F_6N_2O$
Formula weight	308.19
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	C2/c
a/Å	10.9802(18)
b/Å	11.6601(11)
c/Å	10.2792(18)
α/	90
β/	114.43(2)

γ/	90
Volume/Å^3	1198.2(4)
Z	4
ρ_{calc}g/cm^3	1.708
μ/mm^{-1}	0.174
F(000)	616.0
Crystal size/mm^3	0.14 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/	5.368 to 49.954
Index ranges	-11 ≤ h ≤ 13, -13 ≤ k ≤ 13, -12 ≤ l ≤ 12
Reflections collected	2098
Independent reflections	1055 [R_{int} = 0.0280, R_{sigma} = 0.0357]
Data/restraints/parameters	1055/0/96
Goodness-of-fit on F^2	1.017
Final R indexes [I>=2σ (I)]	R_1 = 0.0402, wR_2 = 0.1021
Final R indexes [all data]	R_1 = 0.0459, wR_2 = 0.1073

Table 8 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 4a.

Atom	*x*	*y*	*z*	U(eq)
F1	4637.0(10)	1207.6(8)	4312.1(10)	33.4(3)
F3	5823.4(11)	1299.2(9)	6580.8(10)	35.8(3)
F2	3969.6(10)	2224.2(9)	5629.7(11)	38.2(4)
O1	5000	5016.5(14)	2500	29.2(4)
N1	5104.9(14)	3488.5(12)	3975.0(14)	22.3(4)
C5	5781.0(17)	2947.5(14)	5223.4(16)	22.1(4)
C1	5684.1(17)	4406.7(15)	3745.9(17)	22.9(4)

C6	5061.0(18)	1921.7(15)	5435.6(17)	25.9(4)
C2	6897.2(18)	4855.1(16)	4696.1(18)	29.3(5)
C4	7002.3(18)	3293.9(16)	6246.5(18)	27.6(4)
C3	7555.9(18)	4282.2(17)	5965(2)	32.7(5)

Table 9 Anisotropic Displacement Parameters ($Å^2×10^3$) for 4a.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1	36.0(7)	23.4(6)	32.5(6)	-2.6(4)	6.0(5)	-8.5(5)
F3	37.2(7)	31.7(7)	31.4(6)	8.6(4)	6.9(5)	2.3(5)
F2	28.4(7)	33.2(6)	58.5(7)	6.1(5)	23.5(6)	0.4(5)
O1	36.4(11)	17.0(9)	32.4(9)	0	12.4(8)	0
N1	18.4(8)	18.1(7)	28.0(8)	-2.5(6)	7.2(6)	0.9(6)
C5	19.0(10)	21.3(9)	24.7(9)	-4.6(7)	7.9(7)	1.2(7)
C1	22.0(10)	18.6(9)	28.4(9)	-3.2(7)	10.7(7)	2.7(7)
C6	21.9(10)	25.6(10)	26.2(9)	1.4(7)	6.1(7)	2.3(8)
C2	26.0(11)	24.0(10)	42.0(10)	-10.7(8)	18.2(8)	-8.1(8)
C4	21.3(10)	30.7(10)	25.8(9)	-5.7(7)	4.8(7)	1.0(8)
C3	20.8(10)	35.9(11)	36.5(10)	-14.9(9)	6.9(8)	-8.2(8)

Table 10 Bond Lengths for 4a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	C6	1.3413(19)	N1	C1	1.315(2)
F3	C6	1.3411(19)	C5	C6	1.499(3)
F2	C6	1.341(2)	C5	C4	1.379(2)
O1	$C1^1$	1.3836(18)	C1	C2	1.388(2)

O1	C1	1.3836(18)	C2	C3	1.375(3)
N1	C5	1.345(2)	C4	C3	1.388(3)

Table 11 Bond Angles for 4a.

Atom	Atom	Atom	Angle/	Atom	Atom	Atom	Angle/
C1[1]	O1	C1	118.15(17)	F1	C6	C5	112.73(13)
C1	N1	C5	115.83(14)	F3	C6	F1	106.75(14)
N1	C5	C6	113.39(14)	F3	C6	F2	106.48(13)
N1	C5	C4	124.72(16)	F3	C6	C5	112.60(14)
C4	C5	C6	121.87(16)	F2	C6	C5	111.68(14)
O1	C1	C2	116.97(15)	C3	C2	C1	117.39(16)
N1	C1	O1	117.80(14)	C5	C4	C3	117.11(17)
N1	C1	C2	125.11(15)	C2	C3	C4	119.82(16)
F1	C6	F2	106.15(13)				

Table 12 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 4a.

Atom	*x*	*y*	*z*	U(eq)
H2	7250.61	5517.16	4483.02	35
H4	7436.28	2883.29	7088.95	33
H3	8370.29	4556.04	6632.3	39