Supplementary Material (ESI) for Chemical Communications

Supporting Information of

Hydrogen Bonding Assisted Tautomerization of Pyridine Moieties in the Coordination Sphere of an Ir(I) Complex

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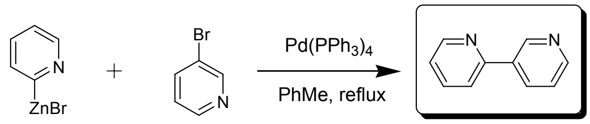
General procedures

All manipulations were carried out using standard Schlenk techniques or in nitrogen-filled glove-box, except where otherwise noted. All solvent were distilled under N_2 before use and stored glove-box. $CDCl_3$ was dried by 4Å molecular sieve and CD_2Cl_2, DMSO-d_6 were obtained in sealed ampules from CIL and were used without further purification. Air-sensitive product were stored and weighted in glove-box.

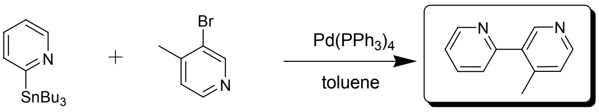
NMR spectra were obtained on a Bruker DPX 300, AMX400 or 500 spectrometer. All spectra were collected at 298K unless otherwise specified. The chemical shift is given as dimensionless δ values and is frequency referenced relative to TMS for ^1H and ^{13}C NMR. Assignment of ^{13}C signals were facilitated by HMQC and HMBC spectra. Elemental analyses were performed in the Division of Chemistry and Biological Chemistry, Nanyang Technological University. HRMS spectra were obtained in EI or ESI mode on a Finnigan MAT95XP GC/HRMS system (Thermo Electron Corp.). X-ray crystallographic analysis was performed on a Bruker X8 APEX diffractometer.

Synthesis of ligands 1, 2 and 3



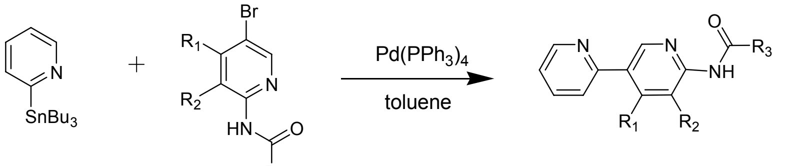
1

Ligand **1** was synthesized from Negishi coupling. 3-Bromopyridine (300 mg, 1.90 mmol) and $Pd(PPh_3)_4$ (110 mg, 5mol %) were dissolved in dry toluene (4 ml), to which was added via syringe a 2-Pyridylzinc bromide solution (0.5 M in THF, 3.8 ml, 1.90 mmol). The mixture was then stirred for 24 hours under reflux. All volatiles were then removed and water was added. The mixture was then extracted with dichloromethane and dried over sodium sulfate. Silica gel chromatography (EtOAc/hexane 1:1) gave **1** as a light-yellow oil (225 mg, 1.44 mmol, 76%). ^1H NMR (500 MHz, $CDCl_3$): δ 9.19 (d, J = 2.2 Hz, 1H), 8.73 (d, J = 4.7 Hz, 1H), 8.65 (d, J = 4.7 Hz, 1H), 8.33 (d, J = 8.0 Hz, 1H), 7.75-7.82 (m, 2H), 7.41 (dd, J = 8.0, J = 2.0 Hz, 1H), 7.29-7.31 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.8, 150.1, 149.9, 148.2, 137.1, 133.9, 134.4, 123.6, 122.9, 120.7. HRMS: 156.0722 (calculated 156.0682)



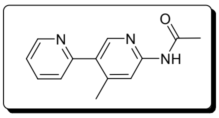
2

Ligand **2** was synthesized from the Stille coupling reaction. 3-Bromo-4-methylpyridine (200 mg, 1.16 mmol) and $Pd(PPh_3)_4$ (67 mg, 5 mol %) were dissolved in dry toluene (4 ml), and to which was added 2-(tri-*n*-butylstannyl)pyridine (475 mg, 1.28 mmol). The mixture was stirring for 24 hours under reflux. After removal of toluene under vacuum, the residue was dissolved in dichloromethane and the palladium black was removed by filtration through Celite. Analytically pure **2** was obtained as an oil after silica gel chromatography using hexanes/ethyl acetate (1:1) as an eluent. Yield: 139 mg (70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.71-8.72 (m, 1H), 8.58 (s, 1H), 8.48 (d, J = 5.1 Hz, 1H), 7.79 (td, J = 7.7, J = 1.8 Hz, 1H), 7.41 (d, J = 7.8 Hz, 1H), 7.29 (dd, J = 7.5, J = 4.7 Hz, 1H), 7.20 (d, J = 5.0 Hz, 1H), 2.40 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.8, 149.9, 149.6, 149.1, 145.3, 136.6, 136.3, 125.6, 124.1, 122.3, 19.8. HRMS: 170.0833 (calculated 170.0838).

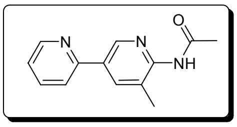


3a: R_1 = Me, R_2 = H, R_3 = Me
3b: R_1 = H, R_2 = Me, R_3 = Me
3c: R_1 = H, R_2 = Me, R_3 = Et
3d: R_1 = R_2 = H, R_3 = Me
3e: R_1 = R_2 =H, R_3 = Et

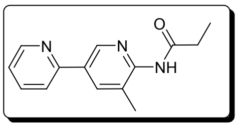
Ligands **3a-e** was synthesized through a directly analogous method for **2**.



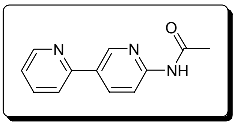
N-(4-methyl-5-(pyridin-2-yl)pyridin-2-yl)acetamide (**3a**), white solid, yield 65%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.92 (br, 1H, NH), 8.74 (d, J = 4.3 Hz, 1H), 8.31 (s, 1H), 8.19 (s, 1H), 7.80 (td, J = 7.8, J = 1.8 Hz, 1H), 7.41 (d, J = 7.8 Hz, 1H), 7.28-7.31 (m, 1H), 2.46 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.9, 156.4, 151.1, 149.7, 148.2, 147.9, 136.5, 132.8, 124.2, 122.2, 115.3, 24.8, 20.5. Anal. Calcd for $C_{13}H_{13}N_3O$ (227.3): C, 68.70; H, 5.77; N, 18.49; Found: C, 68.88; H, 5.31; N, 18.19.



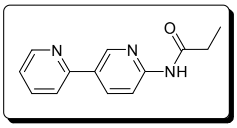
N-(3-methyl-5-(pyridin-2-yl)pyridin-2-yl)acetamide (**3b**), white solid, yield 60%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.83 (s, 1H), 8.80 (br, 1H, NH), 8.72 (d, J = 4.8 Hz, 1H), 8.21 (s, 1H), 7.79 (t, J = 6.7, 1H), 7.72 (d, J = 7.9 Hz, 1H), 7.28-7.30 (m, 1H), 2.38 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.1, 154.4, 150.1, 150.0, 144.0, 138.2, 137.0, 132.8, 127.7, 122.6, 120.4, 24.8, 20.5. Anal. Calcd for $C_{13}H_{13}N_3O$ (227.3): C, 68.70; H, 5.77; N, 18.49; Found: C, 68.56; H, 5.38; N, 18.30.



N-(3-methyl-5-(pyridin-2-yl)pyridin-2-yl)propionamide (**3c**), white solid, yield 67%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 9.05 (br, 1H, N*H*), 8.83 (d, *J* = 2.0 Hz, 1H), 8.70 (d, *J* = 4.2 Hz, 1H), 8.19 (s, 1H), 7.78 (td, *J* = 7.8, *J* = 1.7 Hz, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.27-7.29 (m, 1H), 2.56 (q, *J* = 7.4 Hz, 2H, C*H*$_2$), 2.37 (s, 3H), 1.26 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 173.4, 154.4, 150.3, 149.9, 143.9, 138.3, 137.1, 132.8, 128.2, 122.7, 120.4, 29.9, 18.4, 9.7. Anal. Calcd $C_{14}H_{15}N_3O$ (241.3): C, 69.69; H, 6.27; N, 17.41; Found: C, 69.78; H, 6.01; N, 17.50.



N-(5-(pyridin-2-yl)pyridin-2-yl)acetamide (**3d)**, white solid, yield 78%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.94 (s, 1H), 8.93 (br, 1H, N*H*), 8.70 (d, *J* = 4.7 Hz, 1H), 8.33-8.35 (m, 2H), 7.78 (t, *J* = 7.9 Hz, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.26-7.29 (m, 1H), 2.27 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 168.9, 154.4, 151.9, 150.0, 146.3, 137.0, 136.8, 131.1, 122.5, 120.0, 113.8, 24.8. Anal. Calcd $C_{12}H_{11}N_3O$ (213.2): C, 67.59; H, 5.20; N, 19.71; Found: C, 67.90; H, 5.31; N, 19.51.



N-(5-(pyridin-2-yl)pyridin-2-yl)propionamide (**3e)**, white solid, yield 70%. ^{1}H NMR (500 MHz, CDCl$_3$): 8.93 (s, 1H), 8.71 (d, *J* = 4.5 Hz, 1H), 8.67 (br, 1H, N*H*), 8.32-8.37 (m, 2H), 7.78 (td, *J* = 7.8, *J* = 1.6Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.26-7.29 (m, 1H), 2.48 (q, *J* = 7.5 Hz, 2H), 1.28 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 172.6, 154.5, 151.9, 149.9, 146.3, 137.0, 136.8, 131.0, 122.5, 120.1, 113.7, 30.8, 9.4. Anal. Calcd $C_{13}H_{13}N_3O$ (227.3): C, 68.70; H, 5.77; N, 18.49; Found C, 68.51; H, 5.83; N, 18.64.

Synthesis of iridium complexes 4a-e

General procedure: To a stirred solution of ligands **3a-e** (0.2mmol) in dry acetone (3ml) was added an acetone solution (2 mL) of Ir(COD)$_2$BF$_4$ (0.2 mmol) at room temperature. After stirred for 1 h, the solution became dark green and dark green to black precipitates formed. The solution was concentrated to ca. 0.5 mL, followed by addition of diethyl ether (5 mL). Filtration gives complexes **4a-e** in nearly quantitative yield.

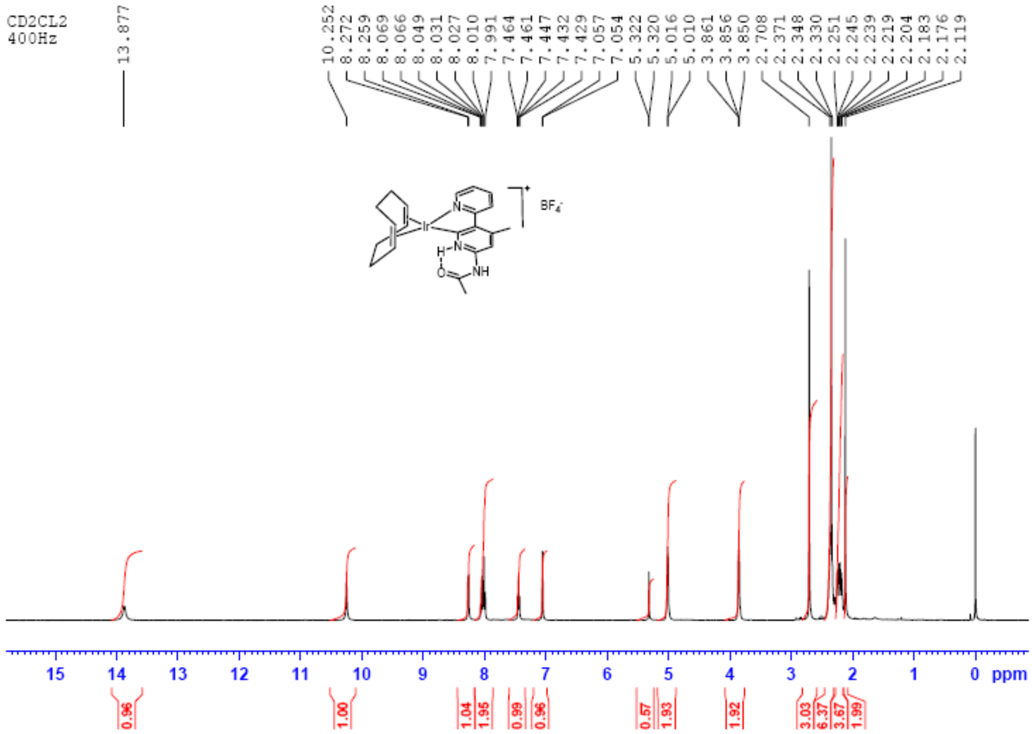
Complex 4a: Complex **4a** was synthesized by following the above general procedure using **3a** and Ir(COD)$_2$BF$_4$ in acetone. Yield: 98%. Single crystals suitable for X-ray analysis were obtained by slow diffusion of ether into a CH$_2$Cl$_2$ solution of **4a** after one day. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 13.9 (br, 1H, N*H* of carbene), 10.3 (br, 1H, N*H* of amide), 8.26 (d, *J* = 5.2 Hz, 1H), 7.99-8.06 (m, 2H), 7.44 (td, *J* = 7.8, *J* = 1.4 Hz, 1H), 7.05 (d, *J* = 1.4 Hz, 1H), 5.01 (d, *J* = 2.4 Hz, 2H, COD), 3.85 (t, *J* = 2.3 Hz, 2H, COD), 2.71 (s, 3H, C*H*$_3$), 2.34 (s, 3H, C*H*$_3$), 2.33-2.37 (m, 3H, COD), 2.17-2.25 (m, 3H, COD), 2.12 (s, 2H, COD). ^{13}C NMR (75 MHz, CD$_2$Cl$_2$): δ 180.0 (Ir-*C*), 175.2, 164.4, 151.8, 150.7, 146.6, 142.2, 141.0, 124.6, 123.5, 112.6, 91.1, 63.9, 32.8, 30.0, 24.1 ppm. Anal. Calcd for C$_{21}$H$_{25}$BF$_4$IrN$_3$O (614.5): C, 41.05; H, 4.10; N, 6.84; Found: C, 41.21; H, 4.31; N, 6.48.

Complex 4b. Complex **4b** was synthesized by following the above general procedure using **3a** and Ir(COD)$_2$BF$_4$ in acetone. Yield: 95%. ^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ 14.2 (br, 1H, N*H* of carbene), 10.8 (br, 1H, N*H* of amide), 8.72 (s, 1H), 8.66 (d, *J* = 5.4 Hz, 1H), 8.33 (d, *J* = 8.0Hz, 1H), 8.14 (t, *J* = 7.7 Hz, 1H), 7.51 (t, *J* = 6.3 Hz, 1H), 3.80 (br, 4H, COD), 2.35 (s, 3H, CH$_3$), 2.34 (s, 3H), 2.27-2.29 (m, 3H, COD), 2.01-2.08 (m, 5H, COD). ^{13}C NMR (75 MHz, DMSO-*d*$_6$): δ 175.4 (Ir-*C*), 175.0, 160.1, 150.5, 147.4, 140.4, 138.8, 137.8, 124.9, 121.1, 116.3, 33.0 (br), 24.8, 16.3. Anal. Calcd for C$_{21}$H$_{25}$BF$_4$IrN$_3$O (614.5): C, 41.05; H, 4.10; N, 6.84; Found: C, 41.43; H, 4.44; N, 6.61.

Complex 4c. Complex **4c** was synthesized by following the above general procedure using **3c** and Ir(COD)$_2$BF$_4$ in acetone. Yield: 97%. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 14.5 (br, 1H, N*H* of carbene), 9.6 (br, 1H, N*H* of amide), 8.32 (d, *J* = 4.3 Hz, 1H), 8.06-8.10 (m, 2H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 6.6 Hz, 1H), 4.92 (br, 2H, COD), 3.88 (br, 2H, COD), 2.84 (q, *J* = 7.4Hz, 2H, C*H*$_2$), 2.69 (s, 3H, C*H*$_3$), 2.38-2.56 (m, 4H, COD), 2.18-2.24 (m, 4H, COD), 1.25 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, CD$_2$Cl$_2$): δ 179.6, 177.6 (Ir-*C*), 163.3, 150.2, 147.2, 142.7, 141.1, 137.7, 125.0, 119.9, 118.4, 90.8, 62.6, 33.1, 30.1, 15.9, 8.3. Anal. Calcd for C$_{22}$H$_{27}$BF$_4$IrN$_3$O (628.5): C, 42.04; H, 4.33; N, 6.69; Found: C, 41.91; H, 4.52 N, 6.60.

Complex 4d. Complex **4d** was synthesized by following the above general procedure using **3d** and Ir(COD)$_2$BF$_4$ in acetone. Yield 96%. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 13.8 (br, 1H, N*H* of carbene), 12.0 (br, 1H, N*H* of amide), 8.74 (d, *J* = 8.6 Hz, 1H), 8.64 (d, *J* = 5.1 Hz, 1H), 8.30 (d, *J* = 7.9 Hz, 1H), 8.14 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 6.2 Hz, 1H), 7.04 (d, *J* = 8.5 Hz, 1H), 3.78 (br, 4H, COD), 2.27 (s, 3H, C*H*$_3$), 2.25-2.28 (m, 4H, COD), 2.03-2.08 (m, 4H, COD) ppm. ^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ 178.7 (Ir-*C*), 174.2, 160.0, 150.4, 149.0, 140.0, 137.9, 137.4, 124.9, 121.0, 106.4, 32.9, 24.7. Anal. Calcd for C$_{20}$H$_{23}$BF$_4$IrN$_3$O (600.4): C, 40.01; H, 3.86; N, 7.00; Found: C, 40.22; H, 3.91; N, 6.85.

Complex 4e. Complex **4e** was synthesized by following the above general procedure using **3e** and Ir(COD)$_2$BF$_4$ in acetone. Yield: 98%. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 14.2 (br, 1H, N*H* of carbene), 10.4 (br, 1H, N*H* of amide), 8.21-8.25 (m, 2H), 8.07 (td, *J* = 8.0, *J* = 1.5 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 6.0 Hz, 1H), 7.30 (dd, *J* = 8.7, *J* = 2.0 Hz, 1H), 5.09 (br, 2H, COD), 3.93 (br, 2H, COD), 2.70 (q, *J* = 7.4 Hz, 1H), 2.36-2.41 (m, 4H, COD), 2.19-2.28 (m, 4H, COD), 1.24 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 178.6 (Ir-*C*), 177.6, 160.0, 150.4, 149.0, 139.9, 137.8, 137.4, 124.8, 121.0, 106.4, 33.0, 31.2, 8.9. Anal. Calcd for $C_{21}H_{25}BF_4IrN_3O$ (614.5): C, 41.05; H, 4.10; N, 6.84; Found 41.24; H, 4.01; N, 6.99.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7.464
7.461
7.447
7.432
7.429
7.057
7.054
5.322
5.320
5.016
5.010
3.861
3.856
3.850
2.708
2.371
2.348
2.330
2.251
2.245
2.239
2.219
2.204
2.183
2.176
2.119
N
Ir
H
N
O
NH
BF4-
+
15
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12
11
10
9
8
7
6
5
4
3
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0
ppm
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1.92
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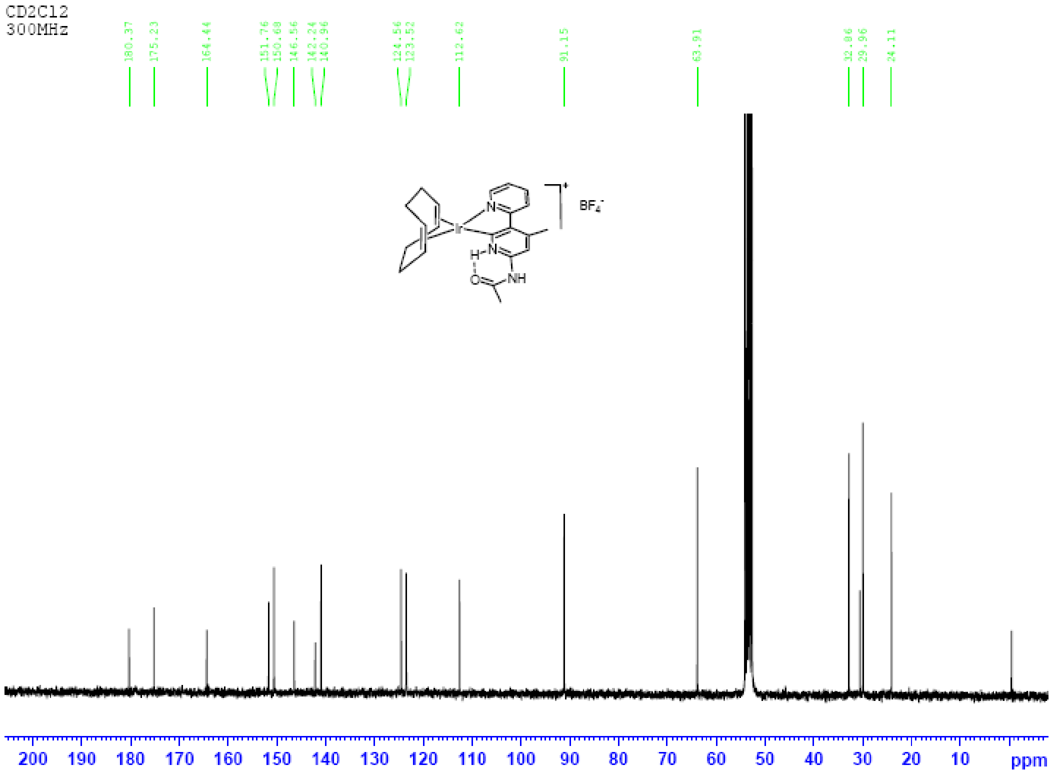
1.99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91.15
63.91
32.96
29.96
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H
N
O
NH
BF4-
+
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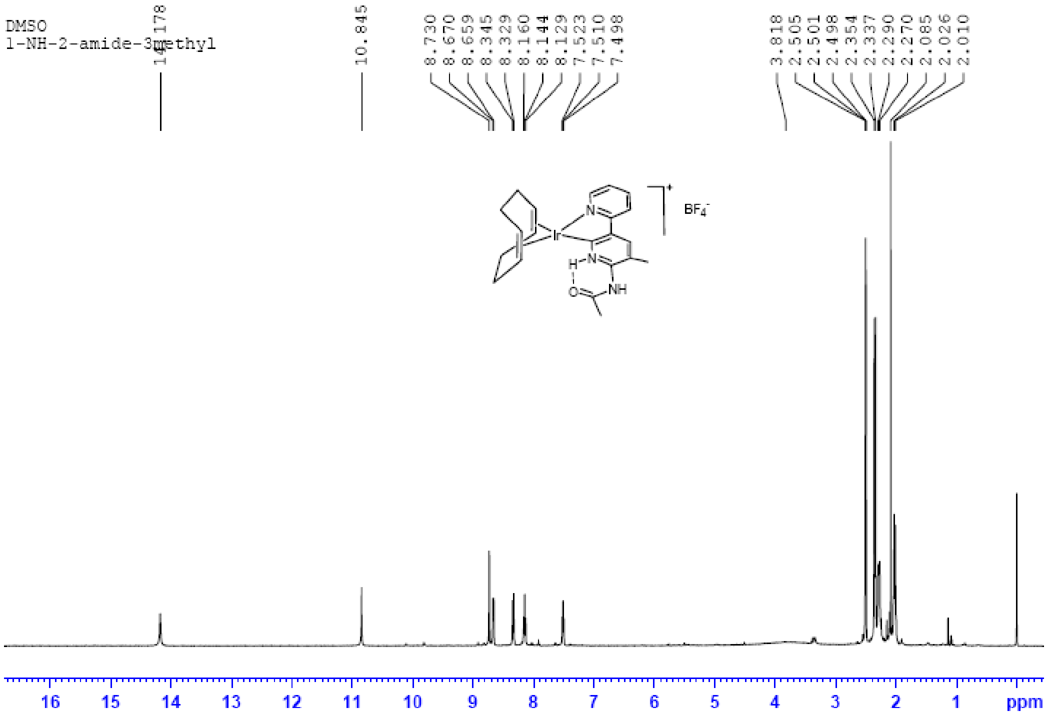
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2.505
2.501
2.498
2.354
2.337
2.290
2.270
2.085
2.026
2.010
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Ir
H
N
O
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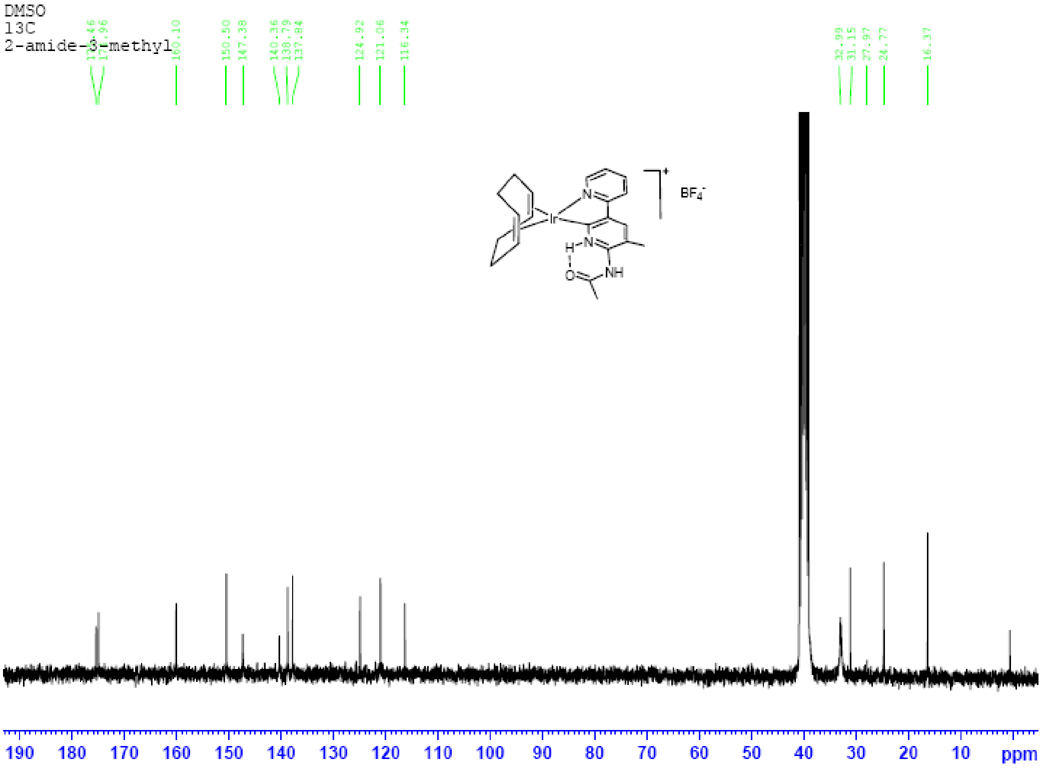
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137.84
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116.34
32.99
31.15
27.97
24.77
16.97
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Ir
H
N
O
NH
+
BF4-
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70
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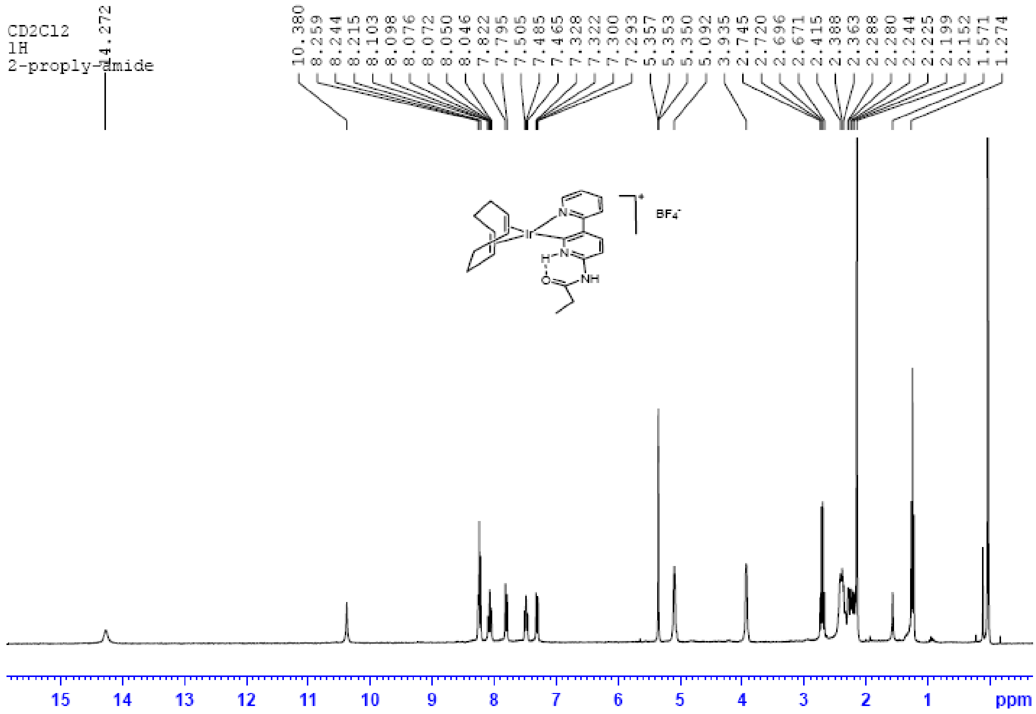
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8.046
7.822
7.795
7.505
7.485
7.465
7.328
7.322
7.300
7.293
5.357
5.353
5.350
5.092
3.935
2.745
2.720
2.696
2.671
2.415
2.388
2.363
2.288
2.280
2.244
2.225
2.199
2.152
1.571
1.274
Ir
N
H
O
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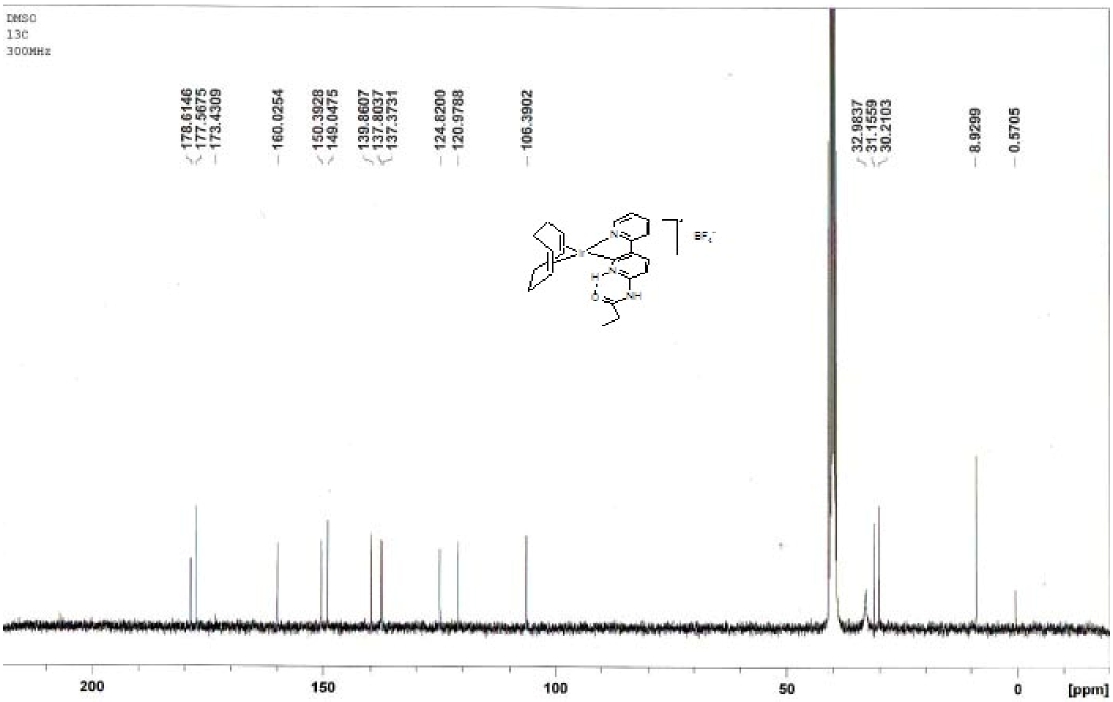
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137.3731
124.8200
120.9788
106.3902
32.9837
31.1559
30.2103
8.9299
0.5705
Ir
N
H
O
NH
BF4-
+
200
150
100
50
0
[ppm]

Table 1. Crystal data and structure refinement for complex **4**a.

Empirical formula	$C_{21}H_{25}BF_4IrN_3O$	
Formula weight	614.45	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 7.7588(2) Å	α= 90°.
	b = 16.9174(5) Å	β= 103.7470(10)°.
	c = 15.9163(5) Å	γ = 90°.
Volume	2029.31(10) $Å^3$	
Z	4	
Density (calculated)	2.011 Mg/m^3	
Absorption coefficient	6.635 mm^{-1}	
F(000)	1192	
Crystal size	0.30 x 0.04 x 0.04 mm^3	
Theta range for data collection	2.41 to 30.54°.	
Index ranges	-11<=h<=11, -24<=k<=24, -20<=l<=22	
Reflections collected	32967	
Independent reflections	6170 [R(int) = 0.0256]	
Completeness to theta = 30.54°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7772 and 0.2408	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6170 / 77 / 343	
Goodness-of-fit on F^2	1.061	
Final R indices [I>2sigma(I)]	R1 = 0.0179, wR2 = 0.0411	
R indices (all data)	R1 = 0.0246, wR2 = 0.0451	
Largest diff. peak and hole	1.377 and -0.610 e•$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **4a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	7498(1)	10208(1)	2914(1)	18(1)
B(1)	1336(5)	7364(2)	2333(2)	35(1)
C(1)	8340(30)	10538(8)	1731(10)	38(4)
C(2)	6801(17)	10959(9)	1745(8)	26(2)
C(1A)	8470(20)	10579(7)	1762(9)	36(3)
C(2A)	6717(18)	10834(9)	1670(8)	37(3)
C(3)	5336(11)	10557(5)	1062(5)	31(2)
C(4)	4289(12)	9961(6)	1492(5)	32(2)
C(3A)	4759(11)	10614(4)	1264(5)	32(2)
C(4A)	4527(11)	9718(5)	1314(4)	29(2)
C(5)	5529(3)	9437(2)	2197(2)	29(1)
C(6)	7214(4)	9108(2)	2251(2)	27(1)
C(7A)	8376(13)	9068(7)	1587(6)	31(2)
C(8A)	8368(13)	9863(4)	1126(5)	30(2)
C(7)	7852(15)	9107(6)	1420(7)	31(2)
C(8)	9088(12)	9802(5)	1359(6)	33(2)
C(9)	9243(3)	11810(1)	3446(2)	25(1)
C(10)	9948(3)	12423(1)	3997(2)	29(1)
C(11)	9927(3)	12361(1)	4851(2)	30(1)
C(12)	9229(3)	11687(1)	5146(2)	26(1)
C(13)	8538(3)	11080(1)	4575(1)	19(1)
C(14)	7787(3)	10325(1)	4798(1)	19(1)
C(15)	7296(3)	9812(1)	4070(1)	18(1)
C(16)	7519(3)	10096(1)	5607(1)	20(1)
C(17)	7979(3)	10578(2)	6418(2)	26(1)
C(18)	6793(3)	9350(1)	5681(1)	22(1)
C(19)	6373(3)	8848(1)	4981(1)	20(1)
C(20)	5424(3)	7524(1)	4408(2)	27(1)
C(21)	4674(5)	6766(2)	4663(2)	41(1)
F(1)	2435(3)	6708(1)	2479(1)	54(1)
F(2)	-103(2)	7195(1)	1626(1)	38(1)
F(3)	680(3)	7530(1)	3049(1)	54(1)
F(4)	2229(3)	8016(1)	2119(1)	57(1)

N(1)	8559(2)	11151(1)	3715(1)	20(1)
N(2)	6635(2)	9089(1)	4212(1)	19(1)
N(3)	5653(3)	8107(1)	5033(1)	24(1)
O(1)	5808(3)	7626(1)	3718(1)	34(1)

Table 3. Bond lengths [Å] and angles [°] for **4a**.

Ir(1)-C(15)	1.999(2)
Ir(1)-N(1)	2.0860(19)
Ir(1)-C(5)	2.123(2)
Ir(1)-C(6)	2.125(2)
Ir(1)-C(2A)	2.200(10)
Ir(1)-C(1)	2.205(11)
Ir(1)-C(2)	2.212(10)
Ir(1)-C(1A)	2.232(9)
B(1)-F(3)	1.383(3)
B(1)-F(1)	1.386(4)
B(1)-F(4)	1.387(4)
B(1)-F(2)	1.413(4)
C(1)-C(2)	1.392(11)
C(1)-C(8)	1.551(11)
C(2)-C(3)	1.532(11)
C(1A)-C(2A)	1.401(11)
C(1A)-C(8A)	1.569(11)
C(2A)-C(3A)	1.548(11)
C(3)-C(4)	1.552(12)
C(4)-C(5)	1.567(8)
C(3A)-C(4A)	1.531(11)
C(4A)-C(5)	1.511(7)
C(5)-C(6)	1.406(4)
C(6)-C(7)	1.518(10)
C(6)-C(7A)	1.544(8)
C(7A)-C(8A)	1.532(10)
C(7)-C(8)	1.534(10)
C(9)-N(1)	1.348(3)
C(9)-C(10)	1.385(3)
C(10)-C(11)	1.367(4)
C(11)-C(12)	1.391(4)
C(12)-C(13)	1.390(3)
C(13)-N(1)	1.378(3)
C(13)-C(14)	1.483(3)
C(14)-C(16)	1.407(3)
C(14)-C(15)	1.425(3)

C(15)-N(2)	1.366(3)
C(16)-C(18)	1.397(3)
C(16)-C(17)	1.497(3)
C(18)-C(19)	1.377(3)
C(19)-N(2)	1.350(3)
C(19)-N(3)	1.383(3)
C(20)-O(1)	1.216(3)
C(20)-N(3)	1.383(3)
C(20)-C(21)	1.503(3)

C(15)-Ir(1)-N(1)	78.44(8)
C(15)-Ir(1)-C(5)	94.90(9)
N(1)-Ir(1)-C(5)	158.03(9)
C(15)-Ir(1)-C(6)	98.20(9)
N(1)-Ir(1)-C(6)	162.35(9)
C(5)-Ir(1)-C(6)	38.64(10)
C(15)-Ir(1)-C(2A)	157.6(5)
N(1)-Ir(1)-C(2A)	99.6(4)
C(5)-Ir(1)-C(2A)	78.6(4)
C(6)-Ir(1)-C(2A)	90.0(5)
C(15)-Ir(1)-C(1)	167.0(5)
N(1)-Ir(1)-C(1)	100.0(5)
C(5)-Ir(1)-C(1)	91.0(5)
C(6)-Ir(1)-C(1)	79.3(4)
C(2A)-Ir(1)-C(1)	35.3(9)
C(15)-Ir(1)-C(2)	155.5(5)
N(1)-Ir(1)-C(2)	93.2(4)
C(5)-Ir(1)-C(2)	84.2(3)
C(6)-Ir(1)-C(2)	96.3(4)
C(2A)-Ir(1)-C(2)	6.3(8)
C(1)-Ir(1)-C(2)	36.7(3)
C(15)-Ir(1)-C(1A)	165.0(5)
N(1)-Ir(1)-C(1A)	97.2(4)
C(5)-Ir(1)-C(1A)	94.1(5)
C(6)-Ir(1)-C(1A)	81.6(3)
C(2A)-Ir(1)-C(1A)	36.8(3)
C(1)-Ir(1)-C(1A)	3.1(10)
C(2)-Ir(1)-C(1A)	37.8(8)

F(3)-B(1)-F(1)	110.9(3)
F(3)-B(1)-F(4)	110.2(2)
F(1)-B(1)-F(4)	110.8(3)
F(3)-B(1)-F(2)	108.8(3)
F(1)-B(1)-F(2)	108.0(2)
F(4)-B(1)-F(2)	108.1(3)
C(2)-C(1)-C(8)	144.8(18)
C(2)-C(1)-Ir(1)	71.9(6)
C(8)-C(1)-Ir(1)	109.6(8)
C(1)-C(2)-C(3)	104.8(16)
C(1)-C(2)-Ir(1)	71.4(6)
C(3)-C(2)-Ir(1)	109.5(7)
C(2A)-C(1A)-C(8A)	105.7(16)
C(2A)-C(1A)-Ir(1)	70.3(6)
C(8A)-C(1A)-Ir(1)	109.8(7)
C(1A)-C(2A)-C(3A)	143.3(16)
C(1A)-C(2A)-Ir(1)	72.8(6)
C(3A)-C(2A)-Ir(1)	107.0(7)
C(2)-C(3)-C(4)	110.7(8)
C(3)-C(4)-C(5)	112.7(6)
C(4A)-C(3A)-C(2A)	109.4(8)
C(5)-C(4A)-C(3A)	108.6(6)
C(6)-C(5)-C(4A)	116.5(4)
C(6)-C(5)-C(4)	132.2(4)
C(4A)-C(5)-C(4)	20.7(3)
C(6)-C(5)-Ir(1)	70.77(14)
C(4A)-C(5)-Ir(1)	116.9(3)
C(4)-C(5)-Ir(1)	106.2(4)
C(5)-C(6)-C(7)	116.0(5)
C(5)-C(6)-C(7A)	131.4(4)
C(7)-C(6)-C(7A)	16.3(6)
C(5)-C(6)-Ir(1)	70.59(15)
C(7)-C(6)-Ir(1)	114.6(4)
C(7A)-C(6)-Ir(1)	111.7(5)
C(8A)-C(7A)-C(6)	110.7(7)
C(7A)-C(8A)-C(1A)	112.0(8)
C(6)-C(7)-C(8)	113.1(8)
C(7)-C(8)-C(1)	107.1(10)

N(1)-C(9)-C(10)	123.0(2)
C(11)-C(10)-C(9)	118.4(2)
C(10)-C(11)-C(12)	119.8(2)
C(13)-C(12)-C(11)	120.3(2)
N(1)-C(13)-C(12)	119.4(2)
N(1)-C(13)-C(14)	114.22(19)
C(12)-C(13)-C(14)	126.3(2)
C(16)-C(14)-C(15)	120.5(2)
C(16)-C(14)-C(13)	127.5(2)
C(15)-C(14)-C(13)	112.03(19)
N(2)-C(15)-C(14)	116.66(19)
N(2)-C(15)-Ir(1)	124.57(16)
C(14)-C(15)-Ir(1)	118.70(15)
C(18)-C(16)-C(14)	118.5(2)
C(18)-C(16)-C(17)	116.0(2)
C(14)-C(16)-C(17)	125.6(2)
C(19)-C(18)-C(16)	120.7(2)
N(2)-C(19)-C(18)	119.3(2)
N(2)-C(19)-N(3)	118.5(2)
C(18)-C(19)-N(3)	122.1(2)
O(1)-C(20)-N(3)	122.1(2)
O(1)-C(20)-C(21)	124.0(2)
N(3)-C(20)-C(21)	113.9(2)
C(9)-N(1)-C(13)	119.1(2)
C(9)-N(1)-Ir(1)	124.50(16)
C(13)-N(1)-Ir(1)	116.40(14)
C(19)-N(2)-C(15)	124.30(19)
C(20)-N(3)-C(19)	126.04(19)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for **4a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir(1)	23(1)	18(1)	12(1)	0(1)	5(1)	0(1)
B(1)	45(2)	37(2)	26(2)	-12(1)	12(1)	-6(1)
C(1)	69(6)	24(5)	26(6)	-7(4)	18(5)	-20(5)
C(2)	55(4)	10(4)	9(3)	0(3)	-3(3)	-6(3)
C(1A)	69(6)	26(5)	27(5)	-1(4)	37(5)	-3(5)
C(2A)	75(5)	14(5)	17(4)	-5(3)	-1(3)	-11(3)
C(3)	31(4)	34(3)	24(3)	7(3)	0(2)	4(3)
C(4)	35(4)	44(5)	15(3)	-3(3)	0(3)	-4(3)
C(3A)	37(4)	33(3)	22(3)	-2(2)	-4(2)	11(3)
C(4A)	32(3)	39(4)	14(3)	-4(2)	0(2)	-1(3)
C(5)	31(1)	36(1)	18(1)	2(1)	2(1)	-11(1)
C(6)	41(1)	26(1)	18(1)	-7(1)	13(1)	-9(1)
C(7A)	38(4)	38(4)	20(4)	-9(3)	15(3)	0(3)
C(8A)	39(4)	26(3)	30(4)	-4(3)	22(3)	4(3)
C(7)	52(6)	16(3)	31(5)	-1(3)	17(4)	1(4)
C(8)	34(4)	41(4)	28(4)	-3(3)	17(3)	0(3)
C(9)	30(1)	22(1)	24(1)	2(1)	7(1)	0(1)
C(10)	30(1)	18(1)	37(2)	2(1)	6(1)	1(1)
C(11)	32(1)	23(1)	35(1)	-8(1)	4(1)	-1(1)
C(12)	30(1)	26(1)	21(1)	-6(1)	5(1)	0(1)
C(13)	19(1)	21(1)	17(1)	-1(1)	4(1)	3(1)
C(14)	19(1)	25(1)	11(1)	-5(1)	0(1)	1(1)
C(15)	19(1)	20(1)	17(1)	0(1)	5(1)	2(1)
C(16)	17(1)	26(1)	15(1)	0(1)	3(1)	4(1)
C(17)	30(1)	34(1)	15(1)	-6(1)	6(1)	-1(1)
C(18)	24(1)	28(1)	14(1)	2(1)	6(1)	3(1)
C(19)	20(1)	24(1)	17(1)	4(1)	5(1)	3(1)
C(20)	32(1)	25(1)	26(1)	1(1)	10(1)	-2(1)
C(21)	63(2)	29(1)	37(2)	-1(1)	24(1)	-12(1)
F(1)	56(1)	52(1)	48(1)	-11(1)	1(1)	9(1)
F(2)	40(1)	50(1)	27(1)	-10(1)	11(1)	-3(1)
F(3)	87(2)	50(1)	32(1)	-17(1)	28(1)	-11(1)
F(4)	60(1)	49(1)	68(1)	-11(1)	29(1)	-19(1)

N(1)	23(1)	19(1)	20(1)	0(1)	6(1)	2(1)
N(2)	23(1)	21(1)	14(1)	0(1)	6(1)	-1(1)
N(3)	31(1)	24(1)	18(1)	2(1)	10(1)	-2(1)
O(1)	50(1)	30(1)	24(1)	-4(1)	16(1)	-9(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2x 10^3) for **4a**.

	x	y	z	U(eq)
H(1)	9348	10916	1914	46
H(2)	6837	11548	1799	32
H(1A)	9452	10974	1827	43
H(2A)	6755	11413	1798	45
H(3A)	5871	10276	641	37
H(3B)	4514	10963	744	37
H(4A)	3575	9614	1040	39
H(4B)	3459	10257	1762	39
H(3A1)	3973	10886	1579	39
H(3A2)	4428	10787	653	39
H(4A1)	3253	9586	1222	35
H(4A2)	4992	9453	859	35
H(5)	4830(40)	9204(17)	2573(17)	35
H(6)	7520(40)	8670(14)	2687(16)	33
H(7A1)	9608	8929	1887	37
H(7A2)	7919	8651	1156	37
H(8A1)	7271	9906	660	36
H(8A2)	9392	9885	856	36
H(7A)	6810	9129	921	38
H(7B)	8487	8606	1381	38
H(8A)	9122	9895	749	39
H(8B)	10307	9688	1697	39
H(9)	9243	11856	2851	31
H(10)	10433	12877	3787	35
H(11)	10388	12776	5242	36
H(12)	9224	11640	5740	31
H(17A)	9266	10660	6588	39
H(17B)	7593	10300	6881	39
H(17C)	7380	11092	6315	39
H(18)	6588	9188	6221	26
H(21A)	3617	6619	4218	61
H(21B)	4350	6840	5217	61
H(21C)	5565	6347	4721	61

H(2N)	6362	8758	3774	23
H(3N)	5309	7996	5508	28

Table 6. Hydrogen bonds for **4a** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2N)...O(1)	0.88	1.96	2.629(3)	131.8
N(3)-H(3N)...F(2)#1	0.88	1.91	2.782(2)	171.7

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+3/2,z+1/2