Supplementary Information (SI) for:

Synthesis and Electronic Investigation of Mono- and Di-substituted 4-Nitro- and 4-Amino-pyrazol-1-yl Bis(pyrazol-1-yl)pyridine-type Ligands and Luminescent Eu(III) Derivatives

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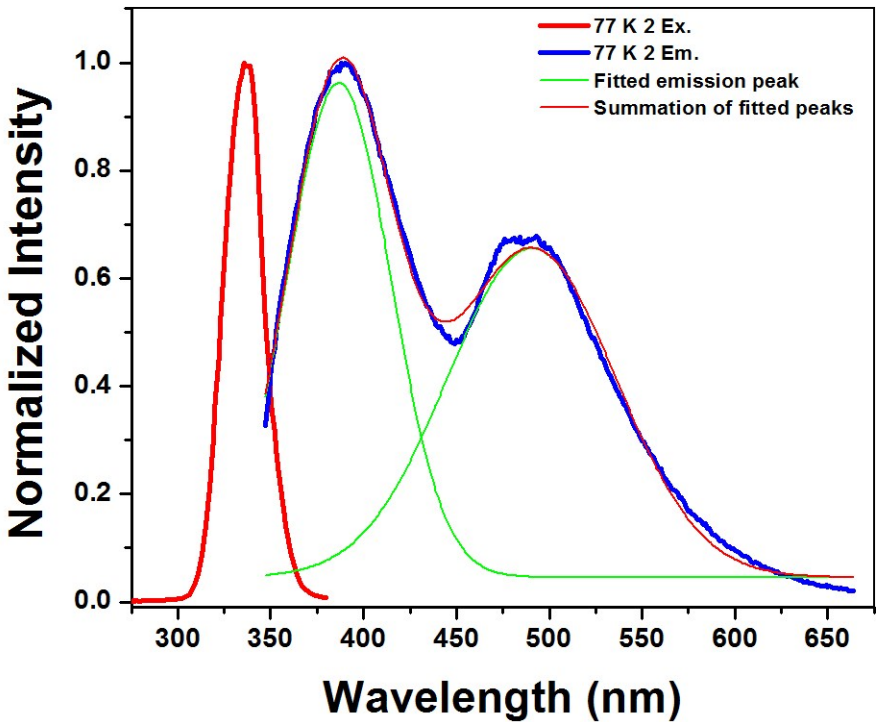

Figure S1: 77 K excitation and emission spectra of 2 in EEET with fitting of emission spectrum peaks.

77 K luminescence measurements were performed by dissolving **2** in 2:2:1:1 diethyl ether: ethyl iodide: ethanol: toluene solvent mixture, then cooling to a solid glass in a quartz liquid nitrogen bath. The spectrum was modeled using a two-peak polynomial fitting function in order to extrapolate the blue edge of phosphorescence for T_1 determination ($R^2 = 0.9963$).

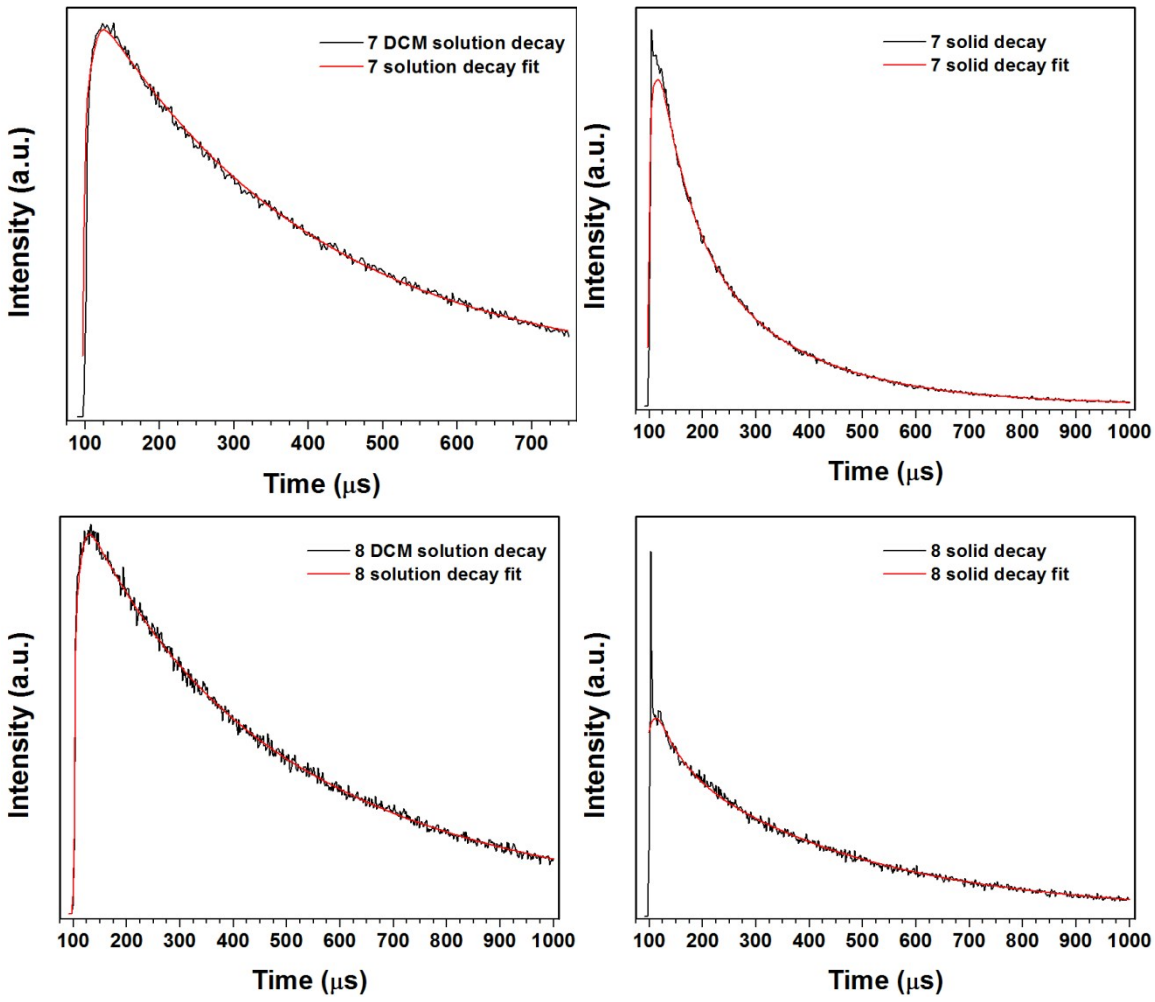

Figure S2: Eu(III) luminescence decays and bi-exponential fits of compounds 7 (top) and 8 (bottom) in DCM solution (left) and solid state (right).

Lifetime measurements were determined by monitoring the λ_{max} of emission in all cases. Specific excitation wavelengths and τ_{obs} values are reported in Table 3 of the main text.

Table S1. Emissive τ_{obs} components of 7 and 8 and the respective contributions of each

Complex	Solvent	τ_1 (μs)	Contribution (%)	τ_2 (μs)	Contribution (%)	χ^2
7	DCM	160 ± 20	20 ± 3	490 ± 10	80 ± 3	1.029
	Solid	41 ± 3	34 ± 2	361 ± 6	66 ± 2	1.030
8	DCM	66 ± 9	13 ± 1	380 ± 10	87.4 ± 0.5	0.994
	Solid	60 ± 2	52.7 ± 0.9	212 ± 2	47.3 ± 0.9	1.056

X-ray

Experimental for $C_{11}H_8N_6O_2$ (5): Crystals grew as large, colorless prisms by slow evaporation from dichloromethane. The data crystal was cut from a larger crystal and had approximate dimensions; 0.62 x 0.42 x 0.30 mm. The data were collected on a Rigaku AFC12 diffractometer with a Saturn 724+ CCD using a graphite monochromator with MoKα radiation (λ = 0.71073Å). A total of 1138 frames of data were collected using ω-scans with a scan range of 0.5° and a counting time of 15 seconds per frame. The data were collected at 100 K using a Rigaku XStream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table S2. Data reduction were performed using the Rigaku Americas Corporation's Crystal Clear version 1.40.[1] The structure was solved by direct methods using SIR2004[2] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2014/7.[3] Structure analysis was aided by use of the programs PLATON98[4] and WinGX.[5] The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0457*P)^2 + (0.2349*P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.0919, with R(F) equal to 0.0332 and a goodness of fit, S, = 1.06. Definitions used for calculating R(F), $R_w(F^2)$ and the goodness of fit, S, are given below.[6] The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[7] All figures were generated using SHELXTL/PC.[8] Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found below.

Table S2. Crystal data and structure refinement for 5.

Empirical formula	C11 H8 N6 O2	
Formula weight	256.23	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 6.0442(17) Å	α= 72.362(7)°.
	b = 8.393(2) Å	β= 89.297(7)°.
c = 11.447(3) Å	γ = 78.103(7)°.	
Volume	540.7(3) $Å^3$	
Z	2	
Density (calculated)	1.574 Mg/m^3	
Absorption coefficient	0.116 mm^{-1}	
F(000)	264	
Crystal size	0.620 x 0.420 x 0.300 mm^3	
Theta range for data collection	3.450 to 27.484°.	
Index ranges	-7<=h<=7, -10<=k<=10, -14<=l<=13	
Reflections collected	7034	
Independent reflections	2419 [R(int) = 0.0191]	
Completeness to theta = 25.242°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.901	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2419 / 0 / 172	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0332, wR2 = 0.0904	
R indices (all data)	R1 = 0.0357, wR2 = 0.0919	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.295 and -0.273 $e.Å^{-3}$	

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 5. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C1	10732(2)	9866(1)	1921(1)	14(1)
C2	12688(2)	10157(1)	2389(1)	16(1)
C3	14079(2)	8766(2)	3223(1)	18(1)
C4	13517(2)	7163(2)	3566(1)	17(1)
C5	11506(2)	7064(1)	3047(1)	13(1)
C6	7192(2)	11144(1)	587(1)	17(1)
C7	6317(2)	12751(2)	-189(1)	20(1)
C8	7963(2)	13714(2)	-153(1)	19(1)
C9	8910(2)	5228(1)	2847(1)	14(1)
C10	8849(2)	3548(1)	3435(1)	15(1)
C11	10735(2)	2870(1)	4279(1)	16(1)
N1	9740(2)	12786(1)	593(1)	18(1)
N2	9241(2)	11200(1)	1046(1)	14(1)
N3	10108(2)	8363(1)	2250(1)	13(1)
N4	10759(2)	5489(1)	3349(1)	14(1)
N5	11906(2)	4059(1)	4235(1)	16(1)
N6	7151(2)	2692(1)	3219(1)	16(1)
O1	5585(1)	3512(1)	2456(1)	20(1)
O2	7352(2)	1166(1)	3819(1)	25(1)

Table S4. Bond lengths [Å] and angles [°] for 5.

C1-N3	1.3338(14)	C7-H7	0.95
C1-C2	1.3999(15)	C8-N1	1.3287(15)
C1-N2	1.4123(14)	C8-H8	0.95
C2-C3	1.3861(16)	C9-N4	1.3490(14)
C2-H2	0.95	C9-C10	1.3743(15)
C3-C4	1.3944(16)	C9-H9	0.95
C3-H3	0.95	C10-C11	1.4080(15)
C4-C5	1.3882(15)	C10-N6	1.4314(14)
C4-H4	0.95	C11-N5	1.3268(15)
C5-N3	1.3304(14)	C11-H11	0.95
C5-N4	1.4271(14)	N1-N2	1.3694(13)
C6-N2	1.3662(15)	N4-N5	1.3735(13)
C6-C7	1.3710(16)	N6-O1	1.2330(13)
C6-H6	0.95	N6-O2	1.2374(13)
C7-C8	1.4130(17)		

N3-C1-C2	124.32(10)	C6-C7-C8	105.08(10)
N3-C1-N2	114.86(10)	C6-C7-H7	127.5
C2-C1-N2	120.82(10)	C8-C7-H7	127.5
C3-C2-C1	116.91(10)	N1-C8-C7	112.02(10)
C3-C2-H2	121.5	N1-C8-H8	124.0
C1-C2-H2	121.5	C7-C8-H8	124.0
C2-C3-C4	120.49(10)	N4-C9-C10	105.06(9)
C2-C3-H3	119.8	N4-C9-H9	127.5
C4-C3-H3	119.8	C10-C9-H9	127.5
C5-C4-C3	116.49(10)	C9-C10-C11	106.93(10)
C5-C4-H4	121.8	C9-C10-N6	125.39(10)
C3-C4-H4	121.8	C11-C10-N6	127.68(10)
N3-C5-C4	125.26(10)	N5-C11-C10	110.39(10)
N3-C5-N4	113.77(9)	N5-C11-H11	124.8
C4-C5-N4	120.97(10)	C10-C11-H11	124.8
N2-C6-C7	106.59(10)	C8-N1-N2	104.20(9)
N2-C6-H6	126.7	C6-N2-N1	112.12(9)
C7-C6-H6	126.7	C6-N2-C1	127.30(10)

N1-N2-C1	120.54(9)	C11-N5-N4	104.51(9)
C5-N3-C1	116.49(10)	O1-N6-O2	124.16(10)
C9-N4-N5	113.10(9)	O1-N6-C10	118.42(10)
C9-N4-C5	125.79(9)	O2-N6-C10	117.42(10)
N5-N4-C5	121.11(9)		

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 5. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	14(1)	13(1)	15(1)	-5(1)	2(1)	-3(1)
C2	17(1)	14(1)	21(1)	-6(1)	3(1)	-7(1)
C3	15(1)	21(1)	22(1)	-7(1)	-1(1)	-7(1)
C4	15(1)	17(1)	17(1)	-3(1)	-1(1)	-4(1)
C5	15(1)	12(1)	14(1)	-5(1)	3(1)	-5(1)
C6	17(1)	17(1)	17(1)	-6(1)	1(1)	-4(1)
C7	21(1)	19(1)	18(1)	-5(1)	-1(1)	-1(1)
C8	26(1)	13(1)	18(1)	-3(1)	3(1)	-2(1)
C9	15(1)	14(1)	14(1)	-4(1)	0(1)	-4(1)
C10	18(1)	13(1)	15(1)	-5(1)	2(1)	-5(1)
C11	20(1)	12(1)	16(1)	-2(1)	0(1)	-4(1)
N1	22(1)	11(1)	21(1)	-3(1)	4(1)	-6(1)
N2	16(1)	11(1)	16(1)	-3(1)	1(1)	-4(1)
N3	14(1)	13(1)	15(1)	-5(1)	1(1)	-4(1)
N4	14(1)	12(1)	14(1)	-3(1)	-1(1)	-4(1)
N5	18(1)	12(1)	16(1)	-1(1)	-2(1)	-2(1)
N6	20(1)	14(1)	16(1)	-6(1)	2(1)	-7(1)
O1	20(1)	21(1)	21(1)	-6(1)	-2(1)	-7(1)
O2	34(1)	14(1)	28(1)	-3(1)	-1(1)	-12(1)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 5.

	x	y	z	U(eq)
H2	13046	11258	2146	20
H3	15425	8905	3564	22
H4	14461	6190	4125	20
H6	6508	10180	770	20
H7	4909	13134	-651	24
H8	7815	14887	-609	23
H9	7875	6031	2222	17
H11	11116	1723	4804	20

Table S7. Torsion angles [°] for 5.

N3-C1-C2-C3	1.87(17)	N3-C1-N2-N1	-177.15(9)
N2-C1-C2-C3	-178.62(10)	C2-C1-N2-N1	3.29(15)
C1-C2-C3-C4	-0.04(17)	C4-C5-N3-C1	1.02(16)
C2-C3-C4-C5	-1.10(17)	N4-C5-N3-C1	-179.22(9)
C3-C4-C5-N3	0.64(17)	C2-C1-N3-C5	-2.32(16)
C3-C4-C5-N4	-179.11(10)	N2-C1-N3-C5	178.14(9)
N2-C6-C7-C8	0.26(12)	C10-C9-N4-N5	0.07(12)
C6-C7-C8-N1	-0.19(13)	C10-C9-N4-C5	-178.82(10)
N4-C9-C10-C11	-0.42(12)	N3-C5-N4-C9	4.37(15)
N4-C9-C10-N6	178.96(10)	C4-C5-N4-C9	-175.86(10)
C9-C10-C11-N5	0.65(13)	N3-C5-N4-N5	-174.44(9)
N6-C10-C11-N5	-178.71(10)	C4-C5-N4-N5	5.34(15)
C7-C8-N1-N2	0.03(12)	C10-C11-N5-N4	-0.58(12)
C7-C6-N2-N1	-0.26(13)	C9-N4-N5-C11	0.32(12)
C7-C6-N2-C1	177.36(10)	C5-N4-N5-C11	179.27(9)
C8-N1-N2-C6	0.14(12)	C9-C10-N6-O1	-0.88(16)
C8-N1-N2-C1	-177.66(9)	C11-C10-N6-O1	178.37(10)
N3-C1-N2-C6	5.42(16)	C9-C10-N6-O2	179.38(11)
C2-C1-N2-C6	-174.14(10)	C11-C10-N6-O2	-1.38(17)

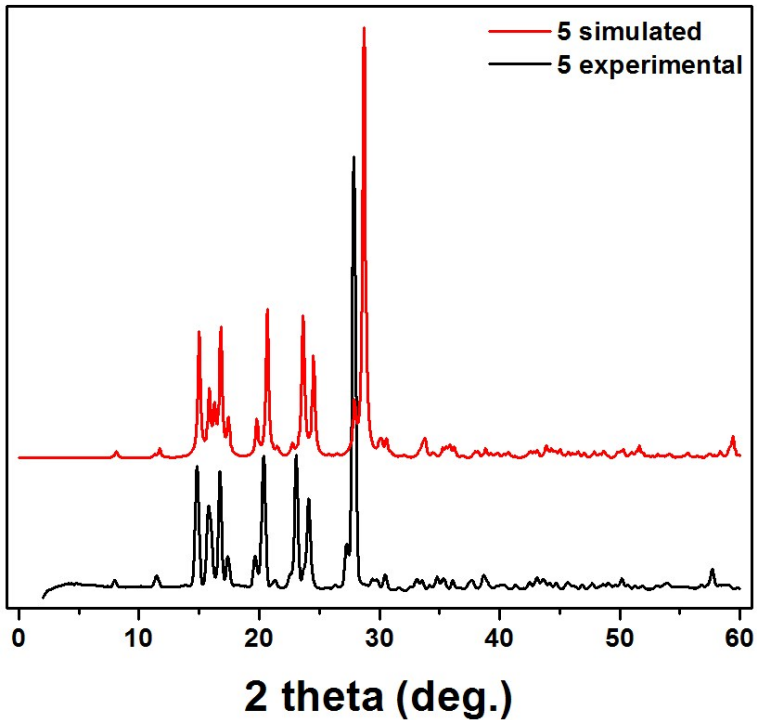

Figure S3: Experimental and simulated X-ray powder diffraction patterns of 5.

X-ray Experimental for $C_{12}H_{11}N_5$ (6): Crystals grew as pale yellow plates by by slow evaporation from dichloromethane. The data crystal had approximate dimensions; 0.18 x 0.06 x 0.06 mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a μ-focus Cu Kα radiation source (λ = 1.5418Å) with collimating mirror monochromators. A total of 965 frames of data were collected using ω-scans with a scan range of 1° and a counting time of 15 seconds per frame with a detector offset of +/- 41.9° and 48 seconds per frame with a detector offset of +/- 111.0°. The data were collected at 173 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table S8. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.37.31.[1] The structure was solved by direct methods using SHELXT[2] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6.[3] Structure analysis was aided by use of the programs PLATON98[4] and WinGX.[5] The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom. The hydrogen atoms on the amine nitrogen, N6, were observed in a ΔF map and refined with isotropic displacement parameters.

The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.1058*P)^2 + (0.3513*P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.214, with R(F) equal to 0.0670 and a goodness of fit, S, = 1.05. Definitions used for calculating R(F), $R_w(F^2)$ and the goodness of fit, S, are given below.[6] The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[7] All figures were generated using SHELXTL/PC.[8] Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found below.

Table S8: Crystal data and structure refinement for 6.

Empirical formula	C12 H11 N5	
Formula weight	225.26	
Temperature	173(2) K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 22.9809(16) Å	α= 90°.
	b = 3.7881(3) Å	β= 104.812(7)°.
	c = 12.2183(9) Å	γ = 90°.
Volume	1028.31(14) $Å^3$	
Z	4	
Density (calculated)	1.455 Mg/m^3	
Absorption coefficient	0.759 mm^{-1}	
F(000)	472	
Crystal size	0.180 x 0.060 x 0.060 mm^3	
Theta range for data collection	3.979 to 75.692°.	
Index ranges	-19<=h<=28, -4<=k<=3, -15<=l<=15	
Reflections collected	5061	
Independent reflections	2060 [R(int) = 0.0500]	
Completeness to theta = 67.684°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.485	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2060 / 0 / 162	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	R1 = 0.0670, wR2 = 0.1865	
R indices (all data)	R1 = 0.0803, wR2 = 0.2137	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.340 and -0.358 $e.Å^{-3}$	

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 6. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C1	6872(1)	5198(6)	3314(2)	25(1)
C2	6825(1)	6797(6)	4314(2)	29(1)
C3	7360(1)	7520(6)	5113(2)	30(1)
C4	7904(1)	6685(6)	4906(2)	29(1)
C5	7895(1)	5066(6)	3874(2)	24(1)
C6	6319(1)	2818(6)	1442(2)	30(1)
C7	5726(1)	2497(7)	897(2)	35(1)
C8	5421(1)	3842(7)	1681(2)	38(1)
C9	8515(1)	2872(6)	2611(2)	26(1)
C10	9113(1)	2104(6)	2793(2)	28(1)
C11	9360(1)	2816(7)	3952(2)	32(1)
N1	5796(1)	4941(6)	2632(2)	34(1)
N2	6351(1)	4305(5)	2470(2)	28(1)
N3	7391(1)	4342(5)	3081(2)	25(1)
N4	8432(1)	4027(5)	3627(2)	25(1)
N5	8951(1)	3970(6)	4457(2)	34(1)
N6	9446(1)	1071(7)	2035(2)	36(1)

Table S10. Bond lengths [Å] and angles [°] for 6.

C1-N3	1.334(3)	C7-H7	0.95
C1-C2	1.393(3)	C8-N1	1.324(3)
C1-N2	1.408(3)	C8-H8	0.95
C2-C3	1.386(3)	C9-C10	1.368(3)
C2-H2	0.95	C9-N4	1.373(3)
C3-C4	1.376(3)	C9-H9	0.95
C3-H3	0.95	C10-N6	1.399(3)
C4-C5	1.397(3)	C10-C11	1.411(3)
C4-H4	0.95	C11-N5	1.323(3)
C5-N3	1.335(3)	C11-H11	0.95
C5-N4	1.401(3)	N1-N2	1.361(3)
C6-C7	1.360(3)	N4-N5	1.354(2)
C6-N2	1.361(3)	N6-H6A	0.90(4)
C6-H6	0.95	N6-H6B	1.04(4)
C7-C8	1.418(4)		

N3-C1-C2	124.5(2)	C6-C7-C8	104.0(2)
N3-C1-N2	115.1(2)	C6-C7-H7	128.0
C2-C1-N2	120.4(2)	C8-C7-H7	128.0
C3-C2-C1	116.8(2)	N1-C8-C7	112.5(2)
C3-C2-H2	121.6	N1-C8-H8	123.7
C1-C2-H2	121.6	C7-C8-H8	123.7
C4-C3-C2	120.6(2)	C10-C9-N4	106.60(19)
C4-C3-H3	119.7	C10-C9-H9	126.7
C2-C3-H3	119.7	N4-C9-H9	126.7
C3-C4-C5	117.5(2)	C9-C10-N6	130.5(2)
C3-C4-H4	121.2	C9-C10-C11	104.6(2)
C5-C4-H4	121.2	N6-C10-C11	124.7(2)
N3-C5-C4	123.7(2)	N5-C11-C10	112.3(2)
N3-C5-N4	115.81(19)	N5-C11-H11	123.9
C4-C5-N4	120.44(19)	C10-C11-H11	123.9
C7-C6-N2	107.5(2)	C8-N1-N2	103.9(2)
C7-C6-H6	126.3	C6-N2-N1	112.07(19)
N2-C6-H6	126.3	C6-N2-C1	127.6(2)

N1-N2-C1	120.3(2)	C11-N5-N4	104.53(18)
C1-N3-C5	116.9(2)	C10-N6-H6A	119(3)
N5-N4-C9	111.94(18)	C10-N6-H6B	114(2)
N5-N4-C5	119.97(18)	H6A-N6-H6B	113(3)
C9-N4-C5	128.06(18)		

Table S11. Anisotropic displacement parameters ($Å^2 x 10^3$) for 6. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	20(1)	26(1)	30(1)	4(1)	9(1)	0(1)
C2	24(1)	32(1)	34(1)	1(1)	14(1)	5(1)
C3	31(1)	32(1)	30(1)	-3(1)	13(1)	2(1)
C4	25(1)	31(1)	30(1)	-2(1)	6(1)	-1(1)
C5	18(1)	28(1)	29(1)	5(1)	9(1)	-1(1)
C6	22(1)	33(1)	35(1)	-2(1)	9(1)	-2(1)
C7	23(1)	37(1)	43(1)	-1(1)	6(1)	-6(1)
C8	16(1)	47(2)	50(1)	4(1)	7(1)	-2(1)
C9	19(1)	34(1)	26(1)	0(1)	7(1)	0(1)
C10	19(1)	34(1)	31(1)	2(1)	6(1)	-1(1)
C11	15(1)	50(1)	32(1)	1(1)	4(1)	-2(1)
N1	18(1)	44(1)	44(1)	2(1)	12(1)	2(1)
N2	16(1)	34(1)	35(1)	3(1)	9(1)	1(1)
N3	19(1)	30(1)	28(1)	2(1)	8(1)	1(1)
N4	16(1)	34(1)	26(1)	-1(1)	5(1)	1(1)
N5	20(1)	50(1)	28(1)	-1(1)	1(1)	2(1)
N6	22(1)	54(1)	34(1)	-2(1)	10(1)	5(1)

Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 6.

	x	y	z	U(eq)
H2	6446	7365	4443	35
H3	7350	8603	5809	36
H4	8273	7190	5444	35
H6	6649	2130	1158	36
H7	5555	1583	160	42
H8	4995	3943	1539	45
H9	8214	2649	1918	32
H11	9773	2501	4328	39
H6A	9716(18)	-690(120)	2240(40)	84(14)
H6B	9189(15)	830(100)	1210(30)	67(11)

Table S13. Torsion angles [°] for 6.

N3-C1-C2-C3	-0.1(4)	N3-C1-N2-C6	-2.8(3)
N2-C1-C2-C3	178.6(2)	C2-C1-N2-C6	178.4(2)
C1-C2-C3-C4	0.2(4)	N3-C1-N2-N1	177.72(18)
C2-C3-C4-C5	-0.6(4)	C2-C1-N2-N1	-1.2(3)
C3-C4-C5-N3	1.0(3)	C2-C1-N3-C5	0.5(3)
C3-C4-C5-N4	-177.6(2)	N2-C1-N3-C5	-178.34(17)
N2-C6-C7-C8	-0.8(3)	C4-C5-N3-C1	-0.9(3)
C6-C7-C8-N1	0.6(3)	N4-C5-N3-C1	177.76(18)
N4-C9-C10-N6	-175.0(2)	C10-C9-N4-N5	-1.1(3)
N4-C9-C10-C11	1.0(3)	C10-C9-N4-C5	-178.8(2)
C9-C10-C11-N5	-0.6(3)	N3-C5-N4-N5	-166.33(19)
N6-C10-C11-N5	175.7(2)	C4-C5-N4-N5	12.4(3)
C7-C8-N1-N2	-0.1(3)	N3-C5-N4-C9	11.2(3)
C7-C6-N2-N1	0.9(3)	C4-C5-N4-C9	-170.1(2)
C7-C6-N2-C1	-178.7(2)	C10-C11-N5-N4	-0.1(3)
C8-N1-N2-C6	-0.5(3)	C9-N4-N5-C11	0.8(3)
C8-N1-N2-C1	179.1(2)	C5-N4-N5-C11	178.7(2)

Table S14. Hydrogen bonds for 6 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N6-H6A...N6#1	0.90(4)	2.27(4)	3.144(3)	165(4)
N6-H6B...N5#2	1.04(4)	2.07(4)	3.064(3)	160(3)

Symmetry transformations used to generate equivalent atoms:

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

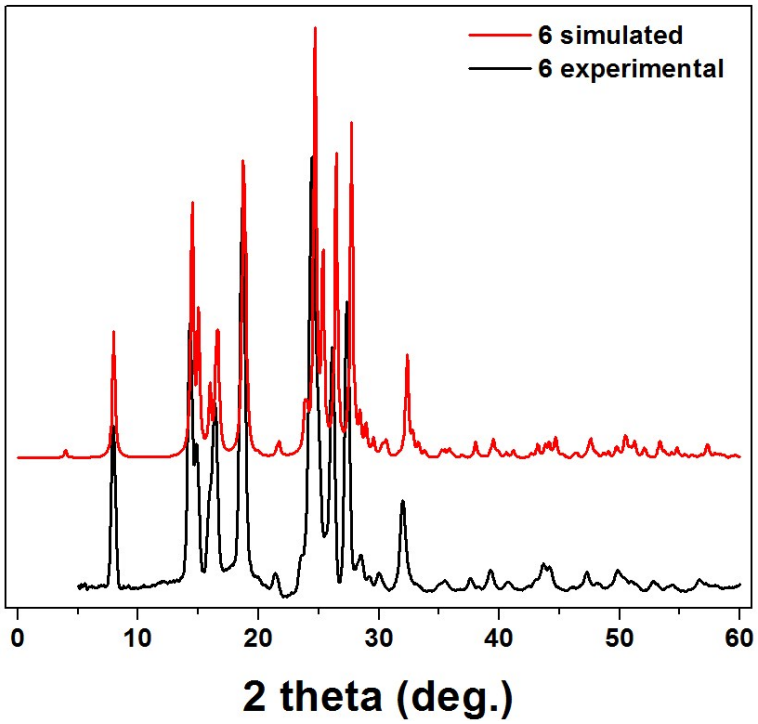

Figure S4: Experimental and simulated X-ray powder diffraction patterns of 6.

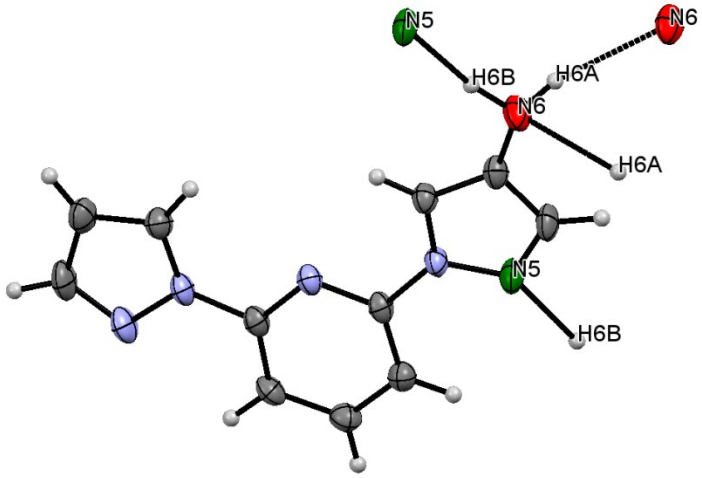

Figure S5: Solid-state structure of 6 showing H-bonding interactions. All atoms participating in H-bonding are labeled; atoms N5 and N6 are colored green and red, respectively, for clarity.

X-ray Experimental for $C_8H_5N_4O_2Br$ (3): Crystals grew as colorless prisms by slow evaporation from dichloromethane. The data crystal had approximate dimensions; 0.39 x 0.18 x 0.046 mm. The data were collected on a Rigaku AFC12 diffractometer with a Saturn 724+ CCD using a graphite monochromator with MoKα radiation (λ = 0.71073Å). A total of 1299 frames of data were collected using ω-scans with a scan range of 0.5° and a counting time of 20 seconds per frame. The data were collected at 100 K using an Rigaku XStream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table S15. Data reduction were performed using the Rigaku Americas Corporation's Crystal Clear version 1.40.[1] The structure was solved by direct methods using SIR2004[2] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6.[3] Structure analysis was aided by use of the programs PLATON98[4] and WinGX.[5] The hydrogen atoms on carbon were located in a ΔF map and refined with isotropic displacement parameters.

The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0328*P)^2 + (0.275*P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.0680, with R(F) equal to 0.0269 and a goodness of fit, S, = 1.10. Definitions used for calculating R(F), $R_w(F^2)$ and the goodness of fit, S, are given below.[6] The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[7] All figures were generated using SHELXTL/PC.[8] Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found below.

Table S15. Crystal data and structure refinement for 3.

Empirical formula	C8 H5 Br N4 O2	
Formula weight	269.07	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 5.1820(14) Å	α= 77.698(7)°.
	b = 8.556(3) Å	β= 81.398(7)°.
	c = 11.285(3) Å	γ = 75.758(7)°.
Volume	471.3(2) $Å^3$	
Z	2	
Density (calculated)	1.896 Mg/m^3	
Absorption coefficient	4.344 mm^{-1}	
F(000)	264	
Crystal size	0.390 x 0.180 x 0.046 mm^3	
Theta range for data collection	3.377 to 27.367°.	
Index ranges	-6<=h<=6, -11<=k<=10, -14<=l<=14	
Reflections collected	6902	
Independent reflections	2125 [R(int) = 0.0408]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.576	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2125 / 0 / 156	
Goodness-of-fit on F^2	1.096	
Final R indices [I>2sigma(I)]	R1 = 0.0269, wR2 = 0.0666	
R indices (all data)	R1 = 0.0288, wR2 = 0.0680	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.662 and -0.446 $e.Å^{-3}$	

Table S16. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 3. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C1	4769(4)	7291(3)	3689(2)	16(1)
C2	6689(4)	8200(3)	3185(2)	18(1)
C3	8305(4)	7763(3)	2159(2)	19(1)
C4	7966(4)	6464(3)	1674(2)	16(1)
C5	5981(4)	5664(2)	2279(2)	14(1)
C6	3538(4)	3485(3)	2338(2)	14(1)
C7	3819(4)	2339(2)	1611(2)	14(1)
C8	5993(4)	2543(3)	720(2)	17(1)
Br1	2457(1)	7866(1)	5082(1)	20(1)
N1	4360(3)	6056(2)	3261(2)	16(1)
N2	5472(3)	4314(2)	1861(2)	14(1)
N3	7025(4)	3744(2)	874(2)	17(1)
N4	2168(3)	1181(2)	1736(2)	15(1)
O1	2461(3)	395(2)	910(2)	22(1)
O2	544(3)	1039(2)	2646(1)	21(1)

Table S17. Bond lengths [Å] and angles [°] for 3.

C1-N1	1.324(3)	C6-N2	1.350(3)
C1-C2	1.393(3)	C6-C7	1.376(3)
C1-Br1	1.904(2)	C6-H6	0.91(3)
C2-C3	1.386(3)	C7-C8	1.412(3)
C2-H2	0.93(3)	C7-N4	1.434(3)
C3-C4	1.397(3)	C8-N3	1.321(3)
C3-H3	0.93(3)	C8-H8	0.97(3)
C4-C5	1.389(3)	N2-N3	1.377(2)
C4-H4	0.93(3)	N4-O2	1.232(2)
C5-N1	1.337(3)	N4-O1	1.232(2)
C5-N2	1.430(3)		

N1-C1-C2	125.2(2)	N2-C6-H6	121.1(18)
N1-C1-Br1	116.03(16)	C7-C6-H6	134.2(18)
C2-C1-Br1	118.77(16)	C6-C7-C8	107.12(18)
C3-C2-C1	117.1(2)	C6-C7-N4	125.84(19)
C3-C2-H2	120.0(17)	C8-C7-N4	127.04(19)
C1-C2-H2	122.9(17)	N3-C8-C7	110.38(19)
C2-C3-C4	120.1(2)	N3-C8-H8	119.1(19)
C2-C3-H3	118.7(18)	C7-C8-H8	130.5(19)
C4-C3-H3	121.2(19)	C1-N1-C5	115.75(18)
C5-C4-C3	116.4(2)	C6-N2-N3	113.33(17)
C5-C4-H4	116.5(17)	C6-N2-C5	126.49(18)
C3-C4-H4	127.1(17)	N3-N2-C5	120.17(17)
N1-C5-C4	125.50(19)	C8-N3-N2	104.49(17)
N1-C5-N2	113.51(18)	O2-N4-O1	124.15(18)
C4-C5-N2	120.98(18)	O2-N4-C7	118.60(17)
N2-C6-C7	104.66(18)	O1-N4-C7	117.25(18)

Table S18. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 3. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	15(1)	15(1)	18(1)	-5(1)	-4(1)	-1(1)
C2	21(1)	15(1)	22(1)	-6(1)	-5(1)	-5(1)
C3	19(1)	17(1)	26(1)	-4(1)	-5(1)	-7(1)
C4	17(1)	16(1)	18(1)	-6(1)	-3(1)	-5(1)
C5	14(1)	11(1)	18(1)	-5(1)	-6(1)	-1(1)
C6	13(1)	16(1)	14(1)	-4(1)	-2(1)	-4(1)
C7	14(1)	12(1)	18(1)	-4(1)	-2(1)	-3(1)
C8	16(1)	17(1)	18(1)	-7(1)	0(1)	-4(1)
Br1	24(1)	18(1)	18(1)	-8(1)	-1(1)	-2(1)
N1	16(1)	14(1)	17(1)	-4(1)	-2(1)	-2(1)
N2	14(1)	14(1)	15(1)	-6(1)	-2(1)	-3(1)
N3	15(1)	18(1)	18(1)	-9(1)	2(1)	-3(1)
N4	16(1)	14(1)	18(1)	-5(1)	-3(1)	-4(1)
O1	25(1)	23(1)	24(1)	-15(1)	3(1)	-10(1)
O2	23(1)	22(1)	19(1)	-7(1)	5(1)	-10(1)

Table S19. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 3.

	x	y	z	U(eq)
H2	6920(50)	9060(30)	3510(20)	19(6)
H3	9590(60)	8360(40)	1800(30)	26(7)
H4	8920(50)	6080(40)	990(30)	24(7)
H6	2370(50)	3770(30)	2990(30)	17(6)
H8	6780(60)	1950(40)	70(30)	30(8)

Table S20. Torsion angles [°] for 3.

N1-C1-C2-C3	-0.4(3)
Br1-C1-C2-C3	-178.97(16)
C1-C2-C3-C4	0.2(3)
C2-C3-C4-C5	-0.6(3)
C3-C4-C5-N1	1.3(3)
C3-C4-C5-N2	-179.78(19)
N2-C6-C7-C8	0.7(2)
N2-C6-C7-N4	-178.44(19)
C6-C7-C8-N3	0.0(3)
N4-C7-C8-N3	179.1(2)
C2-C1-N1-C5	1.1(3)
Br1-C1-N1-C5	179.65(14)
C4-C5-N1-C1	-1.6(3)
N2-C5-N1-C1	179.48(18)
C7-C6-N2-N3	-1.1(2)
C7-C6-N2-C5	178.57(19)
N1-C5-N2-C6	1.9(3)
C4-C5-N2-C6	-177.1(2)
N1-C5-N2-N3	-178.41(17)
C4-C5-N2-N3	2.6(3)
C7-C8-N3-N2	-0.6(2)
C6-N2-N3-C8	1.1(2)
C5-N2-N3-C8	-178.60(19)
C6-C7-N4-O2	-9.2(3)
C8-C7-N4-O2	171.9(2)
C6-C7-N4-O1	170.3(2)
C8-C7-N4-O1	-8.6(3)

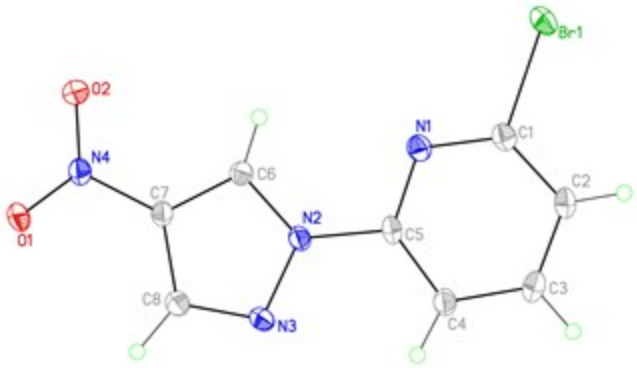

Figure S6: Single crystal structure of 3. Displacement ellipsoids are scaled to the 50% probability level.

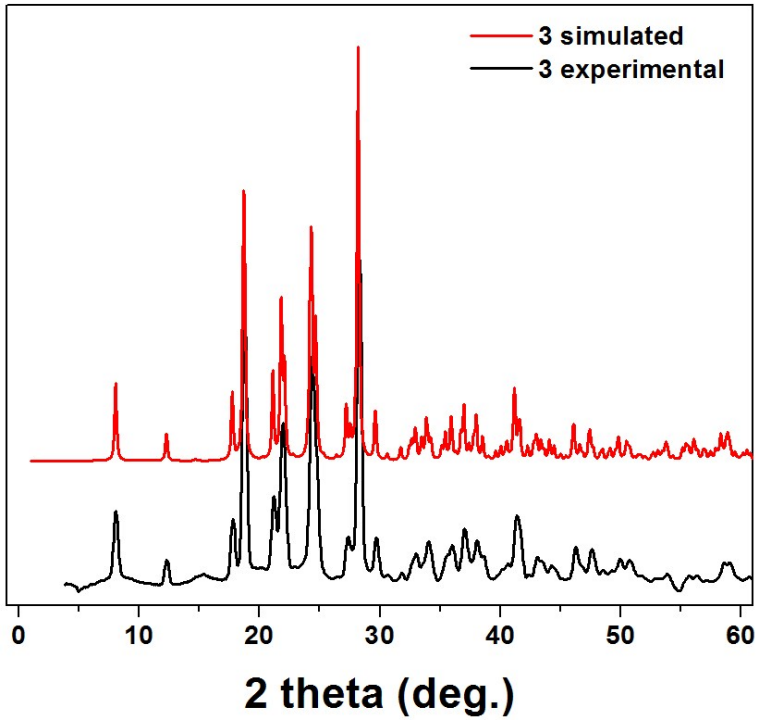

Figure S7: Experimental and simulated X-ray powder diffraction patterns of 3.

Notes and References:

1. CrystalClear 1.40 (2008). Rigaku Americas Corportion, The Woodlands, TX.

2. SIR2004. A program for crystal structure solution. Altomare A., Burla M.C., Caliandro, M., Camalli M., Carrozzini, B., Cascarano G.L., De Caro, L., Giacovazzo C., Polidori G., Spagna R. J. Appl. Cryst. , 2005, 38, 381-388.

3. Sheldrick, G. M. (2015). SHELXL-2014/7. Program for the Refinement of Crystal Structures. Acta Cryst., C71, 9-18.

4. Spek, A. L. (1998). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands.

5. WinGX 1.64. (1999). An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. J. Appl. Cryst. 32. 837-838.

6. $R_w(F^2) = \{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|)^4\}^{1/2}$ where w is the weight given each reflection. $R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|\}$ for reflections with $F_o > 4(\sigma(F_o))$. $S = [\Sigma w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

7. International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.

8. Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.