Electronic Supplementary Information

Versatile bonding and coordination modes of ditriazolylidene ligands in rhodium(III) and iridium(III) complexes

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1. NMR spectra of compounds **5a(I)**, **5a(BF$_4$)**, and **14** S2
2. Details on crystal structure determinations S5

1. NMR spectra of compounds 5a(I), 5a(BF_4), and 14

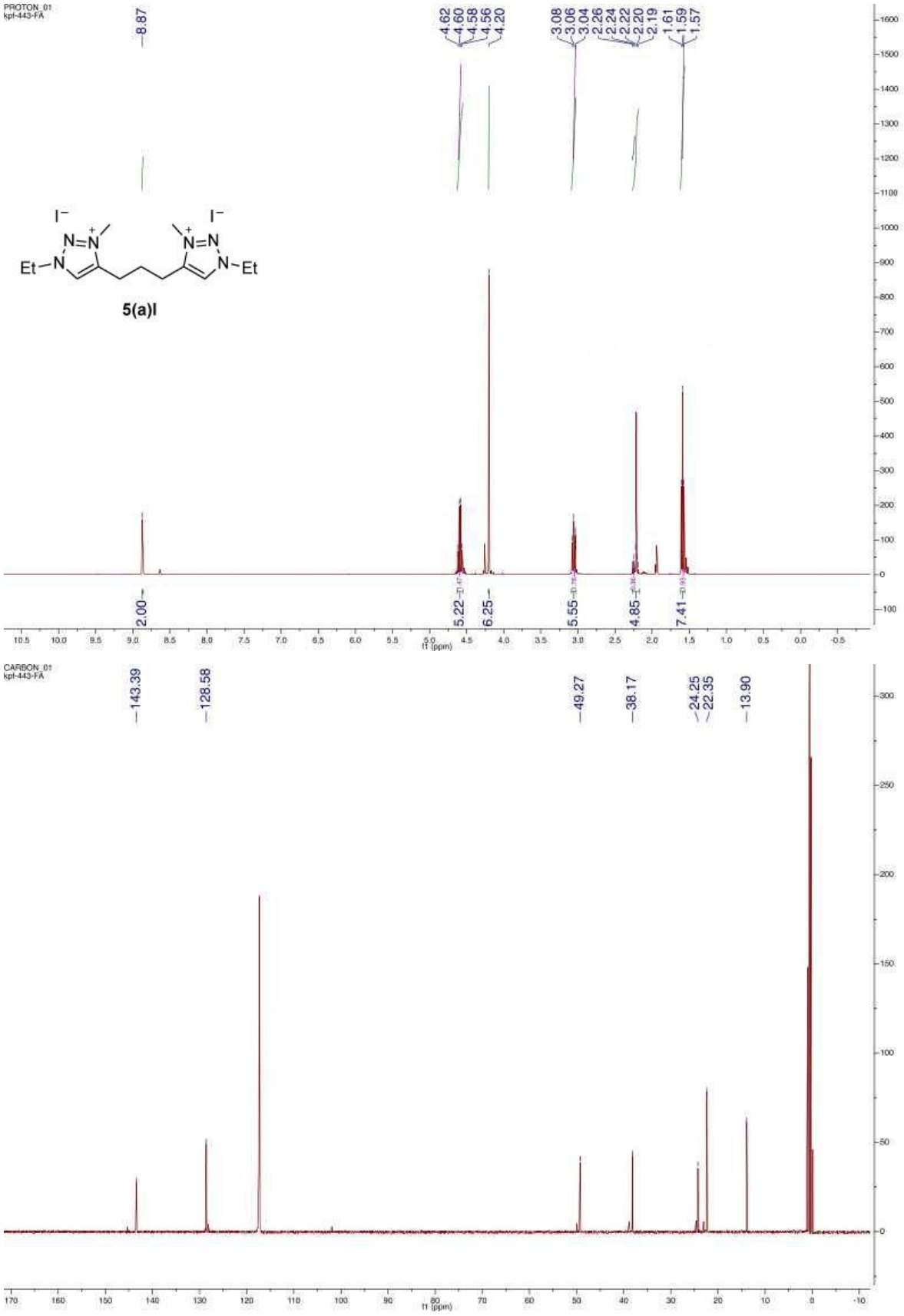

Figure S1. Top: ^{1}H NMR (CD_3CN, 400 MHz); bottom: $^{13}C\{^{1}H\}$ NMR (CD_3CN, 100 MHz).

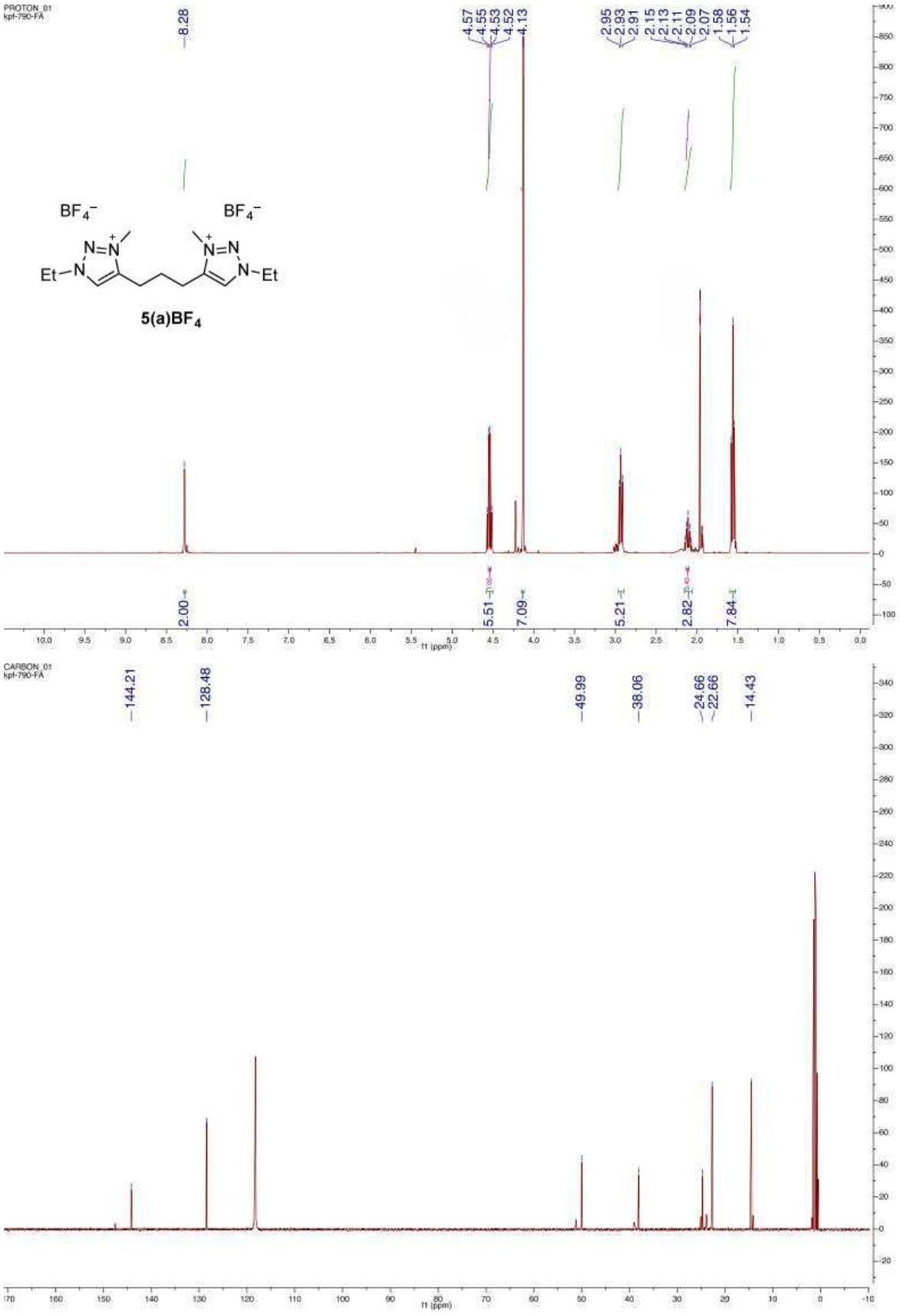

Figure S2. Top: ^{1}H NMR (CD_3CN, 400 MHz); bottom: $^{13}C\{^{1}H\}$ NMR (CD_3CN, 100 MHz).

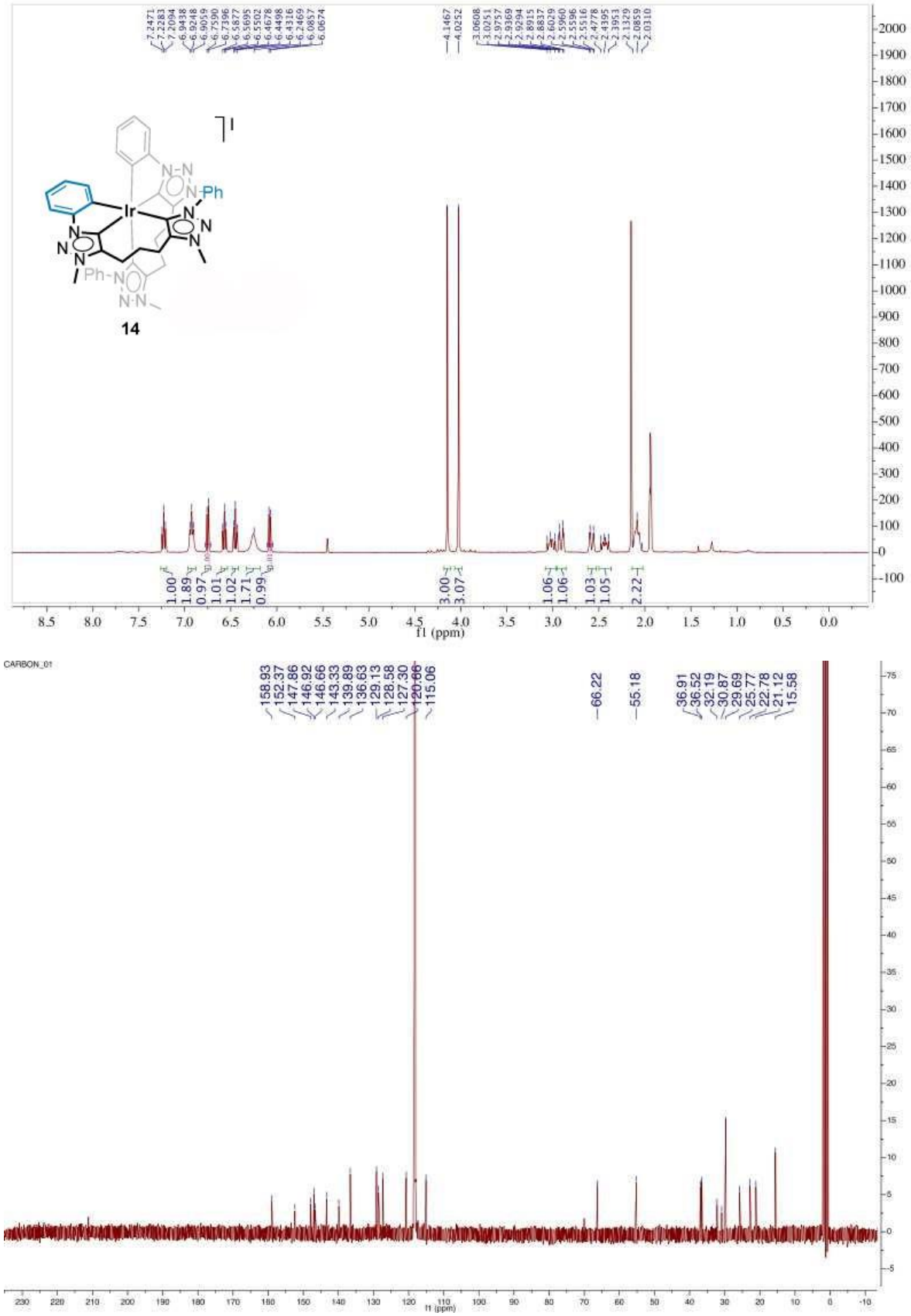

Figure S3. Top: ^{1}H NMR (CD_3CN, 400 MHz); bottom: $^{13}C\{^{1}H\}$ NMR (CD_3CN, 100 MHz).

2. Details on crystal structure determinations

Table S1. Crystal data and structure refinement for complex **7**.

CCDC No.	1477827
Empirical formula	$C_{23}H_{37.48}B_{0.21}N_6O_{0.24}F_{0.84}Cl_{1.79}Rh$
Molecular formula	$[C_{23}H_{37}N_6ClRh]^+\{[Cl]^-\}_{0.79}\{[BF_4]^-\}_{0.21}$ x 0.24 (H_2O) [a)]
Formula weight	586.33
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$ (#14)
Unit cell dimensions	a = 9.4774(4) Å α= 90°.
	b = 17.4666(7) Å β= 92.342(4)°.
	c = 15.7881(6) Å γ = 90°.
Volume	2611.35(18) $Å^3$
Z	4
Density (calculated)	1.491 Mg/m^3
Absorption coefficient	0.867 mm^{-1}
F(000)	1213
Crystal size	0.2270 x 0.1286 x 0.0296 mm^3
Theta range for data collection	2.81 to 26.81°.
Index ranges	–11<=h<=11, –22<=k<=22, –19<=l<=19
Reflections collected	27799
Independent reflections	5534 [R(int) = 0.0483]
Completeness to theta	(= 26.81°) 99.3%
Absorption correction	Analytical
Max. and min. transmission	0.975 and 0.868
Refinement method	Full–matrix least–squares on F^2
Data / restraints / parameters	5534 / 6 / 327 [b)]
Goodness–of–fit on F^2	1.047
Final R indices [I>2sigma(I)]	R1 = 0.0308, wR2 = 0.0679
R indices (all data)	R1 = 0.0367, wR2 = 0.0713
Largest diff. peak and hole	0.560 and –0.759 e.$Å^{-3}$

Table S2. Crystal data and structure refinement for complexes **8** and **9**.

CCDC No.	1477829	1477828
Empirical formula	$C_{31}H_{36}BN_6F_4Rh$	$C_{30}H_{34}BN_6OF_4Rh$
Molecular formula	$[C_{31}H_{36}N_6Rh]^+[BF_4]^-$	$[C_{30}H_{34}N_6ORh]^+[BF_4]^-$
Formula weight	682.38	684.35
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Monoclinic
Space group	Pbca (#61)	$P2_1/n$ (#14)
Unit cell dimensions	a = 15.4355(1) Å α= 90°.	a = 10.3886(3) Å α= 90°.
	b = 16.3463(1) Å β= 90°.	b = 23.2899(4) Å β= 112.792(3)°.
	c = 23.5226(2) Å γ = 90°.	c = 12.8981(3) Å γ = 90°.
Volume	5935.07(7) $Å^3$	2877.01(12) $Å^3$
Z	8	4
Density (calculated)	1.527 Mg/m^3	1.580 Mg/m^3
Absorption coefficient	0.633 mm^{-1}	0.656 mm^{-1}
F(000)	2800	1400
Crystal size	0.2479 x 0.2093 x 0.1640 mm^3	0.2225 x 0.1815 x 0.1246 mm^3
Theta range for data collection	2.95 to 31.00°.	2.77 to 29.67°.
Index ranges	–22<=h<=22, –23<=k<=23, –34<=l<=34	–14<=h<=14, –32<=k<=32, –17<=l<=17
Reflections collected	127462	64653
Independent reflections	9453 [R(int) = 0.0358]	7618 [R(int) = 0.0488]
Completeness to theta	(= 31.00°) 99.9%	(= 28.00°) 99.6%
Absorption correction	Analytical	Analytical
Max. and min. transmission	0.934 and 0.895	0.933 and 0.903
Refinement method	Full–matrix least–squares on F^2	Full–matrix least–squares on F^2
Data / restraints / parameters	9453 / 0 / 395	7618 / 0 / 395
Goodness–of–fit on F^2	1.029	1.221
Final R indices [I>2σ(I)]	R1 = 0.0246, wR2 = 0.0616	R1 = 0.0364, wR2 = 0.0743
R indices (all data)	R1 = 0.0298, wR2 = 0.0650	R1 = 0.0402, wR2 = 0.0759
Largest diff. peak and hole	0.592 and –0.486 e.$Å^{-3}$	0.894 and –0.768 e.$Å^{-3}$

Table S3. Crystal data and structure refinement for complex **13**.

CCDC No.	1477827
Empirical formula	$C_{43}H_{44}N_{12}Cl_2RhI$
Molecular formula	$[C_{42}H_{42}N_{12}Rh]^+[I]^-$ x C H_2Cl_2 [c]
Formula weight	1029.61
Temperature	100(2) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	$P2_1/n$ (#14)
Unit cell dimensions	a = 19.4324(3) Å α= 90°.
	b = 11.1984(2) Å β= 107.720(2)°.
	c = 20.9143(3) Å γ = 90°.
Volume	4335.27(12) $Å^3$
Z	4
Density (calculated)	1.577 Mg/m^3
Absorption coefficient	10.283 mm^{-1}
F(000)	2072
Crystal size	0.2811 x 0.0398 x 0.0142 mm^3
Theta range for data collection	3.72 to 76.91°.
Index ranges	–20<=h<=23, –13<=k<=13, –26<=l<=24
Reflections collected	44951
Independent reflections	9021 [R(int) = 0.0647]
Completeness to theta	(= 76.91°) 98.6%
Absorption correction	Analytical
Max. and min. transmission	0.868 and 0.316
Refinement method	Full–matrix least–squares on F^2
Data / restraints / parameters	9021 / 0 / 509
Goodness–of–fit on F^2	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0495, wR2 = 0.1289
R indices (all data)	R1 = 0.0547, wR2 = 0.1336
Largest diff. peak and hole	1.483 and –1.797 e.$Å^{-3}$

[a] The hydrogen atoms of the water molecule could not be detected; [b] All B–F bond lengths were restrained to be equal using SADI; [c] The solvent could not me modelled in terms of atomic sites. Platon SQUEEZE was used to compensate for the spread electron density.