10.1071/CH15596_AC

Australian Journal of Chemistry 69(7), 759-762

Supplementary Material

Acceleration of the Morita-Baylis-Hillman Reaction using an Ionic Thiourea Organocatalyst

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1-nitrobenzyl-1-methylpyrrolidinium hexafluoridophosphate, (**1**)

p-Nitrobenzyl bromide (1.00 g, 4.63 mmol) was dissolved in 10 mL MeCN and *N*-methylpyrrolidine (0.48 mL, 4.63mmol) was added dropwise at ambient temperature. The reaction vessel was heated using microwave irradiation to 80 °C and held for fifteen minutes. The product was precipitated from the acetonitrile using an equal volume of ethyl acetate, filtered and dried under vacuum. (1.13 g, 81% yield)

MP 168-169 °C, IR (KBr): 2963, 1605, 1528, 1424, 1346 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300MHz) δ 8.35 (d, *J*=8.7Hz, 2H), 7.94 (d, *J*=8.7Hz, 2H), 4.85 (s, 2H), 3.65-3.69 (m, 2H), 3.46-4.51 (m, 2H), 2.97 (s, 3H), 2.14-2.16 (m, 2H),; ^{13}C NMR (DMSO-d_6, 75MHz) δ 149.0, 136.9, 134.6, 124.3, 64.1, 63.5 47.7, 21.2; ESI-MS: Positive Mode Found: m/z 221.9 [100%, $(C_{12}H_{17}N_2O_2)^+$]; Calc. 221.1

N-methyl-*N*-(p-nitrobenzyl)pyrrolidinium bromide (1.23 g, 4.08 mmol) was dissolved in a minimum amount of water and an aqueous solution of HPF_6 (1.25 eq, 0.43 mL) was added dropwise. The product precipitated, was filtered off after 3h and dried under vacuum. The product obtained was a white solid. (1.27 g, 85%).

MP 155-156 °C, IR (KBr): 3081, 1610, 1530, 1431, 1359, 834, 557 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300MHz) δ 8.34 (d, *J*=8.8Hz, 2H), 7.86 (d, *J*=8.8Hz, 2H), 4.72 (s, 2H), 3.58-3.62 (m, 2H), 3.41-3.47 (m, 2H), 2.93 (s, 3H), 2.14-2.16 (m, 2H); ^{13}C NMR (DMSO-d_6, 75MHz) δ 149.0, 136.4, 134.5, 124.3, 64.5, 63.6, 47.8, 21.2; ^{31}P NMR (DMSO-d_6, 121MHz) δ -144.2 (septet, *J*=711.4Hz); ESI-MS: Positive Mode Found: m/z 221.1 [100%, $(C_{12}H_{17}N_2O_2)^+$]; Calc. 221.1 Negative mode: m/z 144.6 [100%, $(PF_6)^-$]; Calc. 144.9

1-aminobenzyl-1-methylpyrrolidinium hexafluoridophosphate, (**2**)

$FeSO_4 \cdot 7H_2O$ (5.75 g, 20.69 mmol) and sodium citrate (0.44 g, 1.72 mmol) were added to 100 mL of H_2O. $NaBH_4$ (1.30 g , 34.49 mmol) was added slowly and the iron was reduced to black Fe^0. The water was decanted and the nanoparticles were washed and decanted twice more with 50 mL of water. *N*-methyl-*N*-(*p*-nitrobenzyl)pyrrolidinium hexafluorophosphate (1.26 g, 3.45 mmol) was added and the reaction was stirred at ambient temperature for 24 hours. The reaction mixture was passed through a vacuum frit to remove water and other aqueous impurities. The residue in the frit was washed with 3x20mL portions of acetonitrile. The acetonitrile from the washings was removed *in vacuo* and the product was dried under vacuum. The product was obtained was a yellow solid. (0.85 g, 73%)

MP 143-144 °C, IR (KBr): 3489, 3401, 2981, 1632, 1426, 835, 558 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300MHz) δ 7.16 (d, *J*=8.4Hz, 2H), 6.60 (d, *J*=8.4Hz, 2H), 5.53 (s, 2NH), 4.30 (s, 2H), 3.44-3.48 (m, 2H), 3.26-3.30 (m, 2H), 2.83 (s, 3H), 2.09 (s, 2H); ^{13}C NMR (DMSO-d_6, 75MHz) δ 150.8, 133.8, 115.4, 114.0, 66.1, 62.3, 47.5, 21.3; ^{31}P NMR (DMSO-d_6, 121MHz) δ -144.2 (septet, *J*=711.3Hz); ESI-MS: Positive Mode Found: m/z 191.2 [99.5%, $(C_{12}H_{19}N_2)^+$]; Calc. 191.1 Negative mode: m/z 144.6 [100%, $(PF_6)^-$]; Calc. 144.9; ESI-HRMS: Positive Mode Found: m/z 191.1535 [99.5%, $(C_{12}H_{19}N_2)^+$]; Calc. 191.1548

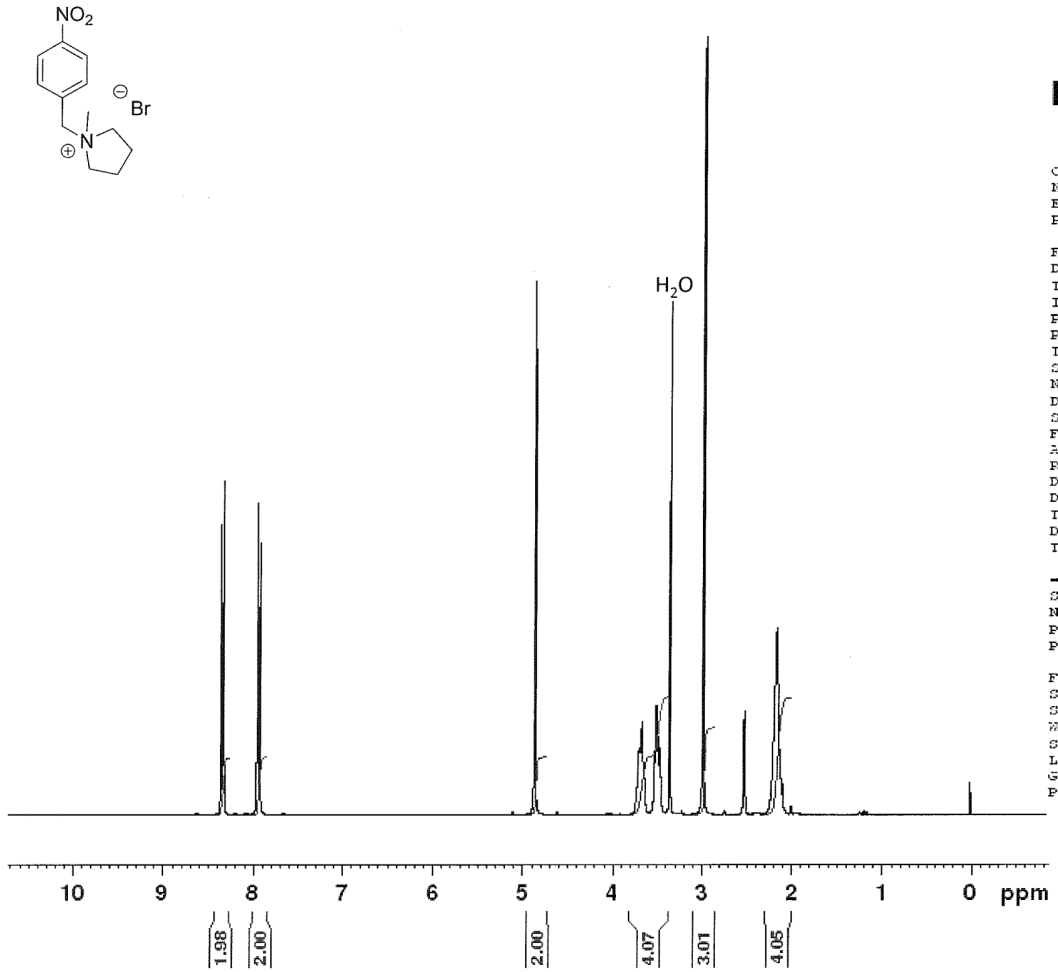
1-[4-({[3,5-di(trifluoromethyl)anilino]carbothioyl}amino)benzyl]-1-methylpyrrolidinium hexafluoridophosphate, (**3**)

N-methyl-*N*-(p-aminobenzyl)pyrrolidinium hexafluorophosphate (0.334g, 0.99 mmol) was dissolved in 5 mL MeCN and 3,5-bis(trifluoromethyl)phenyl isothiocyanate was added (0.18 mL, 0.99 mmol) and was heated to 50 °C under microwave irradiation for two hours. Solvent was removed *in vacuo* and after column chromatography with acetone as the eluting solvent the acetone was removed *in vacuo* and after drying under vacuum was obtained as a pale yellow solid. (0.49g, 81%)

IR (KBr): 3378, 1614, 1537, 1473, 1384, 1280, 1178, 1133, 841, 558 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300MHz) δ 10.46 (s, 1NH), 10.36 (s,1NH), 8.25 (s, 2H), 7.82 (s, 1H), 7.66 (d, *J*=8.6Hz, 2H), 7.56 (d, *J*=8.6Hz, 2H), 4.53 (s, 2H), 3.54-3.58 (m, 2H), 3.36-3.41 (m, 2H), 2.91 (s, 3H), 2.14-2.15 (m, 4H); ^{13}C NMR (DMSO-d_6, 75MHz) δ 180.3, 142.1, 141.0, 133.4, 130.8, 130.4, 125.6, 123.9, 121.9, 65.2, 63.1, 47.7, 21.3; ^{31}P NMR (DMSO-d_6, 121MHz) δ -144.2 (septet, *J*=711.4Hz); ESI-MS: Positive Mode Found: m/z 462.3 [100%, $(C_{21}H_{22}N_3F_6S)^+$]; Calc. 462.1; Negative mode: m/z

144.6 [100%, $(PF_6)^-$]; Calc. 144.9; ESI-HRMS: Positive Mode Found: m/z 462.1424 [100%, $(C_{21}H_{22}N_3F_6S)^+$]; Calc. 462.1439

General Procedure: Ionic thiourea catalyst, (**3**), (0.304g, 10 mol %) was placed in a 50 mL round bottom flask and dissolved in the appropriate solvent (see Table 1**)** with stirring at room temperature. Cyclohex-2-en-1-one (0.49 mL, 5.00 mmol) and benzaldehyde (0.10 mL, 1.00 mmol) were then added sequentially to the reaction mixture. DABCO (0.056g, 10 mol %) was then added to the reaction mixture. The reaction was stirred at room temperature (25°C) for the specified reaction time. Otherwise reactions were heated using a CEM Discover microwave reactor operating at 20W. Upon completion of reaction the organic materials were extracted using 5x10mL portions of diethyl ether. An aliquot of the ether extract was dissolved in $CDCl_3$ and the sample was analyzed *via* ^1H NMR spectroscopy to determine percent conversion to the allylic alcohol product, 2-(hydroxyphenylmethyl)cyclohex-2-en-1-one. To recycle the ionic liquid phase containing the catalyst, **3**, the ionic liquid phase was placed under vacuum to remove any residual ether. Benzaldehyde, cyclohex-2-en-1-one and DABCO were added in the same quantities as in the first run. The mixture was stirred for 48 hours and extracted using the same procedure with 5x10 mL portions of diethyl ether. The third consecutive reaction in [BMPyr][$N(Tf)_2$] was performed using the same procedure as the second and results are summarized in Table 1 (Entries 5a, 5b, 5c).



BRUKER

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RG                128.5
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TE               298.4 K
D1            1.00000000 sec
TD0                   1

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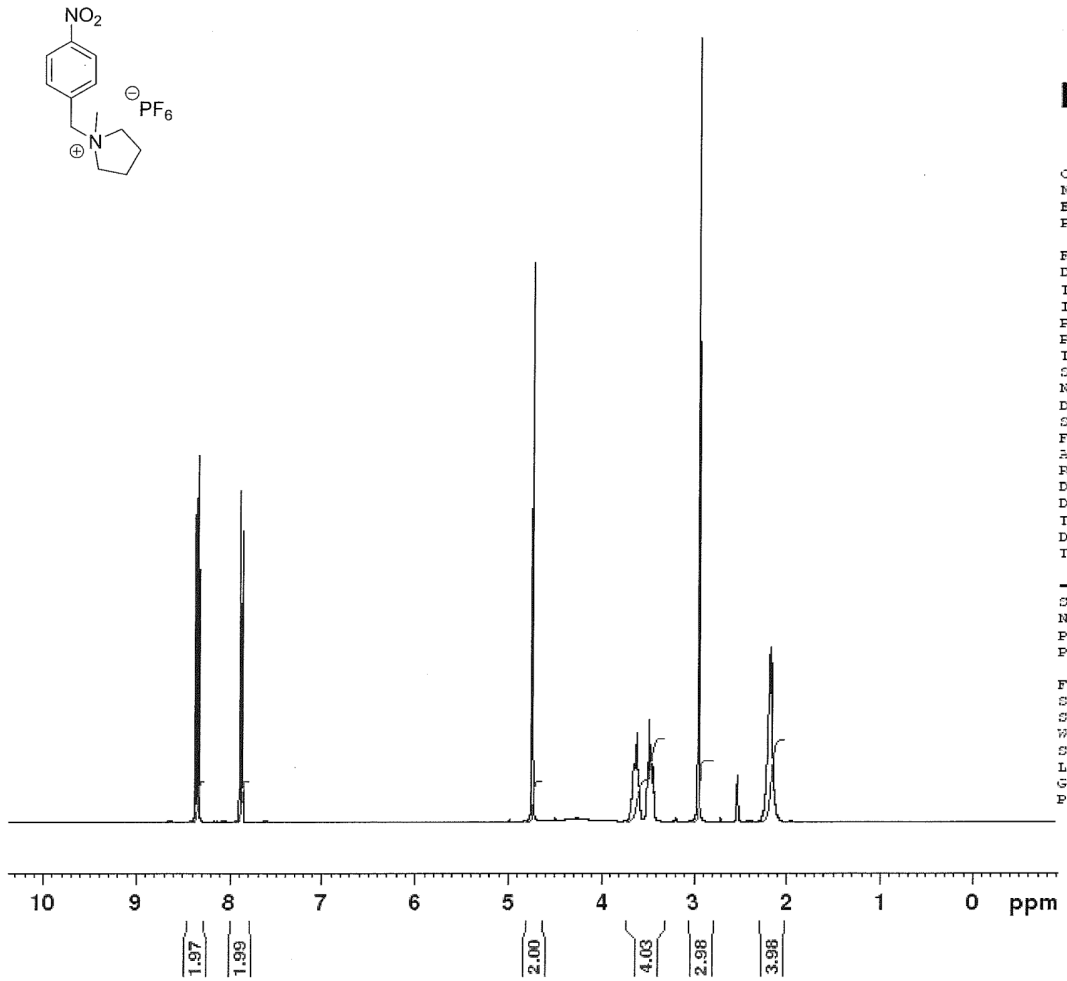

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FIDRES        0.091699 Hz
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P1               16.00 usec
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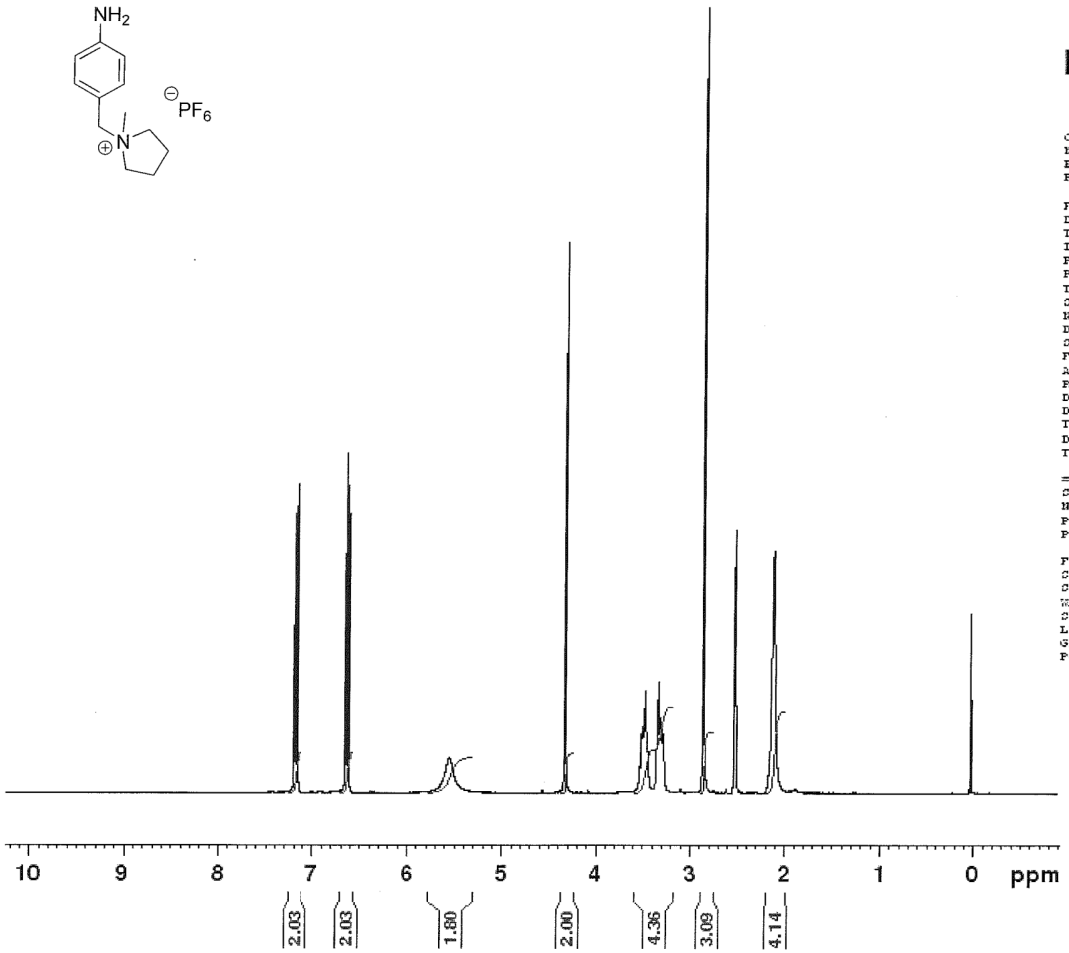

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TD               65536
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DS                    2
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RG                 216.01
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DE                12.21 usec
TE                298.4 K
D1             1.00000000 sec
TD0                   1

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PLW1          5.90000010 W

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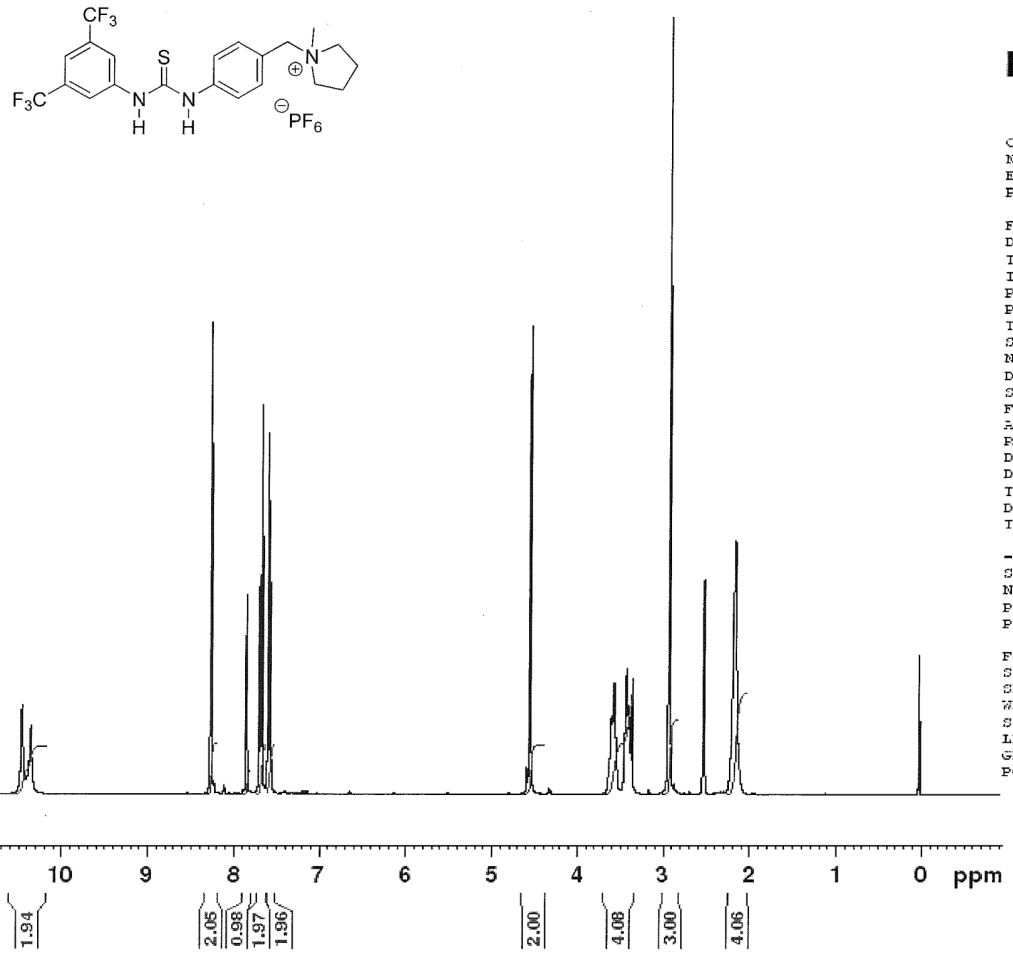

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PULPROG           zg30
TD               65536
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DS                   2
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AQ            5.4525952 sec
RG              216.01
DW               83.200 usec
DE               12.21 usec
TE              298.4 K
D1           1.00000000 sec
TD0                  1

--------- CHANNEL f1 -------
SFO1        300.2618542 MHz
NUC1              1H
P1               16.00 usec
PLW1          5.90000010 W

F2 - Processing parameters
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SF          300.2600000 MHz
WDW               EM
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PC              1.00
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Crystallographic data for the ionic thiourea derivative, 1-[4-({[3,5-di(trifluoromethyl)anilino]carbothioyl}amino)benzyl]-1-methylpyrrolidinium hexafluoridophosphate, (3).

The crystal was attached to the tip of a 300 μm MicroLoop with paratone-N oil. Measurements were made on a Bruker APEXII CCD [1] equipped diffractometer (30 mA, 50 mV) using monochromated Mo Kα radiation (λ = 0.71073 Å) at 125 K. The initial orientation and unit cell were indexed using a least-squares analysis of a random set of reflections collected from three series of 0.5° ω-scans, 10 seconds per frame and 12 frames per series, that were well distributed in reciprocal space. For data collection, four ω-scan frame series were collected with 0.5° wide scans, 30 second frames and 366 frames per series at varying φ angles (φ = 0°, 90°, 180°, 270°). The crystal to detector distance was set to 6 cm and a complete sphere of data was collected. Cell refinement and data reduction were performed with the Bruker SAINT software [2], which corrects for beam inhomogeneity, possible crystal decay, Lorentz and polarisation effects. A multi-scan absorption correction was applied (SADABS [3]). The structure was solved using Superflip [4] and EDMA [5] and refined using a full-matrix least-squares method on F^2 with SHELXL-2014 [6].

The non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to carbon were included at geometrically idealized positions and were not refined. The isotropic thermal parameters of the hydrogen atoms were fixed at $1.2U_{eq}$ of the parent carbon atom, $1.5U_{eq}$ for methyl and OH hydrogens. The only exceptions were the hydrogen atoms bonded to nitrogen. Those hydrogen atoms were allowed to refine isotropically with a weak restraint placed on the N-H bond lengths. The sulphur atom in the cation was found to be disordered over two positions. The occupancy was allowed to refine and found to be 95% for S1A and 5% for S1B. A weak restraint was placed on the two sulphurs to keep their anisotropic displacement parameters similar. One of the CF_3 groups in the cation was found to be disordered. The fluorine atoms in that group were split over two positions and allowed to refine with restraints placed on the C-F distances. The occupancy of the two groups was refined and determined to be 50% for the A atoms and 50% for the B atoms so it was set to that ratio in the final refinement. A restraint was also placed on all the fluorine atoms of the disordered group to make their anisotropic thermal motion more isotropic. The equatorial atoms of the PF_6^- anion were also found to be disordered. Those four fluorine atoms were split over two positions with the occupancy of the A positions refining to 90% and the B positions 10%. The P-F bond distances in the anion were all restrained to be equal and the thermal parameters of the anionic fluorines restrained to be more isotropic. Finally, one of the solvating acetone molecules (that with 50% occupancy) was also found to be disordered. The oxygen atom was split equally over two positions and the hydrogen atoms of the methyl groups were modeled with a 6-position orientation (spinning) rather than the usual three point placement.

Table 1. Crystal data and structure refinement for (**3**).

Identification code	Ionic thiourea derivative, (**3**)	
Empirical formula	$C_{51}\ H_{62}\ F_{24}\ N_6\ O_3\ P_2\ S_2$	
Formula weight	1389.12	
Temperature	125(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P* -1	
Unit cell dimensions	*a* = 9.2648(13) Å	□= 82.916(2)°
	b = 10.2545(15) Å	□= 80.708(2)°
	c = 16.746(2) Å	□ = 71.473(2)°
Volume	1484.3(4) $Å^3$	
Z	1	
Density (calculated)	1.554 Mg/m^3	
Absorption coefficient	0.267 mm^{-1}	
F(000)	712	
Crystal size	0.240 x 0.210 x 0.170 mm^3	
Theta range for data collection	2.101 to 28.754°	
Index ranges	-12<=h<=12, -13<=k<=13, -22<=l<=22	
Reflections collected	17868	
Independent reflections	7066 [R(int) = 0.0197]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7458 and 0.6935	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7066 / 117 / 504	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.0441, wR2 = 0.1126	
R indices (all data)	R1 = 0.0553, wR2 = 0.1207	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.545 and -0.409 $e.Å^{-3}$	

Table 2. 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)
S(1A)	949(2)	5381(1)	2120(1)	23(1)
S(1B)	1710(40)	5200(15)	1985(9)	35(3)
F(1)	2245(2)	11148(2)	-1264(1)	53(1)
F(2)	3290(2)	11098(2)	-216(1)	61(1)
F(3)	4427(2)	9713(2)	-1128(1)	62(1)
F(4A)	797(4)	6989(3)	-1664(1)	43(1)
F(5A)	1252(5)	5352(3)	-747(2)	46(1)
F(6A)	-965(6)	6931(5)	-657(3)	53(1)
F(4B)	-197(6)	7642(5)	-1495(3)	83(1)
F(5B)	1418(6)	5749(6)	-1136(4)	98(2)
F(6B)	-724(6)	6422(5)	-480(3)	52(1)
N(1)	1488(2)	7838(2)	1771(1)	24(1)
N(2)	1452(2)	7047(1)	3085(1)	20(1)
N(3)	3460(2)	3547(1)	6505(1)	20(1)
C(1)	1541(2)	8004(2)	922(1)	21(1)
C(2)	2207(2)	9005(2)	532(1)	23(1)
C(3)	2307(2)	9266(2)	-301(1)	25(1)
C(4)	1752(2)	8554(2)	-773(1)	28(1)
C(5)	1086(2)	7574(2)	-380(1)	28(1)
C(6)	968(2)	7287(2)	459(1)	25(1)
C(7)	3073(2)	10300(2)	-719(1)	31(1)
C(8)	480(3)	6770(2)	-865(1)	40(1)
C(9)	1322(2)	6784(2)	2324(1)	19(1)
C(10)	1638(2)	6148(2)	3801(1)	18(1)
C(11)	2442(2)	4740(2)	3800(1)	20(1)
C(12)	2638(2)	3944(2)	4531(1)	21(1)
C(13)	2048(2)	4524(2)	5273(1)	20(1)
C(14)	1281(2)	5935(2)	5265(1)	21(1)
C(15)	1083(2)	6745(2)	4539(1)	20(1)
C(16)	2134(2)	3622(2)	6059(1)	21(1)

C(17)	3370(2)	2653(2)	7295(1)	25(1)
C(18)	4197(3)	3132(2)	7861(1)	33(1)
C(19)	4301(2)	4551(2)	7492(1)	30(1)
C(20)	3349(2)	4921(2)	6792(1)	25(1)
C(21)	4955(2)	2965(2)	5993(1)	28(1)
P(1)	7406(1)	919(1)	3560(1)	30(1)
F(7A)	8186(4)	32(2)	2794(1)	67(1)
F(8A)	6683(3)	1805(2)	4314(1)	58(1)
F(9A)	6327(3)	2063(2)	3005(2)	71(1)
F(10A)	8532(3)	-225(2)	4088(2)	59(1)
F(7B)	7080(30)	399(17)	2793(8)	50(5)
F(8B)	5847(16)	2199(14)	3476(14)	50(5)
F(9B)	7390(30)	1500(30)	4389(11)	72(7)
F(10B)	8780(20)	-391(19)	3650(20)	85(8)
F(11)	6174(2)	110(2)	3794(1)	73(1)
F(12)	8644(2)	1735(2)	3321(1)	56(1)
O(1)	2327(2)	9521(1)	2775(1)	33(1)
C(22)	2102(3)	10601(2)	3978(1)	42(1)
C(23)	2392(2)	10521(2)	3078(1)	27(1)
C(24)	2810(3)	11676(2)	2576(2)	44(1)
O(2A)	4730(30)	6002(16)	775(13)	52(3)
O(2B)	4840(40)	5560(20)	894(18)	73(5)
C(25)	5471(8)	5972(8)	-603(4)	63(2)
C(26)	4873(6)	5344(6)	187(4)	51(1)
C(27)	4349(9)	4098(8)	158(5)	64(2)

Table 3. Bond lengths [Å] and angles [°] for (**3**).

S(1A)-S(1B)	0.68(3)
S(1A)-C(9)	1.6679(17)
S(1B)-C(9)	1.697(14)
F(1)-C(7)	1.335(2)
F(2)-C(7)	1.323(2)
F(3)-C(7)	1.323(2)
F(4A)-C(8)	1.329(3)
F(5A)-C(8)	1.407(4)
F(6A)-C(8)	1.289(5)
F(4B)-C(8)	1.390(4)
F(5B)-C(8)	1.212(5)
F(6B)-C(8)	1.323(5)
N(1)-C(9)	1.365(2)
N(1)-C(1)	1.406(2)
N(1)-H(1N)	0.824(16)
N(2)-C(9)	1.366(2)
N(2)-C(10)	1.418(2)
N(2)-H(2N)	0.843(15)
N(3)-C(21)	1.492(2)
N(3)-C(20)	1.512(2)
N(3)-C(16)	1.514(2)
N(3)-C(17)	1.521(2)
C(1)-C(6)	1.394(2)
C(1)-C(2)	1.401(2)
C(2)-C(3)	1.381(2)
C(2)-H(2)	0.9500
C(3)-C(4)	1.391(3)
C(3)-C(7)	1.501(2)
C(4)-C(5)	1.388(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.394(2)
C(5)-C(8)	1.504(3)
C(6)-H(6)	0.9500
C(10)-C(15)	1.395(2)
C(10)-C(11)	1.399(2)
C(11)-C(12)	1.389(2)
C(11)-H(11)	0.9500
C(12)-C(13)	1.397(2)
C(12)-H(12)	0.9500
C(13)-C(14)	1.394(2)
C(13)-C(16)	1.510(2)
C(14)-C(15)	1.389(2)
C(14)-H(14)	0.9500

C(15)-H(15)	0.9500
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-C(18)	1.521(3)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-C(19)	1.535(3)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-C(20)	1.520(3)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
P(1)-F(10B)	1.543(13)
P(1)-F(7B)	1.557(11)
P(1)-F(9B)	1.573(13)
P(1)-F(8A)	1.5789(18)
P(1)-F(10A)	1.5847(16)
P(1)-F(11)	1.5884(16)
P(1)-F(9A)	1.5889(17)
P(1)-F(12)	1.5984(15)
P(1)-F(7A)	1.6009(18)
P(1)-F(8B)	1.626(11)
O(1)-C(23)	1.221(2)
C(22)-C(23)	1.495(3)
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-C(24)	1.484(3)
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
O(2A)-C(26)	1.23(2)
O(2A)-C(27)#1	1.65(3)
O(2B)-C(26)	1.22(3)
O(2B)-C(25)#1	1.82(3)
O(2B)-C(27)#1	1.84(3)
C(25)-C(26)	1.501(10)
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(25)-H(25D)	0.9800

C(25)-H(25E)	0.9800
C(25)-H(25F)	0.9800
C(26)-C(26)#1	0.950(10)
C(26)-C(27)#1	1.108(9)
C(26)-C(27)	1.513(10)
C(26)-C(25)#1	1.542(10)
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(27)-H(27D)	0.9800
C(27)-H(27E)	0.9800
C(27)-H(27F)	0.9800

S(1B)-S(1A)-C(9)	80.7(12)
S(1A)-S(1B)-C(9)	76.0(14)
C(9)-N(1)-C(1)	131.94(15)
C(9)-N(1)-H(1N)	116.5(15)
C(1)-N(1)-H(1N)	110.9(15)
C(9)-N(2)-C(10)	129.60(14)
C(9)-N(2)-H(2N)	115.0(14)
C(10)-N(2)-H(2N)	115.4(14)
C(21)-N(3)-C(20)	111.23(14)
C(21)-N(3)-C(16)	110.52(13)
C(20)-N(3)-C(16)	112.73(13)
C(21)-N(3)-C(17)	110.16(13)
C(20)-N(3)-C(17)	102.70(13)
C(16)-N(3)-C(17)	109.21(12)
C(6)-C(1)-C(2)	119.22(15)
C(6)-C(1)-N(1)	125.48(15)
C(2)-C(1)-N(1)	115.28(15)
C(3)-C(2)-C(1)	120.34(16)
C(3)-C(2)-H(2)	119.8
C(1)-C(2)-H(2)	119.8
C(2)-C(3)-C(4)	121.35(16)
C(2)-C(3)-C(7)	120.19(17)
C(4)-C(3)-C(7)	118.43(16)
C(5)-C(4)-C(3)	117.76(16)
C(5)-C(4)-H(4)	121.1
C(3)-C(4)-H(4)	121.1
C(4)-C(5)-C(6)	122.25(17)
C(4)-C(5)-C(8)	119.77(16)
C(6)-C(5)-C(8)	117.97(17)
C(5)-C(6)-C(1)	119.08(16)
C(5)-C(6)-H(6)	120.5
C(1)-C(6)-H(6)	120.5
F(2)-C(7)-F(3)	107.01(18)

F(2)-C(7)-F(1)	106.17(17)
F(3)-C(7)-F(1)	105.57(16)
F(2)-C(7)-C(3)	113.32(15)
F(3)-C(7)-C(3)	112.50(16)
F(1)-C(7)-C(3)	111.74(16)
F(5B)-C(8)-F(6B)	108.4(4)
F(6A)-C(8)-F(4A)	111.0(3)
F(5B)-C(8)-F(4B)	109.5(4)
F(6B)-C(8)-F(4B)	99.5(3)
F(6A)-C(8)-F(5A)	107.1(3)
F(4A)-C(8)-F(5A)	101.3(3)
F(5B)-C(8)-C(5)	115.3(3)
F(6A)-C(8)-C(5)	112.6(3)
F(6B)-C(8)-C(5)	114.1(3)
F(4A)-C(8)-C(5)	114.1(2)
F(4B)-C(8)-C(5)	108.8(2)
F(5A)-C(8)-C(5)	109.9(2)
N(1)-C(9)-N(2)	110.87(14)
N(1)-C(9)-S(1A)	125.39(13)
N(2)-C(9)-S(1A)	123.70(12)
N(1)-C(9)-S(1B)	118.0(6)
N(2)-C(9)-S(1B)	125.9(5)
C(15)-C(10)-C(11)	119.52(14)
C(15)-C(10)-N(2)	116.96(14)
C(11)-C(10)-N(2)	123.33(15)
C(12)-C(11)-C(10)	119.73(15)
C(12)-C(11)-H(11)	120.1
C(10)-C(11)-H(11)	120.1
C(11)-C(12)-C(13)	121.19(15)
C(11)-C(12)-H(12)	119.4
C(13)-C(12)-H(12)	119.4
C(14)-C(13)-C(12)	118.39(15)
C(14)-C(13)-C(16)	120.92(15)
C(12)-C(13)-C(16)	120.52(15)
C(15)-C(14)-C(13)	121.04(15)
C(15)-C(14)-H(14)	119.5
C(13)-C(14)-H(14)	119.5
C(14)-C(15)-C(10)	120.07(15)
C(14)-C(15)-H(15)	120.0
C(10)-C(15)-H(15)	120.0
C(13)-C(16)-N(3)	114.90(13)
C(13)-C(16)-H(16A)	108.5
N(3)-C(16)-H(16A)	108.5
C(13)-C(16)-H(16B)	108.5
N(3)-C(16)-H(16B)	108.5
H(16A)-C(16)-H(16B)	107.5

N(3)-C(17)-C(18)	105.81(14)
N(3)-C(17)-H(17A)	110.6
C(18)-C(17)-H(17A)	110.6
N(3)-C(17)-H(17B)	110.6
C(18)-C(17)-H(17B)	110.6
H(17A)-C(17)-H(17B)	108.7
C(17)-C(18)-C(19)	105.96(15)
C(17)-C(18)-H(18A)	110.5
C(19)-C(18)-H(18A)	110.5
C(17)-C(18)-H(18B)	110.5
C(19)-C(18)-H(18B)	110.5
H(18A)-C(18)-H(18B)	108.7
C(20)-C(19)-C(18)	105.57(15)
C(20)-C(19)-H(19A)	110.6
C(18)-C(19)-H(19A)	110.6
C(20)-C(19)-H(19B)	110.6
C(18)-C(19)-H(19B)	110.6
H(19A)-C(19)-H(19B)	108.8
N(3)-C(20)-C(19)	104.54(14)
N(3)-C(20)-H(20A)	110.8
C(19)-C(20)-H(20A)	110.8
N(3)-C(20)-H(20B)	110.8
C(19)-C(20)-H(20B)	110.8
H(20A)-C(20)-H(20B)	108.9
N(3)-C(21)-H(21A)	109.5
N(3)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
N(3)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
F(10B)-P(1)-F(7B)	90.5(13)
F(10B)-P(1)-F(9B)	97.0(14)
F(7B)-P(1)-F(9B)	168.7(12)
F(8A)-P(1)-F(10A)	91.42(12)
F(10B)-P(1)-F(11)	93.7(9)
F(7B)-P(1)-F(11)	69.1(8)
F(9B)-P(1)-F(11)	101.9(10)
F(8A)-P(1)-F(11)	90.14(12)
F(10A)-P(1)-F(11)	89.17(12)
F(8A)-P(1)-F(9A)	90.05(14)
F(10A)-P(1)-F(9A)	177.95(15)
F(11)-P(1)-F(9A)	92.27(12)
F(10B)-P(1)-F(12)	86.3(9)
F(7B)-P(1)-F(12)	110.8(8)
F(9B)-P(1)-F(12)	78.3(10)
F(8A)-P(1)-F(12)	89.96(11)

F(10A)-P(1)-F(12)	90.95(11)
F(11)-P(1)-F(12)	179.84(10)
F(9A)-P(1)-F(12)	87.61(11)
F(8A)-P(1)-F(7A)	178.29(14)
F(10A)-P(1)-F(7A)	87.96(12)
F(11)-P(1)-F(7A)	91.44(12)
F(9A)-P(1)-F(7A)	90.54(14)
F(12)-P(1)-F(7A)	88.46(11)
F(10B)-P(1)-F(8B)	174.3(11)
F(7B)-P(1)-F(8B)	86.6(10)
F(9B)-P(1)-F(8B)	85.1(11)
F(11)-P(1)-F(8B)	80.6(6)
F(12)-P(1)-F(8B)	99.3(6)
C(23)-C(22)-H(22A)	109.5
C(23)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(23)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
O(1)-C(23)-C(24)	121.71(18)
O(1)-C(23)-C(22)	120.81(18)
C(24)-C(23)-C(22)	117.45(17)
C(23)-C(24)-H(24A)	109.5
C(23)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(23)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(26)-C(25)-H(25A)	109.5
C(26)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(26)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(26)-C(25)-H(25D)	109.5
H(25A)-C(25)-H(25D)	141.1
H(25B)-C(25)-H(25D)	56.3
H(25C)-C(25)-H(25D)	56.3
C(26)-C(25)-H(25E)	109.5
H(25A)-C(25)-H(25E)	56.3
H(25B)-C(25)-H(25E)	141.1
H(25C)-C(25)-H(25E)	56.3
H(25D)-C(25)-H(25E)	109.5
C(26)-C(25)-H(25F)	109.5
H(25A)-C(25)-H(25F)	56.3
H(25B)-C(25)-H(25F)	56.3

H(25C)-C(25)-H(25F)	141.1
H(25D)-C(25)-H(25F)	109.5
H(25E)-C(25)-H(25F)	109.5
O(2B)-C(26)-C(25)	132.5(14)
O(2A)-C(26)-C(25)	114.6(12)
O(2B)-C(26)-C(27)	109.6(14)
O(2A)-C(26)-C(27)	127.5(13)
C(25)-C(26)-C(27)	117.5(5)
C(26)-C(27)-H(27A)	109.5
C(26)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(26)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(26)-C(27)-H(27D)	109.5
H(27A)-C(27)-H(27D)	141.1
H(27B)-C(27)-H(27D)	56.3
H(27C)-C(27)-H(27D)	56.3
C(26)-C(27)-H(27E)	109.5
H(27A)-C(27)-H(27E)	56.3
H(27B)-C(27)-H(27E)	141.1
H(27C)-C(27)-H(27E)	56.3
H(27D)-C(27)-H(27E)	109.5
C(26)-C(27)-H(27F)	109.5
H(27A)-C(27)-H(27F)	56.3
H(27B)-C(27)-H(27F)	56.3
H(27C)-C(27)-H(27F)	141.1
H(27D)-C(27)-H(27F)	109.5
H(27E)-C(27)-H(27F)	109.5

Symmetry transformations used to generate equivalent atoms:

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

Table 4. 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}
S(1A)	37(1)	19(1)	18(1)	0(1)	-6(1)	-14(1)
S(1B)	41(9)	29(5)	33(6)	-1(4)	2(6)	-13(5)
F(1)	60(1)	55(1)	48(1)	33(1)	-17(1)	-31(1)
F(2)	113(1)	59(1)	33(1)	3(1)	-3(1)	-64(1)
F(3)	44(1)	51(1)	81(1)	2(1)	22(1)	-19(1)
F(4A)	74(2)	56(2)	13(1)	-3(1)	-5(1)	-40(2)
F(5A)	73(2)	33(1)	41(2)	-6(1)	-21(2)	-22(1)
F(6A)	42(2)	65(3)	60(2)	-14(2)	-14(2)	-22(2)
F(4B)	121(3)	93(3)	62(2)	23(2)	-60(2)	-58(2)
F(5B)	70(2)	118(3)	118(3)	-89(3)	-6(2)	-19(2)
F(6B)	59(2)	65(3)	48(2)	-17(2)	-4(2)	-39(2)
N(1)	39(1)	21(1)	17(1)	1(1)	-6(1)	-16(1)
N(2)	30(1)	16(1)	16(1)	0(1)	-5(1)	-10(1)
N(3)	22(1)	21(1)	18(1)	3(1)	-5(1)	-9(1)
C(1)	26(1)	21(1)	16(1)	1(1)	-4(1)	-6(1)
C(2)	28(1)	21(1)	21(1)	1(1)	-5(1)	-9(1)
C(3)	28(1)	25(1)	21(1)	4(1)	-2(1)	-8(1)
C(4)	34(1)	34(1)	17(1)	3(1)	-4(1)	-13(1)
C(5)	34(1)	33(1)	20(1)	0(1)	-6(1)	-14(1)
C(6)	32(1)	26(1)	19(1)	2(1)	-4(1)	-13(1)
C(7)	38(1)	34(1)	23(1)	4(1)	-2(1)	-17(1)
C(8)	54(1)	57(1)	20(1)	-2(1)	-6(1)	-32(1)
C(9)	21(1)	19(1)	17(1)	0(1)	-3(1)	-6(1)
C(10)	20(1)	20(1)	17(1)	2(1)	-5(1)	-11(1)
C(11)	24(1)	21(1)	19(1)	-2(1)	-3(1)	-9(1)
C(12)	25(1)	18(1)	21(1)	0(1)	-5(1)	-9(1)
C(13)	20(1)	23(1)	18(1)	3(1)	-5(1)	-10(1)
C(14)	21(1)	26(1)	16(1)	-2(1)	-2(1)	-7(1)
C(15)	20(1)	19(1)	21(1)	-2(1)	-4(1)	-5(1)
C(16)	22(1)	25(1)	20(1)	4(1)	-6(1)	-12(1)
C(17)	32(1)	27(1)	18(1)	8(1)	-8(1)	-13(1)

C(18)	45(1)	32(1)	25(1)	3(1)	-12(1)	-15(1)
C(19)	35(1)	35(1)	25(1)	-1(1)	-6(1)	-17(1)
C(20)	34(1)	21(1)	24(1)	0(1)	-7(1)	-11(1)
C(21)	23(1)	34(1)	25(1)	-1(1)	-3(1)	-5(1)
P(1)	41(1)	22(1)	26(1)	-2(1)	-7(1)	-9(1)
F(7A)	113(2)	56(1)	37(1)	-22(1)	9(1)	-35(1)
F(8A)	73(2)	43(1)	50(1)	-22(1)	18(1)	-11(1)
F(9A)	87(2)	51(1)	85(2)	26(1)	-59(2)	-25(1)
F(10A)	69(1)	41(1)	49(1)	11(1)	-18(1)	8(1)
F(7B)	76(10)	48(7)	34(6)	-11(5)	-14(6)	-21(7)
F(8B)	50(7)	36(6)	57(9)	3(6)	-5(6)	-7(5)
F(9B)	90(12)	76(11)	62(10)	-23(7)	-19(8)	-31(8)
F(10B)	75(10)	70(10)	104(12)	7(8)	-2(8)	-23(7)
F(11)	65(1)	47(1)	115(2)	-8(1)	4(1)	-34(1)
F(12)	56(1)	45(1)	69(1)	-9(1)	7(1)	-23(1)
O(1)	47(1)	24(1)	32(1)	-6(1)	-8(1)	-17(1)
C(22)	54(1)	38(1)	34(1)	-12(1)	-9(1)	-13(1)
C(23)	27(1)	20(1)	34(1)	-5(1)	-9(1)	-4(1)
C(24)	62(2)	28(1)	48(1)	1(1)	-10(1)	-21(1)
O(2A)	58(5)	57(9)	44(6)	-15(6)	-26(4)	-10(7)
O(2B)	72(7)	75(12)	75(9)	-4(8)	-30(6)	-20(10)
C(25)	48(3)	69(4)	60(4)	-12(4)	-4(3)	1(3)
C(26)	35(3)	59(4)	56(4)	-24(2)	-18(2)	3(2)
C(27)	55(4)	59(4)	82(5)	-24(4)	-5(4)	-16(3)

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

	x	y	z	U(eq)
H(1N)	1730(20)	8451(19)	1938(13)	29
H(2N)	1420(20)	7863(16)	3134(13)	24
H(2)	2591	9505	843	28
H(4)	1827	8734	-1346	34
H(6)	504	6612	713	30
H(11)	2851	4330	3300	25
H(12)	3184	2988	4526	25
H(14)	888	6349	5764	25
H(15)	569	7708	4544	24
H(16A)	2216	2677	5941	26
H(16B)	1163	3972	6422	26
H(17A)	3878	1667	7204	30
H(17B)	2287	2776	7528	30
H(18A)	5236	2475	7897	39
H(18B)	3614	3204	8413	39
H(19A)	3883	5244	7900	36
H(19B)	5381	4507	7295	36
H(20A)	2269	5436	6976	30
H(20B)	3771	5489	6352	30
H(21A)	4987	2085	5808	42
H(21B)	5798	2815	6314	42
H(21C)	5062	3613	5522	42
H(22A)	1793	9803	4236	62
H(22B)	1280	11451	4111	62
H(22C)	3041	10601	4176	62
H(24A)	2958	11506	2001	66
H(24B)	3763	11746	2723	66
H(24C)	1984	12540	2672	66
H(25A)	5460	6910	-533	95
H(25B)	4819	6004	-1016	95

H(25C)	6525	5412	-777	95
H(25D)	5743	5307	-1017	95
H(25E)	6383	6213	-535	95
H(25F)	4678	6805	-774	95
H(27A)	3602	4030	636	97
H(27B)	5235	3263	155	97
H(27C)	3869	4194	-335	97
H(27D)	4868	3628	-332	97
H(27E)	3236	4395	149	97
H(27F)	4602	3464	639	97

Table 6. Torsion angles [°] for (**3**).

C(9)-N(1)-C(1)-C(6)	21.1(3)
C(9)-N(1)-C(1)-C(2)	-160.25(18)
C(6)-C(1)-C(2)-C(3)	-0.6(3)
N(1)-C(1)-C(2)-C(3)	-179.38(16)
C(1)-C(2)-C(3)-C(4)	0.2(3)
C(1)-C(2)-C(3)-C(7)	-177.74(17)
C(2)-C(3)-C(4)-C(5)	0.2(3)
C(7)-C(3)-C(4)-C(5)	178.22(18)
C(3)-C(4)-C(5)-C(6)	-0.2(3)
C(3)-C(4)-C(5)-C(8)	-179.55(19)
C(4)-C(5)-C(6)-C(1)	-0.2(3)
C(8)-C(5)-C(6)-C(1)	179.12(18)
C(2)-C(1)-C(6)-C(5)	0.6(3)
N(1)-C(1)-C(6)-C(5)	179.23(17)
C(2)-C(3)-C(7)-F(2)	-14.2(3)
C(4)-C(3)-C(7)-F(2)	167.80(18)
C(2)-C(3)-C(7)-F(3)	107.4(2)
C(4)-C(3)-C(7)-F(3)	-70.6(2)
C(2)-C(3)-C(7)-F(1)	-134.09(19)
C(4)-C(3)-C(7)-F(1)	47.9(2)
C(4)-C(5)-C(8)-F(5B)	85.5(4)
C(6)-C(5)-C(8)-F(5B)	-93.9(4)
C(4)-C(5)-C(8)-F(6A)	-120.9(3)
C(6)-C(5)-C(8)-F(6A)	59.8(3)
C(4)-C(5)-C(8)-F(6B)	-148.0(3)
C(6)-C(5)-C(8)-F(6B)	32.7(4)
C(4)-C(5)-C(8)-F(4A)	6.8(3)
C(6)-C(5)-C(8)-F(4A)	-172.5(3)
C(4)-C(5)-C(8)-F(4B)	-38.0(4)
C(6)-C(5)-C(8)-F(4B)	142.7(3)
C(4)-C(5)-C(8)-F(5A)	119.8(3)
C(6)-C(5)-C(8)-F(5A)	-59.6(3)
C(1)-N(1)-C(9)-N(2)	175.50(17)
C(1)-N(1)-C(9)-S(1A)	-6.5(3)
C(1)-N(1)-C(9)-S(1B)	19.5(11)
C(10)-N(2)-C(9)-N(1)	-167.01(16)
C(10)-N(2)-C(9)-S(1A)	15.0(3)
C(10)-N(2)-C(9)-S(1B)	-13.4(13)
S(1B)-S(1A)-C(9)-N(1)	78.8(12)
S(1B)-S(1A)-C(9)-N(2)	-103.5(12)
S(1A)-S(1B)-C(9)-N(1)	-115.1(11)
S(1A)-S(1B)-C(9)-N(2)	92.9(14)
C(9)-N(2)-C(10)-C(15)	-152.53(17)

C(9)-N(2)-C(10)-C(11)	32.5(3)
C(15)-C(10)-C(11)-C(12)	1.9(2)
N(2)-C(10)-C(11)-C(12)	176.76(15)
C(10)-C(11)-C(12)-C(13)	-0.1(2)
C(11)-C(12)-C(13)-C(14)	-1.4(2)
C(11)-C(12)-C(13)-C(16)	173.96(15)
C(12)-C(13)-C(14)-C(15)	1.1(2)
C(16)-C(13)-C(14)-C(15)	-174.29(15)
C(13)-C(14)-C(15)-C(10)	0.8(2)
C(11)-C(10)-C(15)-C(14)	-2.3(2)
N(2)-C(10)-C(15)-C(14)	-177.43(15)
C(14)-C(13)-C(16)-N(3)	-86.85(19)
C(12)-C(13)-C(16)-N(3)	97.87(18)
C(21)-N(3)-C(16)-C(13)	-60.78(18)
C(20)-N(3)-C(16)-C(13)	64.40(18)
C(17)-N(3)-C(16)-C(13)	177.88(14)
C(21)-N(3)-C(17)-C(18)	83.69(18)
C(20)-N(3)-C(17)-C(18)	-34.88(18)
C(16)-N(3)-C(17)-C(18)	-154.75(15)
N(3)-C(17)-C(18)-C(19)	17.1(2)
C(17)-C(18)-C(19)-C(20)	7.3(2)
C(21)-N(3)-C(20)-C(19)	-78.44(17)
C(16)-N(3)-C(20)-C(19)	156.77(14)
C(17)-N(3)-C(20)-C(19)	39.37(17)
C(18)-C(19)-C(20)-N(3)	-29.05(19)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z

Table 7. Hydrogen bonds for (**3**) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(1)	0.824(16)	2.117(17)	2.8980(19)	158(2)
N(2)-H(2N)...F(10B)#2	0.843(15)	2.62(3)	3.104(19)	118.1(17)
N(2)-H(2N)...O(1)	0.843(15)	2.107(17)	2.8654(19)	149.5(19)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z #2 x-1,y+1,z

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