Self-assembly between 1,4-diazabicyclo[2.2.2]octane and bis(hexafluoroalcohols): solid/liquid phase switching for catalyst recycling

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Supporting information

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General methods and materials

General methods: ^{1}H, ^{13}C and ^{19}F NMR spectra were obtained on Bruker 200 and 300 spectrometers. In all measurements $CDCl_3$ was used as solvent, except where indicated. Chemical shifts (δ) are given in ppm relative to TMS, as internal standard for ^{1}H and ^{13}C NMR, and relative to $CFCl_3$ for ^{19}F NMR. Coupling constants *J* are measured in Hz.
IR spectra have been recorded on a FT Brucker Vector 22 spectrometer.
APCI MS spectra have been obtained on an Esquire-LC Bruker spectrometer.

Materials: All chemicals were used as provided without further purification, except benzaldehyde that was purified by washing with aq. sol. $NaHCO_3$.

NMR spectra of compounds **2-10** match with those reported in the literature. References are given for each compound.

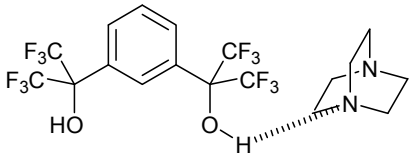
Crystal structure analyses: X-ray crystal structures were determined with Cu-Kα radiation (λ = 1.54178 Å) at 173 K using a Rigaku Saturn CCD with a Rigaku MM007 RA and confocal optics. The data was corrected for Lorentz, polarisation and absorption. The data for the complexes analysed was collected and processed using CrystalClear (Rigaku).[1] The structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure[2] crystallographic software package except for refinement, which was performed using SHELXL-97.[3]

These X-ray data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html CCDC 855431, 855432 or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk.

1 (a) CrystalClear 2.0: Rigaku Corporation, 2004; (b) J. W. P. Flugrath, *Acta Cryst.*, **1999**, *D55*, 1718.
2 CrystalStructure 4.0: Crystal Structure Analysis Package, Rigaku and Rigaku/MSC (2000-2009). 9009 New Trails Dr. The Woodlands TX 77381 USA.
3 G.M. Sheldrick, *Acta Cryst. A*, **2008**, *64*, 112.

Synthesis of 1a and 1b

1,3-Bis-HFAB/DABCO adduct (1a)



A solution of 1,4-diazabicyclo[2.2.2]octane (6 mmol, 672 mg) in dichloromethane (20 mL) was added dropwise to a solution of 1,3-bis-HFAB (6 mmol, 2.46 g) in dichloromethane (20 mL) at room temperature. A solid was immediately formed, which was filtered and then crystallized from toluene (90 mL) to afford **1a** (2.86 g, 91% yield).

White crystals, mp 208-210 °C

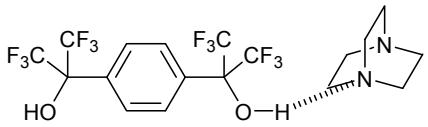
^{19}F NMR (acetone-d_6, 188 MHz) δ = –70.7 (s)

^{1}H NMR (acetone-d_6, 300 MHz) δ = 2.72 (s, 12H), 7.70 (t, J = 8.0, 1H), 7.93 (d, J = 8.1, 2 H), 8.29 (s, 1H), OH n.o.

^{13}C NMR (acetone-d_6, 75 MHz) δ = 48.2, 79.1 (sept, $^{2}J_{C\text{-}F}$ = 29), 125.0 (q, $^{1}J_{C\text{-}F}$ = 288), 127.8, 130.5, 130.8, 133.9.

Anal. Calcd for $C_{18}H_{18}F_{12}N_2O_2$ (522.33): C, 41.39; H, 3.47; N, 5.36. Found: C, 41.43; H, 3.64; N, 5.27.

1,4-Bis-HFAB/DABCO adduct (1b)



A solution of 1,4-diazabicyclo[2.2.2]octane (6 mmol, 672 mg) in dichloromethane (20 mL) was added dropwise to a solution of 1,4-bis-HFAB (6 mmol, 2.46 g) in warm dichloromethane (60 mL). A solid was immediately formed, which was filtered and then crystallized from toluene (150 mL) to afford **1b** (2.80 g, 89% yield).

White crystals, mp 240 °C

^{19}F NMR (acetone-d_6, 188 MHz) δ = –70.7 (s)

^{1}H NMR (acetone-d_6, 200 MHz) δ = 2.71 (s, 12H), 7.94 (s, 4H), OH n.o.

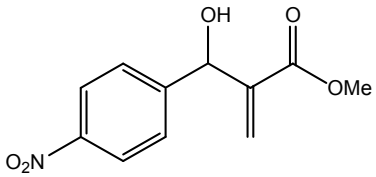
^{13}C NMR (acetone-d_6, 75 MHz) δ = 48.2, 79.1 (sept, $^{2}J_{C\text{-}F}$ = 30), 125.1 (q, $^{1}J_{C\text{-}F}$ = 287), 129.2, 135.3

Anal. Calcd for $C_{18}H_{18}F_{12}N_2O_2$ (522.33): C, 41.39; H, 3.47; N, 5.36. Found: C, 41.47; H, 3.41; N, 5.33.

General procedure for the Morita-Baylis-Hillman reaction catalyzed by 1a or 1b

A 10 mL round-bottomed flask was charged with the aromatic aldehyde (3 mmol), methanol (12 mmol, 384 mg), methyl acrylate (6 mmol, 516 mg) and catalyst **1** (0.6 mmol, 314 mg). The flask was then capped and the reaction mixture was stirred at 20 °C for the time indicated in Table 1. After completion of the reaction (^{1}H NMR monitoring), volatiles were evaporated in vacuo, and dichloromethane (2 mL) was added to precipitate **1**. The solution was filtered, and the filtrate was concentrated to afford the Morita-Baylis-Hillman products **2-7** (if necessary the product was purified by column chromatography; eluent cyclohexane/AcOEt, 60:40). The recovered solid **1** was washed again with dichloromethane (2 mL) and ready to be reused.

Methyl 3-hydroxy-2-methylene-3-(4-nitrophenyl)propanoate (2)[4]



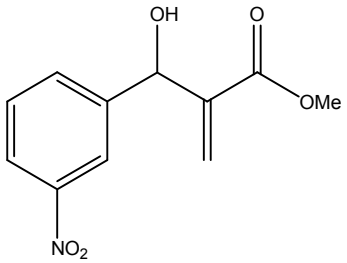
97% yield (1st run)

^{1}H NMR (300 MHz) δ = 3.51 (d, *J* = 5.9, 1H), 3.78 (s, 3H), 5.68(d, *J* = 5.6, 1H), 5.94(d, *J*= 1.2, 1H), 6.44 (d, *J*= 1.1, 1H), 7.57 (d, *J* = 8.5, 2H), 8.35 (d, *J* = 8.7, 2H).

^{13}C NMR (75 MHz) δ = 52.2, 72.5, 123.5, 127.2, 127.3, 140.9, 147.3, 148.6, 166.6.

IR (ν, cm^{-1}): 1517, 1712, 3464.

Methyl 3-hydroxy-2-methylene-3-(3-nitrophenyl)propanoate (3)[5]



85% yield

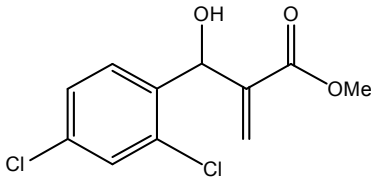
4 J. Cai, Z. Zhou, G. Zhao, C.Tang, *Org. Lett.* **2002**, *4*, 4723.
5 X. Mi, S. Luo, J.-P. Cheng, *J. Org. Chem*. **2005**, *70*, 2338.

^{1}H NMR (300 MHz) δ = 3.26 (d, *J* = 6.3, 1 H), 3.75 (s, 3 H), 5.64 (d, *J* = 6.2, 1H), 5.90 (d, *J*= 1.2, 1 H), 6.42 (d, *J*= 1.3, 1 H), 7.53 (dd, *J* = 8.2, 7.9, 1 H), 7.75 (d, *J* = 7.7, 1 H), 8.16 (d, *J* = 8.2, 1 H), 8.26 (s, 1H)

^{13}C NMR (75 MHz) δ = 52.2, 72.6, 121.5, 122.7, 127.2, 129.3, 132.6, 140.8, 143.5, 148.3, 166.3.

IR (ν, cm^{-1}): 1526, 1713, 3452

Methyl 3-hydroxy-3-(2,4-dichlorophenyl)-2-methylenepropanoate (4)[4]



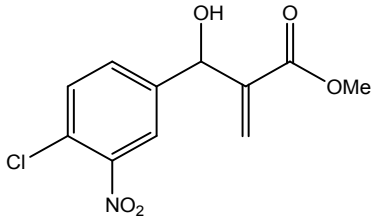
80% yield

^{1}H NMR (300 MHz) δ = 3.27 (d, *J* = 4.8, 1H), 3.79 (s, 3H), 5.58 (d, *J*= 1.2, 1H), 5.92 (d, *J* = 4.6, 1H), 6.34 (d, *J*=1.3, 1H), 7.29 (dd, *J* = 8.4, 2.1, 1H), 7.38 (d, *J* = 2.0, 1H), 7.52 (d, *J* = 8.4, 1H).

^{13}C NMR (75 MHz) δ = 52.1, 68.9, 127.0, 127.1, 129.1, 133.4, 134.1, 136.9, 140.2, 166.8.

IR (ν, cm^{-1}): 1714, 3429.

Methyl 3-hydroxy-3-(4-chloro-3-nitrophenyl)-2-methylenepropanoate (5)[6]



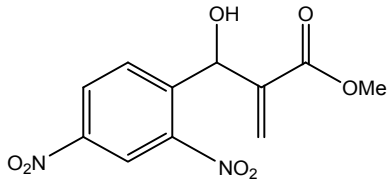
^{1}H NMR (300 MHz)δ = 3.76 (s, 3H), 5.58 (d, *J*= 1.2, 1H), 5.56 (s, *J* = 4.6, 1H), 5.91 (s, *J*=1.3, 1H), 6.41 (s, 1H), 7.50-7.56 (m, *J* = 2.0, 2H), 7.88-7.92 (m, 1H).

^{13}C NMR (75 MHz) δ = 51.8, 70.9, 123.5, 125.4, 126.7, 131.3, 131.4, 140.7, 142.2, 147.2, 165.9.

IR (ν, cm^{-1}): 1704, 3452

6 S.-H. Zhao, H.-R. Zhang, L.-H. Feng, Z.-B. Chen, *J. Mol. Catal. A* **2006**, *258*, 251.

Methyl 3-hydroxy-3-(2,4-dinitrophenyl)-2-methylenepropanoate (6)[7]

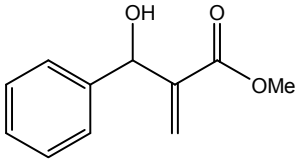


^{1}H NMR (300 MHz) δ = 3.75 (s, 3H), 5.75 (s, 1H), 6.29 (s, 1H), 6.39 (s, 1H), 8.04 (d, *J* = 8.7, 1H), 8.47 (dd, *J* = 8.3, 2.7, 1H), 8.78 (d, *J* = 2.3, 1H).

^{13}C NMR (75 MHz) δ = 52.1, 66.6, 119.7, 126.7, 127.0, 130.6, 140.5, 143.3, 146.9, 147.8, 165.7.

IR (ν, cm^{-1}): 1526, 1708, 3547.

Methyl 3-hydroxy-2-methylene-3-phenyl-propanoate (7)[8]



77% yield

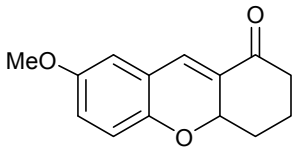
^{1}H NMR (300 MHz) δ = 3.58 (br s, 1H), 3.71 (s, 3H), 5.56 (s, 1H), 5.84 (s, 1H), 6.34 (s, 1H), 7.27-7.40 (m, 5H).

^{13}C NMR (75 MHz) δ = 51.7, 72.7, 125.6, 126.5, 127.6, 128.2, 141.3, 142.0, 166.6.

IR (ν, cm^{-1}): 1717, 3445.

7 O. B. Familoni, P. J. Klaas, K. A. Lobb, V. E. Pakade, P. T. Kaye, *Org. Biomol. Chem.* **2006**, *4*, 3960.
8 D. Basavaiah, K. R. Reddy, N. Kumaragurubaran, *Nat. Protoc.* **2007**, *2*, 2665.

Synthesis of 7-methoxy-2,3,4,4a-tetrahydro-xanthen-1-one (8)[9]



A sealed tube was charged with a solution of 5-methoxysalicylaldehyde (1 mmol, 152 mg) and 2-cyclohexen-1-one (2 mmol, 192 mg) in dioxane (1 mL). **1a** (522 mg) was then added and the mixture was heated to 95 °C under vigorous stirring. After 48 h, the reaction mixture was cooled to room temperature and **1a** crystallized. **1a** was then filtered off, washed with dioxane (2×2 mL) and recovered as white crystals (480 mg, 92%). Solvent was evaporated from the filtrate in vacuo, and the residue was purified by flash chromatography (cyclohexane/AcOEt, 85:15) to afford the product **3** as a yellow solid (189 mg, 82%).

mp 103-105 °C

^{1}H NMR (300 MHz) δ = 1.60-1.75 (m, 1 H), 1.93-2.14 (m, 2H), 2.31-2.49 (m, 2H) 2.52-2.64 (m, 1H), 3.78 (s, 3H), 4.93 (ddd, *J* = 2.2, 6.1, 10.4, 1H), 6.74 (t, *J* = 1.7, 1H), 6.80 (d, *J* = 1.6, 1H), 7.40 (d, *J* = 2.2, 1H).

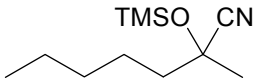
^{13}C NMR (75 MHz) δ = 17.9, 29.6, 38.8, 55.7, 74.6, 113.4, 116.7, 118.2, 122.6, 131.0, 131.5, 149.9, 154.5, 197.3.

IR ν (cm^{-1}) 1674, 2936

APCI *m/z* (rel. int.): 231 $[M+H]^+$ (100)

9 B. Lesch, S. Bräse, *Angew. Chem. Int. Ed*. **2004**, *43*, 115.

Typical procedure for the cyanosilylation of ketones catalysed by 1a: synthesis of 2-methyl-2-(trimethylsilyloxy)-heptanenitrile (9)[10]

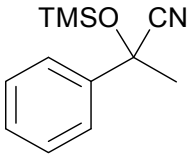


To a mixture of heptan-2-one (1 mmol, 114 mg) and trimethylsilyl cyanide (1.05 mmol, 104 mg) in a 10 mL round-bottomed flask under stirring, catalyst **1a** (0.2 mmol, 105 mg) was added and quickly solubilised. After 4.5 h (^{1}H NMR monitoring), the mixture was heated to 60 °C under vacuum in a rotavapor until a precipitate appears (2-3 h). Dichloromethane was then added to the mixture and filtered. The solid **1a** was recovered (74 mg), and solvents from the filtrate were evaporated in vacuo. The residue was filtered over a short pad of silica with cyclohexane to afford pure silylated cyanohydrin **4a** (196 mg, 92%).

^{1}H NMR (300 MHz) δ = 0.23 (s, 9H), 0.90 (t, *J* = 6.8, 1H), 1.26-1.38 (m, 4H), 1.38-1.6 (m, 2H), 1.56 (s, 3H), 1.62-1.78 (m, 2H).

^{13}C NMR (75 MHz) δ = 1.3, 13.9, 22.4, 23.9, 28.9, 31.4, 43.3, 69.6, 122.2.

2-Phenyl-2-(trimethylsilyloxy)-propionitrile (10)[11]

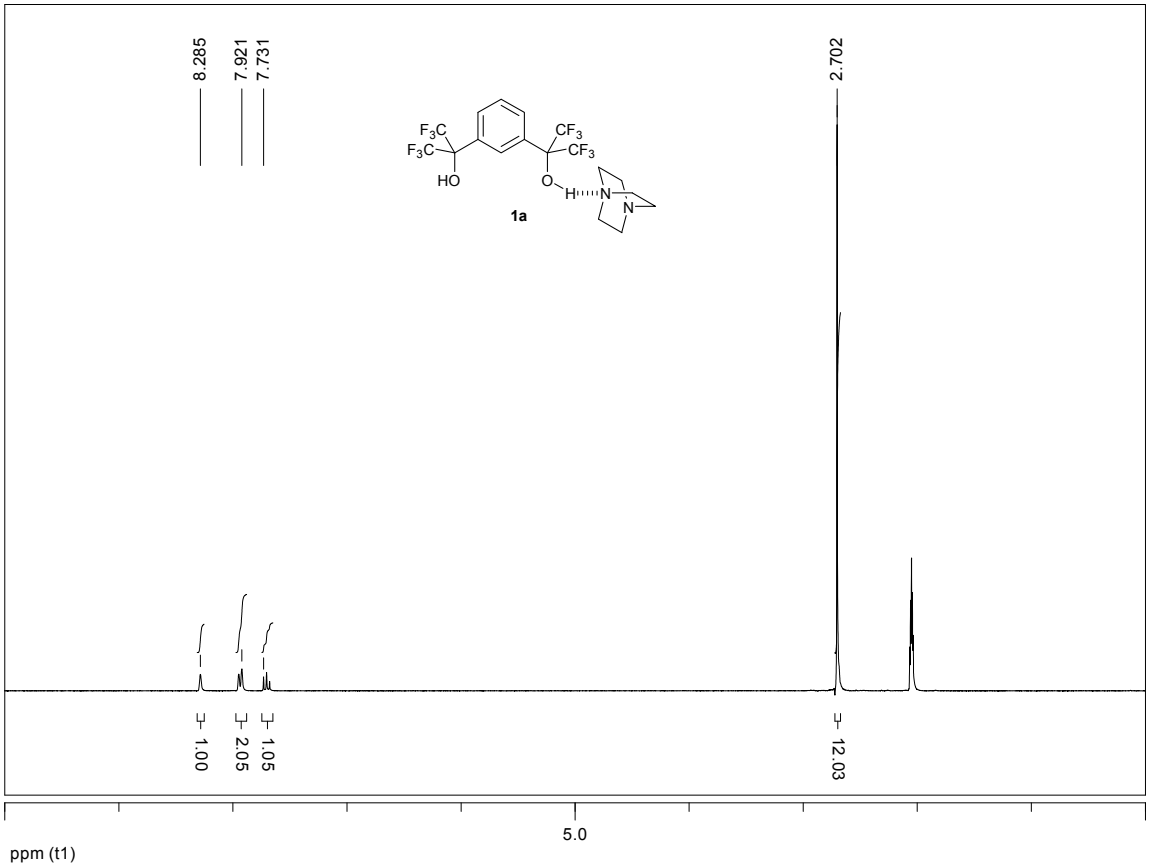


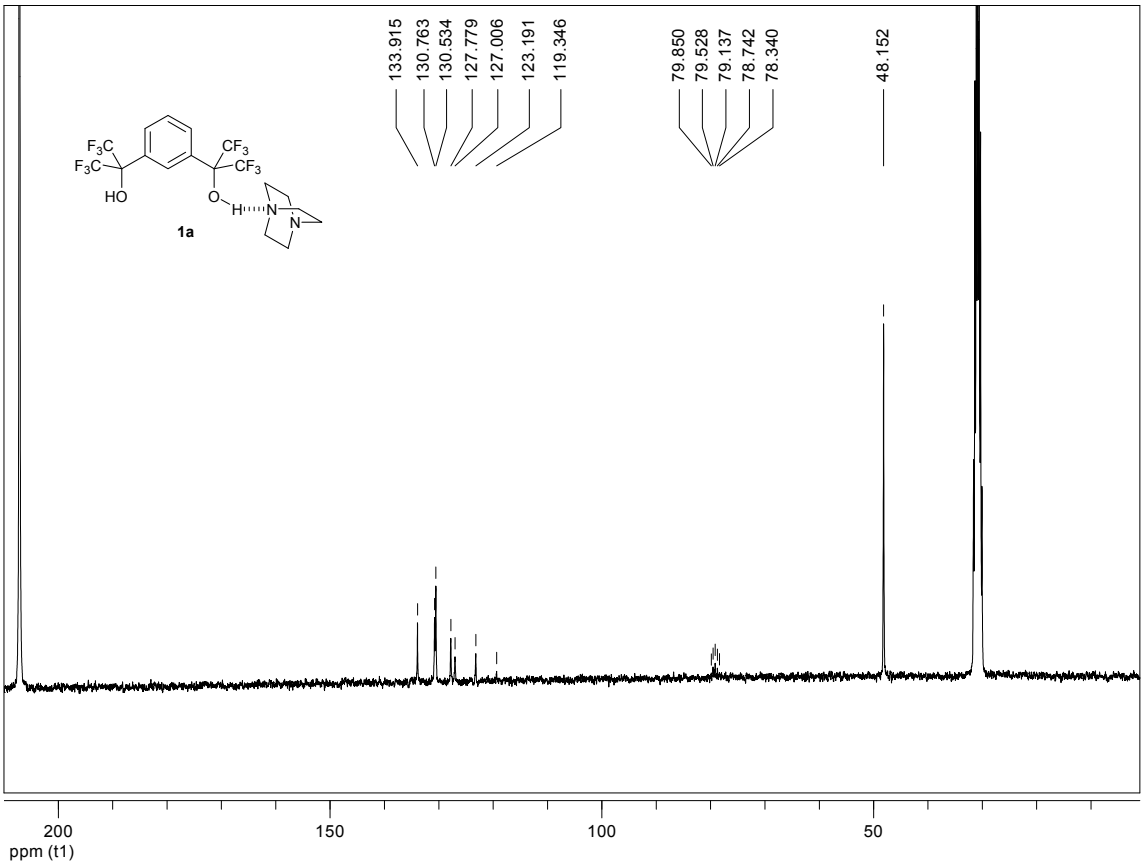
86% yield

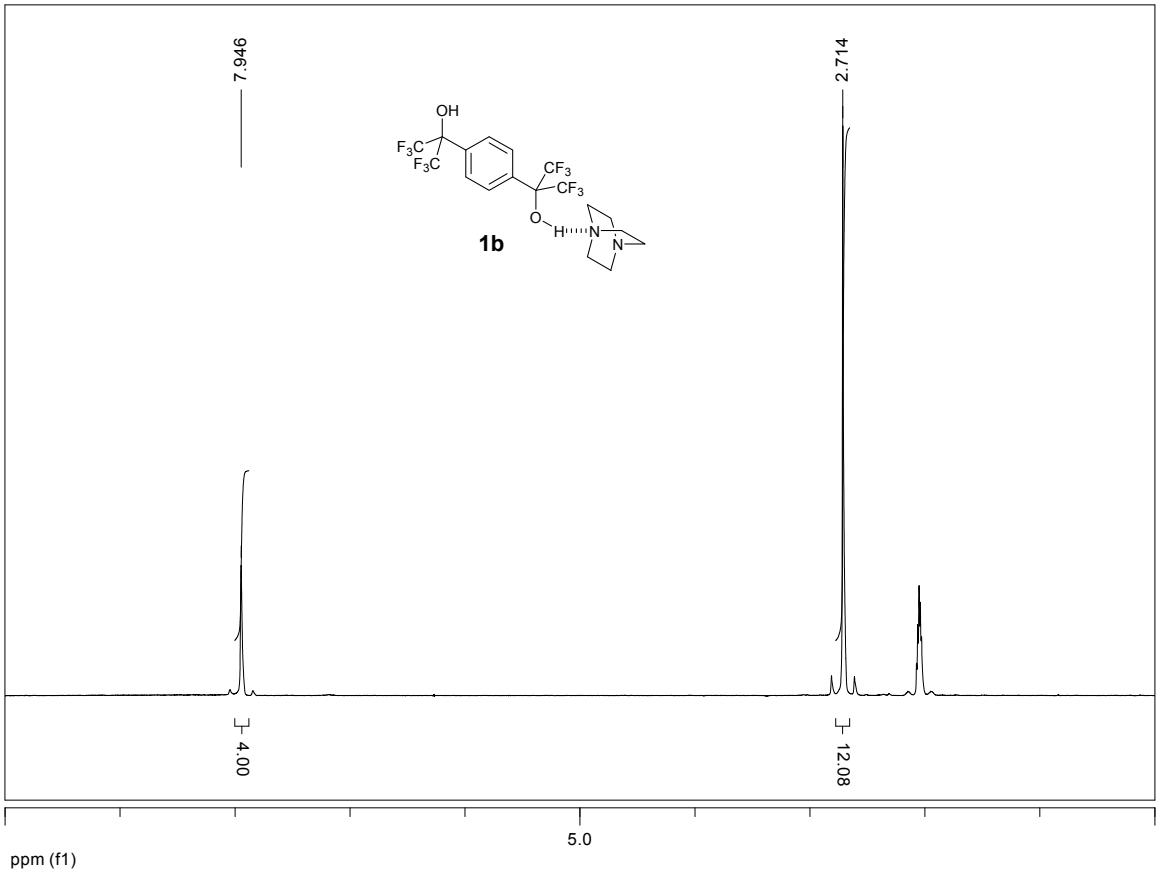
^{1}H NMR (300 MHz) δ = 0.18 (s, 9H), 1.86 (s, 3H), 7.34-7.42 (m, 3H), 7.52-7.57 (m, 2H).

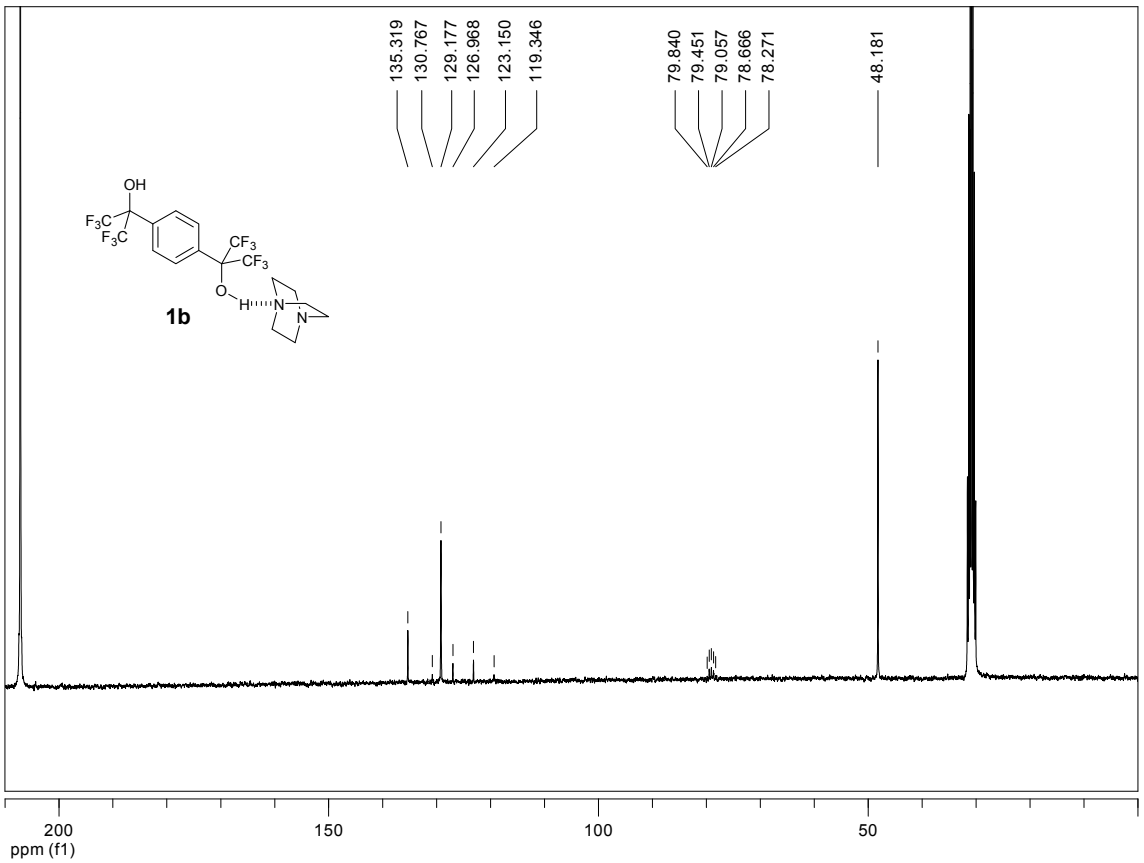
^{13}C NMR (75 MHz) δ = 1.0, 33.6, 71.6, 121.6, 124.6, 128.6, 142.0.

10 T. Sigeru, I. Tsutomu, T. Sadahito, H. Hirofumi, K. Hideki, U. Kenji, *Bull. Chem. Soc. Jpn*. **1987**, *60*, 2173.
11 N. Kurono, M. Yamaguchi, K. Suzuki, T. Ohkuma, *J. Org. Chem.* **2005**, *70*, 6530.

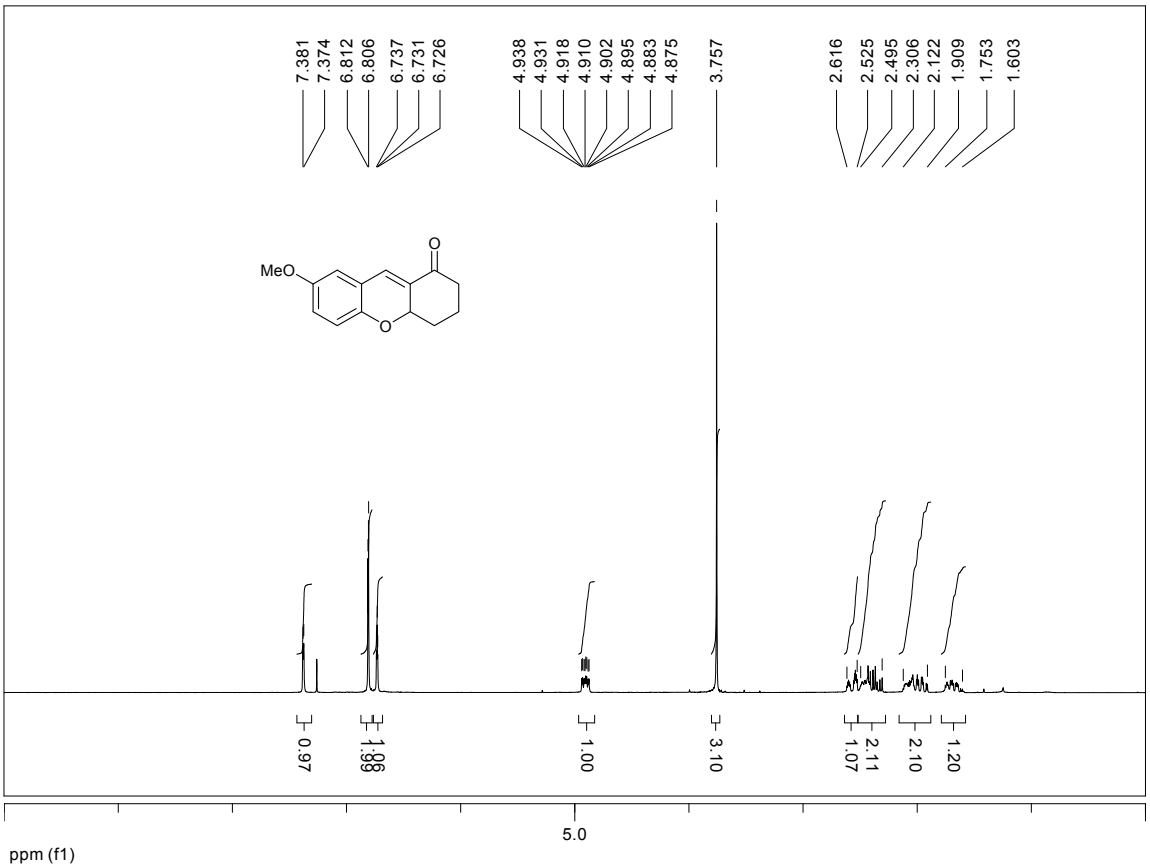


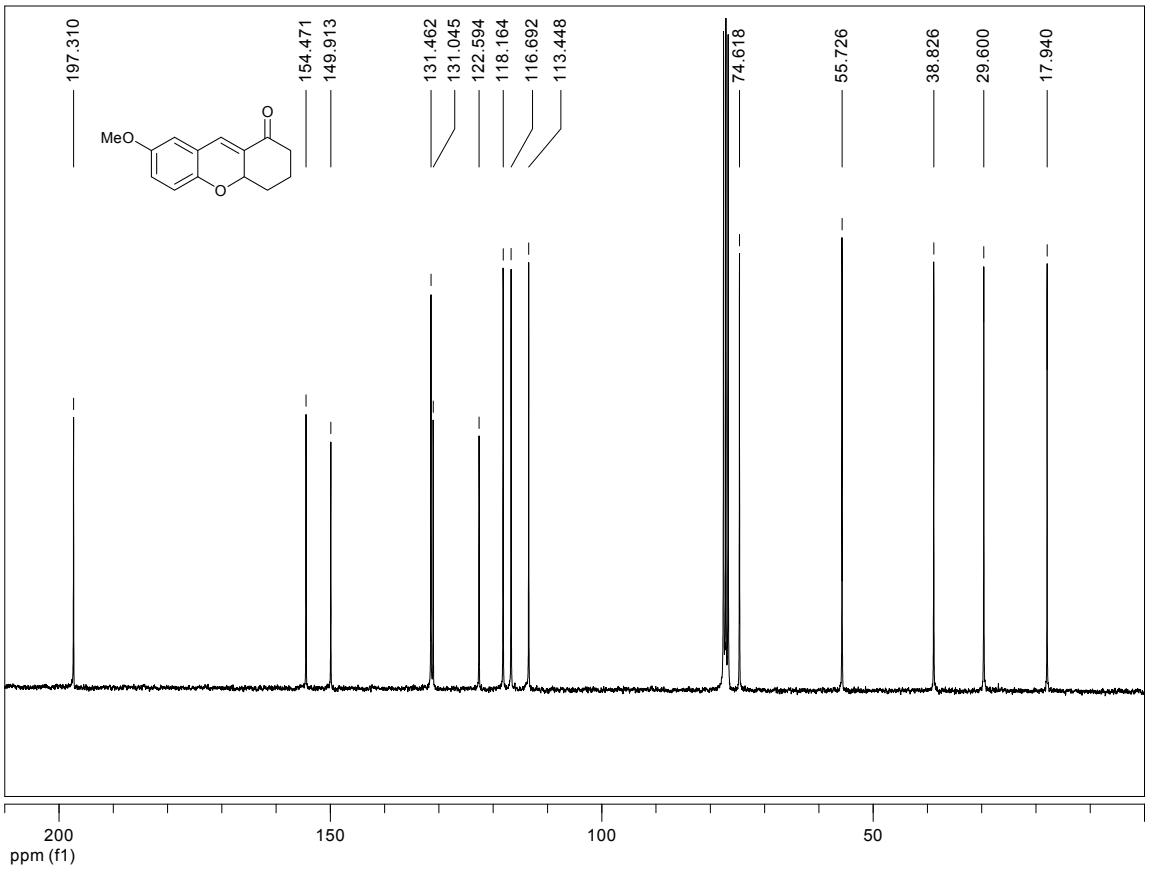






7-methoxy-2,3,4,4a-tetrahydro-xanthen-1-one (8)





X-ray diffraction data for 1a

Table 1. Crystal data and structure refinement for 1a.

Identification code	1a	
Empirical formula	C18 H18 F12 N2 O2	
Formula weight	522.34	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.301(3) Å	α= 80.225(12)°.
	b = 10.979(4) Å	β= 85.04(3)°.
	c = 11.710(3) Å	γ = 89.69(2)°.
Volume	1047.7(6) $Å^3$	
Z	2	
Density (calculated)	1.656 Mg/m^3	
Absorption coefficient	1.634 mm^{-1}	
F(000)	528	
Crystal size	0.20 x 0.10 x 0.01 mm^3	
Theta range for data collection	3.84 to 68.17°.	
Index ranges	-9<=h<=9, -13<=k<=12, -13<=l<=13	
Reflections collected	14359	
Independent reflections	3590 [R(int) = 0.0513]	
Completeness to theta = 67.00°	94.8 %	
Absorption correction	Multiscan	
Max. and min. transmission	1.000 and 0.763	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3590 / 2 / 315	
Goodness-of-fit on F^2	1.088	
Final R indices [I>2sigma(I)]	R1 = 0.0590, wR2 = 0.1634	
R indices (all data)	R1 = 0.0700, wR2 = 0.1770	
Largest diff. peak and hole	0.509 and -0.387 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 1a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	4795(3)	7204(2)	8268(2)	32(1)
C(2)	5394(5)	8135(5)	7275(3)	84(2)
C(3)	4357(5)	8138(5)	6237(3)	77(1)
N(4)	3069(3)	7205(2)	6539(2)	33(1)
C(5)	3128(4)	7535(5)	8567(3)	76(1)
C(6)	2076(4)	7512(5)	7546(3)	63(1)
C(7)	4808(8)	6014(4)	7914(5)	103(2)
C(8)	3778(6)	5999(4)	6872(4)	83(2)
C(11)	237(3)	7025(3)	2970(2)	29(1)
C(12)	-1022(3)	7517(3)	2329(2)	29(1)
C(13)	-1386(3)	7057(3)	1343(2)	28(1)
C(14)	-447(3)	6121(3)	987(2)	38(1)
C(15)	817(4)	5648(3)	1615(3)	41(1)
C(16)	1161(3)	6083(3)	2613(2)	34(1)
C(17)	609(3)	7504(3)	4075(2)	28(1)
O(17)	1793(2)	6786(2)	4616(2)	38(1)
C(18)	1232(3)	8846(3)	3753(2)	35(1)
F(1)	2585(2)	8897(2)	3051(2)	65(1)
F(2)	199(2)	9630(2)	3214(2)	50(1)
F(3)	1587(2)	9307(2)	4690(2)	52(1)
C(19)	-925(3)	7419(3)	4931(2)	38(1)
F(4)	-1586(3)	6301(2)	5093(2)	66(1)
F(5)	-602(2)	7646(2)	5972(1)	61(1)
F(6)	-2085(2)	8215(2)	4582(2)	51(1)
C(20)	-2777(3)	7578(2)	629(2)	28(1)
O(20)	-3170(2)	6741(2)	-78(2)	35(1)
C(21)	-2227(3)	8813(3)	-134(2)	37(1)
F(7)	-1028(2)	8618(2)	-918(2)	57(1)
F(8)	-3427(2)	9353(2)	-716(2)	51(1)
F(9)	-1679(2)	9627(2)	467(2)	48(1)
C(22)	-4306(3)	7776(3)	1436(2)	33(1)
F(10)	-5616(2)	7939(2)	844(2)	47(1)
F(11)	-4190(2)	8752(2)	1965(2)	43(1)

F(12)	-4603(2)	6790(2)	2265(2)	47(1)

Table 3. Bond lengths [Å] and angles [°] for 1a.

N(1)-C(7)	1.435(4)
N(1)-C(5)	1.457(4)
N(1)-C(2)	1.465(5)
C(2)-C(3)	1.548(5)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-N(4)	1.464(4)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
N(4)-C(8)	1.451(5)
N(4)-C(6)	1.465(4)
C(5)-C(6)	1.544(5)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-C(8)	1.552(5)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(11)-C(16)	1.384(4)
C(11)-C(12)	1.393(4)
C(11)-C(17)	1.533(3)
C(12)-C(13)	1.392(3)
C(12)-H(12A)	0.9500
C(13)-C(14)	1.385(4)
C(13)-C(20)	1.536(3)
C(14)-C(15)	1.381(4)
C(14)-H(14A)	0.9500
C(15)-C(16)	1.387(4)
C(15)-H(15A)	0.9500
C(16)-H(16A)	0.9500
C(17)-O(17)	1.385(3)
C(17)-C(18)	1.539(4)
C(17)-C(19)	1.544(4)

O(17)-H(17O)	0.9800(11)
C(18)-F(1)	1.328(3)
C(18)-F(2)	1.332(3)
C(18)-F(3)	1.339(3)
C(19)-F(4)	1.325(4)
C(19)-F(5)	1.334(3)
C(19)-F(6)	1.340(4)
C(20)-O(20)	1.394(3)
C(20)-C(21)	1.539(4)
C(20)-C(22)	1.553(4)
O(20)-H(20O)	0.9800(11)
C(21)-F(9)	1.333(3)
C(21)-F(8)	1.335(3)
C(21)-F(7)	1.336(3)
C(22)-F(11)	1.333(3)
C(22)-F(12)	1.334(3)
C(22)-F(10)	1.335(3)

C(7)-N(1)-C(5)	108.9(4)
C(7)-N(1)-C(2)	109.0(4)
C(5)-N(1)-C(2)	106.0(3)
N(1)-C(2)-C(3)	110.8(3)
N(1)-C(2)-H(2A)	109.5
C(3)-C(2)-H(2A)	109.5
N(1)-C(2)-H(2B)	109.5
C(3)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	108.1
N(4)-C(3)-C(2)	110.4(3)
N(4)-C(3)-H(3A)	109.6
C(2)-C(3)-H(3A)	109.6
N(4)-C(3)-H(3B)	109.6
C(2)-C(3)-H(3B)	109.6
H(3A)-C(3)-H(3B)	108.1
C(8)-N(4)-C(3)	109.3(3)
C(8)-N(4)-C(6)	108.5(3)
C(3)-N(4)-C(6)	107.2(3)
N(1)-C(5)-C(6)	111.4(3)
N(1)-C(5)-H(5A)	109.4

C(6)-C(5)-H(5A)	109.4
N(1)-C(5)-H(5B)	109.4
C(6)-C(5)-H(5B)	109.4
H(5A)-C(5)-H(5B)	108.0
N(4)-C(6)-C(5)	110.1(3)
N(4)-C(6)-H(6A)	109.6
C(5)-C(6)-H(6A)	109.6
N(4)-C(6)-H(6B)	109.6
C(5)-C(6)-H(6B)	109.6
H(6A)-C(6)-H(6B)	108.1
N(1)-C(7)-C(8)	111.8(3)
N(1)-C(7)-H(7A)	109.3
C(8)-C(7)-H(7A)	109.3
N(1)-C(7)-H(7B)	109.3
C(8)-C(7)-H(7B)	109.3
H(7A)-C(7)-H(7B)	107.9
N(4)-C(8)-C(7)	110.0(3)
N(4)-C(8)-H(8A)	109.7
C(7)-C(8)-H(8A)	109.7
N(4)-C(8)-H(8B)	109.7
C(7)-C(8)-H(8B)	109.7
H(8A)-C(8)-H(8B)	108.2
C(16)-C(11)-C(12)	119.8(2)
C(16)-C(11)-C(17)	119.3(2)
C(12)-C(11)-C(17)	121.0(2)
C(13)-C(12)-C(11)	120.8(2)
C(13)-C(12)-H(12A)	119.6
C(11)-C(12)-H(12A)	119.6
C(14)-C(13)-C(12)	119.0(2)
C(14)-C(13)-C(20)	119.2(2)
C(12)-C(13)-C(20)	121.7(2)
C(15)-C(14)-C(13)	120.0(2)
C(15)-C(14)-H(14A)	120.0
C(13)-C(14)-H(14A)	120.0
C(14)-C(15)-C(16)	121.2(3)
C(14)-C(15)-H(15A)	119.4
C(16)-C(15)-H(15A)	119.4
C(11)-C(16)-C(15)	119.1(3)

C(11)-C(16)-H(16A)	120.4
C(15)-C(16)-H(16A)	120.4
O(17)-C(17)-C(11)	109.8(2)
O(17)-C(17)-C(18)	108.6(2)
C(11)-C(17)-C(18)	109.5(2)
O(17)-C(17)-C(19)	108.2(2)
C(11)-C(17)-C(19)	109.9(2)
C(18)-C(17)-C(19)	110.7(2)
C(17)-O(17)-H(17O)	118(2)
F(1)-C(18)-F(2)	107.0(2)
F(1)-C(18)-F(3)	106.8(2)
F(2)-C(18)-F(3)	106.4(2)
F(1)-C(18)-C(17)	110.0(2)
F(2)-C(18)-C(17)	114.3(2)
F(3)-C(18)-C(17)	111.9(2)
F(4)-C(19)-F(5)	107.2(3)
F(4)-C(19)-F(6)	106.4(2)
F(5)-C(19)-F(6)	105.8(2)
F(4)-C(19)-C(17)	110.9(2)
F(5)-C(19)-C(17)	111.9(2)
F(6)-C(19)-C(17)	114.2(2)
O(20)-C(20)-C(13)	109.2(2)
O(20)-C(20)-C(21)	109.5(2)
C(13)-C(20)-C(21)	108.9(2)
O(20)-C(20)-C(22)	108.2(2)
C(13)-C(20)-C(22)	111.0(2)
C(21)-C(20)-C(22)	110.0(2)
C(20)-O(20)-H(20O)	113(2)
F(9)-C(21)-F(8)	107.2(2)
F(9)-C(21)-F(7)	107.0(2)
F(8)-C(21)-F(7)	107.5(2)
F(9)-C(21)-C(20)	113.4(2)
F(8)-C(21)-C(20)	111.6(2)
F(7)-C(21)-C(20)	109.9(2)
F(11)-C(22)-F(12)	107.3(2)
F(11)-C(22)-F(10)	107.0(2)
F(12)-C(22)-F(10)	106.7(2)
F(11)-C(22)-C(20)	113.4(2)

F(12)-C(22)-C(20)	110.8(2)
F(10)-C(22)-C(20)	111.2(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 1a. 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}
N(1)	32(1)	36(1)	31(1)	-10(1)	-9(1)	2(1)
C(2)	74(3)	123(4)	49(2)	13(2)	-27(2)	-49(3)
C(3)	67(2)	114(4)	43(2)	14(2)	-23(2)	-43(2)
N(4)	31(1)	38(1)	31(1)	-9(1)	-7(1)	2(1)
C(5)	41(2)	151(5)	43(2)	-34(2)	-13(2)	15(2)
C(6)	42(2)	110(3)	43(2)	-24(2)	-15(1)	11(2)
C(7)	156(5)	64(3)	119(4)	-55(3)	-113(4)	50(3)
C(8)	120(4)	59(3)	93(3)	-41(2)	-78(3)	42(3)
C(11)	29(1)	31(2)	28(1)	-8(1)	-7(1)	1(1)
C(12)	30(1)	29(2)	32(1)	-11(1)	-8(1)	7(1)
C(13)	28(1)	32(2)	27(1)	-10(1)	-8(1)	4(1)
C(14)	41(2)	45(2)	35(2)	-22(1)	-13(1)	10(1)
C(15)	42(2)	43(2)	46(2)	-23(1)	-18(1)	19(1)
C(16)	31(1)	38(2)	37(2)	-12(1)	-15(1)	11(1)
C(17)	28(1)	32(2)	28(1)	-9(1)	-11(1)	5(1)
O(17)	43(1)	42(1)	35(1)	-14(1)	-21(1)	13(1)
C(18)	37(2)	37(2)	35(2)	-12(1)	-12(1)	1(1)
F(1)	54(1)	59(1)	82(1)	-24(1)	22(1)	-19(1)
F(2)	67(1)	38(1)	50(1)	-5(1)	-29(1)	2(1)
F(3)	71(1)	42(1)	53(1)	-22(1)	-31(1)	4(1)
C(19)	38(2)	50(2)	28(1)	-11(1)	-9(1)	3(1)
F(4)	74(1)	62(1)	57(1)	-5(1)	13(1)	-24(1)
F(5)	47(1)	111(2)	30(1)	-26(1)	-9(1)	11(1)
F(6)	34(1)	81(1)	41(1)	-18(1)	-7(1)	16(1)
C(20)	32(1)	30(2)	27(1)	-11(1)	-10(1)	3(1)
O(20)	42(1)	34(1)	37(1)	-17(1)	-20(1)	9(1)
C(21)	41(2)	37(2)	37(2)	-10(1)	-13(1)	4(1)
F(7)	63(1)	61(1)	42(1)	-2(1)	10(1)	0(1)
F(8)	63(1)	38(1)	53(1)	2(1)	-30(1)	4(1)
F(9)	57(1)	38(1)	50(1)	-7(1)	-17(1)	-12(1)
C(22)	31(1)	33(2)	38(2)	-12(1)	-13(1)	6(1)
F(10)	31(1)	65(1)	51(1)	-23(1)	-17(1)	11(1)
F(11)	37(1)	48(1)	52(1)	-28(1)	-10(1)	11(1)

F(12)	43(1)	47(1)	48(1)	0(1)	0(1)	-2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 1a.

	x	y	z	U(eq)
H(2A)	6533	7956	7036	100
H(2B)	5362	8961	7506	100
H(3A)	3877	8964	6027	92
H(3B)	5052	7963	5554	92
H(5A)	3106	8373	8775	91
H(5B)	2672	6947	9254	91
H(6A)	1198	6890	7785	76
H(6B)	1576	8330	7333	76
H(7A)	4377	5385	8577	124
H(7B)	5936	5793	7692	124
H(8A)	4469	5782	6205	100
H(8B)	2911	5366	7091	100
H(12A)	-1640	8175	2567	35
H(14A)	-671	5805	310	46
H(15A)	1462	5013	1358	49
H(16A)	2020	5739	3046	41
H(17O)	2150(50)	7000(40)	5333(19)	73(12)
H(20O)	-3950(30)	7070(30)	-630(20)	63(11)

Table 6. Torsion angles [°] for 1a.

C(7)-N(1)-C(2)-C(3)	57.6(5)
C(5)-N(1)-C(2)-C(3)	-59.4(5)
N(1)-C(2)-C(3)-N(4)	-0.2(6)
C(2)-C(3)-N(4)-C(8)	-57.9(5)
C(2)-C(3)-N(4)-C(6)	59.6(5)
C(7)-N(1)-C(5)-C(6)	-56.2(5)
C(2)-N(1)-C(5)-C(6)	60.9(5)
C(8)-N(4)-C(6)-C(5)	59.6(4)
C(3)-N(4)-C(6)-C(5)	-58.3(4)
N(1)-C(5)-C(6)-N(4)	-2.1(5)
C(5)-N(1)-C(7)-C(8)	57.7(6)
C(2)-N(1)-C(7)-C(8)	-57.5(6)
C(3)-N(4)-C(8)-C(7)	58.3(5)
C(6)-N(4)-C(8)-C(7)	-58.4(5)
N(1)-C(7)-C(8)-N(4)	-0.3(7)
C(16)-C(11)-C(12)-C(13)	1.3(4)
C(17)-C(11)-C(12)-C(13)	-178.2(2)
C(11)-C(12)-C(13)-C(14)	-1.8(4)
C(11)-C(12)-C(13)-C(20)	179.5(2)
C(12)-C(13)-C(14)-C(15)	0.8(4)
C(20)-C(13)-C(14)-C(15)	179.6(3)
C(13)-C(14)-C(15)-C(16)	0.7(5)
C(12)-C(11)-C(16)-C(15)	0.3(4)
C(17)-C(11)-C(16)-C(15)	179.7(3)
C(14)-C(15)-C(16)-C(11)	-1.3(5)
C(16)-C(11)-C(17)-O(17)	-5.6(3)
C(12)-C(11)-C(17)-O(17)	173.8(2)
C(16)-C(11)-C(17)-C(18)	113.6(3)
C(12)-C(11)-C(17)-C(18)	-66.9(3)
C(16)-C(11)-C(17)-C(19)	-124.6(3)
C(12)-C(11)-C(17)-C(19)	54.9(3)
O(17)-C(17)-C(18)-F(1)	58.9(3)
C(11)-C(17)-C(18)-F(1)	-61.0(3)
C(19)-C(17)-C(18)-F(1)	177.7(2)
O(17)-C(17)-C(18)-F(2)	179.4(2)
C(11)-C(17)-C(18)-F(2)	59.4(3)

C(19)-C(17)-C(18)-F(2)	-61.9(3)
O(17)-C(17)-C(18)-F(3)	-59.6(3)
C(11)-C(17)-C(18)-F(3)	-179.5(2)
C(19)-C(17)-C(18)-F(3)	59.2(3)
O(17)-C(17)-C(19)-F(4)	-69.2(3)
C(11)-C(17)-C(19)-F(4)	50.7(3)
C(18)-C(17)-C(19)-F(4)	171.8(2)
O(17)-C(17)-C(19)-F(5)	50.5(3)
C(11)-C(17)-C(19)-F(5)	170.4(2)
C(18)-C(17)-C(19)-F(5)	-68.5(3)
O(17)-C(17)-C(19)-F(6)	170.6(2)
C(11)-C(17)-C(19)-F(6)	-69.5(3)
C(18)-C(17)-C(19)-F(6)	51.6(3)
C(14)-C(13)-C(20)-O(20)	18.4(3)
C(12)-C(13)-C(20)-O(20)	-162.8(2)
C(14)-C(13)-C(20)-C(21)	-101.1(3)
C(12)-C(13)-C(20)-C(21)	77.6(3)
C(14)-C(13)-C(20)-C(22)	137.6(3)
C(12)-C(13)-C(20)-C(22)	-43.6(3)
O(20)-C(20)-C(21)-F(9)	-173.9(2)
C(13)-C(20)-C(21)-F(9)	-54.5(3)
C(22)-C(20)-C(21)-F(9)	67.3(3)
O(20)-C(20)-C(21)-F(8)	65.0(3)
C(13)-C(20)-C(21)-F(8)	-175.7(2)
C(22)-C(20)-C(21)-F(8)	-53.8(3)
O(20)-C(20)-C(21)-F(7)	-54.1(3)
C(13)-C(20)-C(21)-F(7)	65.2(3)
C(22)-C(20)-C(21)-F(7)	-173.0(2)
O(20)-C(20)-C(22)-F(11)	-165.9(2)
C(13)-C(20)-C(22)-F(11)	74.3(3)
C(21)-C(20)-C(22)-F(11)	-46.3(3)
O(20)-C(20)-C(22)-F(12)	73.3(3)
C(13)-C(20)-C(22)-F(12)	-46.4(3)
C(21)-C(20)-C(22)-F(12)	-167.0(2)
O(20)-C(20)-C(22)-F(10)	-45.2(3)
C(13)-C(20)-C(22)-F(10)	-165.0(2)
C(21)-C(20)-C(22)-F(10)	74.4(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for 1a [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(17)-H(17O)...N(4)	0.9800(11)	1.708(8)	2.678(3)	169(4)
O(20)-H(20O)...N(1)#1	0.9800(11)	1.712(12)	2.662(3)	162(4)

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z-1

X-ray diffraction data for 1b

Table 1. Crystal data and structure refinement for 1b.

Identification code	1b	
Empirical formula	C18 H18 F12 N2 O2	
Formula weight	522.34	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	a = 25.06(2) Å	α= 90°.
	b = 6.782(5) Å	β= 110.81(3)°.
	c = 13.057(15) Å	γ = 90°.
Volume	2075(3) $Å^3$	
Z	4	
Density (calculated)	1.672 Mg/m^3	
Absorption coefficient	1.650 mm^{-1}	
F(000)	1056	
Crystal size	0.12 x 0.10 x 0.05 mm^3	
Theta range for data collection	3.77 to 67.84°.	
Index ranges	-30<=h<=30, -8<=k<=8, -15<=l<=15	
Reflections collected	12652	
Independent reflections	3574 [R(int) = 0.1548]	
Completeness to theta = 67.00°	99.0 %	
Absorption correction	Multiscan	
Max. and min. transmission	1.000 and 0.643	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3574 / 4 / 316	
Goodness-of-fit on F^2	1.330	
Final R indices [I>2sigma(I)]	R1 = 0.1324, wR2 = 0.3253	
R indices (all data)	R1 = 0.1404, wR2 = 0.3567	
Absolute structure parameter	0.6(3)	
Extinction coefficient	0.014(2)	
Largest diff. peak and hole	0.826 and -0.594 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 1b. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	5091(2)	4088(9)	10467(5)	68(1)
C(2)	5387(4)	2583(11)	11265(6)	80(2)
C(3)	5855(4)	3631(12)	12223(6)	81(2)
N(4)	5876(2)	5727(8)	12040(5)	69(1)
C(5)	5496(3)	5063(12)	10072(6)	79(2)
C(6)	5970(4)	6067(14)	11003(6)	85(2)
C(7)	4840(3)	5565(13)	10981(6)	80(2)
C(8)	5312(3)	6551(12)	11923(6)	81(2)
C(11)	3454(3)	1982(11)	7220(5)	68(1)
C(12)	3083(3)	478(11)	6673(6)	76(2)
C(13)	2619(3)	876(10)	5727(6)	69(2)
C(14)	2516(2)	2740(10)	5308(5)	64(1)
C(15)	2891(3)	4288(11)	5853(6)	75(2)
C(16)	3352(3)	3854(11)	6794(6)	77(2)
C(17)	3962(3)	1629(10)	8297(5)	68(2)
O(17)	4302(2)	3304(8)	8545(4)	84(1)
C(18)	4327(3)	-40(13)	8162(7)	87(2)
F(1)	4465(3)	264(16)	7272(5)	150(3)
F(2)	4829(2)	-154(8)	9012(5)	100(2)
F(3)	4102(4)	-1802(9)	8095(9)	184(5)
C(19)	3742(3)	1190(20)	9199(7)	103(3)
F(4)	4163(2)	786(11)	10155(4)	109(2)
F(5)	3386(4)	-170(20)	9028(5)	242(8)
F(6)	3496(3)	2780(20)	9422(6)	184(5)
C(20)	1995(2)	3132(9)	4287(5)	62(1)
O(20)	1709(2)	1381(7)	3944(4)	83(1)
C(21)	1587(3)	4478(12)	4579(6)	75(2)
F(7)	1471(2)	3769(10)	5425(4)	105(2)
F(8)	1078(2)	4638(8)	3750(4)	89(1)
F(9)	1766(2)	6312(8)	4829(5)	104(2)
C(22)	2167(4)	4029(13)	3388(6)	81(2)
F(10)	2405(3)	5839(10)	3618(4)	112(2)
F(11)	1711(2)	4315(7)	2468(4)	88(1)

F(12)	2502(4)	2834(15)	3116(6)	149(3)

Table 3. Bond lengths [Å] and angles [°] for 1b.

N(1)-C(5)	1.451(10)
N(1)-C(2)	1.459(10)
N(1)-C(7)	1.466(10)
C(2)-C(3)	1.550(10)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-N(4)	1.446(10)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
N(4)-C(6)	1.474(10)
N(4)-C(8)	1.476(10)
C(5)-C(6)	1.525(11)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-C(8)	1.525(11)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(11)-C(16)	1.373(11)
C(11)-C(12)	1.393(11)
C(11)-C(17)	1.544(10)
C(12)-C(13)	1.390(10)
C(12)-H(12A)	0.9500
C(13)-C(14)	1.365(10)
C(13)-H(13A)	0.9500
C(14)-C(15)	1.420(9)
C(14)-C(20)	1.522(8)
C(15)-C(16)	1.388(10)
C(15)-H(15A)	0.9500
C(16)-H(16A)	0.9500
C(17)-O(17)	1.388(8)
C(17)-C(19)	1.496(10)
C(17)-C(18)	1.504(11)

O(17)-H(17O)	0.98(2)
C(18)-F(3)	1.312(12)
C(18)-F(1)	1.341(12)
C(18)-F(2)	1.352(9)
C(19)-F(5)	1.247(13)
C(19)-F(6)	1.325(16)
C(19)-F(4)	1.345(10)
C(20)-O(20)	1.377(8)
C(20)-C(22)	1.515(10)
C(20)-C(21)	1.517(10)
O(20)-H(20O)	0.98(2)
C(21)-F(9)	1.324(9)
C(21)-F(7)	1.328(9)
C(21)-F(8)	1.353(9)
C(22)-F(12)	1.303(12)
C(22)-F(11)	1.347(9)
C(22)-F(10)	1.351(11)

C(5)-N(1)-C(2)	109.3(6)
C(5)-N(1)-C(7)	108.6(6)
C(2)-N(1)-C(7)	110.1(6)
N(1)-C(2)-C(3)	107.6(6)
N(1)-C(2)-H(2A)	110.2
C(3)-C(2)-H(2A)	110.2
N(1)-C(2)-H(2B)	110.2
C(3)-C(2)-H(2B)	110.2
H(2A)-C(2)-H(2B)	108.5
N(4)-C(3)-C(2)	112.3(6)
N(4)-C(3)-H(3A)	109.1
C(2)-C(3)-H(3A)	109.1
N(4)-C(3)-H(3B)	109.1
C(2)-C(3)-H(3B)	109.1
H(3A)-C(3)-H(3B)	107.9
C(3)-N(4)-C(6)	109.4(6)
C(3)-N(4)-C(8)	107.5(6)
C(6)-N(4)-C(8)	107.8(6)
N(1)-C(5)-C(6)	111.4(6)
N(1)-C(5)-H(5A)	109.3

C(6)-C(5)-H(5A)	109.3
N(1)-C(5)-H(5B)	109.3
C(6)-C(5)-H(5B)	109.3
H(5A)-C(5)-H(5B)	108.0
N(4)-C(6)-C(5)	109.2(6)
N(4)-C(6)-H(6A)	109.8
C(5)-C(6)-H(6A)	109.8
N(4)-C(6)-H(6B)	109.8
C(5)-C(6)-H(6B)	109.8
H(6A)-C(6)-H(6B)	108.3
N(1)-C(7)-C(8)	109.5(6)
N(1)-C(7)-H(7A)	109.8
C(8)-C(7)-H(7A)	109.8
N(1)-C(7)-H(7B)	109.8
C(8)-C(7)-H(7B)	109.8
H(7A)-C(7)-H(7B)	108.2
N(4)-C(8)-C(7)	110.9(6)
N(4)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8A)	109.5
N(4)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	108.0
C(16)-C(11)-C(12)	118.4(7)
C(16)-C(11)-C(17)	119.1(6)
C(12)-C(11)-C(17)	122.5(6)
C(13)-C(12)-C(11)	120.6(7)
C(13)-C(12)-H(12A)	119.7
C(11)-C(12)-H(12A)	119.7
C(14)-C(13)-C(12)	121.0(6)
C(14)-C(13)-H(13A)	119.5
C(12)-C(13)-H(13A)	119.5
C(13)-C(14)-C(15)	119.1(6)
C(13)-C(14)-C(20)	119.6(5)
C(15)-C(14)-C(20)	121.3(6)
C(16)-C(15)-C(14)	118.8(7)
C(16)-C(15)-H(15A)	120.6
C(14)-C(15)-H(15A)	120.6
C(11)-C(16)-C(15)	122.1(7)

C(11)-C(16)-H(16A)	119.0
C(15)-C(16)-H(16A)	119.0
O(17)-C(17)-C(19)	110.3(7)
O(17)-C(17)-C(18)	107.1(6)
C(19)-C(17)-C(18)	110.5(8)
O(17)-C(17)-C(11)	109.0(6)
C(19)-C(17)-C(11)	109.4(6)
C(18)-C(17)-C(11)	110.5(5)
C(17)-O(17)-H(17O)	123(5)
F(3)-C(18)-F(1)	108.6(9)
F(3)-C(18)-F(2)	104.8(7)
F(1)-C(18)-F(2)	105.6(7)
F(3)-C(18)-C(17)	115.3(8)
F(1)-C(18)-C(17)	109.9(8)
F(2)-C(18)-C(17)	112.0(6)
F(5)-C(19)-F(6)	106.2(11)
F(5)-C(19)-F(4)	107.0(9)
F(6)-C(19)-F(4)	103.5(8)
F(5)-C(19)-C(17)	116.6(8)
F(6)-C(19)-C(17)	110.0(9)
F(4)-C(19)-C(17)	112.6(6)
O(20)-C(20)-C(22)	110.6(6)
O(20)-C(20)-C(21)	106.3(5)
C(22)-C(20)-C(21)	110.9(6)
O(20)-C(20)-C(14)	108.6(5)
C(22)-C(20)-C(14)	111.0(5)
C(21)-C(20)-C(14)	109.2(6)
C(20)-O(20)-H(20O)	136(7)
F(9)-C(21)-F(7)	106.8(7)
F(9)-C(21)-F(8)	105.3(7)
F(7)-C(21)-F(8)	105.8(6)
F(9)-C(21)-C(20)	115.3(6)
F(7)-C(21)-C(20)	110.9(6)
F(8)-C(21)-C(20)	112.1(6)
F(12)-C(22)-F(11)	105.8(7)
F(12)-C(22)-F(10)	110.5(8)
F(11)-C(22)-F(10)	103.6(6)
F(12)-C(22)-C(20)	110.4(7)

F(11)-C(22)-C(20)	111.3(6)
F(10)-C(22)-C(20)	114.6(6)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 1b. 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}
N(1)	61(3)	81(3)	53(3)	-1(2)	7(2)	-5(2)
C(2)	73(3)	78(4)	69(4)	3(3)	1(3)	-5(3)
C(3)	75(4)	91(4)	57(4)	-6(3)	-3(3)	-10(3)
N(4)	68(3)	75(3)	54(3)	-3(2)	10(2)	-4(2)
C(5)	80(4)	96(4)	51(4)	-3(3)	13(3)	-16(4)
C(6)	86(5)	114(6)	50(4)	-2(3)	16(4)	-20(4)
C(7)	61(3)	109(5)	56(4)	-2(3)	1(3)	7(3)
C(8)	74(4)	92(4)	63(4)	-7(3)	9(3)	6(3)
C(11)	62(3)	82(4)	51(3)	0(3)	9(3)	2(3)
C(12)	68(4)	81(4)	62(4)	-2(3)	4(3)	-9(3)
C(13)	61(3)	78(3)	57(4)	-6(3)	7(3)	-4(3)
C(14)	54(3)	75(3)	49(3)	-3(2)	0(2)	-6(3)
C(15)	66(4)	74(4)	70(4)	-6(3)	7(3)	-12(3)
C(16)	68(4)	91(4)	57(4)	0(3)	4(3)	-6(3)
C(17)	68(4)	76(3)	53(3)	-8(3)	12(3)	-7(3)
O(17)	76(3)	89(3)	59(3)	8(2)	-9(2)	-15(3)
C(18)	72(4)	96(5)	63(4)	-20(3)	-12(3)	6(4)
F(1)	105(4)	259(9)	71(4)	-35(4)	15(3)	52(5)
F(2)	72(3)	110(3)	91(4)	-15(2)	-4(3)	16(2)
F(3)	138(6)	83(3)	226(10)	-27(5)	-64(6)	10(3)
C(19)	61(4)	196(11)	47(4)	5(5)	13(3)	-13(5)
F(4)	84(3)	172(5)	56(3)	15(3)	6(2)	-30(3)
F(5)	167(8)	480(20)	50(3)	15(6)	9(4)	-203(12)
F(6)	129(6)	340(15)	77(4)	-5(6)	31(4)	95(8)
C(20)	56(3)	67(3)	52(3)	-1(2)	4(3)	-4(2)
O(20)	84(3)	75(3)	69(3)	-6(2)	1(3)	-7(2)
C(21)	66(4)	90(4)	60(4)	-4(3)	11(3)	-6(3)
F(7)	89(3)	160(5)	68(3)	10(3)	32(2)	0(3)
F(8)	70(3)	108(3)	73(3)	-4(2)	7(2)	7(2)
F(9)	85(3)	93(3)	118(4)	-28(3)	16(3)	3(2)
C(22)	76(4)	104(5)	51(3)	7(3)	9(3)	1(4)
F(10)	107(4)	144(4)	73(3)	8(3)	17(3)	-49(3)
F(11)	85(3)	105(3)	56(2)	9(2)	4(2)	-12(2)

F(12)	148(6)	220(9)	97(4)	39(5)	65(4)	83(6)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 1b.

	x	y	z	U(eq)
H(2A)	5562	1594	10923	96
H(2B)	5115	1898	11539	96
H(3A)	5781	3408	12909	98
H(3B)	6231	3043	12314	98
H(5A)	5293	6058	9515	95
H(5B)	5666	4080	9717	95
H(6A)	6345	5525	11053	103
H(6B)	5970	7500	10858	103
H(7A)	4564	4925	11260	97
H(7B)	4634	6568	10433	97
H(8A)	5311	7987	11786	97
H(8B)	5239	6351	12613	97
H(12A)	3149	-831	6948	91
H(13A)	2369	-165	5366	83
H(15A)	2826	5597	5579	90
H(16A)	3607	4884	7155	92
H(17O)	4600(30)	3510(130)	9260(40)	90(30)
H(20O)	1360(30)	970(170)	3340(70)	120(40)

Table 6. Torsion angles [°] for 1b.

C(5)-N(1)-C(2)-C(3)	60.2(8)
C(7)-N(1)-C(2)-C(3)	-59.0(8)
N(1)-C(2)-C(3)-N(4)	-1.7(10)
C(2)-C(3)-N(4)-C(6)	-57.2(9)
C(2)-C(3)-N(4)-C(8)	59.6(9)
C(2)-N(1)-C(5)-C(6)	-60.6(9)
C(7)-N(1)-C(5)-C(6)	59.5(9)
C(3)-N(4)-C(6)-C(5)	57.4(9)
C(8)-N(4)-C(6)-C(5)	-59.3(9)
N(1)-C(5)-C(6)-N(4)	0.5(10)
C(5)-N(1)-C(7)-C(8)	-59.1(8)
C(2)-N(1)-C(7)-C(8)	60.5(9)
C(3)-N(4)-C(8)-C(7)	-58.3(8)
C(6)-N(4)-C(8)-C(7)	59.6(9)
N(1)-C(7)-C(8)-N(4)	-0.2(9)
C(16)-C(11)-C(12)-C(13)	-0.9(10)
C(17)-C(11)-C(12)-C(13)	177.6(6)
C(11)-C(12)-C(13)-C(14)	0.4(11)
C(12)-C(13)-C(14)-C(15)	-0.1(10)
C(12)-C(13)-C(14)-C(20)	-178.6(6)
C(13)-C(14)-C(15)-C(16)	0.3(10)
C(20)-C(14)-C(15)-C(16)	178.7(6)
C(12)-C(11)-C(16)-C(15)	1.1(11)
C(17)-C(11)-C(16)-C(15)	-177.5(6)
C(14)-C(15)-C(16)-C(11)	-0.8(11)
C(16)-C(11)-C(17)-O(17)	-11.1(9)
C(12)-C(11)-C(17)-O(17)	170.4(6)
C(16)-C(11)-C(17)-C(19)	109.5(9)
C(12)-C(11)-C(17)-C(19)	-69.0(9)
C(16)-C(11)-C(17)-C(18)	-128.6(8)
C(12)-C(11)-C(17)-C(18)	52.9(9)
O(17)-C(17)-C(18)-F(3)	169.7(8)
C(19)-C(17)-C(18)-F(3)	49.5(10)
C(11)-C(17)-C(18)-F(3)	-71.7(10)
O(17)-C(17)-C(18)-F(1)	-67.1(8)
C(19)-C(17)-C(18)-F(1)	172.7(7)

C(11)-C(17)-C(18)-F(1)	51.5(8)
O(17)-C(17)-C(18)-F(2)	49.9(9)
C(19)-C(17)-C(18)-F(2)	-70.3(9)
C(11)-C(17)-C(18)-F(2)	168.5(6)
O(17)-C(17)-C(19)-F(5)	173.2(12)
C(18)-C(17)-C(19)-F(5)	-68.5(13)
C(11)-C(17)-C(19)-F(5)	53.3(14)
O(17)-C(17)-C(19)-F(6)	52.2(9)
C(18)-C(17)-C(19)-F(6)	170.5(7)
C(11)-C(17)-C(19)-F(6)	-67.6(9)
O(17)-C(17)-C(19)-F(4)	-62.6(11)
C(18)-C(17)-C(19)-F(4)	55.7(11)
C(11)-C(17)-C(19)-F(4)	177.5(8)
C(13)-C(14)-C(20)-O(20)	-0.9(8)
C(15)-C(14)-C(20)-O(20)	-179.4(6)
C(13)-C(14)-C(20)-C(22)	-122.8(7)
C(15)-C(14)-C(20)-C(22)	58.7(8)
C(13)-C(14)-C(20)-C(21)	114.7(7)
C(15)-C(14)-C(20)-C(21)	-63.8(7)
O(20)-C(20)-C(21)-F(9)	-173.8(6)
C(22)-C(20)-C(21)-F(9)	-53.4(9)
C(14)-C(20)-C(21)-F(9)	69.2(8)
O(20)-C(20)-C(21)-F(7)	64.7(7)
C(22)-C(20)-C(21)-F(7)	-175.0(6)
C(14)-C(20)-C(21)-F(7)	-52.4(7)
O(20)-C(20)-C(21)-F(8)	-53.3(7)
C(22)-C(20)-C(21)-F(8)	67.0(7)
C(14)-C(20)-C(21)-F(8)	-170.4(5)
O(20)-C(20)-C(22)-F(12)	-60.1(9)
C(21)-C(20)-C(22)-F(12)	-177.8(7)
C(14)-C(20)-C(22)-F(12)	60.6(9)
O(20)-C(20)-C(22)-F(11)	57.1(8)
C(21)-C(20)-C(22)-F(11)	-60.6(8)
C(14)-C(20)-C(22)-F(11)	177.8(6)
O(20)-C(20)-C(22)-F(10)	174.3(7)
C(21)-C(20)-C(22)-F(10)	56.6(9)
C(14)-C(20)-C(22)-F(10)	-65.0(9)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for 1b [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(17)-H(17O)...N(1)	0.98(2)	1.66(2)	2.639(8)	174(8)
O(20)-H(20O)...N(4)#1	0.98(2)	1.71(5)	2.655(7)	160(11)

Symmetry transformations used to generate equivalent atoms:

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