Supplementary Material (ESI) for Organic and Biomolecular Chemistry

A stereoselective synthesis of 6,6,6-trifluoro-L-daunosamine and 6,6,6-trifluoro-L-acosamine.

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Figure 1: HPLC chromatogram of the crude mixture of cycloadducts **12a**—**12d**. The separation was performed on a Phenomonex Luna RP C18 200 mm x 5 mm column using 80% aqueous methanol containing 0.1% TFA as mobile phase at a flow rate of 1 ml min^{-1}.

Figure 2: Partial 282 MHz ^{19}F NMR spectrum in $CDCl_3$, showing the signals for the trifluoroacetamido signals for; (a) the mixture of cycloadducts **12a**—**12d**, (b) **12a**, (c) **12d**, (d) **12c**. Adduct **12a** was obtained by crystallisation from the mixture of adducts. Small quantities of **12c** and **12d** were obtained by HPLC separation of the mixture of adducts.

Figure 3: Partial 282 MHz ^{19}F NMR spectrum in $CDCl_3$ with an increased vertical scale, showing the signals the trifluoroacetamido signals for each amide isomer for; (a) the mixture of cycloadducts **12a** —**12d**, (b) **12a**, (c) **12d**, (d) **12c**.

Figure 4: 300 MHz ^1H NMR spectrum of ethyl 3-amino-2,3,6-trideoxy-6,6,6-trifluoro-β-L-*arabino*-hexopyranoside **14** recorded in D_2O

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Figure 8: 300 MHz ^1H NMR spectrum of ethyl 3-amino-2,3,6-trideoxy-6,6,6-trifluoro-β-L-*lyxo*-hexopyranoside **18** recorded in D_2O.

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Figure 12: Perspective view of one of unique molecules of **16** with displacement ellipsoids drawn at the 50% probability level.

Figure 13: Perspective view of the other unique molecule of **16** with displacement ellipsoids drawn at the 50% probability level.

Figure 14: H-bonding in the X-ray structure of **16**.

Table 1. Crystal data and structure refinement for **16**.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **16**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table 3. Bond lengths [Å] and angles [°] for **16**.

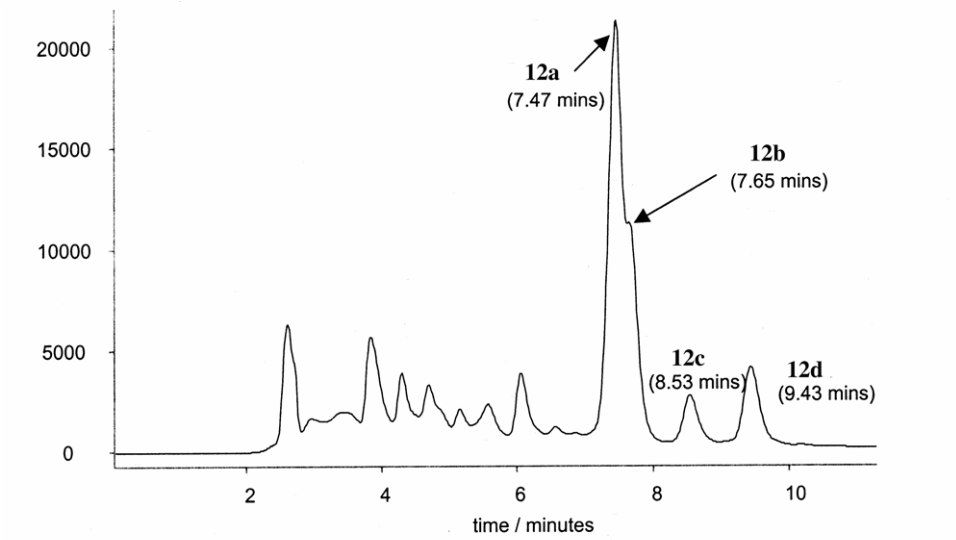
Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **16**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **16**.

Table 6. Torsion angles [°] for **16**.

Table 7. Hydrogen bonds for **16** [Å and °].

Supporting Information



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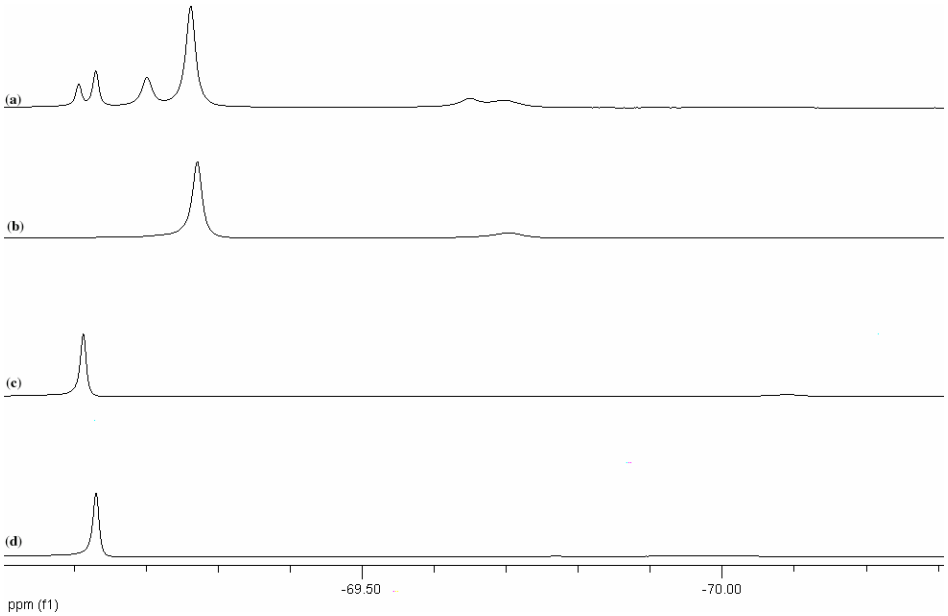

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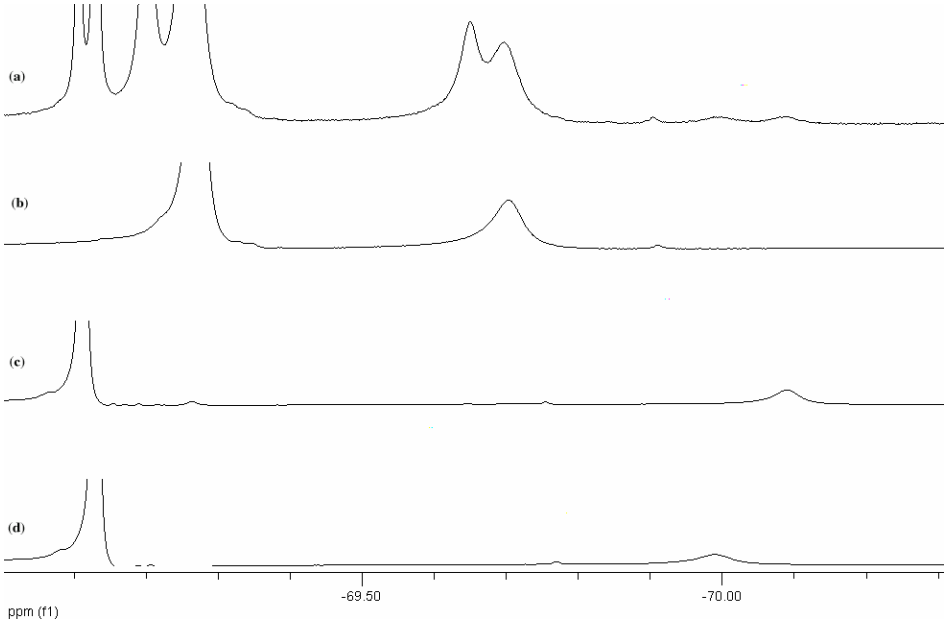

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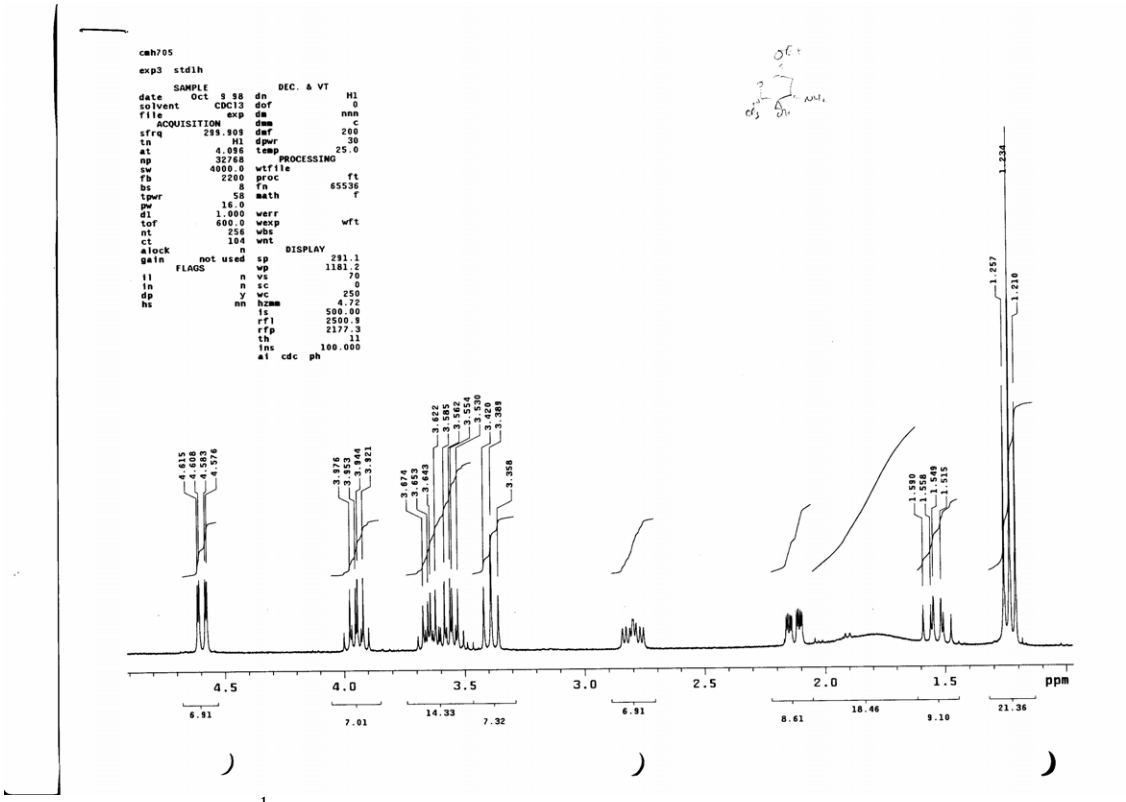

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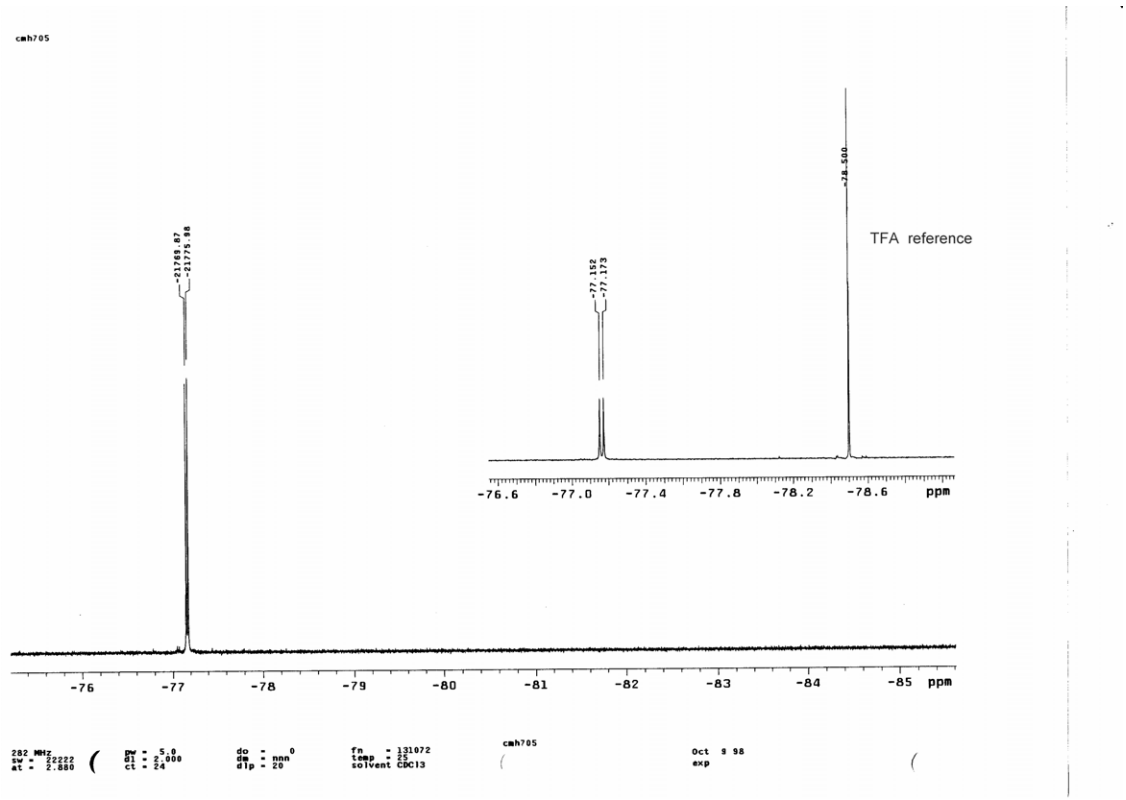

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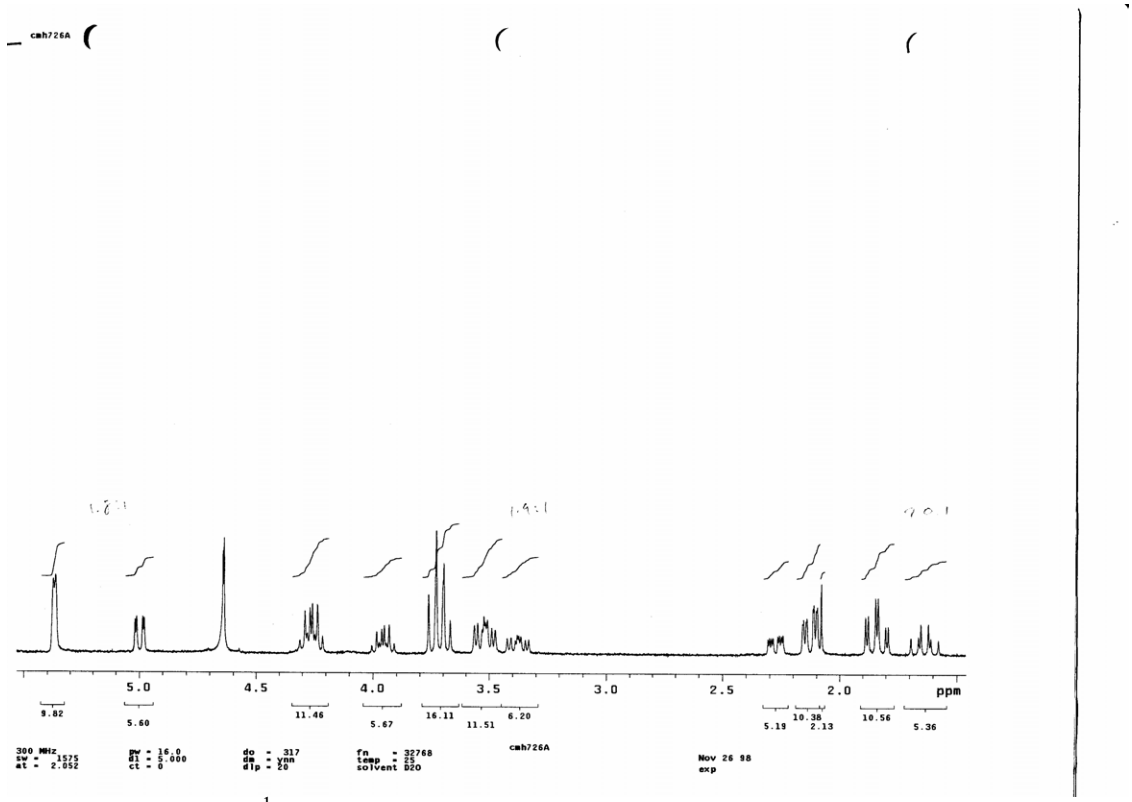

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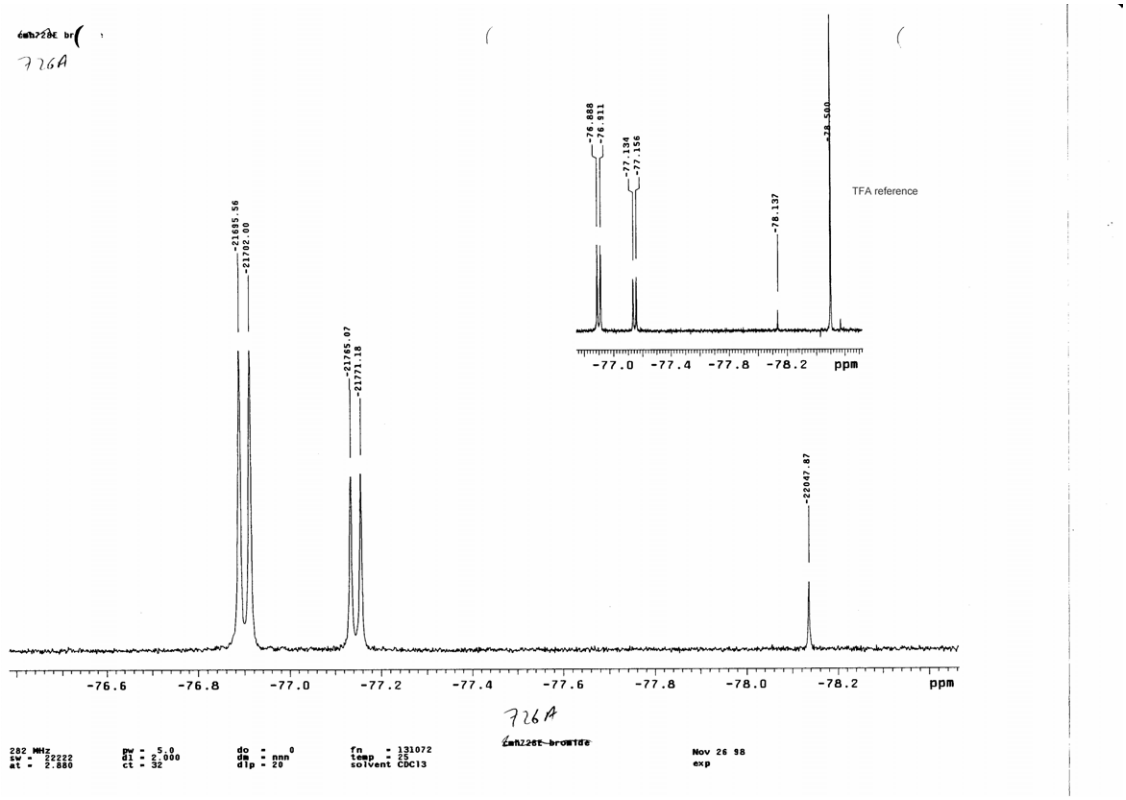
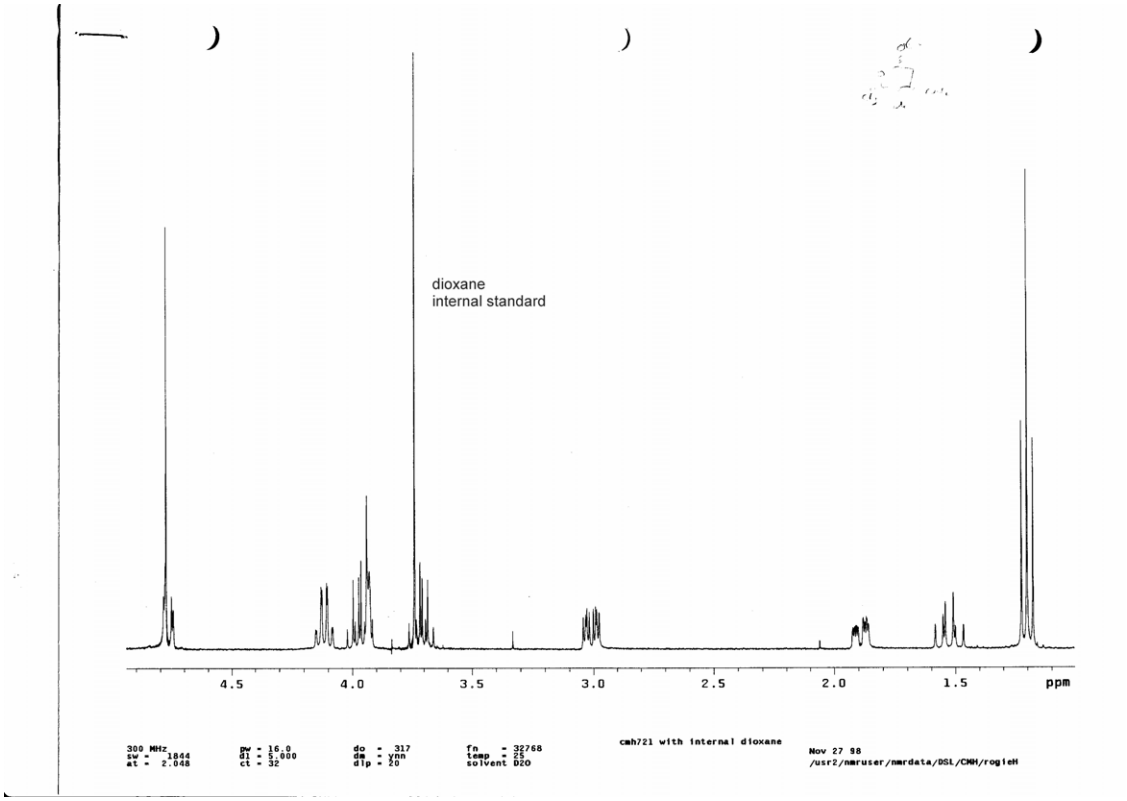


Figure 7: 282 MHz ^{19}F NMR spectrum of 3-amino-2,3,6-trideoxy-6,6,6-trifluoro-L-*arabino*-hexopyranose hydrochloride **15** recorded in D_2O.



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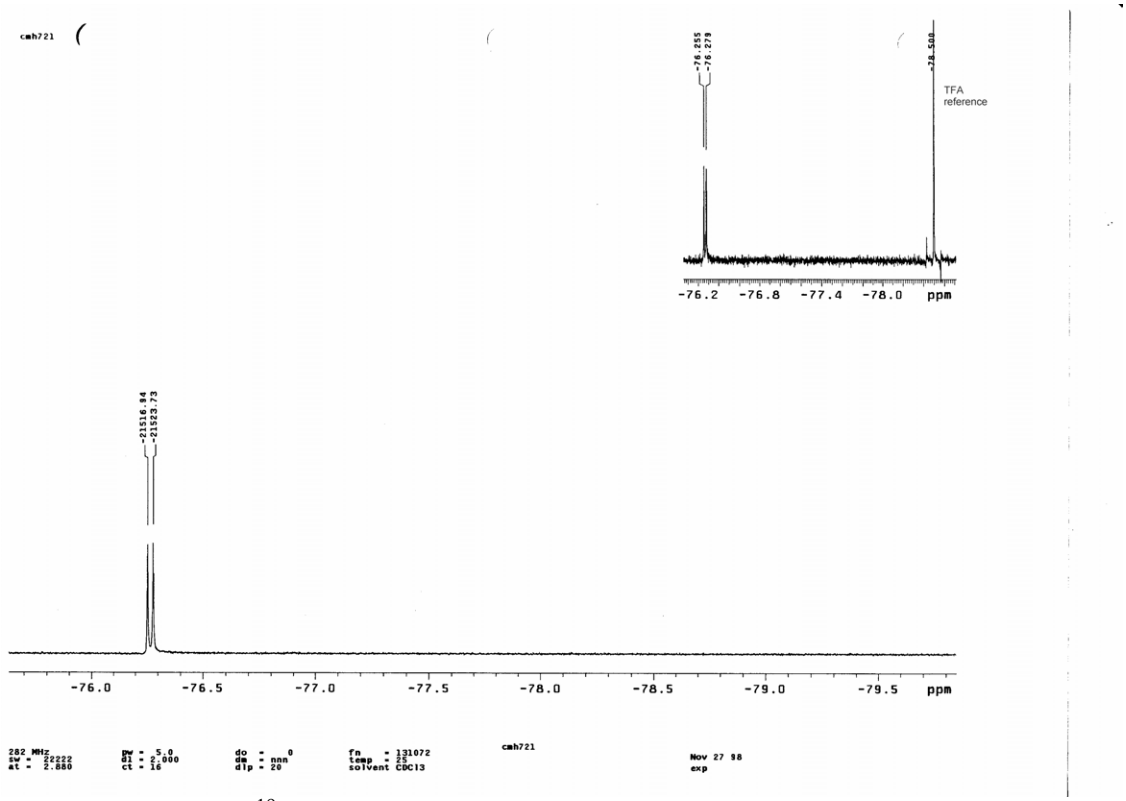

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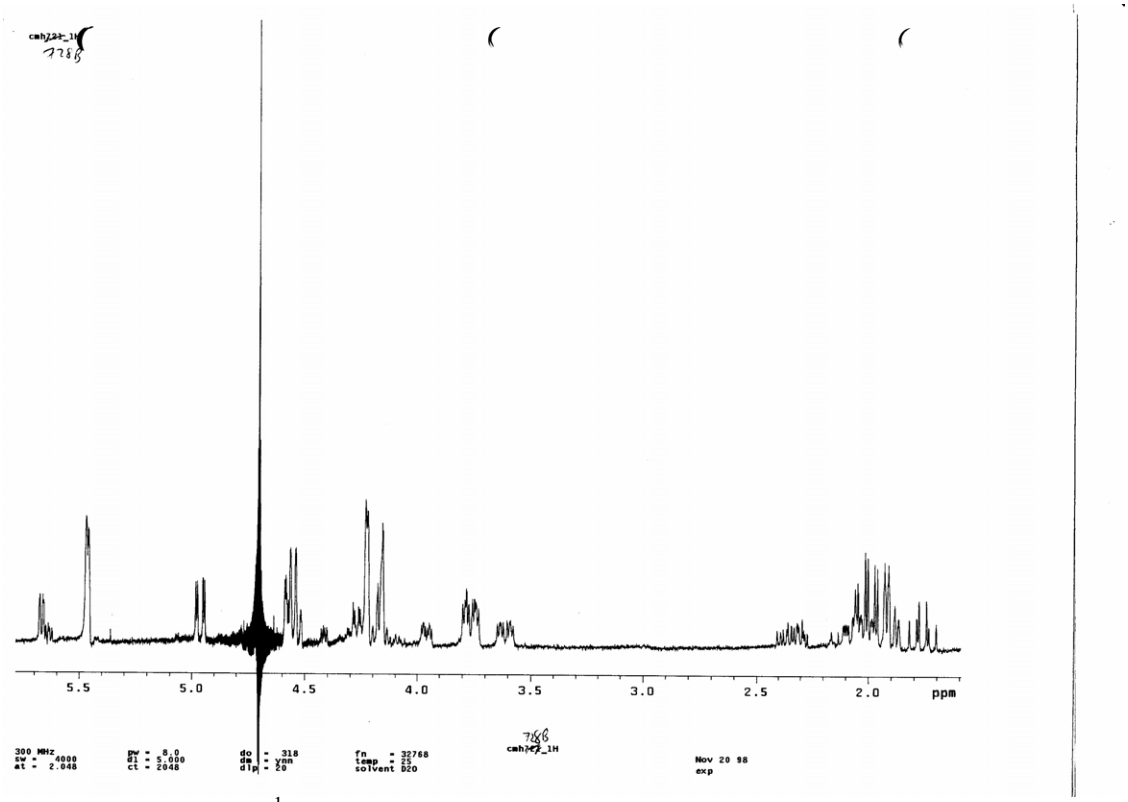

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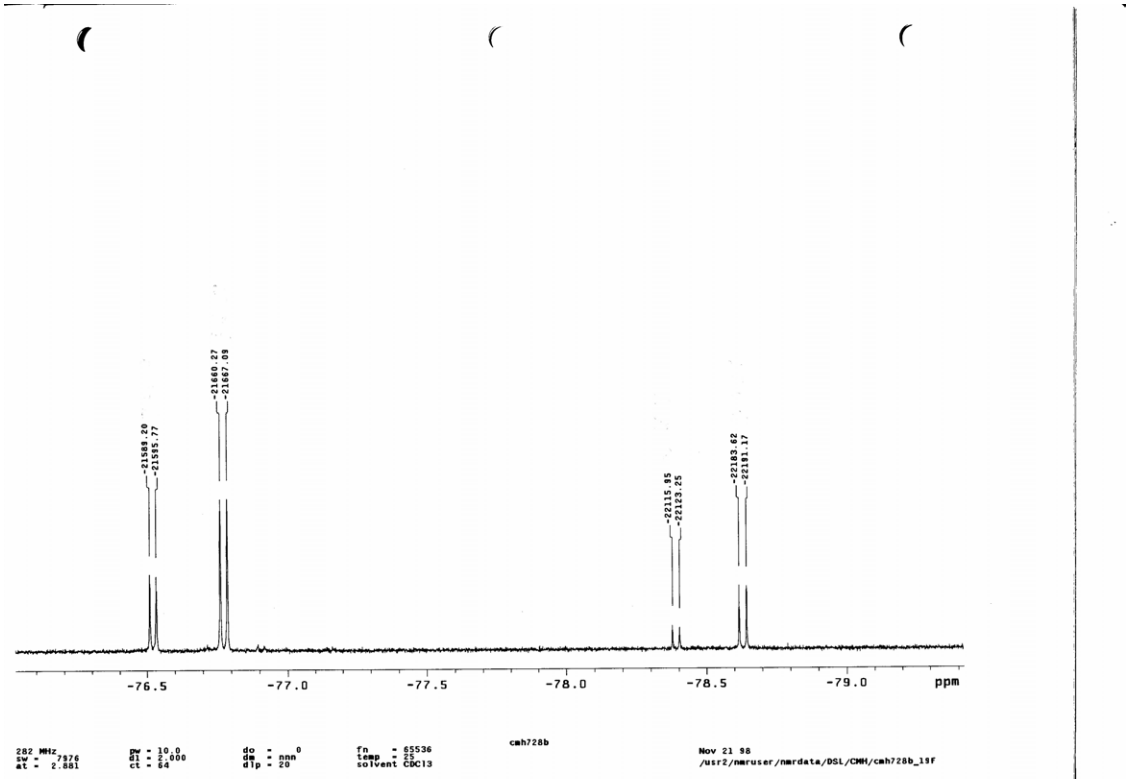

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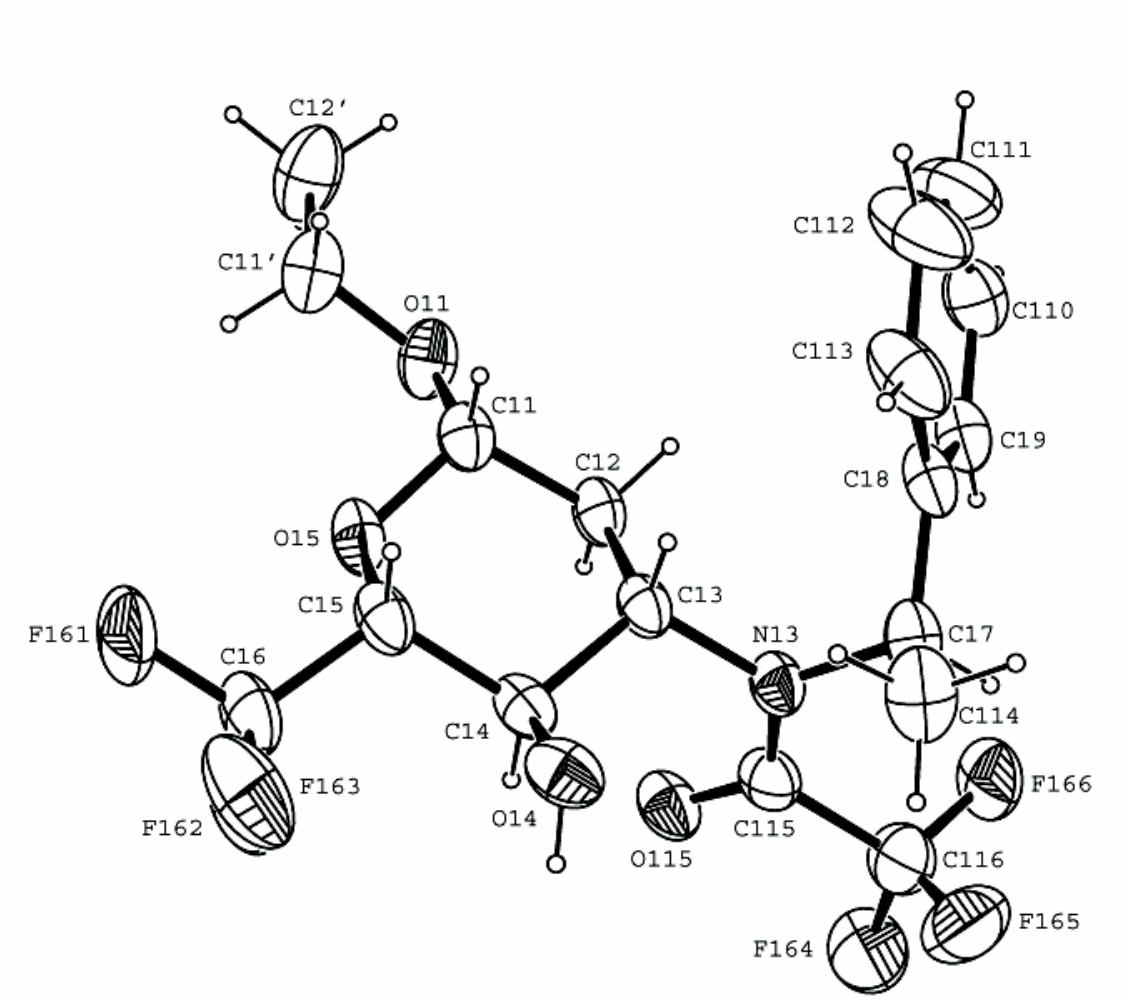

Figure 12: Perspective view of one of unique molecules of **16** with displacement ellipsoids drawn at the 50% probability level.

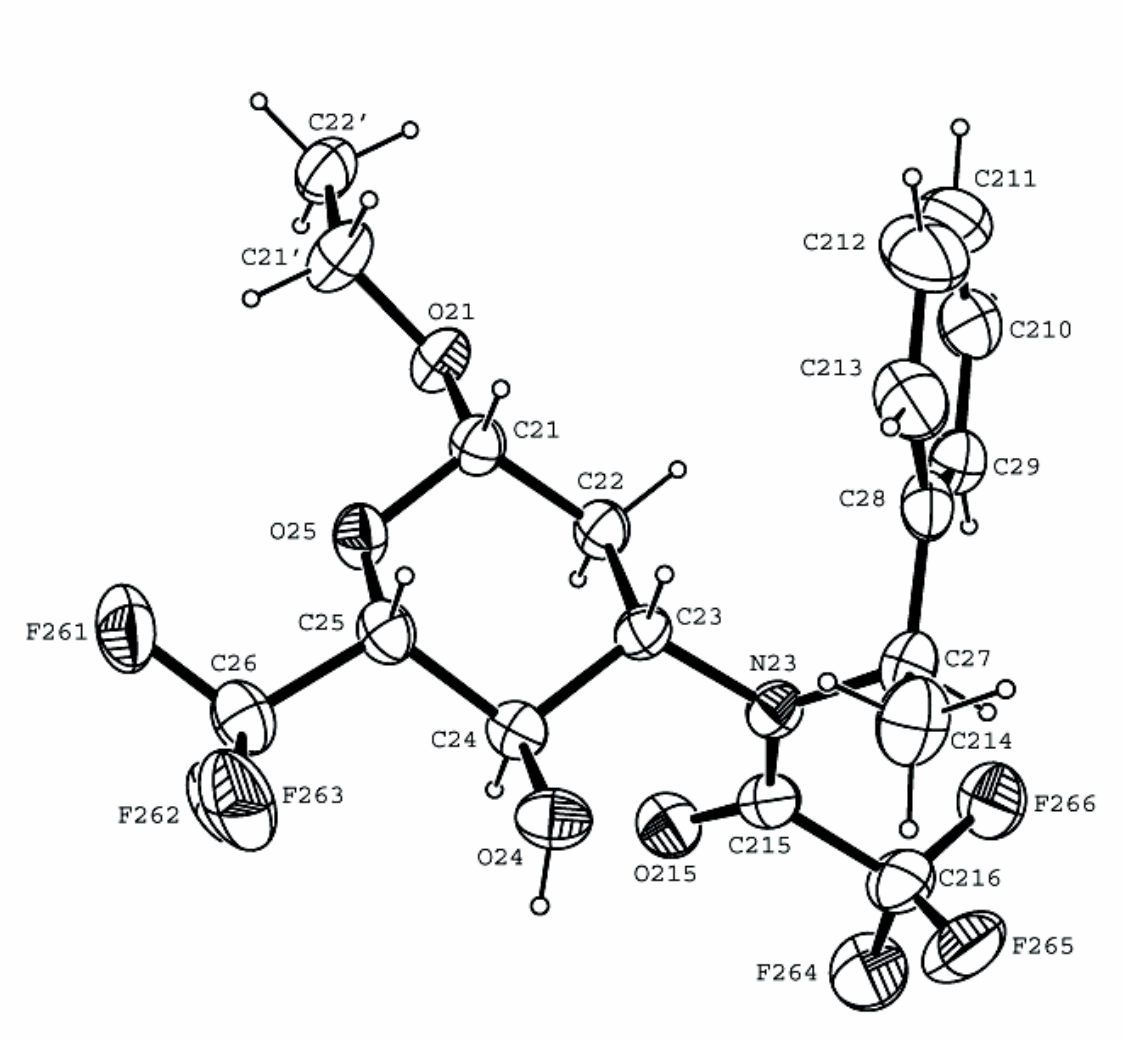

Figure 13: Perspective view of the other unique molecule of **16** with displacement ellipsoids drawn at the 50% probability level.

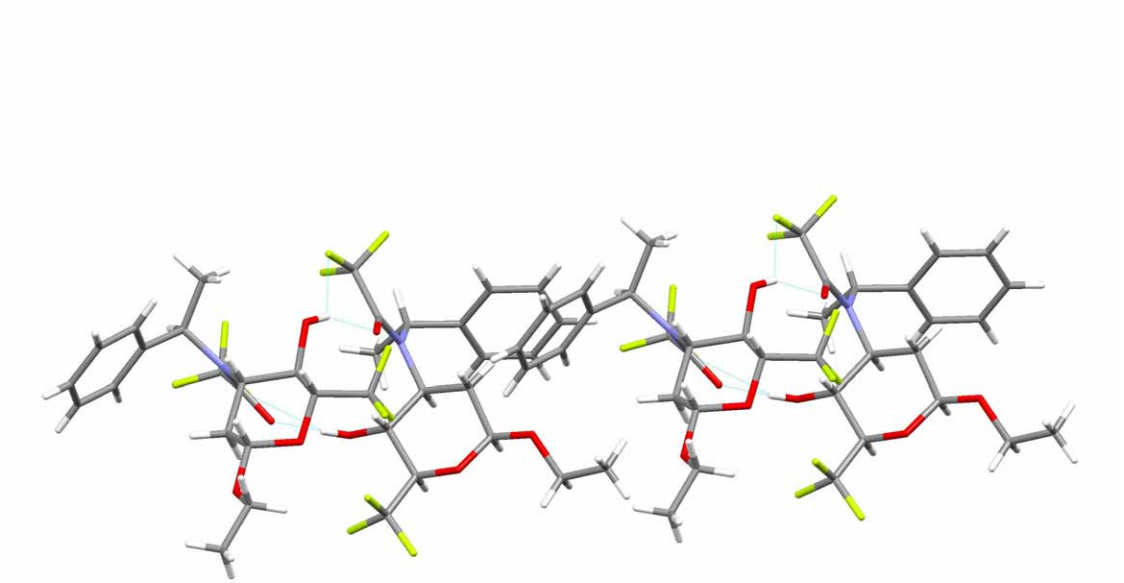

Figure 14: H-bonding in the X-ray structure of **16**.

Table 1. Crystal data and structure refinement for **16**.

Identification code	feda	
Empirical formula	C18 H21 F6 N O4	
Formula weight	429.36	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 9.499(2) Å	α= 113.345(3)°.
	b = 10.601(3) Å	β= 98.080(3)°.
	c = 11.958(3) Å	γ = 103.188(3)°.
Volume	1039.9(4) $Å^3$	
Z	2	
Density (calculated)	1.371 Mg/m^3	
Absorption coefficient	0.131 mm^{-1}	
F(000)	444	
Crystal size	0.8 x 0.5 x 0.4 mm^3	
Theta range for data collection	2.19 to 27.68°.	
Index ranges	-12<=h<=12, -13<=k<=13, -14<=l<=15	
Reflections collected	13093	
Independent reflections	7146 [R(int) = 0.0232]	
Completeness to theta = 27.68°	91.3 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7146 / 3 / 529	
Goodness-of-fit on F^2	0.965	
Final R indices [I>2sigma(I)]	R1 = 0.0311, wR2 = 0.0757	
R indices (all data)	R1 = 0.0366, wR2 = 0.0779	
Absolute structure parameter	-0.4(3)	
Largest diff. peak and hole	0.139 and -0.244 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **16**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(118)	14282(3)	11904(3)	4805(3)	71(1)
C(117)	14663(2)	11880(2)	6058(2)	53(1)
O(12)	13732(1)	10546(1)	5970(1)	46(1)
C(11)	14226(2)	10231(2)	6948(2)	38(1)
C(12)	13288(2)	8730(2)	6680(2)	37(1)
C(13)	13833(2)	8419(2)	7786(2)	33(1)
N(11)	12975(2)	6944(2)	7600(1)	35(1)
C(17)	11534(2)	6691(2)	7641(2)	41(1)
O(13)	10837(1)	7555(1)	7782(1)	46(1)
C(18)	10648(2)	5161(2)	7478(2)	54(1)
F(181)	10406(1)	4134(1)	6318(1)	60(1)
F(182)	11332(2)	4779(2)	8288(1)	76(1)
F(183)	9310(2)	5180(2)	7688(2)	85(1)
C(19)	13792(2)	5838(2)	7321(2)	41(1)
C(110)	14926(2)	6140(2)	8508(2)	54(1)
C(111)	14415(2)	5757(2)	6205(2)	39(1)
C(112)	15935(2)	6352(2)	6335(2)	59(1)
C(113)	16445(3)	6303(3)	5300(3)	83(1)
C(114)	15468(3)	5631(3)	4113(3)	75(1)
C(115)	13955(2)	5031(2)	3966(2)	53(1)
C(116)	13434(2)	5092(2)	5003(2)	41(1)
C(14)	13905(2)	9607(2)	9067(2)	36(1)
O(14)	14751(1)	9402(2)	10027(1)	44(1)
C(15)	14687(2)	11091(2)	9140(2)	39(1)
C(16)	14578(2)	12338(2)	10284(2)	51(1)
F(161)	15162(2)	13610(1)	10276(2)	79(1)
F(162)	13181(1)	12237(1)	10365(1)	64(1)
F(163)	15331(2)	12414(2)	11358(1)	80(1)
O(11)	14053(1)	11271(1)	8088(1)	41(1)

Table 2 (continued). Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for **16**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(218)	9831(2)	5824(2)	4146(2)	47(1)
C(217)	9117(2)	4387(2)	3045(2)	46(1)
O(22)	10047(1)	3494(1)	3086(1)	37(1)
C(21)	9431(2)	2073(2)	2189(2)	32(1)
C(22)	10342(2)	1182(2)	2477(2)	32(1)
C(23)	9667(2)	-366(2)	1451(2)	29(1)
N(21)	10347(1)	-1394(1)	1702(1)	31(1)
C(27)	11756(2)	-1319(2)	1620(2)	34(1)
O(23)	12566(1)	-439(2)	1368(1)	42(1)
C(28)	12426(2)	-2443(2)	1834(2)	46(1)
F(281)	13743(1)	-2320(2)	1547(1)	70(1)
F(282)	11556(2)	-3803(1)	1141(1)	64(1)
F(283)	12692(1)	-2207(1)	3043(1)	55(1)
C(29)	9398(2)	-2379(2)	2119(2)	35(1)
C(210)	8120(2)	-3552(2)	1022(2)	50(1)
C(211)	8947(2)	-1457(2)	3263(2)	36(1)
C(212)	7490(2)	-1395(3)	3227(2)	53(1)
C(213)	7170(3)	-489(4)	4293(3)	72(1)
C(214)	8279(3)	349(3)	5398(2)	68(1)
C(215)	9715(3)	283(3)	5458(2)	52(1)
C(216)	10050(2)	-611(2)	4401(2)	39(1)
C(24)	9637(2)	-444(2)	135(2)	30(1)
O(24)	8814(1)	-1864(1)	-785(1)	37(1)
C(25)	8833(2)	626(2)	1(2)	32(1)
C(26)	8894(2)	788(2)	-1207(2)	40(1)
F(261)	8035(2)	-406(1)	-2218(1)	64(1)
F(262)	8365(1)	1852(1)	-1231(1)	54(1)
F(263)	10273(1)	1090(2)	-1352(1)	60(1)
O(21)	9501(1)	2036(1)	983(1)	34(1)

Table 3. Bond lengths [Å] and angles [°] for **16**.

C(118)-C(117)	1.503(3)	C(218)-C(217)	1.484(3)
C(117)-O(12)	1.441(2)	C(217)-O(22)	1.444(2)
O(12)-C(11)	1.387(2)	O(22)-C(21)	1.379(2)
C(11)-O(11)	1.434(2)	C(21)-O(21)	1.439(2)
C(11)-C(12)	1.515(2)	C(21)-C(22)	1.518(2)
C(12)-C(13)	1.535(2)	C(22)-C(23)	1.521(2)
C(13)-N(11)	1.500(2)	C(23)-N(21)	1.490(2)
C(13)-C(14)	1.529(2)	C(23)-C(24)	1.539(2)
N(11)-C(17)	1.346(2)	N(21)-C(27)	1.342(2)
N(11)-C(19)	1.505(2)	N(21)-C(29)	1.504(2)
C(17)-O(13)	1.222(2)	C(27)-O(23)	1.230(2)
C(17)-C(18)	1.568(3)	C(27)-C(28)	1.560(2)
C(18)-F(181)	1.328(2)	C(28)-F(282)	1.329(2)
C(18)-F(183)	1.333(3)	C(28)-F(281)	1.334(2)
C(18)-F(182)	1.334(3)	C(28)-F(283)	1.341(2)
C(19)-C(111)	1.514(3)	C(29)-C(211)	1.519(3)
C(19)-C(110)	1.526(3)	C(29)-C(210)	1.520(3)
C(111)-C(116)	1.397(3)	C(211)-C(212)	1.397(3)
C(111)-C(112)	1.397(3)	C(211)-C(216)	1.399(3)
C(112)-C(113)	1.379(4)	C(212)-C(213)	1.383(3)
C(113)-C(114)	1.382(4)	C(213)-C(214)	1.377(4)
C(114)-C(115)	1.387(3)	C(214)-C(215)	1.375(3)
C(115)-C(116)	1.382(3)	C(215)-C(216)	1.378(3)
C(14)-O(14)	1.423(2)	C(24)-O(24)	1.413(2)
C(14)-C(15)	1.541(3)	C(24)-C(25)	1.549(2)
C(15)-O(11)	1.418(2)	C(25)-O(21)	1.408(2)
C(15)-C(16)	1.516(3)	C(25)-C(26)	1.529(2)
C(16)-F(162)	1.327(2)	C(26)-F(263)	1.329(2)
C(16)-F(161)	1.340(3)	C(26)-F(261)	1.330(2)
C(16)-F(163)	1.343(3)	C(26)-F(262)	1.343(2)

Table 3 (continued). Bond lengths [Å] and angles [°] for **16**.

O(12)-C(117)-C(118)	108.88(17)	C(111)-C(19)-C(110)	115.77(17)
C(11)-O(12)-C(117)	113.97(13)	C(116)-C(111)-C(112)	118.57(19)
O(12)-C(11)-O(11)	108.33(14)	C(116)-C(111)-C(19)	119.07(16)
O(12)-C(11)-C(12)	109.57(14)	C(112)-C(111)-C(19)	122.35(18)
O(11)-C(11)-C(12)	109.26(14)	C(113)-C(112)-C(111)	120.4(2)
C(11)-C(12)-C(13)	108.60(13)	C(112)-C(113)-C(114)	120.6(2)
N(11)-C(13)-C(14)	112.26(14)	C(113)-C(114)-C(115)	119.7(2)
N(11)-C(13)-C(12)	112.50(13)	C(116)-C(115)-C(114)	120.0(2)
C(14)-C(13)-C(12)	113.10(14)	C(115)-C(116)-C(111)	120.74(18)
C(17)-N(11)-C(13)	118.24(14)	O(14)-C(14)-C(13)	108.47(13)
C(17)-N(11)-C(19)	125.08(14)	O(14)-C(14)-C(15)	109.52(13)
C(13)-N(11)-C(19)	116.62(13)	C(13)-C(14)-C(15)	109.01(14)
O(13)-C(17)-N(11)	125.38(17)	O(11)-C(15)-C(16)	105.24(15)
O(13)-C(17)-C(18)	116.32(16)	O(11)-C(15)-C(14)	112.70(13)
N(11)-C(17)-C(18)	118.30(17)	C(16)-C(15)-C(14)	112.56(16)
F(181)-C(18)-F(183)	106.85(17)	F(162)-C(16)-F(161)	107.09(17)
F(181)-C(18)-F(182)	108.40(18)	F(162)-C(16)-F(163)	106.62(18)
F(183)-C(18)-F(182)	107.33(18)	F(161)-C(16)-F(163)	106.88(15)
F(181)-C(18)-C(17)	112.27(17)	F(162)-C(16)-C(15)	113.14(14)
F(183)-C(18)-C(17)	109.00(18)	F(161)-C(16)-C(15)	111.50(18)
F(182)-C(18)-C(17)	112.71(16)	F(163)-C(16)-C(15)	111.26(17)
N(11)-C(19)-C(111)	108.37(14)	C(15)-O(11)-C(11)	110.60(12)
N(11)-C(19)-C(110)	110.81(15)		

Table 3 (continued). Bond lengths [Å] and angles [°] for **16**.

O(22)-C(217)-C(218)	107.44(14)	O(24)-C(24)-C(25)	109.50(12)
C(21)-O(22)-C(217)	113.60(12)	C(23)-C(24)-C(25)	107.25(13)
O(22)-C(21)-O(21)	107.59(12)	O(21)-C(25)-C(26)	104.86(13)
O(22)-C(21)-C(22)	108.97(12)	O(21)-C(25)-C(24)	112.26(11)
O(21)-C(21)-C(22)	109.88(14)	C(26)-C(25)-C(24)	112.48(14)
C(21)-C(22)-C(23)	107.75(12)	F(263)-C(26)-F(261)	108.39(16)
N(21)-C(23)-C(22)	113.20(12)	F(263)-C(26)-F(262)	106.91(14)
N(21)-C(23)-C(24)	113.70(13)	F(261)-C(26)-F(262)	105.63(13)
C(22)-C(23)-C(24)	111.36(13)	F(263)-C(26)-C(25)	112.82(13)
C(27)-N(21)-C(23)	118.99(13)	F(261)-C(26)-C(25)	111.07(14)
C(27)-N(21)-C(29)	125.28(13)	F(262)-C(26)-C(25)	111.66(16)
C(23)-N(21)-C(29)	115.60(12)	C(25)-O(21)-C(21)	111.36(11)
O(23)-C(27)-N(21)	125.06(15)		
O(23)-C(27)-C(28)	116.69(15)		
N(21)-C(27)-C(28)	118.25(14)		
F(282)-C(28)-F(281)	108.02(17)		
F(282)-C(28)-F(283)	107.31(16)		
F(281)-C(28)-F(283)	106.52(15)		
F(282)-C(28)-C(27)	113.42(14)		
F(281)-C(28)-C(27)	109.23(15)		
F(283)-C(28)-C(27)	112.03(16)		
N(21)-C(29)-C(211)	108.40(13)		
N(21)-C(29)-C(210)	110.93(14)		
C(211)-C(29)-C(210)	115.78(15)		
C(212)-C(211)-C(216)	118.44(19)		
C(212)-C(211)-C(29)	123.10(17)		
C(216)-C(211)-C(29)	118.45(15)		
C(213)-C(212)-C(211)	120.0(2)		
C(214)-C(213)-C(212)	120.4(2)		
C(215)-C(214)-C(213)	120.4(2)		
C(214)-C(215)-C(216)	119.8(2)		
C(215)-C(216)-C(211)	120.93(18)		
O(24)-C(24)-C(23)	108.84(12)		

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **16**. 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}
C(118)	88(2)	50(1)	77(2)	37(1)	3(1)	16(1)
C(117)	54(1)	36(1)	61(1)	19(1)	3(1)	10(1)
O(12)	45(1)	35(1)	48(1)	15(1)	-3(1)	8(1)
C(11)	34(1)	32(1)	40(1)	10(1)	5(1)	10(1)
C(12)	36(1)	27(1)	34(1)	4(1)	3(1)	7(1)
C(13)	28(1)	27(1)	34(1)	5(1)	7(1)	7(1)
N(11)	35(1)	27(1)	34(1)	6(1)	6(1)	8(1)
C(17)	39(1)	36(1)	34(1)	7(1)	8(1)	5(1)
O(13)	33(1)	39(1)	50(1)	6(1)	12(1)	8(1)
C(18)	52(1)	39(1)	55(1)	11(1)	16(1)	2(1)
F(181)	58(1)	33(1)	61(1)	5(1)	9(1)	-2(1)
F(182)	94(1)	64(1)	66(1)	36(1)	23(1)	5(1)
F(183)	62(1)	56(1)	119(1)	23(1)	50(1)	-1(1)
C(19)	40(1)	30(1)	42(1)	8(1)	2(1)	12(1)
C(110)	60(1)	45(1)	47(1)	15(1)	-4(1)	19(1)
C(111)	35(1)	28(1)	42(1)	4(1)	7(1)	14(1)
C(112)	37(1)	54(1)	55(1)	-5(1)	8(1)	11(1)
C(113)	48(1)	77(2)	74(2)	-8(1)	30(1)	1(1)
C(114)	76(2)	65(2)	58(2)	4(1)	37(1)	8(1)
C(115)	63(1)	41(1)	44(1)	7(1)	12(1)	17(1)
C(116)	40(1)	31(1)	45(1)	9(1)	7(1)	15(1)
C(14)	28(1)	35(1)	33(1)	4(1)	8(1)	8(1)
O(14)	38(1)	52(1)	34(1)	12(1)	8(1)	14(1)
C(15)	28(1)	32(1)	40(1)	2(1)	5(1)	7(1)
C(16)	38(1)	32(1)	50(1)	-5(1)	5(1)	1(1)
F(161)	80(1)	28(1)	87(1)	-5(1)	26(1)	-4(1)
F(162)	47(1)	44(1)	70(1)	-5(1)	20(1)	14(1)
F(163)	78(1)	71(1)	42(1)	-14(1)	-8(1)	22(1)
O(11)	37(1)	27(1)	46(1)	5(1)	5(1)	10(1)

Table 4 (continued). Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **16**. 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}
C(218)	61(1)	38(1)	47(1)	19(1)	14(1)	23(1)
C(217)	47(1)	37(1)	49(1)	15(1)	0(1)	20(1)
O(22)	40(1)	28(1)	36(1)	11(1)	0(1)	13(1)
C(21)	33(1)	31(1)	29(1)	13(1)	3(1)	9(1)
C(22)	34(1)	33(1)	27(1)	13(1)	3(1)	10(1)
C(23)	27(1)	29(1)	30(1)	12(1)	6(1)	11(1)
N(21)	30(1)	31(1)	32(1)	14(1)	6(1)	11(1)
C(27)	33(1)	37(1)	29(1)	11(1)	5(1)	14(1)
O(23)	32(1)	54(1)	45(1)	26(1)	12(1)	16(1)
C(28)	46(1)	52(1)	49(1)	24(1)	13(1)	27(1)
F(281)	58(1)	103(1)	93(1)	63(1)	40(1)	58(1)
F(282)	77(1)	47(1)	67(1)	18(1)	16(1)	37(1)
F(283)	54(1)	71(1)	54(1)	36(1)	8(1)	32(1)
C(29)	33(1)	30(1)	42(1)	19(1)	5(1)	7(1)
C(210)	46(1)	37(1)	53(1)	19(1)	-1(1)	1(1)
C(211)	35(1)	41(1)	44(1)	29(1)	11(1)	13(1)
C(212)	40(1)	79(2)	57(1)	43(1)	17(1)	25(1)
C(213)	59(1)	119(2)	78(2)	63(2)	39(1)	54(2)
C(214)	91(2)	99(2)	53(1)	47(2)	40(1)	63(2)
C(215)	71(1)	58(1)	41(1)	29(1)	19(1)	29(1)
C(216)	42(1)	41(1)	41(1)	24(1)	12(1)	17(1)
C(24)	25(1)	35(1)	27(1)	12(1)	4(1)	8(1)
O(24)	34(1)	37(1)	30(1)	6(1)	6(1)	9(1)
C(25)	28(1)	38(1)	29(1)	16(1)	3(1)	8(1)
C(26)	35(1)	50(1)	35(1)	22(1)	5(1)	9(1)
F(261)	80(1)	62(1)	30(1)	19(1)	-6(1)	2(1)
F(262)	57(1)	69(1)	51(1)	41(1)	10(1)	24(1)
F(263)	43(1)	103(1)	54(1)	51(1)	21(1)	23(1)
O(21)	38(1)	33(1)	31(1)	17(1)	4(1)	9(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **16**.

	x	y	z	U(eq)
H(11A)	13227	11840	4587	107
H(11B)	14461	11080	4157	107
H(11C)	14912	12807	4855	107
H(11D)	15731	11953	6289	64
H(11E)	14491	12713	6719	64
H(11)	15302	10281	7036	45
H(12A)	13390	8004	5888	44
H(12B)	12220	8674	6580	44
H(13)	14886	8416	7795	40
H(19)	13032	4878	7053	49
H(11F)	14404	6093	9148	81
H(11G)	15650	7106	8833	81
H(11H)	15453	5416	8304	81
H(112)	16622	6794	7143	71
H(113)	17478	6734	5403	99
H(114)	15831	5580	3400	90
H(115)	13278	4579	3154	64
H(116)	12398	4676	4897	49
H(14)	12872	9553	9175	43
H(14A)	14265	9402	10562	66
H(15)	15768	11190	9181	47

Table 5 (continued). Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3)
for **16**.

	x	y	z	U(eq)
H(21A)	10839	6247	4100	71
H(21B)	9894	5713	4925	71
H(21C)	9230	6461	4140	71
H(21D)	8099	3945	3084	55
H(21E)	9035	4487	2251	55
H(21)	8368	1690	2192	38
H(22A)	10308	1216	3312	38
H(22B)	11399	1572	2491	38
H(23)	8597	-676	1467	34
H(29)	10048	-2873	2402	42
H(21F)	8528	-4141	368	75
H(21G)	7503	-3104	673	75
H(21H)	7506	-4167	1319	75
H(212)	6718	-1975	2469	63
H(213)	6178	-445	4264	86
H(214)	8051	977	6122	81
H(215)	10473	852	6226	62
H(216)	11043	-653	4446	47
H(24)	10678	-173	42	36
H(24A)	9322	-2174	-1293	56
H(25)	7763	274	1	39

Table 6. Torsion angles [°] for **16**.

C(118)-C(117)-O(12)-C(11)	164.57(19)
C(117)-O(12)-C(11)-O(11)	67.91(19)
C(117)-O(12)-C(11)-C(12)	-172.97(17)
O(12)-C(11)-C(12)-C(13)	-178.79(15)
O(11)-C(11)-C(12)-C(13)	-60.24(17)
C(11)-C(12)-C(13)-N(11)	-179.47(14)
C(11)-C(12)-C(13)-C(14)	52.03(18)
C(14)-C(13)-N(11)-C(17)	59.86(18)
C(12)-C(13)-N(11)-C(17)	-69.07(19)
C(14)-C(13)-N(11)-C(19)	-122.80(15)
C(12)-C(13)-N(11)-C(19)	108.26(16)
C(13)-N(11)-C(17)-O(13)	2.4(3)
C(19)-N(11)-C(17)-O(13)	-174.73(18)
C(13)-N(11)-C(17)-C(18)	-178.59(15)
C(19)-N(11)-C(17)-C(18)	4.3(3)
O(13)-C(17)-C(18)-F(181)	110.4(2)
N(11)-C(17)-C(18)-F(181)	-68.7(2)
O(13)-C(17)-C(18)-F(183)	-7.7(3)
N(11)-C(17)-C(18)-F(183)	173.13(17)
O(13)-C(17)-C(18)-F(182)	-126.8(2)
N(11)-C(17)-C(18)-F(182)	54.1(2)
C(17)-N(11)-C(19)-C(111)	123.60(17)
C(13)-N(11)-C(19)-C(111)	-53.54(18)
C(17)-N(11)-C(19)-C(110)	-108.4(2)
C(13)-N(11)-C(19)-C(110)	74.5(2)
N(11)-C(19)-C(111)-C(116)	-73.0(2)
C(110)-C(19)-C(111)-C(116)	161.85(17)
N(11)-C(19)-C(111)-C(112)	105.7(2)
C(110)-C(19)-C(111)-C(112)	-19.5(3)
C(116)-C(111)-C(112)-C(113)	1.1(3)
C(19)-C(111)-C(112)-C(113)	-177.5(2)
C(111)-C(112)-C(113)-C(114)	-1.7(5)
C(112)-C(113)-C(114)-C(115)	1.5(5)
C(113)-C(114)-C(115)-C(116)	-0.8(4)

C(114)-C(115)-C(116)-C(111)	0.3(3)
C(112)-C(111)-C(116)-C(115)	-0.4(3)
C(19)-C(111)-C(116)-C(115)	178.29(17)
N(11)-C(13)-C(14)-O(14)	65.40(16)
C(12)-C(13)-C(14)-O(14)	-165.98(13)
N(11)-C(13)-C(14)-C(15)	-175.41(13)
C(12)-C(13)-C(14)-C(15)	-46.79(17)
O(14)-C(14)-C(15)-O(11)	170.00(13)
C(13)-C(14)-C(15)-O(11)	51.47(17)
O(14)-C(14)-C(15)-C(16)	-71.16(18)
C(13)-C(14)-C(15)-C(16)	170.31(14)
O(11)-C(15)-C(16)-F(162)	68.7(2)
C(14)-C(15)-C(16)-F(162)	-54.4(2)
O(11)-C(15)-C(16)-F(161)	-52.06(19)
C(14)-C(15)-C(16)-F(161)	-175.17(15)
O(11)-C(15)-C(16)-F(163)	-171.27(15)
C(14)-C(15)-C(16)-F(163)	65.62(19)
C(16)-C(15)-O(11)-C(11)	174.27(13)
C(14)-C(15)-O(11)-C(11)	-62.71(17)
O(12)-C(11)-O(11)-C(15)	-173.86(13)
C(12)-C(11)-O(11)-C(15)	66.83(16)
C(218)-C(217)-O(22)-C(21)	173.44(15)
C(217)-O(22)-C(21)-O(21)	71.79(17)
C(217)-O(22)-C(21)-C(22)	-169.12(15)
O(22)-C(21)-C(22)-C(23)	-178.24(13)
O(21)-C(21)-C(22)-C(23)	-60.58(16)
C(21)-C(22)-C(23)-N(21)	-173.24(13)
C(21)-C(22)-C(23)-C(24)	57.17(16)
C(22)-C(23)-N(21)-C(27)	-70.52(18)
C(24)-C(23)-N(21)-C(27)	57.87(18)
C(22)-C(23)-N(21)-C(29)	105.51(15)
C(24)-C(23)-N(21)-C(29)	-126.10(14)
C(23)-N(21)-C(27)-O(23)	1.2(2)
C(29)-N(21)-C(27)-O(23)	-174.39(16)
C(23)-N(21)-C(27)-C(28)	-177.64(14)
C(29)-N(21)-C(27)-C(28)	6.7(2)

O(23)-C(27)-C(28)-F(282)	-127.83(18)
N(21)-C(27)-C(28)-F(282)	51.1(2)
O(23)-C(27)-C(28)-F(281)	-7.3(2)
N(21)-C(27)-C(28)-F(281)	171.68(15)
O(23)-C(27)-C(28)-F(283)	110.49(18)
N(21)-C(27)-C(28)-F(283)	-70.5(2)
C(27)-N(21)-C(29)-C(211)	121.16(16)
C(23)-N(21)-C(29)-C(211)	-54.58(17)
C(27)-N(21)-C(29)-C(210)	-110.67(18)
C(23)-N(21)-C(29)-C(210)	73.59(18)
N(21)-C(29)-C(211)-C(212)	108.87(18)
C(210)-C(29)-C(211)-C(212)	-16.5(2)
N(21)-C(29)-C(211)-C(216)	-70.03(18)
C(210)-C(29)-C(211)-C(216)	164.61(15)
C(216)-C(211)-C(212)-C(213)	1.3(3)
C(29)-C(211)-C(212)-C(213)	-177.56(19)
C(211)-C(212)-C(213)-C(214)	-0.4(3)
C(212)-C(213)-C(214)-C(215)	-0.8(4)
C(213)-C(214)-C(215)-C(216)	1.0(3)
C(214)-C(215)-C(216)-C(211)	0.0(3)
C(212)-C(211)-C(216)-C(215)	-1.1(3)
C(29)-C(211)-C(216)-C(215)	177.82(15)
N(21)-C(23)-C(24)-O(24)	58.87(16)
C(22)-C(23)-C(24)-O(24)	-171.81(12)
N(21)-C(23)-C(24)-C(25)	177.24(12)
C(22)-C(23)-C(24)-C(25)	-53.43(15)
O(24)-C(24)-C(25)-O(21)	173.03(12)
C(23)-C(24)-C(25)-O(21)	55.08(16)
O(24)-C(24)-C(25)-C(26)	-68.98(16)
C(23)-C(24)-C(25)-C(26)	173.07(12)
O(21)-C(25)-C(26)-F(263)	70.70(19)
C(24)-C(25)-C(26)-F(263)	-51.6(2)
O(21)-C(25)-C(26)-F(261)	-167.36(14)
C(24)-C(25)-C(26)-F(261)	70.37(18)
O(21)-C(25)-C(26)-F(262)	-49.74(16)
C(24)-C(25)-C(26)-F(262)	-172.01(13)

C(26)-C(25)-O(21)-C(21)	175.94(12)
C(24)-C(25)-O(21)-C(21)	-61.65(16)
O(22)-C(21)-O(21)-C(25)	-177.45(12)
C(22)-C(21)-O(21)-C(25)	64.04(15)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **16** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(14)-H(14A)...O(23)#1	0.84	2.00	2.7911(18)	156.9
O(14)-H(14A)...F(281)#1	0.84	2.53	3.1427(19)	130.3
O(24)-H(24A)...O(13)#2	0.84	1.94	2.7632(18)	166.5
O(24)-H(24A)...F(183)#2	0.84	2.57	3.124(2)	124.1

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