Test purchase, synthesis and characterization of 3-fluorophenmetrazine (3-FPM) and differentiation from its *ortho*- and *para*-substituted isomers

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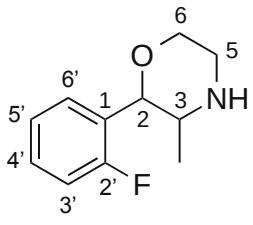
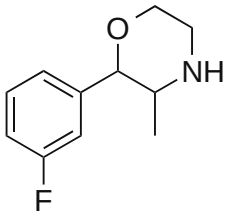
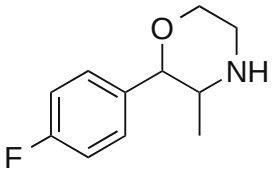


2-Fluorophenmetrazine
(2-FPM)



3-Fluorophenmetrazine
(3-FPM)



4-Fluorophenmetrazine
(4-FPM)

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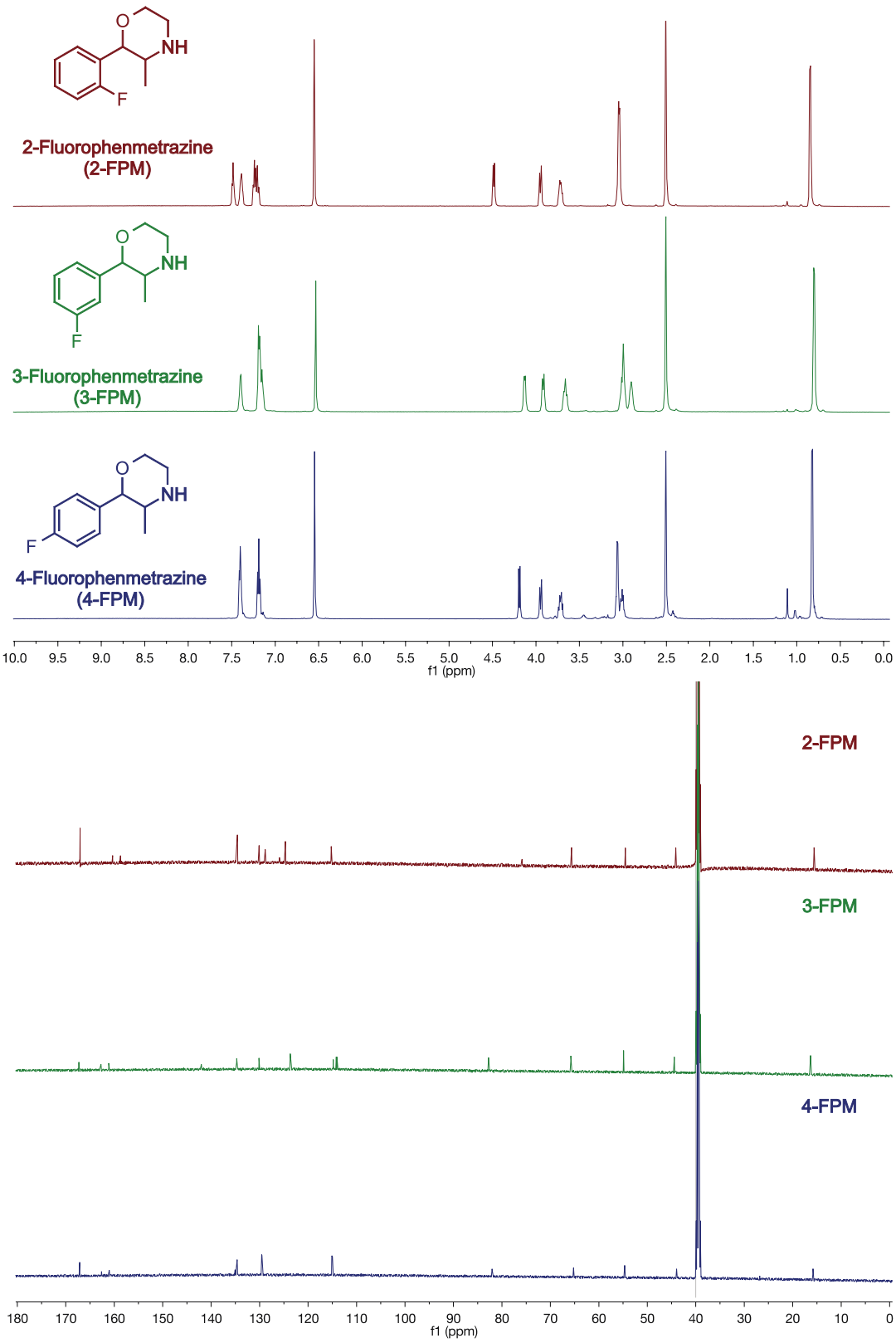
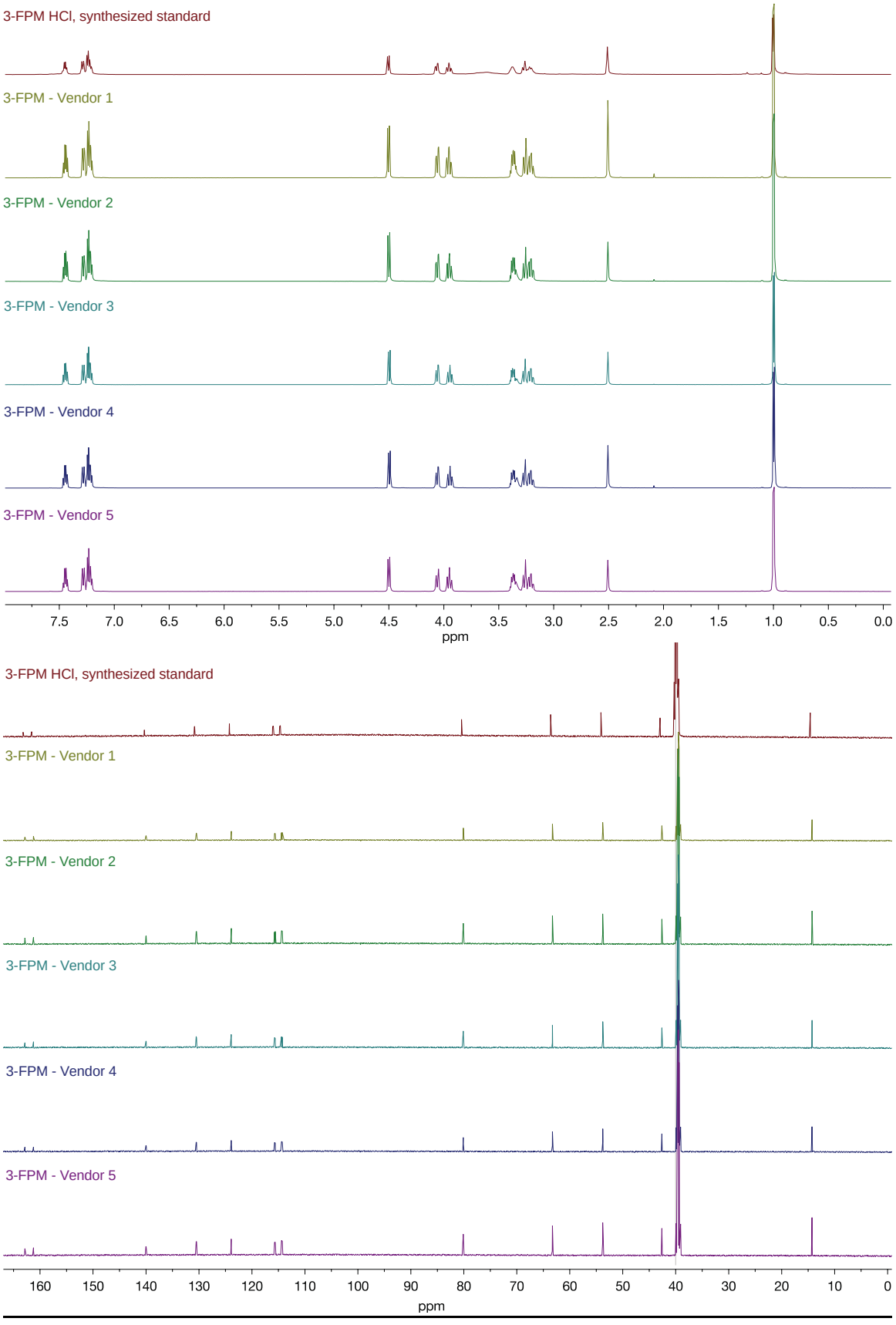
2. ^{1}H and ^{13}C NMR spectra: Synthesized 2-FPM, 3-FPM and 4-FPM fumarate reference standards (d_6-DMSO, 600 / 150 MHz)



3. ^{1}H NMR and ^{13}C NMR spectra: Synthesized 3-FPM vs. all five 3-FPM vendor samples (d_6-DMSO, 600 / 150 MHz)



3-FPM HCl salt synthesized standard

^{1}H NMR (DMSO) δ 7.48–7.41 (m,1H, Ar-CH, [3']), 7.31–7.19 (m, 3H, Ar-CH, [2',4',6']), 4.51 (d, *J* = 9.8 Hz, 1H, CH, [2]), 4.09–3.91 (m, 2H, CH_2, [6]), 3.41–3.33 (m, 1H, CH, [3]), 3.30–3.17 (m, 2H, CH_2, [5]), 1.00 (d, *J* = 6.6 Hz, 3H, CH_3) ppm.^{13}C NMR (DMSO) δ 162.40 (Ar-CF [1']), 140.31 (Ar-CH [5']), 130.80 (Ar-CH [3']), 124.20 (Ar-CH [4']), 115.93 (Ar-CH [2']), 114.70 (Ar-CH [6']), 80.43 (CH [2]), 63.62 (CH_2 [6]), 54.13 (CH [3]), 42.96 (CH_2 [5]), 14.61 (CH_3) ppm. ^{19}F NMR (d_6-DMSO) δ –113.19 ppm.

Vendor one

^{1}H NMR (DMSO) δ 7.48–7.41 (m,1H, Ar-CH, [3]), 7.31–7.18 (m, 3H, Ar-CH, [2',4',6']), 4.50 (d, *J* = 9.8 Hz, 1H, CH, [2]), 4.08–3.92 (m, 2H, CH_2, [6]), 3.41–3.33 (m, 1H, CH, [3]), 3.29–3.16 (m, 2H, CH_2, [5]), 1.00 (d, *J* = 6.7 Hz, 3H, CH_3) ppm.^{13}C NMR (DMSO) δ 161.24 (Ar-CF [1]), 139.95 (Ar-CH [5']), 130.48 (Ar-CH [3']), 123.80 (Ar-CH [4']), 115.57 (Ar-CH [2']), 114.93 (Ar-CH [6']), 80.09 (CH [2]), 63.27 (CH_2 [6]), 53.78 (CH [3]), 42.52 (CH_2 [5]), 14.26 (CH_3) ppm. ^{19}F NMR (d_6-DMSO) δ –113.19 ppm.

Vendor two

^{1}H NMR (DMSO) δ 7.48–7.40 (m,1H, Ar-CH, [3']), 7.31–7.18 (m, 3H, Ar-CH, [2',4',6']), 4.50 (d, *J* = 9.8 Hz, 1H, CH, [2]), 4.09–3.91 (m, 2H, CH_2, [6]), 3.40–3.32 (m, 1H, CH, [3]), 3.30–3.17 (m, 2H, CH_2, [5]), 1.00 (d, *J* = 6.7 Hz, 3H, CH_3) ppm.^{13}C NMR (DMSO) δ 162.05 (Ar-CF [1]), 139.93 (Ar-CH [5']), 130.47 (Ar-CH [3']), 123.80 (Ar-CH [4']), 115.41 (Ar-CH [2']), 114.43 (Ar-CH [6']), 80.10 (CH [2]), 63.27 (CH_2 [6]), 53.78 (CH [3]), 42.61 (CH_2 [5]), 14.27 (CH_3) ppm. ^{19}F NMR (d_6-DMSO) δ –113.19 ppm.

Vendor three

^{1}H NMR (DMSO) δ 7.48–7.41 (m,1H, Ar-CH, [3']), 7.31–7.18 (m, 3H, Ar-CH, [2',4',6']), 4.50 (d, *J* = 9.9 Hz, 1H, CH, [2]), 4.09-3.91 (m, 2H, CH_2, [6]), 3.41–3.33 (m, 1H, CH, [3]), 3.30–3.17 (m, 2H, CH_2, [5]), 1.00 (d, *J* = 6.7 Hz, 3H, CH_3) ppm.^{13}C NMR (DMSO) δ 162.05 (Ar-CF [1]), 139.96 (Ar-CH [5']), 130.48 (Ar-CH [3']), 123.85 (Ar-CH [4']), 115.44 (Ar-CH [2']), 114.21 (Ar-CH [6']), 80.10 (CH [2]), 63.27 (CH_2 [6]), 53.77 (CH [3]), 42.61 (CH_2 [5]), 14.27 (CH_3) ppm. ^{19}F NMR (d_6-DMSO) δ –113.19 ppm.

Vendor four

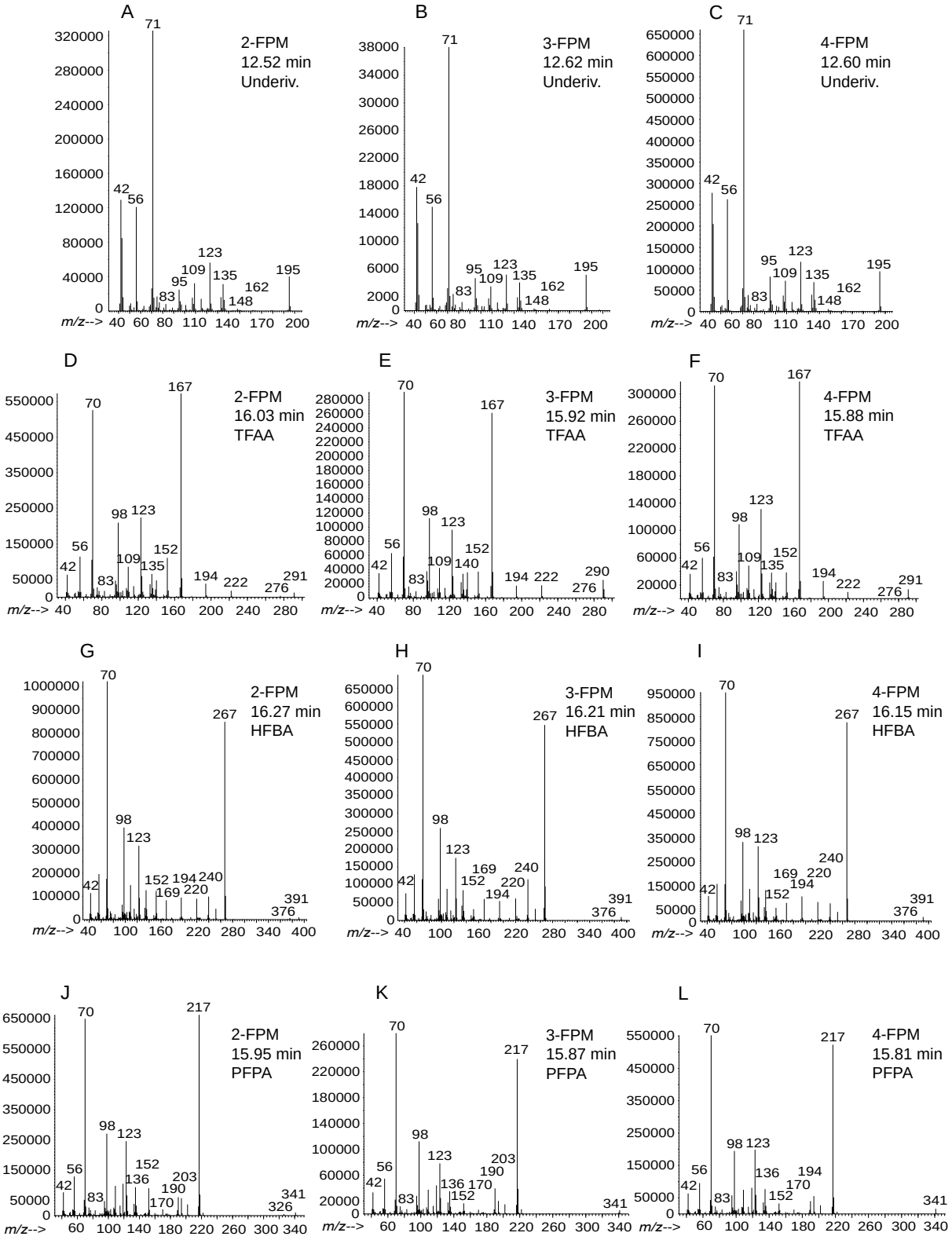
^{1}H NMR (DMSO) δ 7.48–7.41 (m,1H, Ar-CH, [3']), 7.31–7.18 (m, 3H, Ar-CH, [2',4',6']), 4.52 (d, *J* = 9.8 Hz, 1H, CH, [2]), 4.09–3.90 (m, 2H, CH_2, [6]), 3.41–3.33 (m, 1H, CH, [3]), 3.30–3.17 (m, 2H, CH_2, [5]), 1.00 (d, *J* = 6.7 Hz, 3H, CH_3) ppm.^{13}C NMR (DMSO) δ 162.05 (Ar-CF

[1]), 139.99 (Ar-CH [5']), 130.50 (Ar-CH [3']), 123.91 (Ar-CH [4']), 115.65 (Ar-CH [2']), 114.26 (Ar-CH [6']), 80.10 (CH [2]), 63.28 (CH_2 [6]), 53.78 (CH [3]), 42.61 (CH_2 [5]), 14.27 (CH_3) ppm. ^{19}F NMR (d_6-DMSO) δ –113.22 ppm.

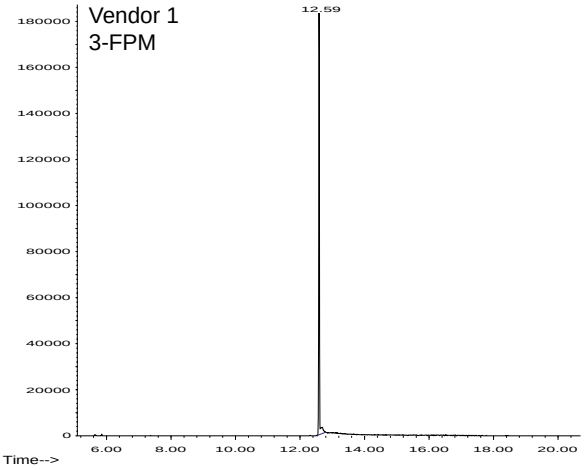
Vendor five

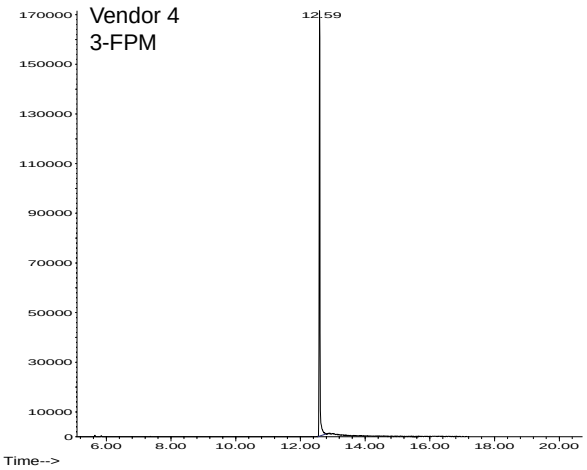
^{1}H NMR (DMSO) δ 7.48–7.41 (m,1H, Ar-CH, [3']), 7.31–7.18 (m, 3H, Ar-CH, [2',4',6']), 4.50 (d, *J* = 9.8 Hz, 1H, CH, [2]), 4.09–3.91 (m, 2H, CH_2, [6]), 3.40–3.32 (m, 1H, CH, [3]), 3.30–3.17 (m, 2H, CH_2, [5]), 1.00 (d, *J* = 6.7 Hz, 3H, CH_3) ppm.^{13}C NMR (DMSO) δ 162.05 (Ar-CF [1]), 139.97 (Ar-CH [5']), 130.49 (Ar-CH [3']), 123.80 (Ar-CH [4']), 115.56 (Ar-CH [2']), 114.32 (Ar-CH [6']), 80.10 (CH [2]), 63.28 (CH_2 [6]), 53.78 (CH [3]), 42.61 (CH_2 [5]), 14.27 (CH_3) ppm. ^{19}F NMR (d_6-DMSO) δ –113.22 ppm.

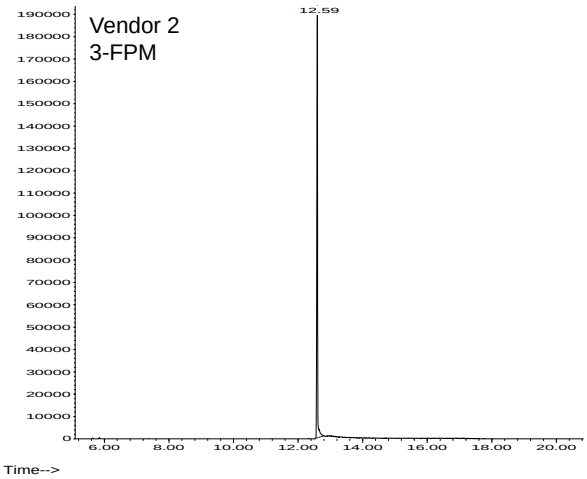
4. Electron Ionization mass spectra for the underivatized [A-C] and derivatized (TFAA [D-F], HFBA [G-I], PFBA [J-L]) FPM isomers (synthesized reference standards)

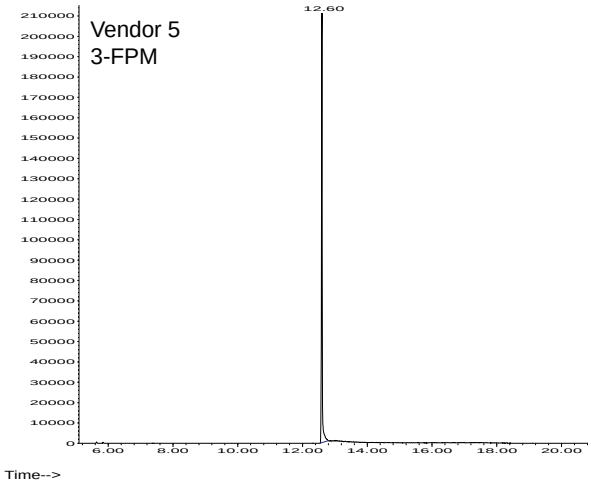


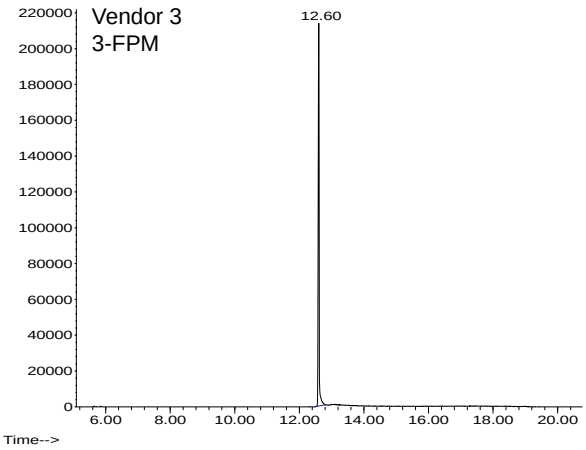
5. GC-MS data obtained from vendor samples (underivatized)



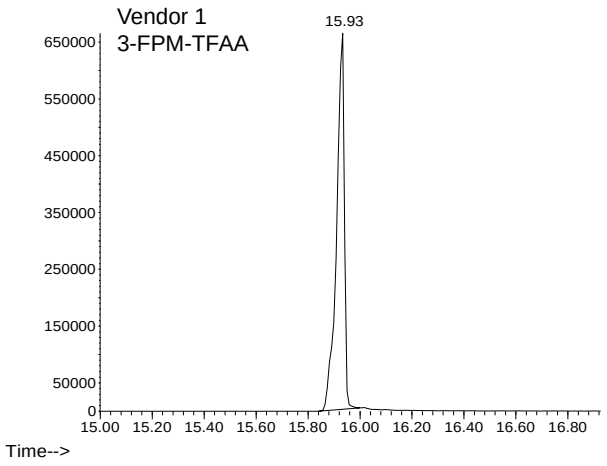


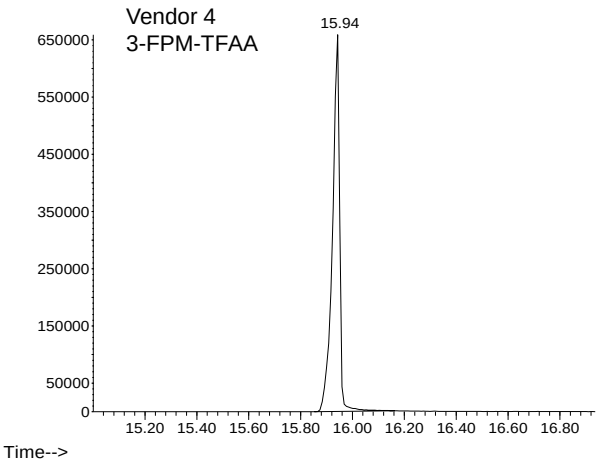


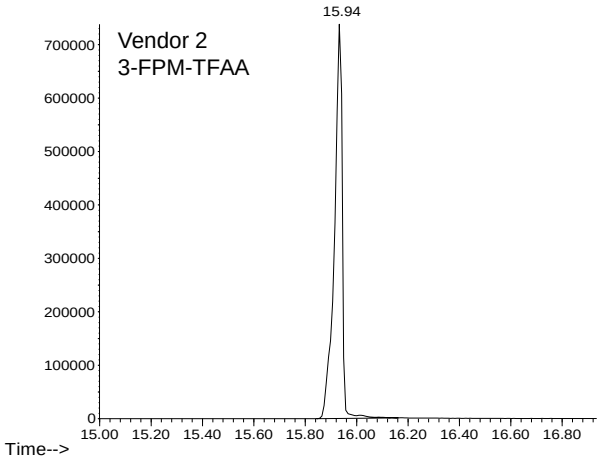


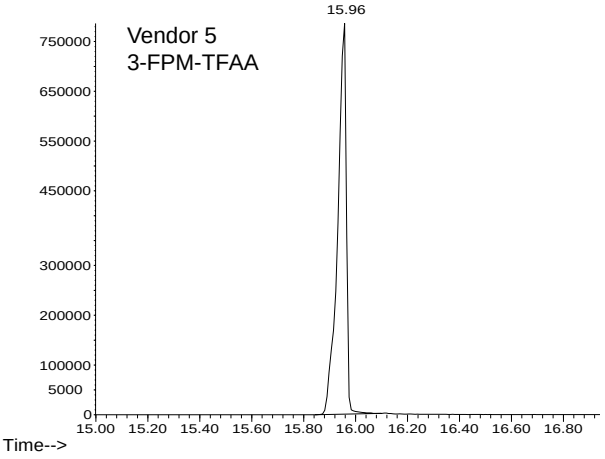


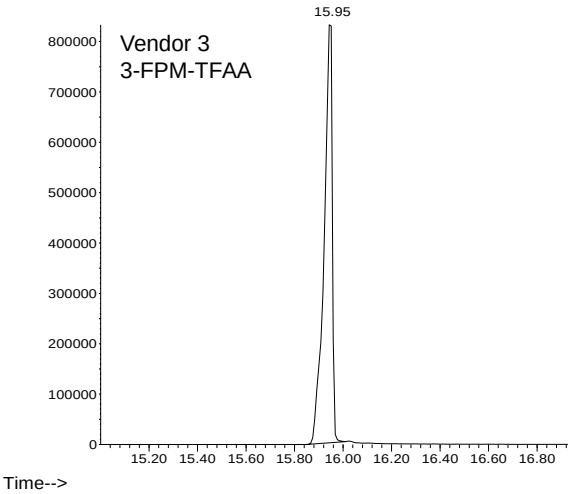
6. GC-MS vendor samples 1 - 5 (3-FPM; derivatized with TFAA)



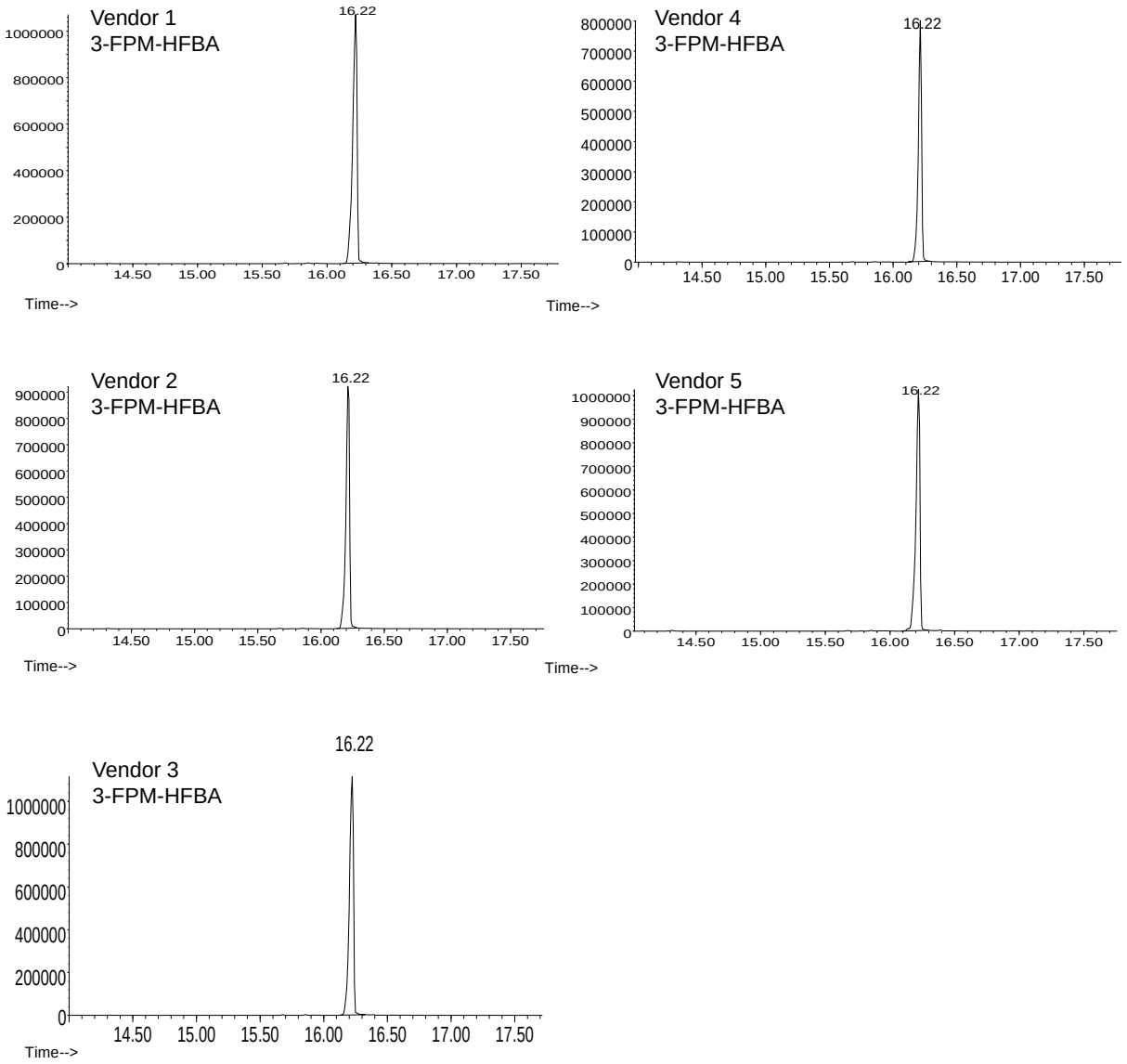




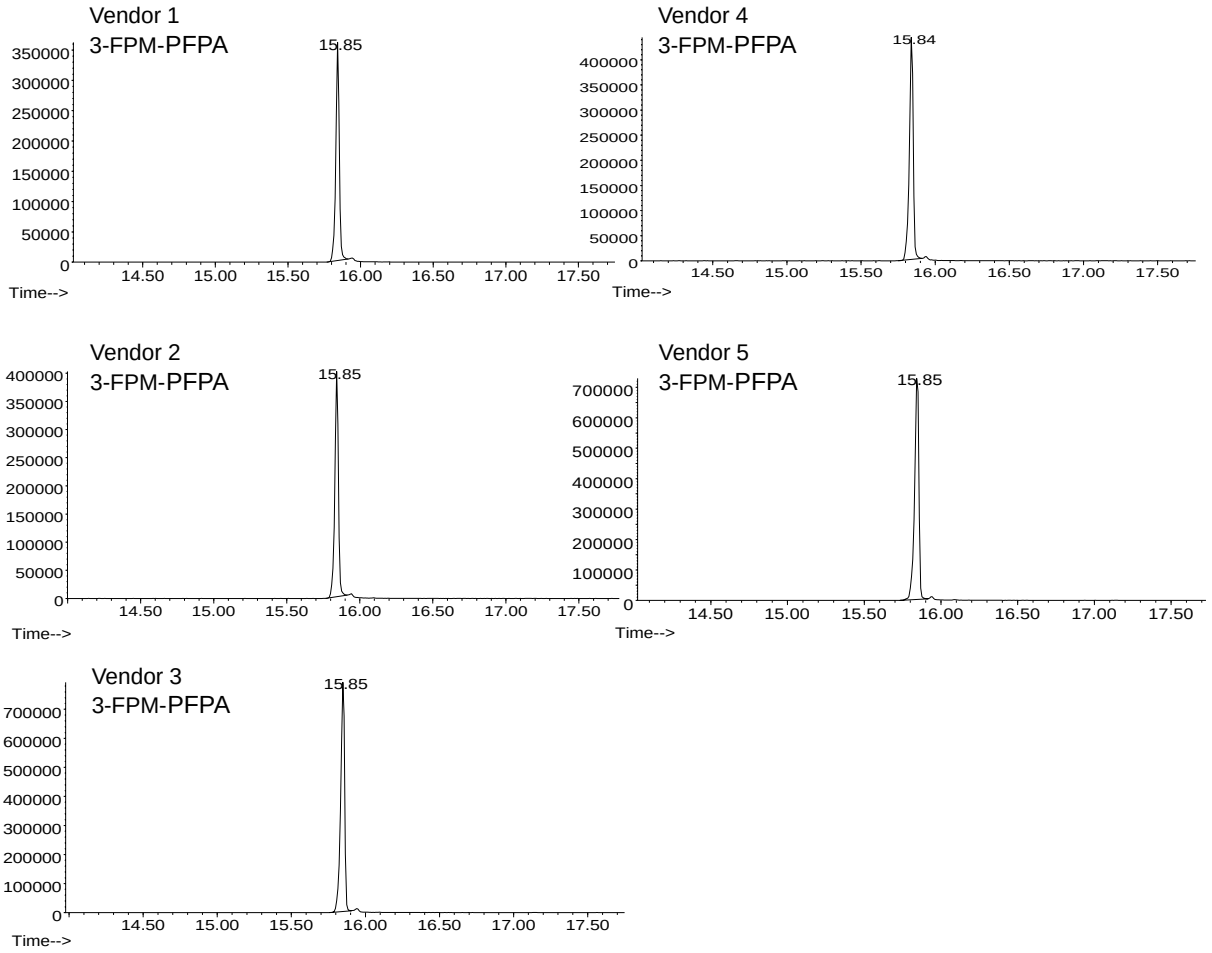




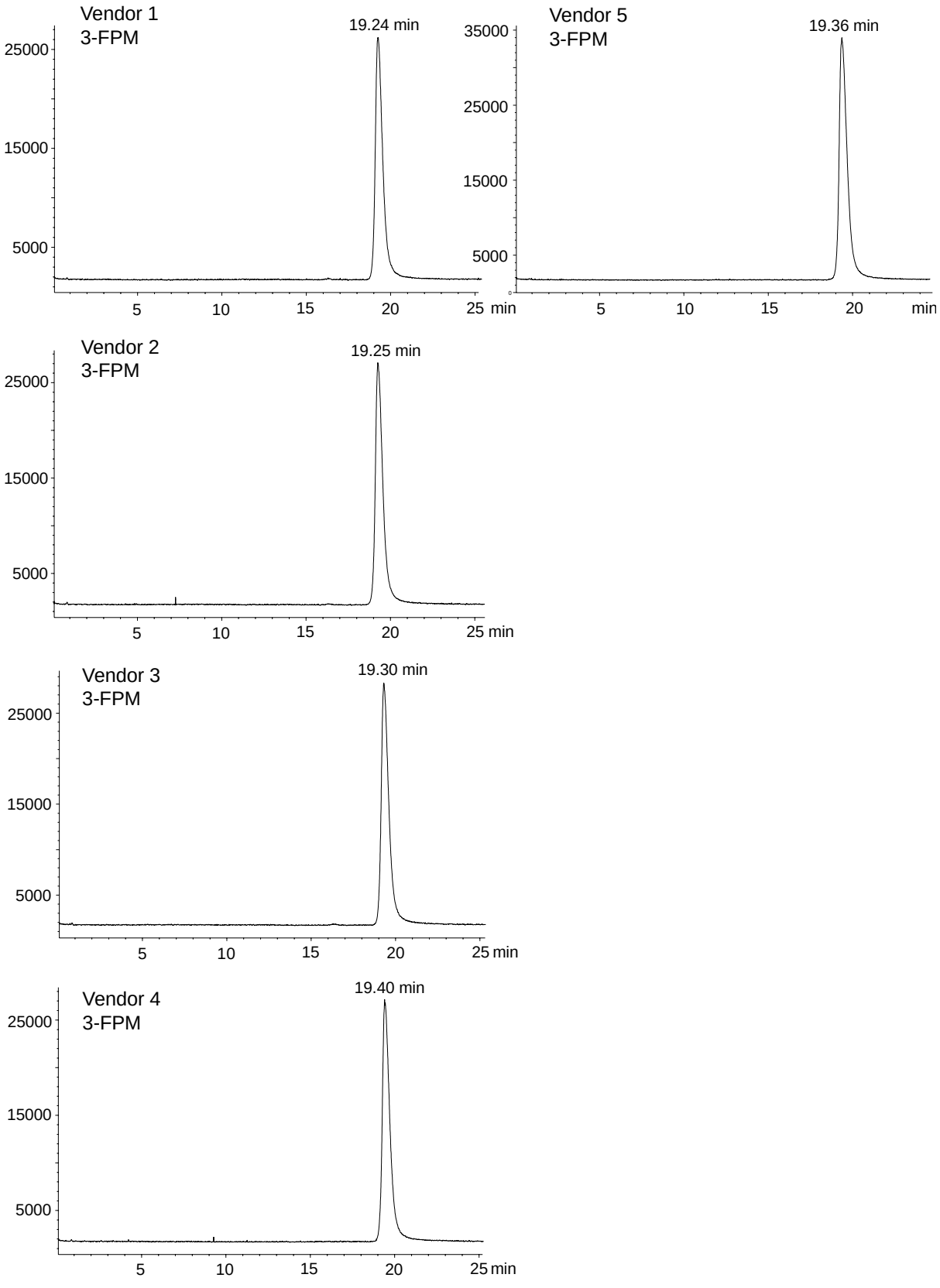
7. GC-MS vendor samples 1 - 5 (3-FPM; derivatized with HFBA)



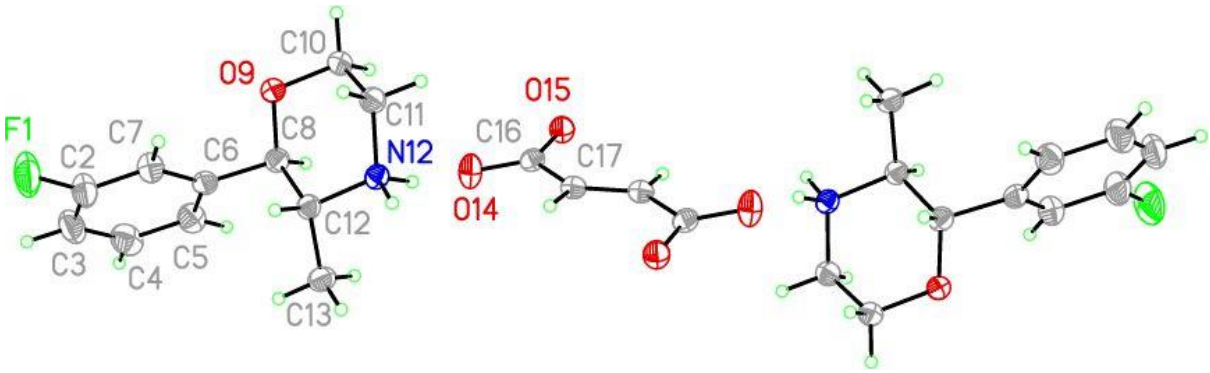
8. GC-MS vendor samples 1 - 5 (3-FPM; derivatized with PFPA)



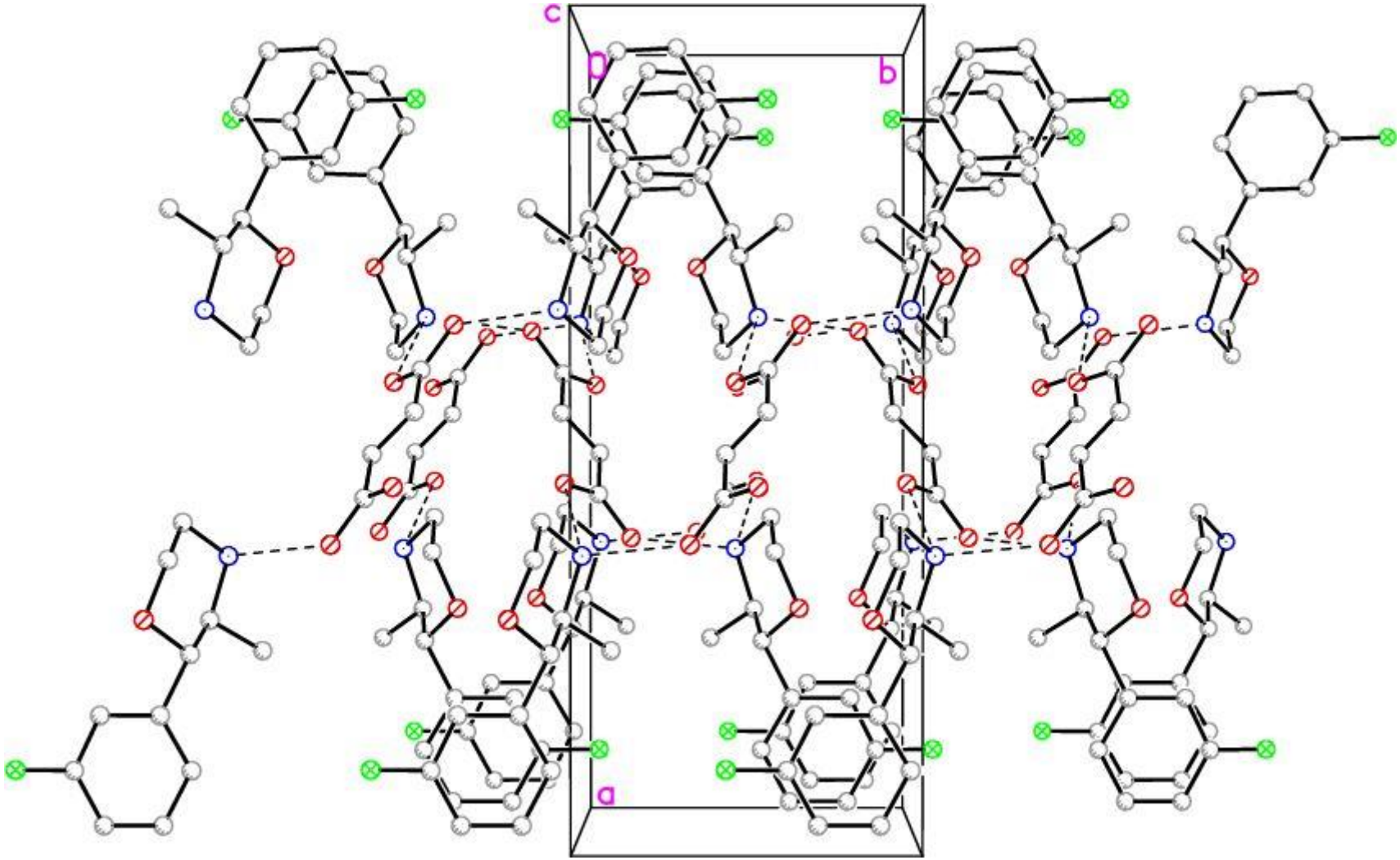
9. LC-Q-MS vendor samples 1 - 5 (3-FPM)



10. X-ray crystal data obtained for synthesized 3-FPM reference standard



Molecular structure of TCD213 (symmetry generated), thermal displacement 50%. Only symmetry unique atoms labeled for clarity



Packing diagram of TCD213 viewed down the c –axis. Hydrogen atoms omitted for clarity. Dashed lines indicate strong hydrogen bonding

Data collection details for TCD213.

Axis	dx/mm	2θ/°	ω/°	φ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	Temperature/K
Omega	50.000	-49.59	299.31	72.00	-64.87	1.90	59	57.00	1.54184	45	0.6	100
Phi	50.000	109.35	77.69	0.45	-23.00	1.90	189	57.00	1.54184	45	0.6	100
Omega	50.000	106.14	152.22	174.20	-82.85	1.90	49	57.00	1.54184	45	0.6	100
Omega	50.000	109.19	343.24	225.00	64.87	1.90	72	57.00	1.54184	45	0.6	100
Phi	50.000	-43.14	348.51	0.45	23.00	1.90	189	57.01	1.54184	45	0.6	100
Omega	50.000	109.19	343.23	300.00	64.88	1.90	72	57.00	1.54184	45	0.6	100
Omega	50.000	-49.59	299.31	216.00	-64.88	1.90	59	57.00	1.54184	45	0.6	100
Phi	50.000	109.35	4.17	0.45	23.00	1.90	189	57.01	1.54184	45	0.6	100
Omega	50.000	109.50	151.33	265.05	-81.57	1.90	50	57.00	1.54184	45	0.6	100
Omega	50.000	-49.59	190.34	144.00	54.74	1.90	70	57.00	1.54184	45	0.6	100
Phi	50.000	94.35	80.80	0.45	-57.06	1.90	189	57.00	1.54184	45	0.6	100
Omega	50.000	-49.59	190.34	36.00	54.74	1.90	70	57.00	1.54184	45	0.6	100
Omega	50.000	-49.59	190.34	108.00	54.74	1.90	70	57.00	1.54184	45	0.6	100
Omega	50.000	109.19	343.24	360.00	64.87	1.90	72	57.00	1.54184	45	0.6	100
Omega	50.000	-49.59	190.34	180.00	54.74	1.90	70	57.00	1.54184	45	0.6	100
Omega	50.000	109.19	96.27	0.00	-54.74	1.90	70	57.00	1.54184	45	0.6	100
Omega	50.000	-11.01	228.92	360.00	54.74	1.90	70	57.00	1.54184	45	0.6	100
Omega	50.000	-49.59	190.34	252.00	54.74	1.90	70	57.00	1.54184	45	0.6	100
Phi	50.000	109.35	95.80	0.45	-57.06	1.90	189	57.00	1.54184	45	0.6	100
Omega	50.000	109.19	96.27	100.00	-54.74	1.90	70	57.00	1.54184	45	0.6	100
Omega	50.000	-49.59	190.34	216.00	54.74	1.90	70	57.00	1.54184	45	0.6	100
Phi	50.000	-2.55	11.00	0.45	57.06	1.90	189	57.00	1.54184	45	0.6	100

Crystal data and structure refinement for TCD213.

Identification code	tcd213	
Empirical formula	$C_{13}H_{16}FNO_3$	
Formula weight	253.27	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 18.7821(8) Å	□= 90°.
	b = 7.7948(3) Å	□= 91.8726(14)°.
	c = 8.7467(4) Å	□ = 90°.
Volume	1279.86(9) $Å^3$	
Z	4	
Density (calculated)	1.314 Mg/m^3	
Absorption coefficient	0.863 mm^{-1}	
F(000)	536	
Crystal size	0.320 x 0.090 x 0.060 mm^3	
Theta range for data collection	2.354 to 70.115°.	
Index ranges	-22≤h≤22, -9≤k≤9, -9≤l≤10	
Reflections collected	14670	
Independent reflections	2421 [R(int) = 0.0367]	
Completeness to theta = 67.679°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.6276	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2421 / 0 / 176	
Goodness-of-fit on F^2	1.081	
Final R indices [I>2σ(I)]	R1 = 0.0516, wR2 = 0.1338	
R indices (all data)	R1 = 0.0544, wR2 = 0.1354	
Largest diff. peak and hole	0.261 and -0.292 $e.Å^{-3}$	

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for TCD213. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	8944(1)	10585(2)	5655(2)	58(1)
C(2)	8935(1)	8860(3)	5963(3)	40(1)
C(3)	9570(1)	8001(4)	6098(3)	43(1)
C(4)	9551(1)	6269(4)	6427(3)	41(1)
C(5)	8903(1)	5436(3)	6608(3)	34(1)
C(6)	8270(1)	6337(3)	6445(2)	26(1)
C(7)	8284(1)	8087(3)	6118(3)	33(1)
C(8)	7555(1)	5464(3)	6572(2)	24(1)
O(9)	7133(1)	6538(2)	7504(2)	27(1)
C(10)	6441(1)	5821(3)	7699(2)	27(1)
C(11)	6040(1)	5724(3)	6190(2)	25(1)
N(12)	6448(1)	4661(2)	5102(2)	22(1)
C(13)	7207(1)	5222(2)	4977(2)	22(1)
C(14)	7599(1)	3898(3)	4040(2)	29(1)
O(15)	6294(1)	1573(2)	6411(2)	32(1)
O(16)	5617(1)	-317(2)	7602(2)	26(1)
C(17)	5753(1)	618(2)	6481(2)	23(1)
C(18)	5252(1)	585(2)	5112(2)	22(1)

Bond lengths [Å] and angles [°] for TCD213.

F(1)-C(2)	1.371(3)	C(3)-C(2)-F(1)	118.7(2)
C(2)-C(3)	1.369(4)	C(3)-C(2)-C(7)	123.5(2)
C(2)-C(7)	1.374(3)	F(1)-C(2)-C(7)	117.8(2)
C(3)-C(4)	1.382(4)	C(2)-C(3)-C(4)	117.9(2)
C(3)-H(3)	0.9500	C(2)-C(3)-H(3)	121.0
C(4)-C(5)	1.394(3)	C(4)-C(3)-H(3)	121.0
C(4)-H(4)	0.9500	C(3)-C(4)-C(5)	120.5(2)
C(5)-C(6)	1.384(3)	C(3)-C(4)-H(4)	119.8
C(5)-H(5)	0.9500	C(5)-C(4)-H(4)	119.8
C(6)-C(7)	1.394(3)	C(6)-C(5)-C(4)	120.2(2)
C(6)-C(8)	1.513(3)	C(6)-C(5)-H(5)	119.9
C(7)-H(7)	0.9500	C(4)-C(5)-H(5)	119.9
C(8)-O(9)	1.427(2)	C(5)-C(6)-C(7)	119.7(2)
C(8)-C(13)	1.534(3)	C(5)-C(6)-C(8)	121.71(19)
C(8)-H(8)	1.0000	C(7)-C(6)-C(8)	118.55(19)
O(9)-C(10)	1.430(2)	C(2)-C(7)-C(6)	118.2(2)
C(10)-C(11)	1.499(3)	C(2)-C(7)-H(7)	120.9
C(10)-H(10A)	0.9900	C(6)-C(7)-H(7)	120.9
C(10)-H(10B)	0.9900	O(9)-C(8)-C(6)	106.83(15)
C(11)-N(12)	1.492(2)	O(9)-C(8)-C(13)	111.33(16)
C(11)-H(11A)	0.9900	C(6)-C(8)-C(13)	110.00(15)
C(11)-H(11B)	0.9900	O(9)-C(8)-H(8)	109.5
N(12)-C(13)	1.499(2)	C(6)-C(8)-H(8)	109.5
N(12)-H(12A)	0.91(3)	C(13)-C(8)-H(8)	109.5
N(12)-H(12B)	0.95(3)	C(8)-O(9)-C(10)	111.30(14)
C(13)-C(14)	1.522(3)	O(9)-C(10)-C(11)	110.28(16)
C(13)-H(13)	1.0000	O(9)-C(10)-H(10A)	109.6
C(14)-H(14A)	0.9800	C(11)-C(10)-H(10A)	109.6
C(14)-H(14B)	0.9800	O(9)-C(10)-H(10B)	109.6
C(14)-H(14C)	0.9800	C(11)-C(10)-H(10B)	109.6
O(15)-C(17)	1.261(2)	H(10A)-C(10)-H(10B)	108.1
O(16)-C(17)	1.255(2)	N(12)-C(11)-C(10)	109.67(16)
C(17)-C(18)	1.500(3)	N(12)-C(11)-H(11A)	109.7
C(18)-C(18)#1	1.324(4)	C(10)-C(11)-H(11A)	109.7
C(18)-H(18)	0.92(2)	N(12)-C(11)-H(11B)	109.7
		C(10)-C(11)-H(11B)	109.7

H(11A)-C(11)-H(11B)	108.2	C(13)-C(14)-H(14A)	109.5
C(11)-N(12)-C(13)	113.18(15)	C(13)-C(14)-H(14B)	109.5
C(11)-N(12)-H(12A)	106.9(15)	H(14A)-C(14)-H(14B)	109.5
C(13)-N(12)-H(12A)	114.9(15)	C(13)-C(14)-H(14C)	109.5
C(11)-N(12)-H(12B)	109.7(14)	H(14A)-C(14)-H(14C)	109.5
C(13)-N(12)-H(12B)	107.7(14)	H(14B)-C(14)-H(14C)	109.5
H(12A)-N(12)-H(12B)	104(2)	O(16)-C(17)-O(15)	124.49(18)
N(12)-C(13)-C(14)	108.63(15)	O(16)-C(17)-C(18)	118.34(17)
N(12)-C(13)-C(8)	110.37(15)	O(15)-C(17)-C(18)	117.16(17)
C(14)-C(13)-C(8)	111.96(16)	C(18)#1-C(18)-C(17)	123.9(2)
N(12)-C(13)-H(13)	108.6	C(18)#1-C(18)-H(18)	118.6(14)
C(14)-C(13)-H(13)	108.6	C(17)-C(18)-H(18)	117.4(14)
C(8)-C(13)-H(13)	108.6		

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

Anisotropic displacement parameters ($Å^2 x\ 10^3$) for TCD213. 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}
F(1)	50(1)	37(1)	89(1)	6(1)	12(1)	-17(1)
C(2)	40(1)	37(1)	44(1)	1(1)	5(1)	-14(1)
C(3)	31(1)	56(2)	41(1)	0(1)	4(1)	-16(1)
C(4)	26(1)	58(2)	39(1)	0(1)	-2(1)	0(1)
C(5)	31(1)	39(1)	31(1)	2(1)	-2(1)	-2(1)
C(6)	28(1)	31(1)	18(1)	-3(1)	1(1)	-4(1)
C(7)	31(1)	33(1)	35(1)	-1(1)	3(1)	-5(1)
C(8)	27(1)	22(1)	22(1)	0(1)	1(1)	-1(1)
O(9)	28(1)	29(1)	25(1)	-6(1)	5(1)	-6(1)
C(10)	29(1)	29(1)	24(1)	-2(1)	6(1)	-5(1)
C(11)	26(1)	25(1)	26(1)	1(1)	3(1)	0(1)
N(12)	24(1)	21(1)	21(1)	0(1)	-1(1)	-1(1)
C(13)	24(1)	21(1)	22(1)	1(1)	1(1)	-1(1)
C(14)	27(1)	33(1)	26(1)	-7(1)	0(1)	1(1)
O(15)	32(1)	29(1)	34(1)	9(1)	-9(1)	-10(1)
O(16)	28(1)	29(1)	22(1)	4(1)	-2(1)	-3(1)

C(17)	26(1)	20(1)	23(1)	-2(1)	1(1)	2(1)
C(18)	24(1)	21(1)	21(1)	1(1)	2(1)	3(1)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for TCD213.

	x	y	z	U(eq)
H(3)	10009	8578	5969	51
H(4)	9984	5641	6531	49
H(5)	8895	4246	6844	40
H(7)	7855	8727	6005	40
H(8)	7622	4321	7076	28
H(10A)	6174	6541	8415	32
H(10B)	6488	4657	8144	32
H(11A)	5565	5208	6333	30
H(11B)	5971	6893	5769	30
H(12A)	6389(13)	3550(40)	5380(30)	33(6)
H(12B)	6229(12)	4730(30)	4110(30)	29(6)
H(13)	7214	6345	4425	27
H(14A)	8084	4299	3872	43
H(14B)	7347	3737	3052	43
H(14C)	7617	2805	4594	43
H(18)	5321(11)	1390(30)	4360(30)	22(5)

Torsion angles [°] for TCD213.

F(1)-C(2)-C(3)-C(4)	179.2(2)
C(7)-C(2)-C(3)-C(4)	-0.9(4)
C(2)-C(3)-C(4)-C(5)	0.2(4)
C(3)-C(4)-C(5)-C(6)	0.6(4)
C(4)-C(5)-C(6)-C(7)	-0.8(3)
C(4)-C(5)-C(6)-C(8)	177.57(19)
C(3)-C(2)-C(7)-C(6)	0.6(4)
F(1)-C(2)-C(7)-C(6)	-179.4(2)
C(5)-C(6)-C(7)-C(2)	0.2(3)
C(8)-C(6)-C(7)-C(2)	-178.23(19)
C(5)-C(6)-C(8)-O(9)	135.24(19)
C(7)-C(6)-C(8)-O(9)	-46.4(2)
C(5)-C(6)-C(8)-C(13)	-103.8(2)
C(7)-C(6)-C(8)-C(13)	74.6(2)
C(6)-C(8)-O(9)-C(10)	-179.91(15)
C(13)-C(8)-O(9)-C(10)	60.0(2)
C(8)-O(9)-C(10)-C(11)	-63.8(2)
O(9)-C(10)-C(11)-N(12)	58.4(2)
C(10)-C(11)-N(12)-C(13)	-51.9(2)
C(11)-N(12)-C(13)-C(14)	171.34(16)
C(11)-N(12)-C(13)-C(8)	48.2(2)
O(9)-C(8)-C(13)-N(12)	-51.4(2)
C(6)-C(8)-C(13)-N(12)	-169.58(15)
O(9)-C(8)-C(13)-C(14)	-172.51(15)
C(6)-C(8)-C(13)-C(14)	69.3(2)
O(16)-C(17)-C(18)-C(18)#1	-12.9(3)
O(15)-C(17)-C(18)-C(18)#1	165.9(2)

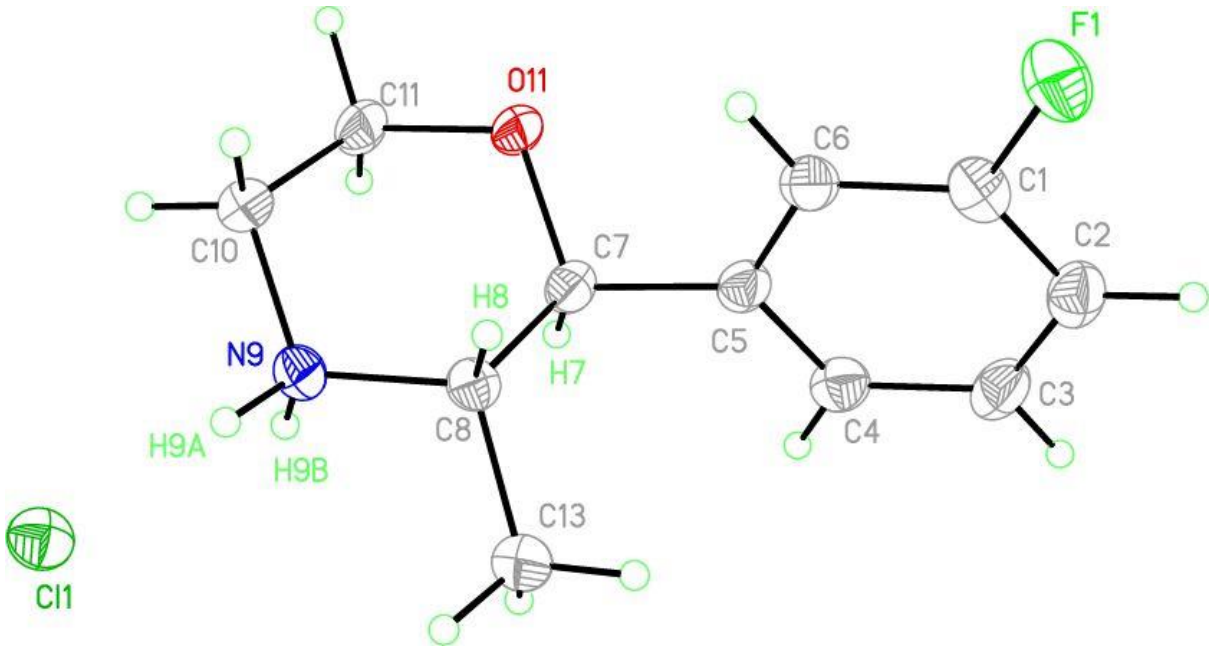
Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y,-z+1

Hydrogen bonds for TCD213 [Å and °].

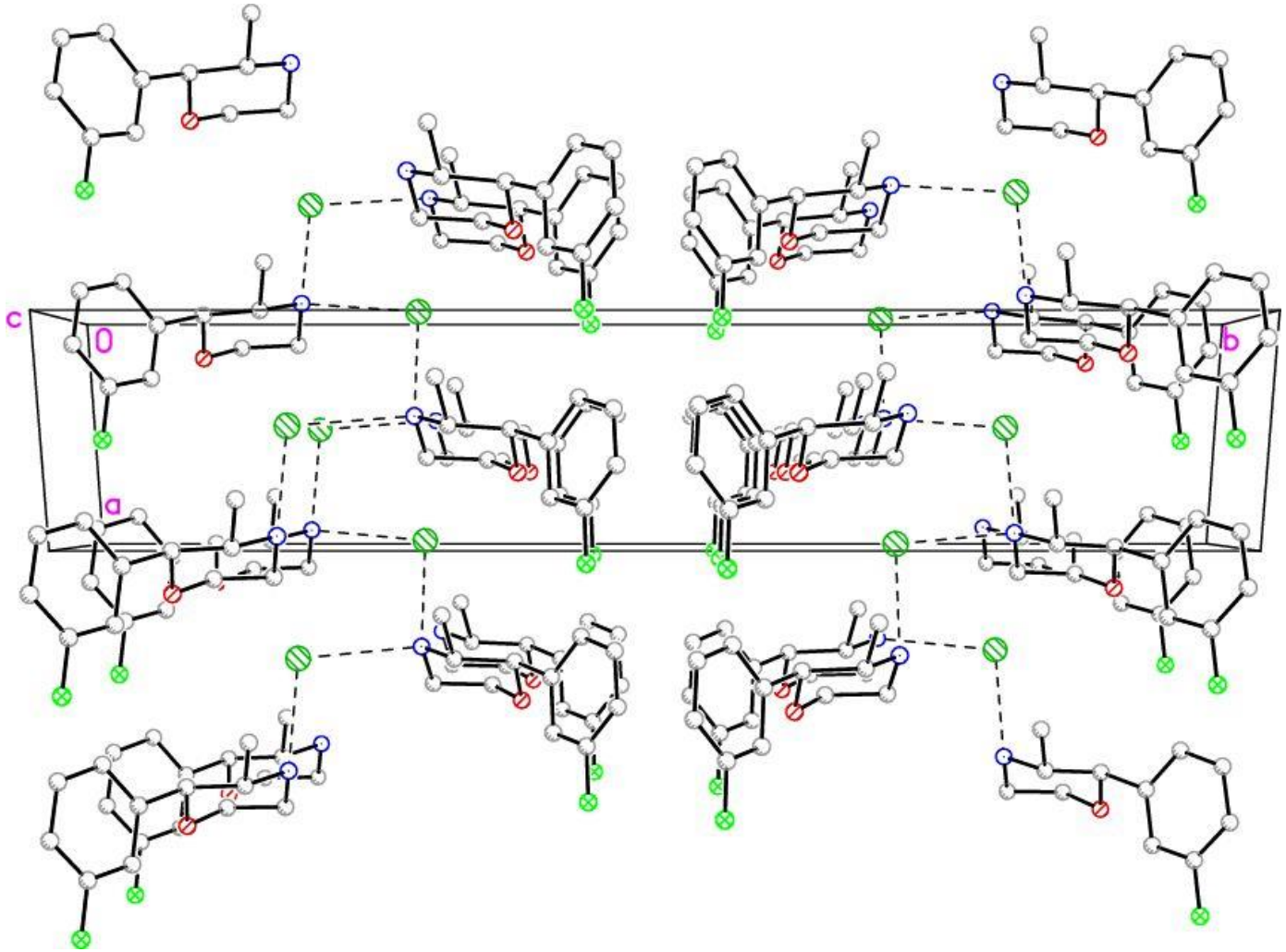
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(3)-H(3)...F(1)#2	0.95	2.55	3.412(3)	151
C(11)-H(11A)...O(16)#3	0.99	2.47	3.417(2)	160
N(12)-H(12A)...O(15)	0.91(3)	1.80(3)	2.685(2)	165(2)
N(12)-H(12B)...O(15)#4	0.95(3)	2.58(2)	3.372(2)	141.7(19)
N(12)-H(12B)...O(16)#4	0.95(3)	1.78(3)	2.693(2)	160(2)
C(13)-H(13)...O(9)#5	1.00	2.36	3.325(2)	163
C(14)-H(14B)...O(15)#4	0.98	2.42	3.326(2)	154

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y,-z+1 #2 -x+2,-y+2,-z+1 #3 -x+1,y+1/2,-z+3/2
#4 x,-y+1/2,z-1/2 #5 x,-y+3/2,z-1/2

11. Additional x-ray crystal data for 3-FPM vendor sample



Asymmetric unit of TCD179. Displacement ellipsoids shown at 50%. Only chiral center and donor hydrogen atoms labeled



Packing diagram of TCD178 viewed down the c-axis. Dashed lines indicate strong hydrogen bonding. Hydrogen atoms omitted for clarity

Data collection details for TCD178.

Axis	dx/mm	2θ/°	ω/°	φ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	Temperature/K
Omega	45.000	17.70	9.07	300.00	-54.74	0.90	137	27.00	0.71073	50	30.0	100
Omega	45.000	17.70	9.07	180.00	-54.74	0.90	137	27.00	0.71073	50	30.0	100
Omega	45.000	17.70	9.07	60.00	-54.74	0.90	137	27.00	0.71073	50	30.0	100
Phi	45.000	17.70	277.61	266.70	23.00	0.90	234	27.00	0.71073	50	30.0	100
Phi	45.000	17.70	8.02	180.20	-57.06	0.90	204	27.00	0.71073	50	30.0	100
Omega	45.000	17.70	9.07	120.00	-54.74	0.90	137	27.00	0.71073	50	30.0	100
Phi	45.000	17.70	355.25	356.20	-23.00	0.90	204	27.00	0.71073	50	30.0	100
Omega	45.000	17.70	9.07	240.00	-54.74	0.90	137	27.00	0.71073	50	30.0	100
Omega	45.000	17.70	9.07	0.00	-54.74	0.90	137	27.00	0.71073	50	30.0	100
Omega	45.000	2.69	353.17	0.00	-54.74	0.90	139	27.00	0.71073	50	30.0	100
Omega	45.000	2.69	353.17	90.00	-54.74	0.90	139	27.00	0.71073	50	30.0	100
Omega	45.000	18.80	262.34	32.98	55.93	0.90	140	27.00	0.71073	50	30.0	100

Crystal data and structure refinement for tcd178.

Identification code	tcd178	
Empirical formula	$C_{11}H_{15}ClFNO$	
Formula weight	231.69	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	a = 6.1009(4) Å	□= 90°.
	b = 29.1650(18) Å	□= 111.322(2)°.
	c = 7.0747(5) Å	□ = 90°.
Volume	1172.66(14) $Å^3$	
Z	4	
Density (calculated)	1.312 Mg/m^3	
Absorption coefficient	0.313 mm^{-1}	
F(000)	488	
Crystal size	0.224 x 0.168 x 0.075 mm^3	
Theta range for data collection	1.396 to 26.410°.	
Index ranges	-7≤h≤7, -35≤k≤36, -8≤l≤8	
Reflections collected	15389	
Independent reflections	2152 [R(int) = 0.0568]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Numerical	
Max. and min. transmission	1.0000 and 0.7644	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2152 / 4 / 145	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2σ(I)]	R1 = 0.0346, wR2 = 0.0664	
R indices (all data)	R1 = 0.0427, wR2 = 0.0687	
Absolute structure parameter	0.03(3)	
Largest diff. peak and hole	0.386 and -0.234 $e.Å^{-3}$	

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for tcd178. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	4715(1)	8004(1)	4430(1)	24(1)
F(1)	10310(4)	5536(1)	10628(3)	36(1)
C(1)	8078(6)	5555(1)	9213(5)	26(1)
C(2)	6351(7)	5300(1)	9544(6)	29(1)
C(3)	4093(7)	5326(1)	8112(6)	30(1)
C(4)	3601(6)	5606(1)	6407(5)	26(1)
C(5)	5381(6)	5861(1)	6123(5)	22(1)
C(6)	7680(6)	5837(1)	7560(5)	23(1)
C(7)	4849(7)	6181(1)	4335(6)	21(1)
C(8)	4682(6)	6680(1)	4970(5)	20(1)
N(9)	4279(5)	6985(1)	3170(4)	21(1)
C(10)	6024(6)	6912(1)	2177(5)	26(1)
O(11)	6664(4)	6137(1)	3521(4)	25(1)
C(11)	6123(7)	6408(1)	1715(5)	28(1)
C(13)	2737(7)	6760(1)	5794(6)	30(1)

Bond lengths [Å] and angles [°] for tcd178.

F(1)-C(1)	1.367(4)	C(3)-C(2)-H(2)	121.1
C(1)-C(6)	1.377(5)	C(2)-C(3)-C(4)	120.5(3)
C(1)-C(2)	1.376(5)	C(2)-C(3)-H(3)	119.7
C(2)-C(3)	1.384(5)	C(4)-C(3)-H(3)	119.7
C(2)-H(2)	0.9500	C(5)-C(4)-C(3)	120.3(3)
C(3)-C(4)	1.396(5)	C(5)-C(4)-H(4)	119.9
C(3)-H(3)	0.9500	C(3)-C(4)-H(4)	119.9
C(4)-C(5)	1.389(5)	C(4)-C(5)-C(6)	119.7(3)
C(4)-H(4)	0.9500	C(4)-C(5)-C(7)	120.7(3)
C(5)-C(6)	1.403(5)	C(6)-C(5)-C(7)	119.5(3)
C(5)-C(7)	1.510(5)	C(1)-C(6)-C(5)	117.8(3)
C(6)-H(6)	0.9500	C(1)-C(6)-H(6)	121.1
C(7)-O(11)	1.427(5)	C(5)-C(6)-H(6)	121.1
C(7)-C(8)	1.537(4)	O(11)-C(7)-C(5)	108.6(3)
C(7)-H(7)	1.0000	O(11)-C(7)-C(8)	110.4(3)
C(8)-N(9)	1.498(4)	C(5)-C(7)-C(8)	110.9(3)
C(8)-C(13)	1.518(5)	O(11)-C(7)-H(7)	109.0
C(8)-H(8)	1.0000	C(5)-C(7)-H(7)	109.0
N(9)-C(10)	1.489(5)	C(8)-C(7)-H(7)	109.0
N(9)-H(9A)	0.918(13)	N(9)-C(8)-C(13)	109.0(3)
N(9)-H(9B)	0.910(14)	N(9)-C(8)-C(7)	108.7(3)
C(10)-C(11)	1.511(5)	C(13)-C(8)-C(7)	113.7(3)
C(10)-H(10A)	0.9900	N(9)-C(8)-H(8)	108.4
C(10)-H(10B)	0.9900	C(13)-C(8)-H(8)	108.4
O(11)-C(11)	1.437(4)	C(7)-C(8)-H(8)	108.4
C(11)-H(11A)	0.9900	C(10)-N(9)-C(8)	113.1(3)
C(11)-H(11B)	0.9900	C(10)-N(9)-H(9A)	107(2)
C(13)-H(13A)	0.9800	C(8)-N(9)-H(9A)	113(2)
C(13)-H(13B)	0.9800	C(10)-N(9)-H(9B)	108(3)
C(13)-H(13C)	0.9800	C(8)-N(9)-H(9B)	112(2)
		H(9A)-N(9)-H(9B)	103(3)
F(1)-C(1)-C(6)	117.9(3)	N(9)-C(10)-C(11)	109.5(3)
F(1)-C(1)-C(2)	118.3(3)	N(9)-C(10)-H(10A)	109.8
C(6)-C(1)-C(2)	123.8(3)	C(11)-C(10)-H(10A)	109.8
C(1)-C(2)-C(3)	117.8(3)	N(9)-C(10)-H(10B)	109.8
C(1)-C(2)-H(2)	121.1	C(11)-C(10)-H(10B)	109.8

H(10A)-C(10)-H(10B)	108.2
C(7)-O(11)-C(11)	110.3(3)
O(11)-C(11)-C(10)	111.0(3)
O(11)-C(11)-H(11A)	109.4
C(10)-C(11)-H(11A)	109.4
O(11)-C(11)-H(11B)	109.4
C(10)-C(11)-H(11B)	109.4
H(11A)-C(11)-H(11B)	108.0
C(8)-C(13)-H(13A)	109.5
C(8)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(8)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5

Anisotropic displacement parameters ($Å^2 x\ 10^3$) for tcd178. 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}
Cl(1)	22(1)	26(1)	22(1)	-1(1)	6(1)	2(1)
F(1)	33(1)	39(1)	29(1)	5(1)	2(1)	4(1)
C(1)	29(2)	24(2)	23(2)	-2(2)	6(2)	3(2)
C(2)	41(2)	24(2)	26(2)	0(2)	17(2)	2(2)
C(3)	35(2)	26(2)	33(2)	0(2)	20(2)	-5(2)
C(4)	26(2)	26(2)	28(2)	-2(2)	12(2)	-1(1)
C(5)	27(2)	21(2)	23(2)	-1(1)	14(2)	1(1)
C(6)	22(2)	22(2)	26(2)	0(1)	10(2)	0(1)
C(7)	20(2)	25(2)	20(2)	2(2)	8(1)	-2(2)
C(8)	16(2)	27(2)	14(2)	3(1)	2(2)	3(1)
N(9)	22(2)	20(2)	20(2)	1(1)	6(1)	2(1)
C(10)	24(2)	28(2)	28(2)	4(2)	14(2)	2(1)
O(11)	32(1)	25(1)	26(1)	4(1)	20(1)	6(1)
C(11)	37(2)	29(2)	26(2)	4(2)	22(2)	4(2)
C(13)	32(2)	30(2)	31(2)	5(2)	16(2)	7(2)

Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for tcd178.

	x	y	z	U(eq)
H(9A)	4330(60)	7291(5)	3490(50)	16(9)
H(2)	6698	5113	10716	35
H(3)	2867	5152	8290	35
H(4)	2043	5623	5437	31
H(6)	8922	6009	7397	28
H(7)	3313	6091	3272	26
H(8)	6217	6766	6045	24
H(10A)	7595	7018	3086	31
H(10B)	5563	7092	904	31
H(11A)	4589	6311	708	33

H(11B)	7340	6358	1117	33
H(13A)	1242	6648	4815	44
H(13B)	2607	7089	6020	44
H(13C)	3107	6596	7081	44
H(9B)	2810(40)	6949(12)	2220(50)	31(10)

Torsion angles [°] for tcd178

F(1)-C(1)-C(2)-C(3)	179.3(3)
C(6)-C(1)-C(2)-C(3)	0.9(5)
C(1)-C(2)-C(3)-C(4)	-0.7(5)
C(2)-C(3)-C(4)-C(5)	0.4(5)
C(3)-C(4)-C(5)-C(6)	-0.1(5)
C(3)-C(4)-C(5)-C(7)	-177.2(3)
F(1)-C(1)-C(6)-C(5)	-179.1(3)
C(2)-C(1)-C(6)-C(5)	-0.6(5)
C(4)-C(5)-C(6)-C(1)	0.2(5)
C(7)-C(5)-C(6)-C(1)	177.4(3)
C(4)-C(5)-C(7)-O(11)	-138.3(3)
C(6)-C(5)-C(7)-O(11)	44.6(4)
C(4)-C(5)-C(7)-C(8)	100.2(4)
C(6)-C(5)-C(7)-C(8)	-76.9(4)
O(11)-C(7)-C(8)-N(9)	56.6(4)
C(5)-C(7)-C(8)-N(9)	177.1(3)
O(11)-C(7)-C(8)-C(13)	178.2(3)
C(5)-C(7)-C(8)-C(13)	-61.3(4)
C(13)-C(8)-N(9)-C(10)	-176.6(3)
C(7)-C(8)-N(9)-C(10)	-52.2(4)
C(8)-N(9)-C(10)-C(11)	52.3(4)
C(5)-C(7)-O(11)-C(11)	175.3(3)
C(8)-C(7)-O(11)-C(11)	-62.9(4)
C(7)-O(11)-C(11)-C(10)	62.9(4)
N(9)-C(10)-C(11)-O(11)	-56.3(4)

Hydrogen bonds for tcd178 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(9)-H(9A)...Cl(1)	0.918(13)	2.169(14)	3.084(3)	175(3)
C(8)-H(8)...Cl(1)#1	1.00	2.65	3.632(3)	167
N(9)-H(9B)...Cl(1)#2	0.910(14)	2.184(17)	3.066(3)	163(3)

Symmetry transformations used to generate equivalent atoms:
#1 x+1/2,-y+3/2,z+1/2 #2 x-1/2,-y+3/2,z-1/2

End of supplementary information