Supporting Information

Fluorinated Aminopyridines: Synthesis, Structure, and Rare Liquid-Liquid Cocrystal Formation Driven by Unusually Short N–H···F–C Hydrogen Bonding

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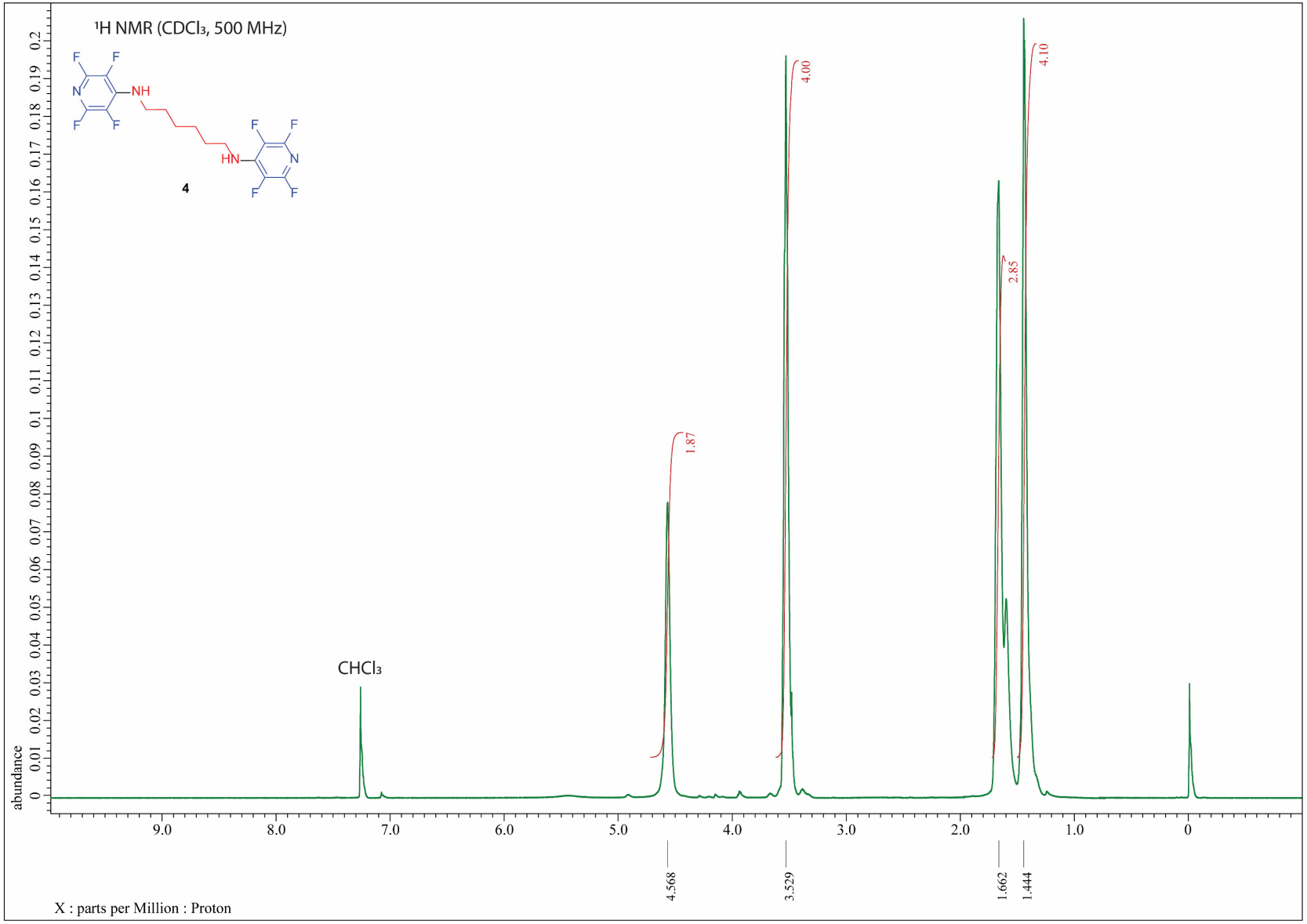

Figure SI1. ^{1}H NMR of N^{1},N^{6}-bis(perfluoropyridine-4-yl)hexane-1,6-diamine (**4**)

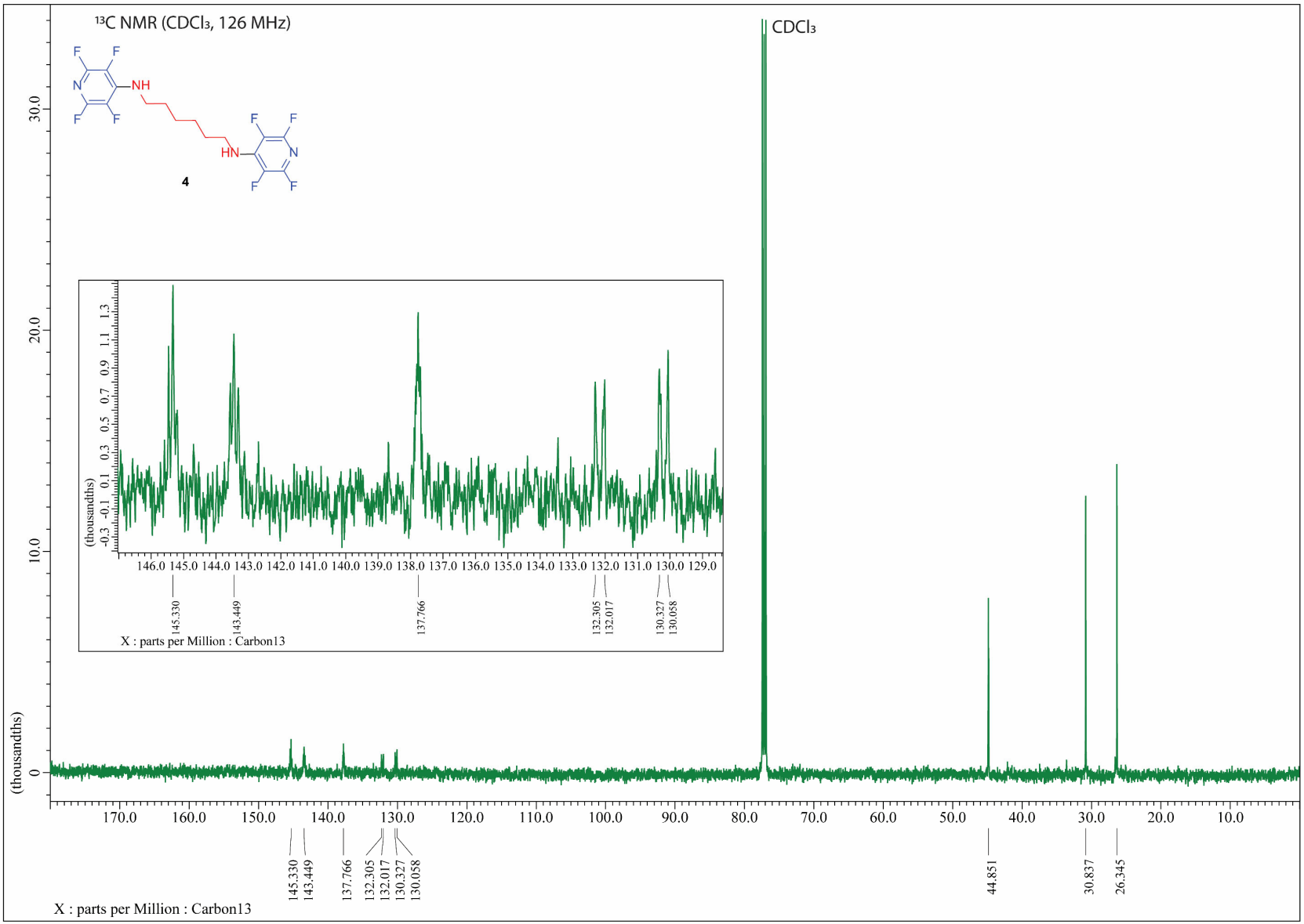

Figure SI2. ^{13}C NMR of *N*^{1},*N*^{6}-bis(perfluoropyridine-4-yl)hexane-1,6-diamine (**4**)

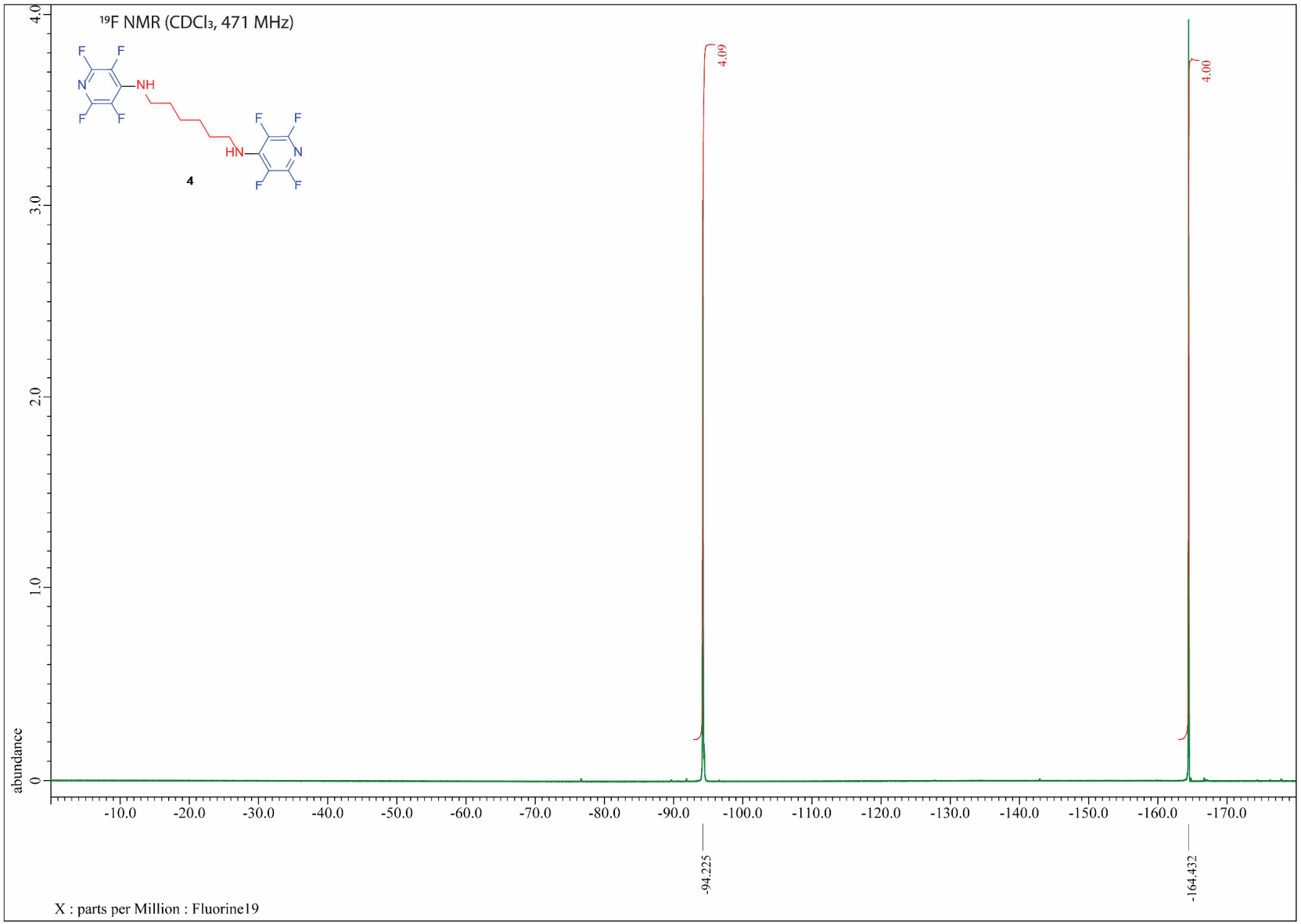

Figure SI3. ^{19}F NMR of N^1,N^6-bis(perfluoropyridine-4-yl)hexane-1,6-diamine (**4**)

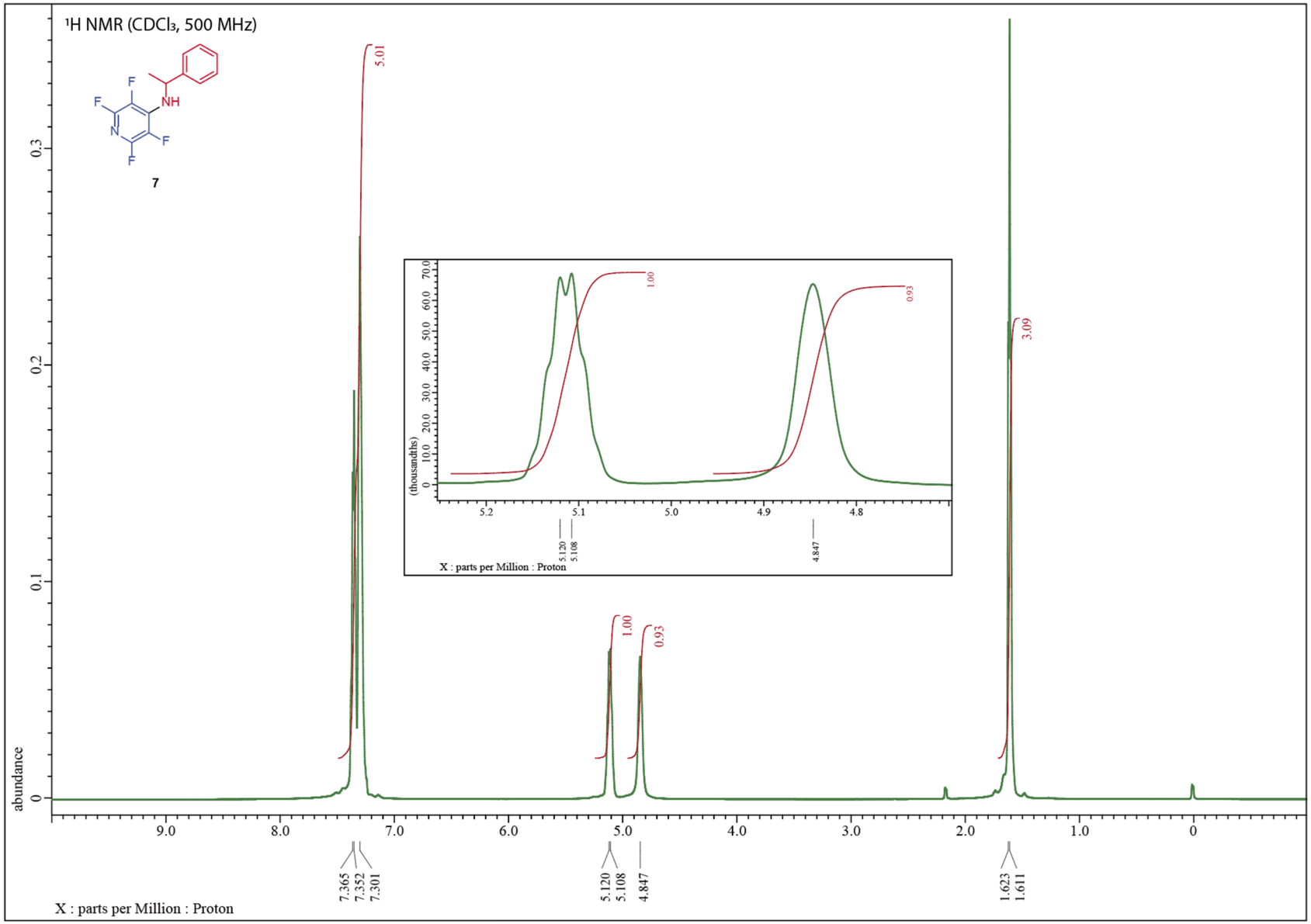

Figure SI4. ^{1}H NMR of 2,3,5,6-tetrafluoro-*N*-(1-phenylethyl)pyridin-4-amine (**7**)

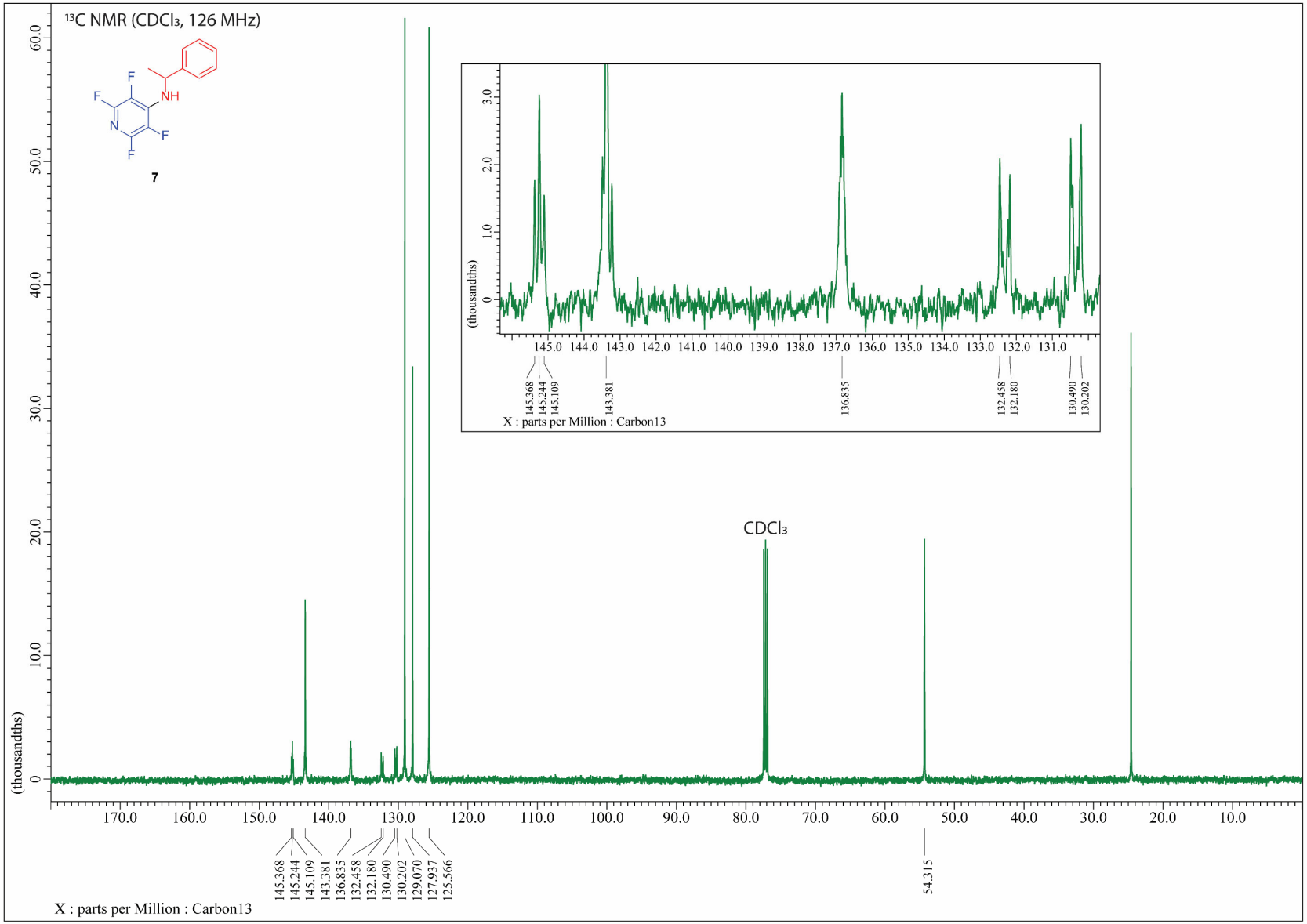

Figure SI5. ^{13}C NMR of 2,3,5,6-tetrafluoro-*N*-(1-phenylethyl)pyridin-4-amine (**7**)

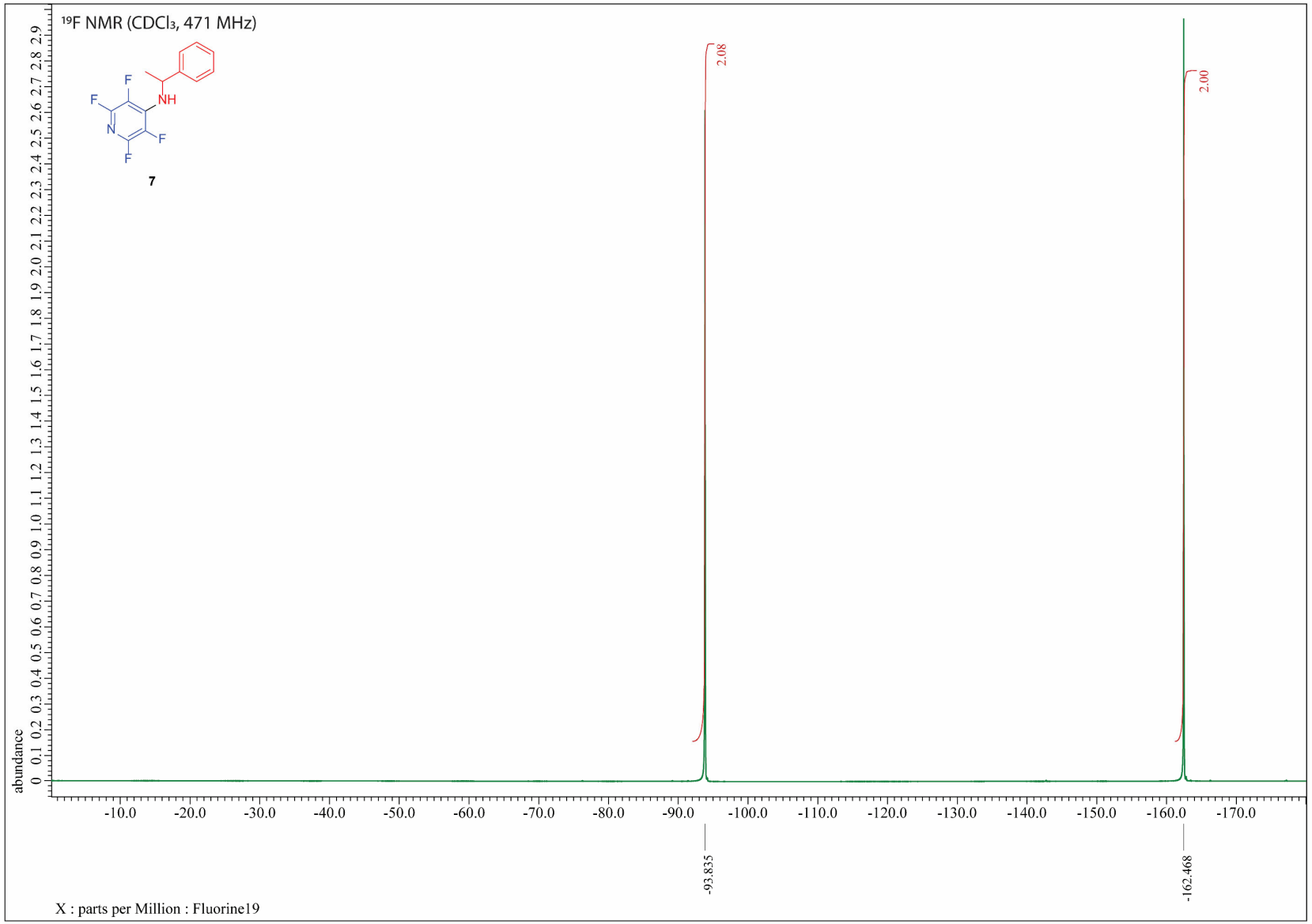

Figure SI6. ^{19}F NMR of 2,3,5,6-tetrafluoro-*N*-(1-phenylethyl)pyridin-4-amine (**7**)

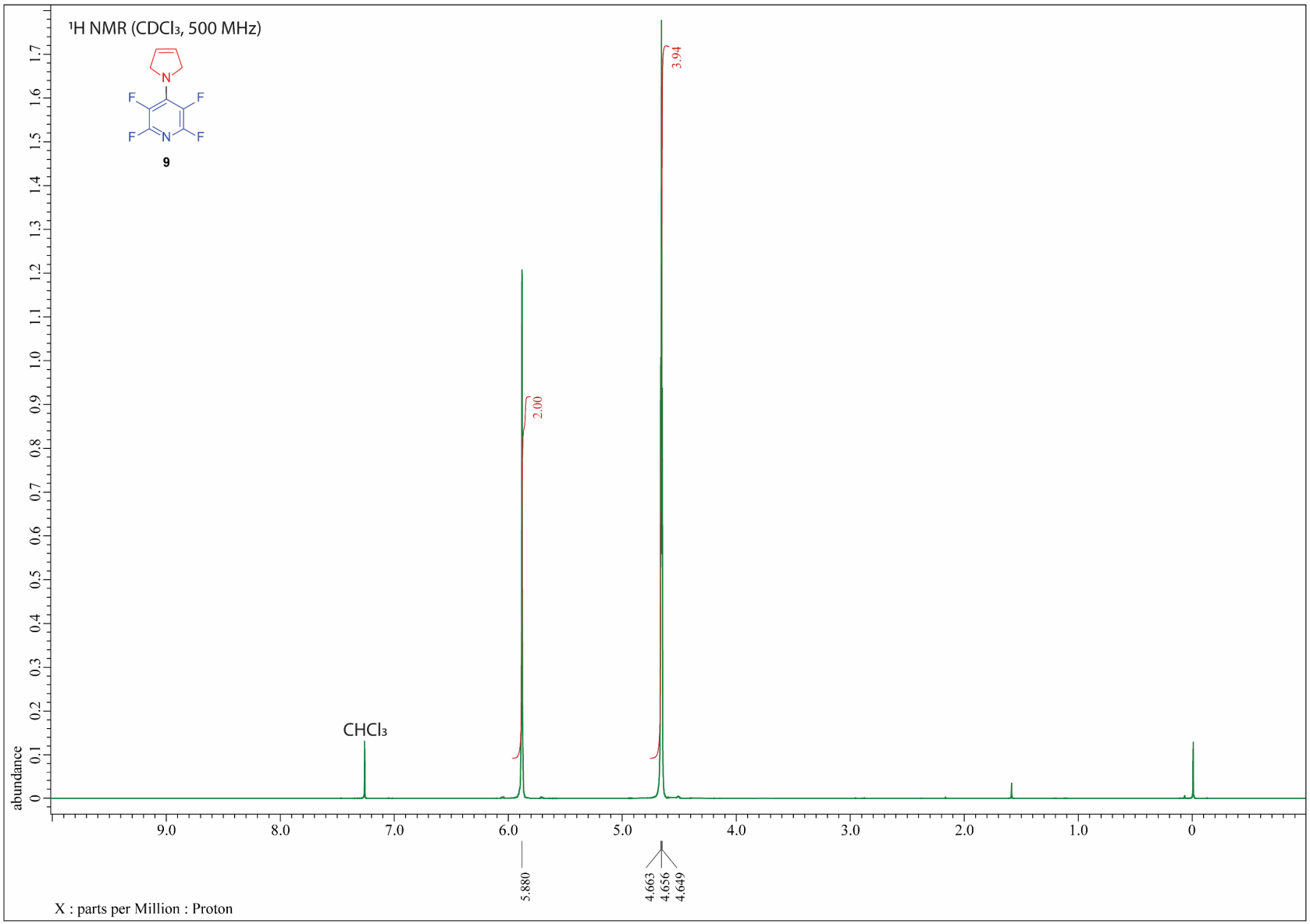

Figure SI7. ^{1}H NMR of 4-(2,5-dihydropyrrol-1-yl)-2,3,5,6-tetrafluoropyridine (**9**)

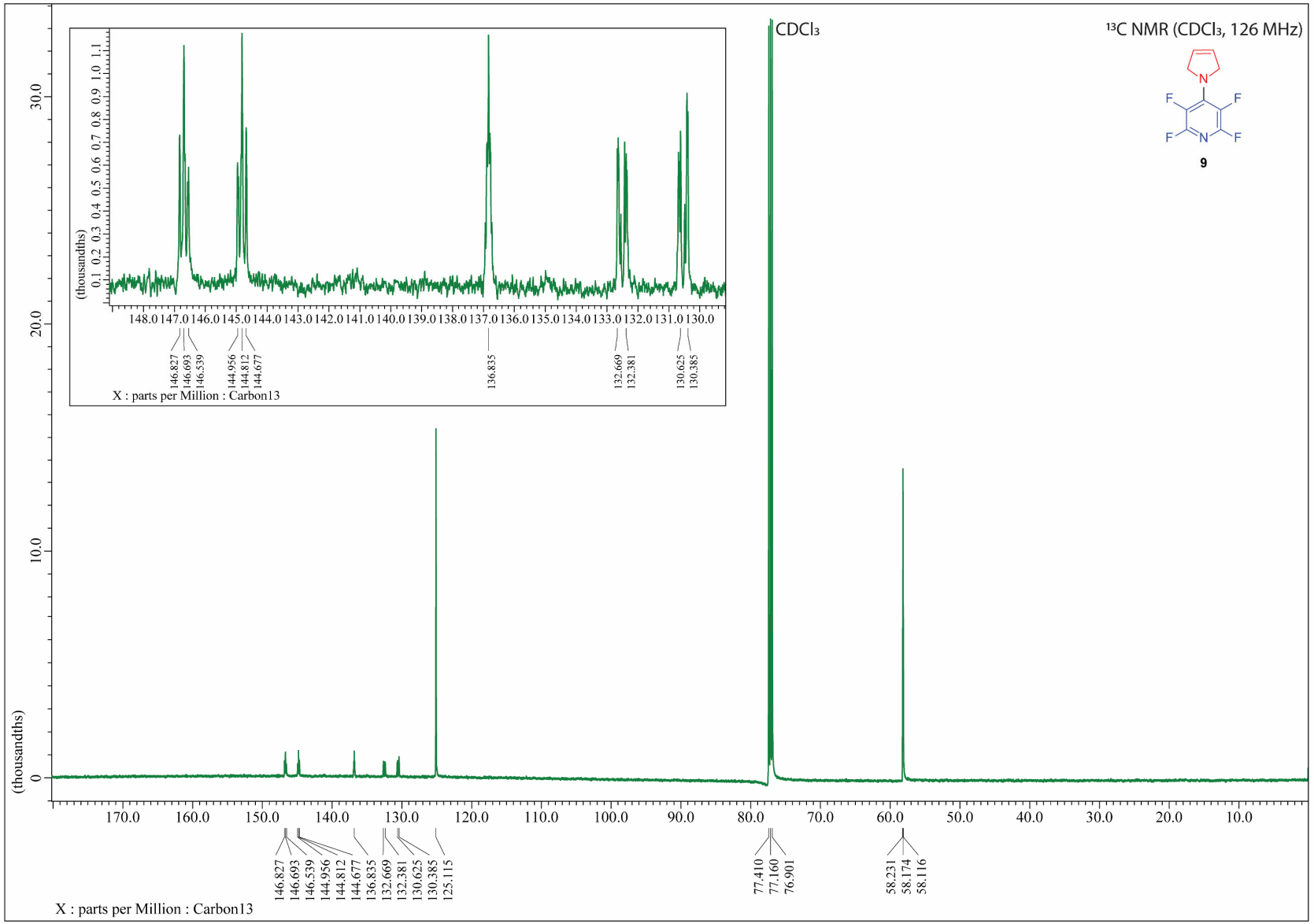

Figure SI8. ^{13}C NMR of 4-(2,5-dihydropyrrol-1-yl)-2,3,5,6-tetrafluoropyridine (**9**)

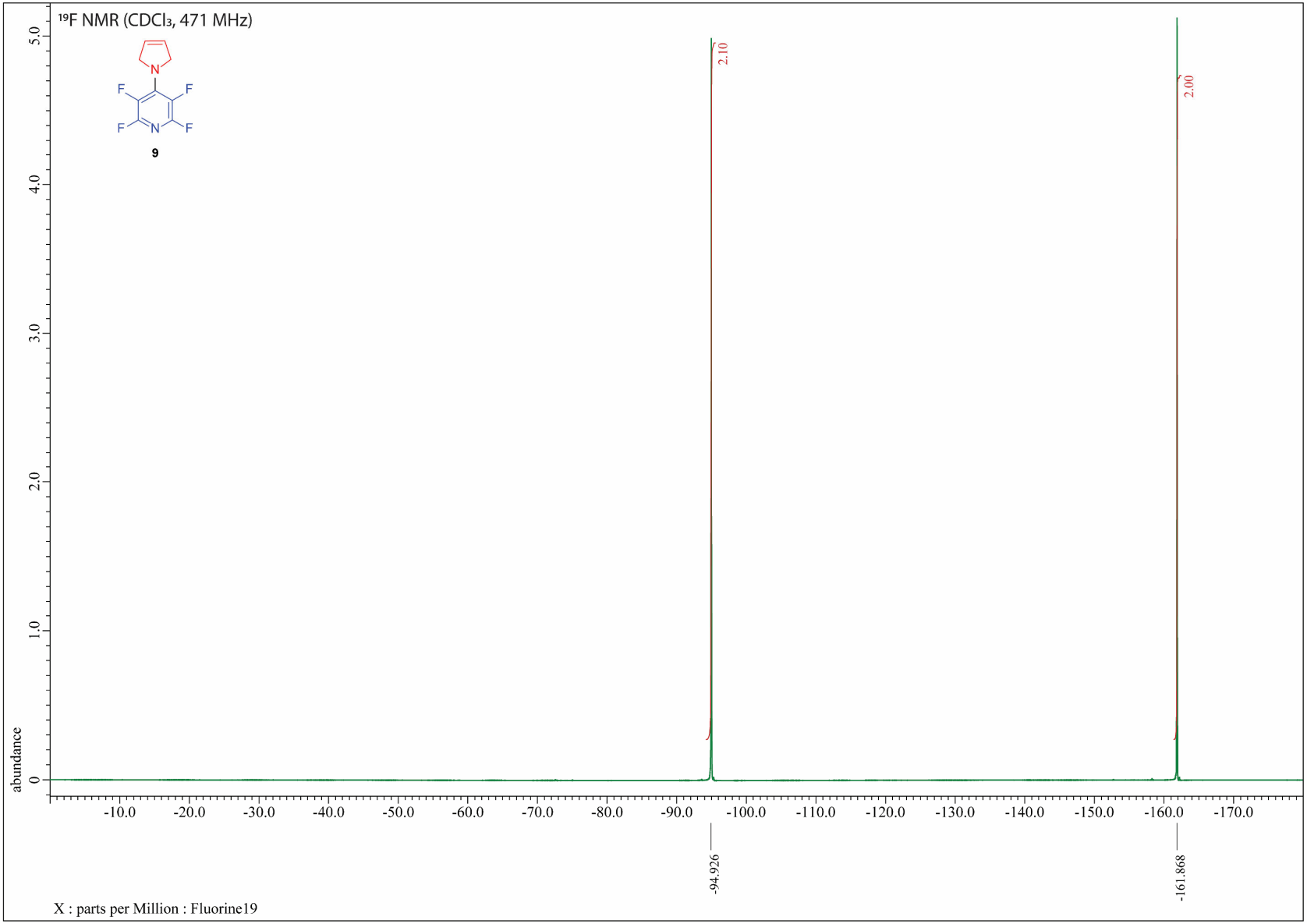

Figure SI9. ^{19}F NMR of 4-(2,5-dihydropyrrol-1-yl)-2,3,5,6-tetrafluoropyridine (**9**)

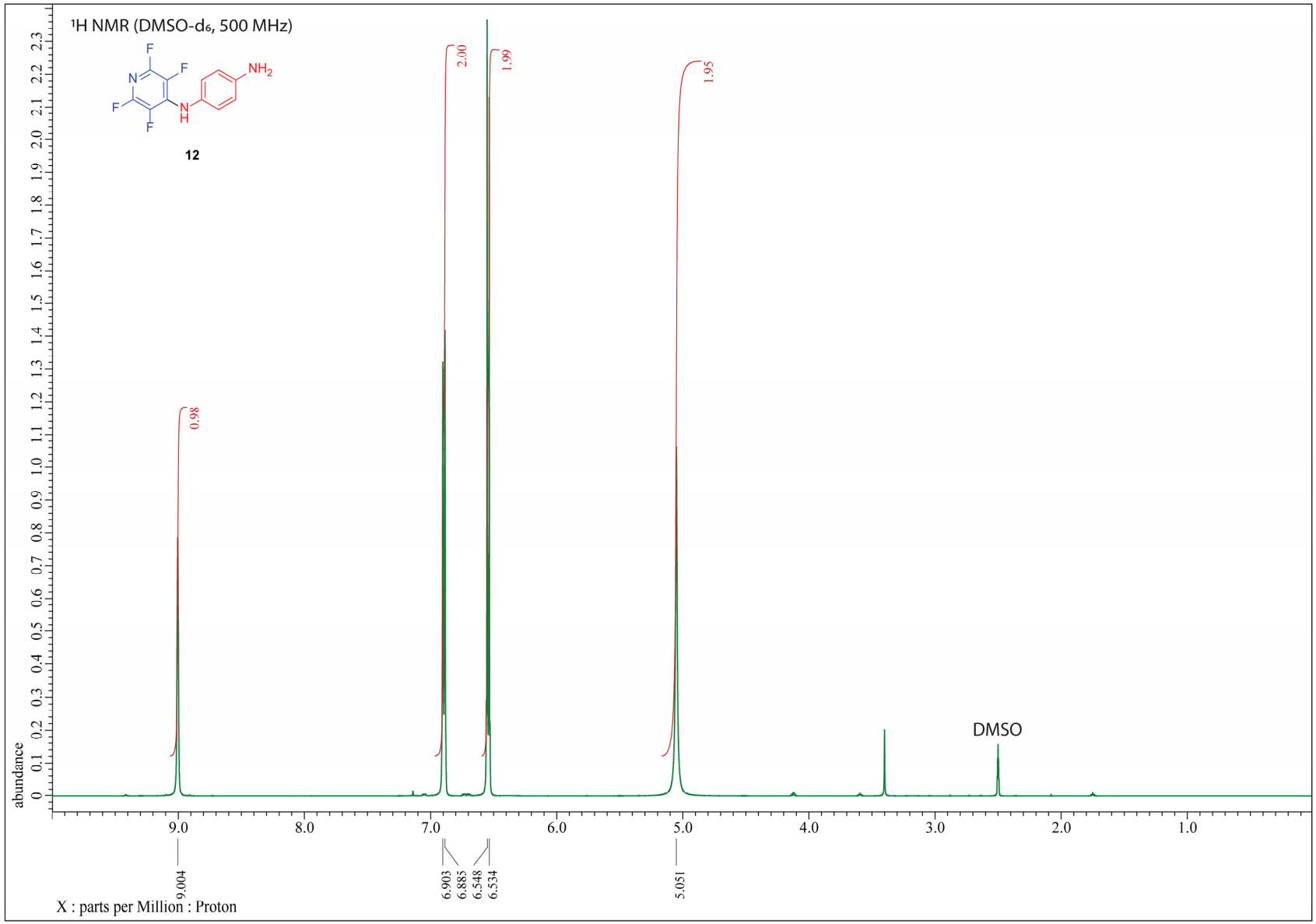

Figure SI10. ^{1}H NMR of *N*^{1}-(perfluoropyridin-4-yl)benzene-1,4-diamine (**12**)

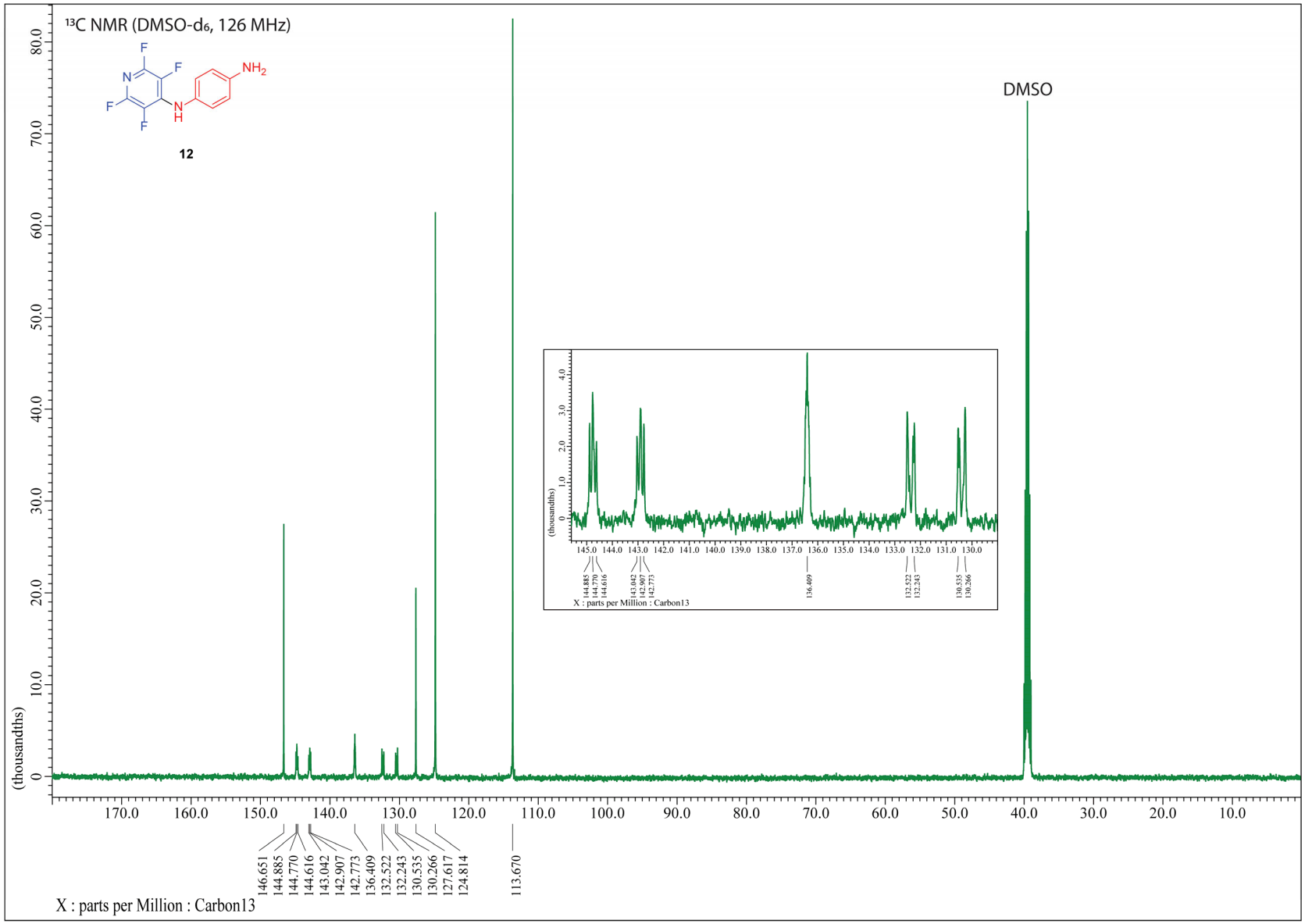

Figure SI11. ^{13}C NMR of *N*^{1}-(perfluoropyridin-4-yl)benzene-1,4-diamine (**12**)

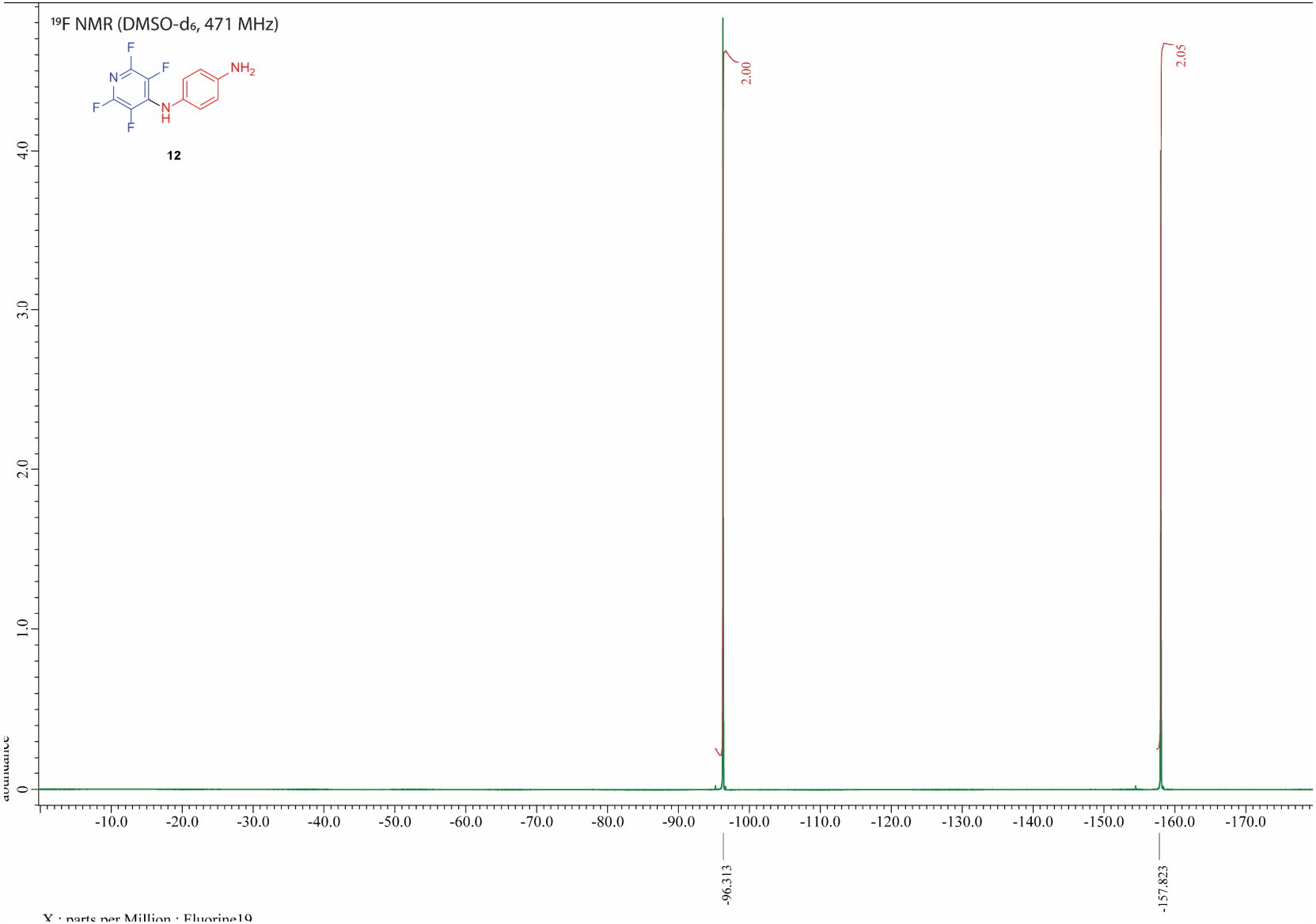

Figure SI12. ^{19}F NMR of *N*^{1}-(perfluoropyridin-4-yl)benzene-1,4-diamine (**12**)

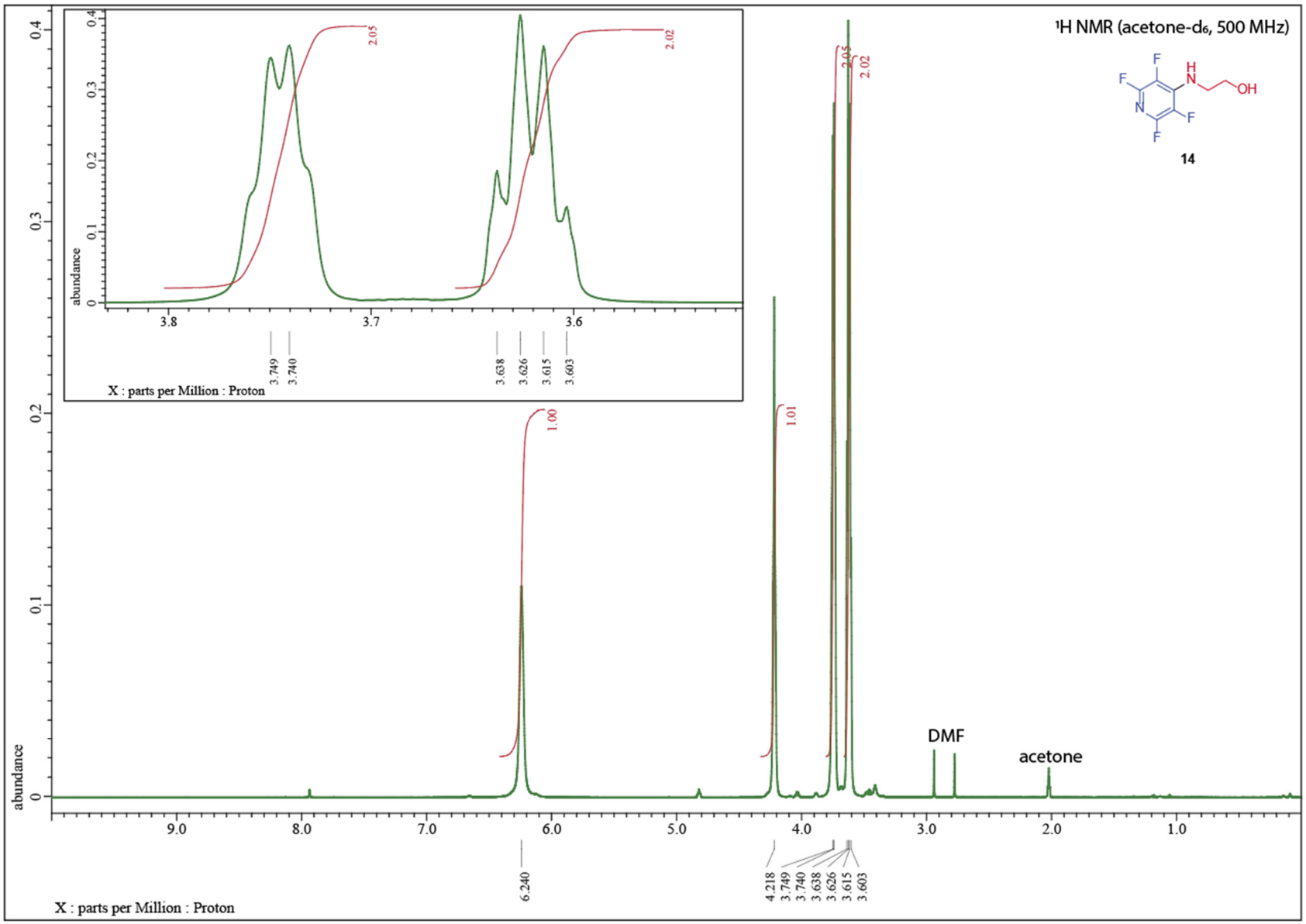

Figure SI13. ^{1}H NMR of 2-((perfluoropyridin-4-yl)amino)ethan-1-ol (**14**)

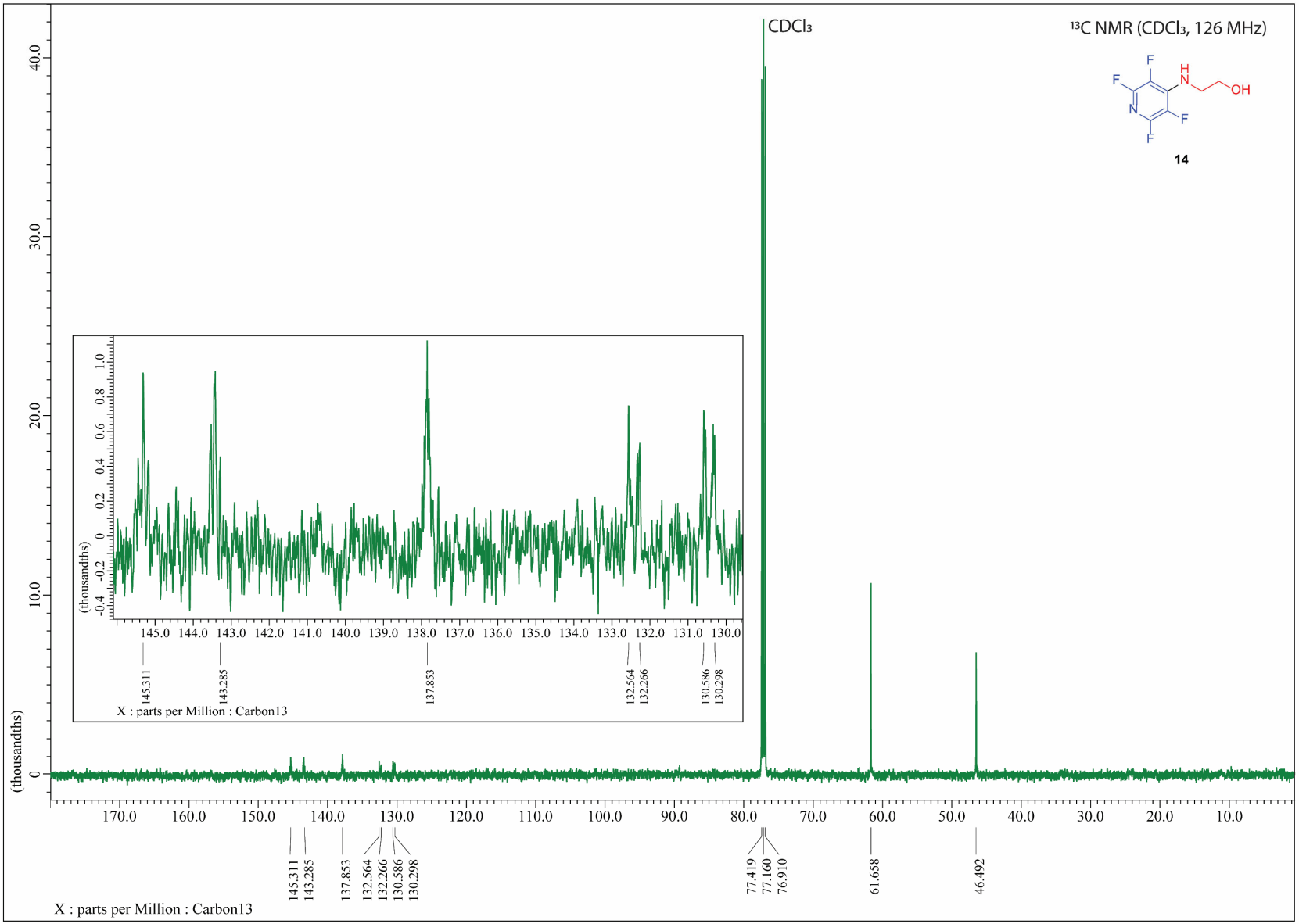

Figure SI14. ^{13}C NMR of 2-((perfluoropyridin-4-yl)amino)ethan-1-ol (**14**)

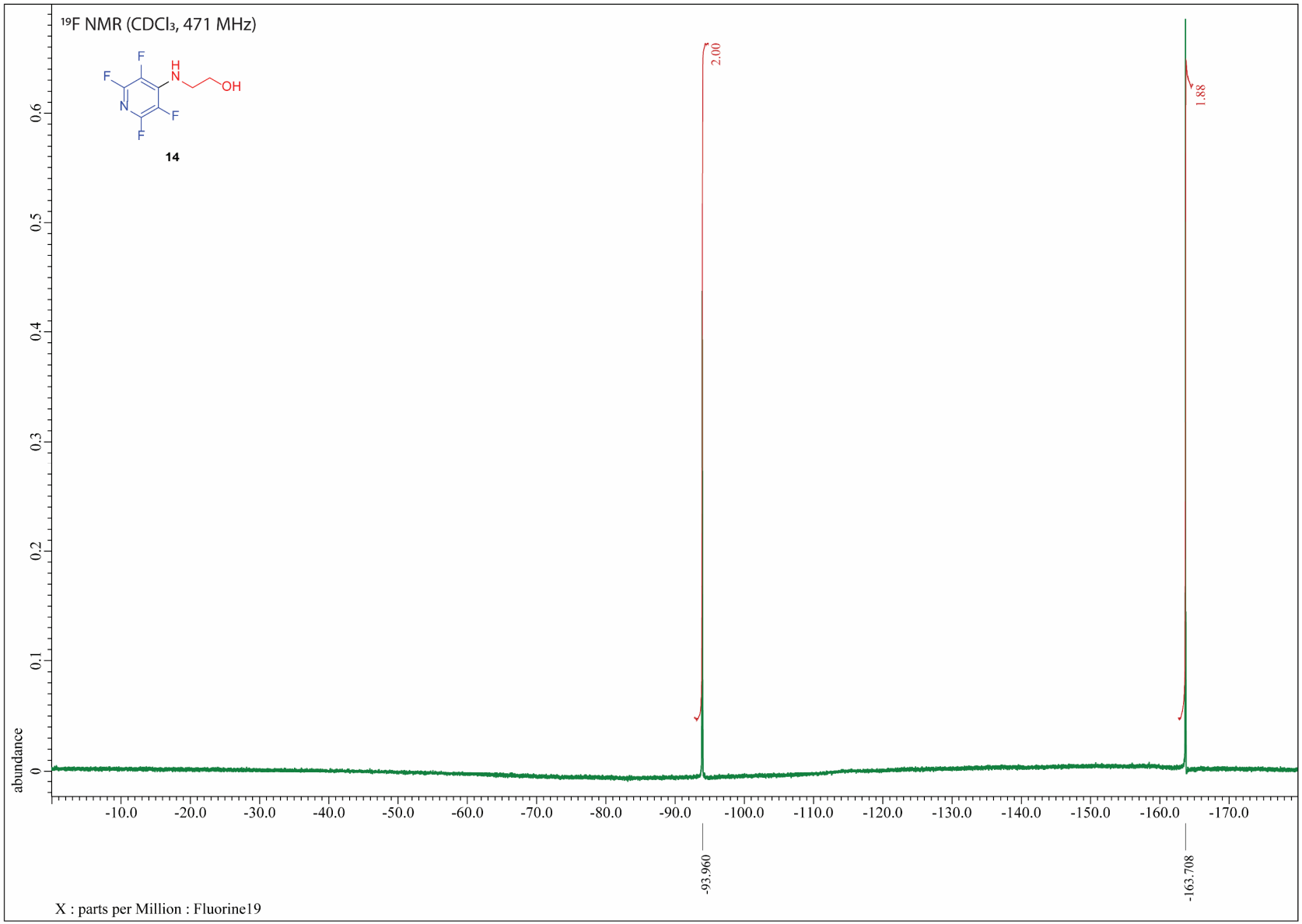

Figure SI15. ^{19}F NMR of 2-((perfluoropyridin-4-yl)amino)ethan-1-ol (**14**)

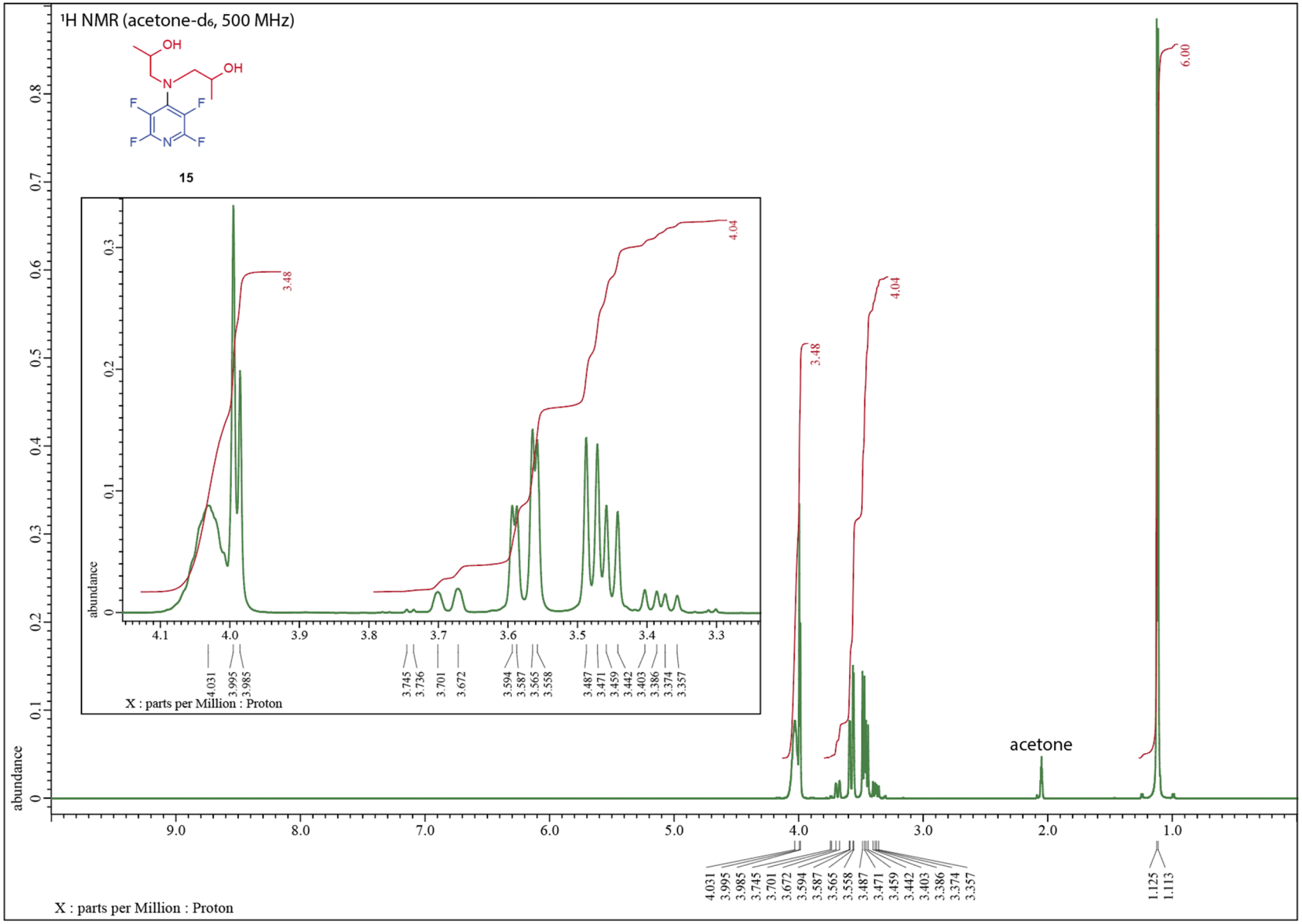

Figure SI16. ^{1}H NMR of 1,1'-((perfluoropyridin-4-yl)azanediyl)bis(propan-2-ol) (**15**)

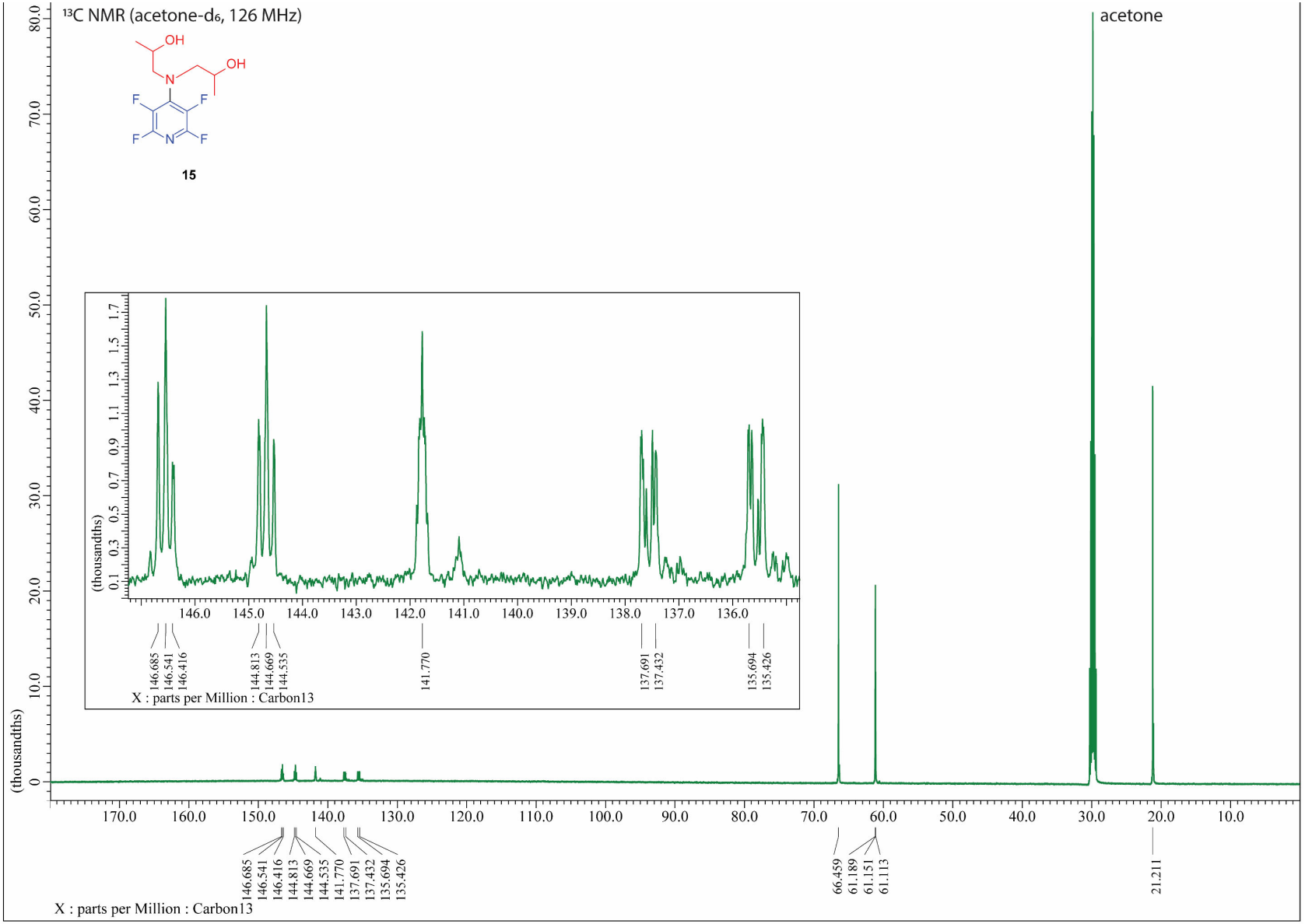

Figure SI17. ^{13}C NMR of 1,1'-((perfluoropyridin-4-yl)azanediyl)bis(propan-2-ol) (**15**)

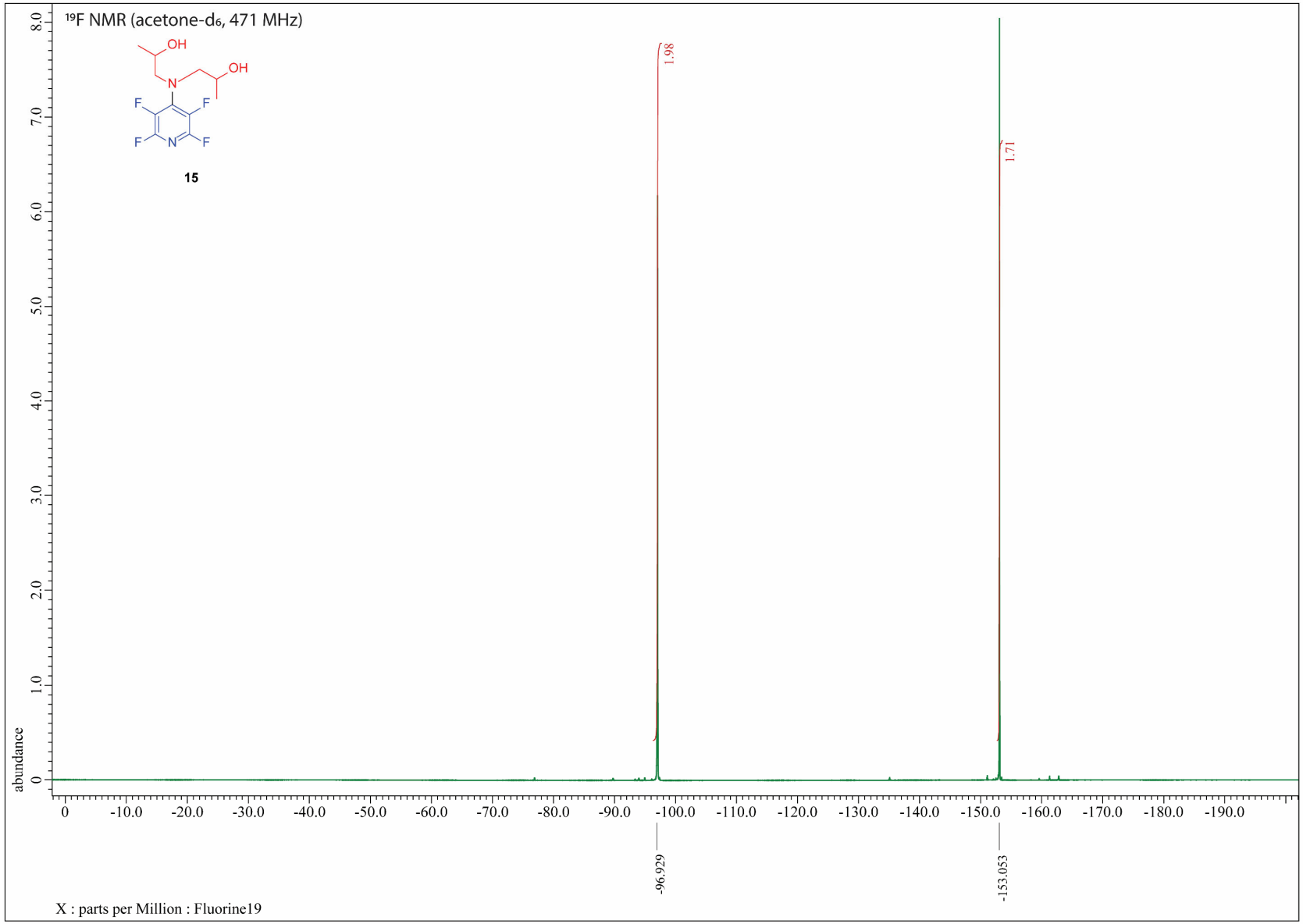

Figure SI18. ^{19}F NMR of 1,1'-((perfluoropyridin-4-yl)azanediyl)bis(propan-2-ol) (**15**)

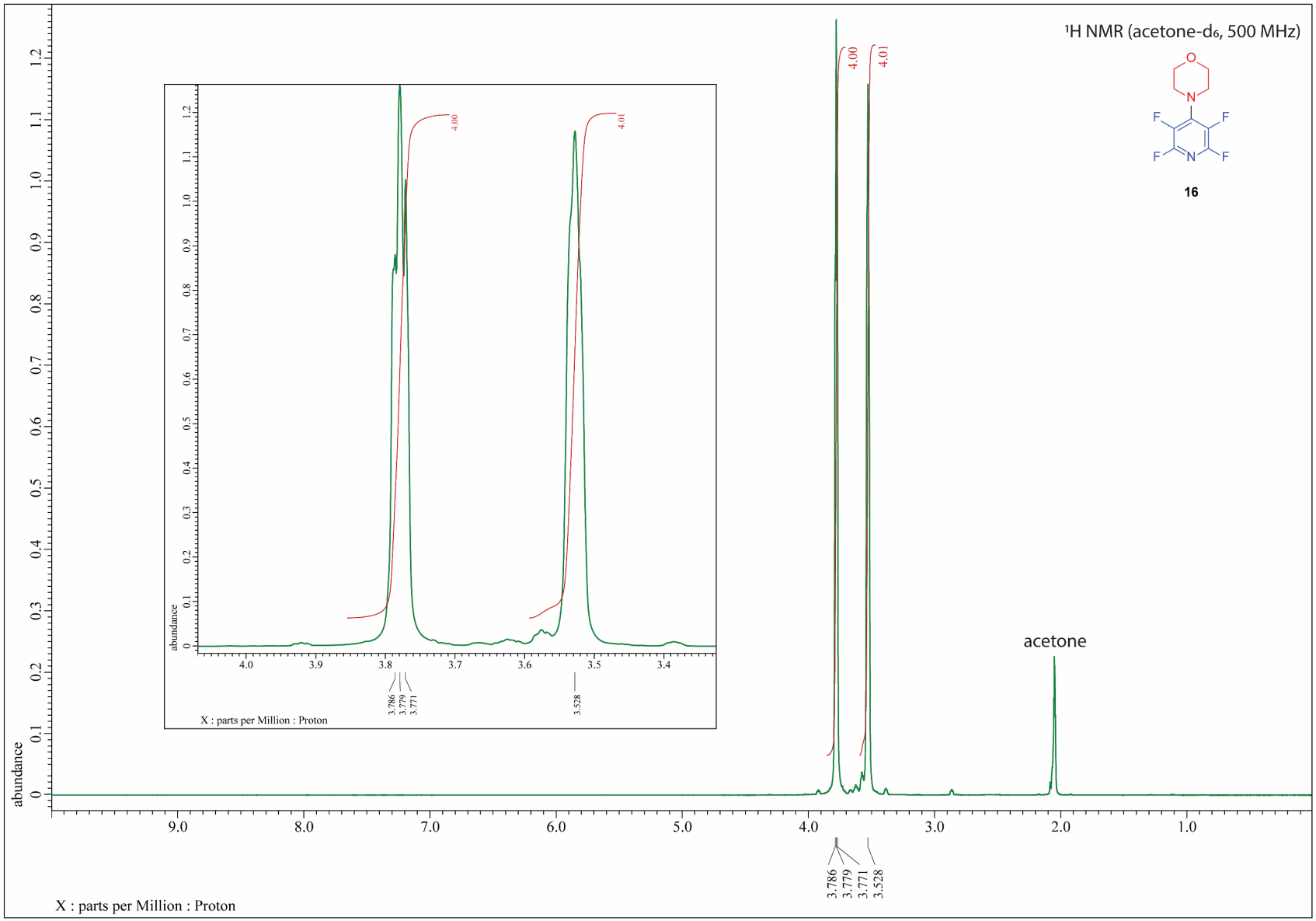

Figure SI19. ^{1}H NMR of 4-(perfluoropyridin-4-yl)morpholine (**16**)

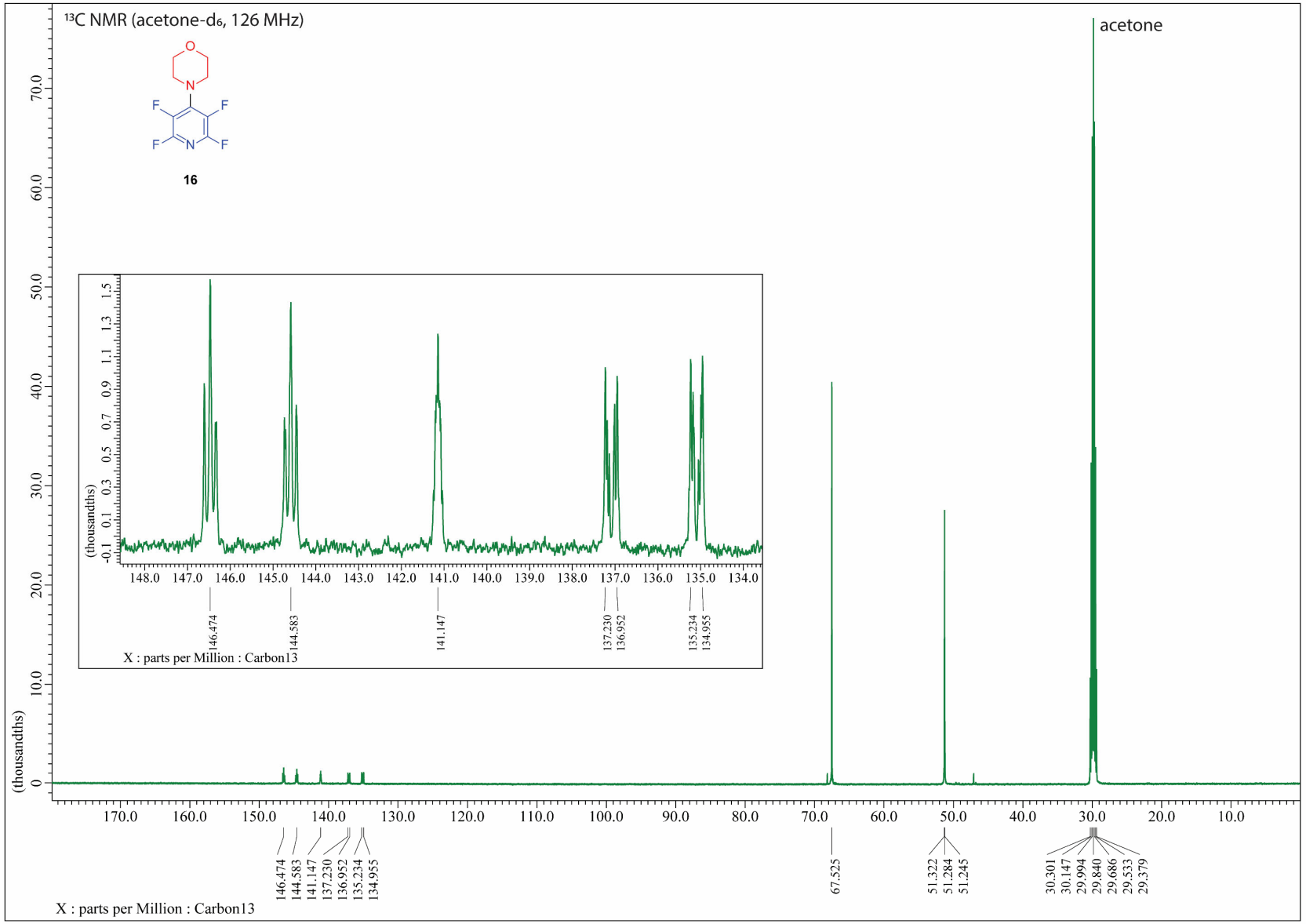

Figure SI20. ^{13}C NMR of 4-(perfluoropyridin-4-yl)morpholine (**16**)

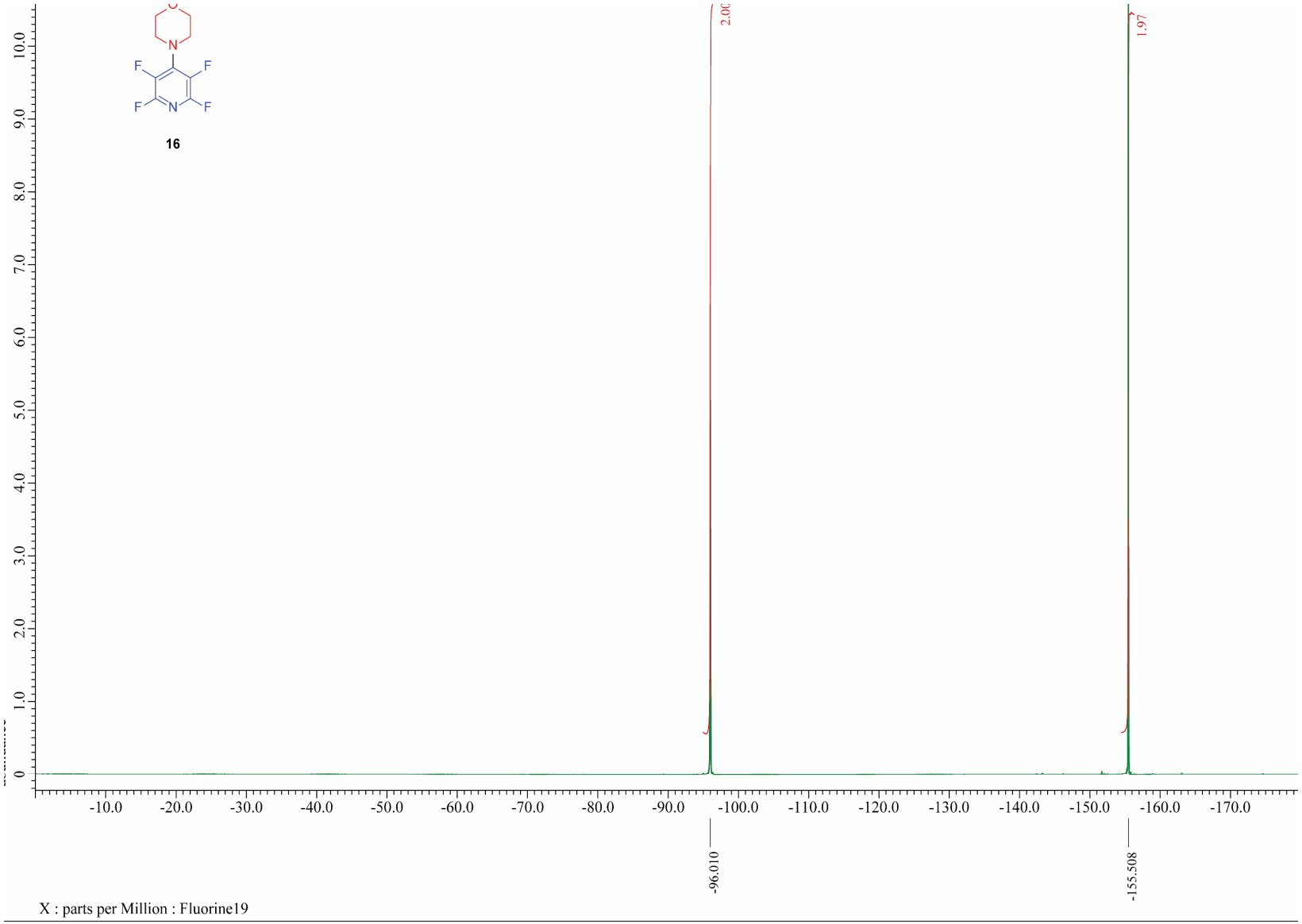

Figure SI21. ^{19}F NMR of 4-(perfluoropyridin-4-yl)morpholine (**16**)

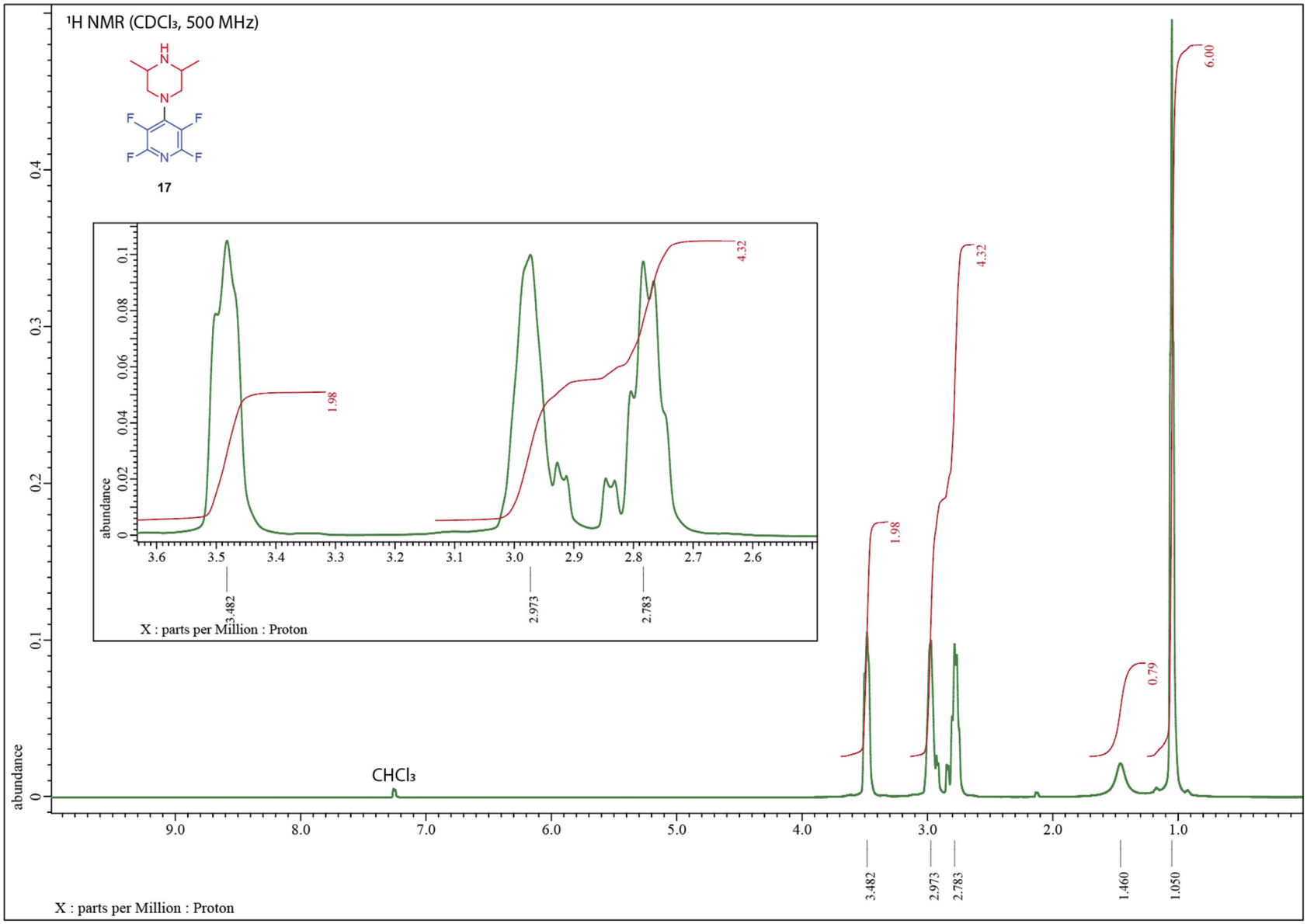

Figure SI22. ^{1}H NMR of 3,5-dimethyl-1-(perfluoropyridin-4-yl)piperazine (**17**)

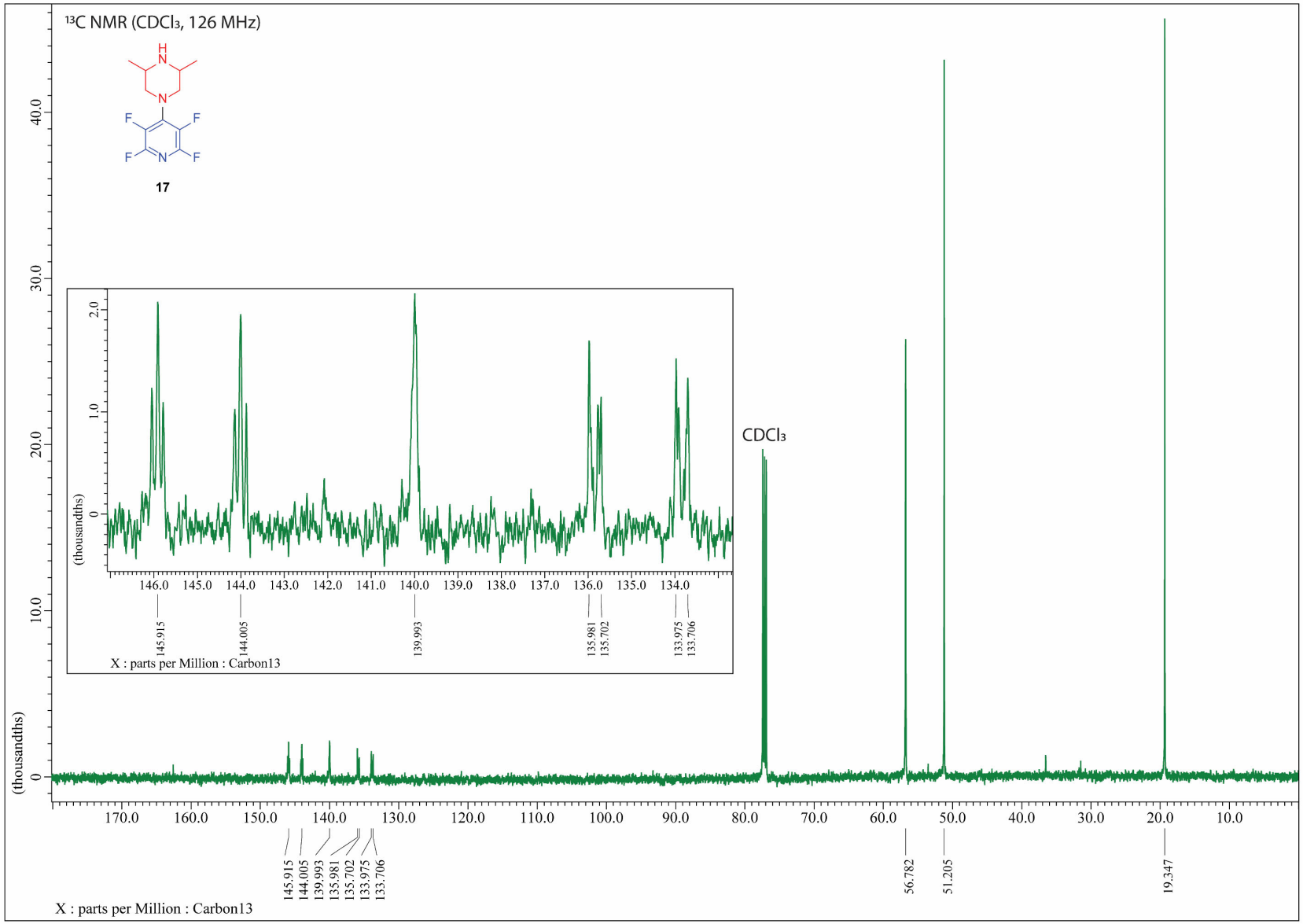

Figure SI23. ^{13}C NMR of 3,5-dimethyl-1-(perfluoropyridin-4-yl)piperazine (**17**)

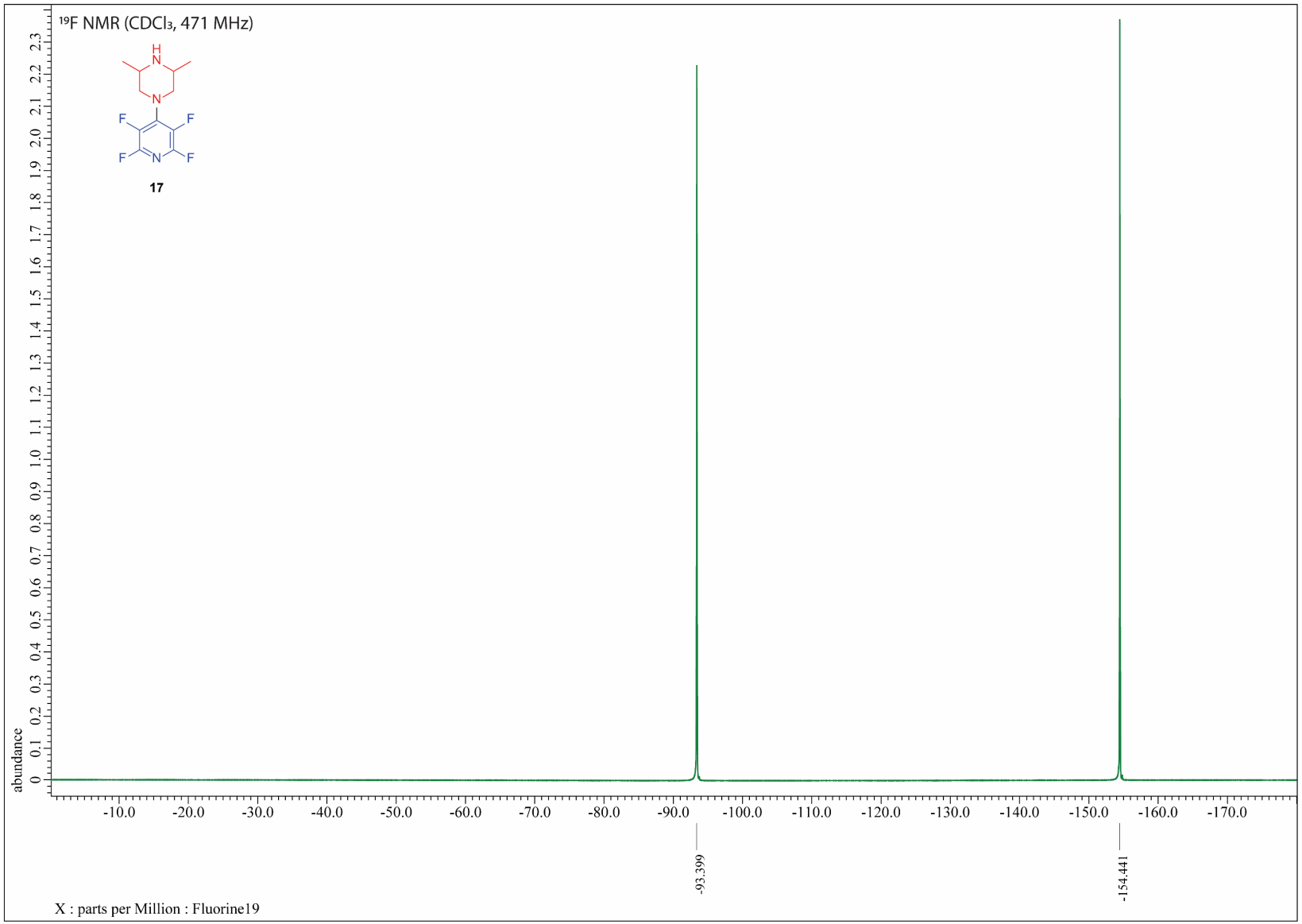

Figure SI24. ^{19}F NMR of 3,5-dimethyl-1-(perfluoropyridin-4-yl)piperazine (**16**)

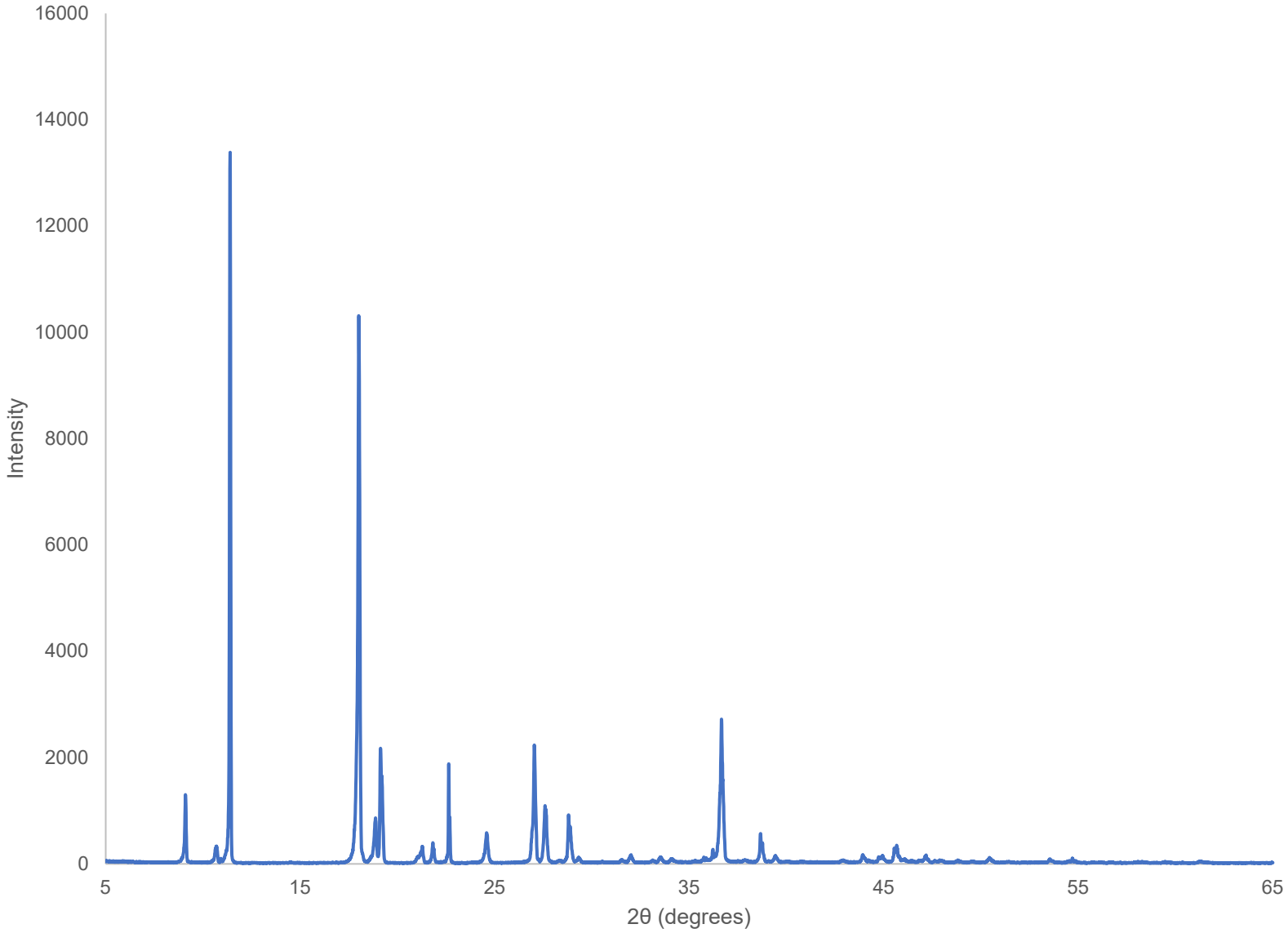

Figure SI25. Powder x-ray diffraction of **18**

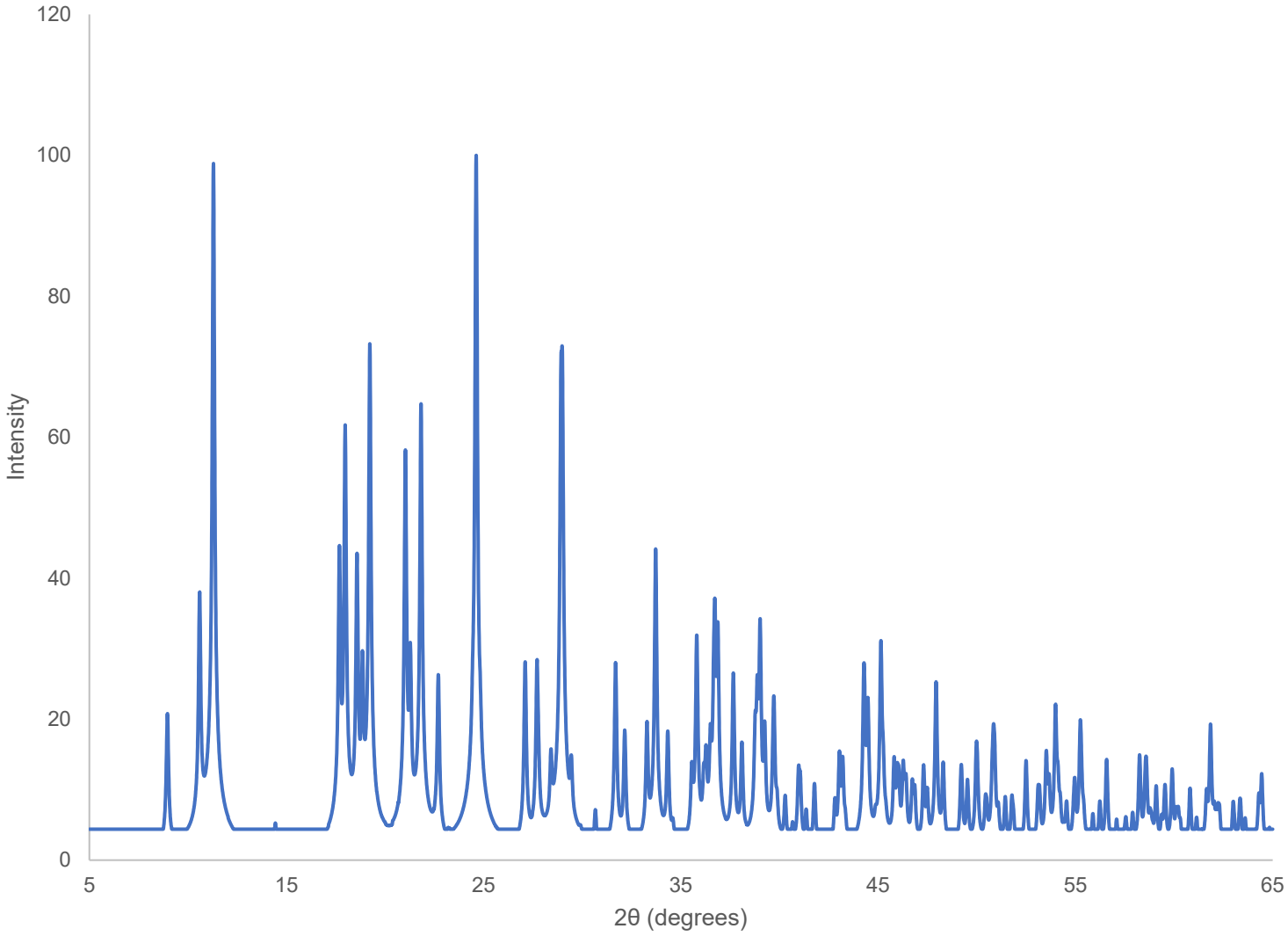

Figure SI26. Predicted powder x-ray diffraction of **18**

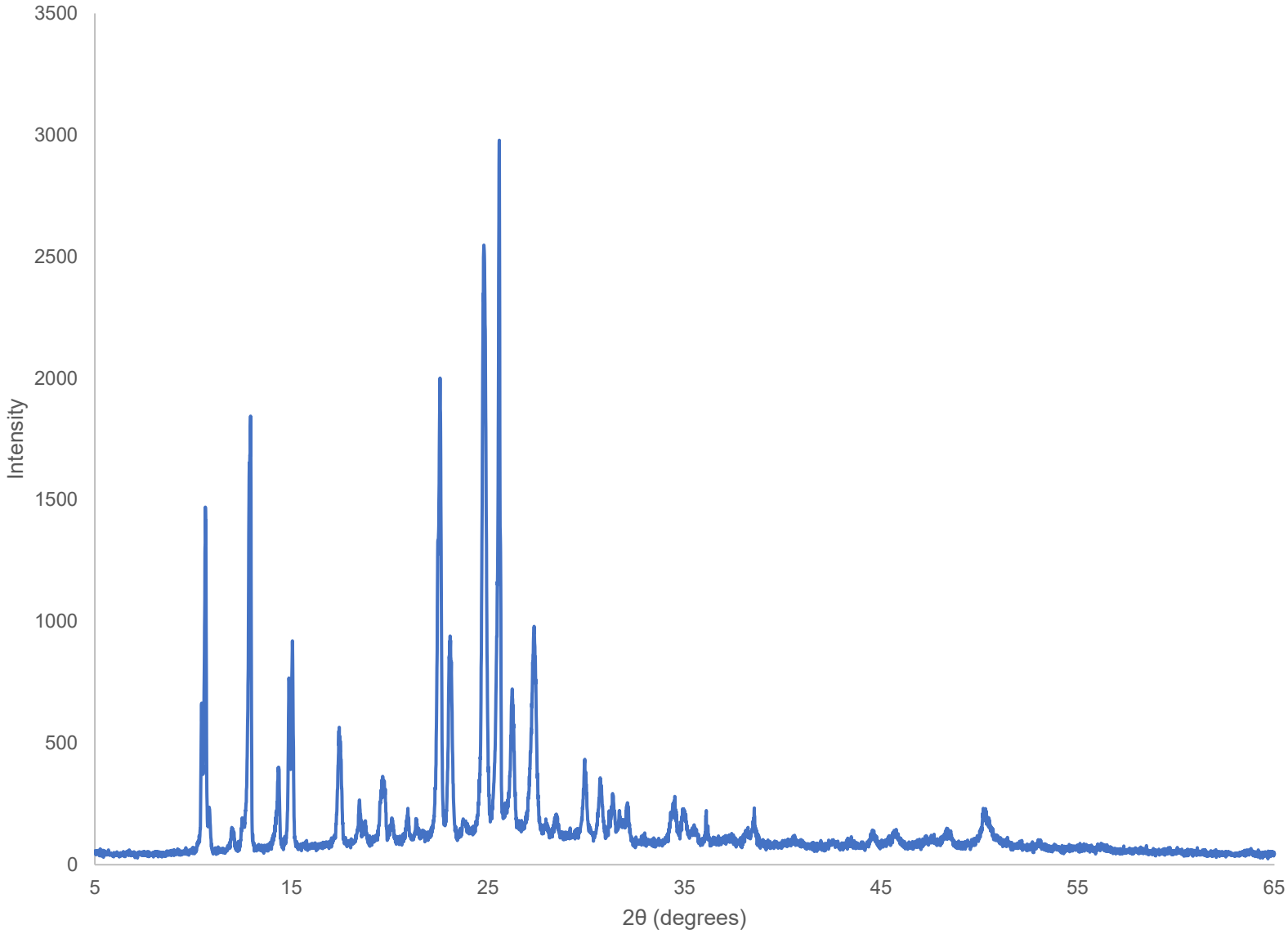

Figure SI27. Powder x-ray diffraction of **19**

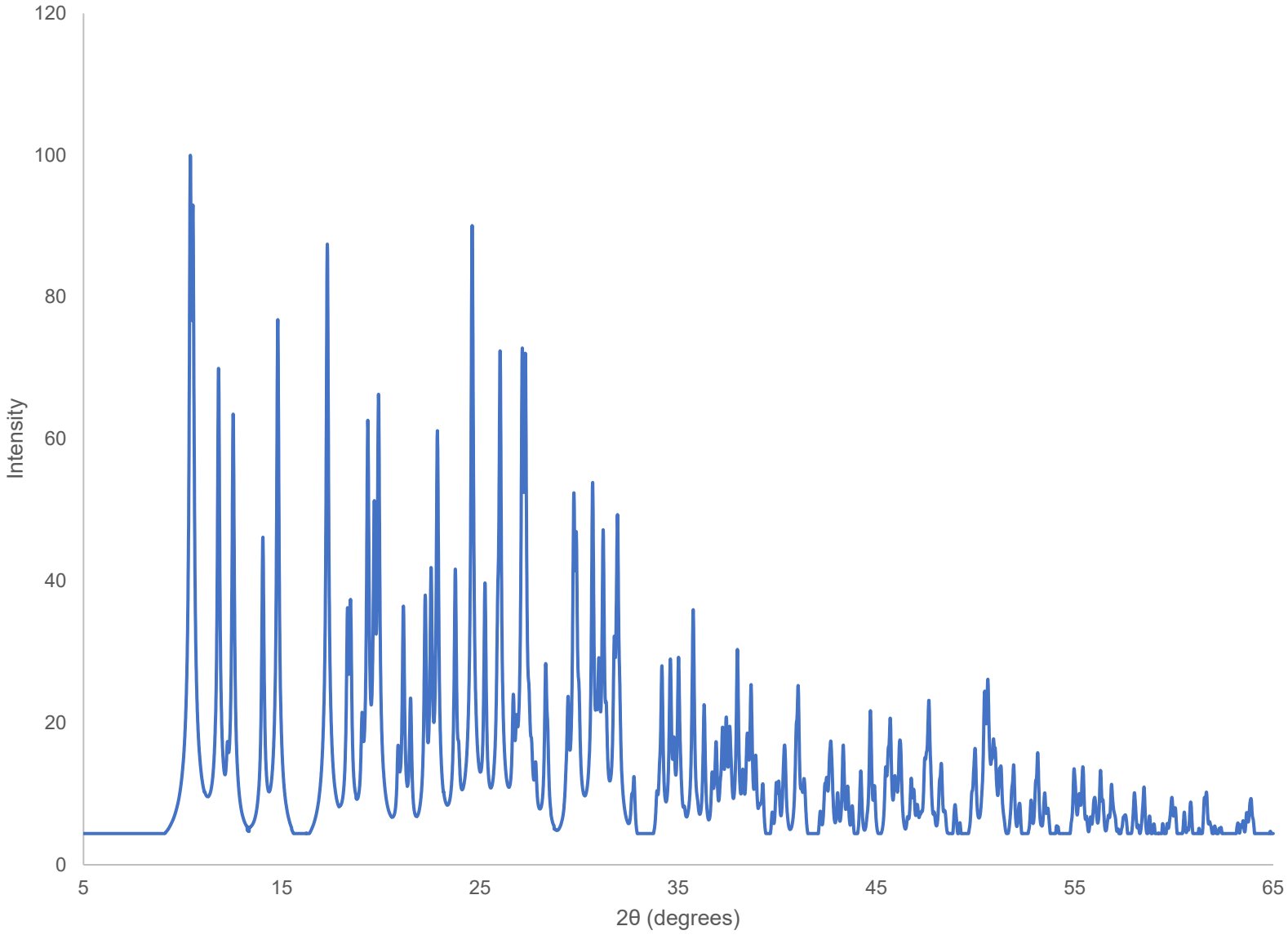

Figure SI28. Predicted powder x-ray diffraction of **19**

Table SI1. Crystallographic Data and Structure Refinement Parameters

	2 poly a	**2 poly b**	**3**	**4**	**5**	**6**
Empirical formula	$C_{12}H_6F_8N_4$	$C_{12}H_6F_8N_4$	$C_{13}H_8F_8N_4$	$C_{16}H_{14}F_8N_4$	$C_{14}H_8F_8N_5$	$C_{19}H_{10}F_{12}N_6$
Formula weight (g/mol)	358.20	358.20	372.23	414.31	401.28	550.33
Crystal system	triclinic	monoclinic	trigonal	triclinic	triclinic	orthorhombic
Space group	$P\bar{1}$	*C*2/*c*	$P3_212$	$P\bar{1}$	$P\bar{1}$	$C222_1$
T (K)	100(2)	293(2)	200(2)	200(2)	194(2)	195(2)
a (Å)	7.6098(3)	14.789(8)	7.8415(5)	5.1158(3)	9.4703(4)	8.3092(4)
b (Å)	12.7754(3)	7.729(4)	7.8415(5)	9.2162(5)	13.0507(5)	13.7094(6)
c (Å)	13.1036(6)	13.470(7)	38.821(2)	17.8911(9)	13.1358(6)	16.9945(8)
α (°)	94.940(2)	90	90	83.186(2)	80.3030(10)	90
β (°)	100.813(2)	123.05(2)	90	89.723(2)	77.4010(10)	90
γ (°)	93.296(2)	90	120	85.492(2)	87.8050(10)	90
V (Å^3)	1243.11(10)	1290.5(12)	2067.3(3)	834.98(8)	1561.77(11)	1935.91(16)
D_{calcd} (g·cm^{-3})	1.914	1.844	1.794	1.648	1.707	1.888
reflns collected	39021	6802	25353	10838	43531	11255
unique reflns	5103	1508	2718	3424	6418	1897
observed reflns	4376	1265	2649	2880	5226	1810
# parameters	449	113	235	262	512	174
R_1 [$I>2\sigma(I)$]	0.0323	0.0512	0.0333	0.0347	0.0328	0.0248
wR_2 [$I>2\sigma(I)$]	0.0801	0.1216	0.0855	0.0842	0.0793	0.0662
R_1 (all)	0.0394	0.0600	0.0344	0.0431	0.0436	0.0265
wR_2 (all)	0.0874	0.1304	0.0861	0.0890	0.0860	0.0672
R(int)	0.0276	0.0201	0.0332	0.0237	0.0288	0.0287
GooF	1.036	1.089	1.179	1.029	1.026	1.077
Flack parameter	N/A	N/A	-0.11(10)	N/A	N/A	0.39(18)
CCDC #	1994733	1994734	1994735	1994736	1994737	1994738

Table SI1 (cont.). Crystallographic Data and Structure Refinement Parameters

	8	**9**	**11**	**13**	**14**
Empirical formula	$C_9H_8F_4N_2$	$C_9H_6F_4N_2$	$C_{11}H_6F_4N_2$	$C_{11}H_7F_4N_3$	$C_7H_6F_4N_2O$
Formula weight (g/mol)	220.17	218.16	242.17	257.20	210.14
Crystal system	orthorhombic	triclinic	orthorhombic	monoclinic	monoclinic
Space group	*Pna*2$_1$	$P\bar{1}$	*Pna*2$_1$	*P*2$_1$/*n*	*P*2$_1$/*n*
T (K)	188(2)	198(2)	100(2)	190(2)	100(2)
a (Å)	13.8300(6)	7.2959(4)	12.036(4)	8.1390(4)	8.0847(4)
b (Å)	10.1160(5)	9.9103(5)	10.696(3)	11.6656(6)	8.8845(4)
c (Å)	6.5854(3)	11.9251(6)	7.794(2)	10.9404(6)	10.9733(5)
α (°)	90	83.3790(10)	90	90	90
β (°)	90	84.7380(10)	90	91.2010(10)	96.975(2)
γ (°)	90	86.1790(10)	90	90	90
V (Å^3)	921.33(7)	851.51(8)	1003.4(5)	1038.52(9)	782.36(6)
D_{calcd} (g·cm^{-3})	1.587	1.702	1.603	1.645	1.784
reflns collected	15198	39728	191633	16102	33266
unique reflns	1884	3483	3465	2139	2856
observed reflns	1432	3007	3021	1878	2431
# parameters	183	272	157	176	135
R_1 [$I>2\sigma(I)$]	0.0428	0.0412	0.0352	0.0318	0.0344
wR_2 [$I>2\sigma(I)$]	0.0934	0.1099	0.0802	0.0844	0.0927
R_1 (all)	0.0610	0.0467	0.0450	0.0372	0.0419
wR_2 (all)	0.1053	0.1173	0.0861	0.0888	0.1007
R(int)	0.0326	0.0280	0.0475	0.0277	0.0315
GooF	1.047	1.052	1.031	1.058	1.024
Flack parameter	0.4(9)	N/A	0.2(3)	N/A	N/A
CCDC #	1994739	1994740	1906424	1994741	1912058

Table SI1 (cont.). Crystallographic Data and Structure Refinement Parameters

	15	**16**	**17·2H$_2$O**	**18**	**19**
Empirical formula	$C_{11}H_{14}F_4N_2O_2$	$C_9H_8F_4N_2O$	$C_{11}H_{17}F_4N_3O_2$	$C_{17}H_{23}F_5N_2$	$C_{11}H_{13}F_5N_2$
Formula weight (g/mol)	282.24	236.17	299.27	350.37	268.23
Crystal system	triclinic	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$C222_1$	$C2/c$
T (K)	186(2)	189(2)	207(2)	100(2)	188(2)
a (Å)	7.4644(4)	8.1474(5)	13.8558(15)	5.1831(12)	18.0262(14)
b (Å)	8.7054(5)	10.3929(6)	7.4780(7)	19.730(5)	7.9890(6)
c (Å)	10.8961(6)	11.3626(7)	13.2055(13)	15.662(4)	18.2560(14)
α (°)	98.501(2)	90	90	90	90
β (°)	98.008(2)	100.798(2)	100.504(3)	90	111.247(2)
γ (°)	115.3230(10)	90	90	90	90
V (Å^3)	616.51(6)	945.09(10)	1345.3(2)	1601.6(6)	2450.4(3)
D_{calcd} (g·cm^{-3})	1.520	1.660	1.478	1.453	1.454
reflns collected	11312	17300	10660	28624	22249
unique reflns	3050	2064	2732	3064	2274
observed reflns	2641	1710	1836	2948	1682
# parameters	231	201	204	114	227
R_1 [$I>2\sigma(I)$]	0.0439	0.0479	0.0471	0.0432	0.0679
wR_2 [$I>2\sigma(I)$]	0.1199	0.1193	0.1131	0.1188	0.1954
R_1 (all)	0.0498	0.0561	0.0805	0.0449	0.0877
wR_2 (all)	0.1262	0.1290	0.1240	0.1209	0.2149
R(int)	0.0276	0.0345	0.0441	0.0542	0.0315
GooF	1.066	1.041	1.030	1.123	1.050
Flack parameter	N/A	N/A	N/A	0.14(19)	N/A
CCDC #	1994742	1994743	1994744	1986043	1994745

Note to Table SI1: The Flack parameters of **6** and **11** are suggestive of some degree of twinning by inversion, and due to the use of Mo radiation, exhibit somewhat high standard uncertainties. Even so, the presence of fluorine provides enough anomalous dispersion to be comfortable with the absolute structure, particularly since the molecules are achiral and the structure analysis is not being used for establishing the absolute configuration. In this way, the data are sufficient for the focus of this study since the resulting hydrogen bonding interactions can still be plainly identified. A test refinement utilizing TWIN/BASF yieled no change in R_1 or wR_2.

Table SI2. Hydrogen-bond geometry (Å, °)

		2 poly a		
D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
C6–H6A···F2	0.99	2.36	2.8908(17)	112.5
C6–H6B···F6	0.99	2.35	3.0215(17)	124.8
C7–H7A···F5	0.99	2.57	3.2730(17)	128
C7–H7A···F6	0.99	2.61	3.5892(17)	169.1
C7–H7B···F12	0.99	2.49	3.3188(17)	141.4
N2–H1N2···F3	0.84(2)	2.31(2)	2.7072(16)	109.6(16)
N2–H1N2···N8	0.84(2)	2.33(2)	3.0871(18)	151.2(18)
N3–H1N3···N5	0.83(2)	2.27(2)	3.0714(17)	161.2(19)
C18–H18A···F10	0.99	2.37	2.9112(17)	113.3
C18–H18B···F14	0.99	2.46	3.0994(17)	121.9
C19–H19A···F9	0.99	2.64	3.1848(17)	114.7
C19–H19B···F4	0.99	2.42	3.1976(17)	135
N6–H1N6···N4	0.855(19)	2.236(19)	3.0121(18)	150.8(16)
N7–H1N7···N1	0.87(2)	2.40(2)	3.2229(18)	158.9(19)

		2 poly b		
D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
C6–H6A···F3	0.97	2.33	2.846(3)	112.3
C6–H6B···F1	0.97	2.51	3.388(3)	149.8
N2–H1N2···F2	0.83(2)	2.34(2)	2.730(2)	109.4(17)
N2–H1N2···N1	0.83(2)	2.45(2)	3.225(2)	155.6(18)

		3		
D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
C6–H6A···F5	0.99	2.5	3.364(3)	146.1
C6–H6B···F2	0.99	2.33	2.845(4)	111.7
C6–H6B···F8	0.99	2.57	3.476(4)	152.2
C7–H7A···F2	0.99	2.6	3.177(3)	117
C8–H8B···F7	0.99	2.31	2.832(3)	111.8
N2–H1N2···N1	0.81(3)	2.45(3)	3.177(4)	150(3)
N3–H1N3···N4	0.81(3)	2.51(3)	3.260(3)	155(3)

		4		
D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
N4–H1N4···N1	0.816(19)	2.53(2)	3.3327(18)	167.4(16)
N2–H1N2···F2	0.827(18)	2.312(17)	2.7019(15)	109.4(14)
N2–H1N2···N3	0.827(18)	2.429(18)	3.1881(18)	153.0(15)
C6–H6B···F3	0.99	2.29	2.8670(17)	116.3
C14–H14A···F6	0.99	2.32	2.8258(17)	111
C14–H14B···F1	0.99	2.55	3.2529(17)	127.6
C15–H15B···F6	0.99	2.59	3.1331(17)	114.7

Table SI2 (cont.). Hydrogen-bond geometry (Å, °)

		5		
D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
N7–H1N7···N3	0.840(18)	2.132(18)	2.9542(16)	166.0(16)
C6–H6A···F16	0.99	2.43	3.2472(18)	140.1
C6–H6B···F1	0.99	2.61	3.4543(17)	143.6
C6–H6B···F2	0.99	2.23	2.8165(17)	116.9
C8–H8D···F7	0.99	2.51	3.1032(16)	118.1
C8–H8D···F11	0.99	2.52	3.1791(16)	124
C20–H20A···F10	0.99	2.3	2.8086(16)	110.6
C21–H21B···F6	0.99	2.56	3.2546(16)	126.7
C21–H21B···F10	0.99	2.56	3.1162(17)	115.5
C22–H22B···F4	0.99	2.58	3.4582(18)	147.5
C23–H23B···F9	0.99	2.53	3.3969(18)	146.3
C23–H23B···F14	0.99	2.21	2.9025(17)	126
N2–H1N2···N10	0.830(18)	2.447(18)	3.2025(18)	151.7(15)
N3–H1N3···N6	0.848(16)	2.645(16)	3.2884(17)	133.7(13)
N4–H1N4···N8	0.841(17)	2.125(17)	2.9501(17)	166.5(15)
N8–H1N8···F9	0.857(16)	2.469(16)	3.2395(14)	149.9(13)
N9–H1N9···N5	0.828(19)	2.387(19)	3.0735(18)	140.8(16)

		6		
D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
N2–H1N2···N1	0.80(3)	2.50(3)	3.255(3)	157(3)
C6–H6B···F2	0.99	2.18	2.914(2)	129.3
C7–H7A···F2	0.99	2.45	3.200(2)	132.3
C7–H7B···F4	0.99	2.6	3.234(2)	121.5
C7–H7B···F6	0.99	2.3	2.915(2)	119.5

		8		
D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
C8B–H8B2···F3	0.99	2.72	3.307(19)	118.3
C9B–H9B1···F4	0.99	2.63	3.51(3)	147.9
C9B–H9B2···F2	0.99	2.58	3.086(19)	111.3

		9		
D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
C9–H9A···F7	0.99	2.53	3.2016(15)	125.3
C15–H15A···F4	0.99	2.56	3.4081(16)	144
C17–H17···N3	0.95	2.67	3.4456(17)	139.8

Table SI2 (cont.). Hydrogen-bond geometry (Å, °)

		11		
D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
N2–H2N···N1	0.85(3)	2.20(3)	3.046(2)	169(3)

		13		
D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
N2–H1N2···N3	0.849(18)	2.175(19)	2.9890(16)	160.5(16)
N3–H2N3···N1	0.870(19)	2.547(19)	3.3264(17)	149.6(15)
C8–H8···F2	0.95	2.57	3.4428(15)	153.7
C11–H11···F1	0.95	2.62	3.3986(16)	139

		14		
D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
N2–H1N1···O1	0.894(17)	1.983(17)	2.8412(11)	160.4(15)
O1–H1O1···N1	0.826(18)	2.096(18)	2.9068(11)	166.9(16)
C7–H7A···F1	0.99	2.51	3.3661(11)	144.5
C7–H7A···F3	0.99	2.5	3.1277(11)	120.7
C7–H7B···F1	0.99	2.63	3.3283(11)	127.3
C7–H7B···F3	0.99	2.52	3.3924(11)	146.9

		15		
D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
O2–HO2···O1A	0.840(16)	1.961(17)	2.781(2)	165(2)
O2–HO2···O1B	0.840(16)	2.15(2)	2.912(11)	151(2)
O1A–HO1A···O2	0.896(16)	1.905(17)	2.773(2)	163(2)
C6A–H6AA···F2	0.99	2.24	2.891(2)	122.3
C7A–H7A···F4	1	2.49	3.3184(16)	139.4
C8A–H8AB···F3	0.98	2.58	3.277(4)	127.8
O1B–HO1B···O2	0.95(2)	2.08(8)	2.912(11)	145(11)
C7B–H7B···F1	1	2.55	3.543(10)	170.7
C8B–H8B1···F3	0.98	2.57	3.07(2)	112.3
C9–H9A···F3	0.99	2.33	2.9364(14)	118.5

		16		
D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
C6A–H6AA···F2	0.99	2.13	2.702(3)	114.8
C6A–H6AA···F2	0.99	2.58	3.331(3)	132.5
C8A–H8AB···F3	0.99	2.42	2.979(4)	115
C9A–H9AB···F3	0.99	2.59	3.566(3)	167.8
C6B–H6BB···F2	0.99	2.54	3.219(6)	125.7
C6B–H6BB···F2	0.99	2.58	3.352(4)	134.9
C9B–H9BA···F3	0.99	2.54	3.507(5)	165.3

Table SI2 (cont.). Hydrogen-bond geometry (Å, °)

17·2H$_2$O				
D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
C6–H6B···F2	0.98	2.18	2.818(2)	121.6
C9–H9A···F1	0.98	2.59	3.458(3)	148.3
C9–H9A···F3	0.98	2.24	2.799(2)	114.8
N3–H1N3···O1	0.83(2)	2.63(2)	3.439(3)	163(2)
O2–H1O2···N1	0.826(10)	2.348(11)	3.158(3)	167(3)
O2–H2O2···O1	0.822(10)	2.05(2)	2.738(3)	141(3)
O1–H2O1···N3	0.884(10)	2.066(16)	2.898(3)	157(3)
18				
D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
N2–H1N2···F3	0.82(5)	2.14(5)	2.9546(12)	170(5)
C5–H5A···F2	0.99	2.35	3.1142(19)	133.5
18				
D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
N2–HNA···F3	0.873(14)	1.893(19)	2.749(4)	166(5)
N2–HNB···F3	0.873(14)	1.869(17)	2.742(4)	176(13)

Note: All hydrogen atoms positions indicated in this table are *before* extension to neutron distances

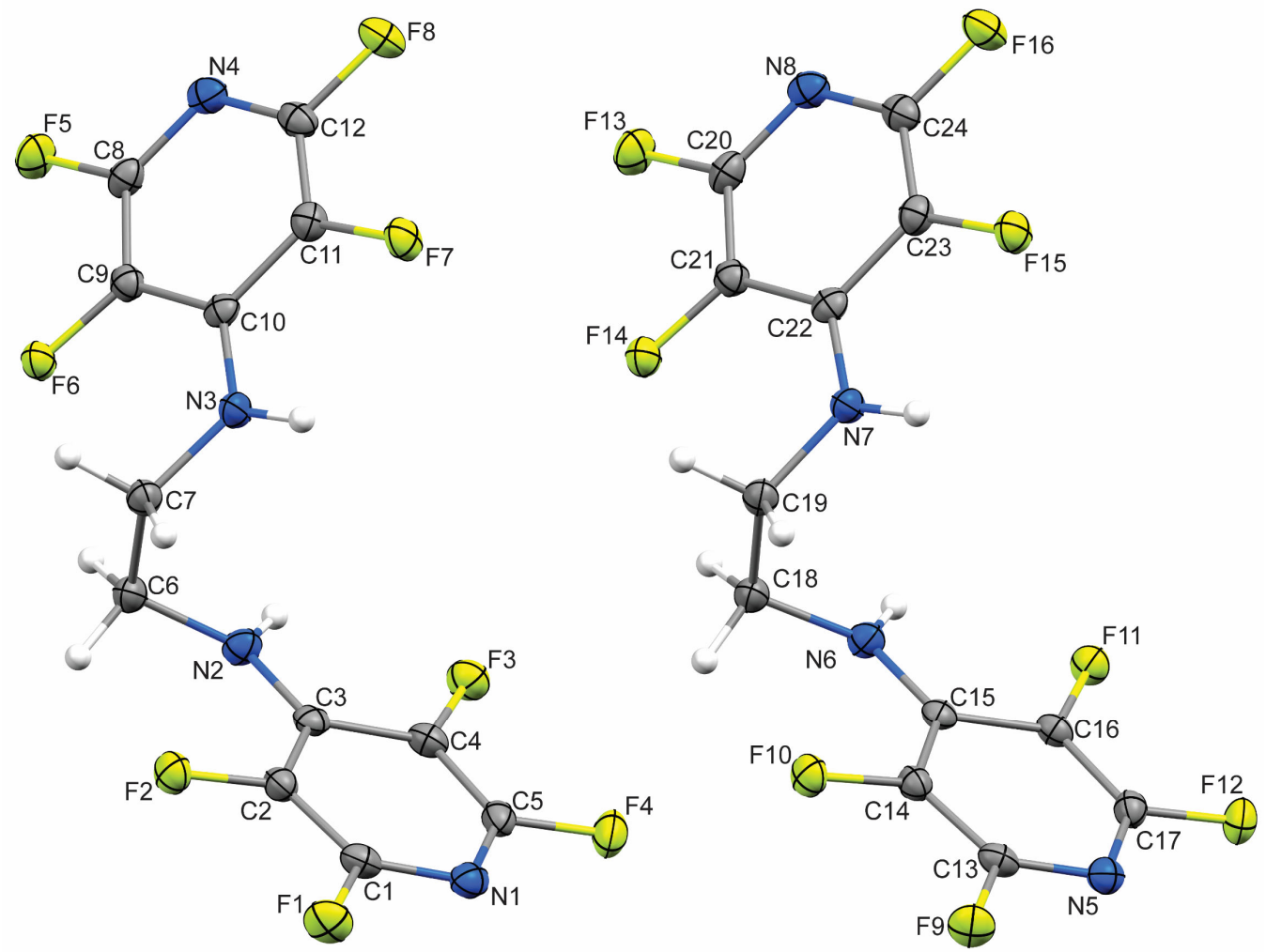

Figure SI29. Molecular stucture of **2 poly a**. Thermal ellipsoids are shown at the 50% probability level.

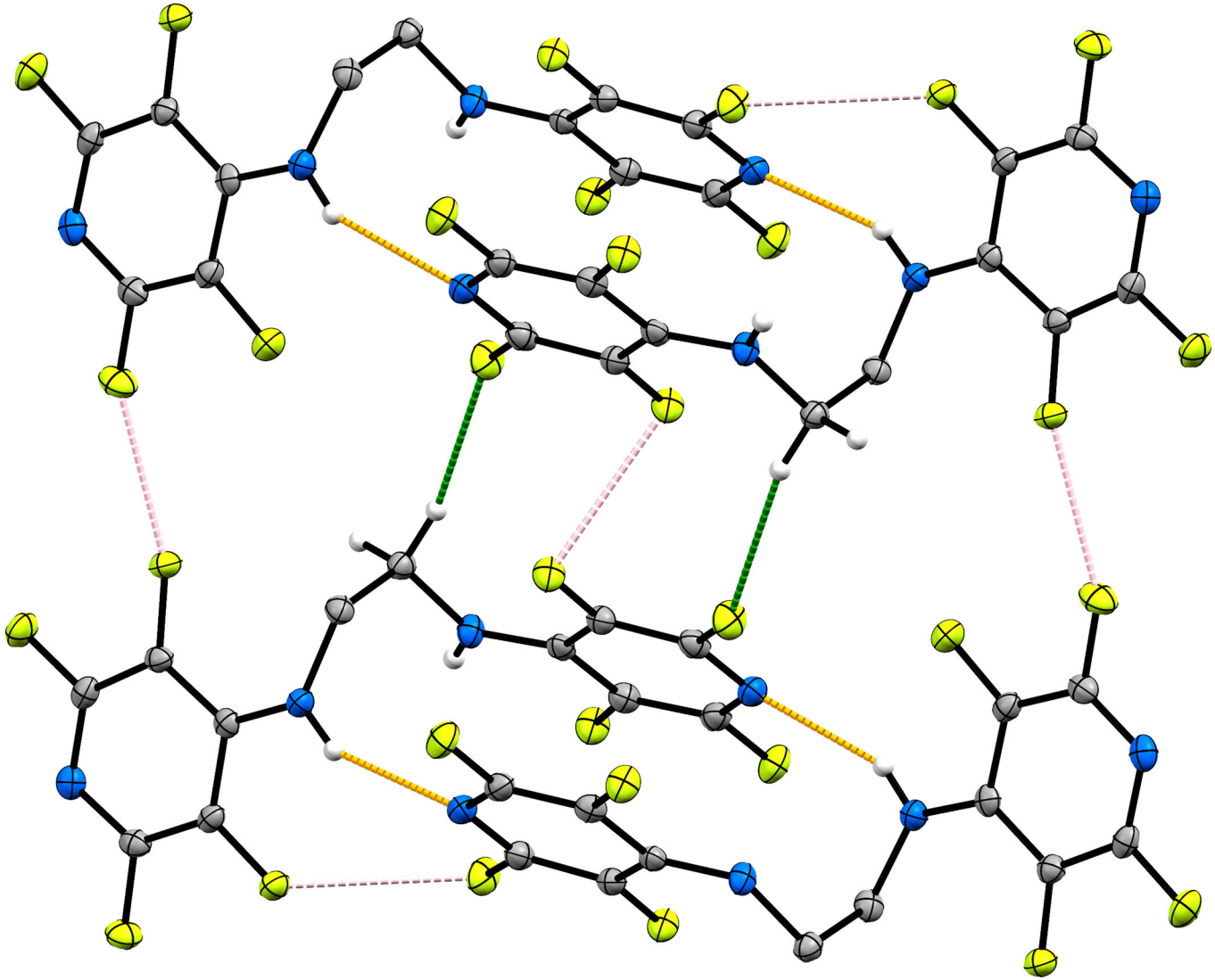

Figure SI30. Solid state packing of **2 poly a**. Intermolecular N–H···$N_{pyridine}$ (orange), C–F···F–C (pink), and C–H···F (green) interactions are indicated by dashed lines. H atoms, except those bound to donor atoms of the indicated intermolecular interactions, have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

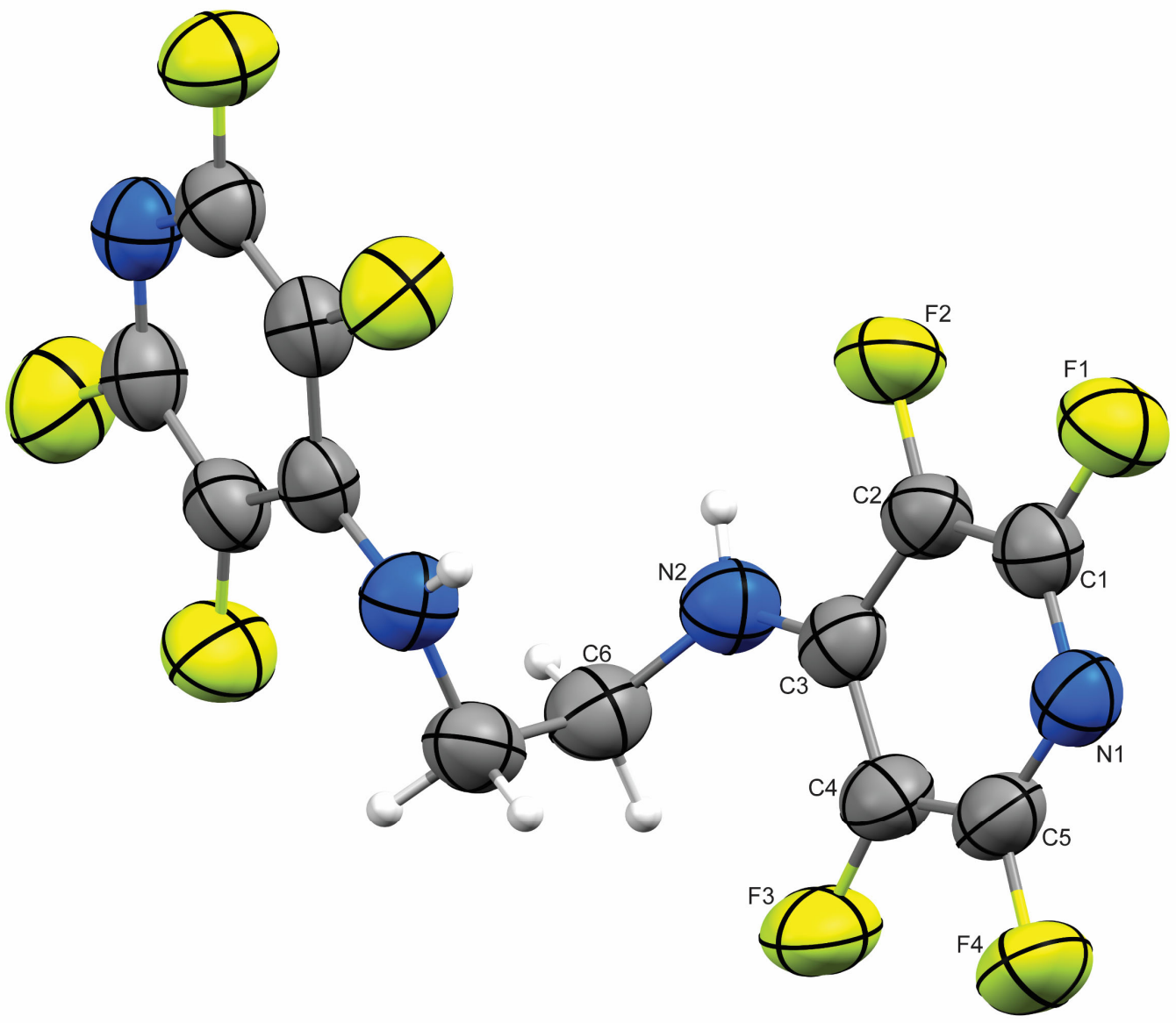

Figure SI31. Molecular stucture of **2 poly b**. Thermal ellipsoids are shown at the 50% probability level.

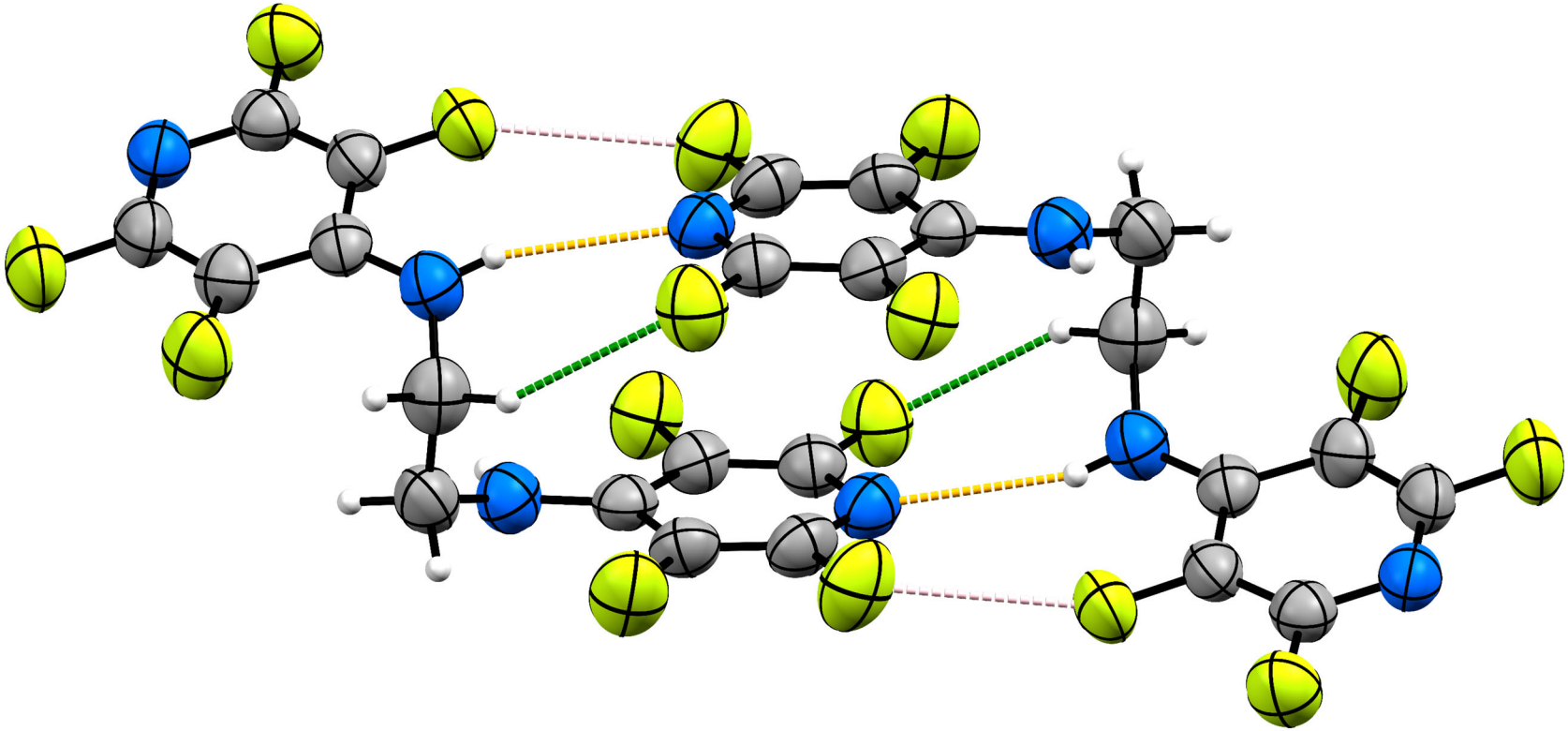

Figure SI32. Solid state packing of **2 poly b**. Intermolecular N–H···$N_{pyridine}$ (orange), C–F···F–C (pink), and C–H···F (green) interactions are indicated by dashed lines. H atoms, except those bound to donor atoms of the indicated intermolecular interactions, have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

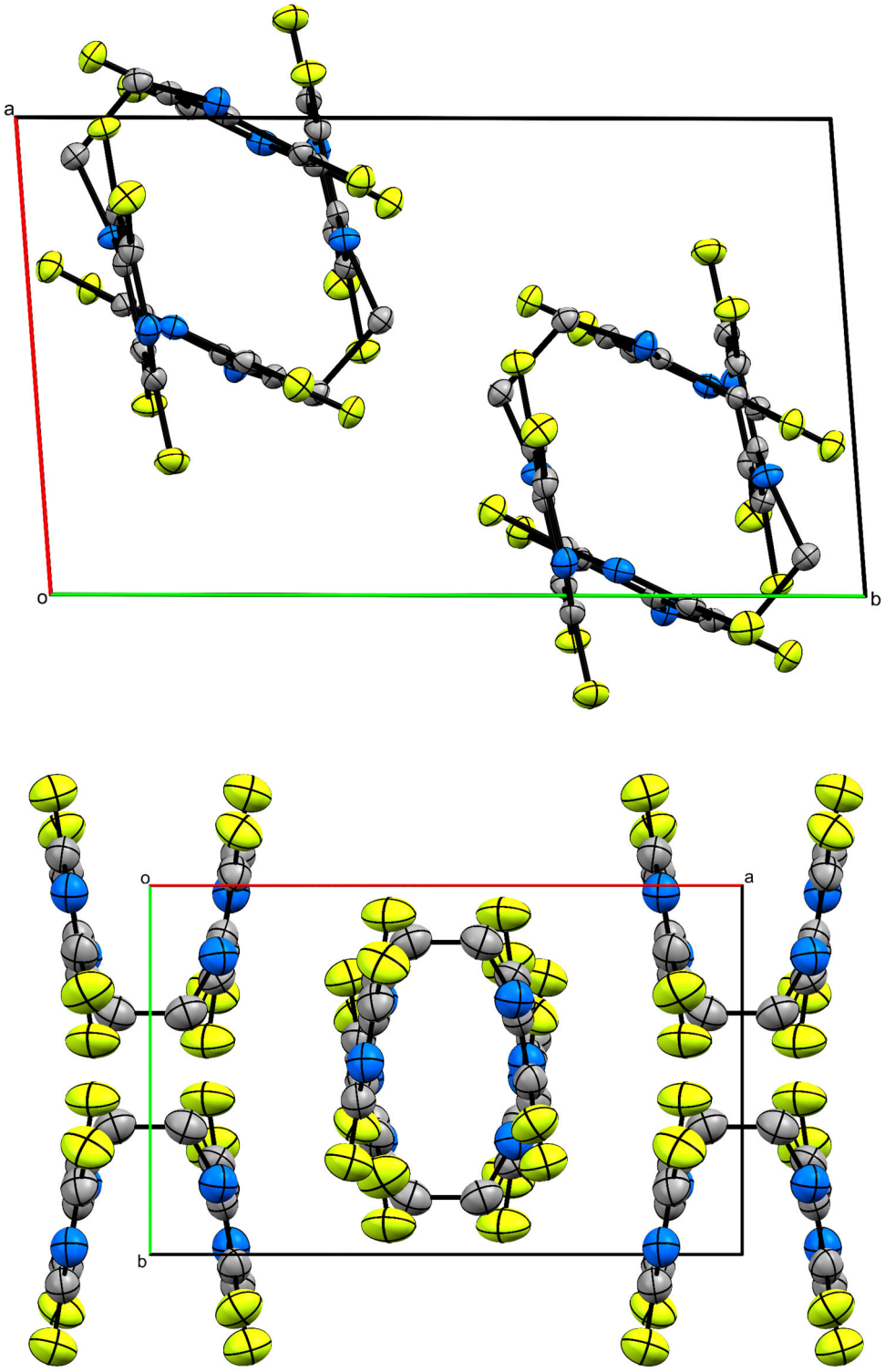

Figure SI33. Unit cell packing of **2 poly a** (top) compared to **2 poly b** (bottom**)** as viewed down the *c* axis. H atoms have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

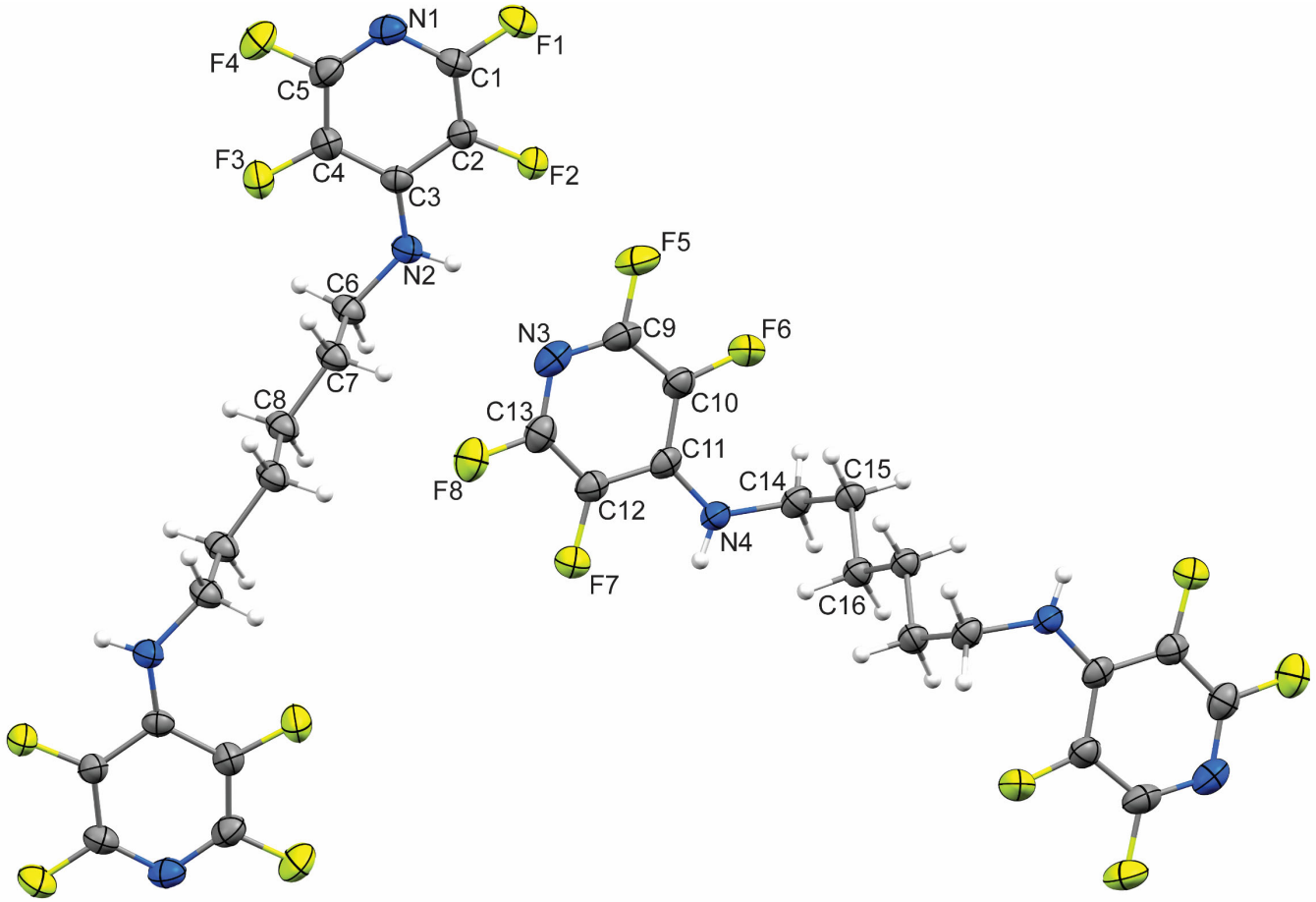

Figure SI34. Molecular stucture of **4**. Thermal ellipsoids are shown at the 50% probability level.

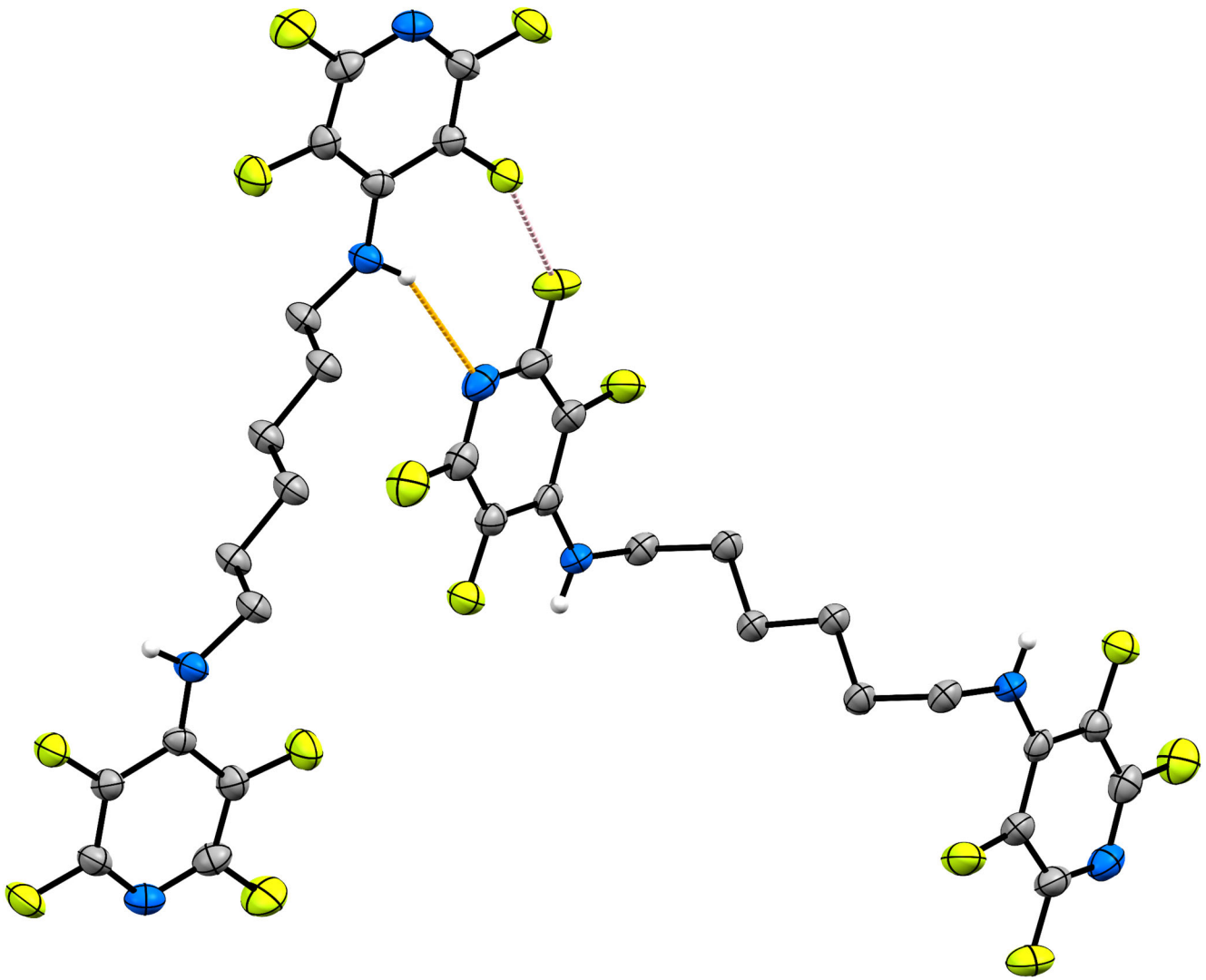

Figure SI35. Solid state packing of **4**. Intermolecular N–H···$N_{pyridine}$ (orange) and C–F···F–C (pink) interactions are indicated by dashed lines. H atoms, except those bound to donor atoms of the indicated intermolecular interactions, have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

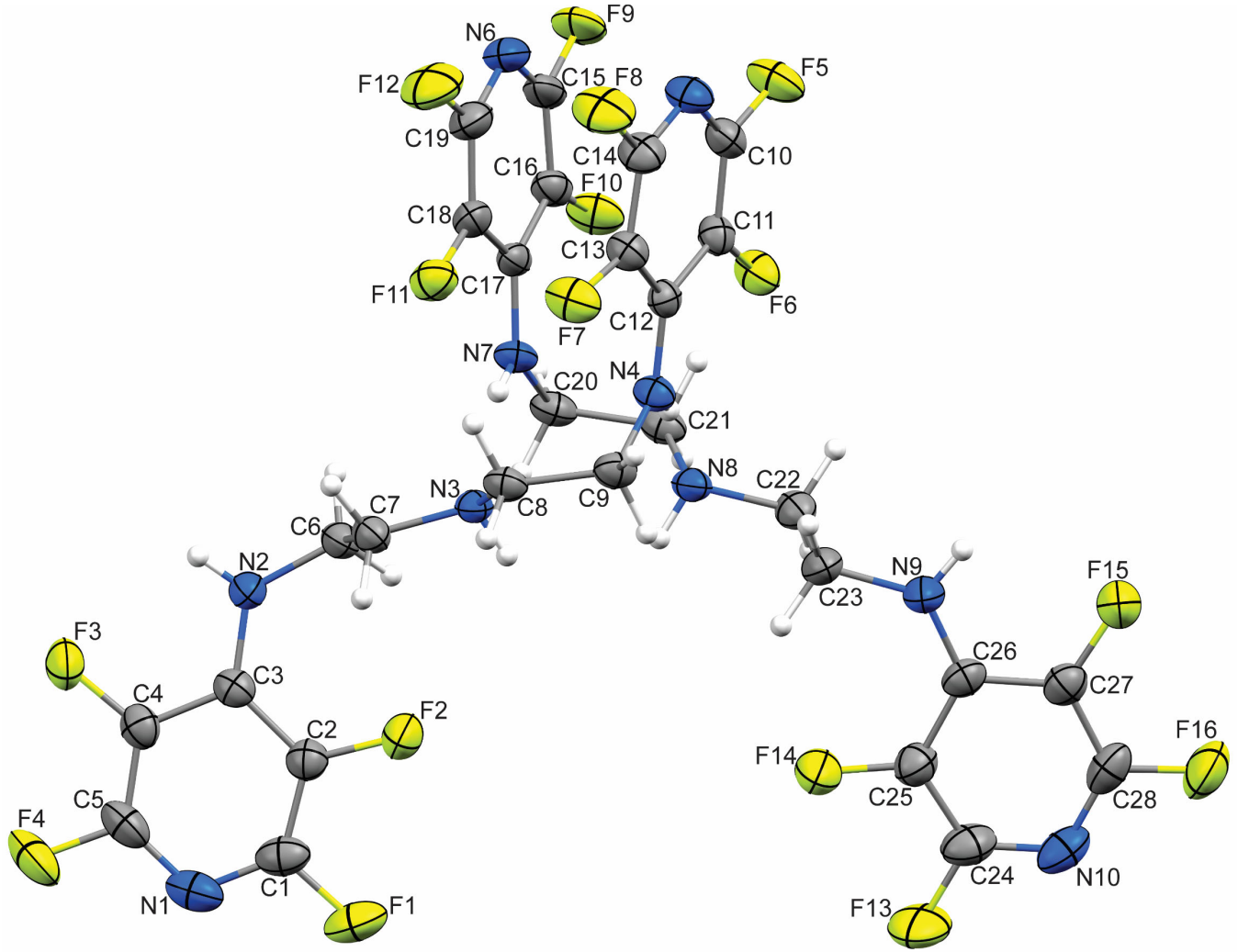

Figure SI36. Molecular stucture of **5**. Thermal ellipsoids are shown at the 50% probability level.

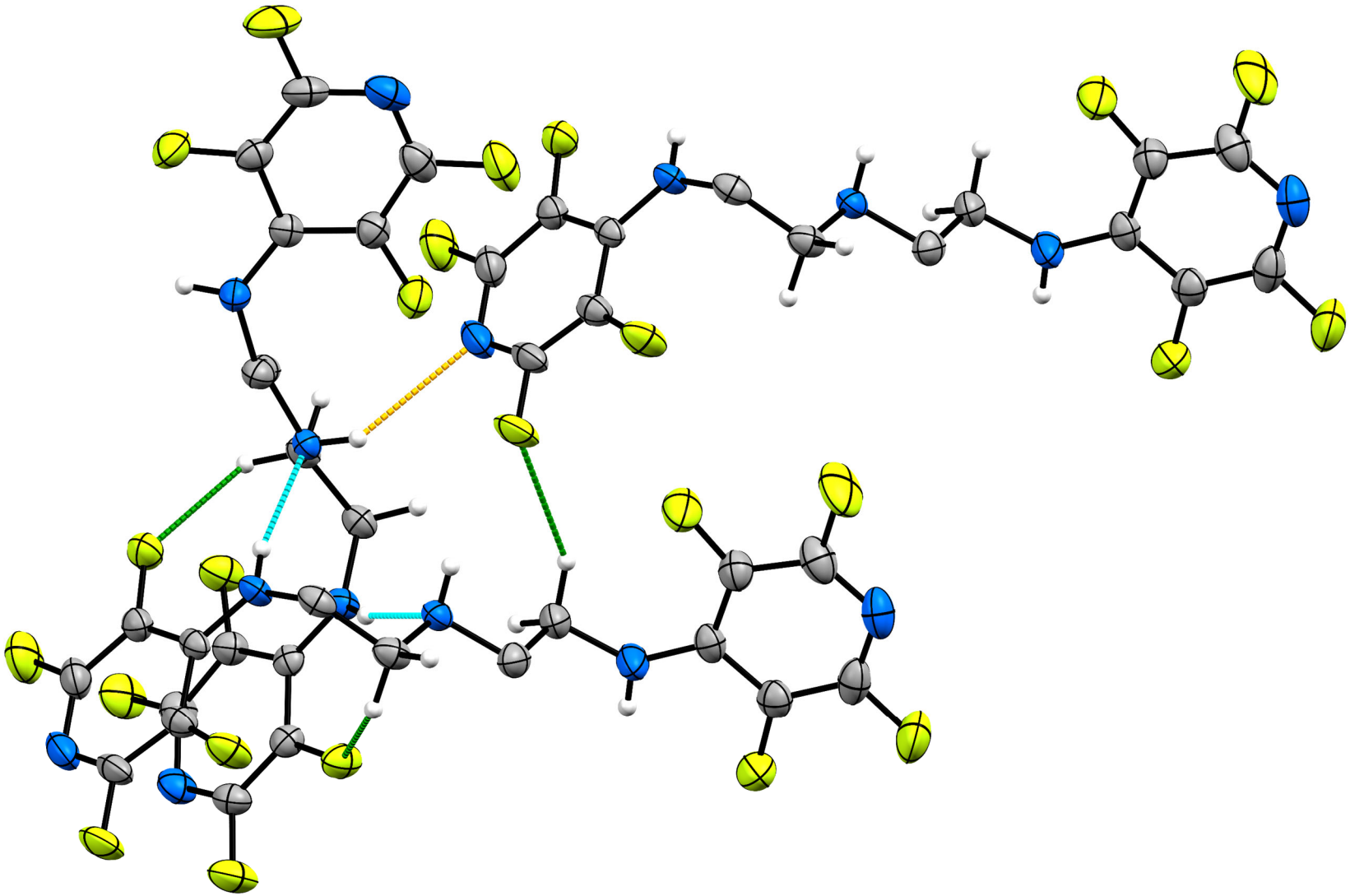

Figure SI37. Solid state packing of **5**. Intermolecular N–H···$N_{pyridine}$ (orange), N–H···N_{amine} (teal), and C–H···F (green) interactions are indicated by dashed lines. H atoms, except those bound to donor atoms of the indicated intermolecular interactions, have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

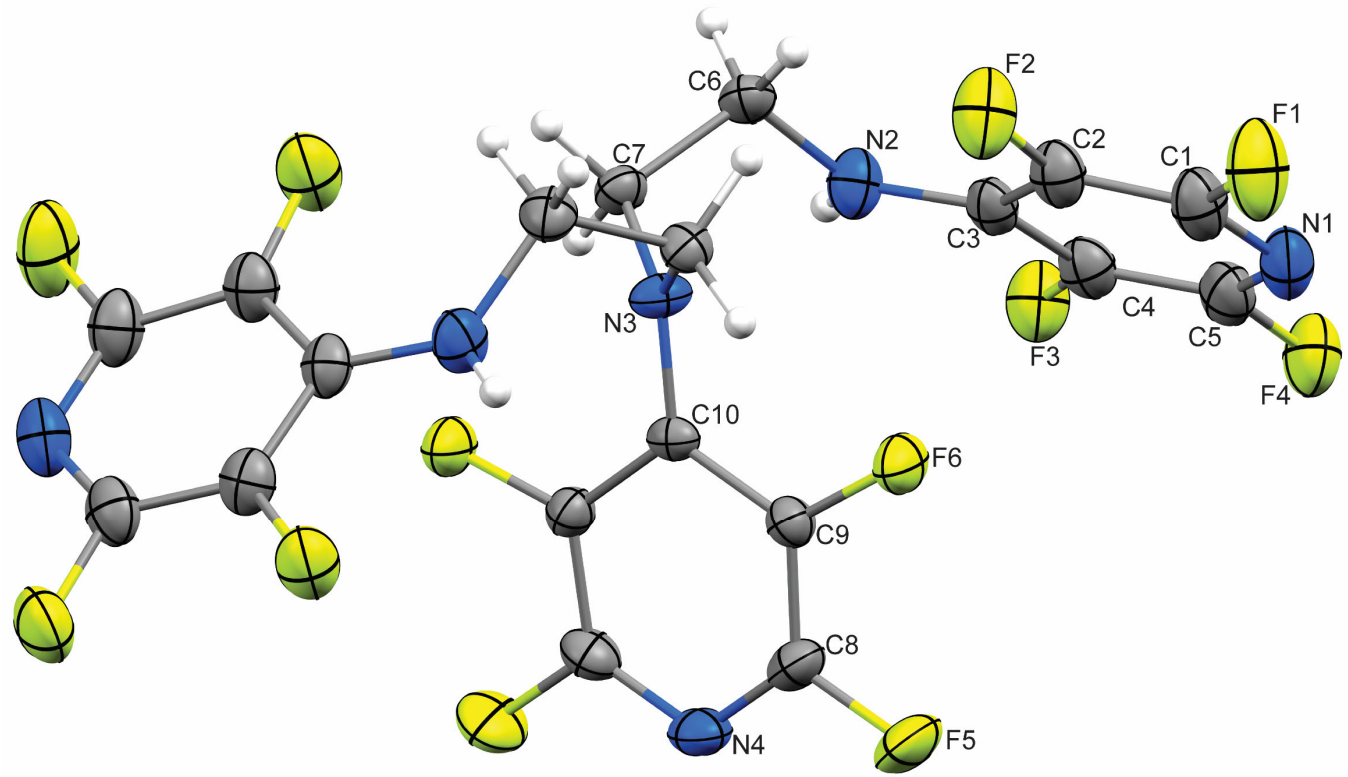

Figure SI38. Molecular stucture of **5**. Thermal ellipsoids are shown at the 50% probability level.

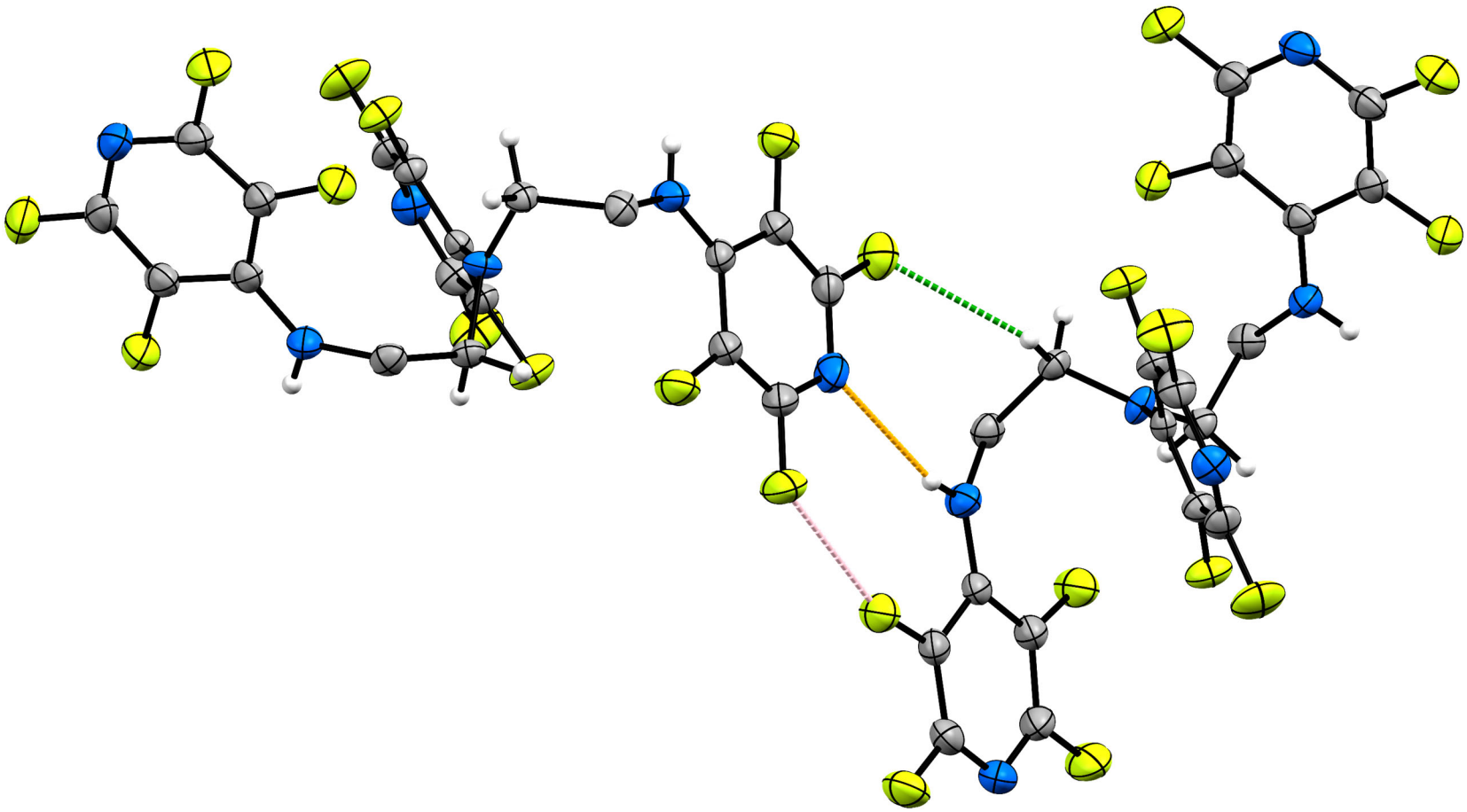

Figure SI39. Solid state packing of **6**. Intermolecular N–H···$N_{pyridine}$ (orange), C–F···F–C (pink), and C–H···F (green) interactions are indicated by dashed lines. H atoms, except those bound to donor atoms of the indicated intermolecular interactions, have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

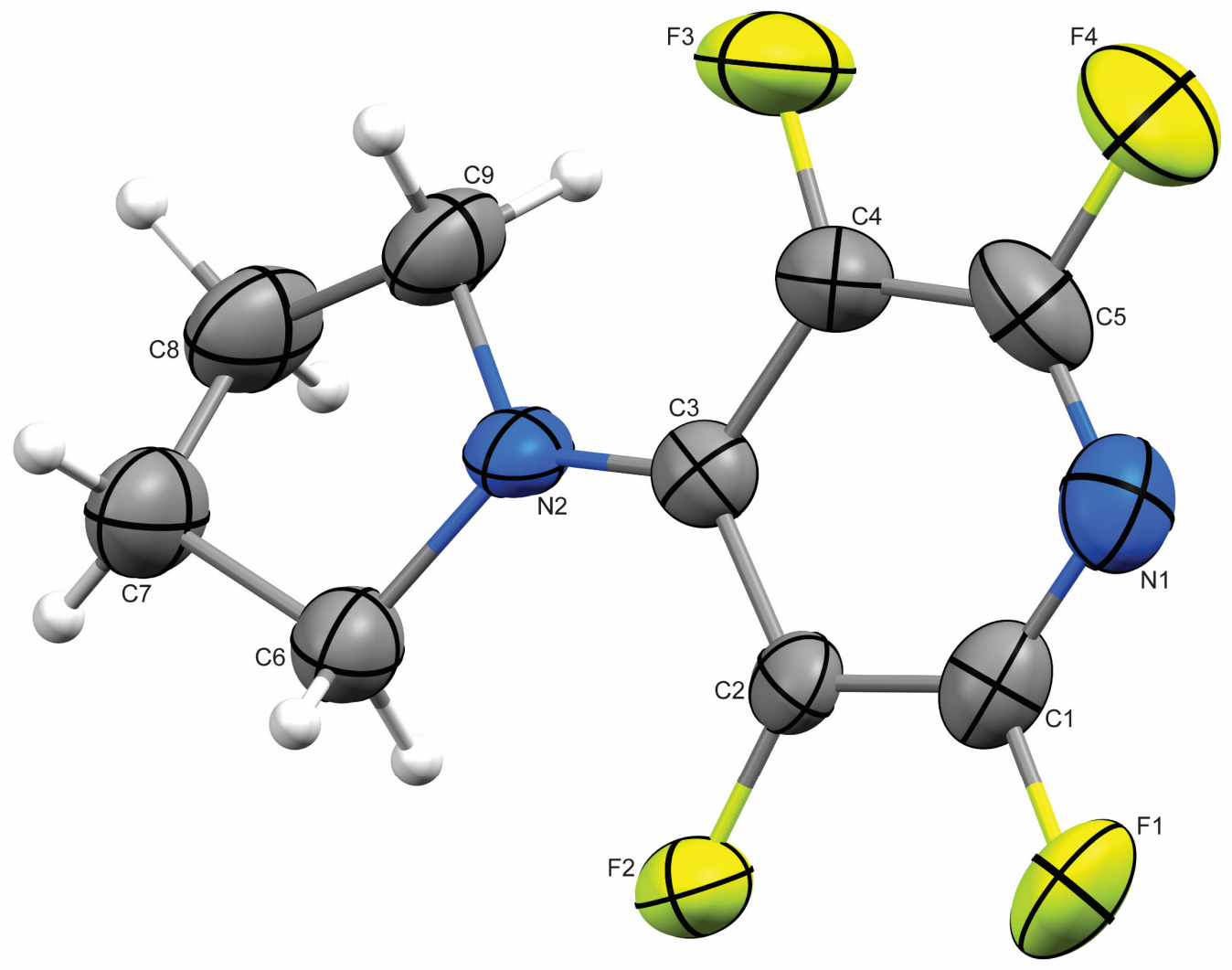

Figure SI40. Molecular stucture of **8**. Thermal ellipsoids are shown at the 50% probability level.

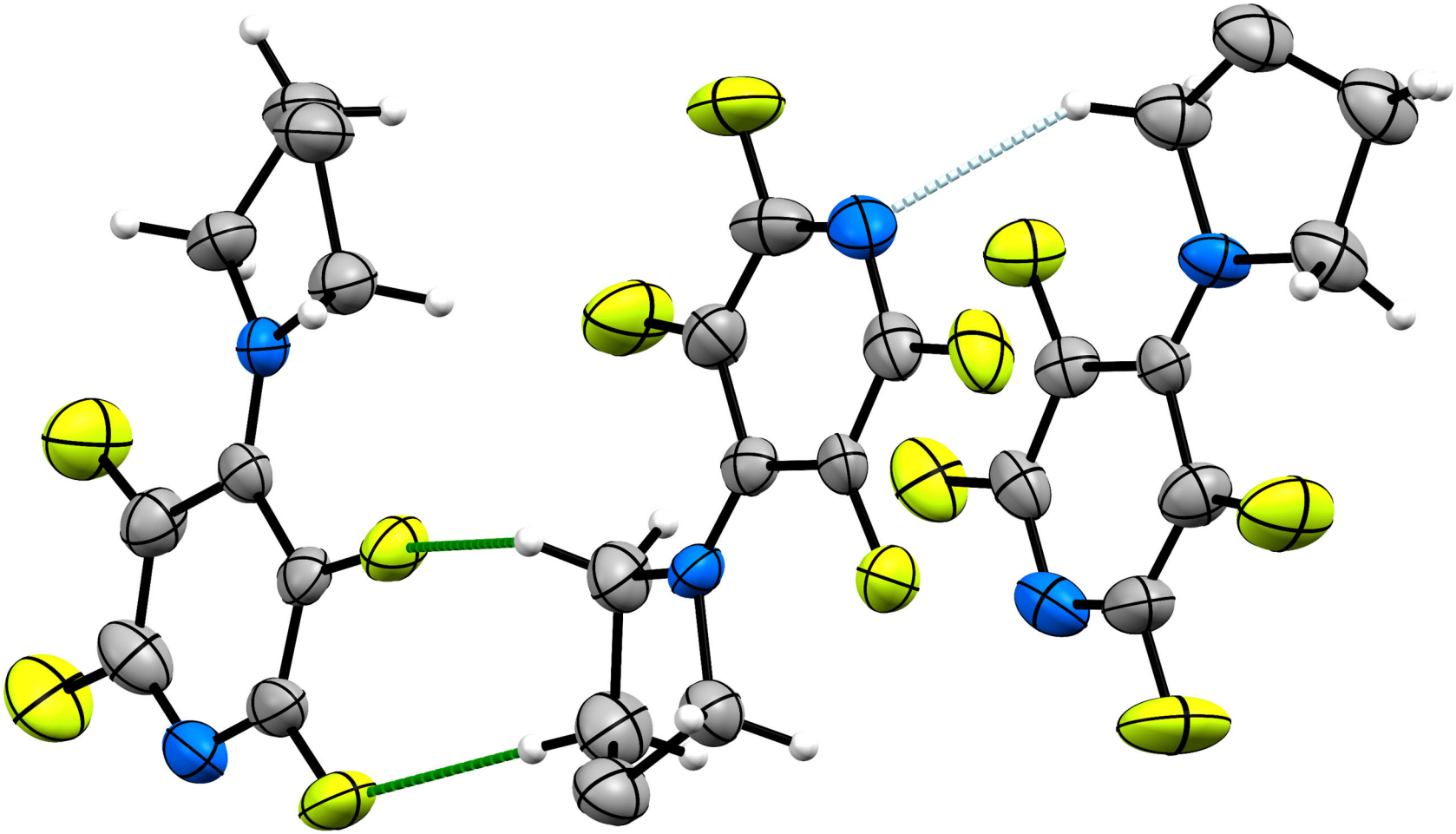

Figure SI41. Solid state packing of **8**. Intermolecular C–H···$N_{pyridine}$ (light blue) and C–H···F (green) interactions are indicated by dashed lines. H atoms, except those bound to donor atoms of the indicated intermolecular interactions, have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

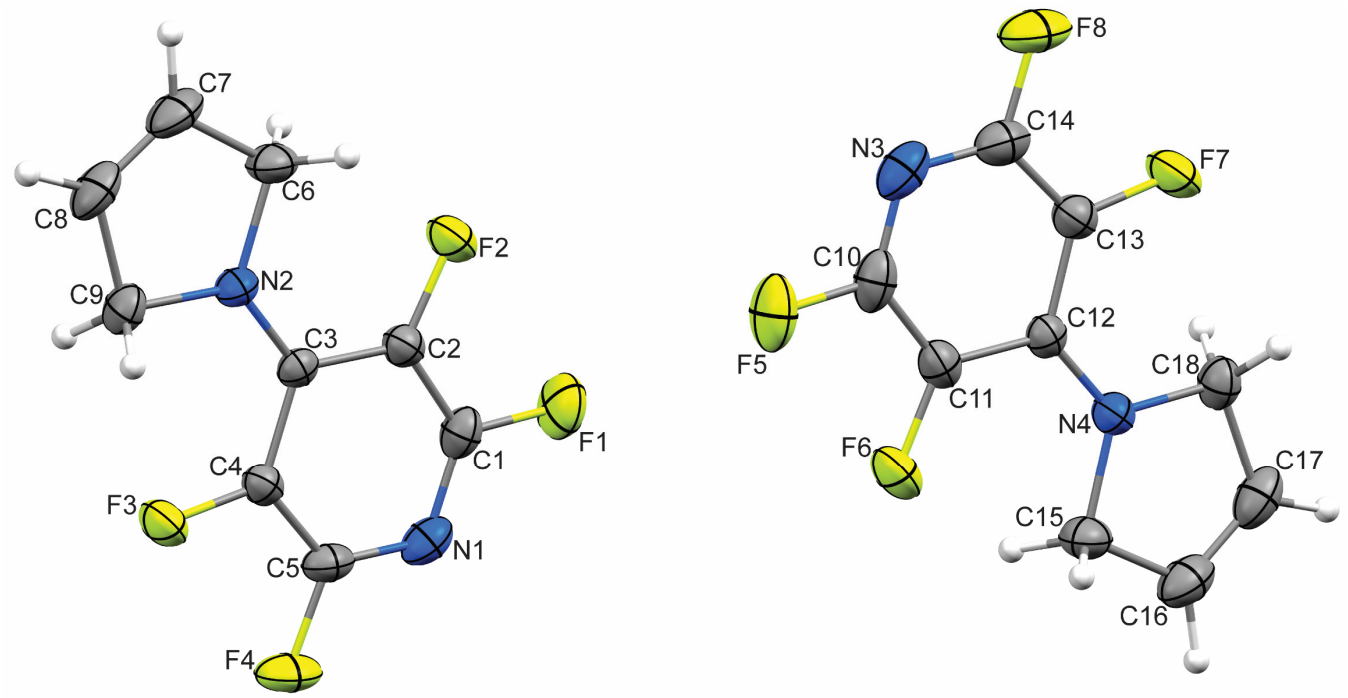

Figure SI42. Molecular stucture of **9**. Thermal ellipsoids are shown at the 50% probability level.

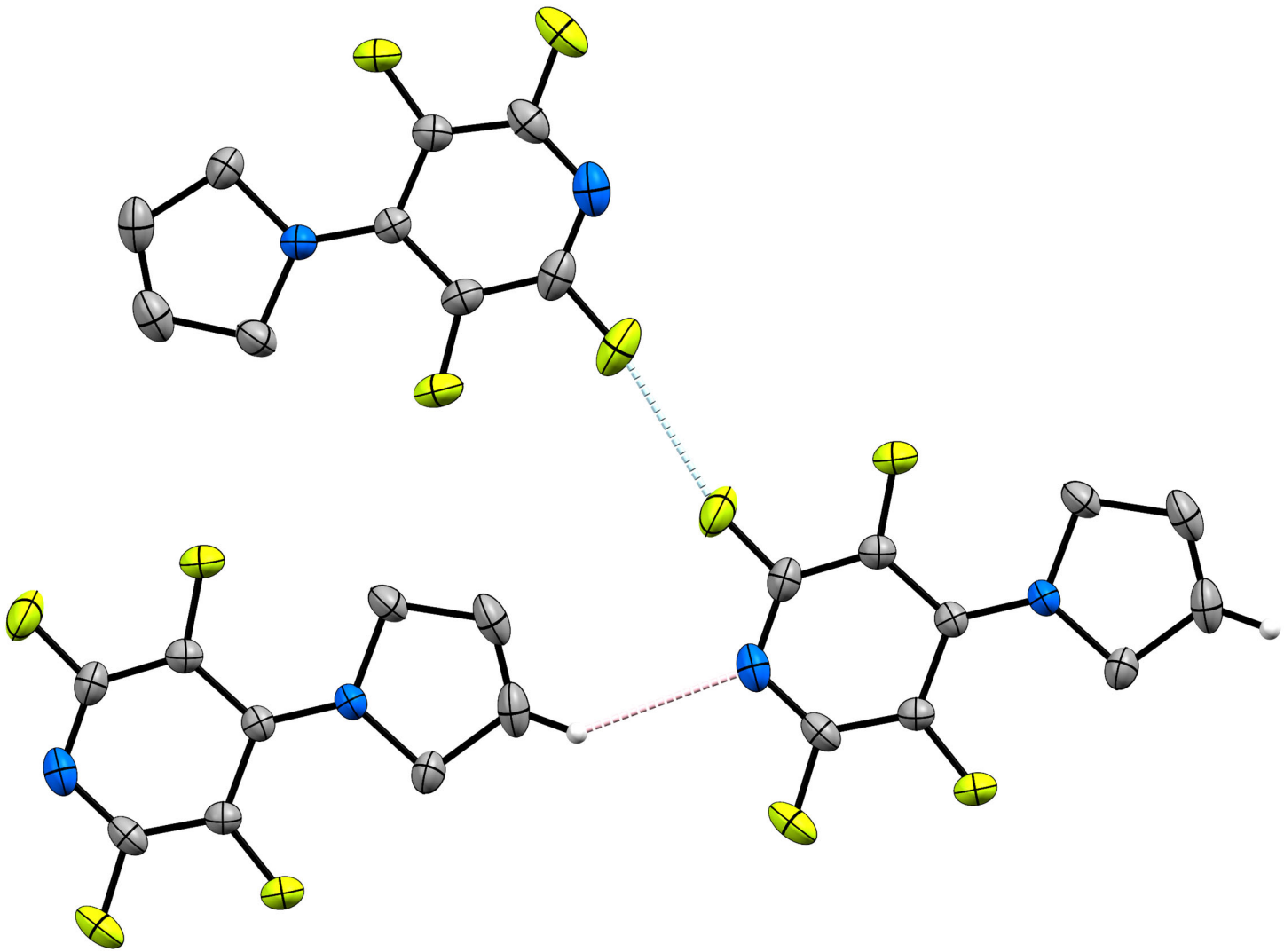

Figure SI43. Solid state packing of **9**. Intermolecular C–H···$N_{pyridine}$ (light blue) and C–F···F–C (pink) interactions are indicated by dashed lines. H atoms, except those bound to donor atoms of the indicated intermolecular interactions, have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

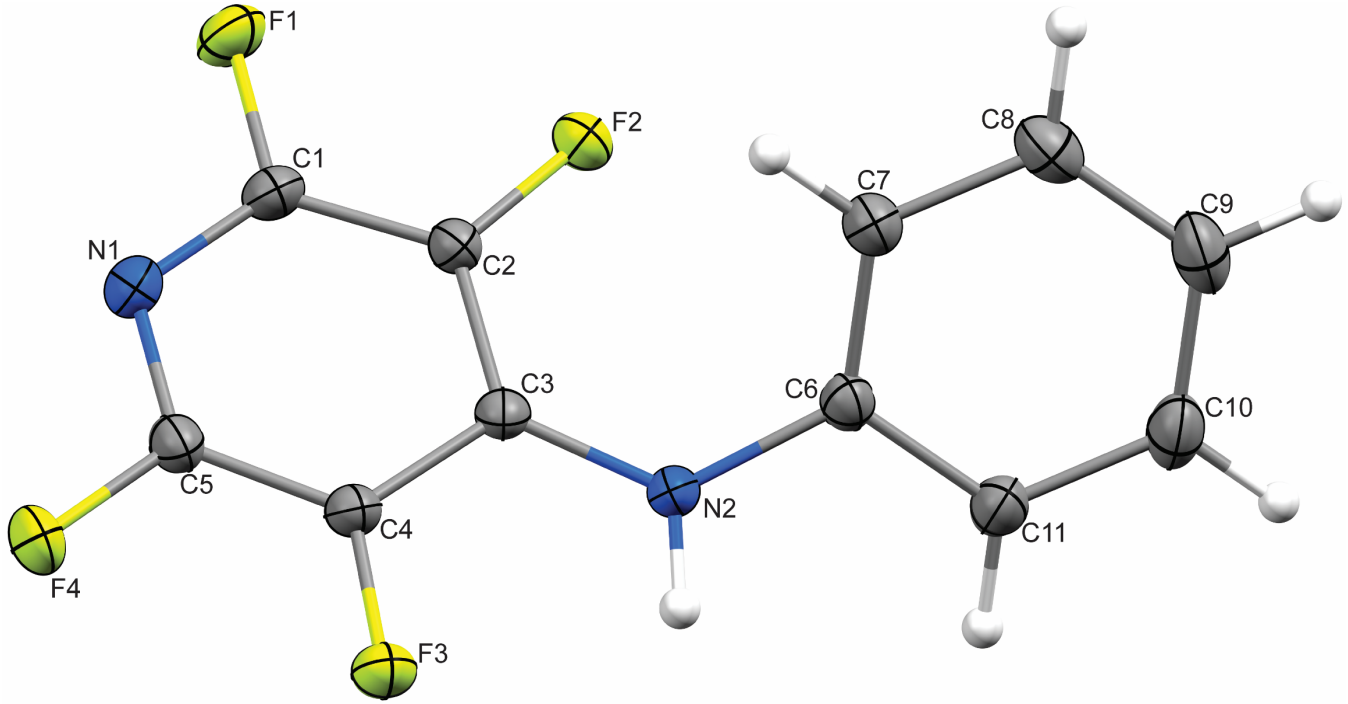

Figure SI44. Molecular stucture of **11**. Thermal ellipsoids are shown at the 50% probability level.

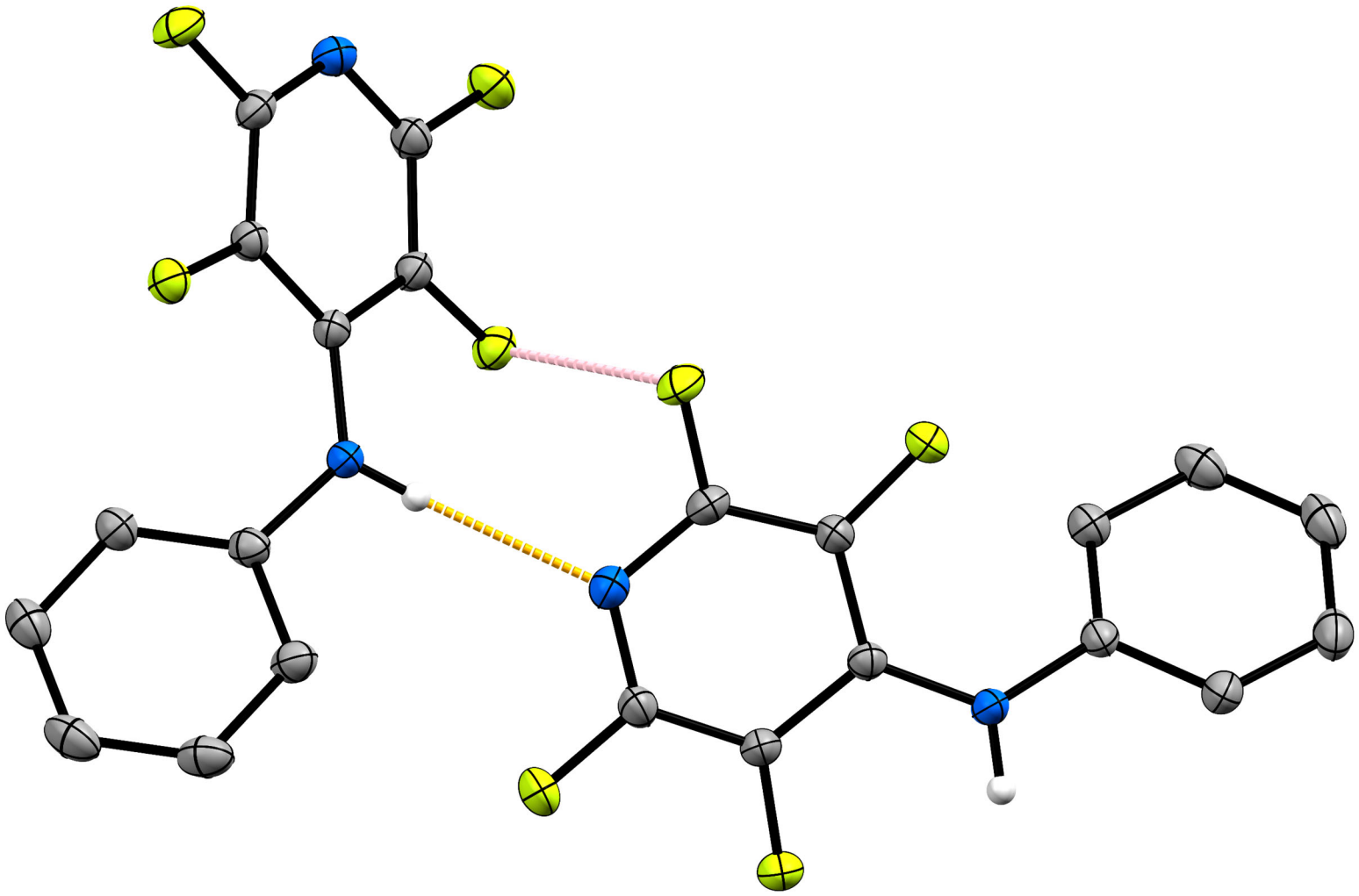

Figure SI45. Solid state packing of **11**. Intermolecular N–H···$N_{pyridine}$ (orange) and C–F···F–C (pink) interactions are indicated by dashed lines. H atoms, except those bound to donor atoms of the indicated intermolecular interactions, have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

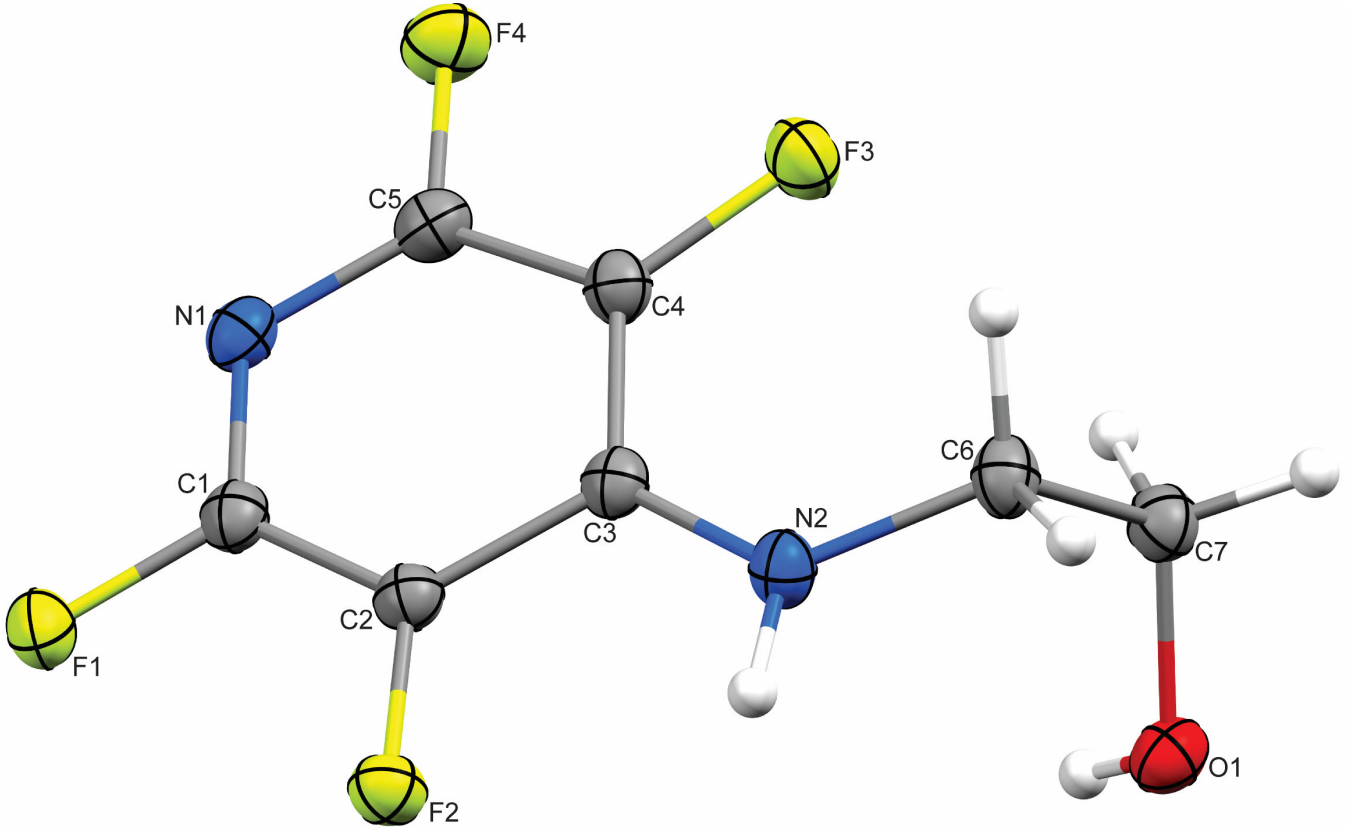

Figure SI46. Molecular stucture of **14**. Thermal ellipsoids are shown at the 50% probability level.

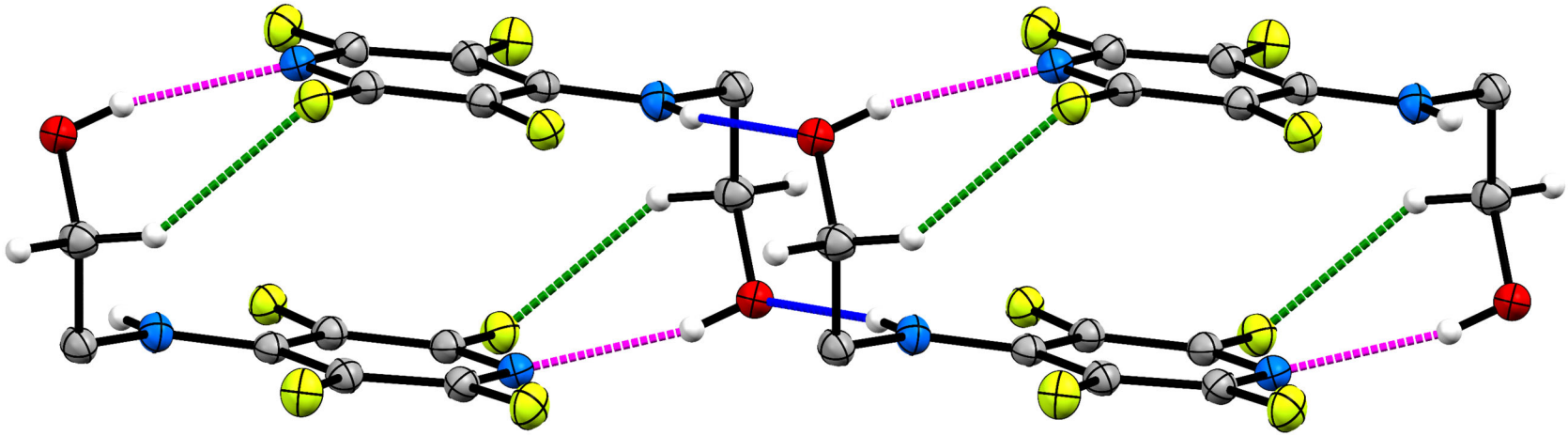

Figure SI47. Solid state packing of **14**. Intermolecular O–H···$N_{pyridine}$ (magenta), N–H···O (blue) and C–H···F (green) interactions are indicated by dashed lines. H atoms, except those bound to donor atoms of the indicated intermolecular interactions, have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

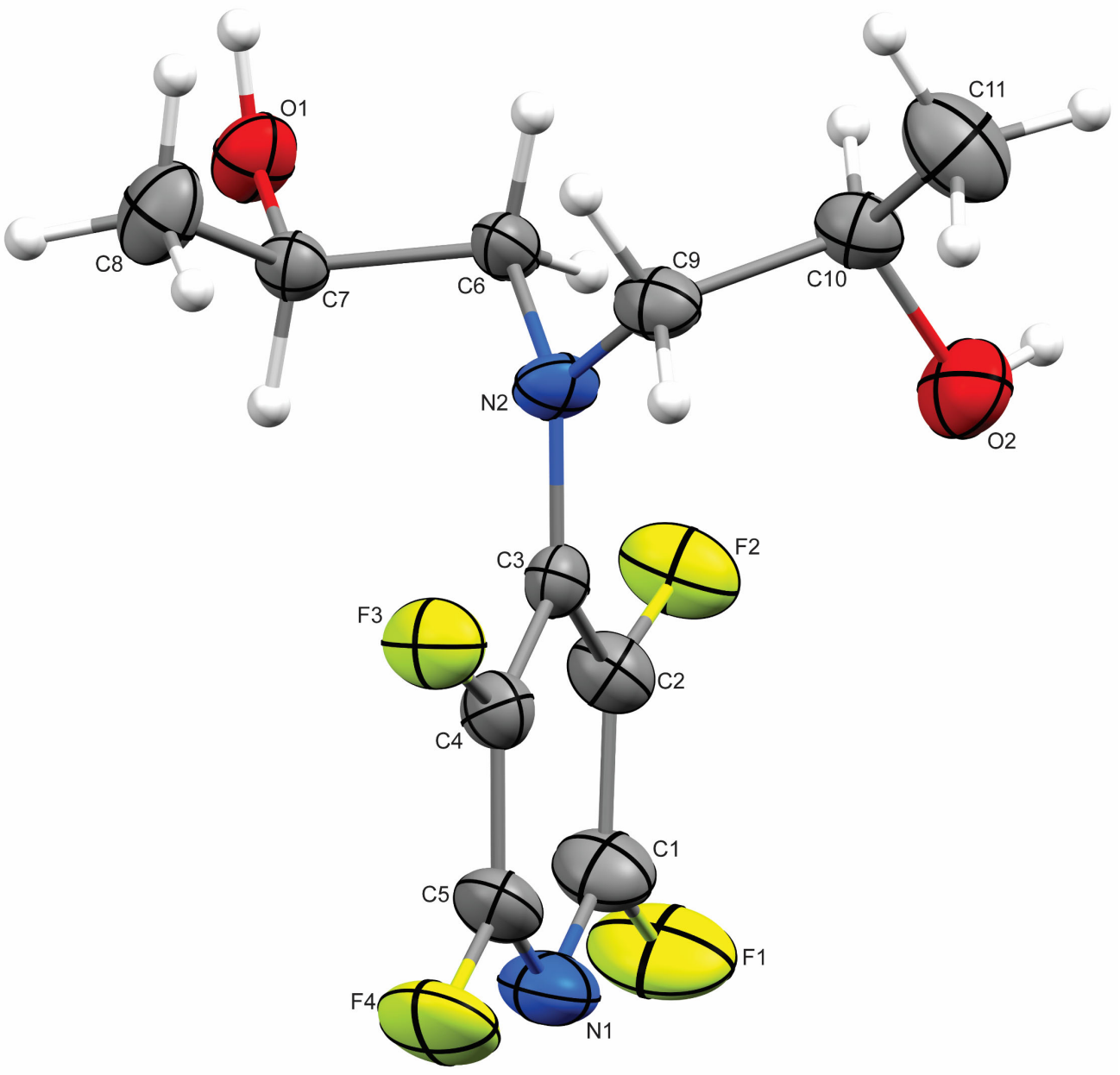

Figure SI48. Molecular stucture of **15**. Thermal ellipsoids are shown at the 50% probability level.

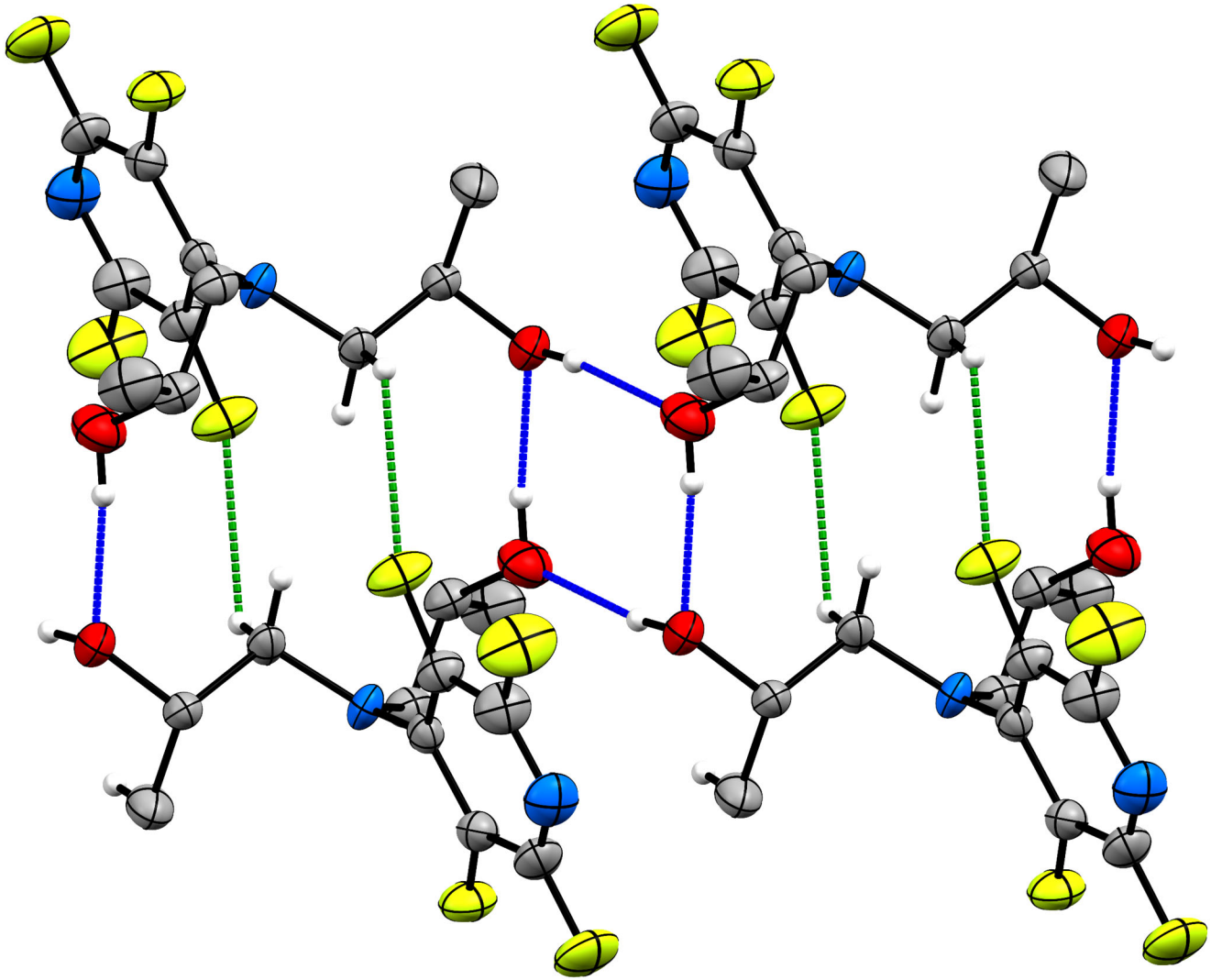

Figure SI49. Solid state packing of **15**. Intermolecular O–H···O (blue) and O–H···F (green) interactions are indicated by dashed lines. H atoms, except those bound to donor atoms of the indicated intermolecular interactions, have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

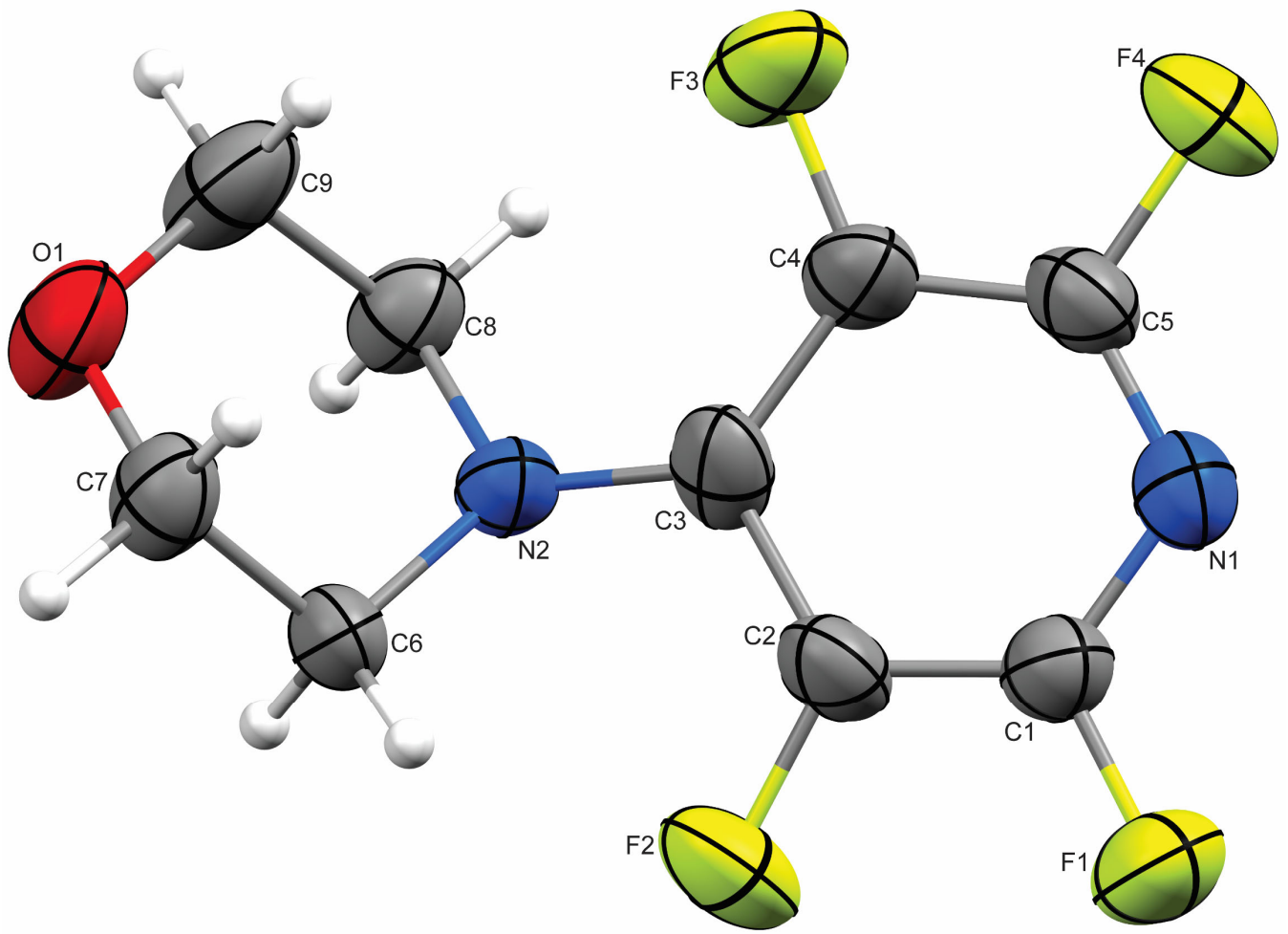

Figure SI50. Molecular stucture of **16**. Thermal ellipsoids are shown at the 50% probability level

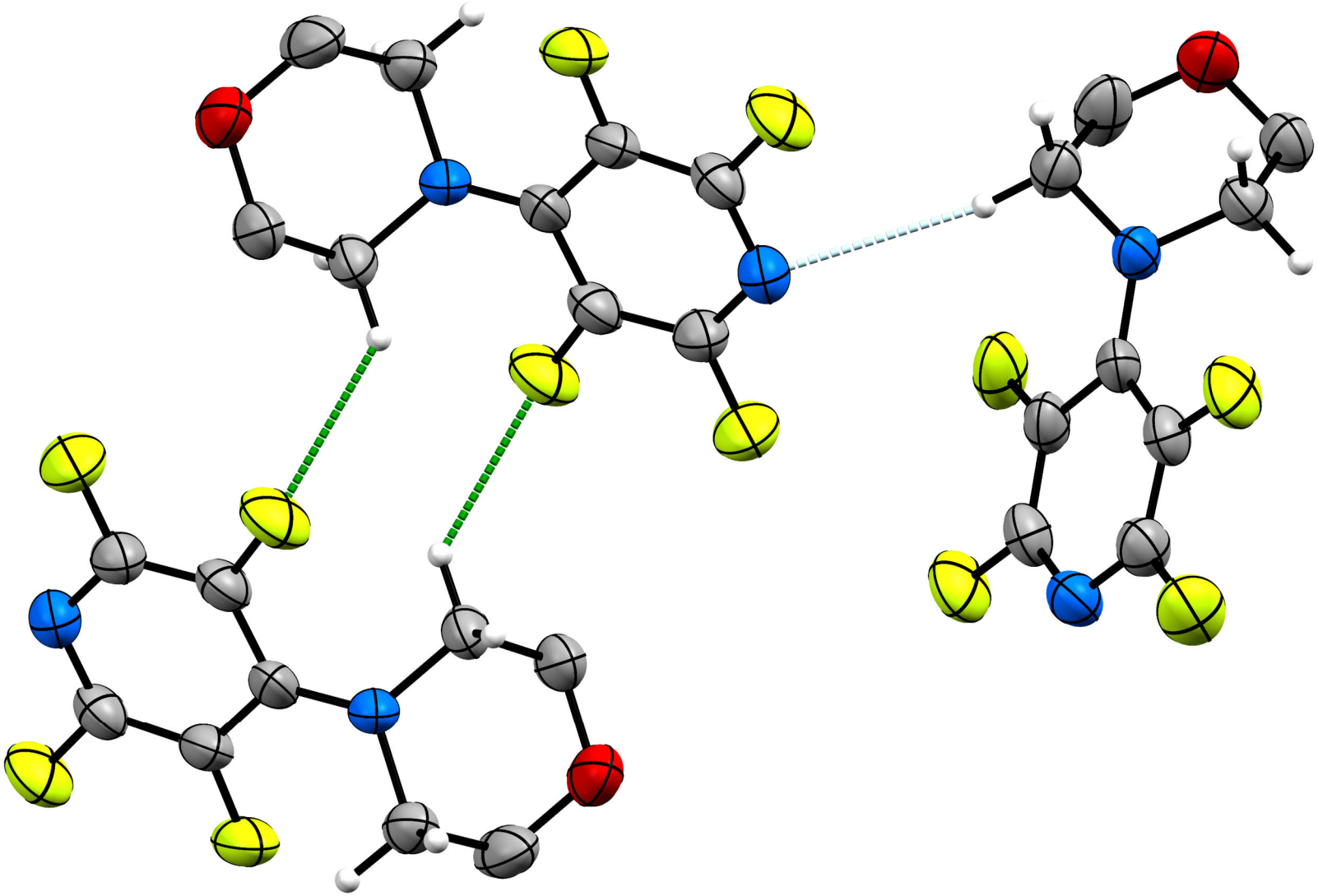

Figure SI51. Solid state packing of **16**. Intermolecular C–H···$N_{pyridine}$ (light blue) and O–H···F (green) interactions are indicated by dashed lines. H atoms, except those bound to donor atoms of the indicated intermolecular interactions, have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

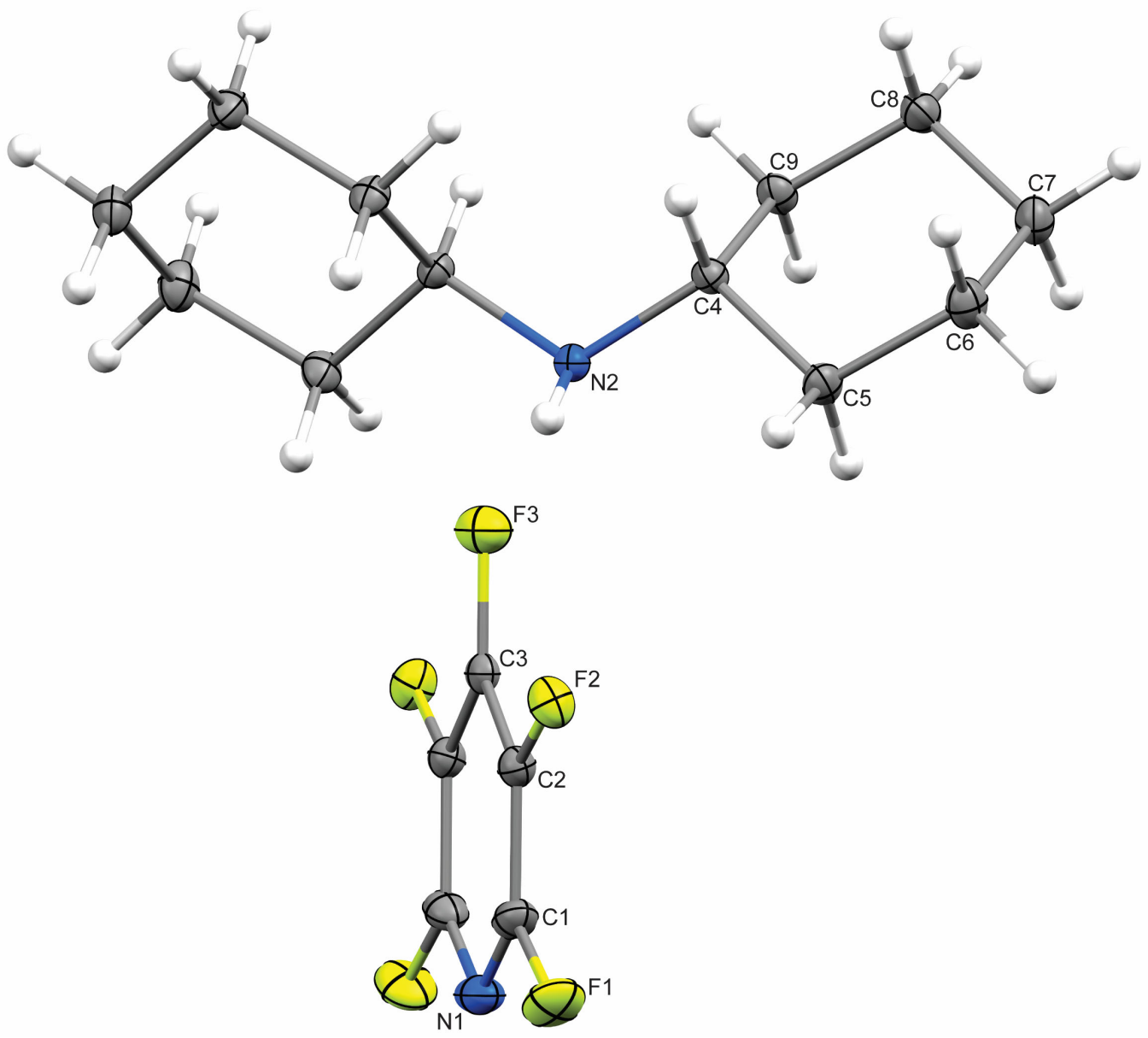

Figure SI52. Molecular stucture of **18**. Thermal ellipsoids are shown at the 50% probability level

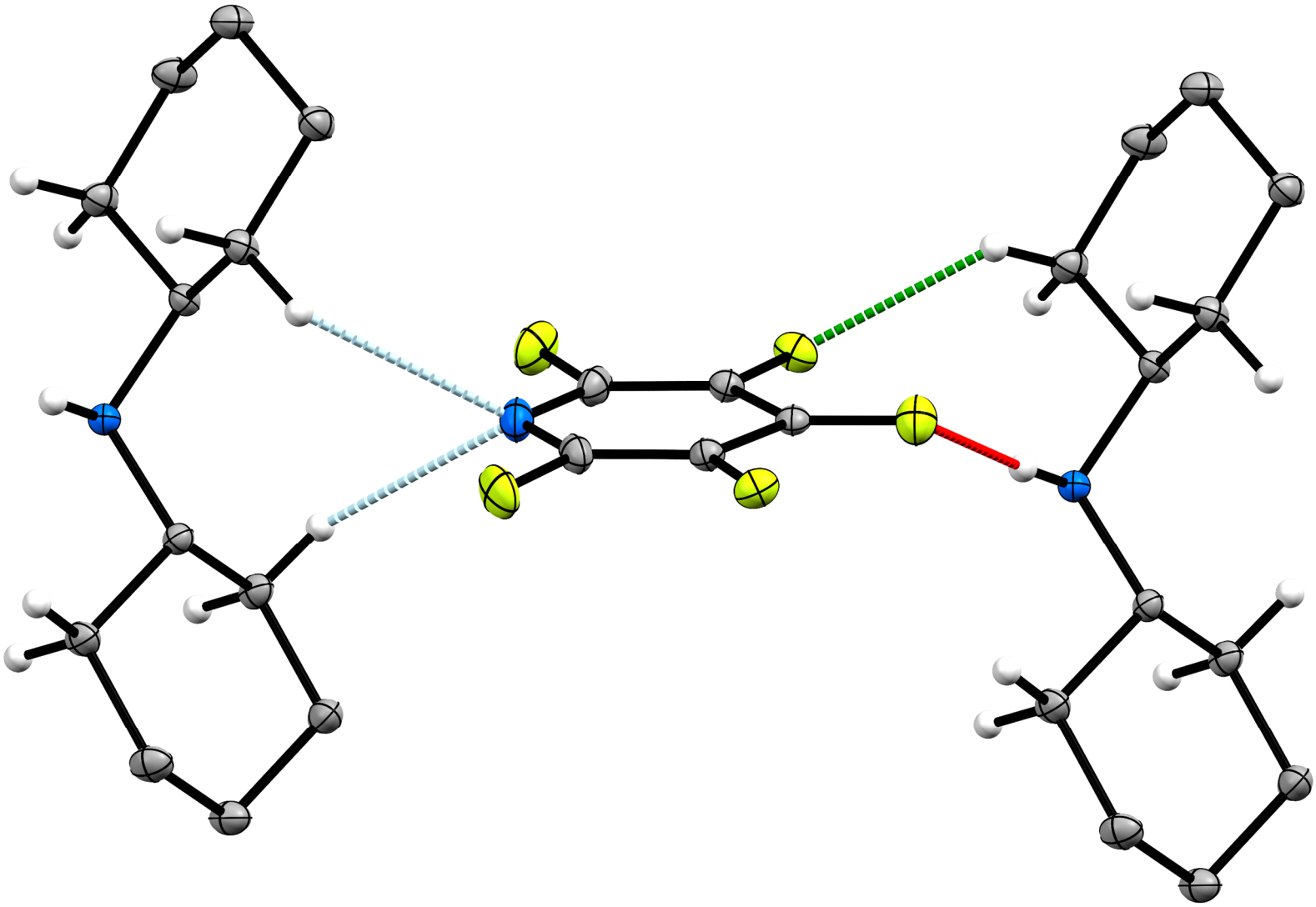

Figure SI53. Solid state packing of **18**. Intermolecular C–H···$N_{pyridine}$ (light blue), N–H···F (red), and C–H···F (green) interactions are indicated by dashed lines. H atoms, except those bound to donor atoms of the indicated intermolecular interactions, have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

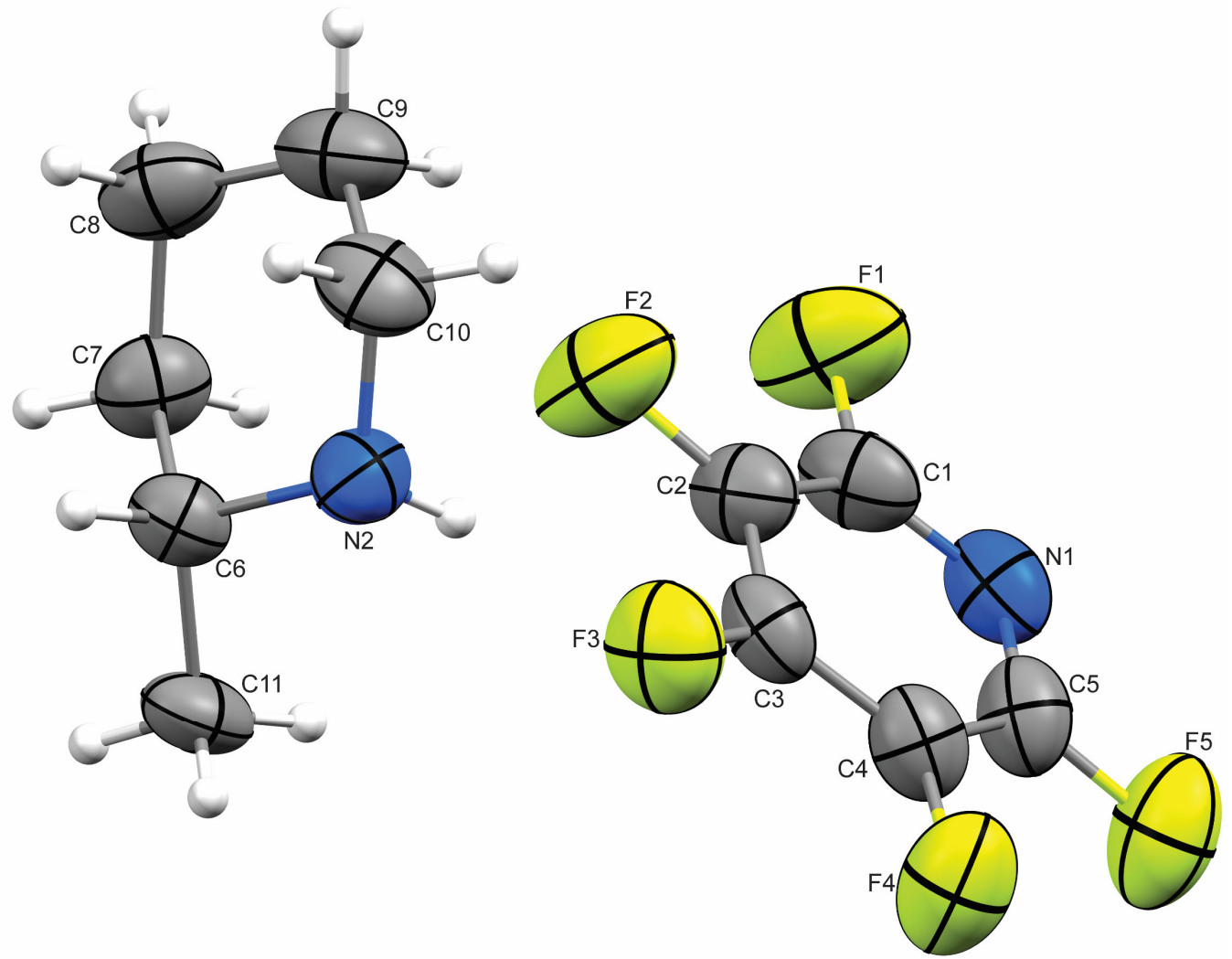

Figure SI54. Molecular stucture of **19**. Thermal ellipsoids are shown at the 50% probability level

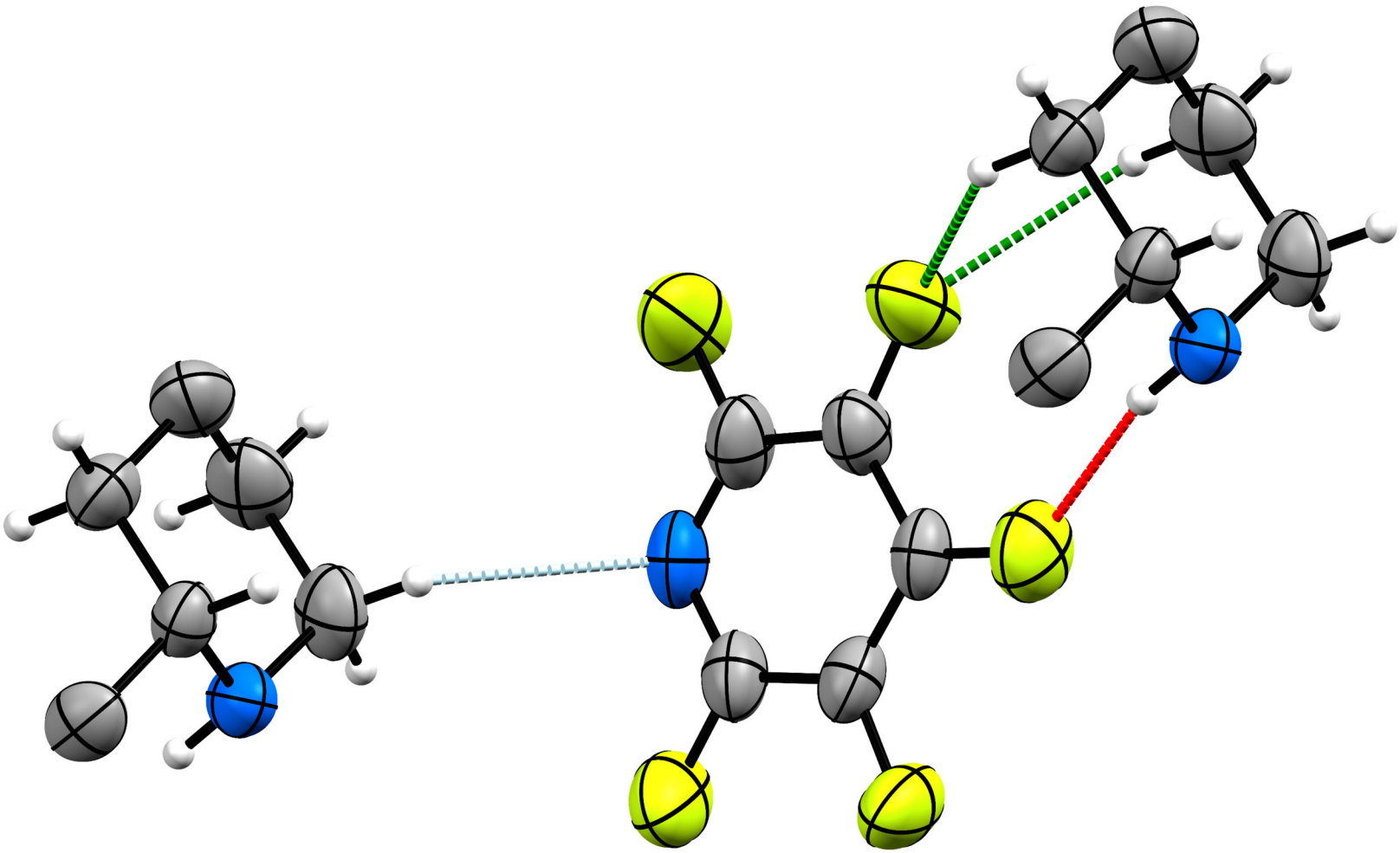

Figure SI55. Solid state packing of **19**. Intermolecular C–H···$N_{pyridine}$ (light blue), N–H···F (red), and C–H···F (green) interactions are indicated by dashed lines. H atoms, except those bound to donor atoms of the indicated intermolecular interactions, have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

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