Supporting Information

A 6'-Fluoro-Substituent in Bicyclo-DNA Increases Affinity to Complementary RNA Presumably by CF---HC Pseudohydrogen Bonds

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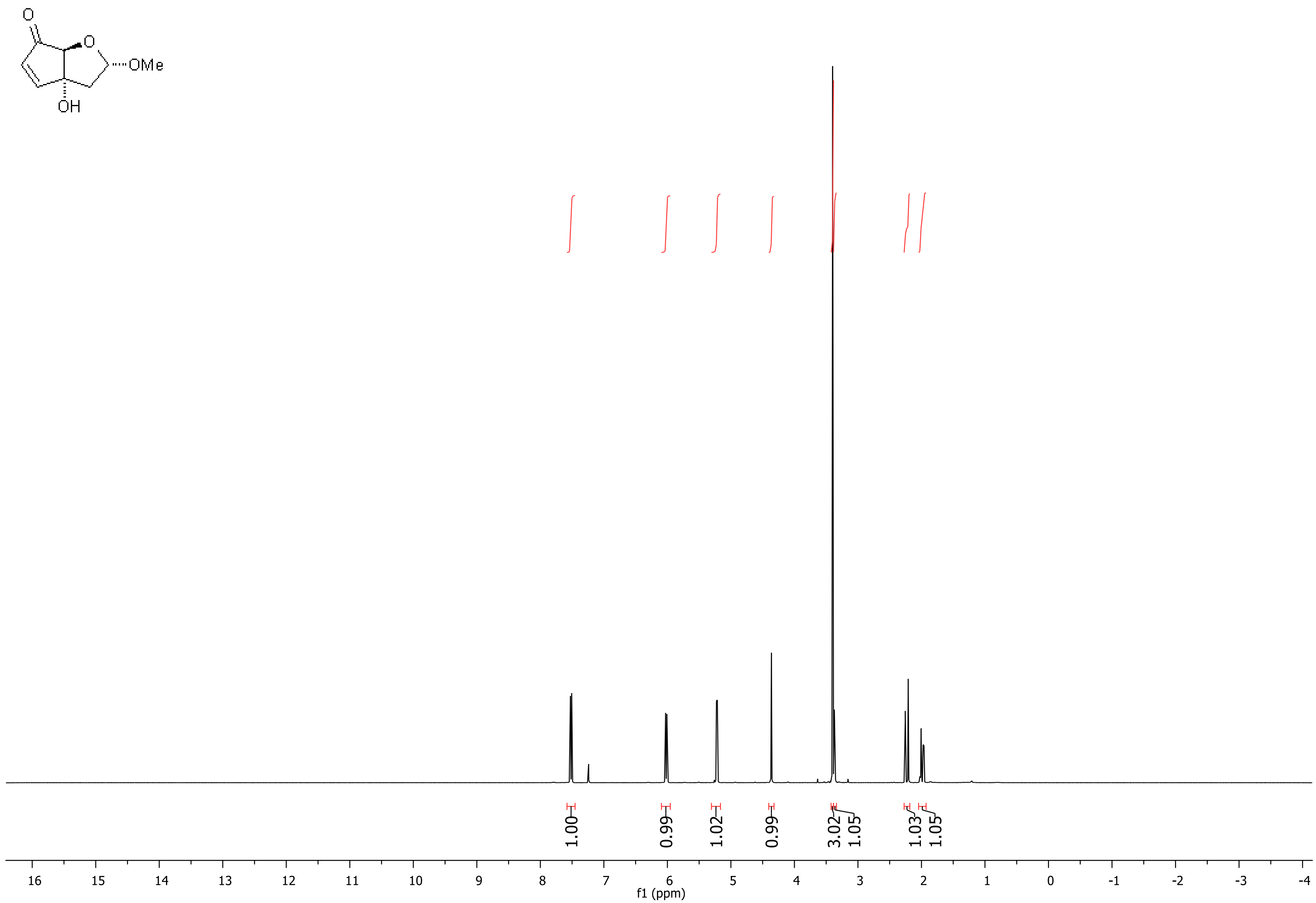


Figure S1: ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **2**

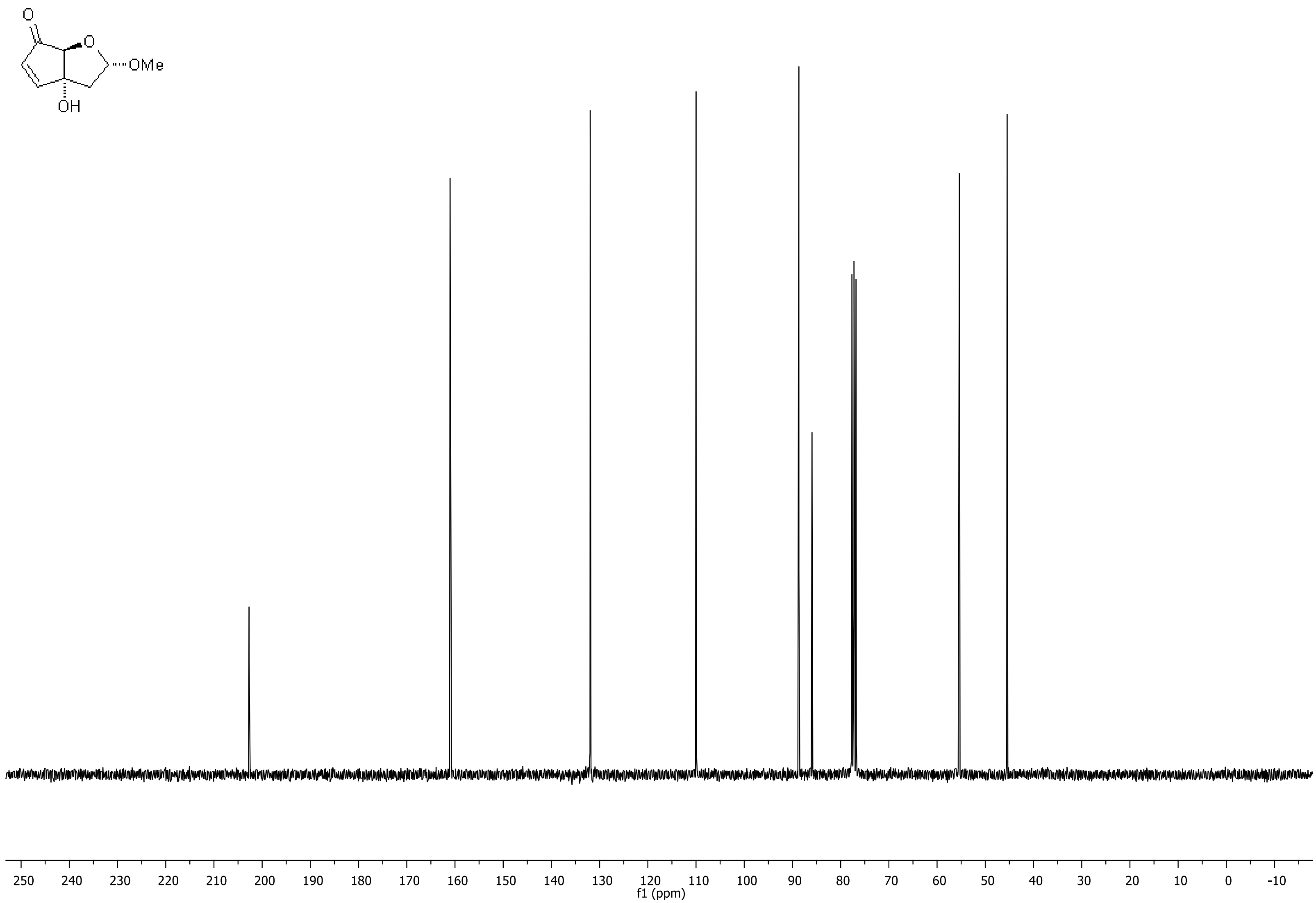


Figure S2: ^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **2**

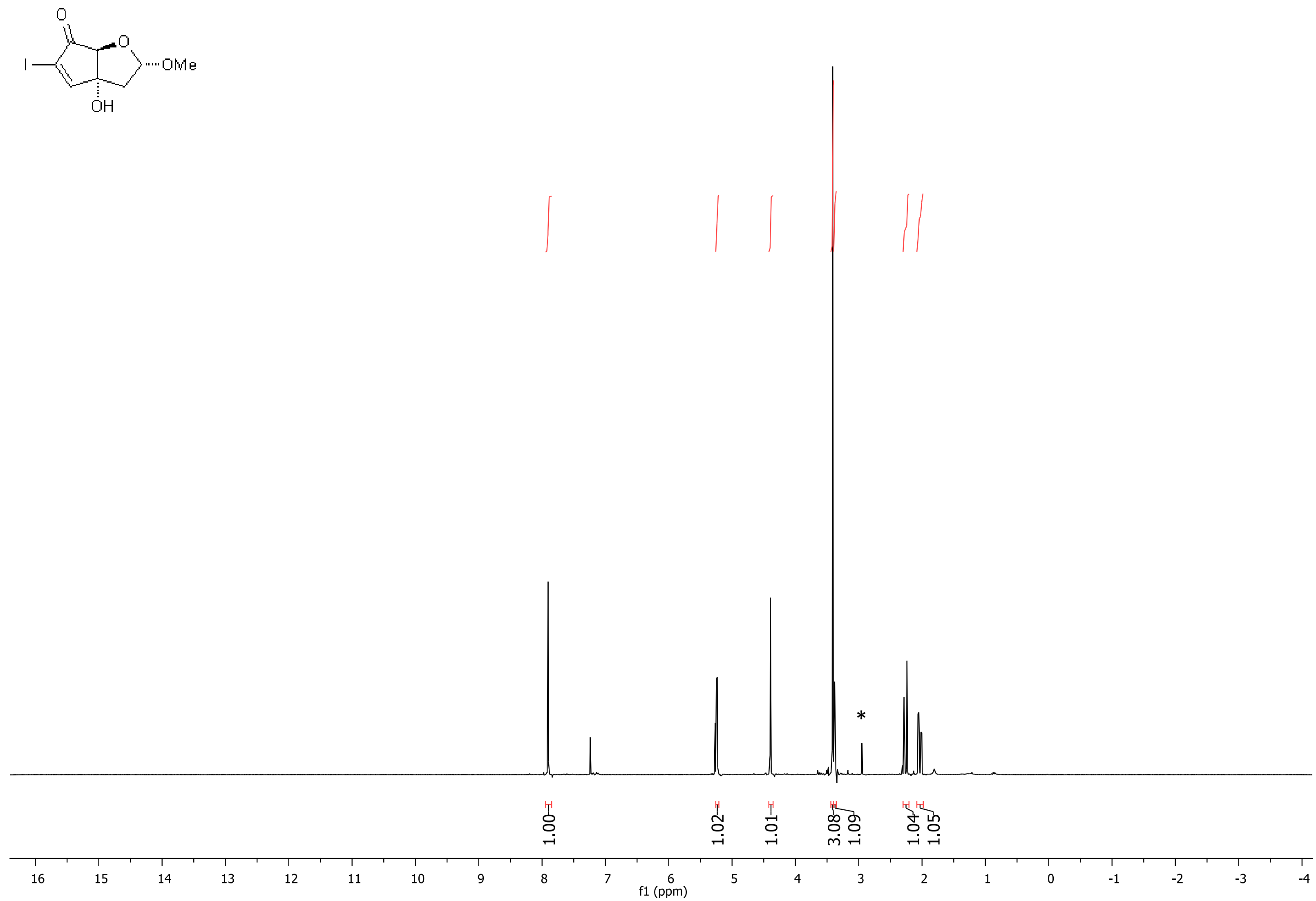
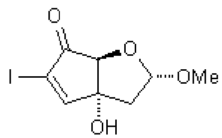


Figure S3: ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **3** (* Unknown impurity)



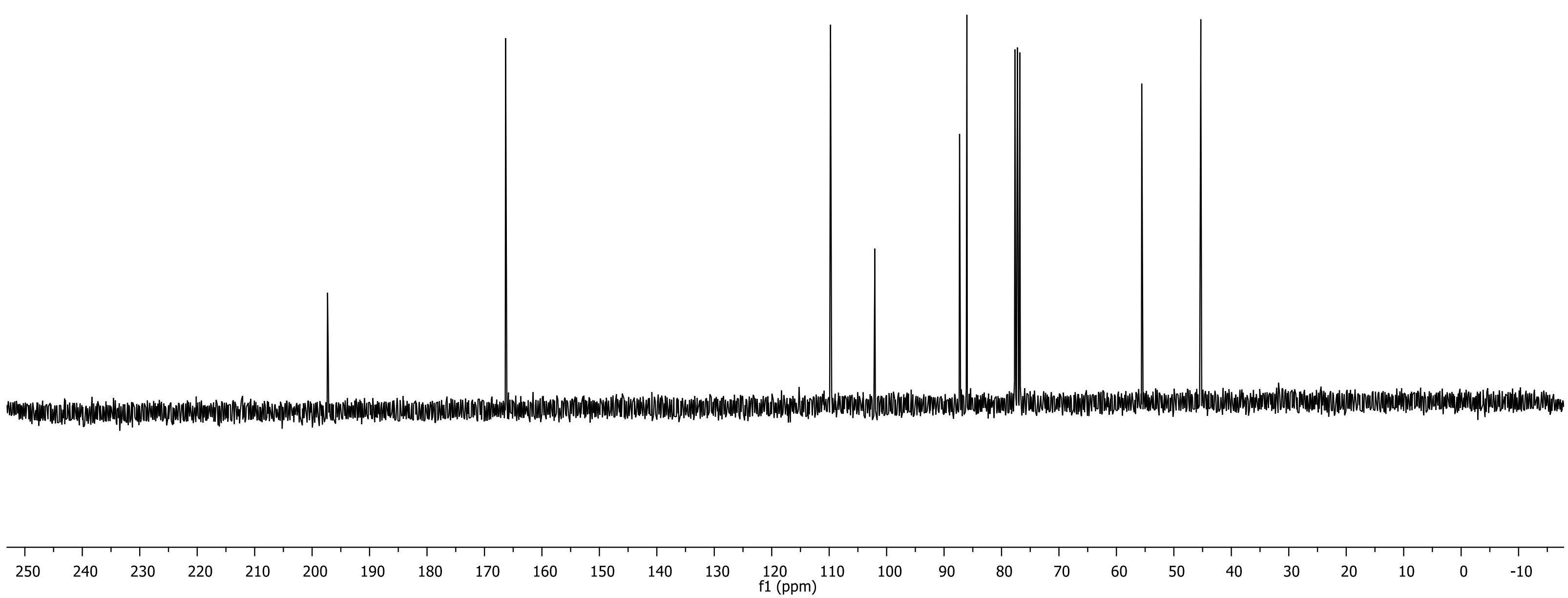


Figure S4: ^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **3**

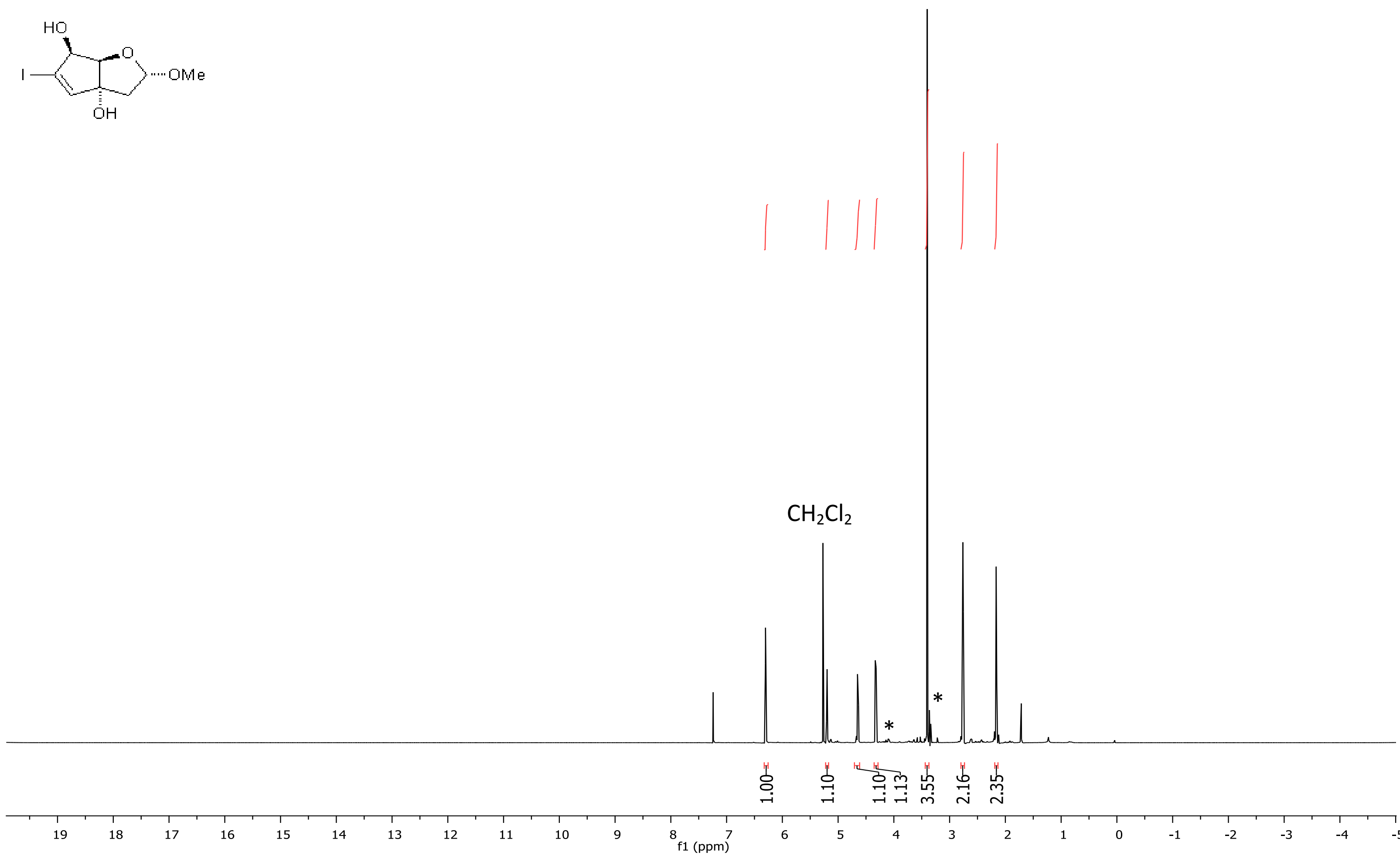
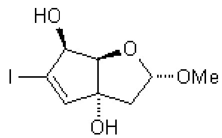


Figure S5: ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **4** (* Unknown impurities)



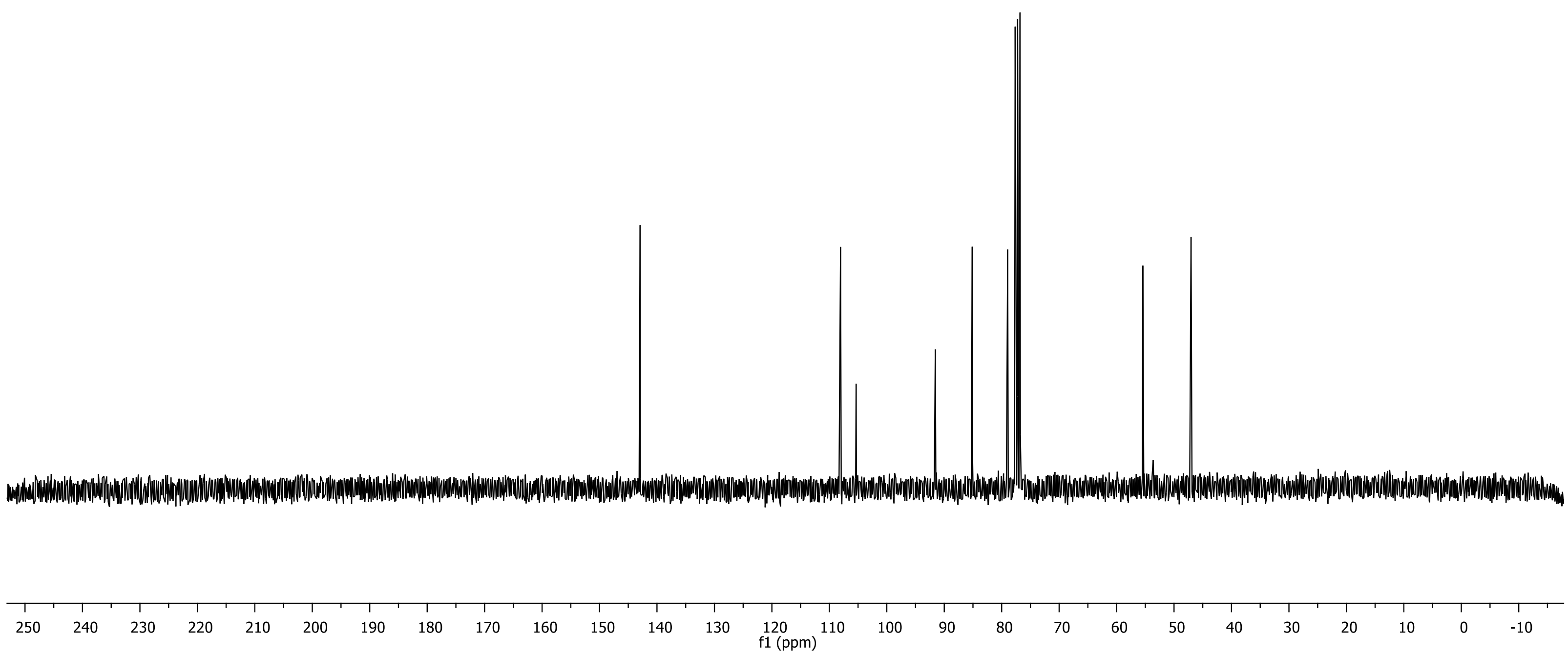


Figure S6: ^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **4**

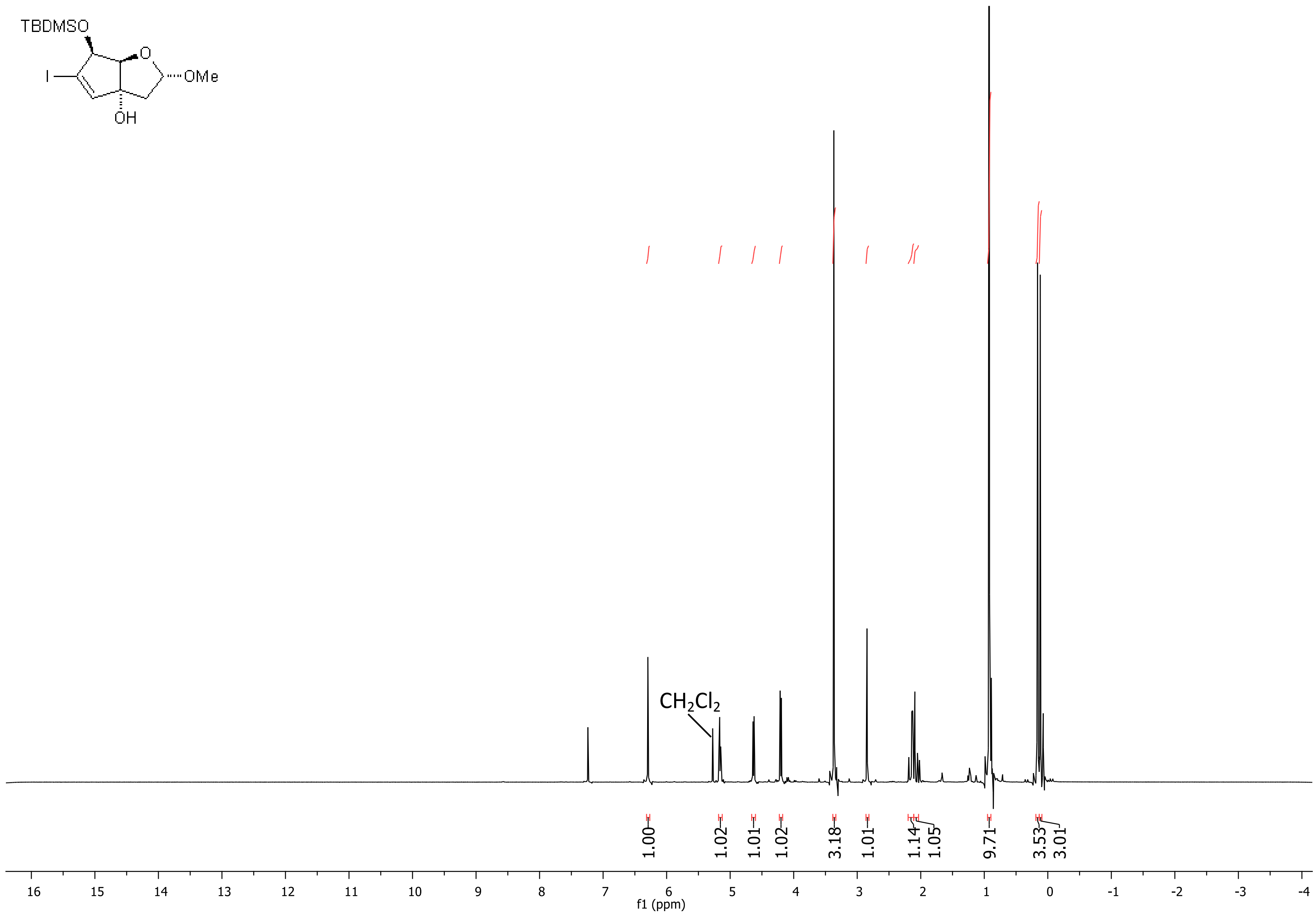


Figure S7: ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **5**

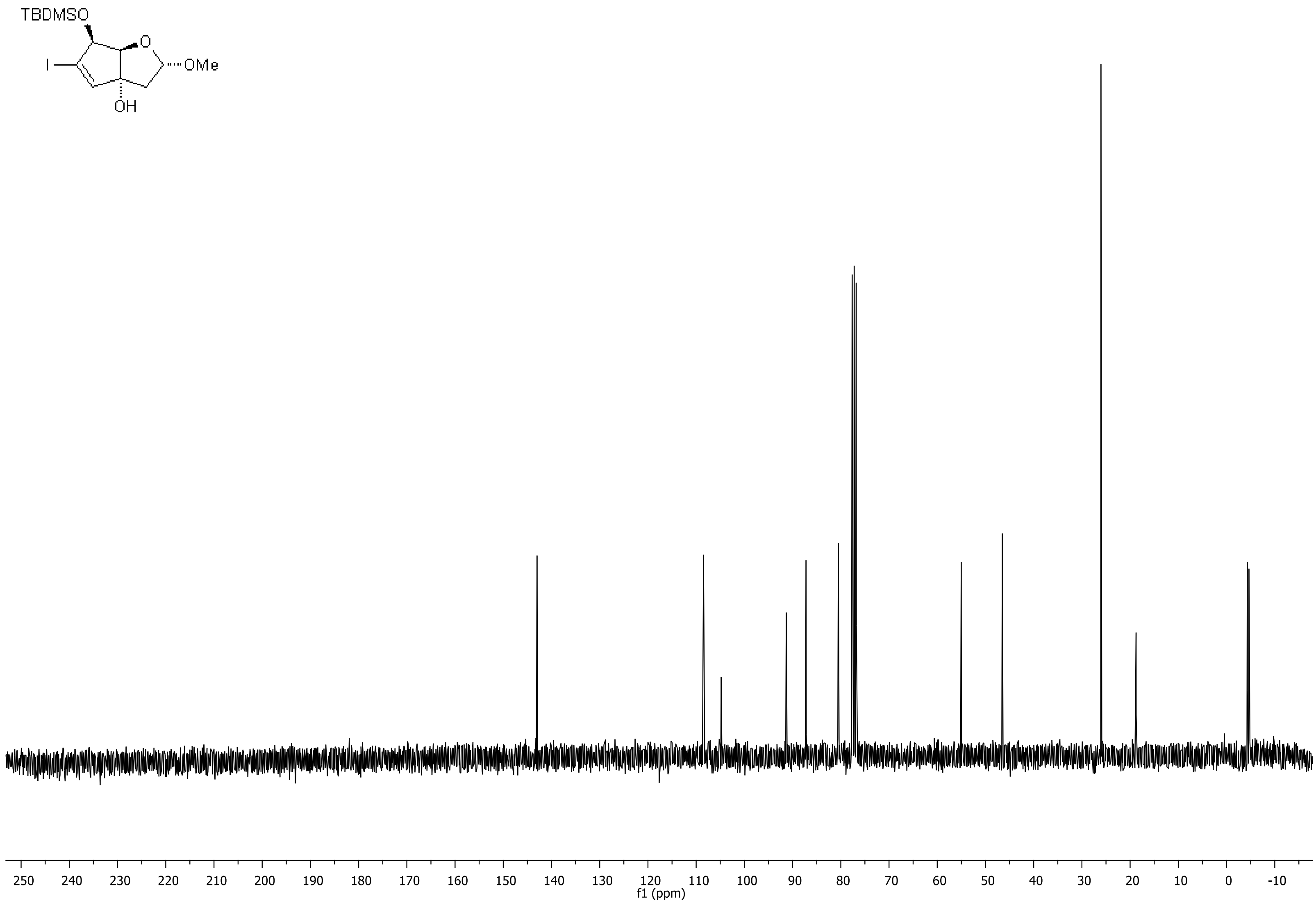


Figure S8: ^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **5**

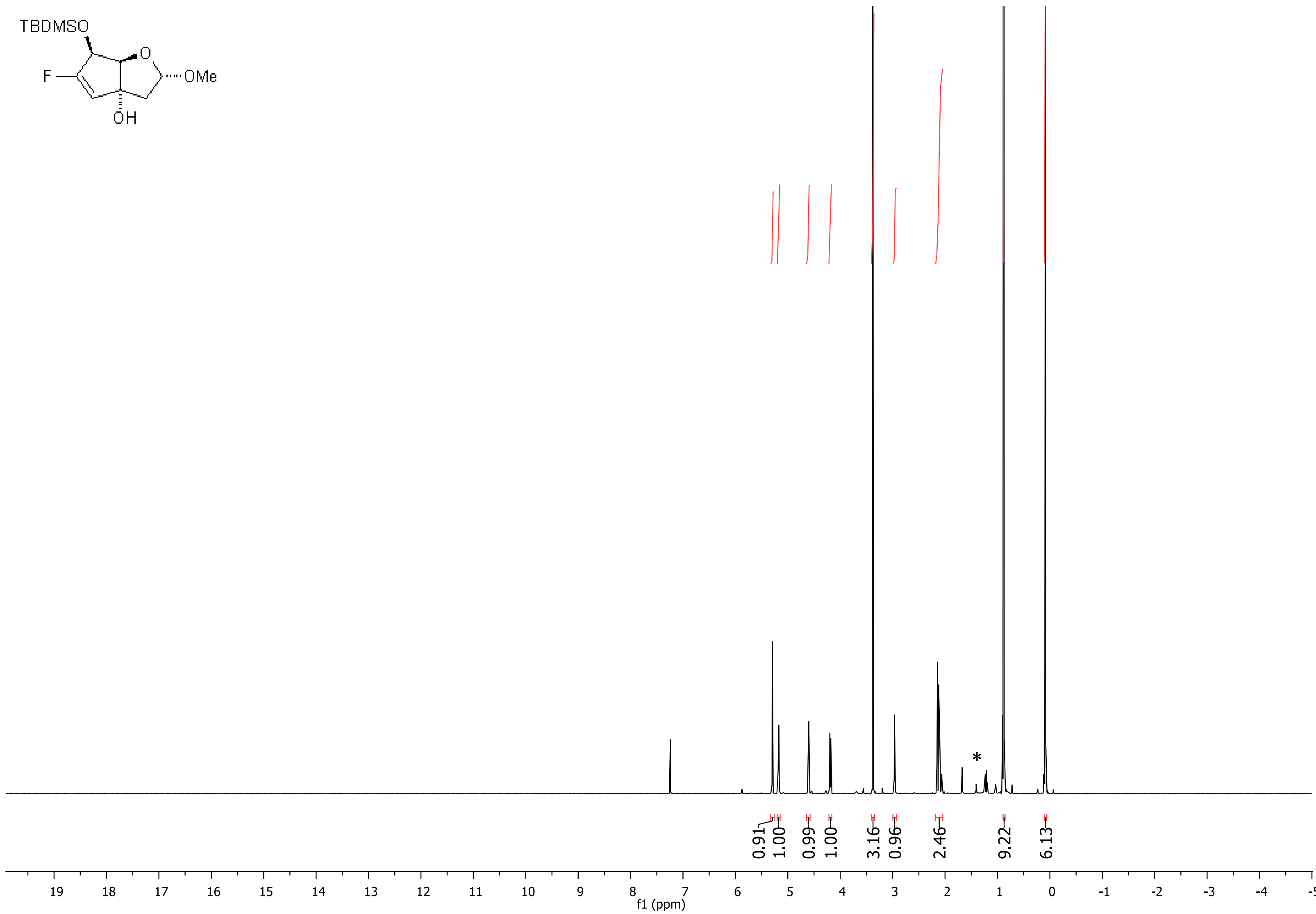


Figure S9: ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **6** (* unknown impurities).

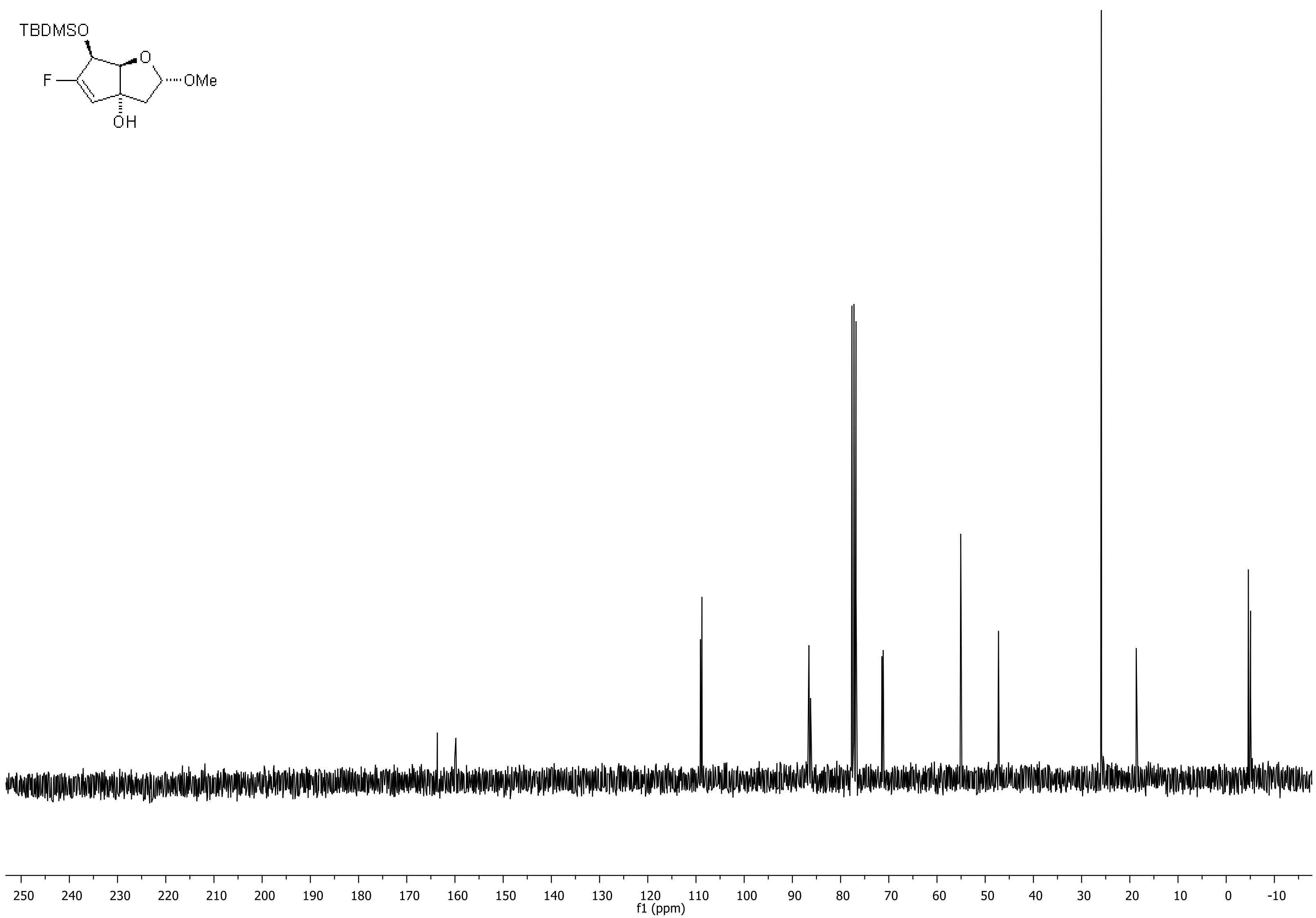


Figure S10: ^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **6**

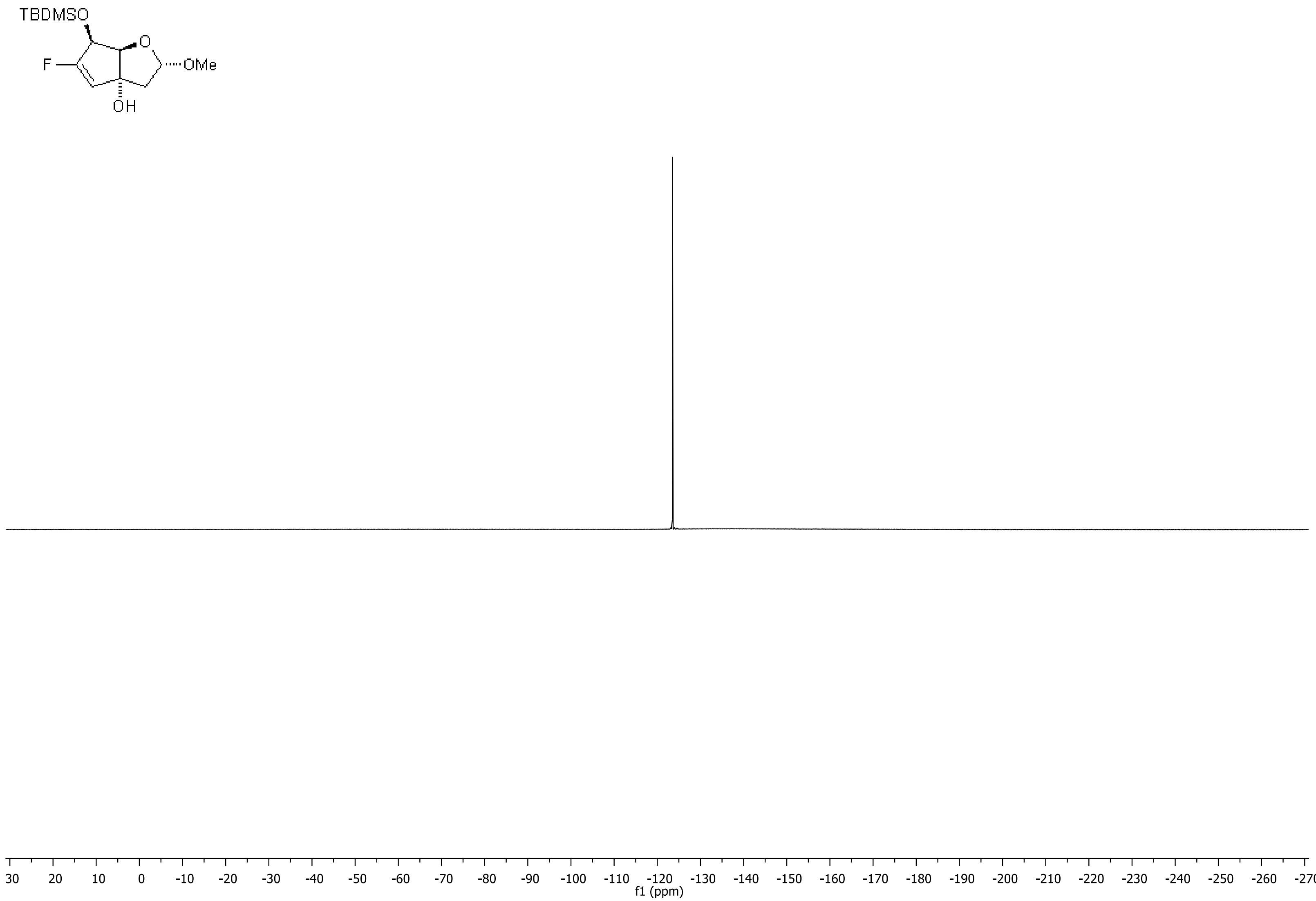


Figure S11: ^{19}F NMR ($CDCl_3$, 376 MHz) spectrum of **6**

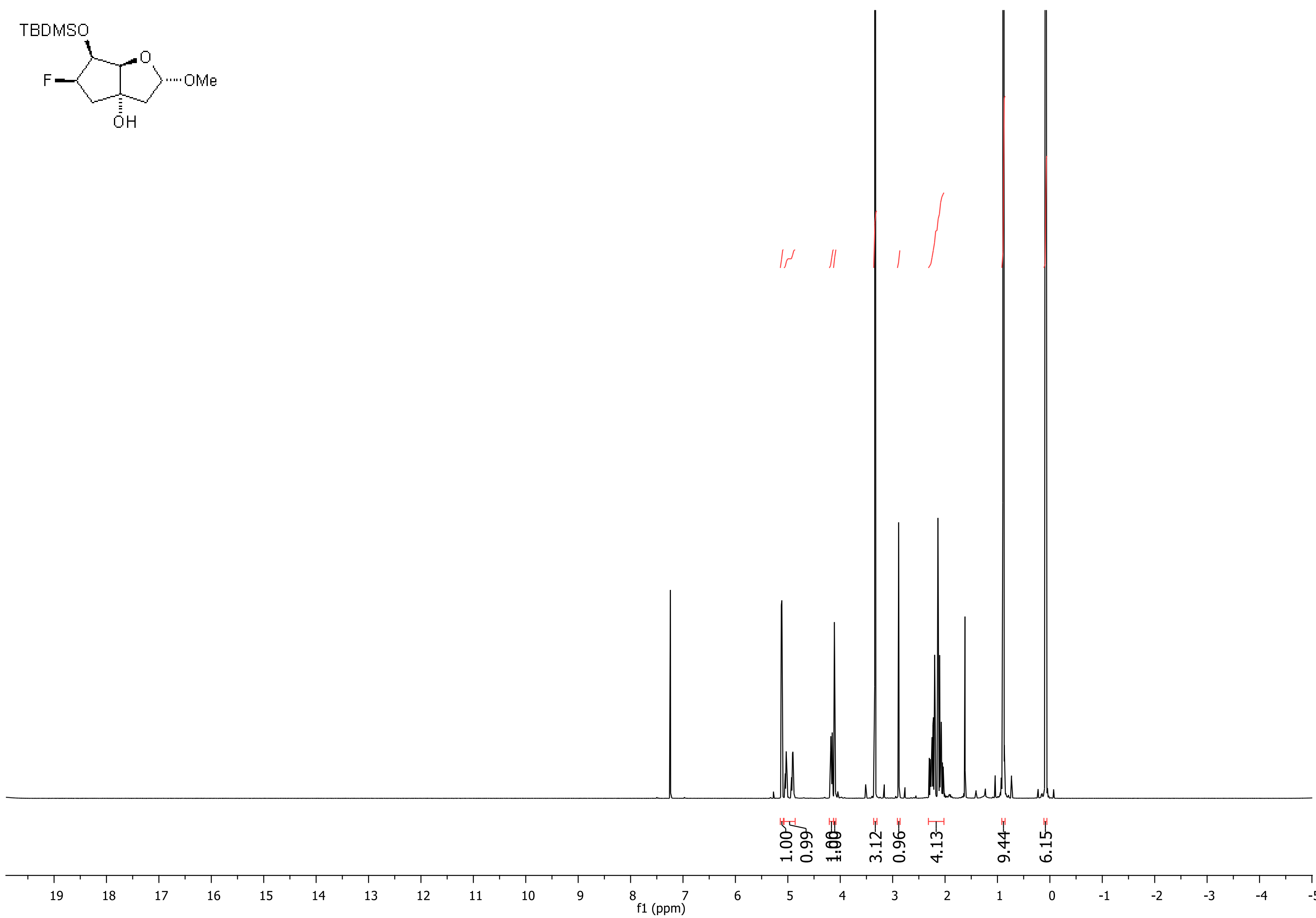


Figure S12: ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **7**

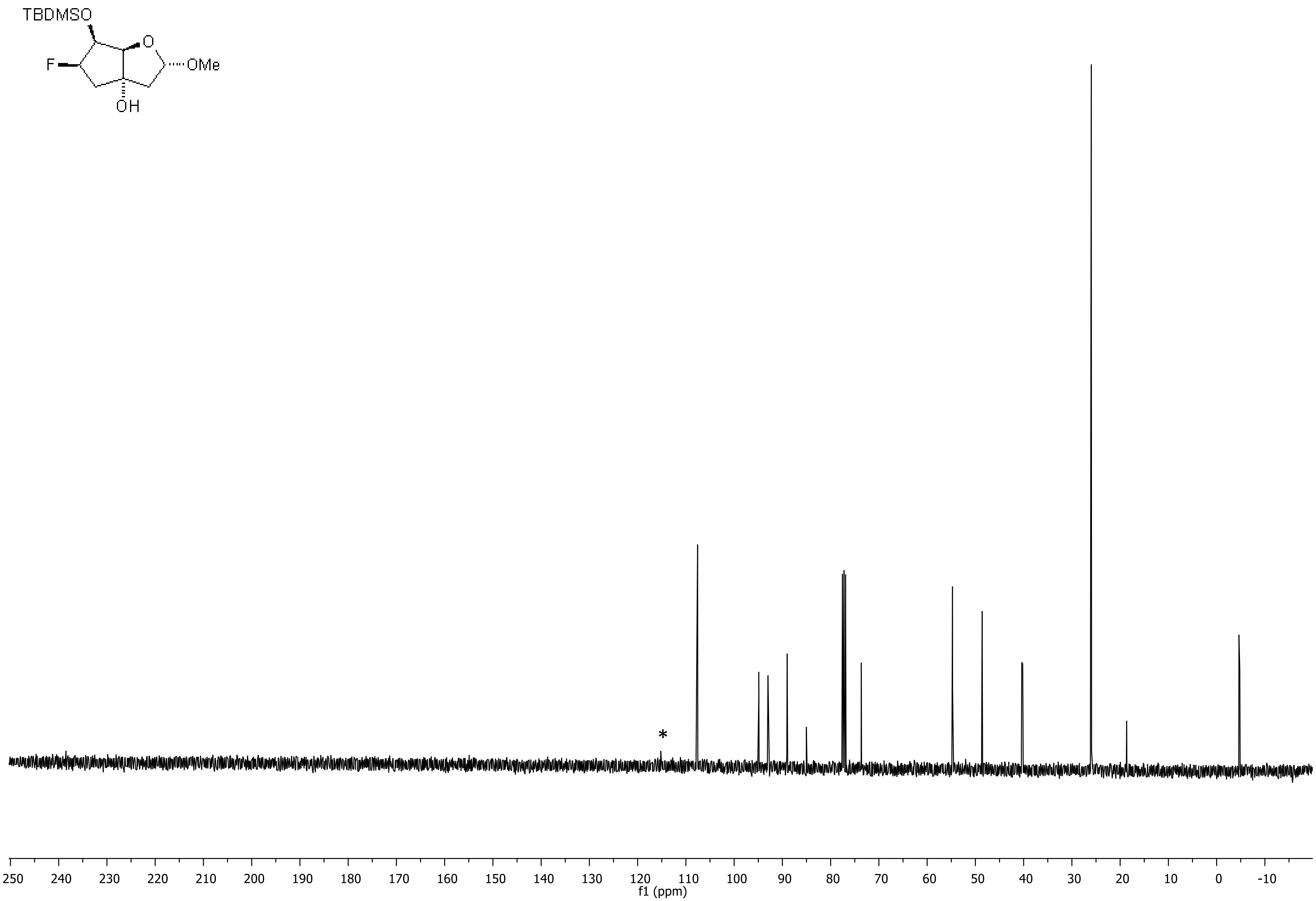


Figure S13: ^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of **7** (* unknown impurity)

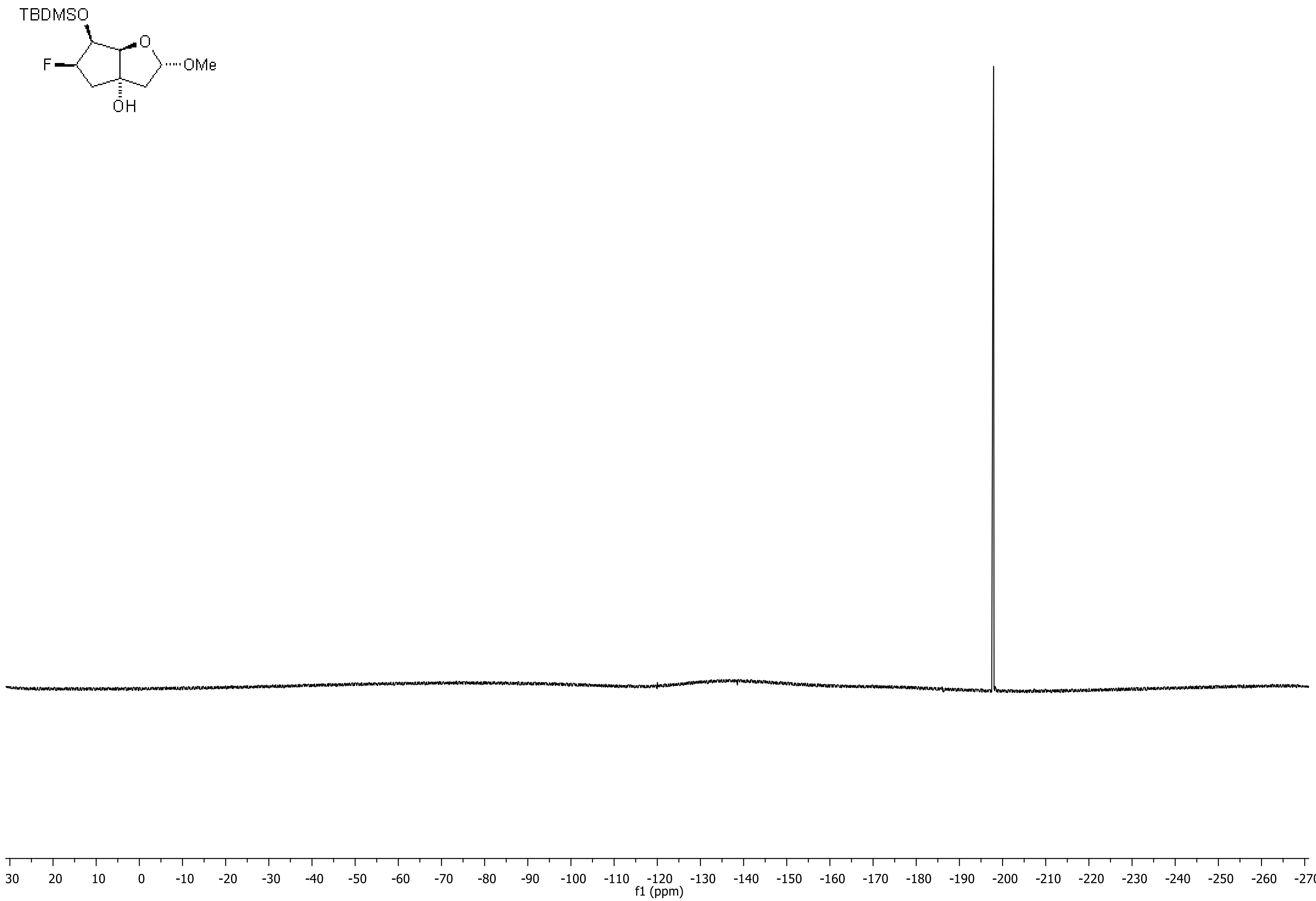


Figure S14: ^{19}F NMR ($CDCl_3$, 376 MHz) spectrum of **7**

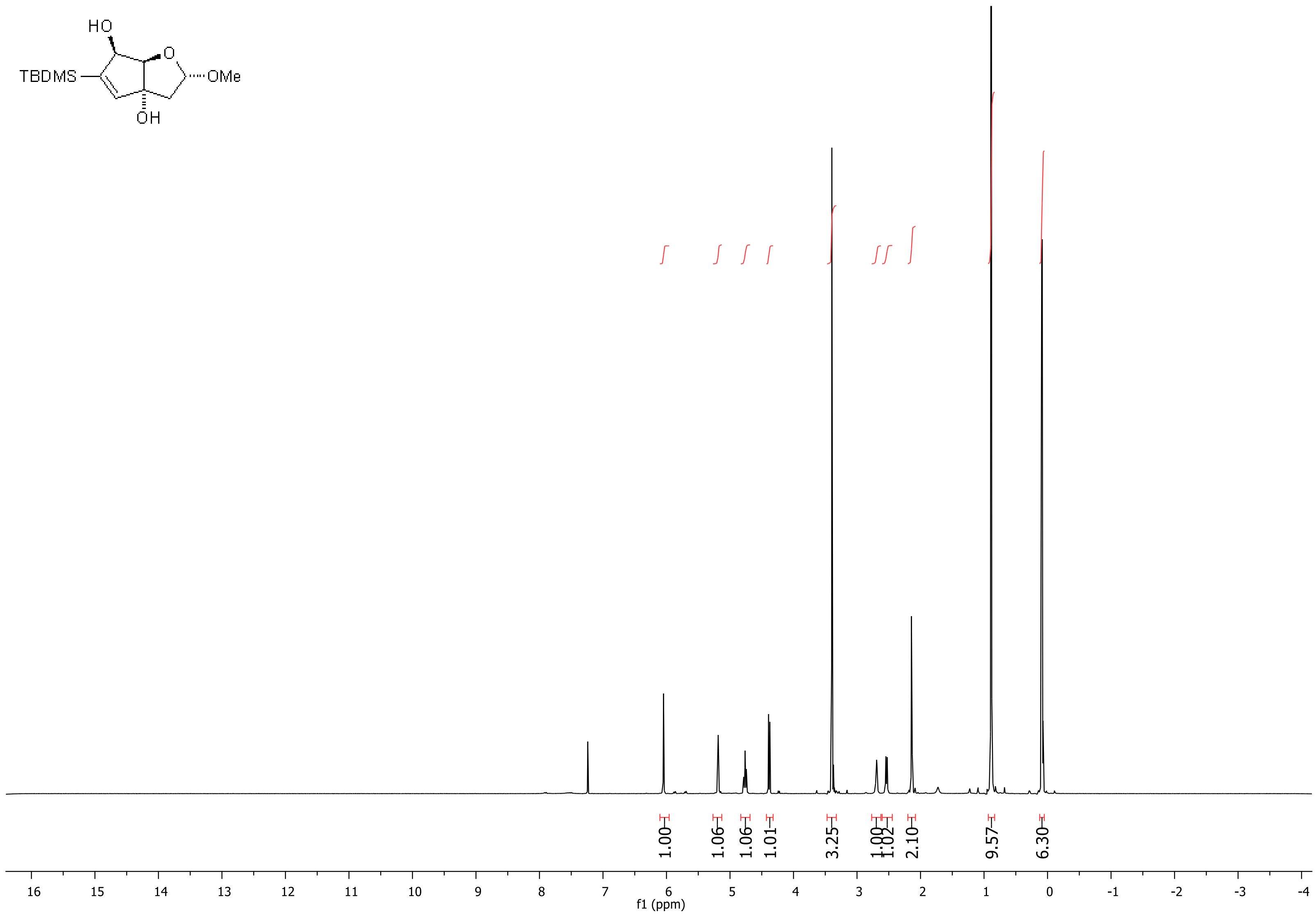


Figure S15: ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **8**

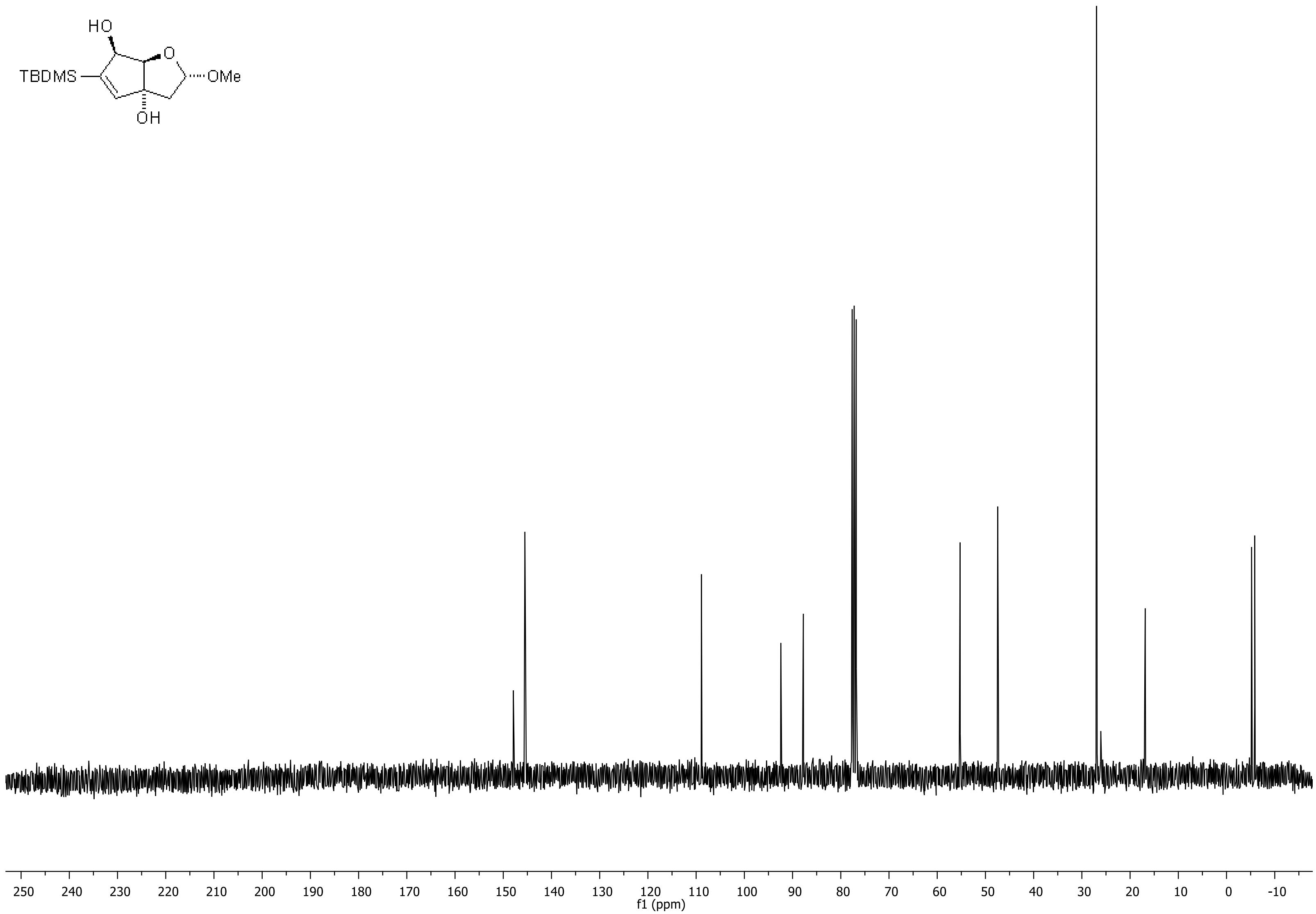


Figure S16: ^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **8**

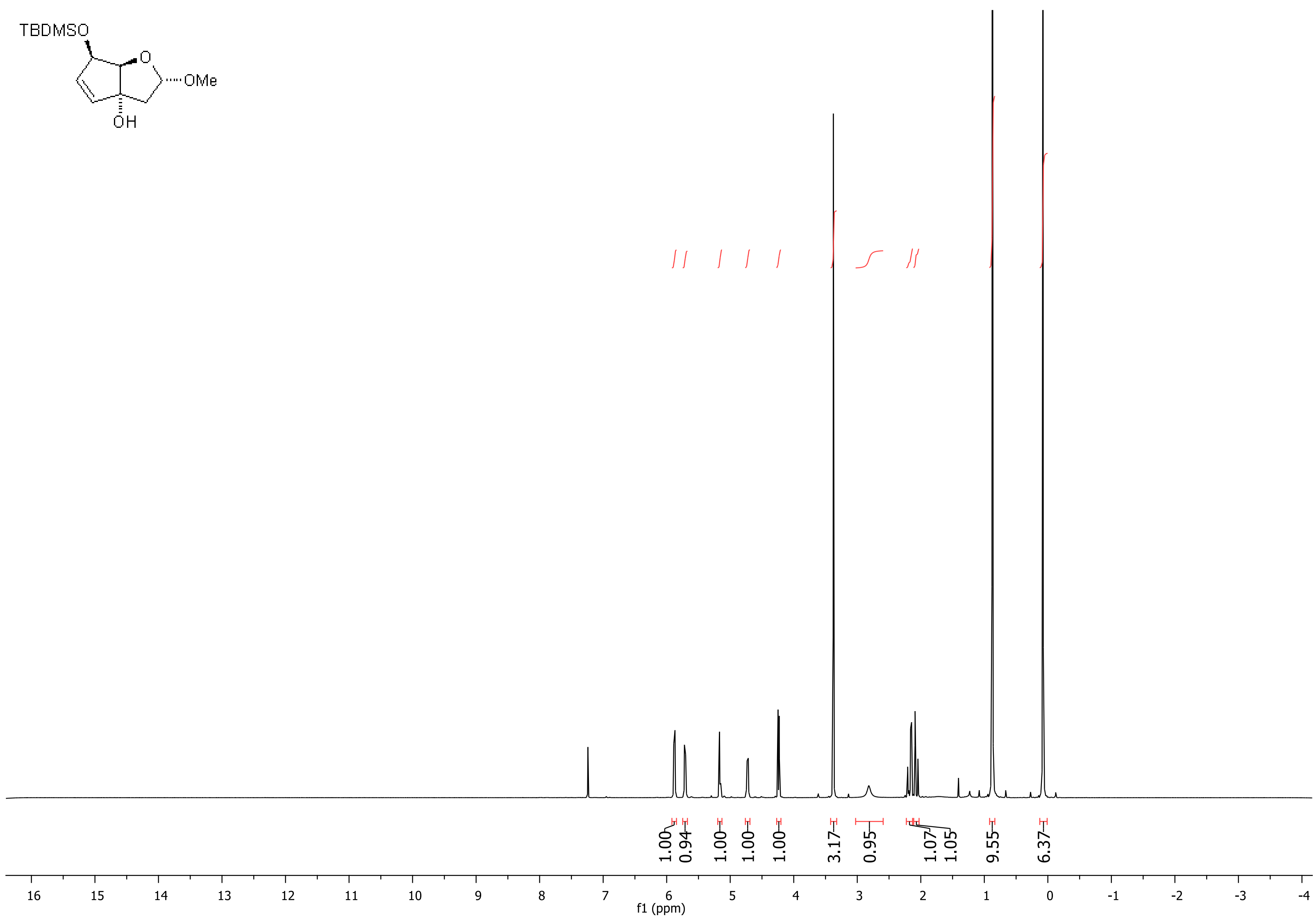


Figure S17: ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **9**

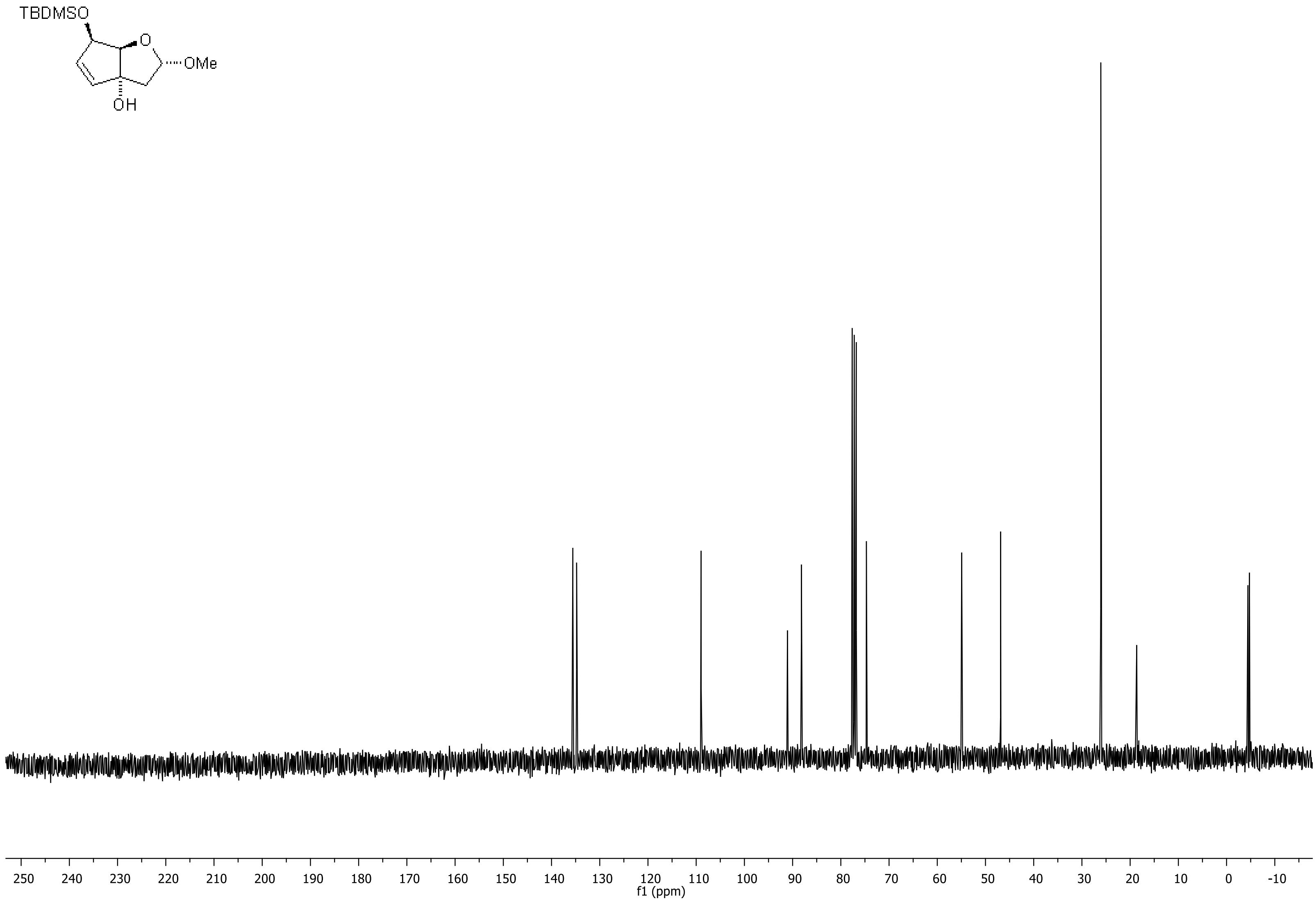


Figure S18: ^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **9**

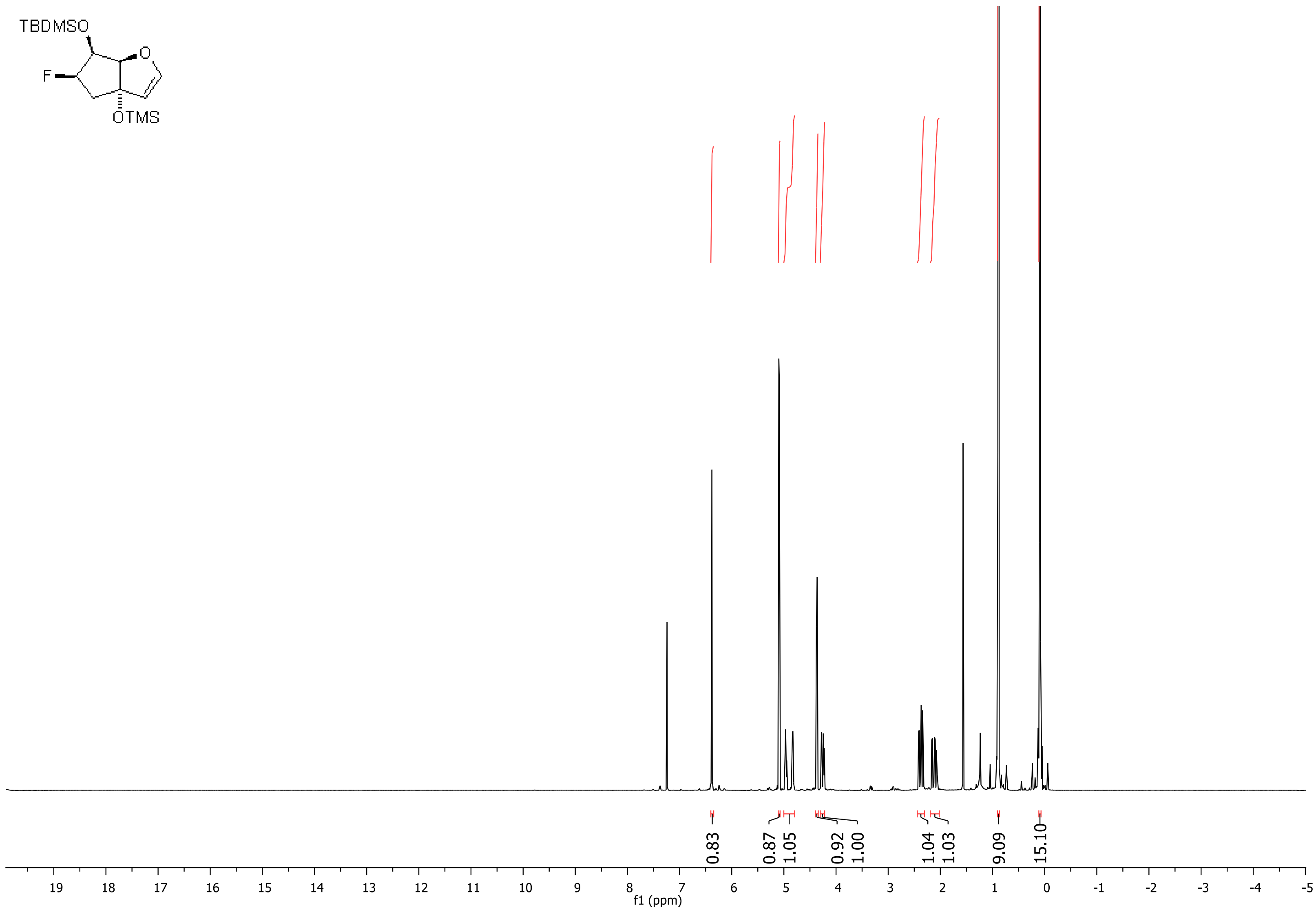


Figure S19: ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **10**

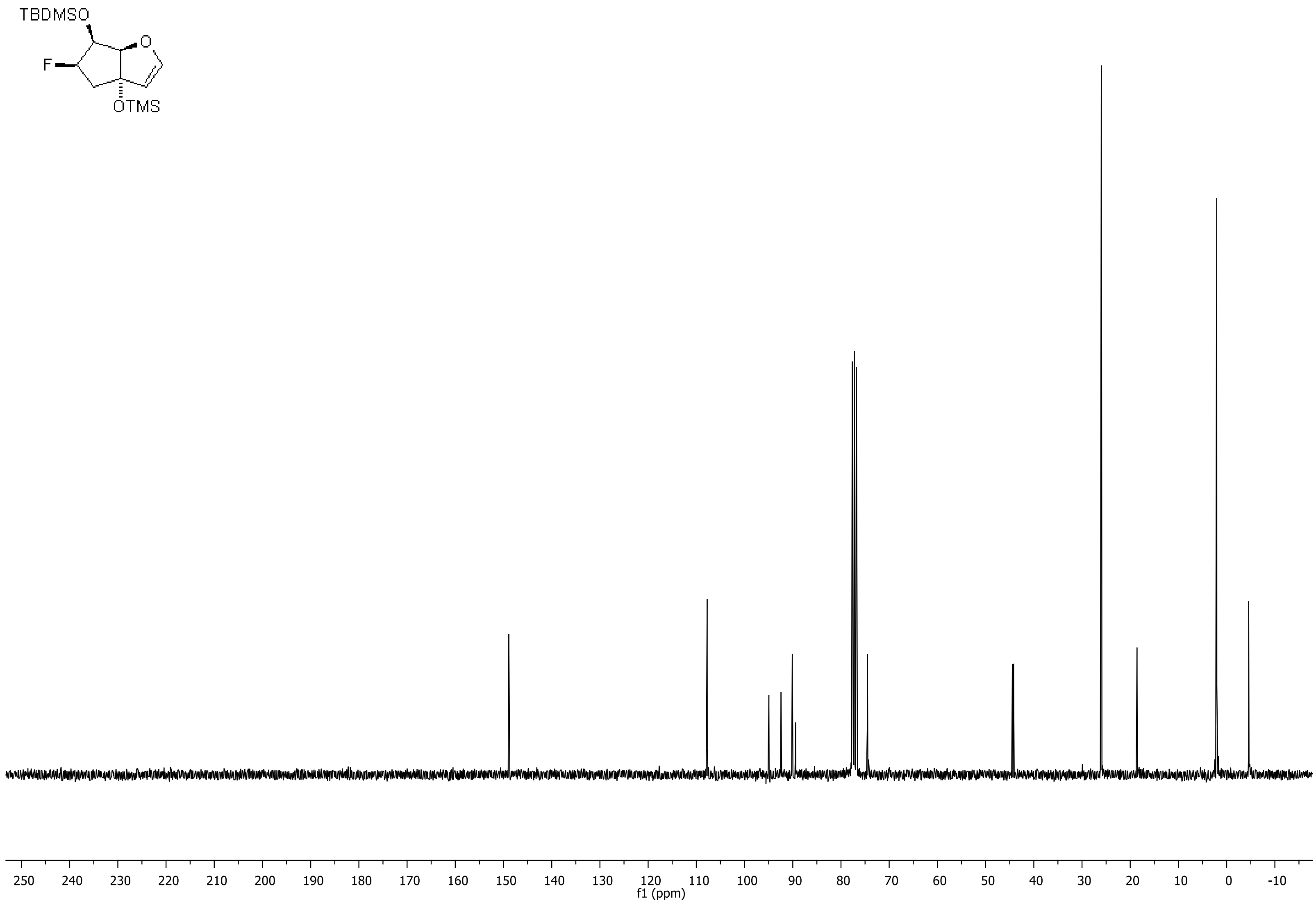


Figure S20: ^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **10**

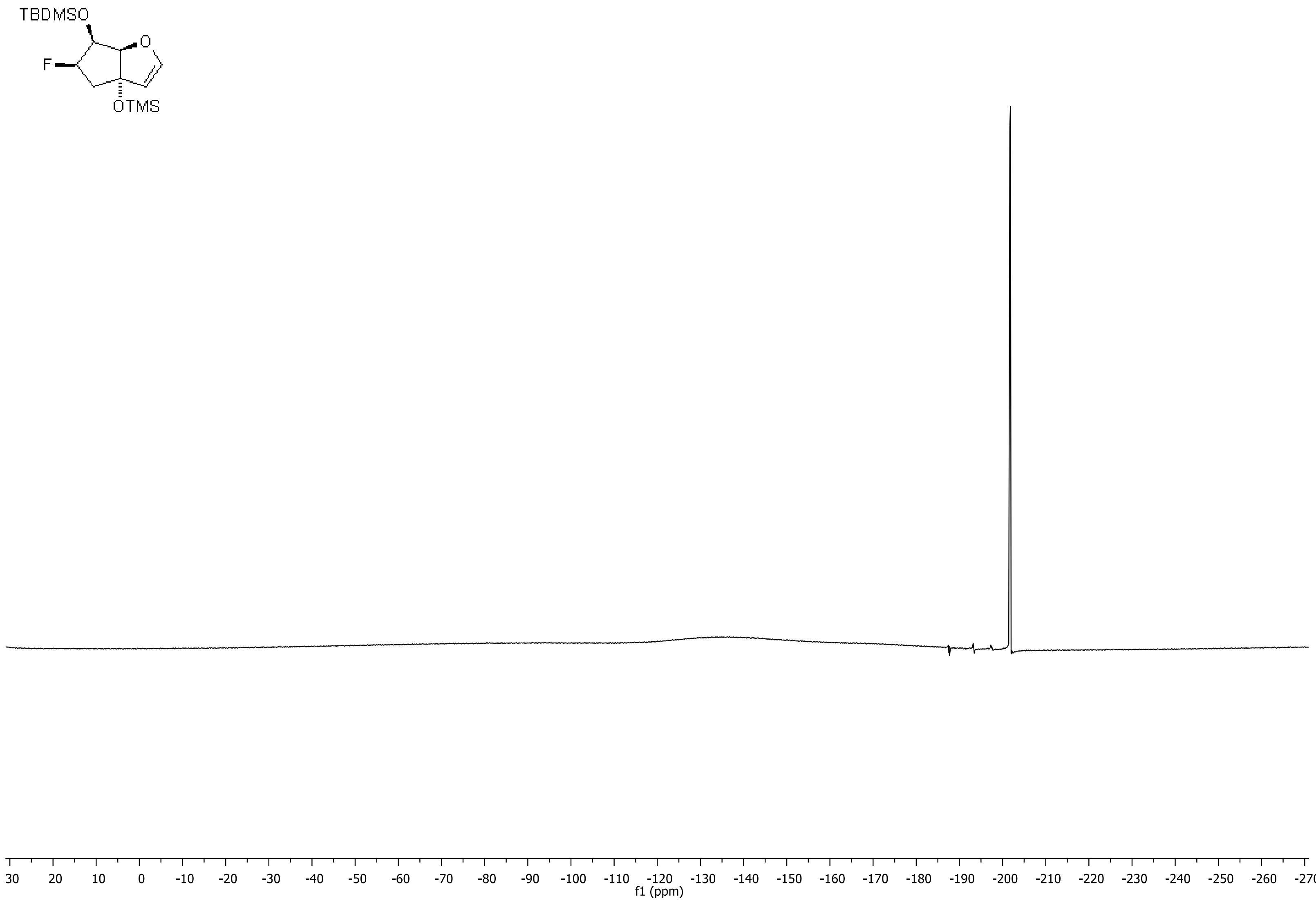


Figure S21: ^{19}F NMR ($CDCl_3$, 376 MHz) spectrum of **10**

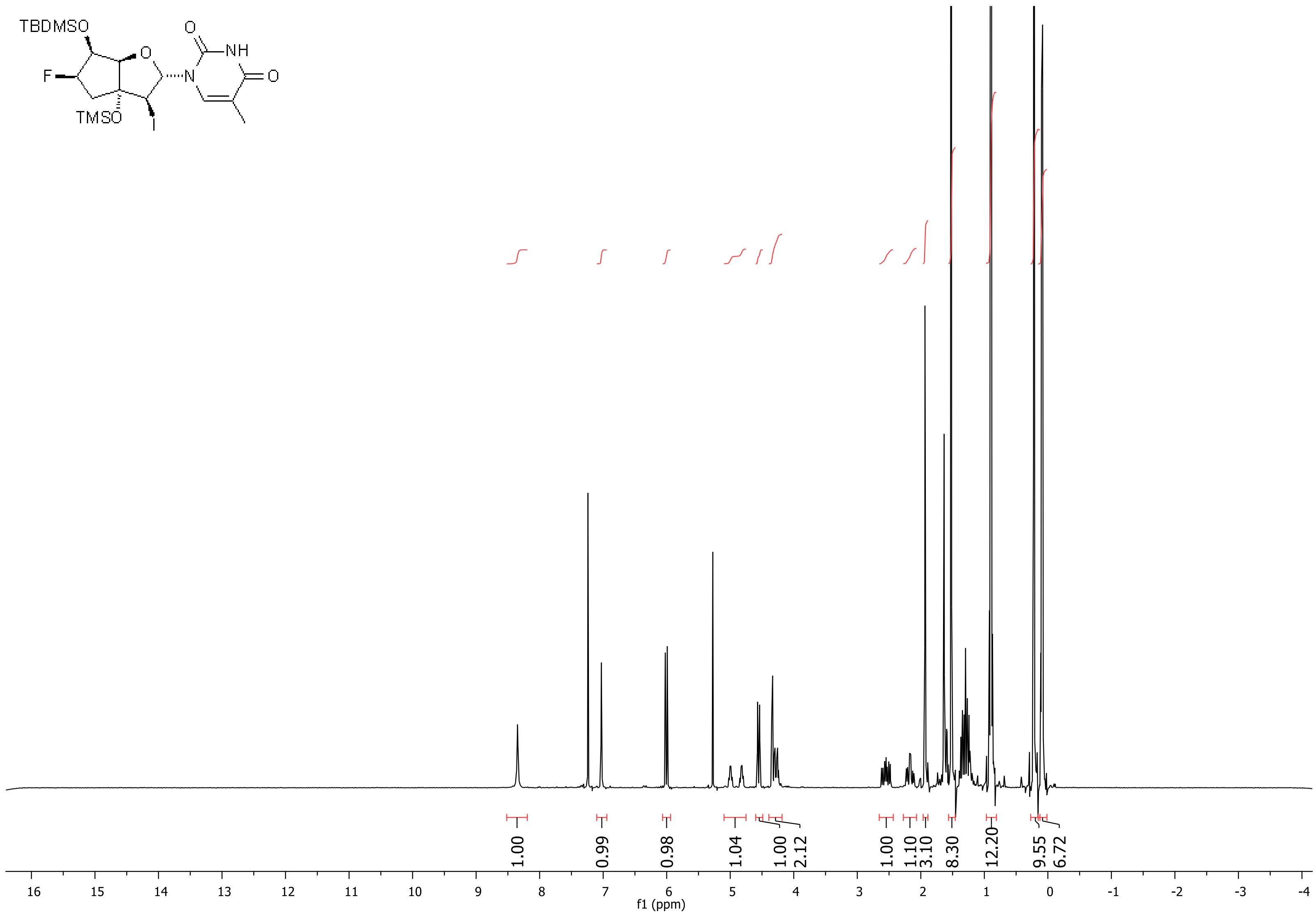


Figure S22: ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **11a**

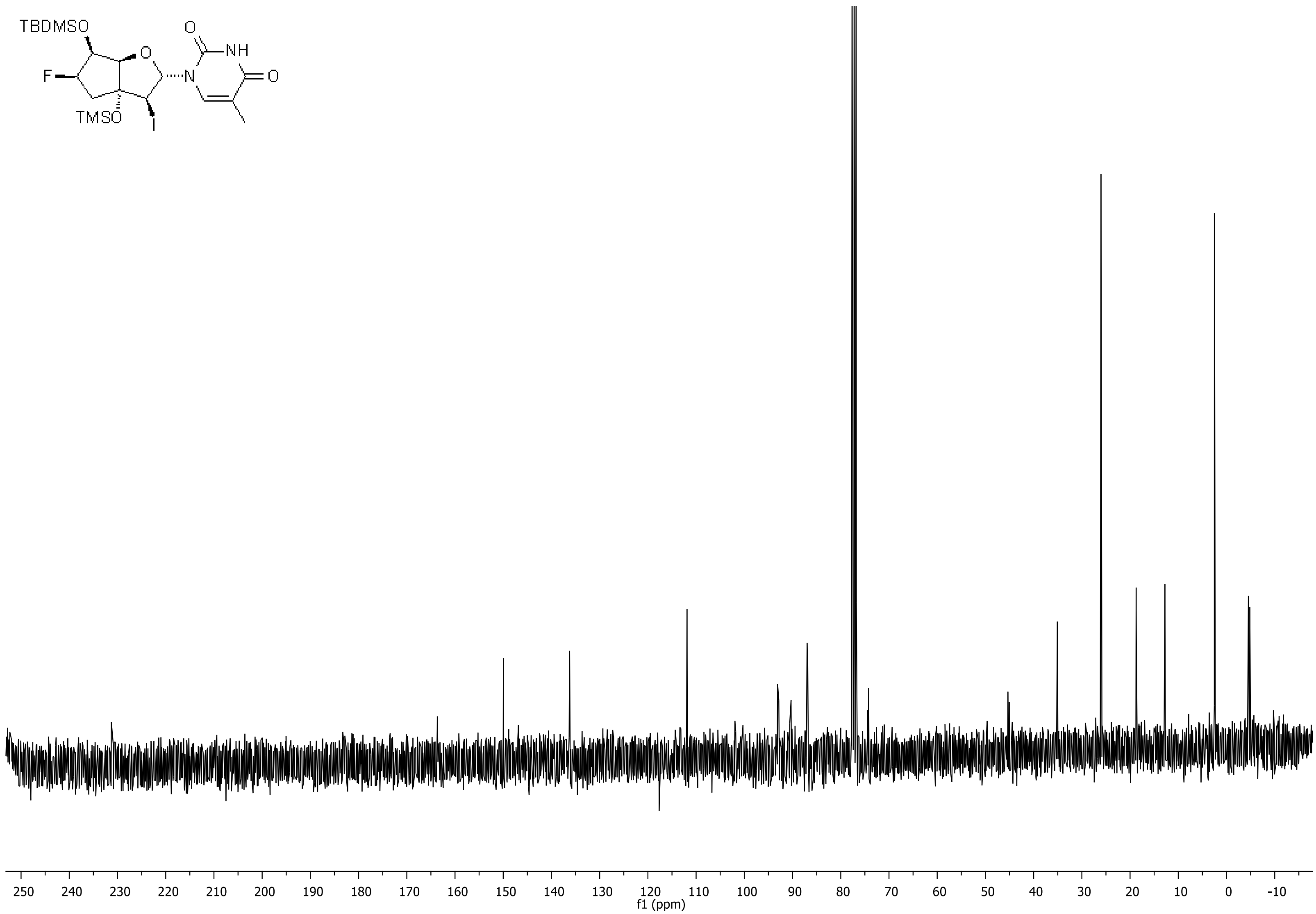


Figure S23: ^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **11a**

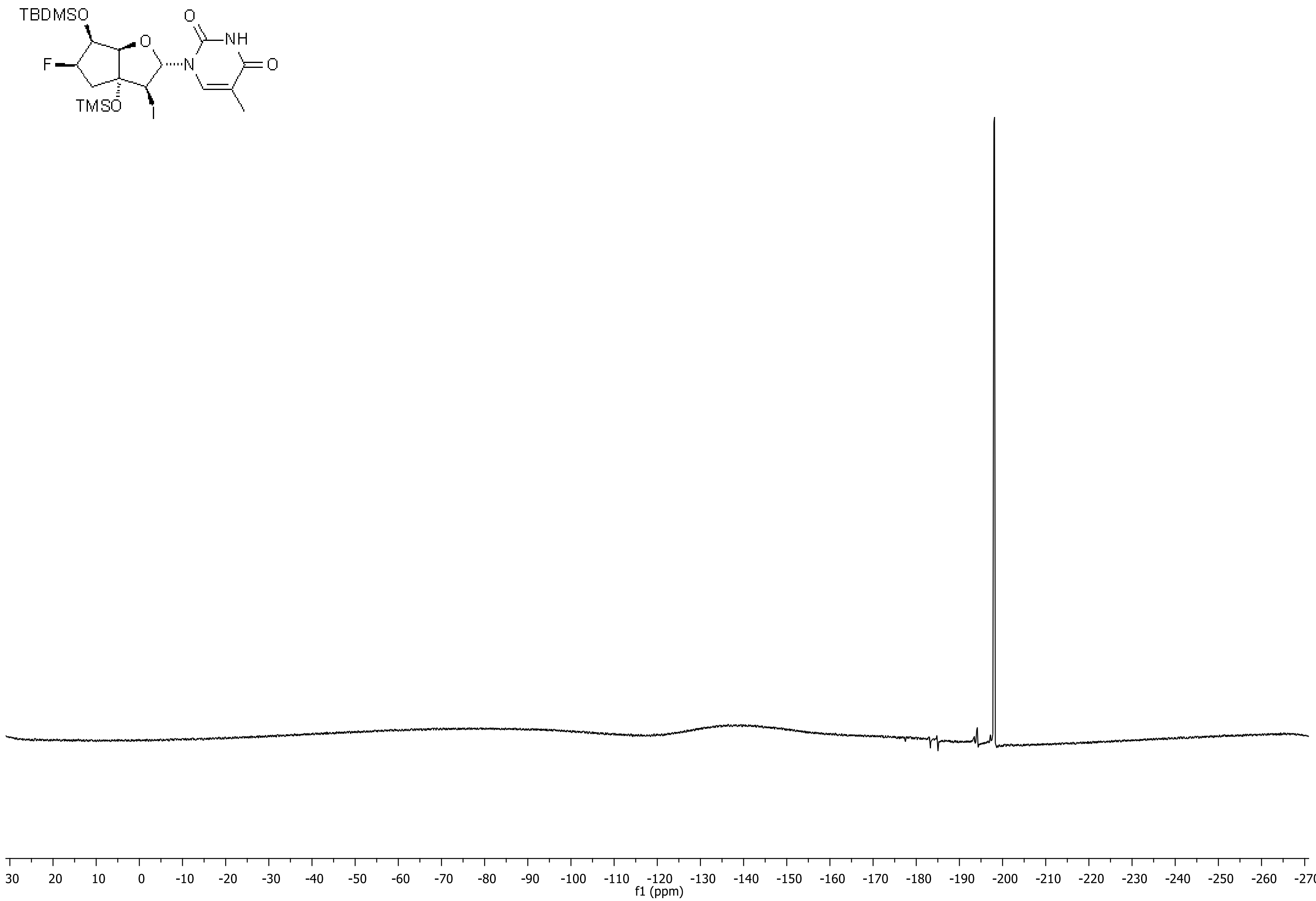


Figure S24: ^{19}F NMR ($CDCl_3$, 376 MHz) spectrum of **11a**

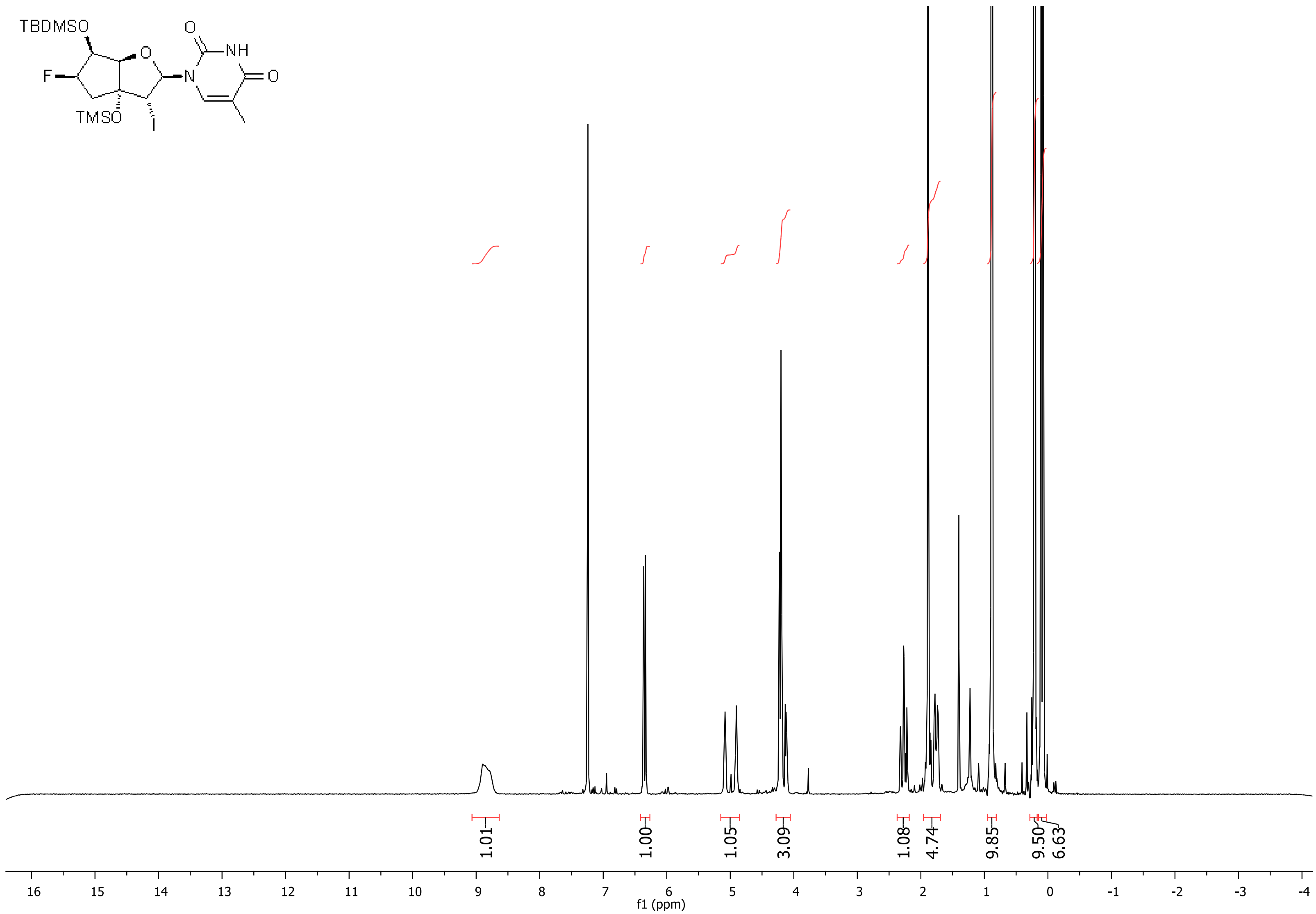
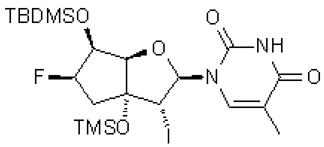


Figure S25: ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **11b**



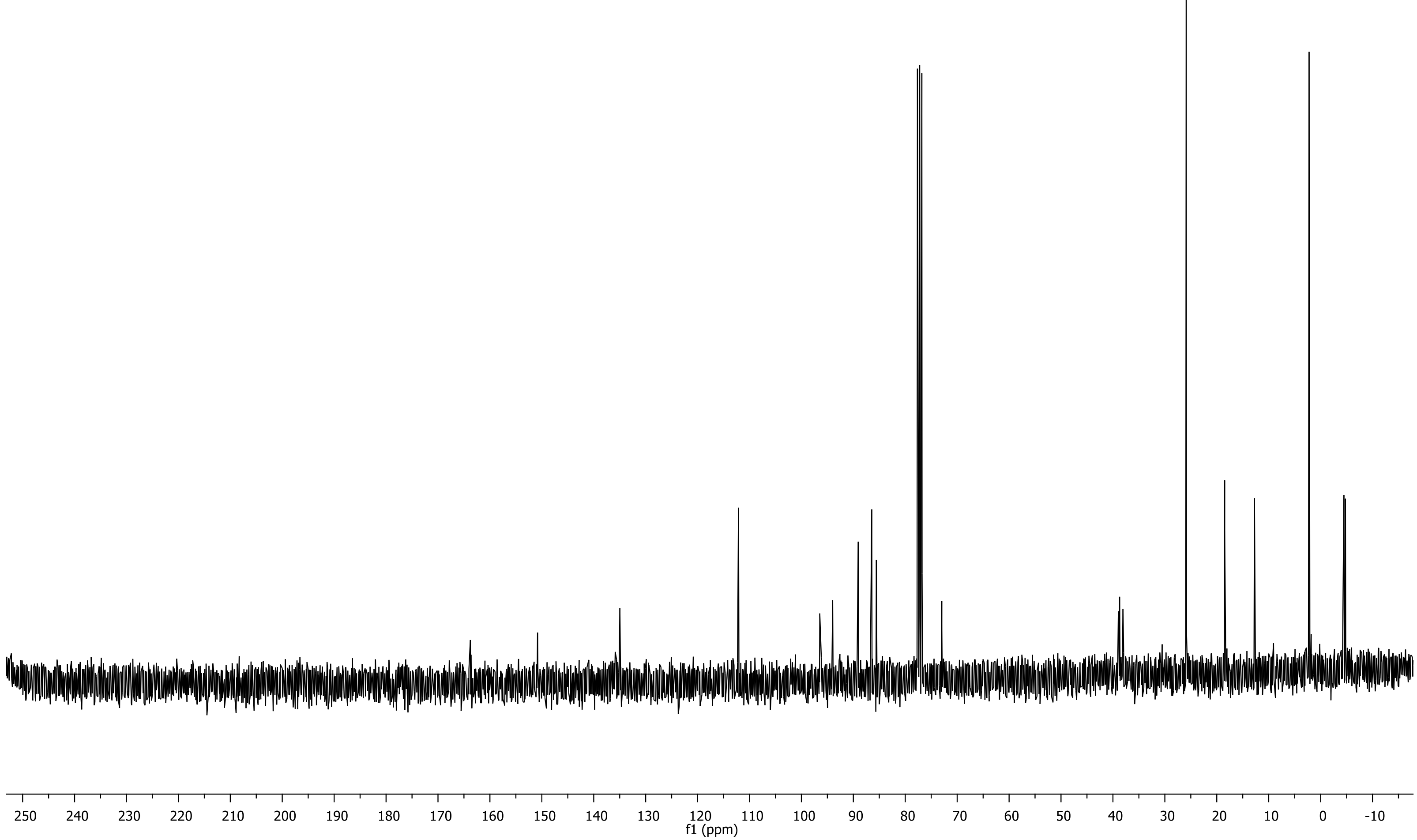


Figure S26: ^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **11b**

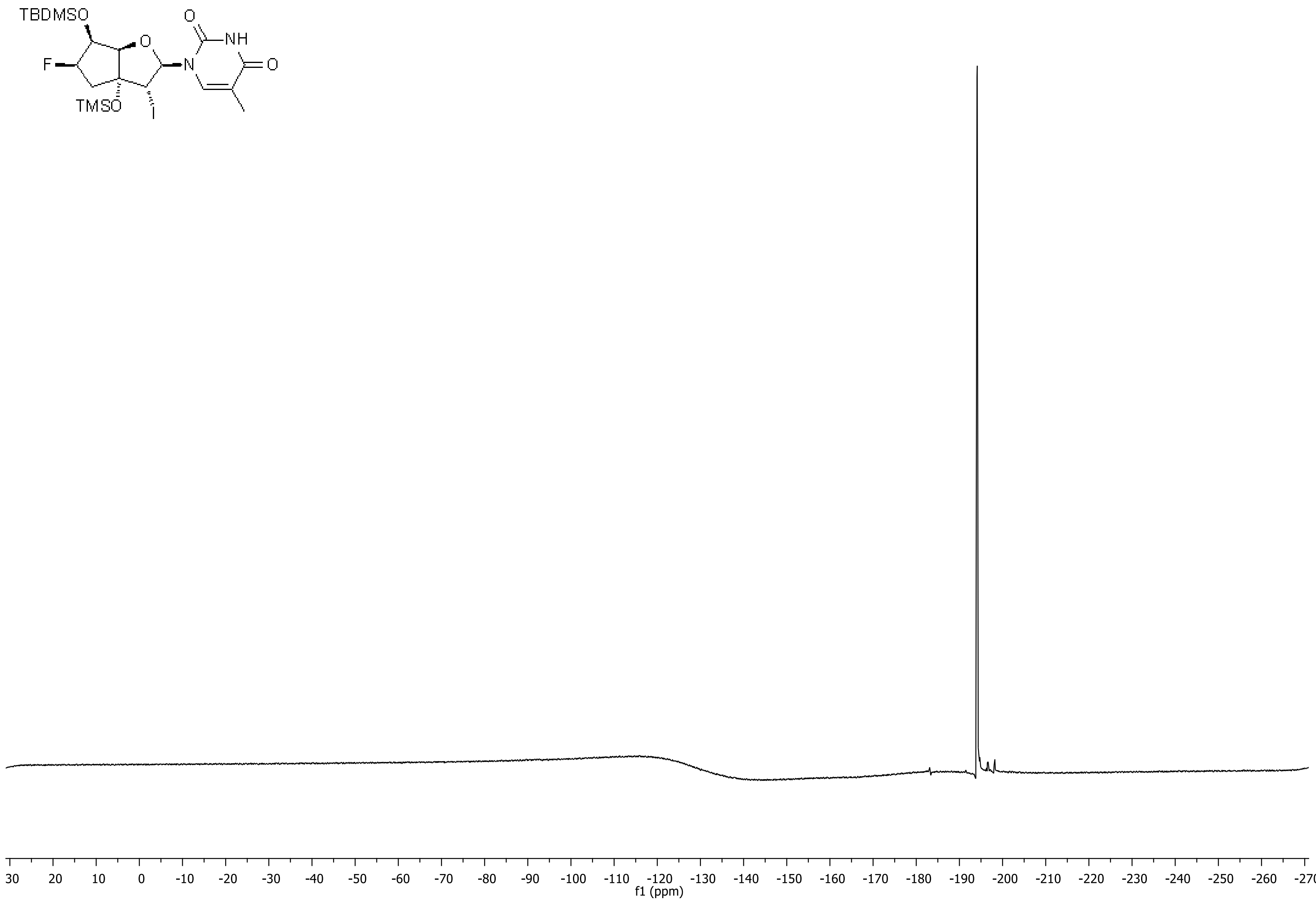
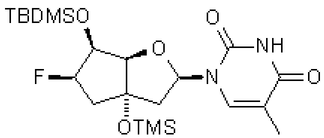


Figure S27: ^{19}F NMR ($CDCl_3$, 376 MHz) spectrum of **11b**



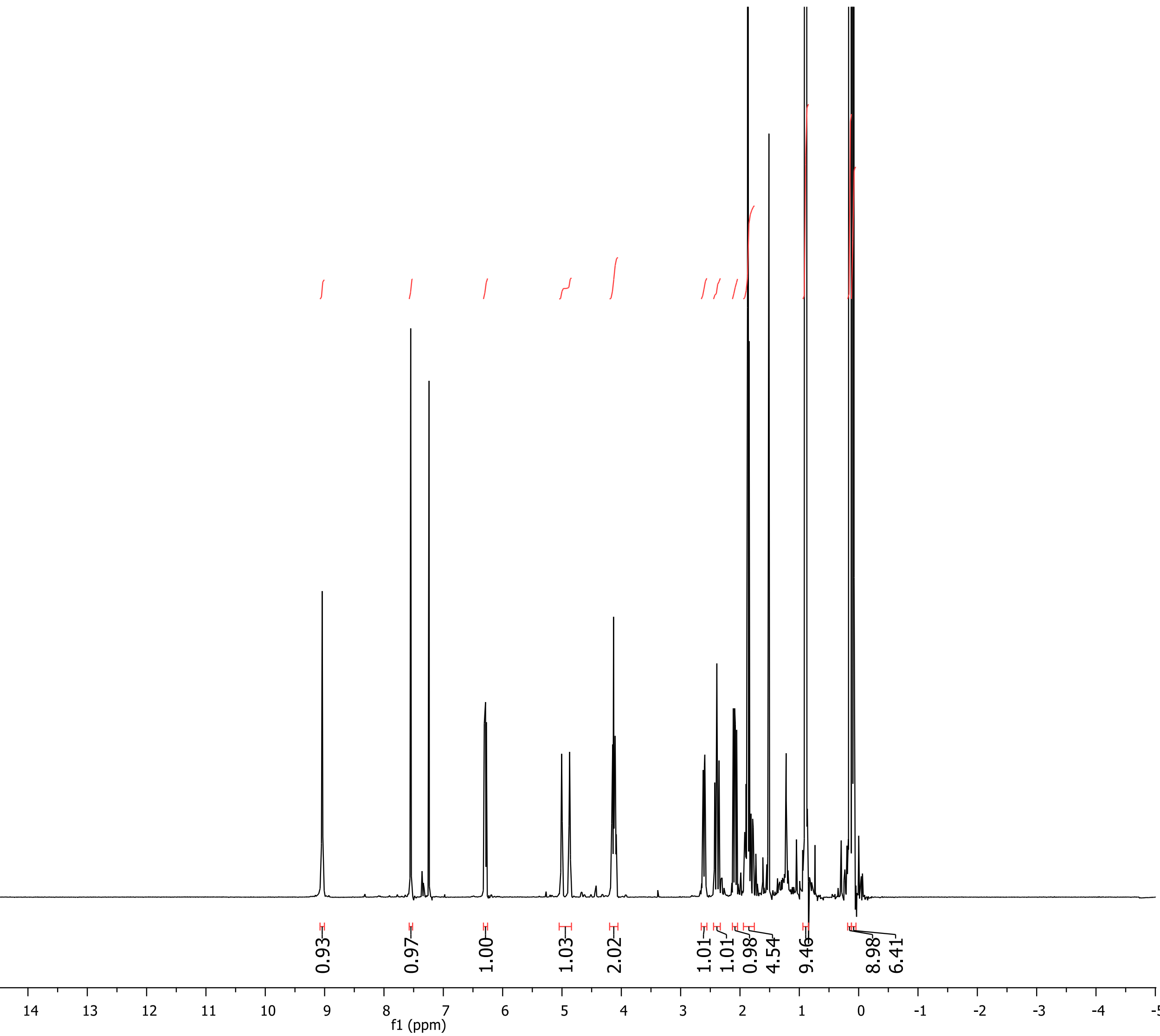


Figure S28: ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **12**

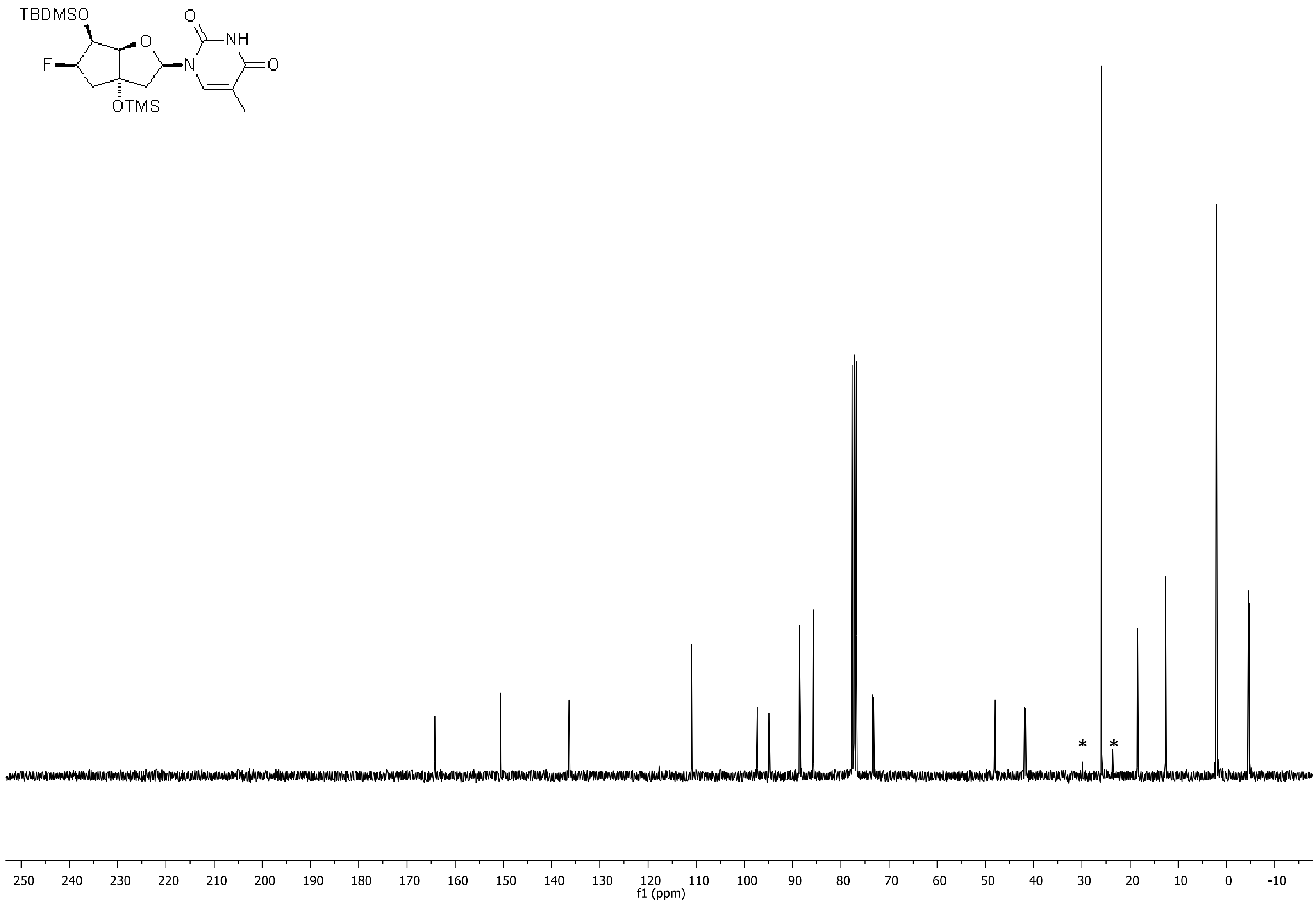


Figure S29: ^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **12** (* unknown impurities).

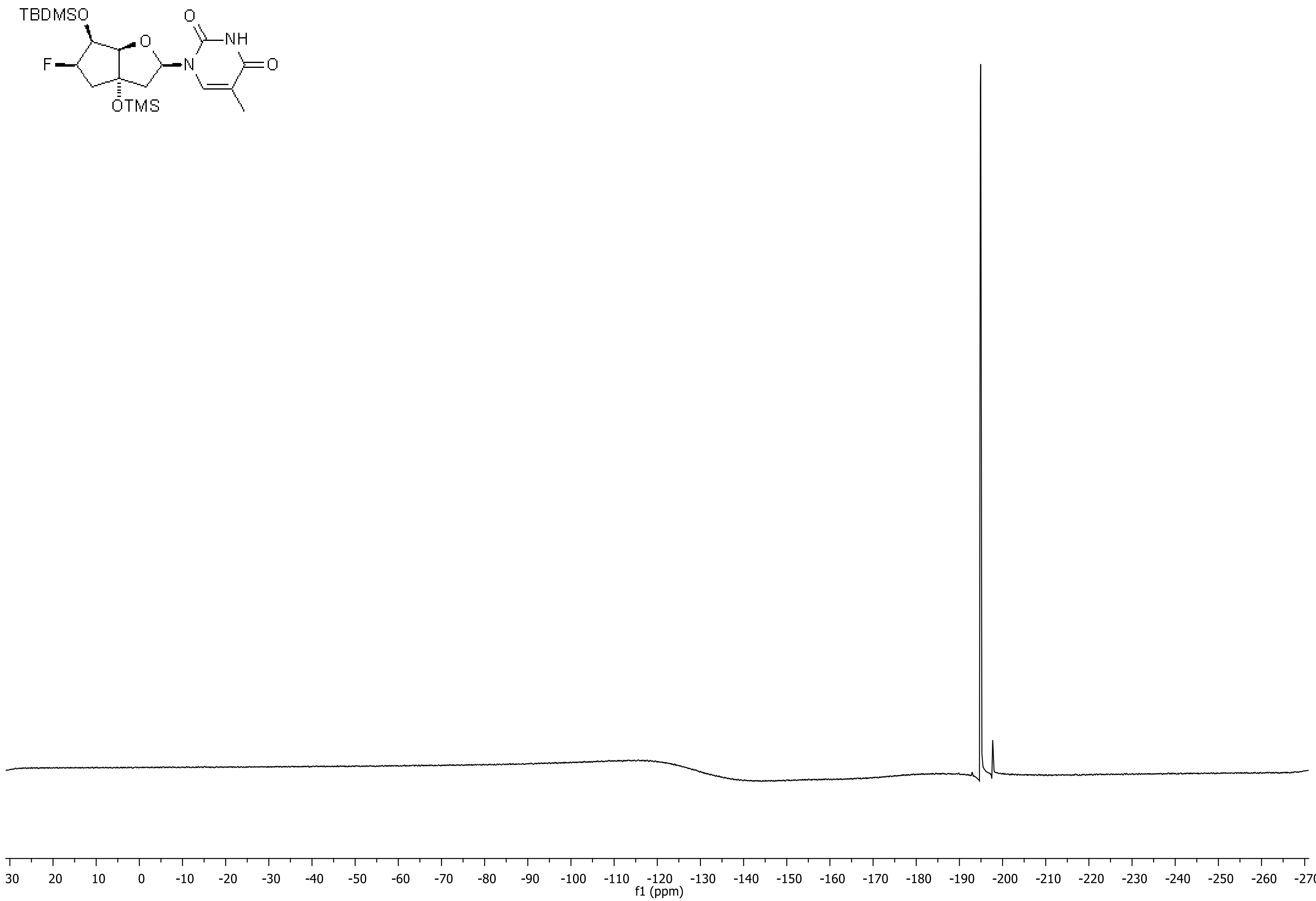
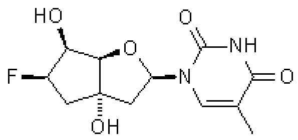


Figure S30: ^{19}F NMR ($CDCl_3$, 376 MHz) spectrum of **12**



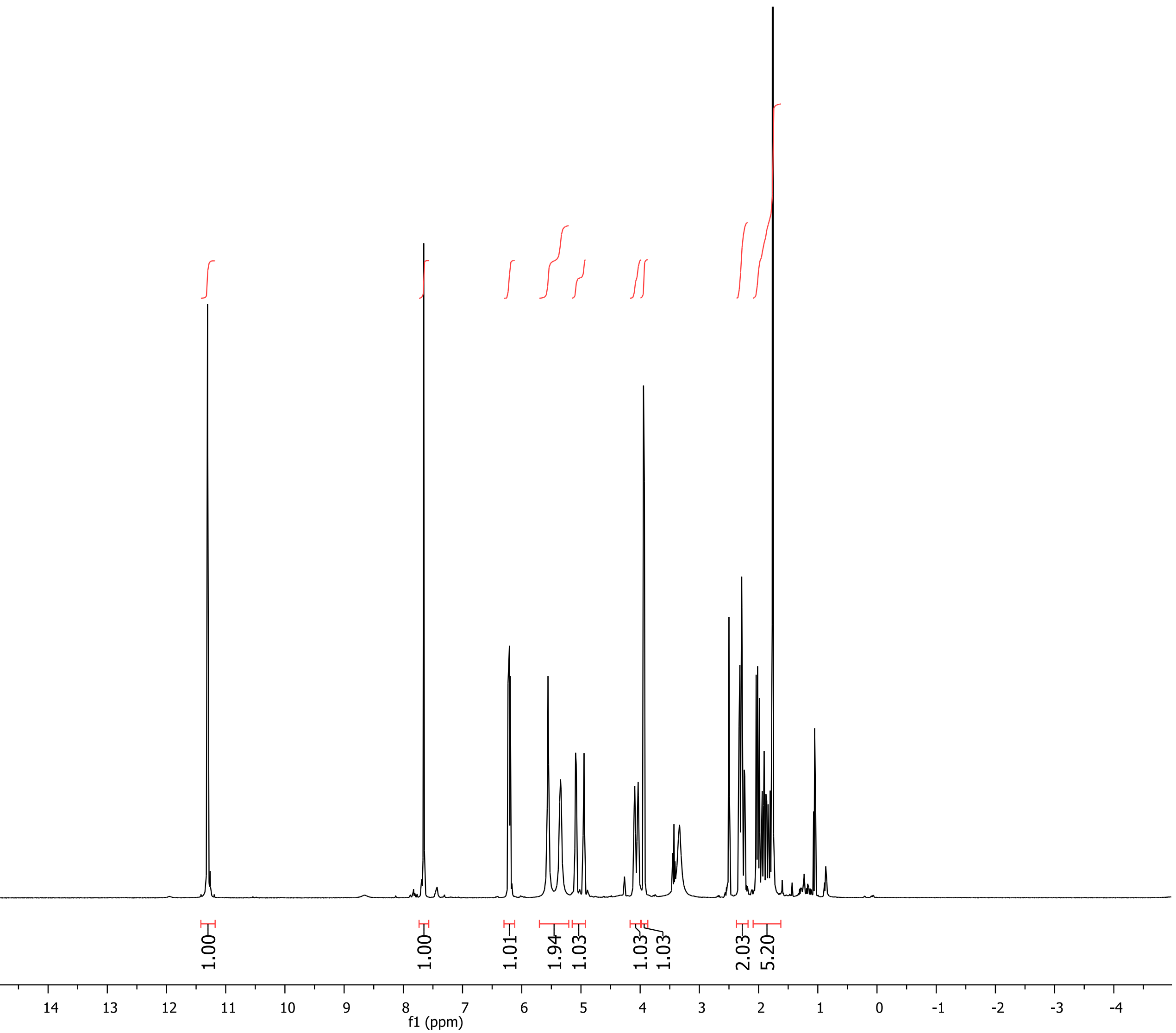


Figure S31: ^{1}H NMR (DMSO-d6, 400 MHz) spectrum of **13**

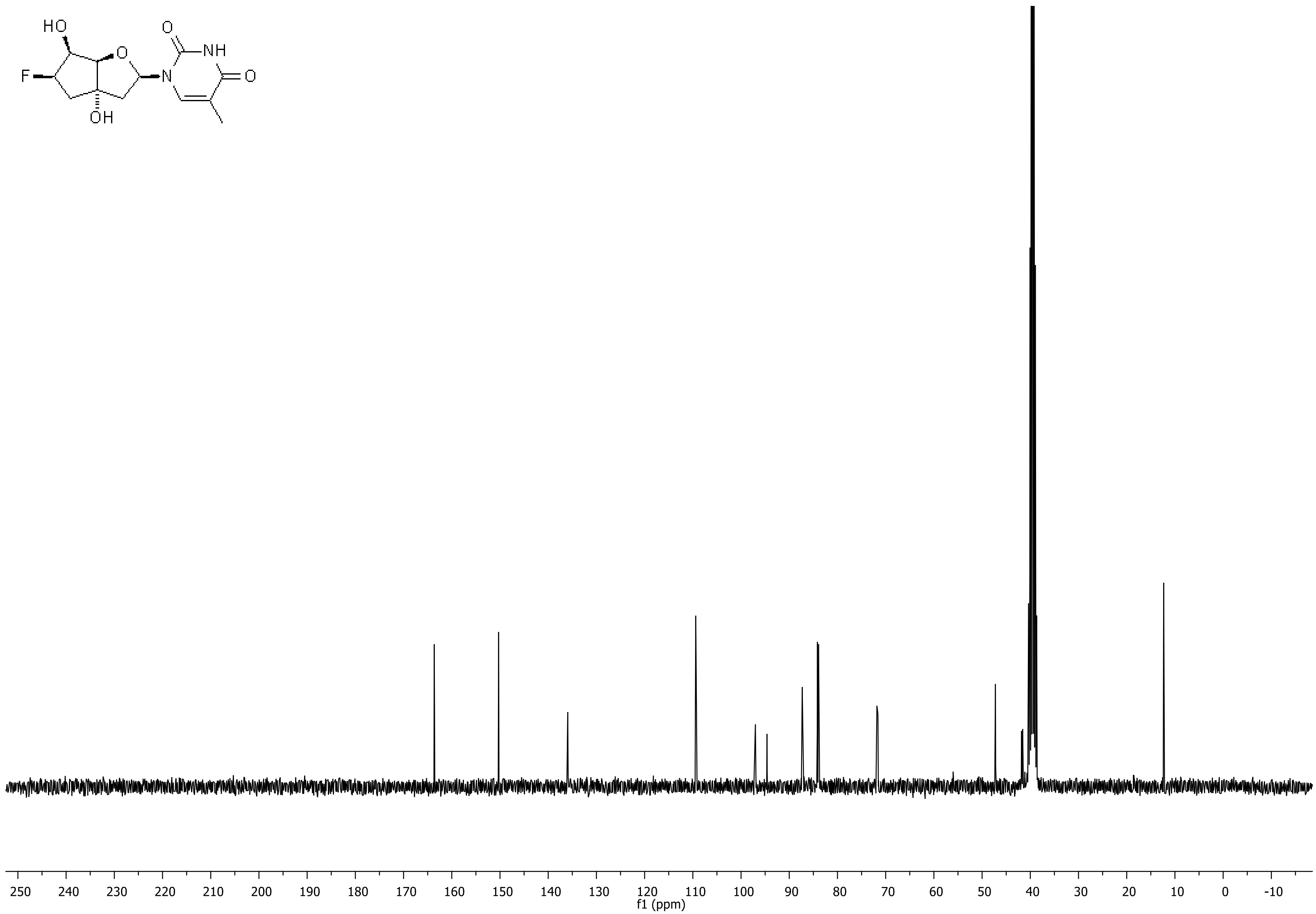
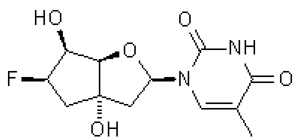


Figure S32: ^{13}C NMR (DMSO-d6, 75 MHz) spectrum of **13**



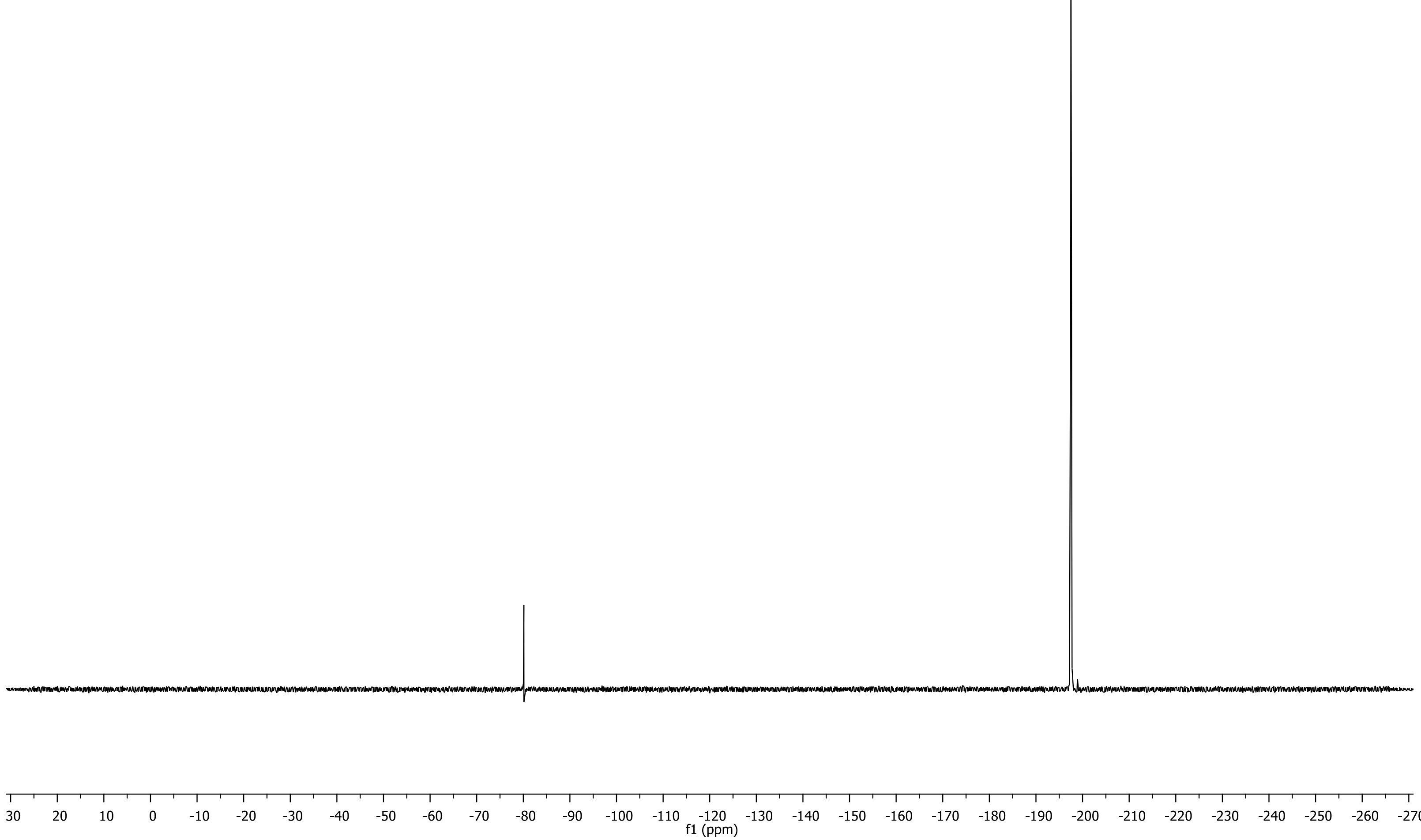
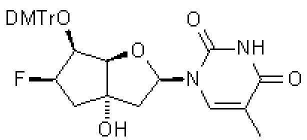


Figure S33: ^{19}F NMR (CD_3OD, 376 MHz) spectrum of **13**



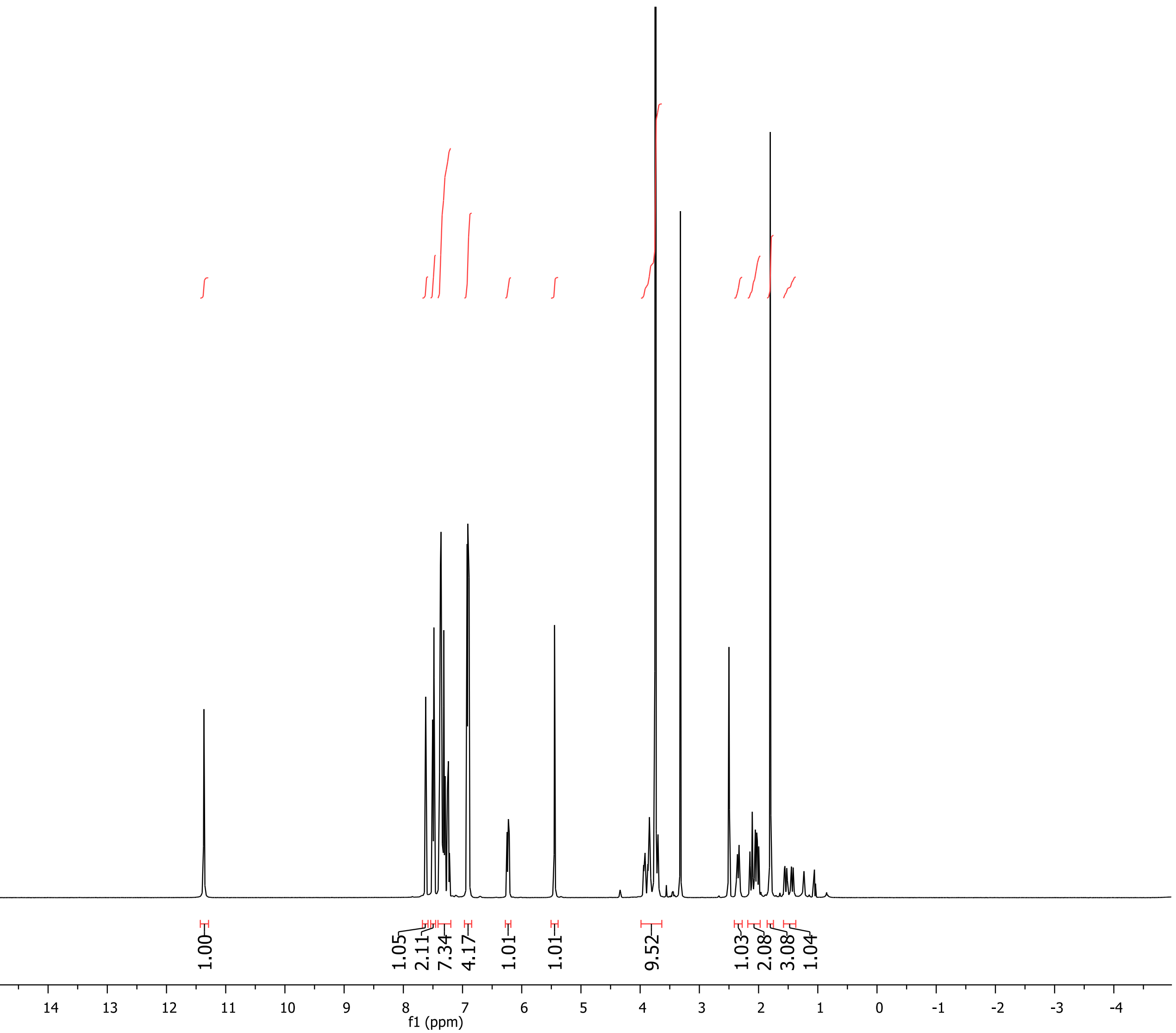


Figure S34: ^{1}H NMR (DMSO-d6, 400 MHz) spectrum of **14**

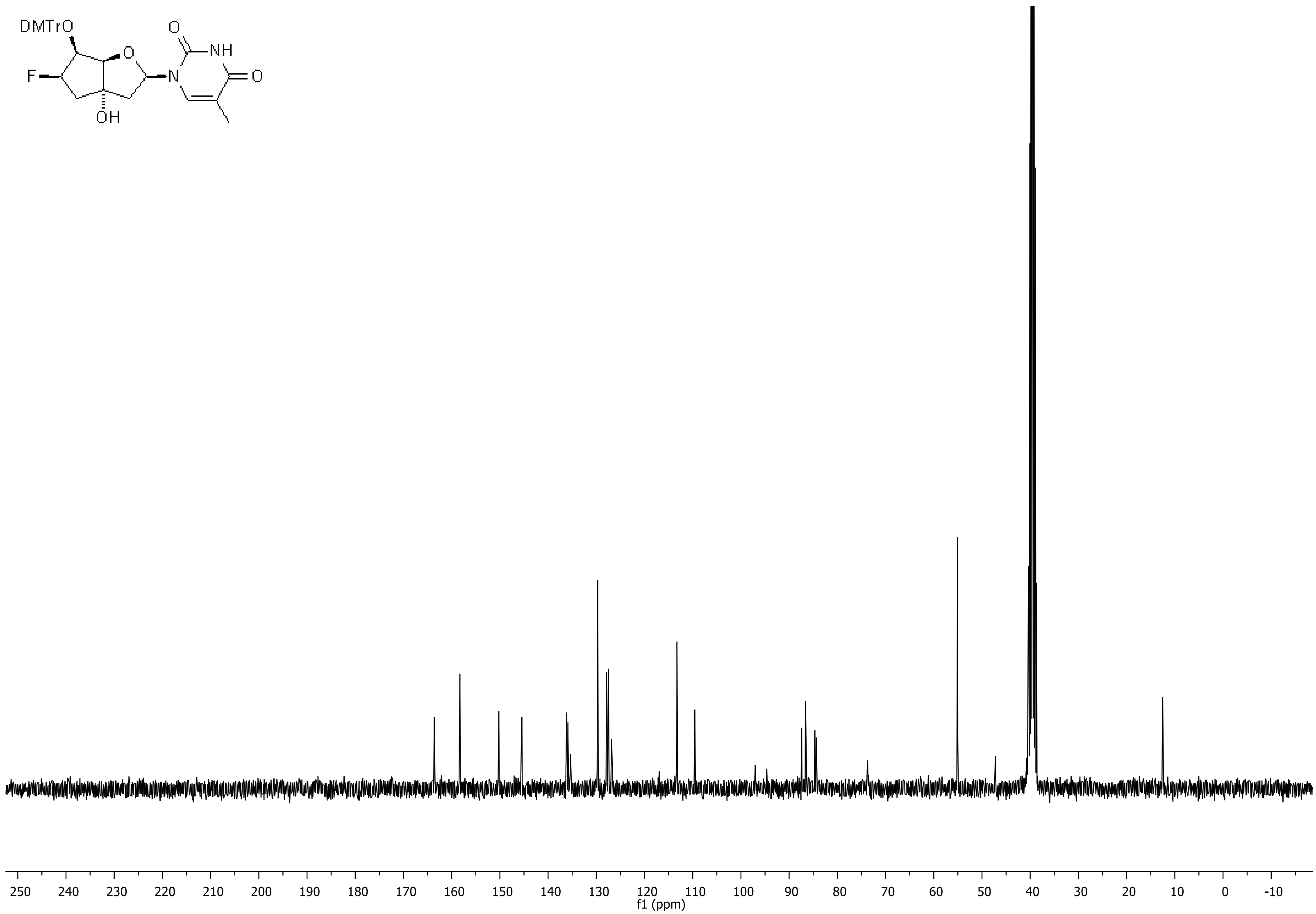


Figure S35: ^{13}C NMR (DMSO-d6, 75 MHz) spectrum of **14**

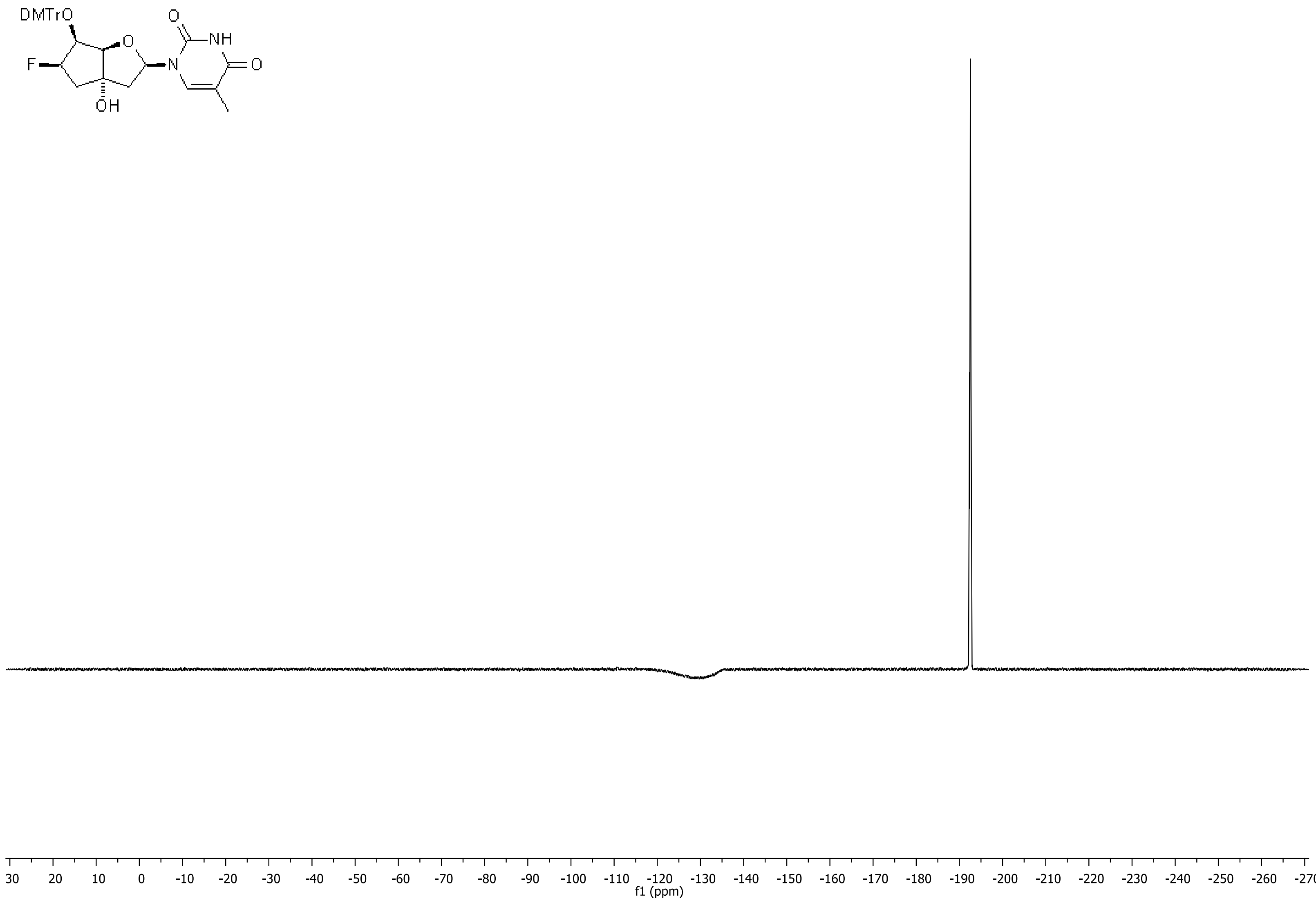


Figure S36: ^{19}F NMR (DMSO-d6, 376 MHz) spectrum of **14**

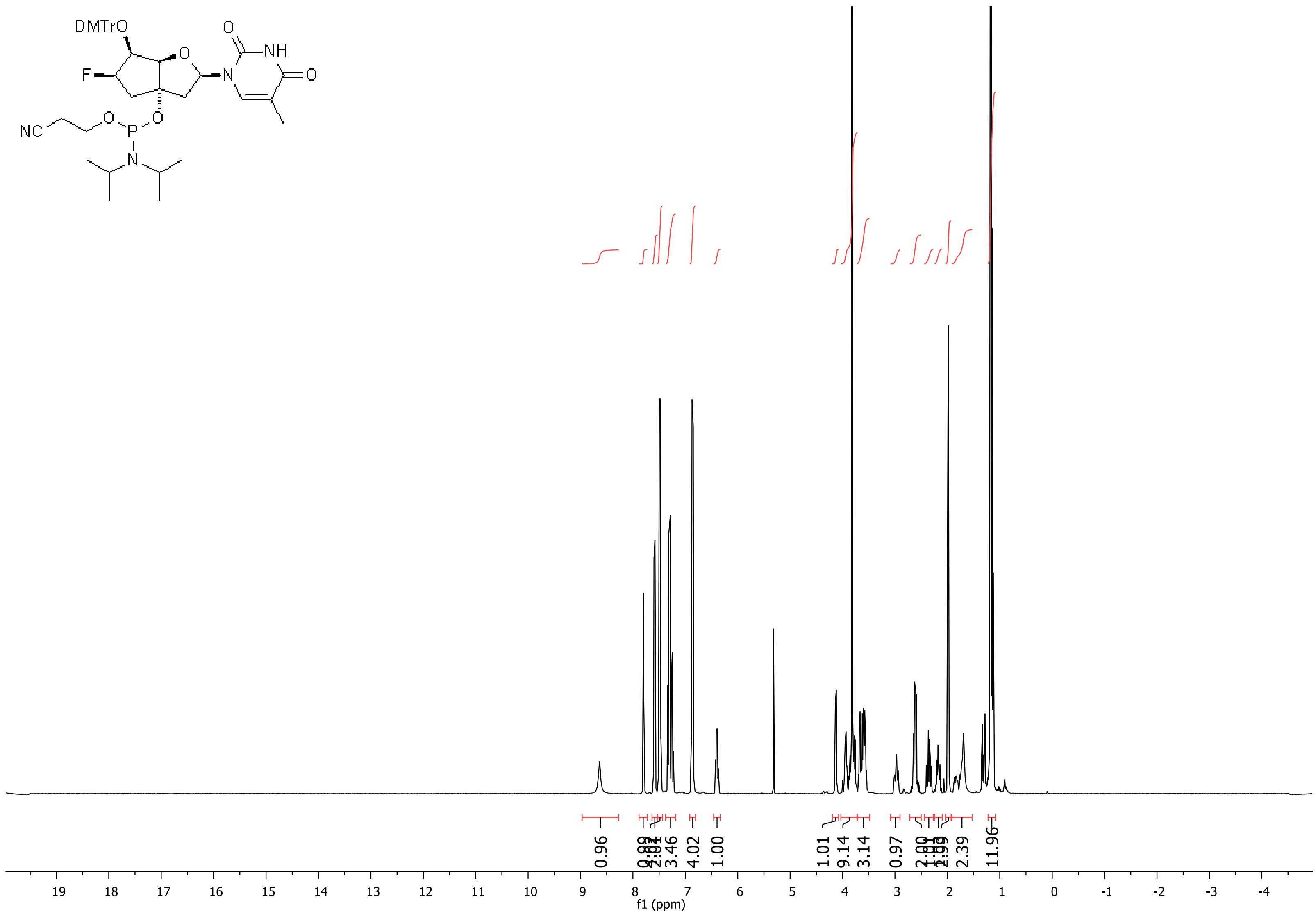


Figure S37: ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **15**

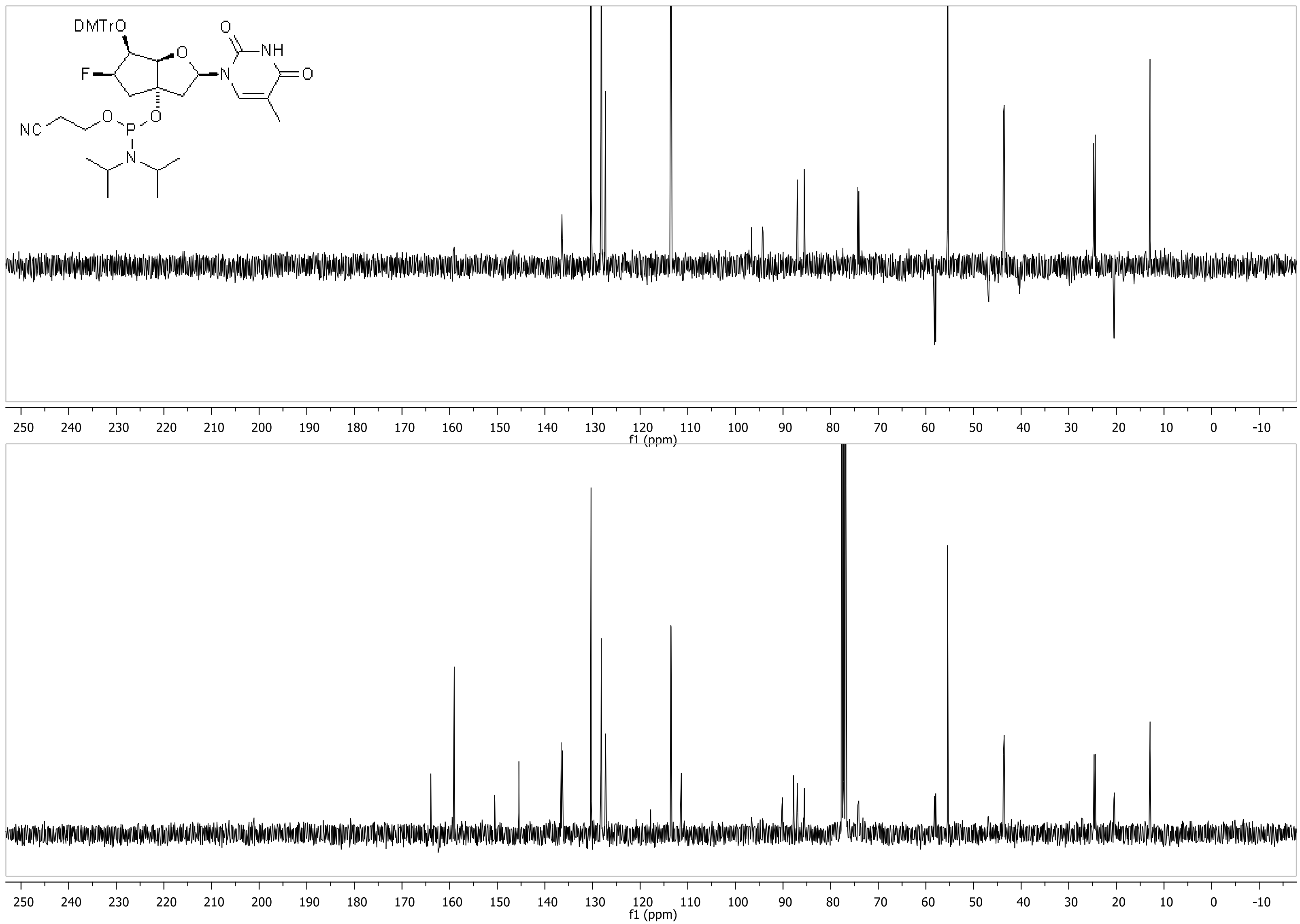


Figure S38: ^{13}C/DEPT NMR ($CDCl_3$, 75 MHz) spectrum of **15**

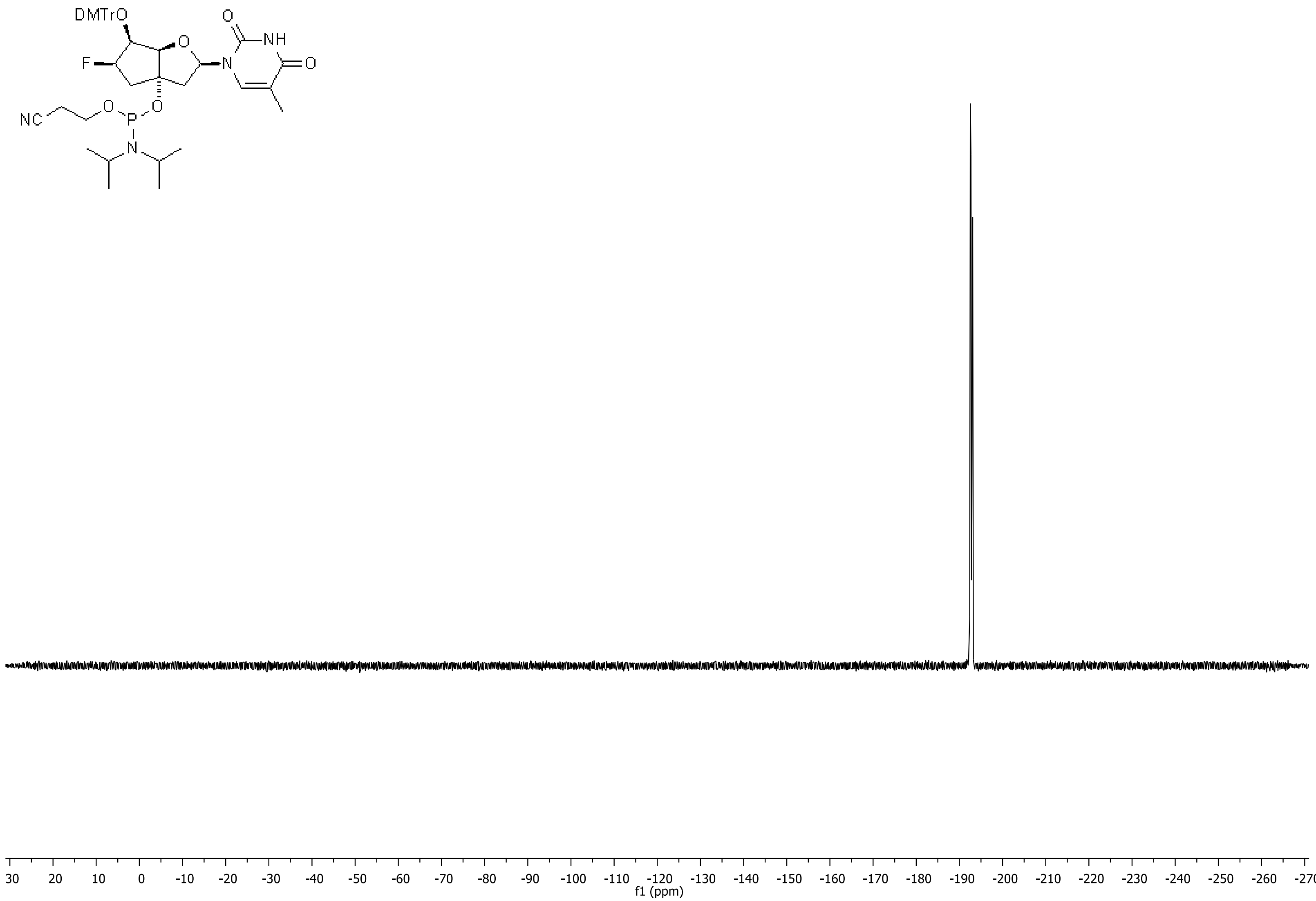


Figure S39: ^{19}F NMR ($CDCl_3$, 376 MHz) spectrum of **15**

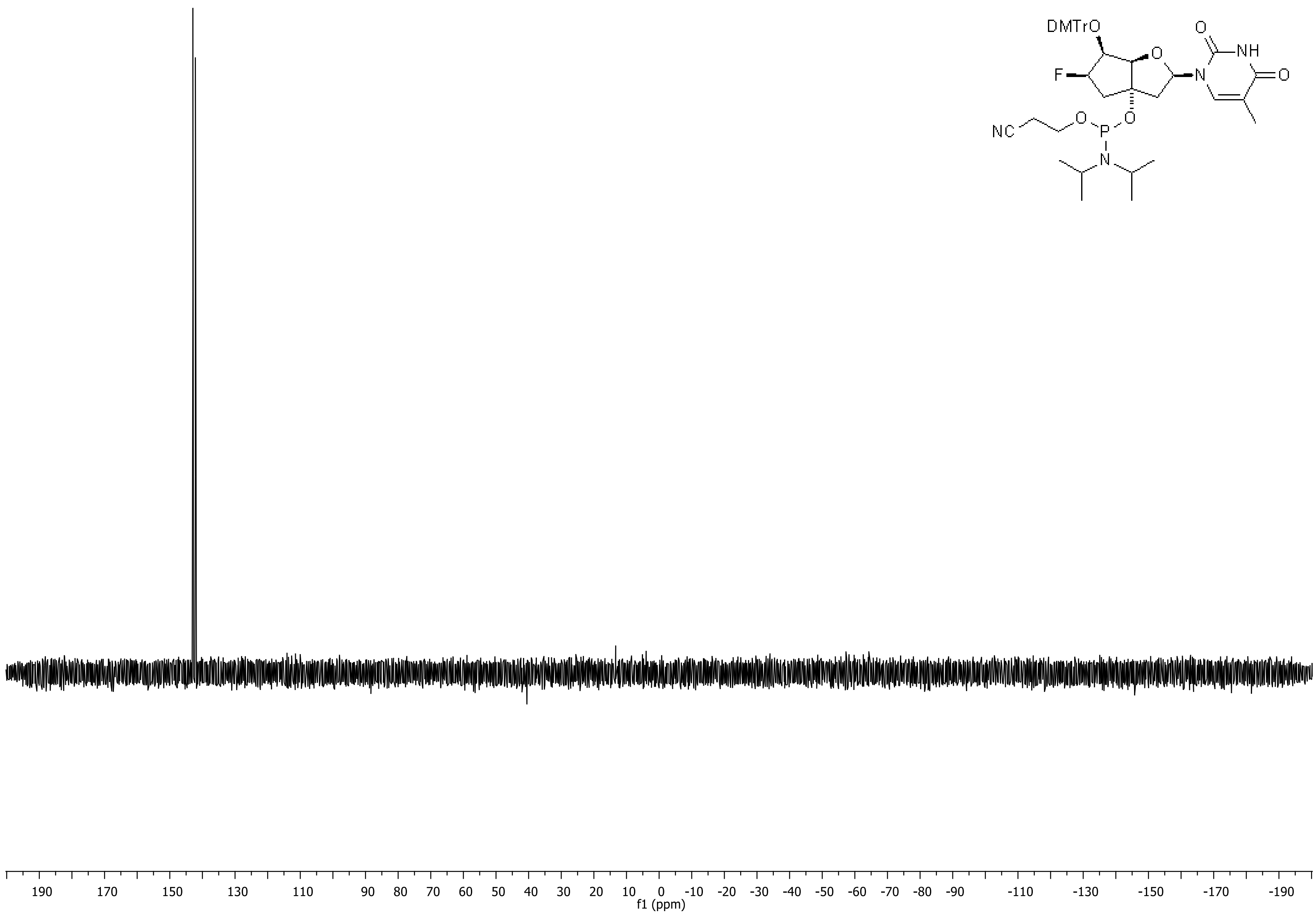


Figure S40: ^{31}P NMR ($CDCl_3$, 122 MHz) spectrum of **15**

Crystal-Structure Determination. –A colorless crystal of compound **13** ($C_{12}H_{15}FN_2O_5$)was mounted in air and used for X-ray structure determination at 173K. All measurements were made on a *Oxford Diffraction SuperNova* area-detector diffractometer using mirror optics monochromated Mo *K*α radiation (λ = 0.71073 Å) and Al filtered. The unit cell constants and an orientation matrix for data collection were obtained from a least-squares refinement of the setting angles of reflections in the range 2° < θ < 27.2°. A total of 561 frames were collected using ω scans, with 80+80 seconds exposure time, a rotation angle of 1.0° per frame and a crystal-detector distance of 65.2 mm.

Data reduction was performed using the *CrysAlisPro* program. The intensities were corrected for Lorentz and polarization effects, and an absorption correction based on the multi-scan method using SCALE3 ABSPACK in *CrysAlisPro* was applied. Data collection and refinement parameters are given in *Table 1.*

The structure was solved by direct methods using *SHELXS-97*, which revealed the positions of all non-hydrogen atoms of the title compound. The non-hydrogen atoms were refined anisotropically. All H-atoms were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2Ueq of its parent atom (1.5Ueq for the methyl groups).

Refinement of the structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. The weighting scheme was based on counting statistics and included a factor to downweight the intense reflections.

All calculations were performed using the *SHELXL-97* program.

The data did not allow assignment of absolute configuration, which was assigned based on the knowledge of the parent compound. Friedel pairs were then merged before the refinement.

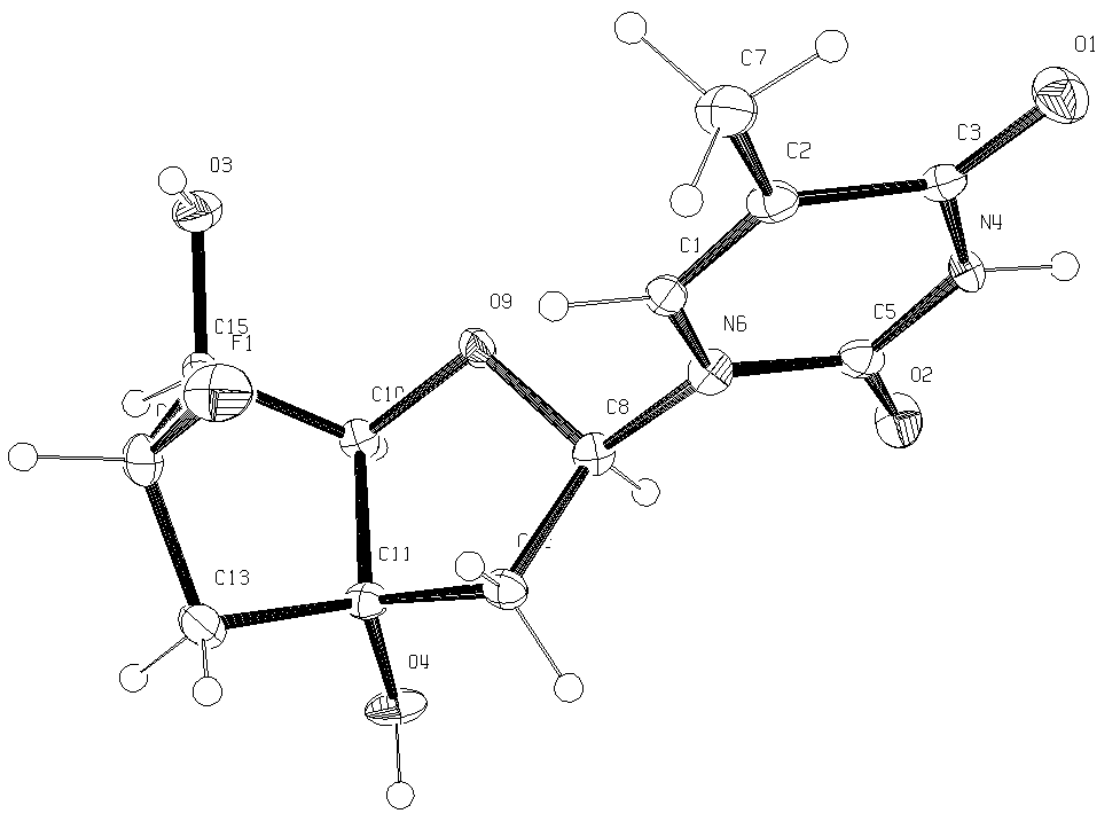


Figure S41: ORTEP view of compound **13**.

Table S1 - Crystal Data and Details of the Structure Determination
for: **13** in P2(1)2(1)2(1)

Crystal Data	
Formula	C12 H15 F N2 O5
Formula Weight	286.26
Crystal System	Orthorhombic
Space group	$P2_12_12_1$ (No. 19)
a, b, c [Angstrom]	6.1167(17) 13.975(2) 14.558(2)
V [Ang**3]	1244.5(4)
Z	4
D(calc) [g/cm**3]	1.528
Mu(MoKa) [/mm]	0.129
F(000)	600
Crystal Size [mm]	0.10 x 0.03 x 0.02
Data Collection	
Temperature (K)	173
Radiation [Angstrom]	MoKa 0.71073
Theta Min-Max [Deg]	2.0, 27.2
Dataset	7:-7; 16:-16 ; 17:-17
Tot., Uniq. Data, R(int)	9404, 1348, 0.1046
Observed data [I > 2.0 sigma(I)]	1050

Refinement

Nref, Npar	1348, 181
R, wR2, S	0.0827, 0.1418, 1.053
R, wR2 [I > 2.0 sigma(I)]	0.0589, 0.13
Max. and Av. Shift/Error	0.008, 0.001
Min. and Max. Resd. Dens. [e/Ang^3]	-0.37, 0.32

Table S2 - Final Coordinates and Equivalent Isotropic Displacement Parameters of the non-Hydrogen atoms for: **13** in P2(1)2(1)2(1)

Atom	x	y	z	U(eq) [Ang^2]
F1	-0.1977(6)	0.2464(3)	0.0962(2)	0.0402(11)
O1	0.4259(7)	0.6673(3)	-0.0174(3)	0.0340(14)
O2	0.6465(7)	0.4699(3)	0.2110(2)	0.0320(12)
O3	0.1204(7)	0.1193(3)	0.0323(2)	0.0312(11)
O4	0.1652(7)	0.2029(3)	0.3499(2)	0.0308(13)
O9	0.2905(6)	0.2673(2)	0.1314(2)	0.0222(11)
N4	0.5205(7)	0.5670(3)	0.0972(3)	0.0210(12)
N6	0.3192(8)	0.4350(3)	0.1397(3)	0.0230(12)
C1	0.1662(9)	0.4597(4)	0.0736(3)	0.0227(17)
C2	0.1852(9)	0.5370(4)	0.0190(3)	0.0240(16)
C3	0.3802(9)	0.5964(4)	0.0285(3)	0.0200(16)
C5	0.5076(9)	0.4881(4)	0.1529(3)	0.0243(17)
C7	0.0144(9)	0.5664(5)	-0.0500(4)	0.0333(19)
C8	0.2932(9)	0.3467(4)	0.1928(3)	0.0223(17)
C10	0.2147(9)	0.1874(4)	0.1847(3)	0.0197(17)
C11	0.0726(9)	0.2285(4)	0.2636(3)	0.0213(16)
C12	0.0838(9)	0.3375(4)	0.2472(3)	0.0227(17)
C13	-0.1562(10)	0.1839(4)	0.2483(3)	0.0317(17)
C14	-0.1657(9)	0.1617(4)	0.1469(4)	0.0307(17)
C15	0.0657(9)	0.1238(4)	0.1264(3)	0.0233(17)

U(eq) = 1/3 of the trace of the orthogonalized U Tensor

Table S3 - Hydrogen Atom Positions and Isotropic Displacement Parameters for: **13** in P2(1)2(1)2(1)

Atom	x	y	z	U(iso) [Ang^2]
H1	0.04144	0.41989	0.06637	0.0271
H3	0.02079	0.14486	0.00114	0.0468
H4	0.63445	0.60414	0.10659	0.0252
H4A	0.08833	0.22561	0.39248	0.0466
H7A	0.06078	0.62542	-0.08074	0.0496
H7B	-0.12488	0.57750	-0.01843	0.0496
H7C	-0.00396	0.51556	-0.09568	0.0496

H8	0.42031	0.33984	0.23546	0.0267
H10	0.34049	0.14993	0.20973	0.0234
H12A	-0.04375	0.36039	0.21162	0.0271
H12B	0.09225	0.37307	0.30591	0.0271
H13A	-0.17348	0.12484	0.28519	0.0378
H13B	-0.27274	0.22961	0.26568	0.0378
H14	-0.28028	0.11278	0.13281	0.0366
H15	0.07518	0.05733	0.15162	0.0281

===

The Temperature Factor has the Form of Exp(-T) Where

T = 8*(Pi**2)*U*(Sin(Theta)/Lambda)**2 for Isotropic Atoms

Table S4 - (An)isotropic Displacement Parameters
for: **13** in P2(1)2(1)2(1)

Atom	U(1,1) or U	U(2,2)	U(3,3)	U(2,3)	U(1,3)	U(1,2)
F1	0.0244(19)	0.062(2)	0.0341(17)	0.0028(17)	-0.0092(17)	0.0106(18)
O1	0.037(3)	0.034(2)	0.031(2)	0.0118(19)	-0.005(2)	-0.003(2)
O2	0.028(2)	0.033(2)	0.035(2)	0.0065(17)	-0.010(2)	-0.002(2)
O3	0.033(2)	0.039(2)	0.0215(18)	-0.0020(16)	-0.001(2)	-0.002(2)
O4	0.042(3)	0.034(2)	0.0165(18)	0.0013(15)	0.000(2)	0.017(2)
O9	0.0190(19)	0.0211(19)	0.0266(19)	-0.0024(16)	0.0079(18)	-0.0039(16)
N4	0.018(2)	0.021(2)	0.024(2)	0.001(2)	0.003(2)	-0.0059(19)
N6	0.021(2)	0.023(2)	0.025(2)	0.001(2)	-0.003(2)	0.004(2)
C1	0.015(3)	0.029(3)	0.024(3)	-0.008(2)	0.007(2)	-0.004(2)
C2	0.019(3)	0.032(3)	0.021(2)	-0.002(2)	0.001(3)	0.003(2)
C3	0.019(3)	0.026(3)	0.015(2)	-0.003(2)	-0.001(2)	0.003(2)
C5	0.026(3)	0.025(3)	0.022(3)	-0.002(2)	0.006(3)	0.005(2)
C7	0.023(3)	0.051(4)	0.026(3)	-0.001(3)	-0.002(3)	-0.003(3)
C8	0.021(3)	0.021(3)	0.025(3)	0.000(2)	0.000(3)	0.002(2)
C10	0.015(3)	0.019(3)	0.025(3)	0.001(2)	0.000(2)	0.005(2)
C11	0.019(3)	0.028(3)	0.017(2)	0.002(2)	-0.002(2)	0.003(2)
C12	0.019(3)	0.026(3)	0.023(3)	0.000(2)	0.003(2)	0.002(2)
C13	0.028(3)	0.039(3)	0.028(3)	0.005(3)	0.006(3)	-0.008(3)
C14	0.020(3)	0.038(3)	0.034(3)	-0.002(3)	-0.003(3)	-0.009(3)
C15	0.026(3)	0.018(3)	0.026(3)	0.000(2)	0.006(3)	-0.004(2)

===

The Temperature Factor has the Form of Exp(-T) Where

T = 8*(Pi**2)*U*(Sin(Theta)/Lambda)**2 for Isotropic Atoms

T = 2*(Pi**2)*Sumij(h(i)*h(j)*U(i,j)*Astar(i)*Astar(j)), for Anisotropic Atoms. Astar(i) are Reciprocal Axial Lengths and h(i) are the Reflection Indices.

Table S5 - Bond Distances (Angstrom)
for: **13** in P2(1)2(1)2(1)

F1	-C14	1.409(7)	C10	-C15	1.530(7)

O1	-C3	1.227(7)	C10	-C11	1.551(7)
O2	-C5	1.226(6)	C11	-C12	1.543(8)
O3	-C15	1.412(5)	C11	-C13	1.548(8)
O4	-C11	1.424(6)	C13	-C14	1.510(7)
O9	-C8	1.425(6)	C14	-C15	1.540(8)
O9	-C10	1.437(6)	C1	-H1	0.9500
O3	-H3	0.8400	C7	-H7A	0.9800
O4	-H4A	0.8400	C7	-H7B	0.9800
N4	-C5	1.371(7)	C7	-H7C	0.9800
N4	-C3	1.380(7)	C8	-H8	1.0000
N6	-C5	1.384(7)	C10	-H10	1.0000
N6	-C8	1.465(7)	C12	-H12A	0.9900
N6	-C1	1.386(7)	C12	-H12B	0.9900
N4	-H4	0.8800	C13	-H13A	0.9900
C1	-C2	1.346(7)	C13	-H13B	0.9900
C2	-C3	1.460(8)	C14	-H14	1.0000
C2	-C7	1.506(8)	C15	-H15	1.0000
C8	-C12	1.511(7)			

Table S6 - Bond Angles (Degrees)
for: **13** in P2(1)2(1)2(1)

C8	-O9	-C10	105.7(3)	C10	-C11	-C13	104.5(4)
C15	-O3	-H3	109.00	O4	-C11	-C10	109.7(4)
C11	-O4	-H4A	109.00	O4	-C11	-C13	112.7(4)
C3	-N4	-C5	129.2(5)	C8	-C12	-C11	101.7(4)
C1	-N6	-C8	120.2(4)	C11	-C13	-C14	105.0(4)
C1	-N6	-C5	121.7(4)	F1	-C14	-C13	110.2(4)
C5	-N6	-C8	118.0(4)	F1	-C14	-C15	108.4(4)
C5	-N4	-H4	115.00	C13	-C14	-C15	103.0(4)
C3	-N4	-H4	115.00	O3	-C15	-C14	114.9(4)
N6	-C1	-C2	123.5(5)	C10	-C15	-C14	103.9(4)
C1	-C2	-C7	123.6(5)	O3	-C15	-C10	115.0(4)
C3	-C2	-C7	118.3(5)	N6	-C1	-H1	118.00
C1	-C2	-C3	118.1(5)	C2	-C1	-H1	118.00
O1	-C3	-C2	126.4(5)	C2	-C7	-H7A	109.00
N4	-C3	-C2	114.0(4)	C2	-C7	-H7B	109.00
O1	-C3	-N4	119.6(5)	C2	-C7	-H7C	110.00
O2	-C5	-N4	122.4(5)	H7A	-C7	-H7B	109.00
O2	-C5	-N6	124.2(5)	H7A	-C7	-H7C	109.00
N4	-C5	-N6	113.4(4)	H7B	-C7	-H7C	109.00
O9	-C8	-N6	109.0(3)	O9	-C8	-H8	109.00
N6	-C8	-C12	116.1(5)	N6	-C8	-H8	109.00
O9	-C8	-C12	104.6(4)	C12	-C8	-H8	109.00
O9	-C10	-C11	107.0(4)	O9	-C10	-H10	111.00
O9	-C10	-C15	110.1(4)	C11	-C10	-H10	111.00
C11	-C10	-C15	107.0(4)	C15	-C10	-H10	111.00
C10	-C11	-C12	103.1(4)	C8	-C12	-H12A	111.00

C12	-C11	-C13	114.5(4)	C8	-C12	-H12B	111.00
O4	-C11	-C12	111.5(4)	C11	-C12	-H12A	111.00
C11	-C12	-H12B	111.00	F1	-C14	-H14	112.00
H12A	-C12	-H12B	109.00	C13	-C14	-H14	112.00
C11	-C13	-H13A	111.00	C15	-C14	-H14	112.00
C11	-C13	-H13B	111.00	O3	-C15	-H15	108.00
C14	-C13	-H13A	111.00	C10	-C15	-H15	108.00
C14	-C13	-H13B	111.00	C14	-C15	-H15	108.00
H13A	-C13	-H13B	109.00				

Table S7 - Torsion Angles (Degrees)
for: **13** in P2(1)2(1)2(1)

C8	-O9	-C10	-C15	142.2(4)
C10	-O9	-C8	-N6	-167.0(4)
C10	-O9	-C8	-C12	-42.1(5)
C8	-O9	-C10	-C11	26.2(5)
C3	-N4	-C5	-N6	-3.8(7)
C5	-N4	-C3	-O1	-176.3(5)
C5	-N4	-C3	-C2	4.1(8)
C3	-N4	-C5	-O2	179.1(5)
C5	-N6	-C1	-C2	-1.4(8)
C5	-N6	-C8	-C12	126.5(5)
C1	-N6	-C5	-N4	2.2(7)
C1	-N6	-C8	-C12	-58.2(6)
C1	-N6	-C5	-O2	179.2(5)
C8	-N6	-C5	-O2	-5.7(7)
C1	-N6	-C8	-O9	59.6(6)
C8	-N6	-C5	-N4	177.3(4)
C8	-N6	-C1	-C2	-176.5(5)
C5	-N6	-C8	-O9	-115.6(5)
N6	-C1	-C2	-C7	-177.2(5)
N6	-C1	-C2	-C3	1.6(8)
C7	-C2	-C3	-N4	176.2(5)
C1	-C2	-C3	-N4	-2.7(7)
C1	-C2	-C3	-O1	177.7(5)
C7	-C2	-C3	-O1	-3.4(8)
N6	-C8	-C12	-C11	160.5(4)
O9	-C8	-C12	-C11	40.2(4)
O9	-C10	-C11	-O4	-119.6(4)
O9	-C10	-C11	-C12	-0.7(5)
O9	-C10	-C11	-C13	119.3(4)
C15	-C10	-C11	-O4	122.4(5)
C15	-C10	-C11	-C12	-118.7(4)
C15	-C10	-C11	-C13	1.3(5)
O9	-C10	-C15	-O3	33.2(6)
O9	-C10	-C15	-C14	-93.2(5)
C11	-C10	-C15	-O3	149.2(4)

C11	-C10	-C15	-C14	22.8(5)
O4	-C11	-C12	-C8	94.6(4)
C10	-C11	-C12	-C8	-23.1(5)
C13	-C11	-C12	-C8	-136.0(4)
O4	-C11	-C13	-C14	-144.6(4)
C10	-C11	-C13	-C14	-25.6(5)
C12	-C11	-C13	-C14	86.5(5)
C11	-C13	-C14	-F1	-75.5(5)
C11	-C13	-C14	-C15	39.9(5)
F1	-C14	-C15	-O3	-48.5(6)
F1	-C14	-C15	-C10	78.1(5)
C13	-C14	-C15	-O3	-165.2(5)
C13	-C14	-C15	-C10	-38.7(5)

Table S8 - Contact Distances(Angstrom)
for: **13** in P2(1)2(1)2(1)

F1	.O3	2.794(6)	O2	.H12A_d	2.4400
F1	.O9_a	3.186(5)	O4	.H4_h	1.9500
F1	.O9	3.044(5)	O9	.H1	2.7900
F1	.C12	3.069(6)	O9	.H3_f	2.6900
F1	.O3_b	2.874(5)	N4	.O4_e	2.810(6)
F1	.H3	2.3900	N6	.O3_f	3.200(6)
F1	.H12A	2.5000	N4	.H13A_i	2.8400
F1	.H1	2.8600	N4	.H7B_d	2.7500
F1	.H3_b	2.7000	N6	.H3_f	2.6400
O1	.O4_c	2.708(6)	C1	.O3_f	3.364(7)
O2	.C12_d	3.295(7)	C5	.O3_f	3.162(6)
O3	.C5_b	3.162(6)	C12	.F1	3.069(6)
O3	.F1	2.794(6)	C12	.O2_a	3.295(7)
O3	.O9	2.728(5)	C1	.H3_f	2.8300
O3	.N6_b	3.200(6)	C1	.H12A	2.7600
O3	.C1_b	3.364(7)	C1	.H13A_i	3.0900
O3	.F1_f	2.874(5)	C2	.H14_f	3.0500
O4	.O1_g	2.708(6)	C3	.H13A_i	3.0200
O4	.N4_h	2.810(6)	C5	.H3_f	2.9100
O9	.F1	3.044(5)	C5	.H13A_i	2.9400
O9	.O3	2.728(5)	C7	.H14_f	3.0500
O9	.F1_d	3.186(5)	C12	.H1	2.8800
O1	.H7A	2.4900	C14	.H12A	3.0300
O1	.H12B_c	2.6400	H1	.F1	2.8600
O1	.H4A_c	1.9900	H1	.O9	2.7900
O2	.H10_e	2.7700	H1	.C12	2.8800
O2	.H8	2.3100	H1	.H12A	2.3300
O2	.H15_e	2.9000	H3	.F1	2.3900
H3	.F1_f	2.7000	H12A	.F1	2.5000
H3	.O9_b	2.6900	H12A	.O2_a	2.4400
H3	.N6_b	2.6400	H12A	.C1	2.7600

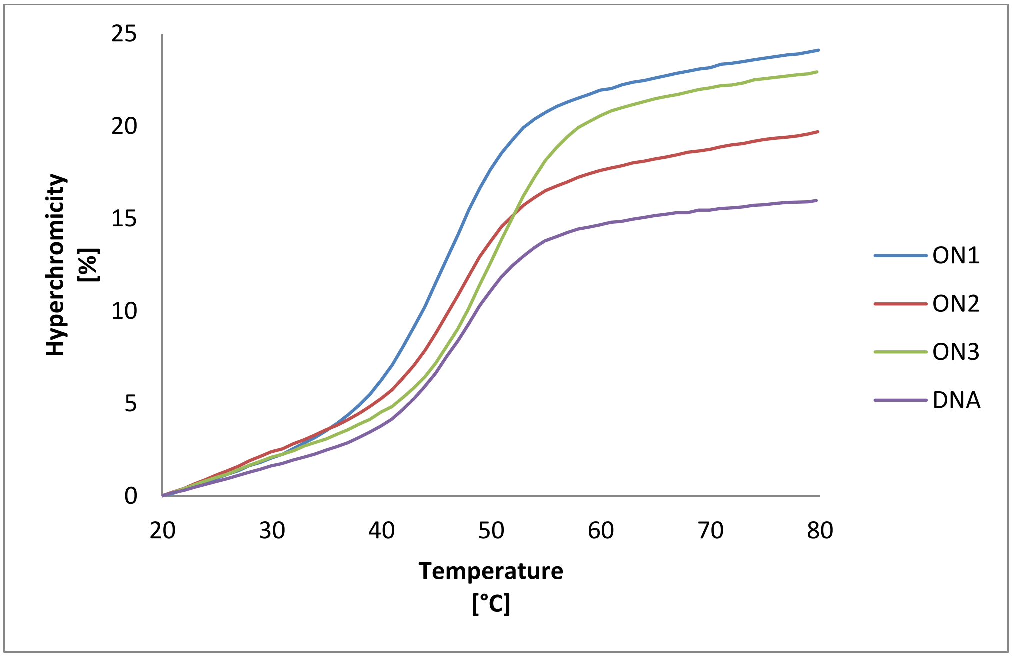
H3	.C1_b	2.8300	H12A	.C14	3.0300
H3	.C5_b	2.9100	H12A	.H1	2.3300
H4	.H7B_d	2.3700	H12A	.H13B	2.4300
H4	.O4_e	1.9500	H12B	.H4A	2.4200
H4	.H4A_e	2.4000	H12B	.O1_g	2.6400
H4A	.H12B	2.4200	H13A	.N4_j	2.8400
H4A	.O1_g	1.9900	H13A	.C1_j	3.0900
H4A	.H4_h	2.4000	H13A	.C3_j	3.0200
H7A	.O1	2.4900	H13A	.C5_j	2.9400
H7B	.N4_a	2.7500	H13B	.H8_a	2.4700
H7B	.H4_a	2.3700	H13B	.H12A	2.4300
H7C	.H14_f	2.3200	H14	.C2_b	3.0500
H8	.O2	2.3100	H14	.C7_b	3.0500
H8	.H13B_d	2.4700	H14	.H7C_b	2.3200
H10	.O2_h	2.7700	H15	.O2_h	2.9000

Table S9 - Hydrogen Bonds (Angstrom, Deg)
for: **13** in P2(1)2(1)2(1)

O3	-- H3	.. F1	0.8400	2.3900	2.794(6)	110.00	.
N4	-- H4	.. O4	0.8800	1.9500	2.810(6)	165.00	4_655
O4	-- H4A	.. O1	0.8400	1.9900	2.708(6)	143.00	2_565
C7	-- H7A	.. O1	0.9800	2.4900	2.924(7)	107.00	.
C8	-- H8	.. O2	1.0000	2.3100	2.776(7)	107.00	.
C12	-- H12A	.. F1	0.9900	2.5000	3.069(6)	116.00	.
C12	-- H12A	.. O2	0.9900	2.4400	3.295(7)	145.00	1_455

Translation of Symmetry Code to Equiv.Pos

a =[1455.00] = -1+x,y,z
b =[3455.00] = -1/2+x,1/2-y,-z
c =[2564.00] = 1/2-x,1-y,-1/2+z
d =[1655.00] = 1+x,y,z
e =[4655.00] = 1-x,1/2+y,1/2-z
f =[3555.00] = 1/2+x,1/2-y,-z
g =[2565.00] = 1/2-x,1-y,1/2+z
h =[4645.00] = 1-x,-1/2+y,1/2-z
i =[4555.00] = -x,1/2+y,1/2-z
j =[4545.00] = -x,-1/2+y,1/2-z



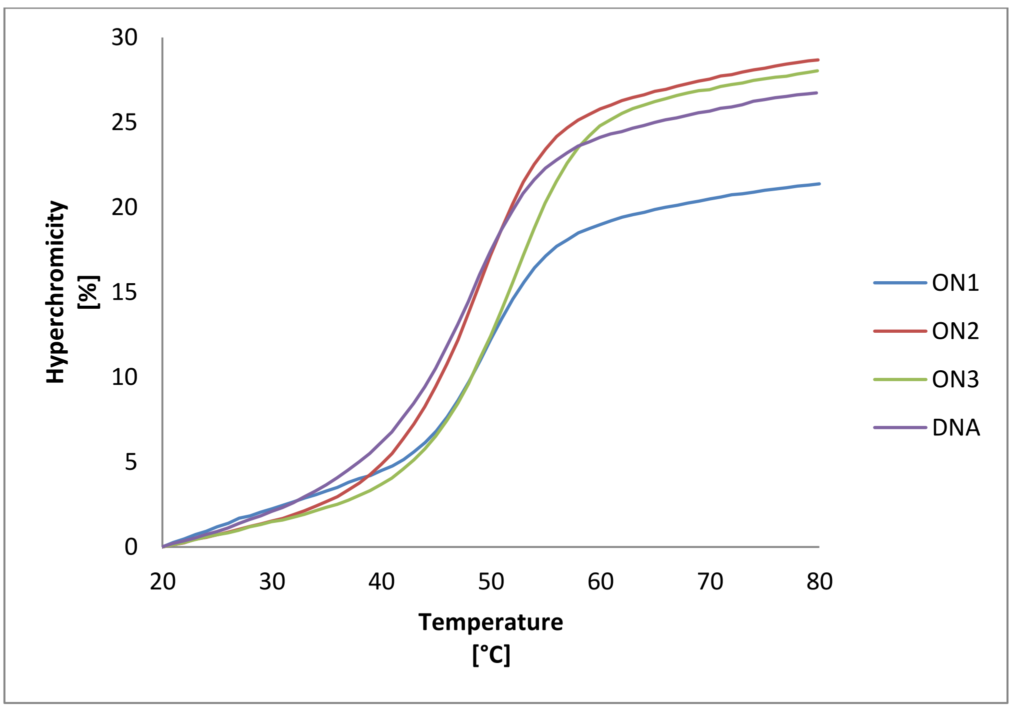
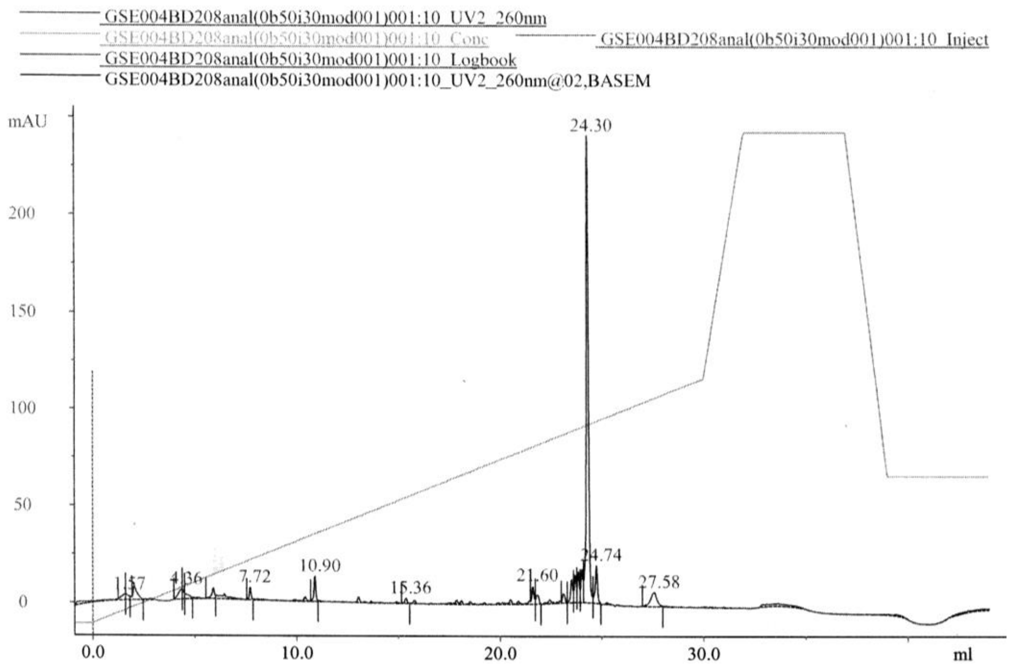


Figure S42: Melting curves of 6’F-bcT in oligonucleotides vs DNA (top) and vs RNA(bottom). Conditions: 1.2 µM single strands in 150 mM NaCl and 10 mM NaH_2PO_4 at pH 7.0



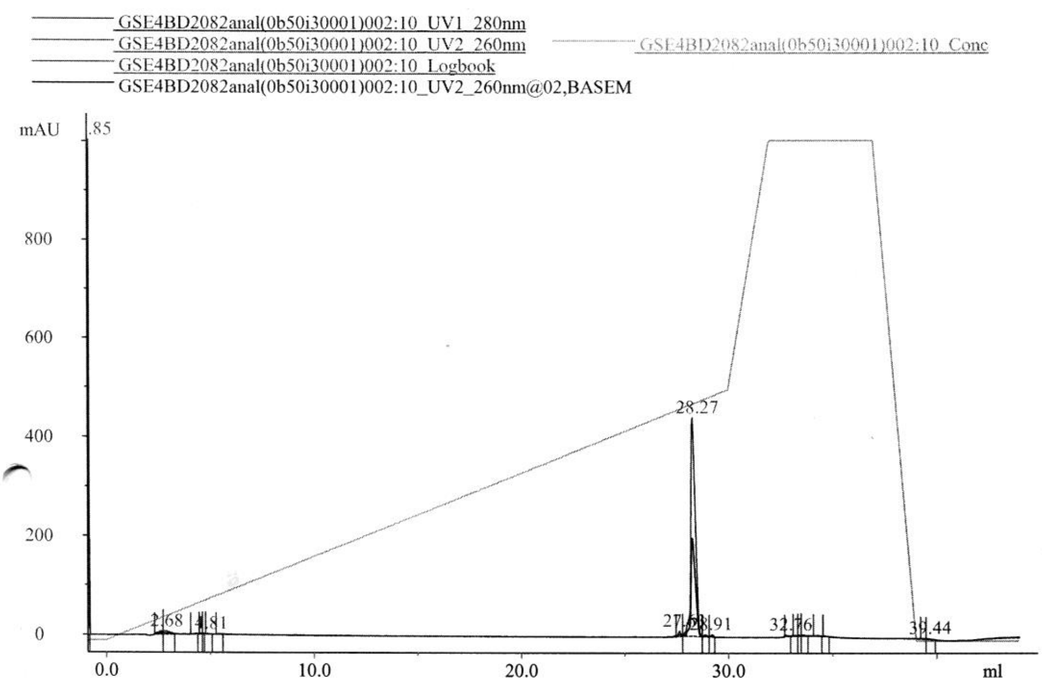
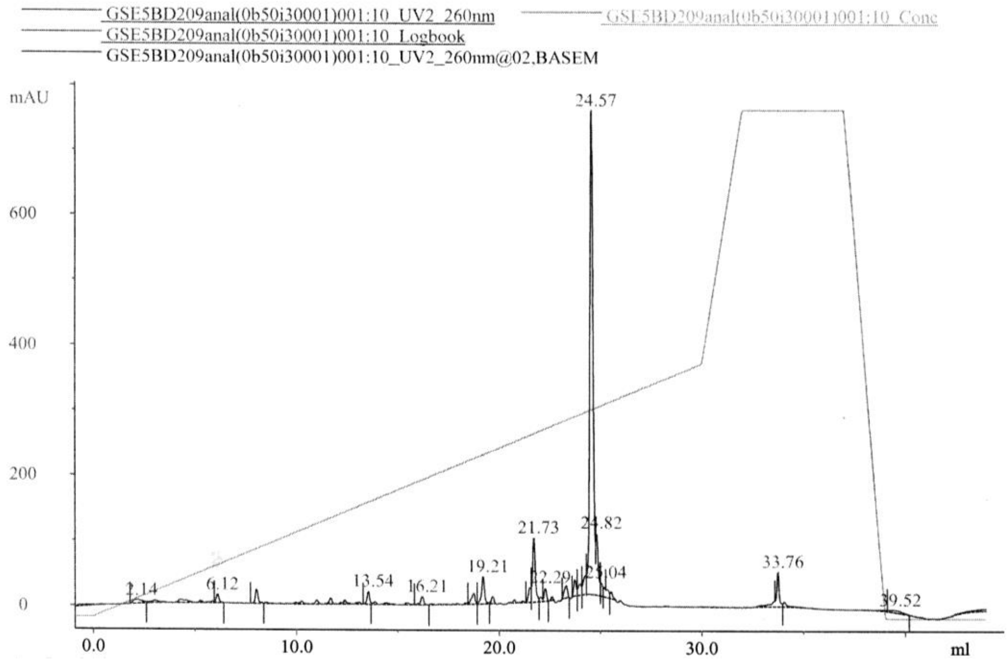


Figure S43: HPLC traces of **ON1** as crude mixture (top) and after purification (bottom). Conditions: Dionex DNA Pac-PA100 (top), Dionex DNA Pac-PA200 (bottom); Buffer A: 25 mM Trizma in H_2O, buffer B 25 mM Trizma, 1.25 M NaCl in H_2O, pH 8.0, 0 to 50% B in A over 30 min with 1 mL/min.



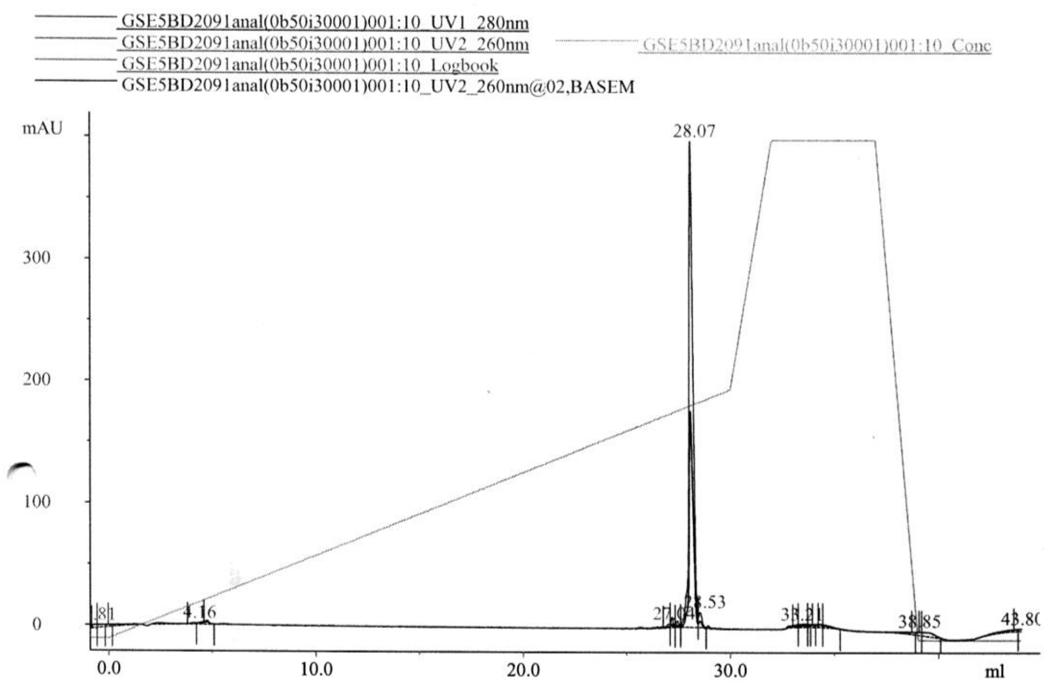
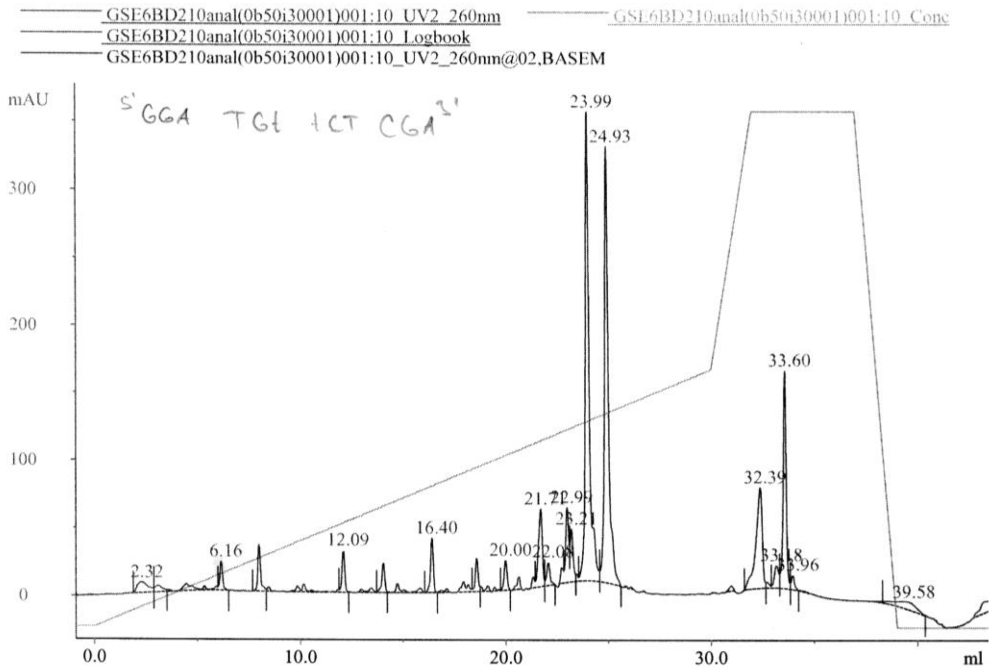


Figure S44: HPLC traces of **ON2** as crude mixture (top) and after purification (bottom). Conditions: Dionex DNA Pac-PA100 (top), Dionex DNA Pac-PA200 (bottom); Buffer A: 25 mM Trizma in H_2O, buffer B 25 mM Trizma, 1.25 M NaCl in H_2O, pH 8.0, 0 to 50% B in A over 30 min with 1 mL/min.



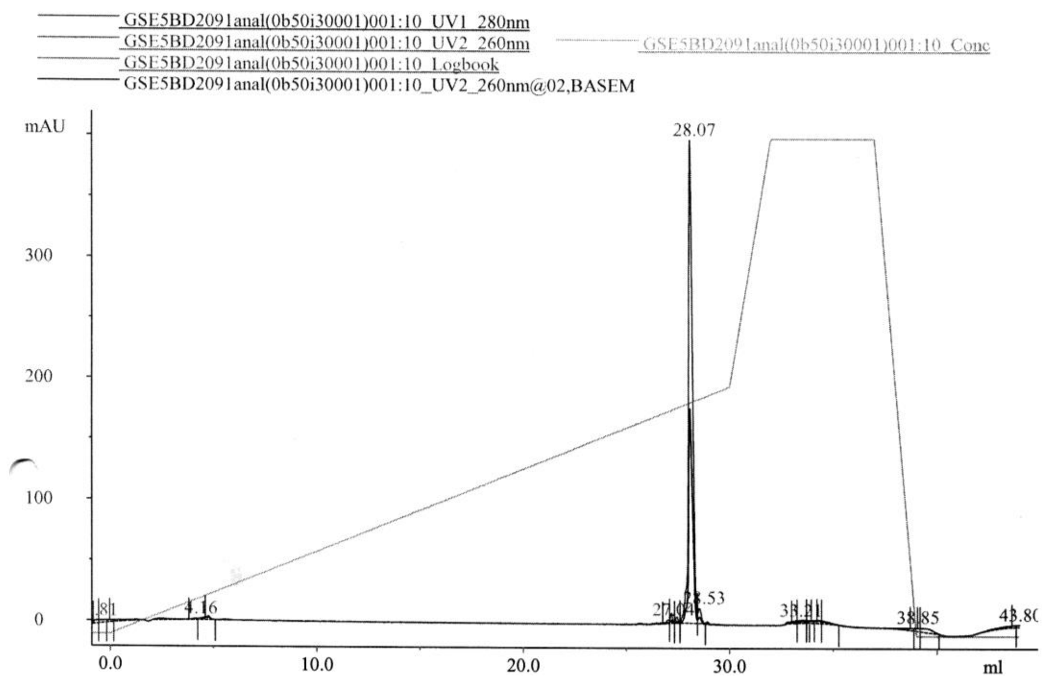


Figure S45: HPLC traces of **ON3** as crude mixture (top) and after purification (bottom). Conditions: Dionex DNA Pac-PA100 (top), Dionex DNA Pac-PA200 (bottom); Buffer A: 25 mM Trizma in H_2O, buffer B 25 mM Trizma, 1.25 M NaCl in H_2O, pH 8.0, 0 to 50% B in A over 30 min with 1 mL/min.

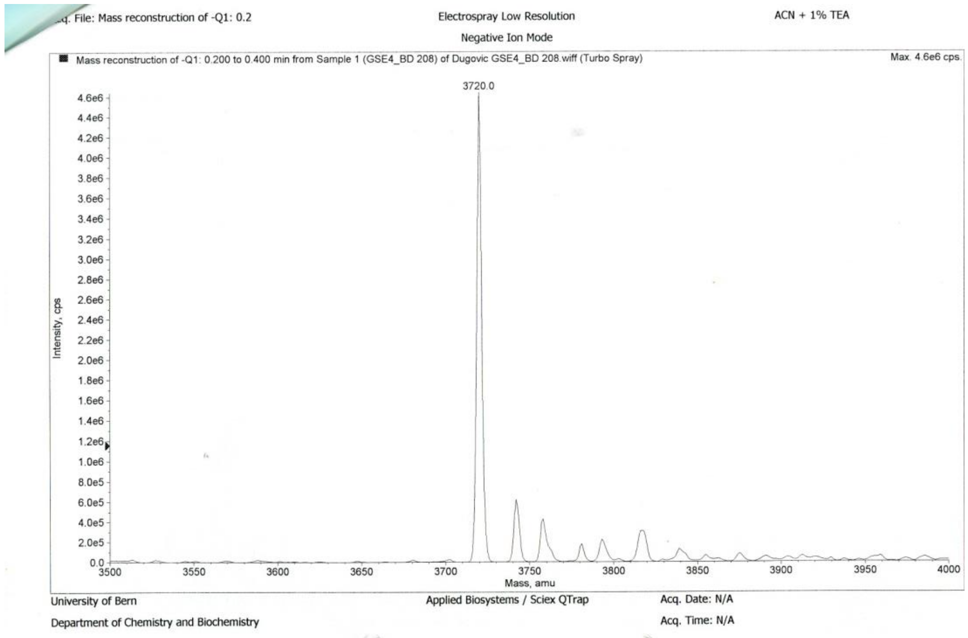


Figure S46: Reconstruction of a ESI−-MS of **ON1**.

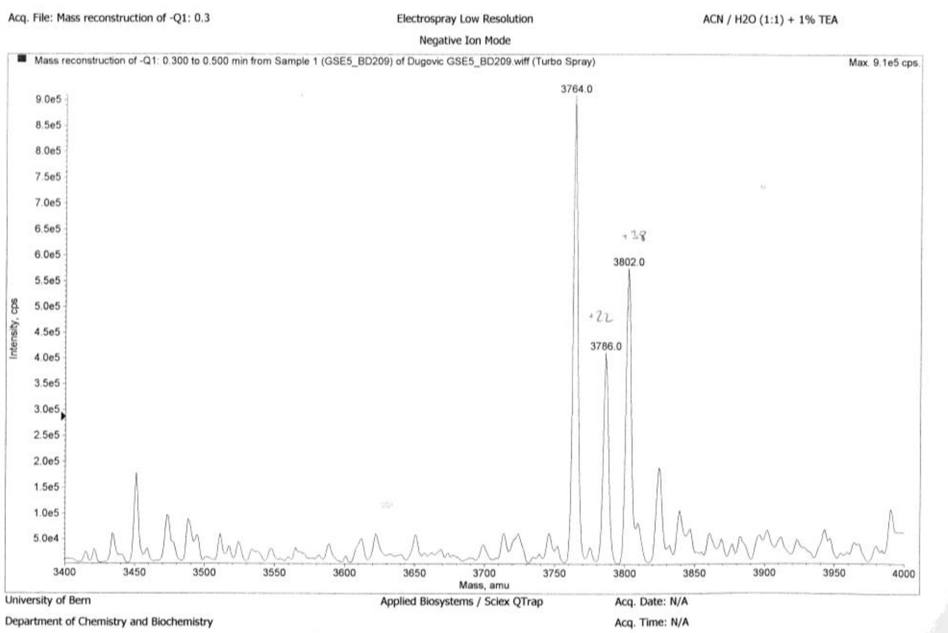


Figure S47: Reconstruction of ESI−-MS of **ON2** (see also Table S10)

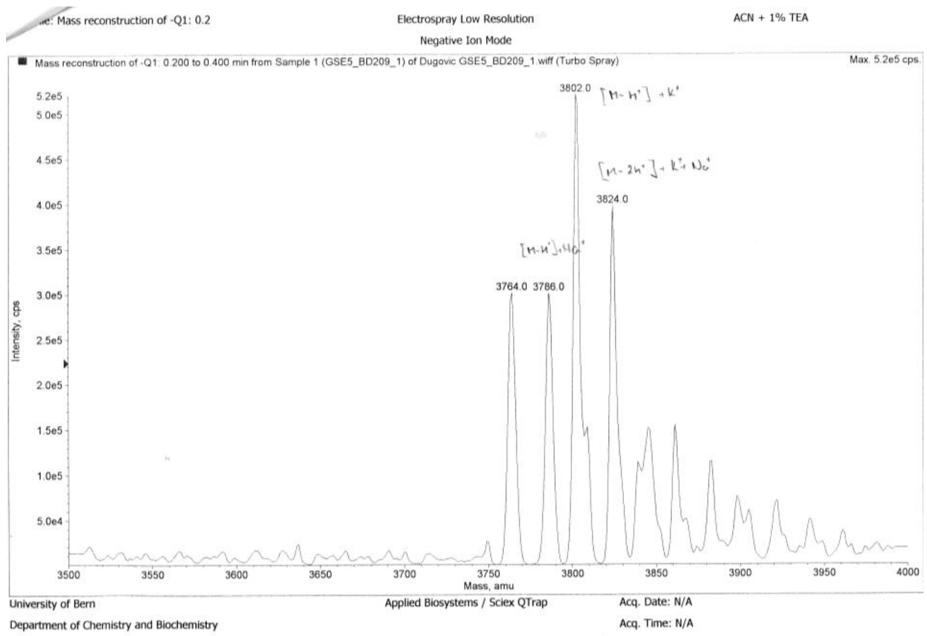


Figure S48: Reconstruction of ESI−-MS of **ON3**