Catalyst-Free and Solvent-Controlled Divergent Synthesis of Difluoromethylene-Containing *S*-Heterocycles

Jun-Xiong He,[†] Zhi-Hao Zhang,[†] Bo-Shuai Mu,[†] Xiao-Yuan Cui,[†] Jian Zhou,[†,§] and Jin-Sheng Yu*[,†,#]

[†] *Shanghai Engineering Research Center of Molecular Therapeutics and New Drug Development, and Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200062, China. E-mail: jsyu@chem.ecnu.edu.cn*

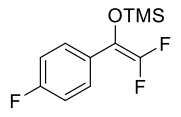
[§] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, CAS, Shanghai 200032, China.*

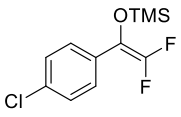
[#] *Key Laboratory of Tropical Medicinal Resource Chemistry of Ministry of Education, Hainan Normal University, Haikou 571158, P R China.*

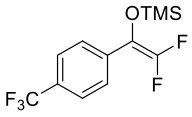
1. The structure and serial number of difluoroenoxysilanes 1 and products 4.

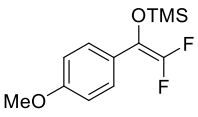
The structure and serial number of difluoroenoxysilanes **1** and C2-adducts **4** were shown below for clear.

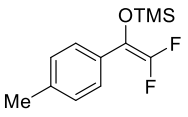
Table S1. The structure and serial number of difluoroenoxysilanes **1**.

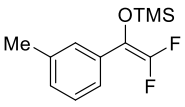

1b

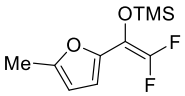

1c

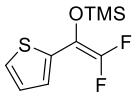

1j

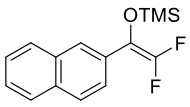

1d


1e


1f


1g


1h


1k

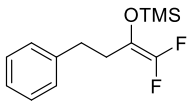
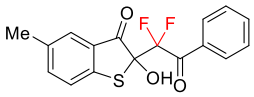
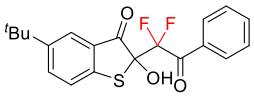
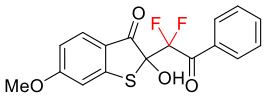
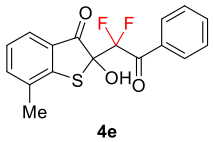

1i

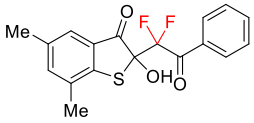
Table S2. The structure and serial number of C2-adducts **4**.

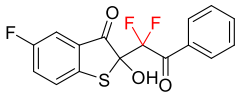

4b

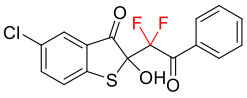

4c

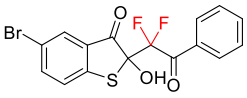

4d

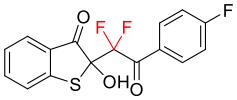

4e

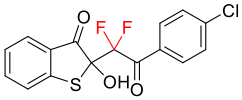

4f

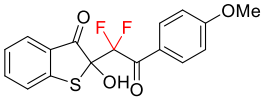

4g

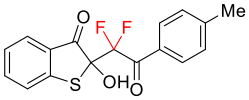

4h

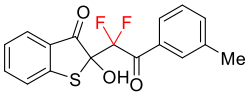

4i

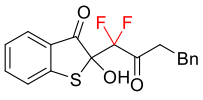

4j

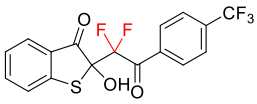

4k

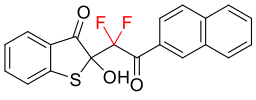

4l


4m


4n


4q


4r

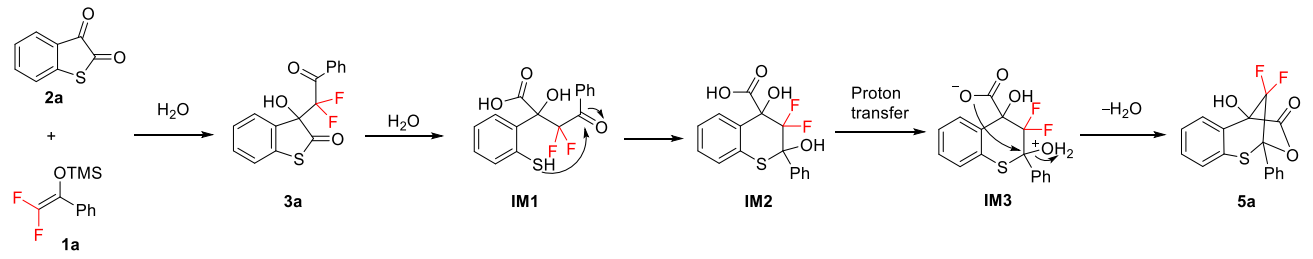

4s

2. The possible pathway for the formation of product 5

According to the observation of experimental result, the reaction of benzo[*b*]thiophene-2,3-diones **1a** and difluoroenoxysilane **2a** in H_2O delivered the 3-difluoroalkyl substituted 3-hydroxylbenzothiophen-2-one **3a** firstly, which was subsequently converted into the bridged seven-membered *S*-heterocycle **5a** through the following possible pathway.

The thioester moiety of **3a** was attacked by solvent H_2O and proceeded a ring-opening reaction to deliver an intermediate **IM1**. The thiophenol anion of **IM1** then reacted with the ketone moiety, because the presence of difluoromethyl makes the ketone group more reactive. Subsequently, the resultant intermediate **IM2** went through a cyclization to provide the bridged seven-membered *S*-heterocycle **5a**. The experimental result of **3a** and CH_3NH_2 in ethanol also supports the possibility of this hypothesis (Scheme 2B in the main text).

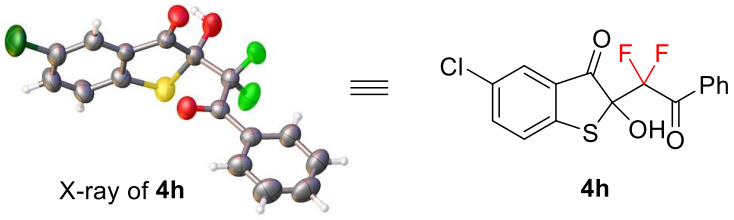
Plausible pathway



3. X-Ray crystal data of 4h, 5a, and 5i

Single crystals of **4h**, **5a**, and **5i** were obtained by slow diffusion of its solution in *n*-hexane/EtOAc at room temperature in air.

Data intensity of **4h**[1] was collected using a 'XtaLAB AFC12 (RINC) ' diffractometer at 292.69(11) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. Crystal data for **4h**: $C_{16}H_9ClF_2O_3S$, T = 292.69(11) K, monoclinic, $P2_1/c$, a = 15.5043(10) Å, b = 15.5994(10) Å, c = 6.4142(4) Å, α = 90°, β = 96.411(6)°, γ = 90°, V = 1541.62(17) Å^3. Z = 4, ρ_{calc} = 1.528 g/cm^3. 13850 reflections collected, 2747 [R_{int} = 0.0636, R_{sigma} = 0.0396] independent reflections, R_1 = 0.0547, wR_2 = 0.1379 ($I >= 2\sigma(I)$, final), R_1 = 0.0697, wR_2 = 0.1472 (all data), GOF = 1.027, and 209 parameters.



ORTEP, ellipsoids set at 50% probability.

Table S3. Crystal data and structure refinement for **4h**.

Identification code	**4h**
Empirical formula	$C_{16}H_9ClF_2O_3S$
Formula weight	354.74
Temperature/K	292.69(11)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.5043(10)
b/Å	15.5994(10)

[3] Supplementary crystallographic data have been deposited at Cambridge Crystallographic Data Center (CCDC number: 2056189).

c/Å	6.4142(4)
α/°	90
β/°	96.411(6)
γ/°	90
Volume/Å^3	1541.62(17)
Z	4
ρ_{calc}g/cm^3	1.528
μ/mm^{-1}	3.778
F(000)	720.0
Crystal size/mm^3	0.32 × 0.16 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.066 to 134.118
Index ranges	-18 ≤ h ≤ 18, -18 ≤ k ≤ 18, -5 ≤ l ≤ 7
Reflections collected	13850
Independent reflections	2747 [R_{int} = 0.0636, R_{sigma} = 0.0396]
Data/restraints/parameters	2747/0/209
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0547, wR_2 = 0.1379
Final R indexes [all data]	R_1 = 0.0697, wR_2 = 0.1472
Largest diff. peak/hole / e Å^{-3}	0.53/-0.23

Table S4. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **4h**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	7434.0(5)	4300.0(6)	7272.2(11)	60.8(3)
Cl1	3604.2(6)	3338.9(8)	4150(2)	99.3(4)
F2	8756.3(12)	3791.1(11)	2485(3)	68.0(5)
F1	8998.6(12)	4599.9(14)	5252(3)	72.6(6)
O3	7089.8(13)	4970.4(14)	2342(3)	59.0(5)
O1	8320.3(14)	3000.3(14)	5695(4)	68.1(6)
O2	6982.7(14)	2974.8(14)	2142(3)	65.1(6)

C1	6164.2(18)	3612.2(17)	4677(4)	43.9(6)
C10	7875.6(19)	5004.1(17)	2583(4)	45.4(6)
C7	7786.7(18)	3693.3(18)	5066(4)	48.0(7)
C11	8386(2)	5667.0(18)	1626(4)	49.5(7)
C9	8355.4(18)	4274.5(18)	3861(4)	48.2(6)
C8	6946.8(18)	3395.9(17)	3714(4)	47.7(7)
C6	6339.3(19)	4066.6(19)	6533(4)	49.8(7)
C2	5329.5(19)	3376.1(19)	3914(5)	52.2(7)
C3	4664(2)	3612(2)	5057(5)	59.7(8)
C16	9282(2)	5651(2)	1695(5)	61.0(8)
C4	4825(2)	4067(2)	6897(6)	67.4(9)
C5	5658(2)	4291(2)	7657(5)	62.7(8)
C12	7920(2)	6334(2)	567(5)	66.6(9)
C15	9715(3)	6290(2)	739(6)	73.8(10)
C13	8359(3)	6957(3)	-392(7)	87.7(12)
C14	9248(3)	6940(3)	-292(6)	86.3(12)

Table S5. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **4h**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
S1	54.6(5)	82.3(6)	45.6(4)	-11.0(4)	6.1(3)	-8.1(4)
Cl1	45.2(5)	126.1(9)	125.1(9)	-6.1(7)	3.4(5)	-8.1(5)
F2	65.3(12)	61.5(11)	83.9(12)	11.0(9)	38.4(9)	9.6(9)
F1	52.4(11)	91.7(14)	70.4(12)	22.9(10)	-8.2(9)	-20.0(9)
O3	46.3(12)	65.9(13)	64.7(13)	9.1(10)	5.7(9)	2.0(10)
O1	53.2(13)	64.2(13)	90.0(17)	29.1(12)	21.9(11)	6.6(11)
O2	65.7(14)	67.1(13)	65.8(14)	-25.8(11)	21.8(11)	-6.9(11)
C1	45.2(15)	40.8(14)	47.1(15)	2.5(11)	11.1(12)	1.9(11)
C10	51.0(16)	46.9(15)	38.7(14)	-2.8(11)	6.3(12)	1.2(13)
C7	44.0(15)	48.6(15)	52.6(16)	6.6(12)	10.9(12)	3.0(12)
C11	61.1(18)	47.3(15)	39.9(14)	-2.1(12)	5.5(12)	-3.0(13)

C9	43.3(15)	52.7(16)	48.8(15)	3.1(13)	6.1(12)	-1.2(13)
C8	50.2(16)	42.9(14)	51.5(16)	-3.0(12)	13.1(13)	-2.2(12)
C6	55.1(17)	53.4(16)	42.0(15)	-1.1(12)	10.9(12)	5.1(13)
C2	49.5(17)	53.9(17)	53.2(17)	-1.4(13)	5.6(13)	-3.3(13)
C3	44.9(17)	63.9(19)	71(2)	7.2(16)	7.7(15)	2.6(14)
C16	63(2)	64.2(19)	56.3(18)	9.1(15)	9.4(15)	-6.7(16)
C4	55(2)	78(2)	73(2)	-7.7(18)	23.6(16)	9.5(17)
C5	62(2)	73(2)	56.3(18)	-14.3(16)	18.5(15)	4.0(16)
C12	78(2)	58.7(19)	62(2)	11.4(16)	5.2(17)	2.1(17)
C15	77(2)	81(2)	65(2)	12.4(19)	17.1(17)	-21.1(19)
C13	109(3)	73(2)	80(3)	29(2)	7(2)	-3(2)
C14	118(4)	73(2)	70(2)	18(2)	19(2)	-28(2)

Table S6. Bond Lengths for **4h**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C7	1.835(3)	C7	C9	1.533(4)
S1	C6	1.749(3)	C7	C8	1.553(4)
Cl1	C3	1.734(3)	C11	C16	1.385(4)
F2	C9	1.363(3)	C11	C12	1.399(4)
F1	C9	1.360(3)	C6	C5	1.388(4)
O3	C10	1.212(3)	C2	C3	1.381(4)
O1	C7	1.393(3)	C3	C4	1.376(5)
O2	C8	1.210(3)	C16	C15	1.383(5)
C1	C8	1.461(4)	C4	C5	1.374(5)
C1	C6	1.386(4)	C12	C13	1.371(5)
C1	C2	1.382(4)	C15	C14	1.373(6)
C10	C11	1.477(4)	C13	C14	1.373(6)
C10	C9	1.544(4)			

Table S7. Bond Angles for **4h**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°

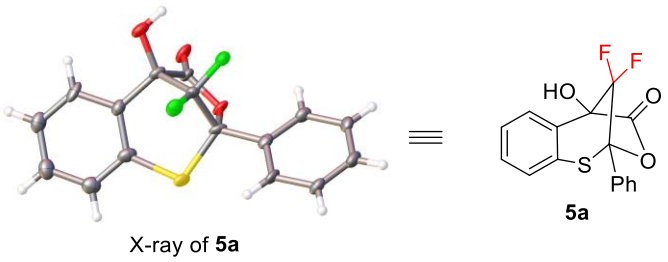
C6	S1	C7	92.71(13)	F1	C9	C7	108.1(2)
C6	C1	C8	112.9(3)	C7	C9	C10	115.7(2)
C2	C1	C8	125.3(3)	O2	C8	C1	126.6(3)
C2	C1	C6	121.8(3)	O2	C8	C7	120.9(3)
O3	C10	C11	123.7(3)	C1	C8	C7	112.2(2)
O3	C10	C9	117.0(2)	C1	C6	S1	115.5(2)
C11	C10	C9	119.2(2)	C1	C6	C5	119.2(3)
O1	C7	S1	113.3(2)	C5	C6	S1	125.3(2)
O1	C7	C9	104.4(2)	C3	C2	C1	117.8(3)
O1	C7	C8	111.3(2)	C2	C3	Cl1	119.5(3)
C9	C7	S1	108.75(19)	C4	C3	Cl1	119.3(3)
C9	C7	C8	112.9(2)	C4	C3	C2	121.2(3)
C8	C7	S1	106.35(18)	C15	C16	C11	120.5(3)
C16	C11	C10	123.8(3)	C5	C4	C3	120.6(3)
C16	C11	C12	119.4(3)	C4	C5	C6	119.4(3)
C12	C11	C10	116.8(3)	C13	C12	C11	119.3(4)
F2	C9	C10	106.9(2)	C14	C15	C16	119.4(4)
F2	C9	C7	109.2(2)	C12	C13	C14	120.8(4)
F1	C9	F2	106.1(2)	C15	C14	C13	120.6(3)
F1	C9	C10	110.3(2)				

Table S8. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **4h**.

Atom	***x***	***y***	***z***	**U(eq)**
H1	8047.98	2652.96	6323.93	102
H2	5219.47	3068.15	2671.66	63
H16	9595.03	5206.48	2388.56	73
H4	4366.32	4223.37	7634.51	81
H5	5765.06	4589.72	8912.95	75
H12	7318.41	6354.31	513.57	80
H15	10316.81	6279.11	794.58	89

H13	8050.66	7395.9	-1119.01	105
H14	9536.51	7374.03	-927.75	104

Data intensity of **5a**[2] was collected using a 'XtaLAB AFC12 (RINC)' diffractometer at 100.01(13) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. Crystal data for **5a**: $C_{16}H_{10}F_2O_3S$, T = 100.01(13) K, monoclinic, $P2_1$, a = 7.10550(10) Å, b = 11.4391(2) Å, c = 34.0389(6) Å, α = 90°, β = 89.638(2)°, γ = 90°, V = 2766.64(8) Å^3. Z = 8, ρ_{calc} = 1.538 g/cm^3. 26426 reflections collected, 9020 [R_{int} = 0.0969, R_{sigma} = 0.0720] independent reflections, R_1 = 0.0749, wR_2 = 0.2019 (I >= 2σ(I), final), R_1 = 0.0789, wR_2 = 0.2053 (all data), GOF = 1.066, and 797 parameters.



X-ray of **5a**

ORTEP, ellipsoids set at 50% probability

Table S9. Crystal data and structure refinement for **5a.**

Identification code	**5a**
Empirical formula	$C_{16}H_{10}F_2O_3S$
Formula weight	320.30
Temperature/K	100.01(13)
Crystal system	monoclinic
Space group	$P2_1$

[2] Supplementary crystallographic data have been deposited at Cambridge Crystallographic Data Center (CCDC number: 2056190).

a/Å	7.10550(10)
b/Å	11.4391(2)
c/Å	34.0389(6)
α/°	90
β/°	89.638(2)
γ/°	90
Volume/Å^3	2766.64(8)
Z	8
ρ_{calc}g/cm^3	1.538
μ/mm^{-1}	2.407
F(000)	1312.0
Crystal size/mm^3	0.32 × 0.16 × 0.14
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.792 to 134.156
Index ranges	-8 ≤ h ≤ 4, -13 ≤ k ≤ 13, -40 ≤ l ≤ 40
Reflections collected	26426
Independent reflections	9020 [R_{int} = 0.0969, R_{sigma} = 0.0720]
Data/restraints/parameters	9020/1/797
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0749, wR_2 = 0.2019
Final R indexes [all data]	R_1 = 0.0789, wR_2 = 0.2053
Largest diff. peak/hole / e Å^{-3}	0.56/-0.70

Table S10. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **5a**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
C1	254(9)	-5210(6)	9352.7(19)	18.9(14)

C2	112(9)	-5404(7)	9757.8(19)	21.9(15)
C3	1460(10)	-6027(7)	9955(2)	25.6(16)
C4	3011(11)	-6451(7)	9760(2)	29.1(17)
C5	3193(11)	-6299(7)	9355(2)	29.4(18)
C6	1836(9)	-5662(6)	9150.5(19)	20.7(15)
C7	321(10)	-4521(7)	8521(2)	23.6(16)
C8	-265(10)	-3303(7)	9055.2(19)	22.0(15)
C9	-1222(9)	-4494(7)	9144.9(18)	19.5(15)
C10	-1495(9)	-4913(6)	8729.3(18)	16.5(13)
C11	180(10)	-4357(7)	8083(2)	24.0(16)
C12	653(9)	-5245(7)	7821.5(17)	22.5(14)
C13	463(9)	-5089(7)	7412.9(17)	23.3(15)
C14	-263(9)	-4011(7)	7275.7(19)	23.3(15)
C15	-783(9)	-3164(7)	7534.1(18)	24.0(15)
C16	-570(9)	-3323(7)	7940.0(17)	22.1(14)
F1	-1828(6)	-6076(4)	8690.0(11)	23.7(9)
F2	-3025(5)	-4368(4)	8566.3(11)	23.3(9)
O1	-2836(7)	-4421(5)	9377.7(13)	24.3(11)
O2	-244(7)	-2448(5)	9247.7(14)	26.5(12)
O3	628(7)	-3398(5)	8702.1(13)	21.6(11)
S1	2241(2)	-5484.9(18)	8640.9(5)	26.2(5)
C17	-1721(9)	-898(7)	5852.6(19)	24.7(16)
C18	-3071(11)	-1552(7)	5649(2)	27.4(17)
C19	-2941(11)	-1673(7)	5241(2)	31.1(18)
C20	-1467(10)	-1174(7)	5039(2)	27.8(17)
C21	-130(9)	-532(7)	5232.0(18)	21.7(15)
C22	-200(10)	-397(7)	5640.1(19)	21.5(15)
C23	1230(10)	378(7)	5841.0(18)	20.9(15)
C24	170(10)	1532(7)	5925.4(18)	22.9(16)
C25	-255(10)	315(7)	6466(2)	25.2(16)

C26	1592(9)	2(7)	6259.9(18)	20.0(14)
C27	-152(9)	525(7)	6903.8(19)	21.0(15)
C28	-752(9)	1556(7)	7070.0(18)	25.2(15)
C29	-601(9)	1719(7)	7476.4(18)	21.6(14)
C30	200(10)	890(7)	7711.0(19)	24.5(16)
C31	756(9)	-164(7)	7548.7(17)	26.2(16)
C32	604(10)	-356(7)	7144.7(17)	25.0(15)
F3	2052(6)	-1146(4)	6298.2(11)	24.6(9)
F4	3054(5)	622(4)	6412.1(11)	25.6(10)
O4	-726(7)	1407(5)	6277.1(13)	22.1(11)
O5	67(8)	2377(5)	5728.6(14)	30.1(13)
O6	2812(7)	494(5)	5601.0(14)	25.6(12)
S2	-2040(2)	-759.0(19)	6364.1(5)	26.1(5)
C33	4700(10)	5199(7)	5754.3(19)	21.5(15)
C34	4796(10)	5566(8)	5366(2)	29.8(18)
C35	3388(11)	6263(7)	5215(2)	27.3(16)
C36	1887(11)	6608(8)	5440(2)	34.2(18)
C37	1755(11)	6231(8)	5830(2)	28.9(17)
C38	3156(10)	5528(7)	5992(2)	25.9(16)
C39	4787(9)	4109(7)	6543.6(18)	18.3(14)
C40	5236(10)	3161(7)	5940.7(18)	20.3(15)
C41	6195(10)	4368(7)	5909.0(18)	21.8(15)
C42	6566(9)	4609(7)	6343.6(19)	19.8(14)
C43	4914(9)	3767(7)	6970(2)	22.4(15)
C44	5603(9)	4566(7)	7234.3(17)	21.8(14)
C45	5676(9)	4295(7)	7636.2(17)	24.4(16)
C46	5079(9)	3224(7)	7760(2)	23.5(16)
C47	4344(9)	2413(7)	7497.4(18)	24.2(15)
C48	4297(9)	2675(7)	7093.9(18)	22.3(15)
F5	8093(5)	3982(4)	6461.7(11)	23.1(9)

F6	6935(5)	5736(4)	6431.2(11)	25.1(9)
O7	5154(7)	2416(5)	5707.5(13)	28.9(12)
O8	4421(6)	3077(5)	6306.0(13)	20.5(11)
O9	7800(7)	4366(5)	5670.0(13)	24.4(11)
S3	2873(2)	5148.7(17)	6488.2(5)	24.6(4)
C49	-3012(10)	517(7)	9008(2)	25.3(16)
C50	-1623(11)	1224(8)	9163(2)	29.7(17)
C51	-1826(11)	1680(8)	9540(2)	32.0(18)
C52	-3396(11)	1397(7)	9761(2)	30.0(17)
C53	-4795(10)	709(7)	9609(2)	26.6(17)
C54	-4640(10)	255(7)	9232(2)	22.6(15)
C55	-6159(9)	-551(7)	9079.2(18)	20.2(15)
C56	-5287(9)	-1797(6)	9063.7(18)	18.5(14)
C57	-4663(9)	-913(7)	8452.4(19)	20.4(14)
C58	-6426(9)	-335(7)	8633.4(18)	18.9(14)
C59	-4834(9)	-1283(7)	8031(2)	22.5(15)
C60	-5625(9)	-2368(7)	7943.1(18)	23.9(15)
C61	-5870(9)	-2700(7)	7555.9(19)	24.4(15)
C62	-5358(10)	-1950(8)	7257(2)	28.2(17)
C63	-4549(9)	-890(7)	7336.5(18)	25.3(15)
C64	-4297(9)	-544(7)	7731.8(17)	23.9(15)
F7	-7975(5)	-916(4)	8513.0(11)	21.5(9)
F8	-6656(6)	789(4)	8529.8(11)	25.7(9)
O10	-4446(6)	-1937(5)	8702.2(13)	20.8(11)
O11	-5290(7)	-2516(5)	9303.2(13)	27.6(12)
O12	-7788(7)	-487(5)	9303.8(13)	25.8(12)
S4	-2641(2)	37.8(18)	8520.8(5)	26.9(5)

Table S11. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **5a**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**

C1	23(3)	18(4)	16(3)	-1(3)	3(2)	0(3)
C2	27(3)	26(4)	13(3)	4(3)	8(3)	-6(3)
C3	39(4)	27(4)	11(3)	5(3)	0(3)	-3(3)
C4	35(4)	32(5)	20(4)	6(3)	-1(3)	2(3)
C5	37(4)	38(5)	13(3)	-5(3)	6(3)	14(3)
C6	22(3)	24(4)	16(3)	-4(3)	3(3)	5(3)
C7	29(4)	29(4)	13(3)	-8(3)	9(3)	2(3)
C8	31(4)	27(4)	8(3)	1(3)	9(3)	3(3)
C9	23(3)	29(4)	6(3)	3(3)	8(2)	3(3)
C10	20(3)	20(4)	10(3)	0(3)	4(2)	6(3)
C11	25(4)	35(4)	12(3)	-4(3)	6(3)	-1(3)
C12	24(3)	32(4)	12(3)	-1(3)	6(2)	1(3)
C13	28(3)	30(4)	12(3)	-1(3)	7(2)	-3(3)
C14	21(3)	36(4)	13(3)	4(3)	2(3)	-2(3)
C15	26(3)	34(4)	12(3)	6(3)	3(3)	1(3)
C16	25(3)	28(4)	13(3)	-1(3)	6(2)	-2(3)
F1	34(2)	20(2)	17.2(19)	0.7(16)	2.7(16)	-6.2(17)
F2	21.1(19)	34(3)	14.6(18)	7.2(17)	2.0(15)	2.2(17)
O1	24(2)	33(3)	16(2)	1(2)	11.7(19)	6(2)
O2	38(3)	25(3)	16(2)	-5(2)	12(2)	-2(2)
O3	31(3)	26(3)	8(2)	-4.4(19)	8.6(18)	-1(2)
S1	26.0(9)	40.8(13)	11.8(7)	-2.2(7)	4.8(6)	11.3(7)
C17	20(3)	38(5)	16(3)	3(3)	5(3)	-3(3)
C18	35(4)	35(5)	12(3)	5(3)	5(3)	-7(3)
C19	37(4)	36(5)	20(4)	-9(3)	-2(3)	-7(3)
C20	34(4)	39(5)	11(3)	-4(3)	0(3)	9(3)
C21	25(3)	29(4)	11(3)	-4(3)	7(2)	2(3)
C22	27(4)	25(4)	13(3)	0(3)	1(3)	4(3)
C23	26(4)	30(4)	7(3)	-1(3)	9(3)	-6(3)
C24	33(4)	27(4)	8(3)	4(3)	8(3)	-8(3)

C25	34(4)	29(4)	13(3)	2(3)	6(3)	-2(3)
C26	22(3)	27(4)	11(3)	-1(3)	4(2)	-5(3)
C27	23(3)	32(4)	8(3)	9(3)	4(2)	-1(3)
C28	25(4)	37(5)	13(3)	1(3)	2(2)	1(3)
C29	25(3)	26(4)	14(3)	-4(3)	4(2)	1(3)
C30	27(4)	37(5)	9(3)	-1(3)	6(3)	-5(3)
C31	25(3)	45(5)	8(3)	6(3)	-2(2)	1(3)
C32	33(4)	29(4)	13(3)	-2(3)	5(3)	8(3)
F3	36(2)	22(2)	15.3(19)	-1.2(16)	1.6(16)	3.9(18)
F4	25(2)	36(3)	15.9(19)	-9.6(18)	3.2(15)	-4.9(18)
O4	34(3)	25(3)	8(2)	6(2)	8.2(18)	4(2)
O5	43(3)	32(3)	15(2)	3(2)	12(2)	3(2)
O6	23(2)	37(3)	16(2)	-4(2)	12.4(19)	-8(2)
S2	27.7(9)	39.8(13)	10.7(7)	2.8(7)	3.6(6)	-8.6(7)
C33	25(3)	26(4)	13(3)	4(3)	3(3)	-7(3)
C34	26(4)	46(5)	18(3)	6(3)	5(3)	-17(3)
C35	35(4)	26(4)	21(3)	5(3)	-2(3)	-8(3)
C36	39(4)	39(5)	25(4)	2(4)	-10(3)	-5(4)
C37	28(4)	39(5)	20(3)	-7(3)	1(3)	1(3)
C38	26(4)	37(5)	15(3)	-4(3)	4(3)	1(3)
C39	21(3)	22(4)	12(3)	-8(3)	6(2)	-6(3)
C40	29(4)	25(4)	7(3)	-6(3)	7(3)	0(3)
C41	24(3)	30(4)	11(3)	-5(3)	7(2)	0(3)
C42	22(3)	22(4)	16(3)	3(3)	1(3)	-2(3)
C43	18(3)	35(4)	14(3)	0(3)	5(3)	-2(3)
C44	25(3)	31(4)	9(3)	2(3)	4(2)	-7(3)
C45	27(4)	36(5)	10(3)	-1(3)	3(2)	0(3)
C46	24(4)	36(4)	11(3)	5(3)	2(3)	3(3)
C47	24(4)	32(4)	16(3)	8(3)	7(3)	1(3)
C48	25(3)	30(4)	12(3)	6(3)	2(2)	-5(3)

F5	20.2(19)	32(2)	17.4(18)	7.4(17)	3.1(15)	0.0(17)
F6	30(2)	31(2)	14.2(19)	-0.3(17)	2.3(16)	-9.3(18)
O7	43(3)	32(3)	12(2)	1(2)	11(2)	-7(2)
O8	25(2)	25(3)	11(2)	-1(2)	8.3(18)	-5(2)
O9	28(3)	29(3)	16(2)	0(2)	13.2(19)	0(2)
S3	25.1(9)	37.3(11)	11.4(7)	-1.6(7)	4.7(6)	4.7(8)
C49	23(4)	34(4)	19(3)	8(3)	3(3)	1(3)
C50	30(4)	34(5)	25(4)	6(3)	-2(3)	-2(3)
C51	36(4)	33(5)	27(4)	-4(4)	-8(3)	1(3)
C52	39(4)	32(4)	19(3)	-2(3)	-5(3)	6(3)
C53	29(4)	36(5)	15(3)	-6(3)	1(3)	17(3)
C54	25(3)	26(4)	17(3)	-3(3)	2(3)	3(3)
C55	20(3)	27(4)	13(3)	5(3)	6(2)	3(3)
C56	22(3)	22(4)	12(3)	-1(3)	7(3)	0(3)
C57	16(3)	30(4)	15(3)	8(3)	6(2)	1(3)
C58	21(3)	21(4)	15(3)	0(3)	5(2)	-5(3)
C59	19(3)	30(4)	18(3)	-3(3)	3(3)	5(3)
C60	25(4)	32(4)	14(3)	2(3)	3(2)	1(3)
C61	22(3)	27(4)	23(3)	-10(3)	4(3)	1(3)
C62	26(4)	44(5)	15(3)	-7(3)	3(3)	0(3)
C63	29(4)	31(4)	16(3)	-2(3)	7(3)	4(3)
C64	24(3)	38(5)	10(3)	-3(3)	5(2)	0(3)
F7	22.0(19)	25(2)	16.9(18)	-0.8(17)	3.1(15)	1.4(17)
F8	33(2)	26(2)	17.6(19)	5.2(17)	1.0(16)	2.3(18)
O10	26(2)	25(3)	11(2)	2(2)	8.8(18)	4(2)
O11	39(3)	33(3)	11(2)	0(2)	7(2)	6(2)
O12	27(3)	35(3)	16(2)	2(2)	8.6(19)	3(2)
S4	23.9(8)	43.7(12)	13.0(7)	0.0(8)	4.4(6)	-8.4(8)

Table S12. Bond Lengths for **5a**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.400(9)	C33	C34	1.387(9)
C1	C6	1.412(9)	C33	C38	1.411(9)
C1	C9	1.511(9)	C33	C41	1.521(10)
C2	C3	1.372(10)	C34	C35	1.381(11)
C3	C4	1.371(11)	C35	C36	1.367(11)
C4	C5	1.395(10)	C36	C37	1.396(11)
C5	C6	1.397(10)	C37	C38	1.396(11)
C6	S1	1.768(6)	C38	S3	1.754(7)
C7	C10	1.536(9)	C39	C42	1.542(9)
C7	C11	1.506(9)	C39	C43	1.507(9)
C7	O3	1.442(9)	C39	O8	1.456(8)
C7	S1	1.804(8)	C39	S3	1.817(7)
C8	C9	1.552(10)	C40	C41	1.544(10)
C8	O2	1.177(9)	C40	O7	1.166(9)
C8	O3	1.360(7)	C40	O8	1.372(7)
C9	C10	1.508(9)	C41	C42	1.529(8)
C9	O1	1.392(7)	C41	O9	1.396(7)
C10	F1	1.358(8)	C42	F5	1.363(8)
C10	F2	1.373(7)	C42	F6	1.350(9)
C11	C12	1.390(10)	C43	C44	1.375(10)
C11	C16	1.387(11)	C43	C48	1.388(11)
C12	C13	1.410(8)	C44	C45	1.404(8)
C13	C14	1.417(11)	C45	C46	1.363(11)
C14	C15	1.358(10)	C46	C47	1.393(10)
C15	C16	1.403(8)	C47	C48	1.407(8)
C17	C18	1.404(10)	C49	C50	1.385(11)
C17	C22	1.418(9)	C49	C54	1.413(9)
C17	S2	1.762(7)	C49	S4	1.764(7)

C18	C19	1.396(10)	C50	C51	1.391(11)
C19	C20	1.374(11)	C51	C52	1.381(11)
C20	C21	1.372(10)	C52	C53	1.373(11)
C21	C22	1.398(9)	C53	C54	1.388(9)
C22	C23	1.515(10)	C54	C55	1.513(10)
C23	C24	1.546(11)	C55	C56	1.555(10)
C23	C26	1.513(9)	C55	C58	1.550(8)
C23	O6	1.392(7)	C55	O12	1.386(7)
C24	O4	1.360(7)	C56	O10	1.374(7)
C24	O5	1.179(9)	C56	O11	1.158(9)
C25	C26	1.527(9)	C57	C58	1.542(9)
C25	C27	1.510(9)	C57	C59	1.502(9)
C25	O4	1.446(9)	C57	O10	1.456(8)
C25	S2	1.801(8)	C57	S4	1.818(7)
C26	F3	1.359(9)	C58	F7	1.352(8)
C26	F4	1.363(8)	C58	F8	1.343(9)
C27	C28	1.375(11)	C59	C60	1.396(11)
C27	C32	1.408(10)	C59	C64	1.376(10)
C28	C29	1.401(8)	C60	C61	1.384(9)
C29	C30	1.366(10)	C61	C62	1.379(11)
C30	C31	1.382(11)	C62	C63	1.369(11)
C31	C32	1.397(8)	C63	C64	1.415(8)

Table S13. Bond Angles for **5a**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C2	C1	C6	118.3(6)	C34	C33	C38	119.9(7)
C2	C1	C9	120.1(6)	C34	C33	C41	119.2(6)
C6	C1	C9	121.5(5)	C38	C33	C41	120.7(6)
C3	C2	C1	121.1(6)	C35	C34	C33	119.9(7)
C4	C3	C2	120.6(6)	C36	C35	C34	121.5(7)

C3	C4	C5	120.2(7)	C35	C36	C37	119.4(8)
C4	C5	C6	119.8(7)	C38	C37	C36	120.6(7)
C1	C6	S1	124.1(5)	C33	C38	S3	124.8(6)
C5	C6	C1	119.9(6)	C37	C38	C33	118.7(6)
C5	C6	S1	116.0(5)	C37	C38	S3	116.5(5)
C10	C7	S1	110.5(5)	C42	C39	S3	108.9(5)
C11	C7	C10	115.7(6)	C43	C39	C42	117.9(5)
C11	C7	S1	110.8(5)	C43	C39	S3	108.6(4)
O3	C7	C10	101.0(5)	O8	C39	C42	101.8(5)
O3	C7	C11	109.0(6)	O8	C39	C43	109.7(6)
O3	C7	S1	109.3(5)	O8	C39	S3	109.7(4)
O2	C8	C9	128.8(6)	O7	C40	C41	129.1(6)
O2	C8	O3	123.4(7)	O7	C40	O8	122.9(7)
O3	C8	C9	107.7(6)	O8	C40	C41	108.1(5)
C1	C9	C8	105.3(6)	C33	C41	C40	105.9(6)
C10	C9	C1	111.1(6)	C33	C41	C42	110.3(6)
C10	C9	C8	98.8(5)	C42	C41	C40	99.9(5)
O1	C9	C1	109.7(5)	O9	C41	C33	111.6(6)
O1	C9	C8	114.7(6)	O9	C41	C40	113.4(6)
O1	C9	C10	116.3(6)	O9	C41	C42	114.8(6)
C9	C10	C7	103.2(5)	C41	C42	C39	102.4(5)
F1	C10	C7	112.8(5)	F5	C42	C39	109.1(6)
F1	C10	C9	115.3(6)	F5	C42	C41	109.5(6)
F1	C10	F2	105.4(5)	F6	C42	C39	114.6(6)
F2	C10	C7	110.2(5)	F6	C42	C41	114.9(6)
F2	C10	C9	110.0(5)	F6	C42	F5	106.3(5)
C12	C11	C7	121.7(7)	C44	C43	C39	118.8(7)
C16	C11	C7	118.7(6)	C44	C43	C48	120.9(6)
C16	C11	C12	119.4(6)	C48	C43	C39	120.3(6)
C11	C12	C13	121.0(7)	C43	C44	C45	120.4(7)

C12	C13	C14	118.2(6)	C46	C45	C44	119.2(7)
C15	C14	C13	120.4(6)	C45	C46	C47	121.1(6)
C14	C15	C16	121.0(7)	C46	C47	C48	119.8(7)
C11	C16	C15	120.0(6)	C43	C48	C47	118.6(7)
C8	O3	C7	112.3(5)	C40	O8	C39	111.7(5)
C6	S1	C7	100.0(3)	C38	S3	C39	100.4(3)
C18	C17	C22	119.0(6)	C50	C49	C54	120.0(7)
C18	C17	S2	116.9(5)	C50	C49	S4	116.0(5)
C22	C17	S2	124.1(5)	C54	C49	S4	123.9(6)
C19	C18	C17	120.2(7)	C49	C50	C51	120.1(7)
C20	C19	C18	120.2(7)	C52	C51	C50	119.6(8)
C21	C20	C19	120.6(6)	C53	C52	C51	120.9(7)
C20	C21	C22	121.0(7)	C52	C53	C54	120.7(7)
C17	C22	C23	121.2(6)	C49	C54	C55	121.8(6)
C21	C22	C17	118.9(7)	C53	C54	C49	118.6(7)
C21	C22	C23	119.6(6)	C53	C54	C55	119.5(6)
C22	C23	C24	104.8(6)	C54	C55	C56	106.6(5)
C26	C23	C22	112.2(6)	C54	C55	C58	109.3(5)
C26	C23	C24	98.8(5)	C58	C55	C56	99.5(5)
O6	C23	C22	109.4(5)	O12	C55	C54	112.0(6)
O6	C23	C24	114.7(6)	O12	C55	C56	113.5(6)
O6	C23	C26	116.0(6)	O12	C55	C58	115.1(5)
O4	C24	C23	107.4(6)	O10	C56	C55	107.9(5)
O5	C24	C23	128.8(6)	O11	C56	C55	128.9(6)
O5	C24	O4	123.8(7)	O11	C56	O10	123.1(6)
C26	C25	S2	110.8(5)	C58	C57	S4	109.5(5)
C27	C25	C26	116.4(6)	C59	C57	C58	115.6(5)
C27	C25	S2	109.7(5)	C59	C57	S4	111.1(5)
O4	C25	C26	101.4(5)	O10	C57	C58	101.6(5)
O4	C25	C27	108.3(6)	O10	C57	C59	109.9(6)

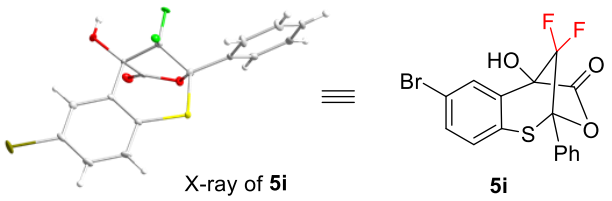
O4	C25	S2	109.7(5)	O10	C57	S4	108.6(4)
C23	C26	C25	102.5(6)	C57	C58	C55	102.6(5)
F3	C26	C23	114.0(6)	F7	C58	C55	108.9(5)
F3	C26	C25	112.9(6)	F7	C58	C57	109.2(6)
F3	C26	F4	106.4(5)	F8	C58	C55	115.2(6)
F4	C26	C23	110.2(6)	F8	C58	C57	113.9(5)
F4	C26	C25	111.0(6)	F8	C58	F7	106.9(6)
C28	C27	C25	121.7(6)	C60	C59	C57	119.4(6)
C28	C27	C32	119.5(6)	C64	C59	C57	120.7(7)
C32	C27	C25	118.8(7)	C64	C59	C60	119.9(7)
C27	C28	C29	119.7(7)	C61	C60	C59	120.1(7)
C30	C29	C28	121.3(7)	C62	C61	C60	119.9(7)
C29	C30	C31	119.4(6)	C63	C62	C61	120.9(7)
C30	C31	C32	120.4(7)	C62	C63	C64	119.5(7)
C31	C32	C27	119.5(7)	C59	C64	C63	119.7(7)
C24	O4	C25	112.0(5)	C56	O10	C57	112.5(5)
C17	S2	C25	99.6(3)	C49	S4	C57	101.1(3)

Table S14. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **5a**.

Atom	***x***	***y***	***z***	**U(eq)**
H2	-913.45	-5105.22	9896.03	26
H3	1320.89	-6163.5	10222.5	31
H4	3944.68	-6840.93	9898.02	35
H5	4213.91	-6620.44	9220.9	35
H12	1100.24	-5952.76	7917.65	27
H13	805.73	-5677.12	7238	28
H14	-384.5	-3882.55	7007.28	28
H15	-1287.69	-2467.85	7440.53	29
H16	-930.68	-2734.49	8113.44	27
H1	-3636.67	-4035.52	9263.46	36

H18	-4054.24	-1906.58	5785.44	33
H19	-3854.84	-2091.63	5106.52	37
H20	-1374.54	-1272.81	4768.15	33
H21	837.02	-181.74	5089.38	26
H28	-1255.28	2143.04	6913.33	30
H29	-1055.56	2404.83	7588.88	26
H30	369.46	1032.7	7977.34	29
H31	1235.09	-748.58	7709.47	31
H32	999.47	-1060.78	7035.79	30
H6	3519.09	986.56	5693.95	38
H34	5806.64	5343.36	5208.21	36
H35	3463.18	6504.09	4954.71	33
H36	963	7088.2	5334.98	41
H37	724.58	6451.17	5982.47	35
H44	6023.41	5291.06	7146.28	26
H45	6126.76	4839.31	7815.41	29
H46	5163.99	3030.97	8025.22	28
H47	3886.03	1700.09	7588.34	29
H48	3862.81	2128.32	6913.7	27
H9	8360.9	3745.11	5696.51	37
H50	-551.46	1395.3	9015.85	36
H51	-909.69	2172.72	9642.36	38
H52	-3506.89	1675.3	10017.08	36
H53	-5858.64	544.93	9759.5	32
H60	-5988.42	-2868.44	8145.09	29
H61	-6379.16	-3428.14	7497.49	29
H62	-5564.88	-2166.25	6997.28	34
H63	-4167.2	-402.23	7132.44	30
H64	-3772.15	180.67	7789.12	29
H12A	-8502.28	-1017.3	9240.91	39

Data intensity of **5i**[3] was collected using a 'XtaLAB AFC12 (RINC)' diffractometer at 99.94(18) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. Crystal data for **5i**: $C_{16}H_9BrF_2O_3S$, T = 99.94(18) K, triclinic, P-1, a = 7.4596(2) Å, b = 9.2236(3) Å, c = 11.0671(5) Å, α = 106.586(3)°, β = 90.288(3)°, γ = 96.906(3)°, V = 723.87(5) Å^3. Z = 2, ρ_{calc} = 1.832 g/cm^3. 5574 reflections collected, 2507 [R_{int} = 0.0310, R_{sigma} = 0.0296] independent reflections, R_1 = 0.0346, wR_2 = 0.0886 ($I >= 2\sigma(I)$, final), R_1 = 0.0355, wR_2 = 0.0892 (all data), GOF = 1.081, and 209 parameters.



ORTEP, ellipsoids set at 50% probability

Table S15. Crystal data and structure refinement for **5i**.

Identification code	**5i**
Empirical formula	$C_{16}H_9BrF_2O_3S$
Formula weight	399.20
Temperature/K	99.94(18)
Crystal system	triclinic
Space group	P-1
a/Å	7.4596(2)
b/Å	9.2236(3)
c/Å	11.0671(5)
α/°	106.586(3)

[3] Supplementary crystallographic data have been deposited at Cambridge Crystallographic Data Center (CCDC number: 2056188).

β/°	90.288(3)
γ/°	96.906(3)
Volume/Å^3	723.87(5)
Z	2
ρ_{calc}g/cm^3	1.832
μ/mm^{-1}	5.560
F(000)	396.0
Crystal size/mm^3	0.32 × 0.28 × 0.26
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.088 to 134.106
Index ranges	-5 ≤ h ≤ 8, -11 ≤ k ≤ 10, -13 ≤ l ≤ 13
Reflections collected	5574
Independent reflections	2507 [R_{int} = 0.0310, R_{sigma} = 0.0296]
Data/restraints/parameters	2507/18/209
Goodness-of-fit on F^2	1.081
Final R indexes [I>=2σ (I)]	R_1 = 0.0346, wR_2 = 0.0886
Final R indexes [all data]	R_1 = 0.0355, wR_2 = 0.0892
Largest diff. peak/hole / e Å^{-3}	0.72/-0.89

Table S16. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **5i**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	792.9(3)	1686.4(3)	4759.9(2)	17.63(13)
S1	4156.8(7)	8141.5(6)	4103.3(5)	9.25(16)
F1	4021.6(18)	6304.8(15)	400.8(12)	10.0(3)
F2	5559.9(18)	5876.1(15)	1914.5(12)	9.7(3)
O3	1907(2)	3939.8(18)	950.3(15)	10.7(4)
O1	1784(2)	7922.9(18)	2199.0(15)	9.5(3)

O2	-629(2)	6175(2)	1500.2(16)	12.5(4)
C11	3141(3)	6353(3)	4197(2)	7.2(4)
C5	3980(3)	10353(3)	1772(2)	11.2(5)
C15	1660(3)	3777(3)	3341(2)	9.0(5)
C6	4810(3)	9240(3)	2103(2)	8.8(5)
C10	2377(3)	5160(3)	3164(2)	6.5(4)
C8	934(3)	6475(3)	1819(2)	8.4(5)
C16	4010(3)	6331(3)	1641(2)	6.6(4)
C9	2302(3)	5360(3)	1843(2)	6.7(4)
C7	3722(3)	7946(3)	2456(2)	7.5(5)
C14	1721(3)	3591(3)	4543(2)	9.7(5)
C13	2455(3)	4765(3)	5577(2)	11.2(5)
C1	6687(3)	9296(3)	2092(2)	13.5(5)
C3	6883(4)	11546(3)	1381(2)	14.3(5)
C4	5020(4)	11510(3)	1417(2)	12.7(5)
C2	7715(3)	10446(3)	1723(2)	15.1(5)
C12	3157(3)	6144(3)	5400(2)	10.4(5)

Table S17. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **5i**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Br1	19.21(19)	15.53(19)	21.93(19)	14.24(12)	0.33(12)	-4.71(12)
S1	12.7(3)	7.7(3)	4.6(3)	0.1(2)	-1.7(2)	-5.3(2)
F1	13.5(7)	13.5(7)	3.2(6)	3.8(5)	1.2(5)	-1.4(5)
F2	6.3(6)	12.7(7)	9.8(6)	3.4(5)	0.0(5)	0.6(5)
O3	16.1(8)	8.9(8)	3.6(7)	-0.5(6)	-4.0(6)	-5.5(6)
O1	5.7(8)	10.4(8)	11.9(8)	3.4(6)	-0.5(6)	-0.8(6)
O2	5.8(8)	21.2(9)	10.6(8)	6.4(7)	-2.6(6)	-2.4(7)
C11	5.7(11)	9.5(11)	6.0(10)	2.1(9)	0.4(8)	-0.2(8)
C5	12.2(12)	13.2(12)	7.0(11)	1.7(9)	1.5(9)	-0.4(9)
C15	5.5(11)	11.0(11)	9.7(11)	2.3(9)	0.6(8)	-0.8(8)

C6	13.1(12)	7.5(11)	4.6(10)	1.4(8)	0.0(8)	-2.8(9)
C10	3.1(10)	10.4(11)	5.8(10)	2.9(8)	0.0(8)	-1.1(8)
C8	10.0(10)	11.3(10)	3.8(9)	3.4(8)	1.4(8)	-1.7(8)
C16	5.8(11)	9.3(11)	4.2(10)	1.8(8)	-1.3(8)	0.1(8)
C9	8.8(11)	6.0(10)	3.6(10)	0.2(8)	-0.4(8)	-2.7(8)
C7	4.9(10)	9.1(11)	7.2(11)	1.0(9)	-1.9(8)	-0.7(8)
C14	5.6(11)	14.6(12)	11.8(11)	8.0(9)	2.5(9)	2.0(9)
C13	9.1(12)	18.1(12)	8.6(11)	7.6(9)	0.7(9)	1.1(9)
C1	11.9(12)	12.3(12)	17.1(12)	7.6(10)	-2.4(9)	-4.1(9)
C3	20.8(13)	11.4(12)	8.0(11)	2.5(9)	-0.3(9)	-8.7(9)
C4	21.7(13)	9.7(11)	6.0(10)	2.0(9)	0.4(9)	0.2(9)
C2	9.1(12)	17.9(13)	16.9(12)	6.0(10)	-0.7(9)	-6.1(9)
C12	8.5(11)	17.6(13)	4.9(11)	3.1(9)	-0.2(8)	1.3(9)

Table S18. Bond Lengths for **5i**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Br1	C14	1.890(3)	C15	C10	1.389(3)
S1	C11	1.762(2)	C15	C14	1.390(3)
S1	C7	1.804(2)	C6	C7	1.508(3)
F1	C16	1.366(3)	C6	C1	1.395(4)
F2	C16	1.338(3)	C10	C9	1.527(3)
O3	C9	1.395(3)	C8	C9	1.538(3)
O1	C8	1.355(3)	C16	C9	1.523(3)
O1	C7	1.468(3)	C16	C7	1.546(3)
O2	C8	1.193(3)	C14	C13	1.388(4)
C11	C10	1.402(3)	C13	C12	1.384(4)
C11	C12	1.399(3)	C1	C2	1.391(4)
C5	C6	1.391(3)	C3	C4	1.387(4)
C5	C4	1.393(4)	C3	C2	1.388(4)

Table S19. Bond Angles for **5i**.

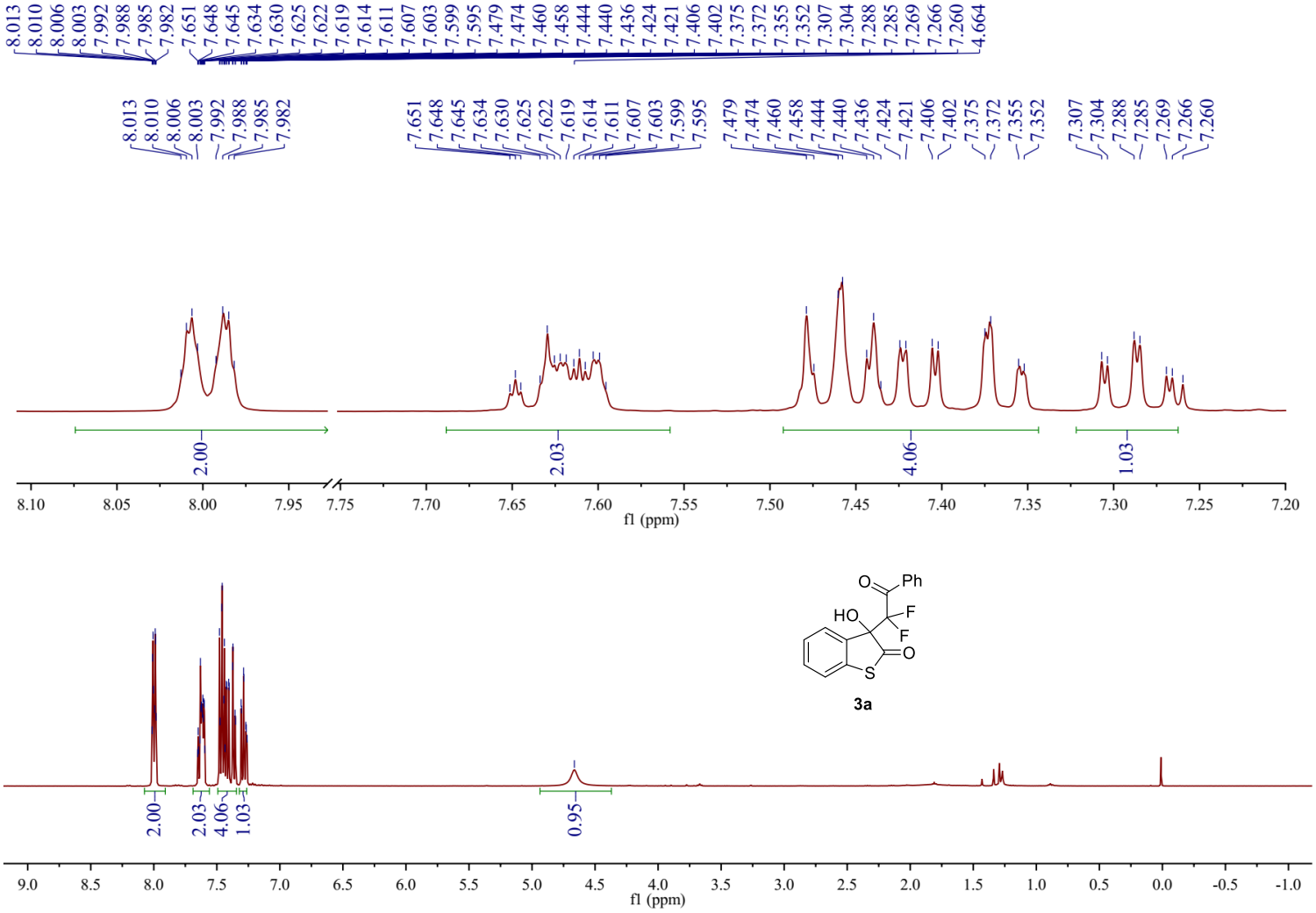
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C11	S1	C7	100.63(11)	O3	C9	C10	109.74(19)
C8	O1	C7	111.13(17)	O3	C9	C8	113.94(18)
C10	C11	S1	124.71(19)	O3	C9	C16	115.68(18)
C12	C11	S1	115.70(18)	C10	C9	C8	108.31(17)
C12	C11	C10	119.6(2)	C16	C9	C10	109.97(18)
C6	C5	C4	120.0(2)	C16	C9	C8	98.59(18)
C10	C15	C14	119.4(2)	O1	C7	S1	110.31(15)
C5	C6	C7	121.4(2)	O1	C7	C6	110.80(18)
C5	C6	C1	119.9(2)	O1	C7	C16	100.49(17)
C1	C6	C7	118.7(2)	C6	C7	S1	109.47(15)
C11	C10	C9	120.9(2)	C6	C7	C16	115.16(19)
C15	C10	C11	119.9(2)	C16	C7	S1	110.31(16)
C15	C10	C9	119.2(2)	C15	C14	Br1	118.87(18)
O1	C8	C9	109.31(19)	C13	C14	Br1	119.63(19)
O2	C8	O1	122.9(2)	C13	C14	C15	121.5(2)
O2	C8	C9	127.7(2)	C12	C13	C14	119.0(2)
F1	C16	C9	108.41(17)	C2	C1	C6	119.7(2)
F1	C16	C7	109.08(18)	C4	C3	C2	120.0(2)
F2	C16	F1	107.38(17)	C3	C4	C5	120.0(2)
F2	C16	C9	115.10(19)	C3	C2	C1	120.3(2)
F2	C16	C7	114.09(18)	C13	C12	C11	120.7(2)
C9	C16	C7	102.55(17)				

Table S20. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **5i**.

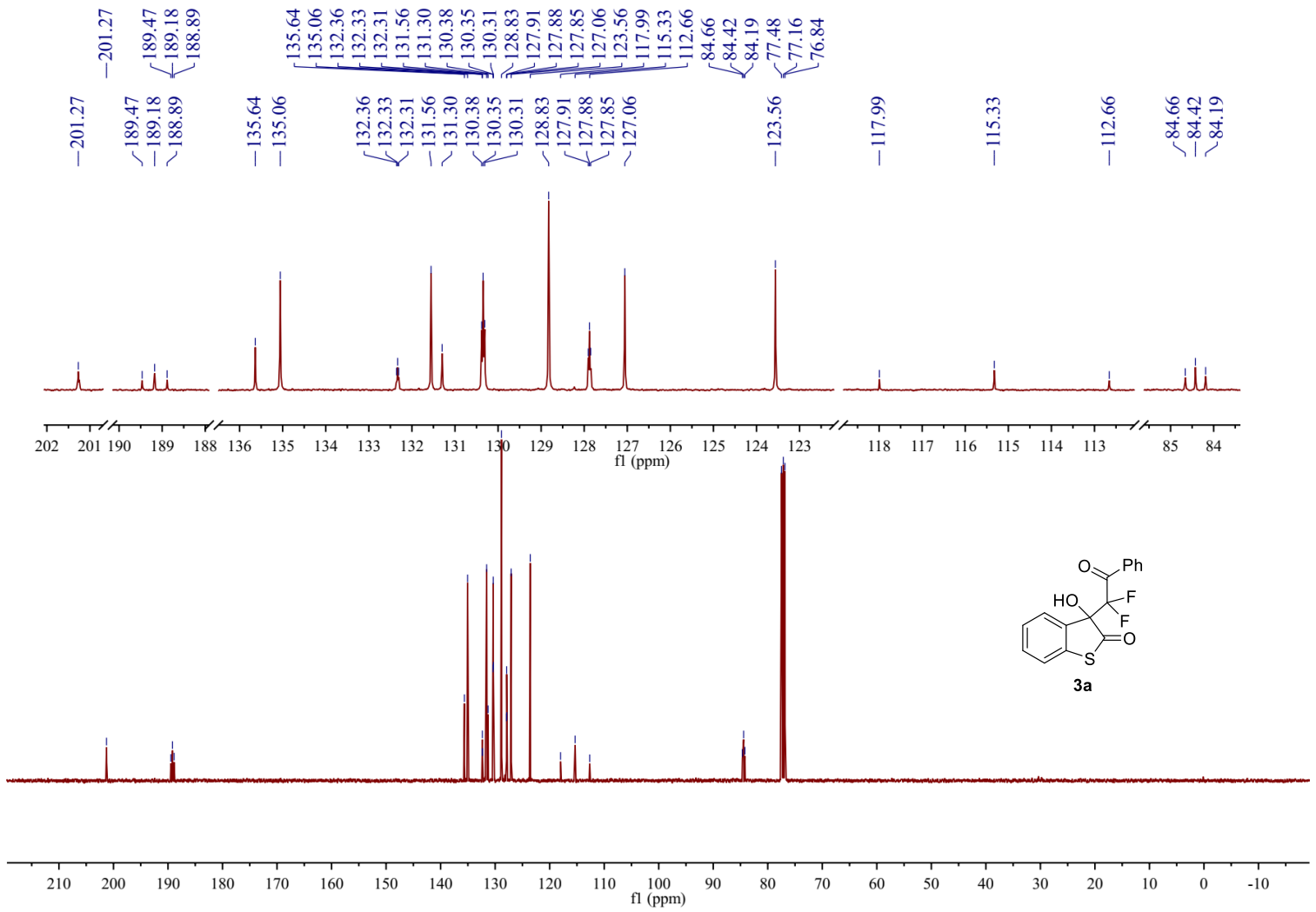
Atom	*x*	*y*	*z*	U(eq)
H3	1754.31	4057.02	251.64	16
H5	2730.12	10324.19	1788.92	13
H15	1144.25	2983.65	2660.92	11
H13	2475.89	4626.4	6376.92	13

H1	7249	8566.77	2330.31	16
H3A	7574.37	12307.04	1126.89	17
H4	4465.14	12259.22	1203.19	15
H2	8964.96	10478.41	1705.75	18
H12	3643.69	6941.05	6088.04	12

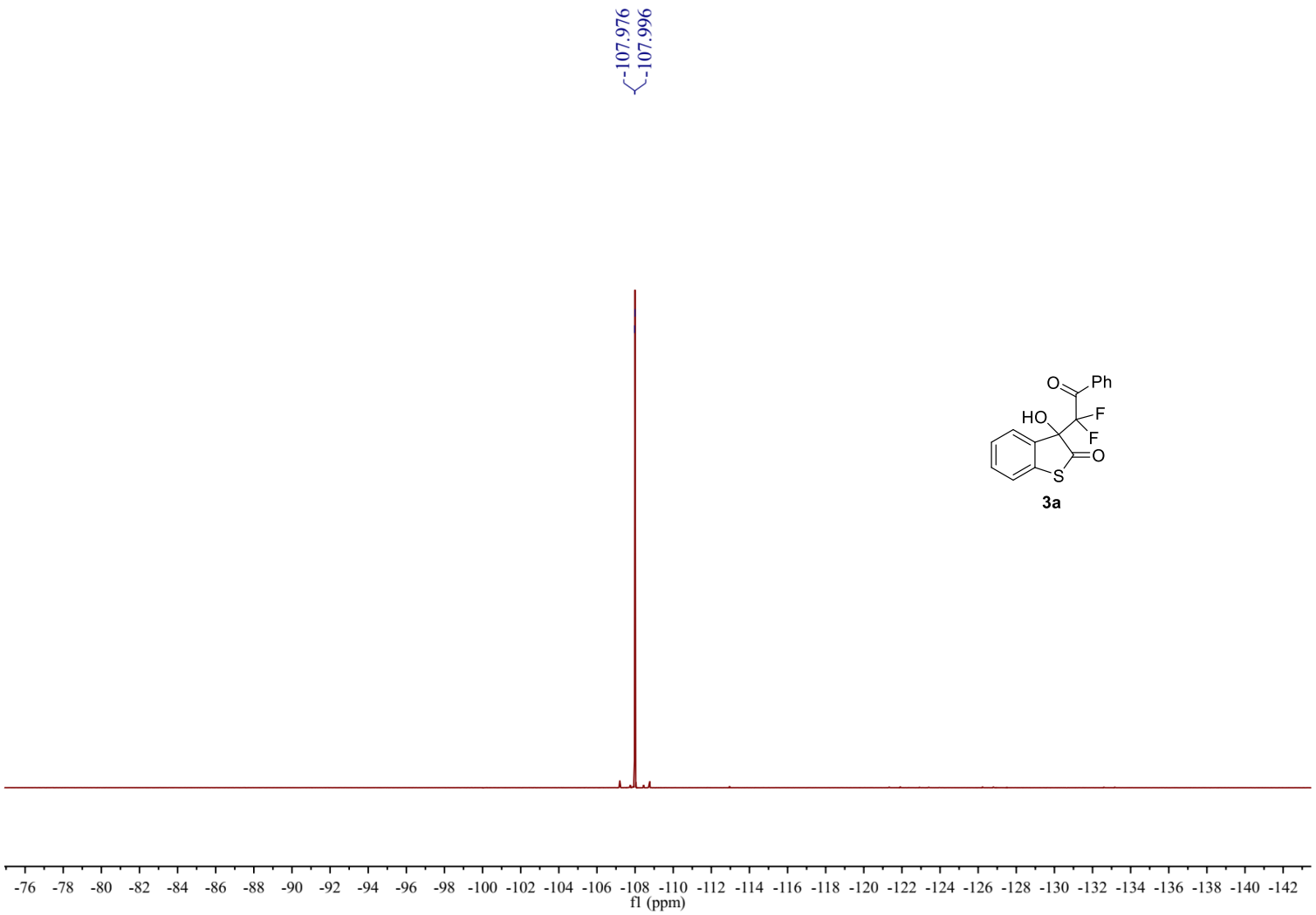
4. ^{1}H, ^{13}C, and ^{19}F NMR spectra



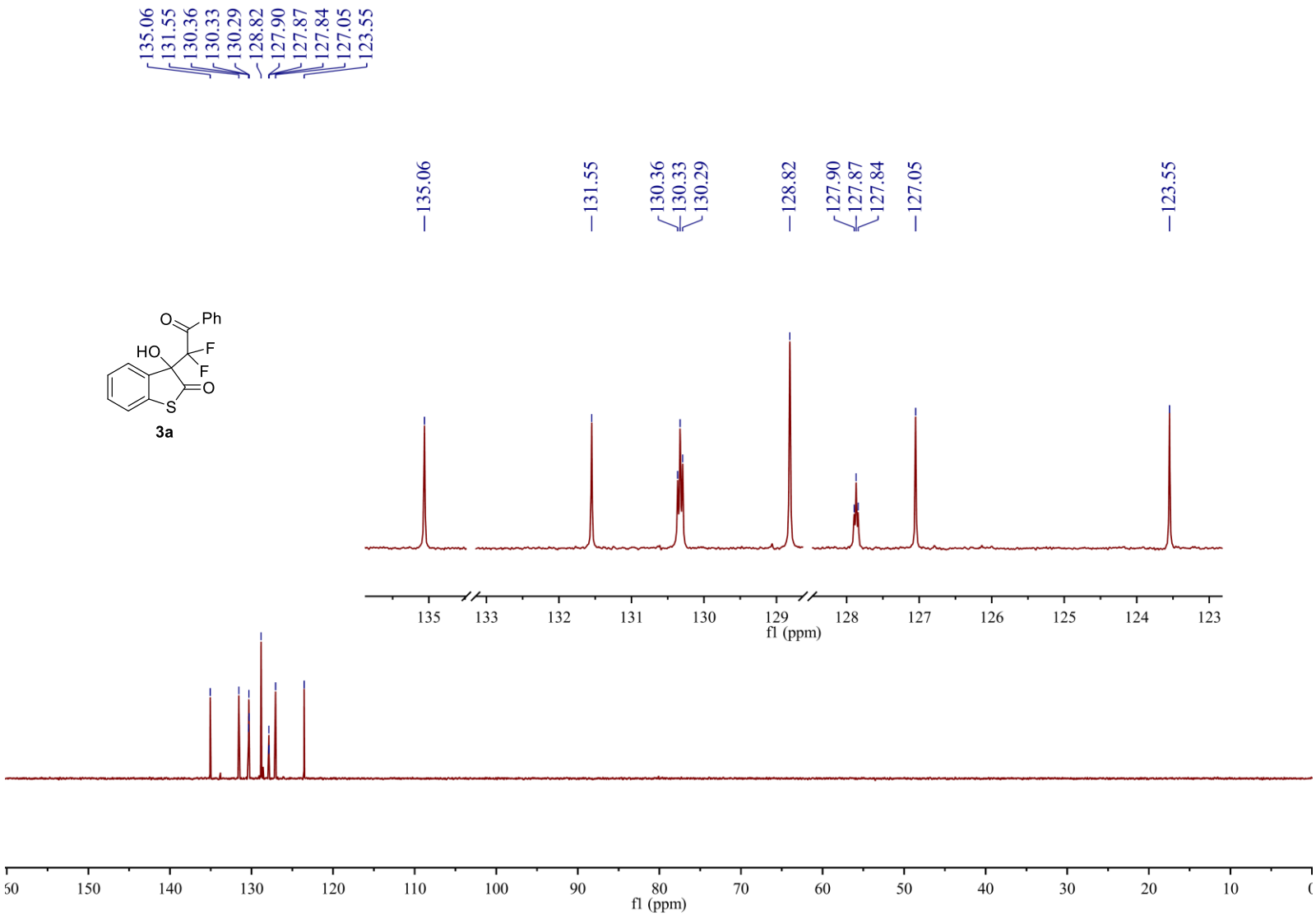
^{1}H NMR spectra of **3a** in $CDCl_3$ (400 MHz)



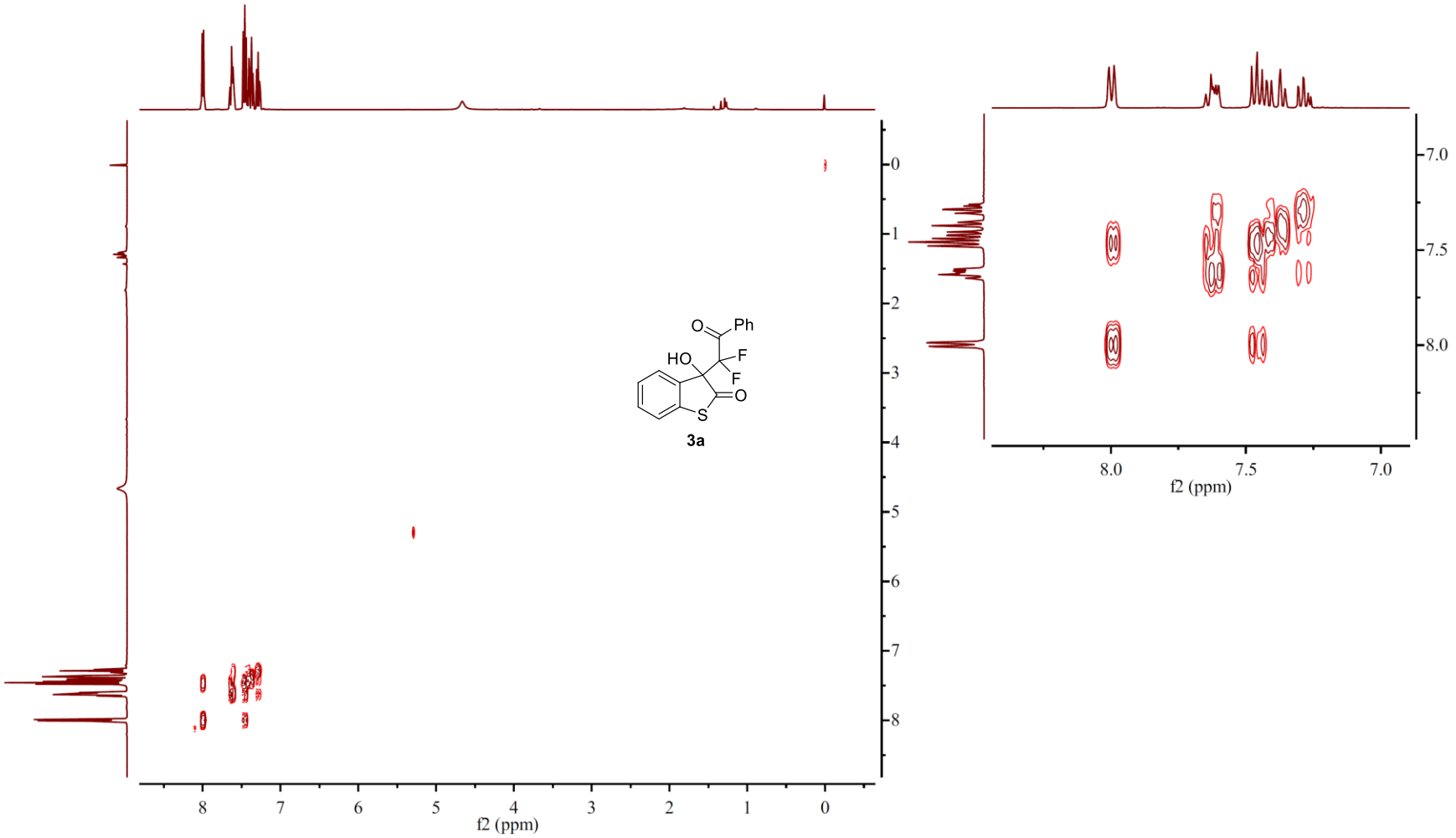
$^{13}C\{^{1}H\}$ NMR spectra of **3a** in $CDCl_3$ (100 MHz)



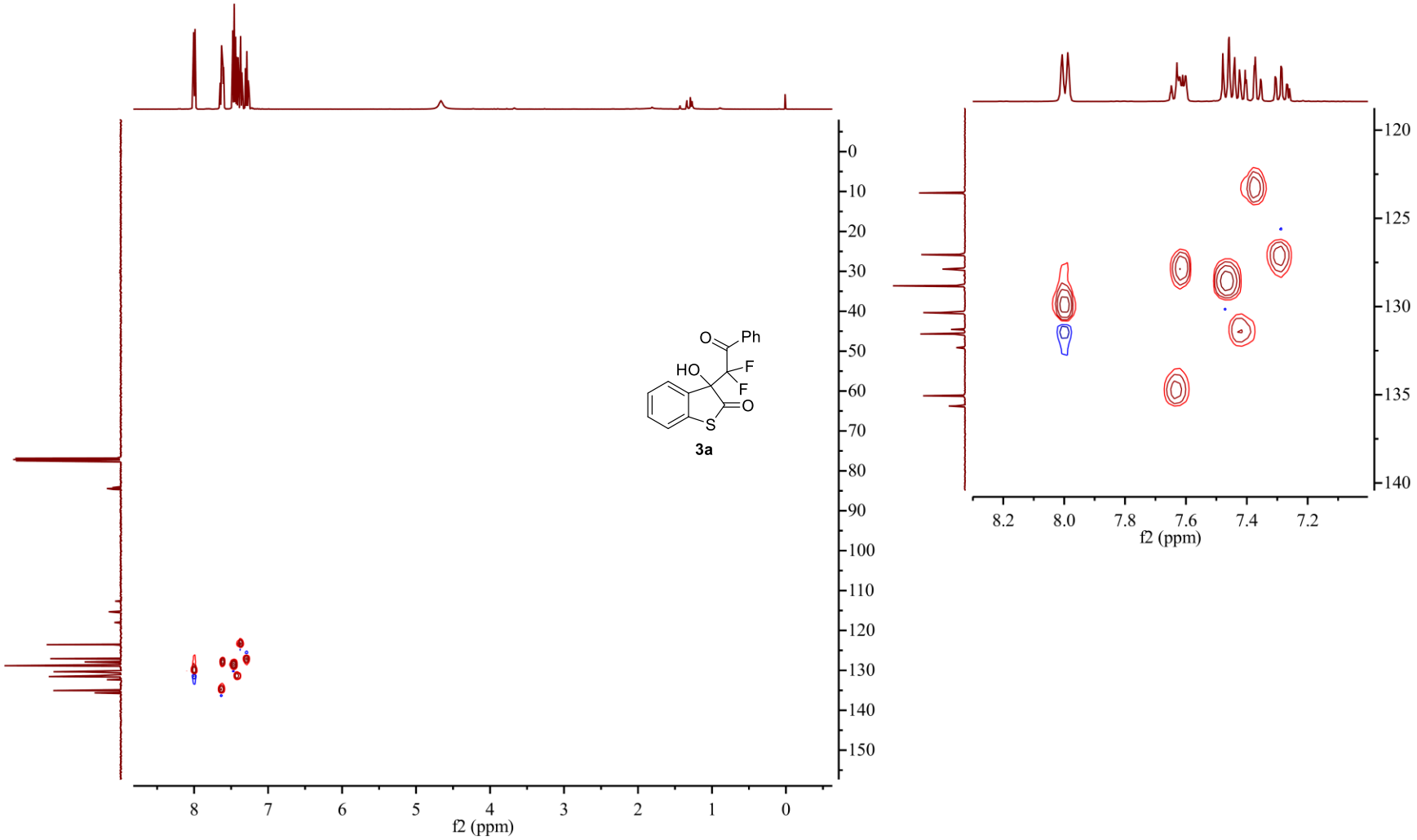
^{19}F NMR spectra of **3a** in $CDCl_3$ (376 MHz)



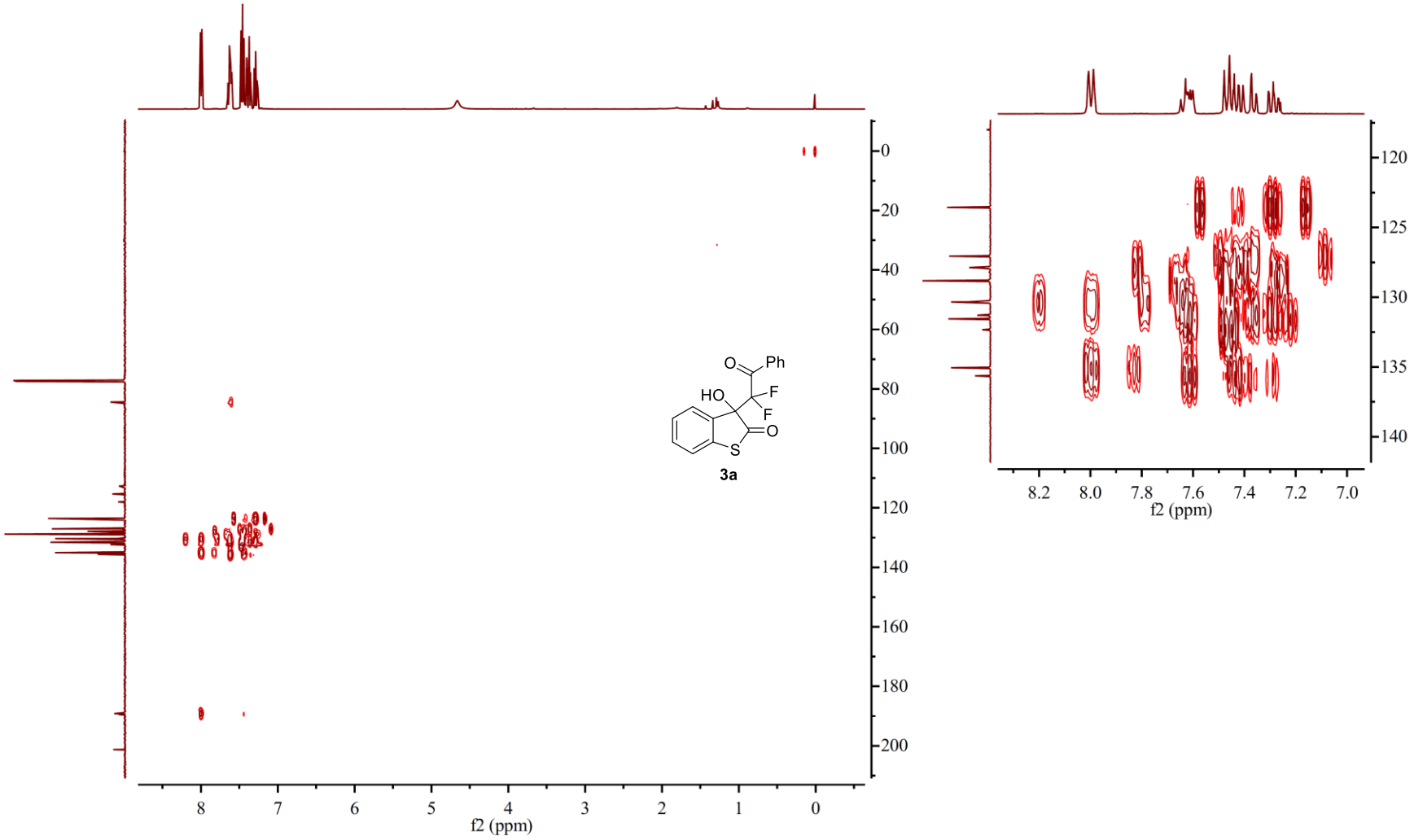
DEPT135 of **3a** in $CDCl_3$ (100 MHz)



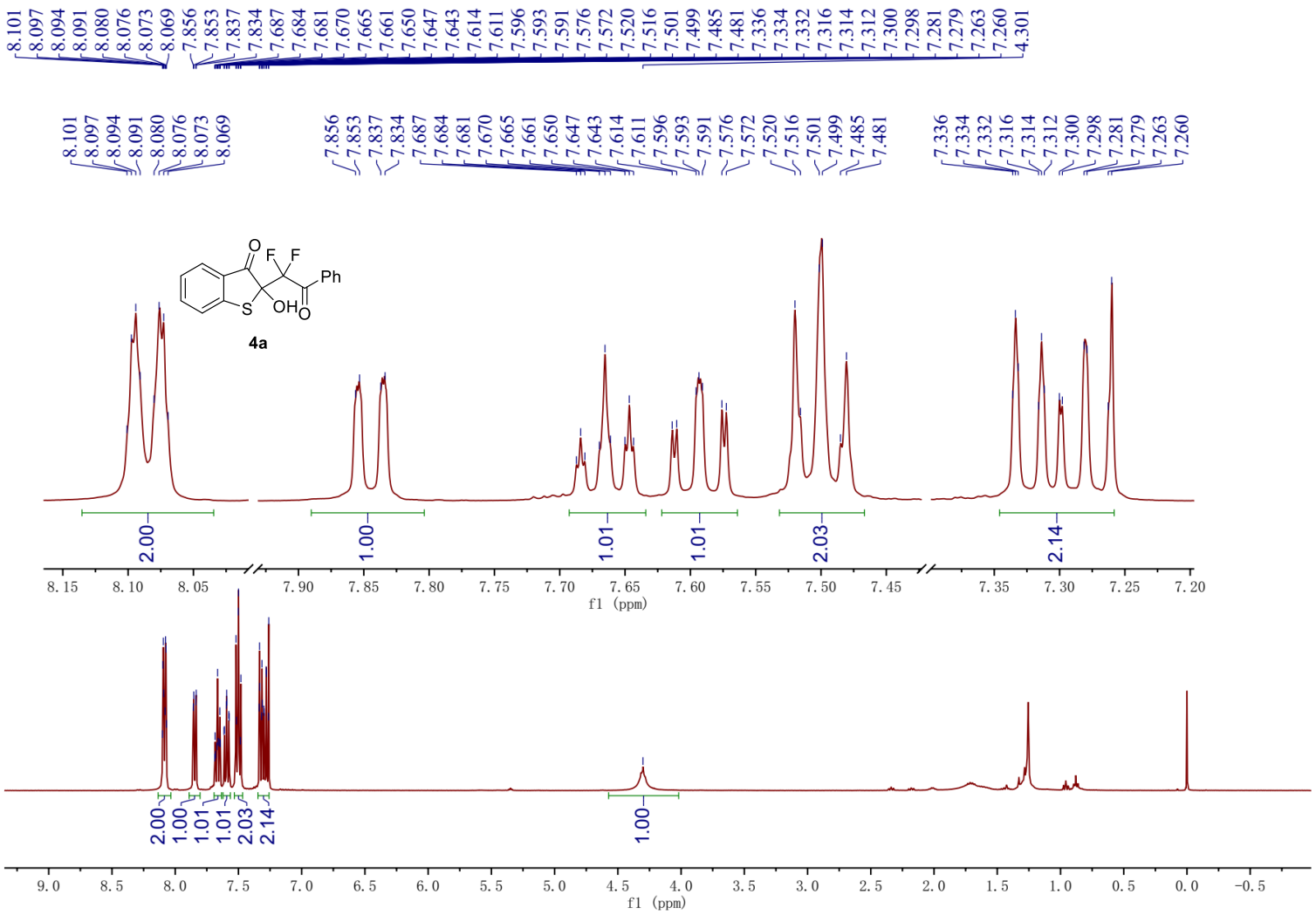
H-H COSY of **3a** in $CDCl_3$



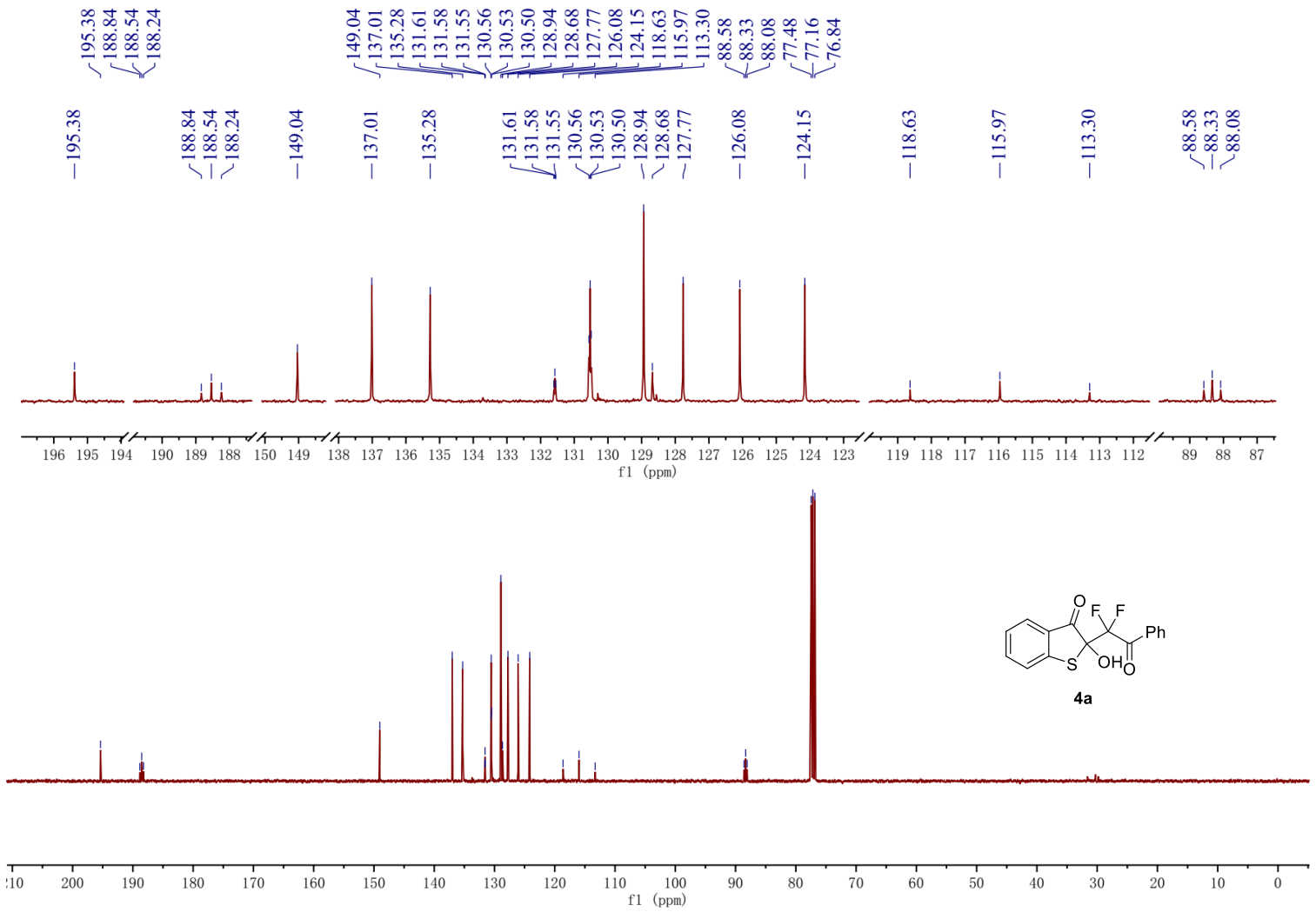
HSQC of **3a** in $CDCl_3$



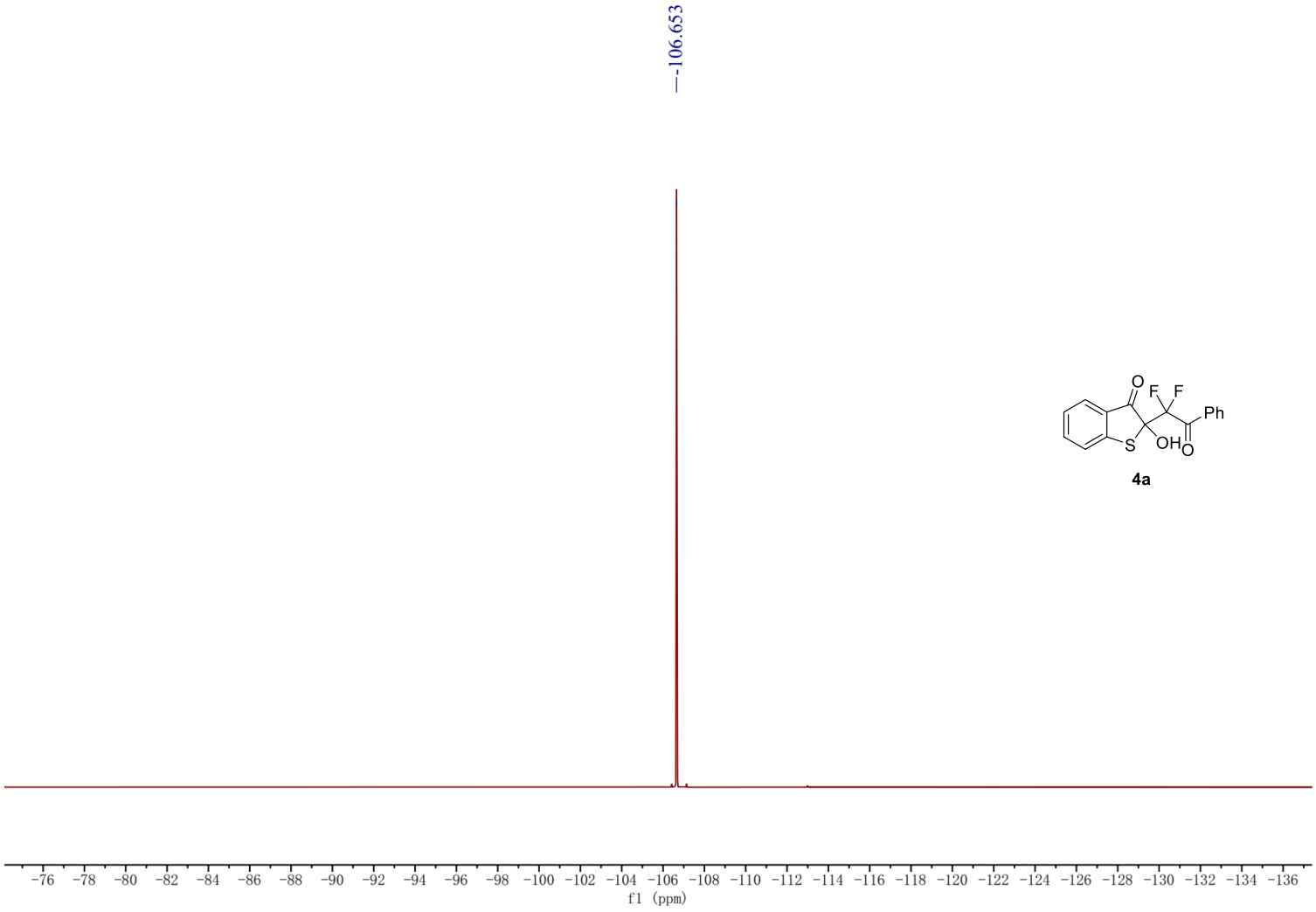
HMBC of **3a** in $CDCl_3$



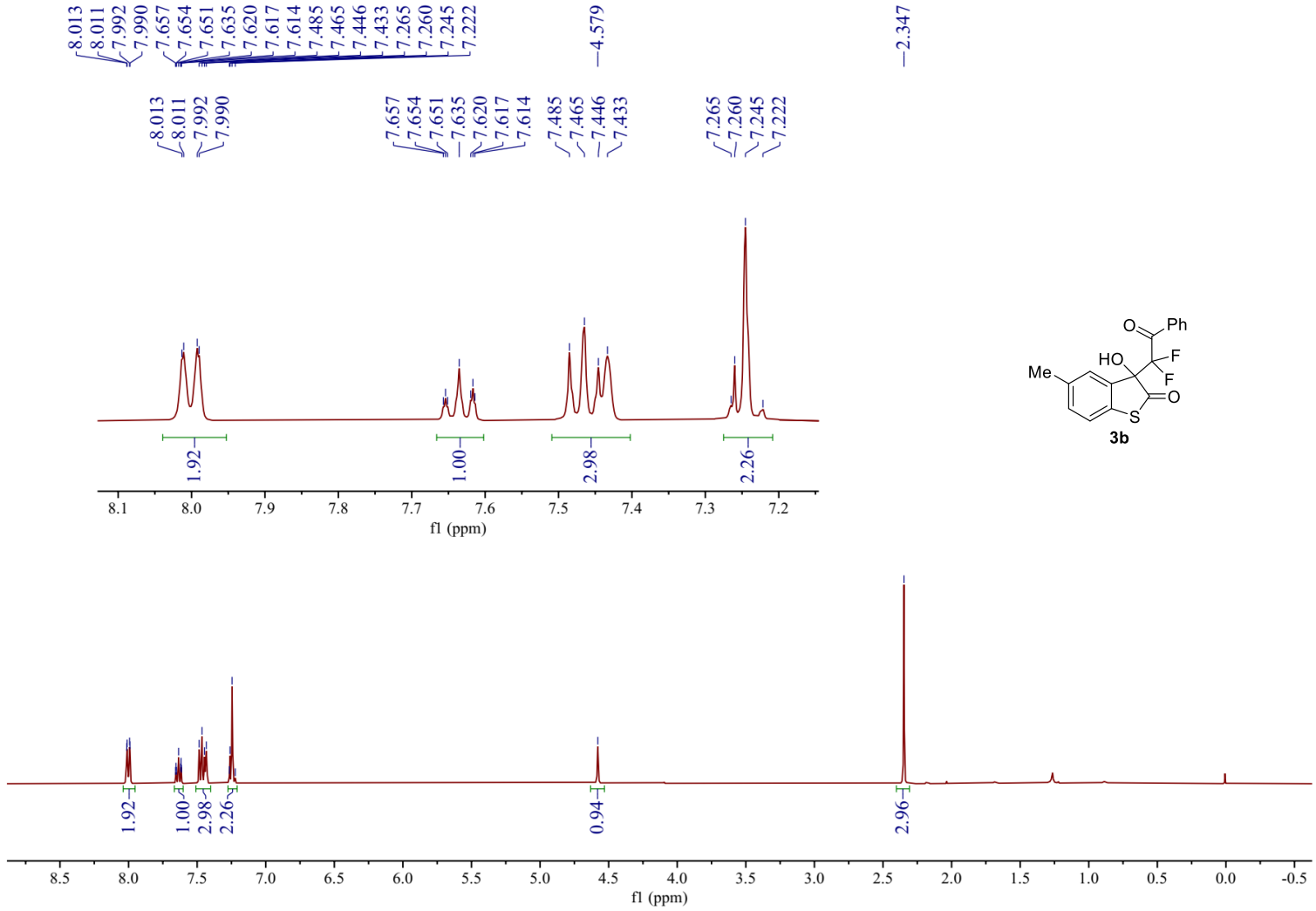
^{1}H NMR spectra of **4a** in $CDCl_3$ (400 MHz)



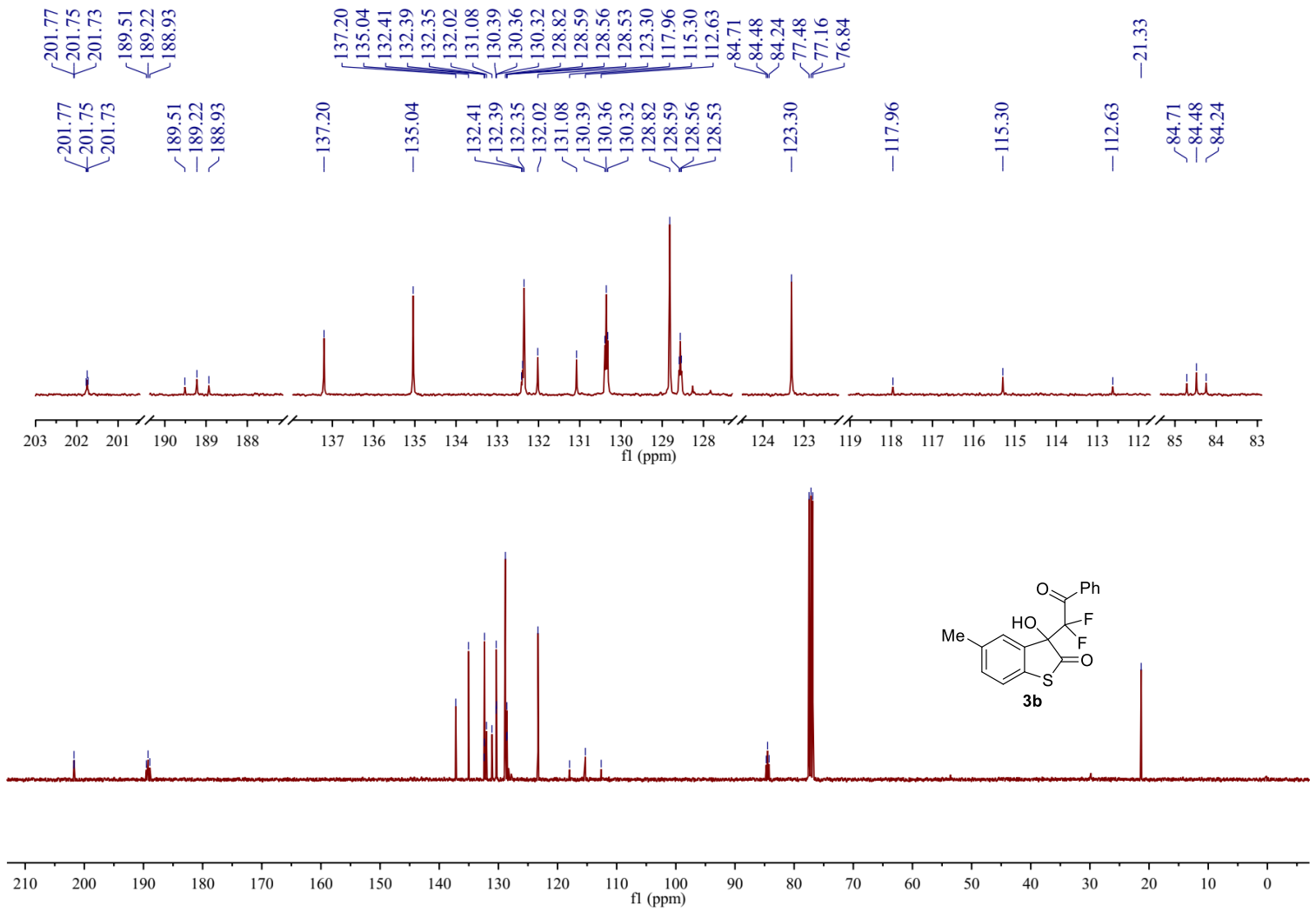
$^{13}C\{^{1}H\}$ NMR spectra of **4a** in $CDCl_3$ (100 MHz)



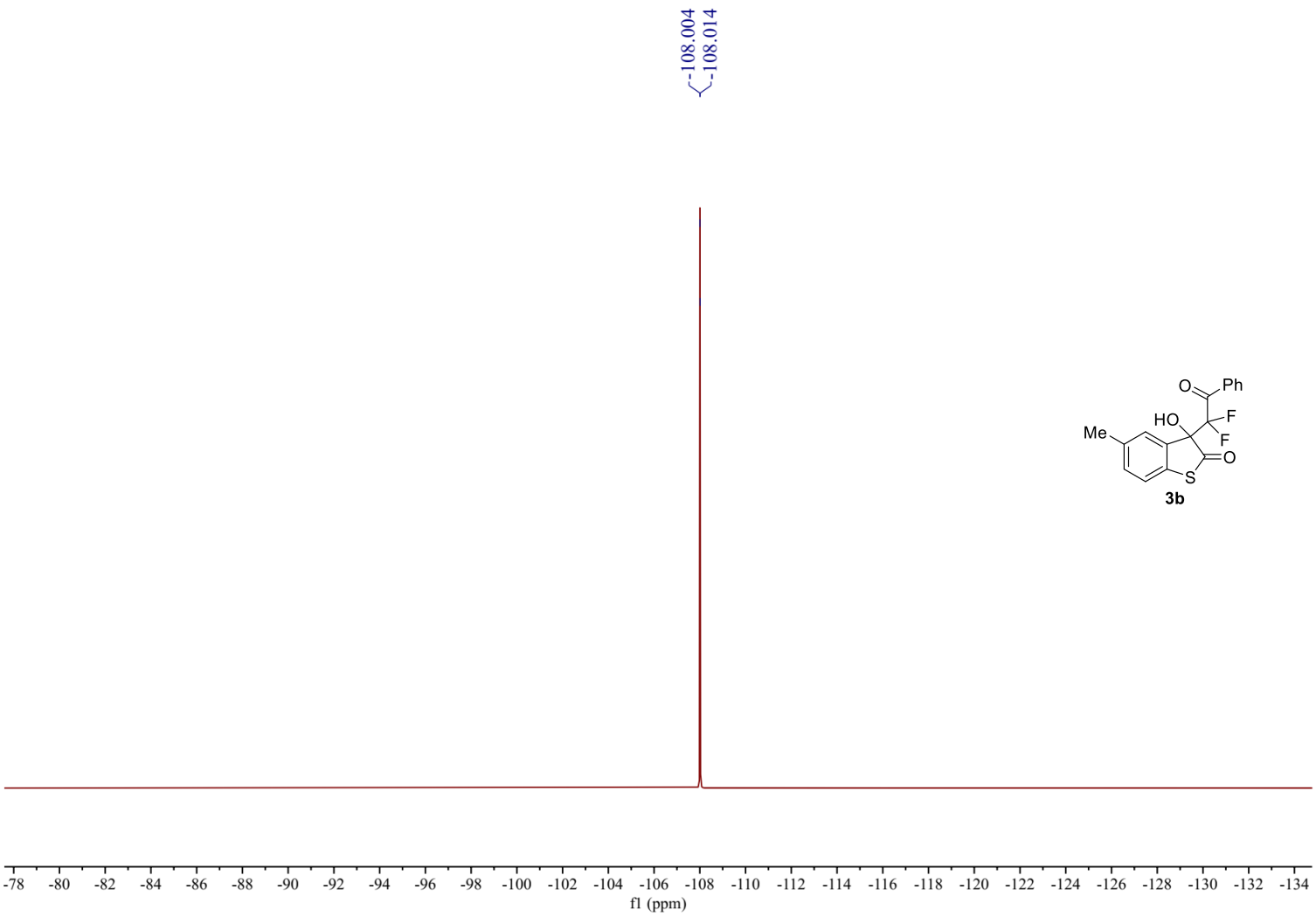
^{19}F NMR spectra of **4a** in $CDCl_3$ (376 MHz)



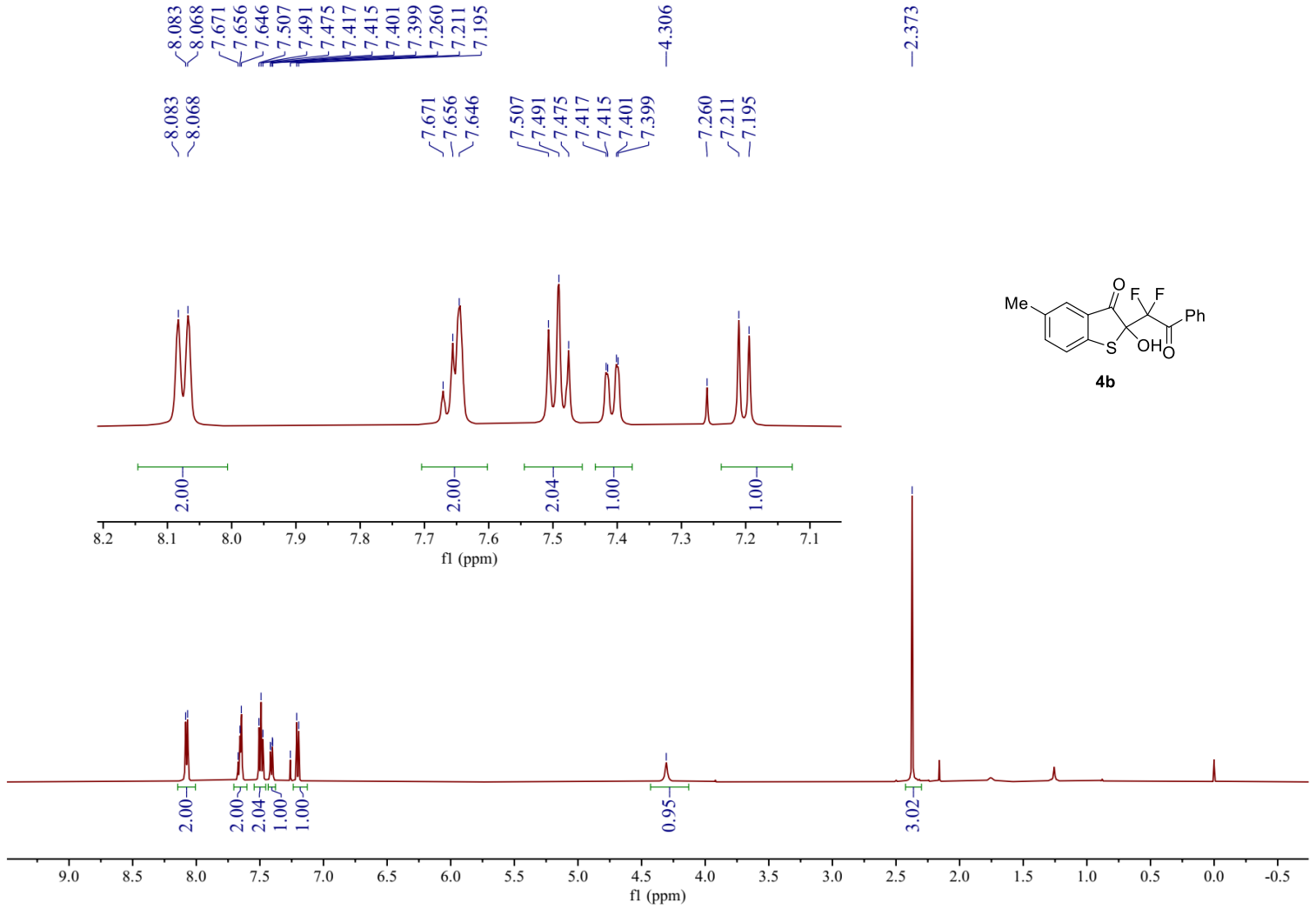
^{1}H NMR spectra of **3b** in $CDCl_3$ (400 MHz)



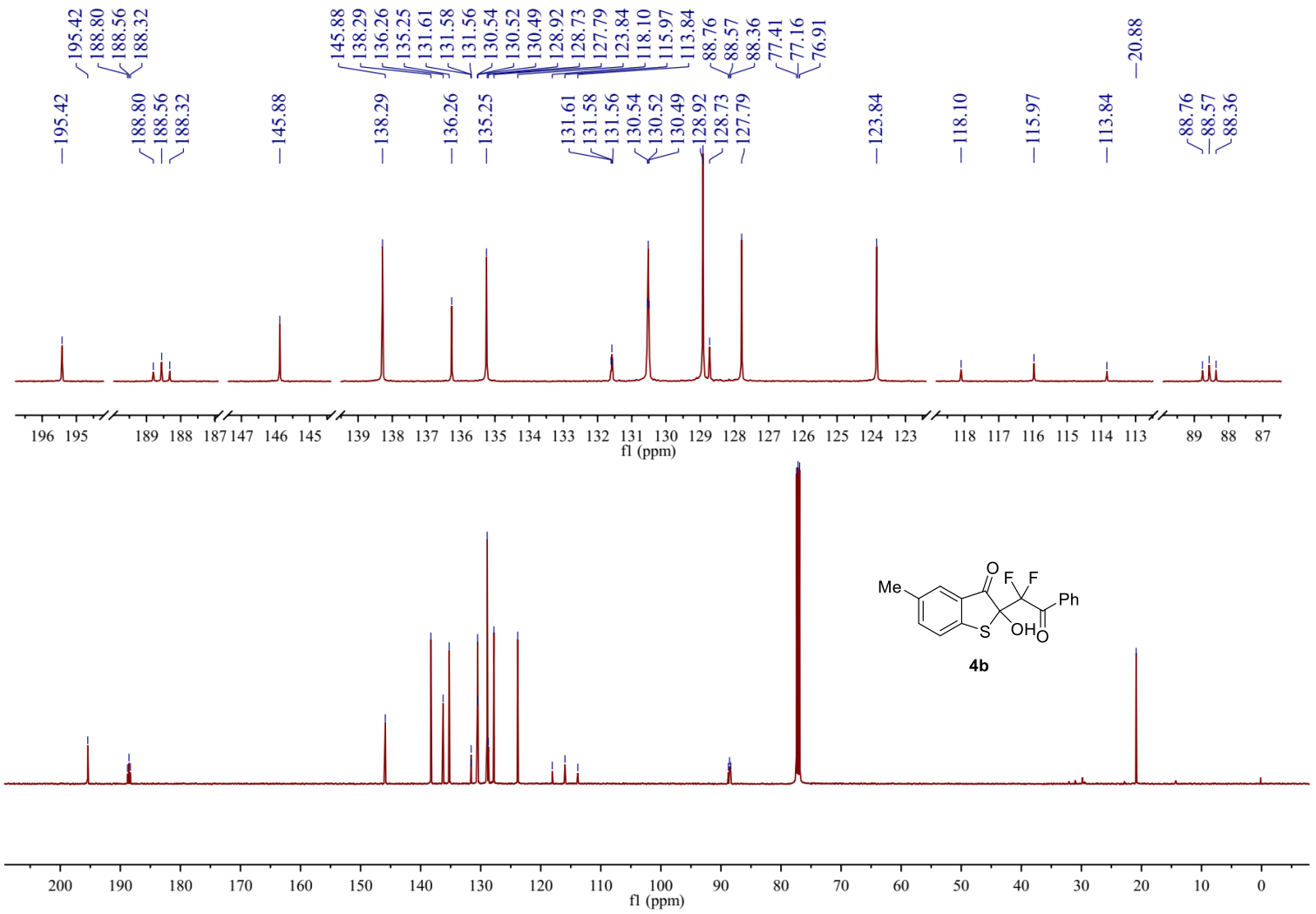
$^{13}C\{^{1}H\}$ NMR spectra of **3b** in $CDCl_3$ (100 MHz)



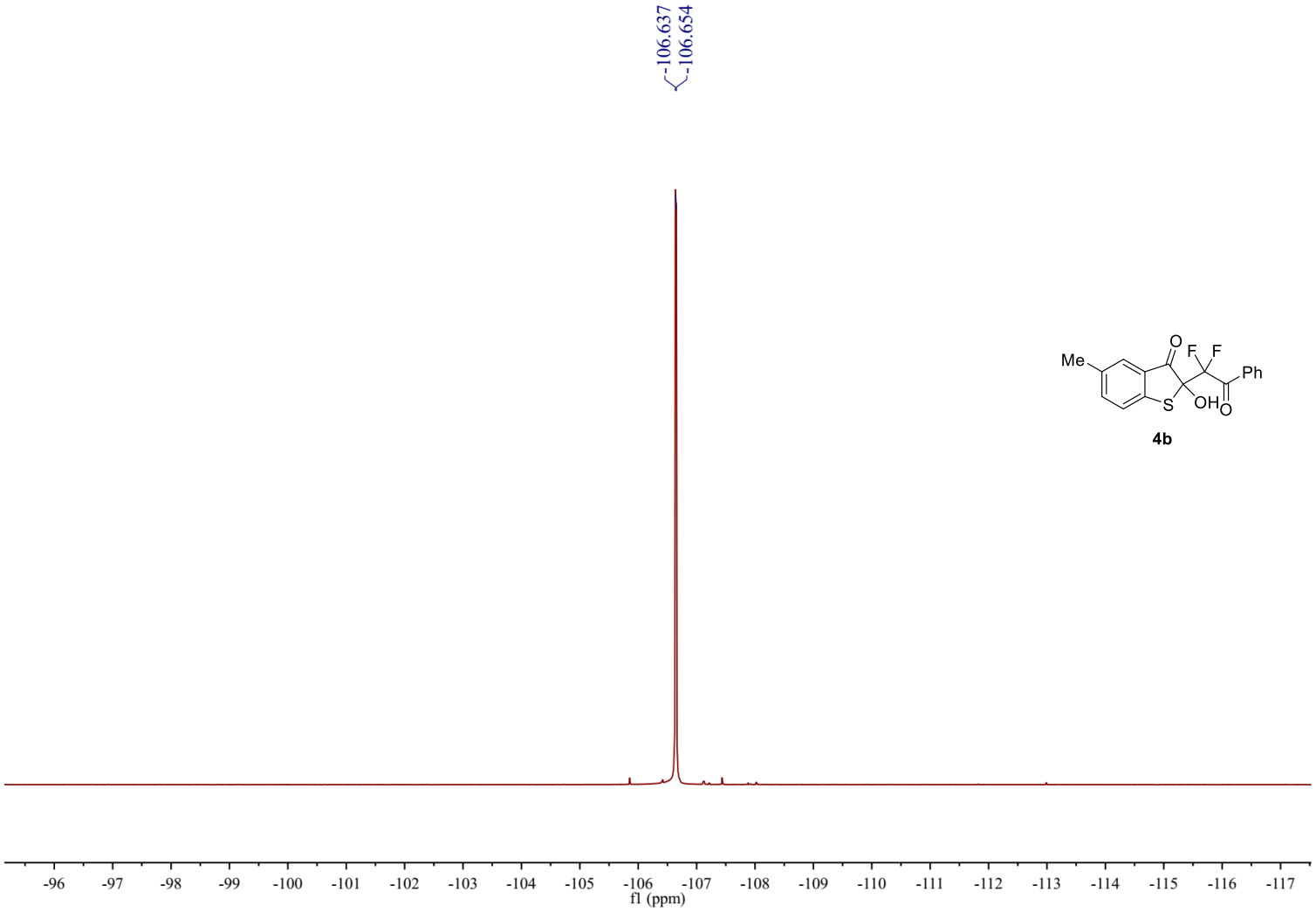
^{19}F NMR spectra of **3b** in $CDCl_3$ (376 MHz)



^{1}H NMR spectra of **4b** in $CDCl_3$ (500 MHz)

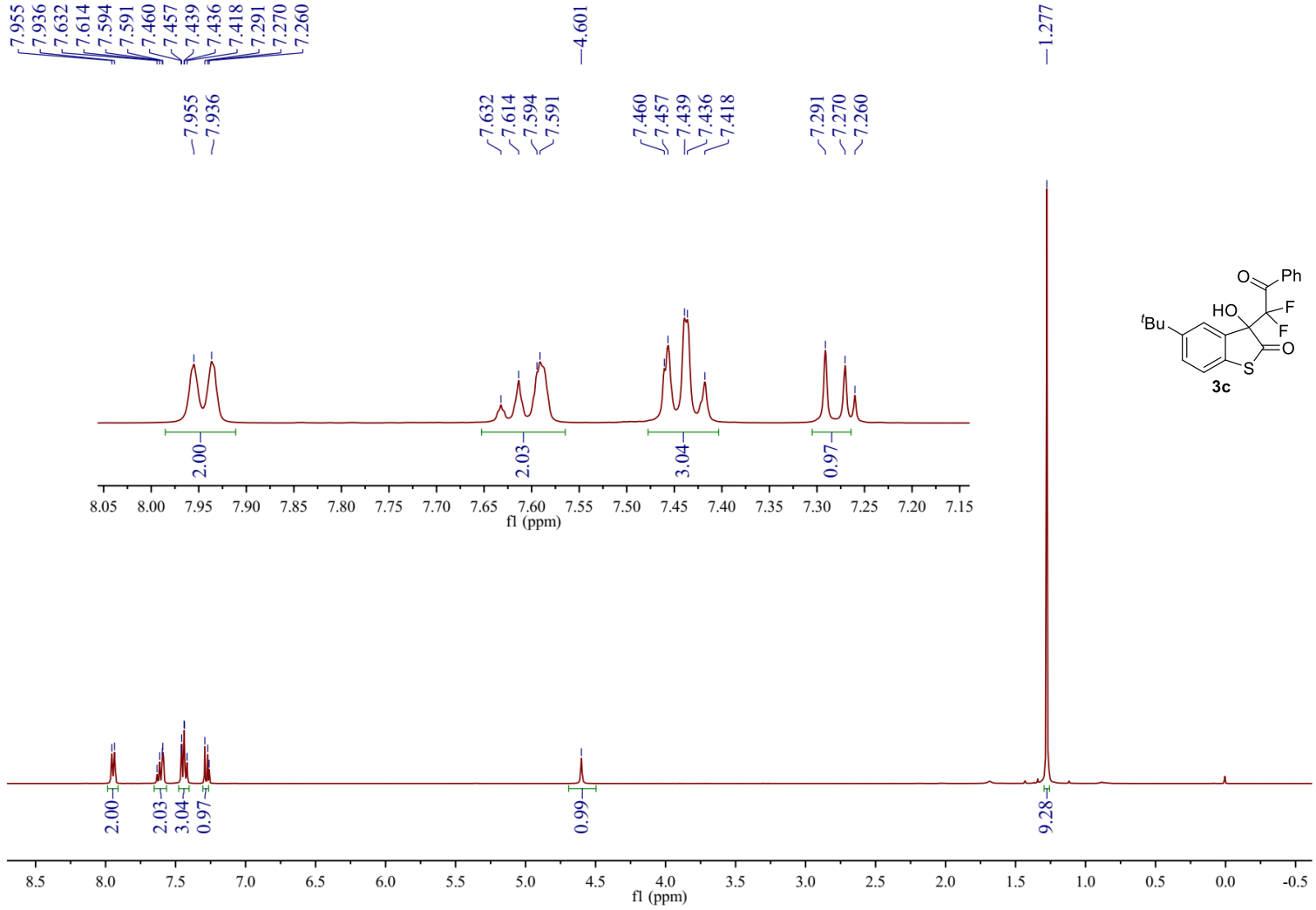


$^{13}C\{^{1}H\}$ NMR spectra of **4b** in $CDCl_3$ (125 MHz)

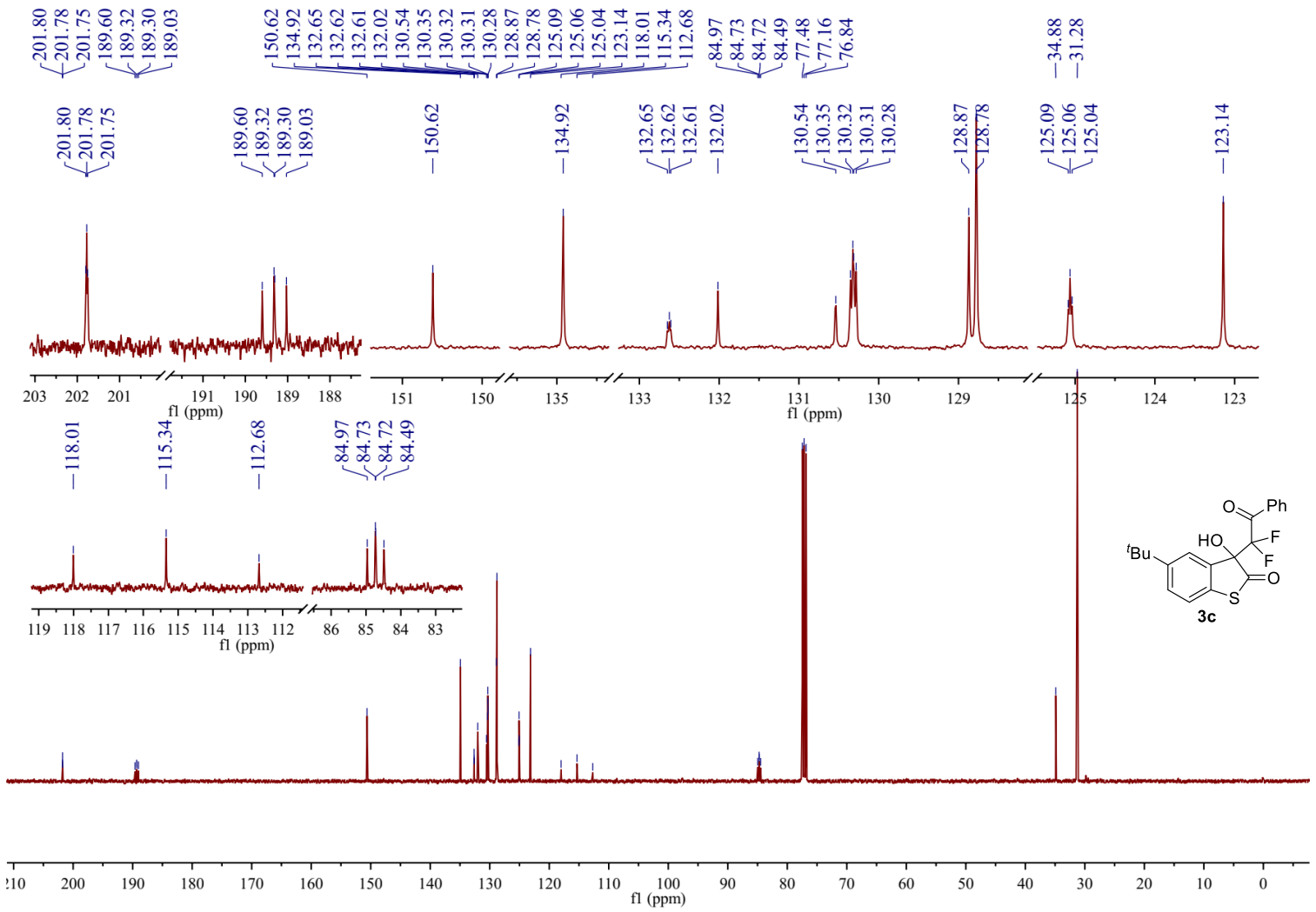


4b

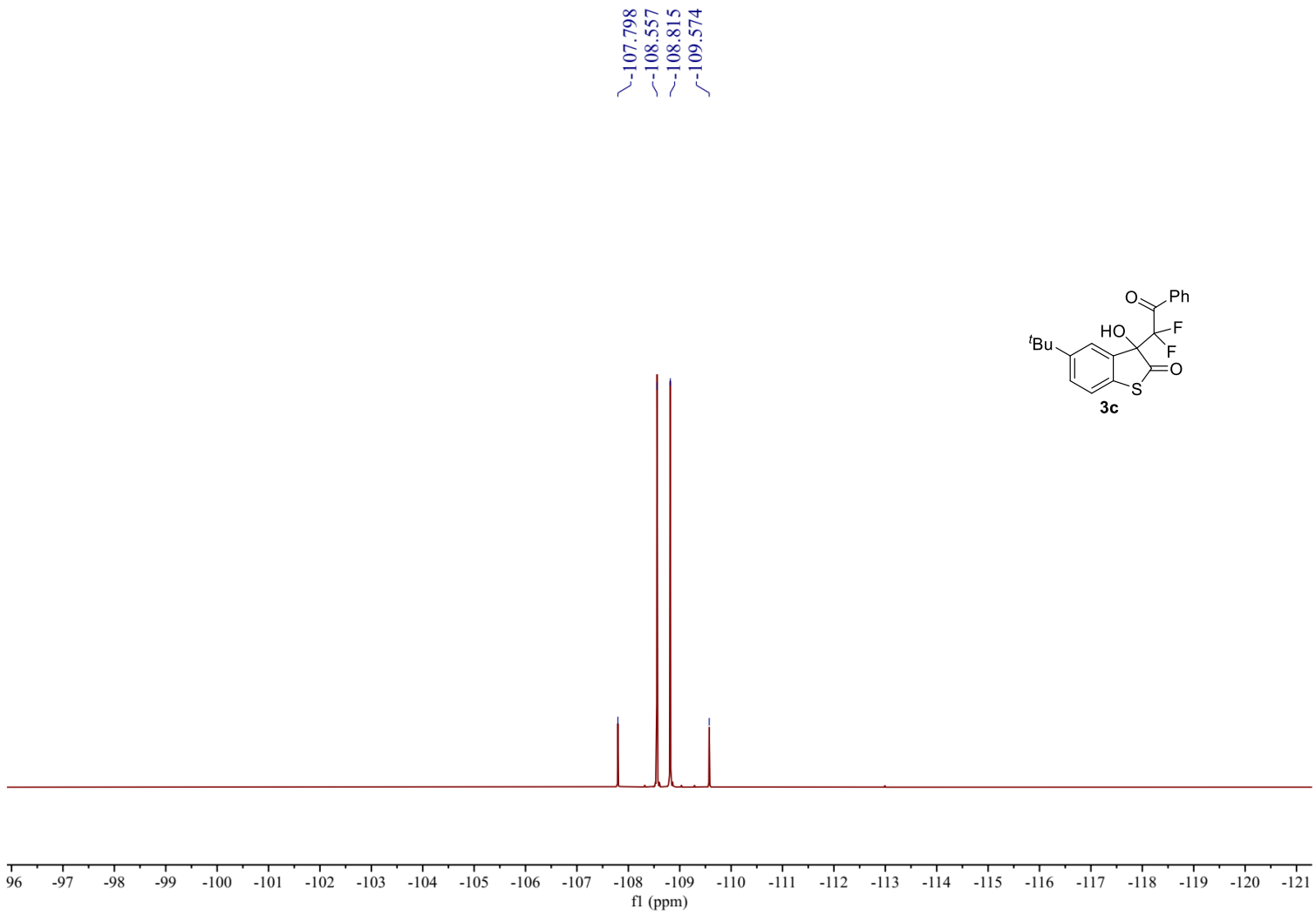
^{19}F NMR spectra of **4b** in $CDCl_3$ (376 MHz)



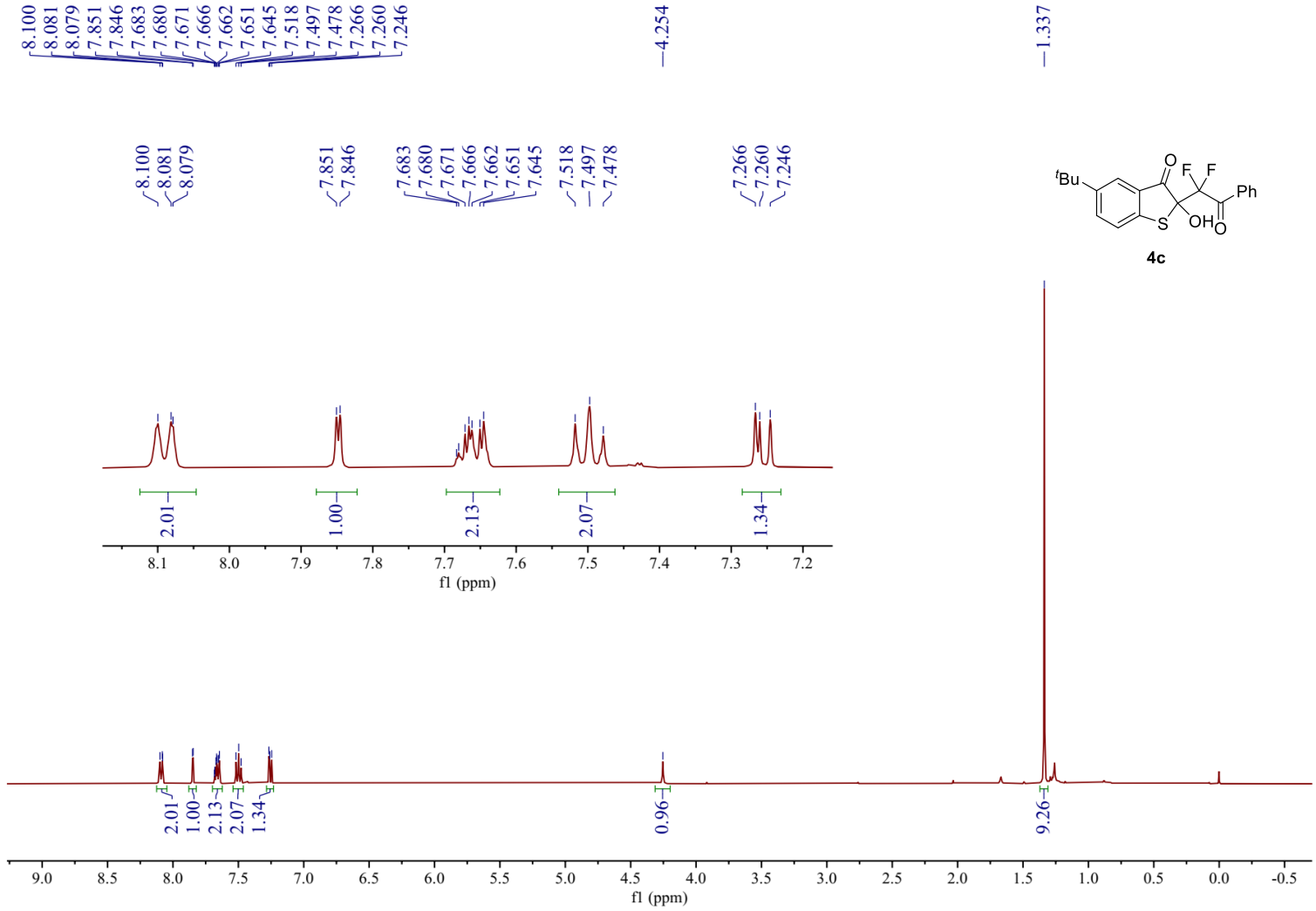
^{1}H NMR spectra of **3c** in $CDCl_3$ (400 MHz)



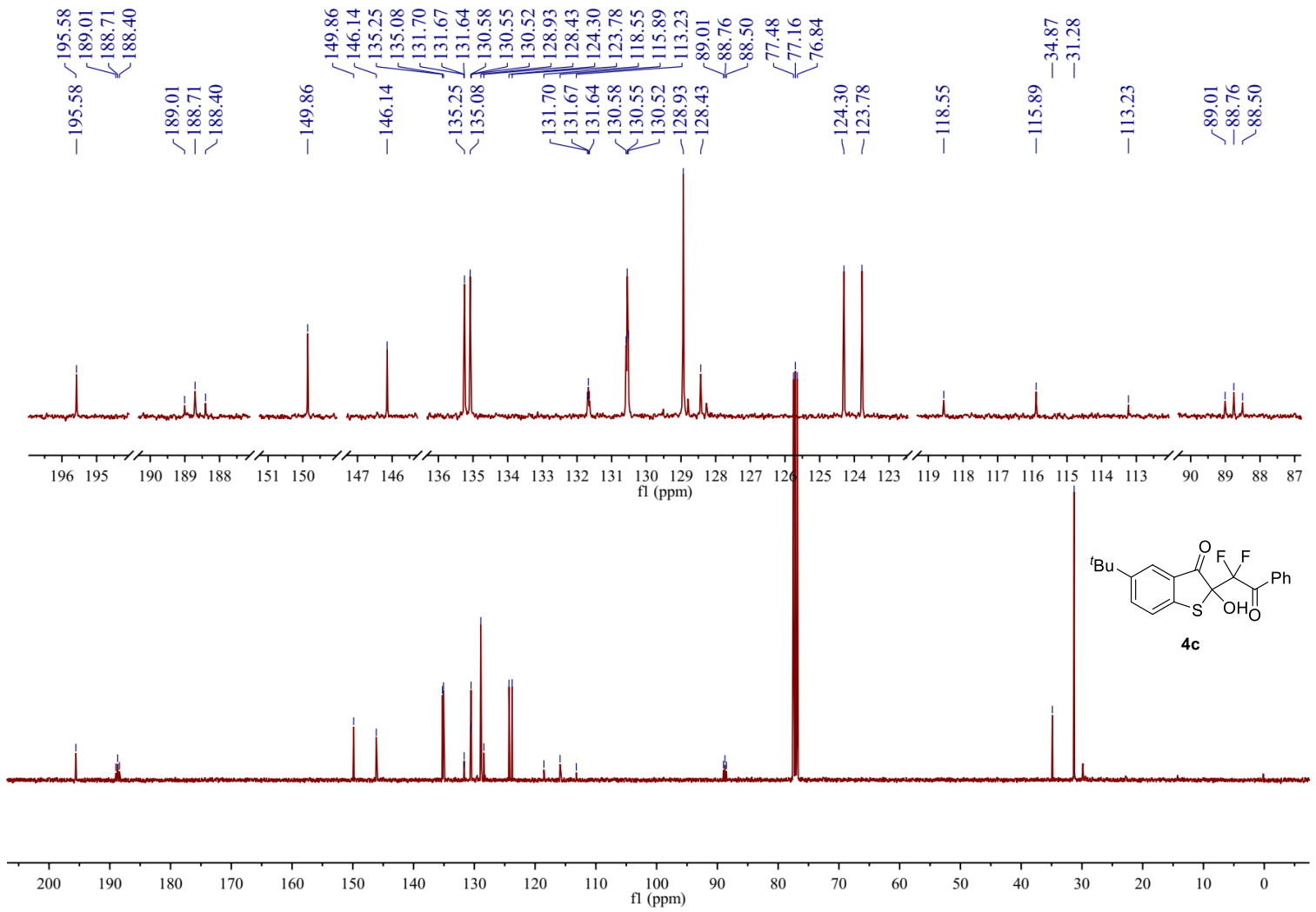
$^{13}C\{^{1}H\}$ NMR spectra of **3c** in $CDCl_3$ (100 MHz)



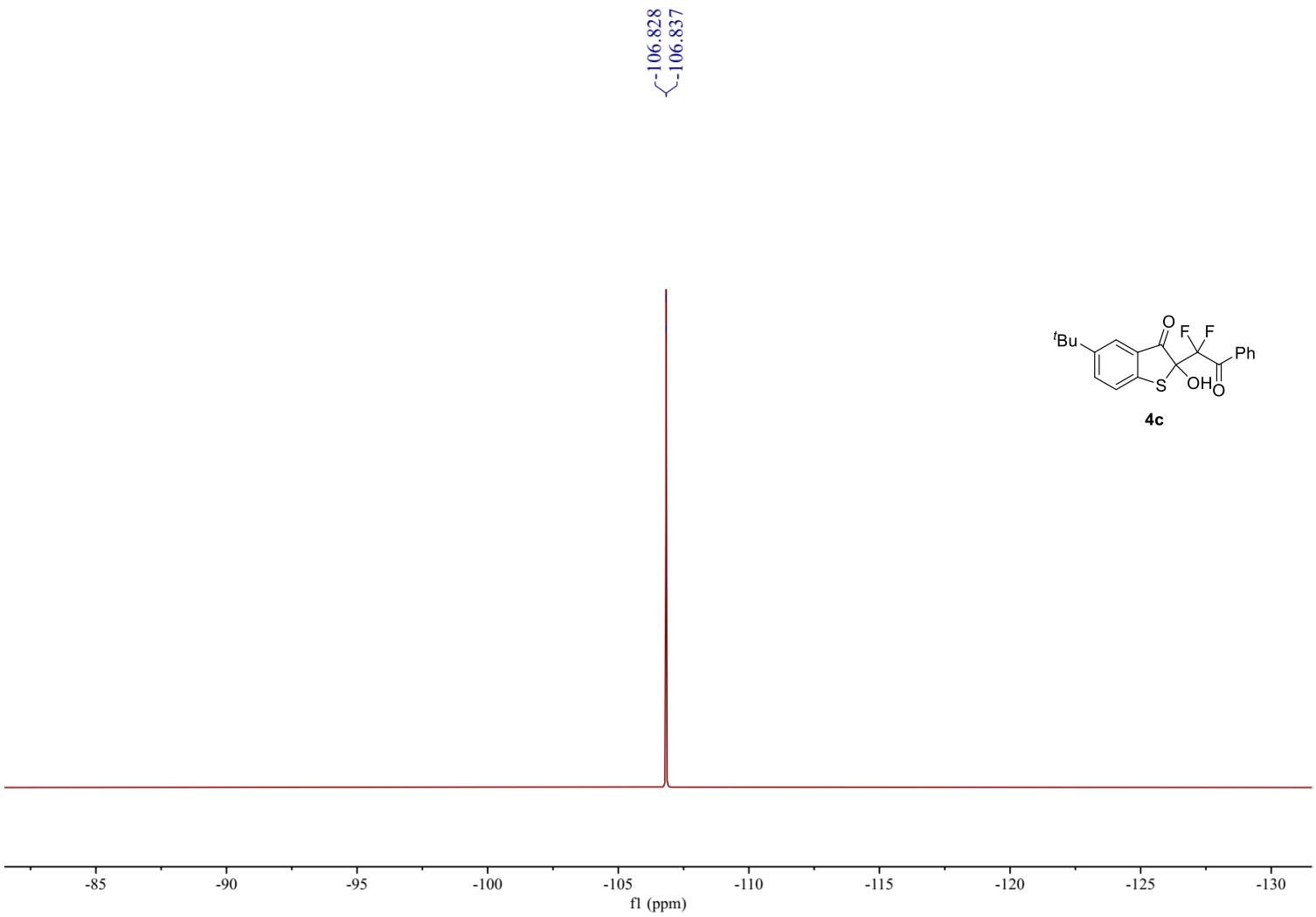
^{19}F NMR spectra of **3c** in $CDCl_3$ (376 MHz)



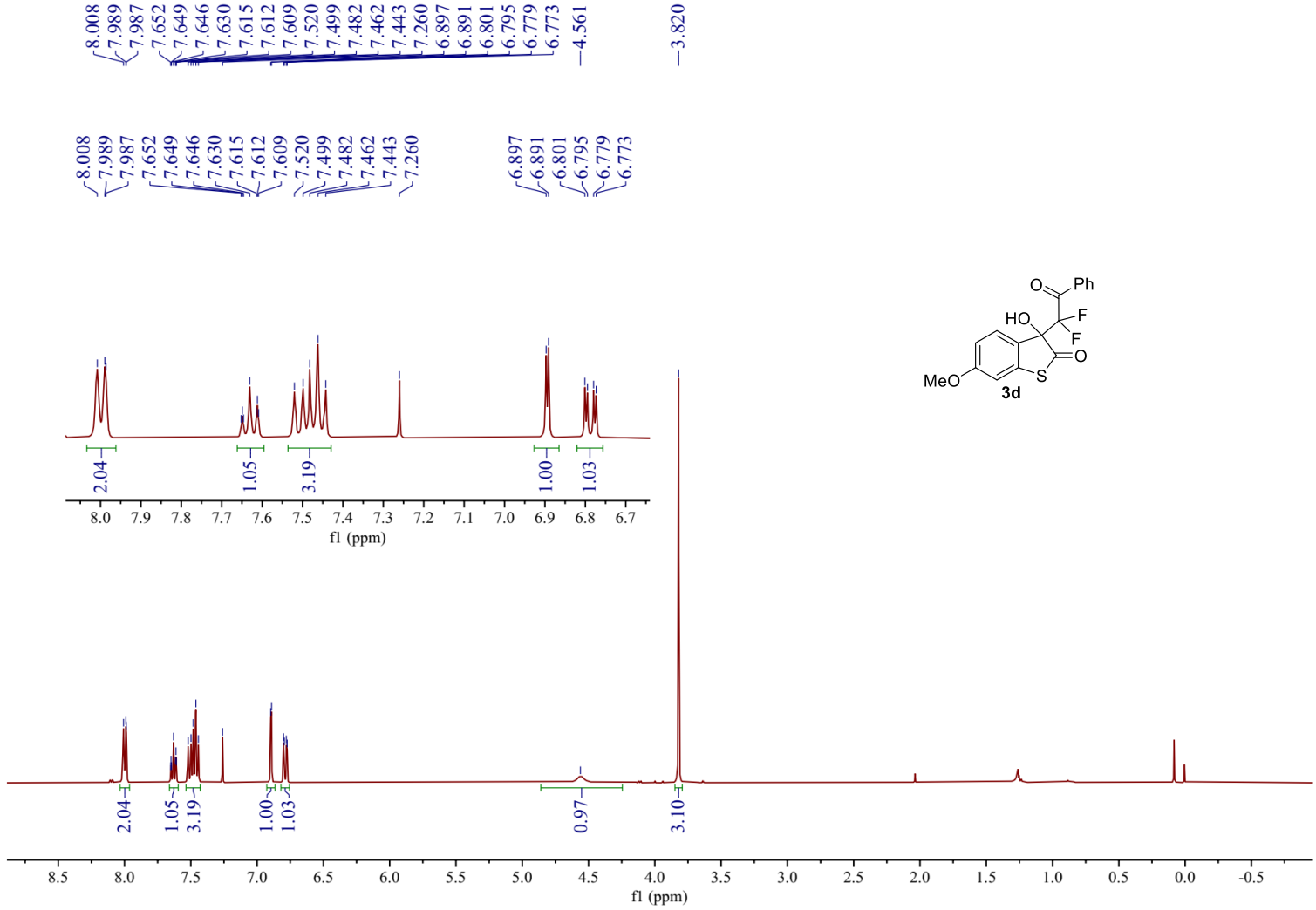
^{1}H NMR spectra of **4c** in $CDCl_3$ (400 MHz)



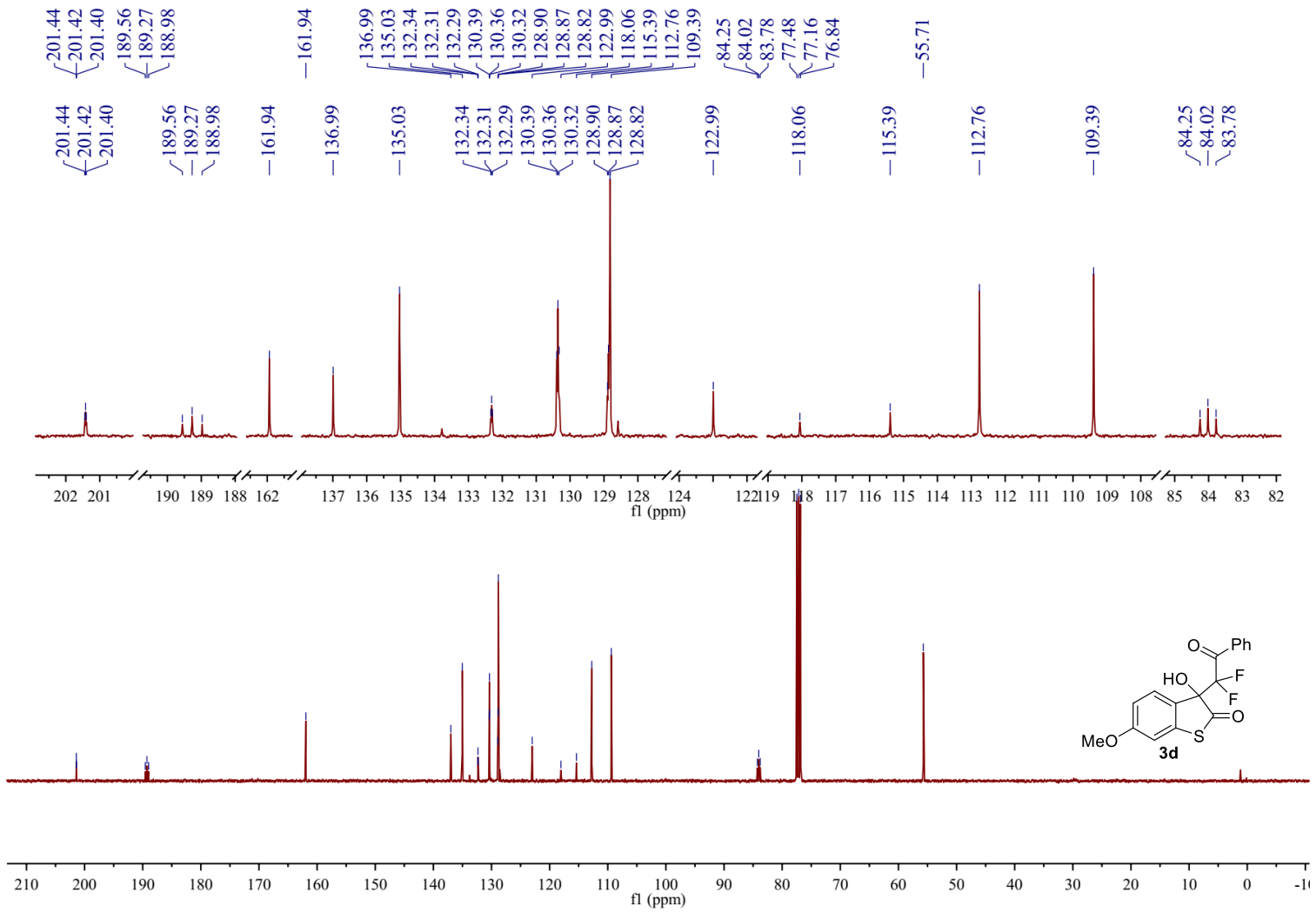
$^{13}C\{^{1}H\}$ NMR spectra of **4c** in $CDCl_3$ (100 MHz)



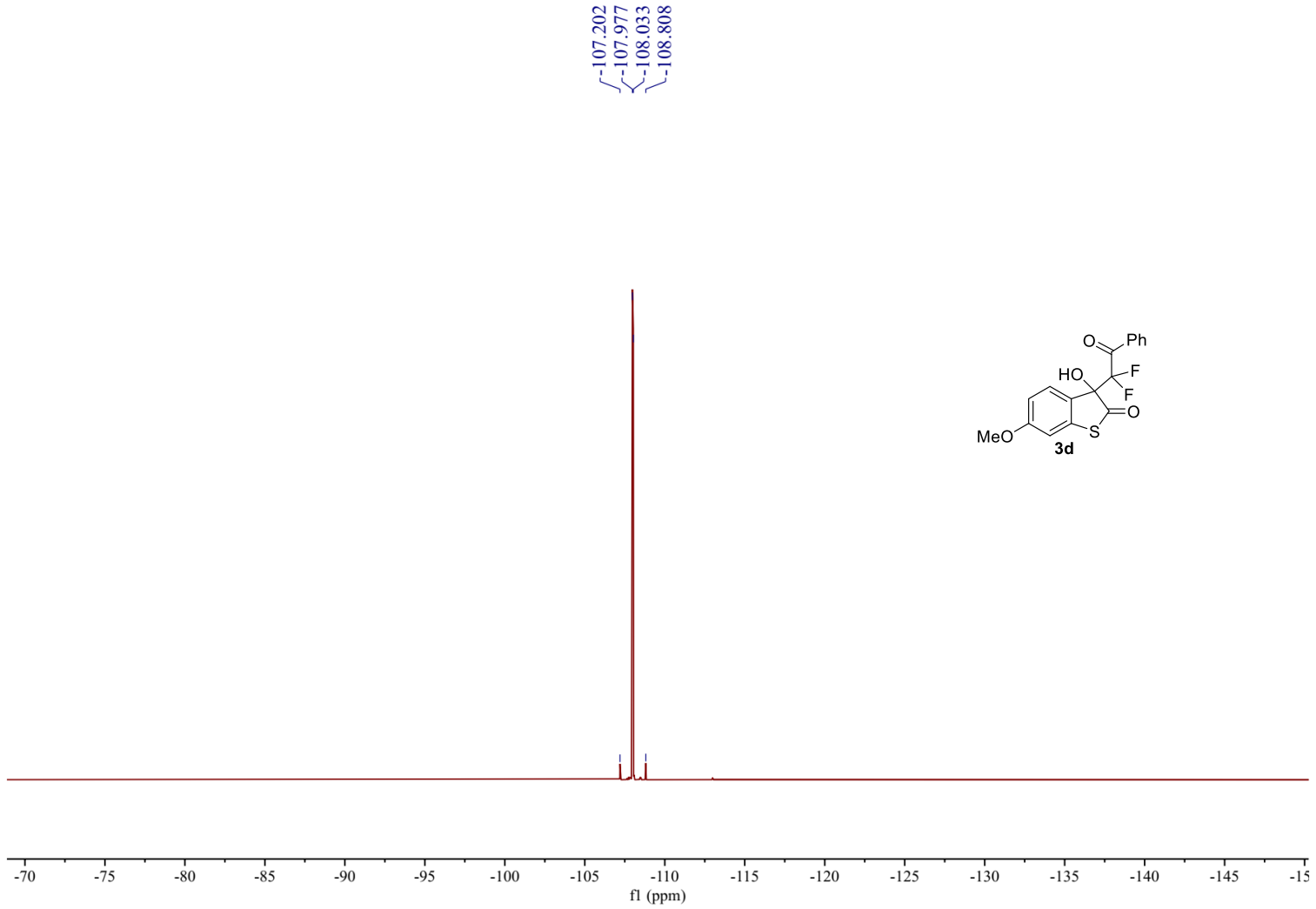
^{19}F NMR spectra of **4c** in $CDCl_3$ (376 MHz)



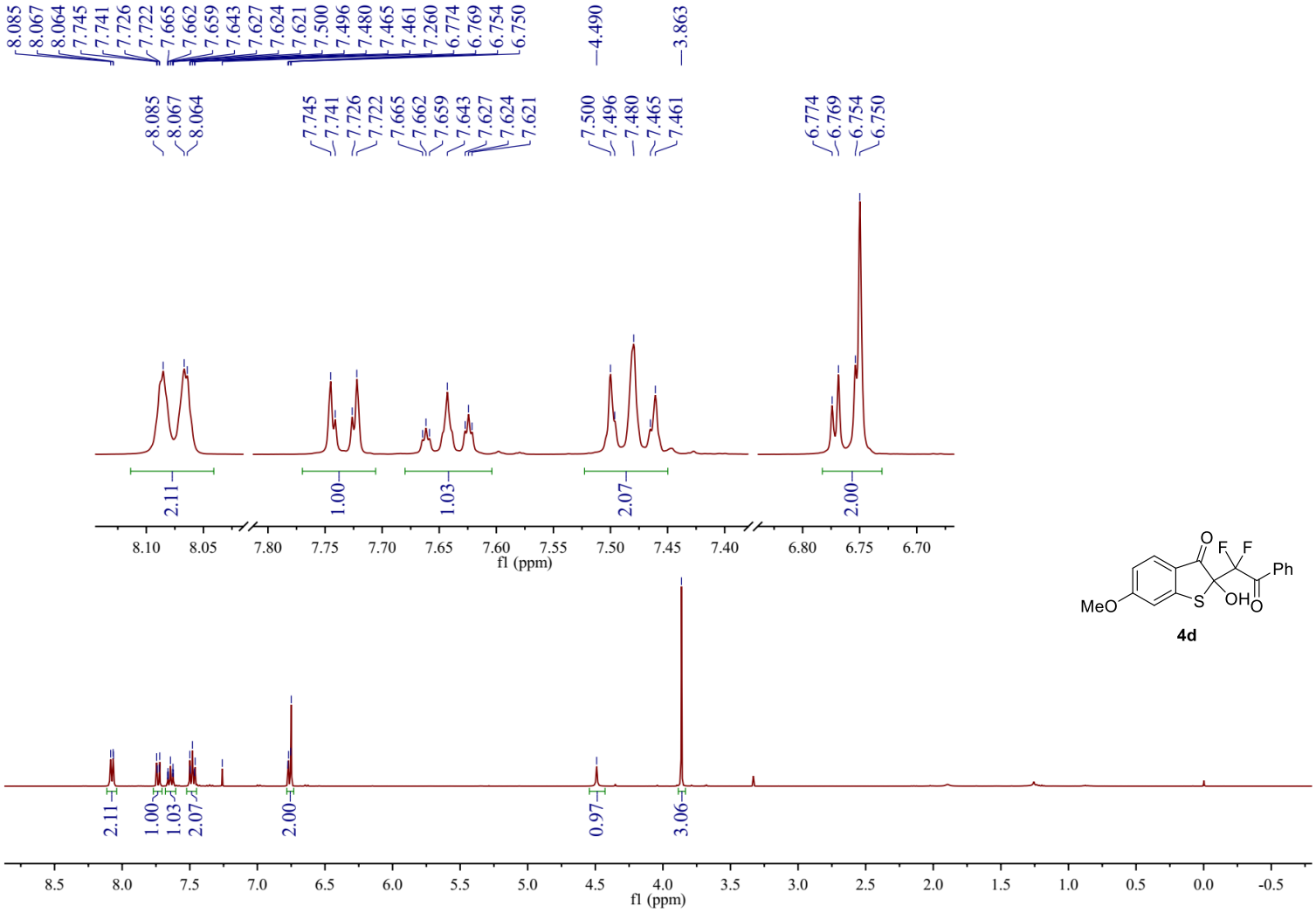
^{1}H NMR spectra of **3d** in $CDCl_3$ (400 MHz)



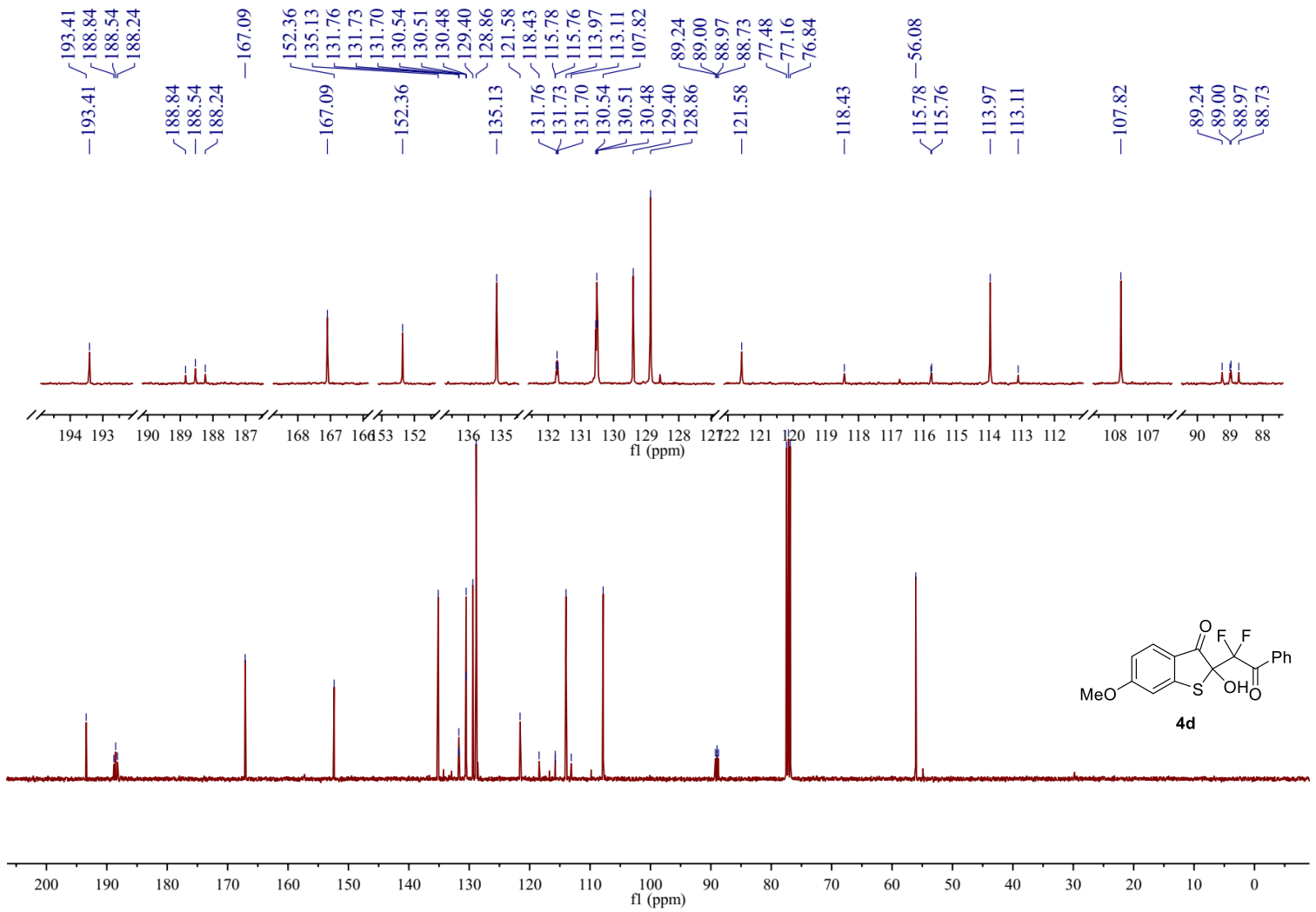
$^{13}C\{^{1}H\}$ NMR spectra of **3d** in $CDCl_3$ (100 MHz)



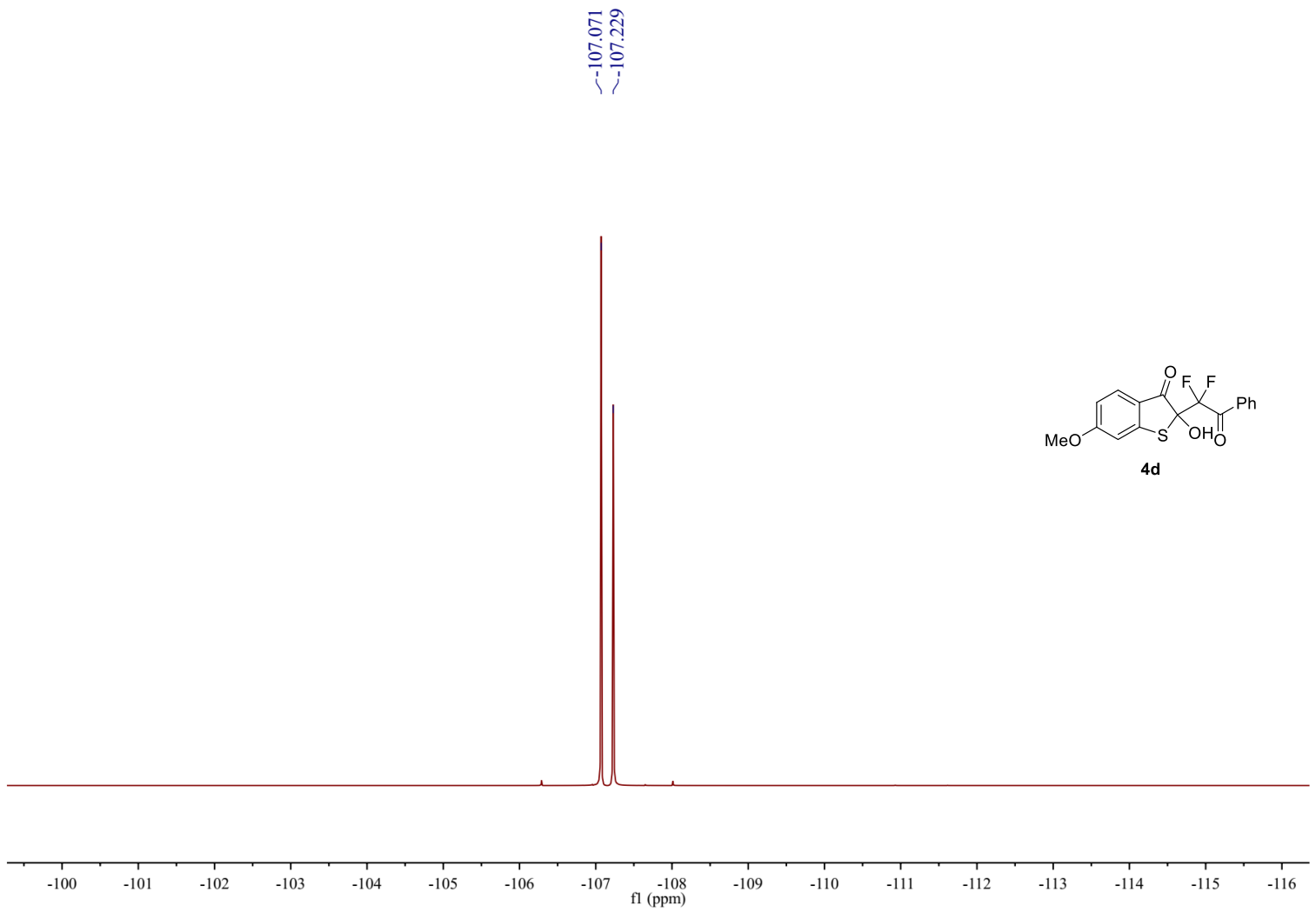
^{19}F NMR spectra of **3d** in $CDCl_3$ (376 MHz)



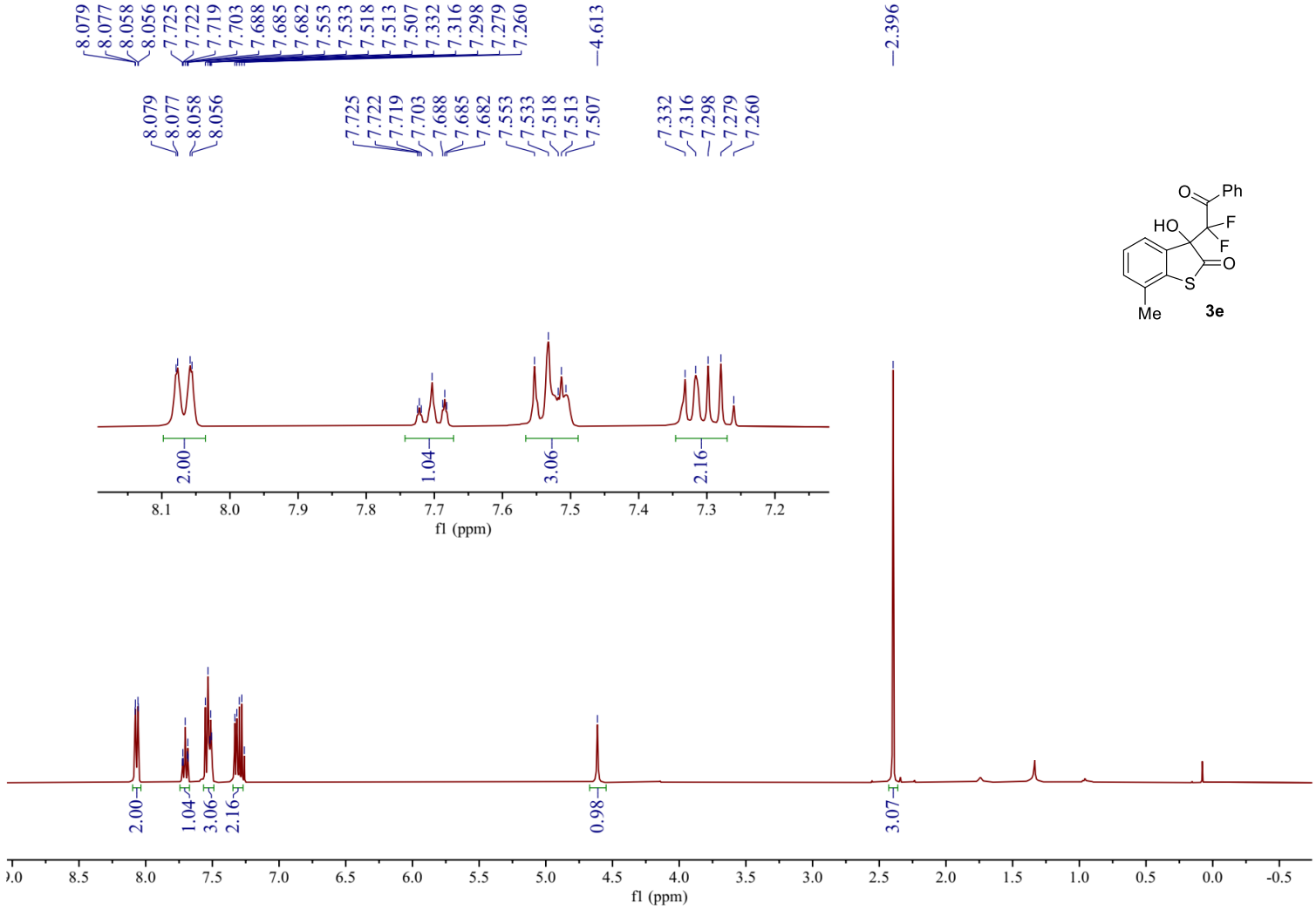
^{1}H NMR spectra of **4d** in $CDCl_3$ (400 MHz)



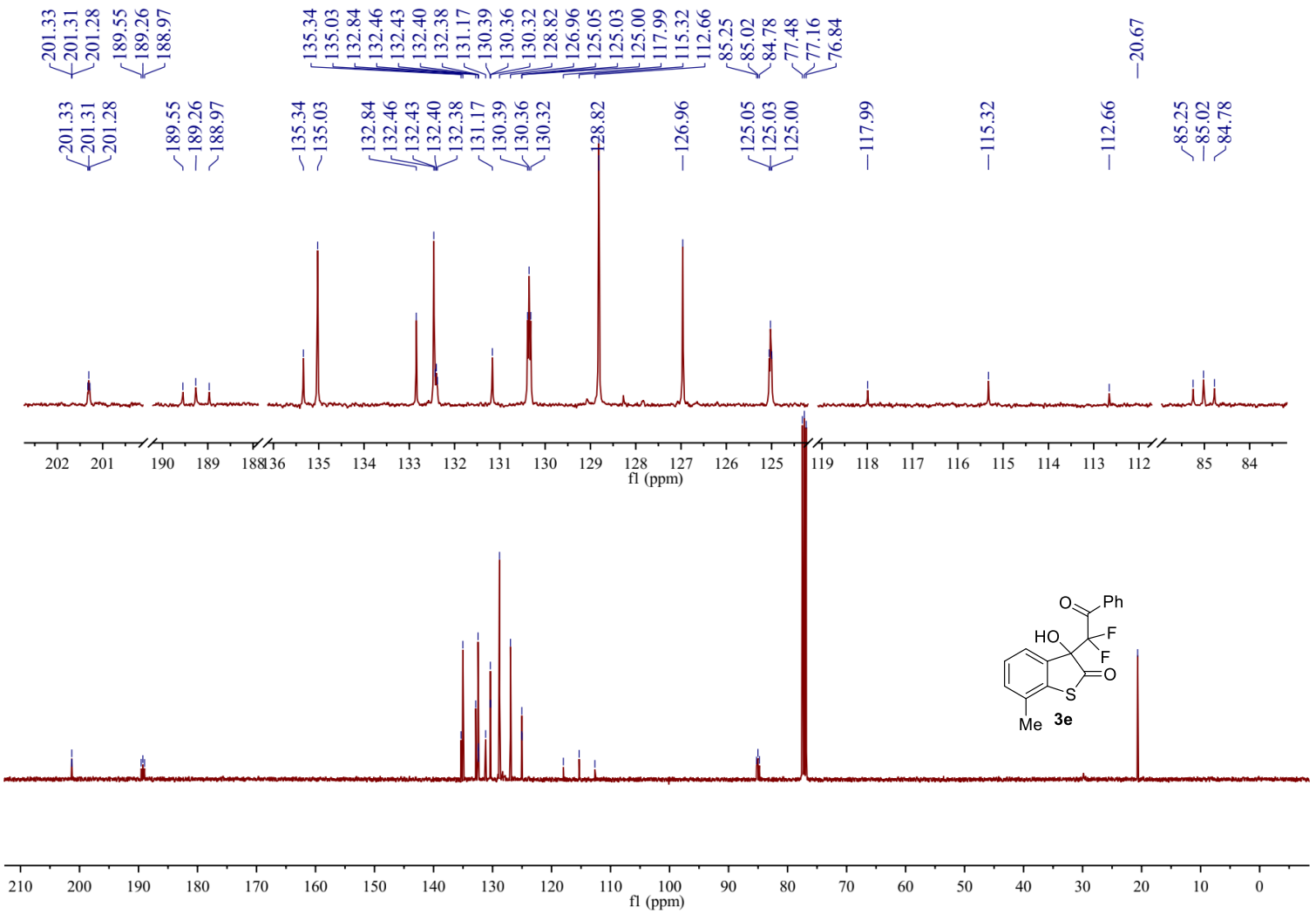
$^{13}C\{^{1}H\}$ NMR spectra of **4d** in $CDCl_3$ (100 MHz)



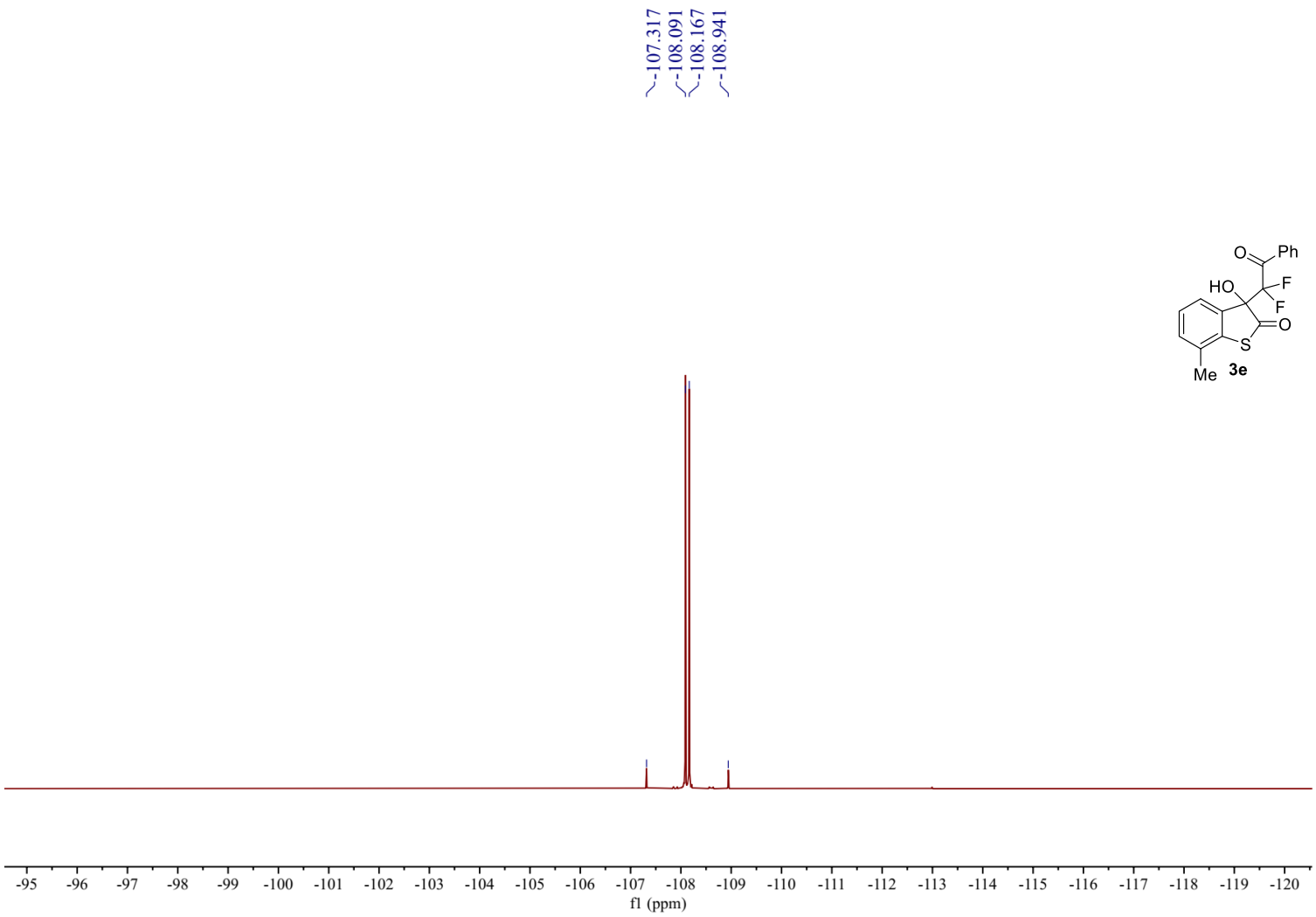
^{19}F NMR spectra of **4d** in $CDCl_3$ (376 MHz)



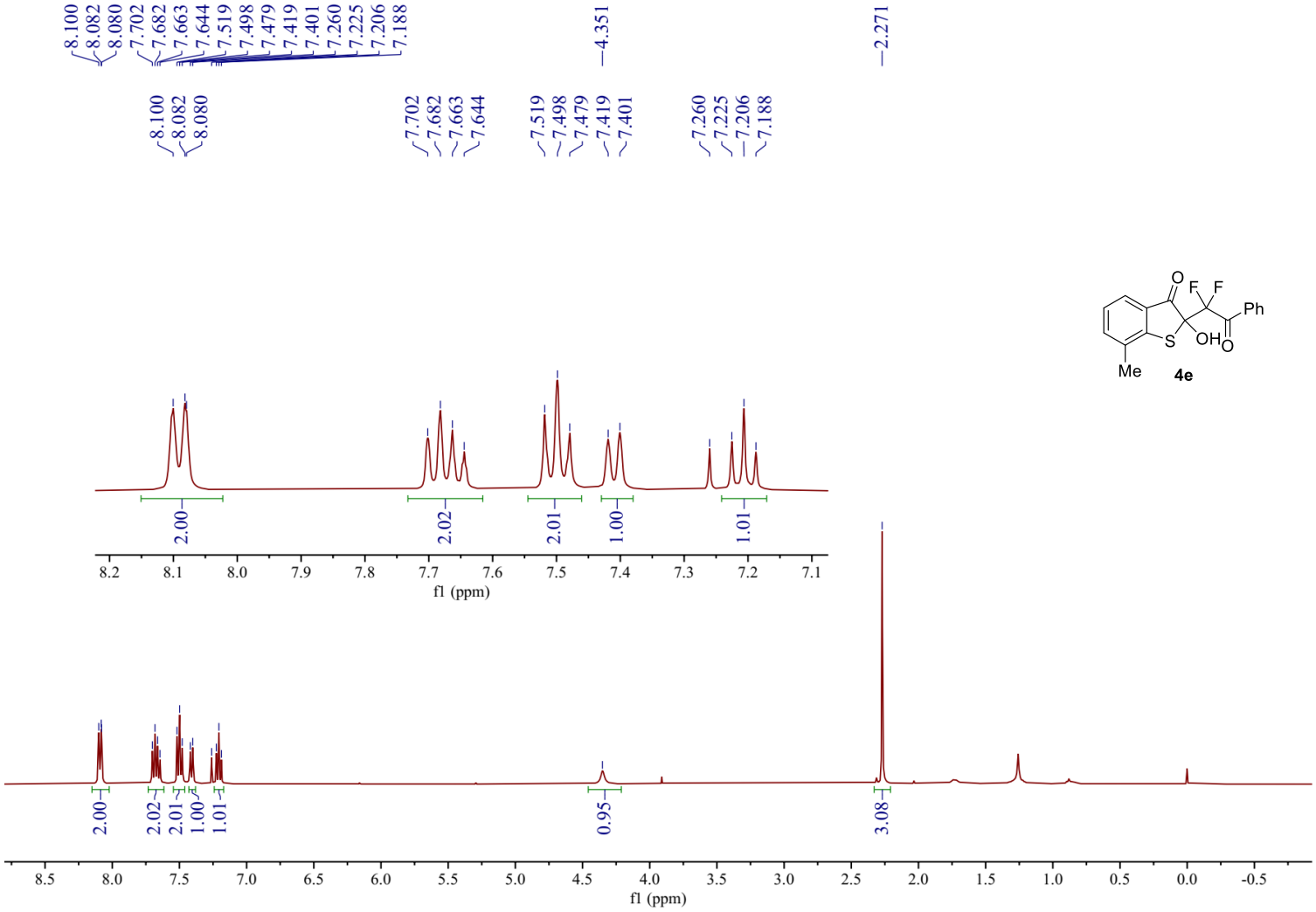
^{1}H NMR spectra of **3e** in $CDCl_3$ (400 MHz)



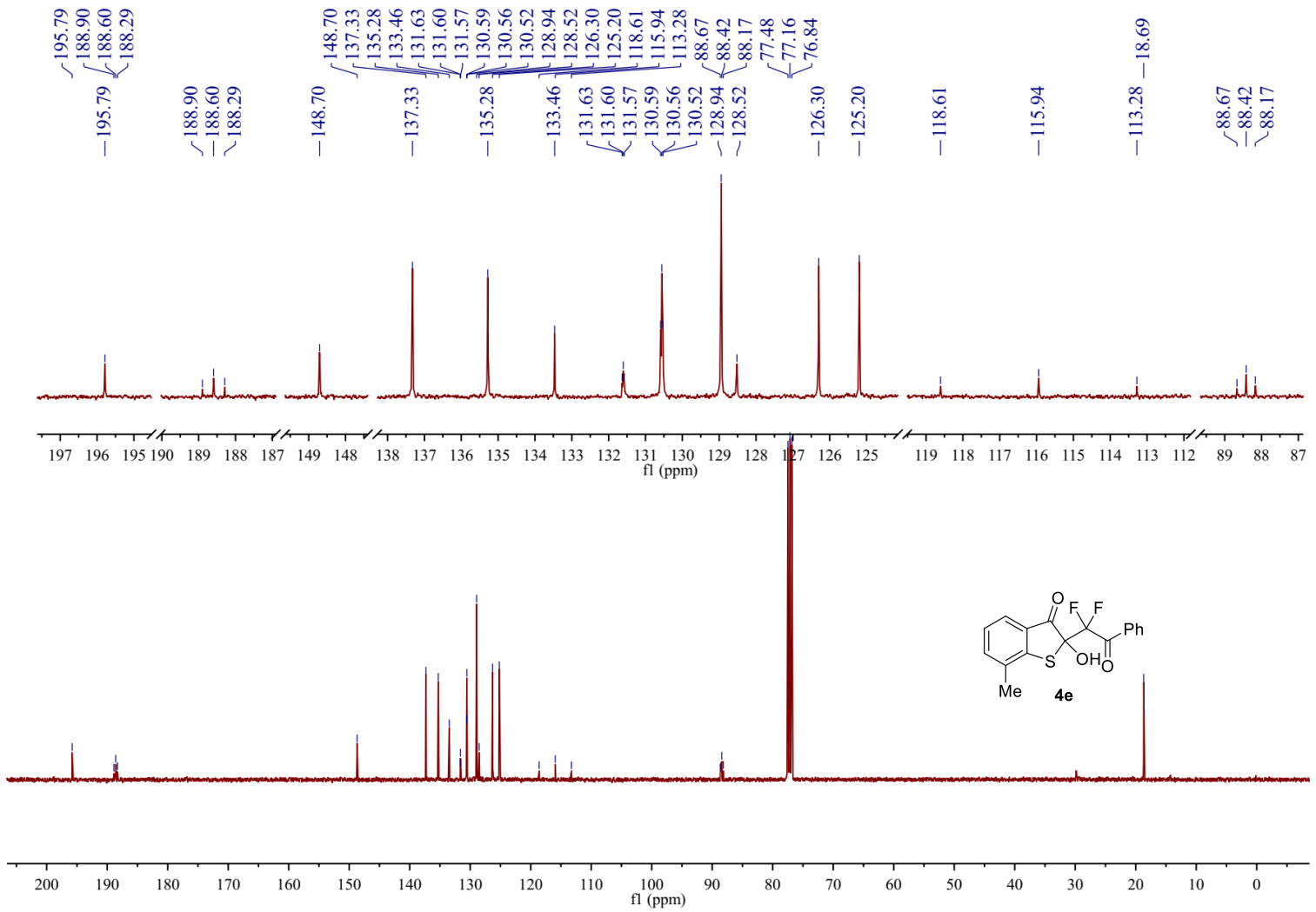
$^{13}C\{^{1}H\}$ NMR spectra of **3e** in $CDCl_3$ (100 MHz)



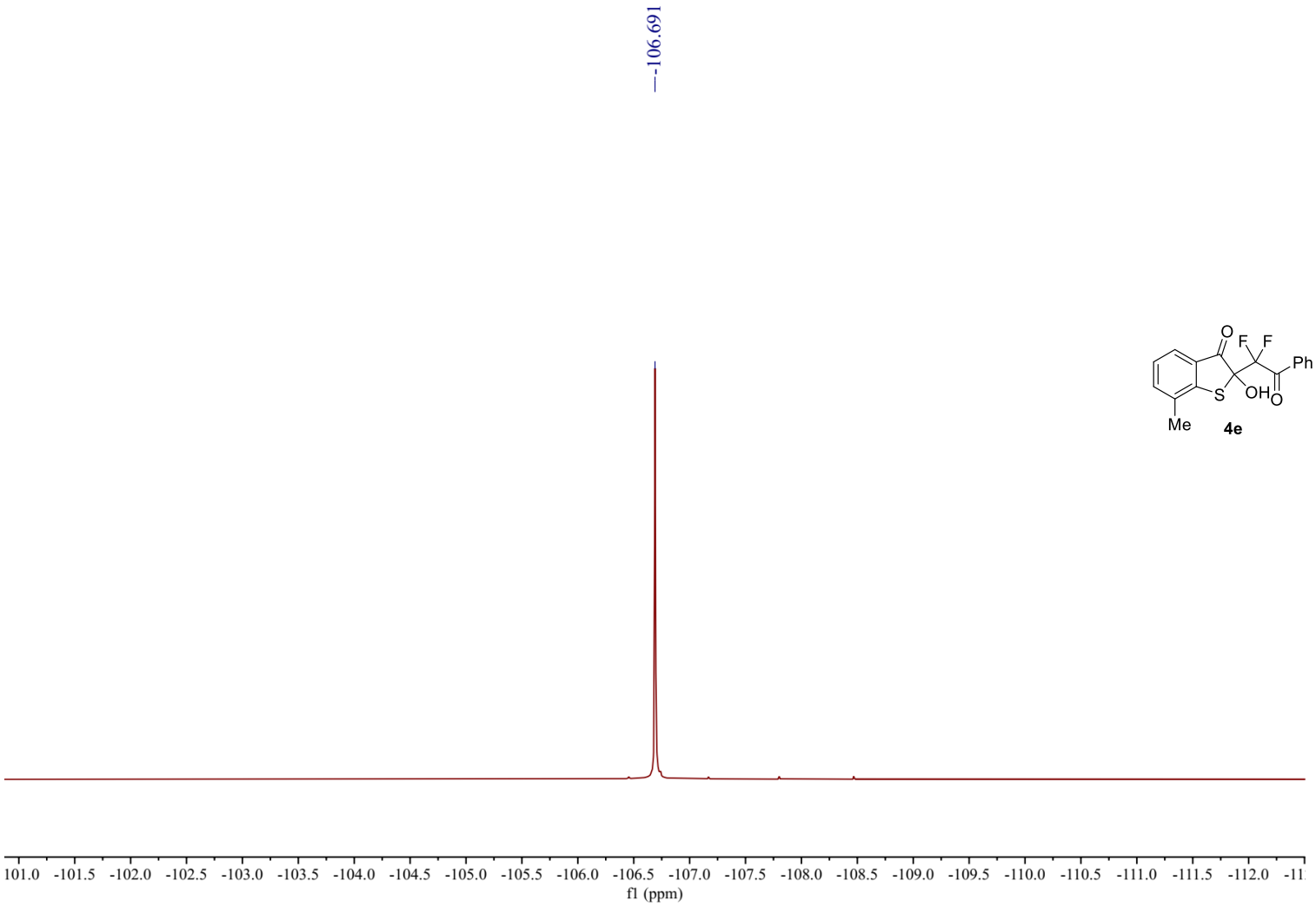
^{19}F NMR spectra of **3e** in $CDCl_3$ (376 MHz)



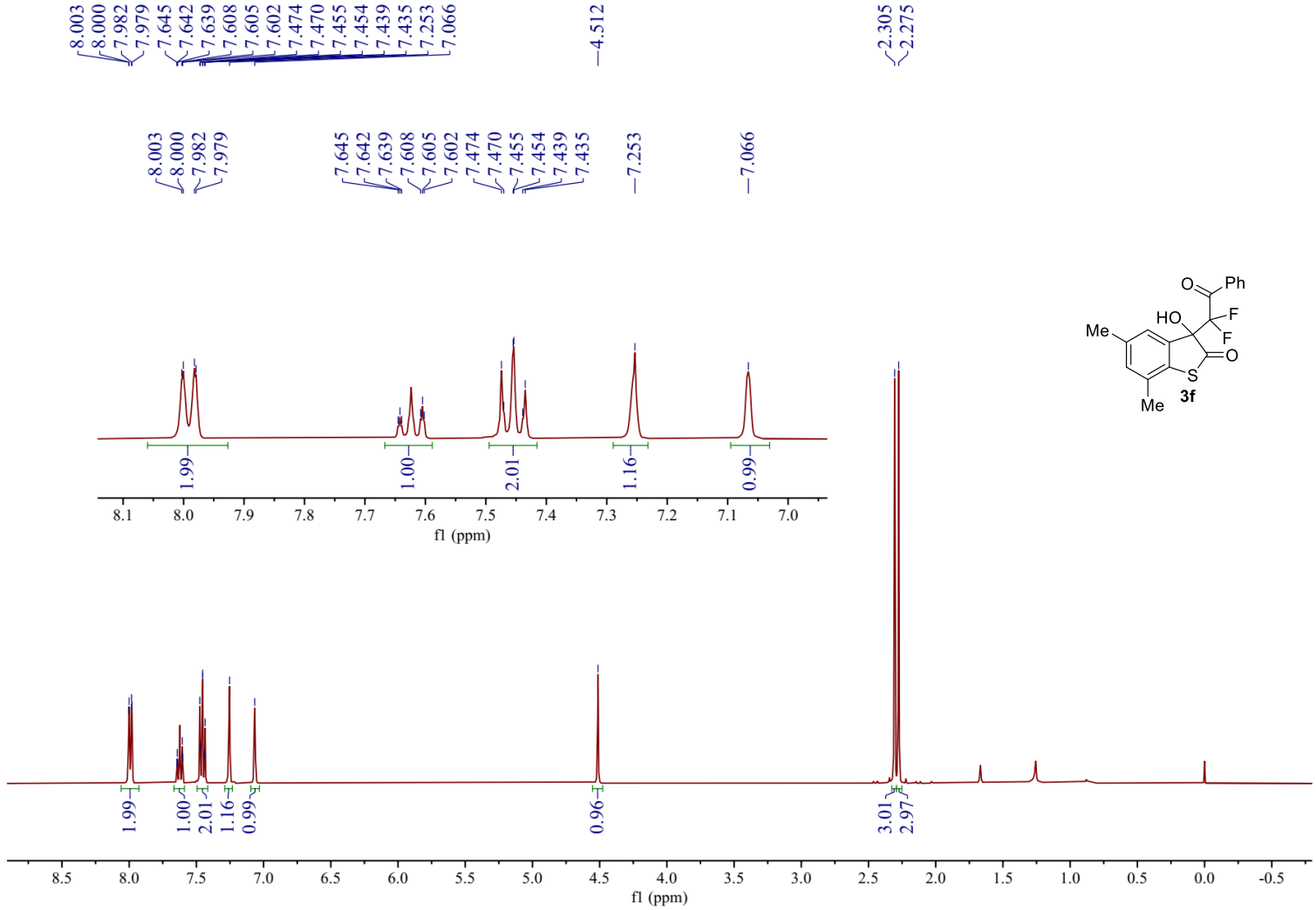
^{1}H NMR spectra of **4e** in $CDCl_3$ (400 MHz)



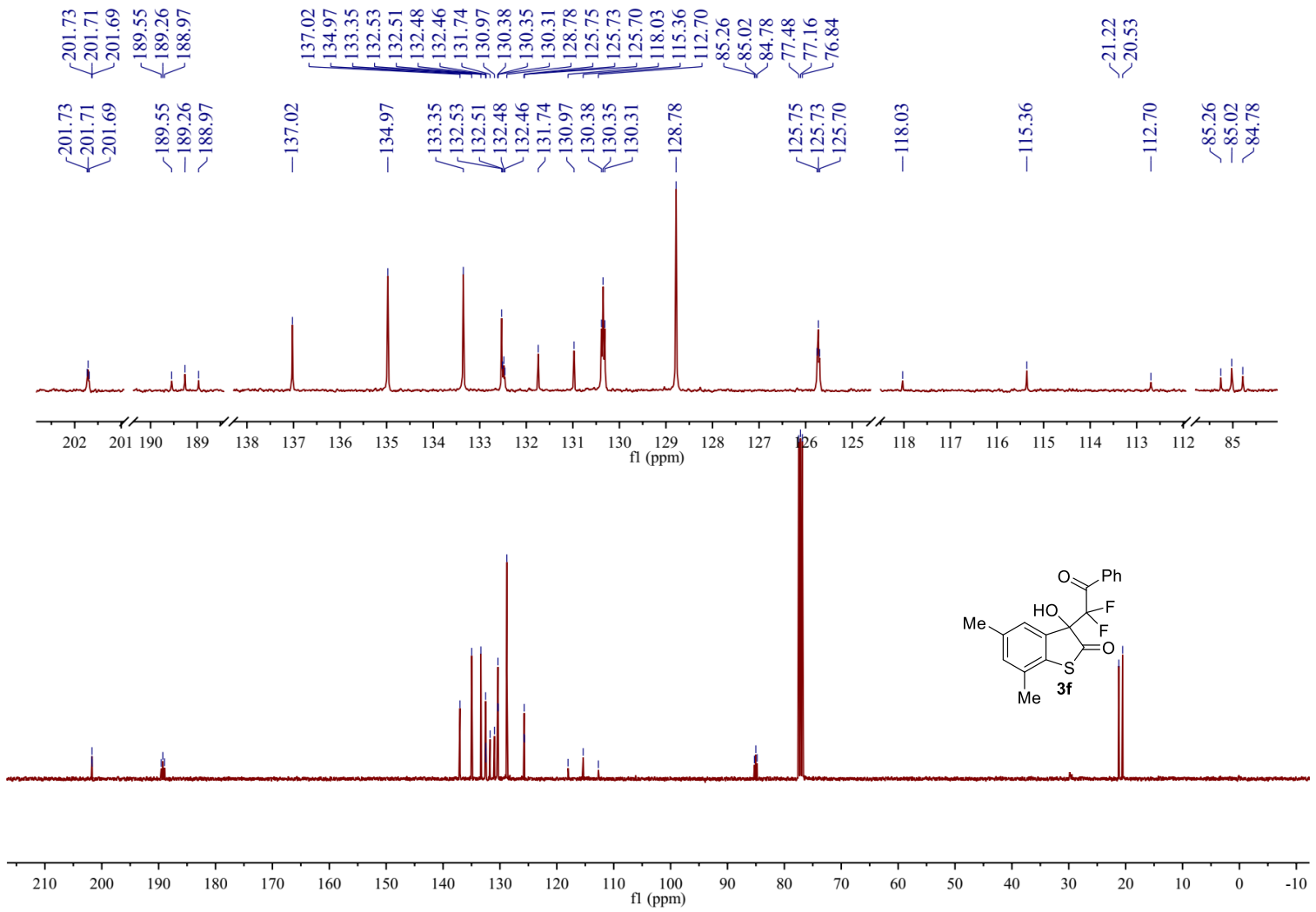
$^{13}C\{^{1}H\}$ NMR spectra of **4e** in $CDCl_3$ (100 MHz)



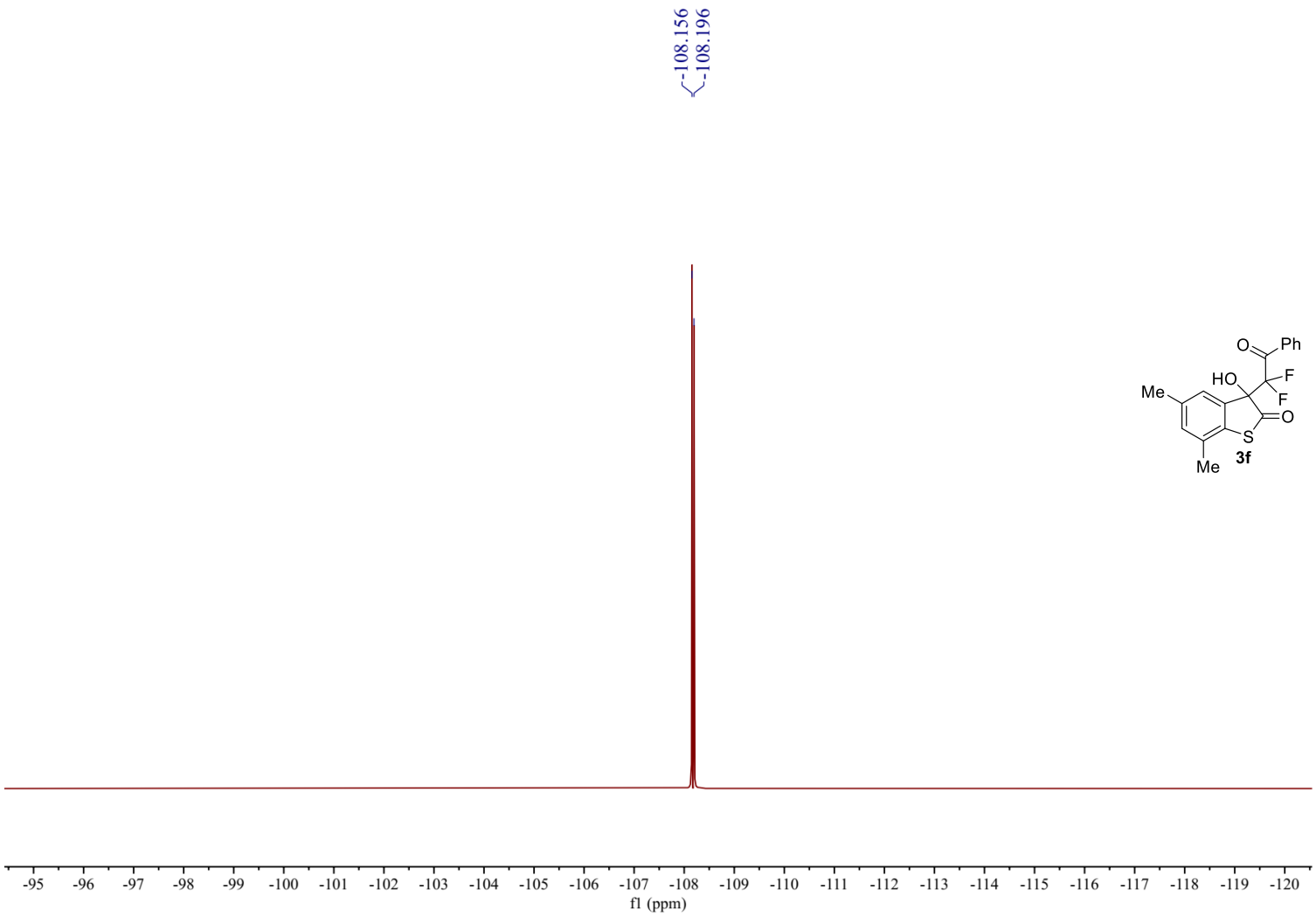
^{19}F NMR spectra of **4e** in $CDCl_3$ (376 MHz)



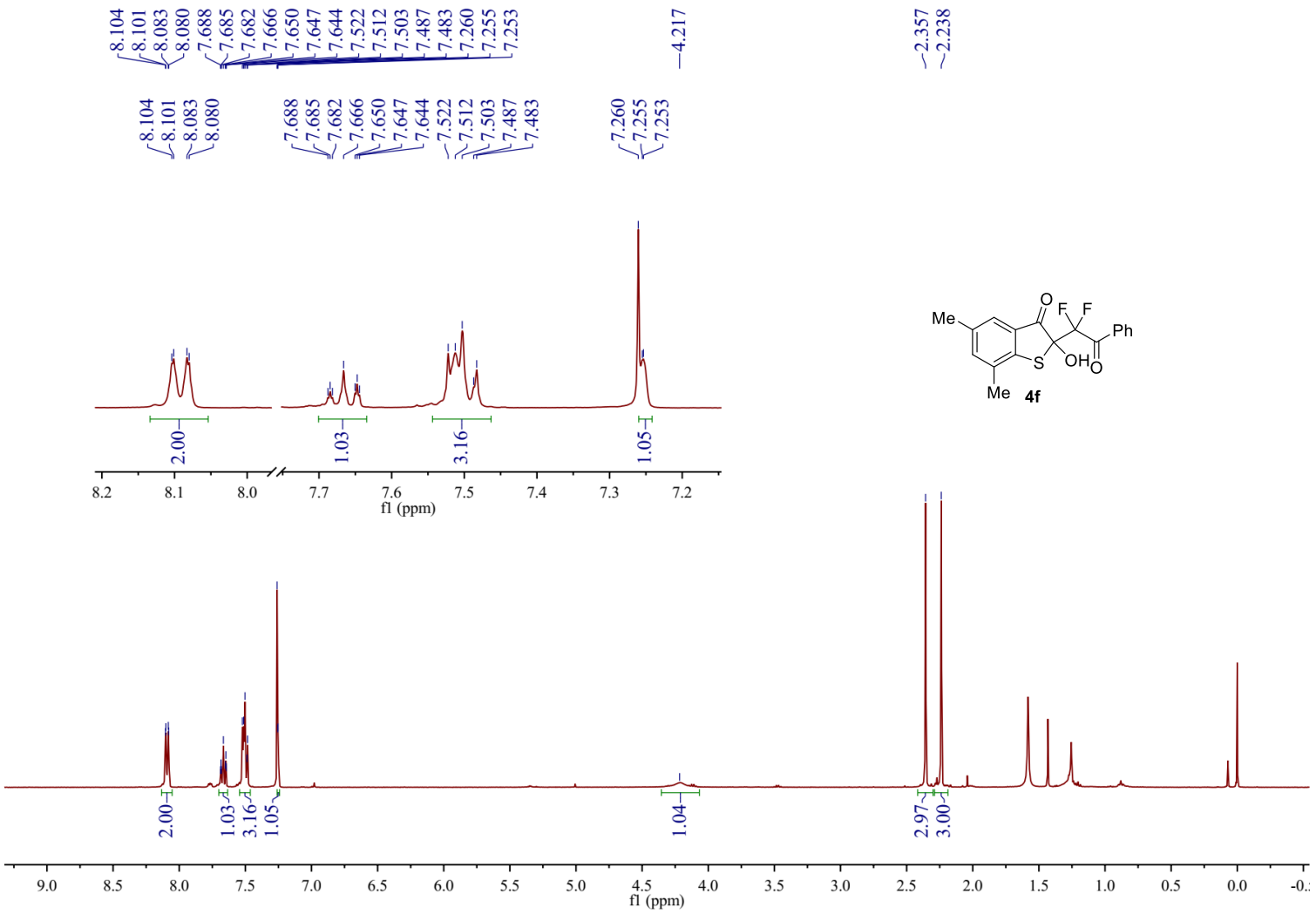
^{1}H NMR spectra of **3f** in $CDCl_3$ (400 MHz)



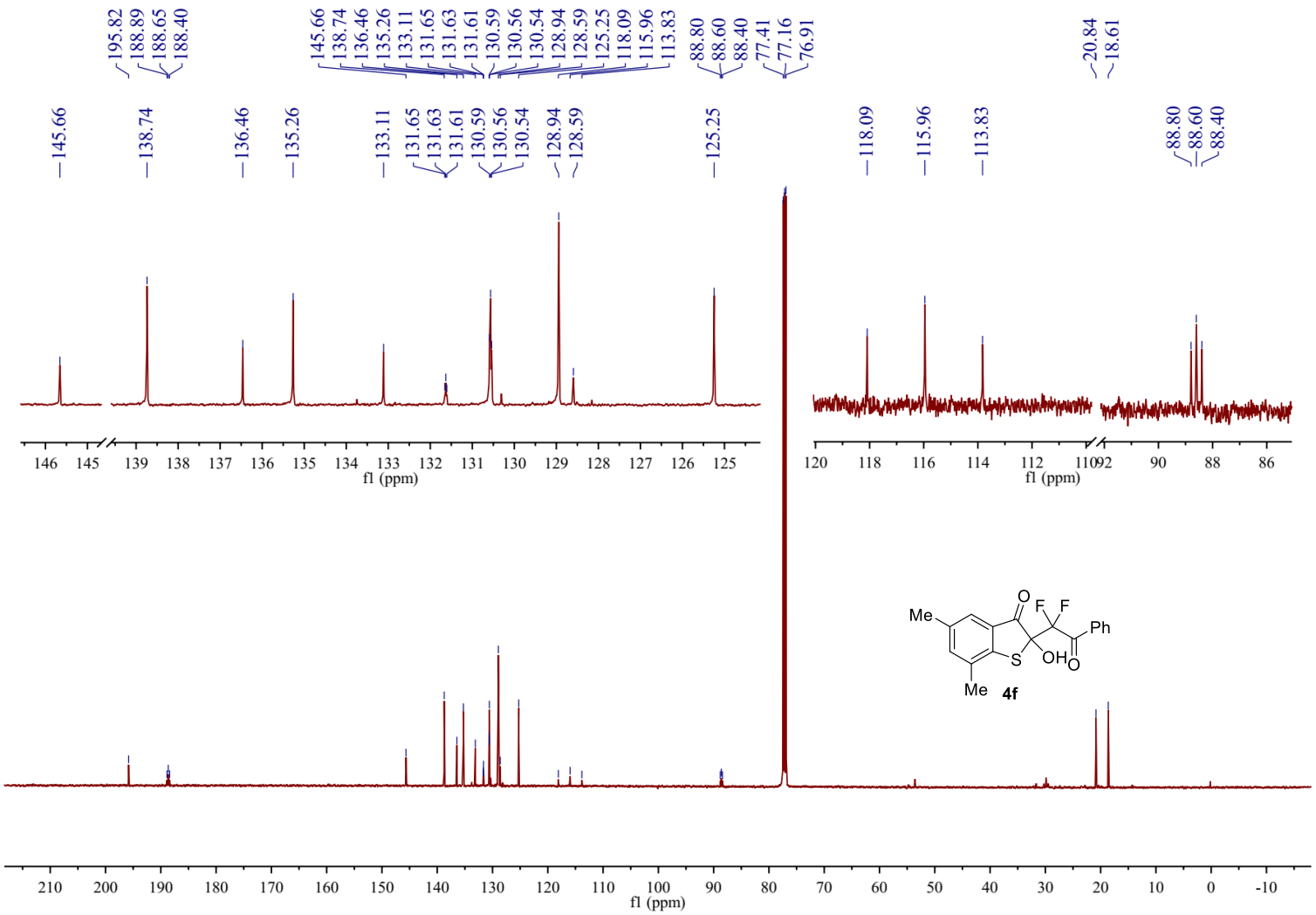
$^{13}C\{^{1}H\}$ NMR spectra of **3f** in $CDCl_3$ (100 MHz)



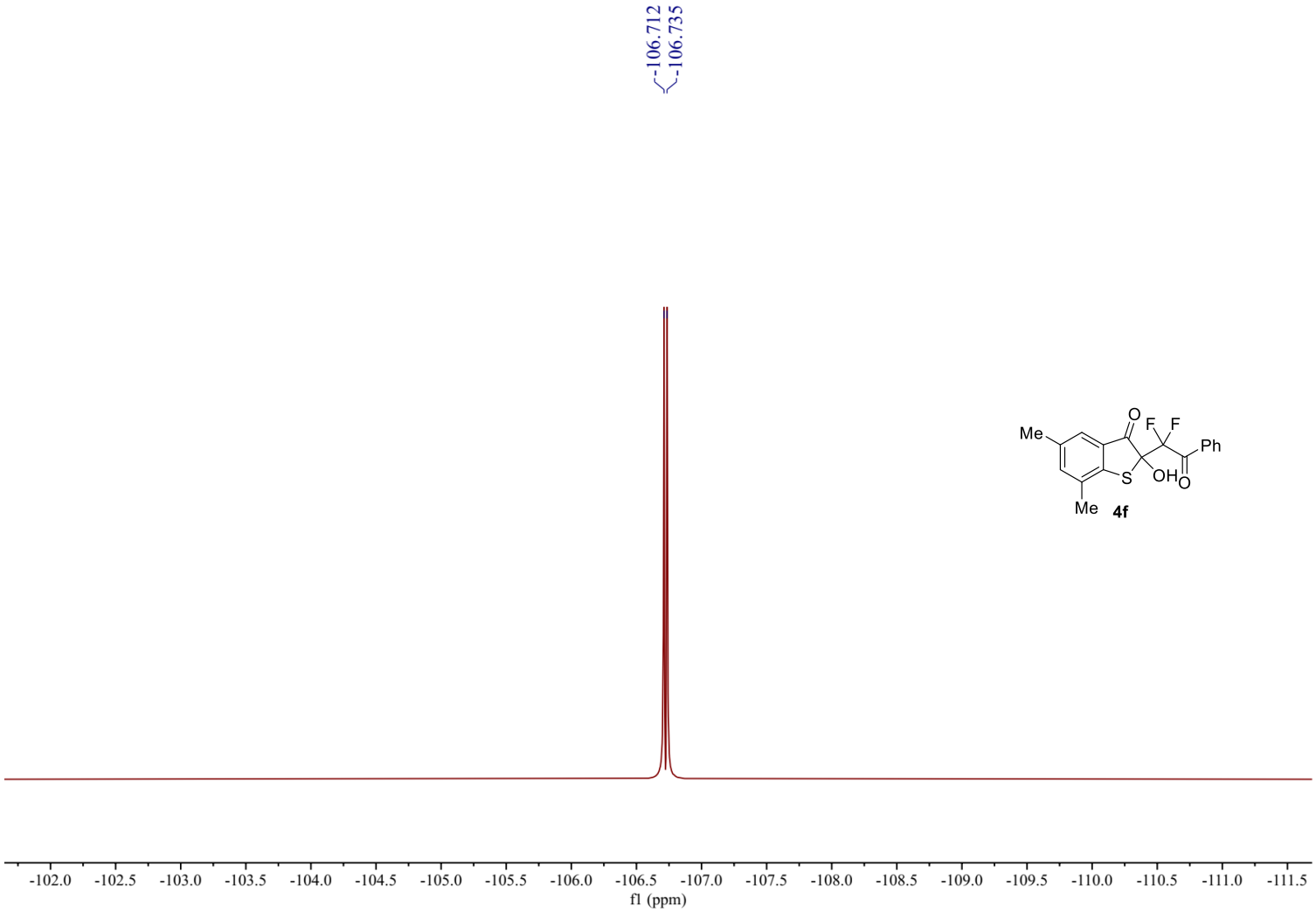
^{19}F NMR spectra of **3f** in $CDCl_3$ (376 MHz)



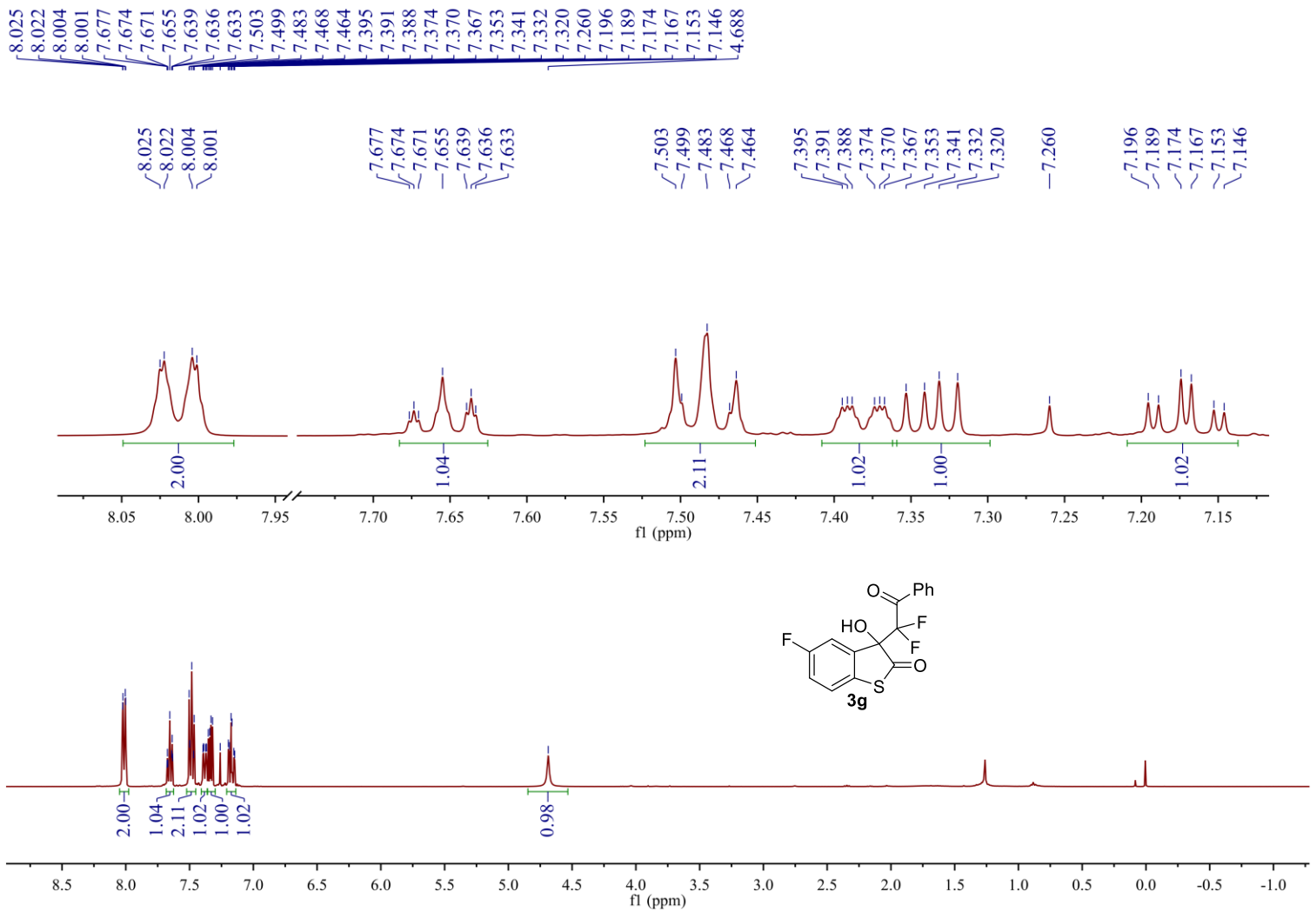
^{1}H NMR spectra of **4f** in $CDCl_3$ (400 MHz)



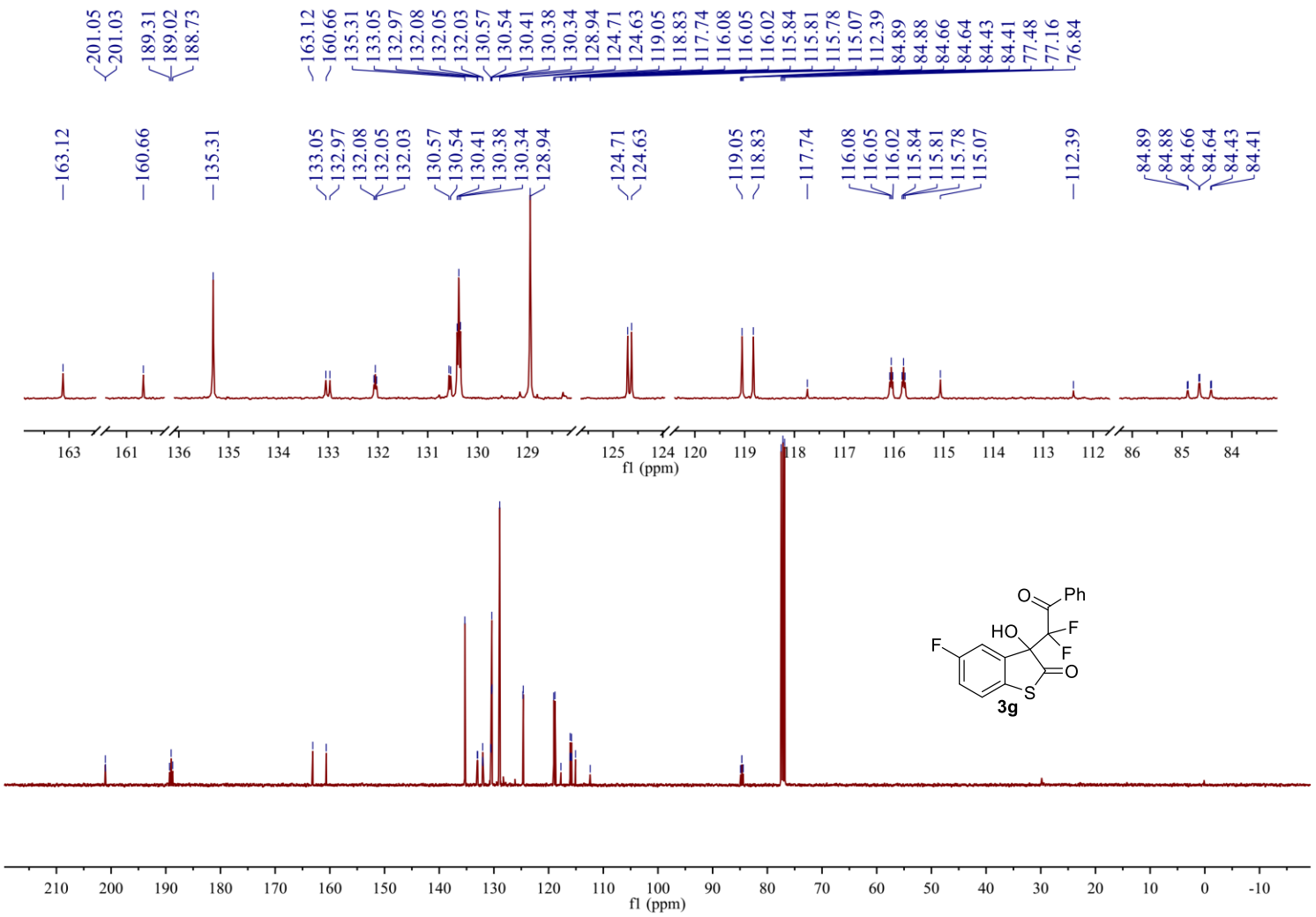
$^{13}C\{^{1}H\}$ NMR spectra of **4f** in $CDCl_3$ (125 MHz)



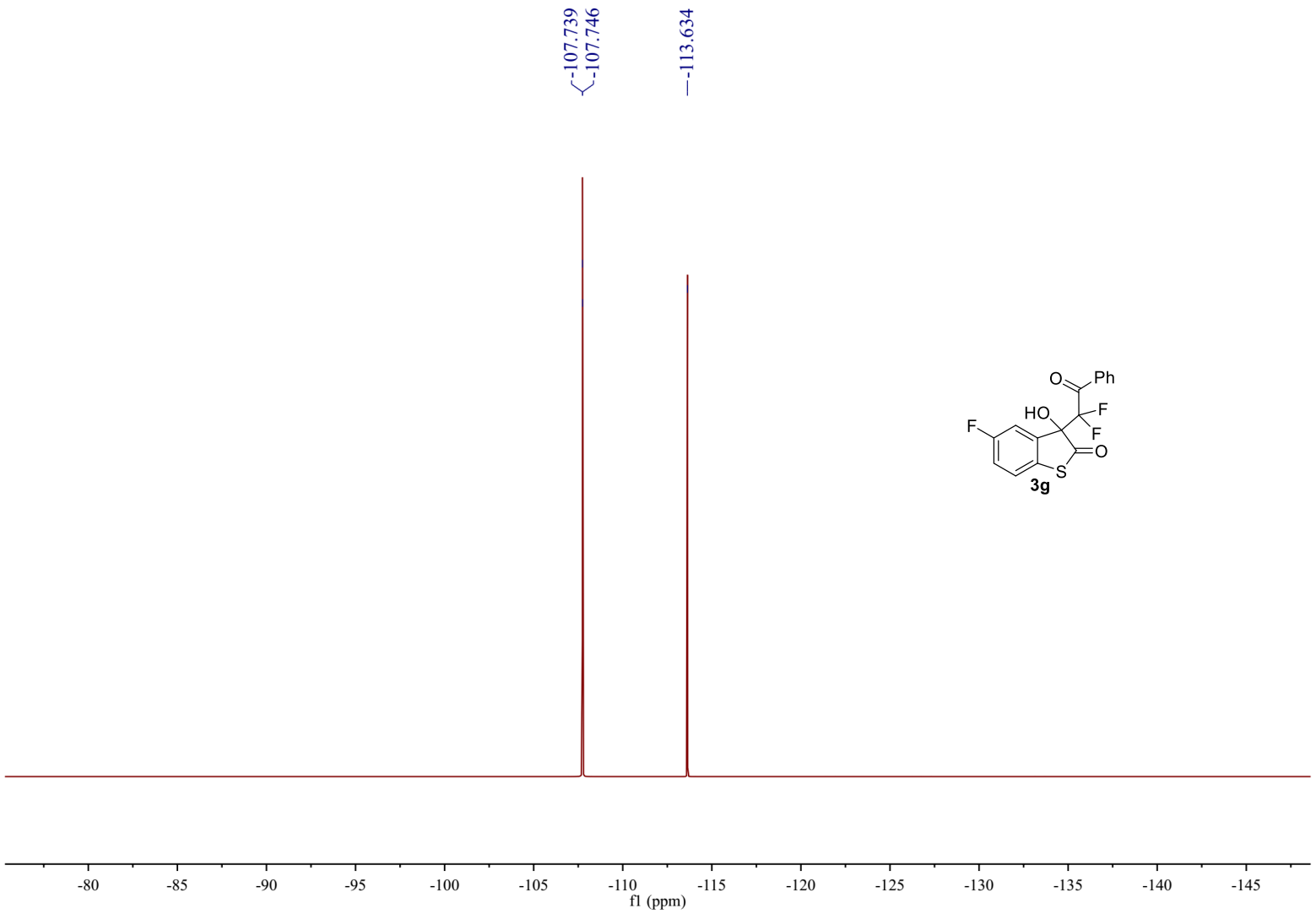
^{19}F NMR spectra of **4f** in $CDCl_3$ (376 MHz)



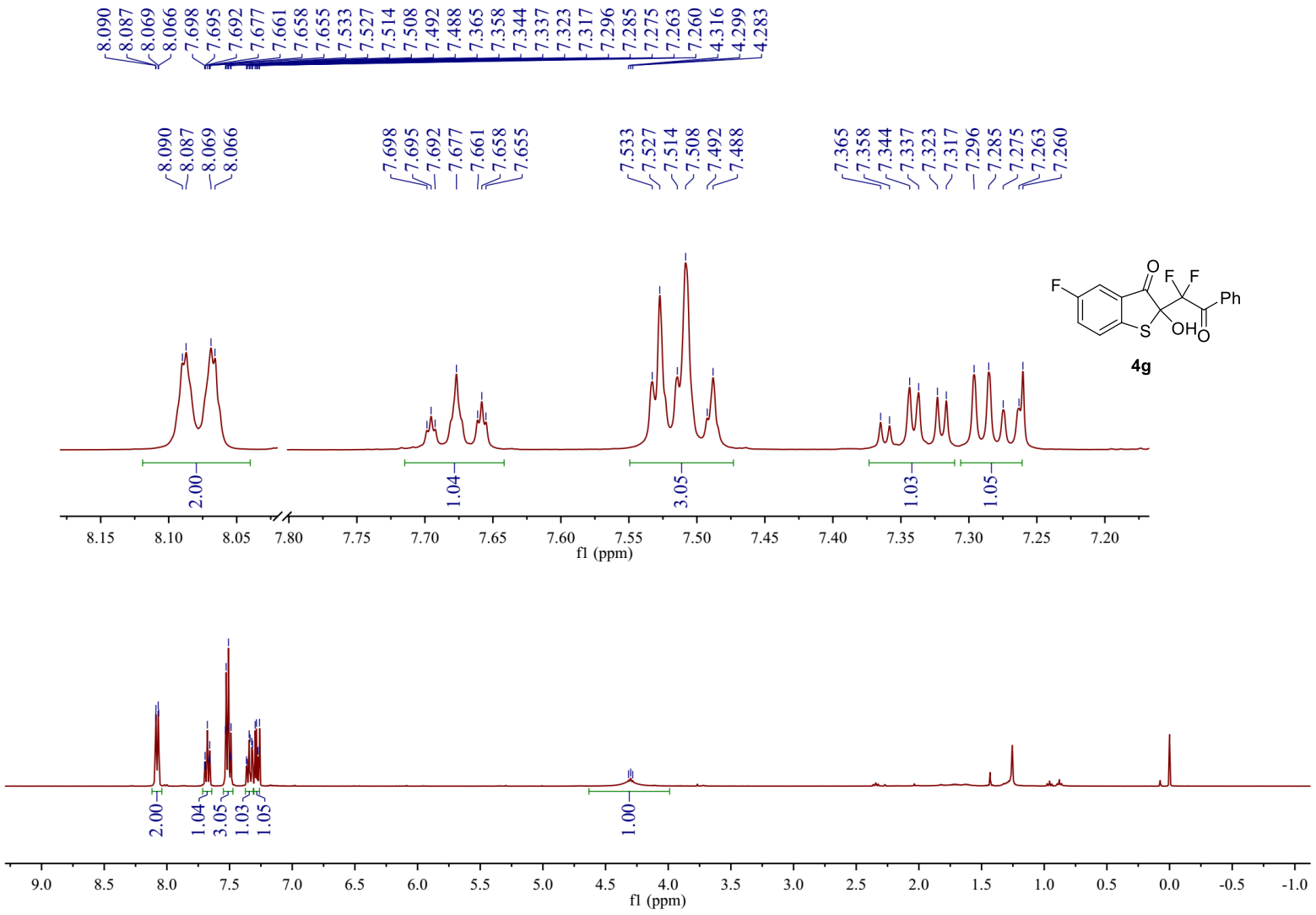
^{1}H NMR spectra of **3g** in $CDCl_3$ (400 MHz)



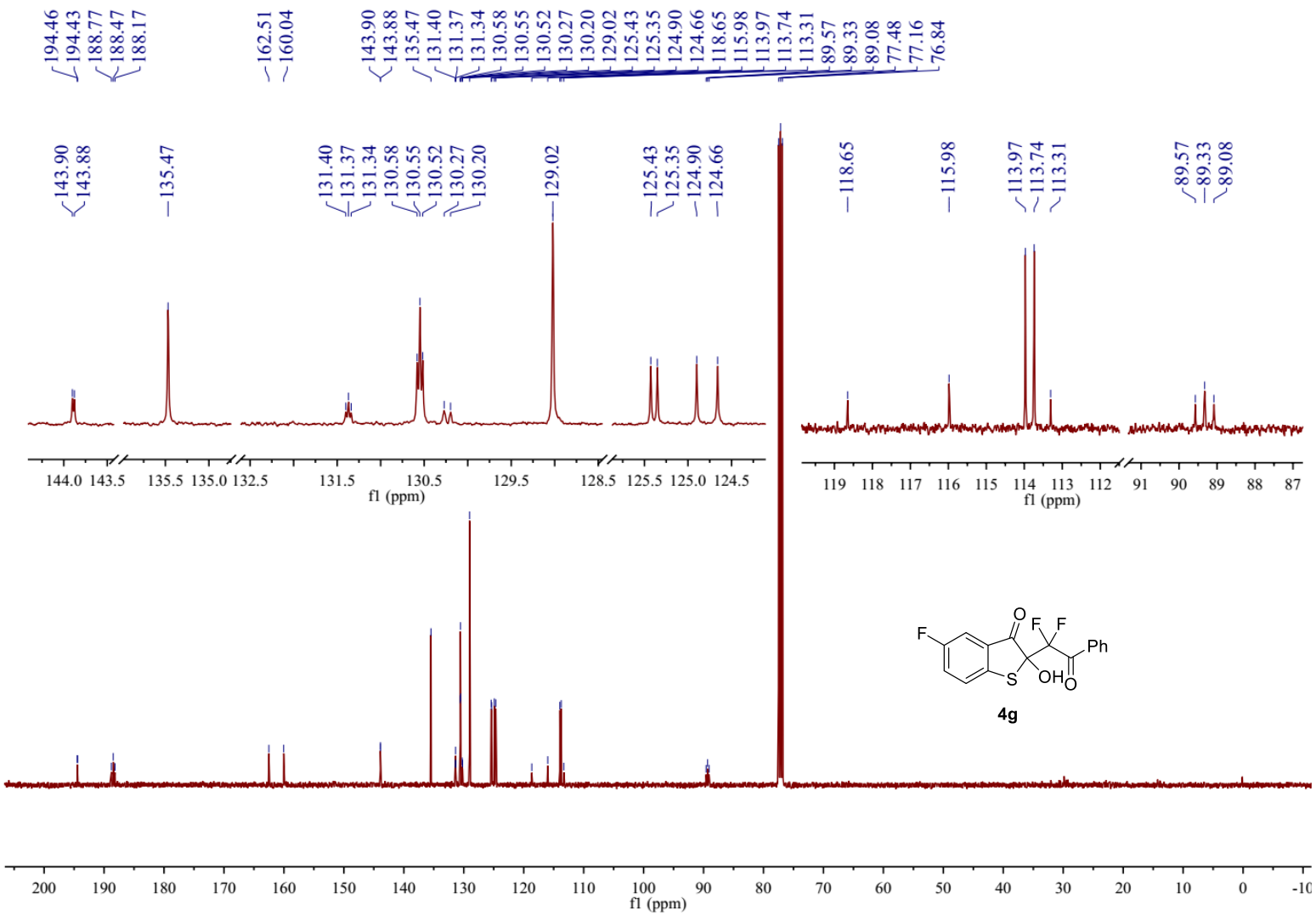
$^{13}C\{^{1}H\}$ NMR spectra of **3g** in $CDCl_3$ (100 MHz)



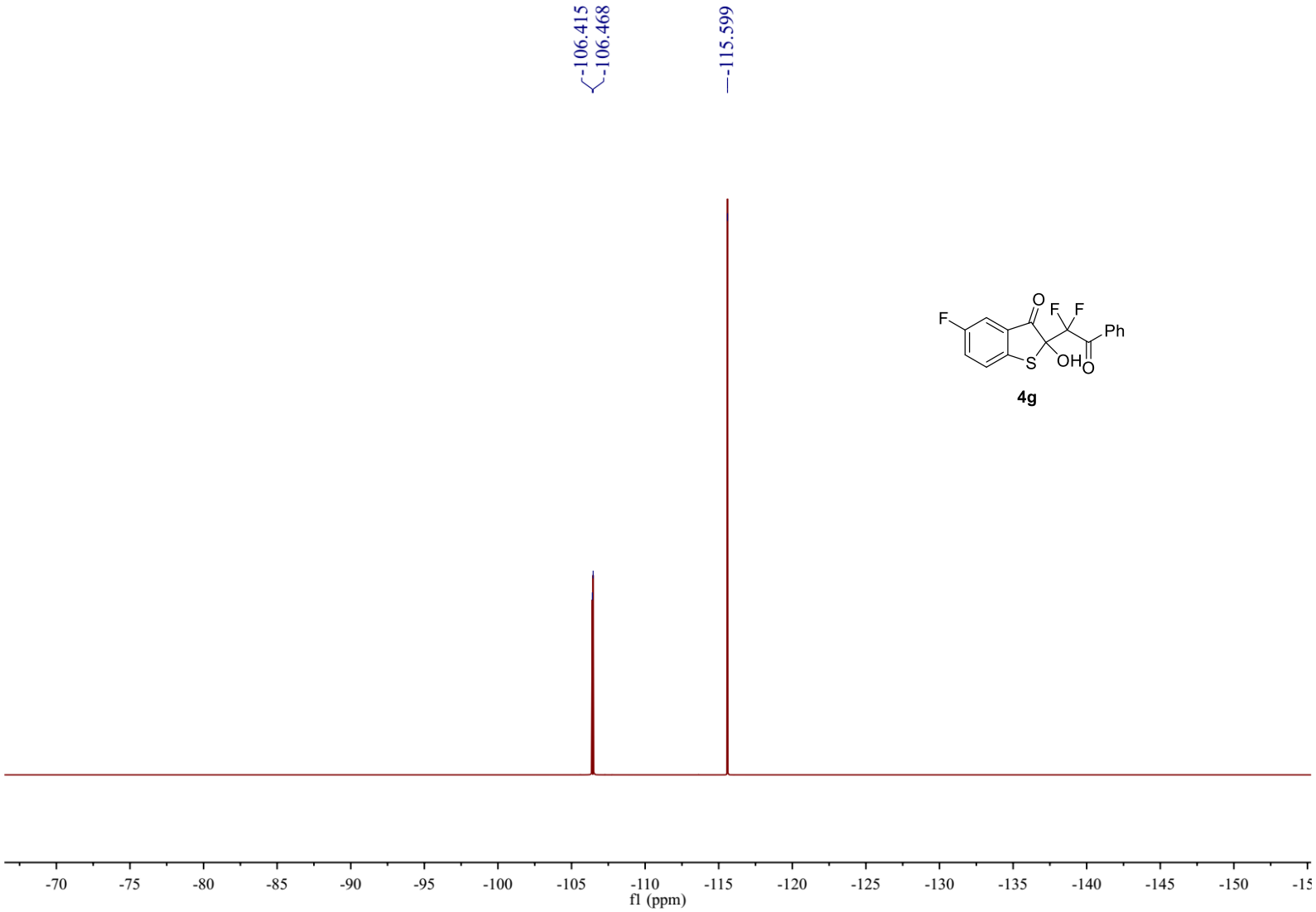
^{19}F NMR spectra of **3g** in $CDCl_3$ (376 MHz)



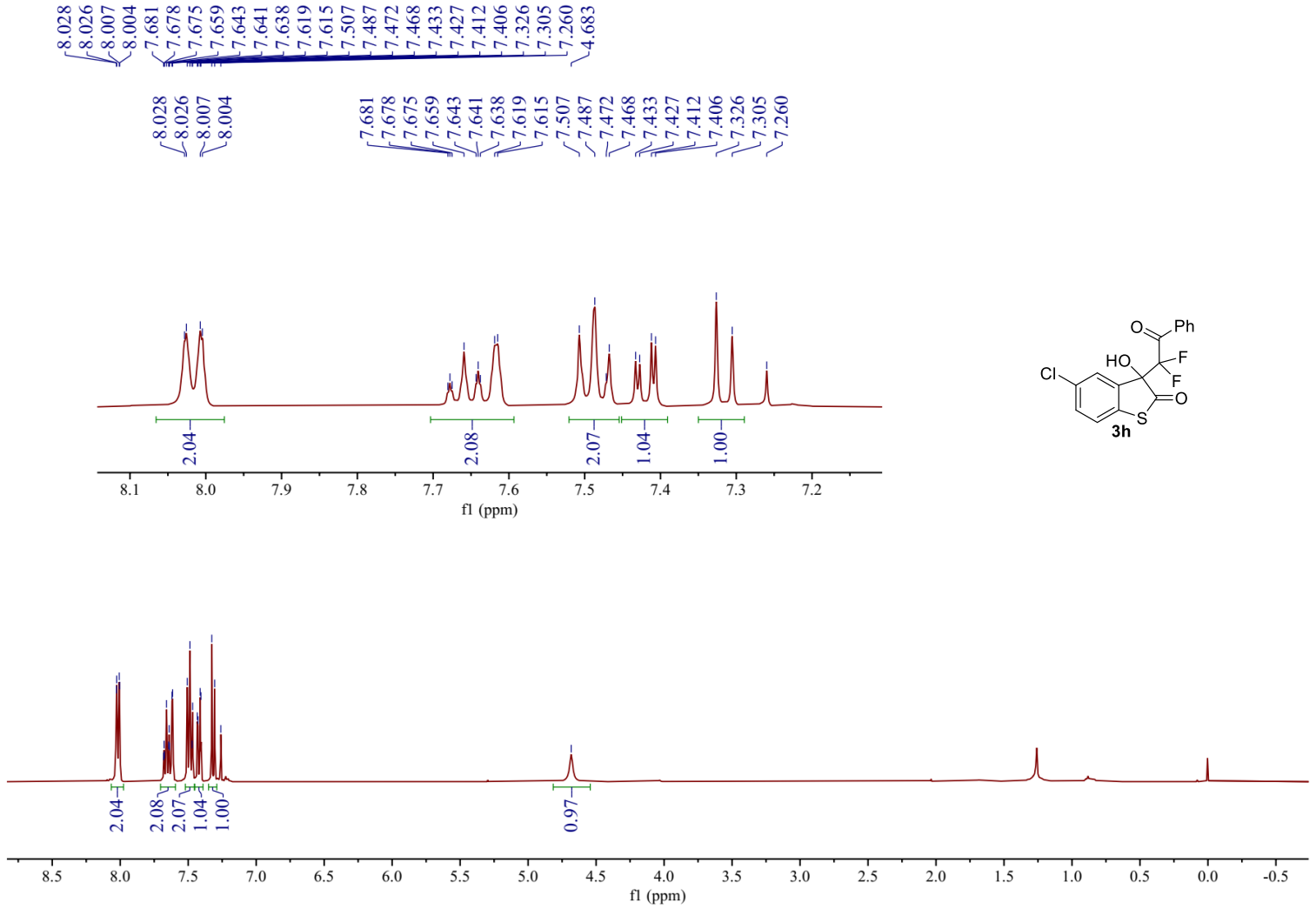
^{1}H NMR spectra of **4g** in $CDCl_3$ (400 MHz)



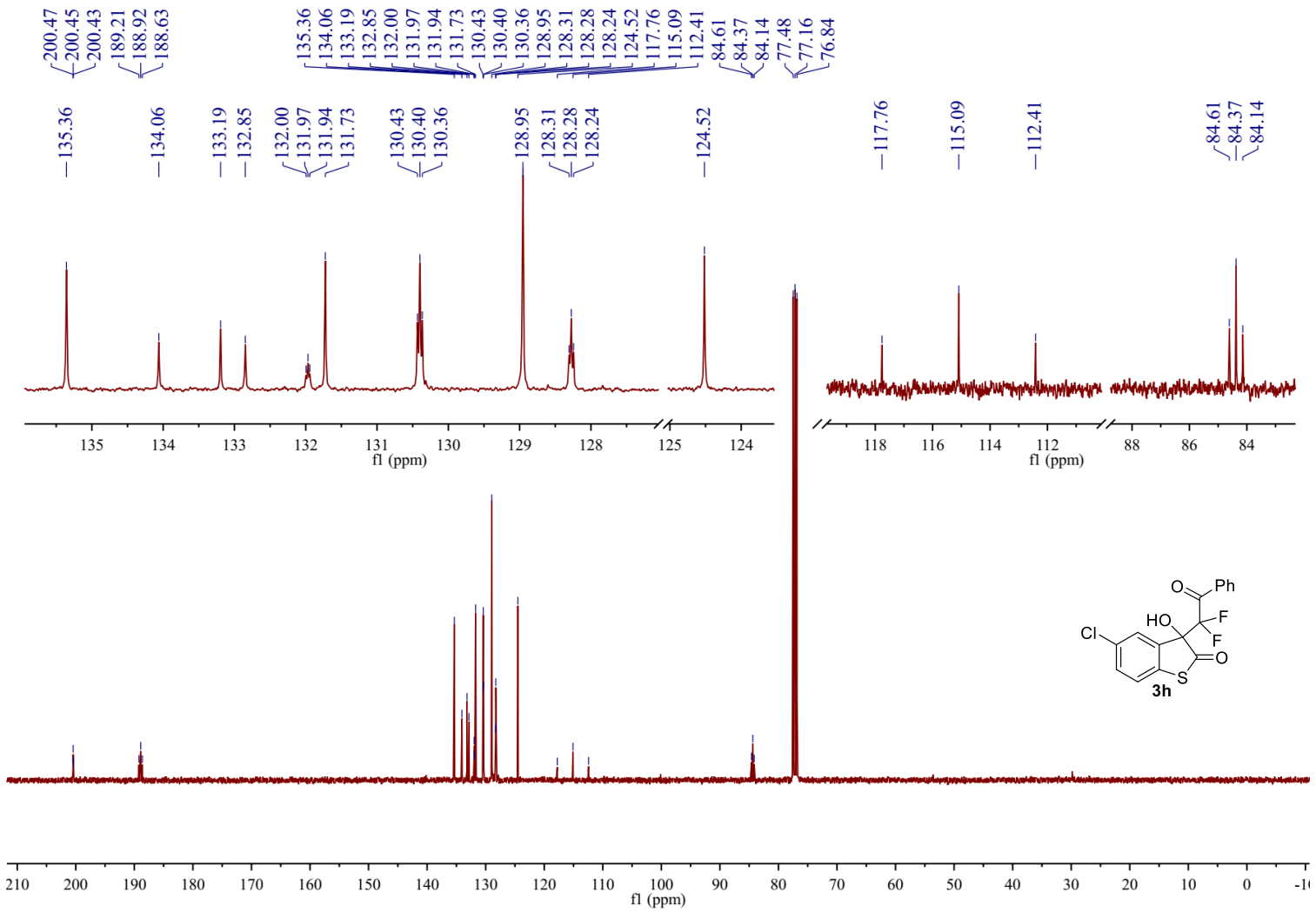
$^{13}C\{^{1}H\}$ NMR spectra of **4g** in $CDCl_3$ (100 MHz)



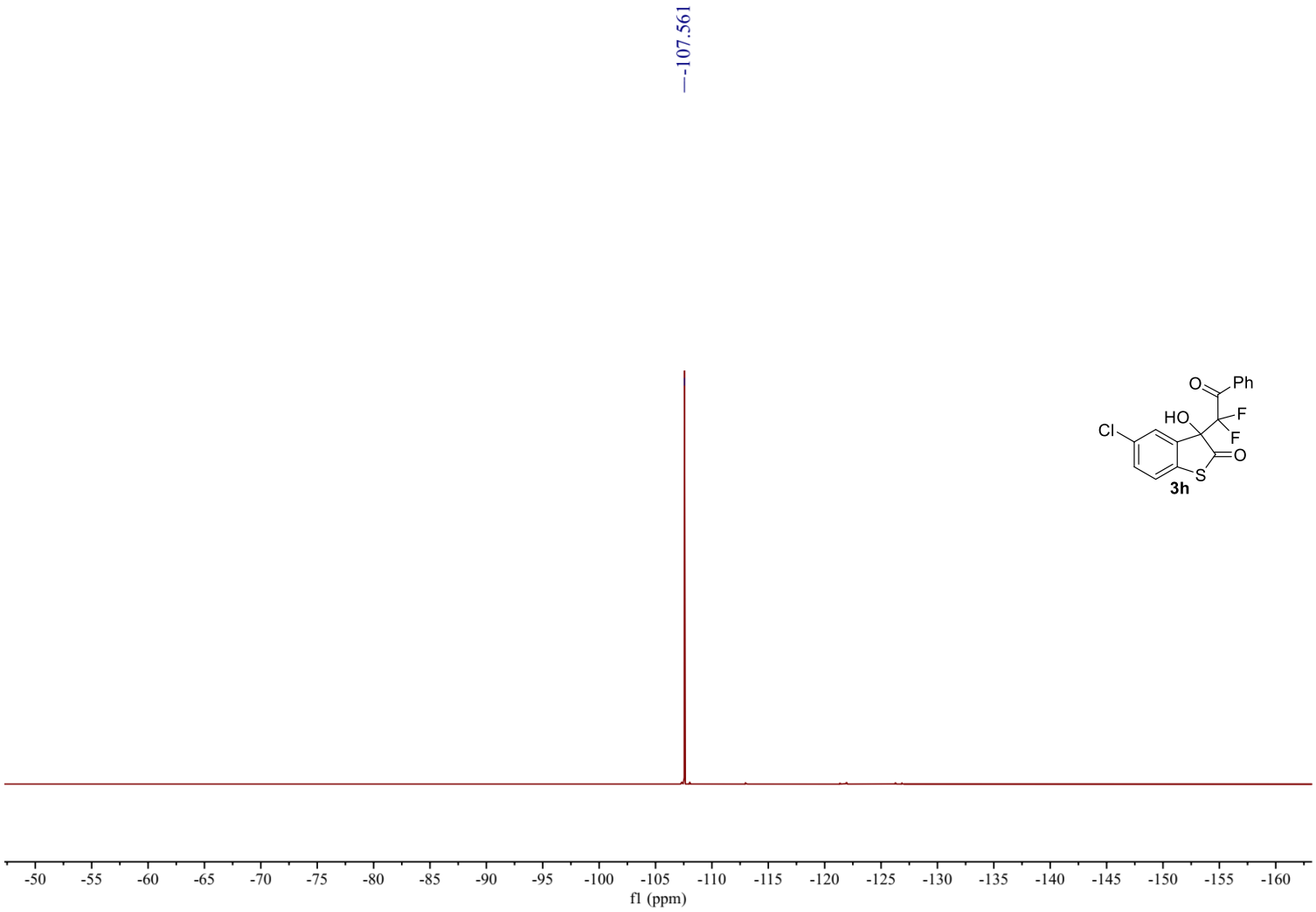
^{19}F NMR spectra of **4g** in $CDCl_3$ (376 MHz)



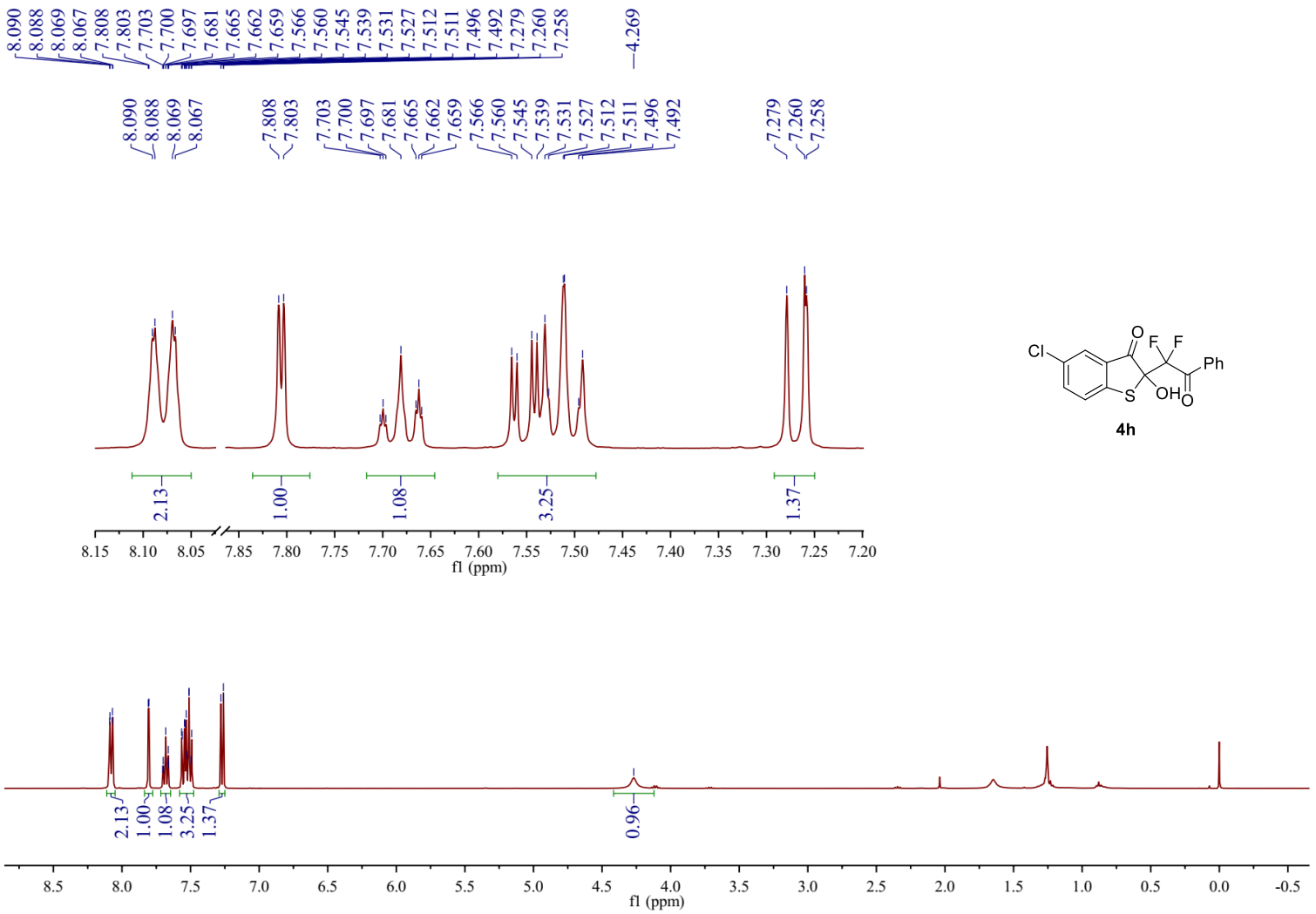
^{1}H NMR spectra of **3h** in $CDCl_3$ (400 MHz)



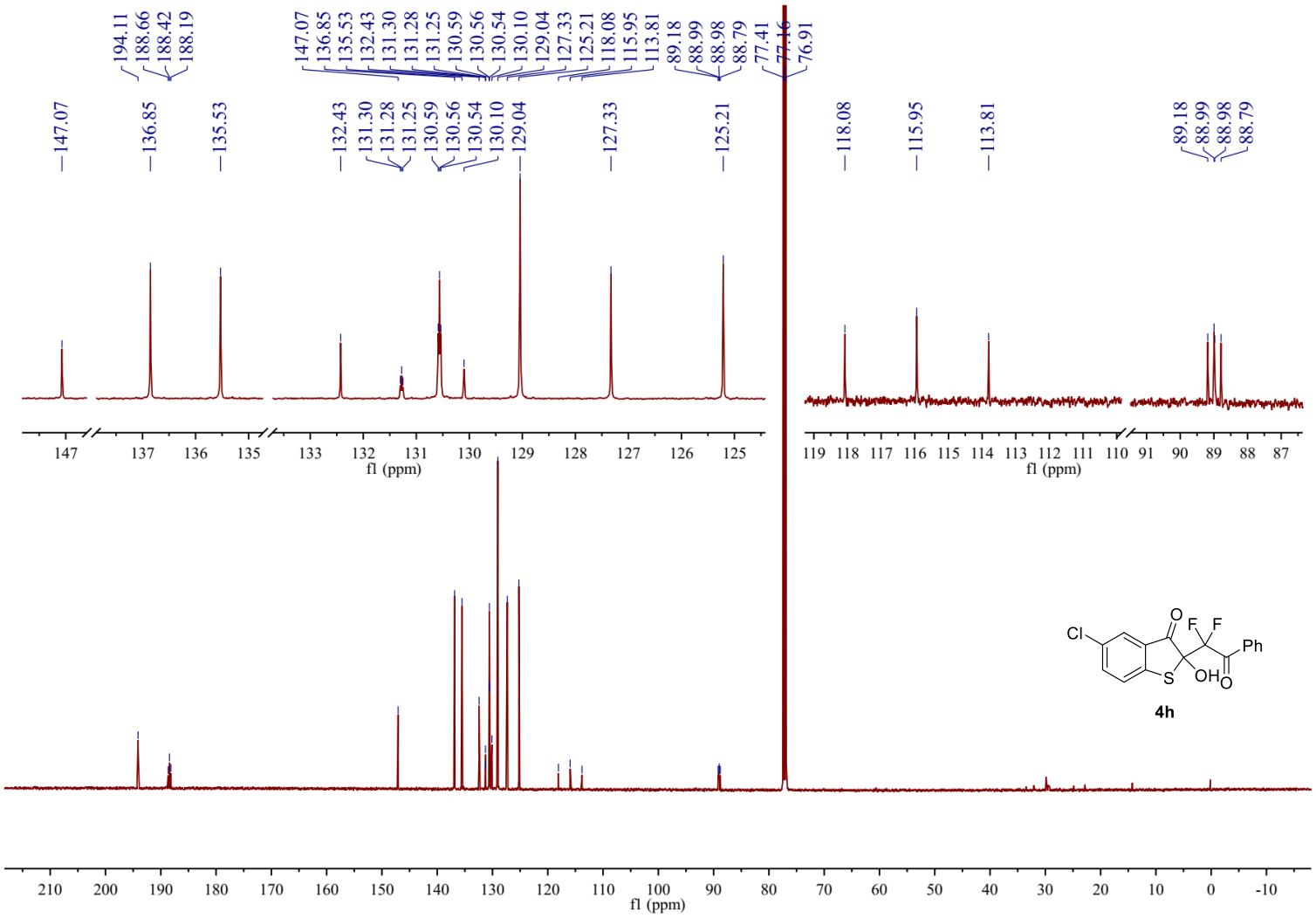
$^{13}C\{^{1}H\}$ NMR spectra of **3h** in $CDCl_3$ (100 MHz)



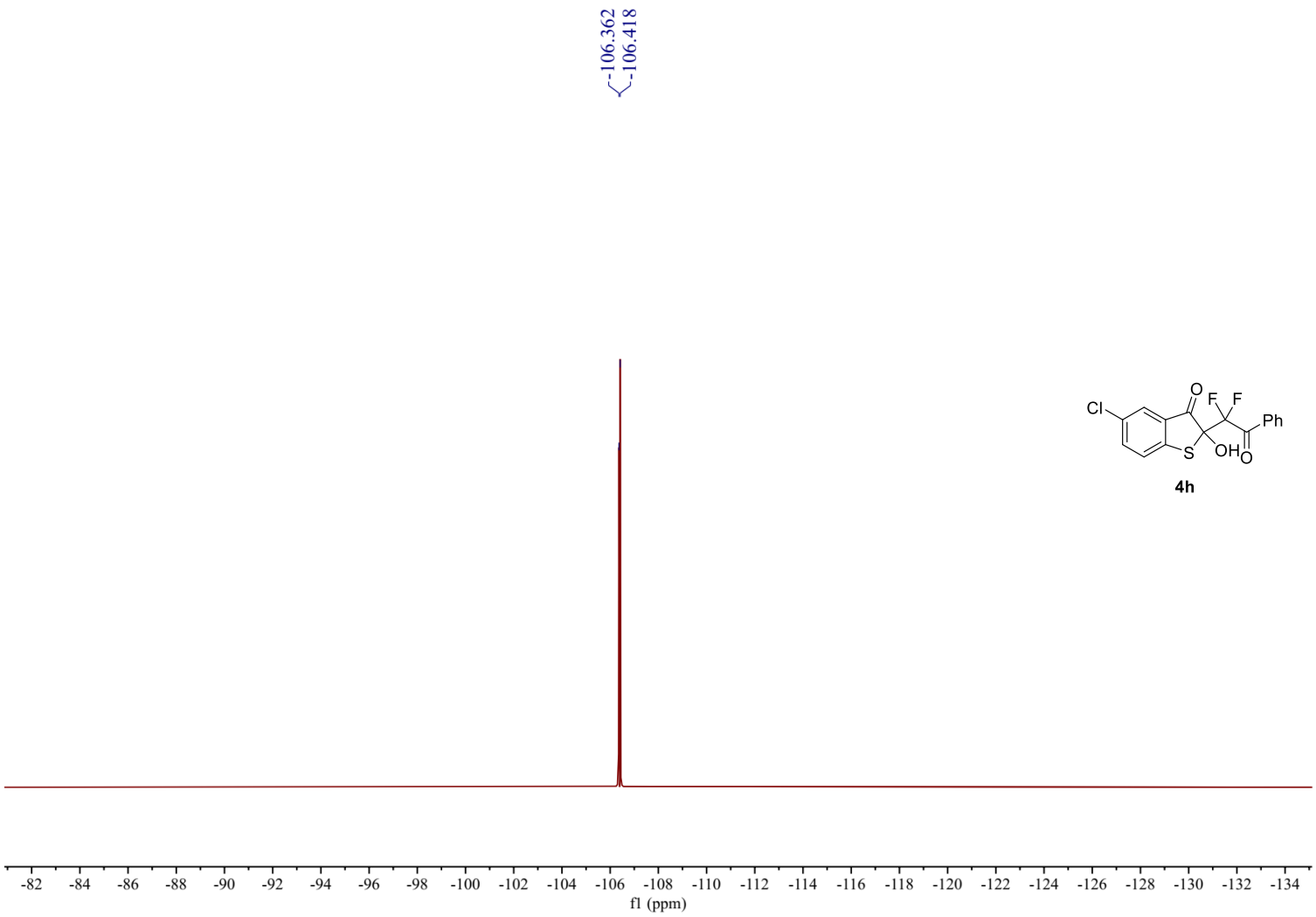
^{19}F NMR spectra of **3h** in $CDCl_3$ (376 MHz)



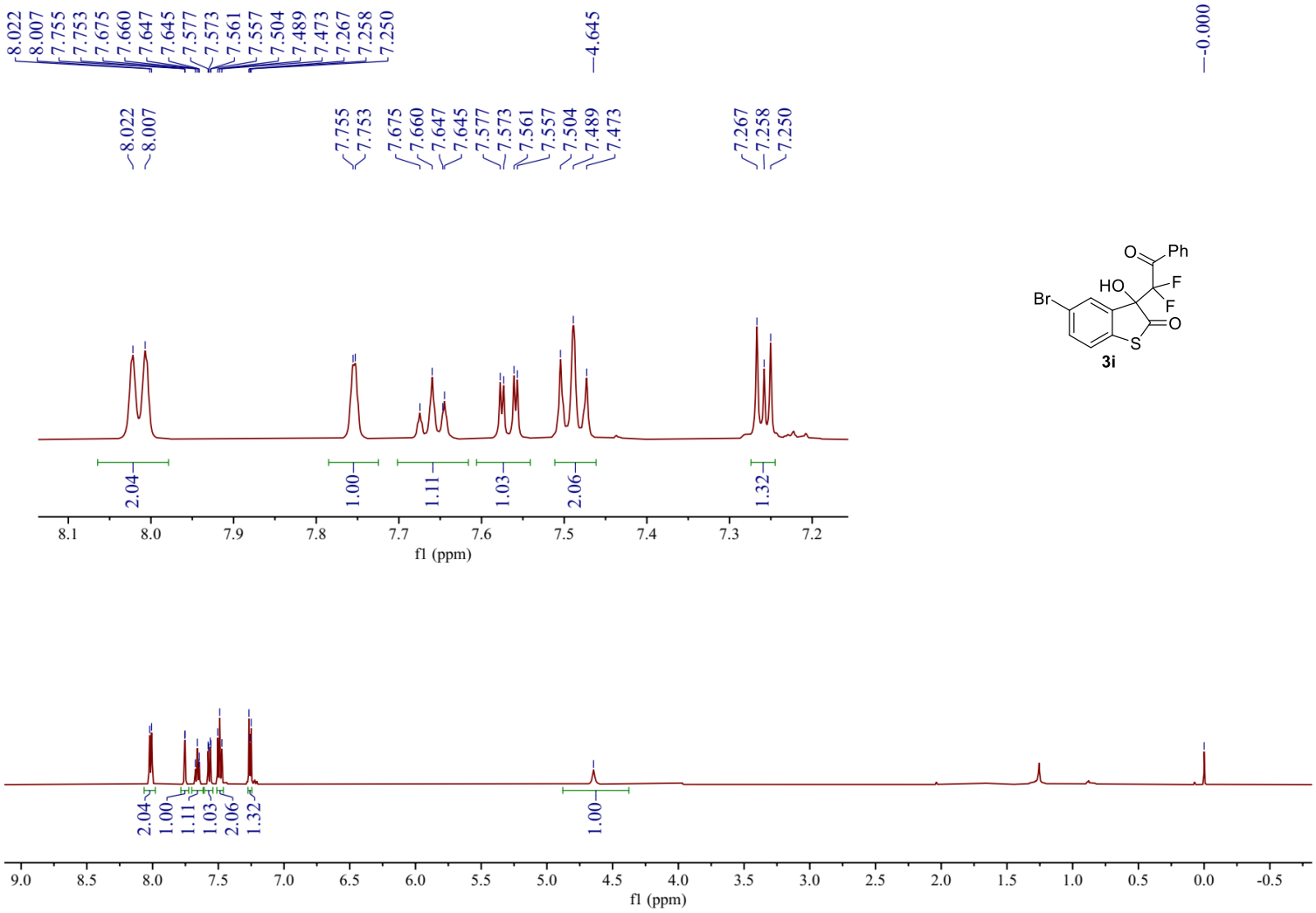
^{1}H NMR spectra of **4h** in $CDCl_3$ (400 MHz)



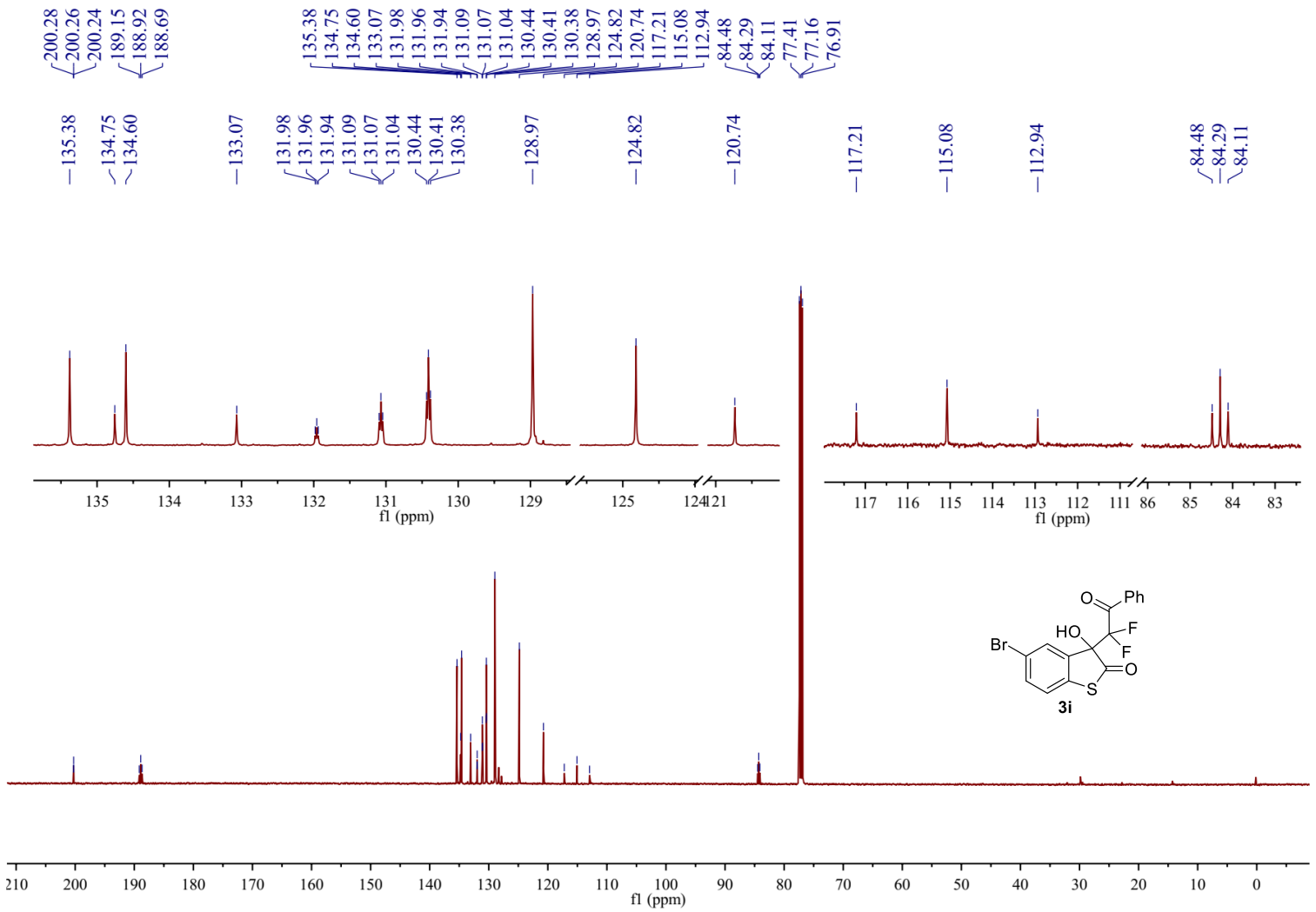
$^{13}C\{^{1}H\}$ NMR spectra of **4h** in $CDCl_3$ (125 MHz)



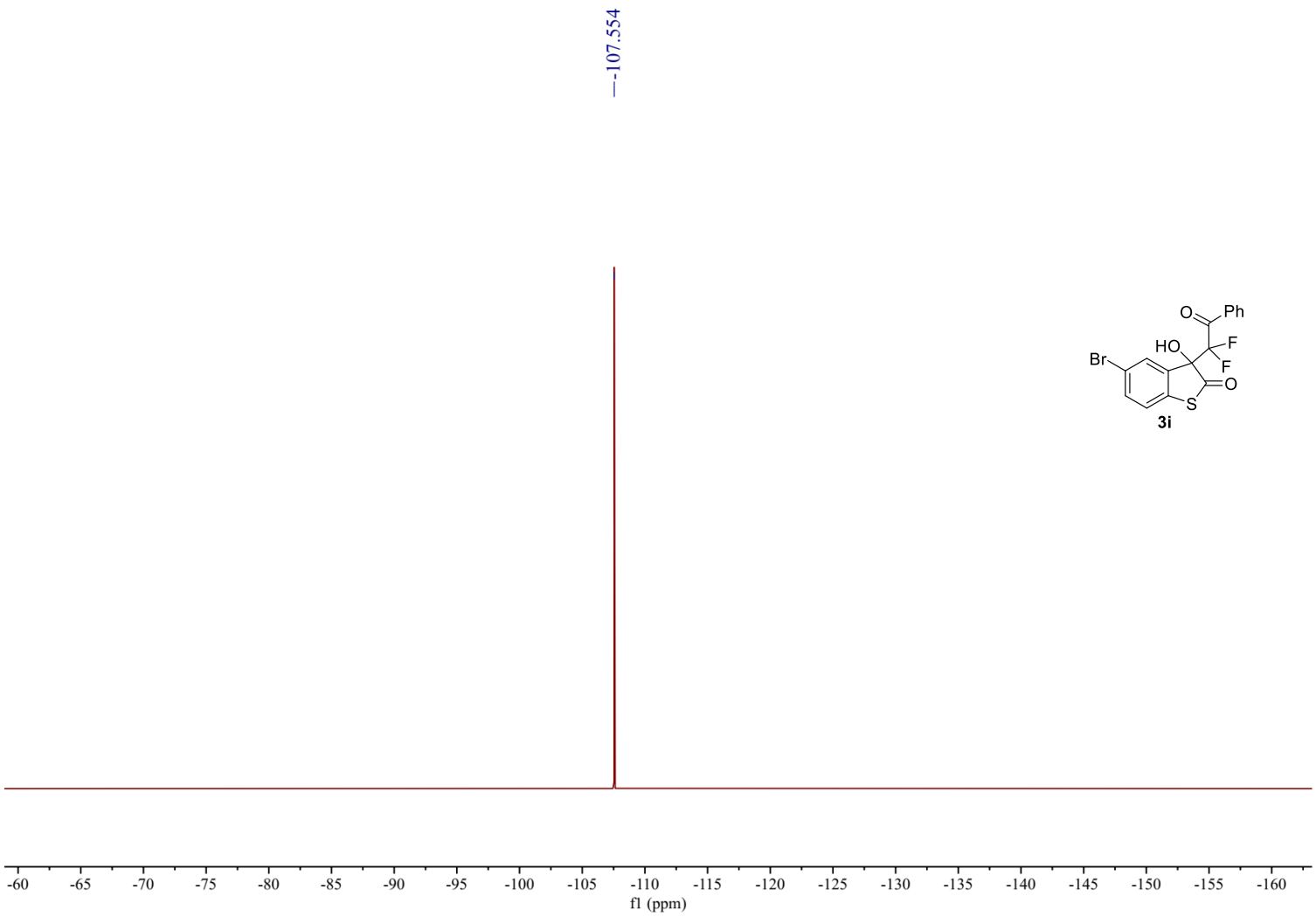
^{19}F NMR spectra of **4h** in $CDCl_3$ (376 MHz)



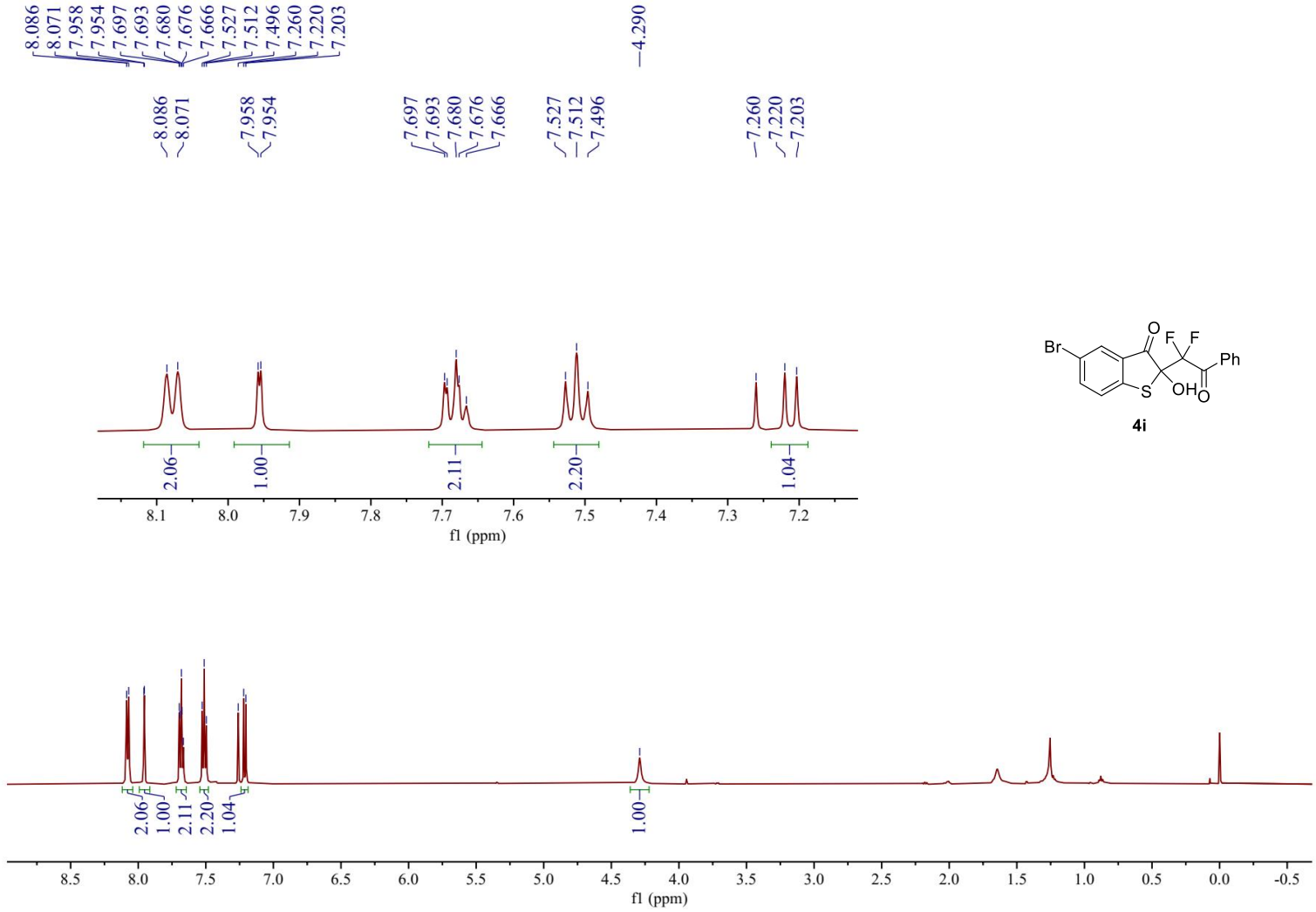
^{1}H NMR spectra of **3i** in $CDCl_3$ (400 MHz)



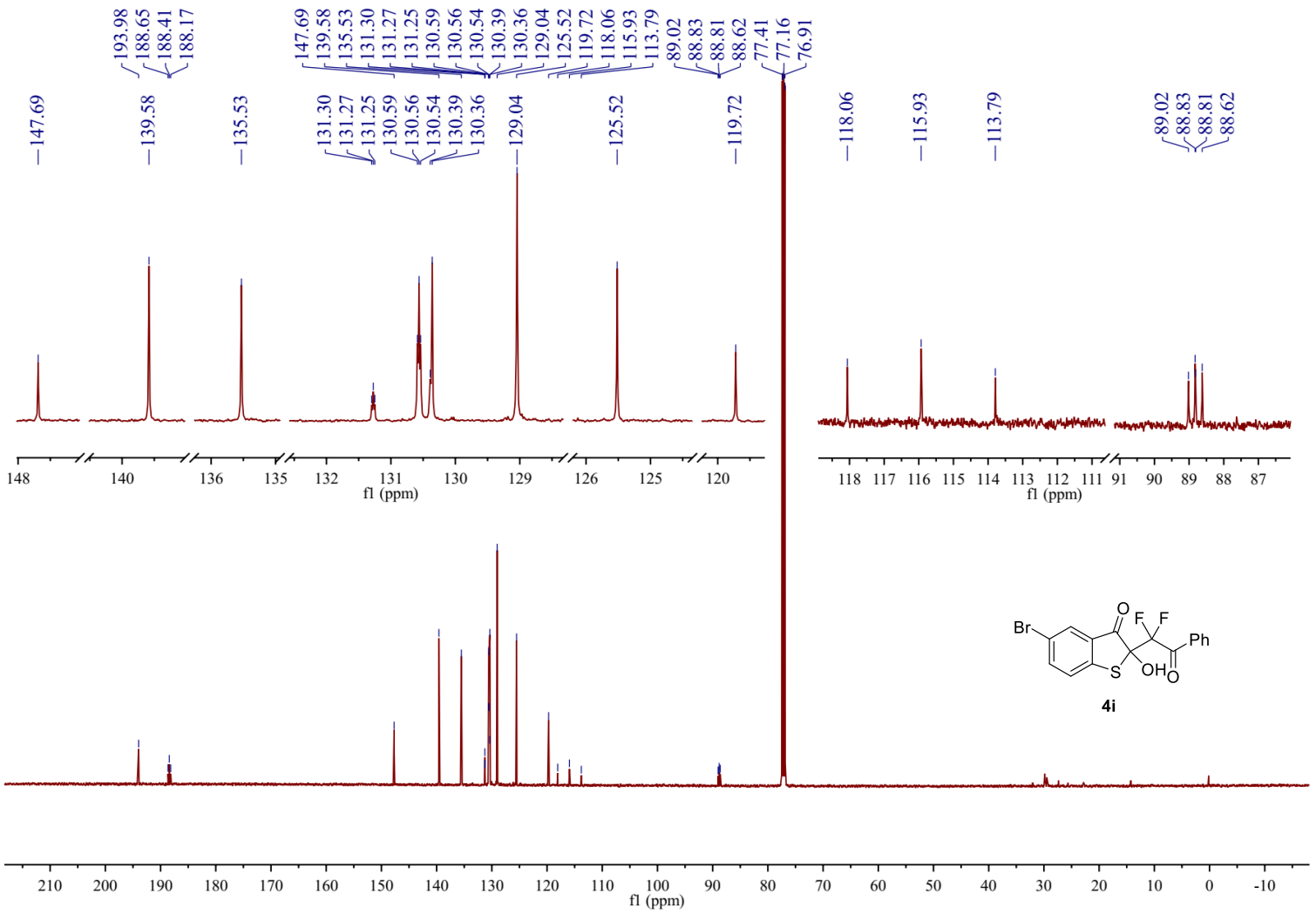
$^{13}C\{^{1}H\}$ NMR spectra of **3i** in $CDCl_3$ (100 MHz)



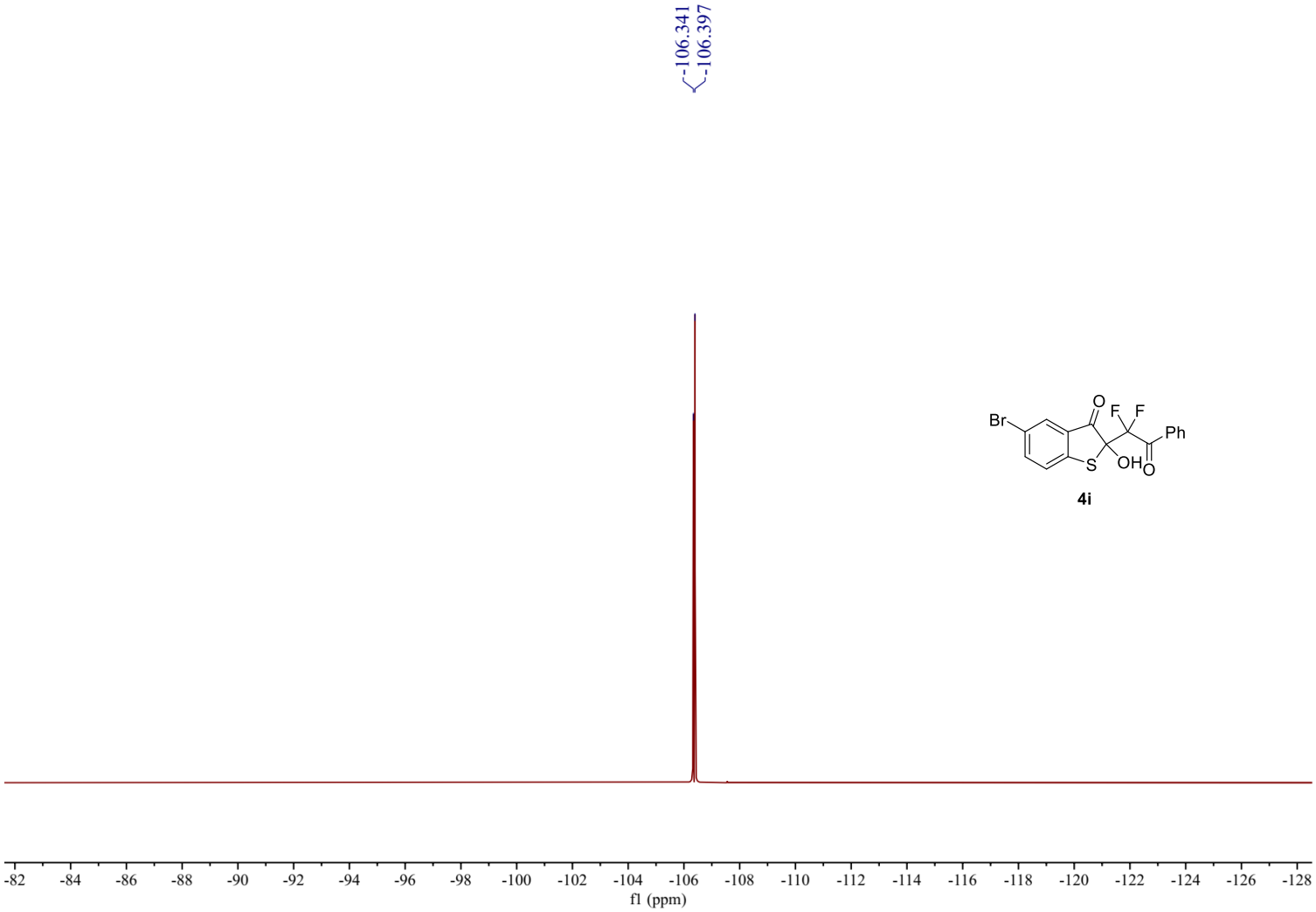
^{19}F NMR spectra of **3i** in $CDCl_3$ (376 MHz)



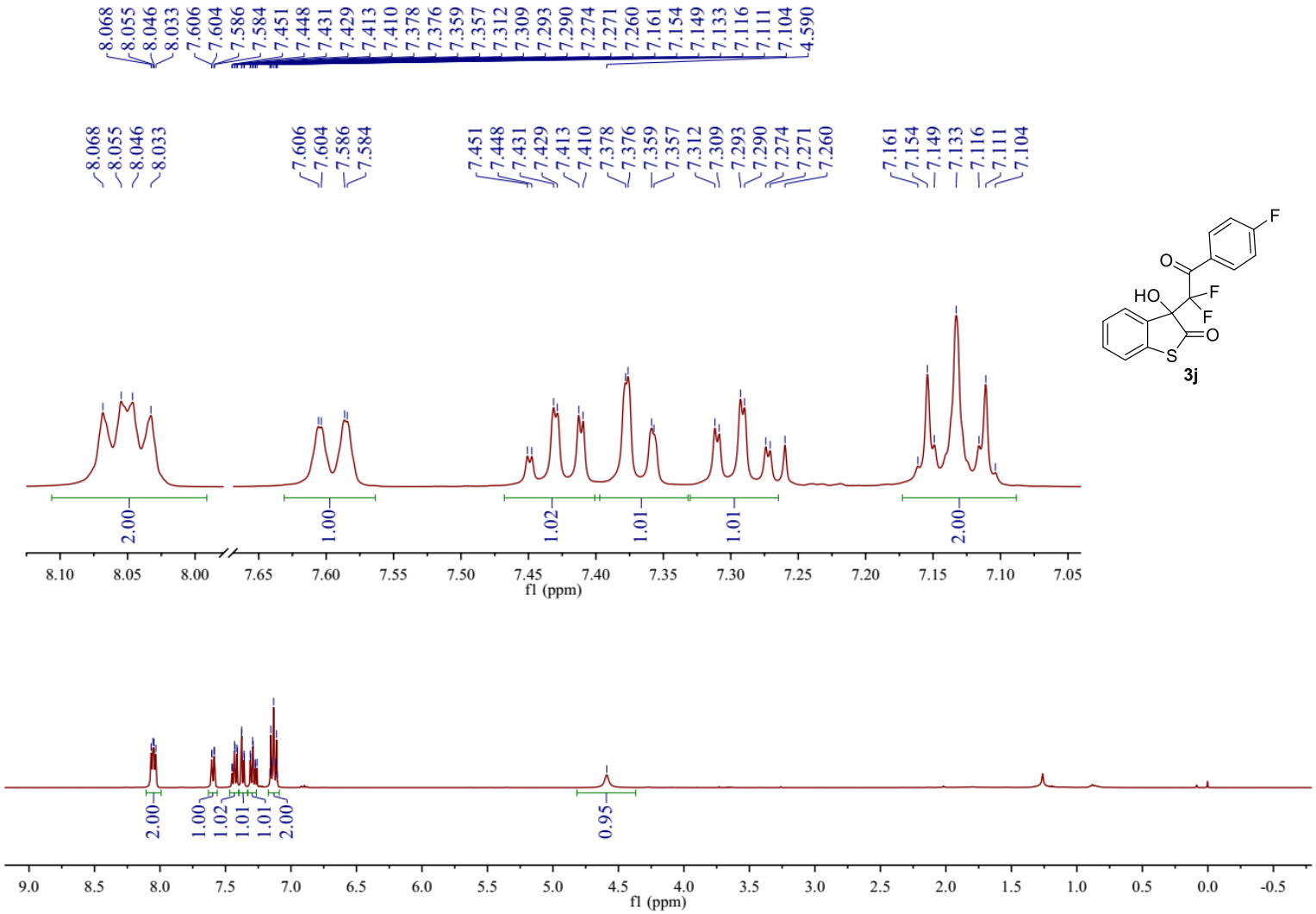
^{1}H NMR spectra of **4i** in $CDCl_3$ (500 MHz)



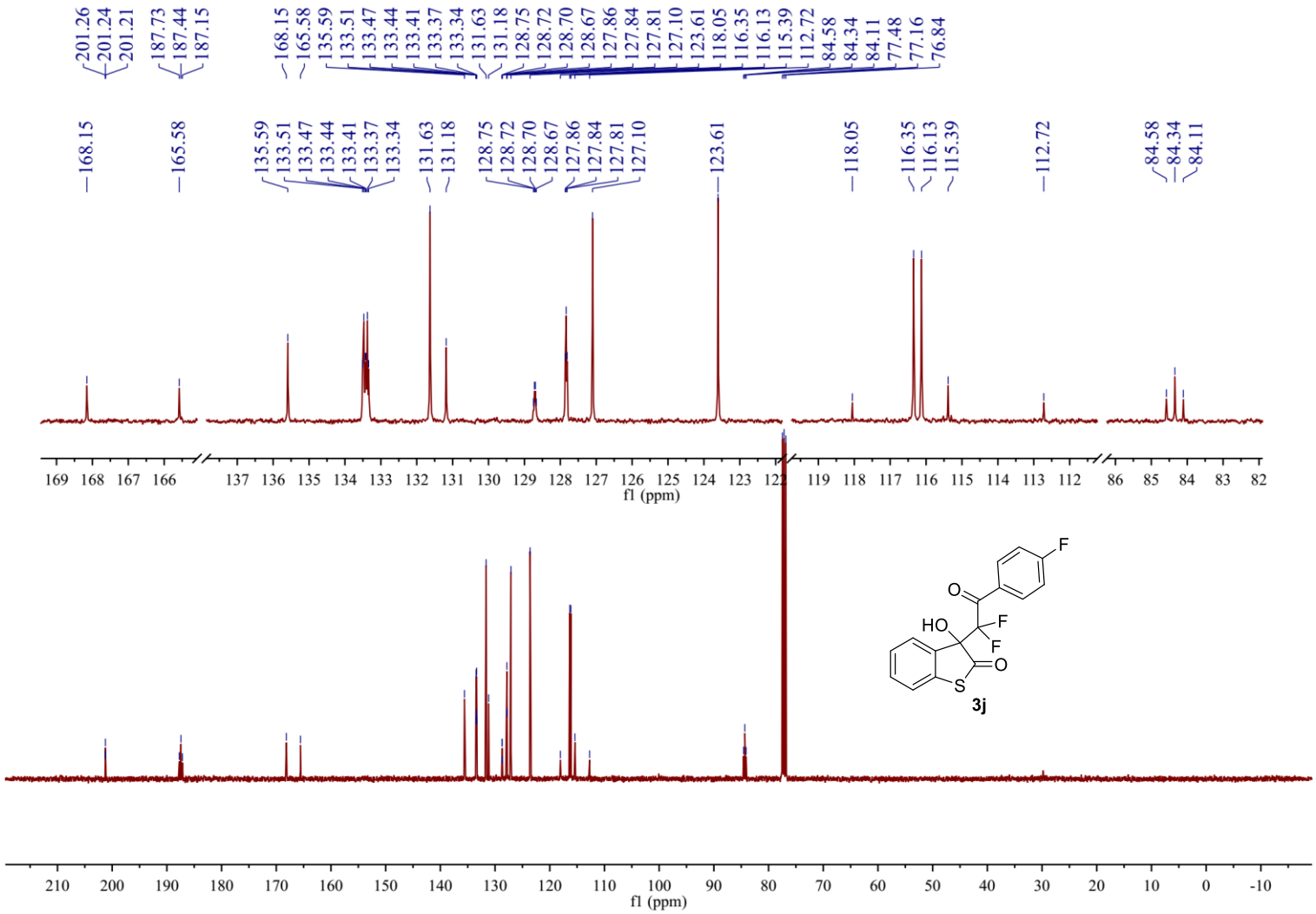
$^{13}C\{^{1}H\}$ NMR spectra of **4i** in $CDCl_3$ (125 MHz)



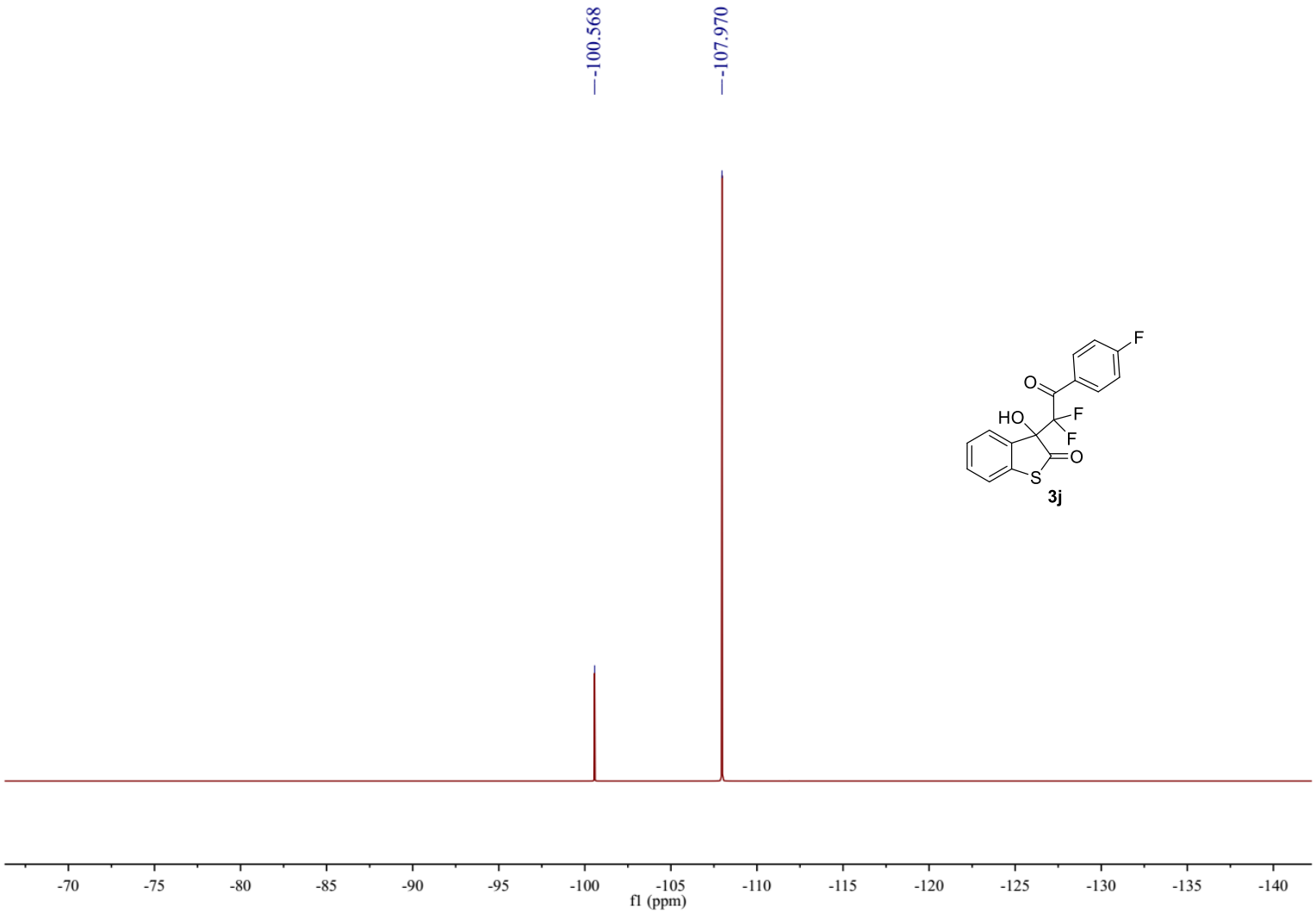
^{19}F NMR spectra of **4i** in $CDCl_3$ (376 MHz)



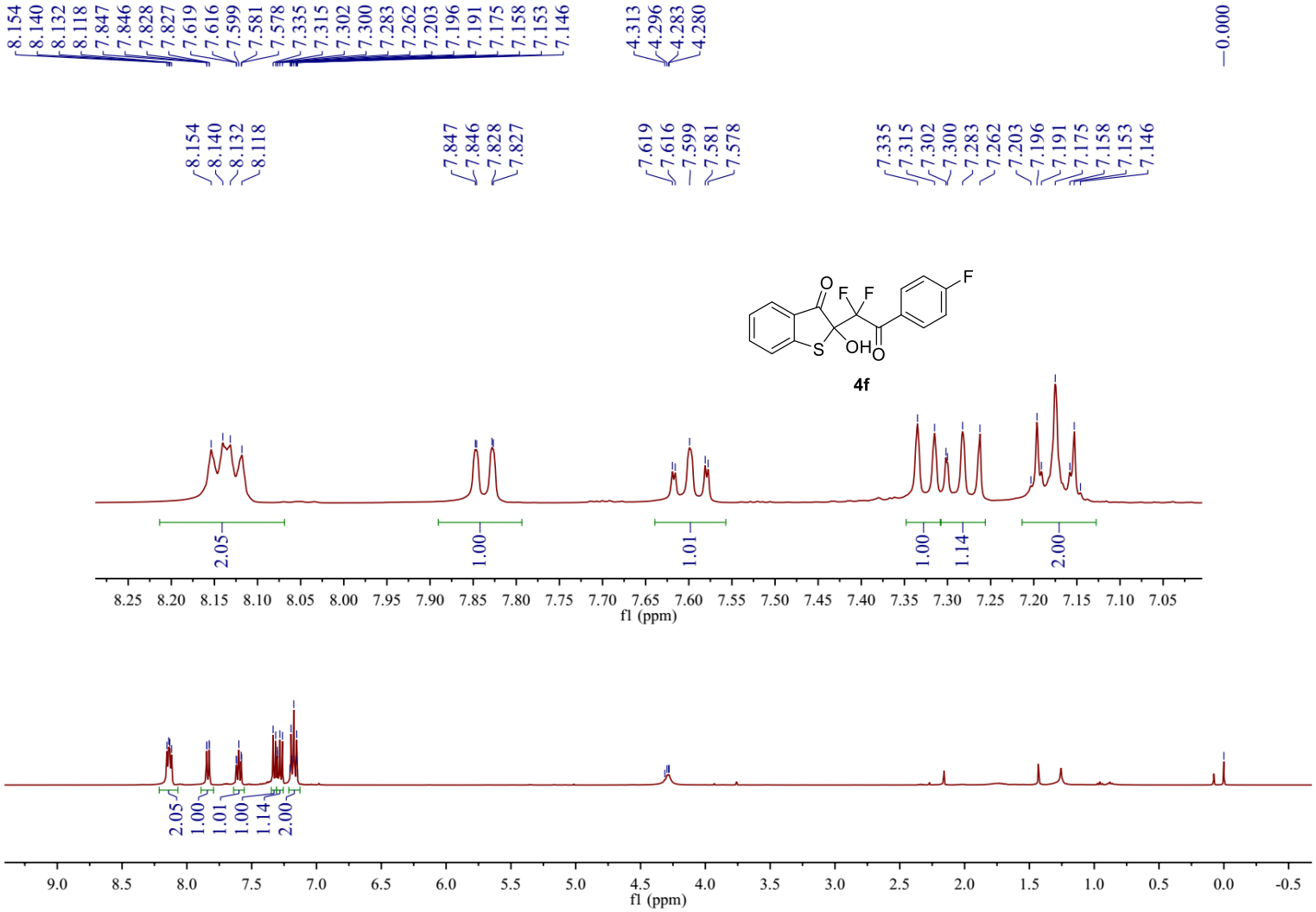
^{1}H NMR spectra of **3j** in $CDCl_3$ (400 MHz)



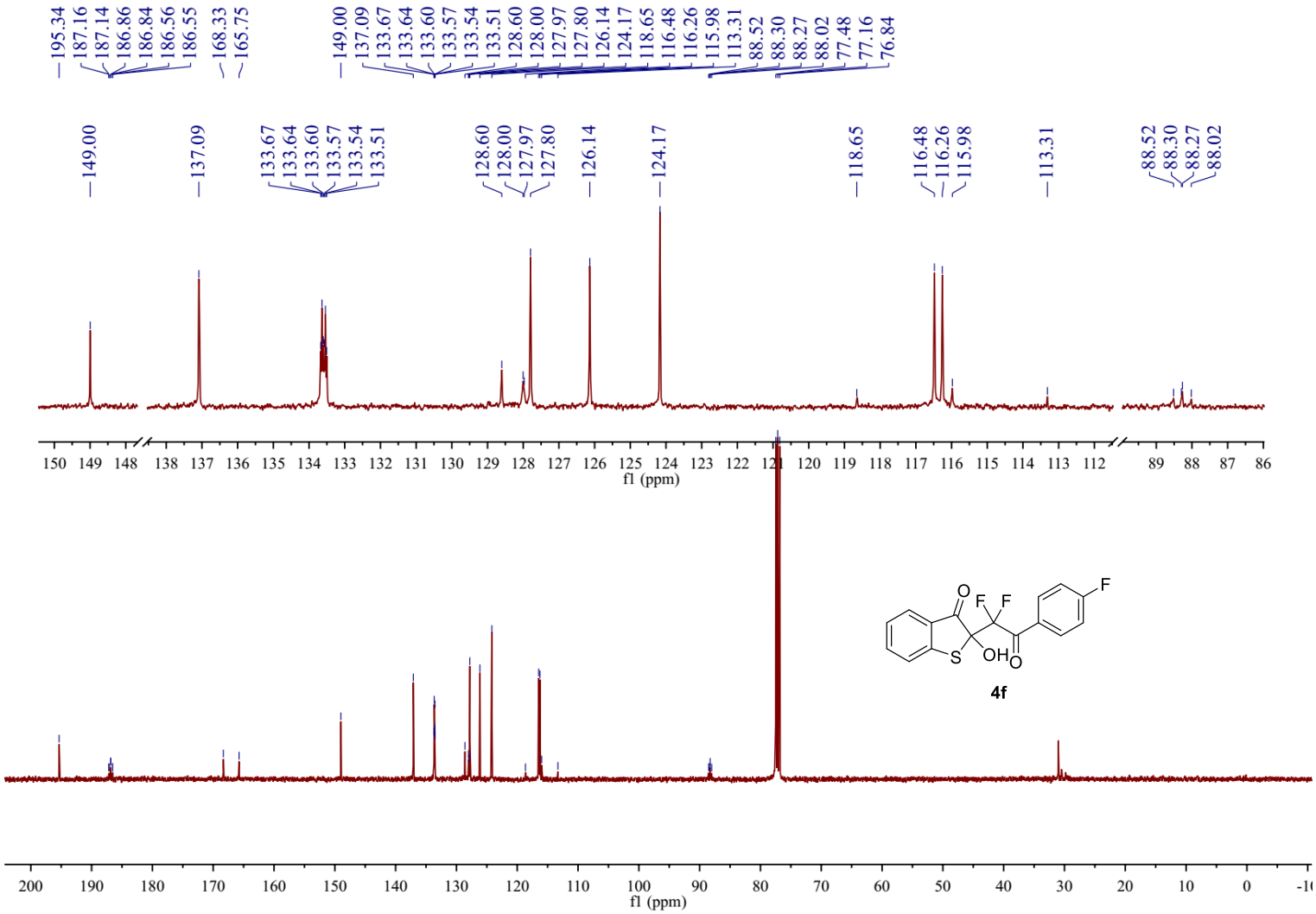
$^{13}C\{^{1}H\}$ NMR spectra of **3j** in $CDCl_3$ (100 MHz)



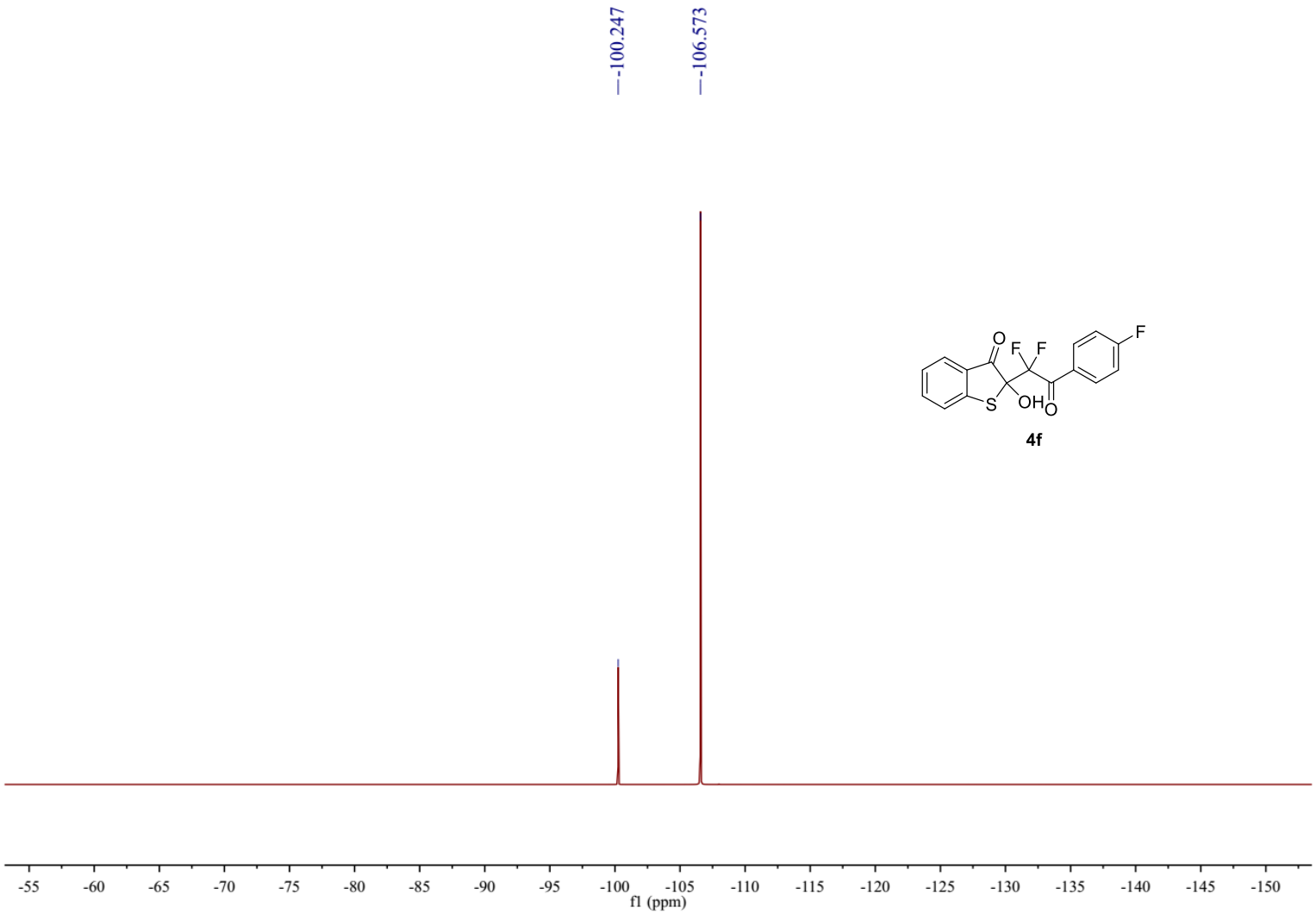
^{19}F NMR spectra of **3j** in $CDCl_3$ (376 MHz)



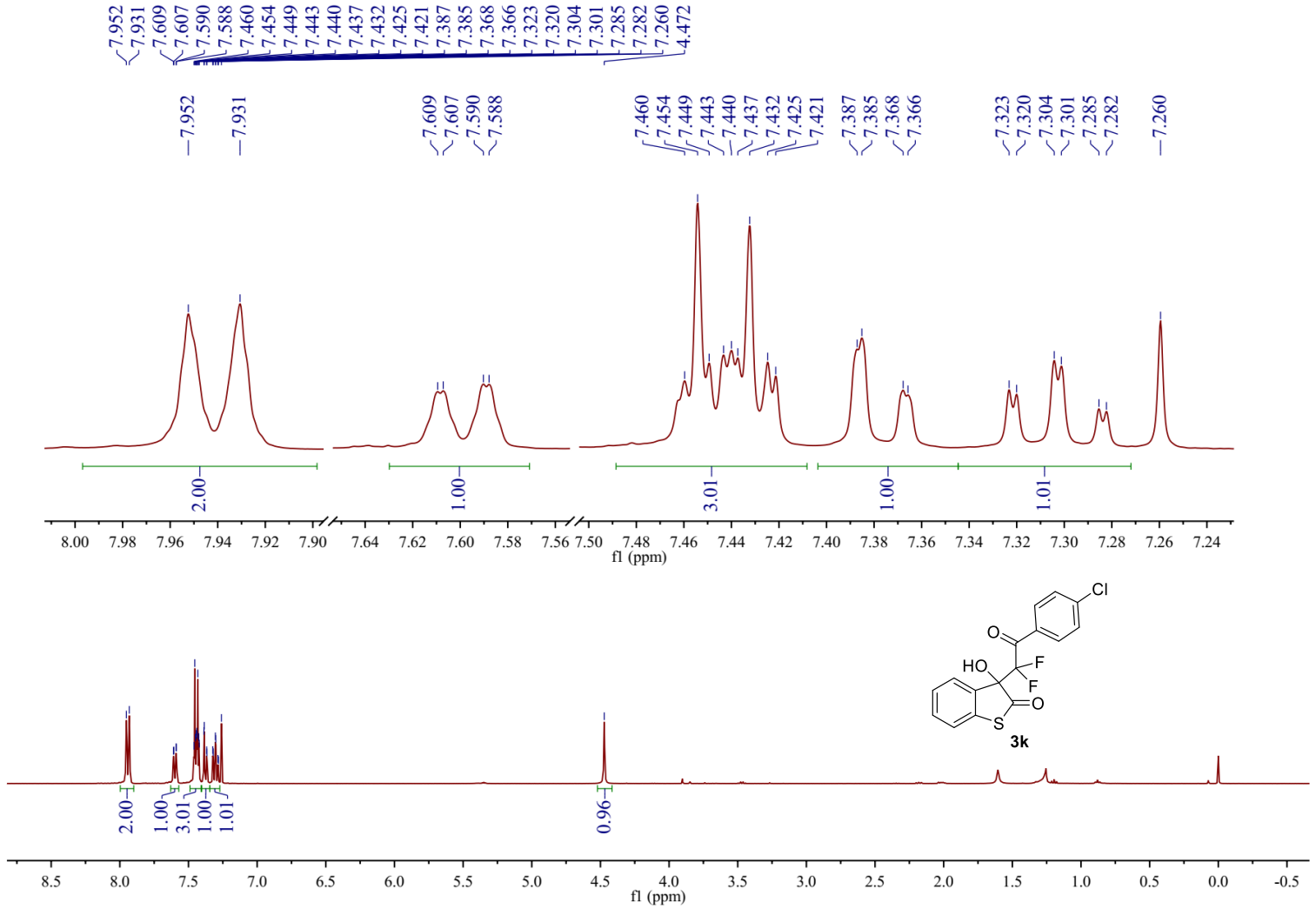
^{1}H NMR spectra of **4j** in $CDCl_3$ (400 MHz)



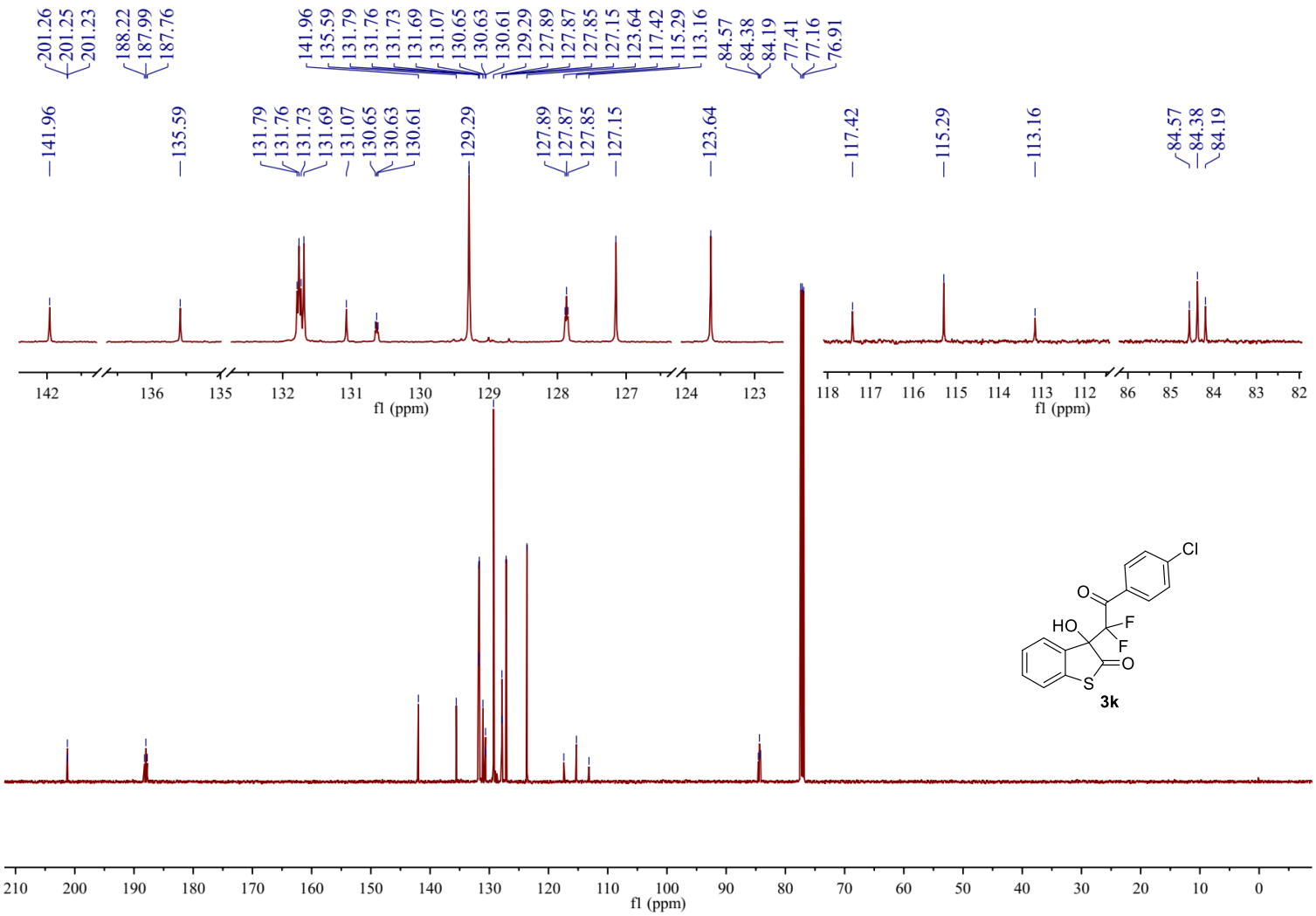
$^{13}C\{^{1}H\}$ NMR spectra of **4j** in $CDCl_3$ (100 MHz)



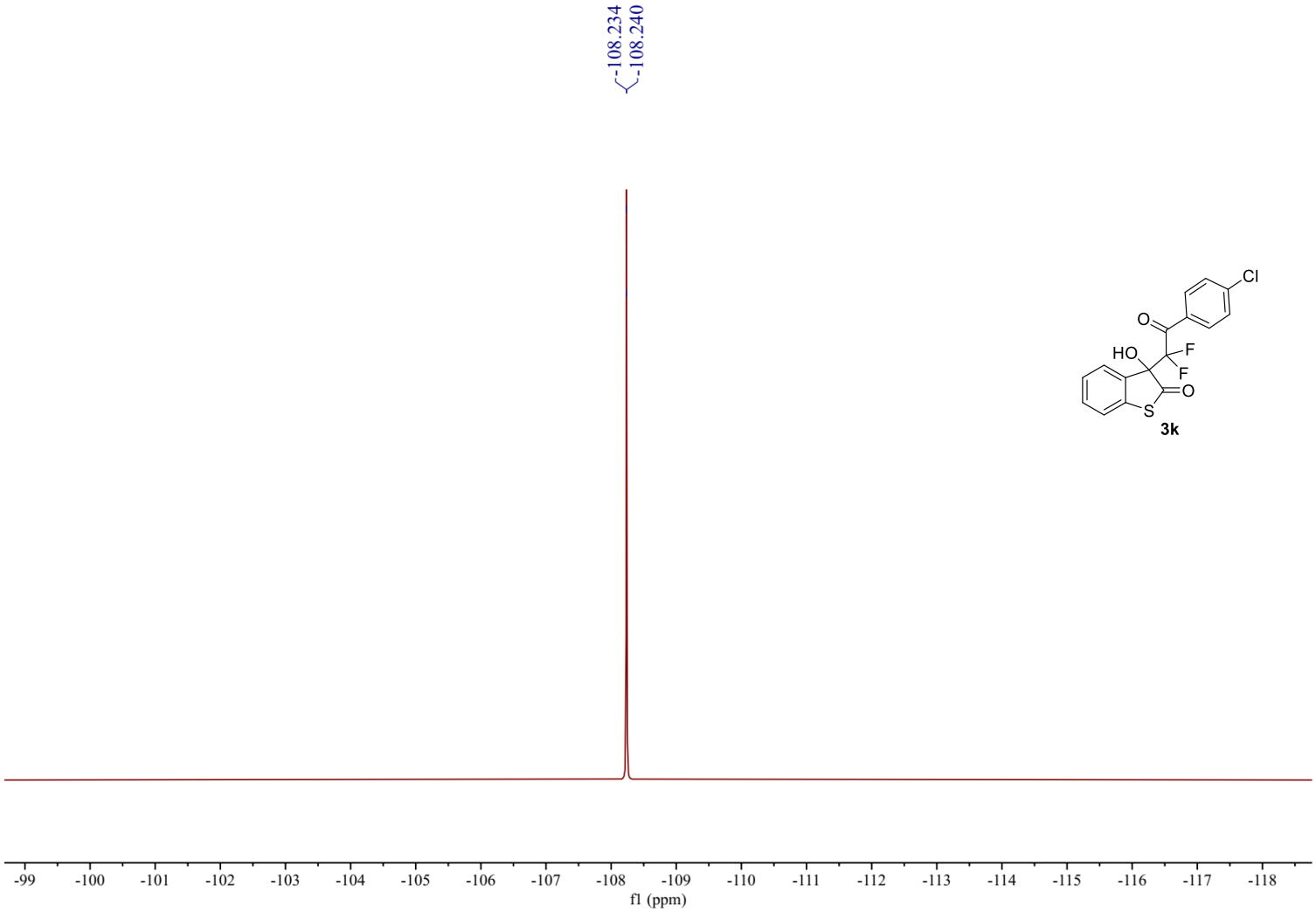
^{19}F NMR spectra of **4j** in $CDCl_3$ (376 MHz)



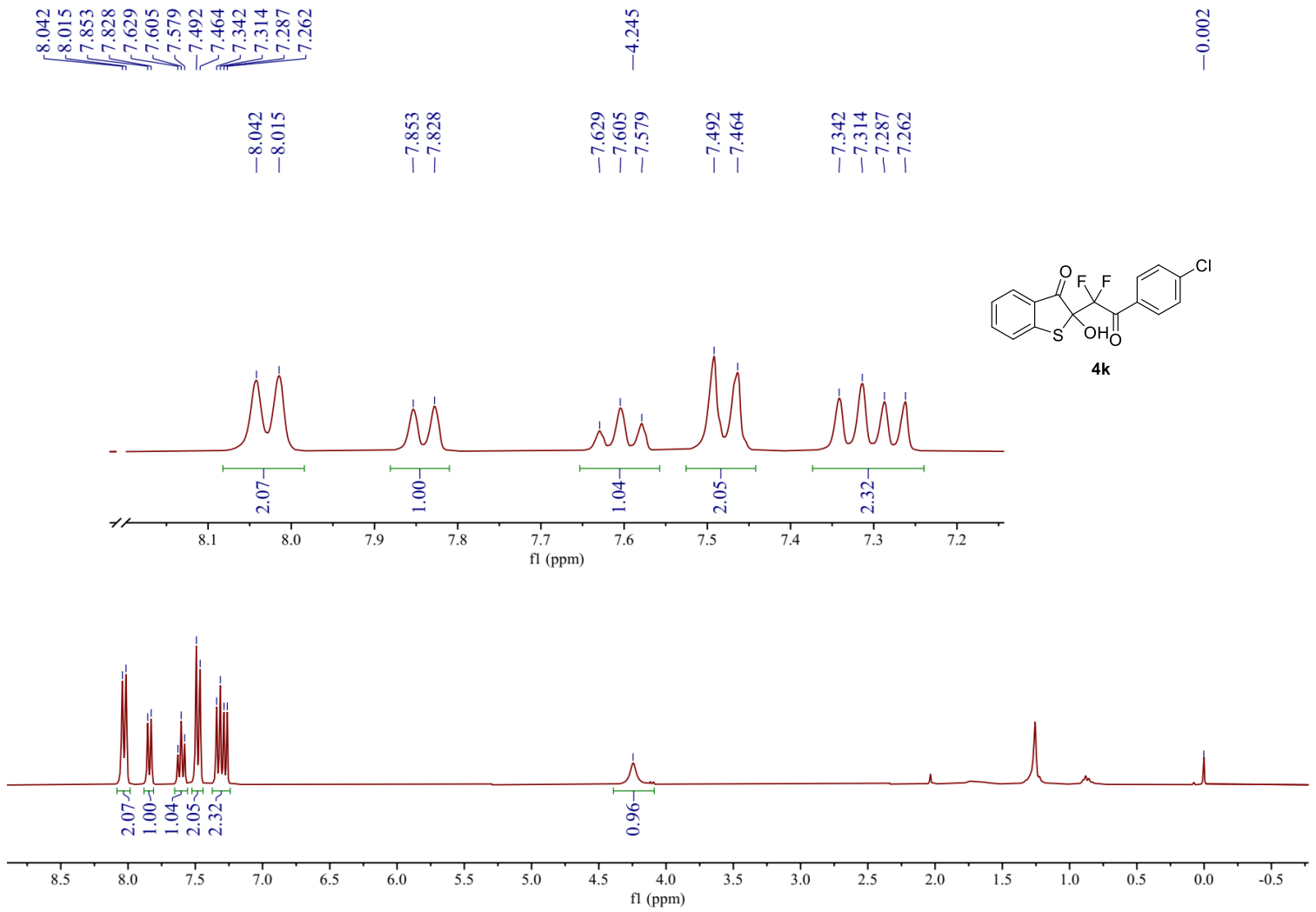
^{1}H NMR spectra of **3k** in $CDCl_3$ (400 MHz)



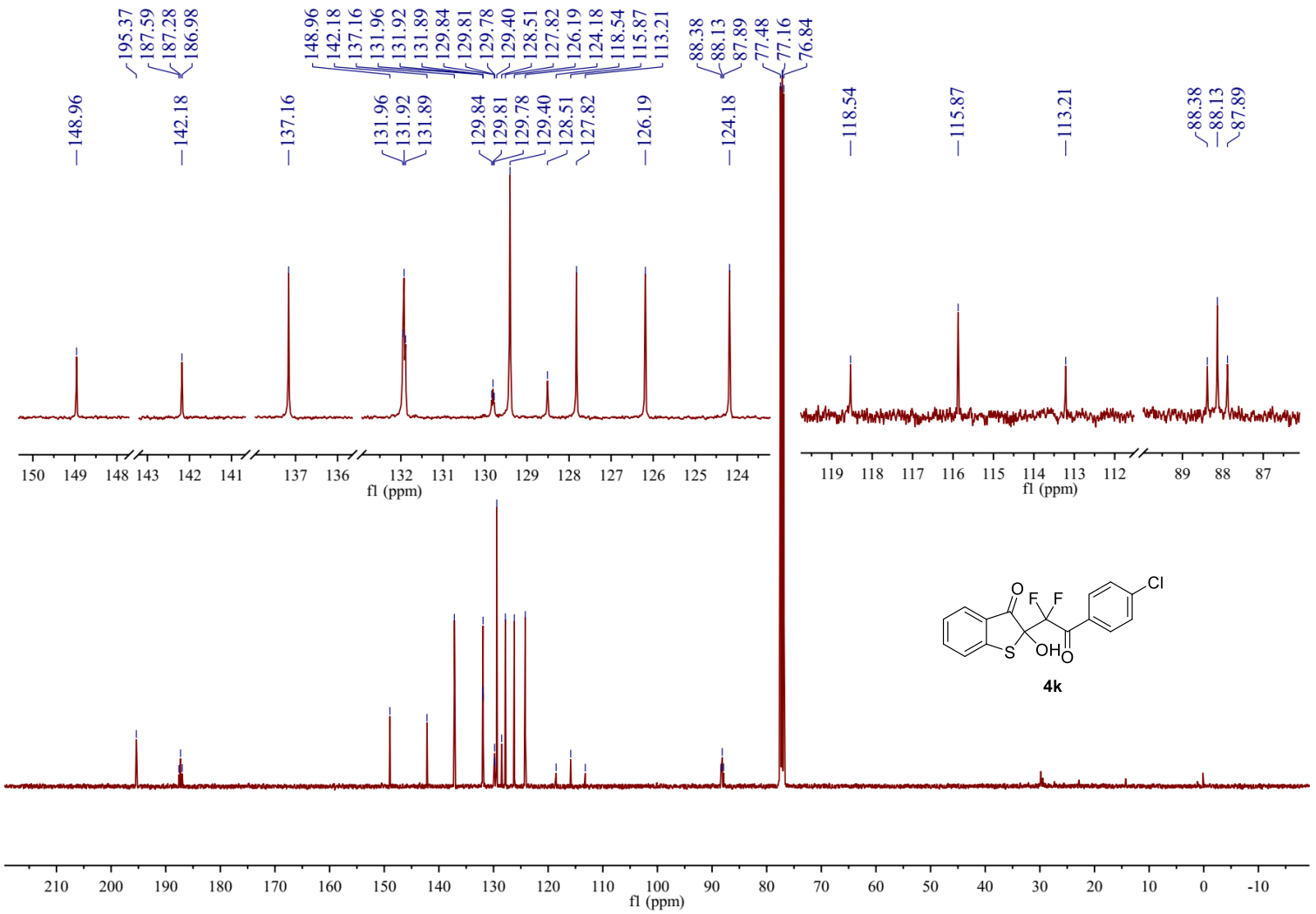
$^{13}C\{^{1}H\}$ NMR spectra of **3k** in $CDCl_3$ (125 MHz)



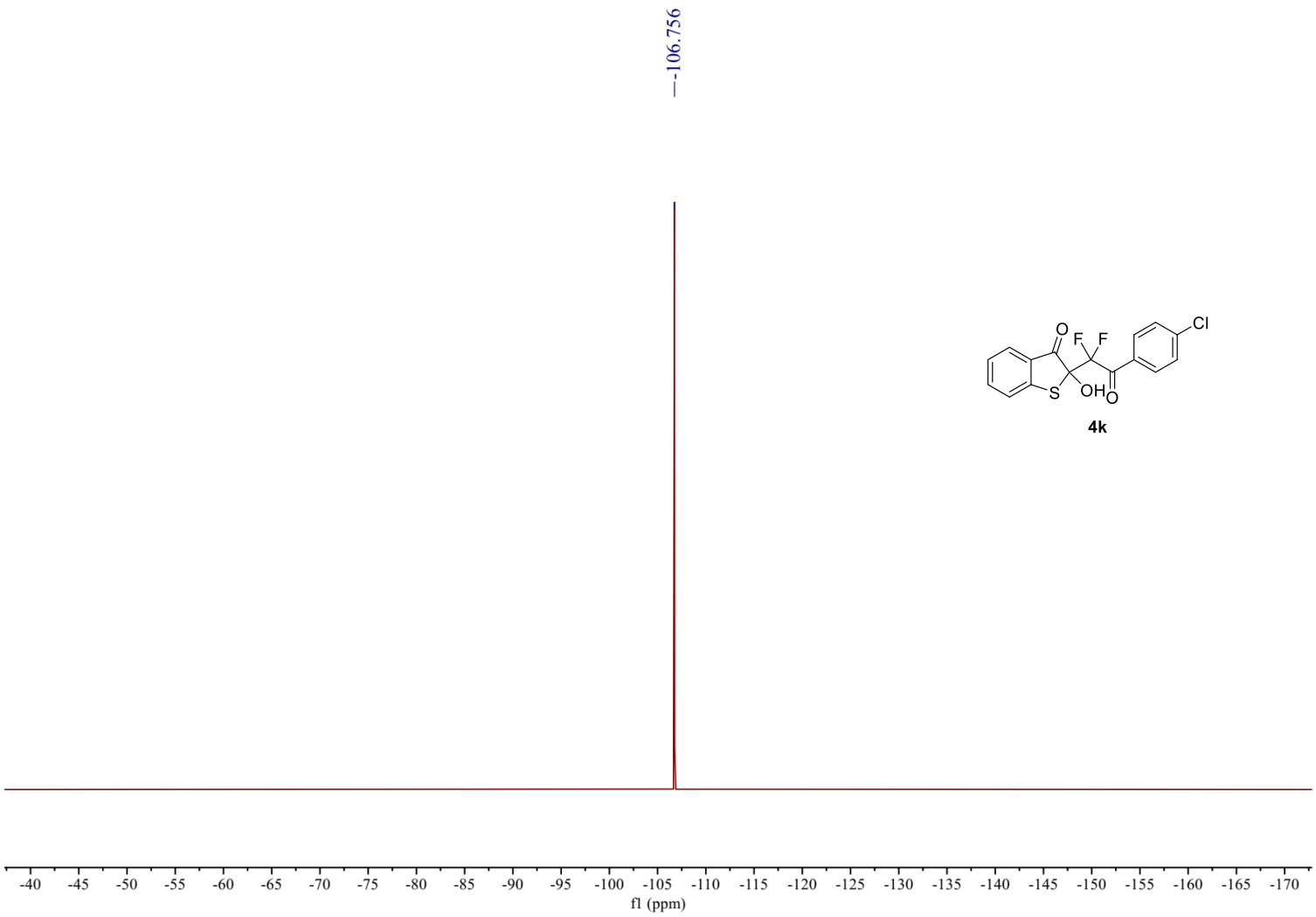
^{19}F NMR spectra of **3k** in $CDCl_3$ (376 MHz)



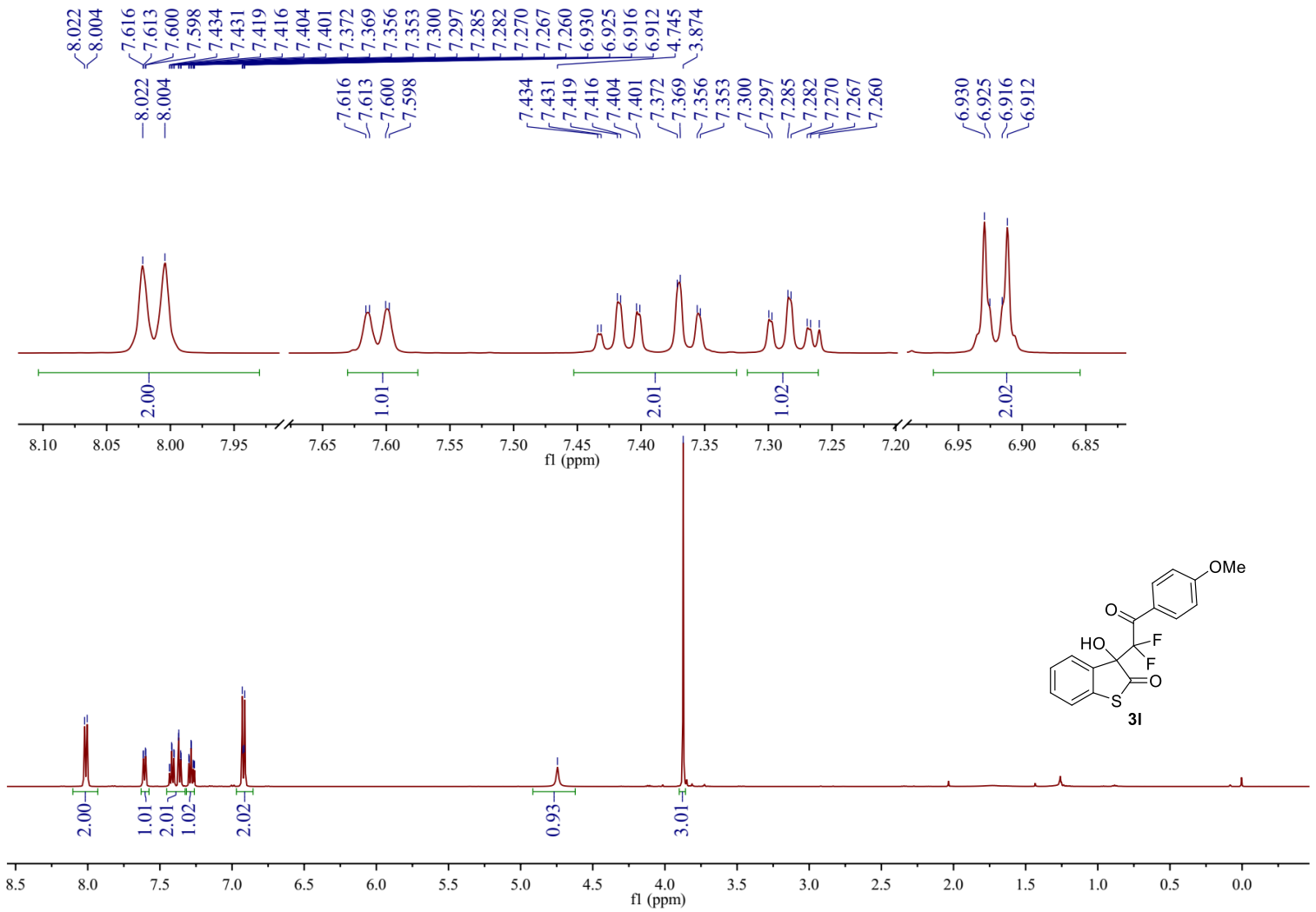
^{1}H NMR spectra of **4k** in $CDCl_3$ (300 MHz)



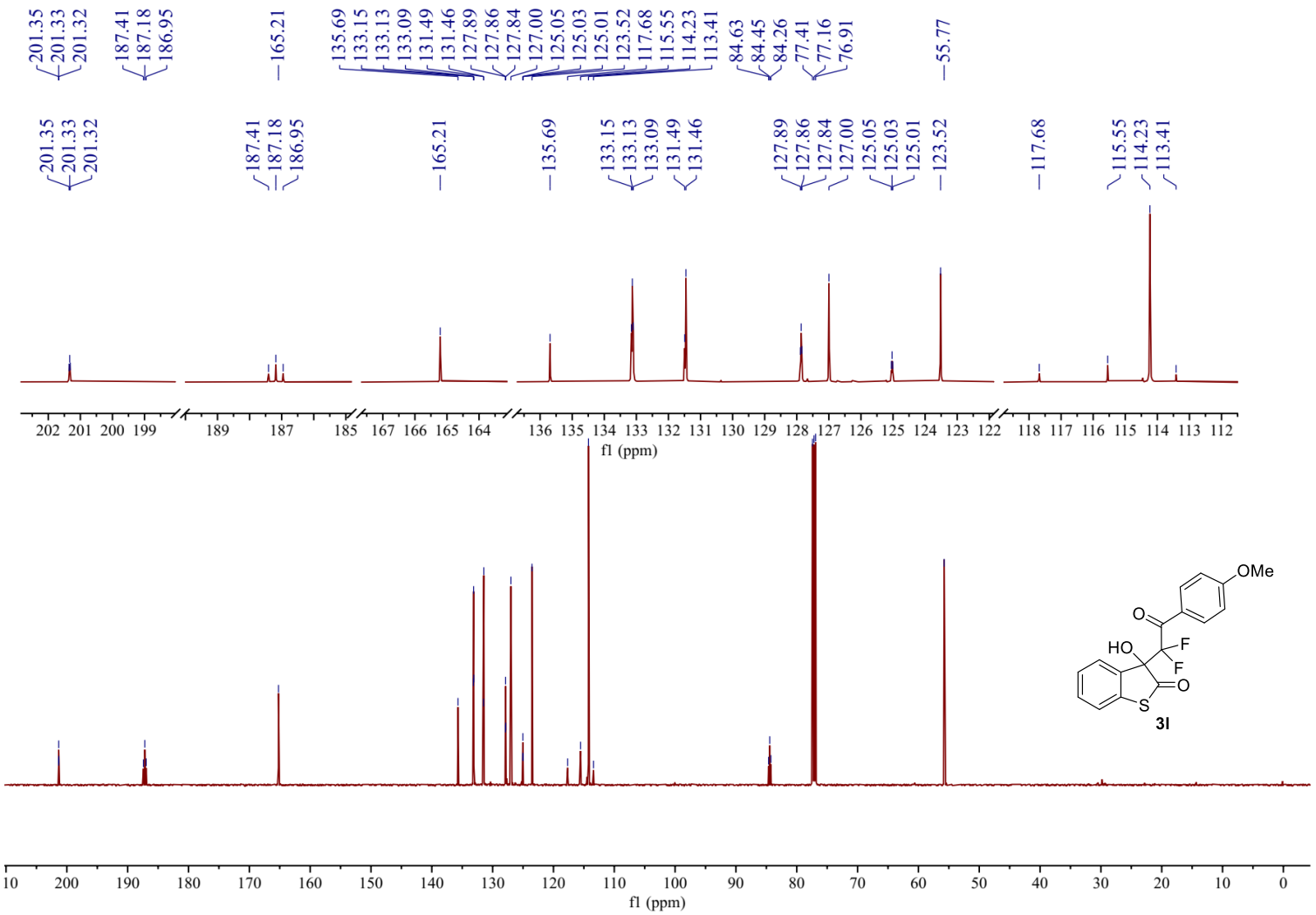
$^{13}C\{^{1}H\}$ NMR spectra of **4k** in $CDCl_3$ (100 MHz)



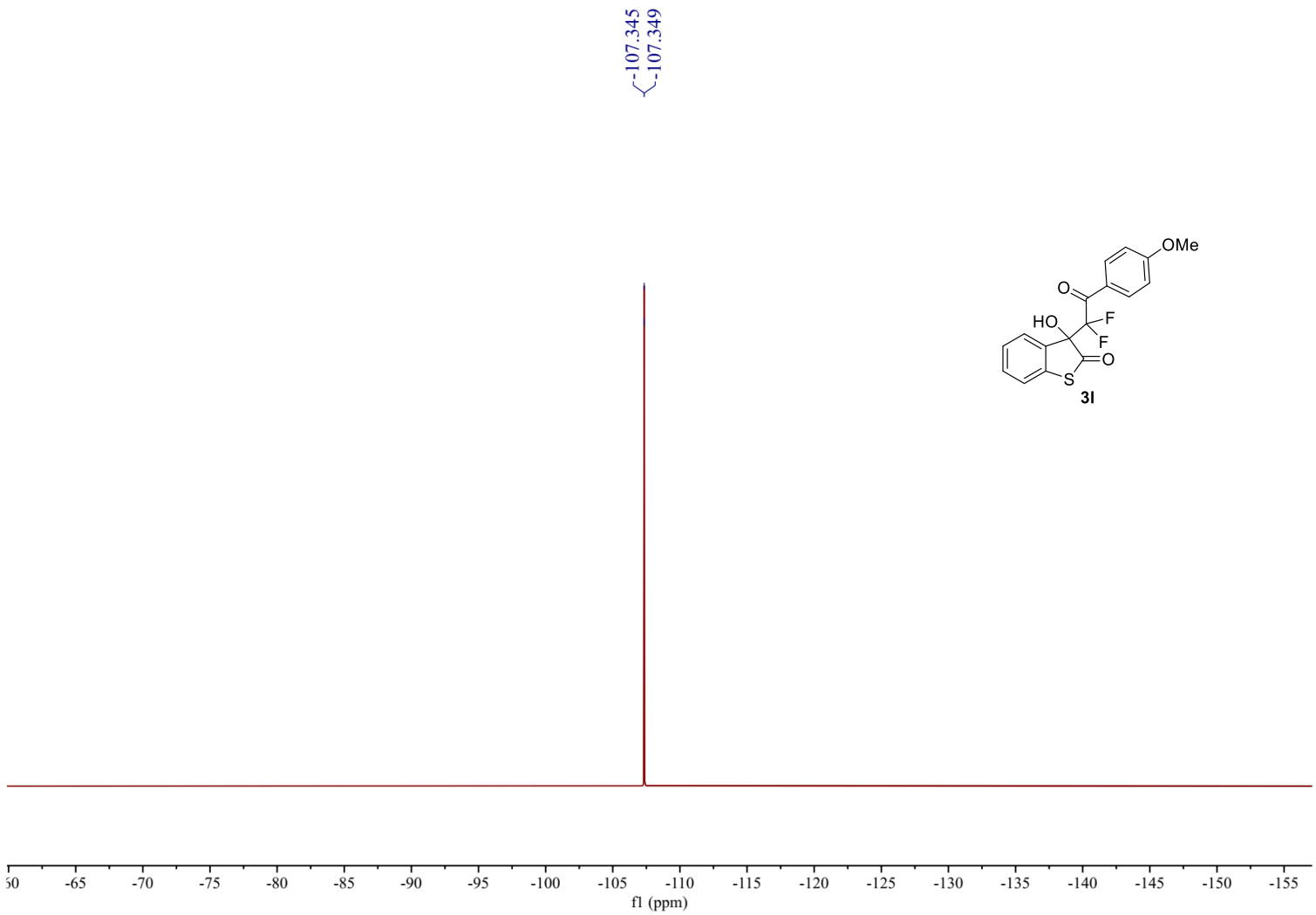
^{19}F NMR spectra of **4k** in $CDCl_3$ (376 MHz)



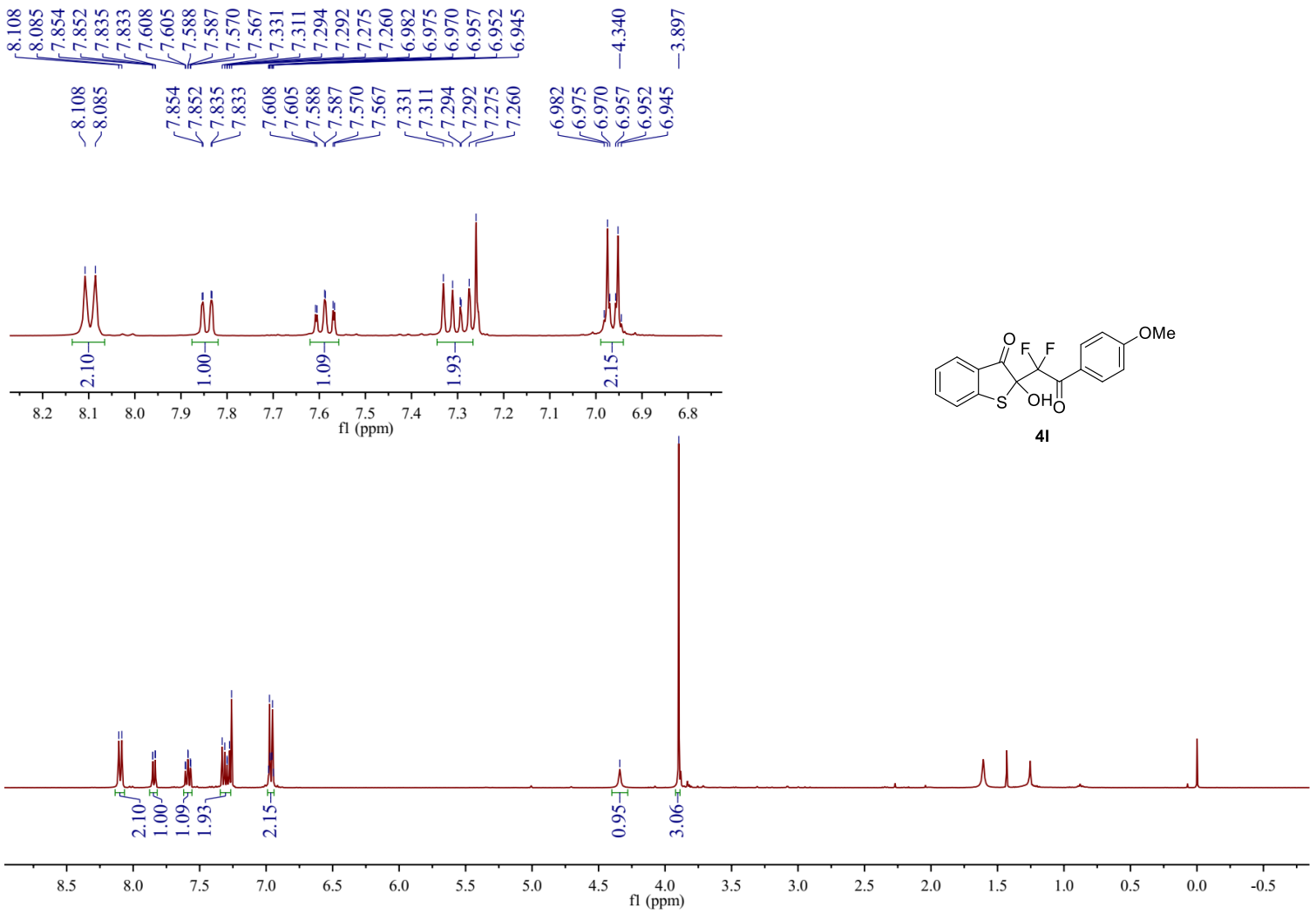
^{1}H NMR spectra of **3l** in $CDCl_3$ (500 MHz)



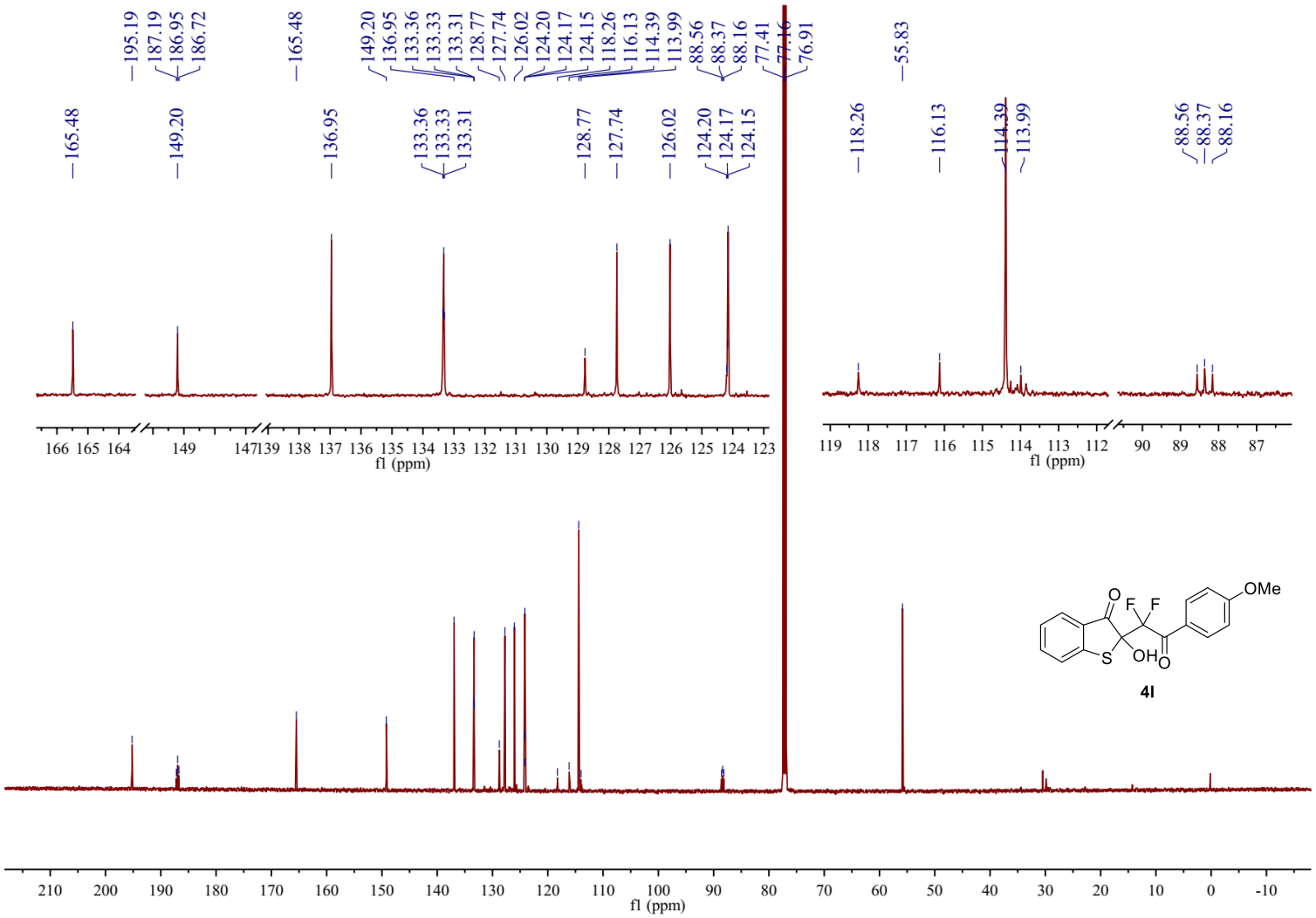
$^{13}C\{^{1}H\}$ NMR spectra of **3l** in $CDCl_3$ (125 MHz)



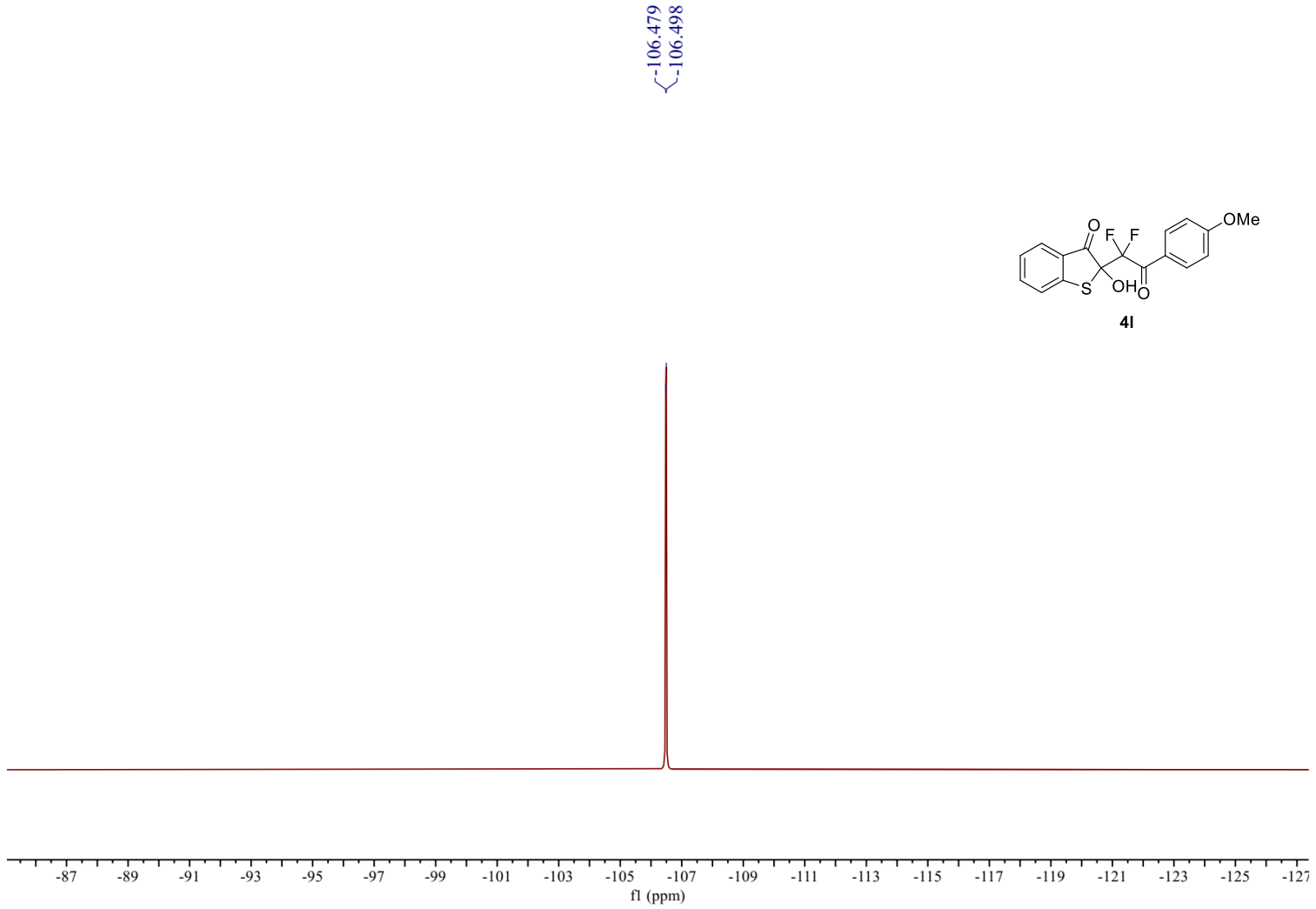
^{19}F NMR spectra of **3l** in $CDCl_3$ (376 MHz)



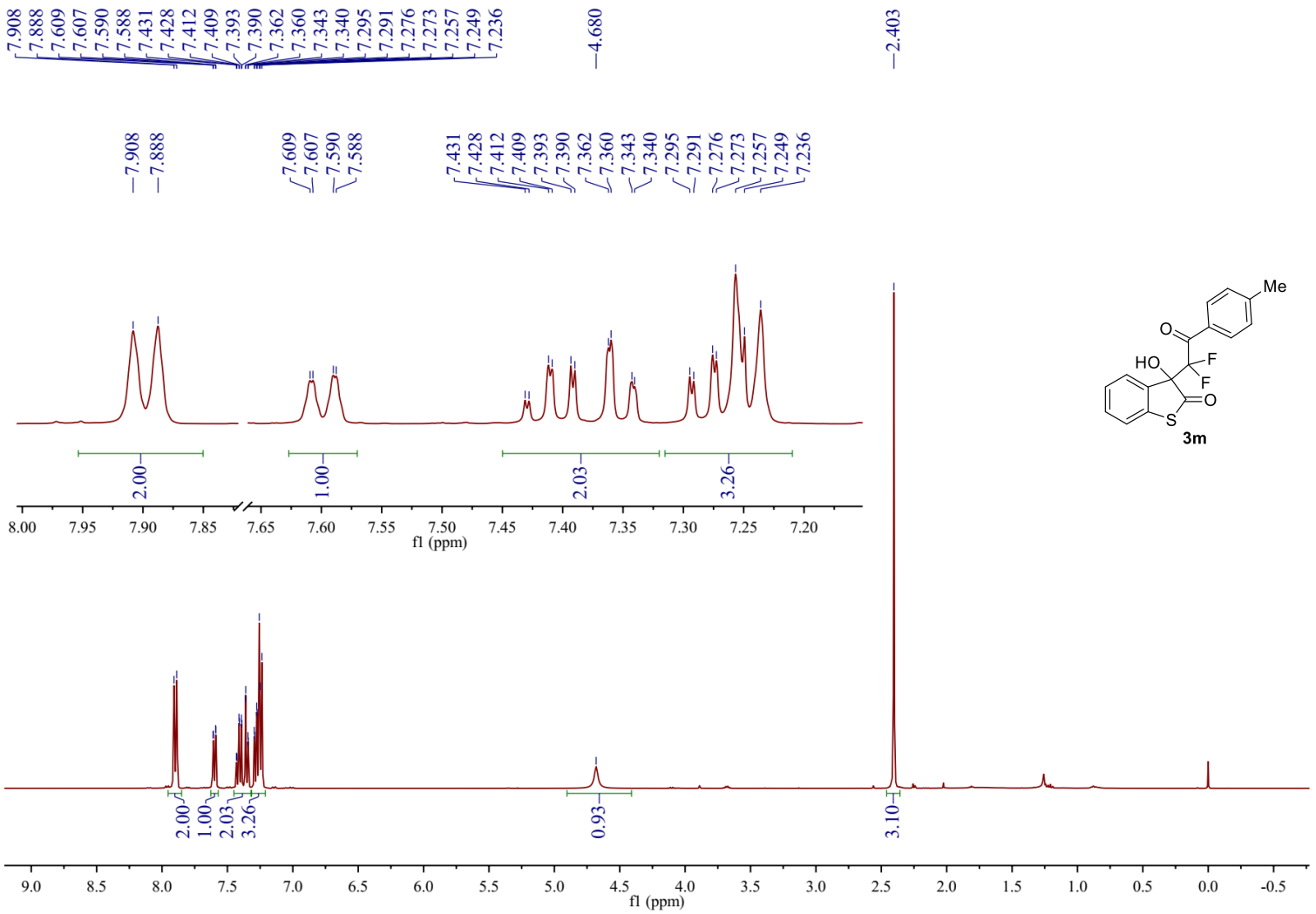
^{1}H NMR spectra of **4l** in $CDCl_3$ (400 MHz)



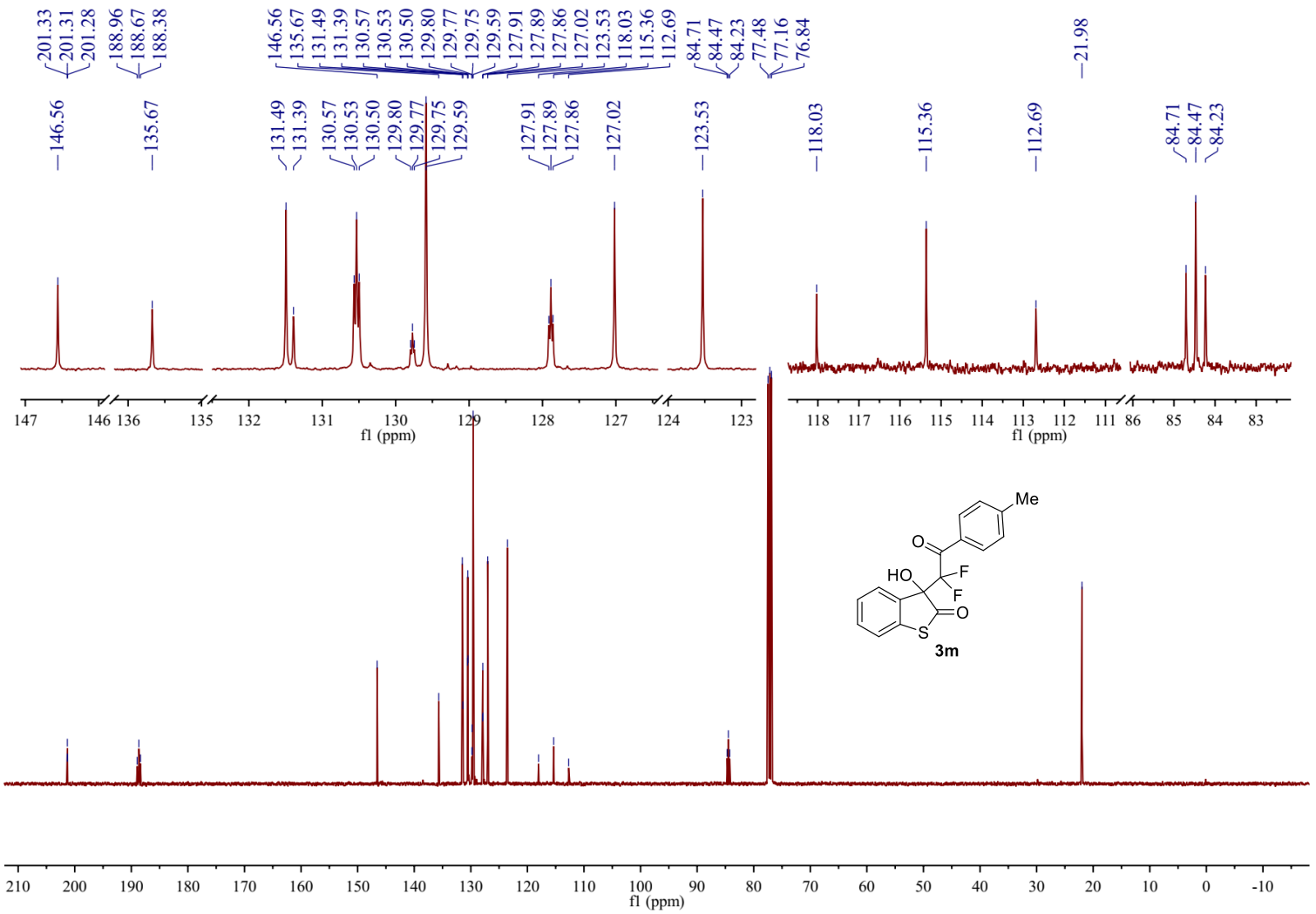
$^{13}C\{^{1}H\}$ NMR spectra of **4l** in $CDCl_3$ (125 MHz)



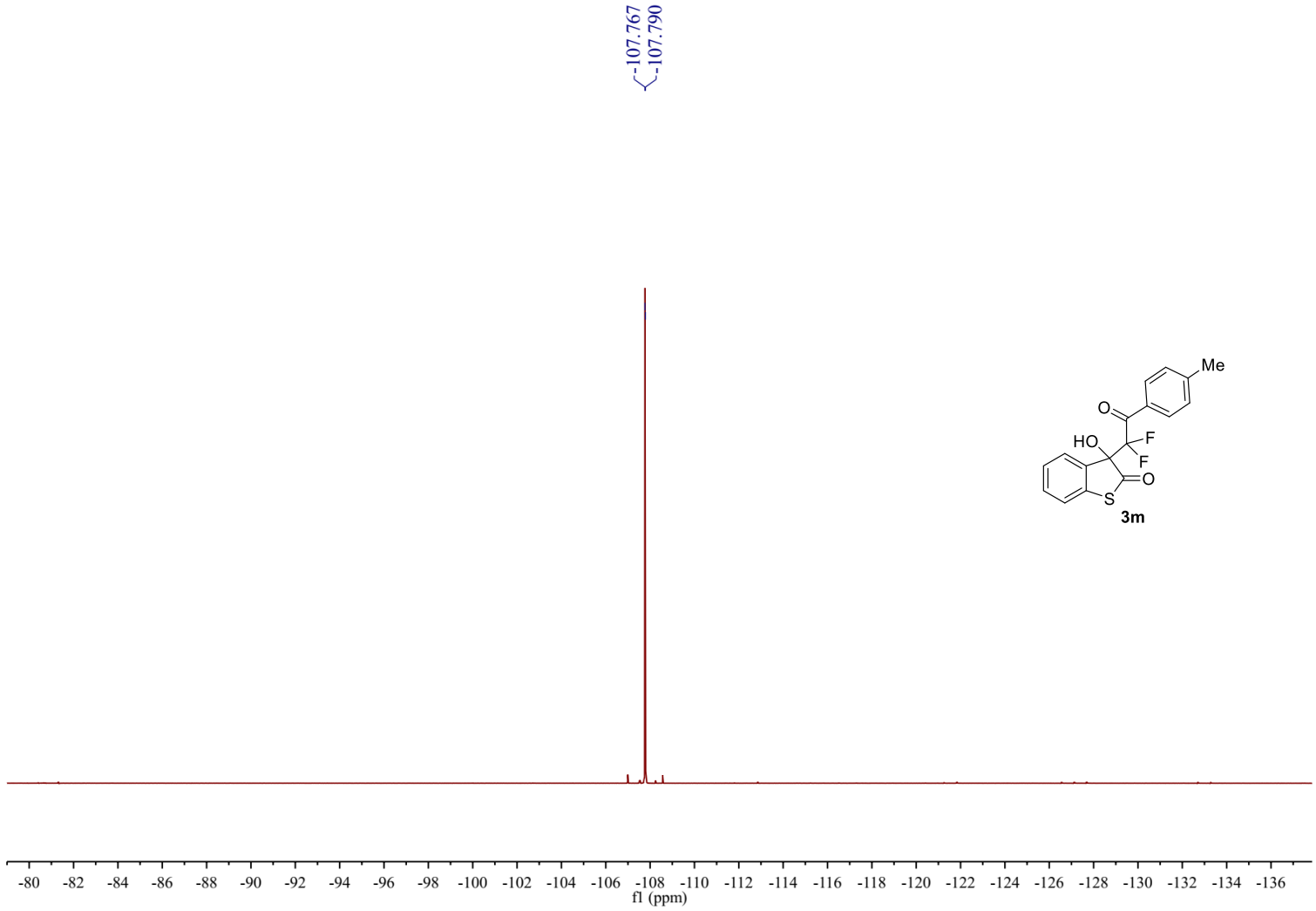
^{19}F NMR spectra of **4l** in $CDCl_3$ (376 MHz)



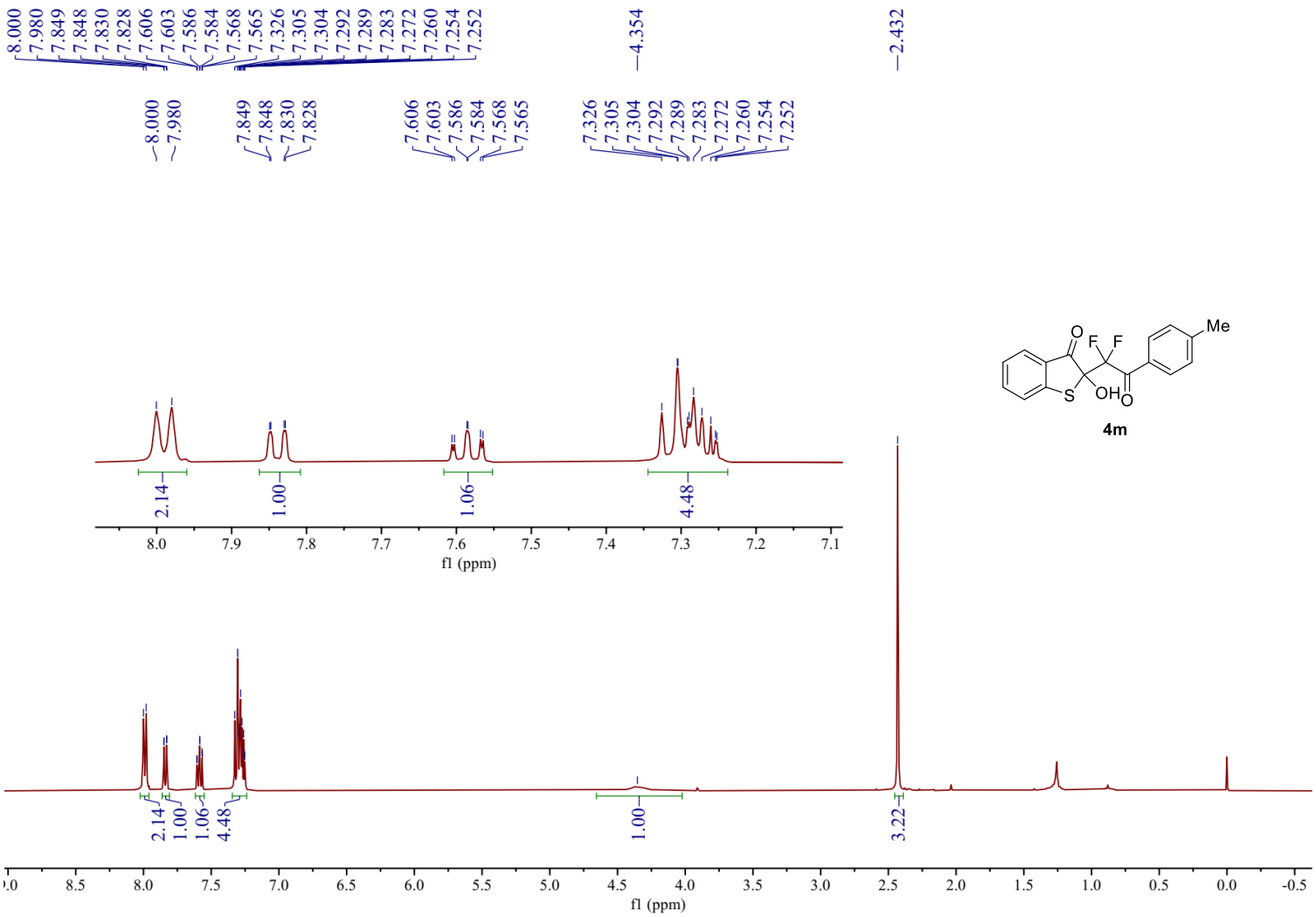
^{1}H NMR spectra of **3m** in $CDCl_3$ (400 MHz)



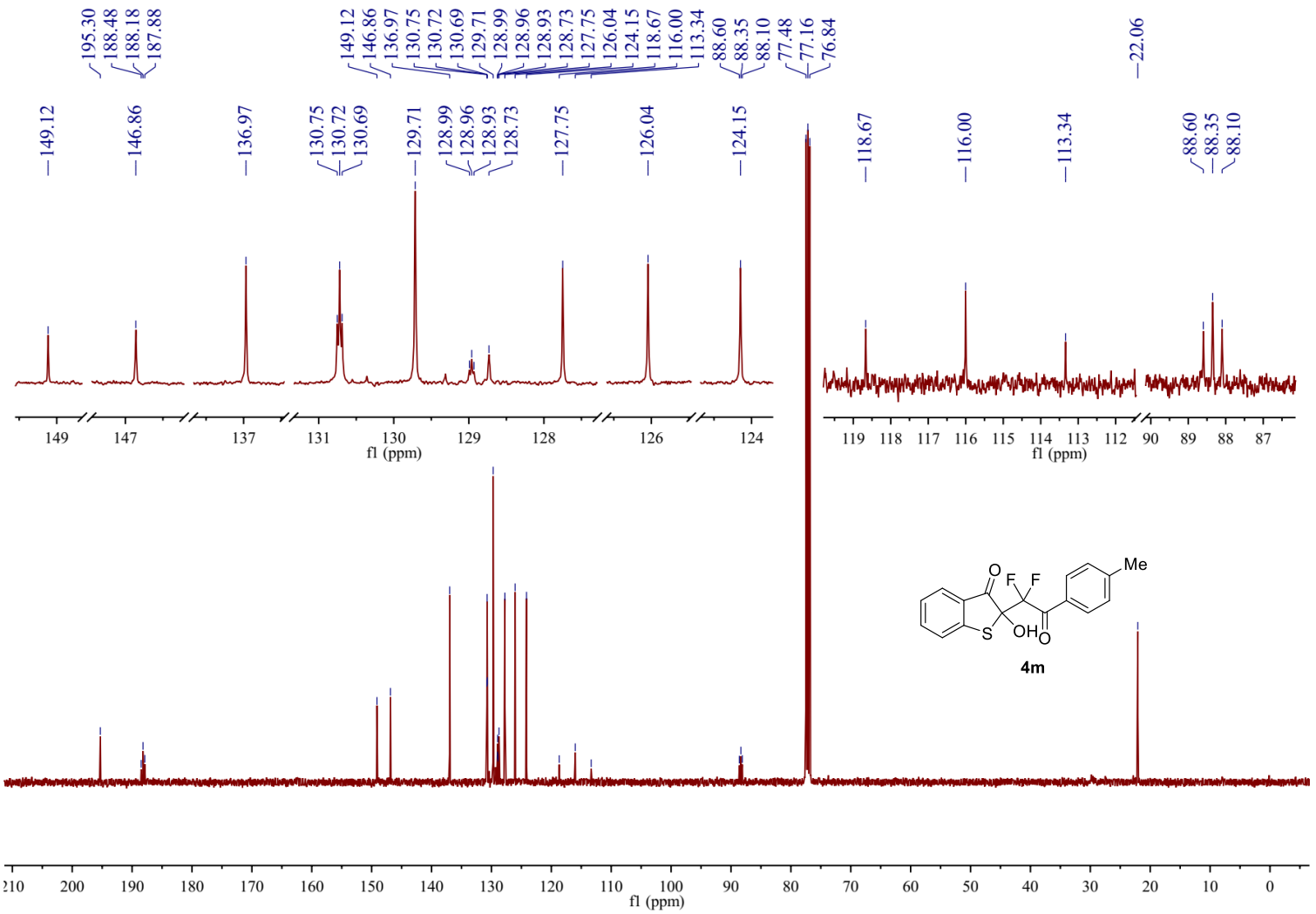
$^{13}C\{^{1}H\}$ NMR spectra of **3m** in $CDCl_3$ (100 MHz)



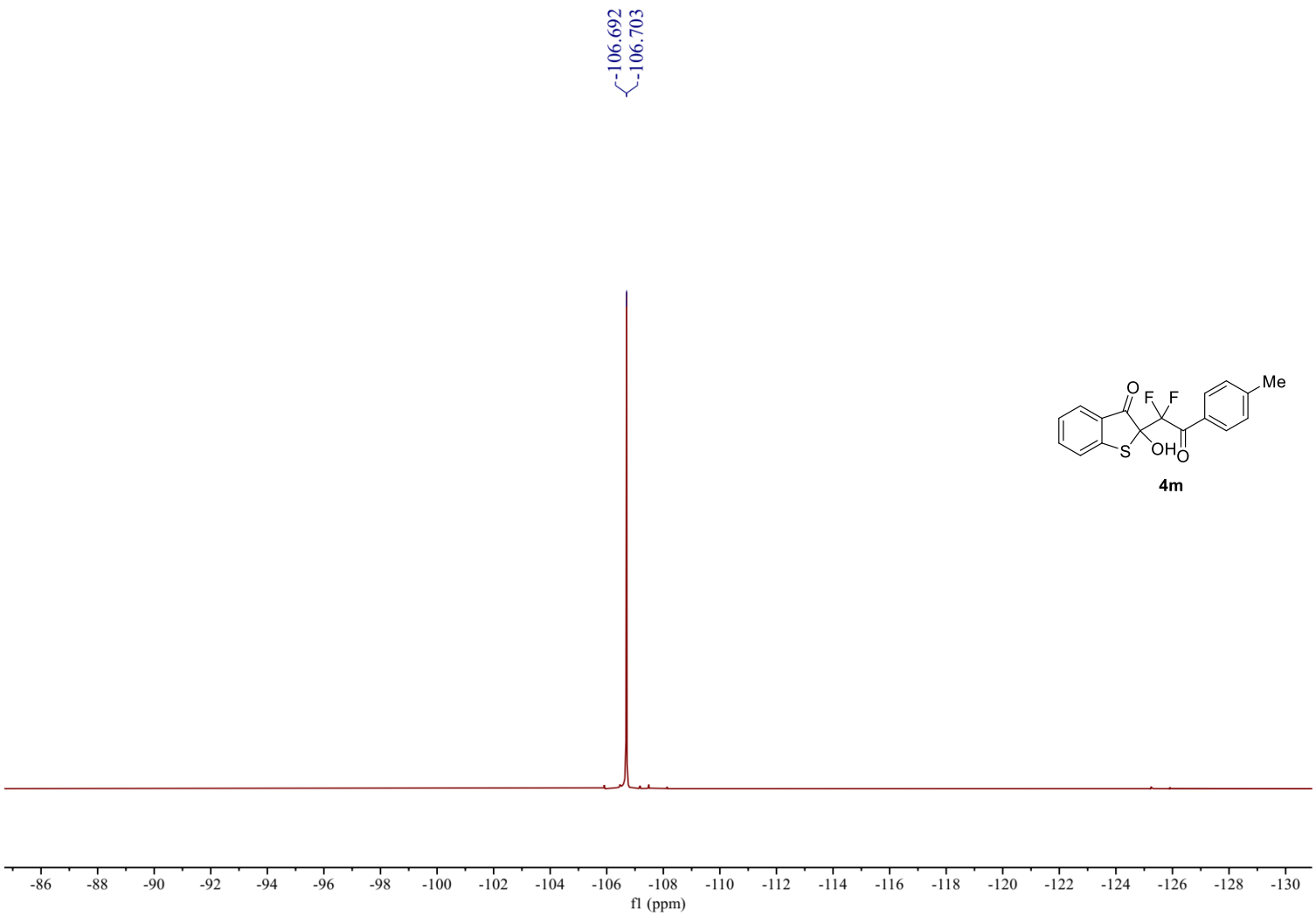
^{19}F NMR spectra of **3m** in $CDCl_3$ (376 MHz)



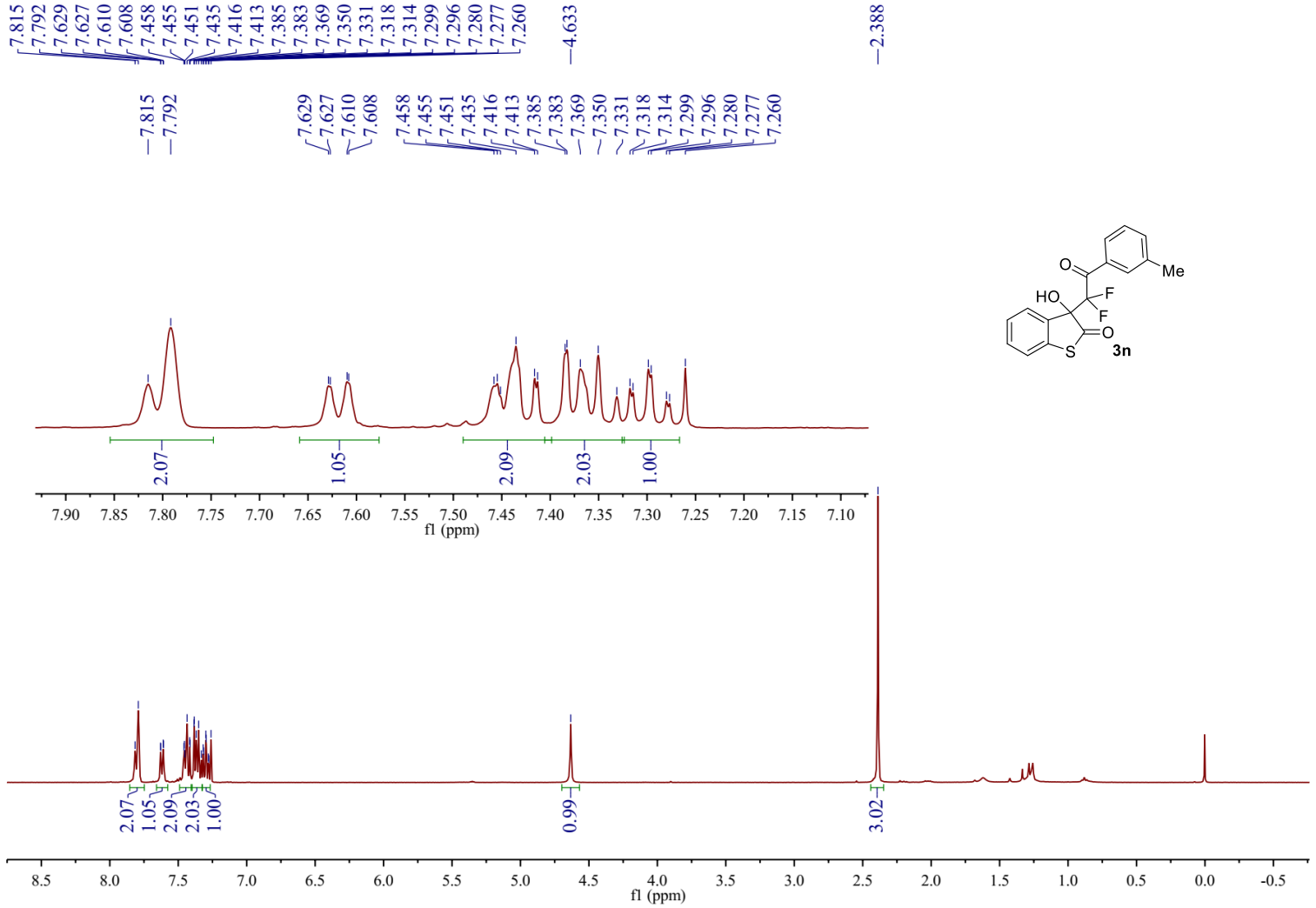
^{1}H NMR spectra of **4m** in $CDCl_3$ (400 MHz)



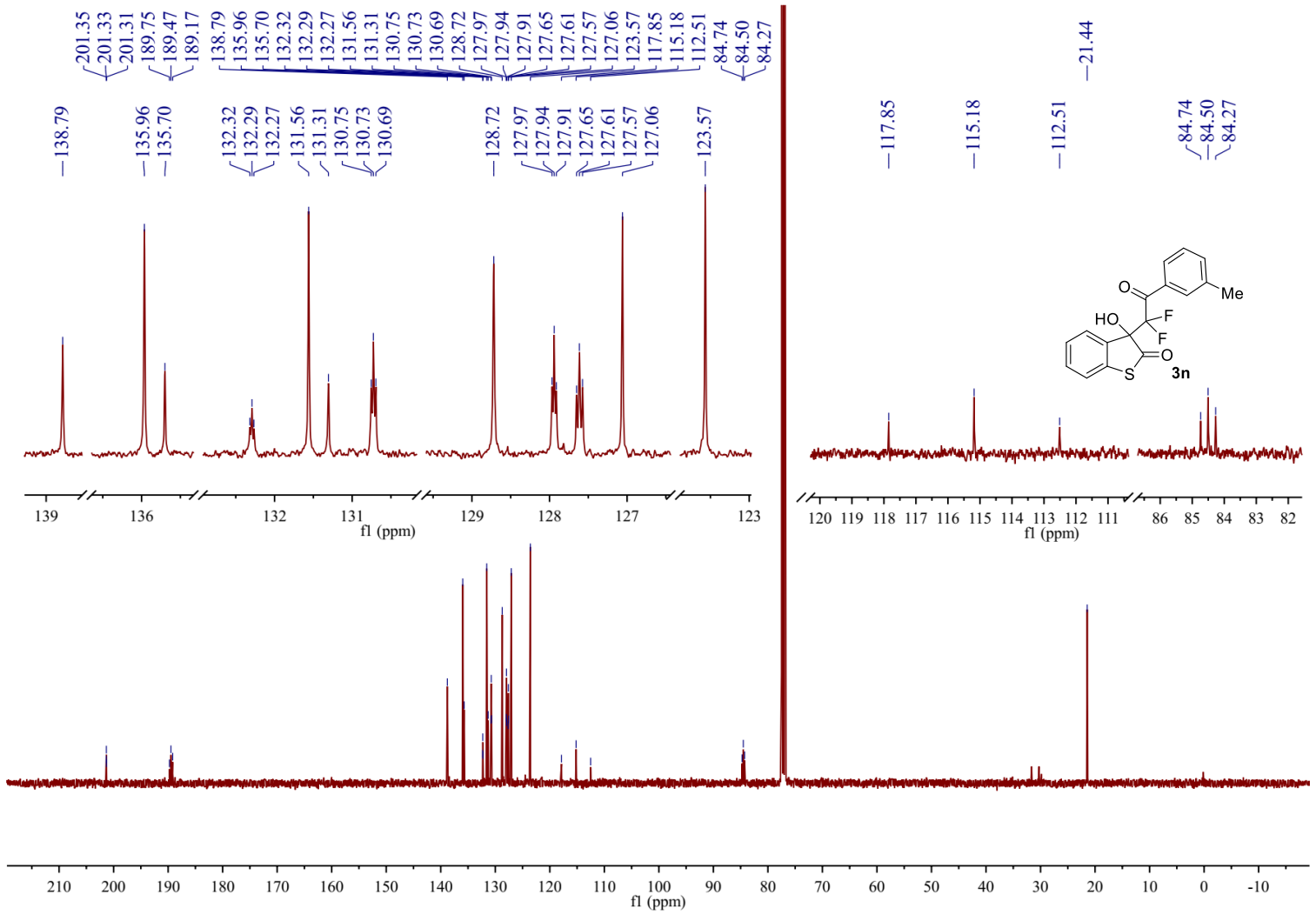
$^{13}C\{^{1}H\}$ NMR spectra of **4m** in $CDCl_3$ (100 MHz)



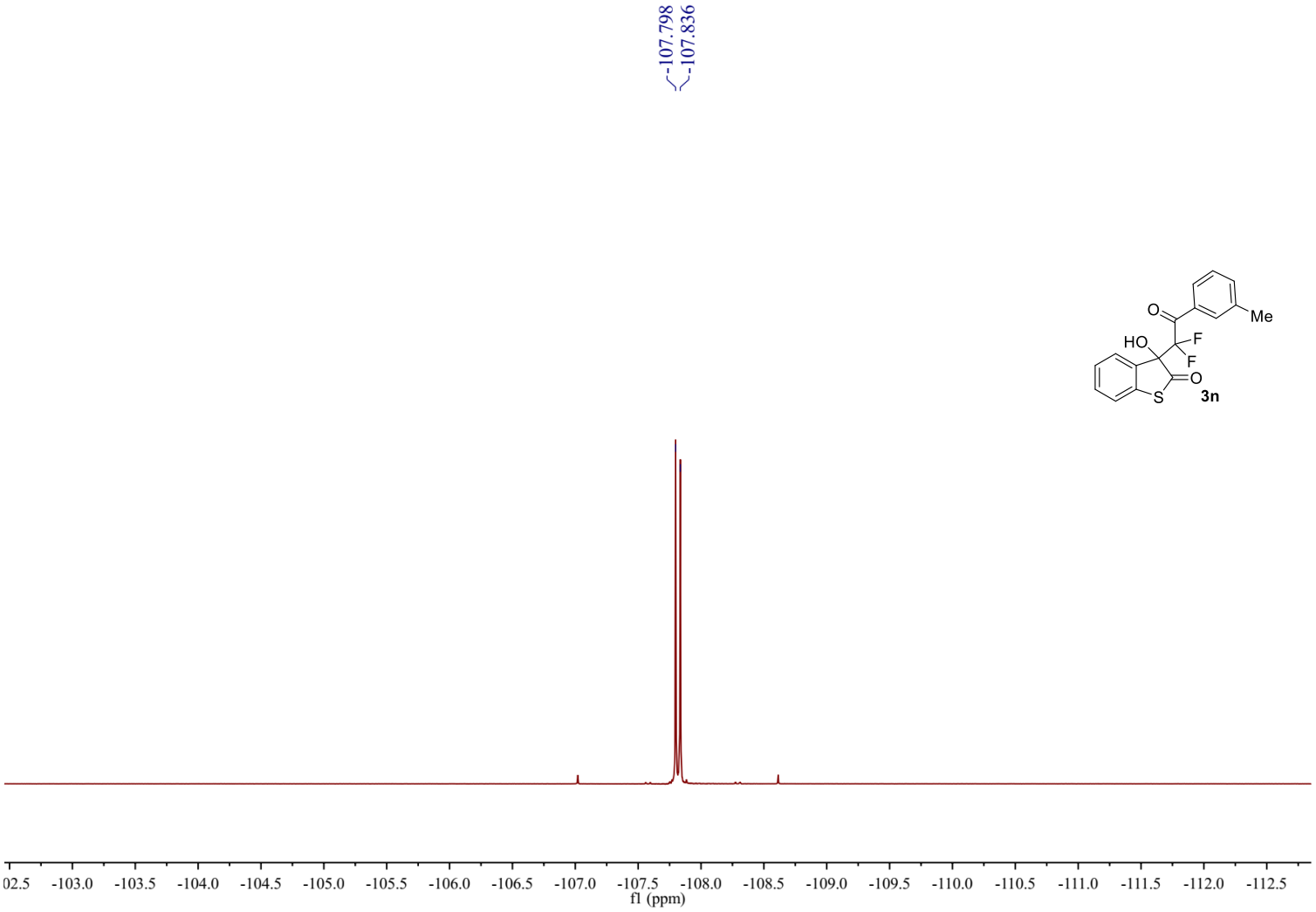
^{19}F NMR spectra of **4m** in $CDCl_3$ (376 MHz)



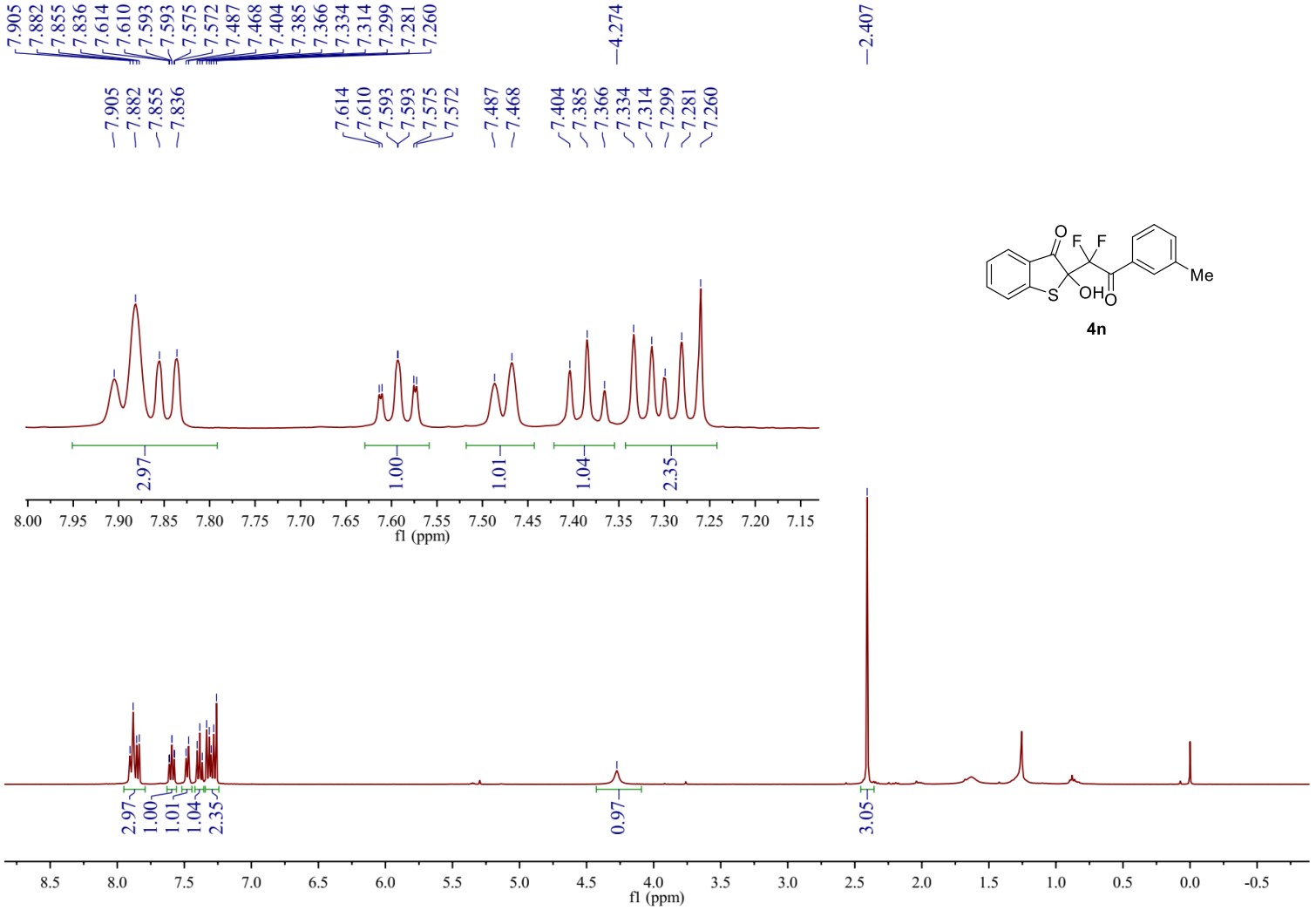
^{1}H NMR spectra of **3n** in $CDCl_3$ (400 MHz)



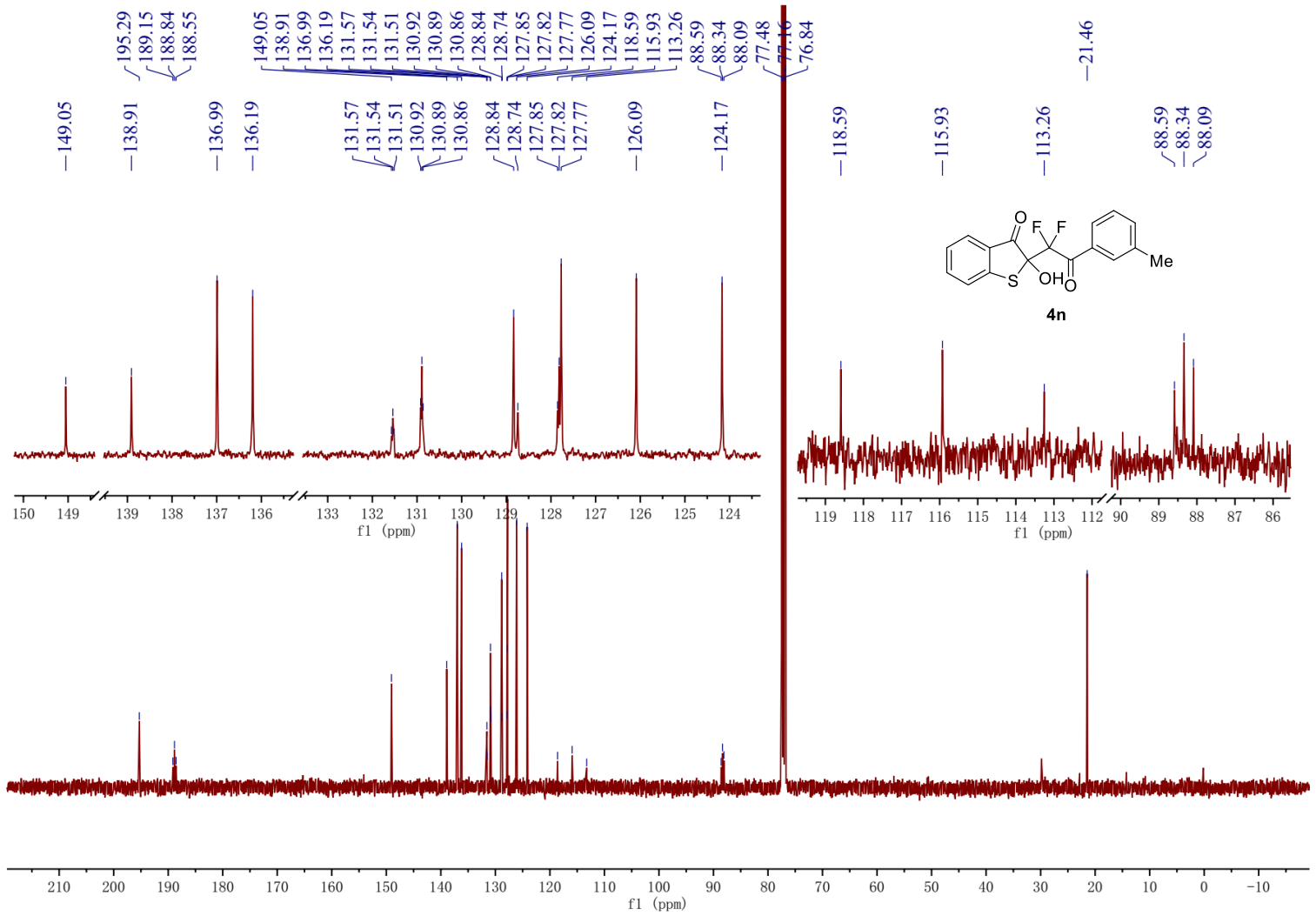
$^{13}C\{^{1}H\}$ NMR spectra of **3n** in $CDCl_3$ (100 MHz)



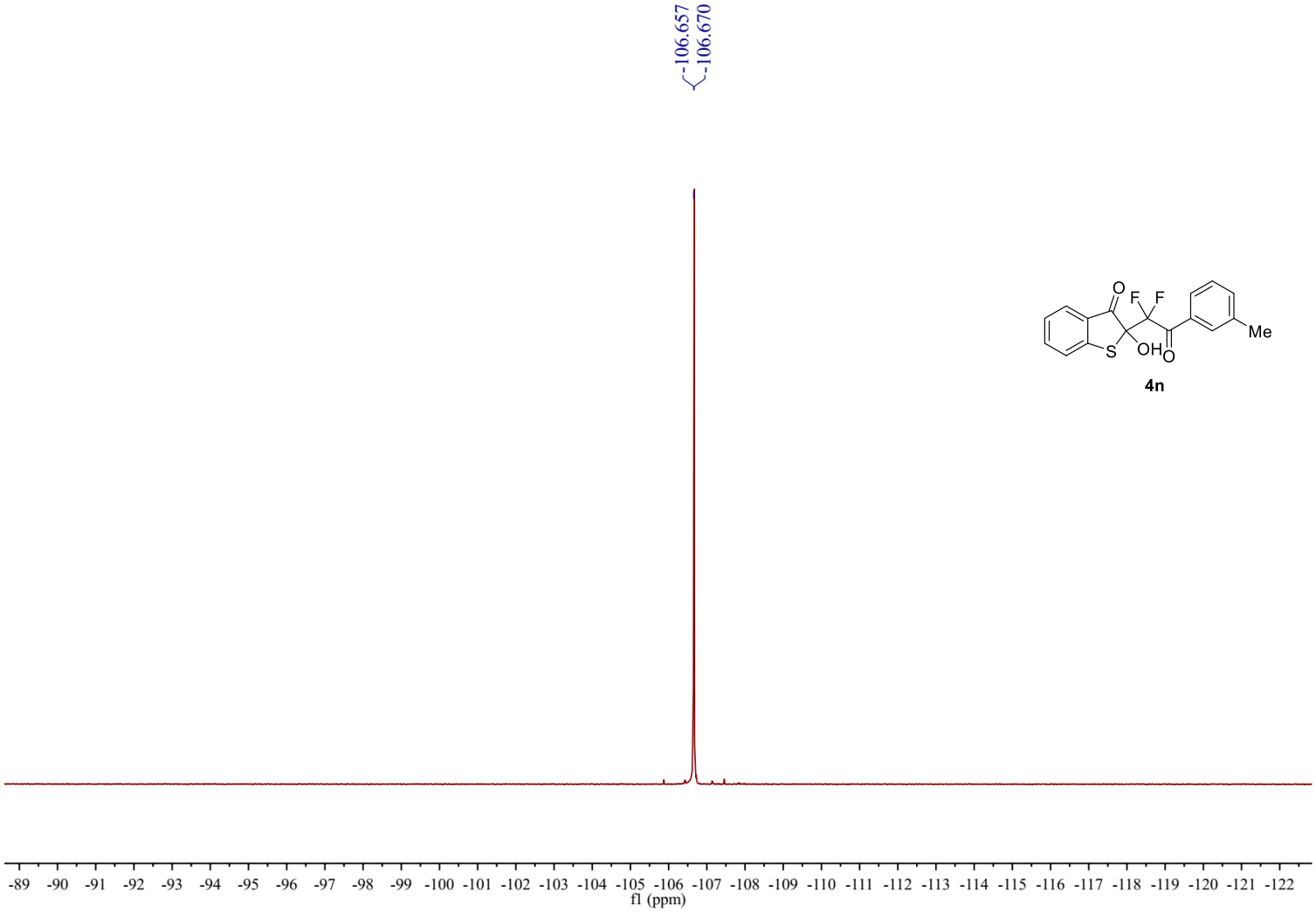
^{19}F NMR spectra of **3n** in $CDCl_3$ (376 MHz)



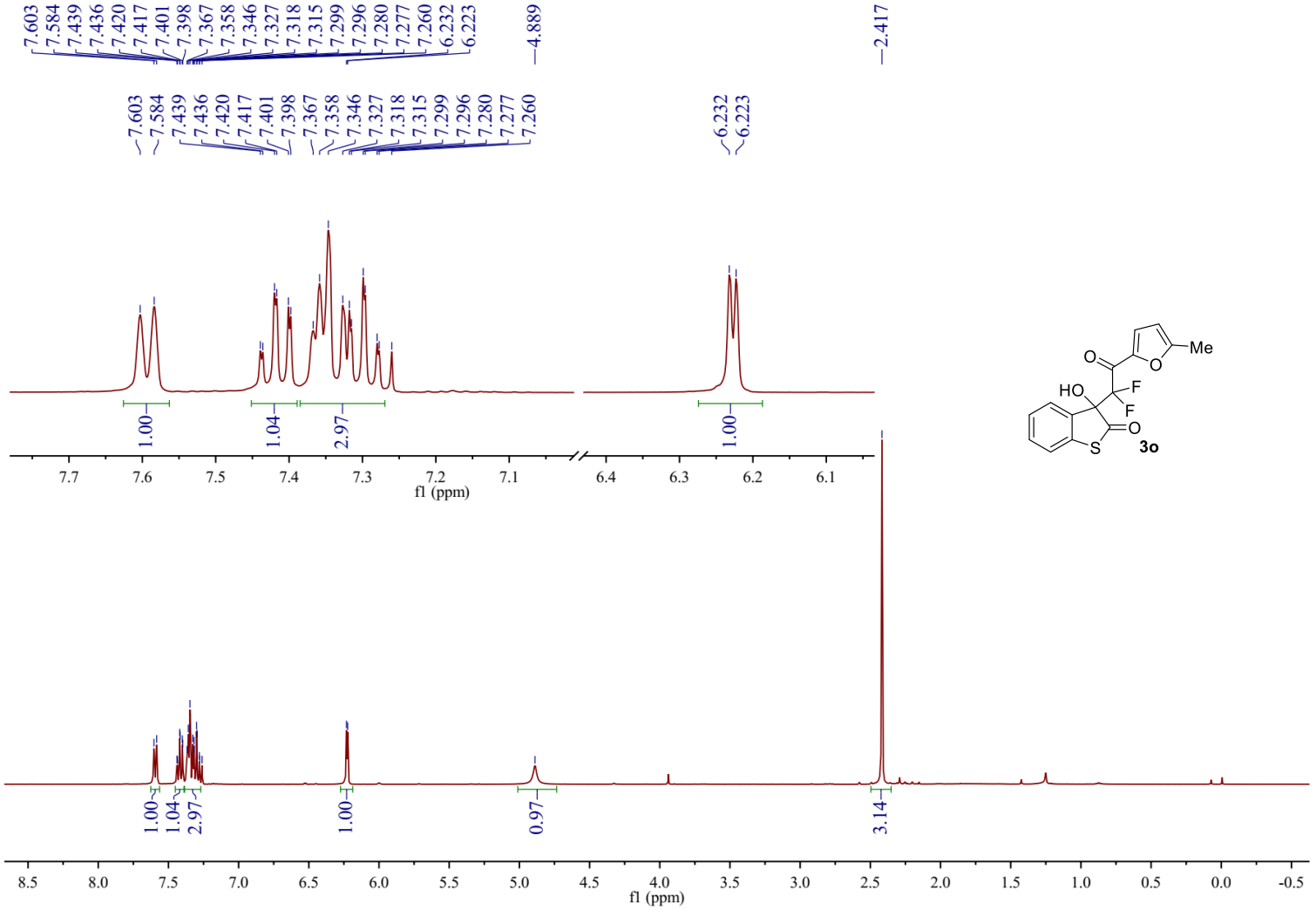
^{1}H NMR spectra of **4n** in $CDCl_3$ (400 MHz)



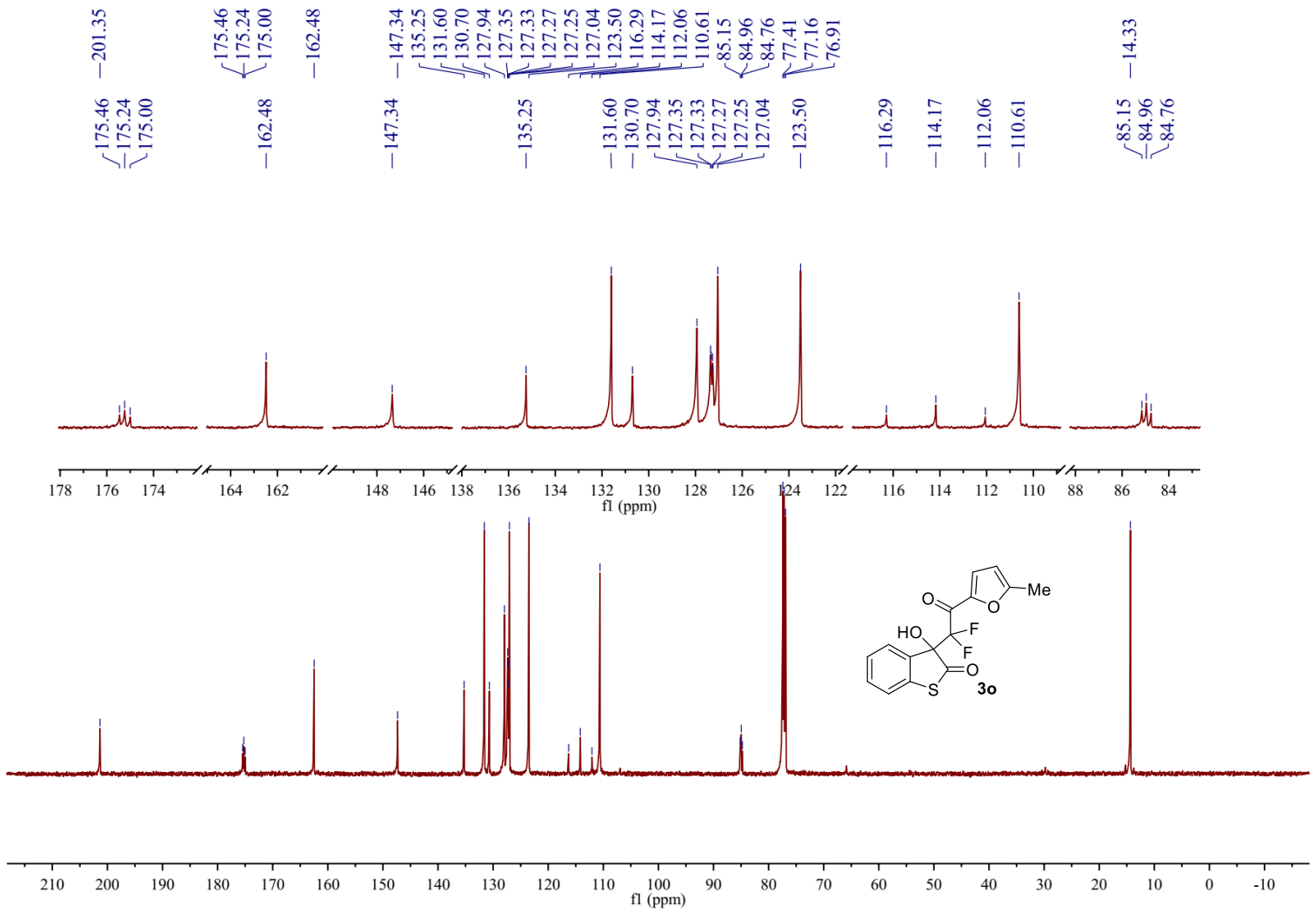
$^{13}C\{^{1}H\}$ NMR spectra of **4n** in $CDCl_3$ (100 MHz)



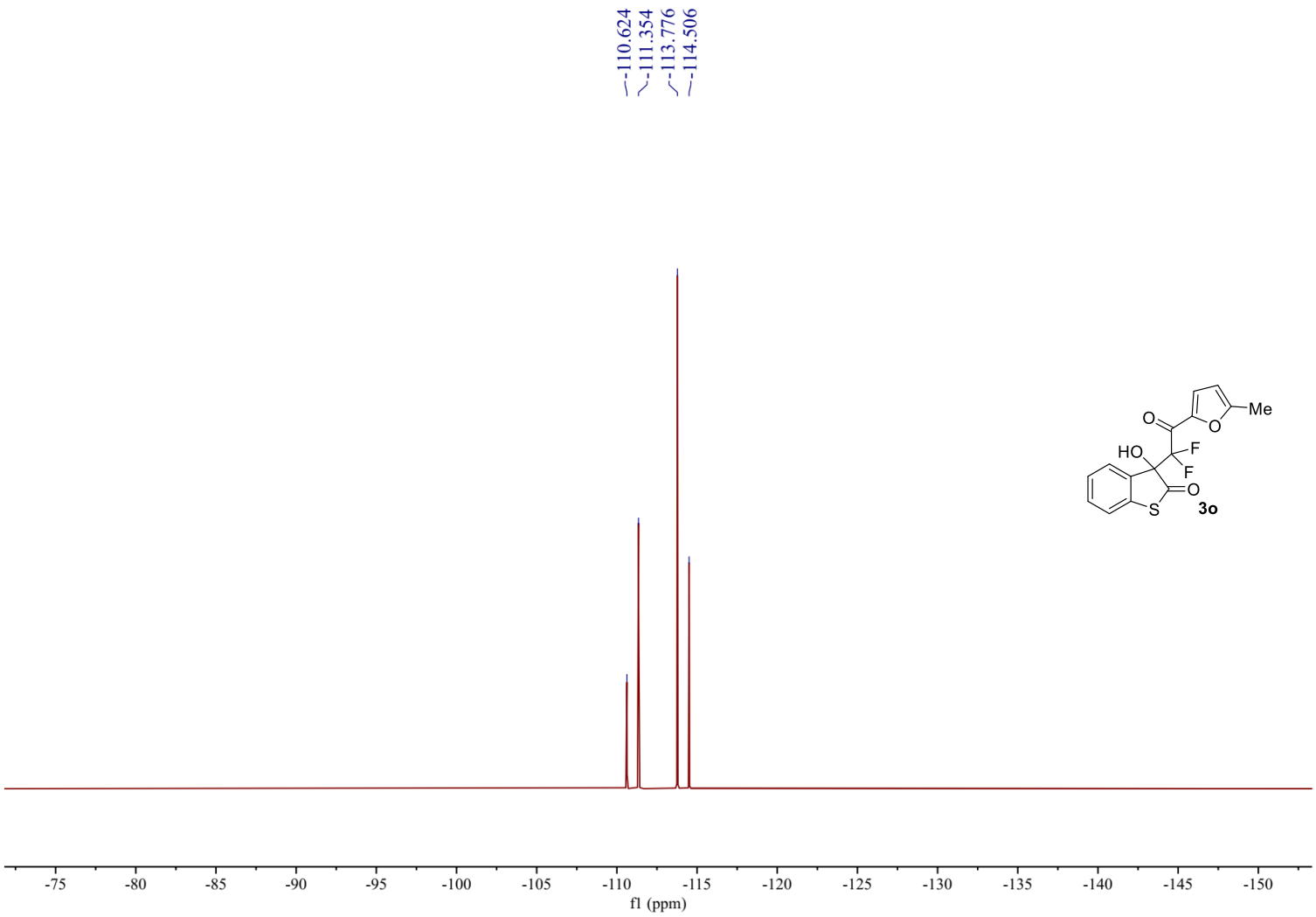
^{19}F NMR spectra of **4n** in $CDCl_3$ (376 MHz)



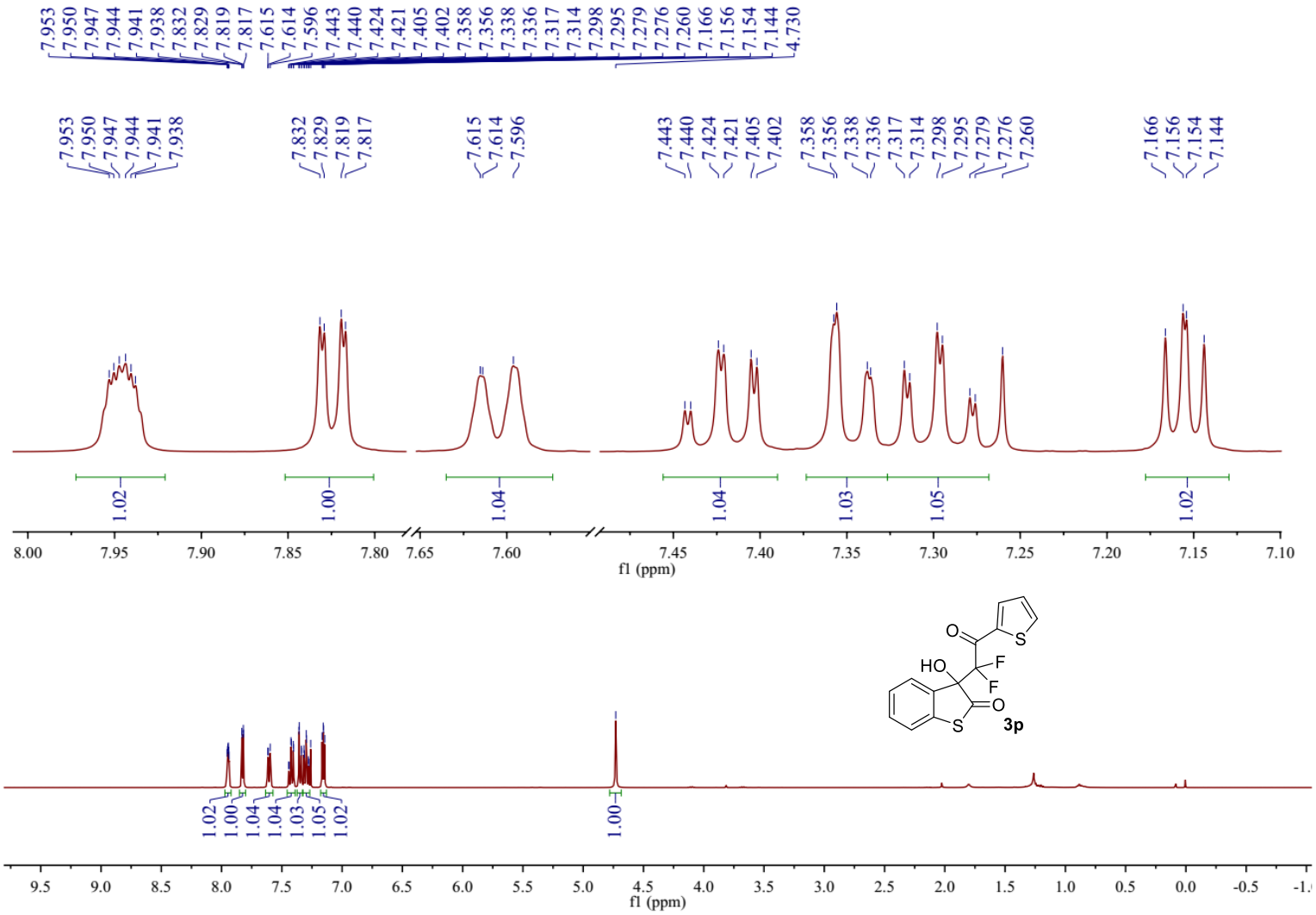
^{1}H NMR spectra of **3o** in $CDCl_3$ (400 MHz)



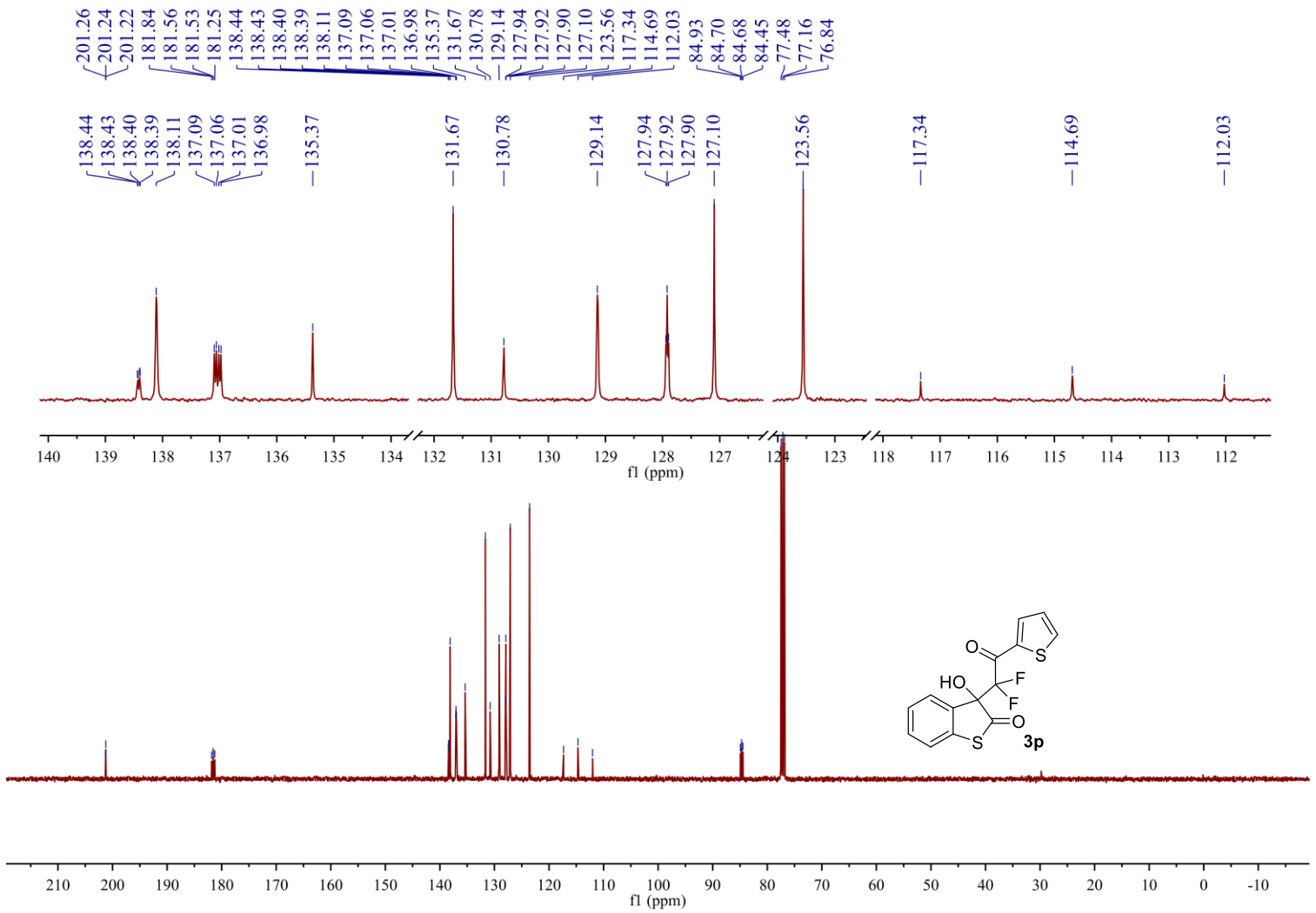
$^{13}C\{^{1}H\}$ NMR spectra of **3o** in $CDCl_3$ (125 MHz)



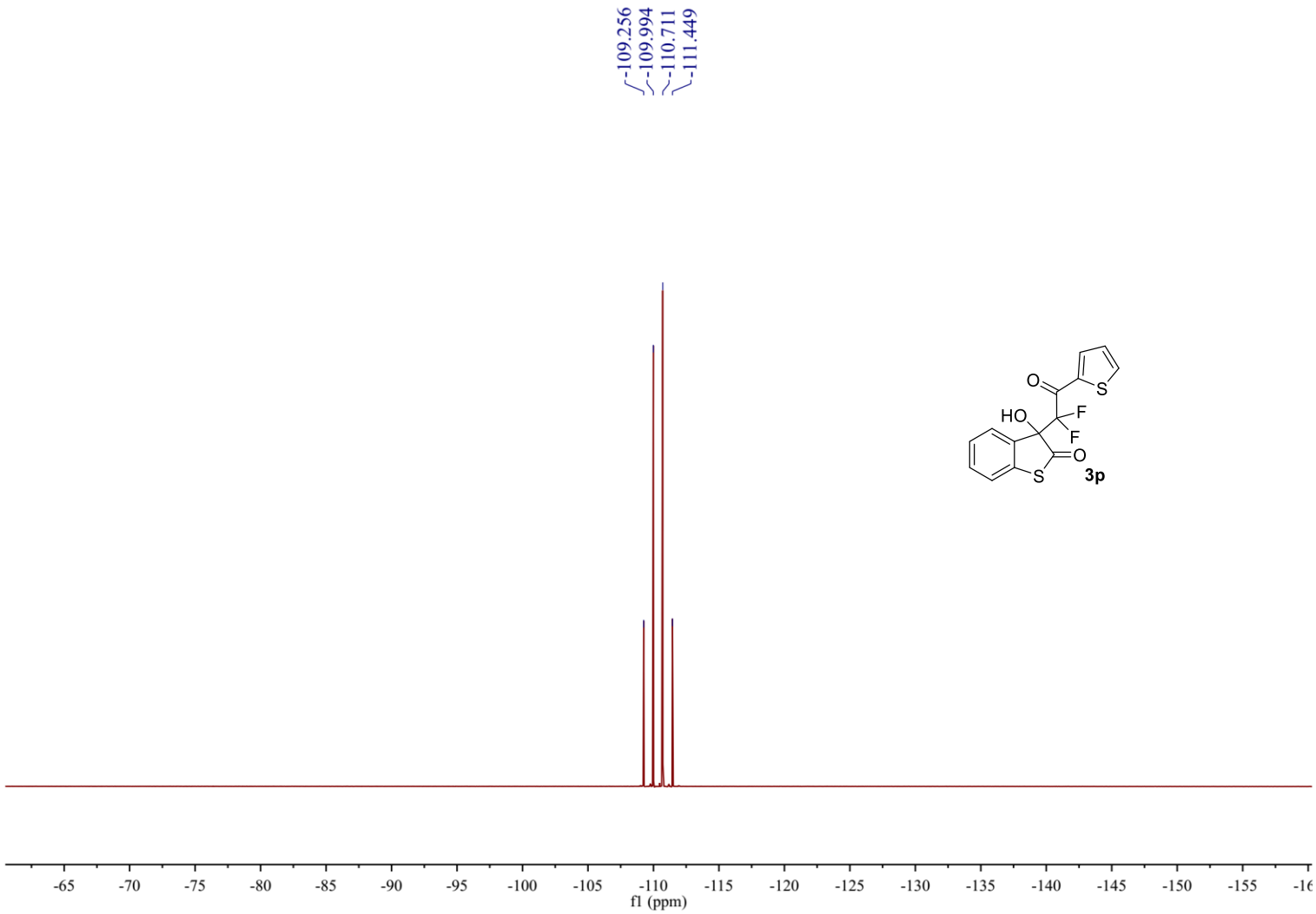
^{19}F NMR spectra of **3o** in $CDCl_3$ (376 MHz)



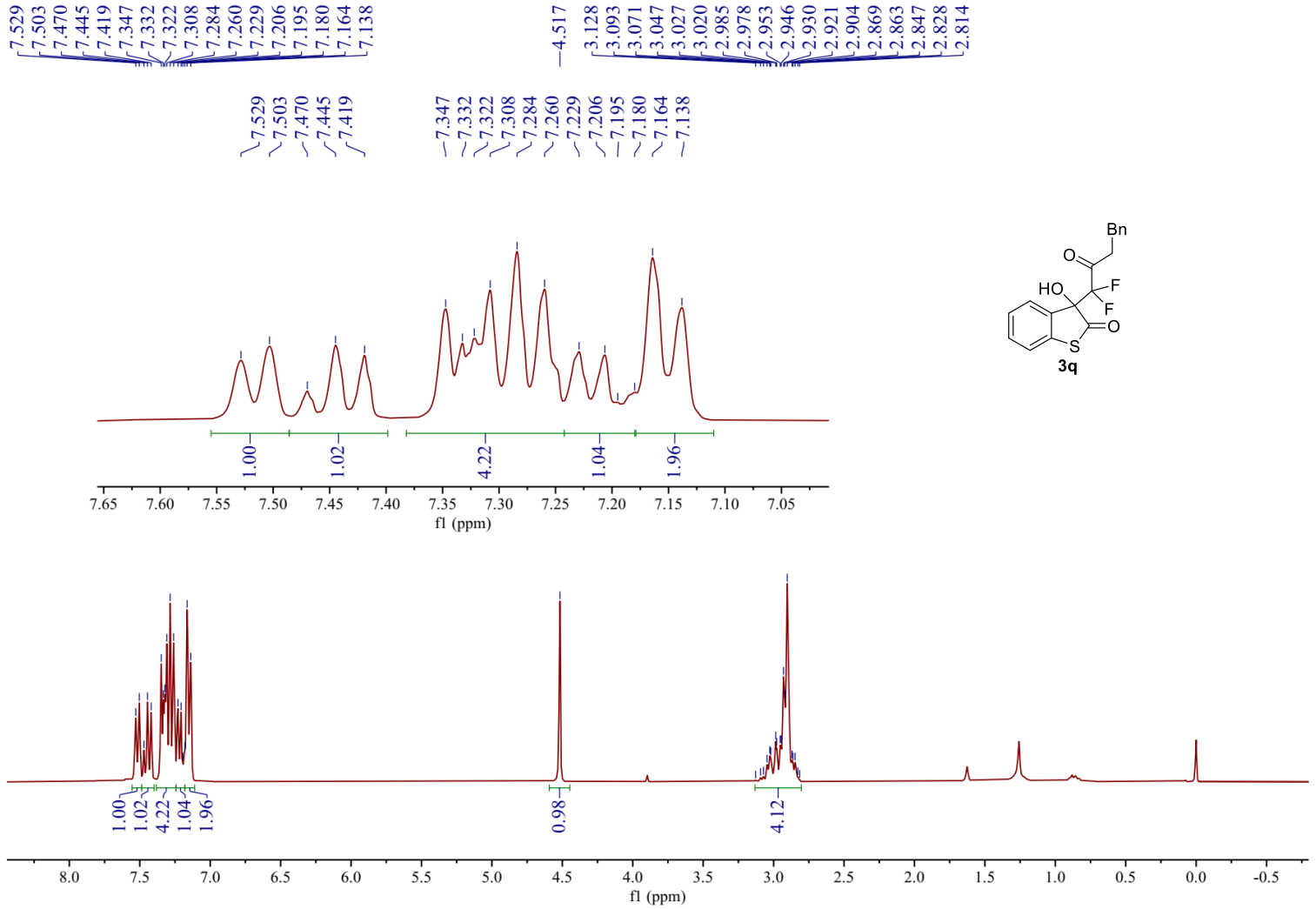
^{1}H NMR spectra of **3p** in $CDCl_3$ (400 MHz)



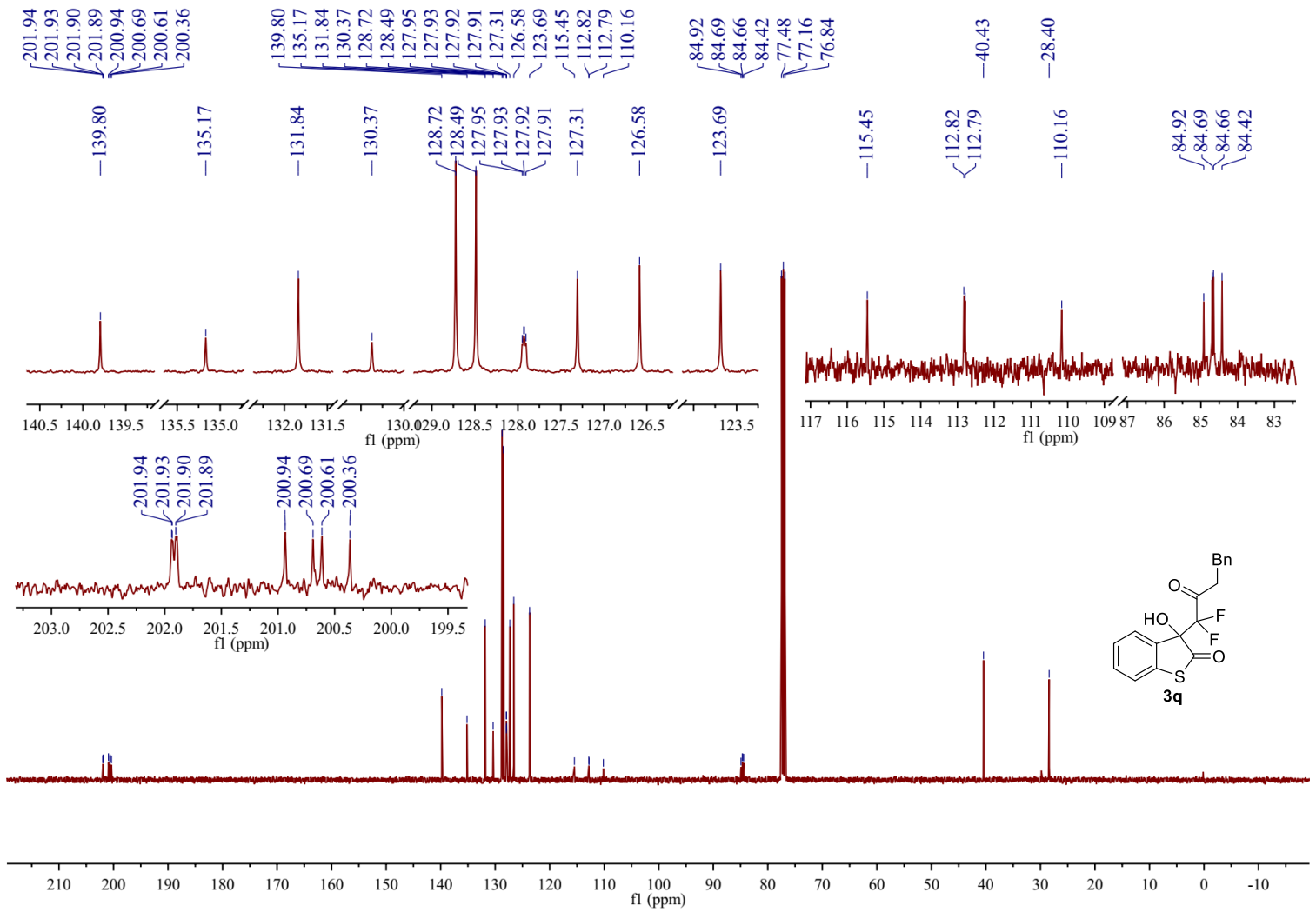
$^{13}C\{^{1}H\}$ NMR spectra of **3p** in $CDCl_3$ (100 MHz)



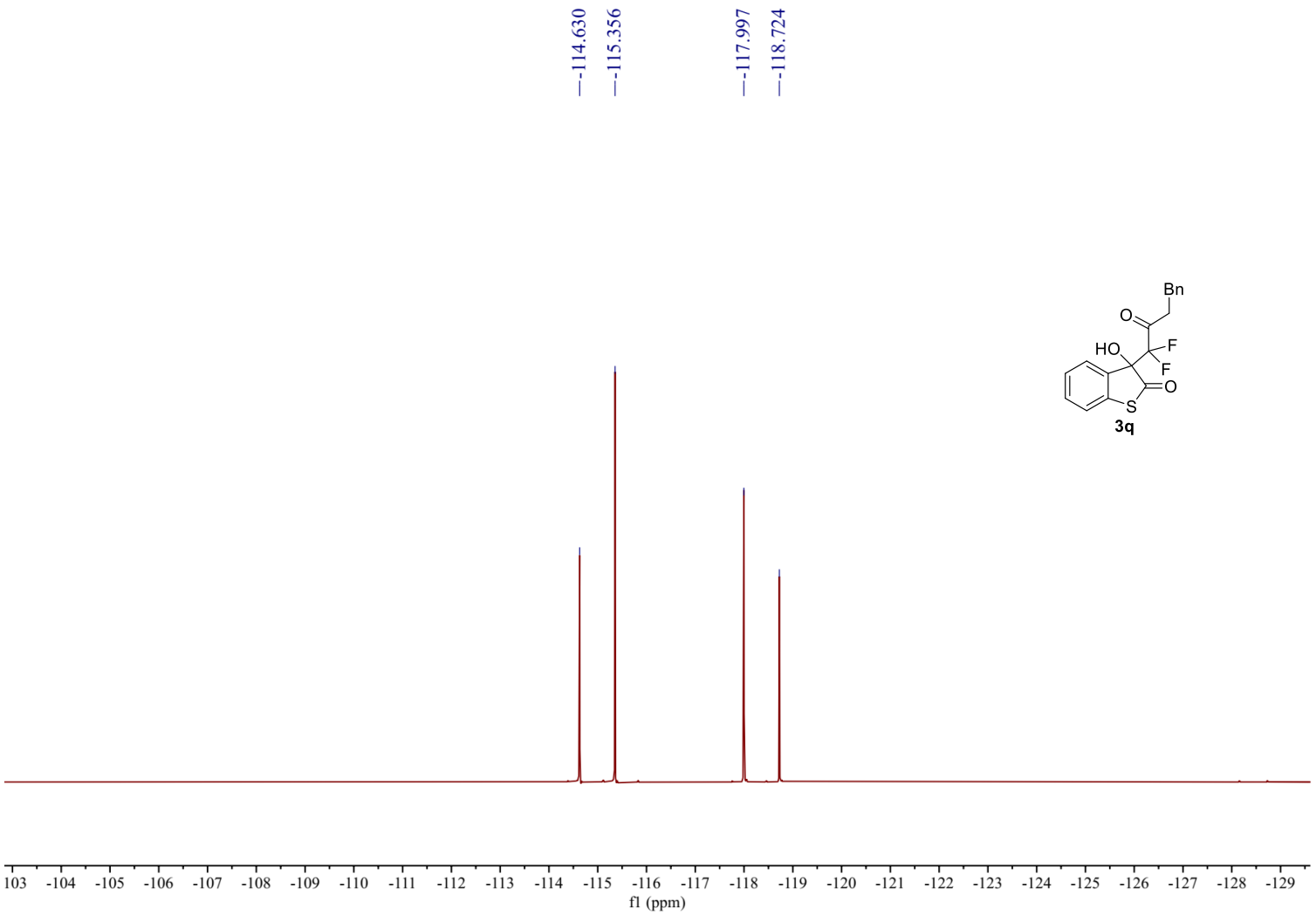
^{19}F NMR spectra of **3p** in $CDCl_3$ (376 MHz)



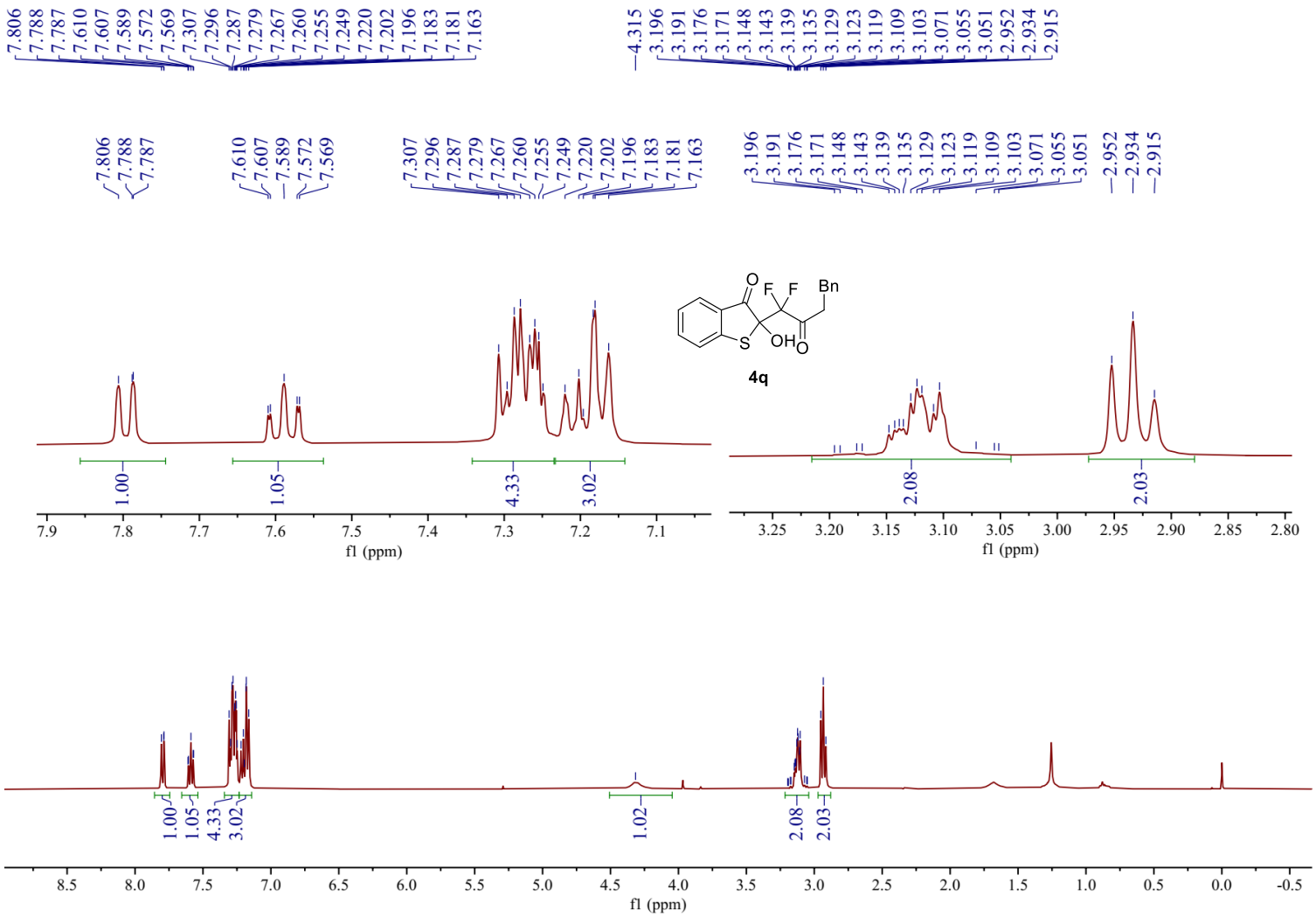
^{1}H NMR spectra of **3q** in $CDCl_3$ (400 MHz)



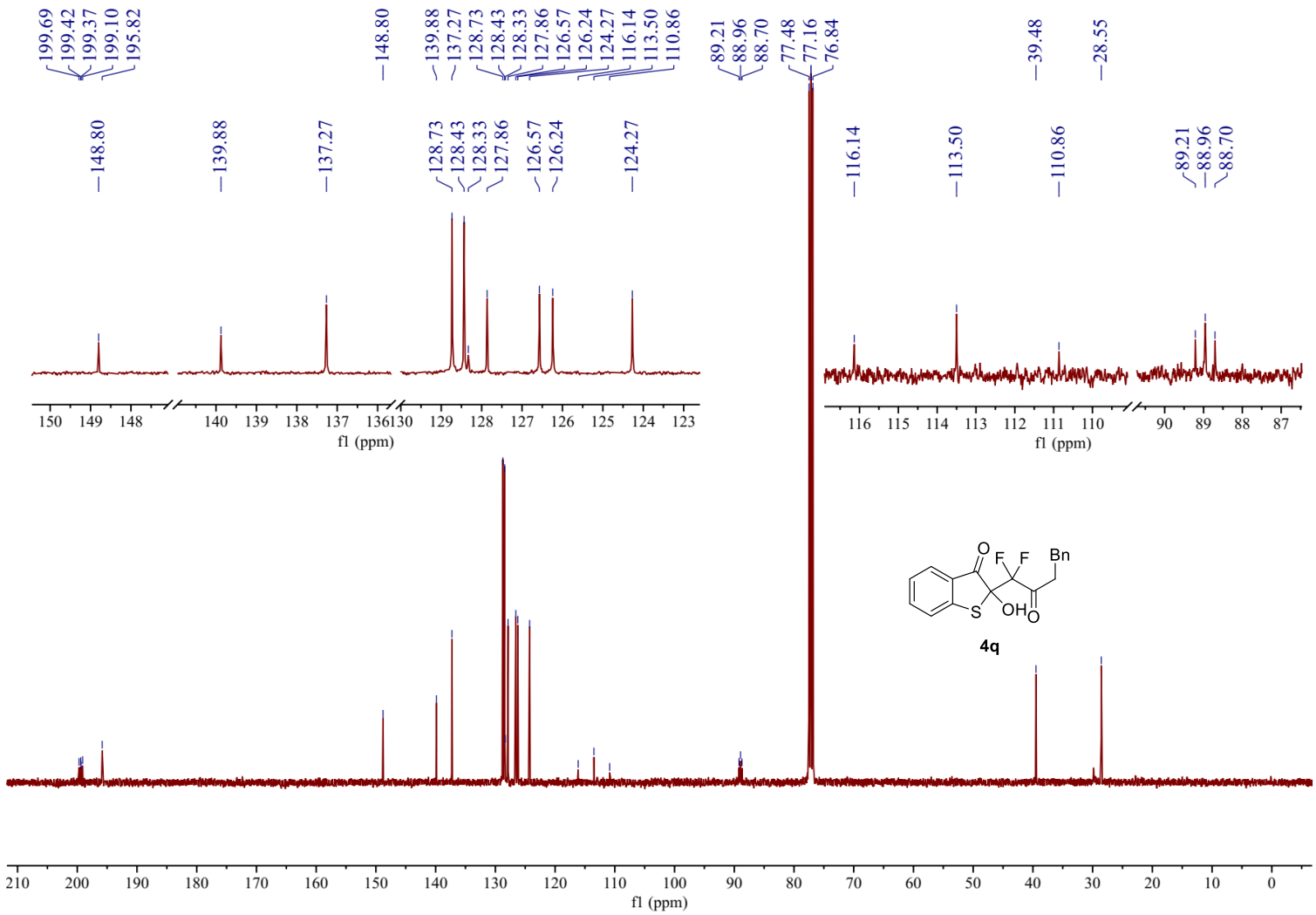
$^{13}C\{^{1}H\}$ NMR spectra of **3q** in $CDCl_3$ (100 MHz)



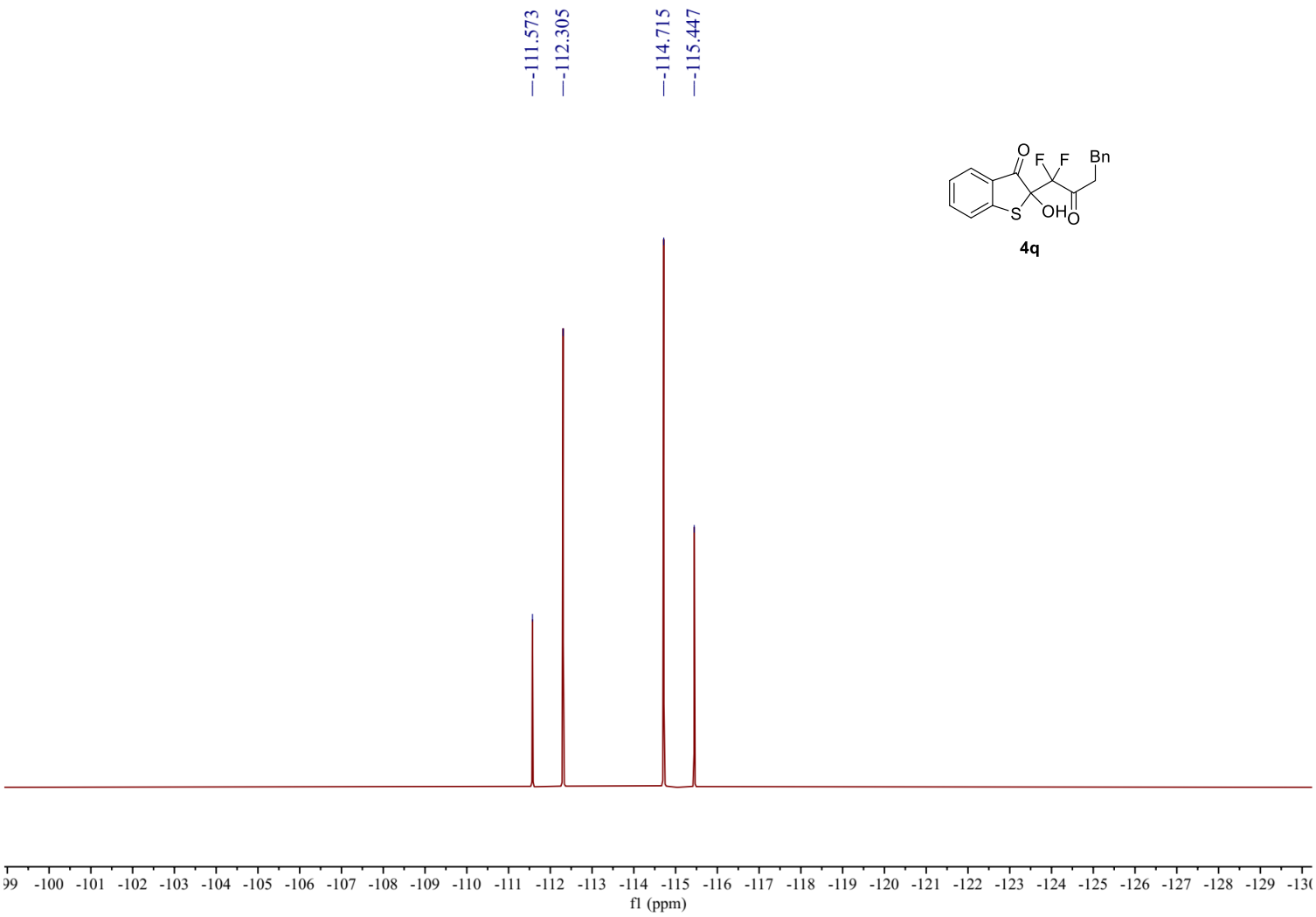
^{19}F NMR spectra of **3q** in $CDCl_3$ (376 MHz)



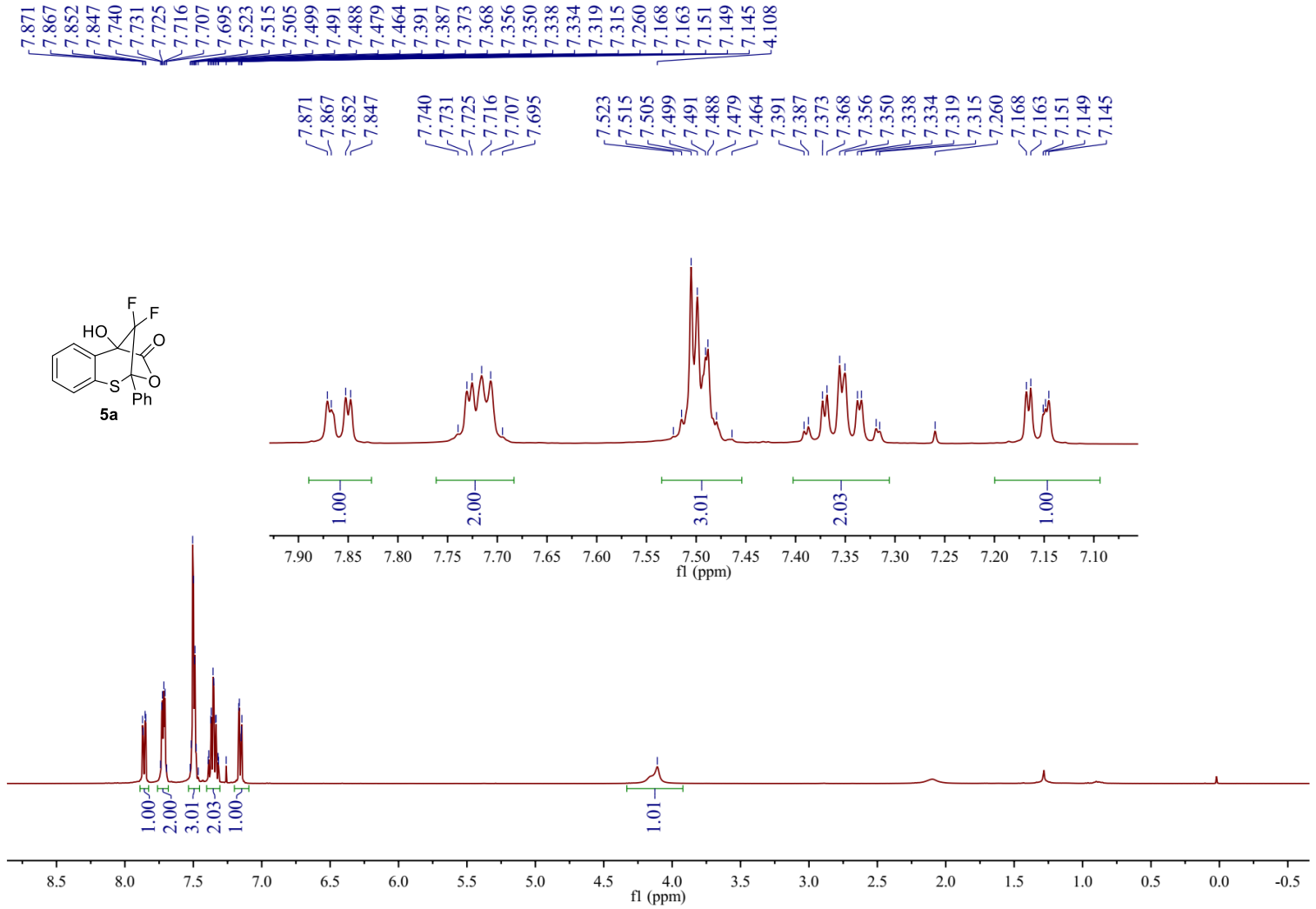
^{1}H NMR spectra of **4q** in $CDCl_3$ (400 MHz)



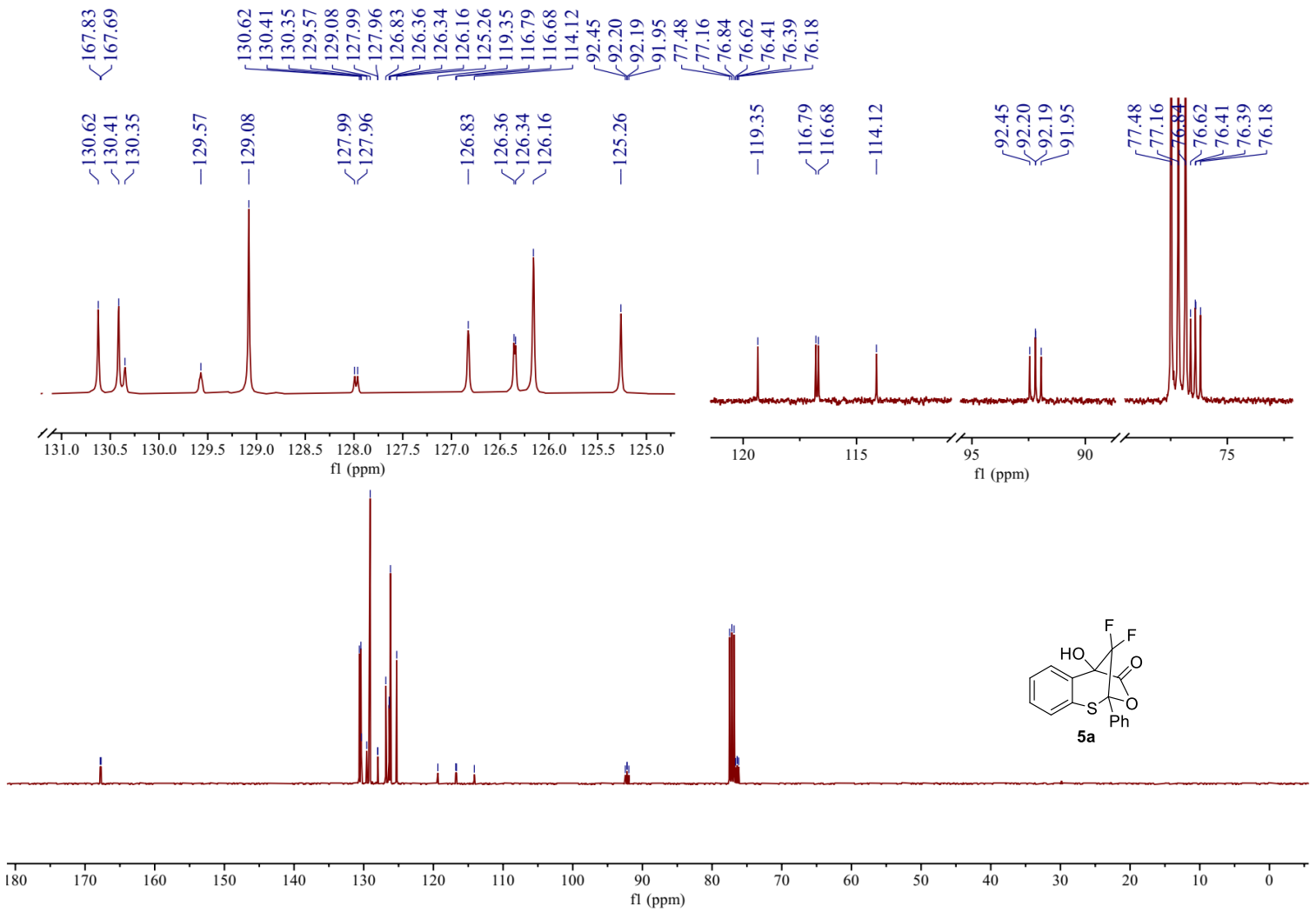
$^{13}C\{^{1}H\}$ NMR spectra of **4q** in $CDCl_3$ (100 MHz)



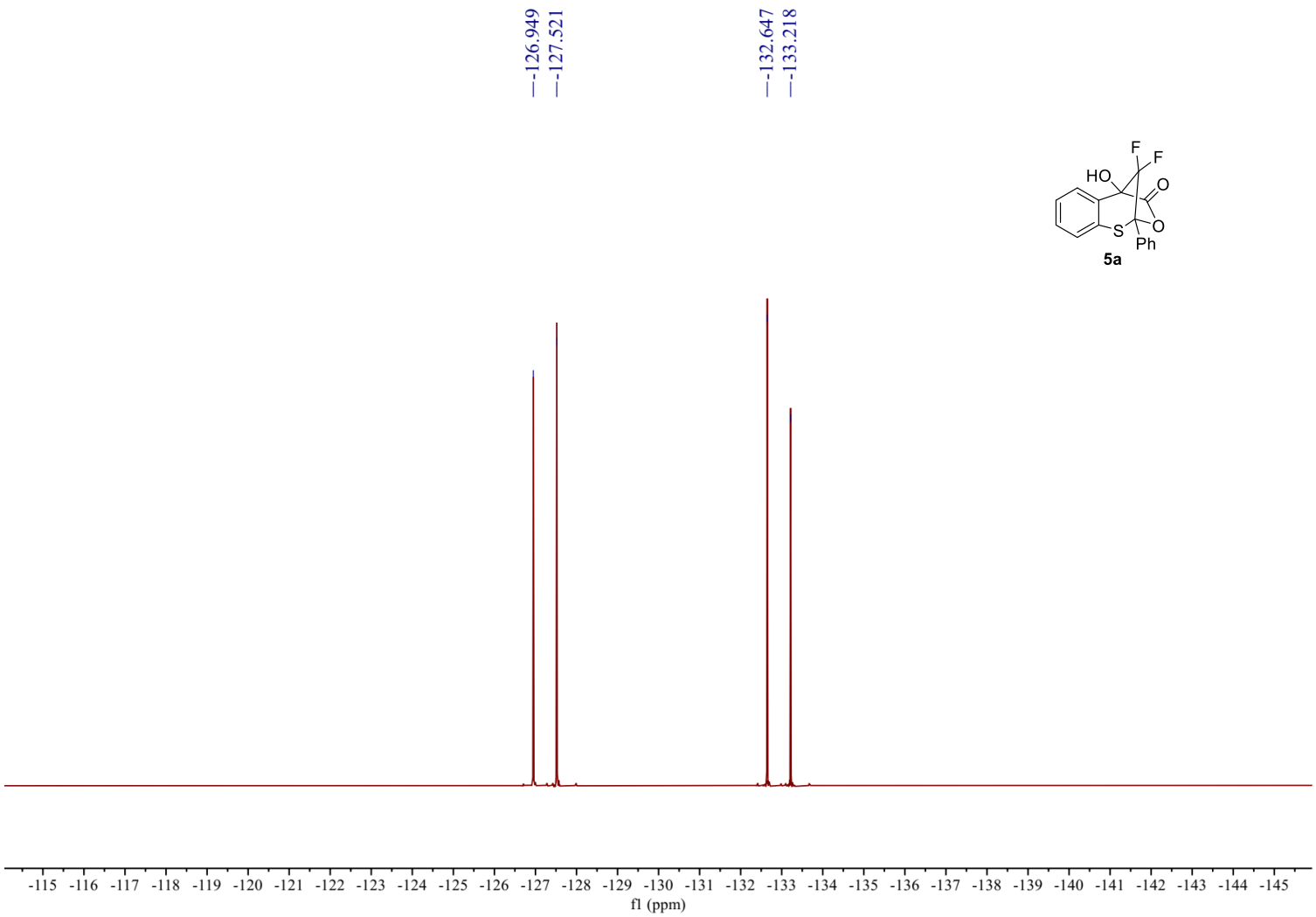
^{19}F NMR spectra of **4q** in $CDCl_3$ (376 MHz)



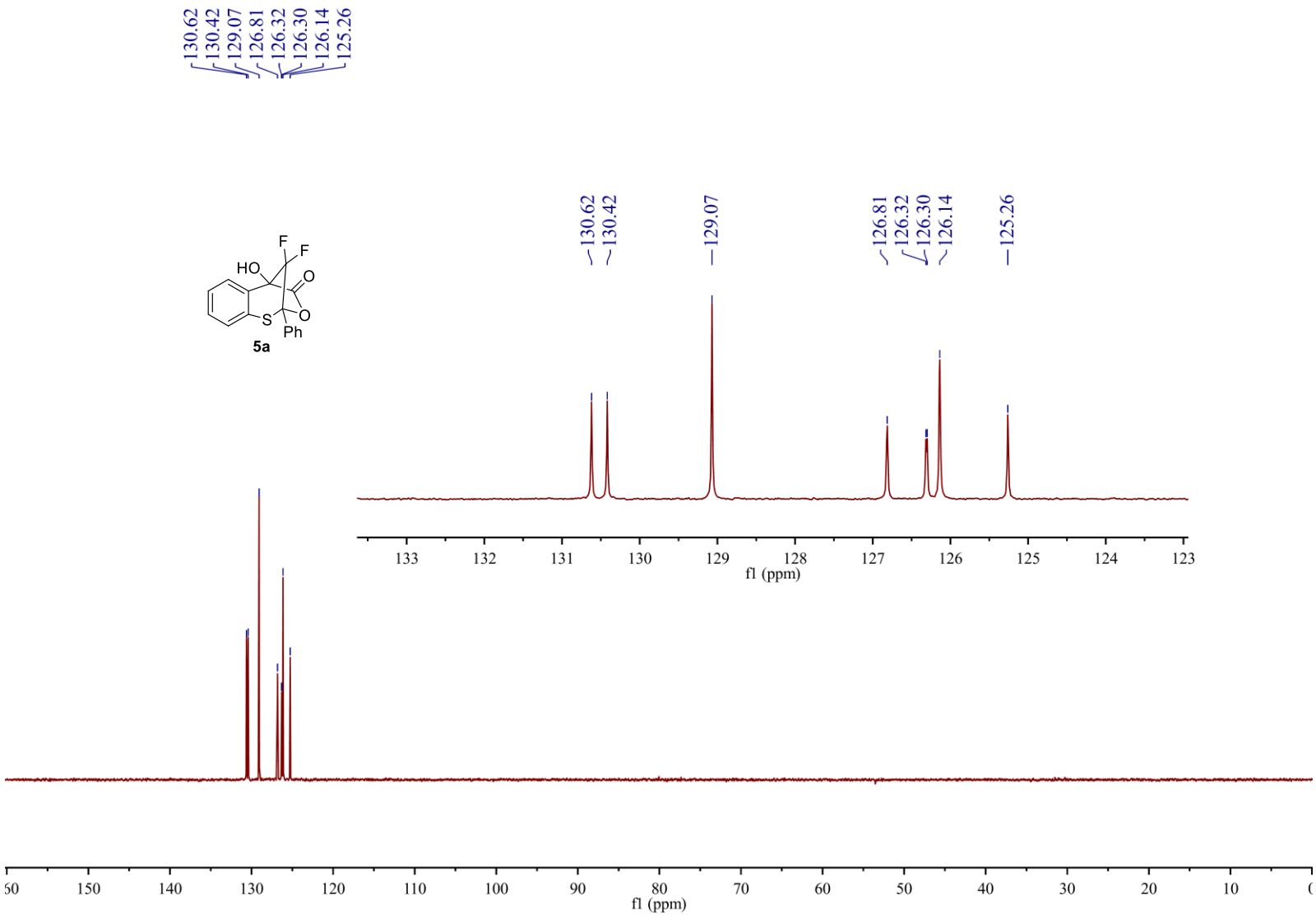
^{1}H NMR spectra of **5a** in $CDCl_3$ (400 MHz)



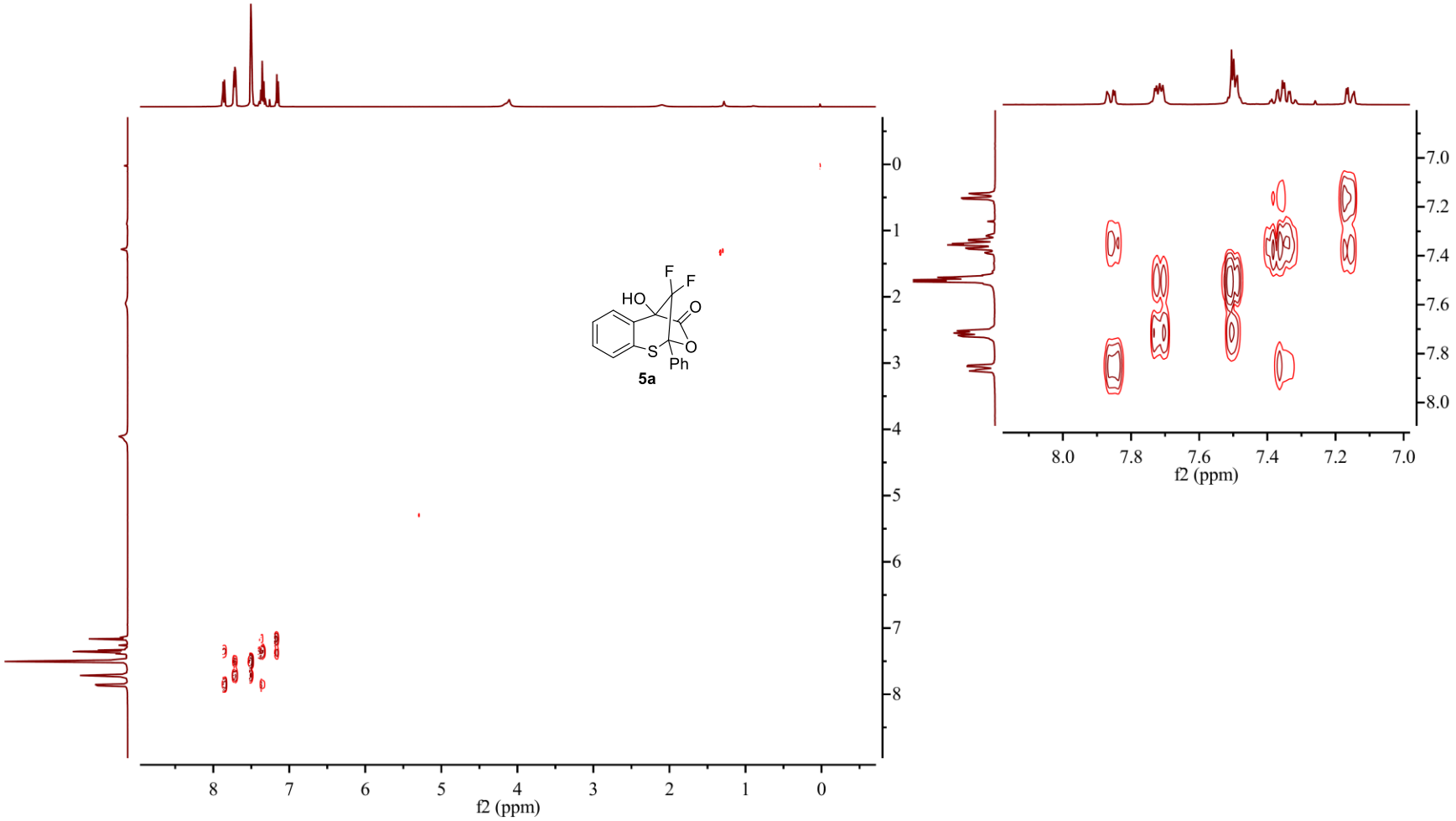
$^{13}C\{^{1}H\}$ NMR spectra of **5a** in $CDCl_3$ (100 MHz)



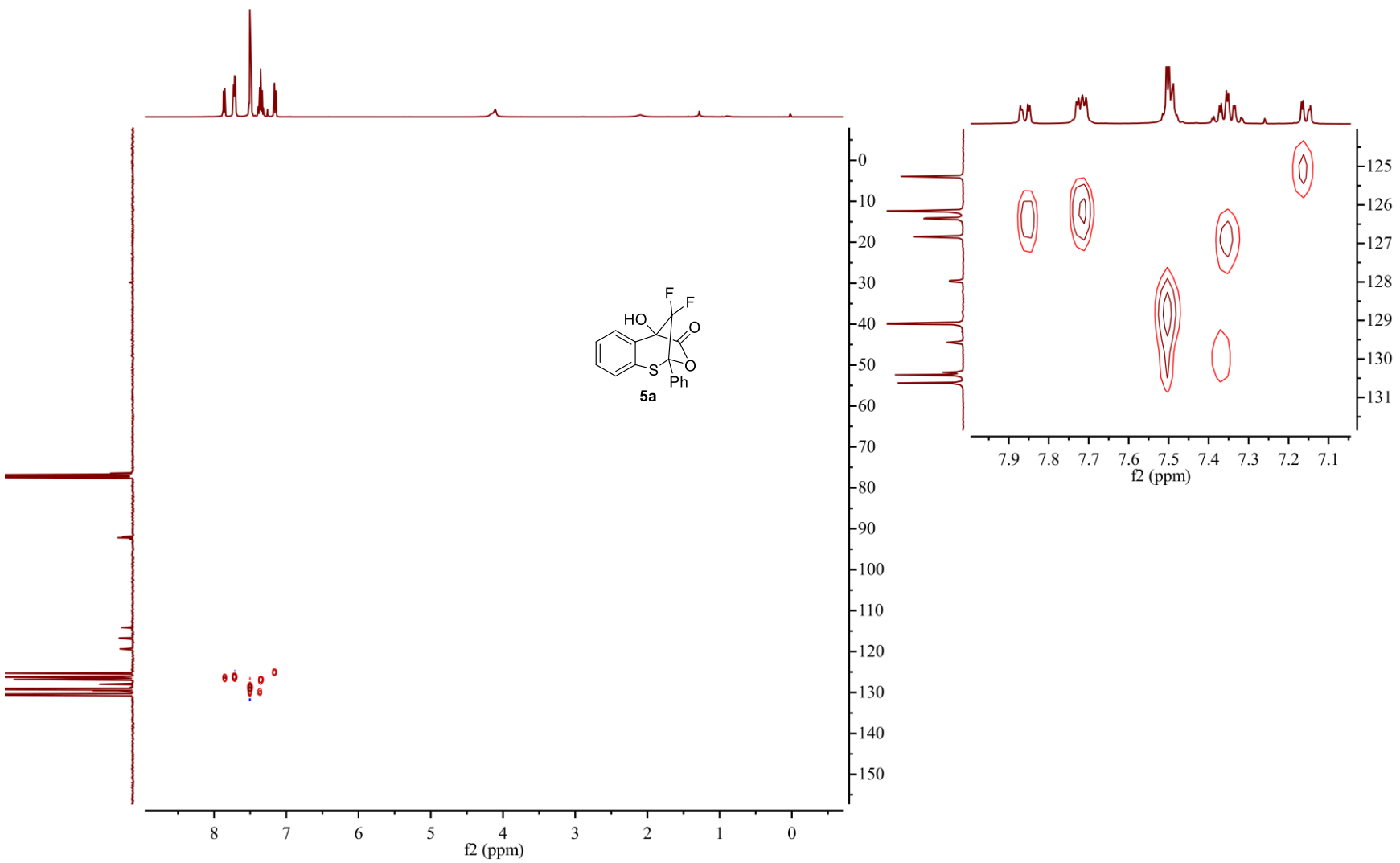
^{19}F NMR spectra of **5a** in $CDCl_3$ (376 MHz)



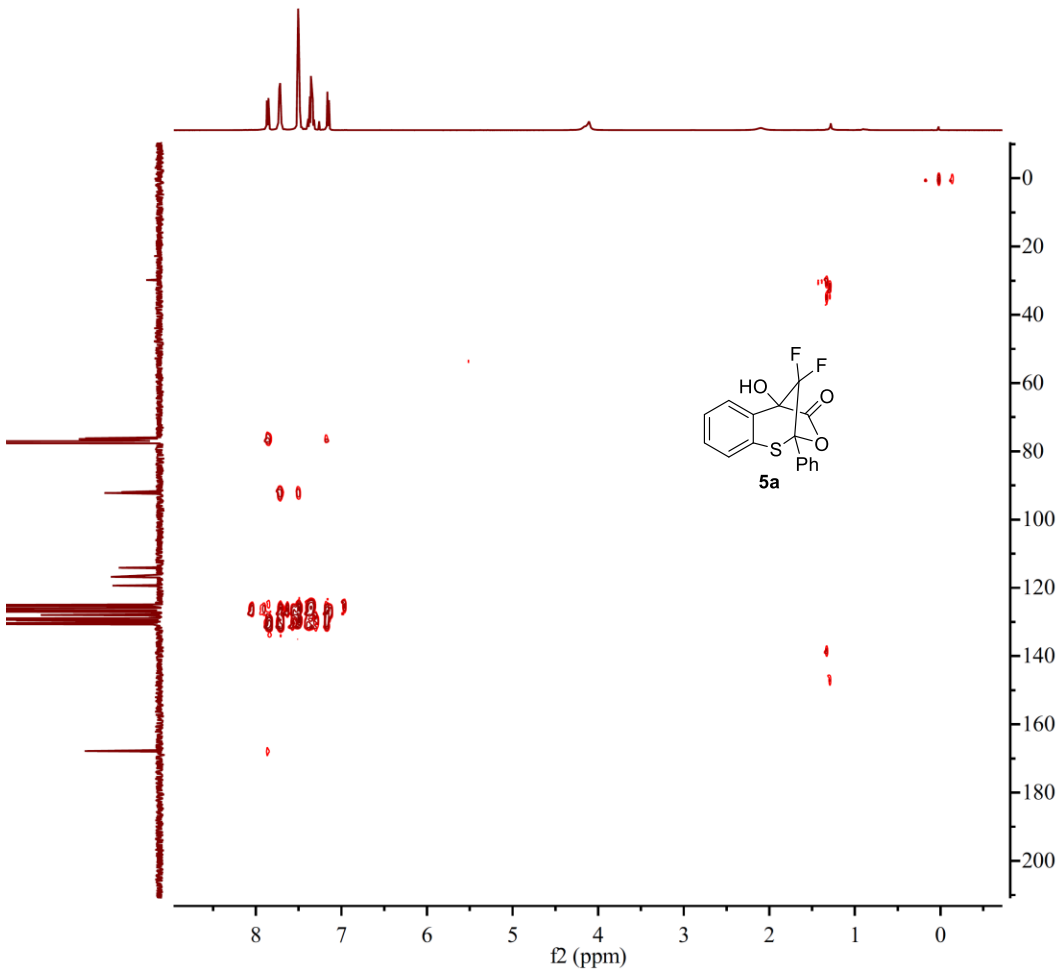
DEPT135 of **5a** in $CDCl_3$ (100 MHz)

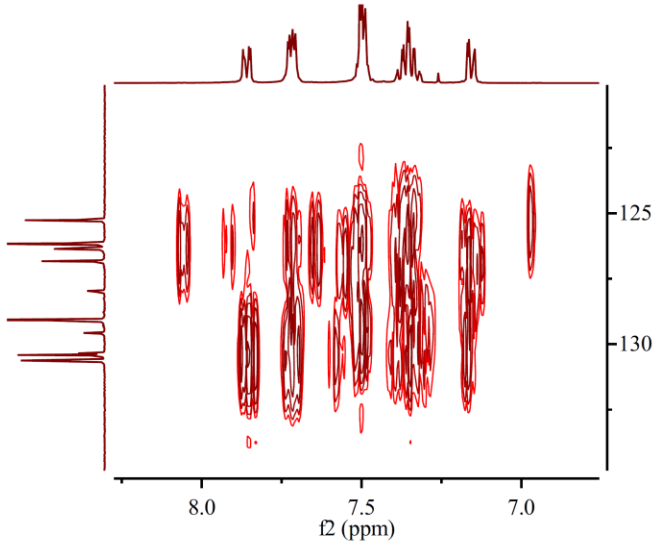


H-H COSY of **5a** in $CDCl_3$

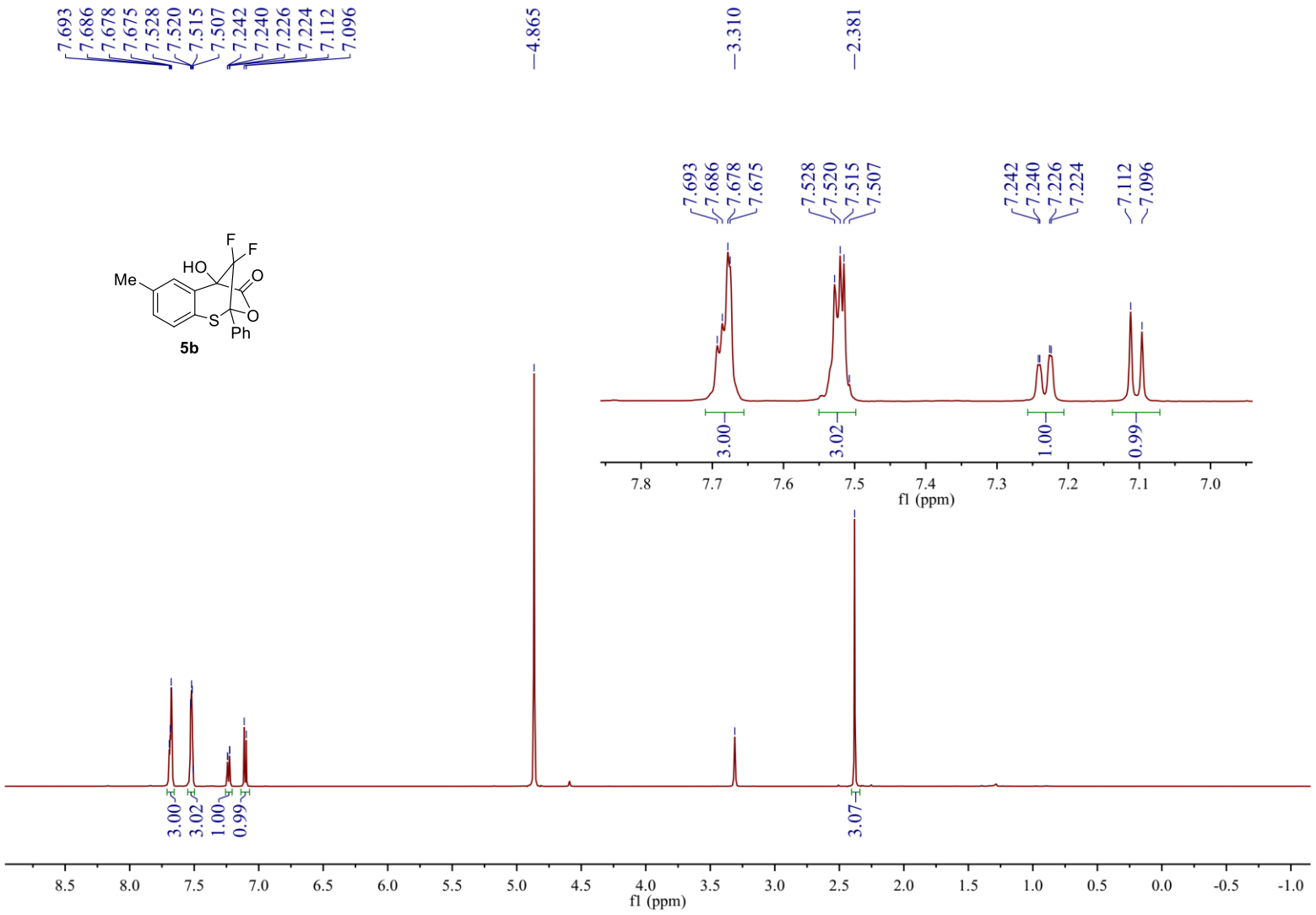


HSQC of **5a** in $CDCl_3$

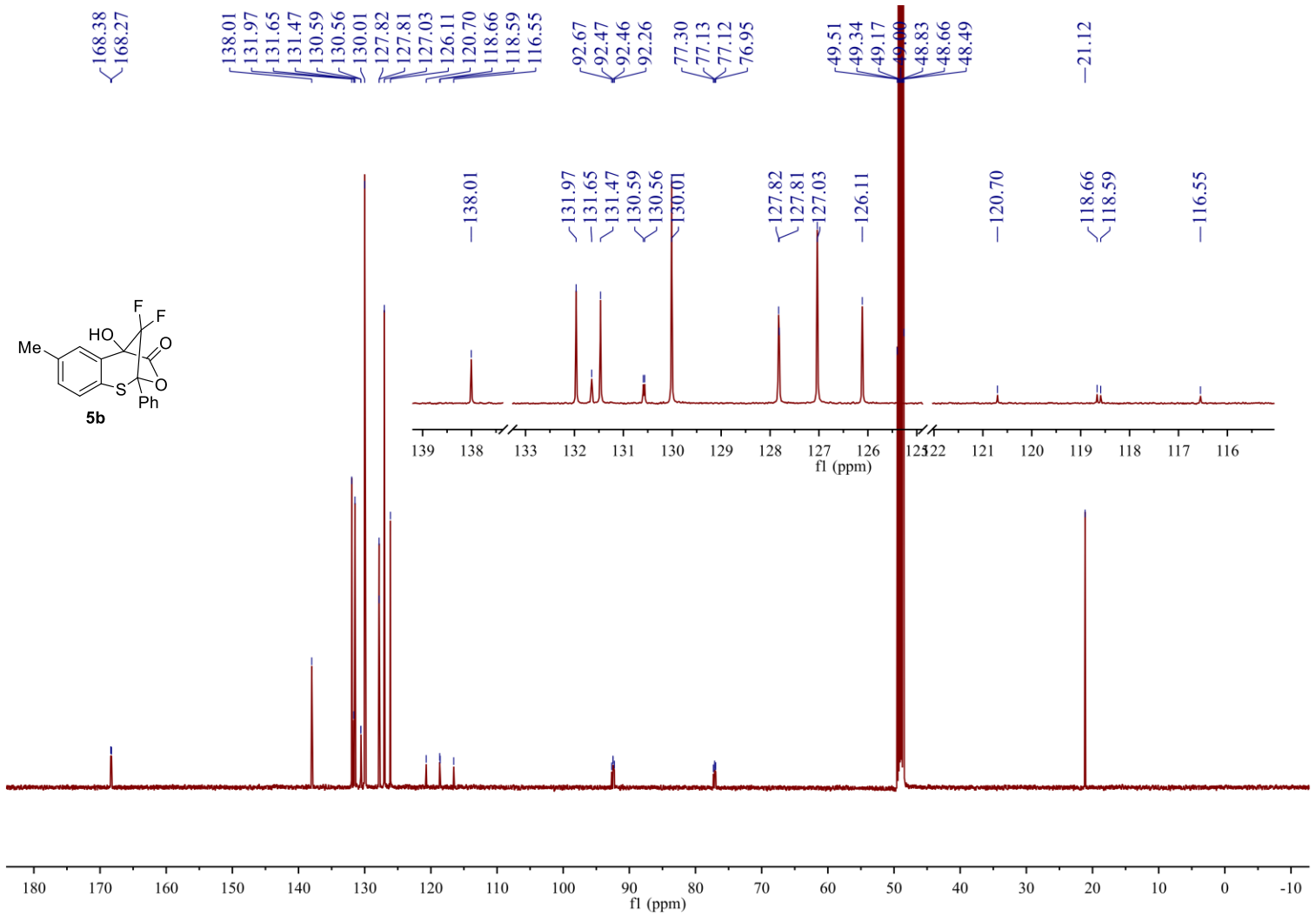




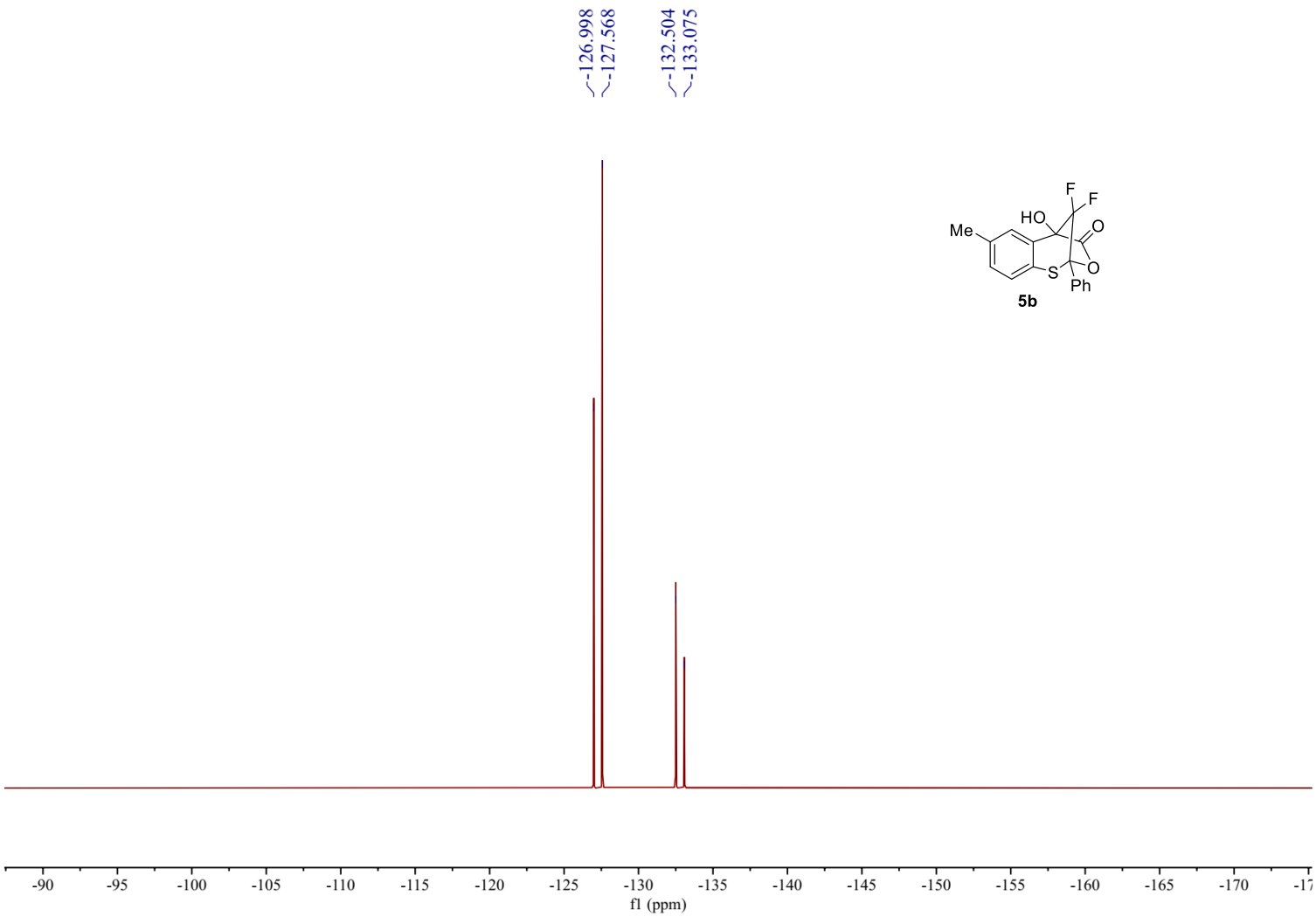
HMBC of **5a** in $CDCl_3$



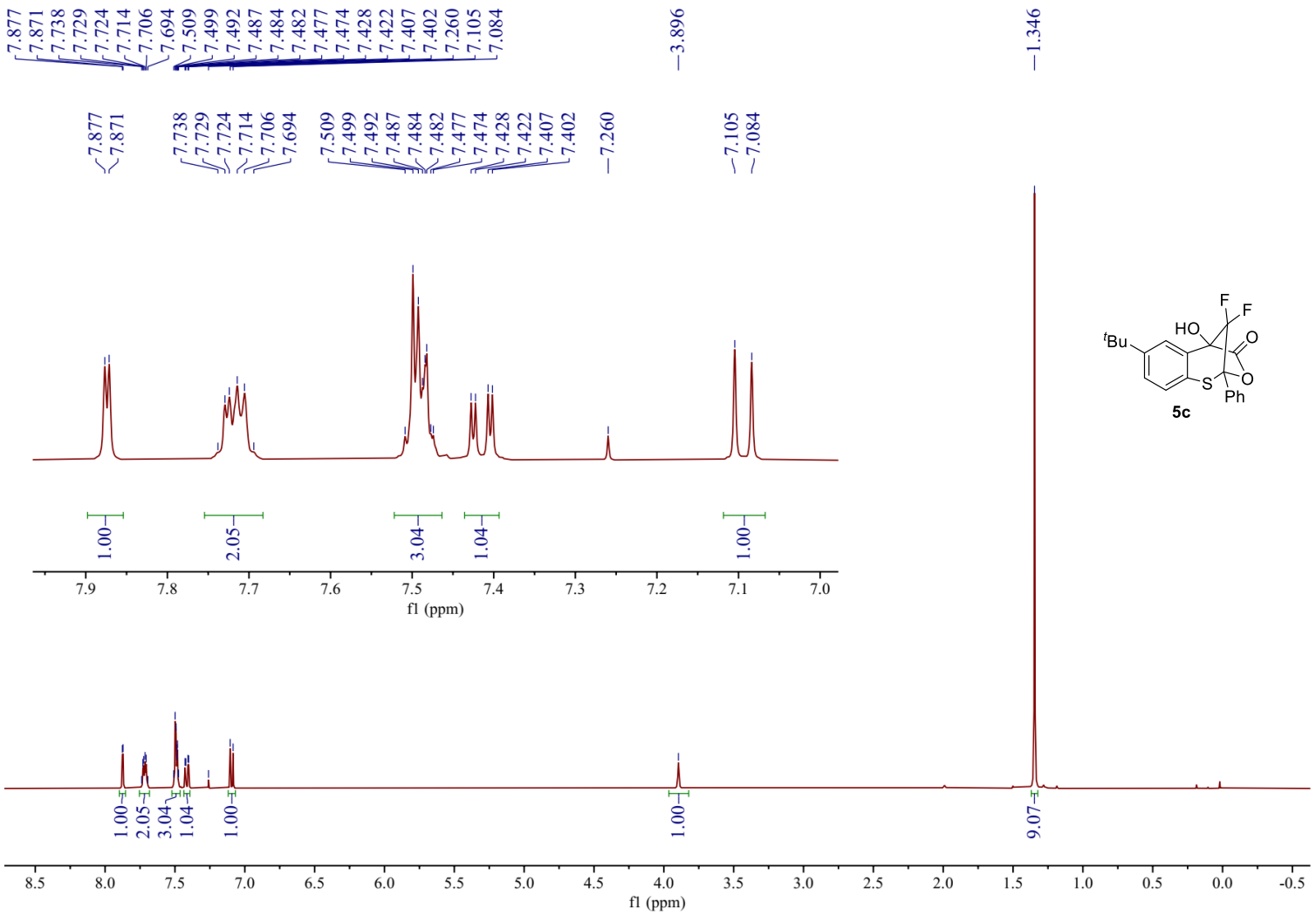
^{1}H NMR spectra of **5b** in CD_3OD (500 MHz)



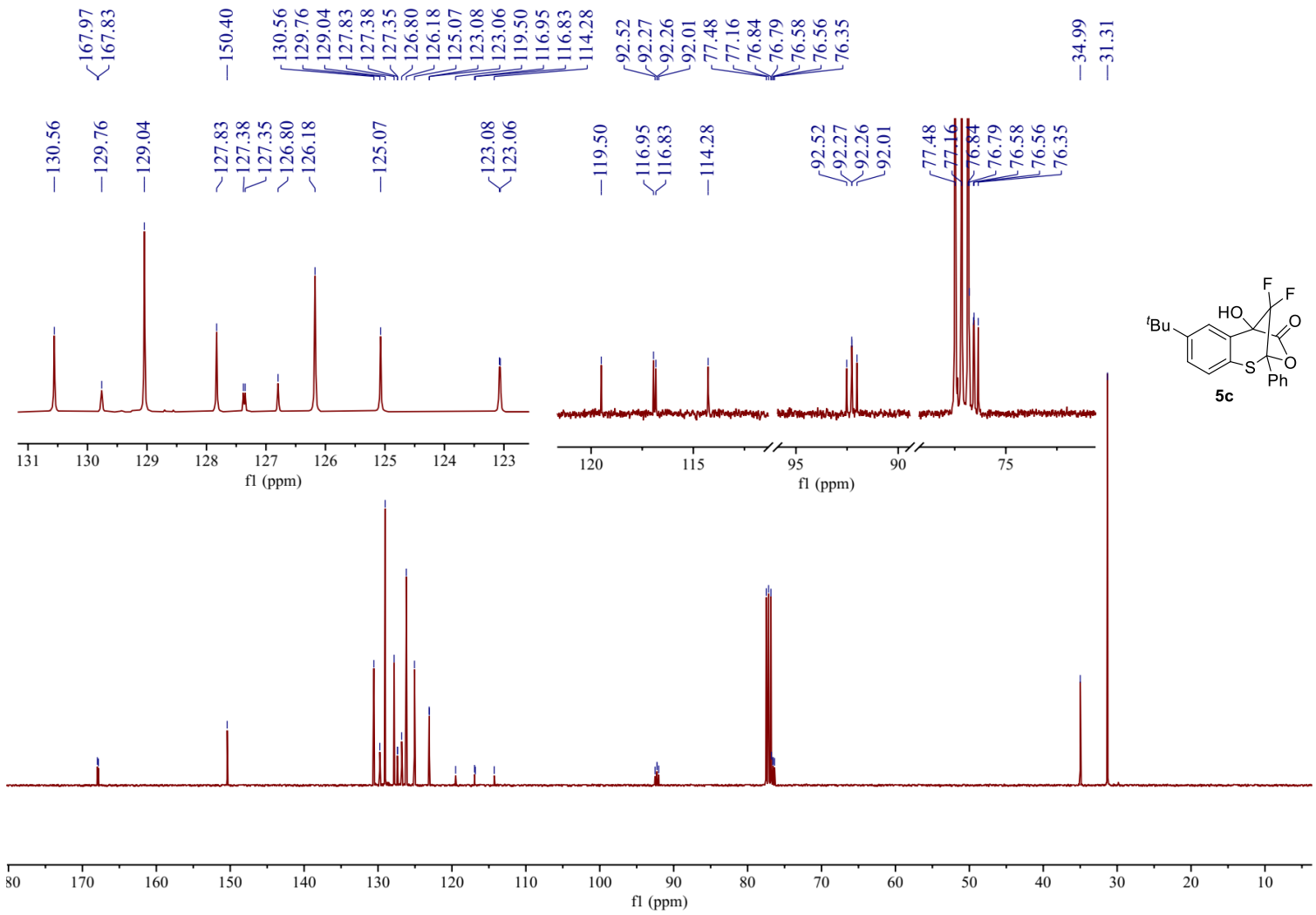
$^{19}C\{^{1}H\}$ NMR spectra of **5b** in CD_3OD (125 MHz)



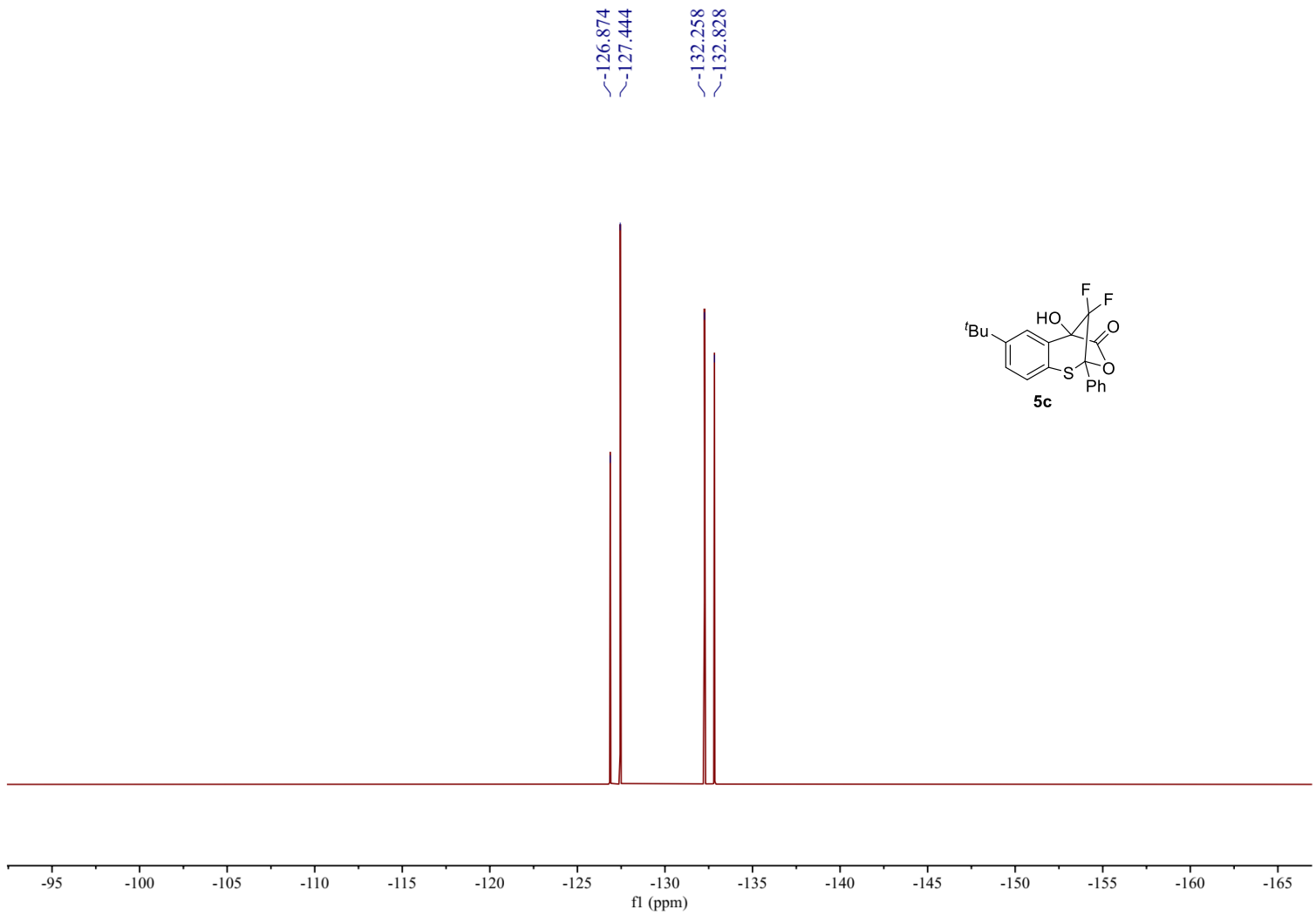
^{19}F NMR spectra of **5b** in $CDCl_3$ (376 MHz)



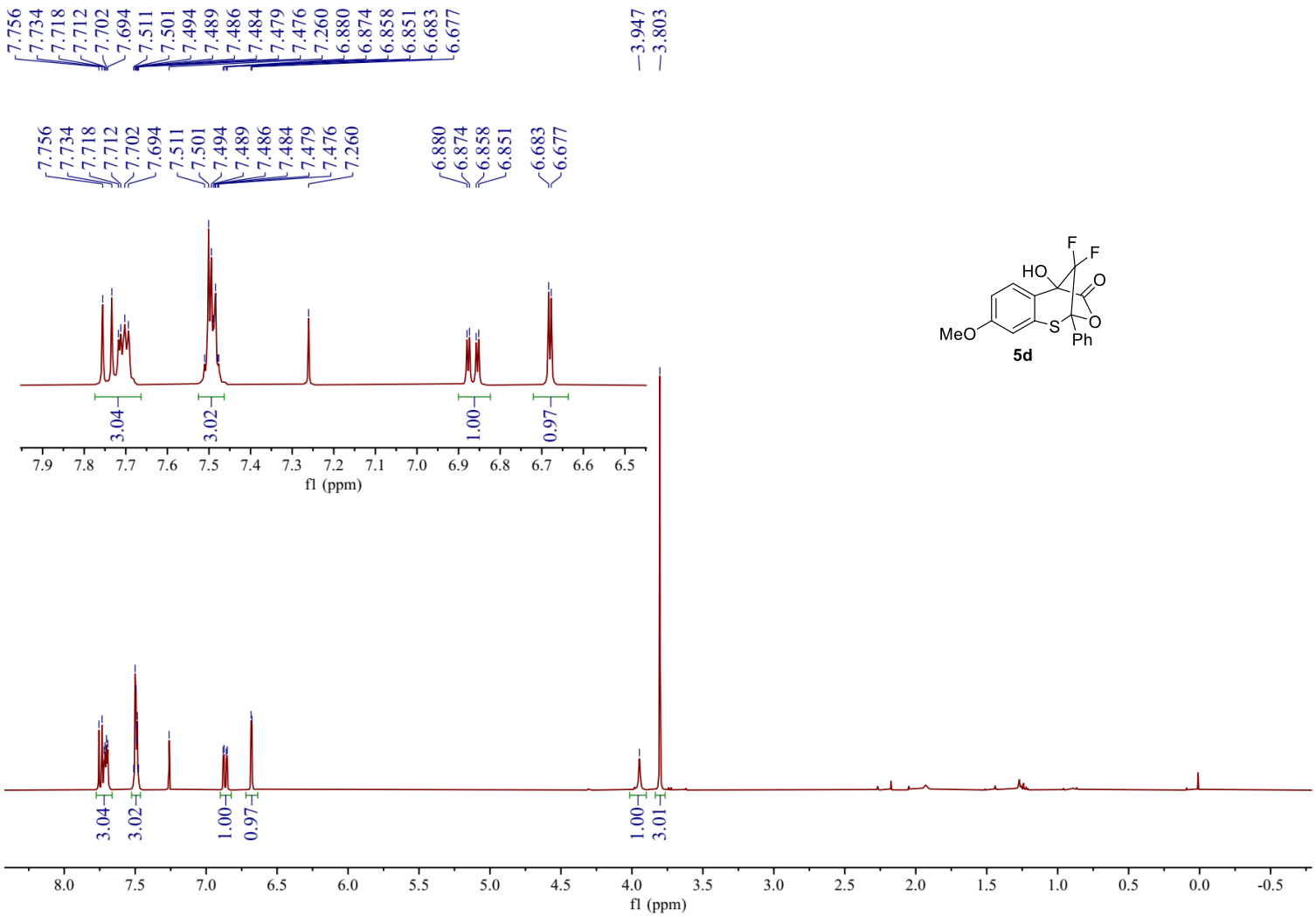
^{1}H NMR spectra of **5c** in $CDCl_3$ (400 MHz)



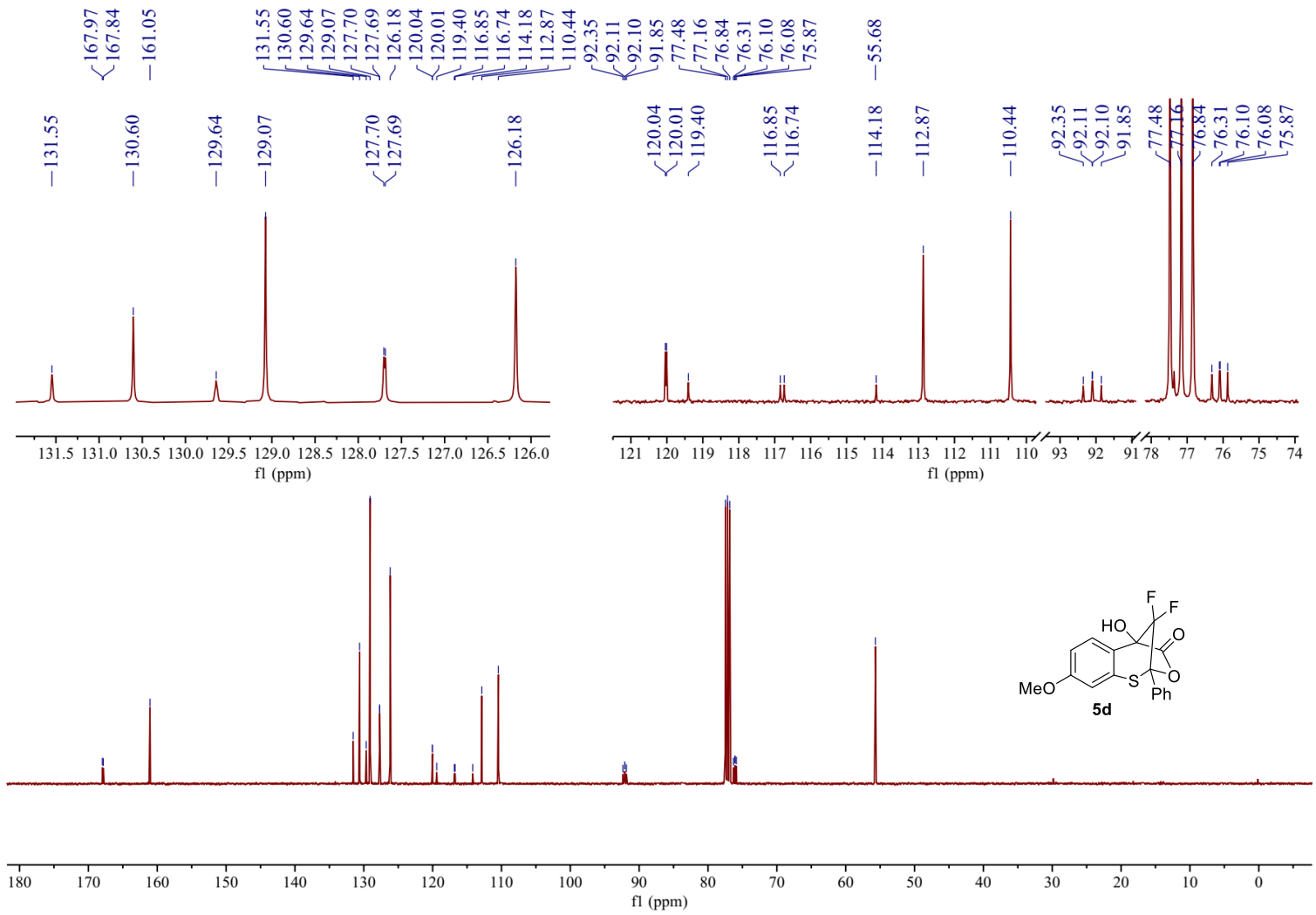
$^{13}C\{^{1}H\}$ NMR spectra of **5c** in $CDCl_3$ (100 MHz)



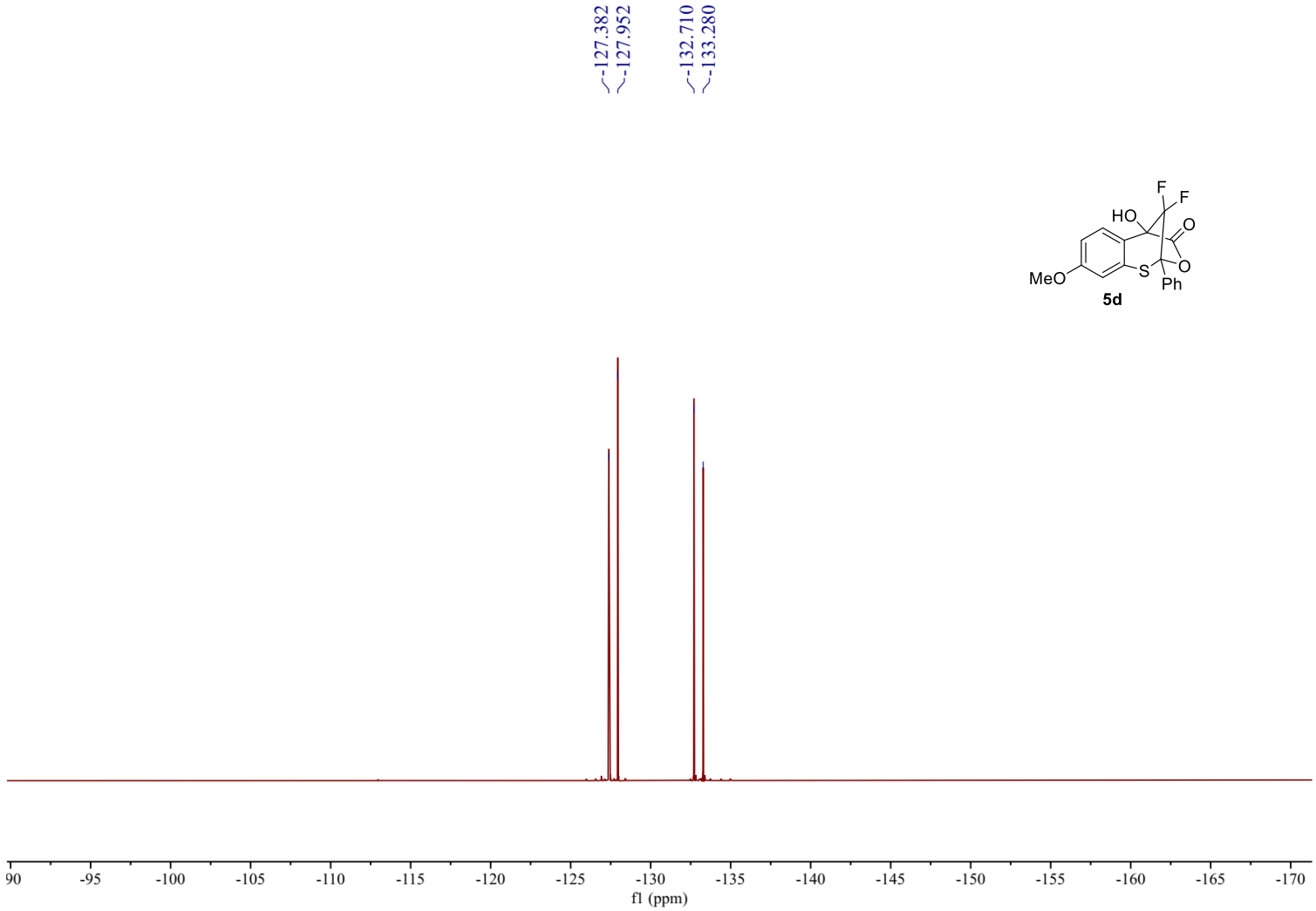
^{19}F NMR spectra of **5c** in $CDCl_3$ (376 MHz)



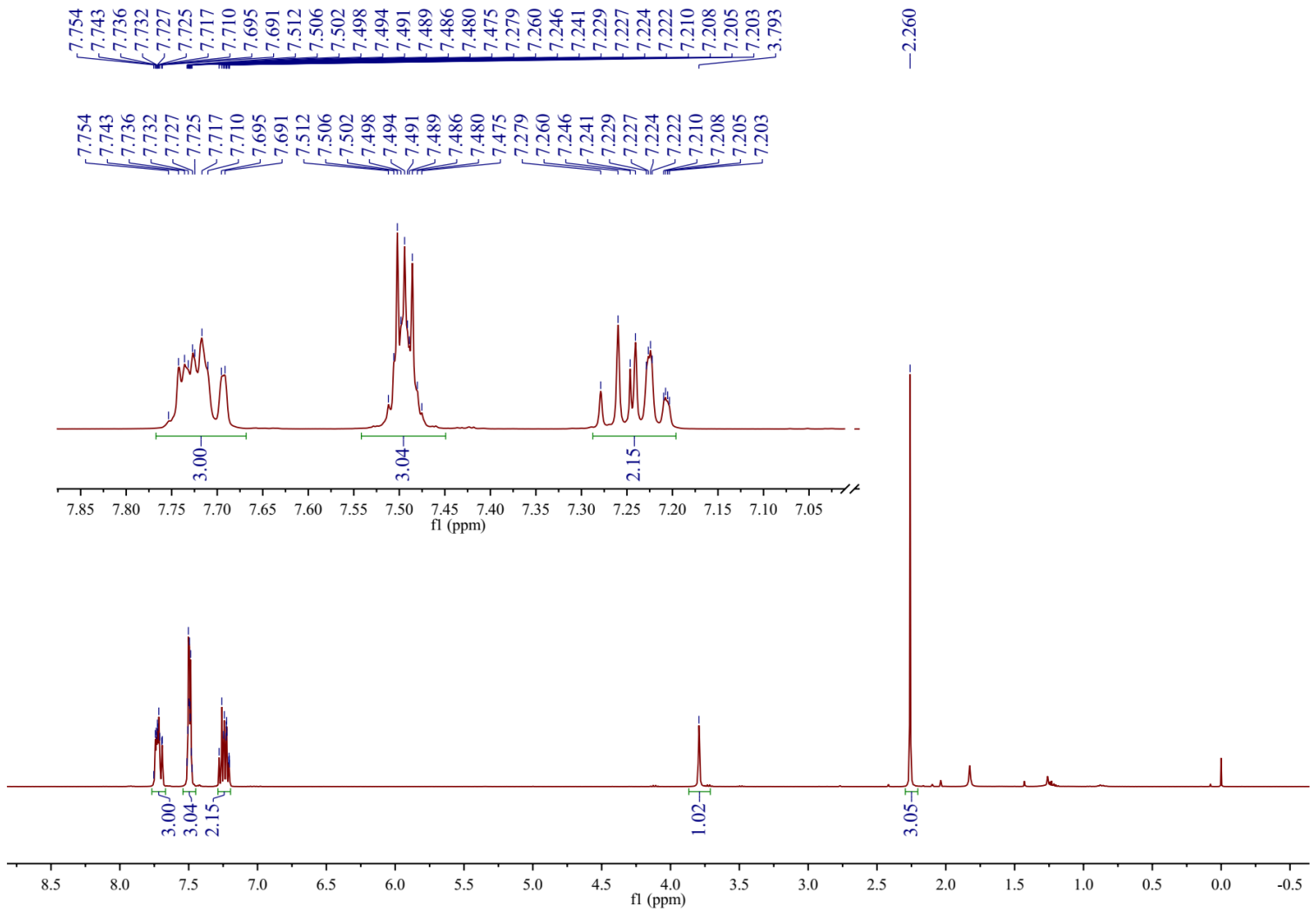
^{1}H NMR spectra of **5d** in $CDCl_3$ (400 MHz)



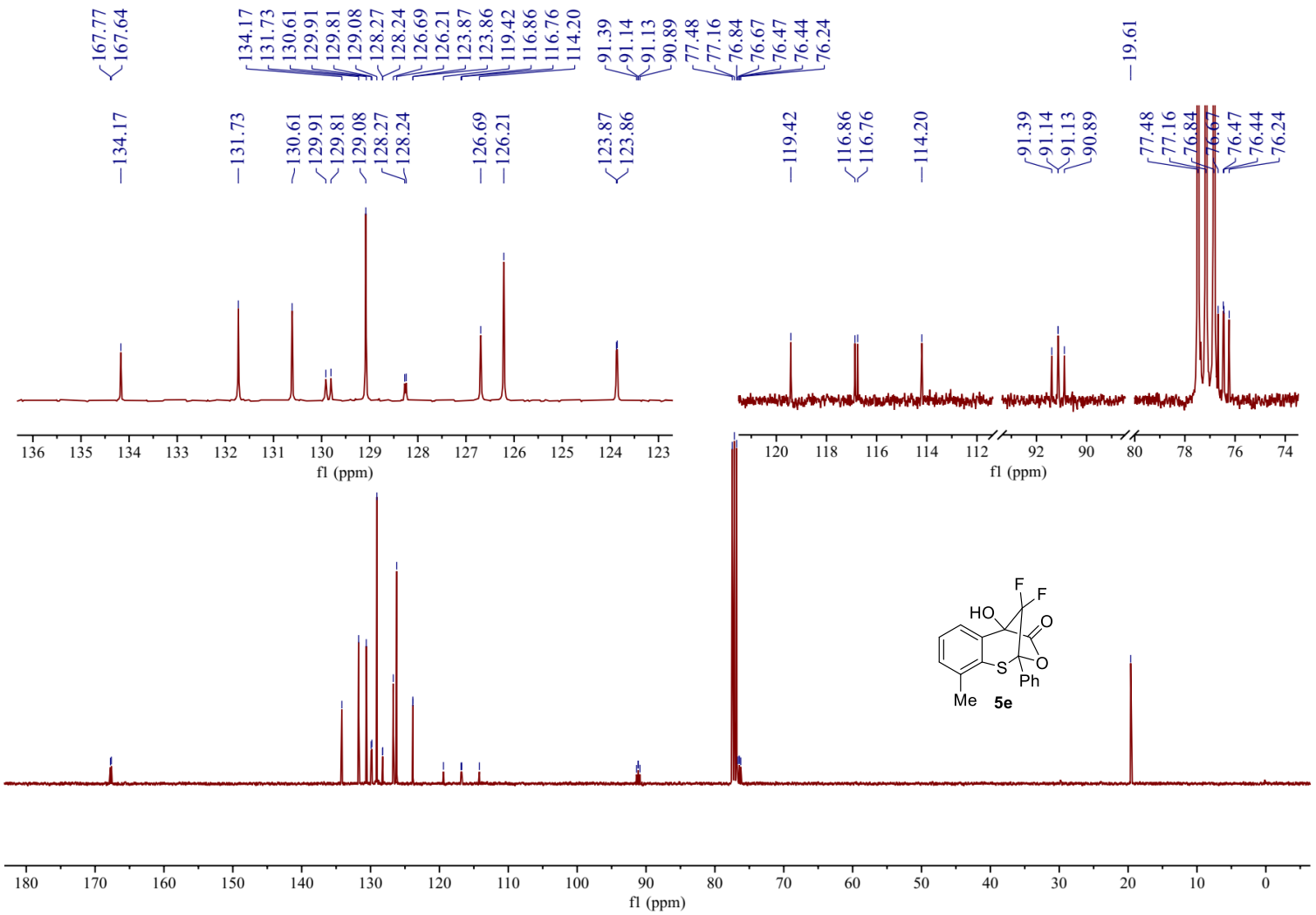
$^{13}C\{^{1}H\}$ NMR spectra of **5d** in $CDCl_3$ (100 MHz)



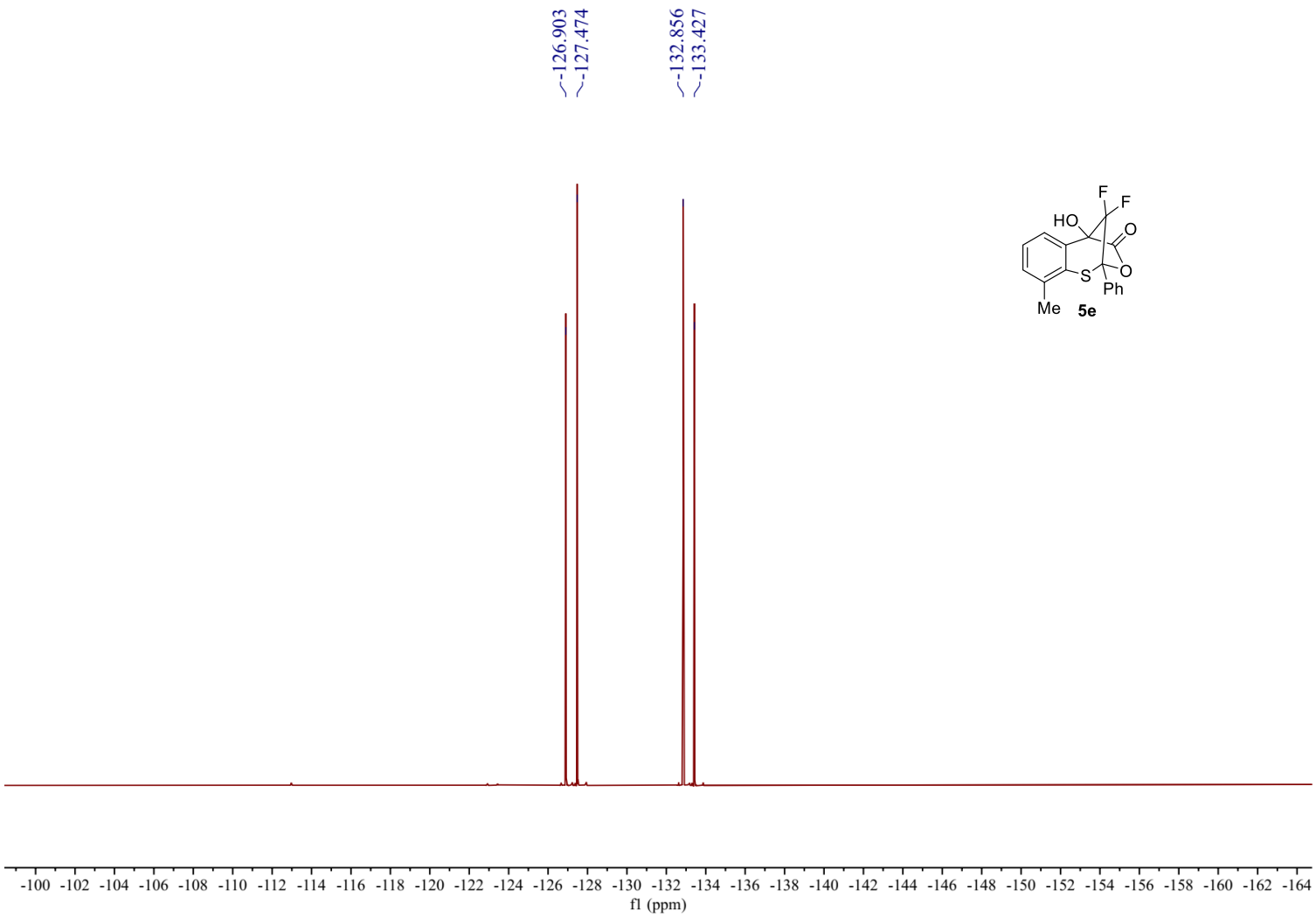
^{19}F NMR spectra of **5d** in $CDCl_3$ (376 MHz)



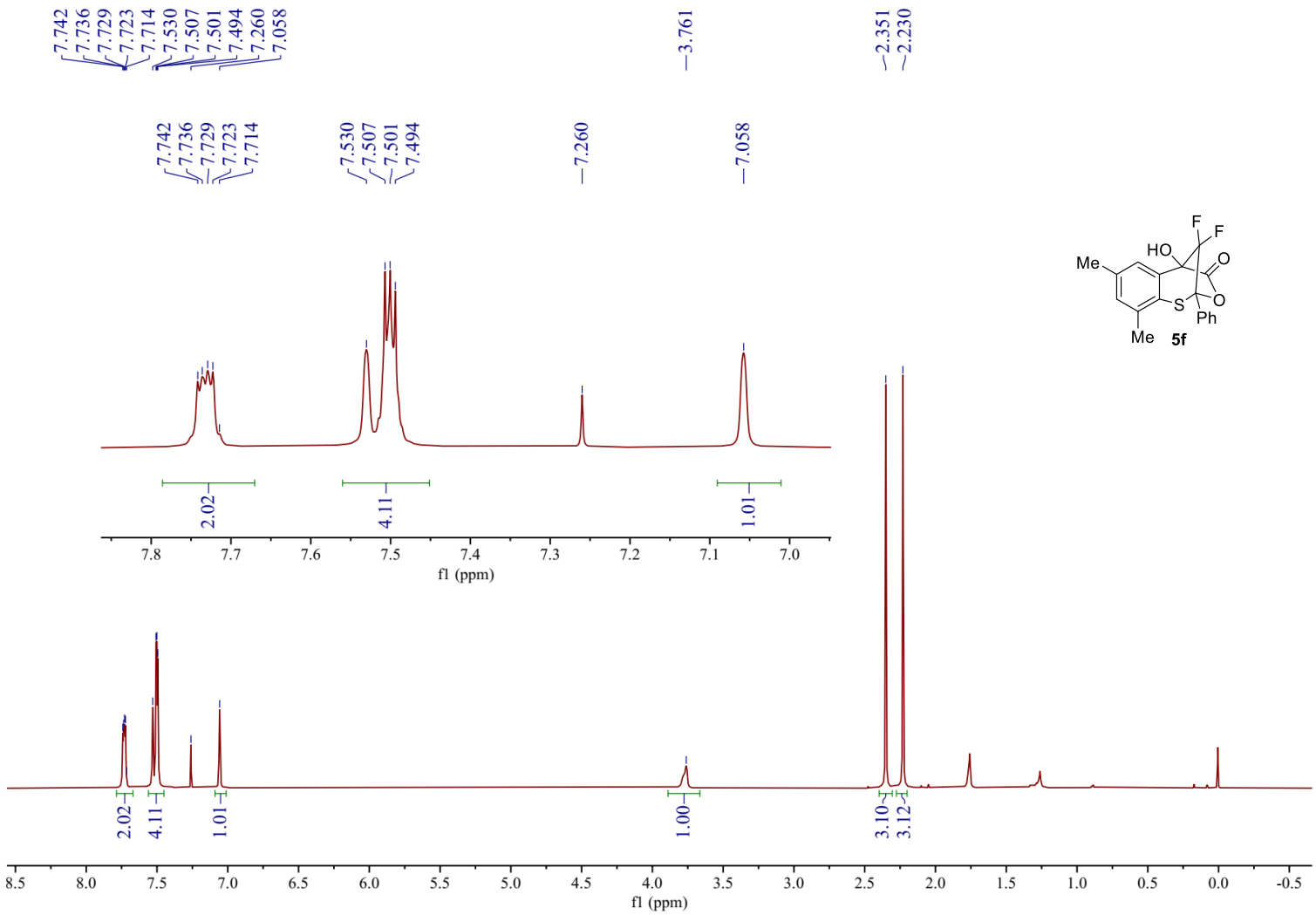
^{1}H NMR spectra of **5e** in $CDCl_3$ (400 MHz)



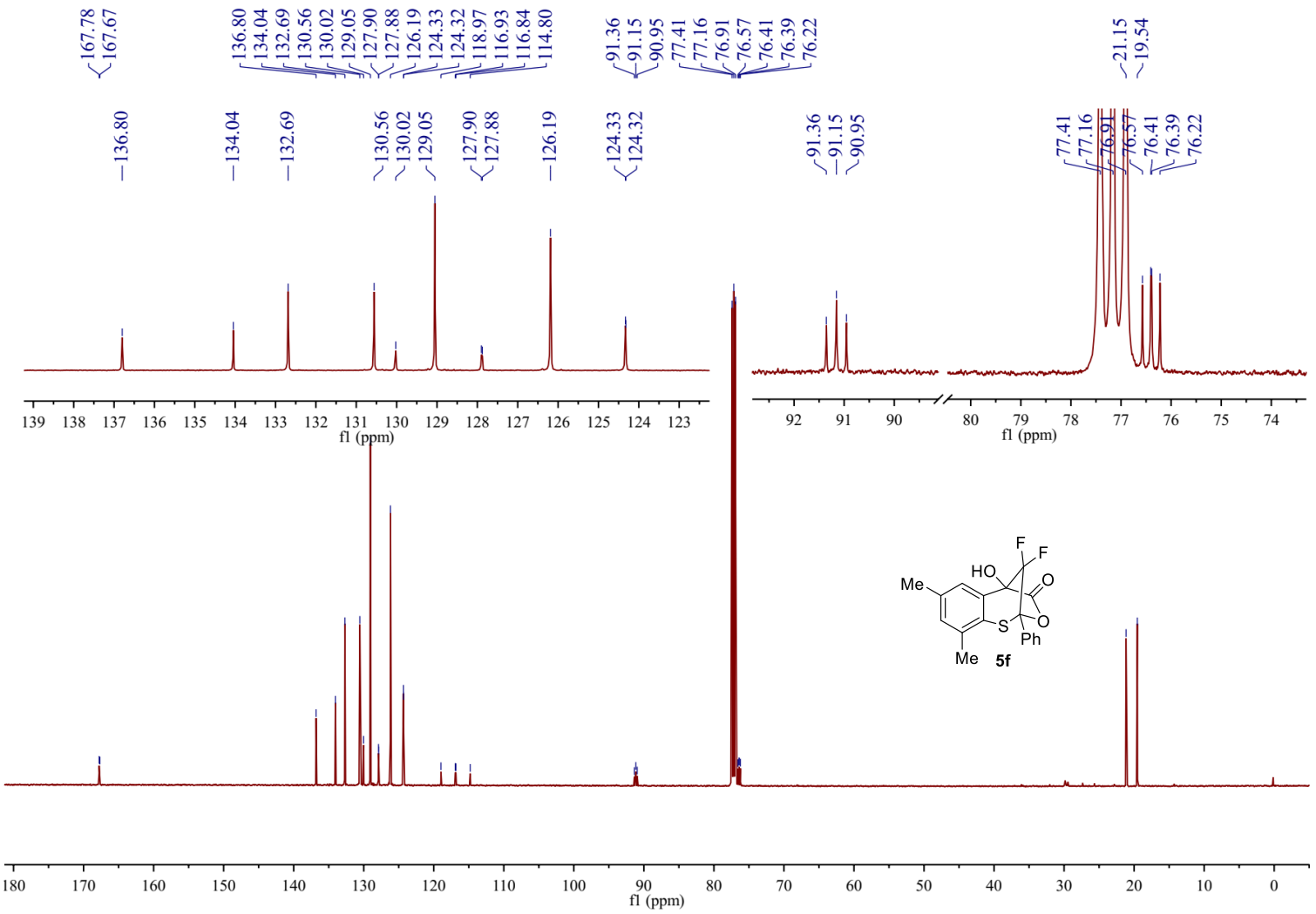
$^{13}C\{^{1}H\}$ NMR spectra of **5e** in $CDCl_3$ (100 MHz)



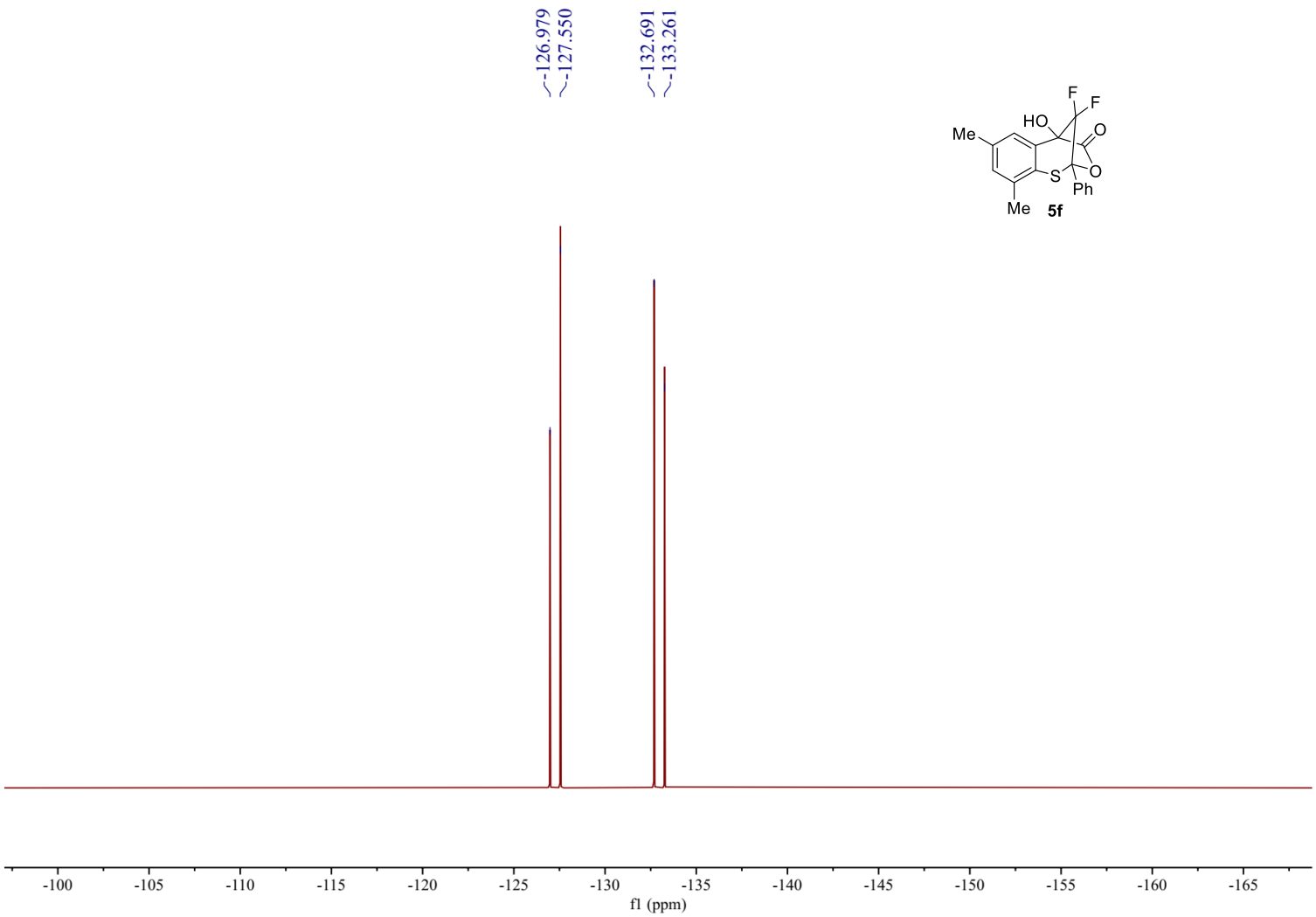
^{19}F NMR spectra of **5e** in $CDCl_3$ (376 MHz)



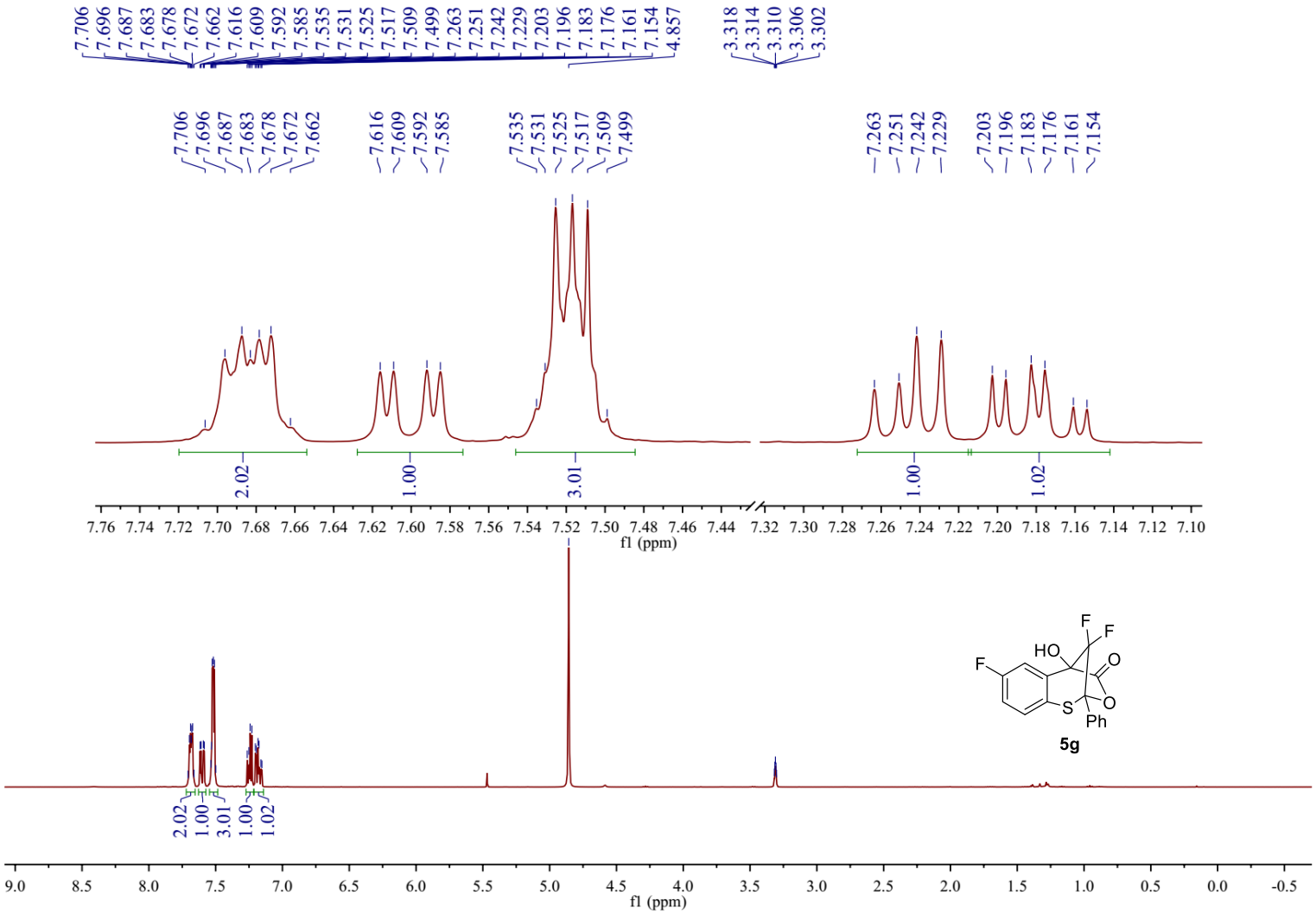
^{1}H NMR spectra of **5f** in $CDCl_3$ (400 MHz)



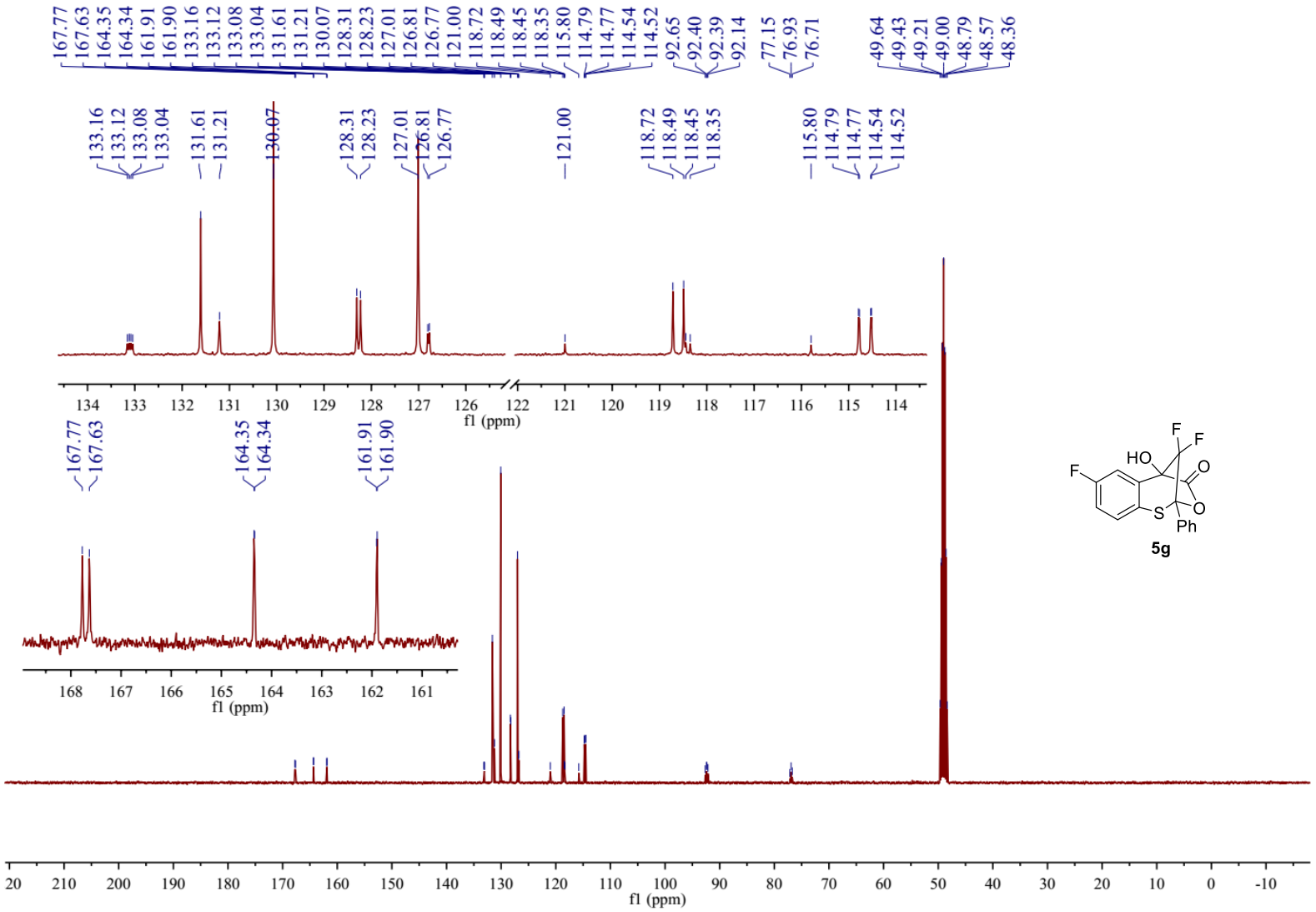
$^{13}C\{^{1}H\}$ NMR spectra of **5f** in $CDCl_3$ (100 MHz)



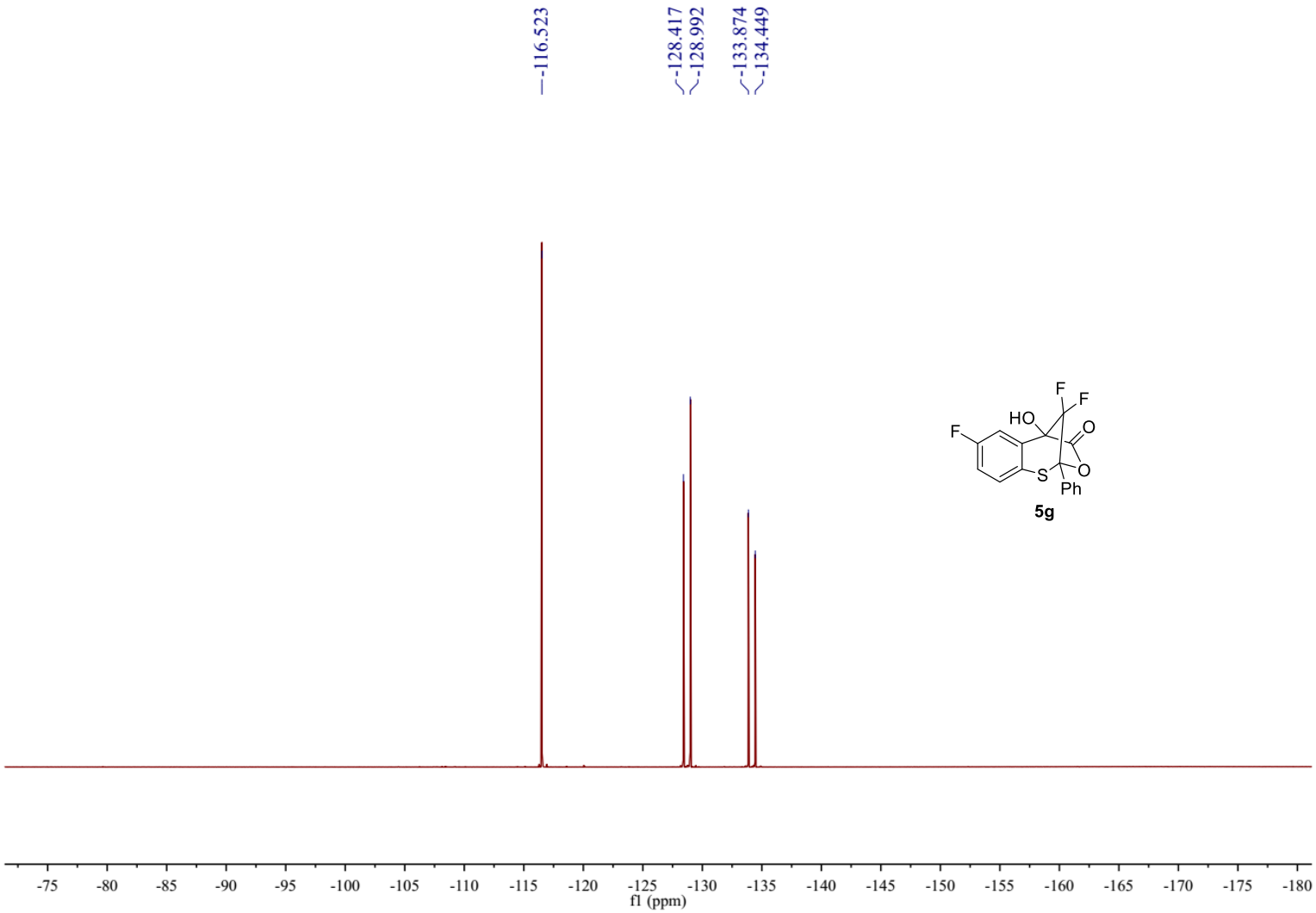
^{19}F NMR spectra of **5f** in $CDCl_3$ (376 MHz)



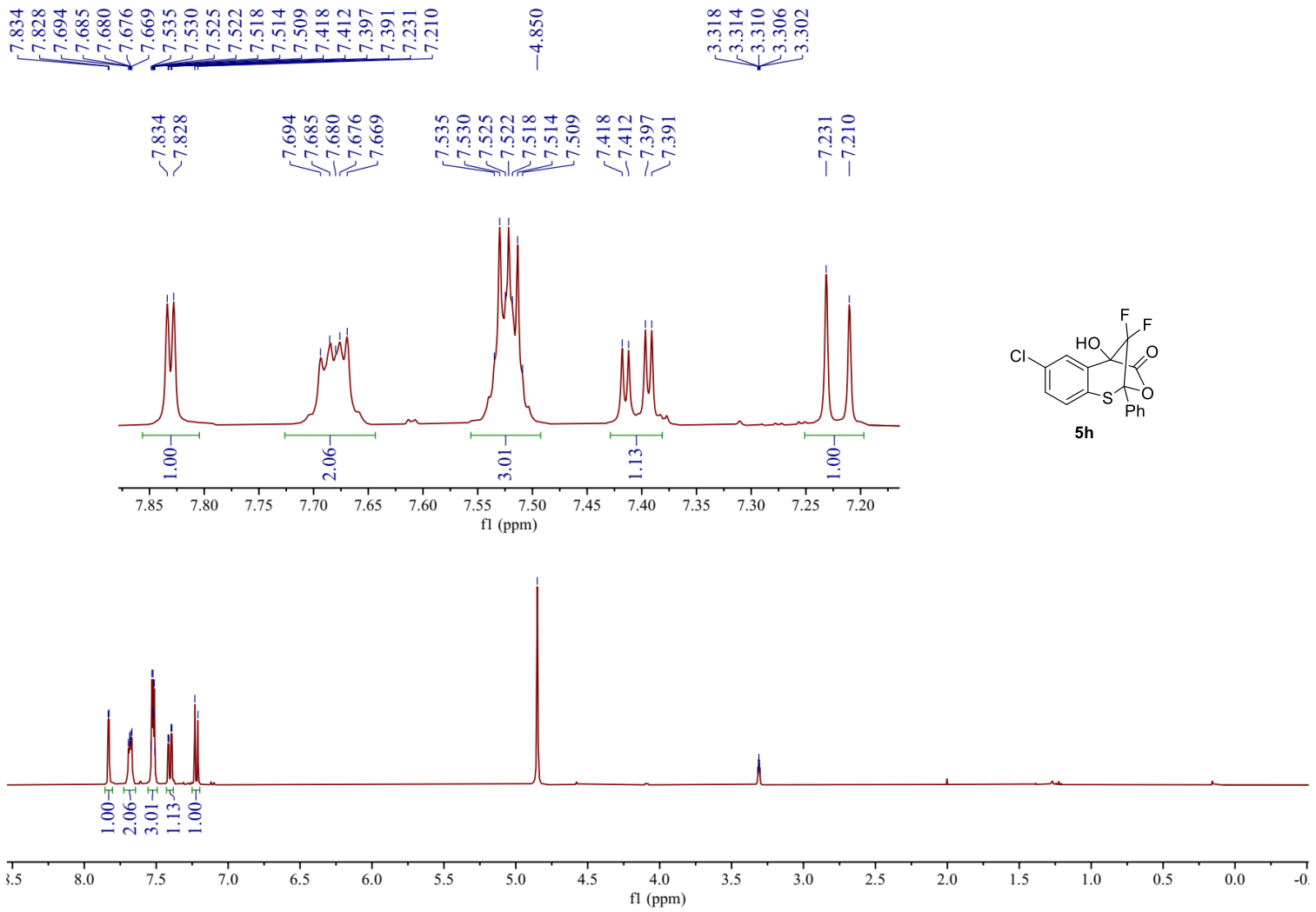
^{1}H NMR spectra of **5g** in CD_3OD (400 MHz)



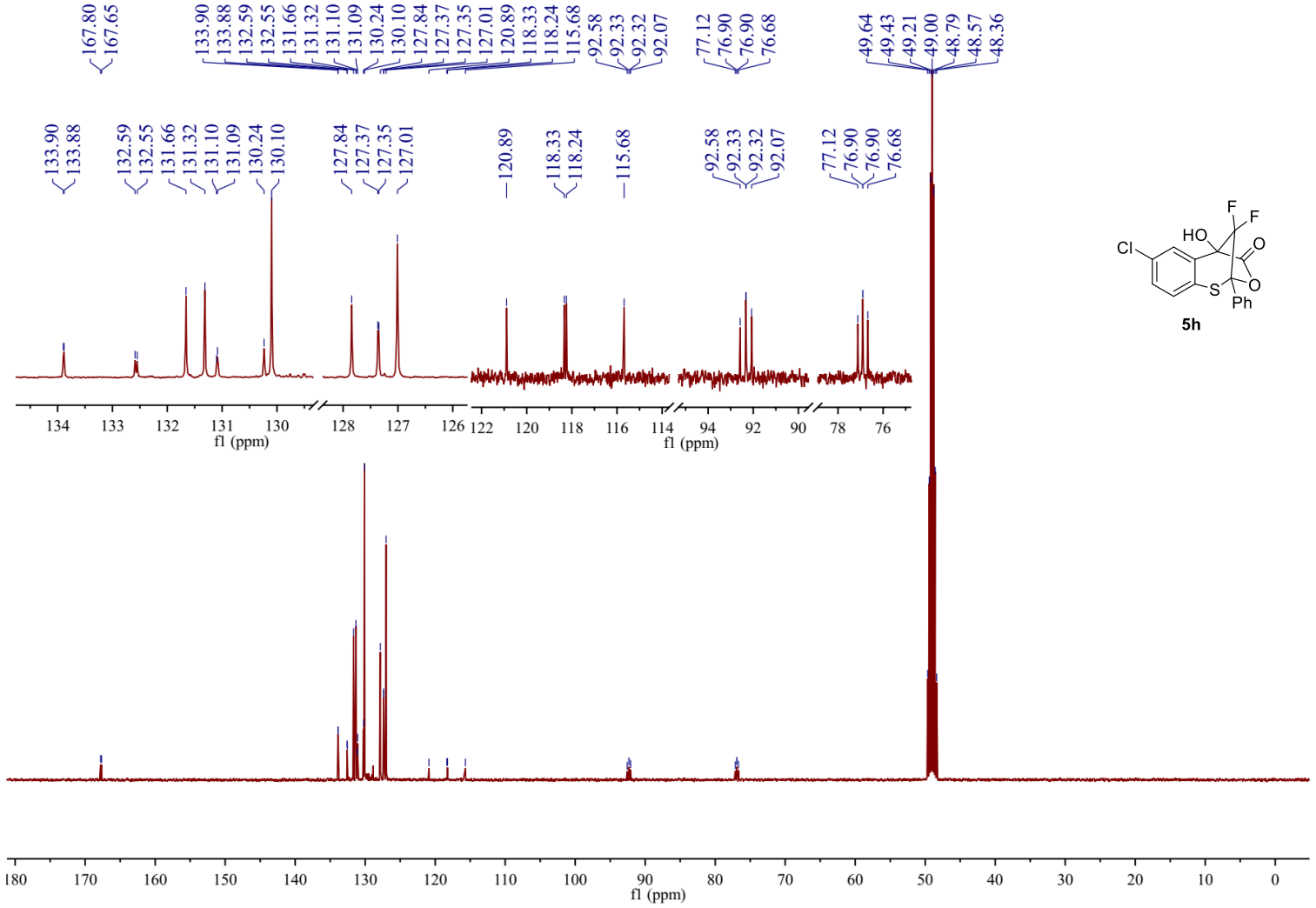
$^{13}C\{^{1}H\}$ NMR spectra of **5g** in CD_3OD (100 MHz)



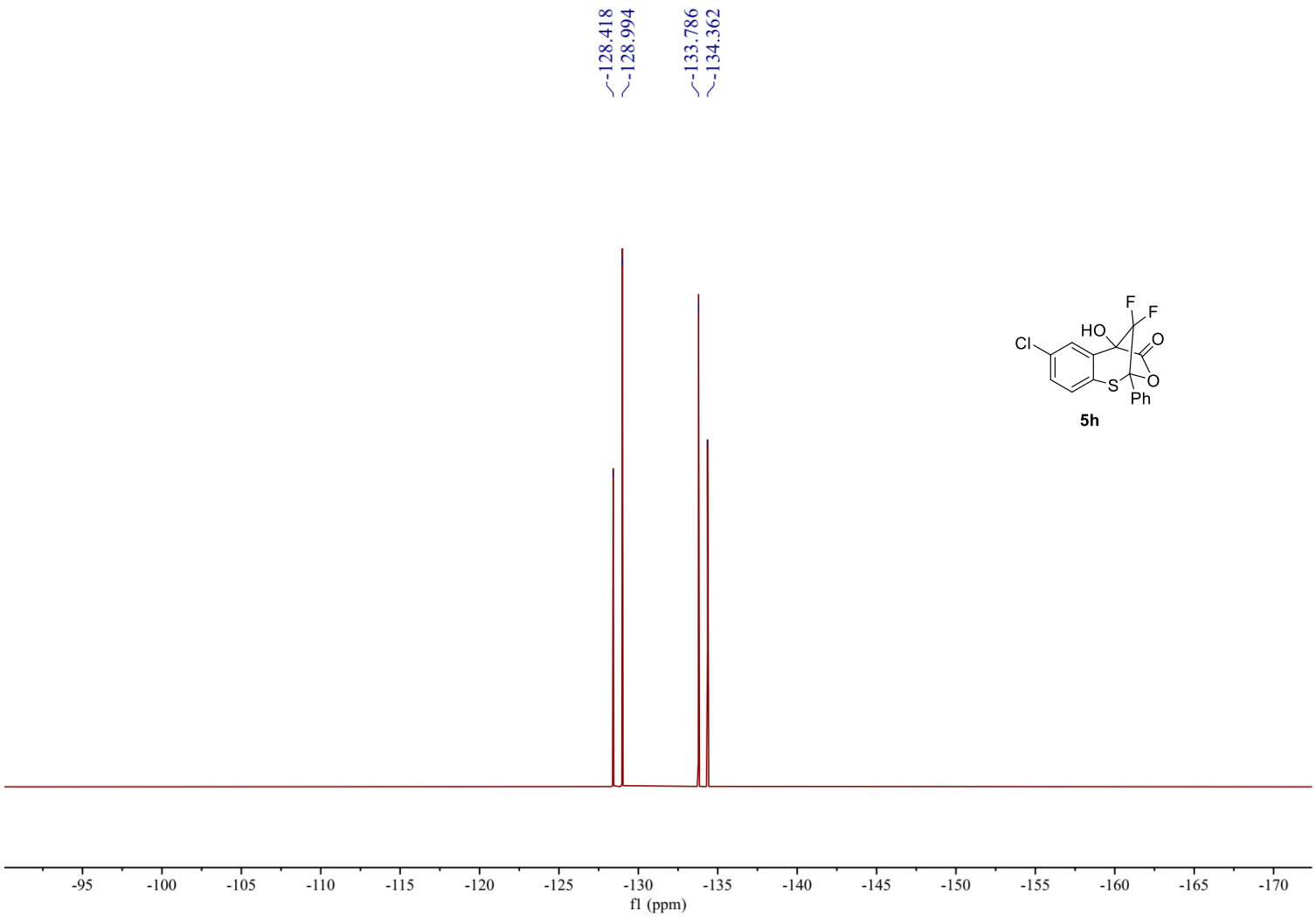
^{19}F NMR spectra of **5g** in CD_3OD (376 MHz)



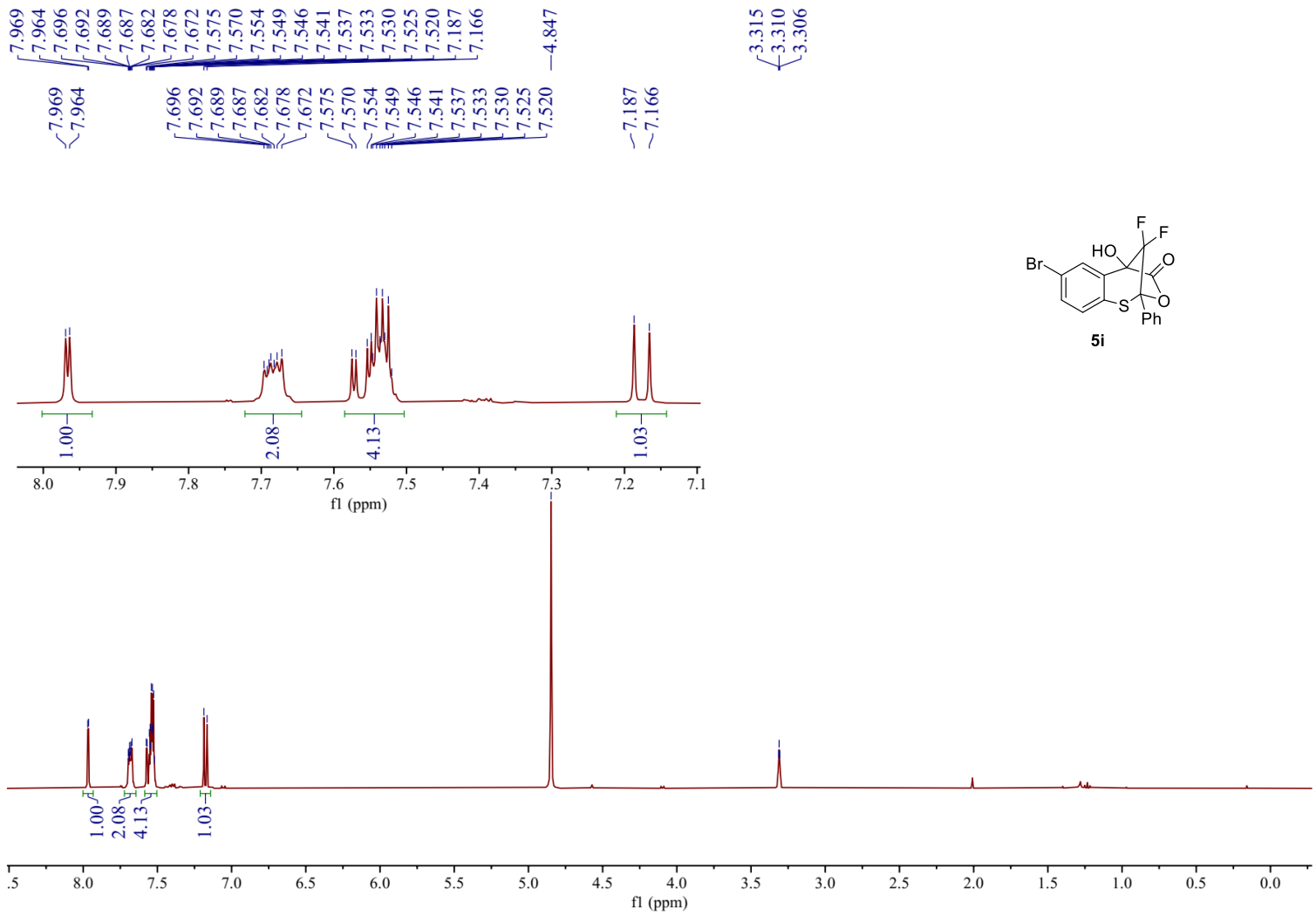
^{1}H NMR spectra of **5h** in CD_3OD (400 MHz)



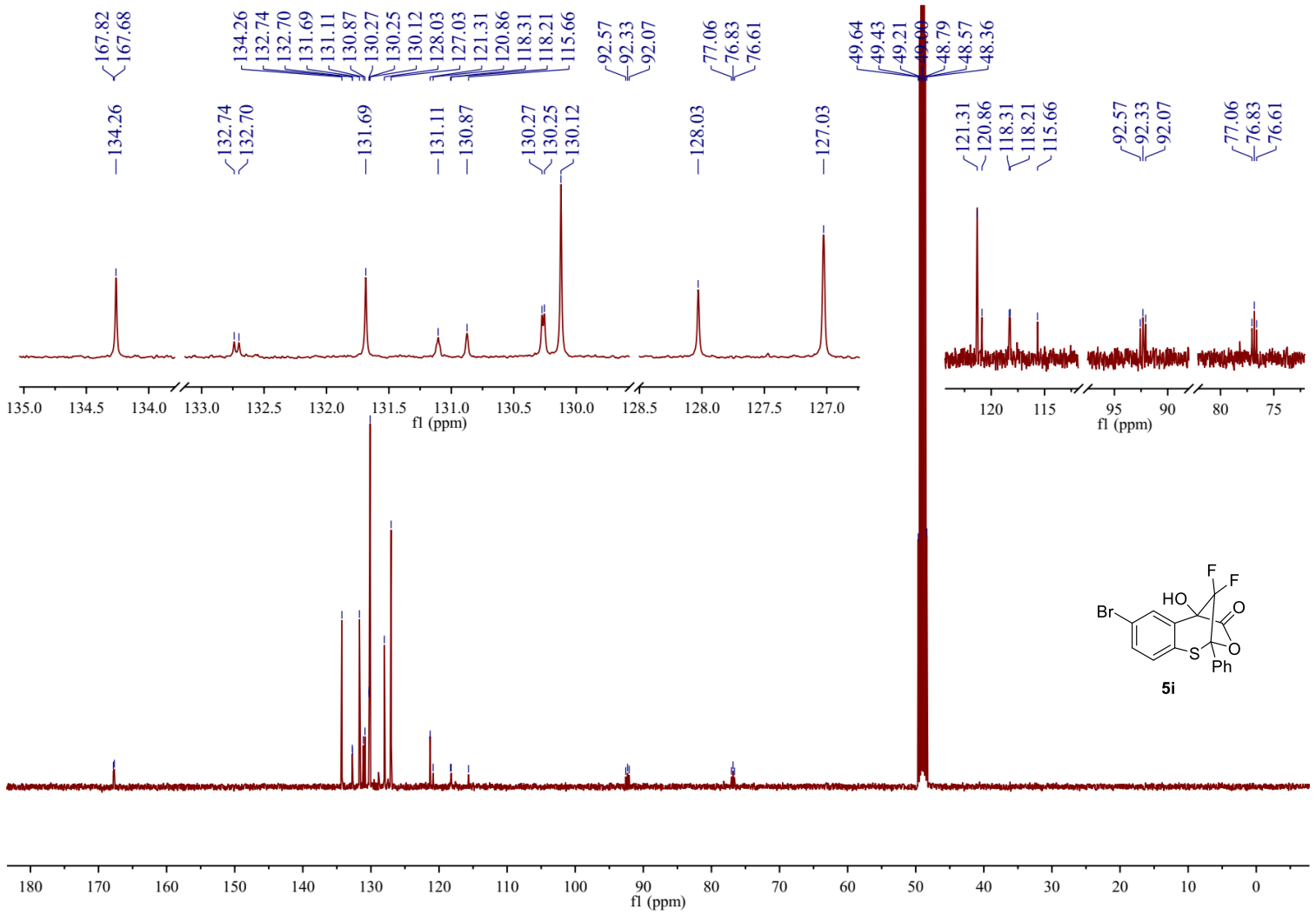
$^{13}C\{^{1}H\}$ NMR spectra of **5h** in CD_3OD (100 MHz)



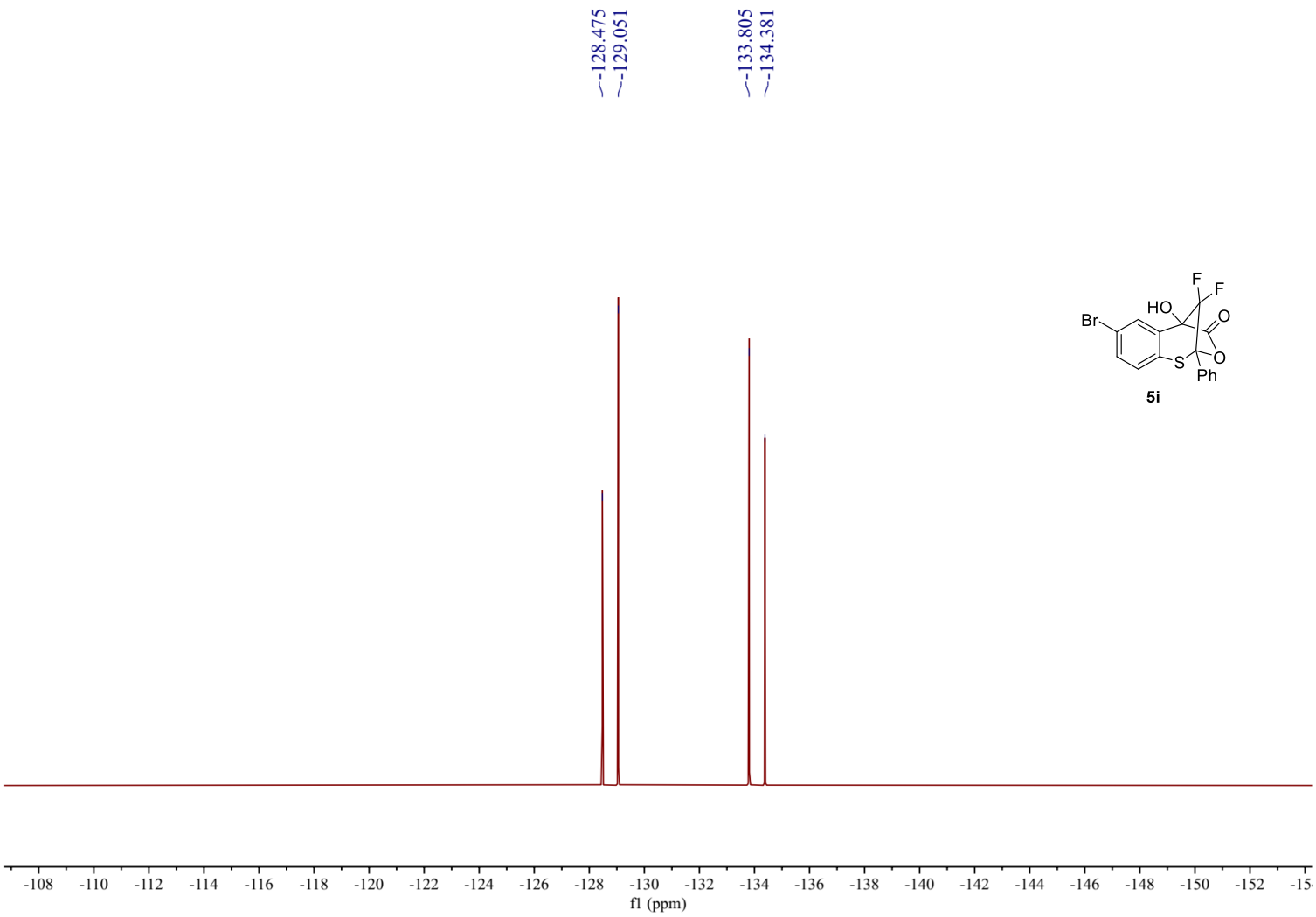
^{19}F NMR spectra of **5h** in CD_3OD (376 MHz)



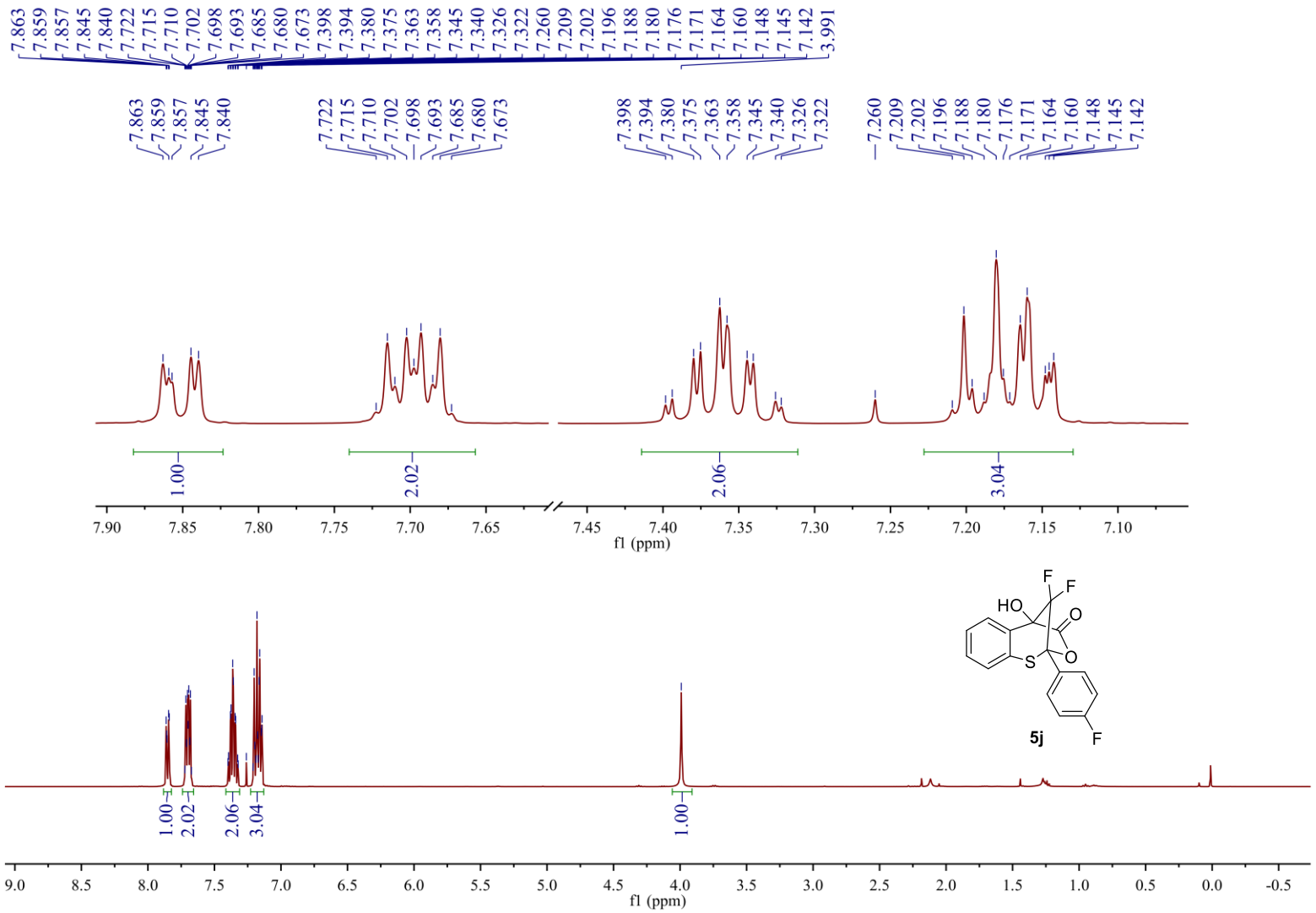
^{1}H NMR spectra of **5i** in CD_3OD (400 MHz)



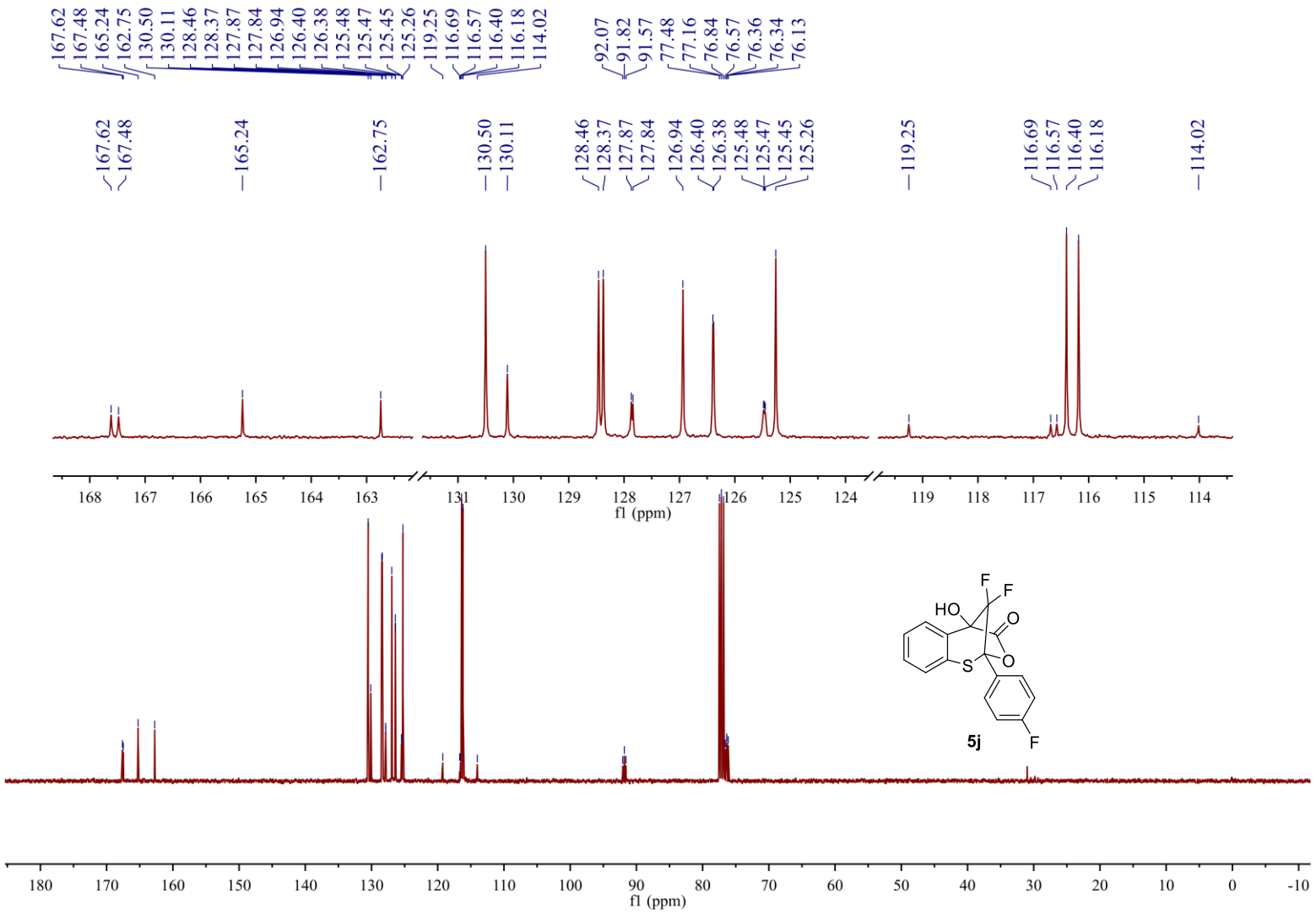
$^{13}C\{^{1}H\}$ NMR spectra of **5i** in CD_3OD (100 MHz)



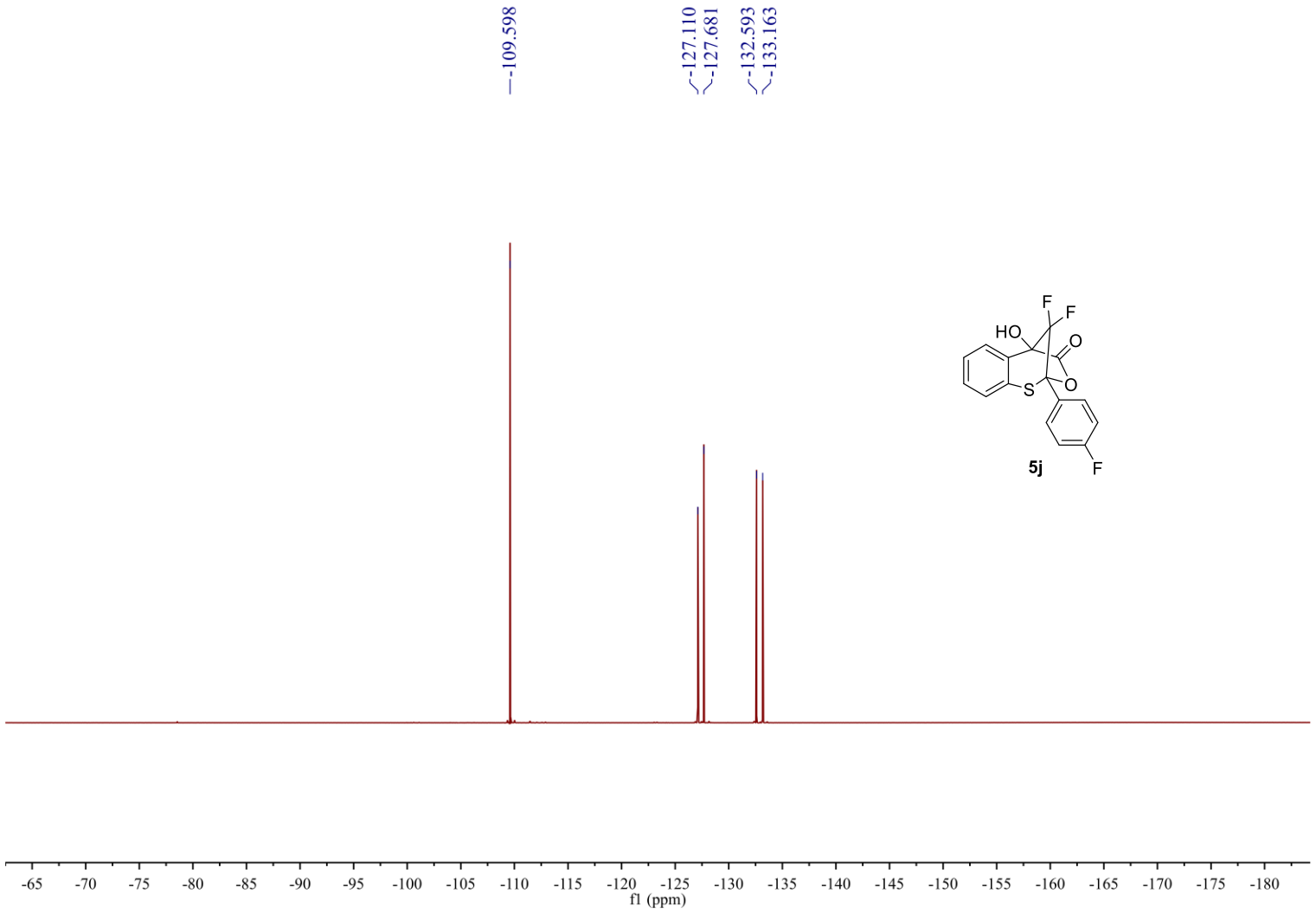
^{19}F NMR spectra of **5i** in CD_3OD (376 MHz)



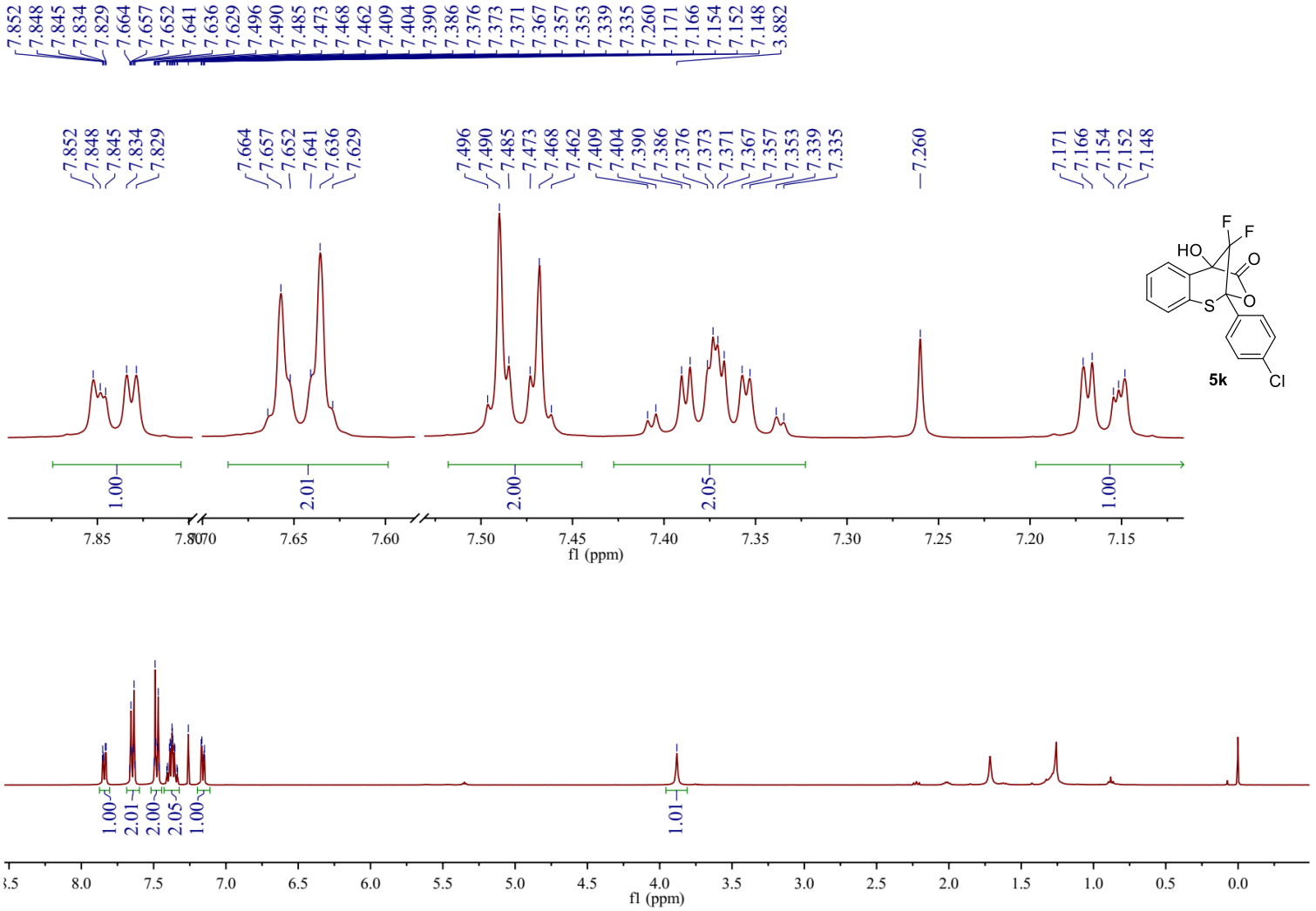
^{1}H NMR spectra of **5j** in $CDCl_3$ (400 MHz)



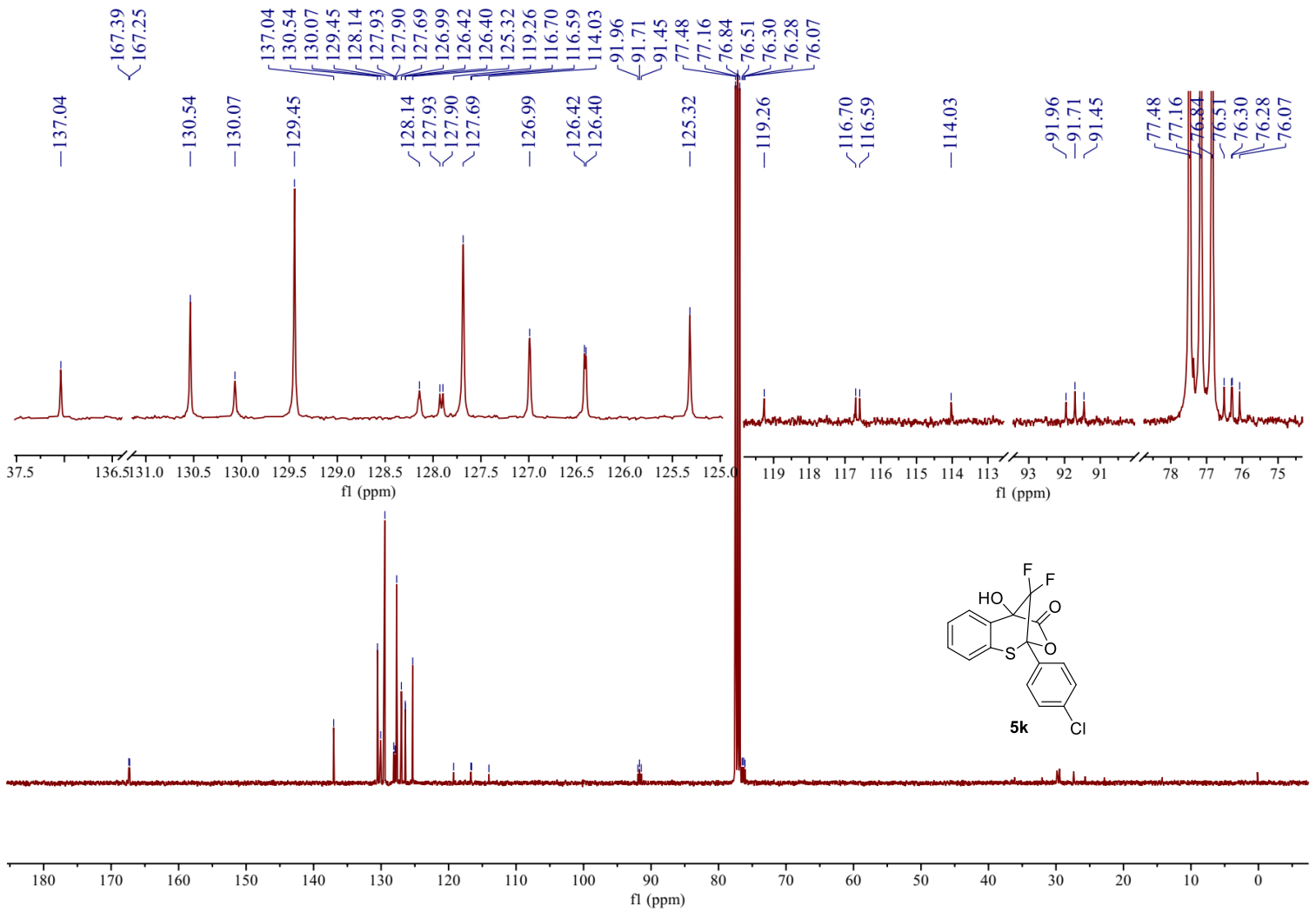
$^{13}C\{^{1}H\}$ NMR spectra of **5j** in $CDCl_3$ (100 MHz)



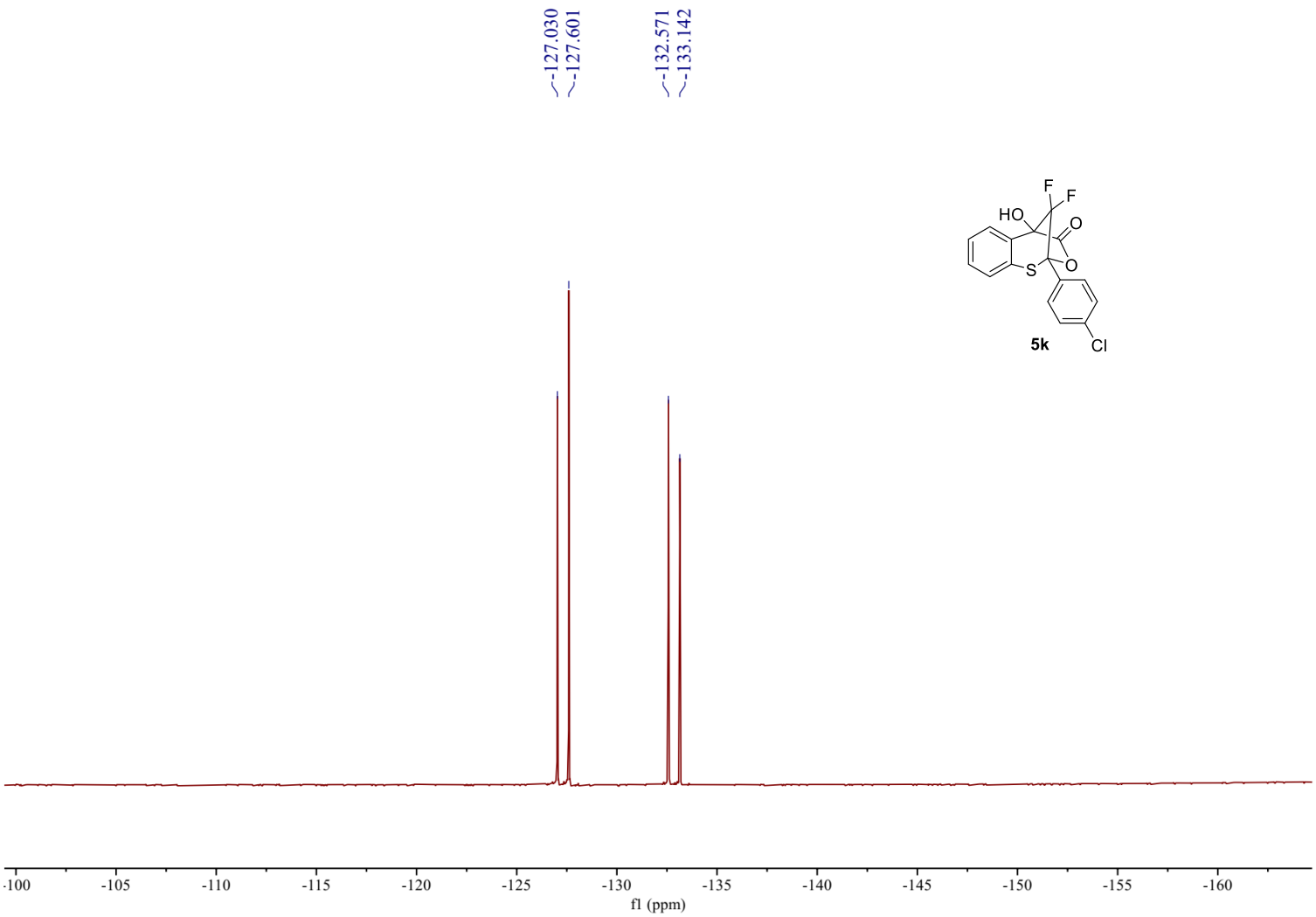
^{19}F NMR spectra of **5j** in $CDCl_3$ (376 MHz)



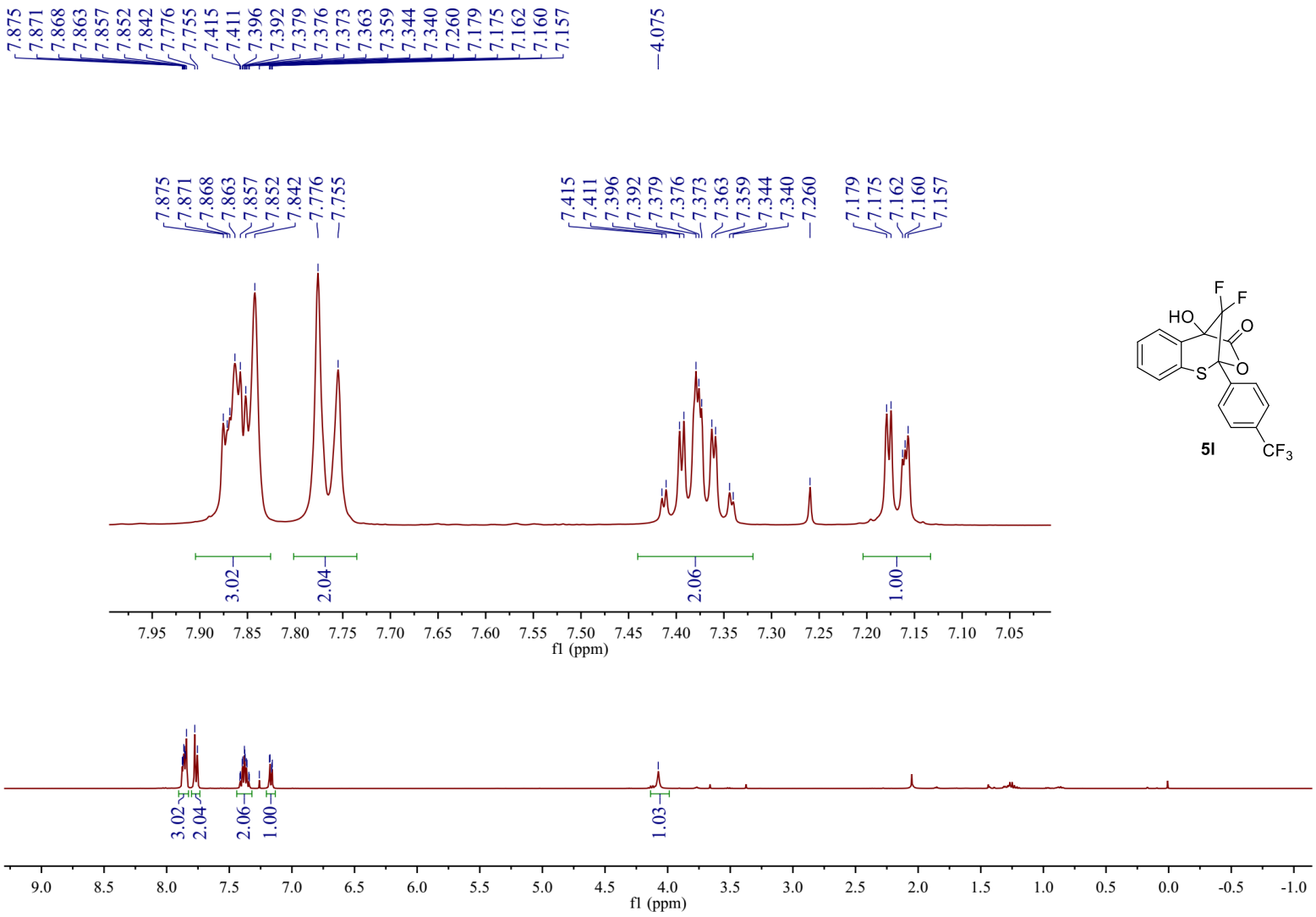
^{1}H NMR spectra of **5k** in $CDCl_3$ (400 MHz)



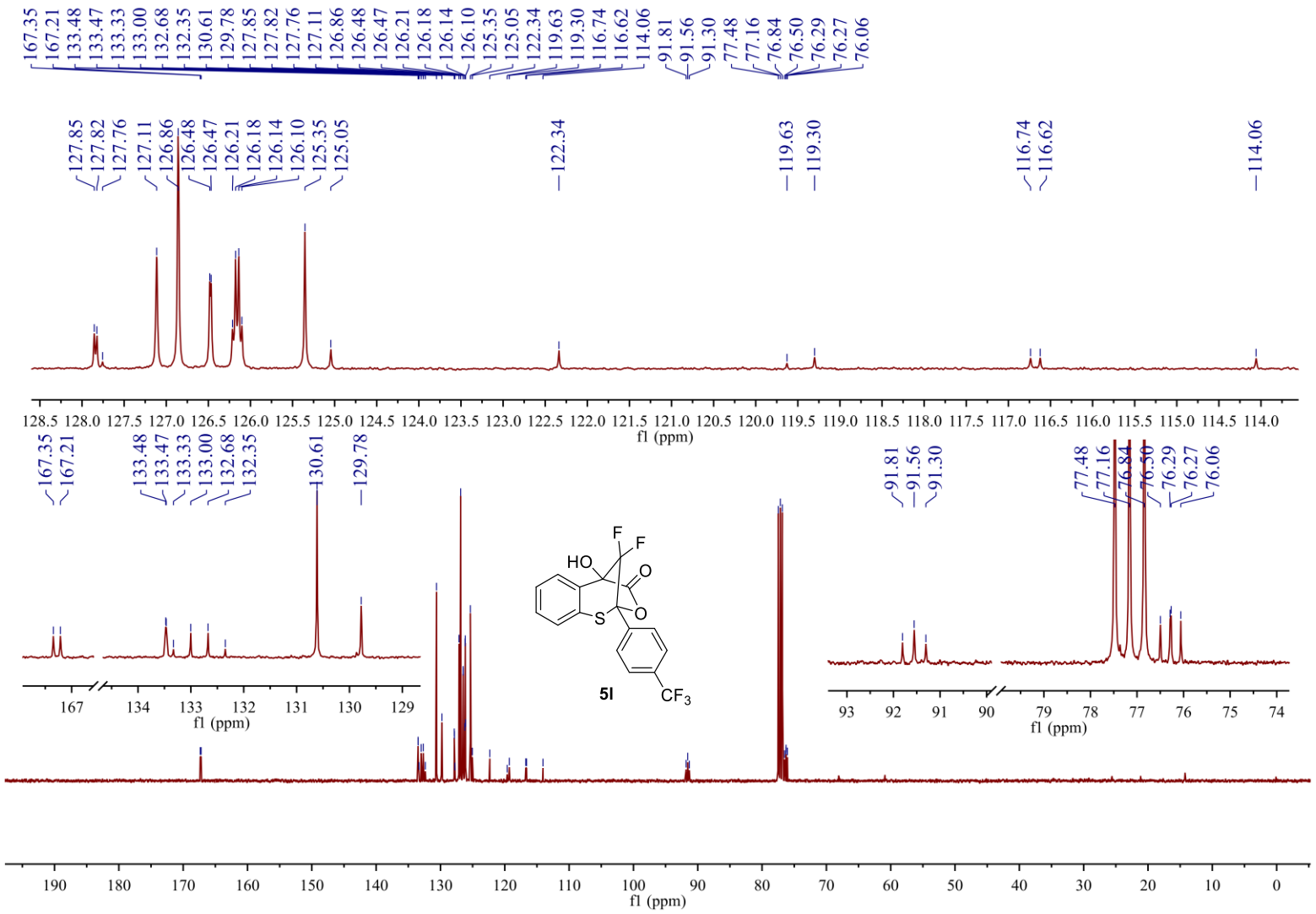
$^{13}C\{^{1}H\}$ NMR spectra of **5k** in $CDCl_3$ (100 MHz)



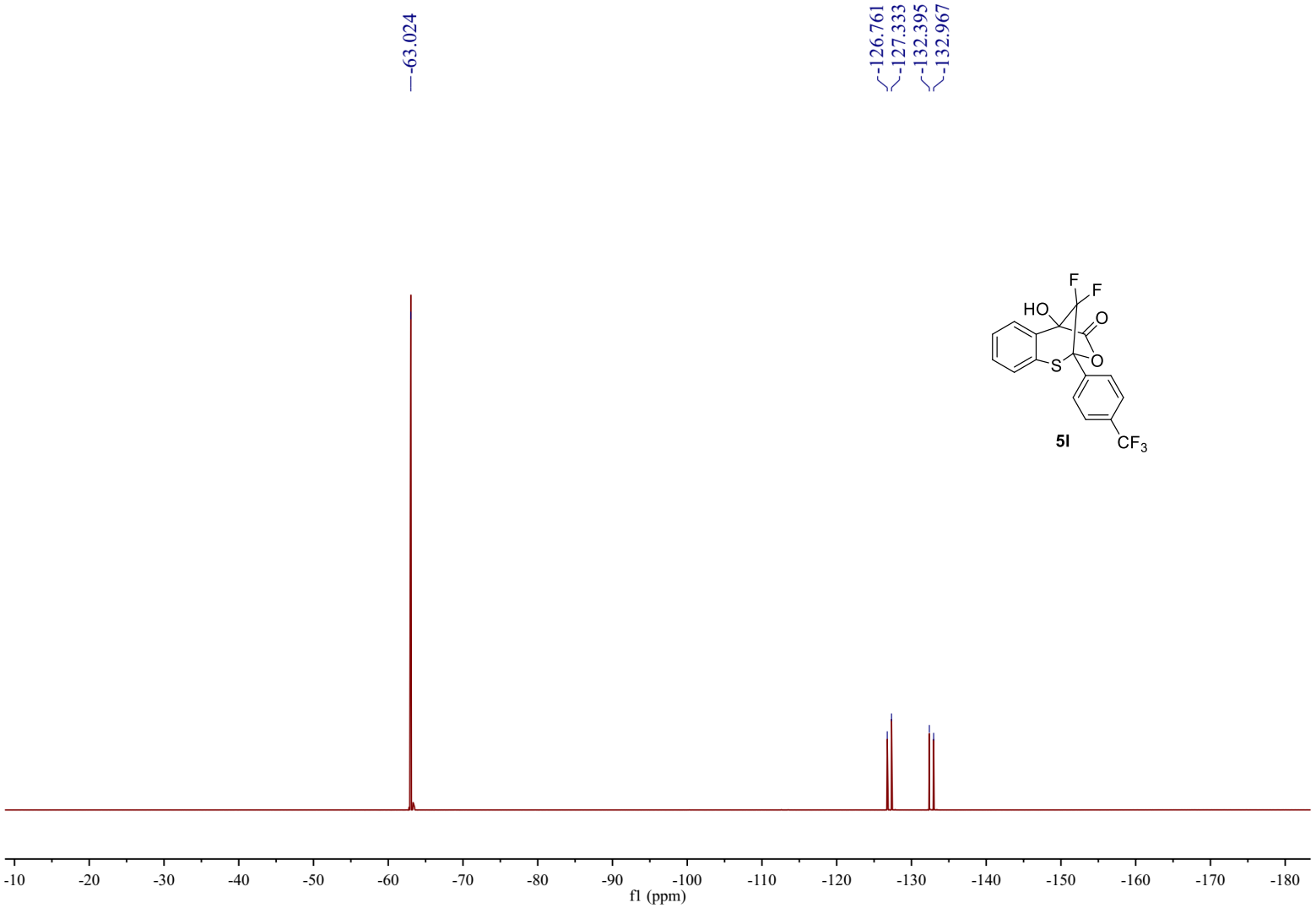
^{19}F NMR spectra of **5k** in $CDCl_3$ (376 MHz)



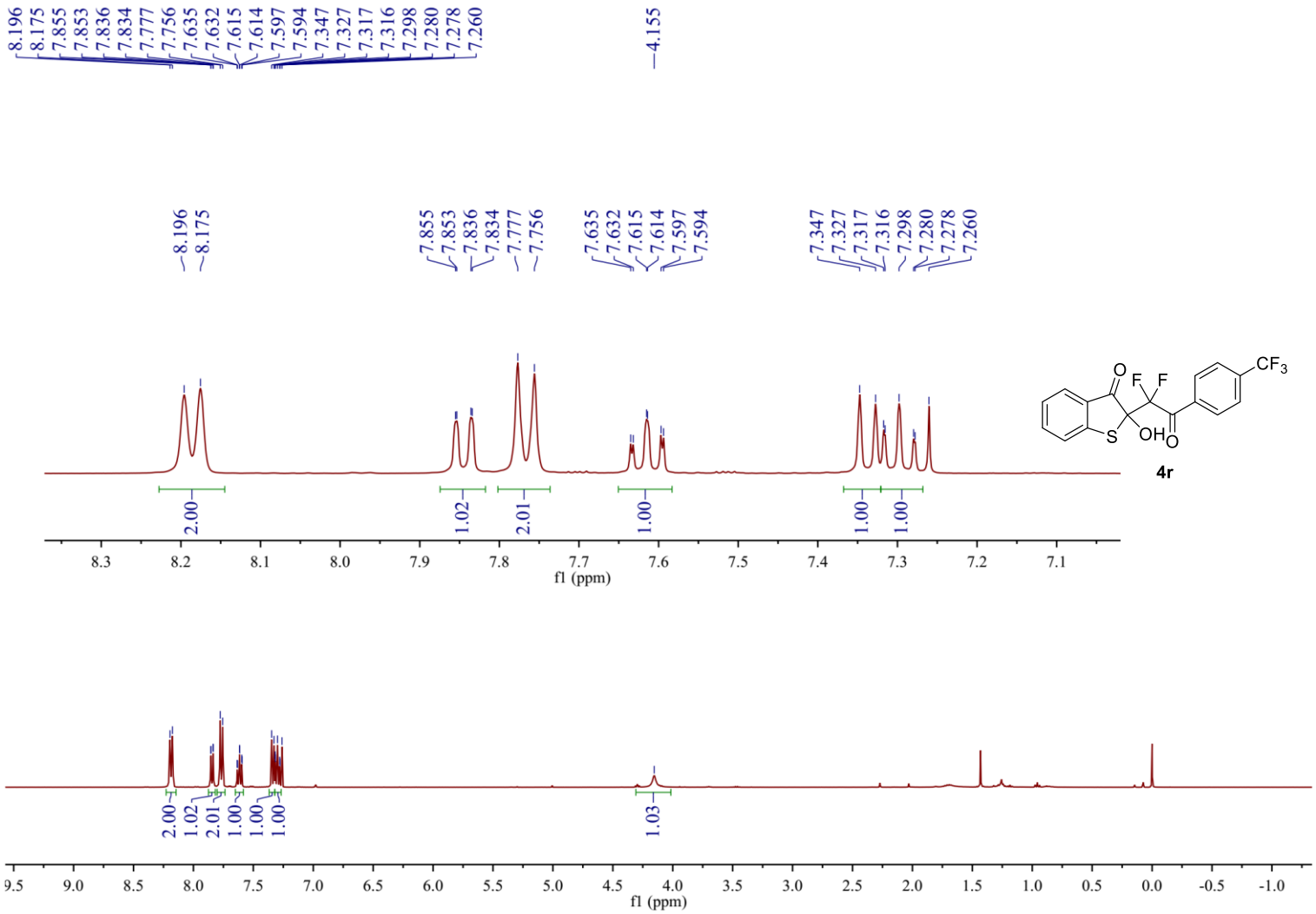
^{1}H NMR spectra of **5l** in $CDCl_3$ (400 MHz)



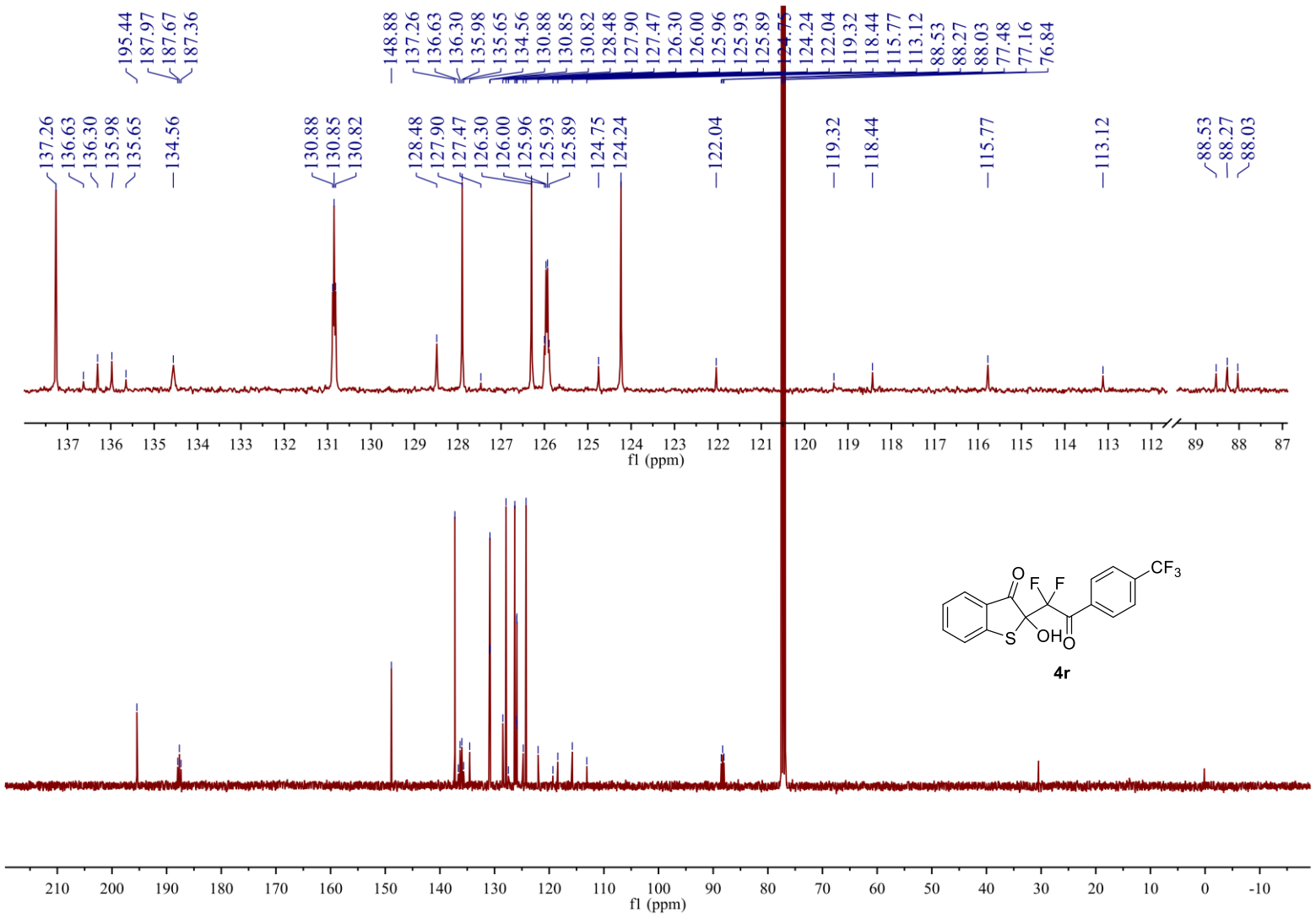
$^{13}C\{^{1}H\}$ NMR spectra of **5l** in $CDCl_3$ (100 MHz)



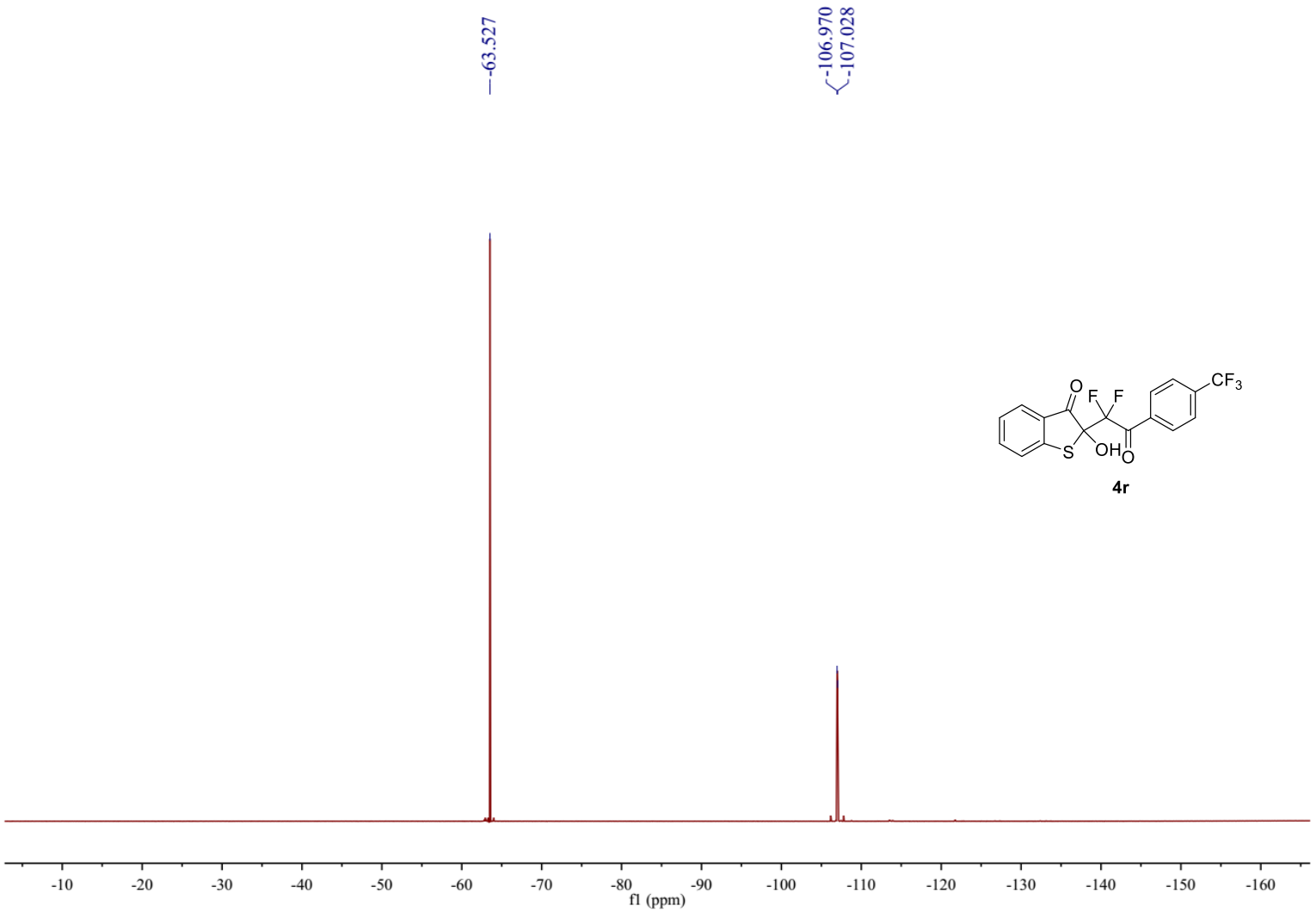
^{19}F NMR spectra of **5l** in $CDCl_3$ (376 MHz)



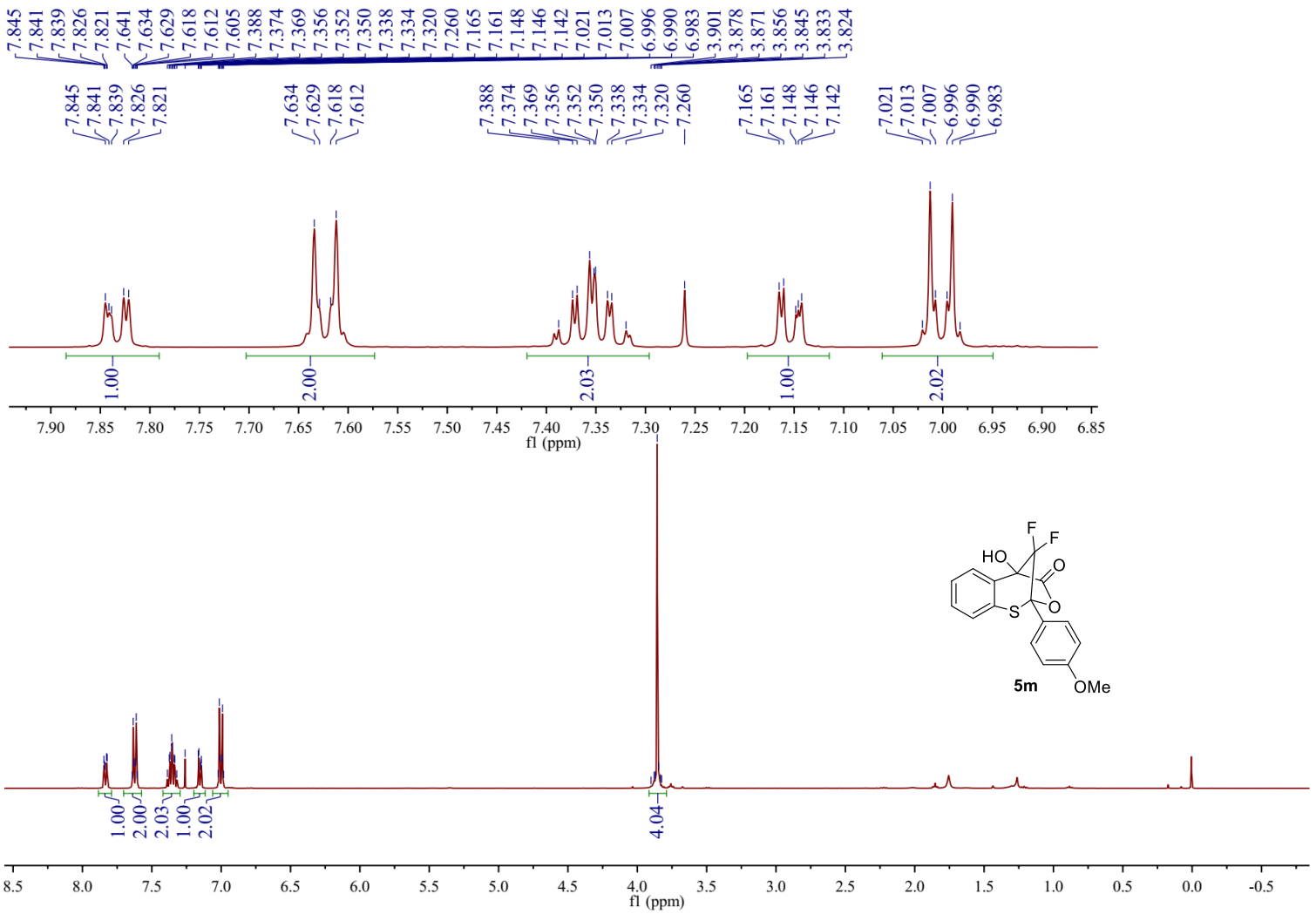
^{1}H NMR spectra of **4r** in $CDCl_3$ (400 MHz)



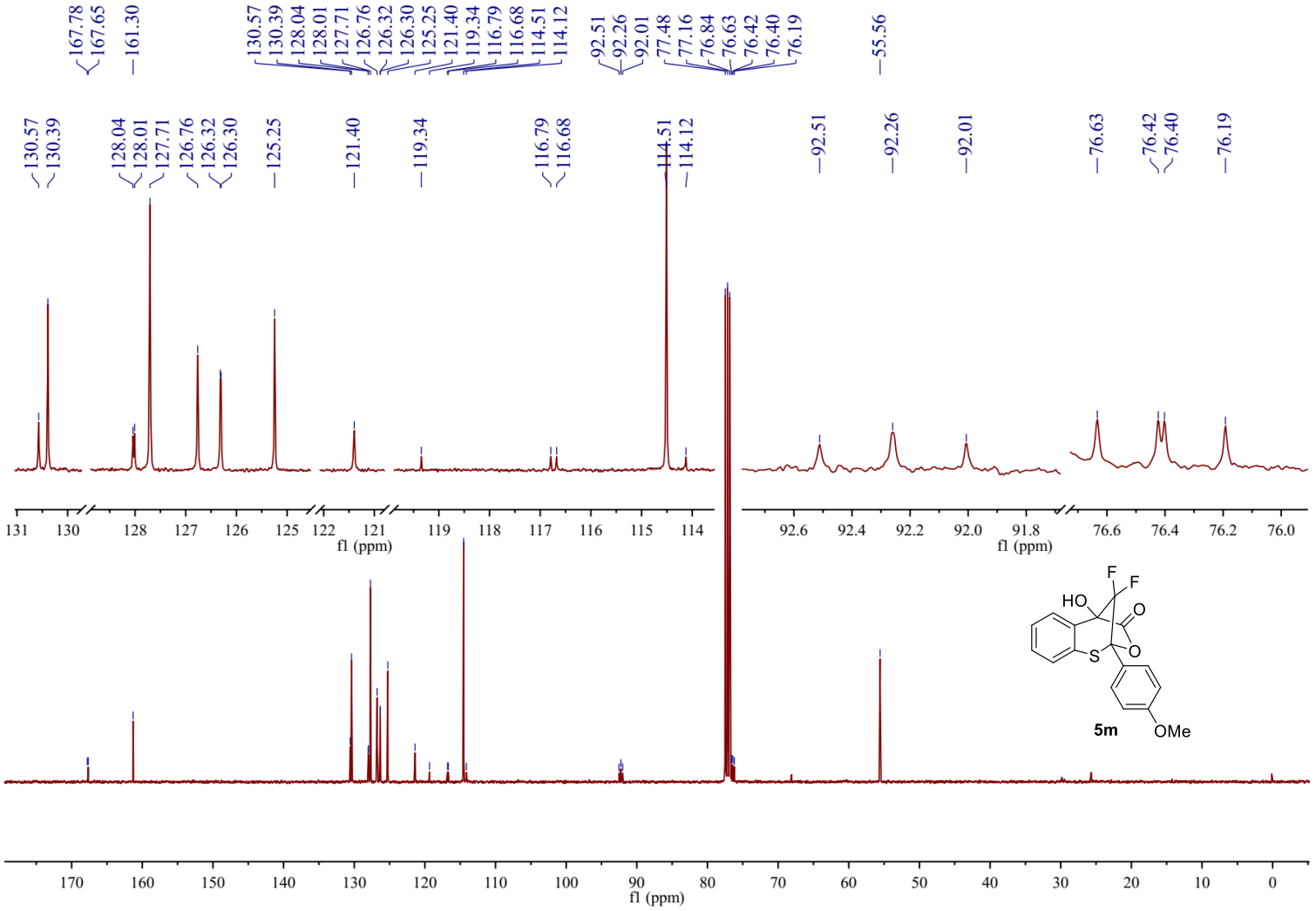
$^{13}C\{^{1}H\}$ NMR spectra of **4r** in $CDCl_3$ (100 MHz)



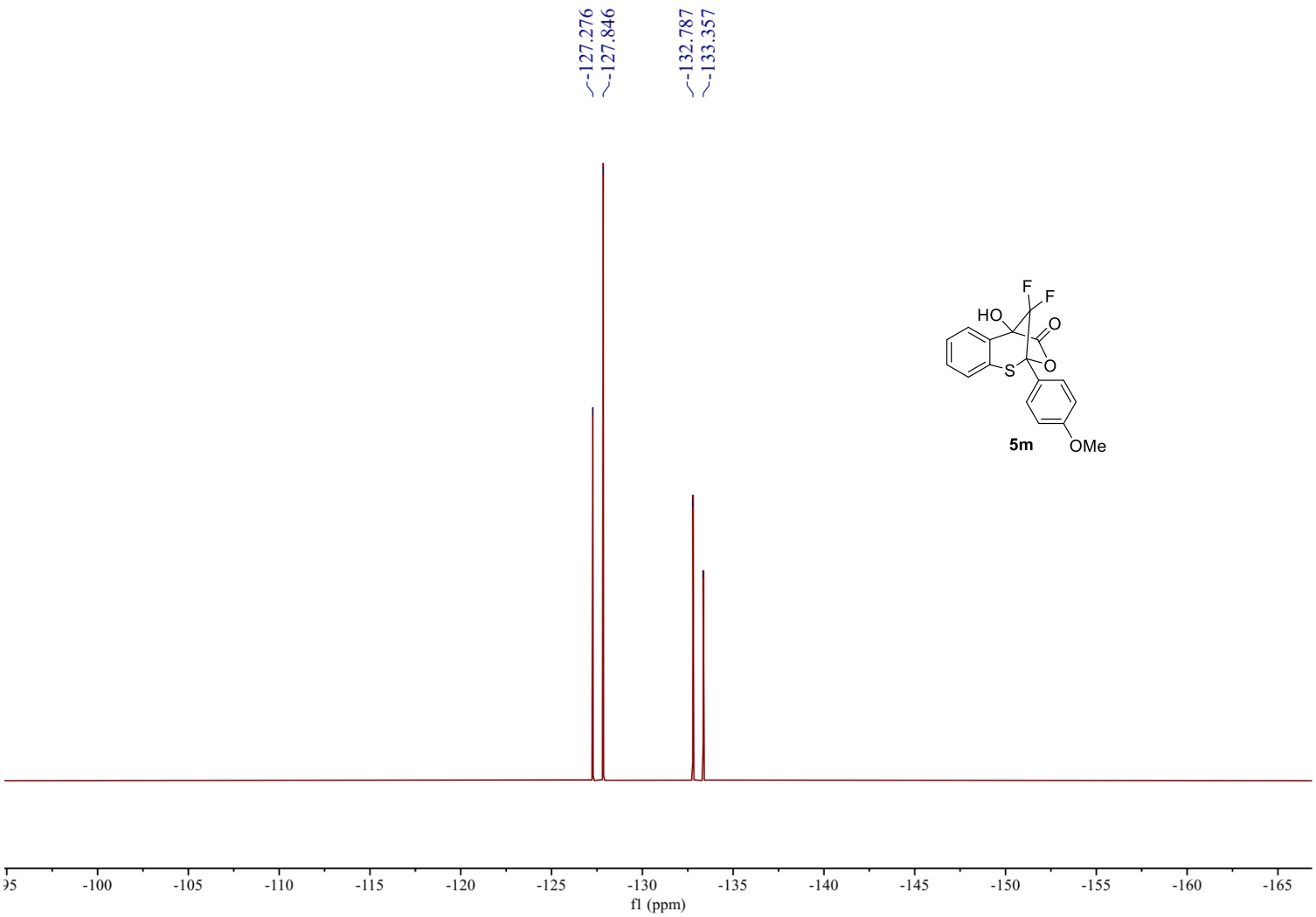
^{19}F NMR spectra of **4r** in $CDCl_3$ (376 MHz)



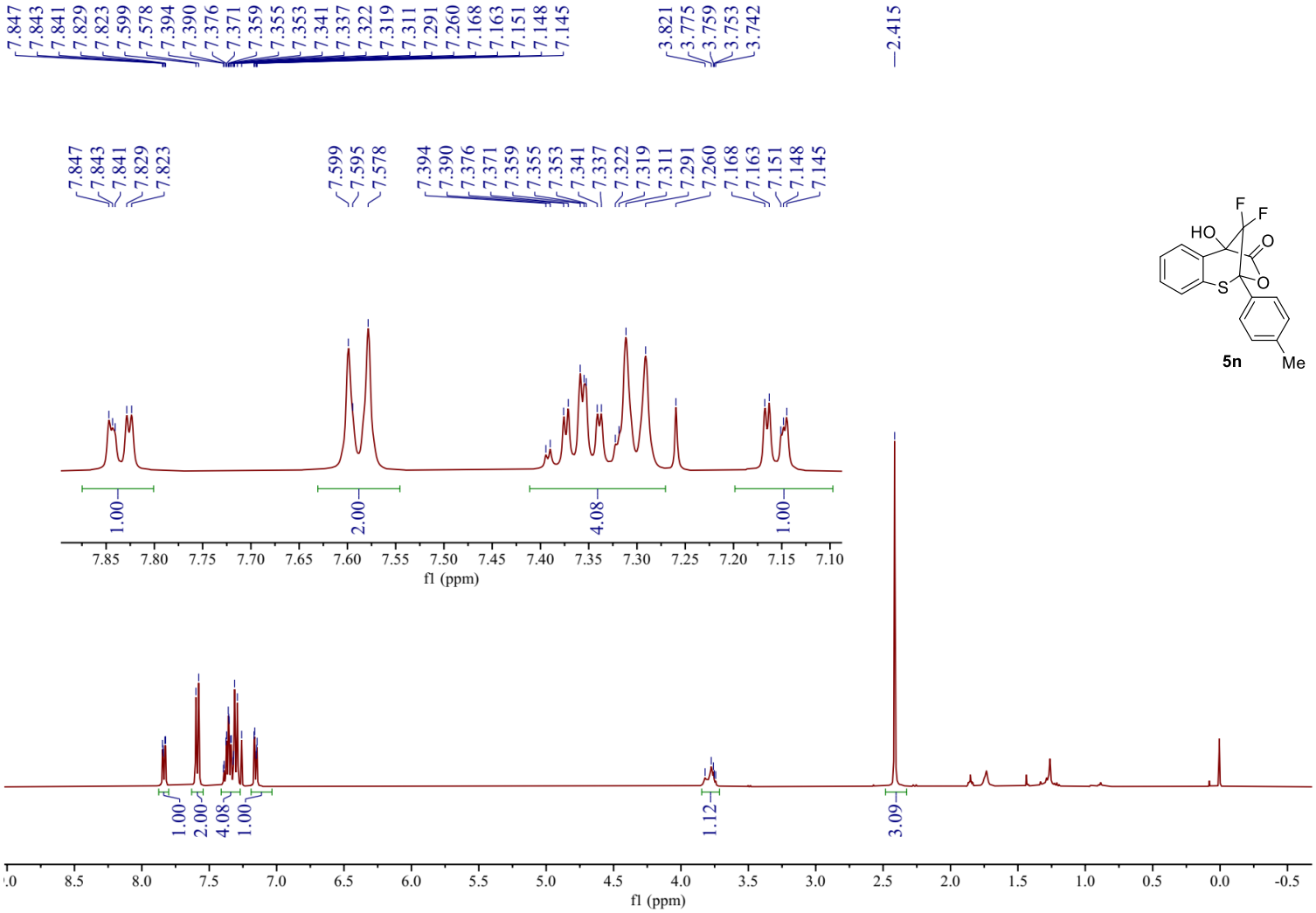
^{1}H NMR spectra of **5m** in $CDCl_3$ (400 MHz)



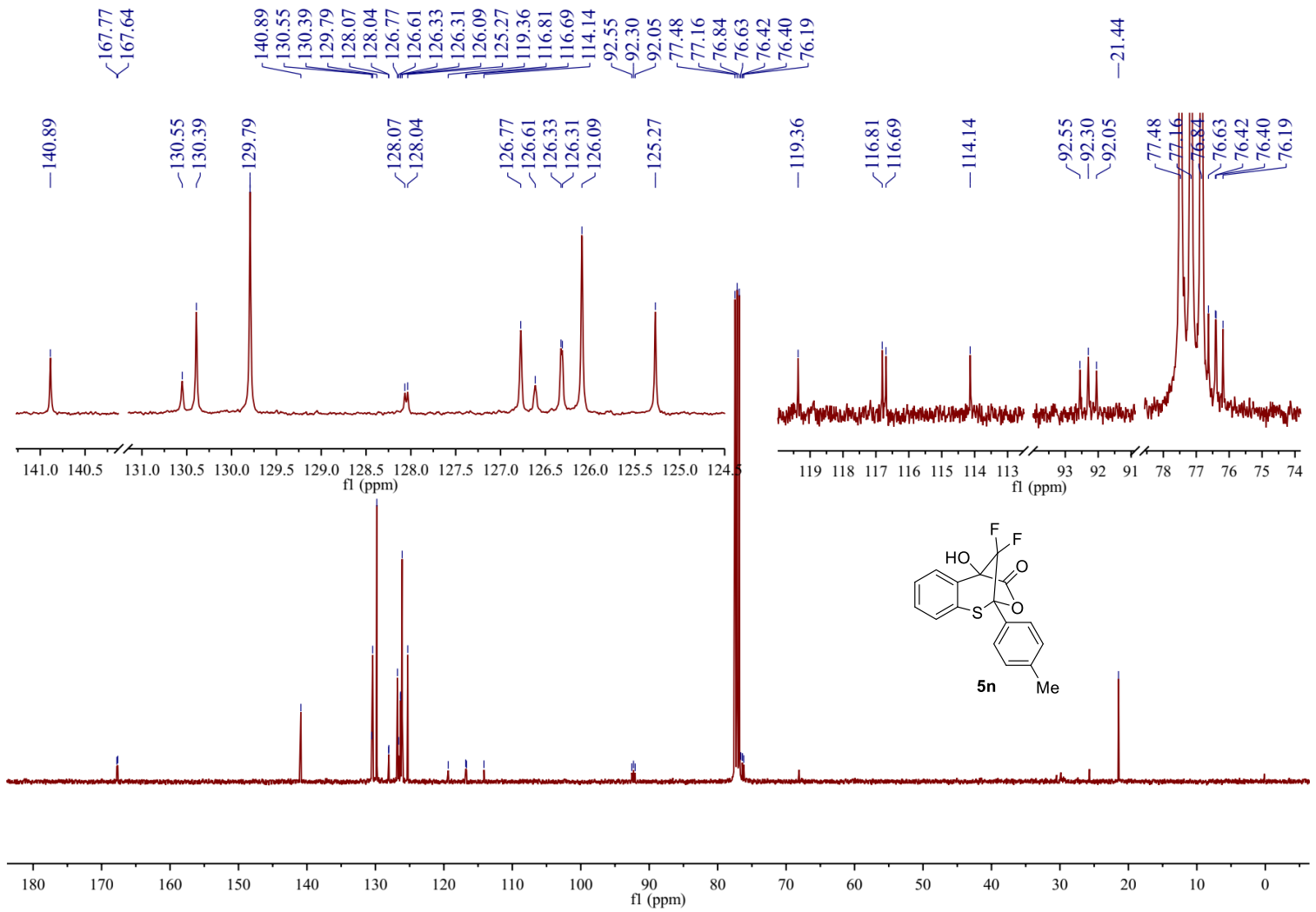
$^{13}C\{^{1}H\}$ NMR spectra of **5m** in $CDCl_3$ (100 MHz)



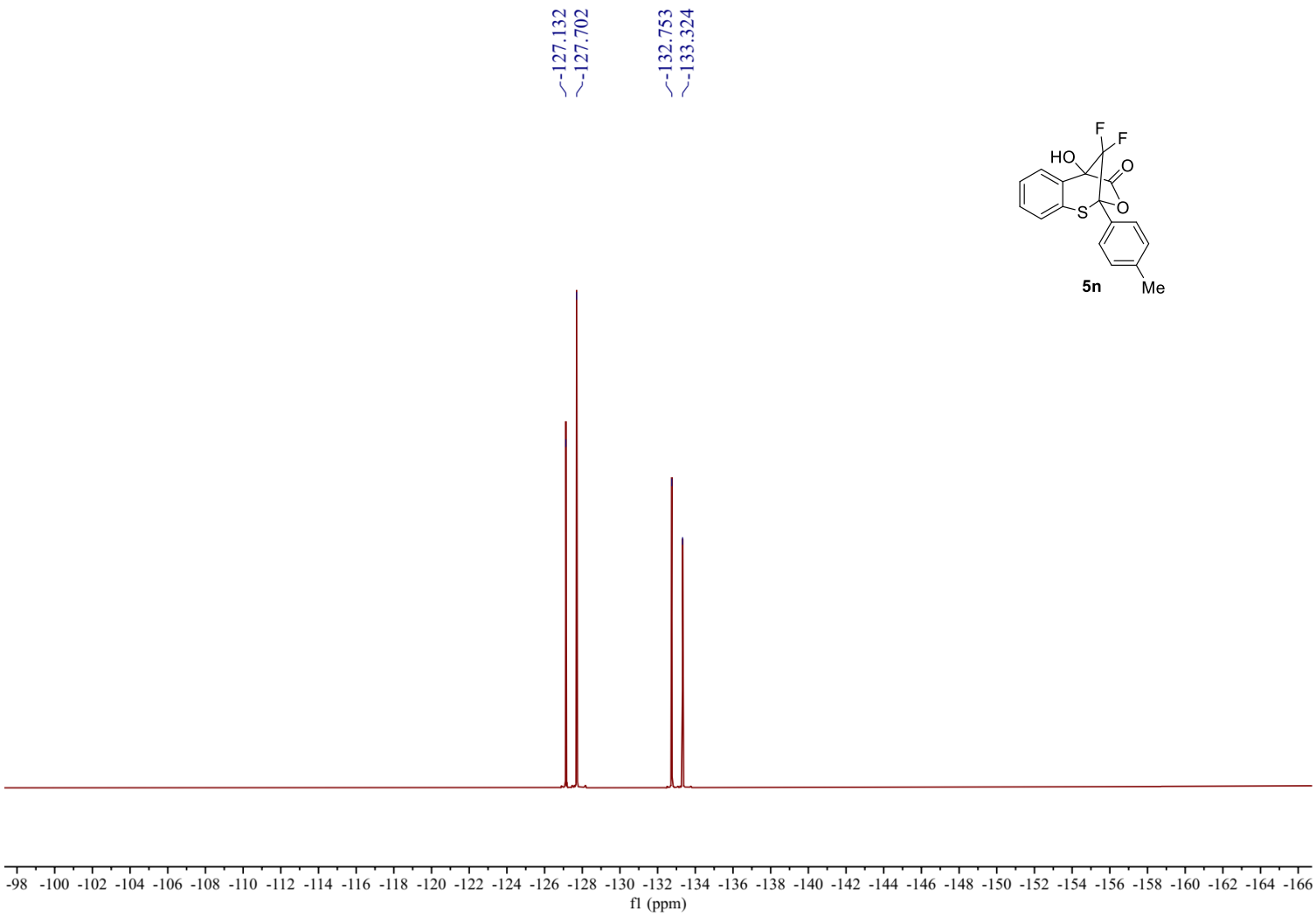
^{19}F NMR spectra of **5m** in $CDCl_3$ (376 MHz)



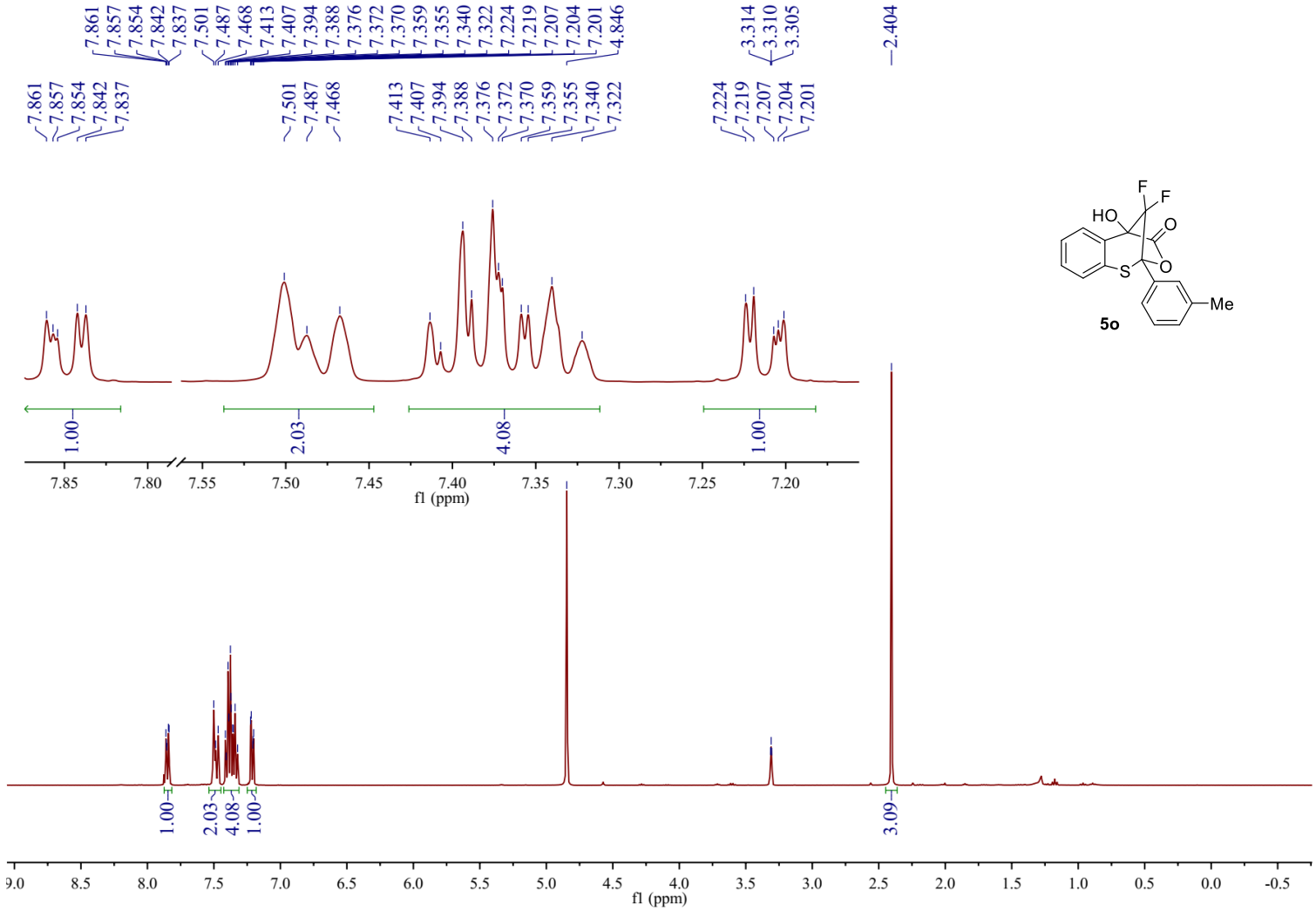
^{1}H NMR spectra of **5n** in $CDCl_3$ (400 MHz)



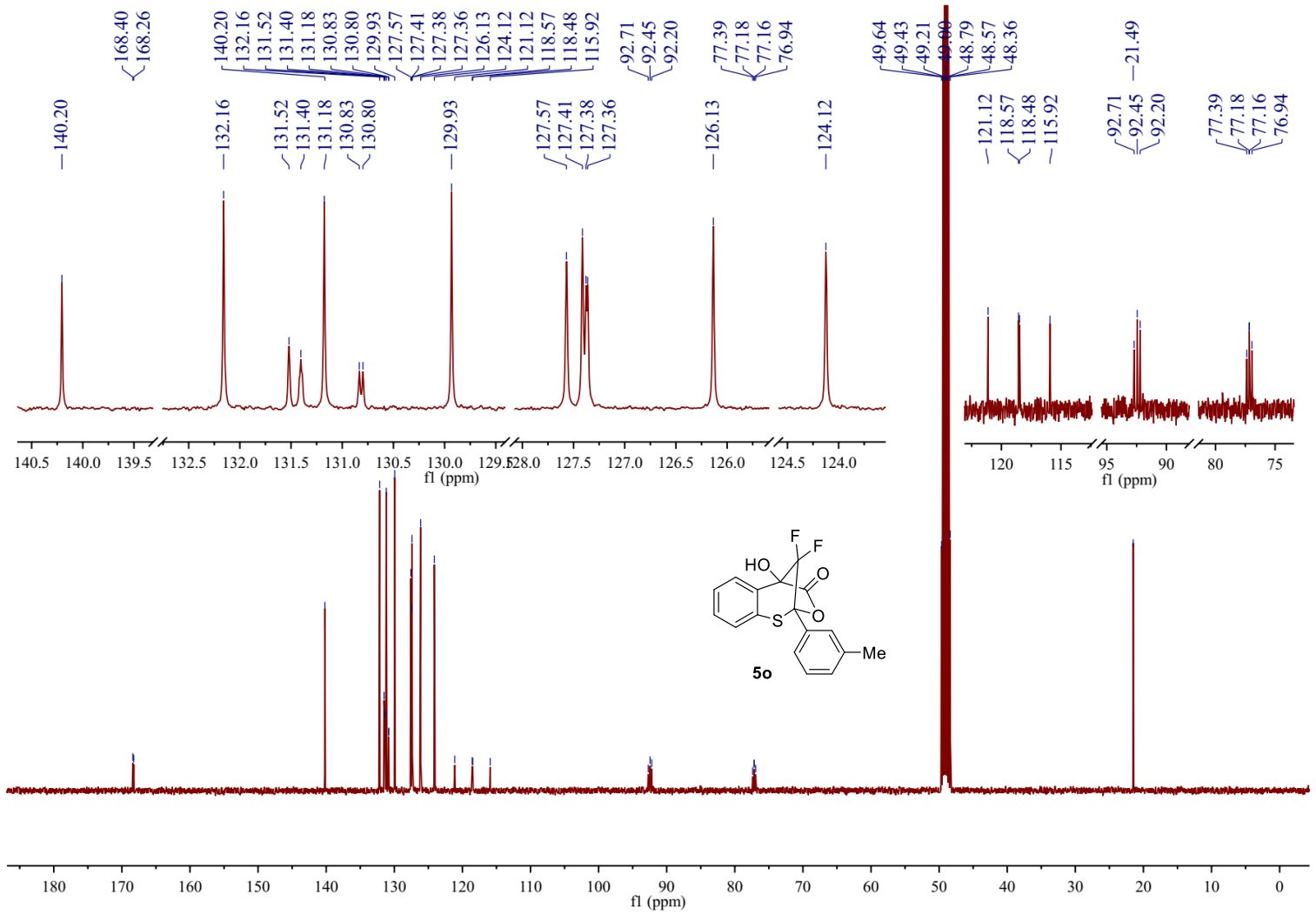
$^{13}C\{^{1}H\}$ NMR spectra of **5n** in $CDCl_3$ (100 MHz)



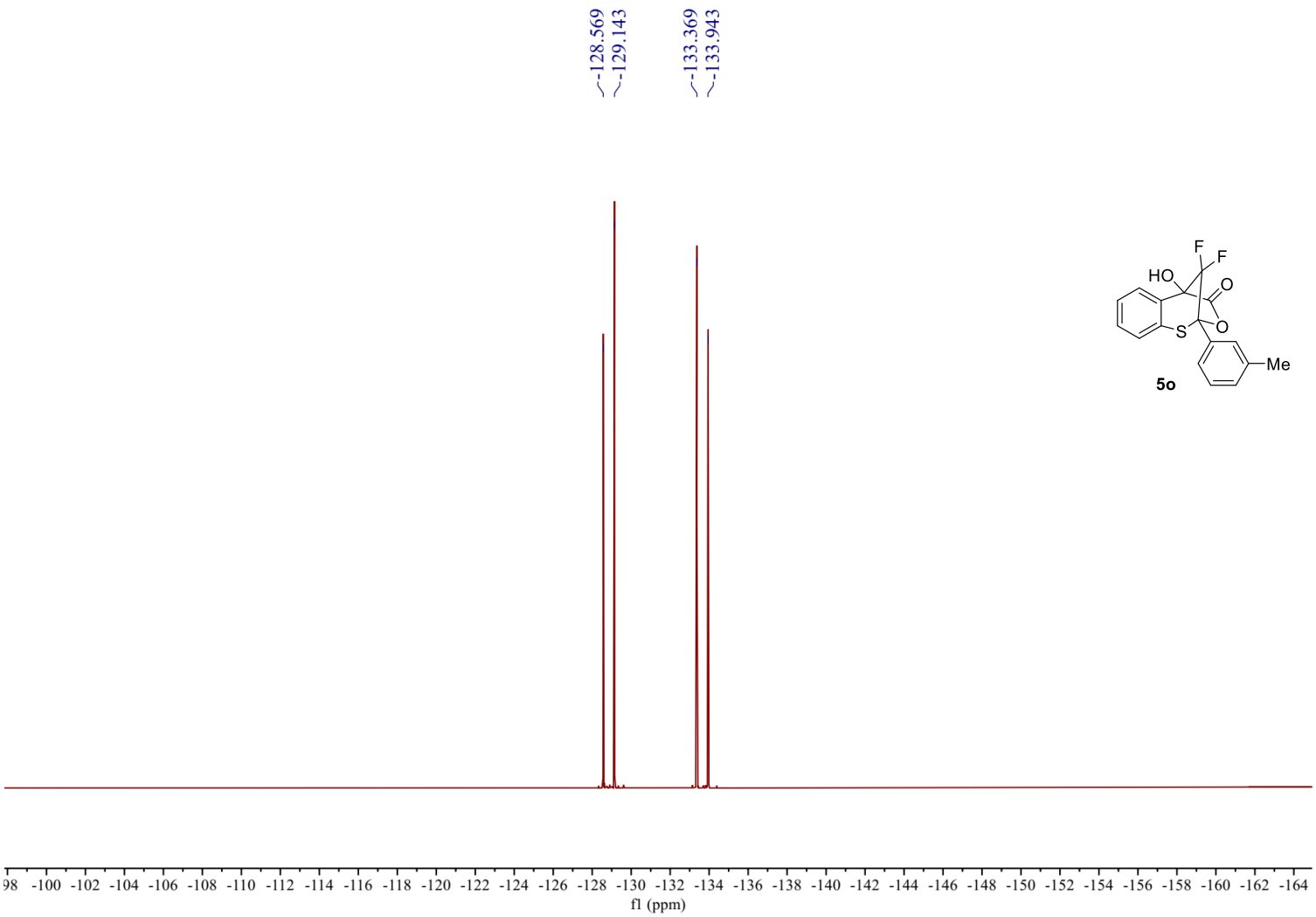
^{19}F NMR spectra of **5n** in $CDCl_3$ (376 MHz)



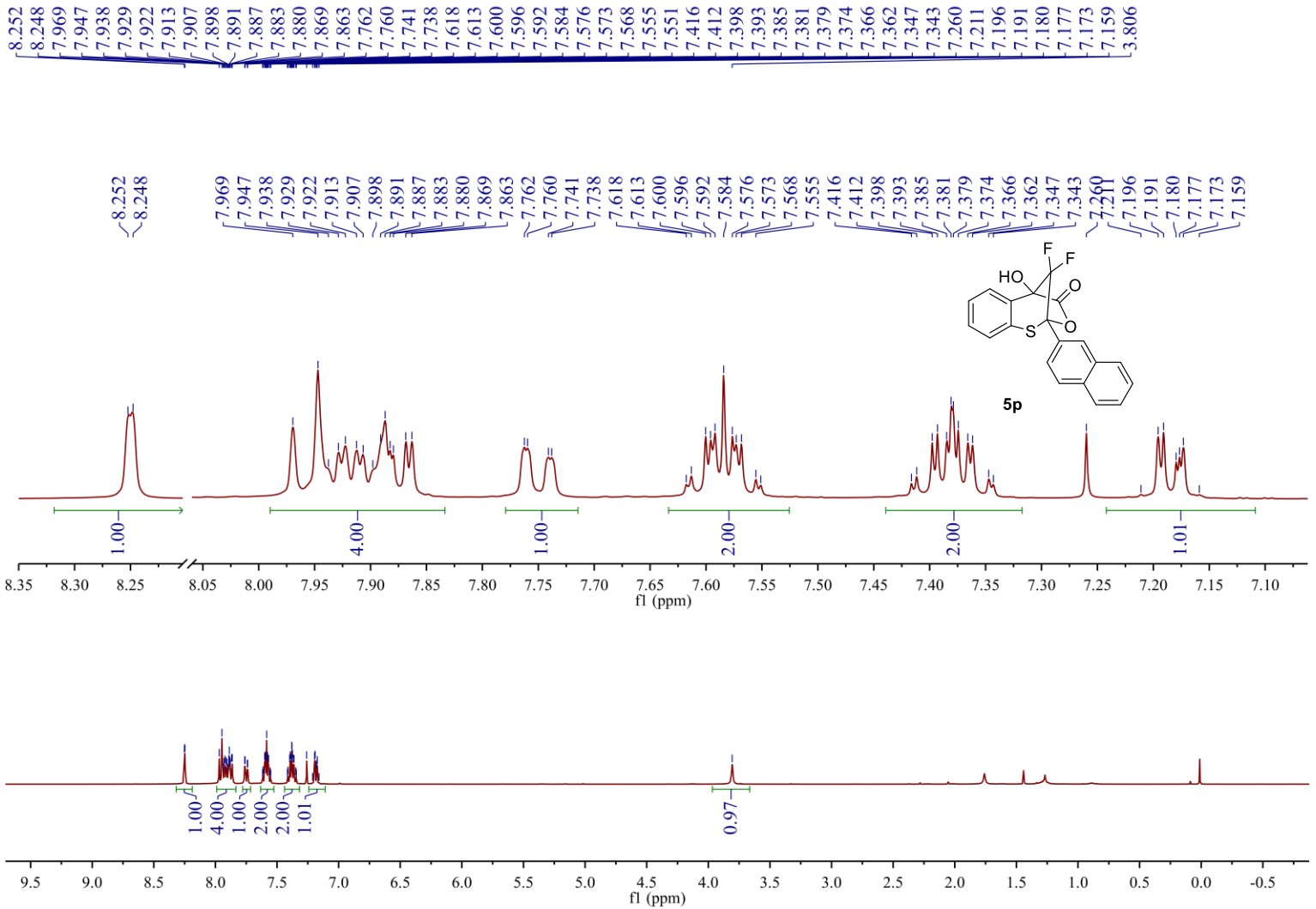
^{1}H NMR spectra of **5o** in CD_3OD (400 MHz)



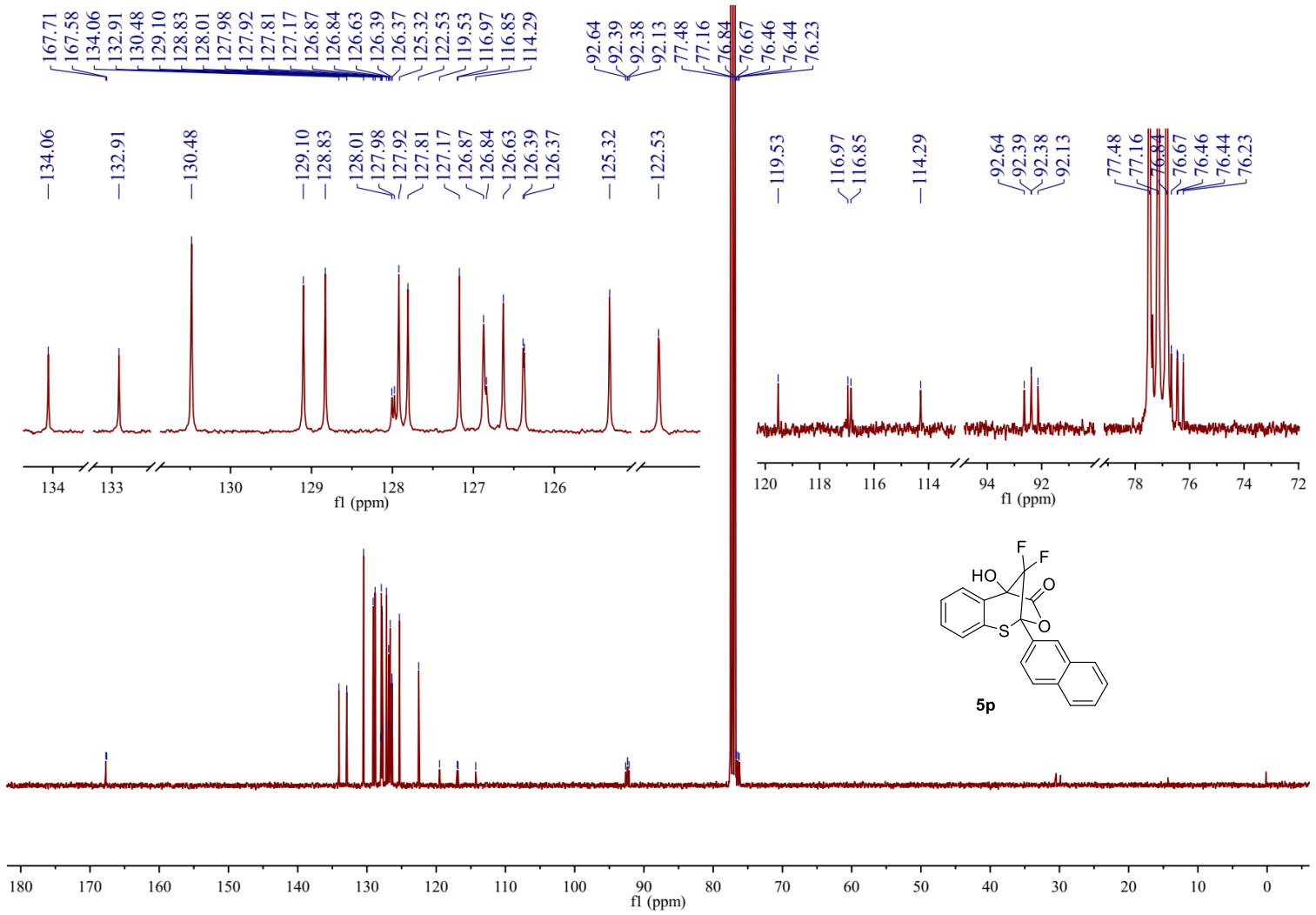
$^{13}C\{^{1}H\}$ NMR spectra of **5o** in CD_3OD (100 MHz)



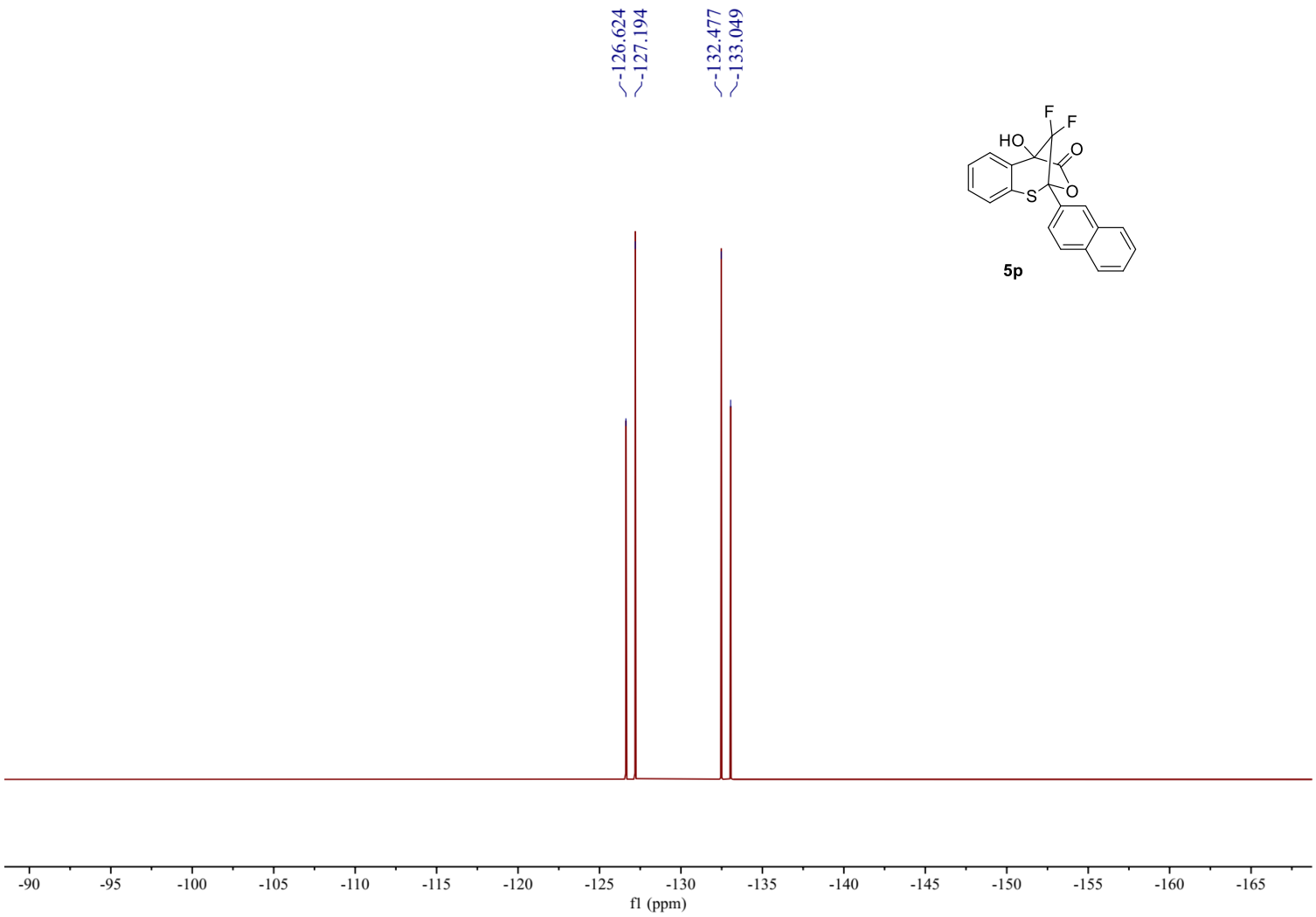
^{19}F NMR spectra of **5o** in CD_3OD (376 MHz)



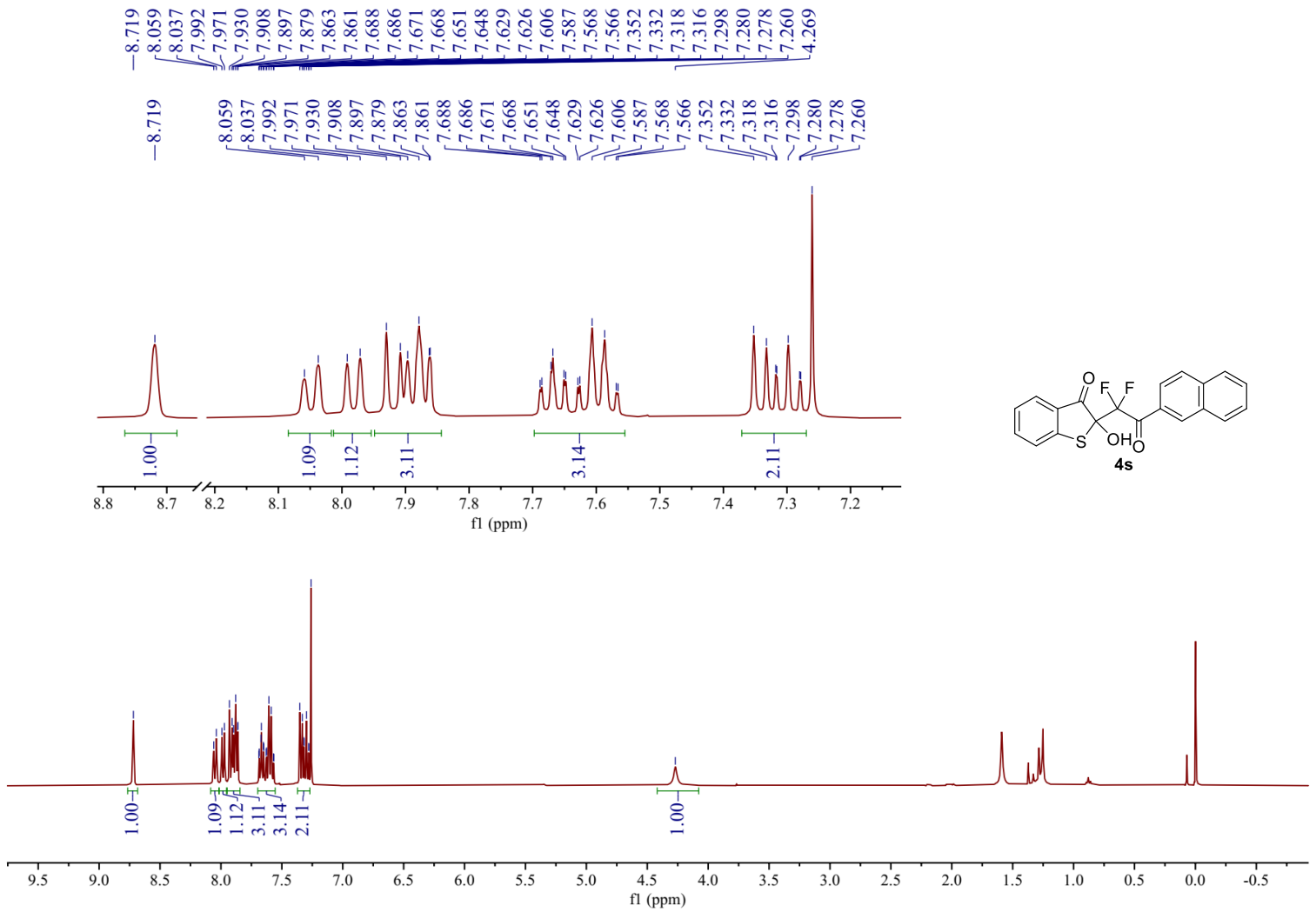
^{1}H NMR spectra of **5p** in $CDCl_3$ (400 MHz)



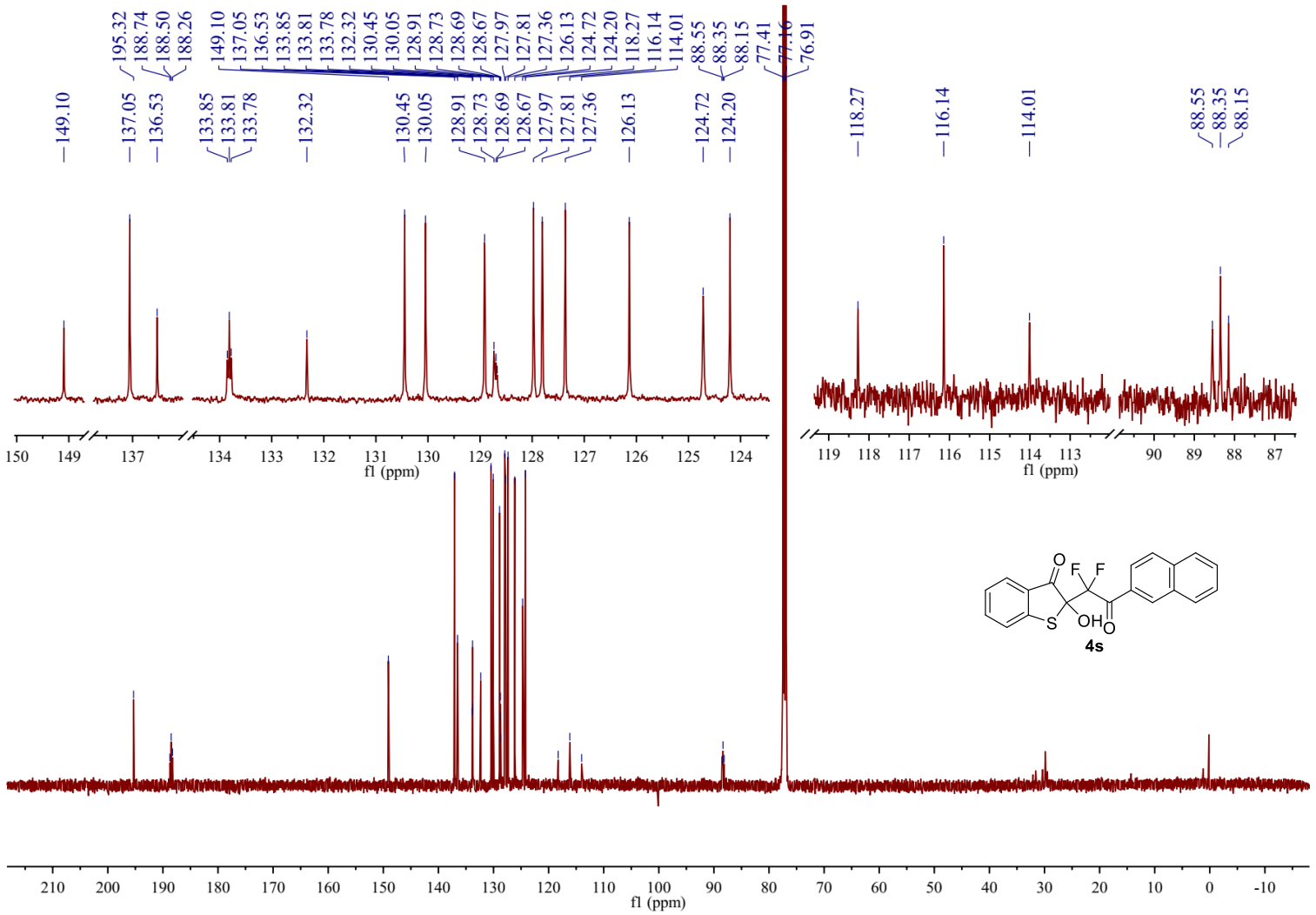
$^{13}C\{^{1}H\}$ NMR spectra of **5p** in $CDCl_3$ (100 MHz)



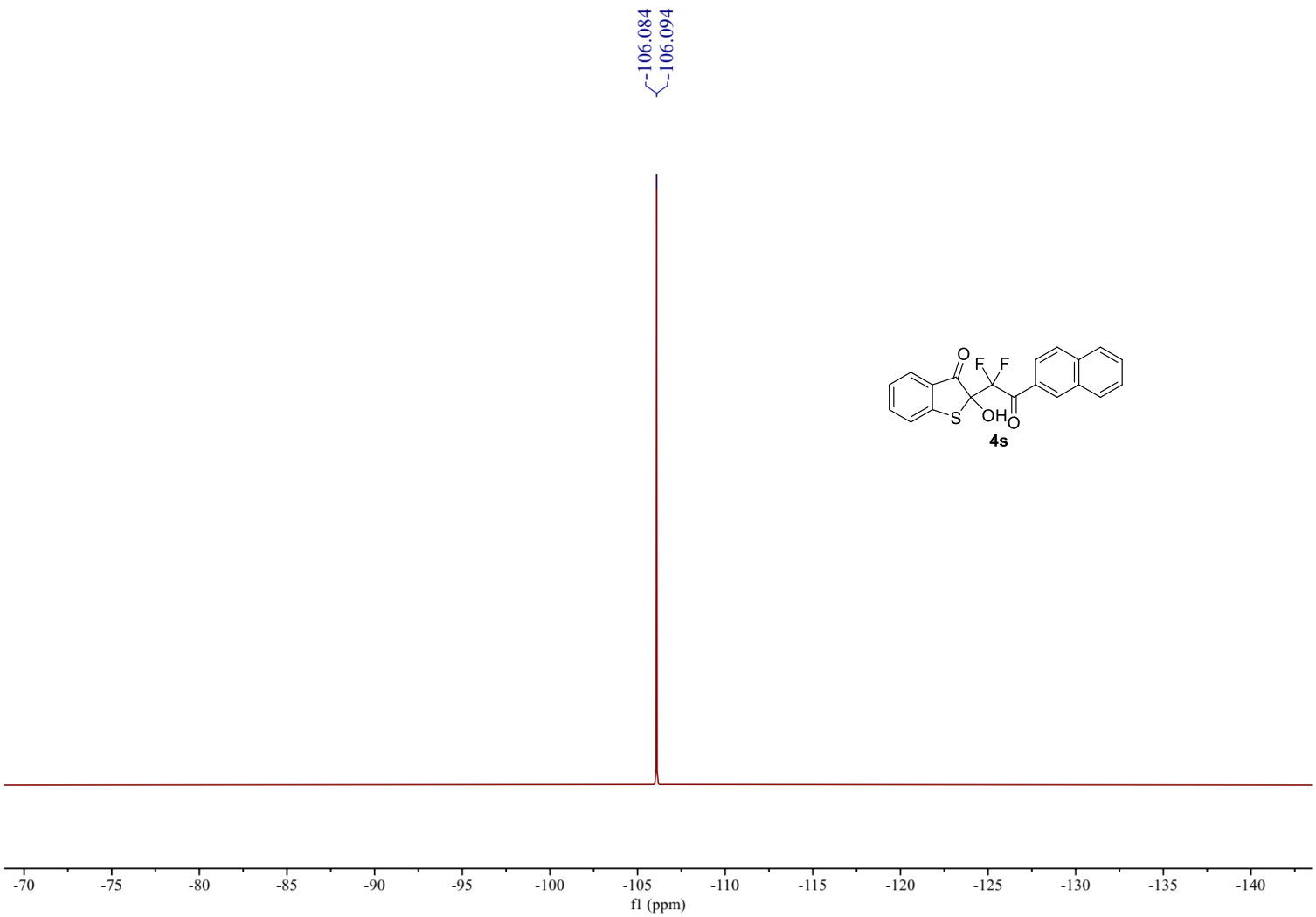
^{19}F NMR spectra of **5p** in $CDCl_3$ (376 MHz)



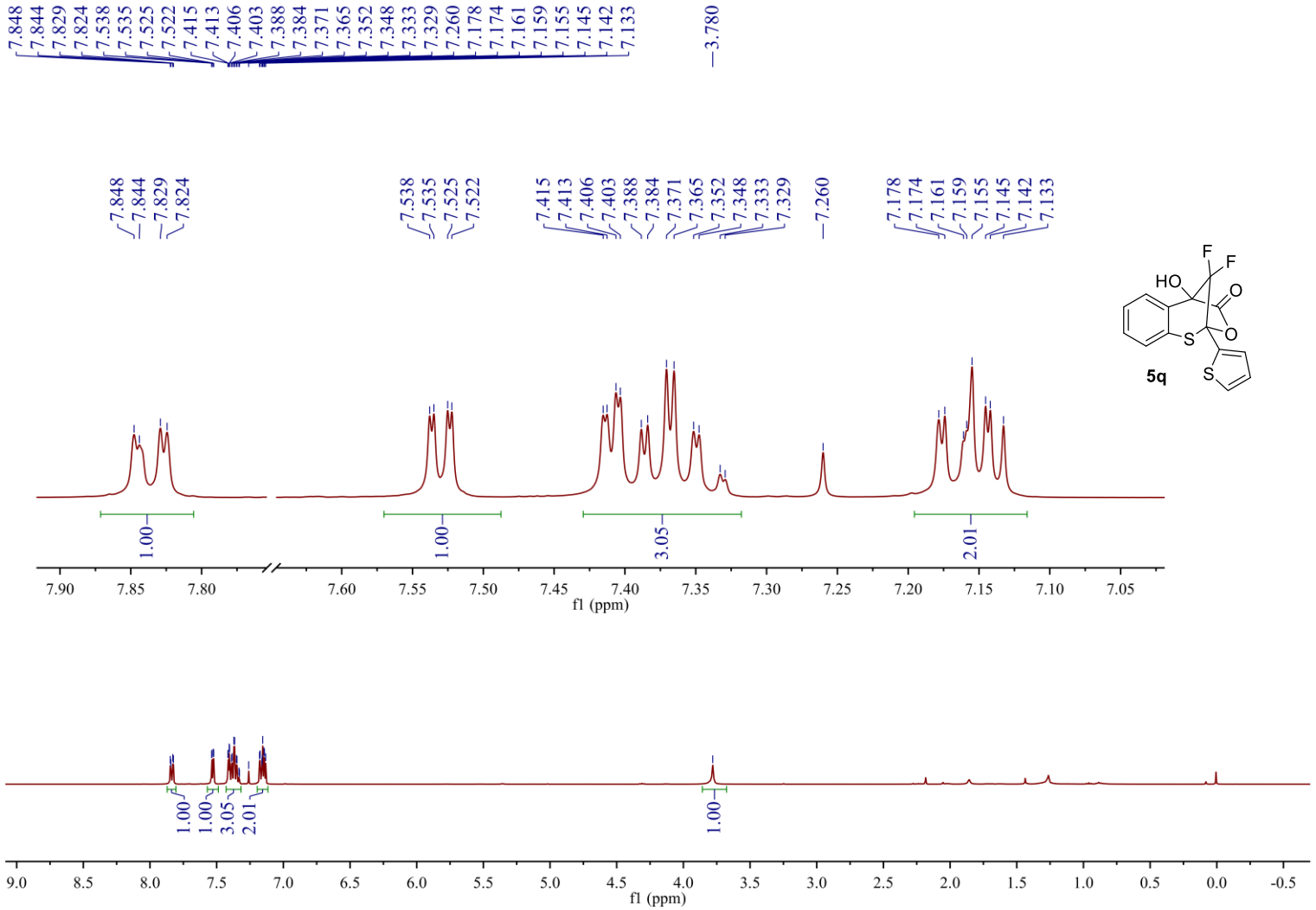
^{1}H NMR spectra of **4s** in $CDCl_3$ (400 MHz)



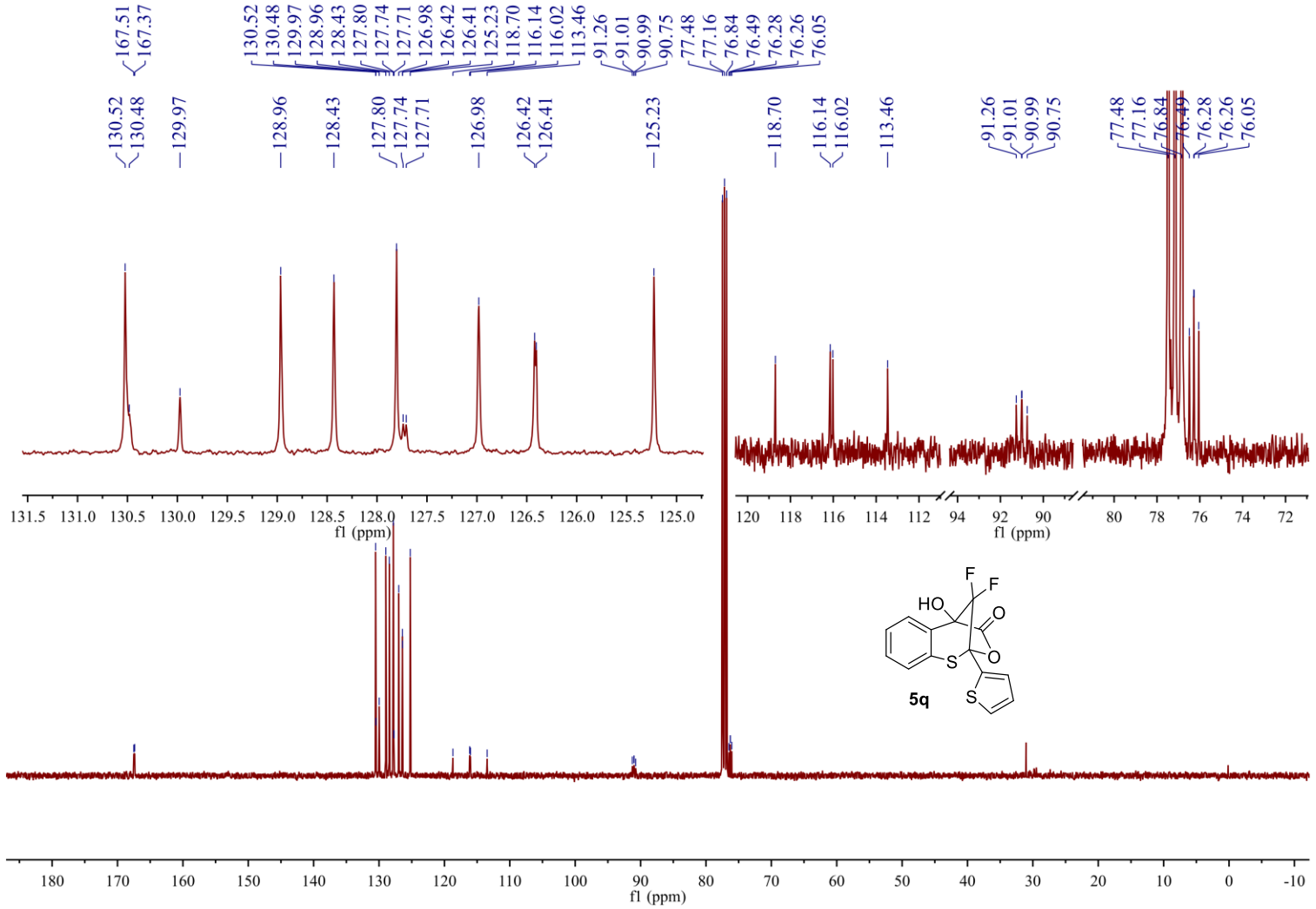
$^{13}C\{^{1}H\}$ NMR spectra of **4s** in $CDCl_3$ (125 MHz)



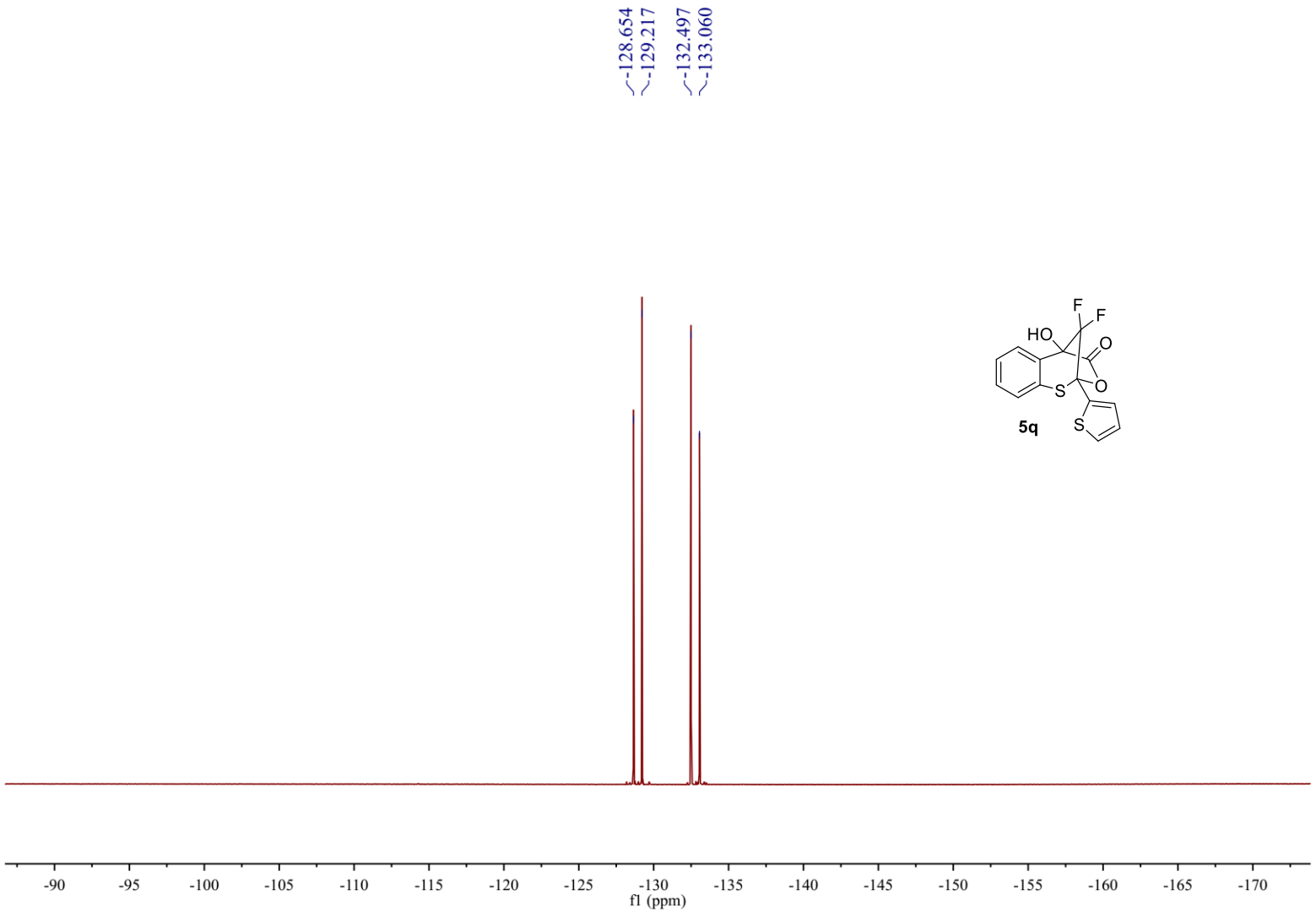
^{19}F NMR spectra of **4s** in $CDCl_3$ (376 MHz)



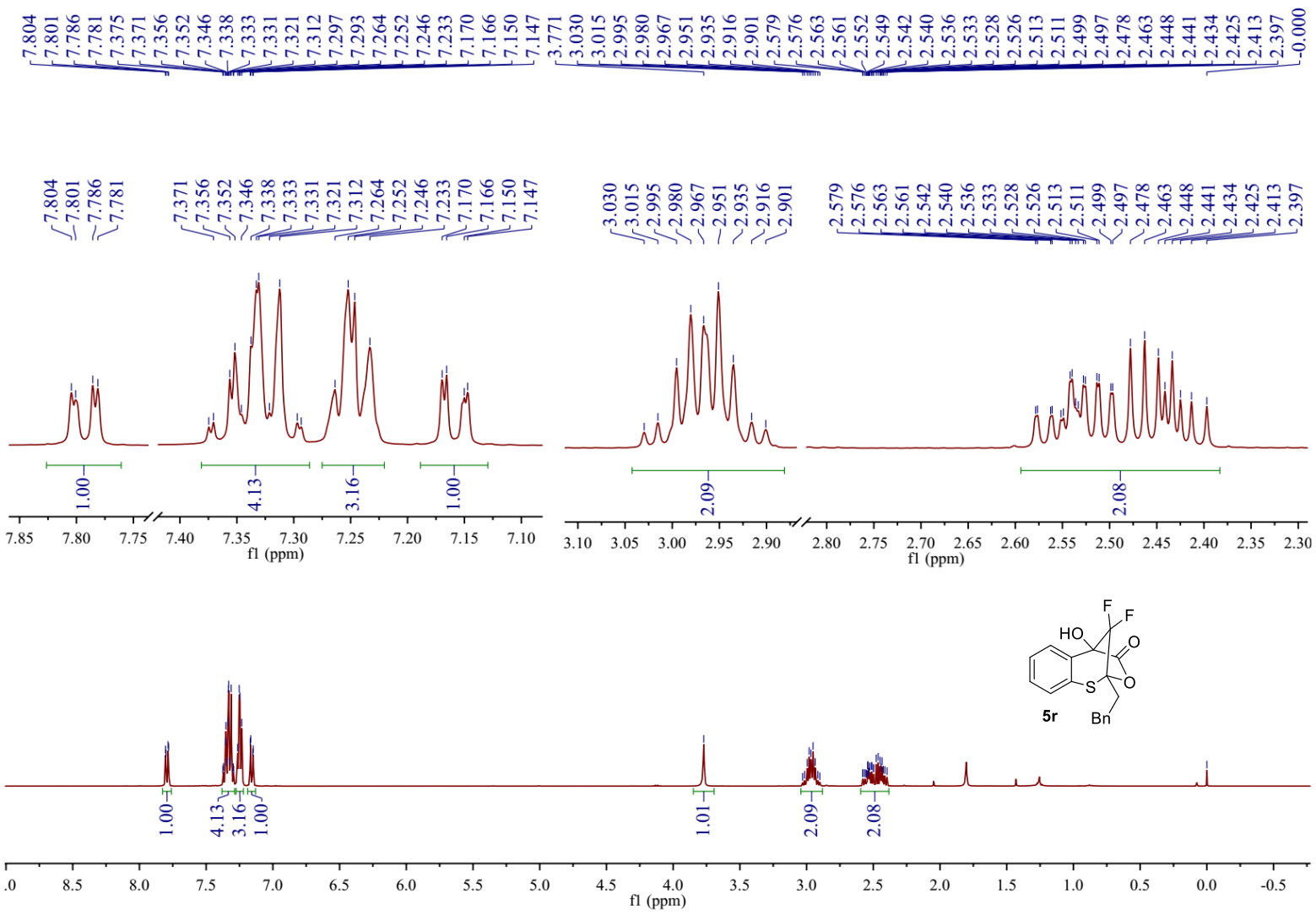
^{1}H NMR spectra of **5q** in $CDCl_3$ (400 MHz)



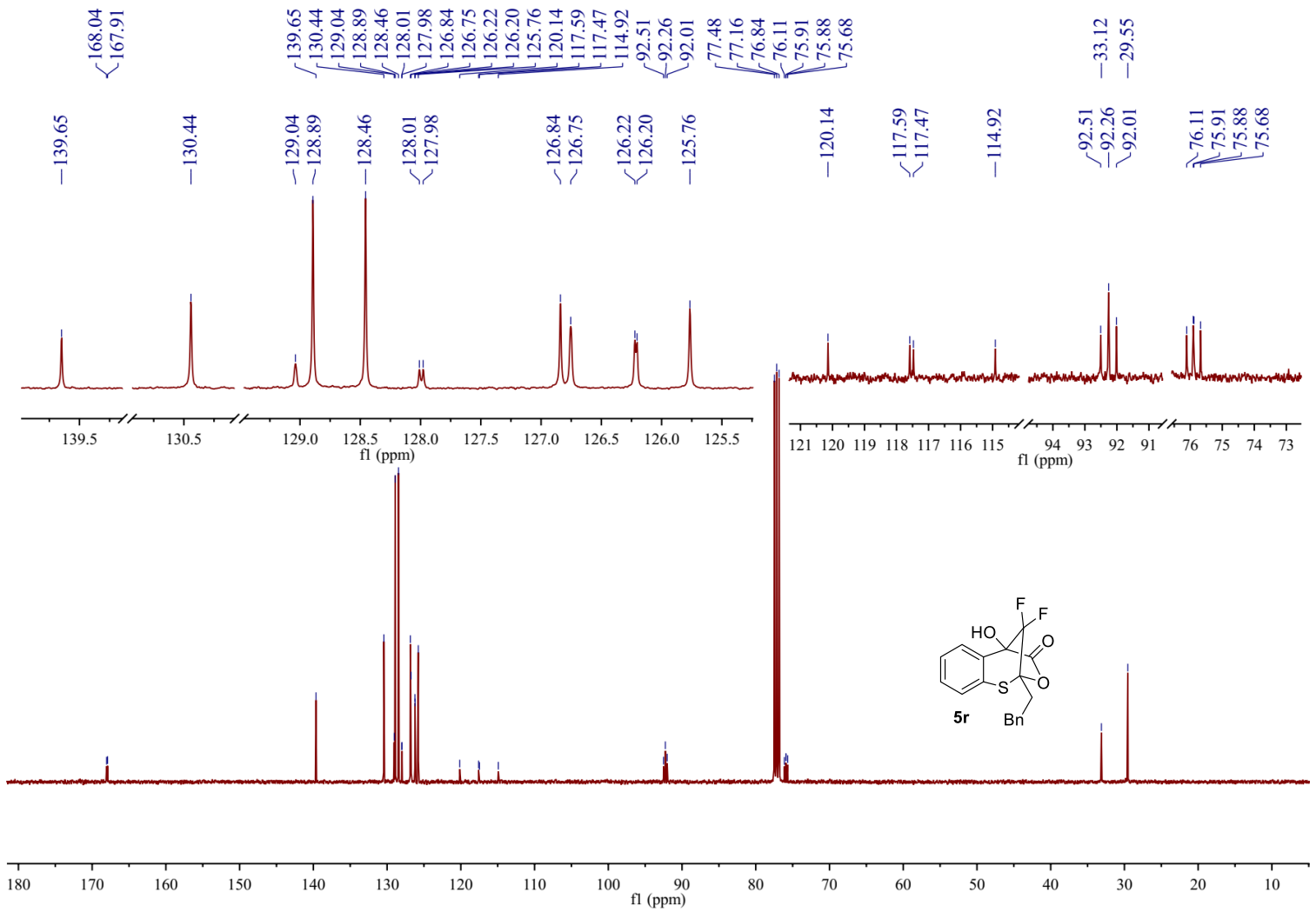
$^{13}C\{^{1}H\}$ NMR spectra of **5q** in $CDCl_3$ (100 MHz)



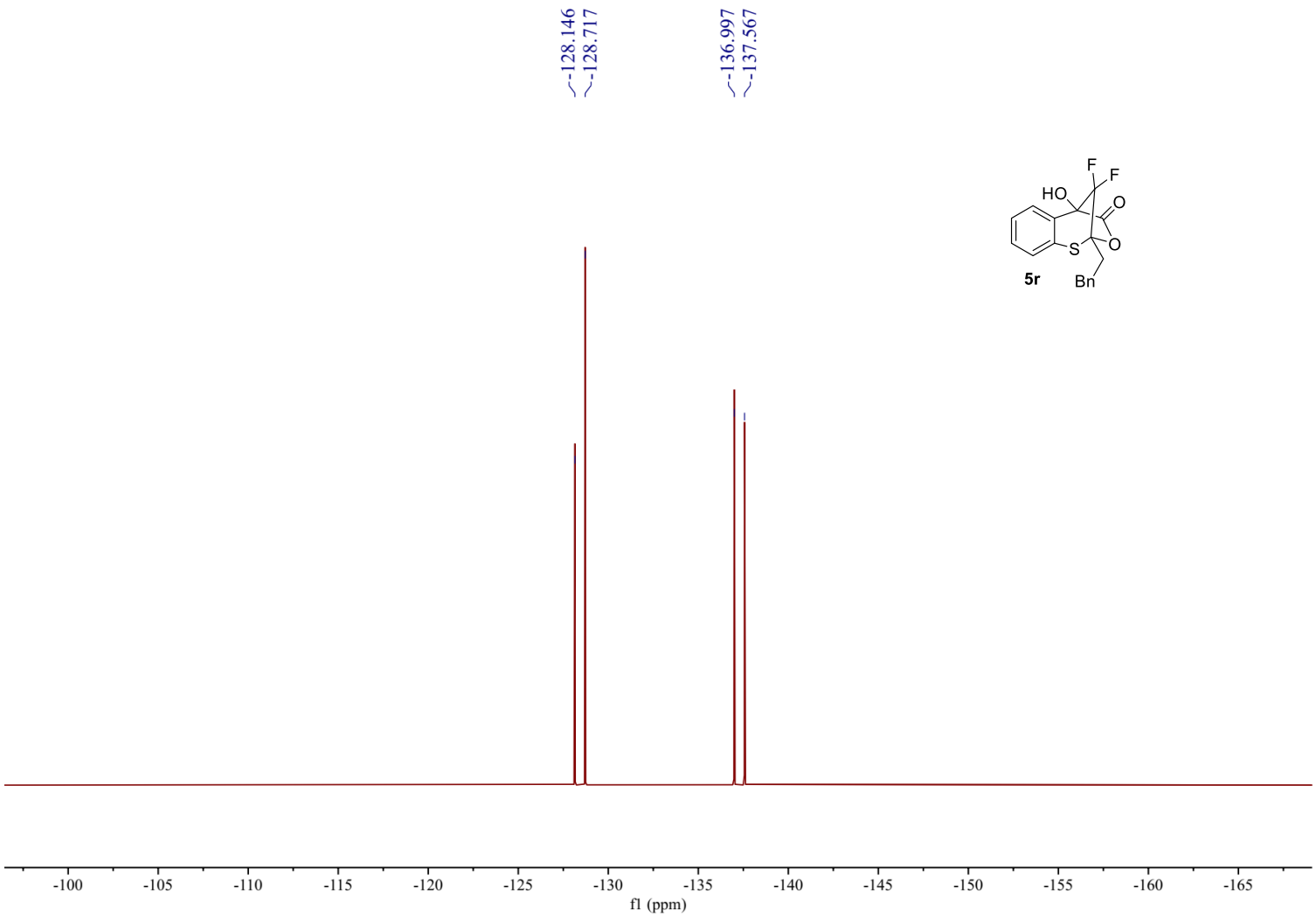
^{19}F NMR spectra of **5q** in $CDCl_3$ (376 MHz)



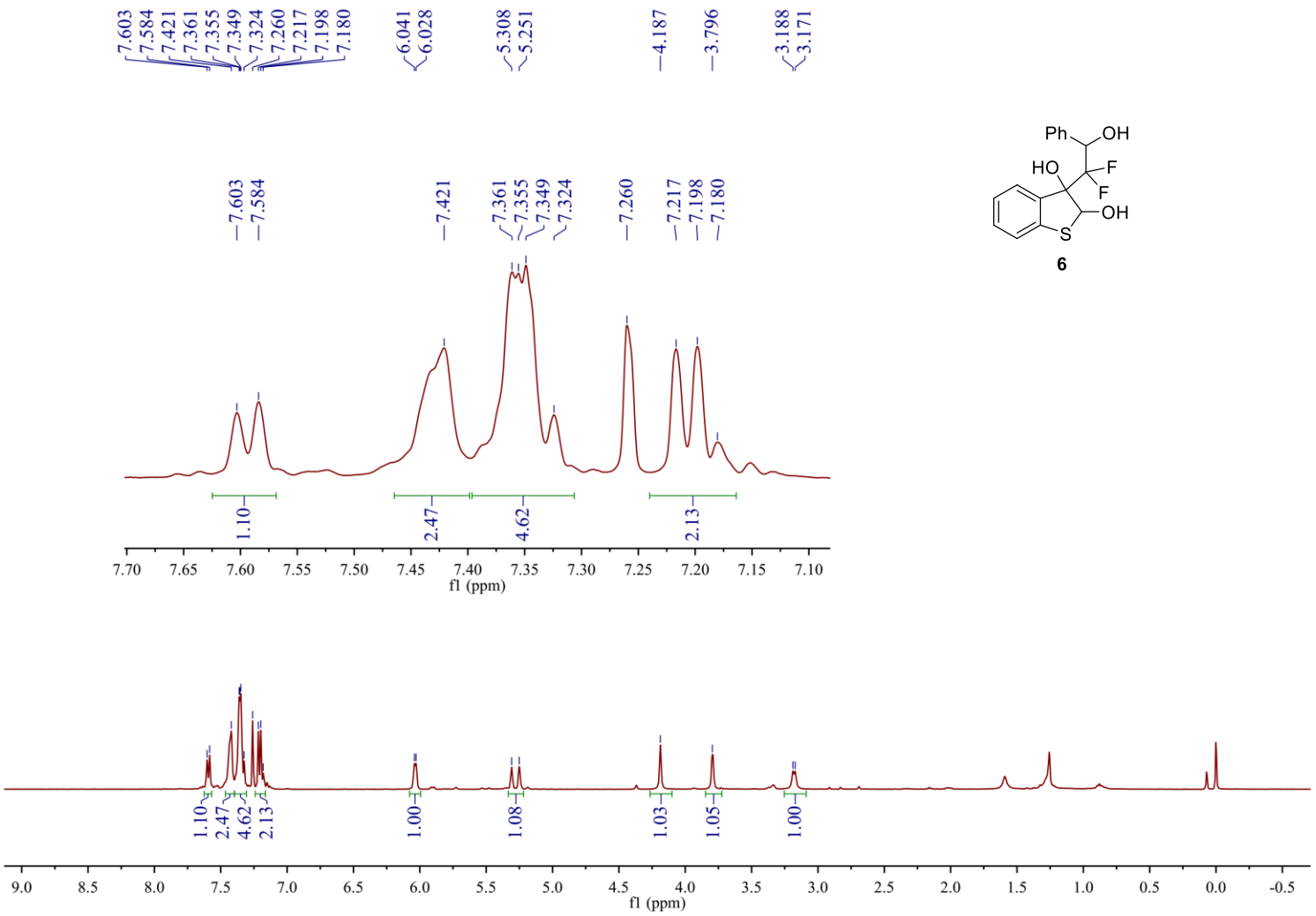
^{1}H NMR spectra of **5r** in $CDCl_3$ (400 MHz)



$^{13}C\{^{1}H\}$ NMR spectra of **5r** in $CDCl_3$ (100 MHz)

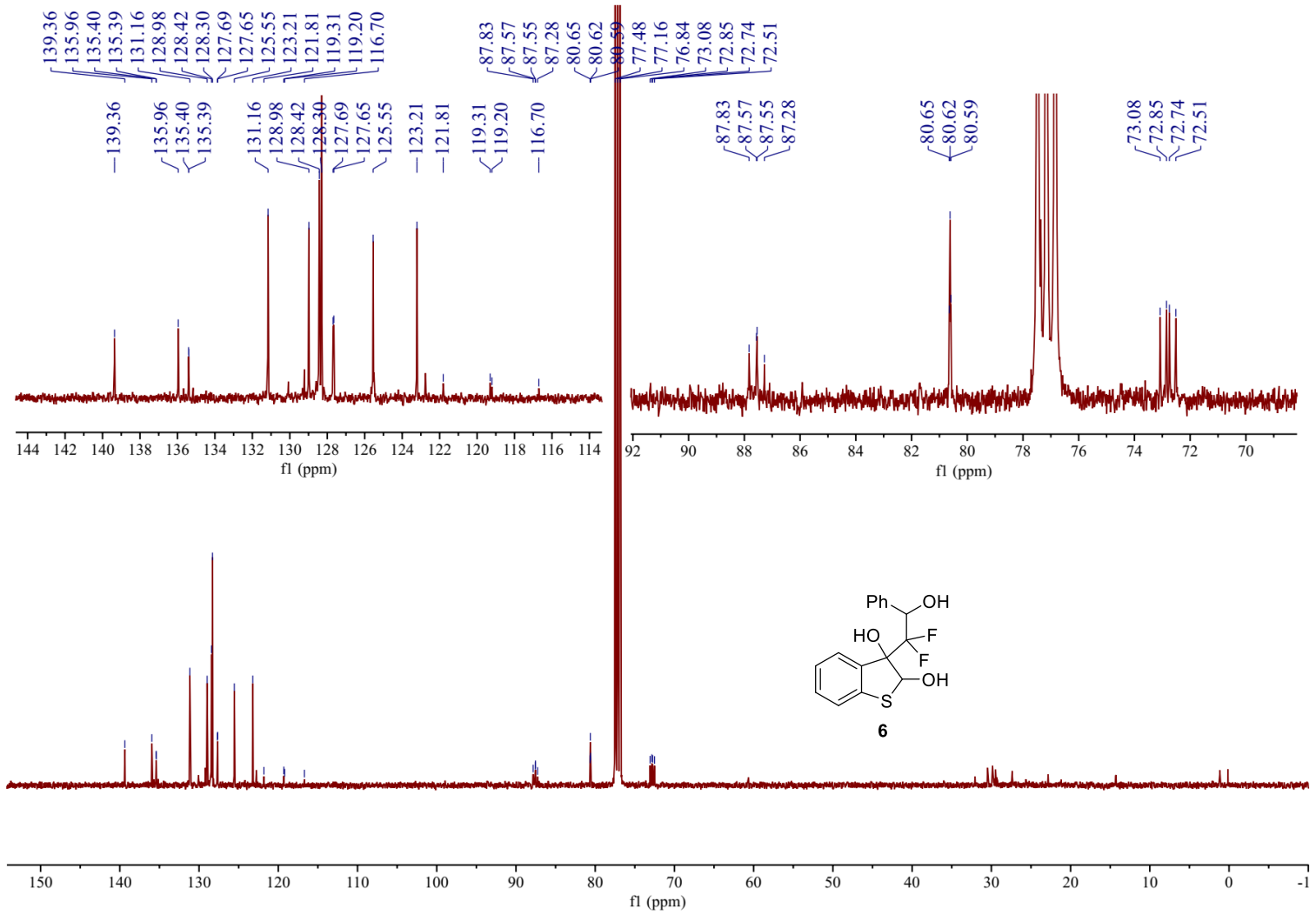


^{19}F NMR spectra of **5r** in $CDCl_3$ (376 MHz)

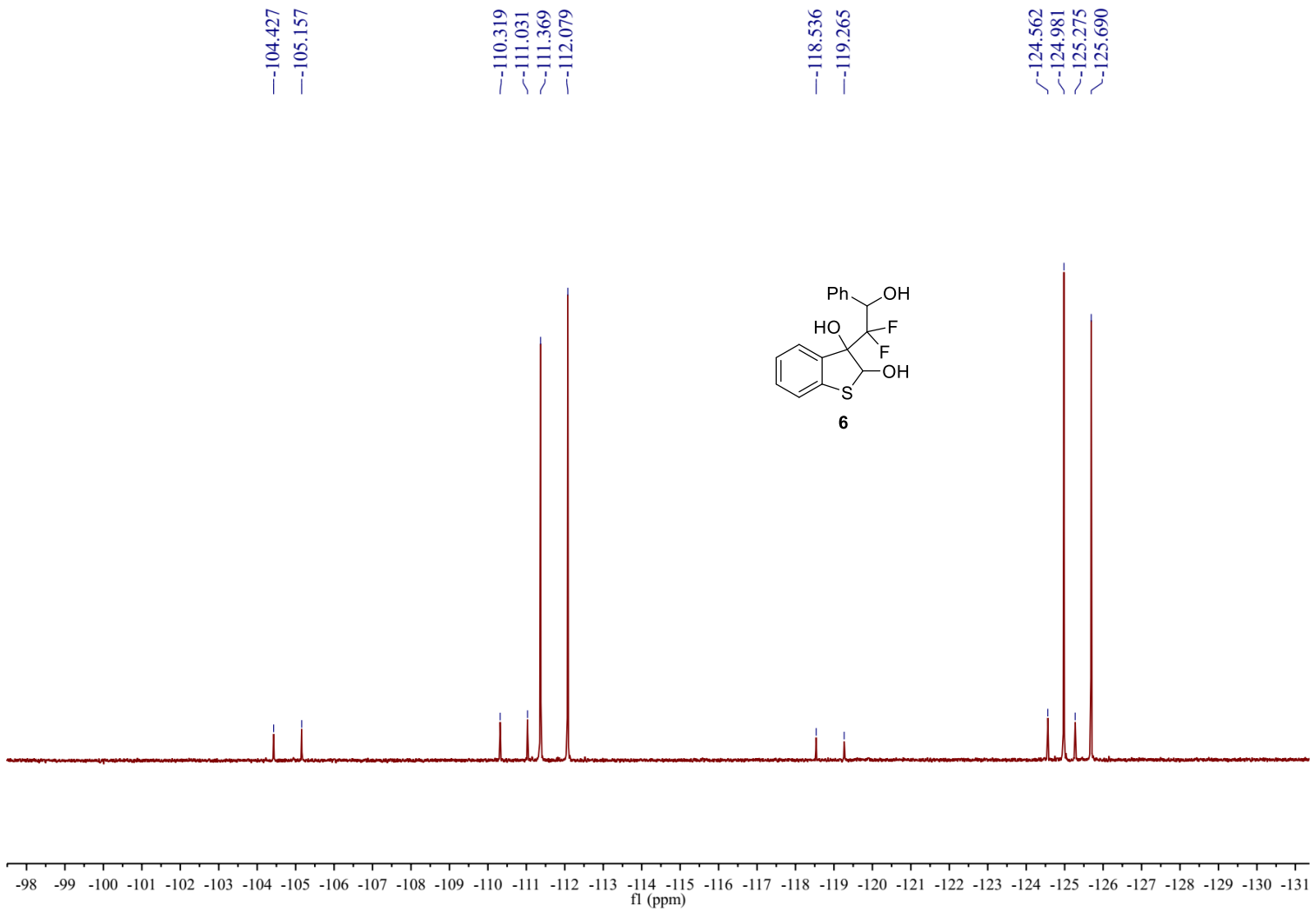


6

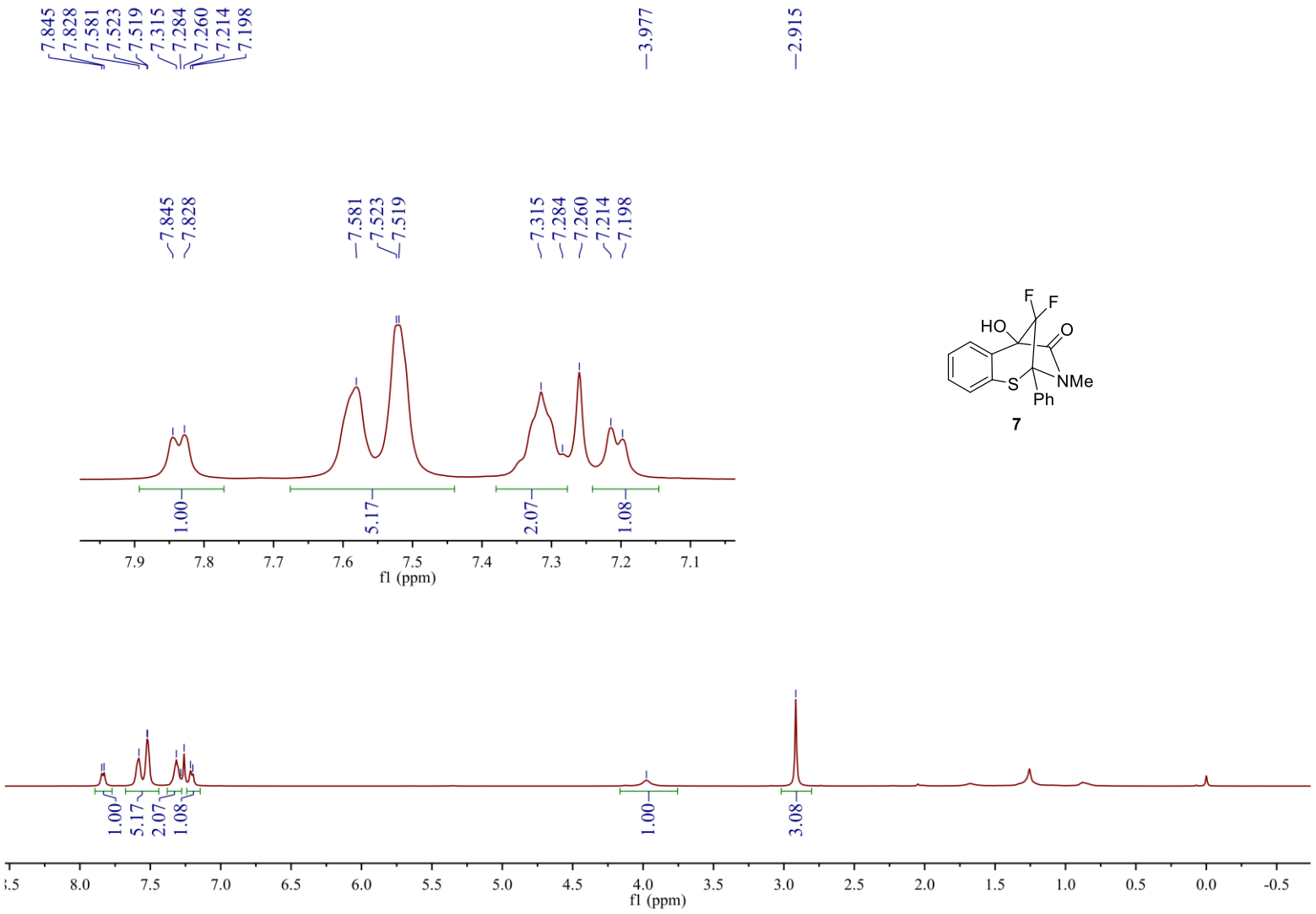
^{1}H NMR spectra of **6** in $CDCl_3$ (400 MHz)



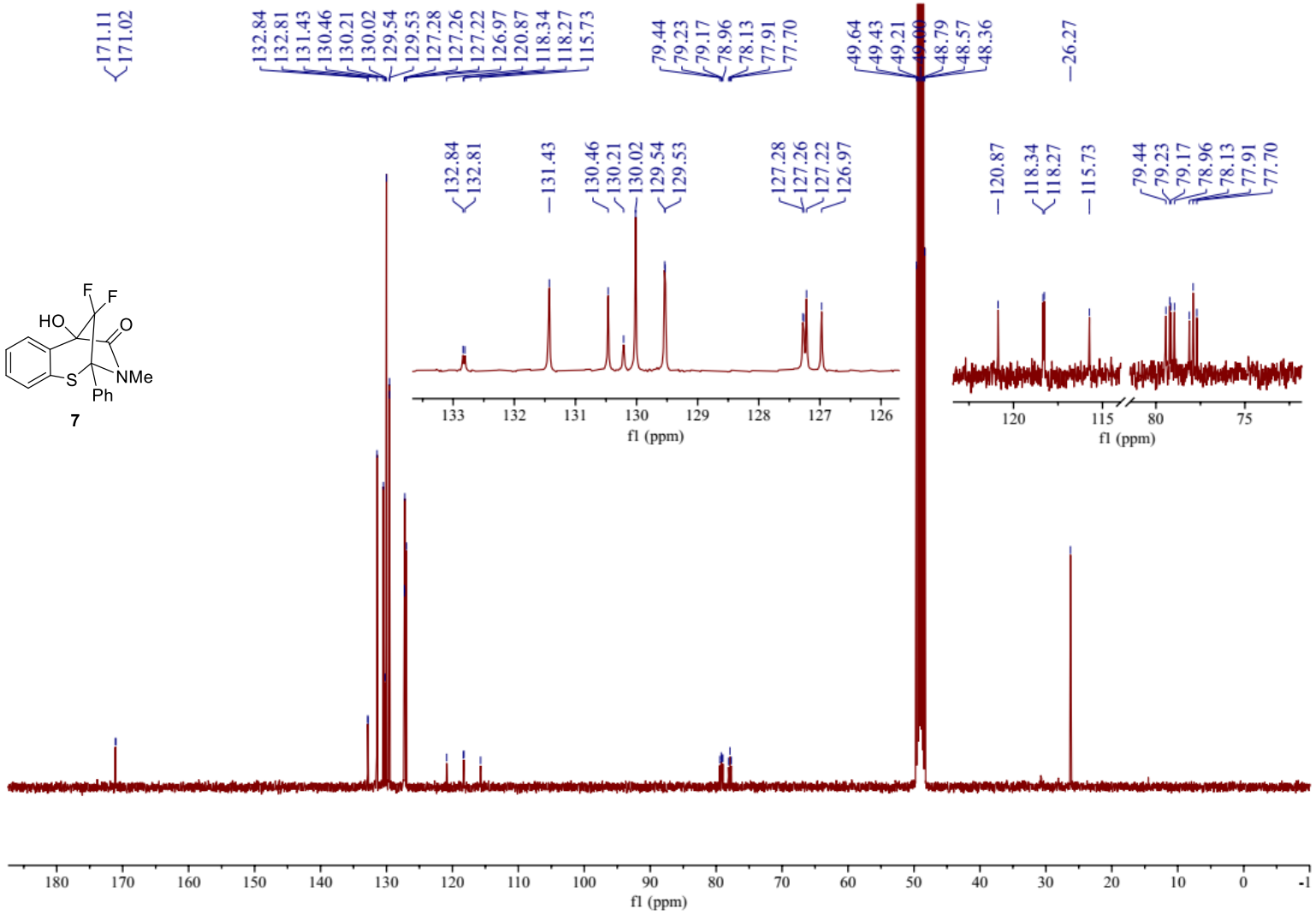
$^{13}C\{^{1}H\}$ NMR spectra of **6** in $CDCl_3$ (100 MHz)



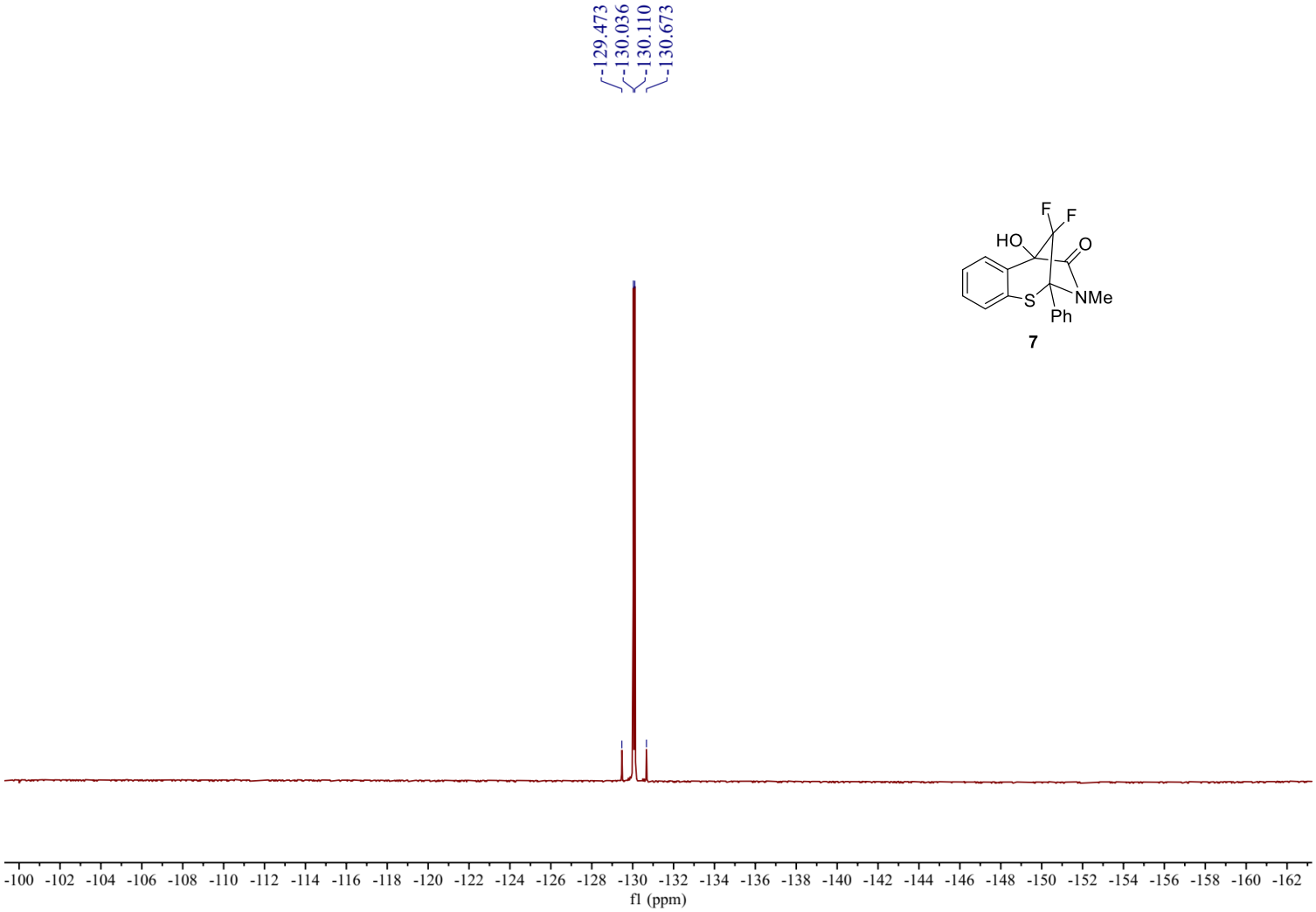
^{19}F NMR spectra of **6** in $CDCl_3$ (376 MHz)



^{1}H NMR spectra of **7** in $CDCl_3$ (400 MHz)



$^{13}C\{^{1}H\}$ NMR spectra of **7** in CD_3OD (100 MHz)



^{19}F NMR spectra of **7** in $CDCl_3$ (376 MHz)