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Supplementary Material

Synthesis and Tautomerism of Curcumin Derivatives and Related Compounds

Á

Hiroyasu Taguchi^a, Daijiro Yanagisawa^a, Shigehiro Morikawa^b, Koichi Hirao^c, Nobuaki

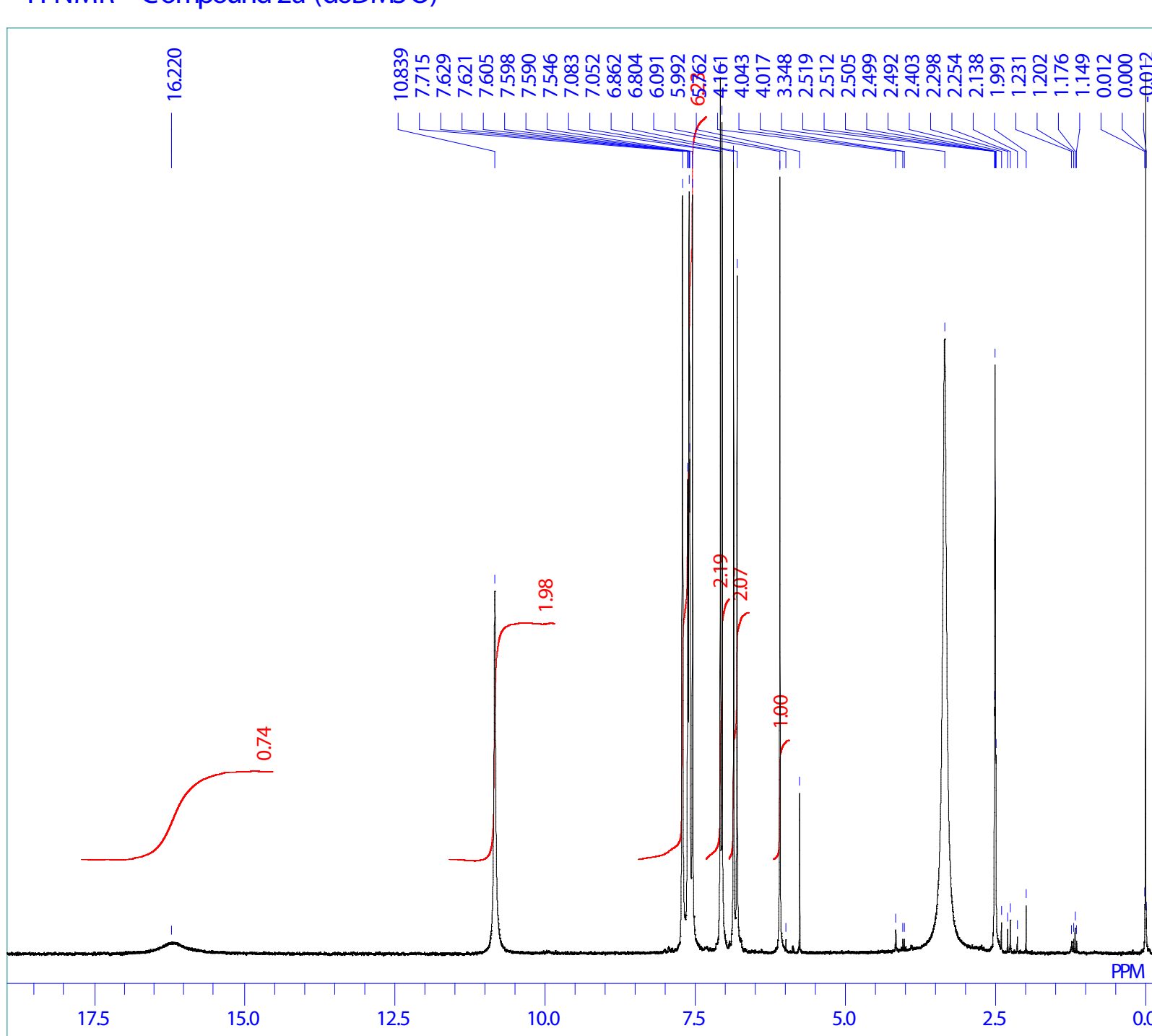
Shirai^c, and Ikuo Tooyama^a

^aMolecular Neuroscience Research Center, Shiga University of Medical Science, Seta
Tsukinowa-cho, Otsu 520-2192, Japan

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Tsukinowa-cho, Otsu 520-2192, Japan

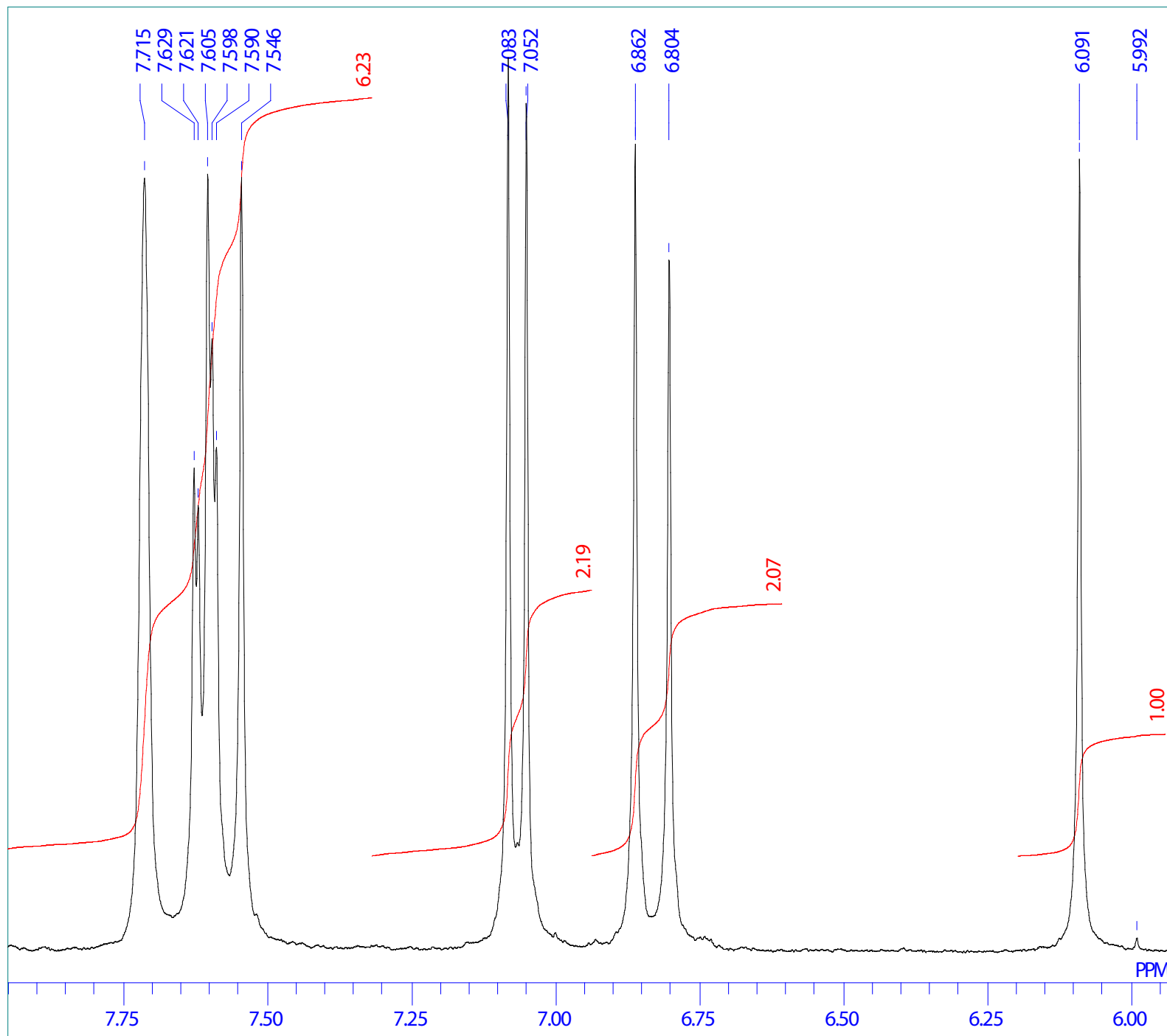
^cNortheastern Industrial Research Center of Shiga Prefecture, 27-39 Mitsuya
Motomachi, Nagahama 526-0024, Japan

¹H NMR Compound 2a (d6DMSO)



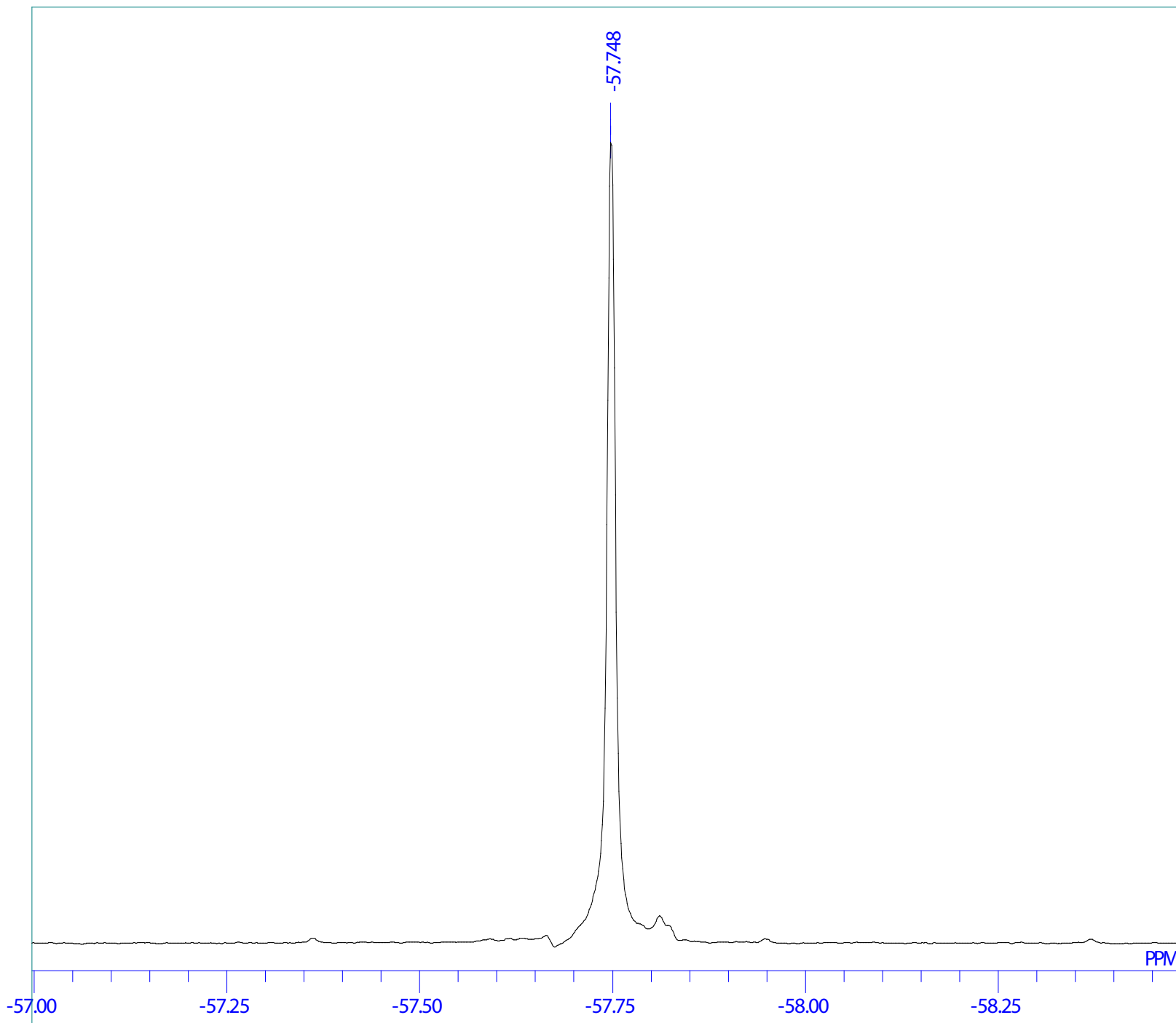
MENUF	NONB
OBNUC	1H
OFR	270.05 MHz
OBSET	112.00 KHz
OBFIN	5800.00 Hz
PW1	12.50 usec
DEADT	49.30 usec
PREDL	0.20000 msec
IWT	1.0000 sec
POINT	65536
SPO	65536
TIMES	32
DUMMY	1
FREQU	10810.80 Hz
FLT	5400 Hz
DELAY	37.00 usec
ACQTM	6.0621 sec
PD	10.0000 sec
ADBIT	16
RGAIN	21
BF	0.50 Hz
T1	0.00
T2	0.00
T3	50.00
T4	60.00
EXMOD	NON
EXPCM	NONSingle.coupledPW1_ACQTM_PD:1H;13C
IRNUC	1H
IFR	270.05 MHz
IRSET	112.00 KHz
IRFIN	5800.00 Hz
IRRPW	50 usec
IRATN	511
DFILE	shiga-Y1spcals
SF	CH5
LKSET	64.40 KHz
LKFN	76.0 Hz
LKLEV	180
LGAIN	20
LKPHS	117
LKSIG	2458
CSPED	16 Hz
FLDC	
FILDF	

¹H NMR Compound 2a (d6DMSO)



MENUF	NONB
OBNUC	1H
OFI	270.05 MHz
OBSET	112.00 KHz
OBFIN	5800.00 Hz
PW1	12.50 usec
DEADT	49.30 usec
PREDL	0.20000 msec
IWT	1.0000 sec
POINT	65536
SPO	65536
TIMES	32
DUMMY	1
FREQU	10810.80 Hz
FLT	5400 Hz
DELAY	37.00 usec
ACQTM	6.0621 sec
PD	10.0000 sec
ADBIT	16
RGAIN	21
BF	0.50 Hz
T1	0.00
T2	0.00
T3	50.00
T4	60.00
EXMOD	NON
EXPCM	NONSinglecoupledPW1_ACQTM_PD:1H;13C
IRNUC	1H
IFR	270.05 MHz
IRSET	112.00 KHz
IRFIN	5800.00 Hz
IRRPW	50 usec
IRATN	511
DFILE	Compound2a_1Hals
SF	CH5
LKSET	64.40 KHz
LKFIN	76.0 Hz
LKLEV	180
LGAIN	20
LKPHS	117
LKSIG	2458
CSPED	16 Hz
FILDC	
FILDF	

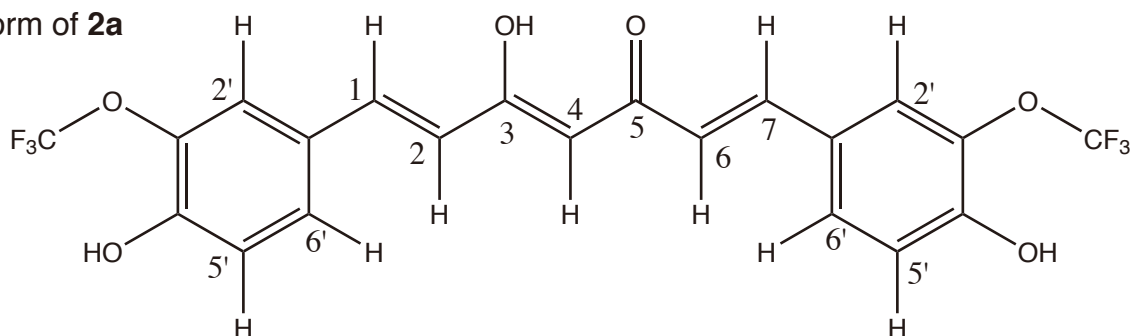
¹⁹F NMR Compound 2a (d6DMSO)



MENUF
OBNUC 19F
OFR 254.05 MHz
OBSET 134.40 KHz
OBFIN 45.10 Hz
PW1 4.00 usec
DEADT 10.00 usec
PREDL 0.00000 msec
INVT 1.0000 sec
POINT 262144
SPO 262144
TIMES 4
DUMMY 1
FREQU 80000.00 Hz
FLT 40000 Hz
DELAY 5.00 usec
ACQTM 0.8192 sec
PD 0.9350 sec
ADBIT 16
RGAIN 24
BF 1.00 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD NON
EXPCM NONSingle.coupledPW1_ACQTM_PD:1H;13C
IRNUC 1H
IFR 270.05 MHz
IRSET 112.00 KHz
IRFIN 5800.00 Hz
IRRPW 50 usec
IRATN 511
DRFILE F-CURCUMINF2.spc.als
SF
LKSET 0.00 KHz
LKFIN 0.0 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 19 Hz
FILDC
FILDF

Assignment for **2a**

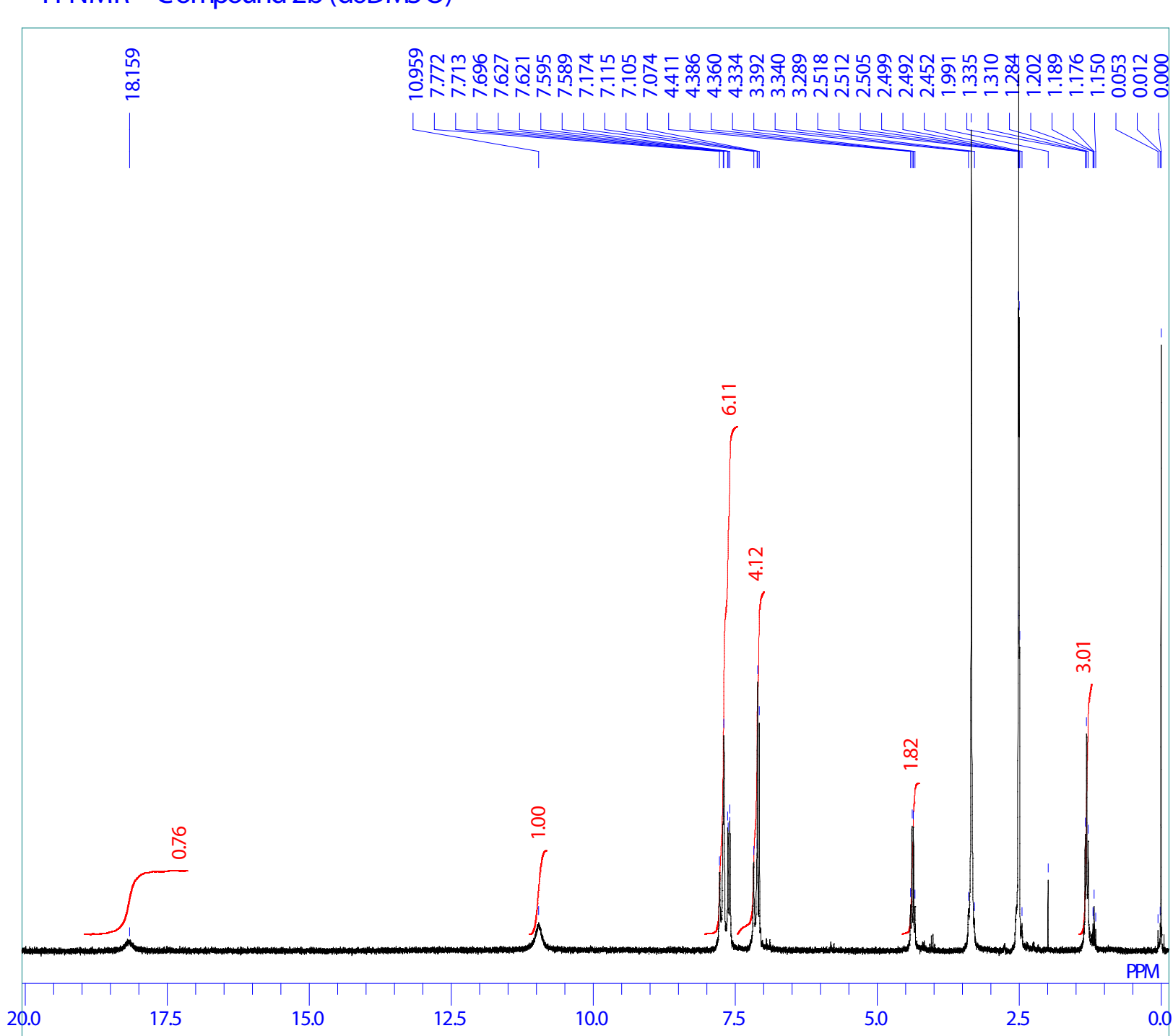
Enol-form of **2a**



- δ_{H} 6.09 (s, 1H, -C(OH)=CHCO-, **H₄**) enol-form
6.83 (d, J 15.8, 2H, -CH=CH-, **H₂** and **H₆**)
7.07 (d, J 8.4, 2H, ArH, **H_{5'}**)
7.58 (d, J 15.8, 2H, -CH=CH-, **H₁** and **H₇**)
7.61 (dd, J 2.2, 8.4, 2H, ArH, **H_{6'}**)
7.72 (br.s, 2H, ArH, **H_{2'}**)
10.84 (s, 2H, OH)
16.22 (br.s, 1H, strongly bound H by hydrogen bonding)

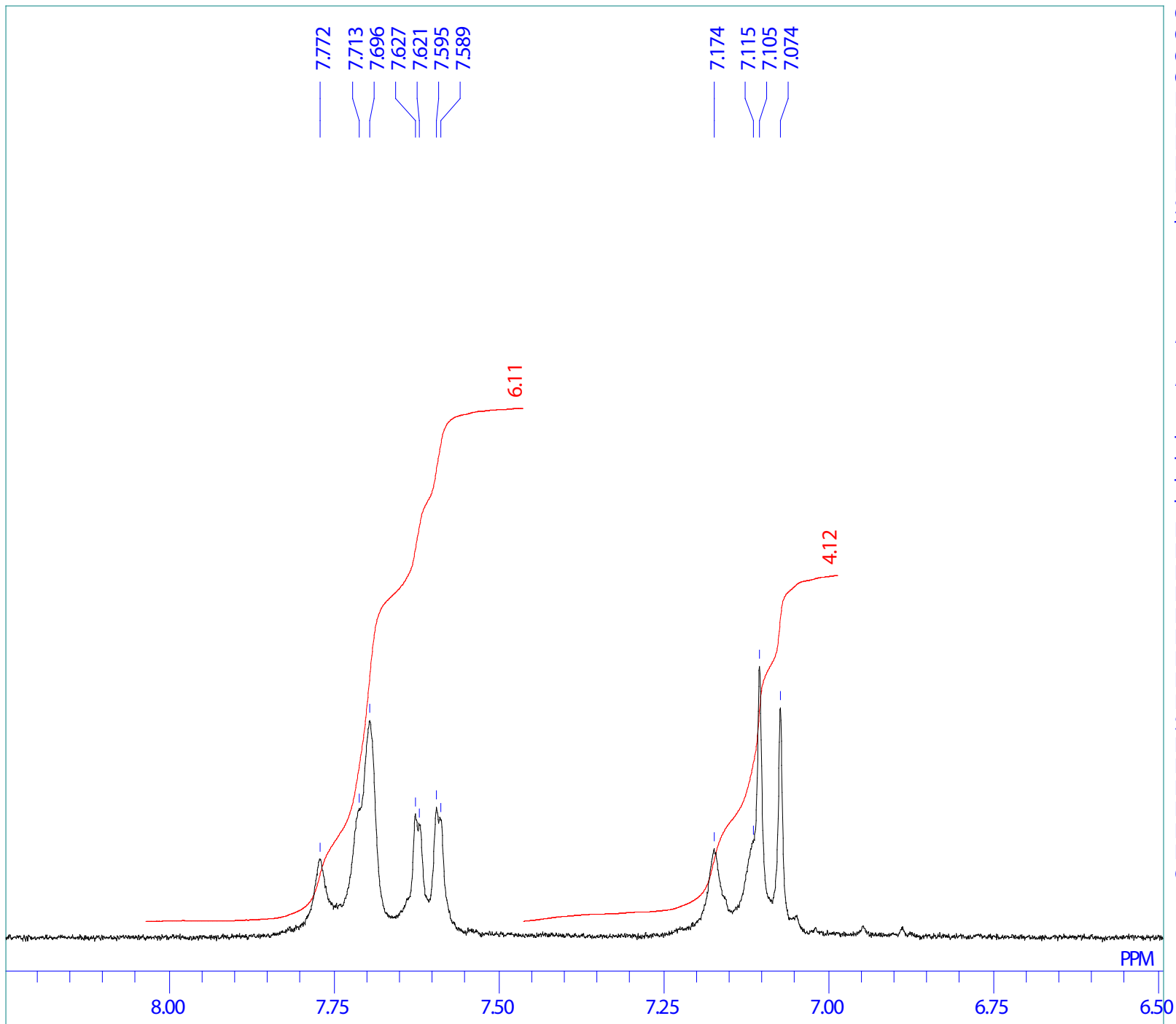
δ_{F} -57.75 (s, -OCF₃)

¹H NMR Compound 2b (d6DMSO)



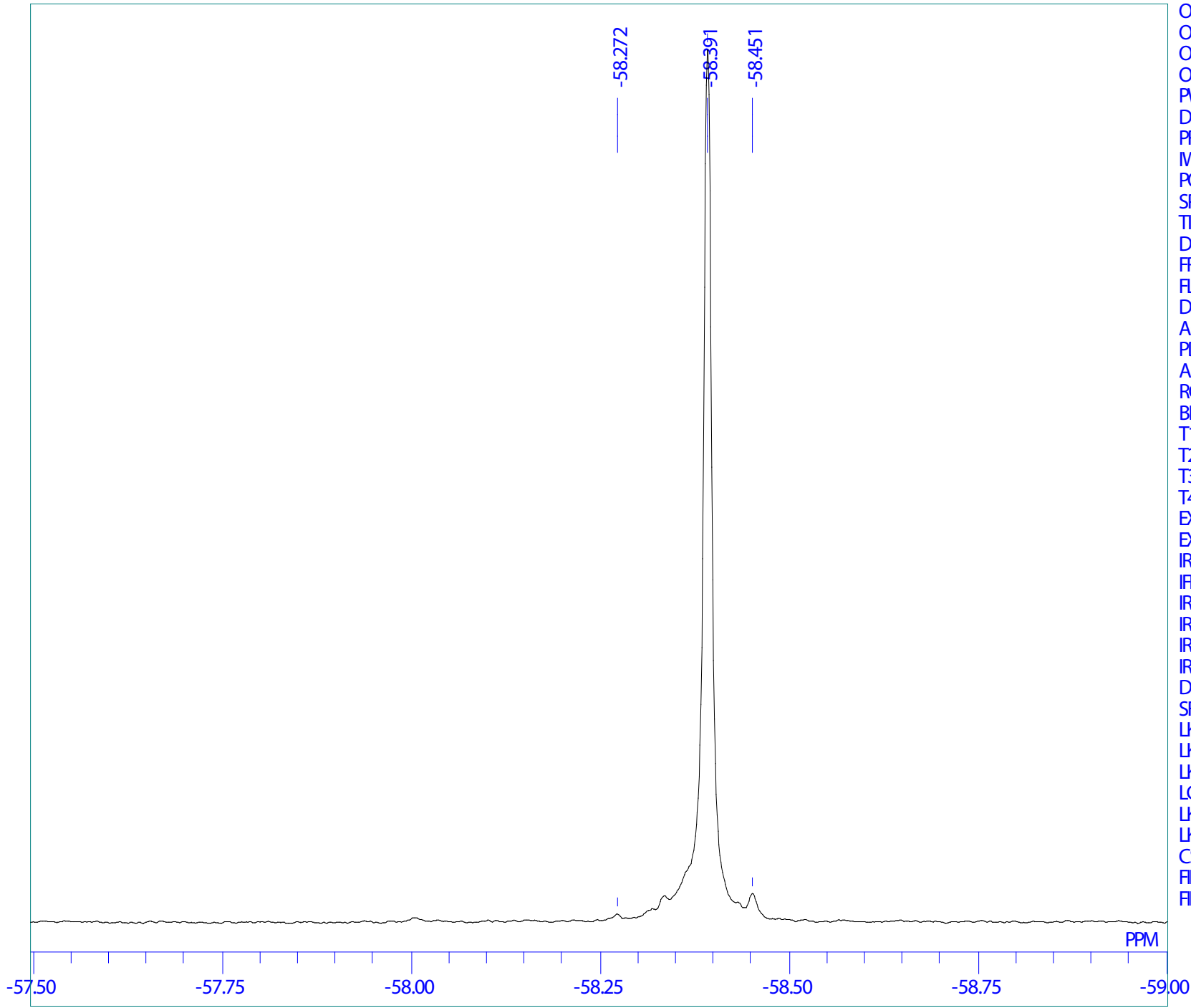
MENUF	NON2
OBNUC	1H
OF	270.05 MHz
OBSET	112.00 KHz
OBFIN	5800.00 Hz
PW1	12.50 usec
DEADT	49.30 usec
PREDL	0.20000 msec
IWT	1.0000 sec
POINT	65536
SPO	65536
TIMES	8
DUMMY	1
FREQU	10810.80 Hz
FLT	5400 Hz
DELAY	37.00 usec
ACQTM	6.0621 sec
PD	0.9350 sec
ADBIT	16
RGAIN	20
BF	0.10 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	NON
EXPCM	NONSinglecoupledPW1_ACQTM_PD:1H;13C
IRNUC	1H
IFR	270.05 MHz
IRSET	112.00 KHz
IRFIN	5800.00 Hz
IRRPW	50 usec
IRATN	511
DRLE	Compound2b_1Hals
SF	F5_INU
LKSET	64.40 KHz
LKFIN	76.0 Hz
LKLEV	170
LGAIN	20
LKPHS	32
LKSIG	1747
CSPED	14 Hz
FLDC	
FLDF	

¹H NMR Compound 2b (d6DMSO)



MENUF NON2
OBNUC 1H
OFR 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.00 Hz
PW1 12.50 usec
DEADT 49.30 usec
PREDL 0.20000 msec
IWT 1.0000 sec
POINT 65536
SPO 65536
TIMES 8
DUMMY 1
FREQU 10810.80 Hz
FLT 5400 Hz
DELAY 37.00 usec
ACQTM 6.0621 sec
PD 0.9350 sec
ADBIT 16
RGAIN 20
BF 0.10 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD NON
EXPCM NONSingle.coupledPW1_ACQTM_PD:1H;13C
IRNUC 1H
IFR 270.05 MHz
IRSET 112.00 KHz
IRFIN 5800.00 Hz
IRRPW 50 usec
IRATN 511
DRFILE Compound2b_1Hals
SF F5_INU
LKSET 64.40 KHz
LKFIN 76.0 Hz
LKLEV 170
LGAIN 20
LKPHS 32
LKSIG 1747
CSPED 14 Hz
FLDC
FLDF

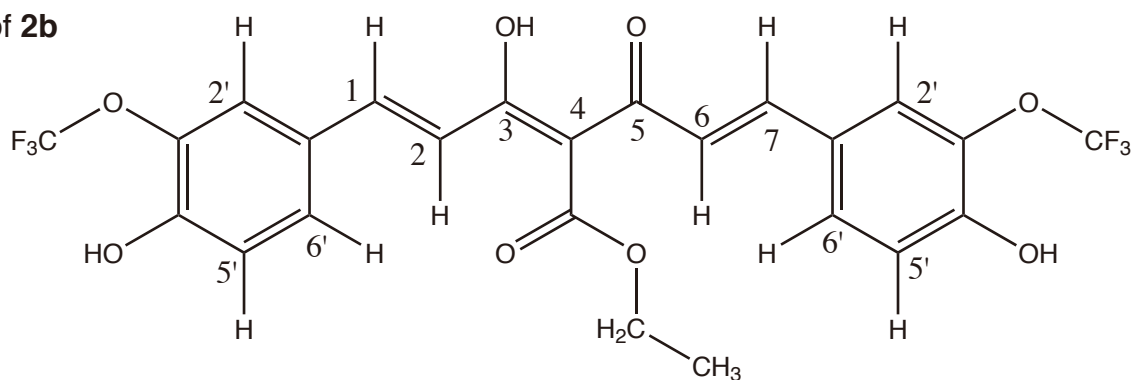
¹⁹F NMR Compound 2b (d6DMSO)



MENUF 19F-SHGAXFH5_INU
OBNUC 19F
OFR 254.05 MHz
OBSET 134.40 KHz
OBFIN 45.10 Hz
PW1 5.00 usec
DEADT 10.00 usec
PREDL 0.20000 msec
IWT 1.0000 sec
POINT 262144
SPO 65536
TIMES 4
DUMMY 1
FREQU 80000.00 Hz
FLT 40000 Hz
DELAY 5.00 usec
ACQTM 0.8192 sec
PD 0.9350 sec
ADBIT 16
RGAIN 24
BF 1.00 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD NON
EXPCM NONSinglecoupledPW1_ACQTM_PD:1H;13C
IRNUC 1H
IFR 270.05 MHz
IRSET 112.00 KHz
IRFIN 5800.00 Hz
IRRPW 50 usec
IRATN 511
DRFILE Shiga-Y12-19Fspc.ALS
SF FH5_INU
LKSET 64.40 KHz
LKFIN 76.0 Hz
LKLEV 170
LGAIN 20
LKPHS 32
LKSIG 1771
CSPED 15 Hz
FILDC
FILDF

Assignment for **2b**

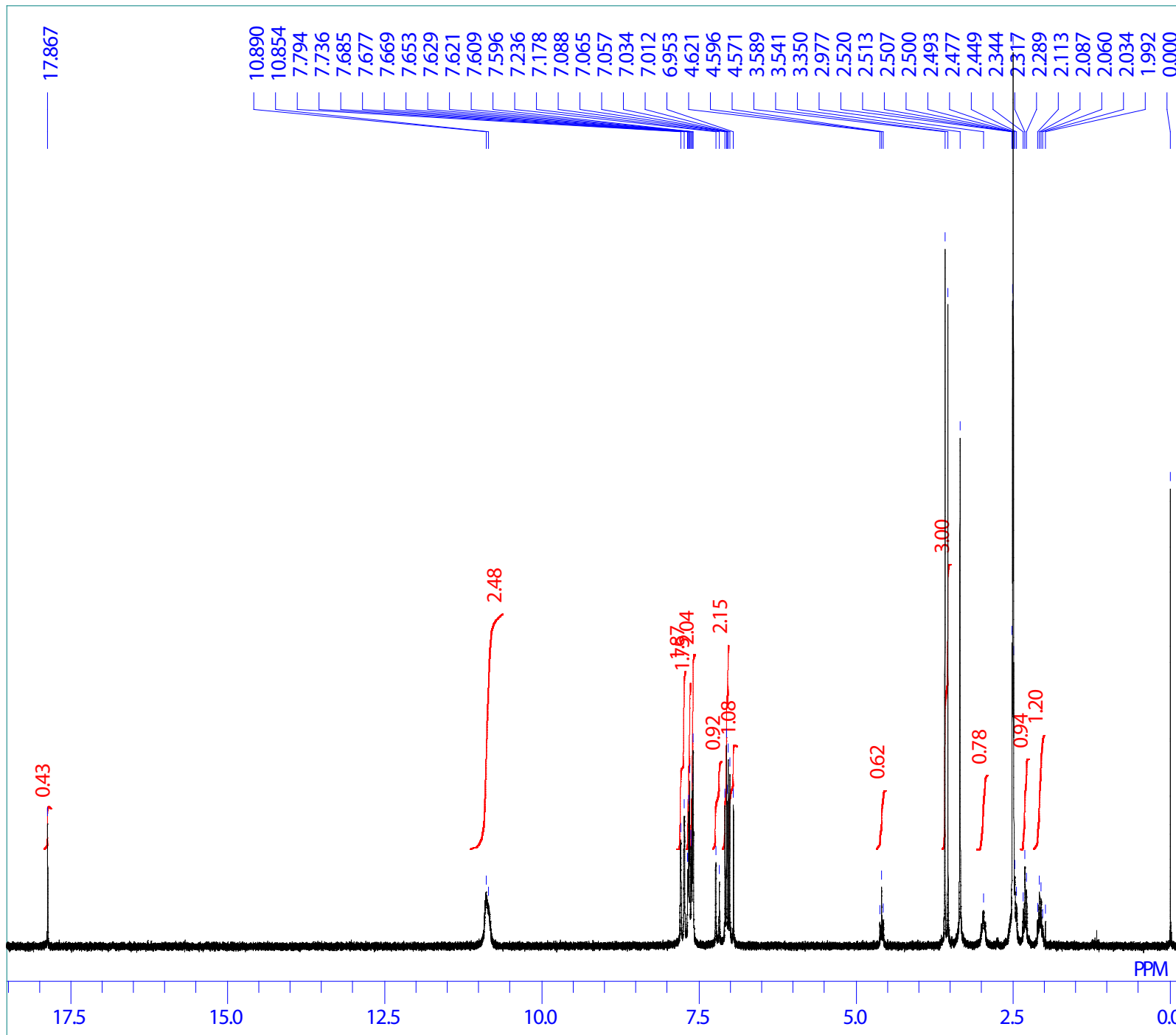
Enol-form of **2b**



- δ_{H} 1.31 (t, J 7.0, 3H, -OCH₂CH₃)
4.37 (q, J 7.0, 2H, -OCH₂CH₃)
7.09 (d, J 8.4, 2H, ArH, **H_{5'}**)
7.14 (d, J 15.9, 2H, -CH=CH-, **H₂** and **H₆**)
7.61 (dd, J 8.6, 1.6, 2H, ArH, **H_{6'}**)
7.70 (br.s., 2H, ArH, **H_{2'}**)
7.74 (d, J 15.9, 2H, -CH=CH-, **H₁** and **H₇**)
10.96 (br.s, 1H, OH)
18.16 (br.s, 1H, strongly bound H by hydrogen bonding)

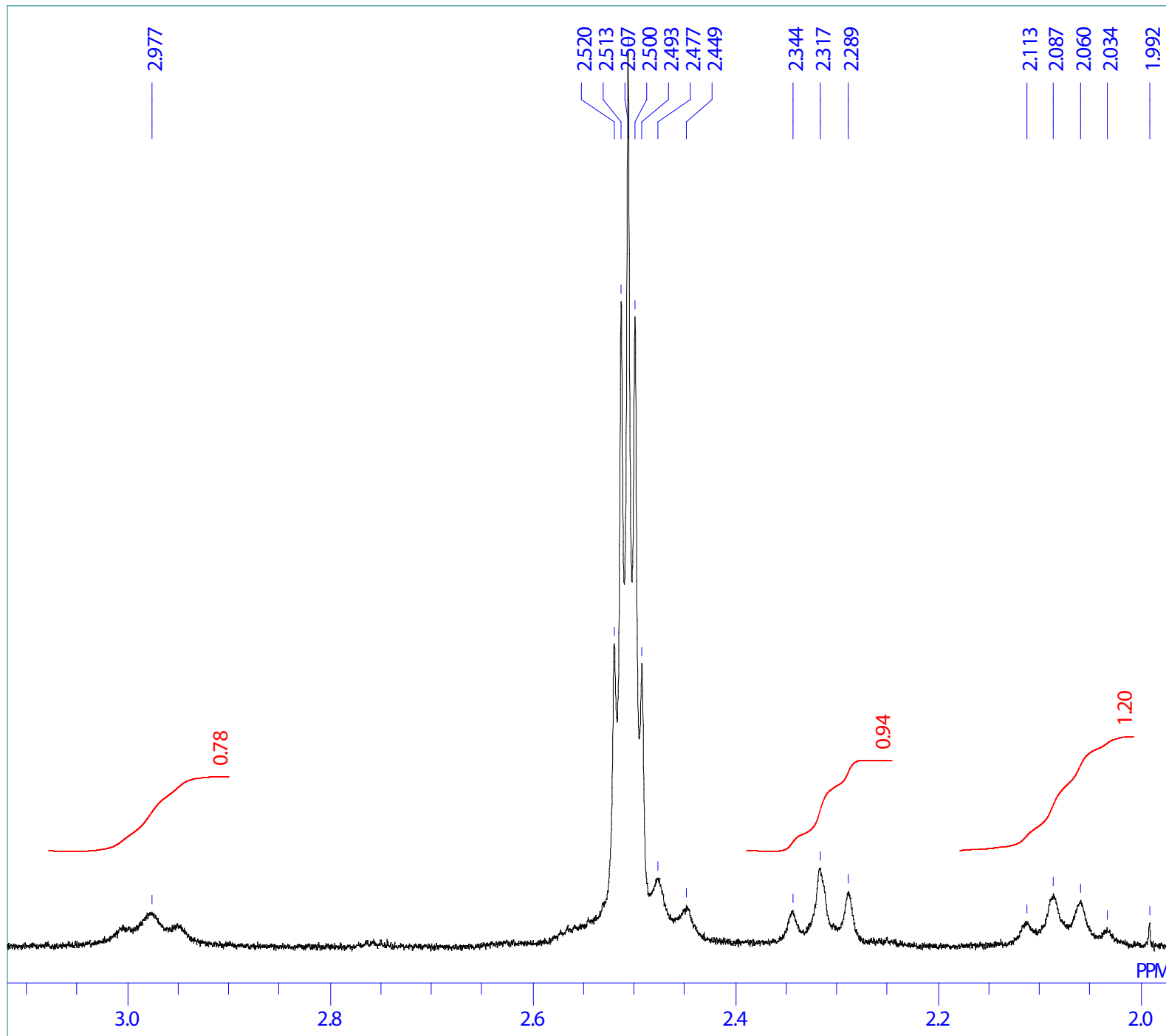
δ_{F} -58.39 (s, -OCF₃)

¹H NMR Compound 2e (d6DMSO)



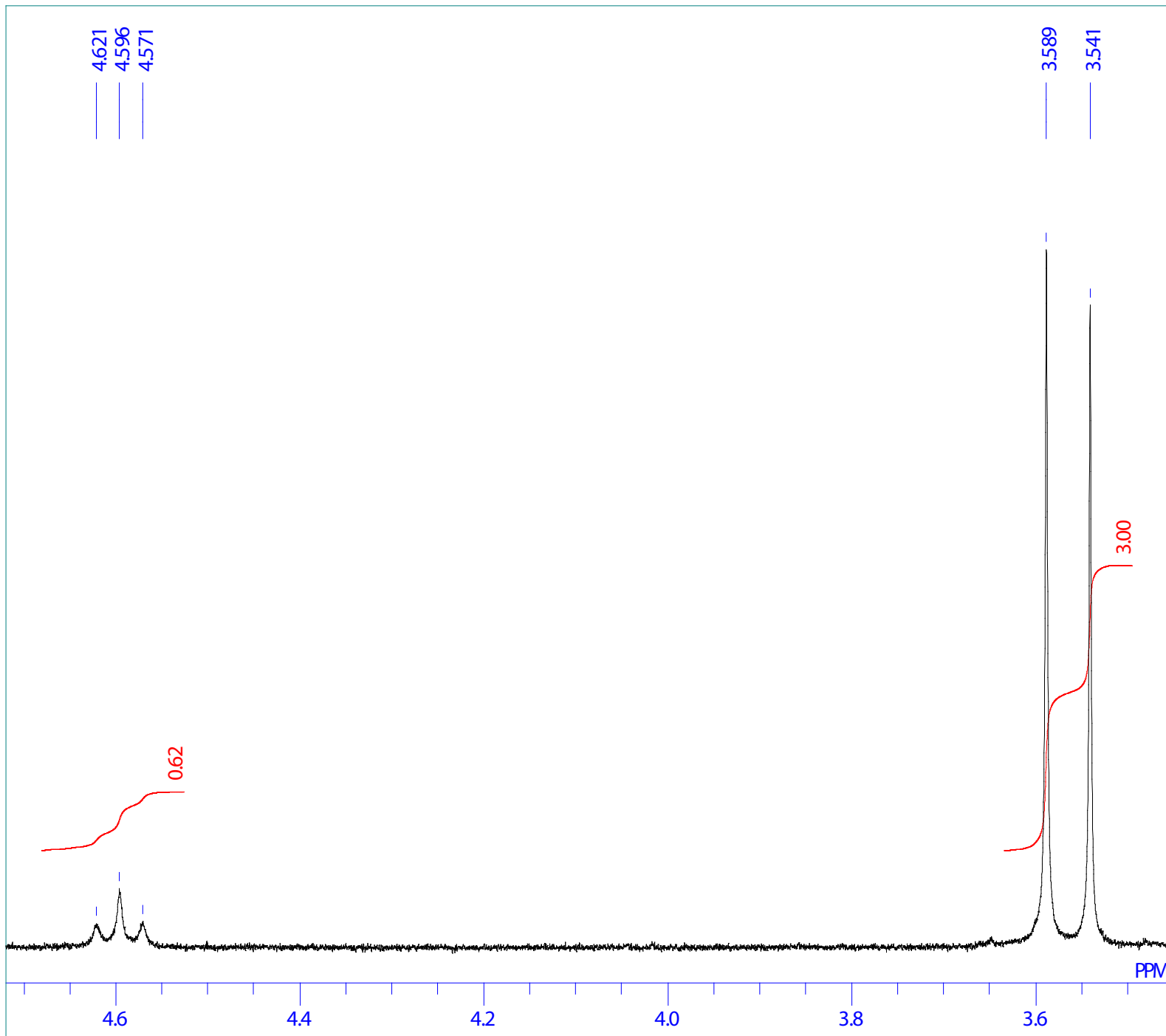
MENUF	NONB
OBNUC	1H
OFR	270.05 MHz
OBSET	112.00 KHz
OBFIN	5800.00 Hz
PW1	12.50 usec
DEADT	49.30 usec
PREDL	0.20000 msec
IWT	1.0000 sec
POINT	262144
SPO	65536
TIMES	8
DUMMY	1
FREQU	10810.81 Hz
FLT	5400 Hz
DELAY	37.00 usec
ACQTM	6.0621 sec
PD	0.9350 sec
ADBIT	16
RGAIN	18
BF	0.01 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	NON
EXPCM	NONSinglecoupledPW1_ACQTM_PD:1H;13C
IRNUC	1H
IFR	270.05 MHz
IRSET	112.00 KHz
IRFIN	5800.00 Hz
IRRPW	50 usec
IRATN	511
DRFILE	Compound2e(d6DMSO)_1Hals
SF	FH5_140306Compound2e(d6DMSO)
LKSET	64.40 KHz
LKFN	76.0 Hz
LKLEV	180
LGAIN	16
LKPHS	82
LKSIG	531
CSPED	16 Hz
FILDC	
FILDF	

¹H NMR Compound 2e (d6DMSO)



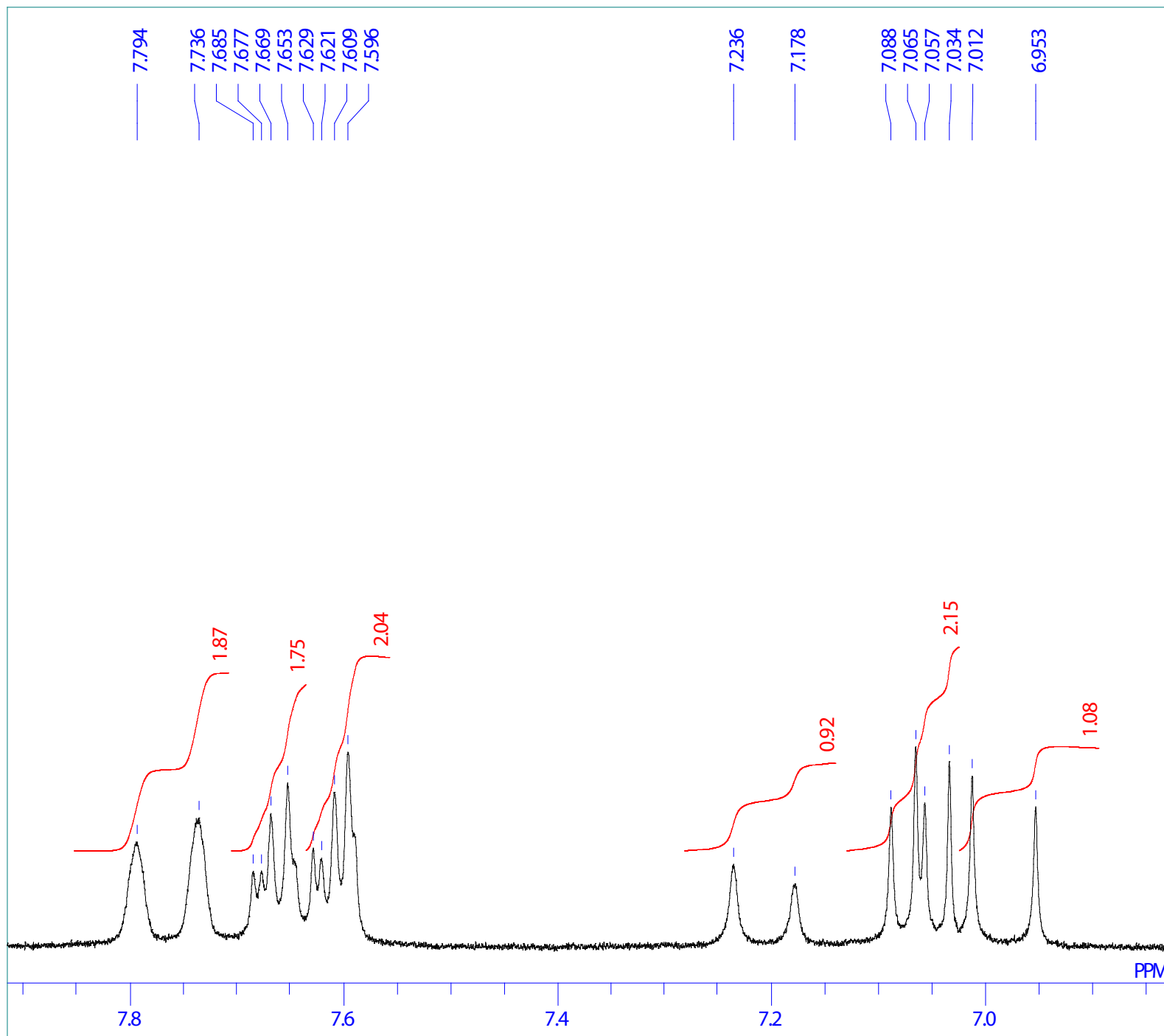
MENUF	NONB
OBNUC	1H
OFR	270.05 MHz
OBSET	112.00 KHz
OBFIN	5800.00 Hz
PW1	12.50 usec
DEADT	49.30 usec
PREDL	0.20000 msec
IWT	1.0000 sec
POINT	262144
SPO	65536
TIMES	8
DUMMY	1
FREQU	10810.81 Hz
FLT	5400 Hz
DELAY	37.00 usec
ACQTM	6.0621 sec
PD	0.9350 sec
ADBIT	16
RGAIN	18
BF	0.01 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	NON
EXPCM	NONSingle.coupledPW1_ACQTM_PD:1H;13C
IRNUC	1H
IFR	270.05 MHz
IRSET	112.00 KHz
IRFIN	5800.00 Hz
IRRPW	50 usec
IRATN	511
DFILE	Compound2e(d6DMSO)_1Hals
SF	FH5_140306Compound2e(d6DMSO)
LKSET	64.40 KHz
LKFN	76.0 Hz
LKLEV	180
LGAIN	16
LKPH5	82
LKSIG	531
CSPED	16 Hz
FILDC	
FILDF	

¹H NMR Compound 2e (d6DMSO)



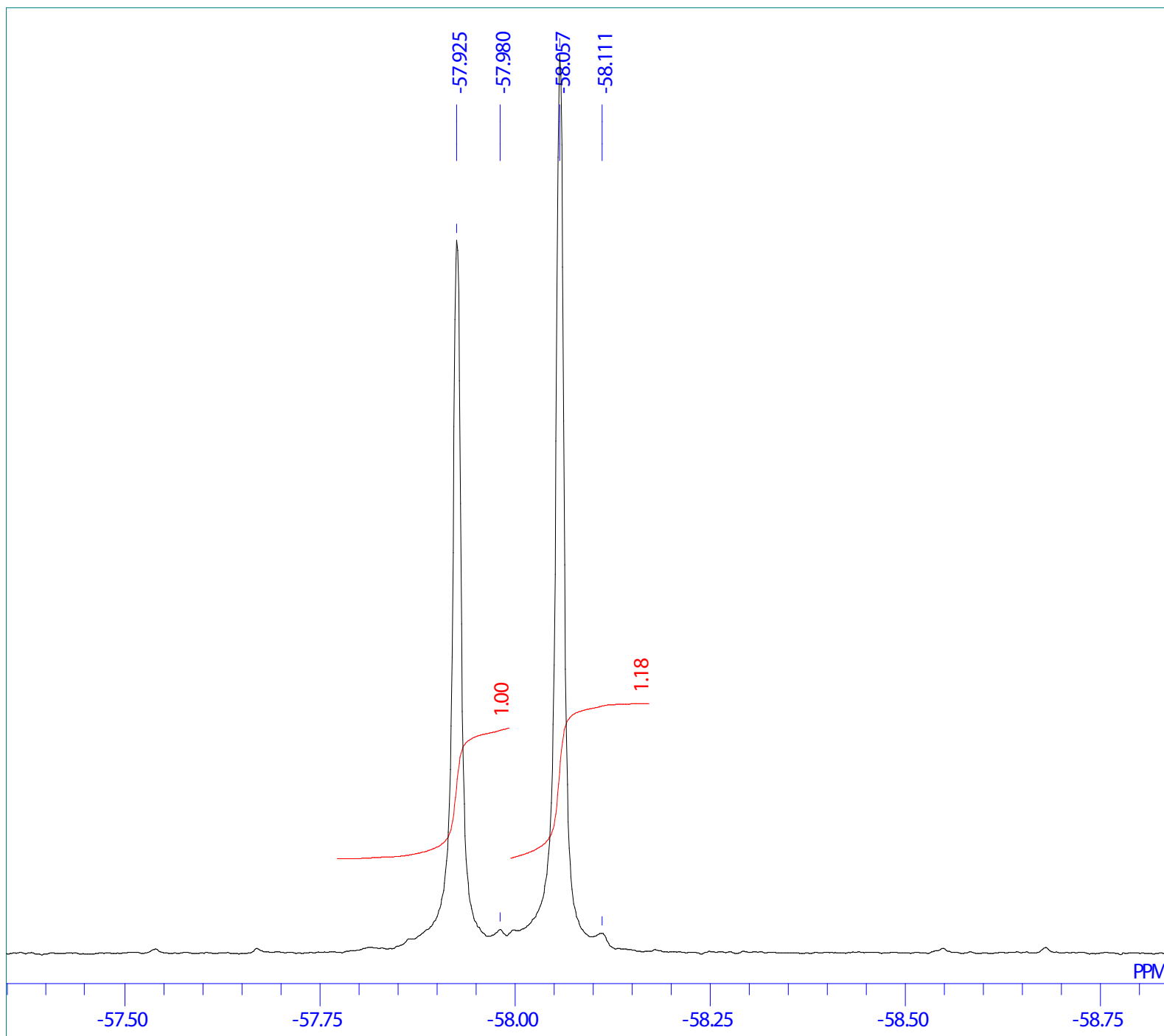
MENUF	NONB
OBNUC	1H
OFFR	270.05 MHz
OBSET	112.00 KHz
OBFIN	5800.00 Hz
PW1	12.50 usec
DEADT	49.30 usec
PREDL	0.20000 msec
IWT	1.0000 sec
POINT	262144
SPO	65536
TIMES	8
DUMMY	1
FREQU	10810.81 Hz
FLT	5400 Hz
DELAY	37.00 usec
ACQTM	6.0621 sec
PD	0.9350 sec
ADBIT	16
RGAIN	18
BF	0.01 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	NON
EXPCM	NONSinglecoupledPW1_ACQTM_PD:1H;13C
IRNUC	1H
IFR	270.05 MHz
IRSET	112.00 KHz
IRFIN	5800.00 Hz
IRRPW	50 usec
IRATN	511
DFILE	Compound2e(d6DMSO)_1Hals
SF	FH5_140306Compound 2e (d6DMSO)
LKSET	64.40 KHz
LKFIN	76.0 Hz
LKLEV	180
LGAIN	16
LKPHS	82
LKSIG	531
CSPED	16 Hz
FILDC	
FILDF	

¹H NMR Compound 2e (d6DMSO)



MENUF NONB
OBNUC 1H
OFR 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.00 Hz
PW1 12.50 usec
DEADT 49.30 usec
PREDL 0.20000 msec
IWT 1.0000 sec
POINT 262144
SPO 65536
TIMES 8
DUMMY 1
FREQU 10810.81 Hz
FLT 5400 Hz
DELAY 37.00 usec
ACQTM 6.0621 sec
PD 0.9350 sec
ADBIT 16
RGAIN 18
BF 0.01 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD NON
EXPCM NONSinglecoupledPW1_ACQTM_PD:1H;13C
IRNUC 1H
IFR 270.05 MHz
IRSET 112.00 KHz
IRFIN 5800.00 Hz
IRRPW 50 usec
IRATN 511
DFILE Compound2e(d6DMSO)_1Hals
SF FH5_140306Compound2e (d6DMSO)
LKSET 64.40 KHz
LKFN 76.0 Hz
LKLEV 180
LGAIN 16
LKPHS 82
LKSIG 531
CSPED 16 Hz
FLDC
FILDF

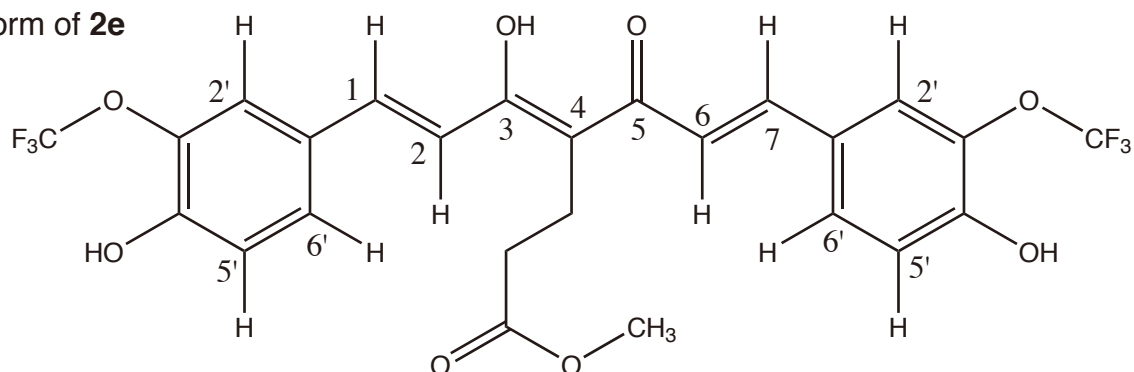
¹⁹F NMR Compound 2e (d6DMSO)



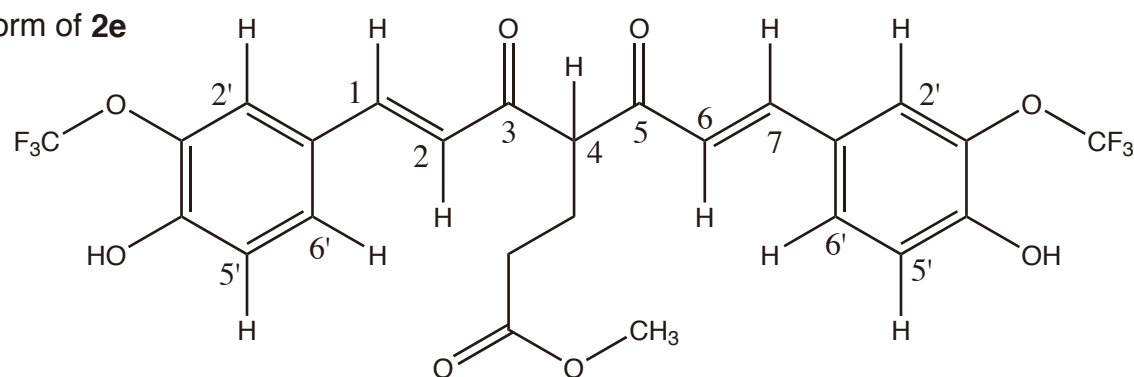
MENUF 19F-SHGAXFH5_140306Compound2e (d6DMSO)
OBNUC 19F
OFR 254.05 MHz
OBSET 135.00 KHz
OBFIN 5700.00 Hz
PW1 5.00 usec
DEADT 10.00 usec
PREDL 0.20000 msec
IWT 1.0000 sec
POINT 262144
SPO 65536
TIMES 8
DUMMY 1
FREQU 80000.00 Hz
FLT 40000 Hz
DELAY 5.00 usec
ACQTM 0.8192 sec
PD 0.9350 sec
ADBIT 16
RGAIN 22
BF 1.00 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD NON
EXPCM NONSingle.coupledPW1_ACQTM_PD:1H;13C
IRNUC 1H
IFR 270.05 MHz
IRSET 112.00 KHz
IRFIN 5800.00 Hz
IRRPW 5800 usec
IRATN 511
DRFILE Compound2e(d6DMSO)_1Hals
SF FH5_140306Compound2e (d6DMSO)
LKSET 64.40 KHz
LKFIN 76.0 Hz
LKLEV 180
LGAIN 16
LKPHS 82
LKSIG 615
CSPED 17 Hz
FILDC
FILDF

Assignment for **2e** in d_6 DMSO

Enol-form of **2e**



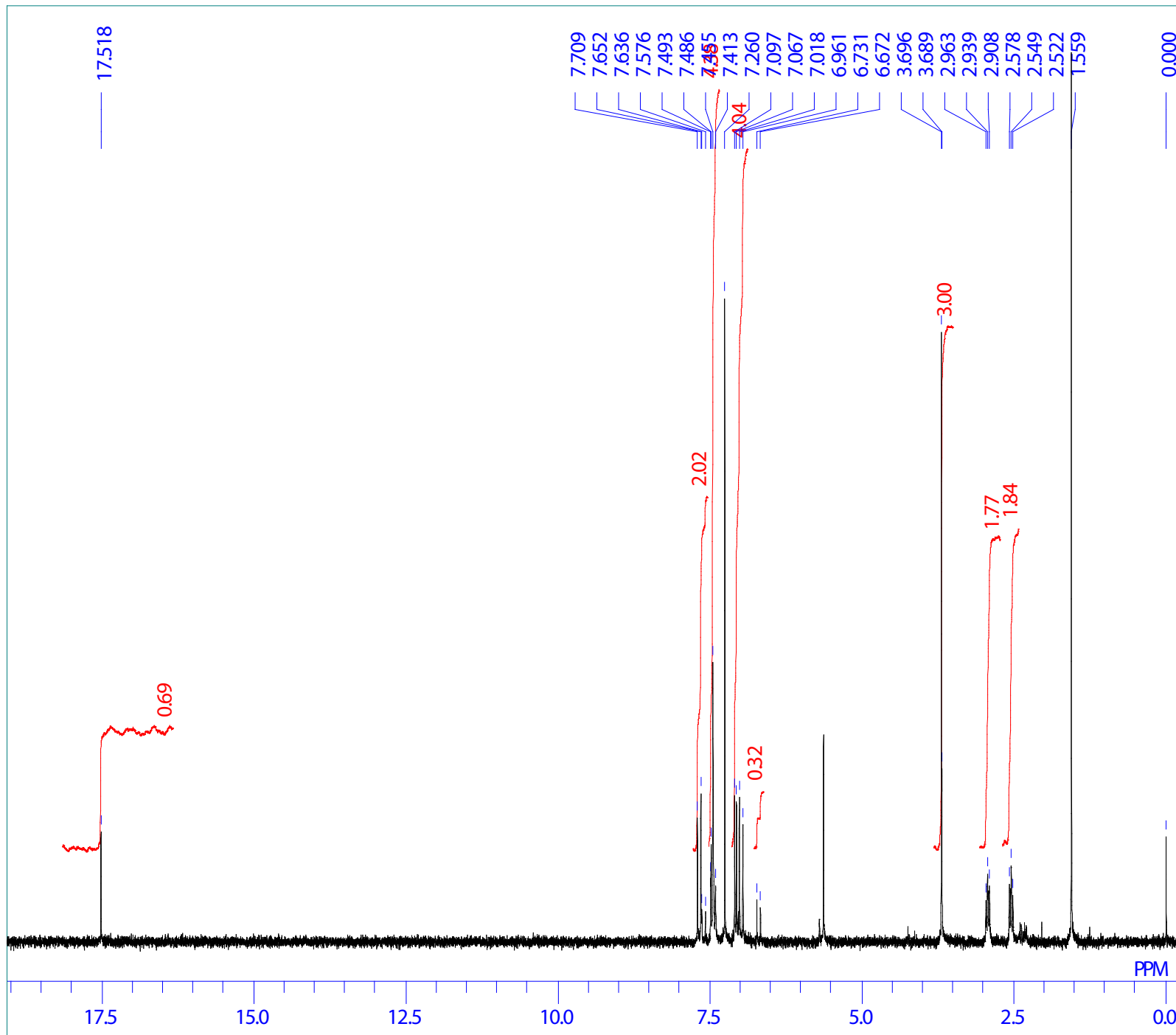
Keto-form of **2e**



- δ_H 2.07 (m) }
 2.32 (m) } 4H
 2.4-2.55 }
 2.98 (m) }
 3.54 (s, $-\text{COOCH}_3$) enol-form } 3H
 3.59 (s, $-\text{COOCH}_3$) keto-form }
 4.60 (t, J 6.8, 0.6H, $-\text{COCHCO}-$, \mathbf{H}_4) keto-form
 6.98 (d, J 15.9, 1.1H, $-\text{CH}=\text{CH}-$, \mathbf{H}_2 and \mathbf{H}_6) keto-form
 7.05 (d, J 8.4, ArH, $\mathbf{H}_{5'}$) keto-form } 2H
 7.07 (d, J 8.4, ArH, $\mathbf{H}_{5'}$) enol-form }
 7.21 (d, J 15.7, 0.9H, $-\text{CH}=\text{CH}-$, \mathbf{H}_2 and \mathbf{H}_6) enol-form
 7.55-7.7 (4H, arom)
 7.77 (br.d, J 15.7, 2H, $-\text{CH}=\text{CH}-$, \mathbf{H}_1 and \mathbf{H}_7) both keto- and enol-form
 10.89 (br, 2H)
 17.87 (s, 0.4H, strongly bound H by hydrogen bonding)

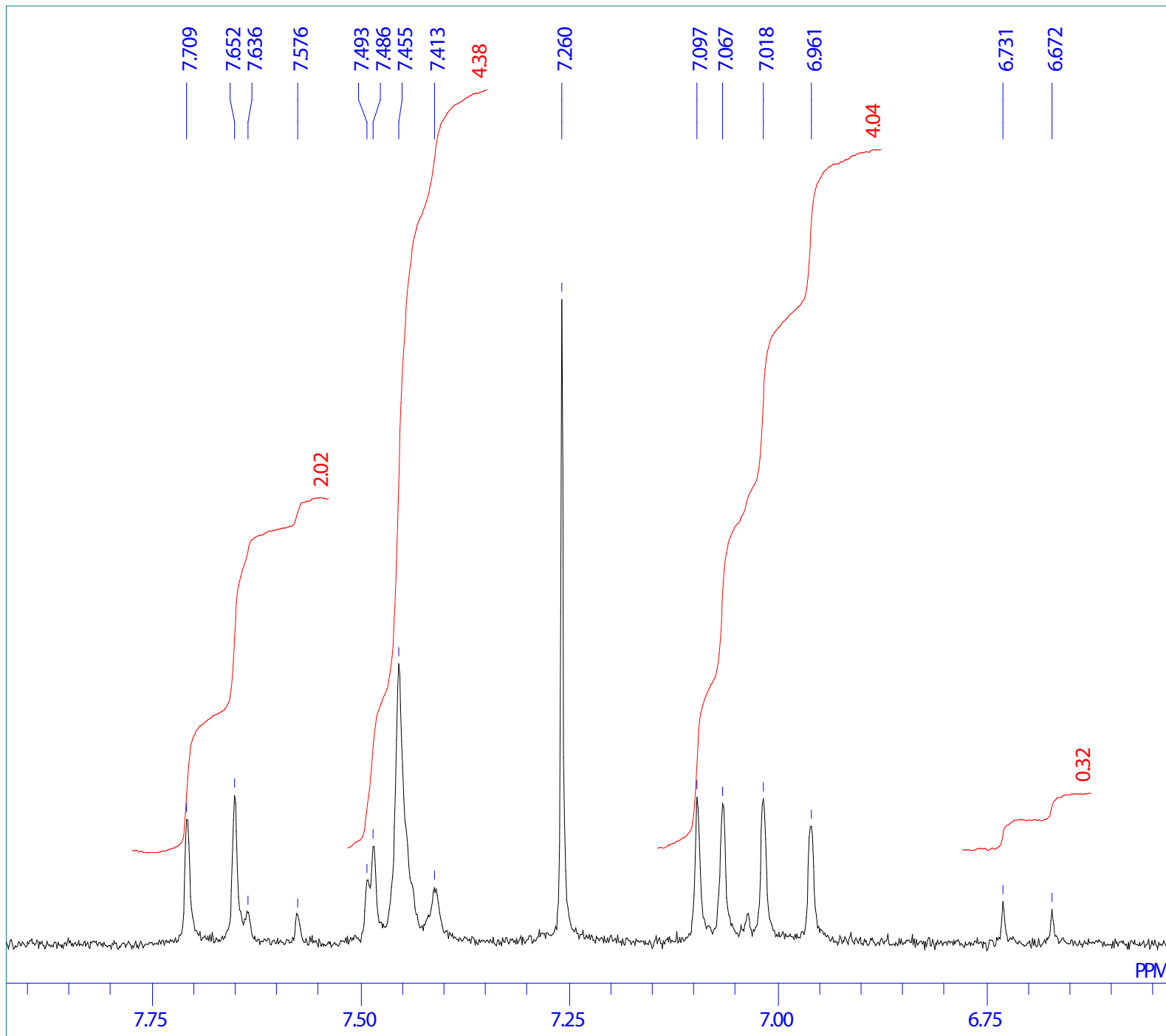
- δ_F -58.06 (s, $-\text{OCF}_3$) keto-form
 -57.93 (s, $-\text{OCF}_3$) enol-form

¹H NMR Compound 2e (CDCl₃)



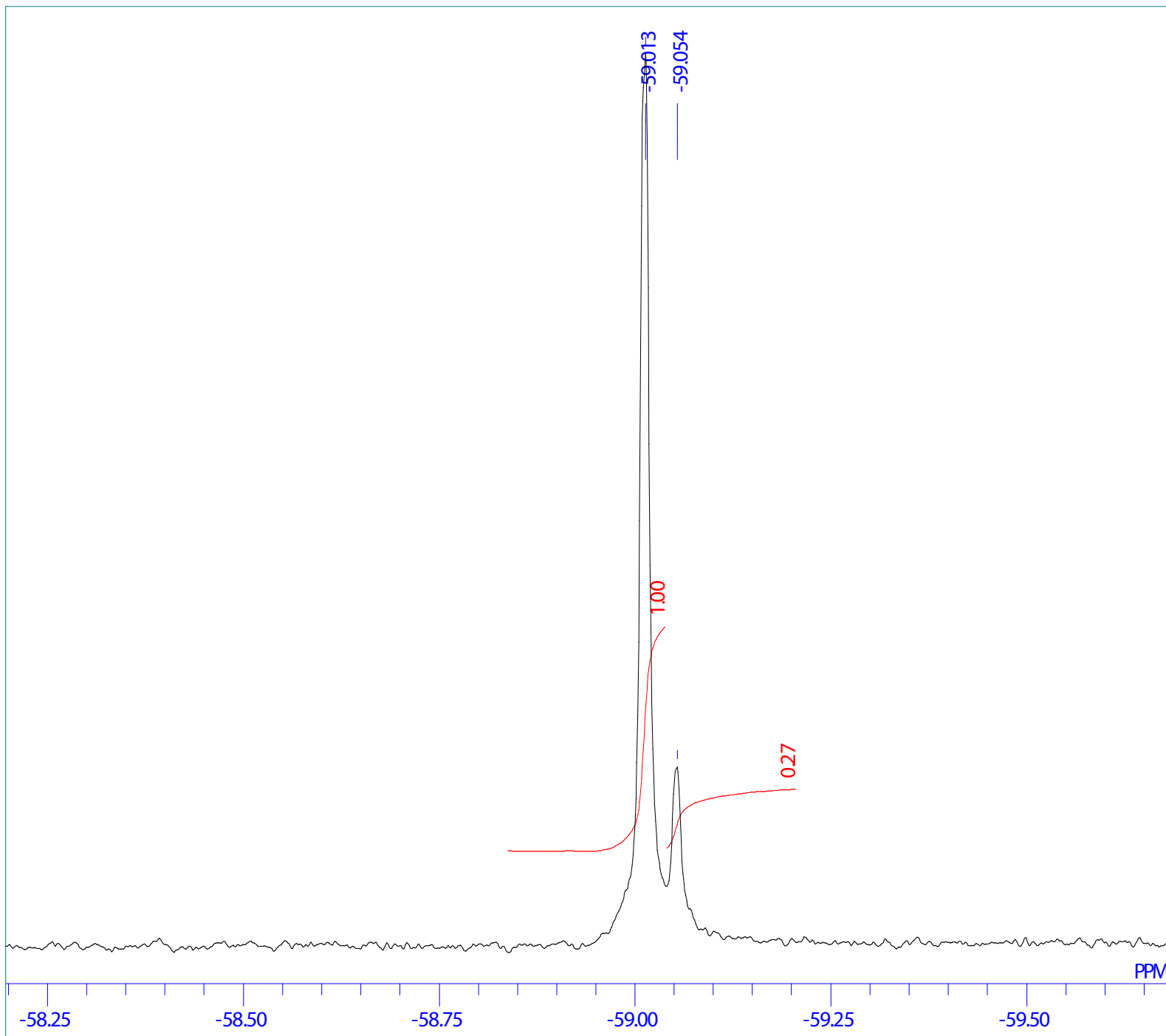
MENUF	NON
OBNUC	1H
OFR	270.05 MHz
OBSET	112.00 KHz
OBFIN	5800.00 Hz
PW1	12.50 usec
DEADT	49.31 usec
PREDL	0.20000 msec
IWT	1.0000 sec
POINT	32768
SPO	32768
TIMES	8
DUMMY	1
FREQU	10810.80 Hz
FLT	5400 Hz
DELAY	37.04 usec
ACQTM	3.0310 sec
PD	0.9350 sec
ADBIT	16
RGAIN	25
BF	0.10 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	NON
EXPCM	NONSinglecoupledPW1_ACQTM_PD:1H;13C
IRNUC	1H
IFR	270.05 MHz
IRSET	112.00 KHz
IRFIN	5800.00 Hz
IRRPW	50 usec
IRATN	511
DFILE	Compound2e(CDCl3)_1Hals
SF	FH5_INU
LKSET	64.60 KHz
LKFN	59.0 Hz
LKLEV	200
LGAIN	20
LKPHS	32
LKSIG	671
CSPED	12 Hz
FILDC	
FILDF	

¹H NMR Compound 2e (CDCl₃)



MENUF	NON
OBNUC	1H
OFI	270.05 MHz
OBSET	112.00 KHz
OBFIN	5800.00 Hz
PW1	12.50 usec
DEADT	49.31 usec
PREDL	0.20000 msec
IWT	1.0000 sec
POINT	32768
SPO	32768
TIMES	8
DUMMY	1
FREQU	10810.80 Hz
FLT	5400 Hz
DELAY	37.04 usec
ACQTM	3.0310 sec
PD	0.9350 sec
ADBIT	16
RGAIN	25
BF	0.10 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	NON
EXPCM	NONSingle.coupledPW1_ACQTM_PD:1H;13C
IRNUC	1H
IFR	270.05 MHz
IRSET	112.00 KHz
IRFIN	5800.00 Hz
IRRPW	50 usec
IRATN	511
DFILE	Cur-COOMespcals
SF	FH5_INU
LKSET	64.60 KHz
LKFIN	59.0 Hz
LKLEV	200
LGAIN	20
LKPHS	32
LKSIG	671
CSPED	12 Hz
FILDC	
FILDF	

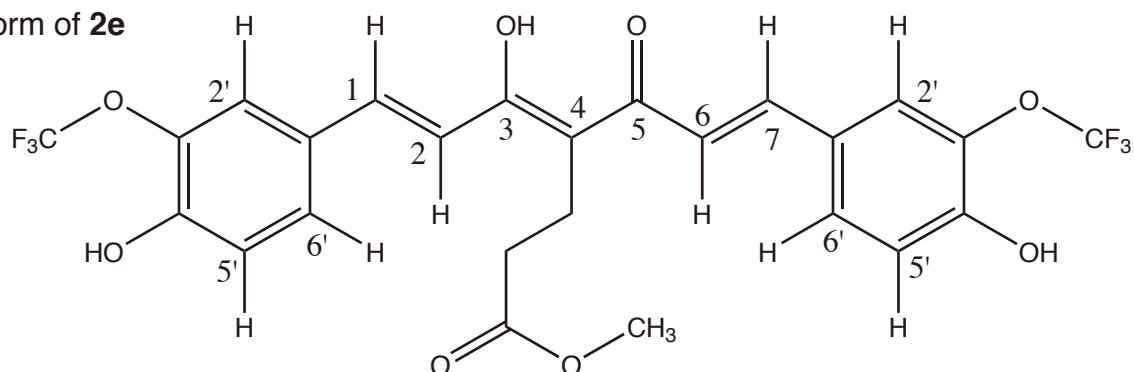
¹⁹F NMR Compound 2e (CDCl₃)



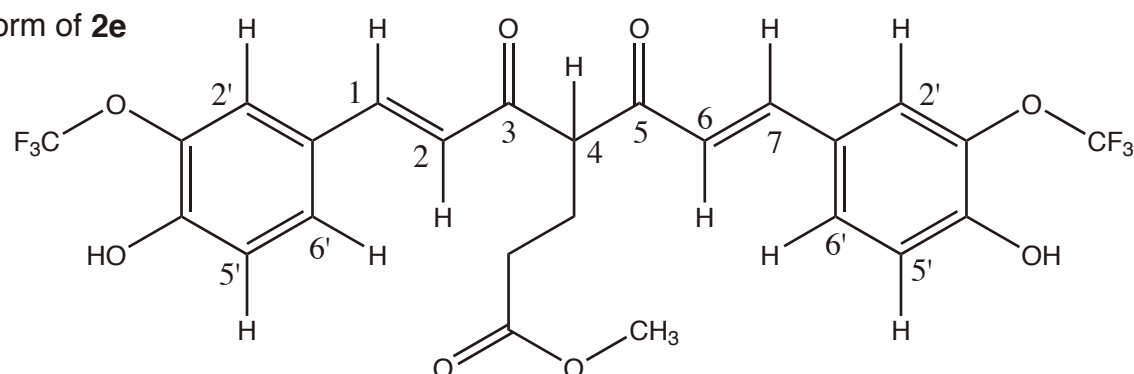
MENUF 19F-SHGAXF5_INU
OBNUC 19F
OFR 254.05 MHz
OBSET 134.40 KHz
OBFIN 45.10 Hz
PW1 5.00 usec
DEADT 10.00 usec
PREDL 0.20000 msec
IWT 1.0000 sec
POINT 262144
SPO 65536
TIMES 4
DUMMY 1
FREQU 80000.00 Hz
FLT 40000 Hz
DELAY 5.00 usec
ACQTM 0.8192 sec
PD 0.9350 sec
ADBIT 16
RGAIN 27
BF 1.00 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD NON
EXPCM NONSinglecoupledPW1_ACQTM_PD:1H;13C
IRNUC 1H
IFR 270.05 MHz
IRSET 112.00 KHz
IRFIN 5800.00 Hz
IRRPW 50 usec
IRATN 511
DRFILE Compound2e_19F.fls
SF F5_INU
LKSET 64.60 KHz
LKFIN 59.0 Hz
LKLEV 200
LGAIN 20
LKPHS 32
LKSIG 688
CSPED 17 Hz
FILDC
FILDF

Assignment for **2e** in CDCl₃

Enol-form of **2e**



Keto-form of **2e**



- δ_{H} 2.55 (m, 2H, -CH₂CH₂COOCH₃)
 2.94 (m, 2H, -CH₂CH₂COOCH₃)
 3.69 (s, 3H, -COOCH₃)
 6.70 (d, J 15.9, 0.3H, -CH=CH-, **H**₂ and **H**₆) keto-form
 6.99 (d, J, 15.4, 1.7H, -CH=CH-, **H**₂ and **H**₆) enol-form
 7.08 (d, J 8.1, 1.7H, ArH, **H**_{5'}) enol-form
 7.4-7.5 (4H, arom) both keto- and enol-form
 7.61 (d, J 15.9, 0.3H, -CH=CH-, **H**₁ and **H**₇) keto-form
 7.68 (d, 15.4, 1.7H, -CH=CH-, **H**₁ and **H**₇) enol-form
 17.52 (s, 0.8H, strongly bound H by hydrogen bonding) enol-form

- δ_{F} -59.05 (s, -OCF₃) keto-form
 -59.01 (s, -OCF₃) enol-form