Essential Parameters for Structural Analysis and Dereplication by ^{1}H NMR Spectroscopy

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■ SUPPORTING INFORMATION

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S1: HNMR and HiFSA Data for Compound 1 (Case Study 1)

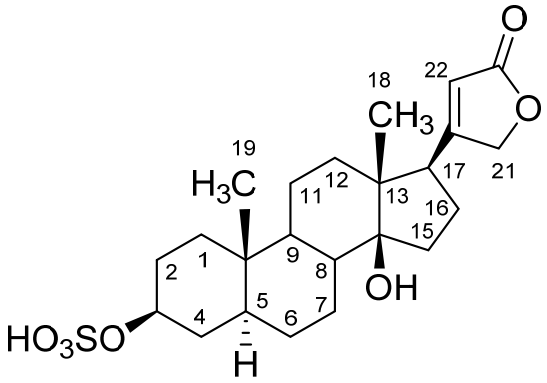
S1a: HiFSA Profile of Uzarigenin-3-sulfate (1)

In CD_3OD (600 MHz, 298 K)

Proton	δ (ppm)	$\Delta\nu_{½}$ (Hz)
H1A	1.0478	1.91
H1B	1.7740	2.19
H2A	2.0134	1.79
H2B	1.5307	1.76
H3A	4.2470	1.80
H4A	1.4155	1.66
H4B	1.8255	1.77
H5A	1.1579	1.96
H6A	1.2731	1.99
H6B	1.3669	2.14
H7A	2.0330	1.96
H7B	1.1116	1.93
H8A	1.5839	2.02
H9A	0.9959	2.15
H11A	**1.2830**	**2.27**
H11B	**1.5246**	**2.18**
H12A	**1.4525**	**2.18**
H12B	**1.4938**	**2.06**
H15A	2.1079	1.71
H15B	1.6954	1.81
H16A	1.8529	1.73
H16B	2.1511	1.82
H17A	2.8217	1.67
H18*	0.8364	1.19
H19*	0.8761	1.44
H21A	5.0209	1.49
H21B	4.9105	0.93
H22A	5.8883	0.89

* The Me groups were assigned based on the ^{1}H-prediction.

Coupling	J(Hz)	Coupling	J(Hz)
H1A / H1B	-13.33	H8A / H7A	3.61
H1A / H18	-0.64	H8A / H7B	12.28
H1A / H2A	3.83	H9A / H11A	12.51
H1A / H2B	13.99	H9A / H11B	3.60
H1B / H2A	3.31	H11A / H11B	-13.55
H1B / H2B	3.96	H12A / H12B	-13.69
H2A / H2B	-12.99	H12A / H11A	13.78
H2A / H4B	1.99	H12A / H11B	3.83
H2A / H3A	4.91	H12A / H19	-0.66
H2B / H3A	11.51	H12B / H11A	3.65
H4A / H5A	12.88	H12B / H11B	3.03
H4A / H4B	-12.63	H15A / H15B	-13.71
H4A / H3A	11.32	H15A / H16A	10.26
H4B / H3A	4.92	H15A / H16B	10.12
H5A / H4B	3.06	H15B / H16A	9.13
H6A / H6B	-13.25	H15B / H16B	1.77
H6A / H5A	12.37	H16A / H16B	-13.87
H6B / H5A	2.98	H17A / H16A	5.53
H7A / H7B	-12.93	H17A / H16B	9.69
H7A / H6A	3.71	H17A / H22A	-0.69
H7A / H6B	2.77	H21A / H21B	-18.32
H7B / H6A	13.20	H22A / H21A	-1.74
H7B / H6B	4.14	H22A / H21B	-1.82
H8A / H9A	11.57		



S1b. Complete HiFSA Profile of Uzarigenin-3-sulfate (1) in CD_3OD (600 MHz, 298 K) using PERCH's parameters (.pms) format

```
* NEW: the lines beginning by * are comment lines !
* To keep all the chemical shifts fixed during iteration
* replace "CHEMICAL SHIFTS(HZ):" by "..SHIFTS(HZ): fixed"
* The couplings can be fixed in the same way

NMR-data: [path]
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CHEMICAL SHIFTS(PPM):
PROTON    2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.09225
 H8A   / 1     1.583875  1*1*1  STAT=Y  PRED= 1.728 RANGE= 0.417 WIDTH(Y)= 2.028 RESP(Y)= 0.9067 HSQC= C8
 H9A   / 1     0.995865  1*1*1  STAT=Y  PRED= 0.965 RANGE= 0.232 WIDTH(Y)= 2.162 RESP(Y)= 0.9030 HSQC= C9
 H17A  / 1     2.821666  1*1*1  STAT=Y  PRED= 2.489 RANGE= 0.322 WIDTH(Y)= 2.059 RESP(Y)= 0.9087 HSQC= C17
 H12A  / 1     1.452478  1*1*1  STAT=Y  PRED= 1.034 RANGE= 0.250 WIDTH(Y)= 2.247 RESP(Y)= 0.8674 HSQC= C12
 H12B  / 1     1.493789  1*1*1  STAT=Y  PRED= 1.649 RANGE= 0.260 WIDTH(Y)= 2.064 RESP(Y)= 0.8989 HSQC= C12
 H11A  / 1     1.282972  1*1*1  STAT=Y  PRED= 1.330 RANGE= 0.212 WIDTH(Y)= 2.293 RESP(Y)= 0.9246 HSQC= C11
 H11B  / 1     1.524588  1*1*1  STAT=Y  PRED= 1.565 RANGE= 0.252 WIDTH(Y)= 2.200 RESP(Y)= 0.8857 HSQC= C11
 H15A  / 1     2.107928  1*1*1  STAT=Y  PRED= 1.809 RANGE= 0.462 WIDTH(Y)= 1.718 RESP(Y)= 0.8625 HSQC= C15
 H15B  / 1     1.695405  1*1*1  STAT=Y  PRED= 1.723 RANGE= 0.265 WIDTH(Y)= 1.854 RESP(Y)= 0.8999 HSQC= C15
 H7A   / 1     2.032966  1*1*1  STAT=Y  PRED= 1.948 RANGE= 0.277 WIDTH(Y)= 1.968 RESP(Y)= 0.8894 HSQC= C7
 H7B   / 1     1.111591  1*1*1  STAT=Y  PRED= 1.167 RANGE= 0.217 WIDTH(Y)= 1.938 RESP(Y)= 0.8698 HSQC= C7
 H16A  / 1     1.852888  1*1*1  STAT=Y  PRED= 1.912 RANGE= 0.437 WIDTH(Y)= 1.743 RESP(Y)= 0.8865 HSQC= C16
 H16B  / 1     2.151134  1*1*1  STAT=Y  PRED= 1.712 RANGE= 0.430 WIDTH(Y)= 1.933 RESP(Y)= 0.9059 HSQC= C16
 H18   / 1     0.876058  1*1*3  STAT=Y  PRED= 0.838 RANGE= 0.225 WIDTH(Y)= 1.465 RESP(Y)= 0.9045 HSQC= C19
 H6A   / 1     1.273053  1*1*1  STAT=Y  PRED= 1.320 RANGE= 0.155 WIDTH(Y)= 1.984 RESP(Y)= 0.9488 HSQC= C6
 H6B   / 1     1.366855  1*1*1  STAT=Y  PRED= 1.342 RANGE= 0.207 WIDTH(Y)= 2.155 RESP(Y)= 0.8995 HSQC= C6
 H1A   / 1     1.047752  1*1*1  STAT=Y  PRED= 0.887 RANGE= 0.152 WIDTH(Y)= 1.991 RESP(Y)= 0.8741 HSQC= C1
 H1B   / 1     1.773988  1*1*1  STAT=Y  PRED= 1.606 RANGE= 0.230 WIDTH(Y)= 2.211 RESP(Y)= 0.9089 HSQC= C1
 H19   / 1     0.836429  1*1*3  STAT=Y  PRED= 0.833 RANGE= 0.150 WIDTH(Y)= 1.254 RESP(Y)= 0.8876 HSQC= C18
 H2A   / 1     2.013384  1*1*1  STAT=Y  PRED= 2.107 RANGE= 0.212 WIDTH(Y)= 1.949 RESP(Y)= 0.8985 HSQC= C2
 H2B   / 1     1.530692  1*1*1  STAT=Y  PRED= 1.849 RANGE= 0.300 WIDTH(Y)= 1.799 RESP(Y)= 0.8772 HSQC= C2
 H4A   / 1     1.415541  1*1*1  STAT=Y  PRED= 1.857 RANGE= 0.372 WIDTH(Y)= 1.665 RESP(Y)= 0.8898 HSQC= C4
 H22A  / 1     5.888342  1*1*1  STAT=Y  PRED= 6.160 RANGE= 0.547 WIDTH(Y)= 0.940 RESP(Y)= 0.9176 HSQC= C22
 H5A   / 1     1.157920  1*1*1  STAT=Y  PRED= 1.135 RANGE= 0.160 WIDTH(Y)= 1.968 RESP(Y)= 0.9201 HSQC= C5
 H4B   / 1     1.825476  1*1*1  STAT=Y  PRED= 1.852 RANGE= 0.260 WIDTH(Y)= 1.773 RESP(Y)= 0.8853 HSQC= C4
 H3A   / 1     4.247007  1*1*1  STAT=Y  PRED= 4.365 RANGE= 0.367 WIDTH(Y)= 1.814 RESP(Y)= 0.8898 HSQC= C3
 H21A  / 1     5.020935  1*1*1  STAT=Y  PRED= 4.903 RANGE= 0.222 WIDTH(Y)= 1.516 RESP(Y)= 0.9583 HSQC= C21
 H21B  / 1     4.910519  1*1*1  STAT=Y  PRED= 4.866 RANGE= 0.202 WIDTH(Y)= 1.310 RESP(Y)= 1.0000 HSQC= C21
MET_H     2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.11343
 MeOH  / 2     3.300116  1*1*1  STAT=Y  PRED= 3.300 RANGE= 0.050 WIDTH(Y)= 1.056 RESP(Y)= 1.0000
MET_D     2*SPIN= 2 SPECIES=2D    POPULATION(Y)=   0.11343
 MET_D1/ 2   -99.999998  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
 MET_D2/ 2   -99.999998  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
MET_OH    2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.79432
 WATER / 3     4.888587  1*1*1  STAT=Y  PRED= 4.891 RANGE= 0.050 WIDTH(Y)= 4.723 RESP(Y)= 1.0000

COUPLING CONSTANTS(HZ):
 J25_26     11.5701   J H8A    H9A      STAT=Y  PRED= 12.490 RANGE= 2.560
 J25_34      3.6052   J H8A    H7A      STAT=Y  PRED= 3.590 RANGE= 3.800
 J25_35     12.2813   J H8A    H7B      STAT=Y  PRED= 12.780 RANGE= 2.560
 J26_30     12.5121   J H9A    H11A     STAT=Y  PRED= 12.590 RANGE= 2.560
 J26_31      3.6044   J H9A    H11B     STAT=Y  PRED= 2.980 RANGE= 2.800
 J27_36      5.5309   J H17A   H16A     STAT=Y  PRED= 3.960 RANGE= 9.200
 J27_37      9.6920   J H17A   H16B     STAT=Y  PRED= 10.720 RANGE= 6.400
 J27_51     -0.6894   J H17A   H22A     STAT=Y  PRED= -2.500 RANGE= 1.200
 J28_29    -13.6932   J H12A   H12B     STAT=Y  PRED= -13.060 RANGE= 1.500
 J28_30     13.7807   J H12A   H11A     STAT=Y  PRED= 12.850 RANGE= 2.560
 J28_31      3.8316   J H12A   H11B     STAT=Y  PRED= 3.800 RANGE= 3.800
 J28_38     -0.6643   J H12A   H19      STAT=Y  PRED= -0.780 RANGE= 0.400
 J29_30      3.6546   J H12B   H11A     STAT=Y  PRED= 3.520 RANGE= 3.800
 J29_31      3.0316   J H12B   H11B     STAT=Y  PRED= 3.040 RANGE= 3.800
 J30_31    -13.5488   J H11A   H11B     STAT=Y  PRED= -13.170 RANGE= 1.500
 J32_33    -13.7061   J H15A   H15B     STAT=Y  PRED= -12.450 RANGE= 2.000
 J32_36     10.2649   J H15A   H16A     STAT=Y  PRED= 6.700 RANGE= 6.000
 J32_37     10.1202   J H15A   H16B     STAT=Y  PRED= 10.340 RANGE= 4.400
 J33_36      9.1272   J H15B   H16A     STAT=Y  PRED= 10.440 RANGE= 4.400
 J33_37      1.7733   J H15B   H16B     STAT=Y  PRED= 1.430 RANGE= 4.800
 J34_35    -12.9331   J H7A    H7B      STAT=Y  PRED= -13.170 RANGE= 1.500
 J34_41      3.7097   J H7A    H6A      STAT=Y  PRED= 4.030 RANGE= 3.800
 J34_42      2.7684   J H7A    H6B      STAT=Y  PRED= 2.410 RANGE= 2.800
 J35_41     13.2040   J H7B    H6A      STAT=Y  PRED= 12.580 RANGE= 2.560
 J35_42      4.1397   J H7B    H6B      STAT=Y  PRED= 4.240 RANGE= 3.800
 J36_37    -13.8660   J H16A   H16B     STAT=Y  PRED= -12.770 RANGE= 2.000
 J41_42    -13.2526   J H6A    H6B      STAT=Y  PRED= -13.210 RANGE= 1.500
 J41_57     12.3742   J H6A    H5A      STAT=Y  PRED= 12.460 RANGE= 2.560
 J42_57      2.9837   J H6B    H5A      STAT=Y  PRED= 2.790 RANGE= 2.800
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 J43_44    -13.3260   J H1A    H1B      STAT=Y  PRED= -13.110 RANGE= 1.500
 J43_45     -0.6363   J H1A    H18      STAT=Y  PRED= -0.790 RANGE= 0.400
 J43_48      3.8301   J H1A    H2A      STAT=Y  PRED= 4.360 RANGE= 3.800
 J43_49     13.9914   J H1A    H2B      STAT=Y  PRED= 12.910 RANGE= 2.560
 J44_48      3.3128   J H1B    H2A      STAT=Y  PRED= 2.510 RANGE= 2.800
 J44_49      3.9635   J H1B    H2B      STAT=Y  PRED= 4.180 RANGE= 3.800
 J48_49    -12.9878   J H2A    H2B      STAT=Y  PRED= -12.860 RANGE= 1.500
 J48_58      1.9948   J H2A    H4B      STAT=Y  PRED= 2.710 RANGE= 1.280
 J48_59      4.9081   J H2A    H3A      STAT=Y  PRED= 4.400 RANGE= 3.800
 J49_59     11.5103   J H2B    H3A      STAT=Y  PRED= 10.140 RANGE= 2.560
 J50_57     12.8753   J H4A    H5A      STAT=Y  PRED= 12.860 RANGE= 2.560
 J50_58    -12.6342   J H4A    H4B      STAT=Y  PRED= -12.830 RANGE= 1.500
 J50_59     11.3207   J H4A    H3A      STAT=Y  PRED= 10.390 RANGE= 2.560
 J51_64     -1.7403   J H22A   H21A     STAT=Y  PRED= -2.060 RANGE= 1.200
 J51_65     -1.8208   J H22A   H21B     STAT=Y  PRED= -2.070 RANGE= 1.200
 J57_58      3.0575   J H5A    H4B      STAT=Y  PRED= 2.960 RANGE= 2.800
 J58_59      4.9156   J H4B    H3A      STAT=Y  PRED= 4.200 RANGE= 3.800
 J64_65    -18.3240   J H21A   H21B     STAT=Y  PRED= -10.080 RANGE= 4.000
 JMETH1      1.6500   J MeOH   MET_D1   STAT=Y  PRED= 1.650 RANGE= 0.150
 JMETH1      1.6500   J MeOH   MET_D2   STAT=Y  PRED= 1.650 RANGE= 0.150

CONTROL PARAMETERS:
       Solvent =  none (def. 99% enriched)
         1.000 =  Concentration (vol%, def=1.0%)
    0.00100000 =  Minimum line-intensity
    0.00100000 =  Diagonalization criterium (not in use)
  600.13002100 =  FIELD(1H,MHz), used to transform shifts to ppms
    7.96588690 =  Left frequency (ppm)
   -0.03494010 =  Right frequency (ppm)
         0.000 =  Acquisition time (s, for QMTLS)
         0.775 =  Line-width (for modes D, P & T, 0=use defaults)
   0.036633096 =  Data-point resolution (Hz)
        52.020 =  GAUSSIAN (%, 0=use default from INF)
         0.000 =  Dispersion contribution (%, 0=use default from INF)
    0.00000000 =  Decoupling frequency (for DORES)

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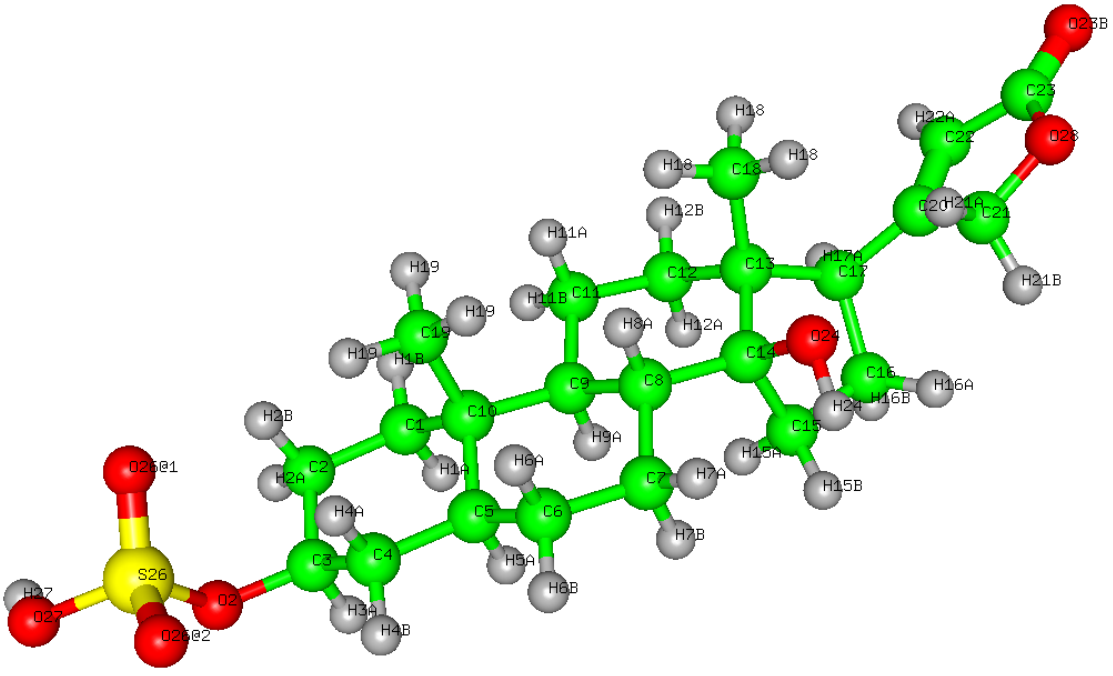
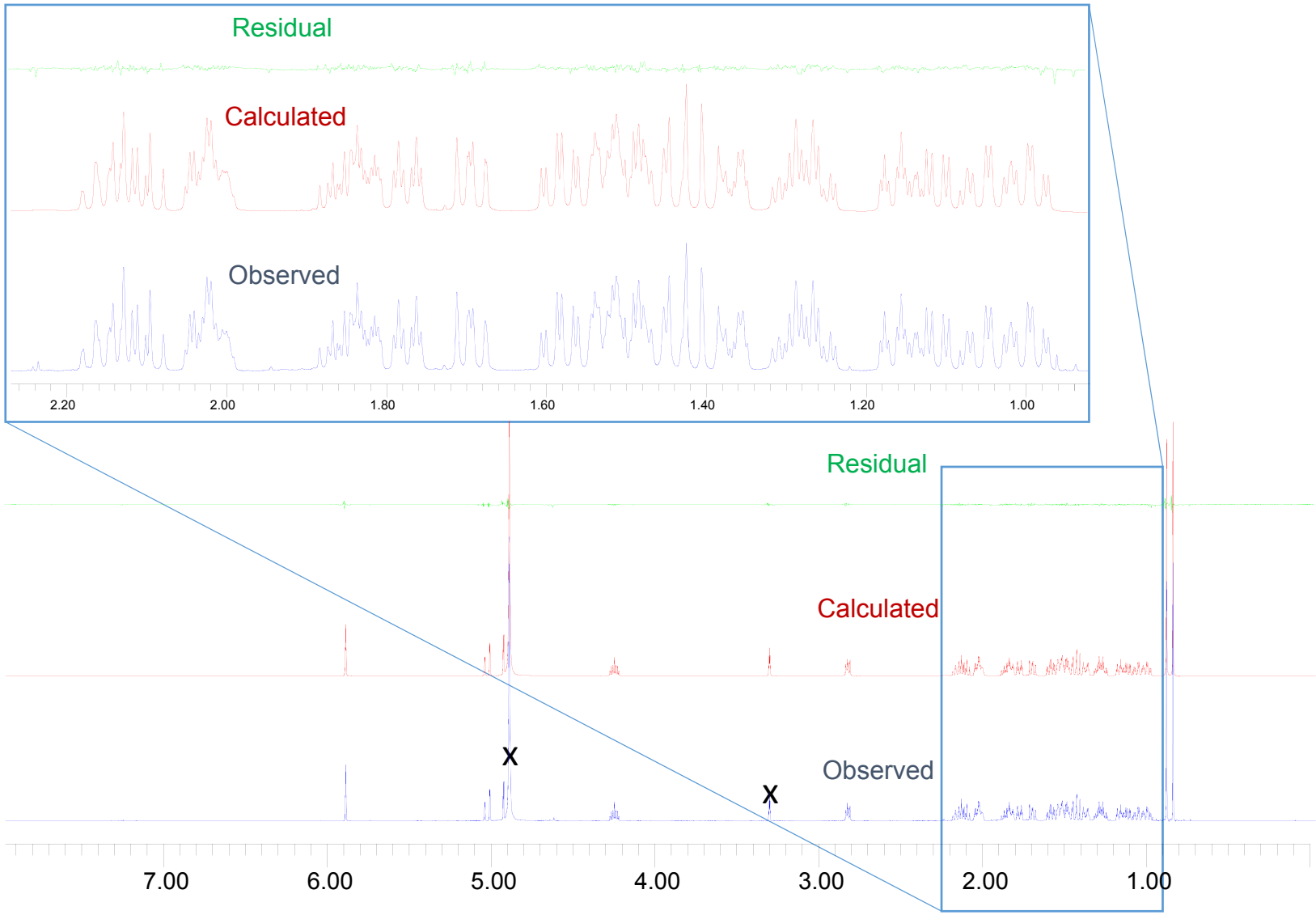


S1c. The ^{1}H NMR Fingerprint of Uzarigenin-3-sulfate (1) in CD_3OD (600 MHz, 298 K)

The X marks on the observed spectrum indicate the solvent signals, CHD_2OD and HOD, which were fitted as well.



S2: HNMR and HiFSA Data for Compound 2 (Case Study 2)

S2a: HiFSA Profile of Progesterone (2)

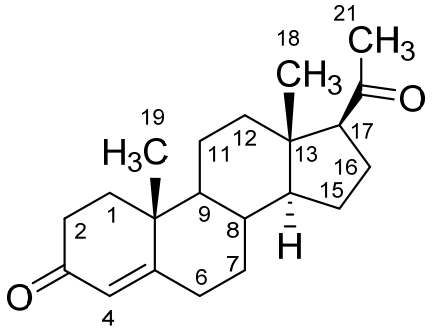
In CD_3OD (900 MHz, 298 K)

Proton	δ (ppm)	$\Delta\nu_{½}$ (Hz)
H1A	1.7420	1.78
H1B	2.1171	1.64
H2A	**2.3177**	**1.42**
H2B	**2.5099**	**1.49**
H4A	5.7374	1.22
H6A	**2.5161**	**1.57**
H6B	**2.3365**	**1.58**
H7A	1.9281	1.64
H7B	1.1016	1.65
H8A	1.6661	1.81
H9A	1.0521	1.85
H11A	1.5394	1.60
H11B	1.6990	1.77
H12A	1.5239	1.79
H12B	2.1126	1.71
H14A	1.2640	1.86
H15A	1.7631	1.61
H15B	1.3136	1.56
H16A	2.1740	1.42
H16B	1.7026	1.42
H17A	2.6701	2.01
H18*	0.6963	1.43
H19*	1.2593	1.42
H21	2.1449	1.15

* The Me groups were assigned based on the ^{1}H-prediction.

Coupling	J(Hz)
H1A / H1B	-13.40
H1A / H19	-0.60
H1A / H2A	4.42
H1A / H2B	14.86
H1B / H2A	3.05
H1B / H2B	5.21
H2A / H2B	-17.04
H2A / H4A	1.00
H6A / H6B	-14.65
H6A / H4A	-1.90
H6B / H4A	-0.56
H7A / H7B	-12.83
H7A / H6A	5.46
H7A / H6B	2.39
H7B / H6A	13.97
H7B / H6B	4.18
H8A / H9A	10.82
H8A / H7A	3.54
H8A / H7B	11.70
H9A / H11A	12.44
H9A / H11B	4.07

Coupling	J(Hz)
H11A / H11B	-13.90
H12A / H12B	-12.48
H12A / H11A	13.26
H12A / H11B	4.26
H12A / H18	-0.55
H12B / H11A	4.10
H12B / H11B	2.86
H14A / H8A	10.83
H14A / H15A	7.31
H14A / H15B	12.66
H15A / H15B	-12.37
H15A / H16A	3.03
H15A / H16B	9.60
H15B / H16A	11.61
H15B / H16B	6.69
H16A / H16B	-13.83
H17A / H16A	9.19
H17A / H16B	9.32



S2b. Complete HiFSA Profile of Progesterone (2) in CD_3OD (900 MHz, 298 K) using PERCH's parameters (.pms) format

```
* NEW: the lines beginning by * are comment lines !
* To keep all the chemical shifts fixed during iteration
* replace "CHEMICAL SHIFTS(HZ):" by "..SHIFTS(HZ): fixed"
* The couplings can be fixed in the same way

NMR-data: [path]
#$œ  Date 19.12.2013;  Time 17:10:13     perch.2ND

CHEMICAL SHIFTS(PPM):  Similarity% = 100.000
PROTON    2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.11964
 H14A  / 1     1.263993  1*1*1  STAT=Y  PRED= 1.264 RANGE= 0.072 WIDTH(Y)= 1.859 RESP(Y)= 1.0000
 H8A   / 1     1.666058  1*1*1  STAT=Y  PRED= 1.666 RANGE= 0.072 WIDTH(Y)= 1.806 RESP(Y)= 1.0000
 H9A   / 1     1.052063  1*1*1  STAT=Y  PRED= 1.052 RANGE= 0.072 WIDTH(Y)= 1.849 RESP(Y)= 1.0000
 H17A  / 1     2.670139  1*1*1  STAT=Y  PRED= 2.670 RANGE= 0.072 WIDTH(Y)= 2.007 RESP(Y)= 1.0000
 H12A  / 1     1.523860  1*1*1  STAT=Y  PRED= 1.524 RANGE= 0.072 WIDTH(Y)= 1.787 RESP(Y)= 1.0000
 H12B  / 1     2.112615  1*1*1  STAT=Y  PRED= 2.113 RANGE= 0.072 WIDTH(Y)= 1.705 RESP(Y)= 1.0000
 H11A  / 1     1.539393  1*1*1  STAT=Y  PRED= 1.539 RANGE= 0.072 WIDTH(Y)= 1.597 RESP(Y)= 1.0000
 H11B  / 1     1.699024  1*1*1  STAT=Y  PRED= 1.699 RANGE= 0.072 WIDTH(Y)= 1.772 RESP(Y)= 1.0000
 H15A  / 1     1.763103  1*1*1  STAT=Y  PRED= 1.763 RANGE= 0.072 WIDTH(Y)= 1.611 RESP(Y)= 1.0000
 H15B  / 1     1.313565  1*1*1  STAT=Y  PRED= 1.314 RANGE= 0.072 WIDTH(Y)= 1.555 RESP(Y)= 1.0000
 H7A   / 1     1.928077  1*1*1  STAT=Y  PRED= 1.928 RANGE= 0.072 WIDTH(Y)= 1.640 RESP(Y)= 1.0000
 H7B   / 1     1.101633  1*1*1  STAT=Y  PRED= 1.102 RANGE= 0.072 WIDTH(Y)= 1.645 RESP(Y)= 1.0000
 H16A  / 1     2.174043  1*1*1  STAT=Y  PRED= 2.174 RANGE= 0.072 WIDTH(Y)= 1.415 RESP(Y)= 1.0000
 H16B  / 1     1.702611  1*1*1  STAT=Y  PRED= 1.703 RANGE= 0.072 WIDTH(Y)= 1.417 RESP(Y)= 1.0000
 H18   / 1     0.696299  1*1*3  STAT=Y  PRED= 0.696 RANGE= 0.072 WIDTH(Y)= 1.425 RESP(Y)= 1.0000
 H6A   / 1     2.516118  1*1*1  STAT=Y  PRED= 2.516 RANGE= 0.072 WIDTH(Y)= 1.567 RESP(Y)= 1.0000
 H6B   / 1     2.336540  1*1*1  STAT=Y  PRED= 2.337 RANGE= 0.072 WIDTH(Y)= 1.580 RESP(Y)= 1.0000
 H1A   / 1     1.742003  1*1*1  STAT=Y  PRED= 1.742 RANGE= 0.072 WIDTH(Y)= 1.779 RESP(Y)= 1.0000
 H1B   / 1     2.117062  1*1*1  STAT=Y  PRED= 2.117 RANGE= 0.072 WIDTH(Y)= 1.638 RESP(Y)= 1.0000
 H19   / 1     1.259275  1*1*3  STAT=Y  PRED= 1.259 RANGE= 0.072 WIDTH(Y)= 1.422 RESP(Y)= 1.0000
 H2A   / 1     2.317691  1*1*1  STAT=Y  PRED= 2.318 RANGE= 0.072 WIDTH(Y)= 1.416 RESP(Y)= 1.0000
 H2B   / 1     2.509924  1*1*1  STAT=Y  PRED= 2.510 RANGE= 0.072 WIDTH(Y)= 1.494 RESP(Y)= 1.0000
 H4A   / 1     5.737395  1*1*1  STAT=Y  PRED= 5.737 RANGE= 0.072 WIDTH(Y)= 1.220 RESP(Y)= 1.0000
 H21   / 1     2.144930  1*1*3  STAT=Y  PRED= 2.145 RANGE= 0.072 WIDTH(Y)= 1.152 RESP(Y)= 1.0000
MET_H     2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.69264
 MeOH  / 2     3.329850  1*1*1  STAT=Y  PRED= 3.330 RANGE= 0.049 WIDTH(Y)= 1.308 RESP(Y)= 1.0000
MET_D     2*SPIN= 2 SPECIES=2D    POPULATION(Y)=   0.69264
 MET_D1/ 2  -100.000002  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
 MET_D2/ 2  -100.000002  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
 MET_D3/ 2  -100.000002  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
MET_OH    2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.17011
 WATER / 3     4.899922  1*1*1  STAT=Y  PRED= 4.900 RANGE= 0.049 WIDTH(Y)= 2.934 RESP(Y)= 1.0000

COUPLING CONSTANTS(HZ):  Similarity% =  26.218
 J24_25     10.8287   J H14A   H8A      STAT=Y  PRED= 10.685 RANGE= 0.100
 J24_32      7.3130   J H14A   H15A     STAT=Y  PRED= 7.255 RANGE= 0.100
 J24_33     12.6579   J H14A   H15B     STAT=Y  PRED= 12.752 RANGE= 0.100
 J25_26     10.8204   J H8A    H9A      STAT=Y  PRED= 10.854 RANGE= 0.100
 J25_34      3.5446   J H8A    H7A      STAT=Y  PRED= 3.549 RANGE= 0.100
 J25_35     11.7014   J H8A    H7B      STAT=Y  PRED= 11.711 RANGE= 0.100
 J26_30     12.4418   J H9A    H11A     STAT=Y  PRED= 12.420 RANGE= 2.570
 J26_31      4.0651   J H9A    H11B     STAT=Y  PRED= 4.084 RANGE= 0.100
 J27_36      9.1884   J H17A   H16A     STAT=Y  PRED= 9.199 RANGE= 0.100
 J27_37      9.3186   J H17A   H16B     STAT=Y  PRED= 9.303 RANGE= 0.100
 J28_29    -12.4787   J H12A   H12B     STAT=Y  PRED= -12.470 RANGE= 0.100
 J28_30     13.2626   J H12A   H11A     STAT=Y  PRED= 13.258 RANGE= 0.100
 J28_31      4.2615   J H12A   H11B     STAT=Y  PRED= 4.283 RANGE= 0.100
 J28_38     -0.5499   J H12A   H18      STAT=Y  PRED= -0.482 RANGE= 0.100
 J29_30      4.1038   J H12B   H11A     STAT=Y  PRED= 4.113 RANGE= 0.100
 J29_31      2.8562   J H12B   H11B     STAT=Y  PRED= 2.860 RANGE= 0.100
 J30_31    -13.8953   J H11A   H11B     STAT=Y  PRED= -13.919 RANGE= 0.100
 J32_33    -12.3670   J H15A   H15B     STAT=Y  PRED= -12.362 RANGE= 0.100
 J32_36      3.0332   J H15A   H16A     STAT=Y  PRED= 3.020 RANGE= 0.100
 J32_37      9.5984   J H15A   H16B     STAT=Y  PRED= 9.611 RANGE= 0.100
 J33_36     11.6147   J H15B   H16A     STAT=Y  PRED= 11.608 RANGE= 0.100
 J33_37      6.6874   J H15B   H16B     STAT=Y  PRED= 6.691 RANGE= 0.100
 J34_35    -12.8262   J H7A    H7B      STAT=Y  PRED= -12.830 RANGE= 0.100
 J34_41      5.4583   J H7A    H6A      STAT=Y  PRED= 5.454 RANGE= 0.100
 J34_42      2.3909   J H7A    H6B      STAT=Y  PRED= 2.385 RANGE= 0.100
 J35_41     13.9716   J H7B    H6A      STAT=Y  PRED= 13.974 RANGE= 0.100
 J35_42      4.1782   J H7B    H6B      STAT=Y  PRED= 4.187 RANGE= 0.100
 J36_37    -13.8262   J H16A   H16B     STAT=Y  PRED= -13.829 RANGE= 0.100
 J41_42    -14.6493   J H6A    H6B      STAT=Y  PRED= -14.654 RANGE= 0.100
 J41_50     -1.9039   J H6A    H4A      STAT=Y  PRED= -1.899 RANGE= 0.100
 J42_50     -0.5646   J H6B    H4A      STAT=Y  PRED= -0.049 RANGE= 0.100
 J43_44    -13.3969   J H1A    H1B      STAT=Y  PRED= -13.386 RANGE= 0.100
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 J43_45      -0.6045   J H1A    H19      STAT=Y  PRED= -0.570 RANGE= 0.100
 J43_48       4.4215   J H1A    H2A      STAT=Y  PRED= 4.417 RANGE= 0.100
 J43_49      14.8637   J H1A    H2B      STAT=Y  PRED= 14.859 RANGE= 0.100
 J44_48       3.0490   J H1B    H2A      STAT=Y  PRED= 3.039 RANGE= 0.100
 J44_49       5.2053   J H1B    H2B      STAT=Y  PRED= 5.206 RANGE= 0.100
 J48_49     -17.0409   J H2A    H2B      STAT=Y  PRED= -17.060 RANGE= 3.400
 J48_50       1.0013   J H2A    H4A      STAT=Y  PRED= 0.976 RANGE= 0.100
 JMETH1       1.6457   J MeOH   MET_D1   STAT=Y  PRED= 1.650 RANGE= 0.300
 JMETH1       1.6457   J MeOH   MET_D2   STAT=Y  PRED= 1.650 RANGE= 0.300

CONTROL PARAMETERS:
       Solvent =  none (def. 99% enriched)
         1.000 =  Concentration (vol%, def=1.0%)
    0.00100000 =  Minimum line-intensity
    0.00100000 =  Diagonalization criterium (not in use)
  899.93200102 =  FIELD(1H,MHz), used to transform shifts to ppms
   10.98591033 =  Left frequency (ppm)
   -0.98817477 =  Right frequency (ppm)
        10.000 =  Acquisition time (s, for QMTLS)
         0.302 =  Line-width (for modes D, P & T, 0=use defaults)
   0.050000000 =  Data-point resolution (Hz)
        43.160 =  GAUSSIAN (%, 0=use default from INF)
         0.000 =  Dispersion contribution (%, 0=use default from INF)
    0.00000000 =  Decoupling frequency (for DORES)

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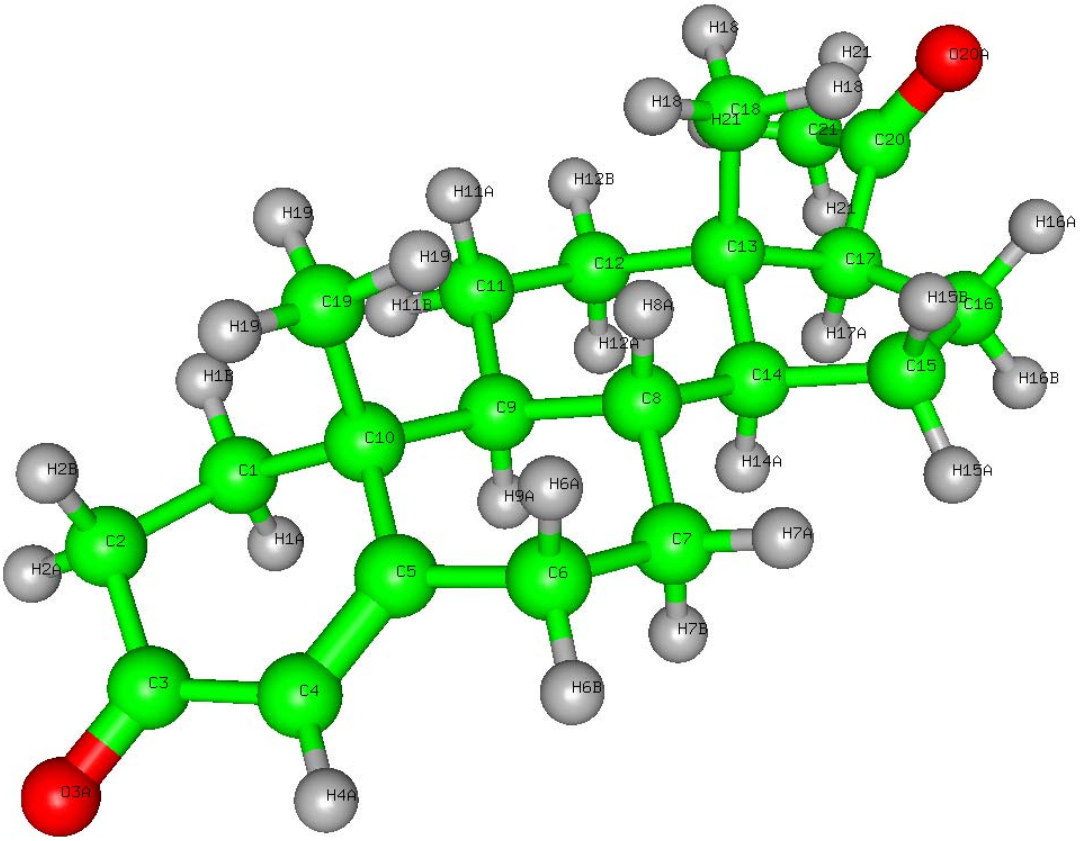
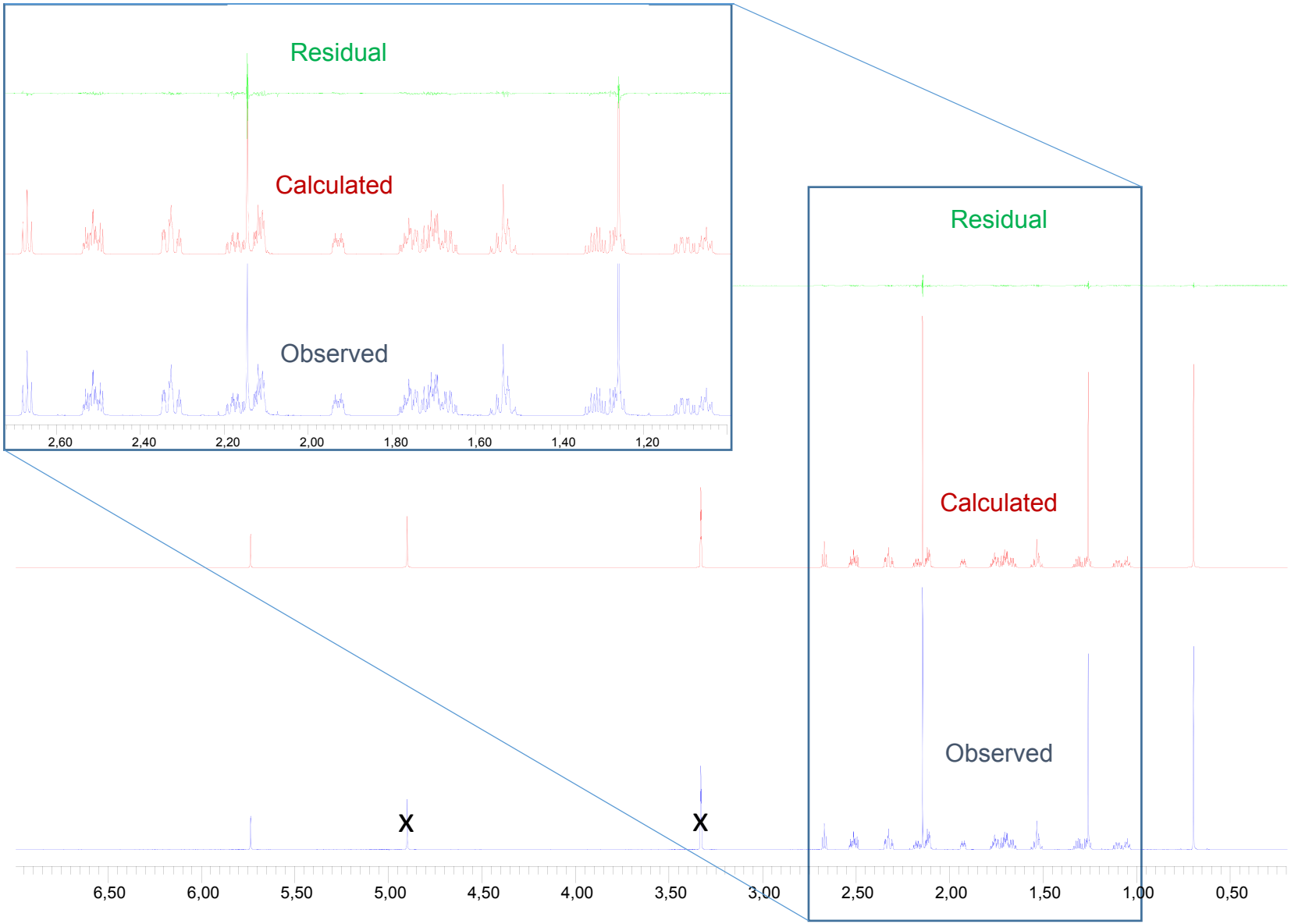


S2c. The ^{1}H NMR Fingerprint of Progesterone (2) in CD_3OD (900 MHz, 298 K)

The X marks on the observed spectrum indicate the solvent signals, CHD_2OD and HOD, which in this case were fitted as well.

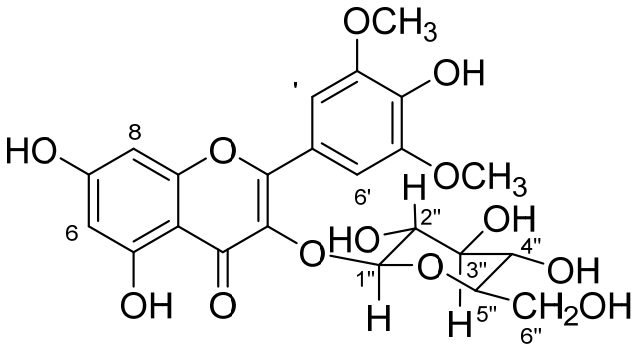


S3: HNMR and HiFSA Data for Compound 3 (Case Study 3)

S3a: HiFSA Profile of Compound 3

In CD_3OD (600 MHz, 298 K)

Proton	δ (ppm)	$\Delta\nu_{1/2}$ (Hz)
H1"	5.4663	0.85
H2"	3.4617	0.99
H3"	3.4473	0.89
H5"	3.2482	1.23
H4"	3.2983	1.66
H6"A	3.5653	1.52
H6"B	3.7467	1.54
H8	6.4193	0.69
H6	6.2088	0.71
H2'_6'	7.5234	0.87
H7'_8'	3.9314	0.92



Coupling			J(Hz)
H1"	/	H2"	7.73
H2"	/	H3"	9.28
H3"	/	H4"	8.80
H5"	/	H4"	9.75
H5"	/	H6"A	5.64
H5"	/	H6"B	2.32
H6"A	/	H6"B	-11.94
H8	/	H6	2.10
H2'_6'	/	H2'_6'	1.82

S3b. Complete HiFSA Profile of Syringetin-3-*O*-β-D-glucoside (3) in CD_3OD (600 MHz, 298 K) using PERCH's parameters (.pms) format

```
* NEW: the lines beginning by * are comment lines !
* To keep all the chemical shifts fixed during iteration
* replace "CHEMICAL SHIFTS(HZ):" by "..SHIFTS(HZ): fixed"
* The couplings can be fixed in the same way

NMR-data: [path]
#$œ  Date  7. 3.2014;  Time 12:46:15     perch.new

CHEMICAL SHIFTS(PPM):
PROTON    2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.02288
 H8    / 1     6.419266  1*1*1  STAT=Y  PRED= 6.419 RANGE= 0.150 WIDTH(Y)= 0.691 RESP(Y)= 1.0000 HSQC= C8
 H6    / 1     6.208833  1*1*1  STAT=Y  PRED= 6.208 RANGE= 0.150 WIDTH(Y)= 0.705 RESP(Y)= 1.0000 HSQC= C6
 H2'_6'/ 1     7.523360  1*2*1  STAT=Y  PRED= 7.577 RANGE= 0.150 WIDTH(Y)= 0.867 RESP(Y)= 1.0000 HSQC= C2_6
 H7'_8'/ 1     3.931432  2*1*3  STAT=Y  PRED= 3.938 RANGE= 0.150 WIDTH(Y)= 0.923 RESP(Y)= 1.0000 HSQC= C7_8
 H1"   / 1     5.466307  1*1*1  STAT=Y  PRED= 5.454 RANGE= 0.150 WIDTH(Y)= 0.851 RESP(Y)= 1.0000 HSQC= C1"
 H2"   / 1     3.461699  1*1*1  STAT=Y  PRED= 3.504 RANGE= 0.150 WIDTH(Y)= 0.988 RESP(Y)= 1.0000 HSQC= C2"
 H3"   / 1     3.447291  1*1*1  STAT=Y  PRED= 3.457 RANGE= 0.150 WIDTH(Y)= 0.893 RESP(Y)= 1.0000 HSQC= C3"
 H5"   / 1     3.248218  1*1*1  STAT=Y  PRED= 3.258 RANGE= 0.150 WIDTH(Y)= 1.229 RESP(Y)= 1.0000 HSQC= C5"
 H4"   / 1     3.298299  1*1*1  STAT=Y  PRED= 3.341 RANGE= 0.150 WIDTH(Y)= 1.663 RESP(Y)= 1.0000 HSQC= C4"
 H6"A  / 1     3.565335  1*1*1  STAT=Y  PRED= 3.715 RANGE= 0.150 WIDTH(Y)= 1.521 RESP(Y)= 1.0000 HSQC= C6"
 H6"B  / 1     3.746671  1*1*1  STAT=Y  PRED= 3.657 RANGE= 0.150 WIDTH(Y)= 1.536 RESP(Y)= 1.0000 HSQC= C6"
MET_H     2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.64187
 MeOH  / 2     3.306004  1*1*1  STAT=Y  PRED= 3.306 RANGE= 0.050 WIDTH(Y)= 0.805 RESP(Y)= 1.0000
MET_D     2*SPIN= 2 SPECIES=2D    POPULATION(Y)=   0.64187
 MET_D1/ 2  -100.000003  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
 MET_D2/ 2  -100.000003  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
MET_OH    2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.27192
 WATER / 3     4.839322  1*1*1  STAT=Y  PRED= 4.839 RANGE= 0.050 WIDTH(Y)= 1.982 RESP(Y)= 1.0000
TMS       2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.06333
 TMS   / 4     0.000143  1*1*1  STAT=Y  PRED= 0.000 RANGE= 0.050 WIDTH(Y)= 0.397 RESP(Y)= 1.0000

COUPLING CONSTANTS(HZ):
 J26_27      2.0990   J H8     H6       STAT=Y  PRED= 2.110 RANGE= 1.790
 J30_31      1.8166   J H2'_6' H2'_6'   STAT=Y  PRED= 1.780 RANGE= 1.790
 J49_50      7.7336   J H1"    H2"      STAT=Y  PRED= 7.310 RANGE= 3.590
 J50_51      9.2783   J H2"    H3"      STAT=Y  PRED= 9.040 RANGE= 3.590
 J51_53      8.7986   J H3"    H4"      STAT=Y  PRED= 9.040 RANGE= 3.590
 J52_53      9.7451   J H5"    H4"      STAT=Y  PRED= 10.500 RANGE= 2.590
 J52_55      5.6420   J H5"    H6"A     STAT=Y  PRED= 5.990 RANGE= 6.400
 J52_56      2.3179   J H5"    H6"B     STAT=Y  PRED= 1.980 RANGE= 3.000
 J55_56    -11.9398   J H6"A   H6"B     STAT=Y  PRED= -12.300 RANGE= 0.600
 JMETH1      1.6450   J MeOH   MET_D1   STAT=Y  PRED= 1.650 RANGE= 0.150
 JMETH1      1.6450   J MeOH   MET_D2   STAT=Y  PRED= 1.650 RANGE= 0.150

CONTROL PARAMETERS:
       Solvent =  none (def. 99% enriched)
         1.000 =  Concentration (vol%, def=1.0%)
    0.00100000 =  Minimum line-intensity
    0.00100000 =  Diagonalization criterium (not in use)
  600.23000000 =  FIELD(1H,MHz), used to transform shifts to ppms
   14.88688909 =  Left frequency (ppm)
   -5.13748487 =  Right frequency (ppm)
         0.000 =  Acquisition time (s, for QMTLS)
         0.371 =  Line-width (for modes D, P & T, 0=use defaults)
   0.183401705 =  Data-point resolution (Hz)
         0.000 =  GAUSSIAN (%, 0=use default from INF)
         0.000 =  Dispersion contribution (%, 0=use default from INF)
    0.00000000 =  Decoupling frequency (for DORES)

END of FILE
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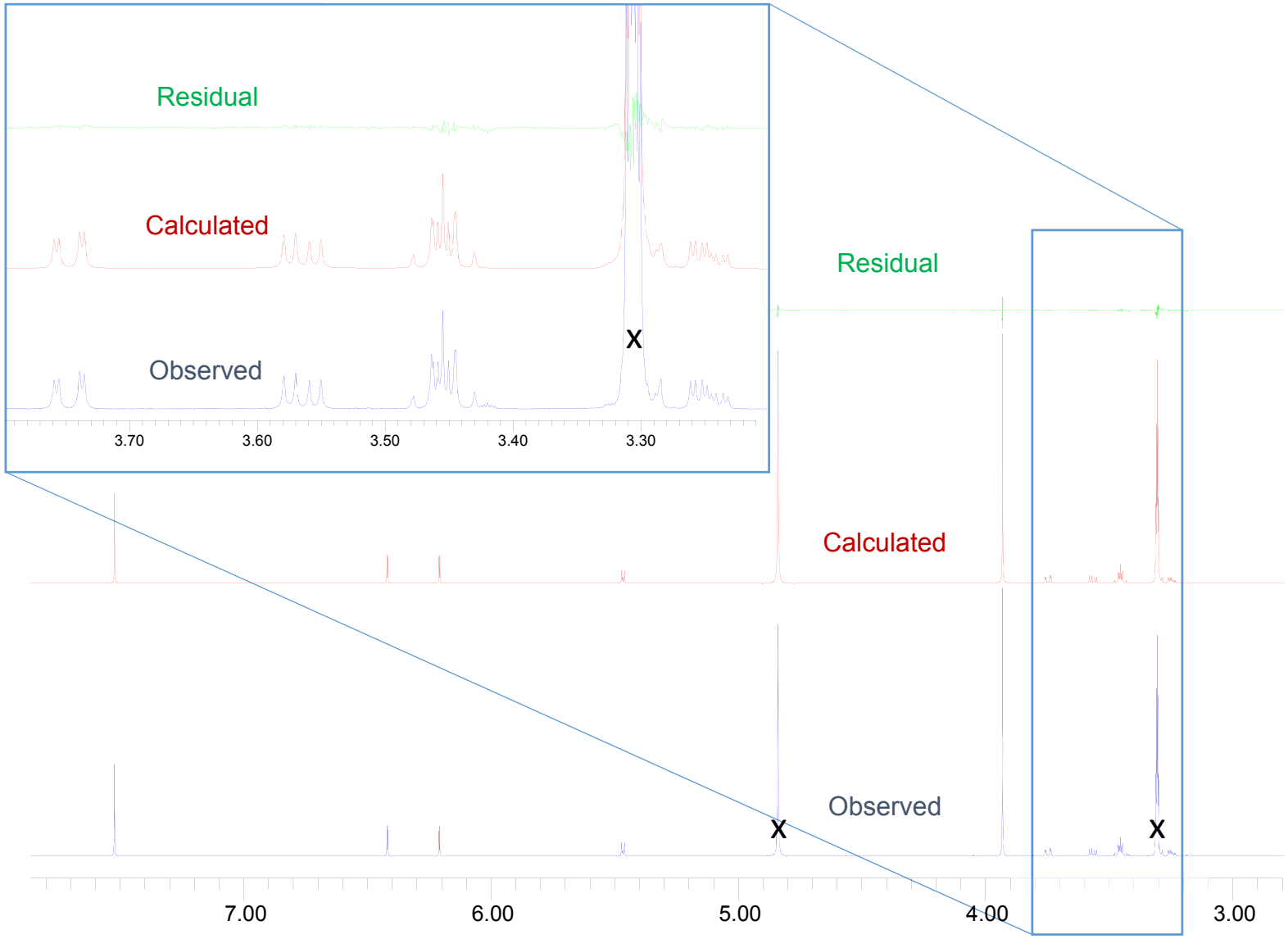
S3c. The ^{1}H NMR Fingerprint of Syringetin-3-*O*-β-D-glucoside (3) in CD_3OD (600 MHz, 298 K)

The X marks on the observed spectrum indicate the solvent signals, CHD_2OD and HOD, which in this case were fitted as well.



S4: HNMR and HiFSA Data for Compound 4 (Case Study 4)

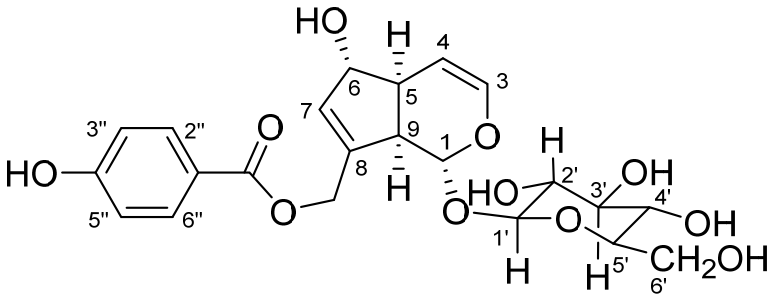
S4a: HiFSA Profile of Agnuside (4)

In CD_3OD (300 MHz, 298 K)

Proton	δ (ppm)	$\Delta\nu_{1/2}$ (Hz)
H1	4.9930	1.01
H1'	4.6958	0.85
H11A	5.0876	1.17
H11B	4.9144	1.23
H2'	3.2422	1.04
H2_6	7.9182	0.73
H3	6.3373	0.98
H3'	3.3760	1.02
H3_5	6.8410	0.74
H4	5.1166	0.87
H4'	3.3178	0.96
H5	2.7012	1.02
H5'	3.2748	1.25
H6	4.4671	1.20
H6'A	3.8465	1.30
H6'B	3.6567	1.40
H7	5.8304	1.05
H9	2.9923	1.18

Coupling	J(Hz)
H1' / H2'	7.91
H2' / H3'	9.28
H3' / H4'	8.85
H3_5 / H3_5	2.25
H4 / H3	6.10
H4' / H5'	9.68
H5 / H6	5.46
H5 / H4	3.90
H5 / H3	-1.99
H5' / H6'A	2.25
H5' / H6'B	5.74
H6 / H7	1.50
H6 / H11A	-2.21
H6 / H11B	-1.71
H6'A / H6'B	-11.97

Coupling	J(Hz)
H7 / H11A	-1.61
H7 / H11B	-1.87
H9 / H5	7.84
H9 / H1	7.34
H9 / H6	-1.93
H9 / H7	-1.23
H9 / H11A	-0.74
H9 / H11B	-0.86
H11A / H11B	-14.75
H2_6 / H2_6	2.58
H2_6 / H3_5	8.61
H3_5 / H2_6	0.35



S4b. Complete HiFSA Profile of Agnuside (4) in CD_3OD (300 MHz, 298 K) using PERCH's parameters (.pms) format

```
* NEW: the lines beginning by * are comment lines !
* To keep all the chemical shifts fixed during iteration
* replace "CHEMICAL SHIFTS(HZ):" by "..SHIFTS(HZ): fixed"
* The couplings can be fixed in the same way

NMR-data: [path]
#$œ  Date  8. 3.2014;  Time 13:30: 6     perch.new

CHEMICAL SHIFTS(PPM):
PROTON    2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.07698
 H9    / 1     2.992252  1*1*1  STAT=Y  WIDTH(Y)= 1.182 RESP(Y)= 1.0000 HSQC= C9
 H5    / 1     2.701207  1*1*1  STAT=Y  WIDTH(Y)= 1.020 RESP(Y)= 1.0000 HSQC= C5
 H1    / 1     4.992977  1*1*1  STAT=Y  WIDTH(Y)= 1.006 RESP(Y)= 1.0000 HSQC= C1
 H6    / 1     4.467097  1*1*1  STAT=Y  WIDTH(Y)= 1.198 RESP(Y)= 1.0000 HSQC= C6
 H7    / 1     5.830424  1*1*1  STAT=Y  WIDTH(Y)= 1.045 RESP(Y)= 1.0000 HSQC= C7
 H1'   / 1     4.695760  1*1*1  STAT=Y  WIDTH(Y)= 0.849 RESP(Y)= 1.0000 HSQC= C1'
 H2'   / 1     3.242201  1*1*1  STAT=Y  WIDTH(Y)= 1.036 RESP(Y)= 1.0000 HSQC= C2'
 H4    / 1     5.116609  1*1*1  STAT=Y  WIDTH(Y)= 0.868 RESP(Y)= 1.0000 HSQC= C4
 H3'   / 1     3.376035  1*1*1  STAT=Y  WIDTH(Y)= 1.018 RESP(Y)= 1.0000 HSQC= C3'
 H4'   / 1     3.317849  1*1*1  STAT=Y  WIDTH(Y)= 0.955 RESP(Y)= 1.0000 HSQC= C4'
 H5'   / 1     3.274789  1*1*1  STAT=Y  WIDTH(Y)= 1.248 RESP(Y)= 1.0000 HSQC= C5'
 H11A  / 1     5.087647  1*1*1  STAT=Y  WIDTH(Y)= 1.167 RESP(Y)= 1.0000 HSQC= C11
 H11B  / 1     4.914419  1*1*1  STAT=Y  WIDTH(Y)= 1.231 RESP(Y)= 1.0000 HSQC= C11
 H3    / 1     6.337333  1*1*1  STAT=Y  WIDTH(Y)= 0.979 RESP(Y)= 1.0000 HSQC= C3
 H6'A  / 1     3.846523  1*1*1  STAT=Y  WIDTH(Y)= 1.295 RESP(Y)= 1.0000 HSQC= C6'
 H6'B  / 1     3.656731  1*1*1  STAT=Y  WIDTH(Y)= 1.399 RESP(Y)= 1.0000 HSQC= C6'
 H2_6  / 1     7.918190  1*2*1  STAT=Y  WIDTH(Y)= 0.734 RESP(Y)= 1.0000 HSQC= C2_6
 H3_5  / 1     6.841045  1*2*1  STAT=Y  WIDTH(Y)= 0.735 RESP(Y)= 1.0000 HSQC= C3_5
MET_H     2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.07520
 MeOH  / 2     3.308142  1*1*1  STAT=Y  PRED= 3.306 RANGE= 0.050 WIDTH(Y)= 0.898 RESP(Y)= 1.0000
MET_D     2*SPIN= 2 SPECIES=2D    POPULATION(Y)=   0.07520
 MET_D1/ 2   -99.999990  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
 MET_D2/ 2   -99.999990  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
TMS       2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.01287
 TMS   / 3    -0.000333  1*1*1  STAT=Y  PRED= -0.010 RANGE= 0.050 WIDTH(Y)= 0.486 RESP(Y)= 1.0000
D2O       2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.83495
 D2O   / 4     4.745296  1*1*1  STAT=Y  PRED= 4.780 RANGE= 0.050 WIDTH(Y)= 2.208 RESP(Y)= 1.0000

COUPLING CONSTANTS(HZ):
 J34_35      7.8354   J H9     H5       STAT=Y  PRED= 7.835 RANGE= 0.001
 J34_36      7.3381   J H9     H1       STAT=Y  PRED= 7.338 RANGE= 0.001
 J34_37     -1.9273   J H9     H6       STAT=Y  PRED= -1.937 RANGE= 0.001
 J34_38     -1.2314   J H9     H7       STAT=Y  PRED= -1.236 RANGE= 0.001
 J34_45     -0.7417   J H9     H11A     STAT=Y  PRED= -0.746 RANGE= 0.001
 J34_46     -0.8637   J H9     H11B     STAT=Y  PRED= -0.866 RANGE= 0.001
 J35_37      5.4602   J H5     H6       STAT=Y  PRED= 5.460 RANGE= 0.001
 J35_41      3.9005   J H5     H4       STAT=Y  PRED= 3.901 RANGE= 0.001
 J35_47     -1.9899   J H5     H3       STAT=Y  PRED= -1.990 RANGE= 0.001
 J37_38      1.4969   J H6     H7       STAT=Y  PRED= 1.481 RANGE= 0.001
 J37_45     -2.2051   J H6     H11A     STAT=Y  PRED= -2.215 RANGE= 0.001
 J37_46     -1.7083   J H6     H11B     STAT=Y  PRED= -1.702 RANGE= 0.001
 J38_45     -1.6078   J H7     H11A     STAT=Y  PRED= -1.603 RANGE= 0.001
 J38_46     -1.8711   J H7     H11B     STAT=Y  PRED= -1.880 RANGE= 0.001
 J39_40      7.9095   J H1'    H2'      STAT=Y  PRED= 7.909 RANGE= 0.001
 J40_42      9.2763   J H2'    H3'      STAT=Y  PRED= 9.276 RANGE= 0.001
 J41_47      6.0985   J H4     H3       STAT=Y  PRED= 6.098 RANGE= 0.001
 J42_43      8.8534   J H3'    H4'      STAT=Y  PRED= 8.852 RANGE= 0.001
 J43_44      9.6820   J H4'    H5'      STAT=Y  PRED= 9.682 RANGE= 0.001
 J44_49      2.2547   J H5'    H6'A     STAT=Y  PRED= 2.254 RANGE= 0.001
 J44_50      5.7399   J H5'    H6'B     STAT=Y  PRED= 5.740 RANGE= 0.001
 J45_46    -14.7461   J H11A   H11B     STAT=Y  PRED= -14.746 RANGE= 0.001
 J49_50    -11.9672   J H6'A   H6'B     STAT=Y  PRED= -11.967 RANGE= 0.001
 J55_56      2.5785   J H2_6   H2_6     STAT=Y  PRED= 2.572 RANGE= 0.001
 J55_57      8.6090   J H2_6   H3_5     STAT=Y  PRED= 8.603 RANGE= 0.001
 J55_58      0.3474   J H3_5   H2_6     STAT=Y  PRED= 0.361 RANGE= 0.001
 J57_58      2.2481   J H3_5   H3_5     STAT=Y  PRED= 2.247 RANGE= 0.001
 JMETH1      1.6500   J MeOH   MET_D1   STAT=Y  PRED= 1.650 RANGE= 0.150
 JMETH1      1.6500   J MeOH   MET_D2   STAT=Y  PRED= 1.650 RANGE= 0.150

CONTROL PARAMETERS:
       Solvent =  none (def. 99% enriched)
         1.000 =  Concentration (vol%, def=1.0%)
    0.00100000 =  Minimum line-intensity
    0.00100000 =  Diagonalization criterium (not in use)
  300.13460000 =  FIELD(1H,MHz), used to transform shifts to ppms
   12.12926954 =  Left frequency (ppm)
```

```
   -0.88577735 =  Right frequency (ppm)
         0.000 =  Acquisition time (s, for QMTLS)
         0.484 =  Line-width (for modes D, P & T, 0=use defaults)
   0.119213397 =  Data-point resolution (Hz)
        25.974 =  GAUSSIAN (%, 0=use default from INF)
         0.000 =  Dispersion contribution (%, 0=use default from INF)
    0.00000000 =  Decoupling frequency (for DORES)

CONSTRAINTS (in equations X0 = 1.0)...use no empty lines
 EQUAL MET_D1   = MET_D2

END of FILE
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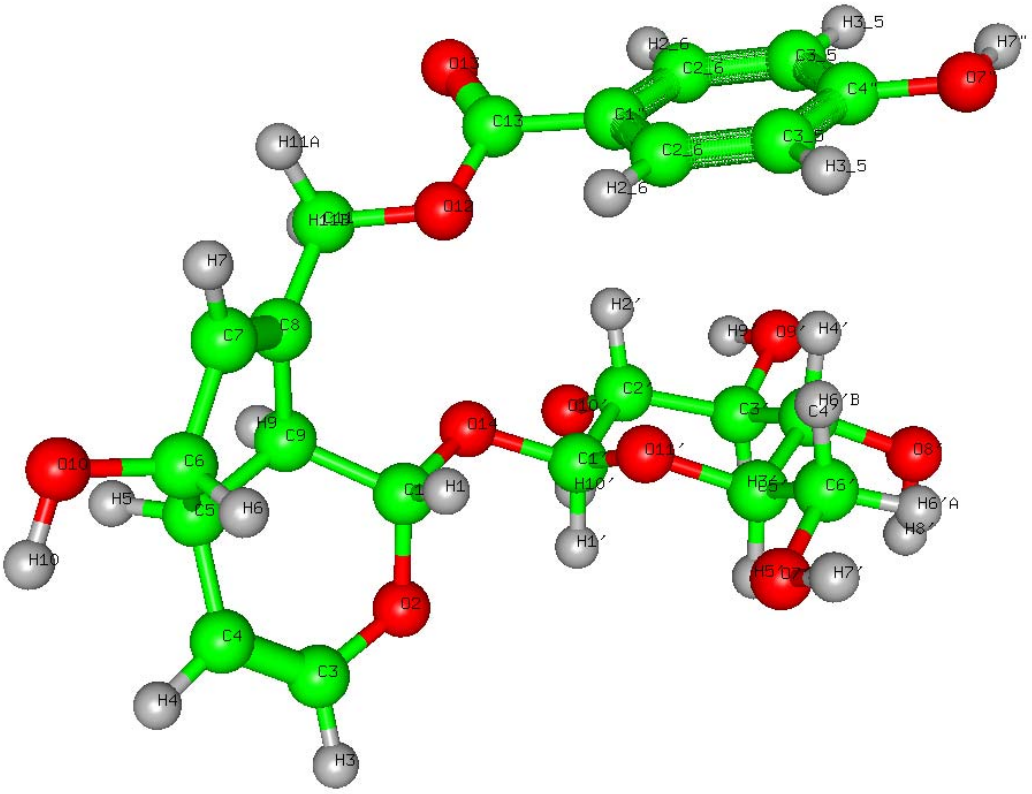
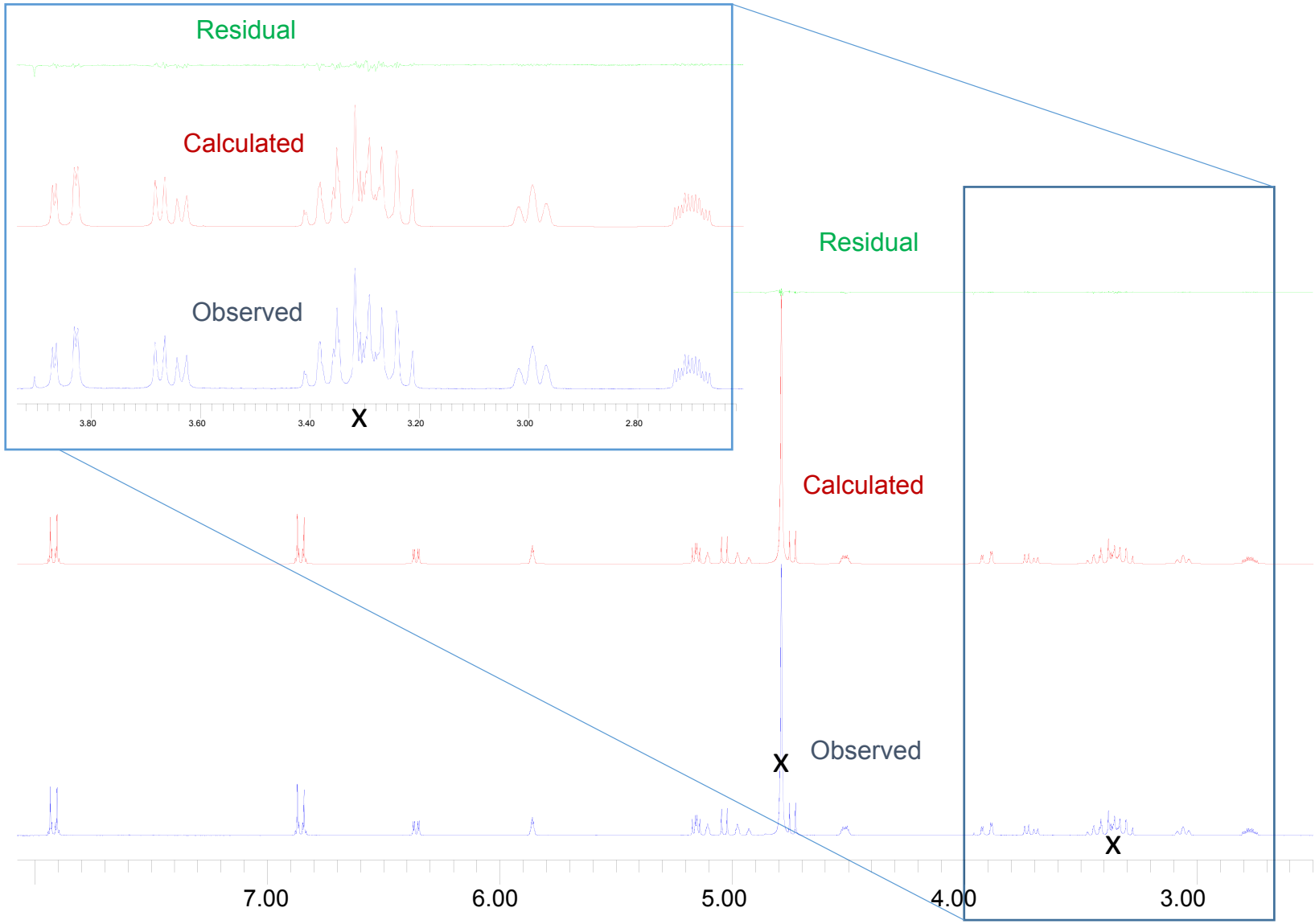


S4c. The ^{1}H NMR Fingerprint of Agnuside (4) in CD_3OD (300 MHz, 298 K)

The X marks on the observed spectrum indicate the solvent signals, CHD_2OD and HOD, which in this case were fitted as well.



S5: Supporting Tables for Case Study 4 (Agnuside, Compound 4)

NMR-parameters derived from different starting values by iterative spectral analysis. All *J*-couplings and chemical shifts were changed randomly and subsequently optimized using iterative full spin analysis. Subsequent D/T-Mode, Linear baseline, Threshold 0.001, Gaussian-contribution 50% (fixed), Dispersion Contribution 0% (fixed)

Starting Values

Starting Values					
δ(A/A')	δ(X/X')	*J*(X,X')	*J*(A /X)	*J*(A,X')	*J*(A ,A')
7.9182	**6.8411**	**2.6329**	**8.6055**	**0.3121**	**2.1721**
7.9182	6.8411	4.0000	8.0000	2.0000	3.0000
8.0182	6.7411	4.0000	8.0000	2.0000	3.0000
7.8182	6.9411	4.0000	8.0000	2.0000	3.0000
7.8182	6.9411	6.0000	10.0000	3.0000	5.0000
7.9182	6.8411	2.0000	5.0000	0.1000	1.0000
7.9182	6.8411	8.0000	12.0000	4.0000	6.0000
7.9182	6.8411	8.0000	12.0000	0.1000	1.0000
7.9182	6.8411	2.0000	3.0000	1.0000	1.5000

Optimized by HiFSA, Fitted Spectral Parameters

	FIT						
	δ(A/A')	δ(X/X')	*J*(X,X')	*J*(A /X)	*J*(A,X')	*J*(A ,A')	RMS
	7.918255	**6.841127**	**2.6354**	**8.6030**	**0.3144**	**2.1687**	**0.06550**
	7.918257	6.841126	2.6321	8.6037	0.3155	2.1690	0.06540
	7.918255	6.841127	2.6365	8.6012	0.3167	2.1633	0.06510
	7.918255	6.841127	2.6365	8.6012	0.3167	2.1633	0.06510
	7.918255	6.841127	2.6349	8.6034	0.3139	2.1698	0.06560
	7.918255	6.841126	2.6348	8.6031	0.3144	2.1684	0.06510
	7.918256	6.841125	2.6341	8.6016	0.3167	2.1674	0.06500
	7.918256	6.841127	2.6349	8.6032	0.3139	2.1695	0.06560
	7.918256	6.841125	2.6352	8.6017	0.3163	2.1667	0.06500
Average	**7.918256**	**6.841126**	**2.6349**	**8.6025**	**0.3154**	**2.1673**	**0.06527**
STDEVP	**0.000001**	**0.000001**	**0.0012**	**0.0009**	**0.0011**	**0.0022**	**0.00023**

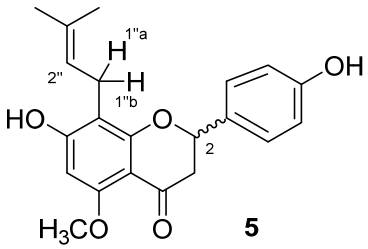
S6: HNMR and HiFSA Data for Compound 5 (Case Study 5)

S6a: HiFSA Profile of Isoxanthohumol (5)

In CD_3OD (500 MHz, 298 K)

Proton	δ (ppm)	$\Delta\nu_{½}$ (Hz)
H2	5.2762	1.48
H3A	2.6598	0.89
H3B	2.9699	0.88
H6	6.1127	0.99
H11	3.7924	0.96
H2'_6'	7.3057	1.04
H3'_5'	6.8093	0.77
H1"A	3.1935	1.55
H1"B	3.2177	1.55
H2"	5.1338	0.92
H4"	1.6147	0.79
H5"	1.5572	1.23

Coupling			J(Hz)
H2	/	H3A	3.00
H2	/	H3B	12.83
H3A	/	H3B	-16.65
H1"A	/	H1"B	-14.08
H1"A	/	H2"	7.37
H1"A	/	H4"	1.17
H1"B	/	H2"	7.14
H1"B	/	H4"	1.21
H2'_6	/	H2'_6	2.39
H2'_6	/	H3'_5	8.44
H3'_5	/	H2'_6	0.34
H2"	/	H4"	-1.29
H2"	/	H5"	-1.39
H3'_5	/	H3'_5	2.68
H4"	/	H5"	-0.41



5

S6b. Complete HiFSA Profile of Isoxanthohumol (5) in CD_3OD (500 MHz, 298 K) using PERCH's Parameters (.pms) Format

```
* NEW: the lines beginning by * are comment lines !
* NEW: the lines beginning by * are comment lines !
* To keep all the chemical shifts fixed during iteration
* replace "CHEMICAL SHIFTS(HZ):" by "..SHIFTS(HZ): fixed"
* The couplings can be fixed in the same way

NMR-data: [path]
#$œ  Date  8. 3.2014;  Time 19:11:48     perch.new

CHEMICAL SHIFTS(PPM):
PROTON    2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   1.00000
 H2    / 1     5.276216  1*1*1  STAT=Y  PRED= 5.358 RANGE= 0.150 WIDTH(Y)= 1.475 RESP(Y)= 0.9264 HSQC= C2
 H3A   / 1     2.659803  1*1*1  STAT=Y  PRED= 2.742 RANGE= 0.150 WIDTH(Y)= 0.890 RESP(Y)= 0.9433 HSQC= C3
 H3B   / 1     2.969928  1*1*1  STAT=Y  PRED= 3.057 RANGE= 0.216 WIDTH(Y)= 0.877 RESP(Y)= 0.9199 HSQC= C3
 H1"A  / 1     3.193542  1*1*1  STAT=Y  PRED= 3.319 RANGE= 0.150 WIDTH(Y)= 1.545 RESP(Y)= 0.9578 HSQC= C1"
 H1"B  / 1     3.217683  1*1*1  STAT=Y  PRED= 3.327 RANGE= 0.150 WIDTH(Y)= 1.550 RESP(Y)= 1.0000 HSQC= C1"
 H6    / 1     6.112698  1*1*1  STAT=Y  PRED= 6.151 RANGE= 0.420 WIDTH(Y)= 0.988 RESP(Y)= 0.9490 HSQC= C6
 H2'_6'/ 1     7.305739  1*2*1  STAT=Y  PRED= 7.328 RANGE= 0.150 WIDTH(Y)= 1.043 RESP(Y)= 0.9759 HSQC= C2_6
 H2"   / 1     5.133838  1*1*1  STAT=Y  PRED= 5.200 RANGE= 0.532 WIDTH(Y)= 0.924 RESP(Y)= 0.9387 HSQC= C2"
 H3'_5'/ 1     6.809348  1*2*1  STAT=Y  PRED= 6.812 RANGE= 0.150 WIDTH(Y)= 0.773 RESP(Y)= 0.9622 HSQC= C3_5
 H11   / 1     3.792368  1*1*3  STAT=Y  PRED= 3.877 RANGE= 0.150 WIDTH(Y)= 0.964 RESP(Y)= 0.9214 HSQC= C11
 H4"   / 1     1.614732  1*1*3  STAT=Y  PRED= 1.746 RANGE= 0.150 WIDTH(Y)= 0.791 RESP(Y)= 0.9219 HSQC= C4"
 H5"   / 1     1.557159  1*1*3  STAT=Y  PRED= 1.658 RANGE= 0.258 WIDTH(Y)= 1.233 RESP(Y)= 0.9252 HSQC= C5"

COUPLING CONSTANTS(HZ):
 J27_28      2.9999   J H2     H3A      STAT=Y  PRED= 2.360 RANGE= 4.400
 J27_29     12.8341   J H2     H3B      STAT=Y  PRED= 11.950 RANGE= 4.000
 J28_29    -16.6478   J H3A    H3B      STAT=Y  PRED= -17.040 RANGE= 3.400
 J30_31    -14.0829   J H1"A   H1"B     STAT=Y  PRED= -18.500 RANGE= 3.400
 J30_35      7.3661   J H1"A   H2"      STAT=Y  PRED= 6.050 RANGE= 4.000
 J30_42      1.1717   J H1"A   H4"      STAT=Y  PRED= 0.650 RANGE= 0.850
 J31_35      7.1420   J H1"B   H2"      STAT=Y  PRED= 9.570 RANGE= 4.000
 J31_42      1.2065   J H1"B   H4"      STAT=Y  PRED= 0.650 RANGE= 0.850
 J33_34      2.3904   J H2'_6' H2'_6'   STAT=Y  PRED= 2.330 RANGE= 1.400
 J33_36      8.4385   J H2'_6' H3'_5'   STAT=Y  PRED= 8.410 RANGE= 0.850
 J33_37      0.3367   J H3'_5' H2'_6'   STAT=Y  PRED= 0.430 RANGE= 0.640
 J35_42     -1.2940   J H2"    H4"      STAT=Y  PRED= -1.650 RANGE= 1.000
 J35_45     -1.3937   J H2"    H5"      STAT=Y  PRED= -1.450 RANGE= 1.290
 J36_37      2.6750   J H3'_5' H3'_5'   STAT=Y  PRED= 2.830 RANGE= 1.400
 J42_45     -0.4121   J H4"    H5"      STAT=Y  PRED= -0.800 RANGE= 1.000

CONTROL PARAMETERS:
       Solvent =  none (def. 99% enriched)
         1.000 =  Concentration (vol%, def=1.0%)
    0.00100000 =  Minimum line-intensity
    0.00100000 =  Diagonalization criterium (not in use)
  500.16300000 =  FIELD(1H,MHz), used to transform shifts to ppms
    7.99982965 =  Left frequency (ppm)
    0.00000000 =  Right frequency (ppm)
         0.000 =  Acquisition time (s, for QMTLS)
         0.756 =  Line-width (for modes D, P & T, 0=use defaults)
   0.123454765 =  Data-point resolution (Hz)
        92.623 =  GAUSSIAN (%, 0=use default from INF)
         0.000 =  Dispersion contribution (%, 0=use default from INF)
    0.00000000 =  Decoupling frequency (for DORES)

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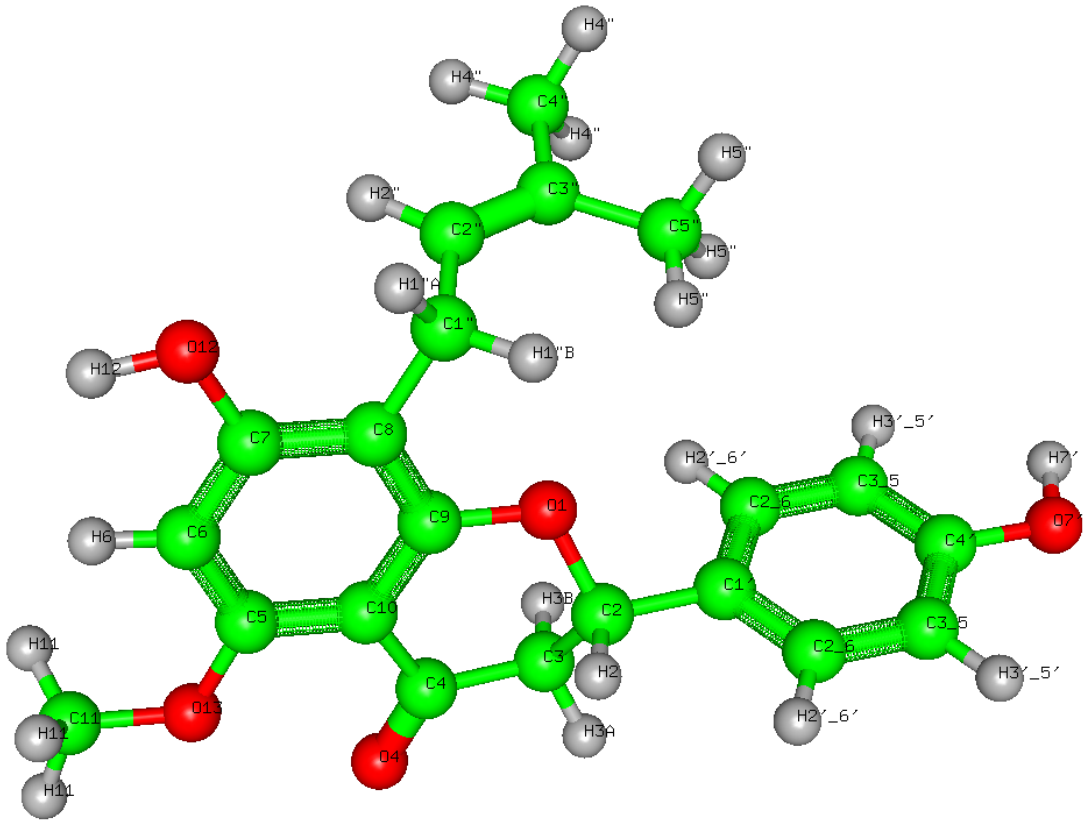
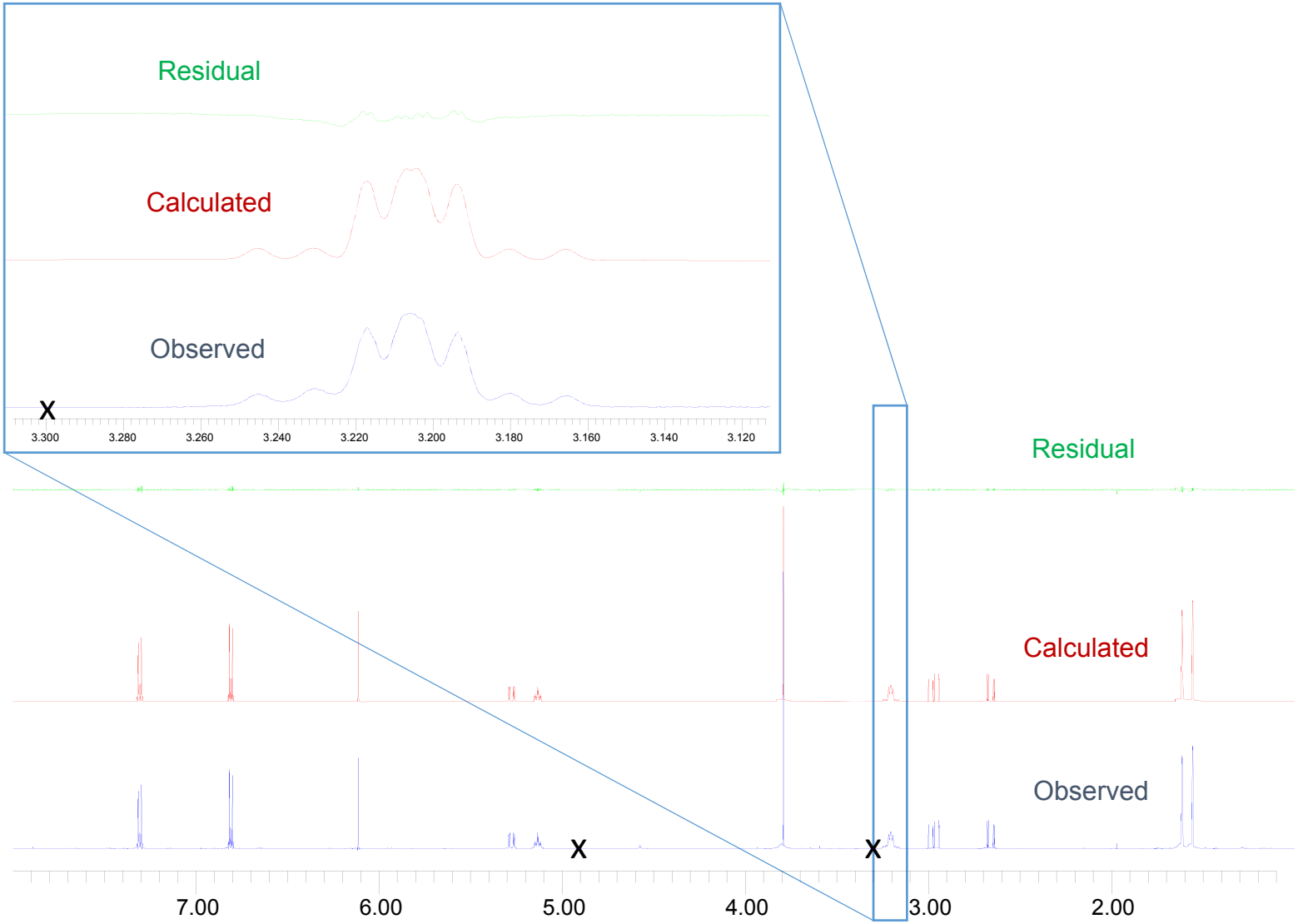

H4"
H4"
C4"
H4"
H5"
C3"
H2"
C2"
C5"
H5"
H5"
H1"A
C1"
H1"B
O12
H12
C7
C8
H3'_5'
H2'_6'
C3_5
H7'
C2_6
C9
O1
O7'
H6
C6
C4'
C1
H3B
C10
C2
C3_5
C5
H11
C3
H2
C2_6
H3'_5'
C4
O13
C11
H2'_6'
H11
H3A
O4
H11

S6c. The ^{1}H NMR Fingerprint of Isoxanthohumol (5) in CD_3OD (500 MHz, 298 K)

The X marks on the observed spectrum indicate that solvent signals, CHD_2OD and HOD, were removed artificially in order to allow the residual to be scaled such that it reflects the differences arising from the compound and non-solvent impurities of the sample, rather than the relatively large solvent signals.



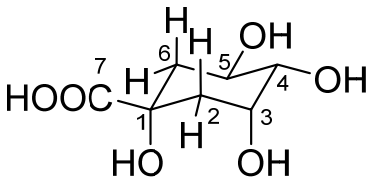
S7: HNMR and HiFSA Data for Compound 6 (Case Study 6)

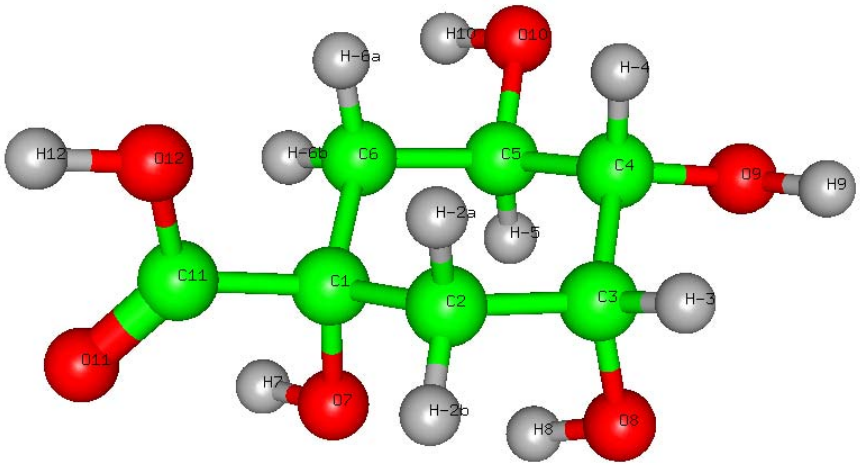
S7a: HiFSA Profile of Quinic Acid (6)

In CD_3OD (360 MHz, 298 K)

Proton	δ (ppm)	$\Delta\nu_{1/2}$ (Hz)
H-2a	2.0457	1.90
H-2b	2.0298	1.13
H-3	4.0830	1.34
H-4	3.3829	1.13
H-5	3.9896	1.21
H-6a	1.8464	1.31
H-6b	2.1190	1.73

Coupling	J(Hz)
H-2a / H-3	3.07
H-2b / H-2a	-14.51
H-2b / H-3	4.04
H-3 / H-4	3.17
H-5 / H-4	9.07
H-6a / H-6b	-13.28
H-6a / H-5	10.91
H-6b / H-2b	2.83
H-6b / H-5	4.69





S7b. Complete HiFSA Profile of Quinic Acid (6) in CD_3OD (360 MHz, 298 K) using PERCH's Parameters (.pms) Format

```
* NEW: the lines beginning by * are comment lines !
* To keep all the chemical shifts fixed during iteration
* replace "CHEMICAL SHIFTS(HZ)" by "..SHIFTS(HZ,fix)"
* The couplings can be fixed in the same way

NMR-data: [path]
#$œ  Date 00.00.0000;  Time 00:00:00  filename
CHEMICAL SHIFTS(PPM): FIT-INDEX= 100.000
PROTON 2*SPIN=1 SPECIES=1H    POPULATION= 1.0000
H-6a/1      1.846350  1*1*1  STAT=Y  PRED= 1.894 RANGE= 0.318 WIDTH= 1.311 RESP= 1.0000 HSQC=C6
H-6b/1      2.118980  1*1*1  STAT=Y  PRED= 2.047 RANGE= 0.332 WIDTH= 1.730 RESP= 1.0000 HSQC=C6
H-2b/1      2.029790  1*1*1  STAT=Y  PRED= 1.979 RANGE= 0.307 WIDTH= 1.127 RESP= 1.0000 HSQC=C2
H-2a/1      2.045740  1*1*1  STAT=Y  PRED= 2.076 RANGE= 0.232 WIDTH= 1.902 RESP= 1.0000 HSQC=C2
H-5 /1      3.989590  1*1*1  STAT=Y  PRED= 3.900 RANGE= 0.501 WIDTH= 1.205 RESP= 1.0000 HSQC=C5
H-3 /1      4.083040  1*1*1  STAT=Y  PRED= 4.076 RANGE= 0.235 WIDTH= 1.339 RESP= 1.0000 HSQC=C3
H-4 /1      3.382940  1*1*1  STAT=Y  PRED= 3.526 RANGE= 0.298 WIDTH= 1.133 RESP= 1.0000 HSQC=C4

COUPLING CONSTANTS(HZ):
J14_15   -13.2822  J  H-6a H-6b  STAT=Y  PRED= -12.530 RANGE= 1.500
J14_18    10.9067  J  H-6a H-5   STAT=Y  PRED=  10.880 RANGE= 2.600
J15_16     2.8301  J  H-6b H-2b  STAT=Y  PRED=  2.670 RANGE= 1.300
J15_18     4.6930  J  H-6b H-5   STAT=Y  PRED=  4.680 RANGE= 3.800
J16_17   -14.5071  J  H-2b H-2a  STAT=Y  PRED= -12.630 RANGE= 1.500
J16_19     4.0377  J  H-2b H-3   STAT=Y  PRED=  2.800 RANGE= 2.800
J17_19     3.0704  J  H-2a H-3   STAT=Y  PRED=  3.030 RANGE= 3.800
J18_20     9.0735  J  H-5  H-4   STAT=Y  PRED=  9.330 RANGE= 3.600
J19_20     3.1721  J  H-3  H-4   STAT=Y  PRED=  3.320 RANGE= 3.800

CONTROL PARAMETERS:
       SOLVENT = None
     REFERENCE = TMS
    0.00000000 = CONCENTRATION (vol%)
       298.000 = TEMPERATURE (vol%, def=1.0%)
  360.13490000 = FIELD(1H,MHz), used to transform shifts to ppms
    0.00100000 = Minimum line-intensity
    0.00100000 = Diagonalization criterium (not used)
    0.00000000 = Left frequency limit(ppm)
    0.00000000 = Right frequency limit(ppm)
         1.127 = Default line-width(Hz)
  0.0000000000 = Data-point resolution(Hz)
         0.000 = Gaussian contribution%
         0.000 = Dispersion contribution%
    0.00000000 = Decoupling frequency (for DORES only)

CONSTRAINTS (in equations X0 = 1.0)...use no empty lines:

CARBON/DEC  2*SPIN=1  SPECIES=13C  POPULATION= 1.0000 OBSERVED equal to PREDICTED
C1  /1   not observed  1*1*1 STAT=DS PRED= 78.190 RANGE= 2.789 WIDTH= 0.500 RESP= 1.0000
C6  /1   not observed  1*1*1 STAT=DS PRED= 41.450 RANGE= 1.753 WIDTH= 0.500 RESP= 1.0000
C2  /1   not observed  1*1*1 STAT=DS PRED= 40.030 RANGE= 2.928 WIDTH= 0.500 RESP= 1.0000
C5  /1   not observed  1*1*1 STAT=DS PRED= 71.380 RANGE= 6.052 WIDTH= 0.500 RESP= 1.0000
C3  /1   not observed  1*1*1 STAT=DS PRED= 72.010 RANGE= 1.893 WIDTH= 0.500 RESP= 1.0000
C4  /1   not observed  1*1*1 STAT=DS PRED= 77.680 RANGE= 9.375 WIDTH= 0.500 RESP= 1.0000
C11 /1   not observed  1*1*1 STAT=DS PRED= 178.960 RANGE= 4.835 WIDTH= 0.500 RESP= 1.0000

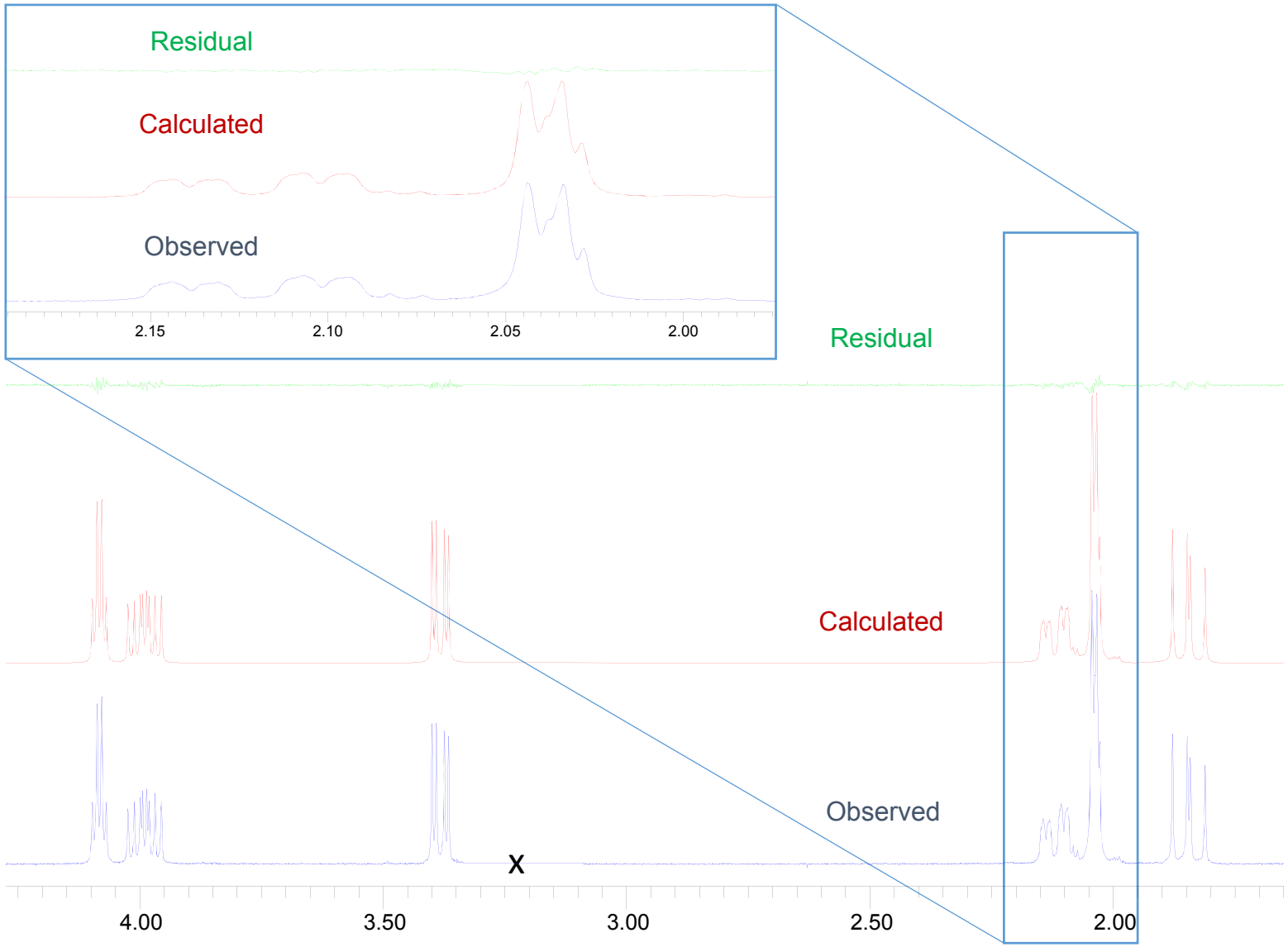
NOE CORRELATIONS():

SCALAR CORRELATIONS():
COSY  1        105.16  H-6a H-6b  STAT=N PRED=   99.21 RANGE= 11.88
COSY  2         86.36  H-6a H-5   STAT=N PRED=   86.14 RANGE= 20.59
COSY  3         22.41  H-6b H-2b  STAT=N PRED=   21.14 RANGE= 10.29
COSY  4         37.16  H-6b H-5   STAT=N PRED=   37.05 RANGE= 30.09
COSY  5        114.86  H-2b H-2a  STAT=N PRED=  100.00 RANGE= 11.88
COSY  6         31.97  H-2b H-3   STAT=N PRED=   22.17 RANGE= 22.17
COSY  7         24.31  H-2a H-3   STAT=N PRED=   23.99 RANGE= 30.09
COSY  8         71.84  H-5  H-4   STAT=N PRED=   73.87 RANGE= 28.50
COSY  9         25.12  H-3  H-4   STAT=N PRED=   26.29 RANGE= 30.09

END of FILE
```

S7c. The ^{1}H NMR Fingerprint of Quinic Acid (6) in CD_3OD (360 MHz, 298 K)

The X mark on the observed spectrum indicate that solvent signal, CHD_2OD, was removed artificially in order to allow the residual to be scaled such that it reflects the differences arising from the compound and non-solvent impurities of the sample, rather than the relatively large solvent signals.



S8: HNMR and HiFSA Data for Compound 7 (Case Study 7)

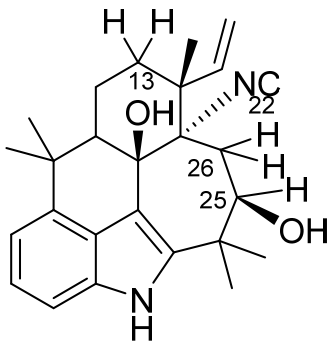
S8a. HiFSA Profile of Ambiguine N Isonitrile (7)

In CD_3OD (900 MHz, 298 K)

Proton	δ (ppm)	$\Delta\nu_{½}$ (Hz)
H5	6.953	1.08
H6	7.030	1.07
H7A	7.091	1.05
H13A	1.520	1.76
H13B	1.991	2.66
H14A	2.143	1.89
H14B	1.811	1.86
H15	2.273	1.58
H17	1.476	1.66
H18	1.452	2.42
H19	1.581	1.74
H20	6.183	0.83
H21A	5.218	1.24
H21B	5.213	1.28
H25	3.948	1.39
H26A	2.980	2.68
H26B	1.967	2.30
H27	1.265	2.51
H28	1.264	1.92

Coupling	*J* (Hz)
H5 / H6	7.28
H5 / H7A	0.67
H6 / H7A	7.94
H13A / H13B	13.53
H13A / H14A	3.17
H13A / H14B	3.47
H13B / H14A	13.91
H13B / H14B	3.49
H14A / H14B	13.11
H14A / H15	12.58

Coupling	*J* (Hz)
H14B / H15	2.36
H19 / H20	0.51
H20 / H21A	10.70
H20 / H21B	17.59
H21A / H21B	1.52
H25 / H26A	10.97
H25 / H26B	1.82
H26A / H26B	14.13
H26A / N	3.37
H26B / N	1.67



7

S8b. Complete HiFSA Profile of Ambiguine N Isonitrile (7) in CD_3OD (900 MHz, 298 K) using PERCH's Parameters (.pms) Format

```
NMR-data: [path]
#$œ  Date 21. 2.2014;  Time 23:38: 6     perch.pms

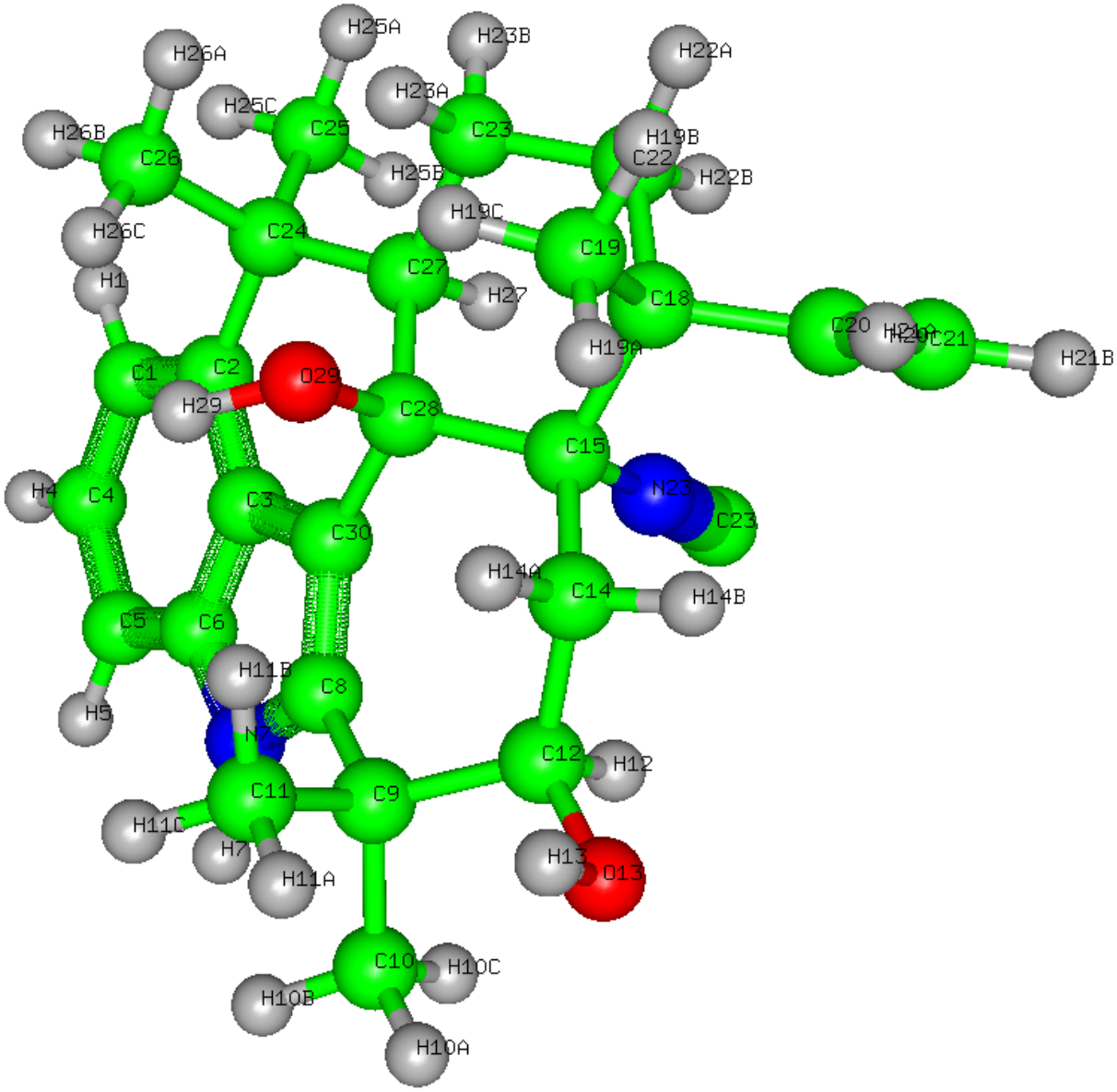
CHEMICAL SHIFTS(PPM):
PROTON    2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.72608
 H5    / 1     6.953274  1*1*1  STAT=Y  PRED= 7.015 RANGE= 0.170 WIDTH(Y)= 1.087 RESP(Y)= 1.0000 HSQC= C5
 H6    / 1     7.029999  1*1*1  STAT=Y  PRED= 6.979 RANGE= 0.170 WIDTH(Y)= 1.066 RESP(Y)= 1.0000 HSQC= C6
 H7A   / 1     7.090594  1*1*1  STAT=Y  PRED= 7.178 RANGE= 0.350 WIDTH(Y)= 1.046 RESP(Y)= 1.0000 HSQC= C7
 H27   / 1     1.265065  1*1*3  STAT=Y  PRED= 1.359 RANGE= 0.366 WIDTH(Y)= 2.508 RESP(Y)= 1.0000 HSQC= C27
 H28   / 1     1.263563  1*1*3  STAT=Y  PRED= 1.273 RANGE= 0.330 WIDTH(Y)= 1.916 RESP(Y)= 1.0000 HSQC= C28
 H25   / 1     3.948152  1*1*1  STAT=Y  PRED= 3.609 RANGE= 0.457 WIDTH(Y)= 1.390 RESP(Y)= 1.0000 HSQC= C25
 H26A  / 1     2.979615  1*1*1  STAT=Y  PRED= 2.014 RANGE= 0.510 WIDTH(Y)= 2.678 RESP(Y)= 1.0000 HSQC= C26
 H26B  / 1     1.966973  1*1*1  STAT=Y  PRED= 1.988 RANGE= 0.458 WIDTH(Y)= 2.300 RESP(Y)= 1.0000 HSQC= C26
 H19   / 1     1.580856  1*1*3  STAT=Y  PRED= 1.441 RANGE= 0.240 WIDTH(Y)= 1.736 RESP(Y)= 1.0000 HSQC= C19
 H20   / 1     6.182991  1*1*1  STAT=Y  PRED= 6.342 RANGE= 0.907 WIDTH(Y)= 0.826 RESP(Y)= 1.0000 HSQC= C20
 H21A  / 1     5.218151  1*1*1  STAT=Y  PRED= 5.082 RANGE= 0.469 WIDTH(Y)= 1.244 RESP(Y)= 1.0000 HSQC= C21
 H21B  / 1     5.213064  1*1*1  STAT=Y  PRED= 5.225 RANGE= 0.400 WIDTH(Y)= 1.280 RESP(Y)= 1.0000 HSQC= C21
 H13A  / 1     1.520034  1*1*1  STAT=Y  PRED= 1.552 RANGE= 0.350 WIDTH(Y)= 1.764 RESP(Y)= 1.0000 HSQC= C13
 H13B  / 1     1.990770  1*1*1  STAT=Y  PRED= 1.308 RANGE= 0.350 WIDTH(Y)= 2.662 RESP(Y)= 1.0000 HSQC= C13
 H14A  / 1     2.142576  1*1*1  STAT=Y  PRED= 1.689 RANGE= 0.370 WIDTH(Y)= 1.887 RESP(Y)= 1.0000 HSQC= C14
 H14B  / 1     1.810806  1*1*1  STAT=Y  PRED= 1.701 RANGE= 0.340 WIDTH(Y)= 1.862 RESP(Y)= 1.0000 HSQC= C14
 H17   / 1     1.476341  1*1*3  STAT=Y  PRED= 1.528 RANGE= 0.270 WIDTH(Y)= 1.661 RESP(Y)= 1.0000 HSQC= C17
 H18   / 1     1.451820  1*1*3  STAT=Y  PRED= 1.364 RANGE= 0.280 WIDTH(Y)= 2.419 RESP(Y)= 1.0000 HSQC= C18
 H15   / 1     2.272871  1*1*1  STAT=Y  PRED= 2.460 RANGE= 0.450 WIDTH(Y)= 1.584 RESP(Y)= 1.0000 HSQC= C15
14N       2*SPIN= 2 SPECIES=1H    POPULATION(Y)=   0.72608
 virtN2/ 1   -20.001645  1*1*1  STAT=N  WIDTH(Y)= 1.497 RESP(Y)= 1.0000 HSQC= C26
GHOST     2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.27392
 G1    / 2     1.505416  1*1*1  STAT=Y  PRED= 1.505 RANGE= 0.170 WIDTH(Y)= 1.865 RESP(Y)= 1.0000
 G2    / 2     1.575734  1*1*1  STAT=Y  WIDTH(Y)= 2.908 RESP(Y)= 1.0000

COUPLING CONSTANTS(HZ):
 J31_32      7.2822   J H5     H6       STAT=Y  PRED= 7.310 RANGE= 0.300
 J31_33      0.6742   J H5     H7A      STAT=Y  PRED= 1.190 RANGE= 0.700
 J32_33      7.9400   J H6     H7A      STAT=Y  PRED= 7.890 RANGE= 0.410
 J40_42     10.9709   J H25    H26A     STAT=Y  PRED= 11.680 RANGE= 1.280
 J40_43      1.8191   J H25    H26B     STAT=Y  PRED= 1.560 RANGE= 1.280
 J42_43     14.1325   J H26A   H26B     STAT=Y  PRED= -12.570 RANGE= 0.750
 VN2         3.3696   J H26A   virtN2   STAT=Y
 34          1.6743   J H26B   virtN2   STAT=Y
 33          0.5123   J H19    H20      STAT=Y
 32         10.7021   J H20    H21A     STAT=Y
 28         17.5941   J H20    H21B     STAT=Y
 24          1.5157   J H21A   H21B     STAT=Y
 21         13.5306   J H13A   H13B     STAT=Y
 23          3.1672   J H13A   H14A     STAT=Y
 25          3.4737   J H13A   H14B     STAT=Y
 26         13.9069   J H13B   H14A     STAT=Y
 22          3.4920   J H13B   H14B     STAT=Y
 29         13.1064   J H14A   H14B     STAT=Y
 31         12.5775   J H14A   H15      STAT=Y
 30          2.4700   J H14B   H15      STAT=Y
 27          2.3635   J H14B   H15      STAT=Y

CONTROL PARAMETERS:
       Solvent =  none (def. 99% enriched)
         1.000 =  Concentration (vol%, def=1.0%)
    0.00100000 =  Minimum line-intensity
    0.00100000 =  Diagonalization criterium (not in use)
  900.00000000 =  FIELD(1H,MHz), used to transform shifts to ppms
    9.50000040 =  Left frequency (ppm)
   -0.75000000 =  Right frequency (ppm)
        10.000 =  Acquisition time (s, for QMTLS)
         0.000 =  Line-width (for modes D, P & T, 0=use defaults)
   0.041308717 =  Data-point resolution (Hz)
        43.149 =  GAUSSIAN (%, 0=use default from INF)
        -9.097 =  Dispersion contribution (%, 0=use default from INF)
    0.00000000 =  Decoupling frequency (for DORES)

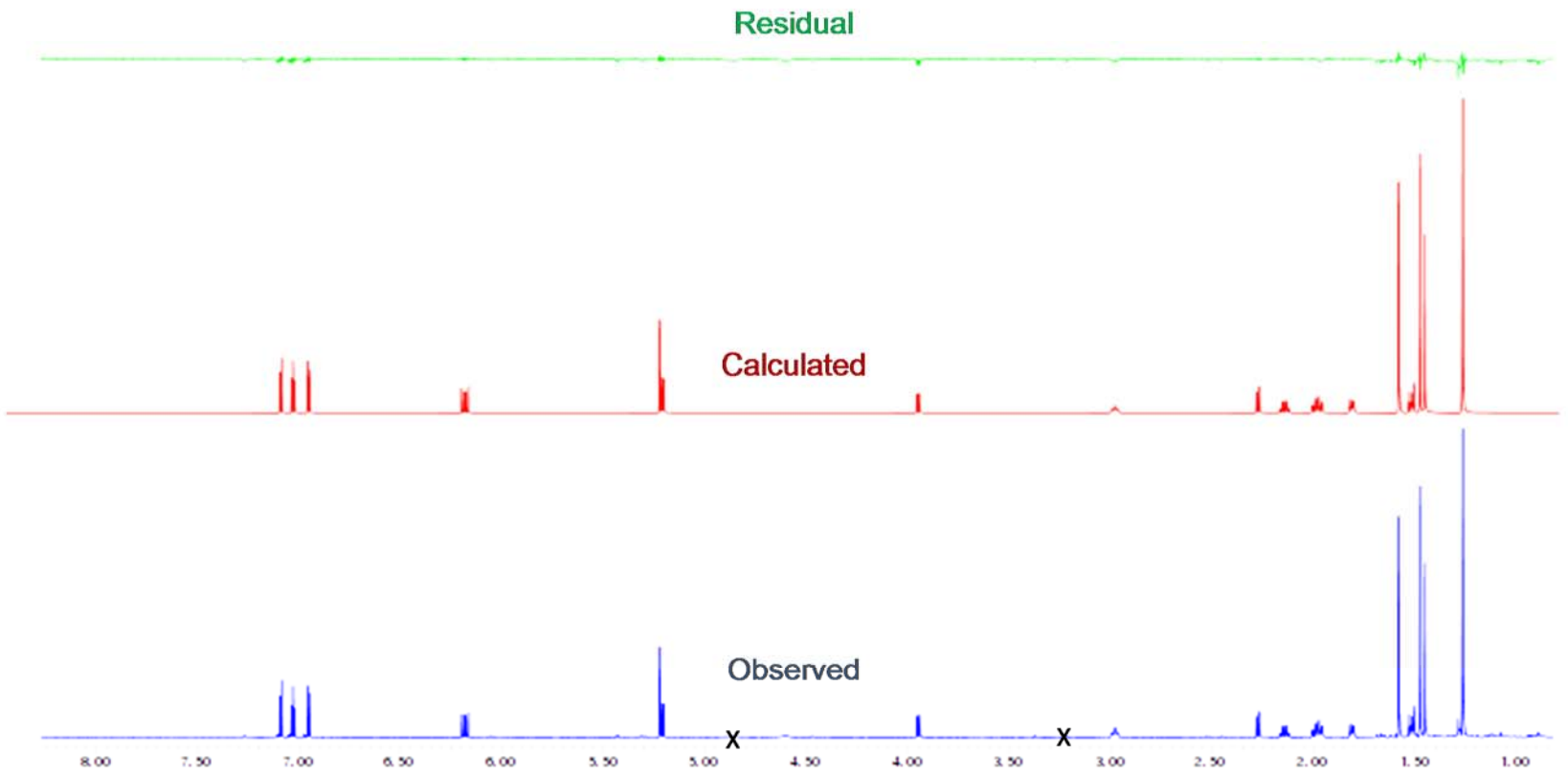
END of FILE
```

S8c. Optimized Structure of 7 for the Initial Prediction of Parameters in PERCH



S8d. The ^{1}H NMR Fingerprint of Ambiguine N Isonitrile (7) in CD_3OD (900 MHz, 298 K)

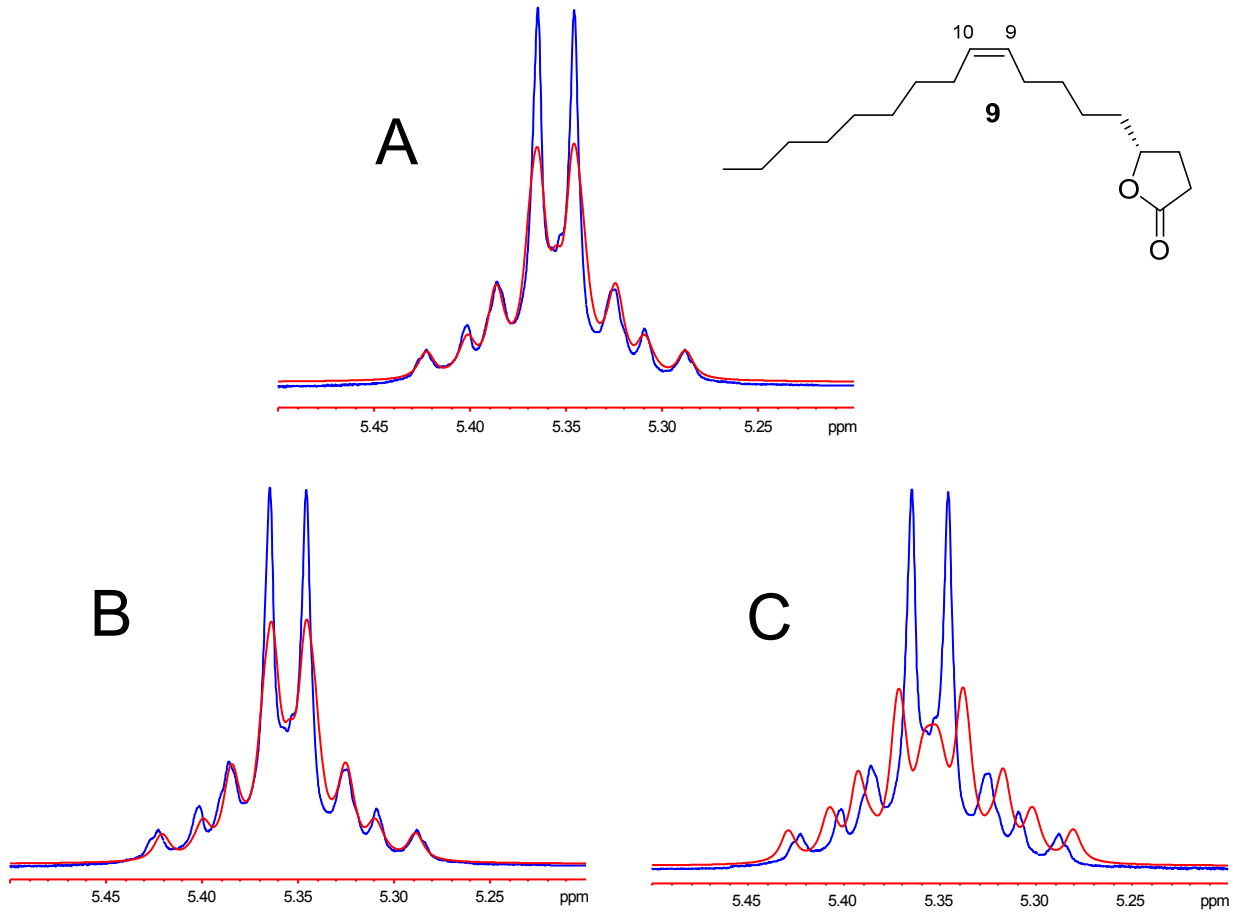
The X marks on the observed spectrum indicate that solvent signals, CHD_2OD and HOD, were removed artificially in order to allow the residual to be scaled such that it reflects the differences arising from the compound and non-solvent impurities of the sample, rather than the relatively large solvent signals.



S9: HNMR Spectral Simulation for Micromolide (9) (Case Study 9) (300 MHz, $CDCl_3$, 298K)

Spectral Simulation using rounded values for the iterated (**A**) chemical shifts of the trans olefinic protons, H-9 and H-10, of **9** demonstrate that even subtle differences in δ values produce notable effects in the simulated spectra (**B** and **C**). The rounding scenarios reflect a minimal change (1-2 ppb, **B**) and the maximum possible deviation (7-8 ppb, **C**) which would still produce the same δ value if two decimal reporting was chosen.

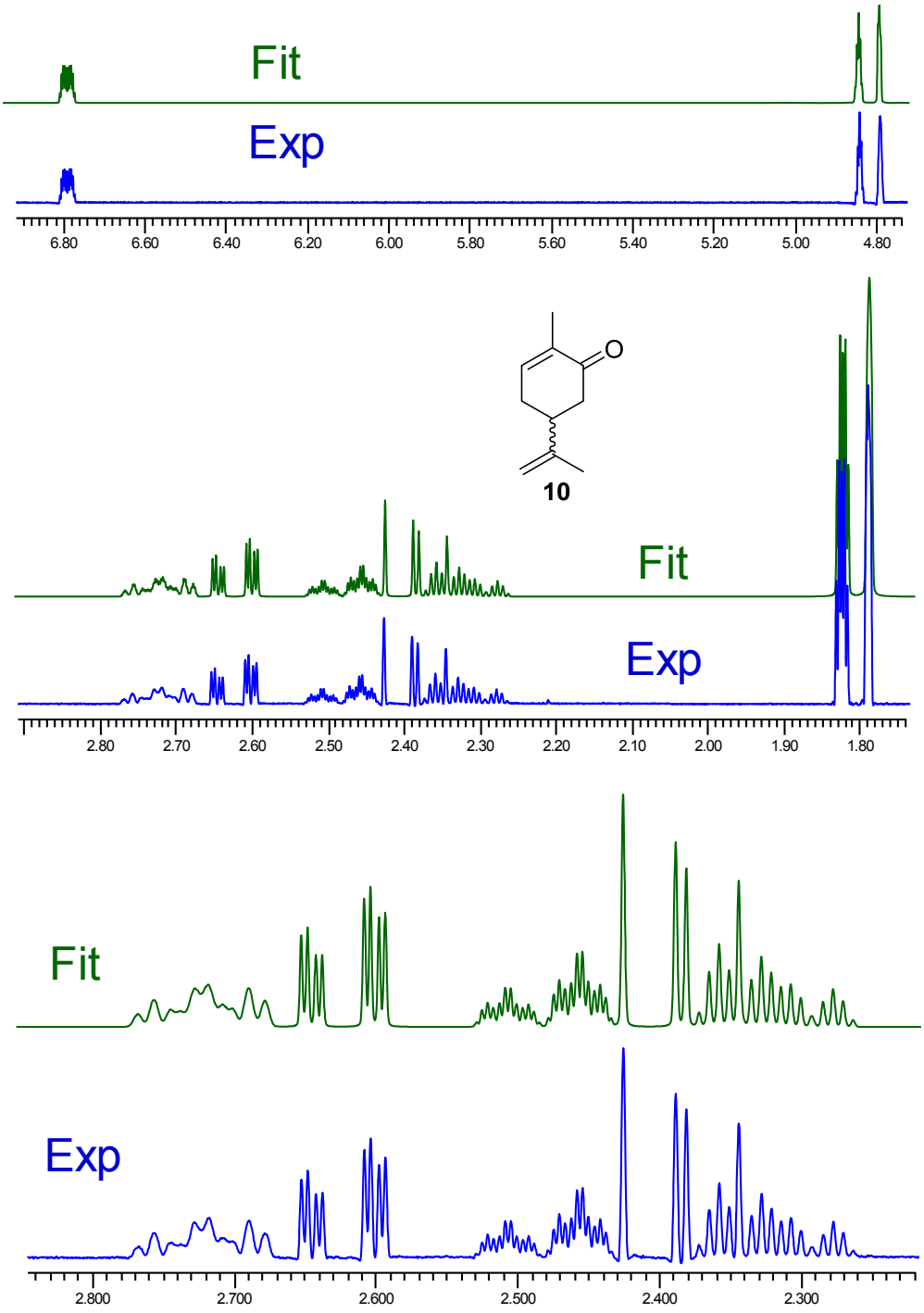
	δ(H-9)	δ(H-10)
A Iteration Result	5.377	5.333
B Sim1 (rounded Δδ=1-2 ppb)	5.375	5.334
C Sim2 (rounded Δδ=7-8 ppb)	5.384	5.325



S10. HNMR and HiFSA Data for Compound 10 (Case Study10)

10a. HiFSA Fingerprint of Carvone (10) (360 MHz, $CDCl_3$, 298K)

Experimental (Exp, in blue) and fitted iteration (Fit, in green).



S10b. Complete HiFSA Profile of Carvone (10) (360 MHz, $CDCl_3$, 298K) using PERCH's Parameters (.pms) Format

```
CHEMICAL SHIFTS (Hz):
protons   2*spin = 1
  6   /1   2446.2529    1*1   Width  0.870 Hz
  5a  /1    892.4883    1*1   Width  0.833 Hz
  5b  /1    836.5308    1*1   Width  1.009 Hz
  4   /1    980.1106    1*1   Width  1.050 Hz
  3a  /1    944.1661    1*1   Width  0.766 Hz
  3b  /1    860.1990    1*1   Width  0.897 Hz
  10  /1    644.0833    1*3   Width  0.917 Hz
  9b  /1   1725.8264    1*1   Width  0.770 Hz
  9a  /1   1744.1284    1*1   Width  1.058 Hz
  7   /1    656.6725    1*3   Width  0.756 Hz

COUPLING CONSTANTS:
  20        6.0233   J 6    5a
  21        2.5568   J 6    5b
  11        1.4505   J 6    7
  23      -18.2493   J 5a   5b
  24        4.4084   J 5a   4
  25        1.6351   J 5a   3a
  19        1.2954   J 5a   7
  26       10.9149   J 5b   4
  18        2.5431   J 5b   7
  28        3.7618   J 4    3a
  29       13.3877   J 4    3b
  15        0.7804   J 4    10
  30        0.9848   J 4    9b
  31       -0.2144   J 4    9a
  32      -16.0705   J 3a   3b
  16        0.3376   J 10   9b
  17        1.4145   J 10   9a
  33        1.6579   J 9b   9a

CONTROL PARAMETERS:
      0.0010 =  The minimum intensity of a line
      0.0010 =  Diagonalization criterium (not in use !)
    3350.347 =  Left frequency limit
    -364.127 =  Right frequency
      0.0000 =  Line-width (for modes D, P & T)
    0.000000 =  Data-point resolution (for mode P)
         0.0 =  GAUSSIAN %
        0.00 =  Dispersion contribution %
      0.0000 =  Decoupling frequency (for DORES)
```

S11: Raw NMR Data & Software-based NMR Analysis

Raw NMR Data. The evaluation of NMR spectra is no longer limited by on-line processing requirements or instrument access, nor is the output format restricted to paper hardcopies. Storing NMR spectral data in digital form is common practice today. In addition to various proprietary data formats from instrument and software vendors, there also have been attempts to standardize the storage of the actual digital spectrum and related information.[41] However, currently there is no standardized open-access format for FID data, regardless of dimension (n-D), in particular not for raw FID data in which the quadrature and/or phase detection schemes are documented and preserved. Analogous to digital photography, digital FID data represents "RAW" file formats, many of which are not fully documented and require reverse engineering approaches in order to be readable. Until appropriate open formats have been defined, the instrument-centered "RAW FID" formats provided by the instrument manufacturers can be widely regarded as the most future proof form of storage. However, adequate precision in HNMR reporting is already achievable with widely available NMR processing software and is a notable means of overcoming this archival limitation, at least for interpreted HNMR spectra. At the same time, the enormous value of FID data to peer review and readership needs to be emphasized.

NMR Software. Tools for off-line post-acquisition processing including Free software (i.e., software source code is available; various sharing models) and other free-of-charge solutions suitable for standard personal computers are widely available (see http://nmrwiki.org/wiki/index.php?title=NMR_Software for a compilation). These tools provide numerous functions for the spectroscopic evaluation, support for the interpretation of NMR spectra, and the extraction of ^{1}H NMR parameters with adequate precision. In some instances, software supports multiplet analysis, extraction of δ/J values, and adaptation to optional journal output formats. Notably, these offerings typically utilize line fitting mechanisms which make first order assumptions and, therefore, are unable to capture the full characteristics of overlapping signals and the widely observed higher order HNMR spectra. It is also noteworthy, that software-

based evaluation of NMR spectra is a routine practice in qHNMR, which adds quantitation as another valuable dimension to the routine ^{1}H NMR analysis of natural products (see [1,2] and references therein). Overall, the determination of chemical shift (δ) values for ^{1}H resonances with an adequate number of decimal places requires no, or only little additional effort when using contemporary NMR analysis software. Providing the original experimental data (raw FID), in addition to the tabulation of the extracted NMR information is an effective way of increasing the reproducibility of HNMR spectra even further and enables others to fully reproduce the spectral analysis.

References

(1) Pauli, G. F.; Jaki, B. U.; Gödecke, T.; Lankin, D. C. *J. Nat. Prod.* **2012**, *75*, 834-851.

(2) Pauli, G. F.; Jaki, B. U.; Lankin, D. C. *J. Nat. Prod.* **2005**, *68*, 133-149.