Supporting Information

Digital NMR Profiles as Building Blocks:

Assembling ^{1}H Fingerprints of Steviol Glycosides

José G. Napolitano,* Charlotte Simmler, James B. McAlpine,

David C. Lankin, Shao-Nong Chen, and Guido F. Pauli*

Department of Medicinal Chemistry and Pharmacognosy, Institute for Tuberculosis Research, and UIC/NIH Center for Botanical Dietary Supplements Research. College of Pharmacy, University of Illinois at Chicago, 833 South Wood Street, Chicago, Illinois 60612, United States

jgnapo@uic.edu; gfp@uic.edu

TABLE OF CONTENT

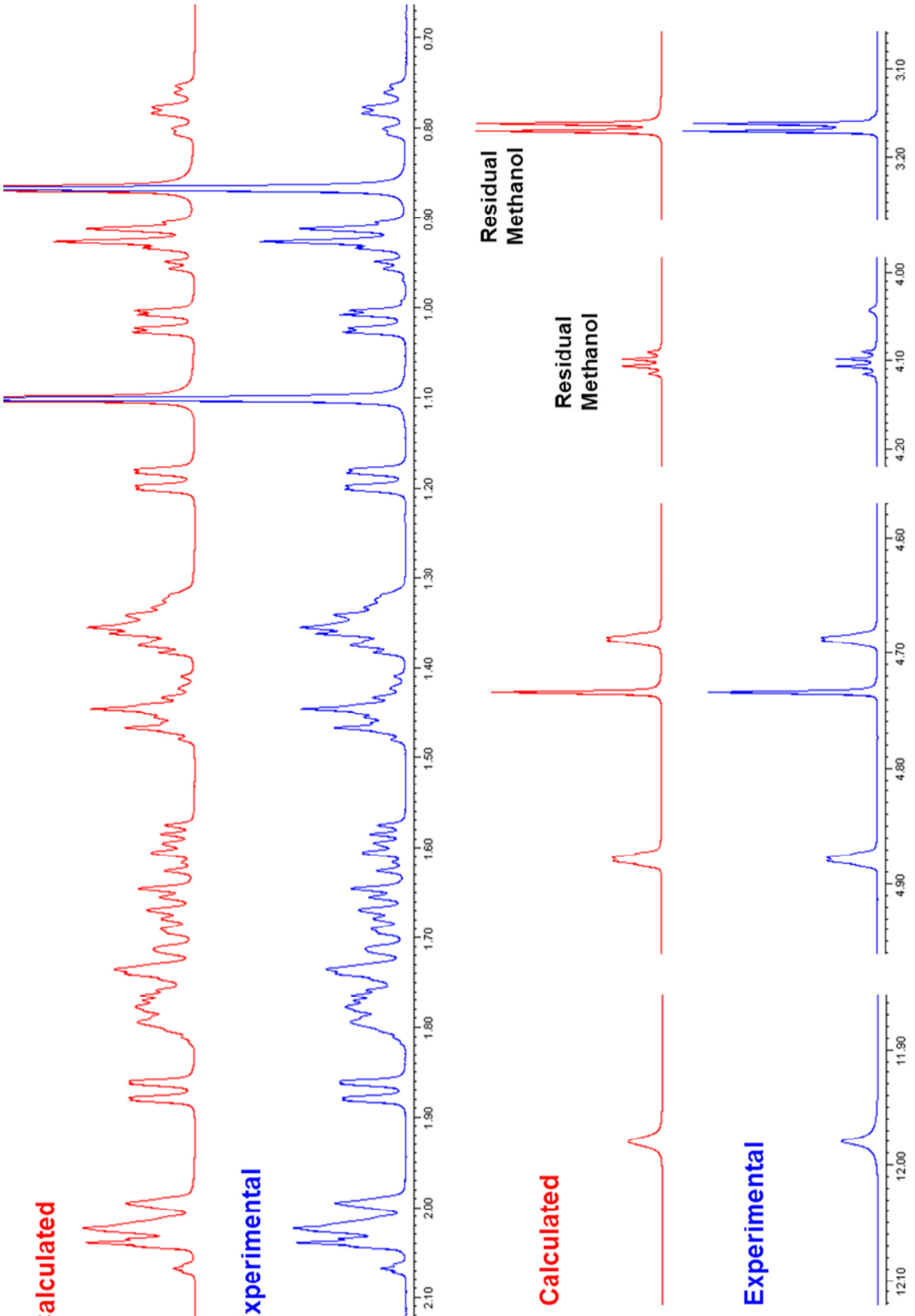
page

S1. The HiFSA profile of steviol (**1**) in DMSO-d_6 [in PERCH parameter (.pms) file 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: c:\HIFSA\Stevia\Steviol
#$œ  Date 10.10.2014;  Time 18:24:58     steviol.pms

CHEMICAL SHIFTS(PPM):
PROTON    2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.05205
 H1A   / 1     0.780095  1*1*1  STAT=Y  PRED= 0.779 RANGE= 0.050 WIDTH(Y)= 2.965 RESP(Y)= 0.9579 HSQC= C1
 H1B   / 1     1.786652  1*1*1  STAT=Y  PRED= 1.778 RANGE= 0.050 WIDTH(Y)= 2.860 RESP(Y)= 0.9901 HSQC= C1
 H2A   / 1     1.775352  1*1*1  STAT=Y  PRED= 1.764 RANGE= 0.050 WIDTH(Y)= 2.883 RESP(Y)= 0.9034 HSQC= C2
 H2B   / 1     1.336829  1*1*1  STAT=Y  PRED= 1.332 RANGE= 0.050 WIDTH(Y)= 2.797 RESP(Y)= 0.9269 HSQC= C2
 H3A   / 1     2.005322  1*1*1  STAT=Y  PRED= 2.000 RANGE= 0.050 WIDTH(Y)= 2.234 RESP(Y)= 0.9312 HSQC= C3
 H3B   / 1     0.929896  1*1*1  STAT=Y  PRED= 0.932 RANGE= 0.050 WIDTH(Y)= 2.524 RESP(Y)= 0.9292 HSQC= C3
 H5A   / 1     1.014807  1*1*1  STAT=Y  PRED= 1.015 RANGE= 0.050 WIDTH(Y)= 2.506 RESP(Y)= 0.9664 HSQC= C5
 H6A   / 1     1.704304  1*1*1  STAT=Y  PRED= 1.700 RANGE= 0.050 WIDTH(Y)= 2.803 RESP(Y)= 0.9192 HSQC= C6
 H6B   / 1     1.745031  1*1*1  STAT=Y  PRED= 1.737 RANGE= 0.050 WIDTH(Y)= 2.776 RESP(Y)= 0.9360 HSQC= C6
 H7A   / 1     1.359640  1*1*1  STAT=Y  PRED= 1.360 RANGE= 0.050 WIDTH(Y)= 2.677 RESP(Y)= 0.9031 HSQC= C7
 H7B   / 1     1.454838  1*1*1  STAT=Y  PRED= 1.449 RANGE= 0.050 WIDTH(Y)= 2.611 RESP(Y)= 0.9915 HSQC= C7
 H9A   / 1     0.918964  1*1*1  STAT=Y  PRED= 0.921 RANGE= 0.050 WIDTH(Y)= 2.972 RESP(Y)= 0.9761 HSQC= C9
 H11A  / 1     1.660380  1*1*1  STAT=Y  PRED= 1.651 RANGE= 0.050 WIDTH(Y)= 3.204 RESP(Y)= 0.9509 HSQC= C11
 H11B  / 1     1.445476  1*1*1  STAT=Y  PRED= 1.429 RANGE= 0.050 WIDTH(Y)= 2.796 RESP(Y)= 0.9007 HSQC= C11
 H12A  / 1     1.357659  1*1*1  STAT=Y  PRED= 1.348 RANGE= 0.025 WIDTH(Y)= 2.742 RESP(Y)= 1.0000 HSQC= C12
 H12B  / 1     1.599403  1*1*1  STAT=Y  PRED= 1.599 RANGE= 0.050 WIDTH(Y)= 2.825 RESP(Y)= 0.9451 HSQC= C12
 H14A  / 1     1.870381  1*1*1  STAT=Y  PRED= 1.869 RANGE= 0.455 WIDTH(Y)= 2.593 RESP(Y)= 0.9685 HSQC= C14
 H14B  / 1     1.189951  1*1*1  STAT=Y  PRED= 1.192 RANGE= 0.050 WIDTH(Y)= 2.546 RESP(Y)= 0.9764 HSQC= C14
 H15A  / 1     2.015428  1*1*1  STAT=Y  PRED= 2.023 RANGE= 0.050 WIDTH(Y)= 2.603 RESP(Y)= 0.9421 HSQC= C15
 H15B  / 1     2.047400  1*1*1  STAT=Y  PRED= 2.052 RANGE= 0.050 WIDTH(Y)= 2.093 RESP(Y)= 0.9264 HSQC= C15
 H17A  / 1     4.878194  1*1*1  STAT=Y  PRED= 4.878 RANGE= 0.025 WIDTH(Y)= 1.665 RESP(Y)= 0.9638 HSQC= C17
 H17B  / 1     4.687131  1*1*1  STAT=Y  PRED= 4.687 RANGE= 0.025 WIDTH(Y)= 1.740 RESP(Y)= 0.9720 HSQC= C17
 H18B  / 1     1.100801  1*1*3  STAT=Y  PRED= 1.101 RANGE= 0.050 WIDTH(Y)= 2.009 RESP(Y)= 0.9314 HSQC= C18
 H20B  / 1     0.866253  1*1*3  STAT=Y  PRED= 0.866 RANGE= 0.050 WIDTH(Y)= 2.279 RESP(Y)= 0.9416 HSQC= C20
 H21A  / 1     4.733292  1*1*1  STAT=Y  PRED= 4.733 RANGE= 0.050 WIDTH(Y)= 1.405 RESP(Y)= 0.9753
 H22A  / 1    11.979751  1*1*1  STAT=Y  PRED= 11.981 RANGE= 0.050 WIDTH(Y)= 5.637 RESP(Y)= 0.7926
DMSO_CH   2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.71336
 DMSO  / 2     2.500022  1*1*1  STAT=Y  PRED= 2.500 RANGE= 0.050 WIDTH(Y)= 1.445 RESP(Y)= 1.0000
DMSO_D    2*SPIN= 2 SPECIES=2D    POPULATION(Y)=   0.71336
 DMSOD1/ 2  -100.000003  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
 DMSOD2/ 2  -100.000003  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
WATER_H   2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.19557
 WATER / 3     3.334570  2*1*1  STAT=Y  PRED= 3.338 RANGE= 0.050 WIDTH(Y)= 1.587 RESP(Y)= 1.0000
MEOH_H    2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.03903
 MEOH1 / 4     3.165037  1*1*3  STAT=Y  PRED= 3.160 RANGE= 0.050 WIDTH(Y)= 1.593 RESP(Y)= 1.0000
 MEOH2 / 4     4.102015  1*1*1  STAT=Y  PRED= 4.010 RANGE= 0.050 WIDTH(Y)= 1.895 RESP(Y)= 1.0000

COUPLING CONSTANTS(HZ):
 J12_13    -12.7498   J H1A    H1B      STAT=Y  PRED= -13.130 RANGE= 1.500
 J17_12     13.7463   J H1A    H2A      STAT=Y  PRED= 12.550 RANGE= 2.560
 J12_18      4.1788   J H1A    H2B      STAT=Y  PRED= 4.380 RANGE= 3.800
 J14_12     -0.6692   J H1A    H20B     STAT=Y  PRED= -0.790 RANGE= 0.400
 J17_13      3.7509   J H1B    H2A      STAT=Y  PRED= 3.880 RANGE= 3.800
 J13_18      2.6839   J H1B    H2B      STAT=Y  PRED= 2.510 RANGE= 2.800
 J13_19      1.3750   J H1B    H3A      STAT=Y  PRED= 2.850 RANGE= 1.280
 J17_18    -13.9964   J H2A    H2B      STAT=Y  PRED= -13.190 RANGE= 1.500
 J17_19      3.3548   J H2A    H3A      STAT=Y  PRED= 3.860 RANGE= 3.800
 J17_20     13.5567   J H2A    H3B      STAT=Y  PRED= 12.570 RANGE= 2.560
 J19_18      2.7383   J H2B    H3A      STAT=Y  PRED= 2.530 RANGE= 2.800
 J20_18      4.1739   J H2B    H3B      STAT=Y  PRED= 4.310 RANGE= 3.800
 J19_20    -13.1052   J H3A    H3B      STAT=Y  PRED= -13.110 RANGE= 1.500
 J21_22     12.2052   J H5A    H6A      STAT=Y  PRED= 12.550 RANGE= 2.560
 J21_23      2.1358   J H5A    H6B      STAT=Y  PRED= 1.710 RANGE= 2.800
 J22_23    -13.8273   J H6A    H6B      STAT=Y  PRED= -13.190 RANGE= 1.500
 J22_24     13.8865   J H6A    H7A      STAT=Y  PRED= 12.990 RANGE= 2.560
 J22_25      2.9928   J H6A    H7B      STAT=Y  PRED= 3.320 RANGE= 3.800
 J23_24      3.4578   J H6B    H7A      STAT=Y  PRED= 3.410 RANGE= 3.800
 J23_25      3.2975   J H6B    H7B      STAT=Y  PRED= 3.190 RANGE= 3.800
 J24_25    -12.8784   J H7A    H7B      STAT=Y  PRED= -13.130 RANGE= 1.500
 J26_1       0.2028   J H9A    H11A     STAT=Y  PRED= 0.490 RANGE= 2.800
 J26_2       8.2034   J H9A    H11B     STAT=Y  PRED= 9.030 RANGE= 3.580
 J26_6       0.8346   J H9A    H14B     STAT=Y  PRED= 2.290 RANGE= 1.100
 J1_2      -15.0120   J H11A   H11B     STAT=Y  PRED= -13.010 RANGE= 1.500
 J3_1        1.3806   J H11A   H12A     STAT=Y  PRED= 1.040 RANGE= 2.800
 J4_1        5.9099   J H11A   H12B     STAT=Y  PRED= 6.480 RANGE= 3.800
 J3_2        6.5580   J H11B   H12A     STAT=Y  PRED= 6.890 RANGE= 3.800
 J4_2       13.7823   J H11B   H12B     STAT=Y  PRED= 11.180 RANGE= 2.800
 J3_4      -11.8435   J H12A   H12B     STAT=Y  PRED= -12.880 RANGE= 1.500
 J3_6        2.6575   J H12A   H14B     STAT=Y  PRED= 2.670 RANGE= 1.280
 J5_6      -10.7418   J H14A   H14B     STAT=Y  PRED= -12.450 RANGE= 2.000
 J7_5        2.5849   J H14A   H15A     STAT=Y  PRED= 1.650 RANGE= 1.280
 J7_8      -17.0549   J H15A   H15B     STAT=Y  PRED= -14.390 RANGE= 3.000
 J7_9       -2.0579   J H15A   H17A     STAT=Y  PRED= -2.030 RANGE= 1.000
 J7_10      -1.5104   J H15A   H17B     STAT=Y  PRED= -1.900 RANGE= 0.950
```

```
 J9_8       -2.8704   J H15B   H17A     STAT=Y  PRED= -2.420 RANGE= 1.200
 J10_8      -2.4953   J H15B   H17B     STAT=Y  PRED= -2.140 RANGE= 1.100
 J9_10       1.5539   J H17A   H17B     STAT=Y  PRED= 2.980 RANGE= 4.000
 JDMSO1      1.7939   J DMSO   DMSOD1   STAT=Y  PRED= 1.700 RANGE= 0.050
 JDMSO1      1.7939   J DMSO   DMSOD2   STAT=Y  PRED= 1.700 RANGE= 0.050
 JMEOH1      5.0000   J MEOH1  MEOH2    STAT=Y  PRED= 5.000 RANGE= 0.050

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)
  600.12700400 =  FIELD(1H,MHz), used to transform shifts to ppms
   22.47832137 =  Left frequency (ppm)
   -7.49157667 =  Right frequency (ppm)
         0.000 =  Acquisition time (s, for QMTLS)
         1.404 =  Line-width (for modes D, P & T, 0=use defaults)
   0.137220373 =  Data-point resolution (Hz)
        42.415 =  GAUSSIAN (%, 0=use default from INF)
        -4.744 =  Dispersion contribution (%, 0=use default from INF)
    0.00000000 =  Decoupling frequency (for DORES)

CONSTRAINTS (in equations X0 = 1.0)...use no empty lines
 EQUAL DMSOD1   = DMSOD2
  1.000 * 1.0 = -41.020 * 1.0  - 1.000 * 1.0
  10.000 * 1.0 = -38.340 * 1.0  - 1.000 * 1.0
  11.000 * 1.0 = -16.670 * 1.0  - 1.000 * 1.0
  12.000 * 1.0 = -36.870 * 1.0  - 1.000 * 1.0
  13.000 * 1.0 = -80.200 * 1.0  - 1.000 * 1.0
  14.000 * 1.0 = -49.010 * 1.0  - 1.000 * 1.0
  15.000 * 1.0 = -48.090 * 1.0  - 1.000 * 1.0
  16.0 * 1.0 = -153.1 * 1.0  - 1.0 * 1.0
  17.0 * 1.0 = -104.2 * 1.0  - 1.0 * 1.0
  18.000 * 1.0 = -28.210 * 1.0  - 1.000 * 1.0
  19.0 * 1.0 = -185.4 * 1.0  - 1.0 * 1.0
  2.000 * 1.0 = -19.040 * 1.0  - 1.000 * 1.0
  20.000 * 1.0 = -14.770 * 1.0  - 1.000 * 1.0
  3.000 * 1.0 = -37.520 * 1.0  - 1.000 * 1.0
  4.000 * 1.0 = -43.240 * 1.0  - 1.000 * 1.0
  5.000 * 1.0 = -55.060 * 1.0  - 1.000 * 1.0
  6.000 * 1.0 = -21.840 * 1.0  - 1.000 * 1.0
  7.000 * 1.0 = -40.820 * 1.0  - 1.000 * 1.0
  8.000 * 1.0 = -42.640 * 1.0  - 1.000 * 1.0
  9.000 * 1.0 = -55.850 * 1.0  - 1.000 * 1.0

END of FILE
```

S2. The ^{1}H fingerprint of steviol (**1**) in DMSO-d_6 (44 mM, 600 MHz, 298 K). The calculated and observed NMR spectra are shown in red and blue, respectively.

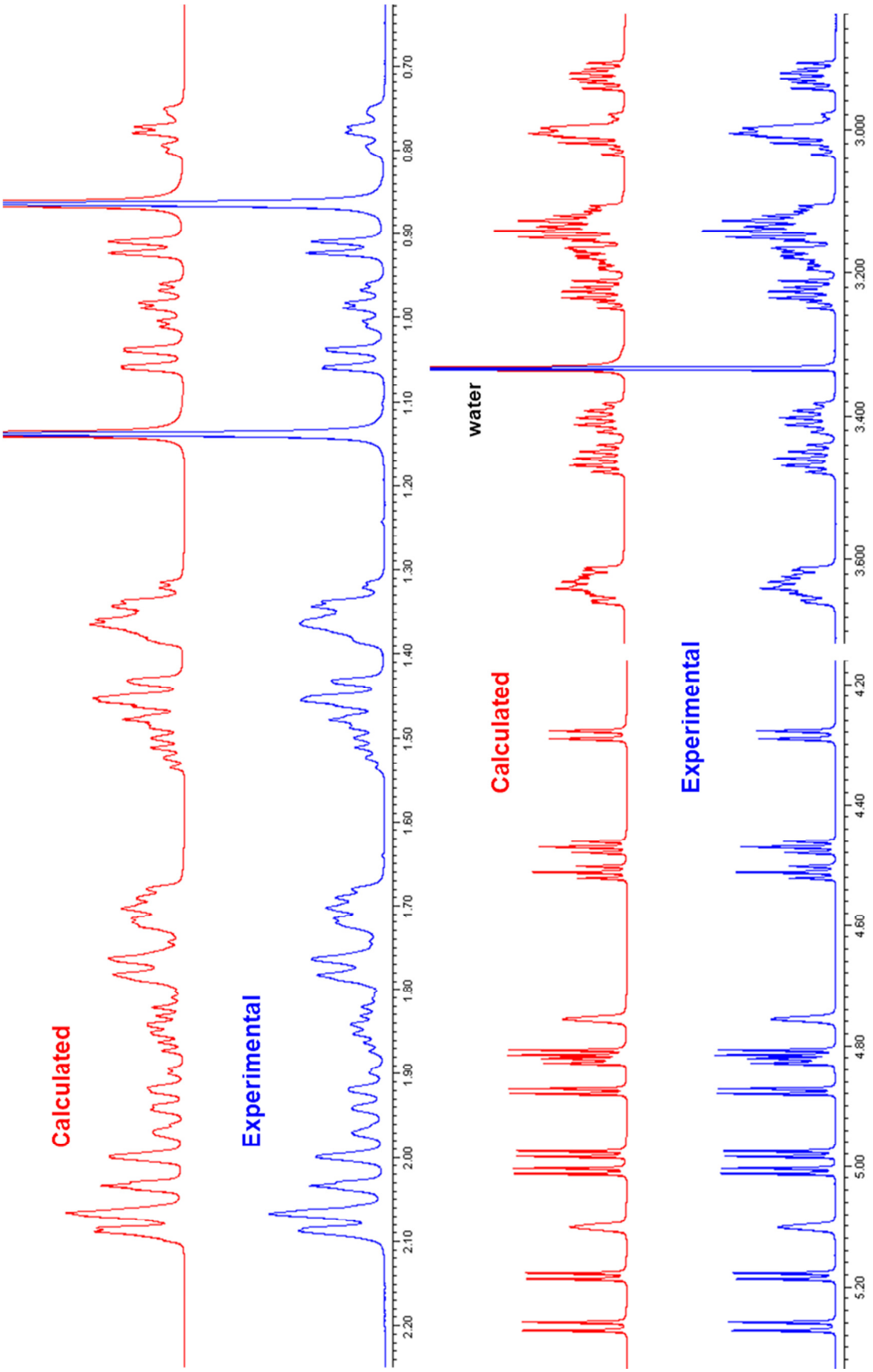


S3. The HiFSA profile of rubusoside (**2**) in DMSO-d_6 [in PERCH parameter (.pms) file format].

```
* 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: c:\HIFSA\Stevia\Rubusoside
#$œ  Date 10.10.2014;  Time 21: 6:43     rubusoside.pms

CHEMICAL SHIFTS(PPM):
PROTON    2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.06075
 H1A   / 1     0.775810  1*1*1  STAT=Y  PRED= 0.779 RANGE= 0.050 WIDTH(Y)= 3.894 RESP(Y)= 0.9579 HSQC= C1
 H1B   / 1     1.771873  1*1*1  STAT=Y  PRED= 1.778 RANGE= 0.050 WIDTH(Y)= 3.704 RESP(Y)= 0.9901 HSQC= C1
 H2A   / 1     1.775486  1*1*1  STAT=Y  PRED= 1.764 RANGE= 0.050 WIDTH(Y)= 3.488 RESP(Y)= 0.9034 HSQC= C2
 H2B   / 1     1.355135  1*1*1  STAT=Y  PRED= 1.332 RANGE= 0.050 WIDTH(Y)= 2.805 RESP(Y)= 0.9269 HSQC= C2
 H3A   / 1     2.079040  1*1*1  STAT=Y  PRED= 2.000 RANGE= 0.050 WIDTH(Y)= 3.184 RESP(Y)= 0.9312 HSQC= C3
 H3B   / 1     0.985283  1*1*1  STAT=Y  PRED= 0.932 RANGE= 0.050 WIDTH(Y)= 3.559 RESP(Y)= 0.9292 HSQC= C3
 H5A   / 1     1.048010  1*1*1  STAT=Y  PRED= 1.015 RANGE= 0.050 WIDTH(Y)= 3.894 RESP(Y)= 0.9664 HSQC= C5
 H6A   / 1     1.928634  1*1*1  STAT=Y  PRED= 1.700 RANGE= 0.050 WIDTH(Y)= 3.922 RESP(Y)= 0.9192 HSQC= C6
 H6B   / 1     1.711646  1*1*1  STAT=Y  PRED= 1.737 RANGE= 0.050 WIDTH(Y)= 3.695 RESP(Y)= 0.9360 HSQC= C6
 H7A   / 1     1.340752  1*1*1  STAT=Y  PRED= 1.360 RANGE= 0.050 WIDTH(Y)= 3.870 RESP(Y)= 0.9031 HSQC= C7
 H7B   / 1     1.467309  1*1*1  STAT=Y  PRED= 1.449 RANGE= 0.050 WIDTH(Y)= 4.055 RESP(Y)= 0.9915 HSQC= C7
 H9A   / 1     0.915919  1*1*1  STAT=Y  PRED= 0.921 RANGE= 0.050 WIDTH(Y)= 3.516 RESP(Y)= 0.9761 HSQC= C9
 H11A  / 1     1.695791  1*1*1  STAT=Y  PRED= 1.651 RANGE= 0.050 WIDTH(Y)= 3.486 RESP(Y)= 0.9509 HSQC= C11
 H11B  / 1     1.500776  1*1*1  STAT=Y  PRED= 1.429 RANGE= 0.050 WIDTH(Y)= 3.863 RESP(Y)= 0.9007 HSQC= C11
 H12A  / 1     1.368745  1*1*1  STAT=Y  PRED= 1.348 RANGE= 0.025 WIDTH(Y)= 3.019 RESP(Y)= 1.0000 HSQC= C12
 H12B  / 1     1.845911  1*1*1  STAT=Y  PRED= 1.599 RANGE= 0.050 WIDTH(Y)= 4.046 RESP(Y)= 0.9451 HSQC= C12
 H14A  / 1     2.076299  1*1*1  STAT=Y  PRED= 1.869 RANGE= 0.455 WIDTH(Y)= 3.655 RESP(Y)= 0.9685 HSQC= C14
 H14B  / 1     1.442310  1*1*1  STAT=Y  PRED= 1.192 RANGE= 0.050 WIDTH(Y)= 3.290 RESP(Y)= 0.9764 HSQC= C14
 H15A  / 1     1.987999  1*1*1  STAT=Y  PRED= 2.023 RANGE= 0.050 WIDTH(Y)= 3.726 RESP(Y)= 0.9421 HSQC= C15
 H15B  / 1     2.043940  1*1*1  STAT=Y  PRED= 2.052 RANGE= 0.050 WIDTH(Y)= 3.826 RESP(Y)= 0.9264 HSQC= C15
 H17A  / 1     5.101198  1*1*1  STAT=Y  PRED= 4.878 RANGE= 0.025 WIDTH(Y)= 2.222 RESP(Y)= 0.9638 HSQC= C17
 H17B  / 1     4.755346  1*1*1  STAT=Y  PRED= 4.687 RANGE= 0.025 WIDTH(Y)= 2.510 RESP(Y)= 0.9720 HSQC= C17
 H18B  / 1     1.137551  1*1*3  STAT=Y  PRED= 1.101 RANGE= 0.050 WIDTH(Y)= 2.685 RESP(Y)= 0.9314 HSQC= C18
 H20B  / 1     0.863457  1*1*3  STAT=Y  PRED= 0.866 RANGE= 0.050 WIDTH(Y)= 3.381 RESP(Y)= 0.9416 HSQC= C20
 GA1   / 1     5.264823  1*1*1  STAT=Y  PRED= 5.565 RANGE= 0.342 WIDTH(Y)= 1.365 RESP(Y)= 0.9078 HSQC= H21
 GA2   / 1     3.146291  1*1*1  STAT=Y  PRED= 3.526 RANGE= 0.200 WIDTH(Y)= 1.588 RESP(Y)= 0.9171 HSQC= C23
 GA3   / 1     3.228384  1*1*1  STAT=Y  PRED= 3.317 RANGE= 0.155 WIDTH(Y)= 1.535 RESP(Y)= 0.8548 HSQC= C26
 GA4   / 1     3.131530  1*1*1  STAT=Y  PRED= 3.387 RANGE= 0.287 WIDTH(Y)= 1.571 RESP(Y)= 0.8374 HSQC= C27
 GA5   / 1     3.179883  1*1*1  STAT=Y  PRED= 3.485 RANGE= 0.247 WIDTH(Y)= 1.710 RESP(Y)= 0.8314 HSQC= C25
 GA6A  / 1     3.458827  1*1*1  STAT=Y  PRED= 3.351 RANGE= 0.450 WIDTH(Y)= 1.979 RESP(Y)= 0.8318 HSQC= C29
 GA6B  / 1     3.626411  1*1*1  STAT=Y  PRED= 3.509 RANGE= 0.232 WIDTH(Y)= 1.878 RESP(Y)= 0.8536 HSQC= C29
 OGA2  / 1     5.180937  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 1.415 RESP(Y)= 0.8978
 OGA3  / 1     5.007395  1*1*1  STAT=Y  PRED= 4.296 RANGE= 1.420 WIDTH(Y)= 1.259 RESP(Y)= 0.8798
 OGA4  / 1     4.978889  1*1*1  STAT=Y  PRED= 4.702 RANGE= 1.565 WIDTH(Y)= 1.230 RESP(Y)= 0.8679
 OGA6  / 1     4.469250  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 1.350 RESP(Y)= 0.8978
 GB1   / 1     4.283265  1*1*1  STAT=Y  PRED= 5.565 RANGE= 0.342 WIDTH(Y)= 1.903 RESP(Y)= 0.9078 HSQC= H21
 GB2   / 1     2.925010  1*1*1  STAT=Y  PRED= 3.526 RANGE= 0.200 WIDTH(Y)= 1.619 RESP(Y)= 0.9171 HSQC= C23
 GB3   / 1     3.123025  1*1*1  STAT=Y  PRED= 3.317 RANGE= 0.155 WIDTH(Y)= 1.422 RESP(Y)= 0.8548 HSQC= C26
 GB4   / 1     3.012271  1*1*1  STAT=Y  PRED= 3.387 RANGE= 0.287 WIDTH(Y)= 1.413 RESP(Y)= 0.8374 HSQC= C27
 GB5   / 1     2.995722  1*1*1  STAT=Y  PRED= 3.485 RANGE= 0.247 WIDTH(Y)= 1.648 RESP(Y)= 0.8314 HSQC= C25
 GB6A  / 1     3.401766  1*1*1  STAT=Y  PRED= 3.351 RANGE= 0.450 WIDTH(Y)= 1.925 RESP(Y)= 0.8318 HSQC= C29
 GB6B  / 1     3.642221  1*1*1  STAT=Y  PRED= 3.509 RANGE= 0.232 WIDTH(Y)= 1.850 RESP(Y)= 0.8536 HSQC= C29
 OGB2  / 1     4.809909  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 1.236 RESP(Y)= 0.8978
 OGB3  / 1     4.874621  1*1*1  STAT=Y  PRED= 4.296 RANGE= 1.420 WIDTH(Y)= 1.222 RESP(Y)= 0.8798
 OGB4  / 1     4.823855  1*1*1  STAT=Y  PRED= 4.702 RANGE= 1.565 WIDTH(Y)= 1.197 RESP(Y)= 0.8679
 OGB6  / 1     4.511059  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 1.486 RESP(Y)= 0.8978
DMSO_CH   2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.84048
 DMSO  / 2     2.500013  1*1*1  STAT=Y  PRED= 2.500 RANGE= 0.050 WIDTH(Y)= 1.329 RESP(Y)= 1.0000
DMSO_D    2*SPIN= 2 SPECIES=2D    POPULATION(Y)=   0.84048
 DMSOD1/ 2  -100.000001  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
 DMSOD2/ 2  -100.000001  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
WATER_H   2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.09878
 WATER / 3     3.331851  2*1*1  STAT=Y  PRED= 3.338 RANGE= 0.050 WIDTH(Y)= 1.054 RESP(Y)= 1.0000

COUPLING CONSTANTS(HZ):
 J12_13    -13.0235   J H1A    H1B      STAT=Y  PRED= -13.130 RANGE= 1.500
 J17_12     12.4391   J H1A    H2A      STAT=Y  PRED= 12.550 RANGE= 2.560
 J12_18      4.4872   J H1A    H2B      STAT=Y  PRED= 4.380 RANGE= 3.800
 J14_12     -0.0900   J H1A    H20B     STAT=Y  PRED= -0.790 RANGE= 0.400
 J17_13      4.2898   J H1B    H2A      STAT=Y  PRED= 3.880 RANGE= 3.800
 J13_18      3.5216   J H1B    H2B      STAT=Y  PRED= 2.510 RANGE= 2.800
 J13_19      1.2723   J H1B    H3A      STAT=Y  PRED= 2.850 RANGE= 1.280
 J17_18    -14.5339   J H2A    H2B      STAT=Y  PRED= -13.190 RANGE= 1.500
 J17_19      4.2070   J H2A    H3A      STAT=Y  PRED= 3.860 RANGE= 3.800
 J17_20     13.2983   J H2A    H3B      STAT=Y  PRED= 12.570 RANGE= 2.560
 J19_18      2.9948   J H2B    H3A      STAT=Y  PRED= 2.530 RANGE= 2.800
 J20_18      4.4682   J H2B    H3B      STAT=Y  PRED= 4.310 RANGE= 3.800
 J19_20    -13.3869   J H3A    H3B      STAT=Y  PRED= -13.110 RANGE= 1.500
 J21_22     12.2242   J H5A    H6A      STAT=Y  PRED= 12.550 RANGE= 2.560
 J21_23      2.0437   J H5A    H6B      STAT=Y  PRED= 1.710 RANGE= 2.800
 J22_23    -13.7595   J H6A    H6B      STAT=Y  PRED= -13.190 RANGE= 1.500
 J22_24     13.2560   J H6A    H7A      STAT=Y  PRED= 12.990 RANGE= 2.560
 J22_25      3.1808   J H6A    H7B      STAT=Y  PRED= 3.320 RANGE= 3.800
 J23_24      3.5762   J H6B    H7A      STAT=Y  PRED= 3.410 RANGE= 3.800
```

```
 J23_25      3.3625   J H6B    H7B      STAT=Y  PRED= 3.190 RANGE= 3.800
 J24_25    -12.5210   J H7A    H7B      STAT=Y  PRED= -13.130 RANGE= 1.500
 J26_1       0.9766   J H9A    H11A     STAT=Y  PRED= 0.490 RANGE= 2.800
 J26_2       8.1506   J H9A    H11B     STAT=Y  PRED= 9.030 RANGE= 3.580
 J26_6       1.3973   J H9A    H14B     STAT=Y  PRED= 2.290 RANGE= 1.100
 J1_2      -14.9148   J H11A   H11B     STAT=Y  PRED= -13.010 RANGE= 1.500
 J3_1        2.1715   J H11A   H12A     STAT=Y  PRED= 1.040 RANGE= 2.800
 J4_1        6.0170   J H11A   H12B     STAT=Y  PRED= 6.480 RANGE= 3.800
 J3_2        6.7922   J H11B   H12A     STAT=Y  PRED= 6.890 RANGE= 3.800
 J4_2       13.2688   J H11B   H12B     STAT=Y  PRED= 11.180 RANGE= 2.800
 J3_4      -11.6314   J H12A   H12B     STAT=Y  PRED= -12.880 RANGE= 1.500
 J3_6        3.0553   J H12A   H14B     STAT=Y  PRED= 2.670 RANGE= 1.280
 J5_6      -11.3992   J H14A   H14B     STAT=Y  PRED= -12.450 RANGE= 2.000
 J7_5        2.7447   J H14A   H15A     STAT=Y  PRED= 1.650 RANGE= 1.280
 J7_8      -16.8669   J H15A   H15B     STAT=Y  PRED= -14.390 RANGE= 3.000
 J7_9       -2.0728   J H15A   H17A     STAT=Y  PRED= -2.030 RANGE= 1.000
 J7_10      -1.5587   J H15A   H17B     STAT=Y  PRED= -1.900 RANGE= 0.950
 J9_8       -3.0038   J H15B   H17A     STAT=Y  PRED= -2.420 RANGE= 1.200
 J10_8      -2.3856   J H15B   H17B     STAT=Y  PRED= -2.140 RANGE= 1.100
 J9_10       1.4829   J H17A   H17B     STAT=Y  PRED= 2.980 RANGE= 4.000
 J38_40      8.2126   J GA1    GA2      STAT=Y  PRED= 7.190 RANGE= 3.580
 J40_43      9.1219   J GA2    GA3      STAT=Y  PRED= 8.920 RANGE= 3.580
 J40_48      5.7658   J GA2    OGA2     STAT=Y  PRED= 4.300 RANGE= 1.000
 J43_46      8.8137   J GA3    GA4      STAT=Y  PRED= 9.140 RANGE= 3.580
 J43_51      5.4074   J GA3    OGA3     STAT=Y  PRED= 4.300 RANGE= 1.000
 J41_46      9.7082   J GA4    GA5      STAT=Y  PRED= 10.550 RANGE= 2.560
 J46_52      5.5423   J GA4    OGA4     STAT=Y  PRED= 4.300 RANGE= 1.000
 J41_49      5.1855   J GA5    GA6A     STAT=Y  PRED= 2.700 RANGE= 3.000
 J41_50      2.1080   J GA5    GA6B     STAT=Y  PRED= 1.280 RANGE= 3.000
 J49_50    -11.8253   J GA6A   GA6B     STAT=Y  PRED= -12.300 RANGE= 0.800
 J49_51      5.9565   J GA6A   OGA6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J50_51      5.2830   J GA6B   OGA6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J48_50      7.7944   J GB1    GB2      STAT=Y  PRED= 7.190 RANGE= 3.580
 J50_53      8.9966   J GB2    GB3      STAT=Y  PRED= 8.920 RANGE= 3.580
 J50_58      5.0219   J GB2    OGB2     STAT=Y  PRED= 4.300 RANGE= 1.000
 J53_56      8.5238   J GB3    GB4      STAT=Y  PRED= 9.140 RANGE= 3.580
 J53_61      4.8856   J GB3    OGB3     STAT=Y  PRED= 4.300 RANGE= 1.000
 J51_56      9.7146   J GB4    GB5      STAT=Y  PRED= 10.550 RANGE= 2.560
 J56_62      5.2828   J GB4    OGB4     STAT=Y  PRED= 4.300 RANGE= 1.000
 J51_59      5.9679   J GB5    GB6A     STAT=Y  PRED= 2.700 RANGE= 3.000
 J51_60      2.2038   J GB5    GB6B     STAT=Y  PRED= 1.280 RANGE= 3.000
 J59_60    -11.5869   J GB6A   GB6B     STAT=Y  PRED= -12.300 RANGE= 0.800
 J59_61      6.0829   J GB6A   OGB6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J60_61      5.7661   J GB6B   OGB6     STAT=Y  PRED= 4.300 RANGE= 3.000
 JDMSO1      1.7939   J DMSO   DMSOD1   STAT=Y  PRED= 1.700 RANGE= 0.050
 JDMSO1      1.7939   J DMSO   DMSOD2   STAT=Y  PRED= 1.700 RANGE= 0.050

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)
   600.12701400 =  FIELD(1H,MHz), used to transform shifts to ppms
    22.47832099 =  Left frequency (ppm)
    -7.49157654 =  Right frequency (ppm)
         0.000 =  Acquisition time (s, for QMTLS)
         1.054 =  Line-width (for modes D, P & T, 0=use defaults)
    0.068609924 =  Data-point resolution (Hz)
        61.986 =  GAUSSIAN (%, 0=use default from INF)
        -5.939 =  Dispersion contribution (%, 0=use default from INF)
     0.00000000 =  Decoupling frequency (for DORES)

CONSTRAINTS (in equations X0 = 1.0)...use no empty lines
 EQUAL DMSOD1   = DMSOD2
  1.000 * 1.0 = -41.020 * 1.0  - 1.000 * 1.0
  10.000 * 1.0 = -38.340 * 1.0  - 1.000 * 1.0
  11.000 * 1.0 = -16.670 * 1.0  - 1.000 * 1.0
  12.000 * 1.0 = -36.870 * 1.0  - 1.000 * 1.0
  13.000 * 1.0 = -80.200 * 1.0  - 1.000 * 1.0
  14.000 * 1.0 = -49.010 * 1.0  - 1.000 * 1.0
  15.000 * 1.0 = -48.090 * 1.0  - 1.000 * 1.0
  16.0 * 1.0 = -153.1 * 1.0  - 1.0 * 1.0
  17.0 * 1.0 = -104.2 * 1.0  - 1.0 * 1.0
  18.000 * 1.0 = -28.210 * 1.0  - 1.000 * 1.0
  19.0 * 1.0 = -185.4 * 1.0  - 1.0 * 1.0
  2.000 * 1.0 = -19.040 * 1.0  - 1.000 * 1.0
  20.000 * 1.0 = -14.770 * 1.0  - 1.000 * 1.0
  3.000 * 1.0 = -37.520 * 1.0  - 1.000 * 1.0
  4.000 * 1.0 = -43.240 * 1.0  - 1.000 * 1.0
  5.000 * 1.0 = -55.060 * 1.0  - 1.000 * 1.0
  6.000 * 1.0 = -21.840 * 1.0  - 1.000 * 1.0
  7.000 * 1.0 = -40.820 * 1.0  - 1.000 * 1.0
  8.000 * 1.0 = -42.640 * 1.0  - 1.000 * 1.0
  9.000 * 1.0 = -55.850 * 1.0  - 1.000 * 1.0

END of FILE
```

S4. The ^{1}H fingerprint of rubusoside (**2**) in DMSO-d_6 (21 mM, 600 MHz, 298 K). The calculated and observed NMR spectra are shown in red and blue, respectively.

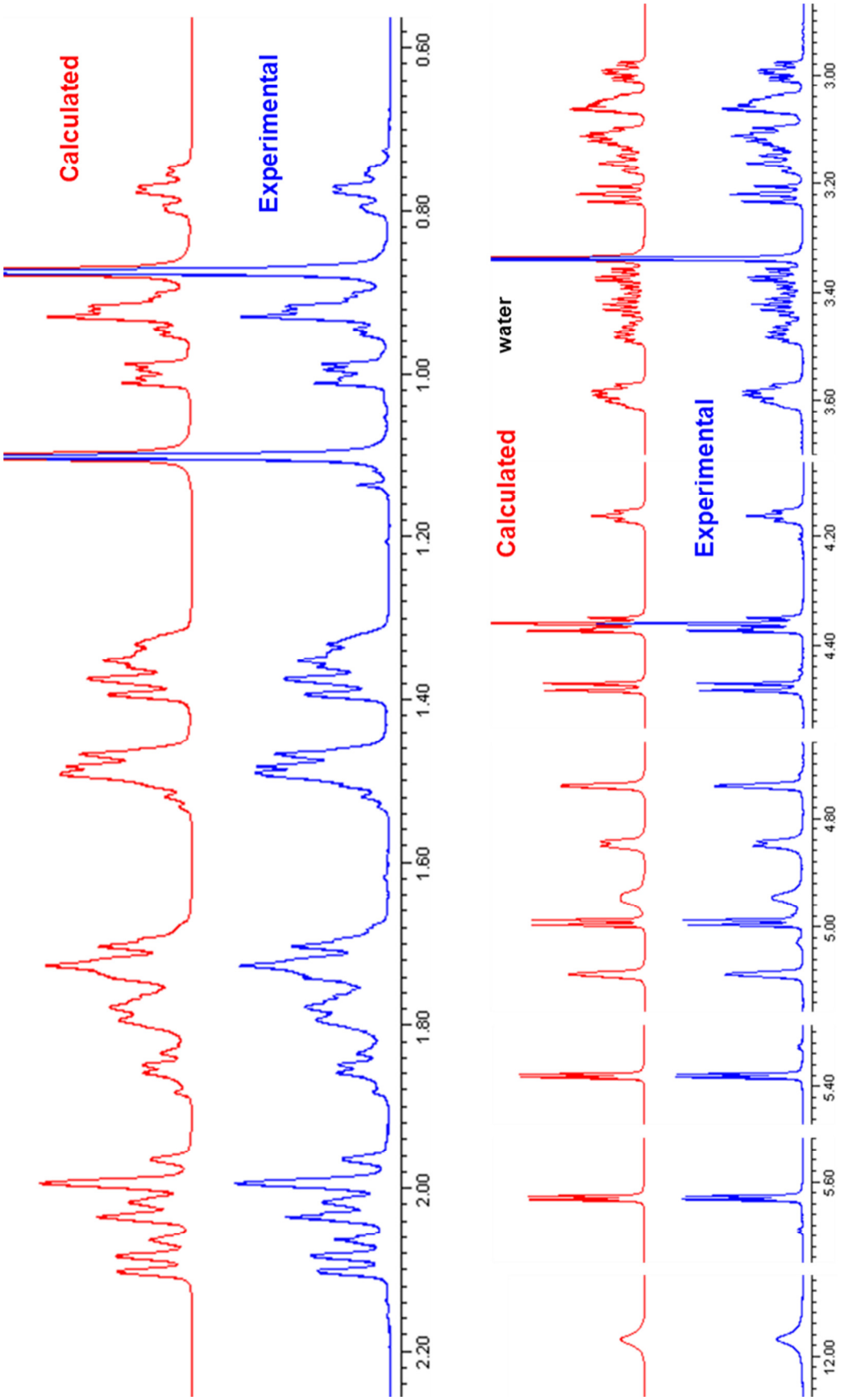


S5. The HiFSA profile of steviolbioside (**3**) in DMSO-d_6 [in PERCH parameter (.pms) file format].

```
* 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: c:\HIFSA\Stevia\Steviolbioside
#$œ  Date 10.10.2014;  Time 21:40:59     stbioside.pms

CHEMICAL SHIFTS(PPM):
PROTON    2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.07934
 H1A   / 1     0.773484  1*1*1  STAT=Y  PRED= 0.779 RANGE= 0.050 WIDTH(Y)= 3.942 RESP(Y)= 0.9579 HSQC= C1
 H1B   / 1     1.785719  1*1*1  STAT=Y  PRED= 1.778 RANGE= 0.050 WIDTH(Y)= 3.999 RESP(Y)= 0.9901 HSQC= C1
 H2A   / 1     1.773902  1*1*1  STAT=Y  PRED= 1.764 RANGE= 0.050 WIDTH(Y)= 3.926 RESP(Y)= 0.9034 HSQC= C2
 H2B   / 1     1.338300  1*1*1  STAT=Y  PRED= 1.332 RANGE= 0.050 WIDTH(Y)= 2.997 RESP(Y)= 0.9269 HSQC= C2
 H3A   / 1     2.005316  1*1*1  STAT=Y  PRED= 2.000 RANGE= 0.050 WIDTH(Y)= 3.037 RESP(Y)= 0.9312 HSQC= C3
 H3B   / 1     0.925708  1*1*1  STAT=Y  PRED= 0.932 RANGE= 0.050 WIDTH(Y)= 3.240 RESP(Y)= 0.9292 HSQC= C3
 H5A   / 1     0.999349  1*1*1  STAT=Y  PRED= 1.015 RANGE= 0.050 WIDTH(Y)= 3.142 RESP(Y)= 0.9664 HSQC= C5
 H6A   / 1     1.714163  1*1*1  STAT=Y  PRED= 1.700 RANGE= 0.050 WIDTH(Y)= 4.661 RESP(Y)= 0.9192 HSQC= C6
 H6B   / 1     1.735628  1*1*1  STAT=Y  PRED= 1.737 RANGE= 0.050 WIDTH(Y)= 4.631 RESP(Y)= 0.9360 HSQC= C6
 H7A   / 1     1.356818  1*1*1  STAT=Y  PRED= 1.360 RANGE= 0.050 WIDTH(Y)= 3.867 RESP(Y)= 0.9031 HSQC= C7
 H7B   / 1     1.476010  1*1*1  STAT=Y  PRED= 1.449 RANGE= 0.050 WIDTH(Y)= 3.866 RESP(Y)= 0.9915 HSQC= C7
 H9A   / 1     0.922105  1*1*1  STAT=Y  PRED= 0.921 RANGE= 0.050 WIDTH(Y)= 3.918 RESP(Y)= 0.9761 HSQC= C9
 H11A  / 1     1.708713  1*1*1  STAT=Y  PRED= 1.651 RANGE= 0.050 WIDTH(Y)= 4.106 RESP(Y)= 0.9509 HSQC= C11
 H11B  / 1     1.495189  1*1*1  STAT=Y  PRED= 1.429 RANGE= 0.050 WIDTH(Y)= 4.091 RESP(Y)= 0.9007 HSQC= C11
 H12A  / 1     1.485211  1*1*1  STAT=Y  PRED= 1.348 RANGE= 0.025 WIDTH(Y)= 3.898 RESP(Y)= 1.0000 HSQC= C12
 H12B  / 1     1.852108  1*1*1  STAT=Y  PRED= 1.599 RANGE= 0.050 WIDTH(Y)= 3.801 RESP(Y)= 0.9451 HSQC= C12
 H14A  / 1     2.092207  1*1*1  STAT=Y  PRED= 1.869 RANGE= 0.455 WIDTH(Y)= 3.957 RESP(Y)= 0.9685 HSQC= C14
 H14B  / 1     1.383991  1*1*1  STAT=Y  PRED= 1.192 RANGE= 0.050 WIDTH(Y)= 3.678 RESP(Y)= 0.9764 HSQC= C14
 H15A  / 1     1.981506  1*1*1  STAT=Y  PRED= 2.023 RANGE= 0.050 WIDTH(Y)= 4.297 RESP(Y)= 0.9421 HSQC= C15
 H15B  / 1     2.045497  1*1*1  STAT=Y  PRED= 2.052 RANGE= 0.050 WIDTH(Y)= 3.345 RESP(Y)= 0.9264 HSQC= C15
 H17A  / 1     5.085833  1*1*1  STAT=Y  PRED= 4.878 RANGE= 0.025 WIDTH(Y)= 3.167 RESP(Y)= 0.9638 HSQC= C17
 H17B  / 1     4.738841  1*1*1  STAT=Y  PRED= 4.687 RANGE= 0.025 WIDTH(Y)= 3.373 RESP(Y)= 0.9720 HSQC= C17
 H18B  / 1     1.100806  1*1*3  STAT=Y  PRED= 1.101 RANGE= 0.050 WIDTH(Y)= 2.608 RESP(Y)= 0.9314 HSQC= C18
 H20B  / 1     0.873701  1*1*3  STAT=Y  PRED= 0.866 RANGE= 0.050 WIDTH(Y)= 3.031 RESP(Y)= 0.9416 HSQC= C20
 H22A  / 1    11.968541  1*1*1  STAT=Y  PRED= 11.981 RANGE= 0.050 WIDTH(Y)= 13.870 RESP(Y)= 0.7926
 GB1   / 1     4.476335  1*1*1  STAT=Y  PRED= 5.565 RANGE= 0.342 WIDTH(Y)= 1.934 RESP(Y)= 0.9078 HSQC= H21
 GB2   / 1     3.218335  1*1*1  STAT=Y  PRED= 3.526 RANGE= 0.200 WIDTH(Y)= 1.888 RESP(Y)= 0.9171 HSQC= C23
 GB3   / 1     3.373393  1*1*1  STAT=Y  PRED= 3.317 RANGE= 0.155 WIDTH(Y)= 1.749 RESP(Y)= 0.8548 HSQC= C26
 GB4   / 1     3.115594  1*1*1  STAT=Y  PRED= 3.387 RANGE= 0.287 WIDTH(Y)= 2.138 RESP(Y)= 0.8374 HSQC= C27
 GB5   / 1     3.049840  1*1*1  STAT=Y  PRED= 3.485 RANGE= 0.247 WIDTH(Y)= 1.675 RESP(Y)= 0.8314 HSQC= C25
 GB6A  / 1     3.421340  1*1*1  STAT=Y  PRED= 3.351 RANGE= 0.450 WIDTH(Y)= 2.189 RESP(Y)= 0.8318 HSQC= C29
 GB6B  / 1     3.584396  1*1*1  STAT=Y  PRED= 3.509 RANGE= 0.232 WIDTH(Y)= 2.147 RESP(Y)= 0.8536 HSQC= C29
 OGB3  / 1     5.628372  1*1*1  STAT=Y  PRED= 4.296 RANGE= 1.420 WIDTH(Y)= 1.678 RESP(Y)= 0.8798
 OGB4  / 1     4.991140  1*1*1  STAT=Y  PRED= 4.702 RANGE= 1.565 WIDTH(Y)= 1.664 RESP(Y)= 0.8679
 OGB6  / 1     4.358285  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 1.773 RESP(Y)= 0.8978
 GC1   / 1     4.365661  1*1*1  STAT=Y  PRED= 5.565 RANGE= 0.342 WIDTH(Y)= 1.705 RESP(Y)= 0.9078 HSQC= H21
 GC2   / 1     2.992140  1*1*1  STAT=Y  PRED= 3.526 RANGE= 0.200 WIDTH(Y)= 1.771 RESP(Y)= 0.9171 HSQC= C23
 GC3   / 1     3.161501  1*1*1  STAT=Y  PRED= 3.317 RANGE= 0.155 WIDTH(Y)= 2.500 RESP(Y)= 0.8548 HSQC= C26
 GC4   / 1     3.115303  1*1*1  STAT=Y  PRED= 3.387 RANGE= 0.287 WIDTH(Y)= 3.989 RESP(Y)= 0.8374 HSQC= C27
 GC5   / 1     3.055040  1*1*1  STAT=Y  PRED= 3.485 RANGE= 0.247 WIDTH(Y)= 1.715 RESP(Y)= 0.8314 HSQC= C25
 GC6A  / 1     3.472896  1*1*1  STAT=Y  PRED= 3.351 RANGE= 0.450 WIDTH(Y)= 2.776 RESP(Y)= 0.8318 HSQC= C29
 GC6B  / 1     3.595517  1*1*1  STAT=Y  PRED= 3.509 RANGE= 0.232 WIDTH(Y)= 2.394 RESP(Y)= 0.8536 HSQC= C29
 OGC2  / 1     5.380007  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 1.594 RESP(Y)= 0.8978
 OGC3  / 1     4.945101  1*1*1  STAT=Y  PRED= 4.296 RANGE= 1.420 WIDTH(Y)= 10.140 RESP(Y)= 0.8798
 OGC4  / 1     4.846038  1*1*1  STAT=Y  PRED= 4.702 RANGE= 1.565 WIDTH(Y)= 4.627 RESP(Y)= 0.8679
 OGC6  / 1     4.161324  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 3.522 RESP(Y)= 0.8978
DMSO_CH   2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.76526
 DMSO  / 2     2.500023  1*1*1  STAT=Y  PRED= 2.500 RANGE= 0.050 WIDTH(Y)= 1.305 RESP(Y)= 1.0000
DMSO_D    2*SPIN= 2 SPECIES=2D    POPULATION(Y)=   0.76526
 DMSOD1/ 2  -100.000001  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
 DMSOD2/ 2  -100.000001  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
WATER_H   2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.15540
 WATER / 3     3.337174  2*1*1  STAT=Y  PRED= 3.338 RANGE= 0.050 WIDTH(Y)= 1.395 RESP(Y)= 1.0000

COUPLING CONSTANTS(HZ):
 J12_13    -12.6475   J H1A    H1B      STAT=Y  PRED= -13.130 RANGE= 1.500
 J17_12     13.6691   J H1A    H2A      STAT=Y  PRED= 12.550 RANGE= 2.560
 J12_18      4.4431   J H1A    H2B      STAT=Y  PRED= 4.380 RANGE= 3.800
 J14_12     -0.0592   J H1A    H20B     STAT=Y  PRED= -0.790 RANGE= 0.400
 J17_13      4.0016   J H1B    H2A      STAT=Y  PRED= 3.880 RANGE= 3.800
 J13_18      2.4597   J H1B    H2B      STAT=Y  PRED= 2.510 RANGE= 2.800
 J13_19      1.2827   J H1B    H3A      STAT=Y  PRED= 2.850 RANGE= 1.280
 J17_18    -13.3639   J H2A    H2B      STAT=Y  PRED= -13.190 RANGE= 1.500
 J17_19      3.5753   J H2A    H3A      STAT=Y  PRED= 3.860 RANGE= 3.800
 J17_20     13.3956   J H2A    H3B      STAT=Y  PRED= 12.570 RANGE= 2.560
 J19_18      2.8951   J H2B    H3A      STAT=Y  PRED= 2.530 RANGE= 2.800
 J20_18      4.3377   J H2B    H3B      STAT=Y  PRED= 4.310 RANGE= 3.800
 J19_20    -13.2039   J H3A    H3B      STAT=Y  PRED= -13.110 RANGE= 1.500
 J21_22     11.7402   J H5A    H6A      STAT=Y  PRED= 12.550 RANGE= 2.560
 J21_23      2.4962   J H5A    H6B      STAT=Y  PRED= 1.710 RANGE= 2.800
 J22_23    -14.0207   J H6A    H6B      STAT=Y  PRED= -13.190 RANGE= 1.500
 J22_24     13.4288   J H6A    H7A      STAT=Y  PRED= 12.990 RANGE= 2.560
 J22_25      3.3044   J H6A    H7B      STAT=Y  PRED= 3.320 RANGE= 3.800
 J23_24      3.9790   J H6B    H7A      STAT=Y  PRED= 3.410 RANGE= 3.800
```

```
 J23_25      3.3795   J H6B    H7B      STAT=Y  PRED= 3.190 RANGE= 3.800
 J24_25    -12.7987   J H7A    H7B      STAT=Y  PRED= -13.130 RANGE= 1.500
 J26_1       0.2816   J H9A    H11A     STAT=Y  PRED= 0.490 RANGE= 2.800
 J26_2       8.4095   J H9A    H11B     STAT=Y  PRED= 9.030 RANGE= 3.580
 J26_6       0.7262   J H9A    H14B     STAT=Y  PRED= 2.290 RANGE= 1.100
 J1_2      -15.0638   J H11A   H11B     STAT=Y  PRED= -13.010 RANGE= 1.500
 J3_1        1.4968   J H11A   H12A     STAT=Y  PRED= 1.040 RANGE= 2.800
 J4_1        6.1771   J H11A   H12B     STAT=Y  PRED= 6.480 RANGE= 3.800
 J3_2        6.8540   J H11B   H12A     STAT=Y  PRED= 6.890 RANGE= 3.800
 J4_2       13.5666   J H11B   H12B     STAT=Y  PRED= 11.180 RANGE= 2.800
 J3_4      -11.5390   J H12A   H12B     STAT=Y  PRED= -12.880 RANGE= 1.500
 J3_6        2.4311   J H12A   H14B     STAT=Y  PRED= 2.670 RANGE= 1.280
 J5_6      -11.3584   J H14A   H14B     STAT=Y  PRED= -12.450 RANGE= 2.000
 J7_5        2.5079   J H14A   H15A     STAT=Y  PRED= 1.650 RANGE= 1.280
 J7_8      -16.9773   J H15A   H15B     STAT=Y  PRED= -14.390 RANGE= 3.000
 J7_9       -1.6991   J H15A   H17A     STAT=Y  PRED= -2.030 RANGE= 1.000
 J7_10      -0.0344   J H15A   H17B     STAT=Y  PRED= -1.900 RANGE= 0.950
 J9_8       -2.9622   J H15B   H17A     STAT=Y  PRED= -2.420 RANGE= 1.200
 J10_8      -2.4830   J H15B   H17B     STAT=Y  PRED= -2.140 RANGE= 1.100
 J9_10       0.3184   J H17A   H17B     STAT=Y  PRED= 2.980 RANGE= 4.000
 J48_50      7.7027   J GB1    GB2      STAT=Y  PRED= 7.190 RANGE= 3.580
 J50_53      9.2232   J GB2    GB3      STAT=Y  PRED= 8.920 RANGE= 3.580
 J53_56      8.7747   J GB3    GB4      STAT=Y  PRED= 9.140 RANGE= 3.580
 J53_61      3.6786   J GB3    OGB3     STAT=Y  PRED= 4.300 RANGE= 1.000
 J51_56      9.6618   J GB4    GB5      STAT=Y  PRED= 10.550 RANGE= 2.560
 J56_62      5.6305   J GB4    OGB4     STAT=Y  PRED= 4.300 RANGE= 1.000
 J51_59      5.5281   J GB5    GB6A     STAT=Y  PRED= 2.700 RANGE= 3.000
 J51_60      2.3008   J GB5    GB6B     STAT=Y  PRED= 1.280 RANGE= 3.000
 J59_60    -11.6534   J GB6A   GB6B     STAT=Y  PRED= -12.300 RANGE= 0.800
 J59_61      6.2549   J GB6A   OGB6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J60_61      5.5488   J GB6B   OGB6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J58_60      7.7985   J GC1    GC2      STAT=Y  PRED= 7.190 RANGE= 3.580
 J60_63      9.0525   J GC2    GC3      STAT=Y  PRED= 8.920 RANGE= 3.580
 J60_68      3.3742   J GC2    OGC2     STAT=Y  PRED= 4.300 RANGE= 1.000
 J63_66      2.1457   J GC3    GC4      STAT=Y  PRED= 9.140 RANGE= 3.580
 J63_71      7.6649   J GC3    OGC3     STAT=Y  PRED= 4.300 RANGE= 1.000
 J61_66      9.3298   J GC4    GC5      STAT=Y  PRED= 10.550 RANGE= 2.560
 J66_72      5.3605   J GC4    OGC4     STAT=Y  PRED= 4.300 RANGE= 1.000
 J61_69      4.5195   J GC5    GC6A     STAT=Y  PRED= 2.700 RANGE= 3.000
 J61_70      2.5522   J GC5    GC6B     STAT=Y  PRED= 1.280 RANGE= 3.000
 J69_70    -11.3319   J GC6A   GC6B     STAT=Y  PRED= -12.300 RANGE= 0.800
 J69_71      5.9254   J GC6A   OGC6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J70_71      4.8659   J GC6B   OGC6     STAT=Y  PRED= 4.300 RANGE= 3.000
 JDMSO1      1.7939   J DMSO   DMSOD1   STAT=Y  PRED= 1.700 RANGE= 0.050
 JDMSO1      1.7939   J DMSO   DMSOD2   STAT=Y  PRED= 1.700 RANGE= 0.050

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)
   600.12701400 =  FIELD(1H,MHz), used to transform shifts to ppms
    22.47832099 =  Left frequency (ppm)
    -7.49157654 =  Right frequency (ppm)
         0.000 =  Acquisition time (s, for QMTLS)
         1.300 =  Line-width (for modes D, P & T, 0=use defaults)
    0.068609924 =  Data-point resolution (Hz)
        41.849 =  GAUSSIAN (%, 0=use default from INF)
        -2.243 =  Dispersion contribution (%, 0=use default from INF)
     0.00000000 =  Decoupling frequency (for DORES)

CONSTRAINTS (in equations X0 = 1.0)...use no empty lines
 EQUAL DMSOD1   = DMSOD2
  1.000 * 1.0 = -41.020 * 1.0  - 1.000 * 1.0
  10.000 * 1.0 = -38.340 * 1.0  - 1.000 * 1.0
  11.000 * 1.0 = -16.670 * 1.0  - 1.000 * 1.0
  12.000 * 1.0 = -36.870 * 1.0  - 1.000 * 1.0
  13.000 * 1.0 = -80.200 * 1.0  - 1.000 * 1.0
  14.000 * 1.0 = -49.010 * 1.0  - 1.000 * 1.0
  15.000 * 1.0 = -48.090 * 1.0  - 1.000 * 1.0
  16.0 * 1.0 = -153.1 * 1.0  - 1.0 * 1.0
  17.0 * 1.0 = -104.2 * 1.0  - 1.0 * 1.0
  18.000 * 1.0 = -28.210 * 1.0  - 1.000 * 1.0
  19.0 * 1.0 = -185.4 * 1.0  - 1.0 * 1.0
  2.000 * 1.0 = -19.040 * 1.0  - 1.000 * 1.0
  20.000 * 1.0 = -14.770 * 1.0  - 1.000 * 1.0
  3.000 * 1.0 = -37.520 * 1.0  - 1.000 * 1.0
  4.000 * 1.0 = -43.240 * 1.0  - 1.000 * 1.0
  5.000 * 1.0 = -55.060 * 1.0  - 1.000 * 1.0
  6.000 * 1.0 = -21.840 * 1.0  - 1.000 * 1.0
  7.000 * 1.0 = -40.820 * 1.0  - 1.000 * 1.0
  8.000 * 1.0 = -42.640 * 1.0  - 1.000 * 1.0
  9.000 * 1.0 = -55.850 * 1.0  - 1.000 * 1.0

END of FILE
```

S6. The ^{1}H fingerprint of steviolbioside (**3**) in DMSO-d_6 (20 mM, 600 MHz, 298 K). The calculated and observed NMR spectra are shown in red and blue, respectively.



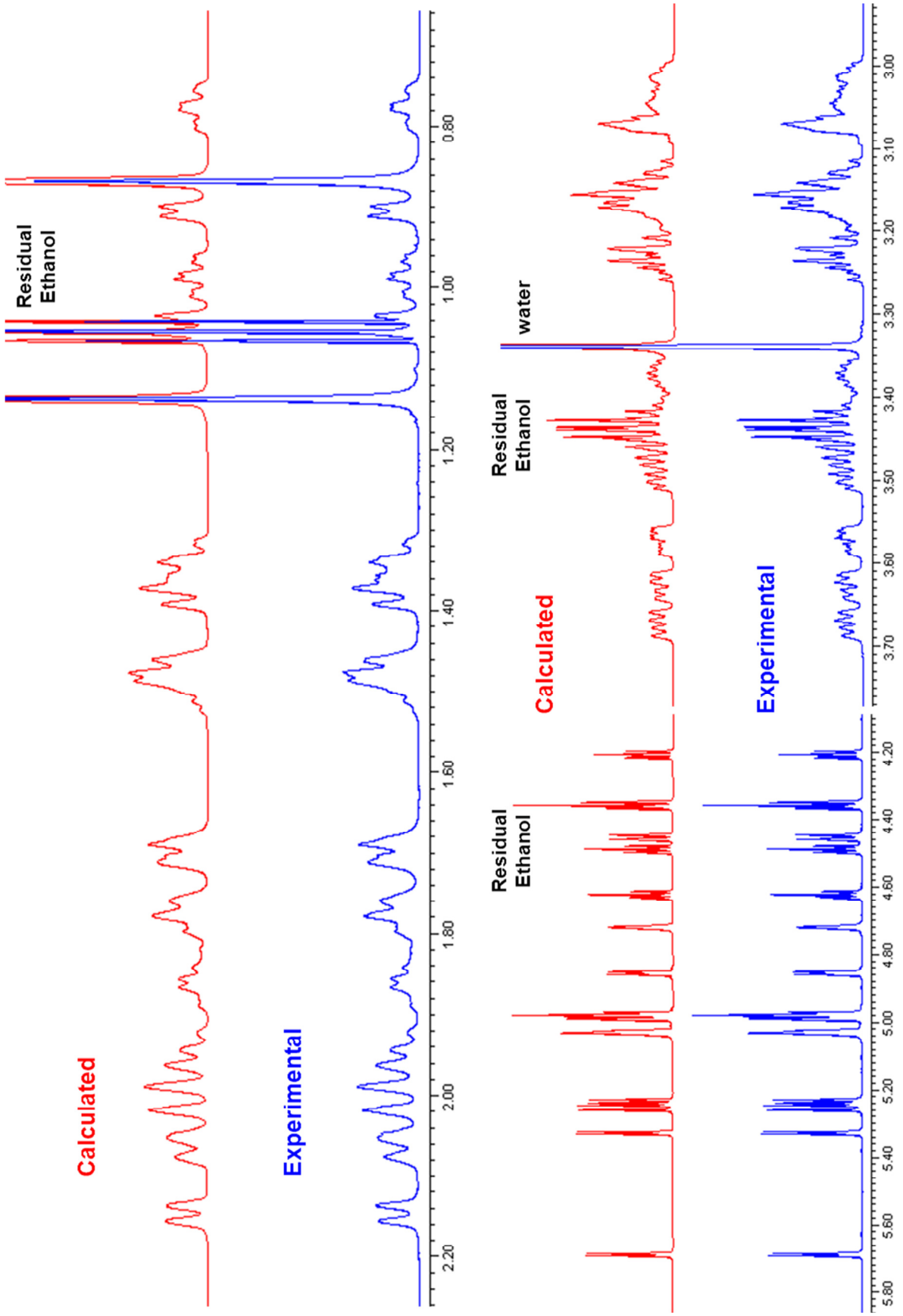
S7. The HiFSA profile of stevioside (**4**) in DMSO-d_6 [in PERCH parameter (.pms) file format].

```
* 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: c:\HIFSA\Stevia\Stevioside
#$œ  Date 10.10.2014;  Time 21:48:44     stevioside.pms

CHEMICAL SHIFTS(PPM):
PROTON    2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.04678
 H1A   / 1     0.775034  1*1*1  STAT=Y  PRED= 0.779 RANGE= 0.050 WIDTH(Y)= 4.815 RESP(Y)= 0.9579 HSQC= C1
 H1B   / 1     1.768496  1*1*1  STAT=Y  PRED= 1.778 RANGE= 0.050 WIDTH(Y)= 4.470 RESP(Y)= 0.9901 HSQC= C1
 H2A   / 1     1.784287  1*1*1  STAT=Y  PRED= 1.764 RANGE= 0.050 WIDTH(Y)= 4.116 RESP(Y)= 0.9034 HSQC= C2
 H2B   / 1     1.356217  1*1*1  STAT=Y  PRED= 1.332 RANGE= 0.050 WIDTH(Y)= 2.908 RESP(Y)= 0.9269 HSQC= C2
 H3A   / 1     2.064530  1*1*1  STAT=Y  PRED= 2.000 RANGE= 0.050 WIDTH(Y)= 3.018 RESP(Y)= 0.9312 HSQC= C3
 H3B   / 1     0.985321  1*1*1  STAT=Y  PRED= 0.932 RANGE= 0.050 WIDTH(Y)= 3.886 RESP(Y)= 0.9292 HSQC= C3
 H5A   / 1     1.043786  1*1*1  STAT=Y  PRED= 1.015 RANGE= 0.050 WIDTH(Y)= 4.749 RESP(Y)= 0.9664 HSQC= C5
 H6A   / 1     1.952114  1*1*1  STAT=Y  PRED= 1.700 RANGE= 0.050 WIDTH(Y)= 4.653 RESP(Y)= 0.9192 HSQC= C6
 H6B   / 1     1.698740  1*1*1  STAT=Y  PRED= 1.737 RANGE= 0.050 WIDTH(Y)= 4.033 RESP(Y)= 0.9360 HSQC= C6
 H7A   / 1     1.336931  1*1*1  STAT=Y  PRED= 1.360 RANGE= 0.050 WIDTH(Y)= 4.040 RESP(Y)= 0.9031 HSQC= C7
 H7B   / 1     1.467720  1*1*1  STAT=Y  PRED= 1.449 RANGE= 0.050 WIDTH(Y)= 4.421 RESP(Y)= 0.9915 HSQC= C7
 H9A   / 1     0.904152  1*1*1  STAT=Y  PRED= 0.921 RANGE= 0.050 WIDTH(Y)= 3.979 RESP(Y)= 0.9761 HSQC= C9
 H11A  / 1     1.695460  1*1*1  STAT=Y  PRED= 1.651 RANGE= 0.050 WIDTH(Y)= 3.665 RESP(Y)= 0.9509 HSQC= C11
 H11B  / 1     1.486654  1*1*1  STAT=Y  PRED= 1.429 RANGE= 0.050 WIDTH(Y)= 4.335 RESP(Y)= 0.9007 HSQC= C11
 H12A  / 1     1.480885  1*1*1  STAT=Y  PRED= 1.348 RANGE= 0.025 WIDTH(Y)= 3.872 RESP(Y)= 1.0000 HSQC= C12
 H12B  / 1     1.859577  1*1*1  STAT=Y  PRED= 1.599 RANGE= 0.050 WIDTH(Y)= 4.397 RESP(Y)= 0.9451 HSQC= C12
 H14A  / 1     2.145290  1*1*1  STAT=Y  PRED= 1.869 RANGE= 0.455 WIDTH(Y)= 4.459 RESP(Y)= 0.9685 HSQC= C14
 H14B  / 1     1.381448  1*1*1  STAT=Y  PRED= 1.192 RANGE= 0.050 WIDTH(Y)= 4.278 RESP(Y)= 0.9764 HSQC= C14
 H15A  / 1     1.977729  1*1*1  STAT=Y  PRED= 2.023 RANGE= 0.050 WIDTH(Y)= 4.473 RESP(Y)= 0.9421 HSQC= C15
 H15B  / 1     2.027777  1*1*1  STAT=Y  PRED= 2.052 RANGE= 0.050 WIDTH(Y)= 3.491 RESP(Y)= 0.9264 HSQC= C15
 H17A  / 1     5.028963  1*1*1  STAT=Y  PRED= 4.878 RANGE= 0.025 WIDTH(Y)= 3.045 RESP(Y)= 0.9638 HSQC= C17
 H17B  / 1     4.717779  1*1*1  STAT=Y  PRED= 4.687 RANGE= 0.025 WIDTH(Y)= 3.834 RESP(Y)= 0.9720 HSQC= C17
 H18B  / 1     1.135823  1*1*3  STAT=Y  PRED= 1.101 RANGE= 0.050 WIDTH(Y)= 3.257 RESP(Y)= 0.9314 HSQC= C18
 H20B  / 1     0.866757  1*1*3  STAT=Y  PRED= 0.866 RANGE= 0.050 WIDTH(Y)= 4.029 RESP(Y)= 0.9416 HSQC= C20
 GA1   / 1     5.250753  1*1*1  STAT=Y  PRED= 5.565 RANGE= 0.342 WIDTH(Y)= 1.692 RESP(Y)= 0.9078 HSQC= H21
 GA2   / 1     3.146778  1*1*1  STAT=Y  PRED= 3.526 RANGE= 0.200 WIDTH(Y)= 1.803 RESP(Y)= 0.9171 HSQC= C23
 GA3   / 1     3.237184  1*1*1  STAT=Y  PRED= 3.317 RANGE= 0.155 WIDTH(Y)= 1.970 RESP(Y)= 0.8548 HSQC= C26
 GA4   / 1     3.136206  1*1*1  STAT=Y  PRED= 3.387 RANGE= 0.287 WIDTH(Y)= 1.797 RESP(Y)= 0.8374 HSQC= C27
 GA5   / 1     3.182600  1*1*1  STAT=Y  PRED= 3.485 RANGE= 0.247 WIDTH(Y)= 2.811 RESP(Y)= 0.8314 HSQC= C25
 GA6A  / 1     3.461519  1*1*1  STAT=Y  PRED= 3.351 RANGE= 0.450 WIDTH(Y)= 2.385 RESP(Y)= 0.8318 HSQC= C29
 GA6B  / 1     3.626204  1*1*1  STAT=Y  PRED= 3.509 RANGE= 0.232 WIDTH(Y)= 2.319 RESP(Y)= 0.8536 HSQC= C29
 OGA2  / 1     5.231801  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 1.882 RESP(Y)= 0.8978
 OGA3  / 1     4.984790  1*1*1  STAT=Y  PRED= 4.296 RANGE= 1.420 WIDTH(Y)= 1.574 RESP(Y)= 0.8798
 OGA4  / 1     4.981474  1*1*1  STAT=Y  PRED= 4.702 RANGE= 1.565 WIDTH(Y)= 1.531 RESP(Y)= 0.8679
 OGA6  / 1     4.486798  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 1.671 RESP(Y)= 0.8978
 GB1   / 1     4.451005  1*1*1  STAT=Y  PRED= 5.565 RANGE= 0.342 WIDTH(Y)= 2.560 RESP(Y)= 0.9078 HSQC= H21
 GB2   / 1     3.221604  1*1*1  STAT=Y  PRED= 3.526 RANGE= 0.200 WIDTH(Y)= 2.435 RESP(Y)= 0.9171 HSQC= C23
 GB3   / 1     3.372479  1*1*1  STAT=Y  PRED= 3.317 RANGE= 0.155 WIDTH(Y)= 2.075 RESP(Y)= 0.8548 HSQC= C26
 GB4   / 1     3.069309  1*1*1  STAT=Y  PRED= 3.387 RANGE= 0.287 WIDTH(Y)= 1.708 RESP(Y)= 0.8374 HSQC= C27
 GB5   / 1     3.070793  1*1*1  STAT=Y  PRED= 3.485 RANGE= 0.247 WIDTH(Y)= 1.821 RESP(Y)= 0.8314 HSQC= C25
 GB6A  / 1     3.417849  1*1*1  STAT=Y  PRED= 3.351 RANGE= 0.450 WIDTH(Y)= 2.276 RESP(Y)= 0.8318 HSQC= C29
 GB6B  / 1     3.671891  1*1*1  STAT=Y  PRED= 3.509 RANGE= 0.232 WIDTH(Y)= 2.813 RESP(Y)= 0.8536 HSQC= C29
 OGB3  / 1     5.687464  1*1*1  STAT=Y  PRED= 4.296 RANGE= 1.420 WIDTH(Y)= 1.818 RESP(Y)= 0.8798
 OGB4  / 1     5.024774  1*1*1  STAT=Y  PRED= 4.702 RANGE= 1.565 WIDTH(Y)= 1.748 RESP(Y)= 0.8679
 OGB6  / 1     4.620924  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 1.883 RESP(Y)= 0.8978
 GC1   / 1     4.351810  1*1*1  STAT=Y  PRED= 5.565 RANGE= 0.342 WIDTH(Y)= 2.155 RESP(Y)= 0.9078 HSQC= H21
 GC2   / 1     3.014400  1*1*1  STAT=Y  PRED= 3.526 RANGE= 0.200 WIDTH(Y)= 2.507 RESP(Y)= 0.9171 HSQC= C23
 GC3   / 1     3.162714  1*1*1  STAT=Y  PRED= 3.317 RANGE= 0.155 WIDTH(Y)= 1.137 RESP(Y)= 0.8548 HSQC= C26
 GC4   / 1     3.162017  1*1*1  STAT=Y  PRED= 3.387 RANGE= 0.287 WIDTH(Y)= 3.848 RESP(Y)= 0.8374 HSQC= C27
 GC5   / 1     3.043839  1*1*1  STAT=Y  PRED= 3.485 RANGE= 0.247 WIDTH(Y)= 2.130 RESP(Y)= 0.8314 HSQC= C25
 GC6A  / 1     3.491978  1*1*1  STAT=Y  PRED= 3.351 RANGE= 0.450 WIDTH(Y)= 2.516 RESP(Y)= 0.8318 HSQC= C29
 GC6B  / 1     3.570773  1*1*1  STAT=Y  PRED= 3.509 RANGE= 0.232 WIDTH(Y)= 2.280 RESP(Y)= 0.8536 HSQC= C29
 OGC2  / 1     5.325737  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 1.680 RESP(Y)= 0.8978
 OGC3  / 1     4.972581  1*1*1  STAT=Y  PRED= 4.296 RANGE= 1.420 WIDTH(Y)= 1.599 RESP(Y)= 0.8798
 OGC4  / 1     4.854051  1*1*1  STAT=Y  PRED= 4.702 RANGE= 1.565 WIDTH(Y)= 1.610 RESP(Y)= 0.8679
 OGC6  / 1     4.204299  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 1.697 RESP(Y)= 0.8978
DMSO_CH   2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.70808
 DMSO  / 2     2.499910  1*1*1  STAT=Y  PRED= 2.500 RANGE= 0.050 WIDTH(Y)= 1.448 RESP(Y)= 1.0000
DMSO_D    2*SPIN= 2 SPECIES=2D    POPULATION(Y)=   0.70808
 DMSOD1/ 2  -100.000001  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
 DMSOD2/ 2  -100.000001  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
WATER_H   2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.20394
 WATER / 3     3.337022  2*1*1  STAT=Y  PRED= 3.338 RANGE= 0.050 WIDTH(Y)= 1.273 RESP(Y)= 1.0000
ETOH_H    2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.04120
 ETOH1 / 4     1.052240  1*1*3  STAT=Y  PRED= 1.060 RANGE= 0.050 WIDTH(Y)= 1.055 RESP(Y)= 1.0000
 ETOH2 / 4     3.436666  1*1*2  STAT=Y  PRED= 3.440 RANGE= 0.050 WIDTH(Y)= 1.124 RESP(Y)= 1.0000
 ETOH3 / 4     4.356153  1*1*1  STAT=Y  PRED= 4.630 RANGE= 0.050 WIDTH(Y)= 1.223 RESP(Y)= 1.0000

COUPLING CONSTANTS(HZ):
 J12_13    -12.4926   J H1A    H1B      STAT=Y  PRED= -13.130 RANGE= 1.500
 J17_12     13.5669   J H1A    H2A      STAT=Y  PRED= 12.550 RANGE= 2.560
 J12_18      4.8980   J H1A    H2B      STAT=Y  PRED= 4.380 RANGE= 3.800
 J14_12     -0.2246   J H1A    H20B     STAT=Y  PRED= -0.790 RANGE= 0.400
 J17_13      3.5672   J H1B    H2A      STAT=Y  PRED= 3.880 RANGE= 3.800
```

```
 J13_18      2.9789   J H1B    H2B      STAT=Y  PRED= 2.510 RANGE= 2.800
 J13_19      3.0597   J H1B    H3A      STAT=Y  PRED= 2.850 RANGE= 1.280
 J17_18    -13.2543   J H2A    H2B      STAT=Y  PRED= -13.190 RANGE= 1.500
 J17_19      4.1862   J H2A    H3A      STAT=Y  PRED= 3.860 RANGE= 3.800
 J17_20     13.3366   J H2A    H3B      STAT=Y  PRED= 12.570 RANGE= 2.560
 J19_18      1.9110   J H2B    H3A      STAT=Y  PRED= 2.530 RANGE= 2.800
 J20_18      4.6637   J H2B    H3B      STAT=Y  PRED= 4.310 RANGE= 3.800
 J19_20    -12.7457   J H3A    H3B      STAT=Y  PRED= -13.110 RANGE= 1.500
 J21_22     12.3404   J H5A    H6A      STAT=Y  PRED= 12.550 RANGE= 2.560
 J21_23      0.3329   J H5A    H6B      STAT=Y  PRED= 1.710 RANGE= 2.800
 J22_23    -11.7131   J H6A    H6B      STAT=Y  PRED= -13.190 RANGE= 1.500
 J22_24     13.4465   J H6A    H7A      STAT=Y  PRED= 12.990 RANGE= 2.560
 J22_25      3.3735   J H6A    H7B      STAT=Y  PRED= 3.320 RANGE= 3.800
 J23_24      4.0671   J H6B    H7A      STAT=Y  PRED= 3.410 RANGE= 3.800
 J23_25      3.6995   J H6B    H7B      STAT=Y  PRED= 3.190 RANGE= 3.800
 J24_25    -12.1329   J H7A    H7B      STAT=Y  PRED= -13.130 RANGE= 1.500
 J26_1       1.2681   J H9A    H11A     STAT=Y  PRED= 0.490 RANGE= 2.800
 J26_2       8.1166   J H9A    H11B     STAT=Y  PRED= 9.030 RANGE= 3.580
 J26_6       1.9535   J H9A    H14B     STAT=Y  PRED= 2.290 RANGE= 1.100
 J1_2      -16.3851   J H11A   H11B     STAT=Y  PRED= -13.010 RANGE= 1.500
 J3_1        3.6498   J H11A   H12A     STAT=Y  PRED= 1.040 RANGE= 2.800
 J4_1        6.1079   J H11A   H12B     STAT=Y  PRED= 6.480 RANGE= 3.800
 J3_2        5.9042   J H11B   H12A     STAT=Y  PRED= 6.890 RANGE= 3.800
 J4_2       12.9223   J H11B   H12B     STAT=Y  PRED= 11.180 RANGE= 2.800
 J3_4      -11.1993   J H12A   H12B     STAT=Y  PRED= -12.880 RANGE= 1.500
 J3_6        2.5663   J H12A   H14B     STAT=Y  PRED= 2.670 RANGE= 1.280
 J5_6      -11.4538   J H14A   H14B     STAT=Y  PRED= -12.450 RANGE= 2.000
 J7_5        3.2644   J H14A   H15A     STAT=Y  PRED= 1.650 RANGE= 1.280
 J7_8      -16.9188   J H15A   H15B     STAT=Y  PRED= -14.390 RANGE= 3.000
 J7_9       -2.0662   J H15A   H17A     STAT=Y  PRED= -2.030 RANGE= 1.000
 J7_10      -0.1080   J H15A   H17B     STAT=Y  PRED= -1.900 RANGE= 0.950
 J9_8       -3.4501   J H15B   H17A     STAT=Y  PRED= -2.420 RANGE= 1.200
 J10_8      -2.7208   J H15B   H17B     STAT=Y  PRED= -2.140 RANGE= 1.100
 J9_10       0.6170   J H17A   H17B     STAT=Y  PRED= 2.980 RANGE= 4.000
 J38_40      8.2096   J GA1    GA2      STAT=Y  PRED= 7.190 RANGE= 3.580
 J40_43      9.0146   J GA2    GA3      STAT=Y  PRED= 8.920 RANGE= 3.580
 J40_48      5.9447   J GA2    OGA2     STAT=Y  PRED= 4.300 RANGE= 1.000
 J43_46      8.8753   J GA3    GA4      STAT=Y  PRED= 9.140 RANGE= 3.580
 J43_51      5.3639   J GA3    OGA3     STAT=Y  PRED= 4.300 RANGE= 1.000
 J41_46      9.8245   J GA4    GA5      STAT=Y  PRED= 10.550 RANGE= 2.560
 J46_52      5.4682   J GA4    OGA4     STAT=Y  PRED= 4.300 RANGE= 1.000
 J41_49      4.9747   J GA5    GA6A     STAT=Y  PRED= 2.700 RANGE= 3.000
 J41_50      2.0809   J GA5    GA6B     STAT=Y  PRED= 1.280 RANGE= 3.000
 J49_50    -11.8162   J GA6A   GA6B     STAT=Y  PRED= -12.300 RANGE= 0.800
 J49_51      5.9130   J GA6A   OGA6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J50_51      5.3363   J GA6B   OGA6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J48_50      7.6636   J GB1    GB2      STAT=Y  PRED= 7.190 RANGE= 3.580
 J50_53      9.2253   J GB2    GB3      STAT=Y  PRED= 8.920 RANGE= 3.580
 J53_56      8.4017   J GB3    GB4      STAT=Y  PRED= 9.140 RANGE= 3.580
 J53_61      3.6005   J GB3    OGB3     STAT=Y  PRED= 4.300 RANGE= 1.000
 J51_56      8.9549   J GB4    GB5      STAT=Y  PRED= 10.550 RANGE= 2.560
 J56_62      5.6759   J GB4    OGB4     STAT=Y  PRED= 4.300 RANGE= 1.000
 J51_59      6.1065   J GB5    GB6A     STAT=Y  PRED= 2.700 RANGE= 3.000
 J51_60      2.0457   J GB5    GB6B     STAT=Y  PRED= 1.280 RANGE= 3.000
 J59_60    -11.5565   J GB6A   GB6B     STAT=Y  PRED= -12.300 RANGE= 0.800
 J59_61      5.9626   J GB6A   OGB6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J60_61      5.7723   J GB6B   OGB6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J58_60      7.7309   J GC1    GC2      STAT=Y  PRED= 7.190 RANGE= 3.580
 J60_63      9.2744   J GC2    GC3      STAT=Y  PRED= 8.920 RANGE= 3.580
 J60_68      3.2533   J GC2    OGC2     STAT=Y  PRED= 4.300 RANGE= 1.000
 J63_66      7.8765   J GC3    GC4      STAT=Y  PRED= 9.140 RANGE= 3.580
 J63_71      4.7796   J GC3    OGC3     STAT=Y  PRED= 4.300 RANGE= 1.000
 J61_66      8.7523   J GC4    GC5      STAT=Y  PRED= 10.550 RANGE= 2.560
 J66_72      5.3220   J GC4    OGC4     STAT=Y  PRED= 4.300 RANGE= 1.000
 J61_69      4.3097   J GC5    GC6A     STAT=Y  PRED= 2.700 RANGE= 3.000
 J61_70      2.4397   J GC5    GC6B     STAT=Y  PRED= 1.280 RANGE= 3.000
 J69_70    -11.2927   J GC6A   GC6B     STAT=Y  PRED= -12.300 RANGE= 0.800
 J69_71      6.1015   J GC6A   OGC6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J70_71      5.2400   J GC6B   OGC6     STAT=Y  PRED= 4.300 RANGE= 3.000
 JDMSO1      1.7939   J DMSO   DMSOD1   STAT=Y  PRED= 1.700 RANGE= 0.050
 JDMSO1      1.7939   J DMSO   DMSOD2   STAT=Y  PRED= 1.700 RANGE= 0.050
 JETOH1      7.0000   J ETOH1  ETOH2    STAT=Y  PRED= 7.000 RANGE= 0.050
 JETOH2      5.0561   J ETOH2  ETOH3    STAT=Y  PRED= 5.000 RANGE= 0.050

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)
   600.12701400 =  FIELD(1H,MHz), used to transform shifts to ppms
    22.47832099 =  Left frequency (ppm)
    -7.49157654 =  Right frequency (ppm)
         0.000 =  Acquisition time (s, for QMTLS)
         1.057 =  Line-width (for modes D, P & T, 0=use defaults)
    0.068609924 =  Data-point resolution (Hz)
        76.574 =  GAUSSIAN (%, 0=use default from INF)
         9.224 =  Dispersion contribution (%, 0=use default from INF)
```

```
    0.00000000 =  Decoupling frequency (for DORES)

CONSTRAINTS (in equations X0 = 1.0)...use no empty lines
 EQUAL DMSOD1   = DMSOD2
  1.000 * 1.0 = -41.020 * 1.0  - 1.000 * 1.0
  10.000 * 1.0 = -38.340 * 1.0  - 1.000 * 1.0
  11.000 * 1.0 = -16.670 * 1.0  - 1.000 * 1.0
  12.000 * 1.0 = -36.870 * 1.0  - 1.000 * 1.0
  13.000 * 1.0 = -80.200 * 1.0  - 1.000 * 1.0
  14.000 * 1.0 = -49.010 * 1.0  - 1.000 * 1.0
  15.000 * 1.0 = -48.090 * 1.0  - 1.000 * 1.0
  16.0 * 1.0 = -153.1 * 1.0  - 1.0 * 1.0
  17.0 * 1.0 = -104.2 * 1.0  - 1.0 * 1.0
  18.000 * 1.0 = -28.210 * 1.0  - 1.000 * 1.0
  19.0 * 1.0 = -185.4 * 1.0  - 1.0 * 1.0
  2.000 * 1.0 = -19.040 * 1.0  - 1.000 * 1.0
  20.000 * 1.0 = -14.770 * 1.0  - 1.000 * 1.0
  3.000 * 1.0 = -37.520 * 1.0  - 1.000 * 1.0
  4.000 * 1.0 = -43.240 * 1.0  - 1.000 * 1.0
  5.000 * 1.0 = -55.060 * 1.0  - 1.000 * 1.0
  6.000 * 1.0 = -21.840 * 1.0  - 1.000 * 1.0
  7.000 * 1.0 = -40.820 * 1.0  - 1.000 * 1.0
  8.000 * 1.0 = -42.640 * 1.0  - 1.000 * 1.0
  9.000 * 1.0 = -55.850 * 1.0  - 1.000 * 1.0

END of FILE
```

S8. The ^{1}H fingerprint of stevioside (**4**) in DMSO-d_6 (29 mM, 600 MHz, 298 K). The calculated and observed NMR spectra are shown in red and blue, respectively.



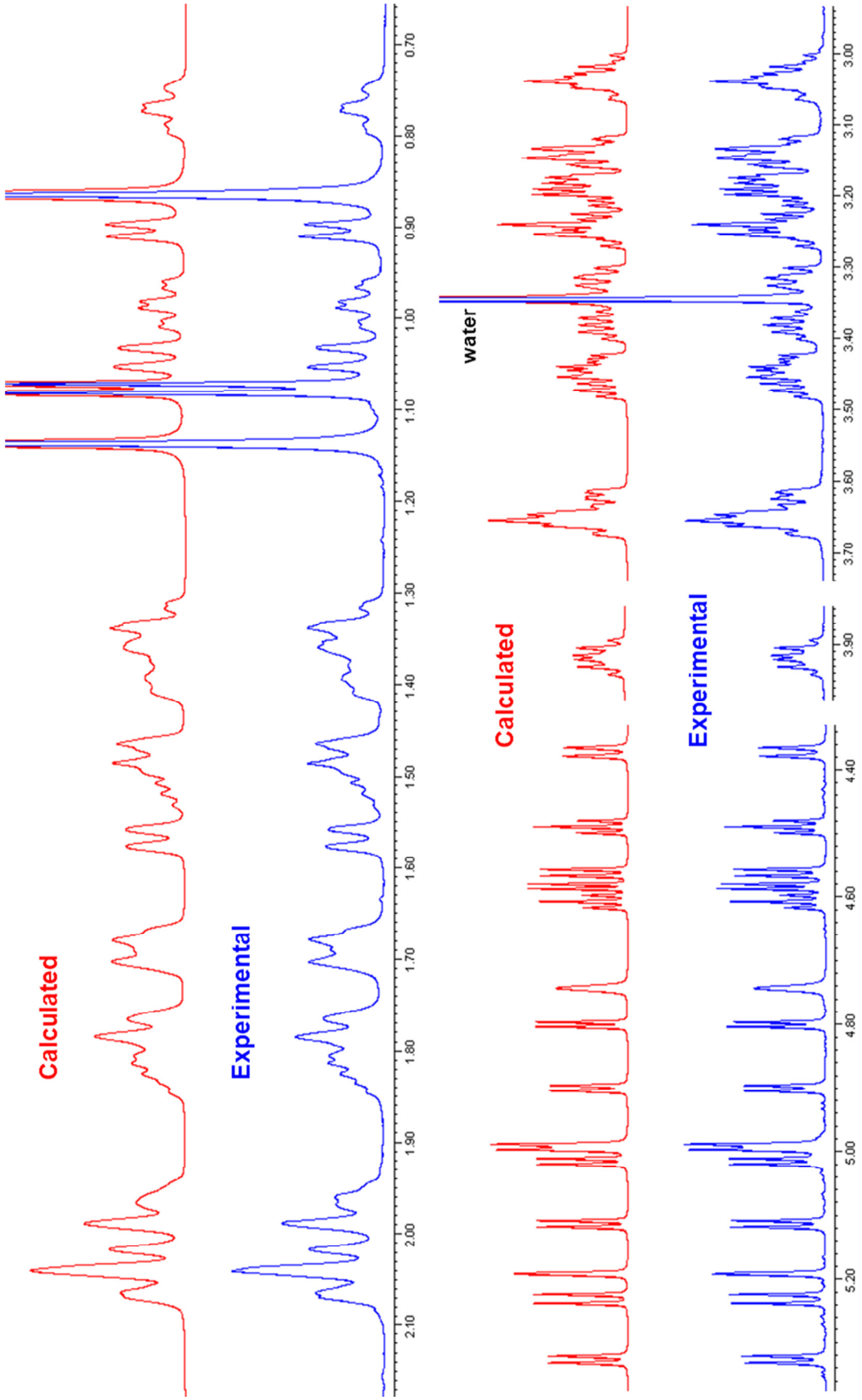
S9. The HiFSA profile of dulcoside A (**5**) in DMSO-d_6 [in PERCH parameter (.pms) file format].

```
* 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: c:\HIFSA\Stevia\DulcosideA
#$œ  Date 10.10.2014;  Time 21:54:51     dulcosideA.pms

CHEMICAL SHIFTS(PPM):
PROTON    2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.07269
 H1A   / 1     0.769600  1*1*1  STAT=Y  PRED= 0.779 RANGE= 0.050 WIDTH(Y)= 4.548 RESP(Y)= 0.9579 HSQC= C1
 H1B   / 1     1.773433  1*1*1  STAT=Y  PRED= 1.778 RANGE= 0.050 WIDTH(Y)= 5.183 RESP(Y)= 0.9901 HSQC= C1
 H2A   / 1     1.793942  1*1*1  STAT=Y  PRED= 1.764 RANGE= 0.050 WIDTH(Y)= 6.158 RESP(Y)= 0.9034 HSQC= C2
 H2B   / 1     1.352028  1*1*1  STAT=Y  PRED= 1.332 RANGE= 0.050 WIDTH(Y)= 3.214 RESP(Y)= 0.9269 HSQC= C2
 H3A   / 1     2.051316  1*1*1  STAT=Y  PRED= 2.000 RANGE= 0.050 WIDTH(Y)= 3.171 RESP(Y)= 0.9312 HSQC= C3
 H3B   / 1     0.984104  1*1*1  STAT=Y  PRED= 0.932 RANGE= 0.050 WIDTH(Y)= 3.712 RESP(Y)= 0.9292 HSQC= C3
 H5A   / 1     1.041781  1*1*1  STAT=Y  PRED= 1.015 RANGE= 0.050 WIDTH(Y)= 4.114 RESP(Y)= 0.9664 HSQC= C5
 H6A   / 1     1.978965  1*1*1  STAT=Y  PRED= 1.700 RANGE= 0.050 WIDTH(Y)= 5.006 RESP(Y)= 0.9192 HSQC= C6
 H6B   / 1     1.693797  1*1*1  STAT=Y  PRED= 1.737 RANGE= 0.050 WIDTH(Y)= 4.405 RESP(Y)= 0.9360 HSQC= C6
 H7A   / 1     1.335765  1*1*1  STAT=Y  PRED= 1.360 RANGE= 0.050 WIDTH(Y)= 4.240 RESP(Y)= 0.9031 HSQC= C7
 H7B   / 1     1.473834  1*1*1  STAT=Y  PRED= 1.449 RANGE= 0.050 WIDTH(Y)= 4.047 RESP(Y)= 0.9915 HSQC= C7
 H9A   / 1     0.903361  1*1*1  STAT=Y  PRED= 0.921 RANGE= 0.050 WIDTH(Y)= 4.440 RESP(Y)= 0.9761 HSQC= C9
 H11A  / 1     1.683915  1*1*1  STAT=Y  PRED= 1.651 RANGE= 0.050 WIDTH(Y)= 5.310 RESP(Y)= 0.9509 HSQC= C11
 H11B  / 1     1.496768  1*1*1  STAT=Y  PRED= 1.429 RANGE= 0.050 WIDTH(Y)= 4.491 RESP(Y)= 0.9007 HSQC= C11
 H12A  / 1     1.393374  1*1*1  STAT=Y  PRED= 1.348 RANGE= 0.025 WIDTH(Y)= 6.522 RESP(Y)= 1.0000 HSQC= C12
 H12B  / 1     1.818426  1*1*1  STAT=Y  PRED= 1.599 RANGE= 0.050 WIDTH(Y)= 5.502 RESP(Y)= 0.9451 HSQC= C12
 H14A  / 1     2.026431  1*1*1  STAT=Y  PRED= 1.869 RANGE= 0.455 WIDTH(Y)= 4.401 RESP(Y)= 0.9685 HSQC= C14
 H14B  / 1     1.566712  1*1*1  STAT=Y  PRED= 1.192 RANGE= 0.050 WIDTH(Y)= 4.588 RESP(Y)= 0.9764 HSQC= C14
 H15A  / 1     1.975000  1*1*1  STAT=Y  PRED= 2.023 RANGE= 0.050 WIDTH(Y)= 4.126 RESP(Y)= 0.9421 HSQC= C15
 H15B  / 1     2.053821  1*1*1  STAT=Y  PRED= 2.052 RANGE= 0.050 WIDTH(Y)= 6.482 RESP(Y)= 0.9264 HSQC= C15
 H17A  / 1     4.991549  1*1*1  STAT=Y  PRED= 4.878 RANGE= 0.025 WIDTH(Y)= 3.536 RESP(Y)= 0.9638 HSQC= C17
 H17B  / 1     4.741988  1*1*1  STAT=Y  PRED= 4.687 RANGE= 0.025 WIDTH(Y)= 3.817 RESP(Y)= 0.9720 HSQC= C17
 H18B  / 1     1.136032  1*1*3  STAT=Y  PRED= 1.101 RANGE= 0.050 WIDTH(Y)= 3.267 RESP(Y)= 0.9314 HSQC= C18
 H20B  / 1     0.864247  1*1*3  STAT=Y  PRED= 0.866 RANGE= 0.050 WIDTH(Y)= 4.237 RESP(Y)= 0.9416 HSQC= C20
 GA1   / 1     5.230042  1*1*1  STAT=Y  PRED= 5.565 RANGE= 0.342 WIDTH(Y)= 1.861 RESP(Y)= 0.9078 HSQC= H21
 GA2   / 1     3.139602  1*1*1  STAT=Y  PRED= 3.526 RANGE= 0.200 WIDTH(Y)= 2.147 RESP(Y)= 0.9171 HSQC= C23
 GA3   / 1     3.250012  1*1*1  STAT=Y  PRED= 3.317 RANGE= 0.155 WIDTH(Y)= 2.119 RESP(Y)= 0.8548 HSQC= C26
 GA4   / 1     3.137602  1*1*1  STAT=Y  PRED= 3.387 RANGE= 0.287 WIDTH(Y)= 2.093 RESP(Y)= 0.8374 HSQC= C27
 GA5   / 1     3.182454  1*1*1  STAT=Y  PRED= 3.485 RANGE= 0.247 WIDTH(Y)= 1.935 RESP(Y)= 0.8314 HSQC= C25
 GA6A  / 1     3.462338  1*1*1  STAT=Y  PRED= 3.351 RANGE= 0.450 WIDTH(Y)= 2.631 RESP(Y)= 0.8318 HSQC= C29
 GA6B  / 1     3.627737  1*1*1  STAT=Y  PRED= 3.509 RANGE= 0.232 WIDTH(Y)= 2.333 RESP(Y)= 0.8536 HSQC= C29
 OGA2  / 1     5.325844  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 2.195 RESP(Y)= 0.8978
 OGA3  / 1     5.014704  1*1*1  STAT=Y  PRED= 4.296 RANGE= 1.420 WIDTH(Y)= 1.943 RESP(Y)= 0.8798
 OGA4  / 1     4.991860  1*1*1  STAT=Y  PRED= 4.702 RANGE= 1.565 WIDTH(Y)= 1.799 RESP(Y)= 0.8679
 OGA6  / 1     4.488581  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 1.753 RESP(Y)= 0.8978
 GB1   / 1     4.370956  1*1*1  STAT=Y  PRED= 5.565 RANGE= 0.342 WIDTH(Y)= 2.793 RESP(Y)= 0.9078 HSQC= H21
 GB2   / 1     3.239020  1*1*1  STAT=Y  PRED= 3.526 RANGE= 0.200 WIDTH(Y)= 2.357 RESP(Y)= 0.9171 HSQC= C23
 GB3   / 1     3.318284  1*1*1  STAT=Y  PRED= 3.317 RANGE= 0.155 WIDTH(Y)= 2.451 RESP(Y)= 0.8548 HSQC= C26
 GB4   / 1     3.023018  1*1*1  STAT=Y  PRED= 3.387 RANGE= 0.287 WIDTH(Y)= 2.069 RESP(Y)= 0.8374 HSQC= C27
 GB5   / 1     3.046462  1*1*1  STAT=Y  PRED= 3.485 RANGE= 0.247 WIDTH(Y)= 2.133 RESP(Y)= 0.8314 HSQC= C25
 GB6A  / 1     3.380396  1*1*1  STAT=Y  PRED= 3.351 RANGE= 0.450 WIDTH(Y)= 2.797 RESP(Y)= 0.8318 HSQC= C29
 GB6B  / 1     3.657217  1*1*1  STAT=Y  PRED= 3.509 RANGE= 0.232 WIDTH(Y)= 2.614 RESP(Y)= 0.8536 HSQC= C29
 OGB3  / 1     5.112100  1*1*1  STAT=Y  PRED= 4.296 RANGE= 1.420 WIDTH(Y)= 1.908 RESP(Y)= 0.8798
 OGB4  / 1     4.899442  1*1*1  STAT=Y  PRED= 4.702 RANGE= 1.565 WIDTH(Y)= 1.964 RESP(Y)= 0.8679
 OGB6  / 1     4.606431  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 2.018 RESP(Y)= 0.8978
 RH1   / 1     5.190868  1*1*1  STAT=Y  PRED= 4.453 RANGE= 0.300 WIDTH(Y)= 2.236 RESP(Y)= 0.9527 HSQC= C33
 RH2   / 1     3.653831  1*1*1  STAT=Y  PRED= 3.609 RANGE= 0.242 WIDTH(Y)= 2.023 RESP(Y)= 0.9502 HSQC= C38
 RH3   / 1     3.437737  1*1*1  STAT=Y  PRED= 3.082 RANGE= 0.582 WIDTH(Y)= 2.240 RESP(Y)= 0.8779 HSQC= C39
 RH4   / 1     3.193912  1*1*1  STAT=Y  PRED= 2.968 RANGE= 0.287 WIDTH(Y)= 2.323 RESP(Y)= 0.9349 HSQC= C37
 RH5   / 1     3.917162  1*1*1  STAT=Y  PRED= 2.961 RANGE= 0.627 WIDTH(Y)= 2.547 RESP(Y)= 0.9335 HSQC= C36
 RH6   / 1     1.075796  1*1*3  STAT=Y  PRED= 0.586 RANGE= 0.262 WIDTH(Y)= 2.533 RESP(Y)= 0.8538 HSQC= C40
 ORH2  / 1     4.582846  1*1*1  STAT=Y  PRED= 4.719 RANGE= 1.395 WIDTH(Y)= 1.574 RESP(Y)= 0.7880
 ORH3  / 1     4.561345  1*1*1  STAT=Y  PRED= 4.127 RANGE= 1.613 WIDTH(Y)= 1.901 RESP(Y)= 0.8379
 ORH4  / 1     4.799351  1*1*1  STAT=Y  PRED= 4.732 RANGE= 1.673 WIDTH(Y)= 1.856 RESP(Y)= 0.8554
DMSO_CH   2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.63632
 DMSO  / 2     2.500036  1*1*1  STAT=Y  PRED= 2.500 RANGE= 0.050 WIDTH(Y)= 1.465 RESP(Y)= 1.0000
DMSO_D    2*SPIN= 2 SPECIES=2D    POPULATION(Y)=   0.63632
 DMSOD1/ 2  -100.000001  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
 DMSOD2/ 2  -100.000001  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
WATER_H   2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.29099
 WATER / 3     3.343032  2*1*1  STAT=Y  PRED= 3.338 RANGE= 0.050 WIDTH(Y)= 1.246 RESP(Y)= 1.0000

COUPLING CONSTANTS(HZ):
 J12_13    -12.3508   J H1A    H1B      STAT=Y  PRED= -13.130 RANGE= 1.500
 J17_12     13.7243   J H1A    H2A      STAT=Y  PRED= 12.550 RANGE= 2.560
 J12_18      4.8051   J H1A    H2B      STAT=Y  PRED= 4.380 RANGE= 3.800
 J14_12     -0.0088   J H1A    H20B     STAT=Y  PRED= -0.790 RANGE= 0.400
 J17_13      4.4009   J H1B    H2A      STAT=Y  PRED= 3.880 RANGE= 3.800
 J13_18      2.2388   J H1B    H2B      STAT=Y  PRED= 2.510 RANGE= 2.800
 J13_19      1.5951   J H1B    H3A      STAT=Y  PRED= 2.850 RANGE= 1.280
 J17_18    -12.6499   J H2A    H2B      STAT=Y  PRED= -13.190 RANGE= 1.500
 J17_19      3.4159   J H2A    H3A      STAT=Y  PRED= 3.860 RANGE= 3.800
 J17_20     12.9429   J H2A    H3B      STAT=Y  PRED= 12.570 RANGE= 2.560
 J19_18      3.4307   J H2B    H3A      STAT=Y  PRED= 2.530 RANGE= 2.800
```

```
 J20_18      4.5157   J H2B    H3B      STAT=Y  PRED= 4.310 RANGE= 3.800
 J19_20    -13.0462   J H3A    H3B      STAT=Y  PRED= -13.110 RANGE= 1.500
 J21_22     12.2827   J H5A    H6A      STAT=Y  PRED= 12.550 RANGE= 2.560
 J21_23      2.4901   J H5A    H6B      STAT=Y  PRED= 1.710 RANGE= 2.800
 J22_23    -13.4373   J H6A    H6B      STAT=Y  PRED= -13.190 RANGE= 1.500
 J22_24     13.6812   J H6A    H7A      STAT=Y  PRED= 12.990 RANGE= 2.560
 J22_25      3.3636   J H6A    H7B      STAT=Y  PRED= 3.320 RANGE= 3.800
 J23_24      4.1555   J H6B    H7A      STAT=Y  PRED= 3.410 RANGE= 3.800
 J23_25      3.8013   J H6B    H7B      STAT=Y  PRED= 3.190 RANGE= 3.800
 J24_25    -12.3785   J H7A    H7B      STAT=Y  PRED= -13.130 RANGE= 1.500
 J26_1       1.4395   J H9A    H11A     STAT=Y  PRED= 0.490 RANGE= 2.800
 J26_2       8.1488   J H9A    H11B     STAT=Y  PRED= 9.030 RANGE= 3.580
 J26_6       0.1724   J H9A    H14B     STAT=Y  PRED= 2.290 RANGE= 1.100
 J1_2      -14.5755   J H11A   H11B     STAT=Y  PRED= -13.010 RANGE= 1.500
 J3_1        1.4291   J H11A   H12A     STAT=Y  PRED= 1.040 RANGE= 2.800
 J4_1        6.3966   J H11A   H12B     STAT=Y  PRED= 6.480 RANGE= 3.800
 J3_2        6.9188   J H11B   H12A     STAT=Y  PRED= 6.890 RANGE= 3.800
 J4_2       13.0395   J H11B   H12B     STAT=Y  PRED= 11.180 RANGE= 2.800
 J3_4      -11.8562   J H12A   H12B     STAT=Y  PRED= -12.880 RANGE= 1.500
 J3_6        3.0246   J H12A   H14B     STAT=Y  PRED= 2.670 RANGE= 1.280
 J5_6      -11.2407   J H14A   H14B     STAT=Y  PRED= -12.450 RANGE= 2.000
 J7_5        2.7762   J H14A   H15A     STAT=Y  PRED= 1.650 RANGE= 1.280
 J7_8      -16.9861   J H15A   H15B     STAT=Y  PRED= -14.390 RANGE= 3.000
 J7_9       -2.6861   J H15A   H17A     STAT=Y  PRED= -2.030 RANGE= 1.000
 J7_10      -2.2098   J H15A   H17B     STAT=Y  PRED= -1.900 RANGE= 0.950
 J9_8       -1.0451   J H15B   H17A     STAT=Y  PRED= -2.420 RANGE= 1.200
 J10_8      -0.8102   J H15B   H17B     STAT=Y  PRED= -2.140 RANGE= 1.100
 J9_10       1.7270   J H17A   H17B     STAT=Y  PRED= 2.980 RANGE= 4.000
 J38_40      8.2370   J GA1    GA2      STAT=Y  PRED= 7.190 RANGE= 3.580
 J40_43      9.2307   J GA2    GA3      STAT=Y  PRED= 8.920 RANGE= 3.580
 J40_48      6.2437   J GA2    OGA2     STAT=Y  PRED= 4.300 RANGE= 1.000
 J43_46      8.7619   J GA3    GA4      STAT=Y  PRED= 9.140 RANGE= 3.580
 J43_51      5.4894   J GA3    OGA3     STAT=Y  PRED= 4.300 RANGE= 1.000
 J41_46      9.6718   J GA4    GA5      STAT=Y  PRED= 10.550 RANGE= 2.560
 J46_52      5.5051   J GA4    OGA4     STAT=Y  PRED= 4.300 RANGE= 1.000
 J41_49      5.1400   J GA5    GA6A     STAT=Y  PRED= 2.700 RANGE= 3.000
 J41_50      2.2096   J GA5    GA6B     STAT=Y  PRED= 1.280 RANGE= 3.000
 J49_50    -11.8380   J GA6A   GA6B     STAT=Y  PRED= -12.300 RANGE= 0.800
 J49_51      5.8914   J GA6A   OGA6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J50_51      5.3438   J GA6B   OGA6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J48_50      7.8628   J GB1    GB2      STAT=Y  PRED= 7.190 RANGE= 3.580
 J50_53      8.8934   J GB2    GB3      STAT=Y  PRED= 8.920 RANGE= 3.580
 J53_56      8.7182   J GB3    GB4      STAT=Y  PRED= 9.140 RANGE= 3.580
 J53_61      5.8420   J GB3    OGB3     STAT=Y  PRED= 4.300 RANGE= 1.000
 J51_56      9.8313   J GB4    GB5      STAT=Y  PRED= 10.550 RANGE= 2.560
 J56_62      5.6038   J GB4    OGB4     STAT=Y  PRED= 4.300 RANGE= 1.000
 J51_59      6.2301   J GB5    GB6A     STAT=Y  PRED= 2.700 RANGE= 3.000
 J51_60      2.5373   J GB5    GB6B     STAT=Y  PRED= 1.280 RANGE= 3.000
 J59_60    -11.6468   J GB6A   GB6B     STAT=Y  PRED= -12.300 RANGE= 0.800
 J59_61      5.8916   J GB6A   OGB6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J60_61      5.7685   J GB6B   OGB6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J56_68      1.6172   J RH1    RH2      STAT=Y  PRED= 2.330 RANGE= 2.800
 J68_69      3.3168   J RH2    RH3      STAT=Y  PRED= 3.420 RANGE= 3.800
 J68_71      4.3703   J RH2    ORH2     STAT=Y  PRED= 4.440 RANGE= 1.500
 J66_69      9.3244   J RH3    RH4      STAT=Y  PRED= 9.590 RANGE= 3.580
 J69_72      6.0126   J RH3    ORH3     STAT=Y  PRED= 4.300 RANGE= 1.000
 J57_66      9.4213   J RH4    RH5      STAT=Y  PRED= 9.940 RANGE= 3.580
 J66_73      4.3603   J RH4    ORH4     STAT=Y  PRED= 4.300 RANGE= 1.000
 J57_59      6.1248   J RH5    RH6      STAT=Y  PRED= 6.250 RANGE= 0.600
 JDMSO1      1.7939   J DMSO   DMSOD1   STAT=Y  PRED= 1.700 RANGE= 0.050
 JDMSO1      1.7939   J DMSO   DMSOD2   STAT=Y  PRED= 1.700 RANGE= 0.050

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)
  600.12701400 =  FIELD(1H,MHz), used to transform shifts to ppms
   22.47832099 =  Left frequency (ppm)
   -7.49157654 =  Right frequency (ppm)
        10.000 =  Acquisition time (s, for QMTLS)
         0.000 =  Line-width (for modes D, P & T, 0=use defaults)
   0.068609924 =  Data-point resolution (Hz)
        60.575 =  GAUSSIAN (%, 0=use default from INF)
         1.746 =  Dispersion contribution (%, 0=use default from INF)
    0.00000000 =  Decoupling frequency (for DORES)

CONSTRAINTS (in equations X0 = 1.0)...use no empty lines
 EQUAL DMSOD1   = DMSOD2
  1.000 * 1.0 = -41.020 * 1.0  - 1.000 * 1.0
  10.000 * 1.0 = -38.340 * 1.0  - 1.000 * 1.0
  11.000 * 1.0 = -16.670 * 1.0  - 1.000 * 1.0
  12.000 * 1.0 = -36.870 * 1.0  - 1.000 * 1.0
  13.000 * 1.0 = -80.200 * 1.0  - 1.000 * 1.0
  14.000 * 1.0 = -49.010 * 1.0  - 1.000 * 1.0
  15.000 * 1.0 = -48.090 * 1.0  - 1.000 * 1.0
  16.0 * 1.0 = -153.1 * 1.0  - 1.0 * 1.0
```

```
  17.0 * 1.0 = -104.2 * 1.0  - 1.0 * 1.0
  18.000 * 1.0 = -28.210 * 1.0  - 1.000 * 1.0
  19.0 * 1.0 = -185.4 * 1.0  - 1.0 * 1.0
  2.000 * 1.0 = -19.040 * 1.0  - 1.000 * 1.0
  20.000 * 1.0 = -14.770 * 1.0  - 1.000 * 1.0
  3.000 * 1.0 = -37.520 * 1.0  - 1.000 * 1.0
  4.000 * 1.0 = -43.240 * 1.0  - 1.000 * 1.0
  5.000 * 1.0 = -55.060 * 1.0  - 1.000 * 1.0
  6.000 * 1.0 = -21.840 * 1.0  - 1.000 * 1.0
  7.000 * 1.0 = -40.820 * 1.0  - 1.000 * 1.0
  8.000 * 1.0 = -42.640 * 1.0  - 1.000 * 1.0
  9.000 * 1.0 = -55.850 * 1.0  - 1.000 * 1.0

END of FILE
```

S10. The ^{1}H fingerprint of dulcoside A (**5**) in DMSO-d_6 (33 mM, 600 MHz, 298 K). The calculated and observed NMR spectra are shown in red and blue, respectively.



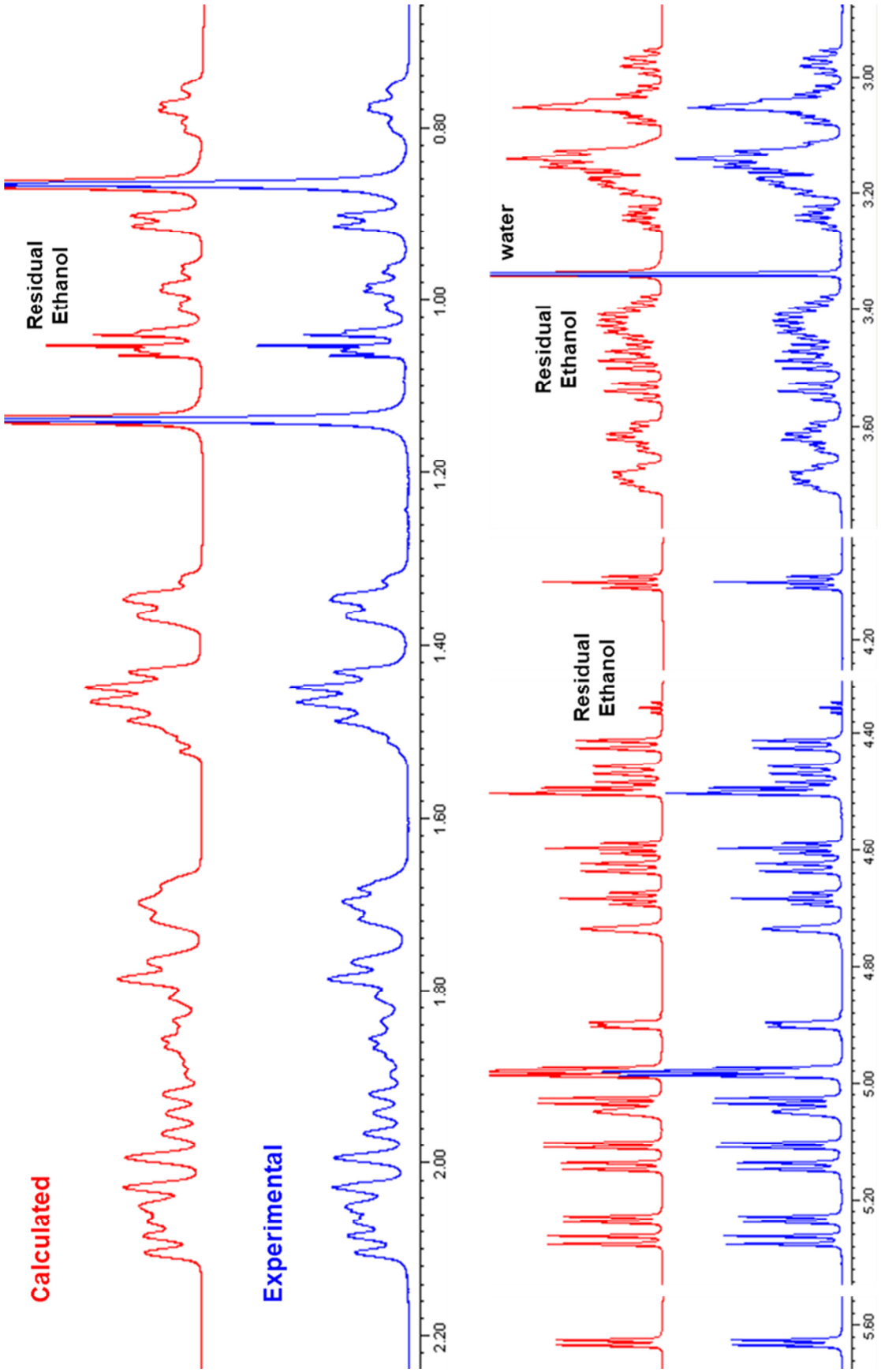
S11. The HiFSA profile of rebaudioside A (**6**) in DMSO-d_6 [in PERCH parameter (.pms) file format].

```
* 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: c:\HIFSA\Stevia\RebA
#$œ  Date 11.10.2014;  Time 21:41:12     rebA.pms

CHEMICAL SHIFTS(PPM):
PROTON    2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.06430
 H1A   / 1     0.776439  1*1*1  STAT=Y  PRED= 0.779 RANGE= 0.050 WIDTH(Y)= 4.929 RESP(Y)= 0.9579 HSQC= C1
 H1B   / 1     1.776161  1*1*1  STAT=Y  PRED= 1.778 RANGE= 0.050 WIDTH(Y)= 5.006 RESP(Y)= 0.9901 HSQC= C1
 H2A   / 1     1.796222  1*1*1  STAT=Y  PRED= 1.764 RANGE= 0.050 WIDTH(Y)= 4.946 RESP(Y)= 0.9034 HSQC= C2
 H2B   / 1     1.355462  1*1*1  STAT=Y  PRED= 1.332 RANGE= 0.050 WIDTH(Y)= 3.612 RESP(Y)= 0.9269 HSQC= C2
 H3A   / 1     2.057578  1*1*1  STAT=Y  PRED= 2.000 RANGE= 0.050 WIDTH(Y)= 3.106 RESP(Y)= 0.9312 HSQC= C3
 H3B   / 1     0.985909  1*1*1  STAT=Y  PRED= 0.932 RANGE= 0.050 WIDTH(Y)= 4.618 RESP(Y)= 0.9292 HSQC= C3
 H5A   / 1     1.047221  1*1*1  STAT=Y  PRED= 1.015 RANGE= 0.050 WIDTH(Y)= 5.355 RESP(Y)= 0.9664 HSQC= C5
 H6A   / 1     1.929700  1*1*1  STAT=Y  PRED= 1.700 RANGE= 0.050 WIDTH(Y)= 5.298 RESP(Y)= 0.9192 HSQC= C6
 H6B   / 1     1.708444  1*1*1  STAT=Y  PRED= 1.737 RANGE= 0.050 WIDTH(Y)= 4.795 RESP(Y)= 0.9360 HSQC= C6
 H7A   / 1     1.344957  1*1*1  STAT=Y  PRED= 1.360 RANGE= 0.050 WIDTH(Y)= 4.973 RESP(Y)= 0.9031 HSQC= C7
 H7B   / 1     1.476214  1*1*1  STAT=Y  PRED= 1.449 RANGE= 0.050 WIDTH(Y)= 4.878 RESP(Y)= 0.9915 HSQC= C7
 H9A   / 1     0.907643  1*1*1  STAT=Y  PRED= 0.921 RANGE= 0.050 WIDTH(Y)= 4.537 RESP(Y)= 0.9761 HSQC= C9
 H11A  / 1     1.688225  1*1*1  STAT=Y  PRED= 1.651 RANGE= 0.050 WIDTH(Y)= 5.695 RESP(Y)= 0.9509 HSQC= C11
 H11B  / 1     1.490198  1*1*1  STAT=Y  PRED= 1.429 RANGE= 0.050 WIDTH(Y)= 5.126 RESP(Y)= 0.9007 HSQC= C11
 H12A  / 1     1.451865  1*1*1  STAT=Y  PRED= 1.348 RANGE= 0.025 WIDTH(Y)= 5.880 RESP(Y)= 1.0000 HSQC= C12
 H12B  / 1     1.859251  1*1*1  STAT=Y  PRED= 1.599 RANGE= 0.050 WIDTH(Y)= 5.441 RESP(Y)= 0.9451 HSQC= C12
 H14A  / 1     2.093945  1*1*1  STAT=Y  PRED= 1.869 RANGE= 0.455 WIDTH(Y)= 4.836 RESP(Y)= 0.9685 HSQC= C14
 H14B  / 1     1.438310  1*1*1  STAT=Y  PRED= 1.192 RANGE= 0.050 WIDTH(Y)= 4.067 RESP(Y)= 0.9764 HSQC= C14
 H15A  / 1     1.982807  1*1*1  STAT=Y  PRED= 2.023 RANGE= 0.050 WIDTH(Y)= 5.387 RESP(Y)= 0.9421 HSQC= C15
 H15B  / 1     2.038472  1*1*1  STAT=Y  PRED= 2.052 RANGE= 0.050 WIDTH(Y)= 5.151 RESP(Y)= 0.9264 HSQC= C15
 H17A  / 1     5.047577  1*1*1  STAT=Y  PRED= 4.878 RANGE= 0.025 WIDTH(Y)= 4.325 RESP(Y)= 0.9638 HSQC= C17
 H17B  / 1     4.735090  1*1*1  STAT=Y  PRED= 4.687 RANGE= 0.025 WIDTH(Y)= 4.404 RESP(Y)= 0.9720 HSQC= C17
 H18B  / 1     1.137858  1*1*3  STAT=Y  PRED= 1.101 RANGE= 0.050 WIDTH(Y)= 3.515 RESP(Y)= 0.9314 HSQC= C18
 H20B  / 1     0.865215  1*1*3  STAT=Y  PRED= 0.866 RANGE= 0.050 WIDTH(Y)= 4.459 RESP(Y)= 0.9416 HSQC= C20
 GA1   / 1     5.268449  1*1*1  STAT=Y  PRED= 5.565 RANGE= 0.342 WIDTH(Y)= 1.728 RESP(Y)= 0.9078 HSQC= H21
 GA2   / 1     3.134209  1*1*1  STAT=Y  PRED= 3.526 RANGE= 0.200 WIDTH(Y)= 3.620 RESP(Y)= 0.9171 HSQC= C23
 GA3   / 1     3.239257  1*1*1  STAT=Y  PRED= 3.317 RANGE= 0.155 WIDTH(Y)= 1.918 RESP(Y)= 0.8548 HSQC= C26
 GA4   / 1     3.129266  1*1*1  STAT=Y  PRED= 3.387 RANGE= 0.287 WIDTH(Y)= 3.730 RESP(Y)= 0.8374 HSQC= C27
 GA5   / 1     3.186219  1*1*1  STAT=Y  PRED= 3.485 RANGE= 0.247 WIDTH(Y)= 2.247 RESP(Y)= 0.8314 HSQC= C25
 GA6A  / 1     3.396356  1*1*1  STAT=Y  PRED= 3.351 RANGE= 0.450 WIDTH(Y)= 2.376 RESP(Y)= 0.8318 HSQC= C29
 GA6B  / 1     3.693565  1*1*1  STAT=Y  PRED= 3.509 RANGE= 0.232 WIDTH(Y)= 2.391 RESP(Y)= 0.8536 HSQC= C29
 OGA2  / 1     5.232683  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 2.029 RESP(Y)= 0.8978
 OGA3  / 1     4.981146  1*1*1  STAT=Y  PRED= 4.296 RANGE= 1.420 WIDTH(Y)= 1.617 RESP(Y)= 0.8798
 OGA4  / 1     4.975743  1*1*1  STAT=Y  PRED= 4.702 RANGE= 1.565 WIDTH(Y)= 1.564 RESP(Y)= 0.8679
 OGA6  / 1     4.596433  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 1.676 RESP(Y)= 0.8978
 GB1   / 1     4.462464  1*1*1  STAT=Y  PRED= 5.565 RANGE= 0.342 WIDTH(Y)= 3.011 RESP(Y)= 0.9078 HSQC= H21
 GB2   / 1     3.485860  1*1*1  STAT=Y  PRED= 3.526 RANGE= 0.200 WIDTH(Y)= 2.523 RESP(Y)= 0.9171 HSQC= C23
 GB3   / 1     3.537517  1*1*1  STAT=Y  PRED= 3.317 RANGE= 0.155 WIDTH(Y)= 2.459 RESP(Y)= 0.8548 HSQC= C26
 GB4   / 1     3.140933  1*1*1  STAT=Y  PRED= 3.387 RANGE= 0.287 WIDTH(Y)= 1.706 RESP(Y)= 0.8374 HSQC= C27
 GB5   / 1     3.164798  1*1*1  STAT=Y  PRED= 3.485 RANGE= 0.247 WIDTH(Y)= 2.584 RESP(Y)= 0.8314 HSQC= C25
 GB6A  / 1     3.459111  1*1*1  STAT=Y  PRED= 3.351 RANGE= 0.450 WIDTH(Y)= 2.313 RESP(Y)= 0.8318 HSQC= C29
 GB6B  / 1     3.625055  1*1*1  STAT=Y  PRED= 3.509 RANGE= 0.232 WIDTH(Y)= 3.579 RESP(Y)= 0.8536 HSQC= C29
 OGB4  / 1     4.501016  1*1*1  STAT=Y  PRED= 4.702 RANGE= 1.565 WIDTH(Y)= 1.764 RESP(Y)= 0.8679
 OGB6  / 1     4.492673  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 1.584 RESP(Y)= 0.8978
 GC1   / 1     4.628839  1*1*1  STAT=Y  PRED= 5.565 RANGE= 0.342 WIDTH(Y)= 2.551 RESP(Y)= 0.9078 HSQC= H21
 GC2   / 1     2.973995  1*1*1  STAT=Y  PRED= 3.526 RANGE= 0.200 WIDTH(Y)= 2.553 RESP(Y)= 0.9171 HSQC= C23
 GC3   / 1     3.138851  1*1*1  STAT=Y  PRED= 3.317 RANGE= 0.155 WIDTH(Y)= 1.841 RESP(Y)= 0.8548 HSQC= C26
 GC4   / 1     3.050044  1*1*1  STAT=Y  PRED= 3.387 RANGE= 0.287 WIDTH(Y)= 1.667 RESP(Y)= 0.8374 HSQC= C27
 GC5   / 1     3.049883  1*1*1  STAT=Y  PRED= 3.485 RANGE= 0.247 WIDTH(Y)= 1.589 RESP(Y)= 0.8314 HSQC= C25
 GC6A  / 1     3.425120  1*1*1  STAT=Y  PRED= 3.351 RANGE= 0.450 WIDTH(Y)= 3.751 RESP(Y)= 0.8318 HSQC= C29
 GC6B  / 1     3.606473  1*1*1  STAT=Y  PRED= 3.509 RANGE= 0.232 WIDTH(Y)= 2.524 RESP(Y)= 0.8536 HSQC= C29
 OGC2  / 1     5.141521  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 2.034 RESP(Y)= 0.8978
 OGC3  / 1     4.982919  1*1*1  STAT=Y  PRED= 4.296 RANGE= 1.420 WIDTH(Y)= 1.579 RESP(Y)= 0.8798
 OGC4  / 1     4.898931  1*1*1  STAT=Y  PRED= 4.702 RANGE= 1.565 WIDTH(Y)= 1.733 RESP(Y)= 0.8679
 OGC6  / 1     4.099578  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 1.719 RESP(Y)= 0.8978
 GD1   / 1     4.418061  1*1*1  STAT=Y  PRED= 5.565 RANGE= 0.342 WIDTH(Y)= 2.400 RESP(Y)= 0.9078 HSQC= H21
 GD2   / 1     3.034697  1*1*1  STAT=Y  PRED= 3.526 RANGE= 0.200 WIDTH(Y)= 2.061 RESP(Y)= 0.9171 HSQC= C23
 GD3   / 1     3.142994  1*1*1  STAT=Y  PRED= 3.317 RANGE= 0.155 WIDTH(Y)= 1.661 RESP(Y)= 0.8548 HSQC= C26
 GD4   / 1     3.059512  1*1*1  STAT=Y  PRED= 3.387 RANGE= 0.287 WIDTH(Y)= 1.874 RESP(Y)= 0.8374 HSQC= C27
 GD5   / 1     3.185242  1*1*1  STAT=Y  PRED= 3.485 RANGE= 0.247 WIDTH(Y)= 1.991 RESP(Y)= 0.8314 HSQC= C25
 GD6A  / 1     3.418615  1*1*1  STAT=Y  PRED= 3.351 RANGE= 0.450 WIDTH(Y)= 3.166 RESP(Y)= 0.8318 HSQC= C29
 GD6B  / 1     3.680778  1*1*1  STAT=Y  PRED= 3.509 RANGE= 0.232 WIDTH(Y)= 2.819 RESP(Y)= 0.8536 HSQC= C29
 OGD2  / 1     5.628618  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 1.924 RESP(Y)= 0.8978
 OGD3  / 1     5.105333  1*1*1  STAT=Y  PRED= 4.296 RANGE= 1.420 WIDTH(Y)= 1.697 RESP(Y)= 0.8798
 OGD4  / 1     5.029260  1*1*1  STAT=Y  PRED= 4.702 RANGE= 1.565 WIDTH(Y)= 1.604 RESP(Y)= 0.8679
 OGD6  / 1     4.681769  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 1.936 RESP(Y)= 0.8978
DMSO_CH   2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.78165
 DMSO  / 2     2.500037  1*1*1  STAT=Y  PRED= 2.500 RANGE= 0.050 WIDTH(Y)= 1.386 RESP(Y)= 1.0000
DMSO_D    2*SPIN= 2 SPECIES=2D    POPULATION(Y)=   0.78165
 DMSOD1/ 2  -100.000001  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
 DMSOD2/ 2  -100.000001  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
WATER_H   2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.14734
 WATER / 3     3.336916  2*1*1  STAT=Y  PRED= 3.338 RANGE= 0.050 WIDTH(Y)= 1.538 RESP(Y)= 1.0000
ETOH_H    2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.00672
```

```
 ETOH1 / 4     1.051882  1*1*3  STAT=Y  PRED= 1.060 RANGE= 0.050 WIDTH(Y)= 0.998 RESP(Y)= 1.0000
 ETOH2 / 4     3.436263  1*1*2  STAT=Y  PRED= 3.440 RANGE= 0.050 WIDTH(Y)= 0.997 RESP(Y)= 1.0000
 ETOH3 / 4     4.355242  1*1*1  STAT=Y  PRED= 4.630 RANGE= 0.050 WIDTH(Y)= 1.023 RESP(Y)= 1.0000

COUPLING CONSTANTS(HZ):
 J12_13    -12.5140   J H1A    H1B      STAT=Y  PRED= -13.130 RANGE= 1.500
 J17_12     14.0074   J H1A    H2A      STAT=Y  PRED= 12.550 RANGE= 2.560
 J12_18      5.2986   J H1A    H2B      STAT=Y  PRED= 4.380 RANGE= 3.800
 J14_12     -0.0689   J H1A    H20B     STAT=Y  PRED= -0.790 RANGE= 0.400
 J17_13      4.1940   J H1B    H2A      STAT=Y  PRED= 3.880 RANGE= 3.800
 J13_18      3.4388   J H1B    H2B      STAT=Y  PRED= 2.510 RANGE= 2.800
 J13_19      3.1226   J H1B    H3A      STAT=Y  PRED= 2.850 RANGE= 1.280
 J17_18    -12.9881   J H2A    H2B      STAT=Y  PRED= -13.190 RANGE= 1.500
 J17_19      4.1645   J H2A    H3A      STAT=Y  PRED= 3.860 RANGE= 3.800
 J17_20     14.0460   J H2A    H3B      STAT=Y  PRED= 12.570 RANGE= 2.560
 J19_18      1.9339   J H2B    H3A      STAT=Y  PRED= 2.530 RANGE= 2.800
 J20_18      4.8775   J H2B    H3B      STAT=Y  PRED= 4.310 RANGE= 3.800
 J19_20    -12.3568   J H3A    H3B      STAT=Y  PRED= -13.110 RANGE= 1.500
 J21_22     12.2268   J H5A    H6A      STAT=Y  PRED= 12.550 RANGE= 2.560
 J21_23      1.9806   J H5A    H6B      STAT=Y  PRED= 1.710 RANGE= 2.800
 J22_23    -13.1188   J H6A    H6B      STAT=Y  PRED= -13.190 RANGE= 1.500
 J22_24     14.2307   J H6A    H7A      STAT=Y  PRED= 12.990 RANGE= 2.560
 J22_25      3.4659   J H6A    H7B      STAT=Y  PRED= 3.320 RANGE= 3.800
 J23_24      4.0568   J H6B    H7A      STAT=Y  PRED= 3.410 RANGE= 3.800
 J23_25      3.4963   J H6B    H7B      STAT=Y  PRED= 3.190 RANGE= 3.800
 J24_25    -11.9249   J H7A    H7B      STAT=Y  PRED= -13.130 RANGE= 1.500
 J26_1       1.1766   J H9A    H11A     STAT=Y  PRED= 0.490 RANGE= 2.800
 J26_2       8.0742   J H9A    H11B     STAT=Y  PRED= 9.030 RANGE= 3.580
 J26_6       1.7522   J H9A    H14B     STAT=Y  PRED= 2.290 RANGE= 1.100
 J1_2      -14.8153   J H11A   H11B     STAT=Y  PRED= -13.010 RANGE= 1.500
 J3_1        4.0450   J H11A   H12A     STAT=Y  PRED= 1.040 RANGE= 2.800
 J4_1        6.0550   J H11A   H12B     STAT=Y  PRED= 6.480 RANGE= 3.800
 J3_2        6.7453   J H11B   H12A     STAT=Y  PRED= 6.890 RANGE= 3.800
 J4_2       12.9566   J H11B   H12B     STAT=Y  PRED= 11.180 RANGE= 2.800
 J3_4      -11.0057   J H12A   H12B     STAT=Y  PRED= -12.880 RANGE= 1.500
 J3_6        3.6938   J H12A   H14B     STAT=Y  PRED= 2.670 RANGE= 1.280
 J5_6      -11.5467   J H14A   H14B     STAT=Y  PRED= -12.450 RANGE= 2.000
 J7_5        3.1100   J H14A   H15A     STAT=Y  PRED= 1.650 RANGE= 1.280
 J7_8      -16.9583   J H15A   H15B     STAT=Y  PRED= -14.390 RANGE= 3.000
 J7_9       -1.8989   J H15A   H17A     STAT=Y  PRED= -2.030 RANGE= 1.000
 J7_10      -0.9307   J H15A   H17B     STAT=Y  PRED= -1.900 RANGE= 0.950
 J9_8       -3.0845   J H15B   H17A     STAT=Y  PRED= -2.420 RANGE= 1.200
 J10_8      -2.2089   J H15B   H17B     STAT=Y  PRED= -2.140 RANGE= 1.100
 J9_10       0.0776   J H17A   H17B     STAT=Y  PRED= 2.980 RANGE= 4.000
 J38_40      8.1814   J GA1    GA2      STAT=Y  PRED= 7.190 RANGE= 3.580
 J40_43      9.3156   J GA2    GA3      STAT=Y  PRED= 8.920 RANGE= 3.580
 J40_48      5.7851   J GA2    OGA2     STAT=Y  PRED= 4.300 RANGE= 1.000
 J43_46      8.5190   J GA3    GA4      STAT=Y  PRED= 9.140 RANGE= 3.580
 J43_51      5.3022   J GA3    OGA3     STAT=Y  PRED= 4.300 RANGE= 1.000
 J41_46      9.9534   J GA4    GA5      STAT=Y  PRED= 10.550 RANGE= 2.560
 J46_52      5.5141   J GA4    OGA4     STAT=Y  PRED= 4.300 RANGE= 1.000
 J41_49      6.9818   J GA5    GA6A     STAT=Y  PRED= 2.700 RANGE= 3.000
 J41_50      2.3264   J GA5    GA6B     STAT=Y  PRED= 1.280 RANGE= 3.000
 J49_50    -11.7188   J GA6A   GA6B     STAT=Y  PRED= -12.300 RANGE= 0.800
 J49_51      5.4851   J GA6A   OGA6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J50_51      5.0936   J GA6B   OGA6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J48_50      7.7805   J GB1    GB2      STAT=Y  PRED= 7.190 RANGE= 3.580
 J50_53      9.1744   J GB2    GB3      STAT=Y  PRED= 8.920 RANGE= 3.580
 J53_56      8.4747   J GB3    GB4      STAT=Y  PRED= 9.140 RANGE= 3.580
 J51_56      8.5028   J GB4    GB5      STAT=Y  PRED= 10.550 RANGE= 2.560
 J56_62      2.3517   J GB4    OGB4     STAT=Y  PRED= 4.300 RANGE= 1.000
 J51_59      4.5411   J GB5    GB6A     STAT=Y  PRED= 2.700 RANGE= 3.000
 J51_60      1.0131   J GB5    GB6B     STAT=Y  PRED= 1.280 RANGE= 3.000
 J59_60    -11.6290   J GB6A   GB6B     STAT=Y  PRED= -12.300 RANGE= 0.800
 J59_61      5.8943   J GB6A   OGB6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J60_61      5.3619   J GB6B   OGB6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J58_60      7.8593   J GC1    GC2      STAT=Y  PRED= 7.190 RANGE= 3.580
 J60_63      9.3751   J GC2    GC3      STAT=Y  PRED= 8.920 RANGE= 3.580
 J60_68      6.6384   J GC2    OGC2     STAT=Y  PRED= 4.300 RANGE= 1.000
 J63_66      8.6451   J GC3    GC4      STAT=Y  PRED= 9.140 RANGE= 3.580
 J63_71      4.6778   J GC3    OGC3     STAT=Y  PRED= 4.300 RANGE= 1.000
 J61_66      9.1993   J GC4    GC5      STAT=Y  PRED= 10.550 RANGE= 2.560
 J66_72      5.0819   J GC4    OGC4     STAT=Y  PRED= 4.300 RANGE= 1.000
 J61_69      4.8390   J GC5    GC6A     STAT=Y  PRED= 2.700 RANGE= 3.000
 J61_70      2.4894   J GC5    GC6B     STAT=Y  PRED= 1.280 RANGE= 3.000
 J69_70    -11.1977   J GC6A   GC6B     STAT=Y  PRED= -12.300 RANGE= 0.800
 J69_71      5.7276   J GC6A   OGC6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J70_71      5.6674   J GC6B   OGC6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J68_80      7.9562   J GD1    GD2      STAT=Y  PRED= 7.190 RANGE= 3.580
 J70_73      9.0207   J GD2    GD3      STAT=Y  PRED= 8.920 RANGE= 3.580
 J70_78      5.1506   J GD2    OGD2     STAT=Y  PRED= 4.300 RANGE= 1.000
 J73_76      8.5632   J GD3    GD4      STAT=Y  PRED= 9.140 RANGE= 3.580
 J73_81      5.0233   J GD3    OGD3     STAT=Y  PRED= 4.300 RANGE= 1.000
 J71_76      9.8494   J GD4    GD5      STAT=Y  PRED= 10.550 RANGE= 2.560
 J76_82      5.6049   J GD4    OGD4     STAT=Y  PRED= 4.300 RANGE= 1.000
 J71_79      4.6446   J GD5    GD6A     STAT=Y  PRED= 2.700 RANGE= 3.000
 J71_80      2.3039   J GD5    GD6B     STAT=Y  PRED= 1.280 RANGE= 3.000
```

```
 J79_80    -11.4564   J GD6A   GD6B     STAT=Y  PRED= -12.300 RANGE= 0.800
 J79_81      6.0898   J GD6A   OGD6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J80_81      5.7502   J GD6B   OGD6     STAT=Y  PRED= 4.300 RANGE= 3.000
 JDMSO1      1.7939   J DMSO   DMSOD1   STAT=Y  PRED= 1.700 RANGE= 0.050
 JDMSO1      1.7939   J DMSO   DMSOD2   STAT=Y  PRED= 1.700 RANGE= 0.050
 JETOH1      7.0000   J ETOH1  ETOH2    STAT=Y  PRED= 7.000 RANGE= 0.050
 JETOH2      5.0977   J ETOH2  ETOH3    STAT=Y  PRED= 5.000 RANGE= 0.050

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)
  600.12701400 =  FIELD(1H,MHz), used to transform shifts to ppms
   22.47832099 =  Left frequency (ppm)
   -7.49157654 =  Right frequency (ppm)
         0.000 =  Acquisition time (s, for QMTLS)
         0.991 =  Line-width (for modes D, P & T, 0=use defaults)
   0.068609924 =  Data-point resolution (Hz)
        63.801 =  GAUSSIAN (%, 0=use default from INF)
        -2.951 =  Dispersion contribution (%, 0=use default from INF)
    0.00000000 =  Decoupling frequency (for DORES)

CONSTRAINTS (in equations X0 = 1.0)...use no empty lines
 EQUAL DMSOD1   = DMSOD2
  1.000 * 1.0 = -41.020 * 1.0  - 1.000 * 1.0
  10.000 * 1.0 = -38.340 * 1.0  - 1.000 * 1.0
  11.000 * 1.0 = -16.670 * 1.0  - 1.000 * 1.0
  12.000 * 1.0 = -36.870 * 1.0  - 1.000 * 1.0
  13.000 * 1.0 = -80.200 * 1.0  - 1.000 * 1.0
  14.000 * 1.0 = -49.010 * 1.0  - 1.000 * 1.0
  15.000 * 1.0 = -48.090 * 1.0  - 1.000 * 1.0
  16.0 * 1.0 = -153.1 * 1.0  - 1.0 * 1.0
  17.0 * 1.0 = -104.2 * 1.0  - 1.0 * 1.0
  18.000 * 1.0 = -28.210 * 1.0  - 1.000 * 1.0
  19.0 * 1.0 = -185.4 * 1.0  - 1.0 * 1.0
  2.000 * 1.0 = -19.040 * 1.0  - 1.000 * 1.0
  20.000 * 1.0 = -14.770 * 1.0  - 1.000 * 1.0
  3.000 * 1.0 = -37.520 * 1.0  - 1.000 * 1.0
  4.000 * 1.0 = -43.240 * 1.0  - 1.000 * 1.0
  5.000 * 1.0 = -55.060 * 1.0  - 1.000 * 1.0
  6.000 * 1.0 = -21.840 * 1.0  - 1.000 * 1.0
  7.000 * 1.0 = -40.820 * 1.0  - 1.000 * 1.0
  8.000 * 1.0 = -42.640 * 1.0  - 1.000 * 1.0
  9.000 * 1.0 = -55.850 * 1.0  - 1.000 * 1.0

END of FILE
```

S12. The ^{1}H fingerprint of rebaudioside A (**6**) in DMSO-d_6 (23 mM, 600 MHz, 298 K). The calculated and observed NMR spectra are shown in red and blue, respectively.



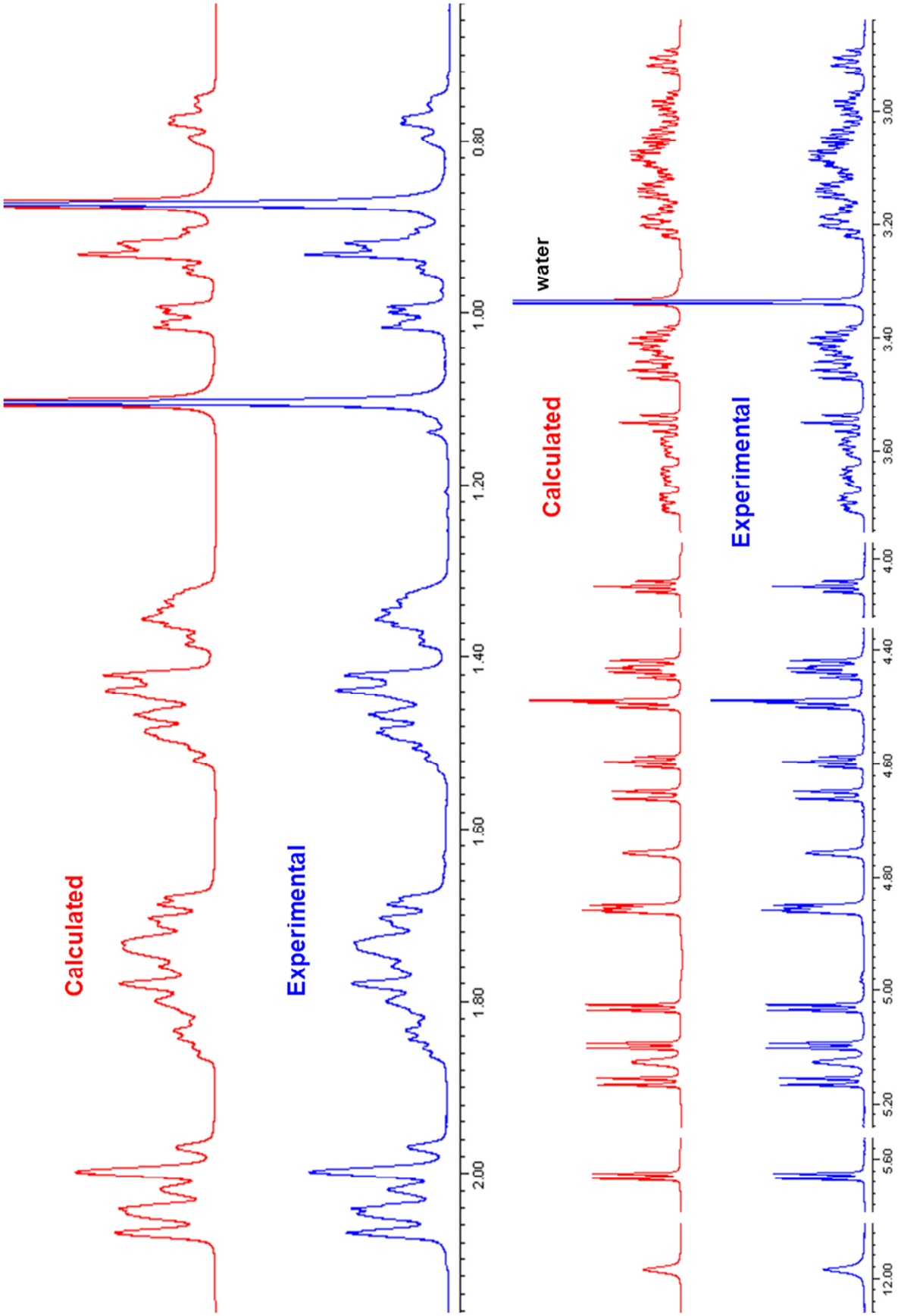
S13. The HiFSA profile of rebaudioside B (**7**) in DMSO-d_6 [in PERCH parameter (.pms) file format].

```
* 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: c:\HIFSA\Stevia\RebB
#$œ  Date 10.10.2014;  Time 22:21:16     rebB.pms

CHEMICAL SHIFTS(PPM):
PROTON    2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.05345
 H1A   / 1     0.775844  1*1*1  STAT=Y  PRED= 0.779 RANGE= 0.050 WIDTH(Y)= 3.120 RESP(Y)= 0.9579 HSQC= C1
 H1B   / 1     1.788191  1*1*1  STAT=Y  PRED= 1.778 RANGE= 0.050 WIDTH(Y)= 3.881 RESP(Y)= 0.9901 HSQC= C1
 H2A   / 1     1.769866  1*1*1  STAT=Y  PRED= 1.764 RANGE= 0.050 WIDTH(Y)= 3.927 RESP(Y)= 0.9034 HSQC= C2
 H2B   / 1     1.339855  1*1*1  STAT=Y  PRED= 1.332 RANGE= 0.050 WIDTH(Y)= 2.967 RESP(Y)= 0.9269 HSQC= C2
 H3A   / 1     2.008302  1*1*1  STAT=Y  PRED= 2.000 RANGE= 0.050 WIDTH(Y)= 3.427 RESP(Y)= 0.9312 HSQC= C3
 H3B   / 1     0.928436  1*1*1  STAT=Y  PRED= 0.932 RANGE= 0.050 WIDTH(Y)= 3.699 RESP(Y)= 0.9292 HSQC= C3
 H5A   / 1     1.004385  1*1*1  STAT=Y  PRED= 1.015 RANGE= 0.050 WIDTH(Y)= 3.476 RESP(Y)= 0.9664 HSQC= C5
 H6A   / 1     1.718759  1*1*1  STAT=Y  PRED= 1.700 RANGE= 0.050 WIDTH(Y)= 4.710 RESP(Y)= 0.9192 HSQC= C6
 H6B   / 1     1.742223  1*1*1  STAT=Y  PRED= 1.737 RANGE= 0.050 WIDTH(Y)= 4.667 RESP(Y)= 0.9360 HSQC= C6
 H7A   / 1     1.361382  1*1*1  STAT=Y  PRED= 1.360 RANGE= 0.050 WIDTH(Y)= 4.050 RESP(Y)= 0.9031 HSQC= C7
 H7B   / 1     1.437099  1*1*1  STAT=Y  PRED= 1.449 RANGE= 0.050 WIDTH(Y)= 4.037 RESP(Y)= 0.9915 HSQC= C7
 H9A   / 1     0.925089  1*1*1  STAT=Y  PRED= 0.921 RANGE= 0.050 WIDTH(Y)= 4.015 RESP(Y)= 0.9761 HSQC= C9
 H11A  / 1     1.694365  1*1*1  STAT=Y  PRED= 1.651 RANGE= 0.050 WIDTH(Y)= 4.208 RESP(Y)= 0.9509 HSQC= C11
 H11B  / 1     1.501259  1*1*1  STAT=Y  PRED= 1.429 RANGE= 0.050 WIDTH(Y)= 4.146 RESP(Y)= 0.9007 HSQC= C11
 H12A  / 1     1.475871  1*1*1  STAT=Y  PRED= 1.348 RANGE= 0.025 WIDTH(Y)= 3.934 RESP(Y)= 1.0000 HSQC= C12
 H12B  / 1     1.836642  1*1*1  STAT=Y  PRED= 1.599 RANGE= 0.050 WIDTH(Y)= 3.765 RESP(Y)= 0.9451 HSQC= C12
 H14A  / 1     2.059247  1*1*1  STAT=Y  PRED= 1.869 RANGE= 0.455 WIDTH(Y)= 4.087 RESP(Y)= 0.9685 HSQC= C14
 H14B  / 1     1.428830  1*1*1  STAT=Y  PRED= 1.192 RANGE= 0.050 WIDTH(Y)= 3.770 RESP(Y)= 0.9764 HSQC= C14
 H15A  / 1     1.985623  1*1*1  STAT=Y  PRED= 2.023 RANGE= 0.050 WIDTH(Y)= 4.279 RESP(Y)= 0.9421 HSQC= C15
 H15B  / 1     2.050203  1*1*1  STAT=Y  PRED= 2.052 RANGE= 0.050 WIDTH(Y)= 3.769 RESP(Y)= 0.9264 HSQC= C15
 H17A  / 1     5.125521  1*1*1  STAT=Y  PRED= 4.878 RANGE= 0.025 WIDTH(Y)= 3.832 RESP(Y)= 0.9638 HSQC= C17
 H17B  / 1     4.756877  1*1*1  STAT=Y  PRED= 4.687 RANGE= 0.025 WIDTH(Y)= 3.782 RESP(Y)= 0.9720 HSQC= C17
 H18B  / 1     1.102598  1*1*3  STAT=Y  PRED= 1.101 RANGE= 0.050 WIDTH(Y)= 2.936 RESP(Y)= 0.9314 HSQC= C18
 H20B  / 1     0.872515  1*1*3  STAT=Y  PRED= 0.866 RANGE= 0.050 WIDTH(Y)= 3.555 RESP(Y)= 0.9416 HSQC= C20
 H22A  / 1    11.984351  1*1*1  STAT=Y  PRED= 11.981 RANGE= 0.050 WIDTH(Y)= 6.451 RESP(Y)= 0.7926
 GB1   / 1     4.493111  1*1*1  STAT=Y  PRED= 5.565 RANGE= 0.342 WIDTH(Y)= 2.238 RESP(Y)= 0.9078 HSQC= H21
 GB2   / 1     3.457088  1*1*1  STAT=Y  PRED= 3.526 RANGE= 0.200 WIDTH(Y)= 1.964 RESP(Y)= 0.9171 HSQC= C23
 GB3   / 1     3.549127  1*1*1  STAT=Y  PRED= 3.317 RANGE= 0.155 WIDTH(Y)= 2.053 RESP(Y)= 0.8548 HSQC= C26
 GB4   / 1     3.203939  1*1*1  STAT=Y  PRED= 3.387 RANGE= 0.287 WIDTH(Y)= 1.753 RESP(Y)= 0.8374 HSQC= C27
 GB5   / 1     3.094971  1*1*1  STAT=Y  PRED= 3.485 RANGE= 0.247 WIDTH(Y)= 2.090 RESP(Y)= 0.8314 HSQC= C25
 GB6A  / 1     3.407142  1*1*1  STAT=Y  PRED= 3.351 RANGE= 0.450 WIDTH(Y)= 1.996 RESP(Y)= 0.8318 HSQC= C29
 GB6B  / 1     3.643427  1*1*1  STAT=Y  PRED= 3.509 RANGE= 0.232 WIDTH(Y)= 2.367 RESP(Y)= 0.8536 HSQC= C29
 OGB4  / 1     4.489201  1*1*1  STAT=Y  PRED= 4.702 RANGE= 1.565 WIDTH(Y)= 1.532 RESP(Y)= 0.8679
 OGB6  / 1     4.436331  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 1.650 RESP(Y)= 0.8978
 GC1   / 1     4.653912  1*1*1  STAT=Y  PRED= 5.565 RANGE= 0.342 WIDTH(Y)= 2.082 RESP(Y)= 0.9078 HSQC= H21
 GC2   / 1     2.911058  1*1*1  STAT=Y  PRED= 3.526 RANGE= 0.200 WIDTH(Y)= 2.144 RESP(Y)= 0.9171 HSQC= C23
 GC3   / 1     3.132942  1*1*1  STAT=Y  PRED= 3.317 RANGE= 0.155 WIDTH(Y)= 2.110 RESP(Y)= 0.8548 HSQC= C26
 GC4   / 1     2.986647  1*1*1  STAT=Y  PRED= 3.387 RANGE= 0.287 WIDTH(Y)= 2.082 RESP(Y)= 0.8374 HSQC= C27
 GC5   / 1     3.080448  1*1*1  STAT=Y  PRED= 3.485 RANGE= 0.247 WIDTH(Y)= 2.063 RESP(Y)= 0.8314 HSQC= C25
 GC6A  / 1     3.430941  1*1*1  STAT=Y  PRED= 3.351 RANGE= 0.450 WIDTH(Y)= 2.561 RESP(Y)= 0.8318 HSQC= C29
 GC6B  / 1     3.591710  1*1*1  STAT=Y  PRED= 3.509 RANGE= 0.232 WIDTH(Y)= 2.385 RESP(Y)= 0.8536 HSQC= C29
 OGC2  / 1     5.159273  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 1.674 RESP(Y)= 0.8978
 OGC3  / 1     4.857861  1*1*1  STAT=Y  PRED= 4.296 RANGE= 1.420 WIDTH(Y)= 1.983 RESP(Y)= 0.8798
 OGC4  / 1     4.853732  1*1*1  STAT=Y  PRED= 4.702 RANGE= 1.565 WIDTH(Y)= 1.572 RESP(Y)= 0.8679
 OGC6  / 1     4.047087  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 1.584 RESP(Y)= 0.8978
 GD1   / 1     4.423299  1*1*1  STAT=Y  PRED= 5.565 RANGE= 0.342 WIDTH(Y)= 2.010 RESP(Y)= 0.9078 HSQC= H21
 GD2   / 1     3.036506  1*1*1  STAT=Y  PRED= 3.526 RANGE= 0.200 WIDTH(Y)= 1.773 RESP(Y)= 0.9171 HSQC= C23
 GD3   / 1     3.144461  1*1*1  STAT=Y  PRED= 3.317 RANGE= 0.155 WIDTH(Y)= 1.679 RESP(Y)= 0.8548 HSQC= C26
 GD4   / 1     3.067099  1*1*1  STAT=Y  PRED= 3.387 RANGE= 0.287 WIDTH(Y)= 1.848 RESP(Y)= 0.8374 HSQC= C27
 GD5   / 1     3.184629  1*1*1  STAT=Y  PRED= 3.485 RANGE= 0.247 WIDTH(Y)= 1.991 RESP(Y)= 0.8314 HSQC= C25
 GD6A  / 1     3.399675  1*1*1  STAT=Y  PRED= 3.351 RANGE= 0.450 WIDTH(Y)= 2.226 RESP(Y)= 0.8318 HSQC= C29
 GD6B  / 1     3.690730  1*1*1  STAT=Y  PRED= 3.509 RANGE= 0.232 WIDTH(Y)= 2.085 RESP(Y)= 0.8536 HSQC= C29
 OGD2  / 1     5.628404  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 1.594 RESP(Y)= 0.8978
 OGD3  / 1     5.096671  1*1*1  STAT=Y  PRED= 4.296 RANGE= 1.420 WIDTH(Y)= 1.459 RESP(Y)= 0.8798
 OGD4  / 1     5.028968  1*1*1  STAT=Y  PRED= 4.702 RANGE= 1.565 WIDTH(Y)= 1.424 RESP(Y)= 0.8679
 OGD6  / 1     4.595012  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 1.550 RESP(Y)= 0.8978
DMSO_CH   2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.79946
 DMSO  / 2     2.500032  1*1*1  STAT=Y  PRED= 2.500 RANGE= 0.050 WIDTH(Y)= 1.268 RESP(Y)= 1.0000
DMSO_D    2*SPIN= 2 SPECIES=2D    POPULATION(Y)=   0.79946
 DMSOD1/ 2  -100.000001  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
 DMSOD2/ 2  -100.000001  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
WATER_H   2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.14709
 WATER / 3     3.336154  2*1*1  STAT=Y  PRED= 3.338 RANGE= 0.050 WIDTH(Y)= 1.302 RESP(Y)= 1.0000

COUPLING CONSTANTS(HZ):
 J12_13    -12.0306   J H1A    H1B      STAT=Y  PRED= -13.130 RANGE= 1.500
 J17_12     14.2935   J H1A    H2A      STAT=Y  PRED= 12.550 RANGE= 2.560
 J12_18      4.9450   J H1A    H2B      STAT=Y  PRED= 4.380 RANGE= 3.800
 J14_12     -0.1780   J H1A    H20B     STAT=Y  PRED= -0.790 RANGE= 0.400
 J17_13      3.8064   J H1B    H2A      STAT=Y  PRED= 3.880 RANGE= 3.800
 J13_18      3.0622   J H1B    H2B      STAT=Y  PRED= 2.510 RANGE= 2.800
 J13_19      2.8669   J H1B    H3A      STAT=Y  PRED= 2.850 RANGE= 1.280
 J17_18    -12.7266   J H2A    H2B      STAT=Y  PRED= -13.190 RANGE= 1.500
 J17_19      3.5299   J H2A    H3A      STAT=Y  PRED= 3.860 RANGE= 3.800
```

```
 J17_20     13.4122   J H2A    H3B      STAT=Y  PRED= 12.570 RANGE= 2.560
 J19_18      2.1457   J H2B    H3A      STAT=Y  PRED= 2.530 RANGE= 2.800
 J20_18      4.5718   J H2B    H3B      STAT=Y  PRED= 4.310 RANGE= 3.800
 J19_20    -12.5550   J H3A    H3B      STAT=Y  PRED= -13.110 RANGE= 1.500
 J21_22     11.8210   J H5A    H6A      STAT=Y  PRED= 12.550 RANGE= 2.560
 J21_23      2.3659   J H5A    H6B      STAT=Y  PRED= 1.710 RANGE= 2.800
 J22_23    -13.8083   J H6A    H6B      STAT=Y  PRED= -13.190 RANGE= 1.500
 J22_24     14.7294   J H6A    H7A      STAT=Y  PRED= 12.990 RANGE= 2.560
 J22_25      3.7816   J H6A    H7B      STAT=Y  PRED= 3.320 RANGE= 3.800
 J23_24      3.5067   J H6B    H7A      STAT=Y  PRED= 3.410 RANGE= 3.800
 J23_25      5.7672   J H6B    H7B      STAT=Y  PRED= 3.190 RANGE= 3.800
 J24_25    -11.8882   J H7A    H7B      STAT=Y  PRED= -13.130 RANGE= 1.500
 J26_1       0.9744   J H9A    H11A     STAT=Y  PRED= 0.490 RANGE= 2.800
 J26_2       7.9560   J H9A    H11B     STAT=Y  PRED= 9.030 RANGE= 3.580
 J26_6       0.0399   J H9A    H14B     STAT=Y  PRED= 2.290 RANGE= 1.100
 J1_2      -15.0885   J H11A   H11B     STAT=Y  PRED= -13.010 RANGE= 1.500
 J3_1        1.9258   J H11A   H12A     STAT=Y  PRED= 1.040 RANGE= 2.800
 J4_1        6.0978   J H11A   H12B     STAT=Y  PRED= 6.480 RANGE= 3.800
 J3_2        2.6706   J H11B   H12A     STAT=Y  PRED= 6.890 RANGE= 3.800
 J4_2       14.0330   J H11B   H12B     STAT=Y  PRED= 11.180 RANGE= 2.800
 J3_4      -11.4094   J H12A   H12B     STAT=Y  PRED= -12.880 RANGE= 1.500
 J3_6        3.2469   J H12A   H14B     STAT=Y  PRED= 2.670 RANGE= 1.280
 J5_6      -12.0137   J H14A   H14B     STAT=Y  PRED= -12.450 RANGE= 2.000
 J7_5        3.0003   J H14A   H15A     STAT=Y  PRED= 1.650 RANGE= 1.280
 J7_8      -16.1340   J H15A   H15B     STAT=Y  PRED= -14.390 RANGE= 3.000
 J7_9       -1.6209   J H15A   H17A     STAT=Y  PRED= -2.030 RANGE= 1.000
 J7_10      -0.0375   J H15A   H17B     STAT=Y  PRED= -1.900 RANGE= 0.950
 J9_8       -2.9809   J H15B   H17A     STAT=Y  PRED= -2.420 RANGE= 1.200
 J10_8      -2.4552   J H15B   H17B     STAT=Y  PRED= -2.140 RANGE= 1.100
 J9_10       0.4415   J H17A   H17B     STAT=Y  PRED= 2.980 RANGE= 4.000
 J48_50      7.6703   J GB1    GB2      STAT=Y  PRED= 7.190 RANGE= 3.580
 J50_53      9.0623   J GB2    GB3      STAT=Y  PRED= 8.920 RANGE= 3.580
 J53_56      8.6956   J GB3    GB4      STAT=Y  PRED= 9.140 RANGE= 3.580
 J51_56      9.6569   J GB4    GB5      STAT=Y  PRED= 10.550 RANGE= 2.560
 J56_62      2.3149   J GB4    OGB4     STAT=Y  PRED= 4.300 RANGE= 1.000
 J51_59      5.2987   J GB5    GB6A     STAT=Y  PRED= 2.700 RANGE= 3.000
 J51_60      2.2884   J GB5    GB6B     STAT=Y  PRED= 1.280 RANGE= 3.000
 J59_60    -11.0725   J GB6A   GB6B     STAT=Y  PRED= -12.300 RANGE= 0.800
 J59_61      6.4043   J GB6A   OGB6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J60_61      5.6097   J GB6B   OGB6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J58_60      7.8767   J GC1    GC2      STAT=Y  PRED= 7.190 RANGE= 3.580
 J60_63      9.2543   J GC2    GC3      STAT=Y  PRED= 8.920 RANGE= 3.580
 J60_68      6.8804   J GC2    OGC2     STAT=Y  PRED= 4.300 RANGE= 1.000
 J63_66      8.7537   J GC3    GC4      STAT=Y  PRED= 9.140 RANGE= 3.580
 J63_71      4.5877   J GC3    OGC3     STAT=Y  PRED= 4.300 RANGE= 1.000
 J61_66      9.5810   J GC4    GC5      STAT=Y  PRED= 10.550 RANGE= 2.560
 J66_72      5.2996   J GC4    OGC4     STAT=Y  PRED= 4.300 RANGE= 1.000
 J61_69      5.8522   J GC5    GC6A     STAT=Y  PRED= 2.700 RANGE= 3.000
 J61_70      2.3560   J GC5    GC6B     STAT=Y  PRED= 1.280 RANGE= 3.000
 J69_70    -11.6137   J GC6A   GC6B     STAT=Y  PRED= -12.300 RANGE= 0.800
 J69_71      5.7485   J GC6A   OGC6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J70_71      5.5199   J GC6B   OGC6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J68_80      7.8998   J GD1    GD2      STAT=Y  PRED= 7.190 RANGE= 3.580
 J70_73      9.1681   J GD2    GD3      STAT=Y  PRED= 8.920 RANGE= 3.580
 J70_78      5.3896   J GD2    OGD2     STAT=Y  PRED= 4.300 RANGE= 1.000
 J73_76      8.7266   J GD3    GD4      STAT=Y  PRED= 9.140 RANGE= 3.580
 J73_81      5.0034   J GD3    OGD3     STAT=Y  PRED= 4.300 RANGE= 1.000
 J71_76      9.6876   J GD4    GD5      STAT=Y  PRED= 10.550 RANGE= 2.560
 J76_82      5.6068   J GD4    OGD4     STAT=Y  PRED= 4.300 RANGE= 1.000
 J71_79      6.5514   J GD5    GD6A     STAT=Y  PRED= 2.700 RANGE= 3.000
 J71_80      2.2039   J GD5    GD6B     STAT=Y  PRED= 1.280 RANGE= 3.000
 J79_80    -11.4550   J GD6A   GD6B     STAT=Y  PRED= -12.300 RANGE= 0.800
 J79_81      5.6231   J GD6A   OGD6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J80_81      4.8995   J GD6B   OGD6     STAT=Y  PRED= 4.300 RANGE= 3.000
 JDMSO1      1.7939   J DMSO   DMSOD1   STAT=Y  PRED= 1.700 RANGE= 0.050
 JDMSO1      1.7939   J DMSO   DMSOD2   STAT=Y  PRED= 1.700 RANGE= 0.050

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)
   600.12701400 =  FIELD(1H,MHz), used to transform shifts to ppms
    22.47832099 =  Left frequency (ppm)
    -7.49157654 =  Right frequency (ppm)
          0.000 =  Acquisition time (s, for QMTLS)
          1.268 =  Line-width (for modes D, P & T, 0=use defaults)
    0.068609924 =  Data-point resolution (Hz)
         50.067 =  GAUSSIAN (%, 0=use default from INF)
         -3.799 =  Dispersion contribution (%, 0=use default from INF)
     0.00000000 =  Decoupling frequency (for DORES)

CONSTRAINTS (in equations X0 = 1.0)...use no empty lines
 EQUAL DMSOD1   = DMSOD2
  1.000 * 1.0 = -41.020 * 1.0  - 1.000 * 1.0
  10.000 * 1.0 = -38.340 * 1.0  - 1.000 * 1.0
  11.000 * 1.0 = -16.670 * 1.0  - 1.000 * 1.0
```

```
  12.000 * 1.0 = -36.870 * 1.0  - 1.000 * 1.0
  13.000 * 1.0 = -80.200 * 1.0  - 1.000 * 1.0
  14.000 * 1.0 = -49.010 * 1.0  - 1.000 * 1.0
  15.000 * 1.0 = -48.090 * 1.0  - 1.000 * 1.0
  16.0 * 1.0 = -153.1 * 1.0  - 1.0 * 1.0
  17.0 * 1.0 = -104.2 * 1.0  - 1.0 * 1.0
  18.000 * 1.0 = -28.210 * 1.0  - 1.000 * 1.0
  19.0 * 1.0 = -185.4 * 1.0  - 1.0 * 1.0
  2.000 * 1.0 = -19.040 * 1.0  - 1.000 * 1.0
  20.000 * 1.0 = -14.770 * 1.0  - 1.000 * 1.0
  3.000 * 1.0 = -37.520 * 1.0  - 1.000 * 1.0
  4.000 * 1.0 = -43.240 * 1.0  - 1.000 * 1.0
  5.000 * 1.0 = -55.060 * 1.0  - 1.000 * 1.0
  6.000 * 1.0 = -21.840 * 1.0  - 1.000 * 1.0
  7.000 * 1.0 = -40.820 * 1.0  - 1.000 * 1.0
  8.000 * 1.0 = -42.640 * 1.0  - 1.000 * 1.0
  9.000 * 1.0 = -55.850 * 1.0  - 1.000 * 1.0

END of FILE
```

S14. The ^{1}H fingerprint of rebaudioside B (**7**) in DMSO-d_6 (26 mM, 600 MHz, 298 K). The calculated and observed NMR spectra are shown in red and blue, respectively.



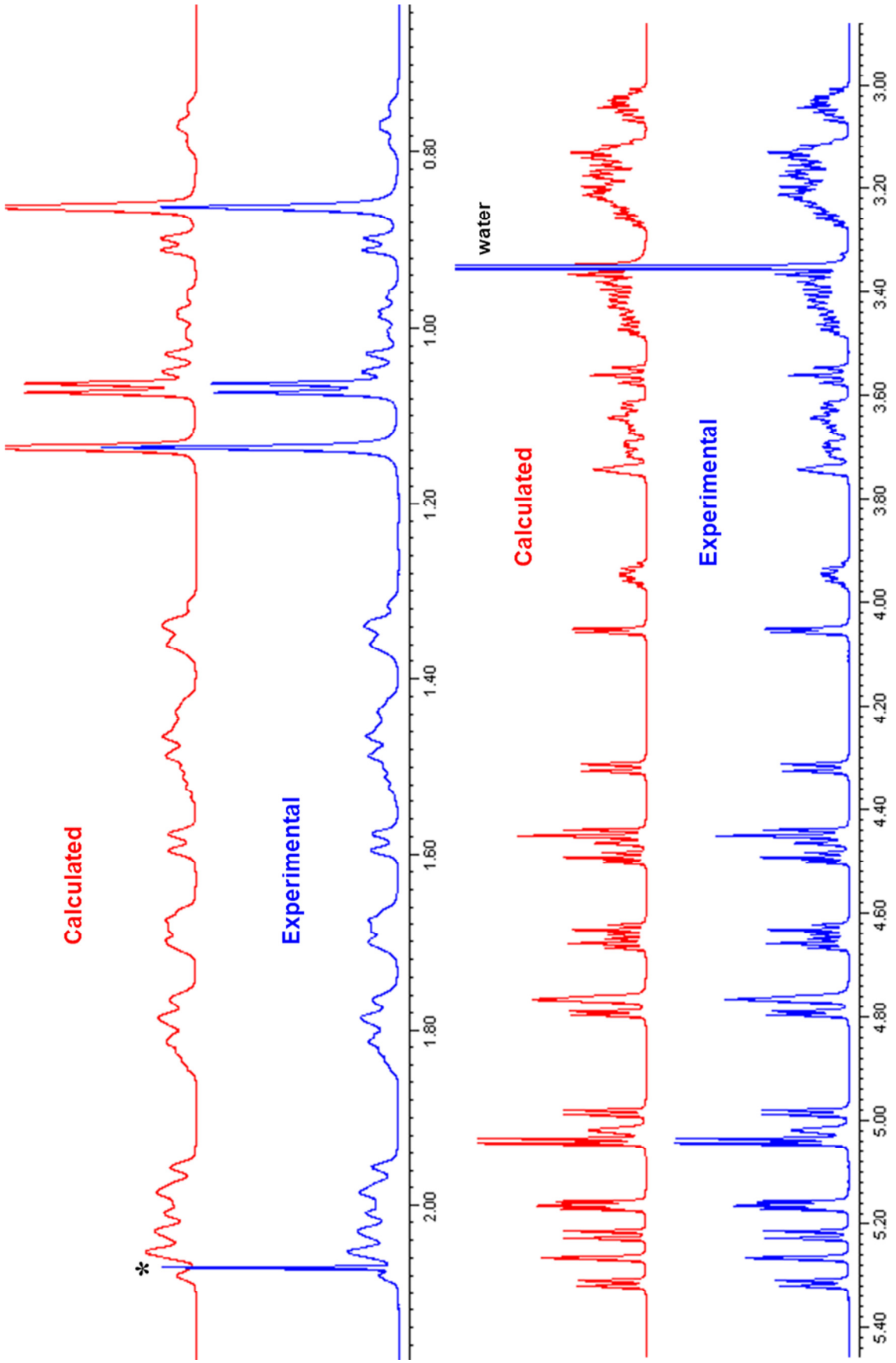
S15. The HiFSA profile of rebaudioside C (**8**) in DMSO-d_6 [in PERCH parameter (.pms) file format].

```
* 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: c:\HIFSA\Stevia\RebC
#$œ  Date 10.10.2014;  Time 22:25:29     rebC.pms

CHEMICAL SHIFTS(PPM):
PROTON    2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.07508
 H1A   / 1     0.768130  1*1*1  STAT=Y  PRED= 0.779 RANGE= 0.050 WIDTH(Y)= 6.377 RESP(Y)= 0.9579 HSQC= C1
 H1B   / 1     1.773877  1*1*1  STAT=Y  PRED= 1.778 RANGE= 0.050 WIDTH(Y)= 6.057 RESP(Y)= 0.9901 HSQC= C1
 H2A   / 1     1.797458  1*1*1  STAT=Y  PRED= 1.764 RANGE= 0.050 WIDTH(Y)= 5.239 RESP(Y)= 0.9034 HSQC= C2
 H2B   / 1     1.351259  1*1*1  STAT=Y  PRED= 1.332 RANGE= 0.050 WIDTH(Y)= 4.089 RESP(Y)= 0.9269 HSQC= C2
 H3A   / 1     2.046577  1*1*1  STAT=Y  PRED= 2.000 RANGE= 0.050 WIDTH(Y)= 3.335 RESP(Y)= 0.9312 HSQC= C3
 H3B   / 1     0.983335  1*1*1  STAT=Y  PRED= 0.932 RANGE= 0.050 WIDTH(Y)= 5.163 RESP(Y)= 0.9292 HSQC= C3
 H5A   / 1     1.038975  1*1*1  STAT=Y  PRED= 1.015 RANGE= 0.050 WIDTH(Y)= 5.681 RESP(Y)= 0.9664 HSQC= C5
 H6A   / 1     1.985168  1*1*1  STAT=Y  PRED= 1.700 RANGE= 0.050 WIDTH(Y)= 5.435 RESP(Y)= 0.9192 HSQC= C6
 H6B   / 1     1.692668  1*1*1  STAT=Y  PRED= 1.737 RANGE= 0.050 WIDTH(Y)= 5.013 RESP(Y)= 0.9360 HSQC= C6
 H7A   / 1     1.336611  1*1*1  STAT=Y  PRED= 1.360 RANGE= 0.050 WIDTH(Y)= 5.482 RESP(Y)= 0.9031 HSQC= C7
 H7B   / 1     1.474303  1*1*1  STAT=Y  PRED= 1.449 RANGE= 0.050 WIDTH(Y)= 5.864 RESP(Y)= 0.9915 HSQC= C7
 H9A   / 1     0.904006  1*1*1  STAT=Y  PRED= 0.921 RANGE= 0.050 WIDTH(Y)= 5.302 RESP(Y)= 0.9761 HSQC= C9
 H11A  / 1     1.679438  1*1*1  STAT=Y  PRED= 1.651 RANGE= 0.050 WIDTH(Y)= 6.109 RESP(Y)= 0.9509 HSQC= C11
 H11B  / 1     1.501121  1*1*1  STAT=Y  PRED= 1.429 RANGE= 0.050 WIDTH(Y)= 5.316 RESP(Y)= 0.9007 HSQC= C11
 H12A  / 1     1.438531  1*1*1  STAT=Y  PRED= 1.348 RANGE= 0.025 WIDTH(Y)= 7.104 RESP(Y)= 1.0000 HSQC= C12
 H12B  / 1     1.818989  1*1*1  STAT=Y  PRED= 1.599 RANGE= 0.050 WIDTH(Y)= 5.090 RESP(Y)= 0.9451 HSQC= C12
 H14A  / 1     2.018223  1*1*1  STAT=Y  PRED= 1.869 RANGE= 0.455 WIDTH(Y)= 5.332 RESP(Y)= 0.9685 HSQC= C14
 H14B  / 1     1.585353  1*1*1  STAT=Y  PRED= 1.192 RANGE= 0.050 WIDTH(Y)= 5.905 RESP(Y)= 0.9764 HSQC= C14
 H15A  / 1     1.972813  1*1*1  STAT=Y  PRED= 2.023 RANGE= 0.050 WIDTH(Y)= 4.786 RESP(Y)= 0.9421 HSQC= C15
 H15B  / 1     2.063484  1*1*1  STAT=Y  PRED= 2.052 RANGE= 0.050 WIDTH(Y)= 5.607 RESP(Y)= 0.9264 HSQC= C15
 H17A  / 1     5.017816  1*1*1  STAT=Y  PRED= 4.878 RANGE= 0.025 WIDTH(Y)= 4.731 RESP(Y)= 0.9638 HSQC= C17
 H17B  / 1     4.763889  1*1*1  STAT=Y  PRED= 4.687 RANGE= 0.025 WIDTH(Y)= 3.938 RESP(Y)= 0.9720 HSQC= C17
 H18B  / 1     1.135839  1*1*3  STAT=Y  PRED= 1.101 RANGE= 0.050 WIDTH(Y)= 3.760 RESP(Y)= 0.9314 HSQC= C18
 H20B  / 1     0.861623  1*1*3  STAT=Y  PRED= 0.866 RANGE= 0.050 WIDTH(Y)= 4.632 RESP(Y)= 0.9416 HSQC= C20
 GA1   / 1     5.220881  1*1*1  STAT=Y  PRED= 5.565 RANGE= 0.342 WIDTH(Y)= 2.027 RESP(Y)= 0.9078 HSQC= H21
 GA2   / 1     3.134916  1*1*1  STAT=Y  PRED= 3.526 RANGE= 0.200 WIDTH(Y)= 2.023 RESP(Y)= 0.9171 HSQC= C23
 GA3   / 1     3.250284  1*1*1  STAT=Y  PRED= 3.317 RANGE= 0.155 WIDTH(Y)= 2.453 RESP(Y)= 0.8548 HSQC= C26
 GA4   / 1     3.136546  1*1*1  STAT=Y  PRED= 3.387 RANGE= 0.287 WIDTH(Y)= 2.399 RESP(Y)= 0.8374 HSQC= C27
 GA5   / 1     3.179003  1*1*1  STAT=Y  PRED= 3.485 RANGE= 0.247 WIDTH(Y)= 1.930 RESP(Y)= 0.8314 HSQC= C25
 GA6A  / 1     3.461098  1*1*1  STAT=Y  PRED= 3.351 RANGE= 0.450 WIDTH(Y)= 2.927 RESP(Y)= 0.8318 HSQC= C29
 GA6B  / 1     3.626158  1*1*1  STAT=Y  PRED= 3.509 RANGE= 0.232 WIDTH(Y)= 3.044 RESP(Y)= 0.8536 HSQC= C29
 OGA2  / 1     5.313768  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 2.458 RESP(Y)= 0.8978
 OGA3  / 1     5.038462  1*1*1  STAT=Y  PRED= 4.296 RANGE= 1.420 WIDTH(Y)= 2.432 RESP(Y)= 0.8798
 OGA4  / 1     4.983639  1*1*1  STAT=Y  PRED= 4.702 RANGE= 1.565 WIDTH(Y)= 1.918 RESP(Y)= 0.8679
 OGA6  / 1     4.491010  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 1.941 RESP(Y)= 0.8978
 GB1   / 1     4.456313  1*1*1  STAT=Y  PRED= 5.565 RANGE= 0.342 WIDTH(Y)= 3.359 RESP(Y)= 0.9078 HSQC= H21
 GB2   / 1     3.363972  1*1*1  STAT=Y  PRED= 3.526 RANGE= 0.200 WIDTH(Y)= 2.270 RESP(Y)= 0.9171 HSQC= C23
 GB3   / 1     3.559321  1*1*1  STAT=Y  PRED= 3.317 RANGE= 0.155 WIDTH(Y)= 2.623 RESP(Y)= 0.8548 HSQC= C26
 GB4   / 1     3.199388  1*1*1  STAT=Y  PRED= 3.387 RANGE= 0.287 WIDTH(Y)= 1.959 RESP(Y)= 0.8374 HSQC= C27
 GB5   / 1     3.120803  1*1*1  STAT=Y  PRED= 3.485 RANGE= 0.247 WIDTH(Y)= 2.536 RESP(Y)= 0.8314 HSQC= C25
 GB6A  / 1     3.382959  1*1*1  STAT=Y  PRED= 3.351 RANGE= 0.450 WIDTH(Y)= 2.898 RESP(Y)= 0.8318 HSQC= C29
 GB6B  / 1     3.655040  1*1*1  STAT=Y  PRED= 3.509 RANGE= 0.232 WIDTH(Y)= 3.083 RESP(Y)= 0.8536 HSQC= C29
 OGB4  / 1     4.762887  1*1*1  STAT=Y  PRED= 4.702 RANGE= 1.565 WIDTH(Y)= 3.502 RESP(Y)= 0.8679
 OGB6  / 1     4.631116  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 2.285 RESP(Y)= 0.8978
 RH1   / 1     5.265103  1*1*1  STAT=Y  PRED= 4.453 RANGE= 0.300 WIDTH(Y)= 2.737 RESP(Y)= 0.9527 HSQC= C33
 RH2   / 1     3.741521  1*1*1  STAT=Y  PRED= 3.609 RANGE= 0.242 WIDTH(Y)= 3.069 RESP(Y)= 0.9502 HSQC= C38
 RH3   / 1     3.427112  1*1*1  STAT=Y  PRED= 3.082 RANGE= 0.582 WIDTH(Y)= 2.583 RESP(Y)= 0.8779 HSQC= C39
 RH4   / 1     3.217599  1*1*1  STAT=Y  PRED= 2.968 RANGE= 0.287 WIDTH(Y)= 4.111 RESP(Y)= 0.9349 HSQC= C37
 RH5   / 1     3.945094  1*1*1  STAT=Y  PRED= 2.961 RANGE= 0.627 WIDTH(Y)= 2.855 RESP(Y)= 0.9335 HSQC= C36
 RH6   / 1     1.067648  1*1*3  STAT=Y  PRED= 0.586 RANGE= 0.262 WIDTH(Y)= 2.846 RESP(Y)= 0.8538 HSQC= C40
 ORH2  / 1     4.051573  1*1*1  STAT=Y  PRED= 4.719 RANGE= 1.395 WIDTH(Y)= 2.066 RESP(Y)= 0.7880
 ORH3  / 1     4.443468  1*1*1  STAT=Y  PRED= 4.127 RANGE= 1.613 WIDTH(Y)= 1.949 RESP(Y)= 0.8379
 ORH4  / 1     4.791816  1*1*1  STAT=Y  PRED= 4.732 RANGE= 1.673 WIDTH(Y)= 2.164 RESP(Y)= 0.8554
 GD1   / 1     4.316854  1*1*1  STAT=Y  PRED= 5.565 RANGE= 0.342 WIDTH(Y)= 2.653 RESP(Y)= 0.9078 HSQC= H21
 GD2   / 1     3.025455  1*1*1  STAT=Y  PRED= 3.526 RANGE= 0.200 WIDTH(Y)= 2.473 RESP(Y)= 0.9171 HSQC= C23
 GD3   / 1     3.168194  1*1*1  STAT=Y  PRED= 3.317 RANGE= 0.155 WIDTH(Y)= 1.997 RESP(Y)= 0.8548 HSQC= C26
 GD4   / 1     3.047268  1*1*1  STAT=Y  PRED= 3.387 RANGE= 0.287 WIDTH(Y)= 2.163 RESP(Y)= 0.8374 HSQC= C27
 GD5   / 1     3.212035  1*1*1  STAT=Y  PRED= 3.485 RANGE= 0.247 WIDTH(Y)= 3.048 RESP(Y)= 0.8314 HSQC= C25
 GD6A  / 1     3.404695  1*1*1  STAT=Y  PRED= 3.351 RANGE= 0.450 WIDTH(Y)= 2.958 RESP(Y)= 0.8318 HSQC= C29
 GD6B  / 1     3.702565  1*1*1  STAT=Y  PRED= 3.509 RANGE= 0.232 WIDTH(Y)= 3.238 RESP(Y)= 0.8536 HSQC= C29
 OGD2  / 1     5.165184  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 2.047 RESP(Y)= 0.8978
 OGD3  / 1     5.159532  1*1*1  STAT=Y  PRED= 4.296 RANGE= 1.420 WIDTH(Y)= 1.906 RESP(Y)= 0.8798
 OGD4  / 1     5.038376  1*1*1  STAT=Y  PRED= 4.702 RANGE= 1.565 WIDTH(Y)= 1.614 RESP(Y)= 0.8679
 OGD6  / 1     4.658077  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 2.113 RESP(Y)= 0.8978
DMSO_CH   2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.56433
 DMSO  / 2     2.500030  1*1*1  STAT=Y  PRED= 2.500 RANGE= 0.050 WIDTH(Y)= 1.568 RESP(Y)= 1.0000
DMSO_D    2*SPIN= 2 SPECIES=2D    POPULATION(Y)=   0.56433
 DMSOD1/ 2  -100.000001  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
 DMSOD2/ 2  -100.000001  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
WATER_H   2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.36059
 WATER / 3     3.349003  2*1*1  STAT=Y  PRED= 3.338 RANGE= 0.050 WIDTH(Y)= 1.588 RESP(Y)= 1.0000

COUPLING CONSTANTS(HZ):
 J12_13    -12.5950   J H1A    H1B      STAT=Y  PRED= -13.130 RANGE= 1.500
```

```
 J17_12     12.8882   J H1A    H2A      STAT=Y  PRED= 12.550 RANGE= 2.560
 J12_18      5.0216   J H1A    H2B      STAT=Y  PRED= 4.380 RANGE= 3.800
 J14_12     -0.0670   J H1A    H20B     STAT=Y  PRED= -0.790 RANGE= 0.400
 J17_13      3.0840   J H1B    H2A      STAT=Y  PRED= 3.880 RANGE= 3.800
 J13_18      3.7195   J H1B    H2B      STAT=Y  PRED= 2.510 RANGE= 2.800
 J13_19      3.3772   J H1B    H3A      STAT=Y  PRED= 2.850 RANGE= 1.280
 J17_18    -13.3265   J H2A    H2B      STAT=Y  PRED= -13.190 RANGE= 1.500
 J17_19      4.1810   J H2A    H3A      STAT=Y  PRED= 3.860 RANGE= 3.800
 J17_20     13.6598   J H2A    H3B      STAT=Y  PRED= 12.570 RANGE= 2.560
 J19_18      2.1675   J H2B    H3A      STAT=Y  PRED= 2.530 RANGE= 2.800
 J20_18      4.8673   J H2B    H3B      STAT=Y  PRED= 4.310 RANGE= 3.800
 J19_20    -12.9973   J H3A    H3B      STAT=Y  PRED= -13.110 RANGE= 1.500
 J21_22     12.4398   J H5A    H6A      STAT=Y  PRED= 12.550 RANGE= 2.560
 J21_23      1.0224   J H5A    H6B      STAT=Y  PRED= 1.710 RANGE= 2.800
 J22_23    -13.6402   J H6A    H6B      STAT=Y  PRED= -13.190 RANGE= 1.500
 J22_24     13.1423   J H6A    H7A      STAT=Y  PRED= 12.990 RANGE= 2.560
 J22_25      2.9869   J H6A    H7B      STAT=Y  PRED= 3.320 RANGE= 3.800
 J23_24      4.4684   J H6B    H7A      STAT=Y  PRED= 3.410 RANGE= 3.800
 J23_25      3.4358   J H6B    H7B      STAT=Y  PRED= 3.190 RANGE= 3.800
 J24_25    -12.3831   J H7A    H7B      STAT=Y  PRED= -13.130 RANGE= 1.500
 J26_1       0.0081   J H9A    H11A     STAT=Y  PRED= 0.490 RANGE= 2.800
 J26_2       8.1001   J H9A    H11B     STAT=Y  PRED= 9.030 RANGE= 3.580
 J26_6       0.1676   J H9A    H14B     STAT=Y  PRED= 2.290 RANGE= 1.100
 J1_2      -14.4815   J H11A   H11B     STAT=Y  PRED= -13.010 RANGE= 1.500
 J3_1        1.2577   J H11A   H12A     STAT=Y  PRED= 1.040 RANGE= 2.800
 J4_1        5.8111   J H11A   H12B     STAT=Y  PRED= 6.480 RANGE= 3.800
 J3_2        6.4977   J H11B   H12A     STAT=Y  PRED= 6.890 RANGE= 3.800
 J4_2       12.8127   J H11B   H12B     STAT=Y  PRED= 11.180 RANGE= 2.800
 J3_4      -10.9509   J H12A   H12B     STAT=Y  PRED= -12.880 RANGE= 1.500
 J3_6        2.3412   J H12A   H14B     STAT=Y  PRED= 2.670 RANGE= 1.280
 J5_6      -11.2862   J H14A   H14B     STAT=Y  PRED= -12.450 RANGE= 2.000
 J7_5        2.9338   J H14A   H15A     STAT=Y  PRED= 1.650 RANGE= 1.280
 J7_8      -16.7761   J H15A   H15B     STAT=Y  PRED= -14.390 RANGE= 3.000
 J7_9       -2.0671   J H15A   H17A     STAT=Y  PRED= -2.030 RANGE= 1.000
 J7_10      -0.0086   J H15A   H17B     STAT=Y  PRED= -1.900 RANGE= 0.950
 J9_8       -2.5458   J H15B   H17A     STAT=Y  PRED= -2.420 RANGE= 1.200
 J10_8      -0.0067   J H15B   H17B     STAT=Y  PRED= -2.140 RANGE= 1.100
 J9_10       0.7624   J H17A   H17B     STAT=Y  PRED= 2.980 RANGE= 4.000
 J38_40      8.2231   J GA1    GA2      STAT=Y  PRED= 7.190 RANGE= 3.580
 J40_43      9.0490   J GA2    GA3      STAT=Y  PRED= 8.920 RANGE= 3.580
 J40_48      6.4084   J GA2    OGA2     STAT=Y  PRED= 4.300 RANGE= 1.000
 J43_46      8.8842   J GA3    GA4      STAT=Y  PRED= 9.140 RANGE= 3.580
 J43_51      5.2628   J GA3    OGA3     STAT=Y  PRED= 4.300 RANGE= 1.000
 J41_46     10.3655   J GA4    GA5      STAT=Y  PRED= 10.550 RANGE= 2.560
 J46_52      5.3953   J GA4    OGA4     STAT=Y  PRED= 4.300 RANGE= 1.000
 J41_49      5.1122   J GA5    GA6A     STAT=Y  PRED= 2.700 RANGE= 3.000
 J41_50      1.8108   J GA5    GA6B     STAT=Y  PRED= 1.280 RANGE= 3.000
 J49_50    -11.7635   J GA6A   GA6B     STAT=Y  PRED= -12.300 RANGE= 0.800
 J49_51      5.8706   J GA6A   OGA6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J50_51      5.3959   J GA6B   OGA6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J48_50      7.9075   J GB1    GB2      STAT=Y  PRED= 7.190 RANGE= 3.580
 J50_53      9.2013   J GB2    GB3      STAT=Y  PRED= 8.920 RANGE= 3.580
 J53_56      8.4433   J GB3    GB4      STAT=Y  PRED= 9.140 RANGE= 3.580
 J51_56      9.5249   J GB4    GB5      STAT=Y  PRED= 10.550 RANGE= 2.560
 J56_62      5.5294   J GB4    OGB4     STAT=Y  PRED= 4.300 RANGE= 1.000
 J51_59      6.0800   J GB5    GB6A     STAT=Y  PRED= 2.700 RANGE= 3.000
 J51_60      2.3623   J GB5    GB6B     STAT=Y  PRED= 1.280 RANGE= 3.000
 J59_60    -11.6465   J GB6A   GB6B     STAT=Y  PRED= -12.300 RANGE= 0.800
 J59_61      5.9260   J GB6A   OGB6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J60_61      5.8411   J GB6B   OGB6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J56_68      1.4424   J RH1    RH2      STAT=Y  PRED= 2.330 RANGE= 2.800
 J68_69      3.4424   J RH2    RH3      STAT=Y  PRED= 3.420 RANGE= 3.800
 J68_71      3.9662   J RH2    ORH2     STAT=Y  PRED= 4.440 RANGE= 1.500
 J66_69      9.3054   J RH3    RH4      STAT=Y  PRED= 9.590 RANGE= 3.580
 J69_72      6.7193   J RH3    ORH3     STAT=Y  PRED= 4.300 RANGE= 1.000
 J57_66      9.3255   J RH4    RH5      STAT=Y  PRED= 9.940 RANGE= 3.580
 J66_73      4.3321   J RH4    ORH4     STAT=Y  PRED= 4.300 RANGE= 1.000
 J57_59      6.0389   J RH5    RH6      STAT=Y  PRED= 6.250 RANGE= 0.600
 J68_80      7.8401   J GD1    GD2      STAT=Y  PRED= 7.190 RANGE= 3.580
 J70_73      8.8413   J GD2    GD3      STAT=Y  PRED= 8.920 RANGE= 3.580
 J70_78      4.8805   J GD2    OGD2     STAT=Y  PRED= 4.300 RANGE= 1.000
 J73_76      8.6026   J GD3    GD4      STAT=Y  PRED= 9.140 RANGE= 3.580
 J73_81      5.2589   J GD3    OGD3     STAT=Y  PRED= 4.300 RANGE= 1.000
 J71_76      9.6578   J GD4    GD5      STAT=Y  PRED= 10.550 RANGE= 2.560
 J76_82      5.6050   J GD4    OGD4     STAT=Y  PRED= 4.300 RANGE= 1.000
 J71_79      6.7829   J GD5    GD6A     STAT=Y  PRED= 2.700 RANGE= 3.000
 J71_80      1.8981   J GD5    GD6B     STAT=Y  PRED= 1.280 RANGE= 3.000
 J79_80    -11.3721   J GD6A   GD6B     STAT=Y  PRED= -12.300 RANGE= 0.800
 J79_81      5.4333   J GD6A   OGD6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J80_81      4.9892   J GD6B   OGD6     STAT=Y  PRED= 4.300 RANGE= 3.000
 JDMSO1      1.7939   J DMSO   DMSOD1   STAT=Y  PRED= 1.700 RANGE= 0.050
 JDMSO1      1.7939   J DMSO   DMSOD2   STAT=Y  PRED= 1.700 RANGE= 0.050

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)
  600.12701400 =  FIELD(1H,MHz), used to transform shifts to ppms
   22.47832099 =  Left frequency (ppm)
   -7.49157654 =  Right frequency (ppm)
         0.000 =  Acquisition time (s, for QMTLS)
         1.500 =  Line-width (for modes D, P & T, 0=use defaults)
   0.068609924 =  Data-point resolution (Hz)
        63.526 =  GAUSSIAN (%, 0=use default from INF)
        -0.819 =  Dispersion contribution (%, 0=use default from INF)
    0.00000000 =  Decoupling frequency (for DORES)

CONSTRAINTS (in equations X0 = 1.0)...use no empty lines
 EQUAL DMSOD1   = DMSOD2
  1.000 * 1.0 = -41.020 * 1.0  - 1.000 * 1.0
  10.000 * 1.0 = -38.340 * 1.0  - 1.000 * 1.0
  11.000 * 1.0 = -16.670 * 1.0  - 1.000 * 1.0
  12.000 * 1.0 = -36.870 * 1.0  - 1.000 * 1.0
  13.000 * 1.0 = -80.200 * 1.0  - 1.000 * 1.0
  14.000 * 1.0 = -49.010 * 1.0  - 1.000 * 1.0
  15.000 * 1.0 = -48.090 * 1.0  - 1.000 * 1.0
  16.0 * 1.0 = -153.1 * 1.0  - 1.0 * 1.0
  17.0 * 1.0 = -104.2 * 1.0  - 1.0 * 1.0
  18.000 * 1.0 = -28.210 * 1.0  - 1.000 * 1.0
  19.0 * 1.0 = -185.4 * 1.0  - 1.0 * 1.0
  2.000 * 1.0 = -19.040 * 1.0  - 1.000 * 1.0
  20.000 * 1.0 = -14.770 * 1.0  - 1.000 * 1.0
  3.000 * 1.0 = -37.520 * 1.0  - 1.000 * 1.0
  4.000 * 1.0 = -43.240 * 1.0  - 1.000 * 1.0
  5.000 * 1.0 = -55.060 * 1.0  - 1.000 * 1.0
  6.000 * 1.0 = -21.840 * 1.0  - 1.000 * 1.0
  7.000 * 1.0 = -40.820 * 1.0  - 1.000 * 1.0
  8.000 * 1.0 = -42.640 * 1.0  - 1.000 * 1.0
  9.000 * 1.0 = -55.850 * 1.0  - 1.000 * 1.0
 IGNORE(HZ):  1246.074 to  1239.040

END of FILE
```

S16. The ^{1}H fingerprint of rebaudioside C (**8**) in DMSO-d_6 (35 mM, 600 MHz, 298 K). The calculated and observed NMR spectra are shown in red and blue, respectively. (*) denotes unidentified impurities.

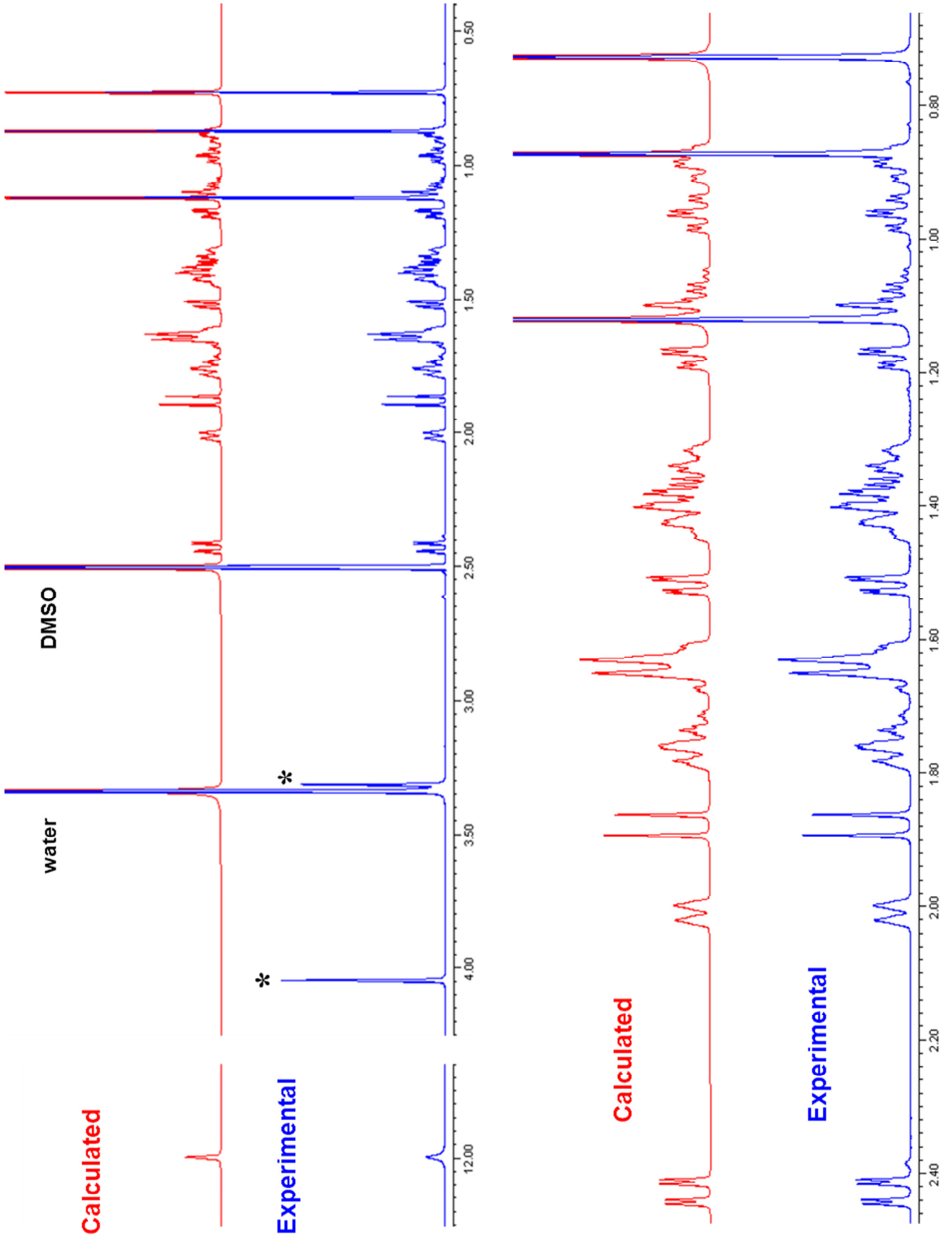


S17. The HiFSA profile of isosteviol (**9**) in DMSO-d_6 [in PERCH parameter (.pms) file format].

```
* 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: c:\HIFSA\Stevia\Isosteviol
#$œ  Date 10.10.2014;  Time 22:27:54     isosteviol.pms

CHEMICAL SHIFTS(PPM):
PROTON    2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.03294
 H1A   / 1     0.886279  1*1*1  STAT=Y  PRED= 0.779 RANGE= 0.050 WIDTH(Y)= 3.428 RESP(Y)= 0.9579 HSQC= C1
 H1B   / 1     1.637285  1*1*1  STAT=Y  PRED= 1.778 RANGE= 0.050 WIDTH(Y)= 3.898 RESP(Y)= 0.9901 HSQC= C1
 H2A   / 1     1.745874  1*1*1  STAT=Y  PRED= 1.764 RANGE= 0.050 WIDTH(Y)= 2.405 RESP(Y)= 0.9034 HSQC= C2
 H2B   / 1     1.328132  1*1*1  STAT=Y  PRED= 1.332 RANGE= 0.050 WIDTH(Y)= 2.338 RESP(Y)= 0.9269 HSQC= C2
 H3A   / 1     2.008950  1*1*1  STAT=Y  PRED= 2.000 RANGE= 0.050 WIDTH(Y)= 2.294 RESP(Y)= 0.9312 HSQC= C3
 H3B   / 1     0.960618  1*1*1  STAT=Y  PRED= 0.932 RANGE= 0.050 WIDTH(Y)= 2.475 RESP(Y)= 0.9292 HSQC= C3
 H5A   / 1     1.108461  1*1*1  STAT=Y  PRED= 1.015 RANGE= 0.050 WIDTH(Y)= 2.570 RESP(Y)= 0.9664 HSQC= C5
 H6A   / 1     1.640488  1*1*1  STAT=Y  PRED= 1.700 RANGE= 0.050 WIDTH(Y)= 2.292 RESP(Y)= 0.9192 HSQC= C6
 H6B   / 1     1.770152  1*1*1  STAT=Y  PRED= 1.737 RANGE= 0.050 WIDTH(Y)= 2.849 RESP(Y)= 0.9360 HSQC= C6
 H7A   / 1     1.402968  1*1*1  STAT=Y  PRED= 1.360 RANGE= 0.050 WIDTH(Y)= 2.195 RESP(Y)= 0.9031 HSQC= C7
 H7B   / 1     1.639577  1*1*1  STAT=Y  PRED= 1.449 RANGE= 0.050 WIDTH(Y)= 2.697 RESP(Y)= 0.9915 HSQC= C7
 H9A   / 1     1.176851  1*1*1  STAT=Y  PRED= 1.062 RANGE= 0.405 WIDTH(Y)= 2.610 RESP(Y)= 0.9093 HSQC= C9
 H11A  / 1     1.626487  1*1*1  STAT=Y  PRED= 1.337 RANGE= 0.422 WIDTH(Y)= 3.526 RESP(Y)= 0.9765 HSQC= C11
 H11B  / 1     1.084846  1*1*1  STAT=Y  PRED= 1.019 RANGE= 0.280 WIDTH(Y)= 2.489 RESP(Y)= 0.8590 HSQC= C11
 H12A  / 1     1.429645  1*1*1  STAT=Y  PRED= 1.622 RANGE= 0.472 WIDTH(Y)= 2.235 RESP(Y)= 0.8935 HSQC= C12
 H12B  / 1     1.364991  1*1*1  STAT=Y  PRED= 1.115 RANGE= 0.227 WIDTH(Y)= 2.343 RESP(Y)= 0.8643 HSQC= C12
 H14A  / 1     1.877328  1*1*1  STAT=Y  PRED= 1.966 RANGE= 0.482 WIDTH(Y)= 1.991 RESP(Y)= 0.9171 HSQC= C14
 H14B  / 1     2.426231  1*1*1  STAT=Y  PRED= 2.250 RANGE= 0.355 WIDTH(Y)= 2.053 RESP(Y)= 0.8874 HSQC= C14
 H15A  / 1     1.389487  1*1*1  STAT=Y  PRED= 1.238 RANGE= 0.245 WIDTH(Y)= 2.125 RESP(Y)= 0.8888 HSQC= C15
 H15B  / 1     1.516894  1*1*1  STAT=Y  PRED= 1.337 RANGE= 0.320 WIDTH(Y)= 1.979 RESP(Y)= 0.9128 HSQC= C15
 H17C  / 1     0.871010  1*1*3  STAT=Y  PRED= 0.937 RANGE= 0.157 WIDTH(Y)= 1.591 RESP(Y)= 0.8890 HSQC= C17
 H18B  / 1     1.119657  1*1*3  STAT=Y  PRED= 1.101 RANGE= 0.050 WIDTH(Y)= 1.853 RESP(Y)= 0.9314 HSQC= C18
 H20B  / 1     0.726281  1*1*3  STAT=Y  PRED= 0.866 RANGE= 0.050 WIDTH(Y)= 2.174 RESP(Y)= 0.9416 HSQC= C20
 H22A  / 1    11.994823  1*1*1  STAT=Y  PRED= 11.981 RANGE= 0.050 WIDTH(Y)= 5.637 RESP(Y)= 0.7926
DMSO_CH   2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.71069
 DMSO  / 2     2.500041  1*1*1  STAT=Y  PRED= 2.500 RANGE= 0.050 WIDTH(Y)= 1.341 RESP(Y)= 1.0000
DMSO_D    2*SPIN= 2 SPECIES=2D    POPULATION(Y)=   0.71069
 DMSOD1/ 2  -100.000001  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
 DMSOD2/ 2  -100.000001  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
WATER_H   2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.25637
 WATER / 3     3.337302  2*1*1  STAT=Y  PRED= 3.338 RANGE= 0.050 WIDTH(Y)= 2.342 RESP(Y)= 1.0000

COUPLING CONSTANTS(HZ):
 J12_13    -12.7869   J H1A    H1B      STAT=Y  PRED= -13.130 RANGE= 1.500
 J17_12     13.3378   J H1A    H2A      STAT=Y  PRED= 12.550 RANGE= 2.560
 J12_18      4.2832   J H1A    H2B      STAT=Y  PRED= 4.380 RANGE= 3.800
 J14_12     -0.0020   J H1A    H20B     STAT=Y  PRED= -0.790 RANGE= 0.400
 J17_13      3.8296   J H1B    H2A      STAT=Y  PRED= 3.880 RANGE= 3.800
 J13_18      2.7004   J H1B    H2B      STAT=Y  PRED= 2.510 RANGE= 2.800
 J13_19      1.4897   J H1B    H3A      STAT=Y  PRED= 2.850 RANGE= 1.280
 J17_18    -14.1319   J H2A    H2B      STAT=Y  PRED= -13.190 RANGE= 1.500
 J17_19      3.3576   J H2A    H3A      STAT=Y  PRED= 3.860 RANGE= 3.800
 J17_20     13.5610   J H2A    H3B      STAT=Y  PRED= 12.570 RANGE= 2.560
 J19_18      2.8763   J H2B    H3A      STAT=Y  PRED= 2.530 RANGE= 2.800
 J20_18      4.1150   J H2B    H3B      STAT=Y  PRED= 4.310 RANGE= 3.800
 J19_20    -13.0921   J H3A    H3B      STAT=Y  PRED= -13.110 RANGE= 1.500
 J21_22     12.0666   J H5A    H6A      STAT=Y  PRED= 12.550 RANGE= 2.560
 J21_23      2.7290   J H5A    H6B      STAT=Y  PRED= 1.710 RANGE= 2.800
 J22_23    -14.2098   J H6A    H6B      STAT=Y  PRED= -13.190 RANGE= 1.500
 J22_24     13.8929   J H6A    H7A      STAT=Y  PRED= 12.990 RANGE= 2.560
 J22_25      3.0333   J H6A    H7B      STAT=Y  PRED= 3.320 RANGE= 3.800
 J23_24      3.6977   J H6B    H7A      STAT=Y  PRED= 3.410 RANGE= 3.800
 J23_25      2.7683   J H6B    H7B      STAT=Y  PRED= 3.190 RANGE= 3.800
 J24_25    -13.0603   J H7A    H7B      STAT=Y  PRED= -13.130 RANGE= 1.500
 J16_18      4.3705   J H9A    H11A     STAT=Y  PRED= 4.170 RANGE= 3.800
 J16_19     12.6465   J H9A    H11B     STAT=Y  PRED= 12.400 RANGE= 2.560
 J16_26      0.0515   J H9A    H14A     STAT=Y  PRED= 1.810 RANGE= 0.890
 J18_19    -14.0757   J H11A   H11B     STAT=Y  PRED= -13.160 RANGE= 1.500
 J18_31      1.5285   J H11A   H12A     STAT=Y  PRED= 1.150 RANGE= 3.000
 J18_22      5.6424   J H11A   H12B     STAT=Y  PRED= 6.170 RANGE= 3.800
 J19_31      5.5922   J H11B   H12A     STAT=Y  PRED= 6.320 RANGE= 3.800
 J19_22     13.4654   J H11B   H12B     STAT=Y  PRED= 11.380 RANGE= 2.800
 J31_22    -12.4565   J H12A   H12B     STAT=Y  PRED= -13.200 RANGE= 1.500
 J31_39      2.6726   J H12A   H15B     STAT=Y  PRED= 2.750 RANGE= 1.280
 J26_27    -18.4276   J H14A   H14B     STAT=Y  PRED= -15.930 RANGE= 4.000
 J27_38      3.6461   J H14B   H15A     STAT=Y  PRED= 1.480 RANGE= 1.200
 J38_39    -11.3961   J H15A   H15B     STAT=Y  PRED= -12.660 RANGE= 2.000
 JDMSO1      1.7939   J DMSO   DMSOD1   STAT=Y  PRED= 1.700 RANGE= 0.050
 JDMSO1      1.7939   J DMSO   DMSOD2   STAT=Y  PRED= 1.700 RANGE= 0.050

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)
  600.13153100 =  FIELD(1H,MHz), used to transform shifts to ppms
   13.31091501 =  Left frequency (ppm)
   -1.00377999 =  Right frequency (ppm)
        10.000 =  Acquisition time (s, for QMTLS)
         0.000 =  Line-width (for modes D, P & T, 0=use defaults)
   0.068609932 =  Data-point resolution (Hz)
        63.251 =  GAUSSIAN (%, 0=use default from INF)
         5.347 =  Dispersion contribution (%, 0=use default from INF)
    0.00000000 =  Decoupling frequency (for DORES)

CONSTRAINTS (in equations X0 = 1.0)...use no empty lines
 EQUAL H11A     = H15B
 EQUAL DMSOD1   = DMSOD2
 IGNORE(HZ):  1573.488 to  1560.842
 IGNORE(HZ):  1436.106 to  1424.075
 IGNORE(HZ):  1995.481 to  1978.842
 IGNORE(HZ):  2448.136 to  2397.794

END of FILE
```

S18. The ^{1}H fingerprint of isosteviol (**9**) in DMSO-d_6 (37 mM, 600 MHz, 298 K). The calculated and observed NMR spectra are shown in red and blue, respectively. (*) denotes unidentified impurities.

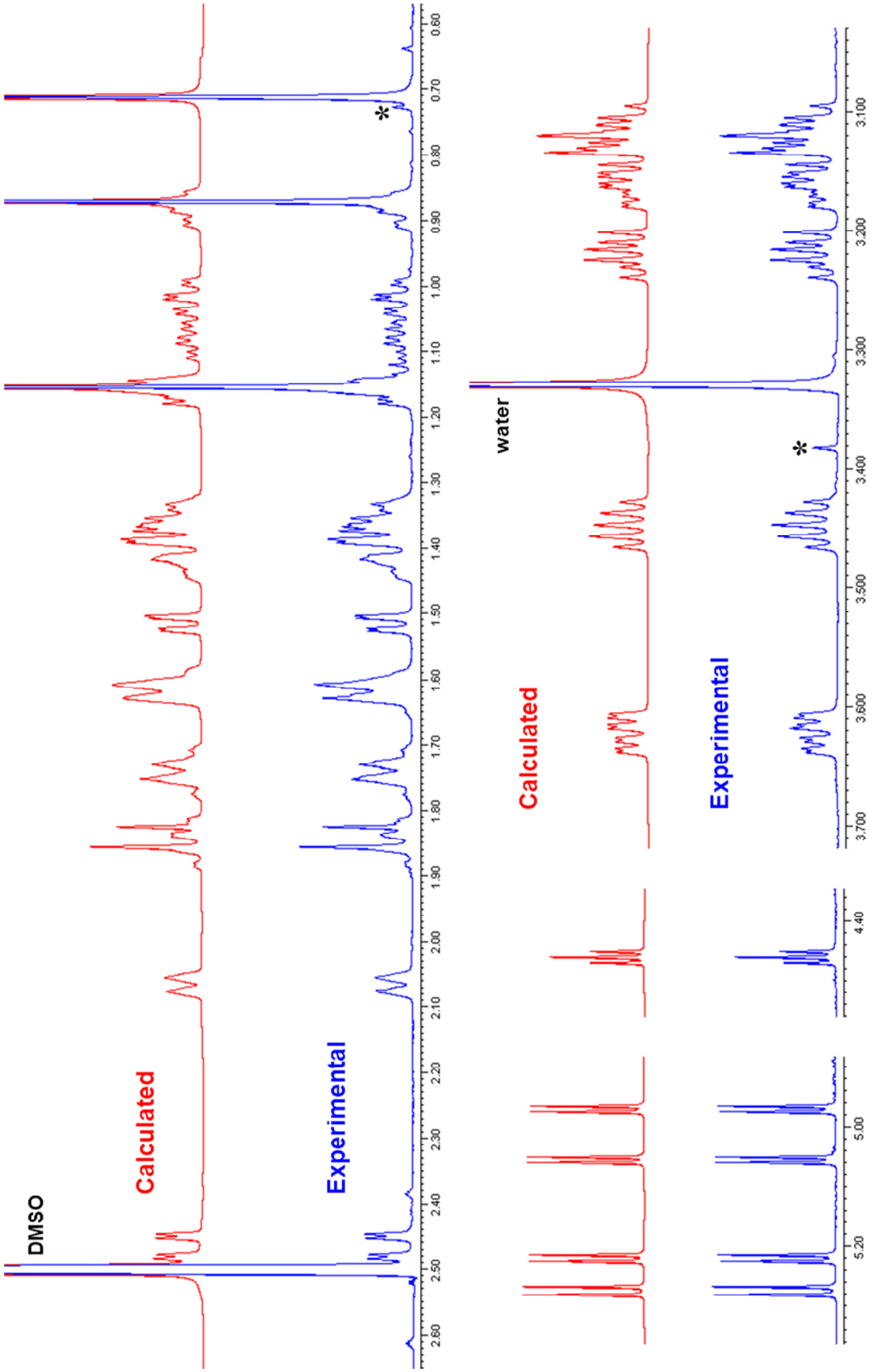


S19. The HiFSA profile of isosteviol monoside (**10**) in DMSO-d_6 [in PERCH parameter (.pms) file format].

```
* 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: c:\HIFSA\Stevia\Isosteviol_monoside
#$œ  Date 10.10.2014;  Time 22:29:40     isomono.pms

CHEMICAL SHIFTS(PPM):
PROTON    2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.03511
 H1A   / 1     0.880956  1*1*1  STAT=Y  PRED= 0.779 RANGE= 0.050 WIDTH(Y)= 3.950 RESP(Y)= 0.9579 HSQC= C1
 H1B   / 1     1.620338  1*1*1  STAT=Y  PRED= 1.778 RANGE= 0.050 WIDTH(Y)= 3.923 RESP(Y)= 0.9901 HSQC= C1
 H2A   / 1     1.740285  1*1*1  STAT=Y  PRED= 1.764 RANGE= 0.050 WIDTH(Y)= 2.763 RESP(Y)= 0.9034 HSQC= C2
 H2B   / 1     1.344453  1*1*1  STAT=Y  PRED= 1.332 RANGE= 0.050 WIDTH(Y)= 2.565 RESP(Y)= 0.9269 HSQC= C2
 H3A   / 1     2.064758  1*1*1  STAT=Y  PRED= 2.000 RANGE= 0.050 WIDTH(Y)= 2.859 RESP(Y)= 0.9312 HSQC= C3
 H3B   / 1     1.016195  1*1*1  STAT=Y  PRED= 0.932 RANGE= 0.050 WIDTH(Y)= 2.976 RESP(Y)= 0.9292 HSQC= C3
 H5A   / 1     1.155233  1*1*1  STAT=Y  PRED= 1.015 RANGE= 0.050 WIDTH(Y)= 3.983 RESP(Y)= 0.9664 HSQC= C5
 H6A   / 1     1.847084  1*1*1  STAT=Y  PRED= 1.700 RANGE= 0.050 WIDTH(Y)= 3.137 RESP(Y)= 0.9192 HSQC= C6
 H6B   / 1     1.740230  1*1*1  STAT=Y  PRED= 1.737 RANGE= 0.050 WIDTH(Y)= 3.030 RESP(Y)= 0.9360 HSQC= C6
 H7A   / 1     1.391935  1*1*1  STAT=Y  PRED= 1.360 RANGE= 0.050 WIDTH(Y)= 3.131 RESP(Y)= 0.9031 HSQC= C7
 H7B   / 1     1.614156  1*1*1  STAT=Y  PRED= 1.449 RANGE= 0.050 WIDTH(Y)= 3.525 RESP(Y)= 0.9915 HSQC= C7
 H9A   / 1     1.160477  1*1*1  STAT=Y  PRED= 1.062 RANGE= 0.405 WIDTH(Y)= 2.638 RESP(Y)= 0.9093 HSQC= C9
 H11A  / 1     1.608357  1*1*1  STAT=Y  PRED= 1.337 RANGE= 0.422 WIDTH(Y)= 3.519 RESP(Y)= 0.9765 HSQC= C11
 H11B  / 1     1.073988  1*1*1  STAT=Y  PRED= 1.019 RANGE= 0.280 WIDTH(Y)= 3.035 RESP(Y)= 0.8590 HSQC= C11
 H12A  / 1     1.427082  1*1*1  STAT=Y  PRED= 1.622 RANGE= 0.472 WIDTH(Y)= 2.757 RESP(Y)= 0.8935 HSQC= C12
 H12B  / 1     1.358586  1*1*1  STAT=Y  PRED= 1.115 RANGE= 0.227 WIDTH(Y)= 3.136 RESP(Y)= 0.8643 HSQC= C12
 H14A  / 1     1.840642  1*1*1  STAT=Y  PRED= 1.966 RANGE= 0.482 WIDTH(Y)= 2.509 RESP(Y)= 0.9171 HSQC= C14
 H14B  / 1     2.464578  1*1*1  STAT=Y  PRED= 2.250 RANGE= 0.355 WIDTH(Y)= 2.513 RESP(Y)= 0.8874 HSQC= C14
 H15A  / 1     1.379578  1*1*1  STAT=Y  PRED= 1.238 RANGE= 0.245 WIDTH(Y)= 2.710 RESP(Y)= 0.8888 HSQC= C15
 H15B  / 1     1.514066  1*1*1  STAT=Y  PRED= 1.337 RANGE= 0.320 WIDTH(Y)= 2.496 RESP(Y)= 0.9128 HSQC= C15
 H17C  / 1     0.869964  1*1*3  STAT=Y  PRED= 0.937 RANGE= 0.157 WIDTH(Y)= 1.910 RESP(Y)= 0.8890 HSQC= C17
 H18B  / 1     1.153692  1*1*3  STAT=Y  PRED= 1.101 RANGE= 0.050 WIDTH(Y)= 2.224 RESP(Y)= 0.9314 HSQC= C18
 H20B  / 1     0.711312  1*1*3  STAT=Y  PRED= 0.866 RANGE= 0.050 WIDTH(Y)= 2.724 RESP(Y)= 0.9416 HSQC= C20
 GA1   / 1     5.273875  1*1*1  STAT=Y  PRED= 5.565 RANGE= 0.342 WIDTH(Y)= 1.357 RESP(Y)= 0.9078 HSQC= H21
 GA2   / 1     3.125355  1*1*1  STAT=Y  PRED= 3.526 RANGE= 0.200 WIDTH(Y)= 1.551 RESP(Y)= 0.9171 HSQC= C23
 GA3   / 1     3.218541  1*1*1  STAT=Y  PRED= 3.317 RANGE= 0.155 WIDTH(Y)= 1.544 RESP(Y)= 0.8548 HSQC= C26
 GA4   / 1     3.116650  1*1*1  STAT=Y  PRED= 3.387 RANGE= 0.287 WIDTH(Y)= 1.592 RESP(Y)= 0.8374 HSQC= C27
 GA5   / 1     3.163869  1*1*1  STAT=Y  PRED= 3.485 RANGE= 0.247 WIDTH(Y)= 1.653 RESP(Y)= 0.8314 HSQC= C25
 GA6A  / 1     3.447025  1*1*1  STAT=Y  PRED= 3.351 RANGE= 0.450 WIDTH(Y)= 1.867 RESP(Y)= 0.8318 HSQC= C29
 GA6B  / 1     3.621034  1*1*1  STAT=Y  PRED= 3.509 RANGE= 0.232 WIDTH(Y)= 1.807 RESP(Y)= 0.8536 HSQC= C29
 OGA2  / 1     5.219173  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 1.424 RESP(Y)= 0.8978
 OGA3  / 1     5.054141  1*1*1  STAT=Y  PRED= 4.296 RANGE= 1.420 WIDTH(Y)= 1.396 RESP(Y)= 0.8798
 OGA4  / 1     4.968791  1*1*1  STAT=Y  PRED= 4.702 RANGE= 1.565 WIDTH(Y)= 1.367 RESP(Y)= 0.8679
 OGA6  / 1     4.459874  1*1*1  STAT=Y  PRED= 5.633 RANGE= 1.215 WIDTH(Y)= 1.557 RESP(Y)= 0.8978
DMSO_CH   2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.88049
 DMSO  / 2     2.500009  1*1*1  STAT=Y  PRED= 2.500 RANGE= 0.050 WIDTH(Y)= 1.389 RESP(Y)= 1.0000
DMSO_D    2*SPIN= 2 SPECIES=2D    POPULATION(Y)=   0.88049
 DMSOD1/ 2  -100.000001  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
 DMSOD2/ 2  -100.000001  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
WATER_H   2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.08440
 WATER / 3     3.328898  2*1*1  STAT=Y  PRED= 3.338 RANGE= 0.050 WIDTH(Y)= 1.235 RESP(Y)= 1.0000

COUPLING CONSTANTS(HZ):
 J12_13    -11.6508   J H1A    H1B      STAT=Y  PRED= -13.130 RANGE= 1.500
 J17_12     13.3895   J H1A    H2A      STAT=Y  PRED= 12.550 RANGE= 2.560
 J12_18      5.3514   J H1A    H2B      STAT=Y  PRED= 4.380 RANGE= 3.800
 J14_12     -0.0010   J H1A    H20B     STAT=Y  PRED= -0.790 RANGE= 0.400
 J17_13      3.0715   J H1B    H2A      STAT=Y  PRED= 3.880 RANGE= 3.800
 J13_18      2.3732   J H1B    H2B      STAT=Y  PRED= 2.510 RANGE= 2.800
 J13_19      1.4964   J H1B    H3A      STAT=Y  PRED= 2.850 RANGE= 1.280
 J17_18    -13.4937   J H2A    H2B      STAT=Y  PRED= -13.190 RANGE= 1.500
 J17_19      3.0566   J H2A    H3A      STAT=Y  PRED= 3.860 RANGE= 3.800
 J17_20     13.7842   J H2A    H3B      STAT=Y  PRED= 12.570 RANGE= 2.560
 J19_18      3.4087   J H2B    H3A      STAT=Y  PRED= 2.530 RANGE= 2.800
 J20_18      4.1910   J H2B    H3B      STAT=Y  PRED= 4.310 RANGE= 3.800
 J19_20    -13.0143   J H3A    H3B      STAT=Y  PRED= -13.110 RANGE= 1.500
 J21_22     12.9949   J H5A    H6A      STAT=Y  PRED= 12.550 RANGE= 2.560
 J21_23      5.6510   J H5A    H6B      STAT=Y  PRED= 1.710 RANGE= 2.800
 J22_23    -14.5233   J H6A    H6B      STAT=Y  PRED= -13.190 RANGE= 1.500
 J22_24     13.5977   J H6A    H7A      STAT=Y  PRED= 12.990 RANGE= 2.560
 J22_25      3.3910   J H6A    H7B      STAT=Y  PRED= 3.320 RANGE= 3.800
 J23_24      3.7642   J H6B    H7A      STAT=Y  PRED= 3.410 RANGE= 3.800
 J23_25      1.8332   J H6B    H7B      STAT=Y  PRED= 3.190 RANGE= 3.800
 J24_25    -13.2179   J H7A    H7B      STAT=Y  PRED= -13.130 RANGE= 1.500
 J16_18      9.5578   J H9A    H11A     STAT=Y  PRED= 4.170 RANGE= 3.800
 J16_19     12.2000   J H9A    H11B     STAT=Y  PRED= 12.400 RANGE= 2.560
 J16_26      0.0411   J H9A    H14A     STAT=Y  PRED= 1.810 RANGE= 0.890
 J18_19    -14.5862   J H11A   H11B     STAT=Y  PRED= -13.160 RANGE= 1.500
 J18_31      2.7467   J H11A   H12A     STAT=Y  PRED= 1.150 RANGE= 3.000
 J18_22      5.2313   J H11A   H12B     STAT=Y  PRED= 6.170 RANGE= 3.800
 J19_31      5.5443   J H11B   H12A     STAT=Y  PRED= 6.320 RANGE= 3.800
 J19_22     13.4248   J H11B   H12B     STAT=Y  PRED= 11.380 RANGE= 2.800
 J31_22    -12.4433   J H12A   H12B     STAT=Y  PRED= -13.200 RANGE= 1.500
 J31_39      2.6956   J H12A   H15B     STAT=Y  PRED= 2.750 RANGE= 1.280
```

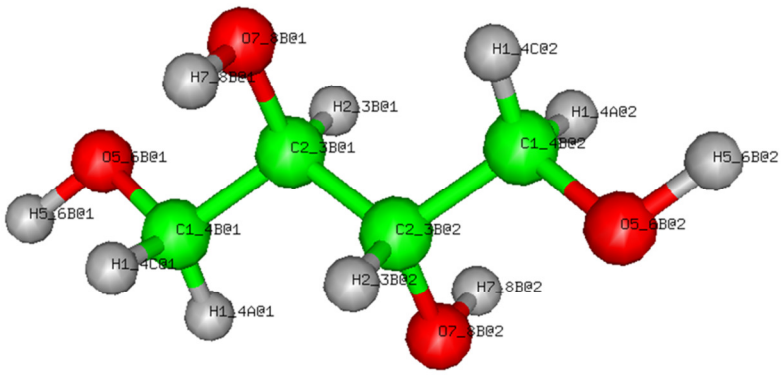
```
 J26_27    -18.6305   J H14A   H14B     STAT=Y  PRED= -15.930 RANGE= 4.000
 J27_38      3.5756   J H14B   H15A     STAT=Y  PRED= 1.480 RANGE= 1.200
 J38_39    -11.3693   J H15A   H15B     STAT=Y  PRED= -12.660 RANGE= 2.000
 J38_40      8.2488   J GA1    GA2      STAT=Y  PRED= 7.190 RANGE= 3.580
 J40_43      9.1213   J GA2    GA3      STAT=Y  PRED= 8.920 RANGE= 3.580
 J40_48      6.3397   J GA2    OGA2     STAT=Y  PRED= 4.300 RANGE= 1.000
 J43_46      8.8402   J GA3    GA4      STAT=Y  PRED= 9.140 RANGE= 3.580
 J43_51      5.2551   J GA3    OGA3     STAT=Y  PRED= 4.300 RANGE= 1.000
 J41_46      9.7543   J GA4    GA5      STAT=Y  PRED= 10.550 RANGE= 2.560
 J46_52      5.5548   J GA4    OGA4     STAT=Y  PRED= 4.300 RANGE= 1.000
 J41_49      5.2613   J GA5    GA6A     STAT=Y  PRED= 2.700 RANGE= 3.000
 J41_50      2.0894   J GA5    GA6B     STAT=Y  PRED= 1.280 RANGE= 3.000
 J49_50    -11.8575   J GA6A   GA6B     STAT=Y  PRED= -12.300 RANGE= 0.800
 J49_51      5.9364   J GA6A   OGA6     STAT=Y  PRED= 4.300 RANGE= 3.000
 J50_51      5.2968   J GA6B   OGA6     STAT=Y  PRED= 4.300 RANGE= 3.000
 JDMSO1      1.7939   J DMSO   DMSOD1   STAT=Y  PRED= 1.700 RANGE= 0.050
 JDMSO1      1.7939   J DMSO   DMSOD2   STAT=Y  PRED= 1.700 RANGE= 0.050

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)
  600.12701400 =  FIELD(1H,MHz), used to transform shifts to ppms
   13.31091512 =  Left frequency (ppm)
   -1.00378002 =  Right frequency (ppm)
         0.000 =  Acquisition time (s, for QMTLS)
         1.235 =  Line-width (for modes D, P & T, 0=use defaults)
   0.068609924 =  Data-point resolution (Hz)
        66.182 =  GAUSSIAN (%, 0=use default from INF)
         1.092 =  Dispersion contribution (%, 0=use default from INF)
    0.00000000 =  Decoupling frequency (for DORES)

CONSTRAINTS (in equations X0 = 1.0)...use no empty lines
 EQUAL H11A     = H15B
 EQUAL DMSOD1   = DMSOD2
 IGNORE(HZ):  1573.488 to  1560.842
 IGNORE(HZ):  1436.106 to  1424.075
 IGNORE(HZ):  2032.754 to  2025.968
 IGNORE(HZ):   389.543 to   355.134

END of FILE
```

S20. The ^{1}H fingerprint of isosteviol monoside (**10**) in DMSO-d_6 (8.3 mM, 600 MHz, 298 K). The calculated and observed NMR spectra are shown in red and blue, respectively. (*) denotes unidentified impurities.



S21. The HiFSA profile of erythritol (**12**) in DMSO-d_6 [in PERCH parameter (.pms) file 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: c:\HIFSA\Stevia\Erythritol
#$œ  Date 10.10.2014;  Time 22:30:49     erythritol.pms

CHEMICAL SHIFTS(PPM):
PROTON    2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.25056
 H1_4A / 1     3.530912  1*2*1  STAT=Y  PRED= 3.408 RANGE= 0.150 WIDTH(Y)= 1.529 RESP(Y)= 0.8448 HSQC= C1_4B
 H1_4C / 1     3.347650  1*2*1  STAT=Y  PRED= 3.445 RANGE= 0.150 WIDTH(Y)= 1.556 RESP(Y)= 0.8652 HSQC= C1_4B
 H2_3B / 1     3.335999  1*2*1  STAT=Y  PRED= 3.441 RANGE= 0.150 WIDTH(Y)= 1.242 RESP(Y)= 1.0000 HSQC= C2_3B
 H5_6B / 1     4.324491  1*2*1  STAT=Y  PRED= 4.386 RANGE= 1.340 WIDTH(Y)= 1.513 RESP(Y)= 0.8604
 H7_8B / 1     4.456002  1*2*1  STAT=Y  PRED= 4.348 RANGE= 0.905 WIDTH(Y)= 1.416 RESP(Y)= 0.8374
DMSO_CH   2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.75601
 DMSO  / 2     2.500182  1*1*1  STAT=Y  PRED= 2.500 RANGE= 0.050 WIDTH(Y)= 1.626 RESP(Y)= 1.0000
DMSO_D    2*SPIN= 2 SPECIES=2D    POPULATION(Y)=   0.75601
 DMSOD1/ 2  -100.000001  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
 DMSOD2/ 2  -100.000001  1*1*1  STAT=Y  PRED= -99.999 RANGE= 0.050 WIDTH(Y)= 1.500 RESP(Y)= 1.0000
WATER_H   2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.00001
 WATER / 3     3.331081  2*1*1  STAT=Y  PRED= 3.338 RANGE= 0.050 WIDTH(Y)= 2.567 RESP(Y)= 1.0000

COUPLING CONSTANTS(HZ):
 J7_8      -10.9203   J H1_4A  H1_4C    STAT=Y  PRED= -12.300 RANGE= 0.600
 J7_9        3.6528   J H1_4A  H2_3B    STAT=Y  PRED= 2.010 RANGE= 3.200
 J7_16       5.9231   J H1_4A  H5_6B    STAT=Y  PRED= 5.100 RANGE= 1.000
 J8_9        6.5599   J H1_4C  H2_3B    STAT=Y  PRED= 7.870 RANGE= 5.600
 J8_16       5.4917   J H1_4C  H5_6B    STAT=Y  PRED= 5.100 RANGE= 1.000
 J9_11       8.4977   J H2_3B  H2_3B    STAT=Y  PRED= 5.510 RANGE= 6.400
 J9_17       5.2693   J H2_3B  H7_8B    STAT=Y  PRED= 4.300 RANGE= 1.000
 JDMSO1      1.7939   J DMSO   DMSOD1   STAT=Y  PRED= 1.700 RANGE= 0.050
 JDMSO1      1.7939   J DMSO   DMSOD2   STAT=Y  PRED= 1.700 RANGE= 0.050

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)
  600.13153100 =  FIELD(1H,MHz), used to transform shifts to ppms
    4.72696384 =  Left frequency (ppm)
    2.14103048 =  Right frequency (ppm)
         0.000 =  Acquisition time (s, for QMTLS)
         1.311 =  Line-width (for modes D, P & T, 0=use defaults)
   0.068609934 =  Data-point resolution (Hz)
        94.921 =  GAUSSIAN (%, 0=use default from INF)
        -5.816 =  Dispersion contribution (%, 0=use default from INF)
    0.00000000 =  Decoupling frequency (for DORES)

CONSTRAINTS (in equations X0 = 1.0)...use no empty lines
 EQUAL DMSOD1   = DMSOD2

END of FILE
```



S22. The ^{1}H fingerprint of erythritol (**12**) in DMSO-d_6 (107 mM, 600 MHz, 298 K). The calculated and observed NMR spectra are shown in red and blue, respectively.