SUPPORTING INFORMATION

Stereochemistry of a Second Riolozane and Other Diterpenoids from *Jatropha dioica*

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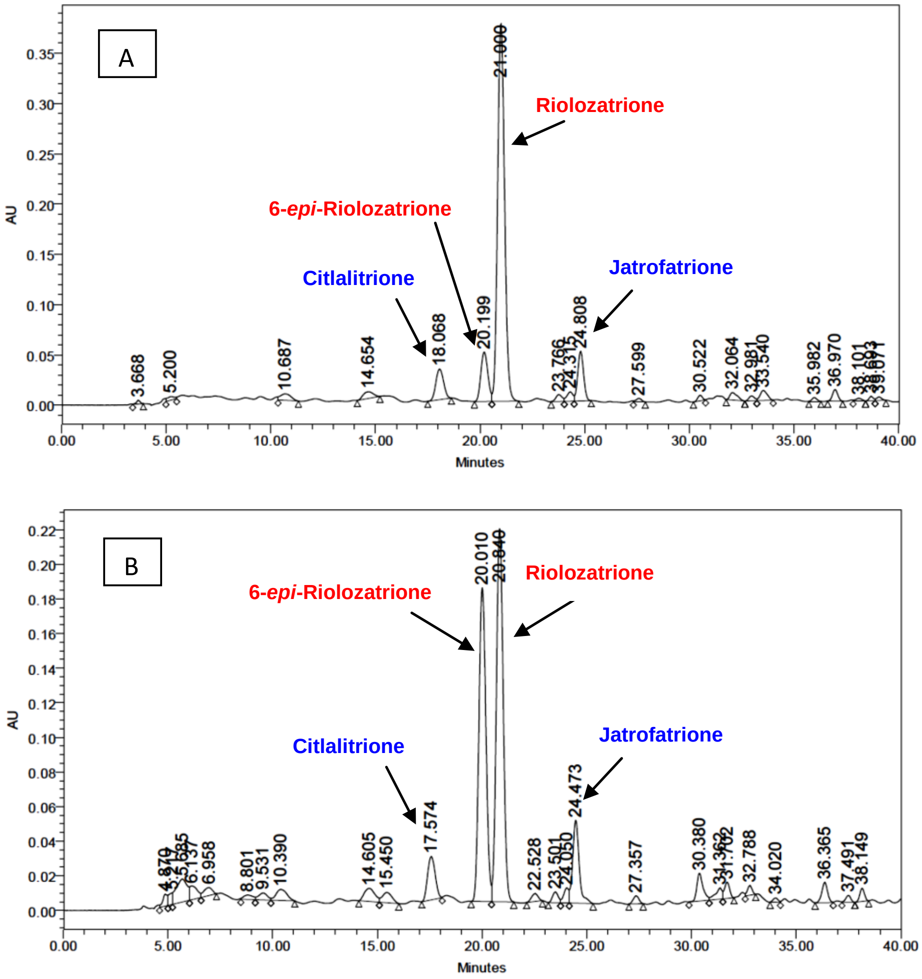
Figure S1. Chromatograms obtained from HPLC analysis for hexane fraction (A) and methylene chloride extract (B) from *J. dioica* roots.

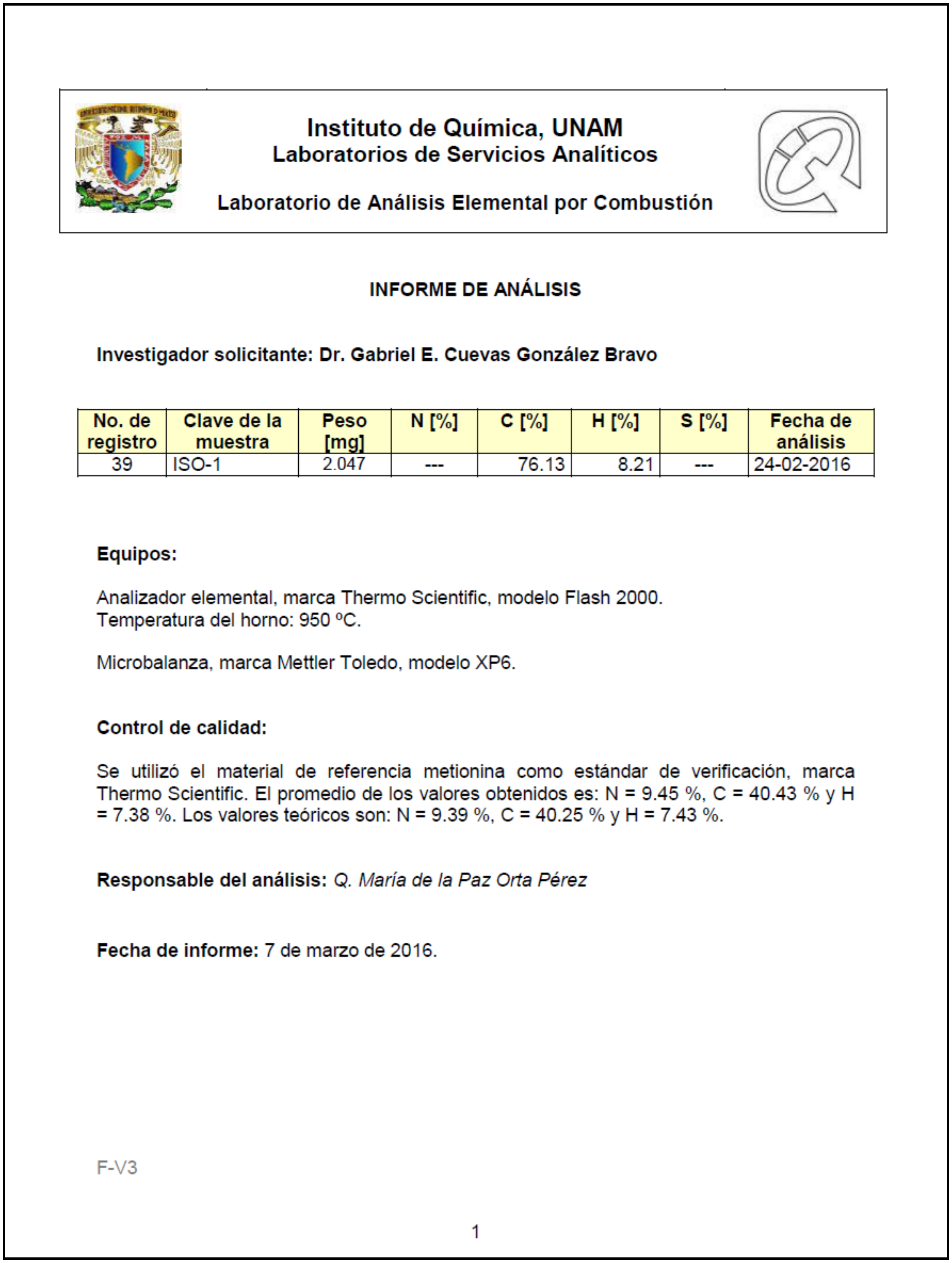


HPLC Analysis Method of obtained extracts from *J. dioica* roots.

HPLC Method.The HPLC analysis of extracts A and B was performed on a Waters liquid chromatograph 1525 linked to a Waters diode array detector 2996, using a Waters AccQ-Tag column and isocratic elution with acetonitrile-water (50:50).

n-Hexane fraction (A): Hydro-methanolic extract of *J. dioica* roots (250 g) at RT, was evaporated at reduced pressure at 40 °C, and subsequent partitioned to obtain fractions of n-hexane, ethyl acetate, and butyl alcohol. DCM extract (B): Dried and powdered roots of *J. dioica* (250 g) were extracted with DCM (3 x 1L) at room temperature to give 3.5 g of concentrated crude extract at reduced pressure.

Figure S2. Elemental analysis of 6-*epi*-Riolozatrione (**2**)



Instituto de Química, UNAM
Laboratorios de Servicios Analíticos

Laboratorio de Análisis Elemental por Combustión

INFORME DE ANÁLISIS

Investigador solicitante: Dr. Gabriel E. Cuevas González Bravo

No. de registro	Clave de la muestra	Peso [mg]	N [%]	C [%]	H [%]	S [%]	Fecha de análisis
39	ISO-1	2.047	---	76.13	8.21	---	24-02-2016

Equipos:

Analizador elemental, marca Thermo Scientific, modelo Flash 2000.
Temperatura del horno: 950 ºC.

Microbalanza, marca Mettler Toledo, modelo XP6.

Control de calidad:

Se utilizó el material de referencia metionina como estándar de verificación, marca Thermo Scientific. El promedio de los valores obtenidos es: N = 9.45 %, C = 40.43 % y H = 7.38 %. Los valores teóricos son: N = 9.39 %, C = 40.25 % y H = 7.43 %.

Responsable del análisis: *Q. María de la Paz Orta Pérez*

Fecha de informe: 7 de marzo de 2016.

F-V3

Figure S3. HRESIMS spectrum of 6-*epi*-Riolozatrione (**2**)

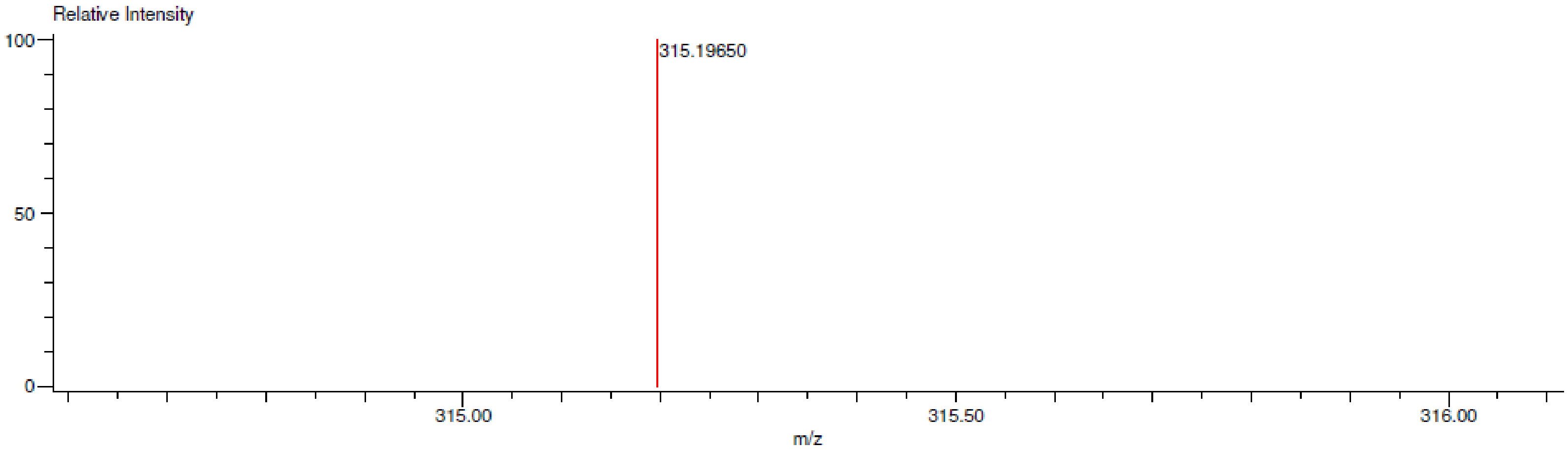
Data:238 Isoriolo
Sample Name:Dr Cuevas Gabriel/Operador:Carmen Garcia-Javier Perez/DART+
Description:
Ionization Mode:ESI+
History:Determine m/z[Peak Detect[Centroid,30,Area];Correct Base[5.0%]];Correct Base[5.0%];Average(MS[1] 0..0)

Acquired:1/27/2016 3:11:32 PM
Operator:AccuTOF
Mass Calibration data:Cal_Peg_600
Created:2/4/2016 3:51:55 PM
Created by:AccuTOF

Charge number:1
Element:^{12}C:0 .. 100, ^{1}H:0 .. 200, ^{16}O:0 .. 6

Tolerance:3.00(mmu)

Unsaturation Number:0.0 .. 30.0 (Fraction:Both)



Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
315.19650	1168548.88	315.19602	0.48	1.54	$^{12}C_{20}{}^{1}H_{27}{}^{16}O_3$	7.5

Figure S4. Infrared spectrum of 6-*epi*-Riolozatrione (**2**)

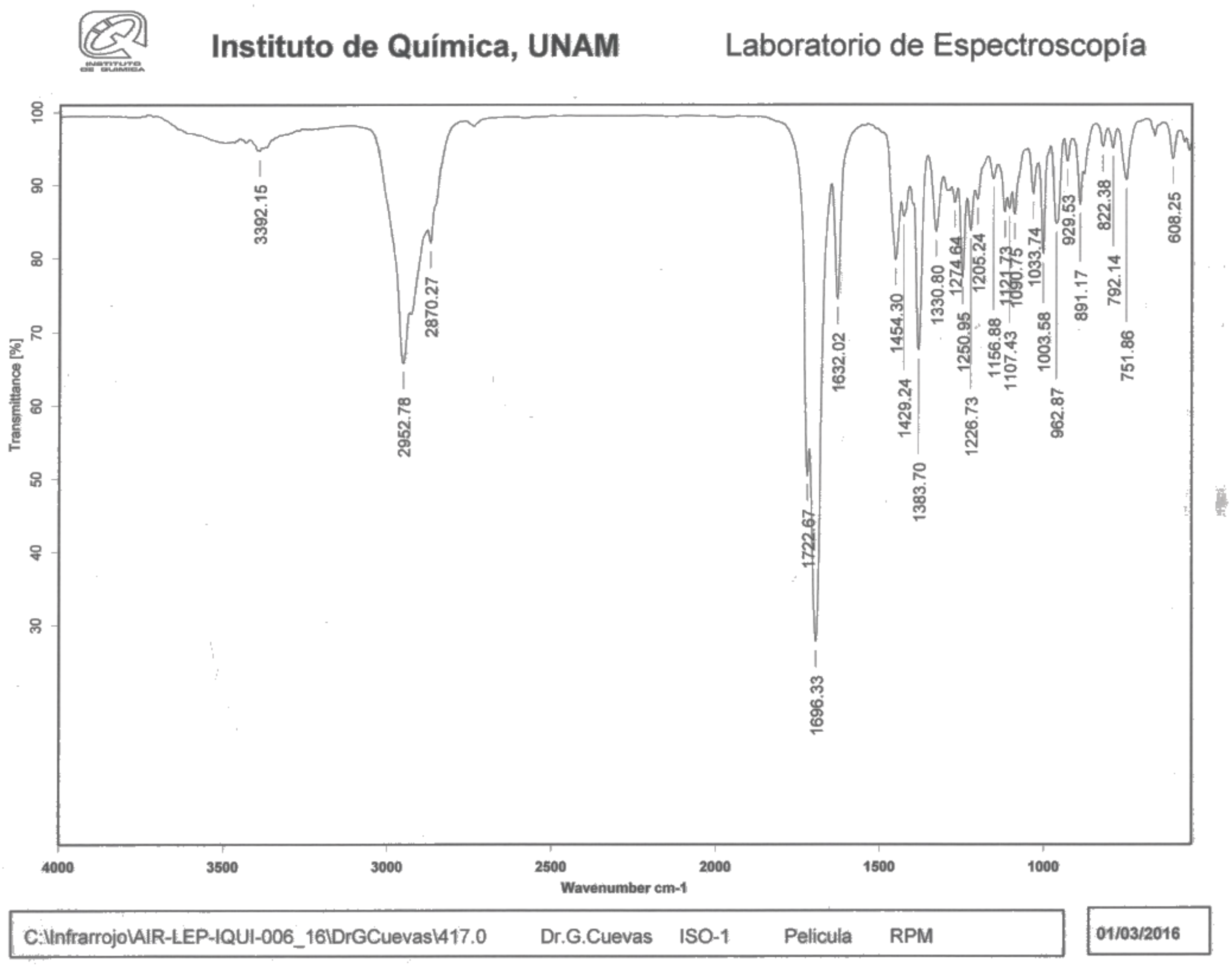


Figure S5. Experimental ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **1** and **2** in $CDCl_3$.

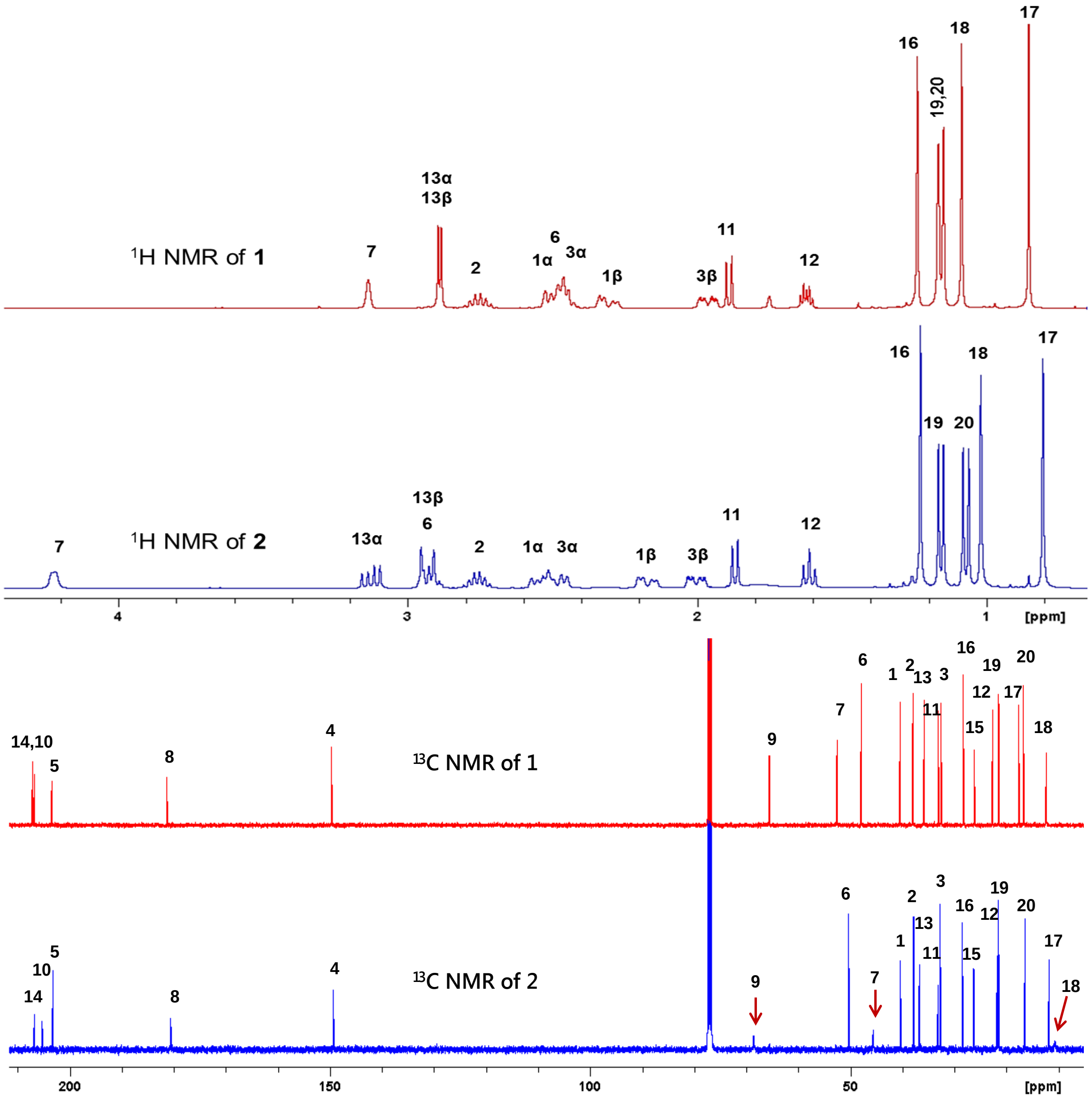
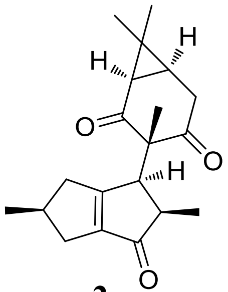


Figure S6. Comparison of the 1D ^{1}H-NMR spectra of compounds **1** and **2** in CD_3OD at 700 MHz, FIDs processed with Lorentzian-Gaussian apodization.



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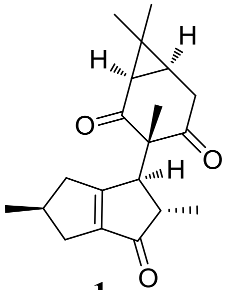

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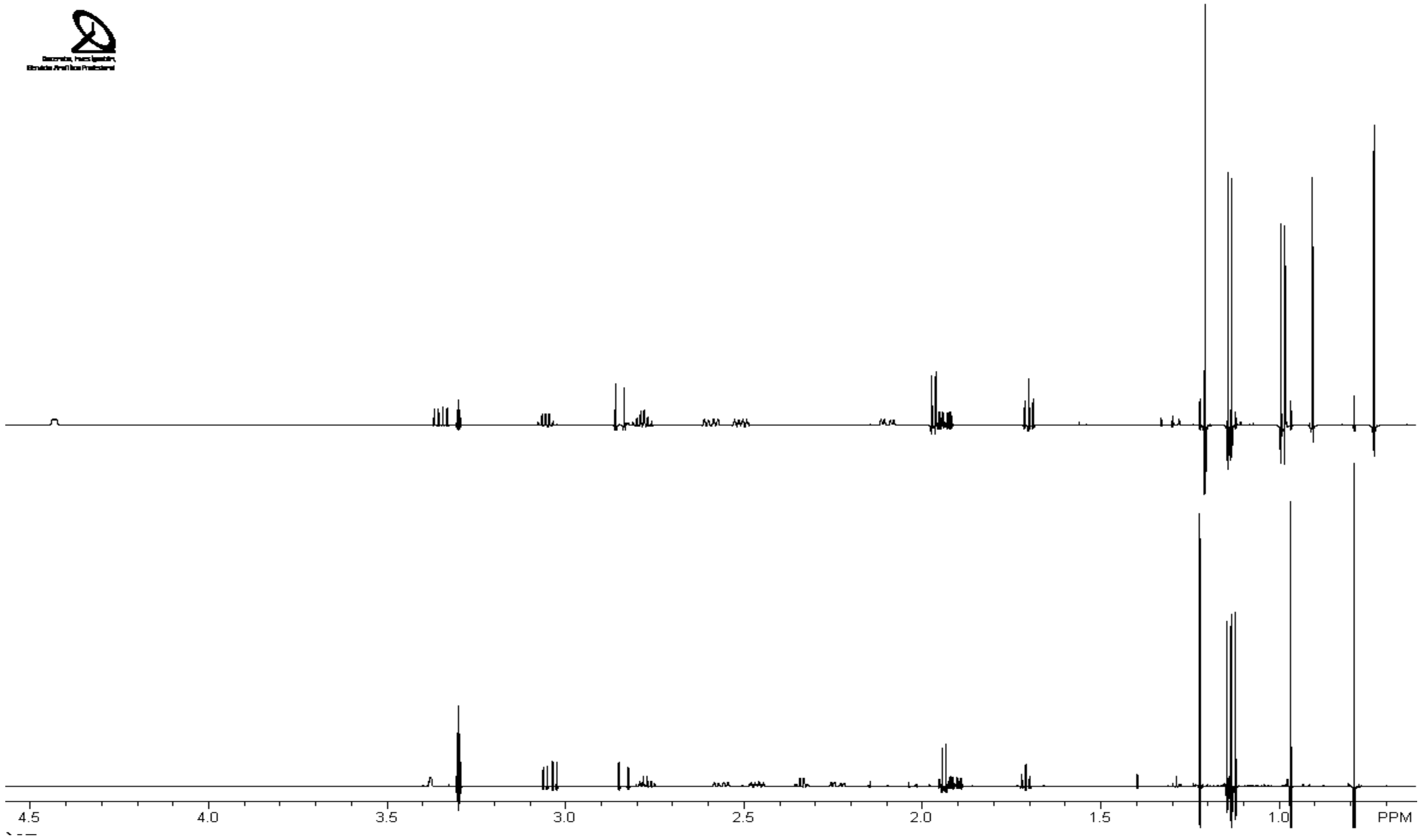

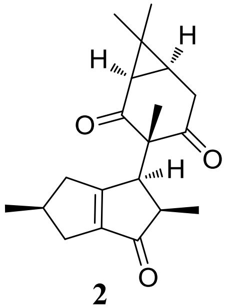

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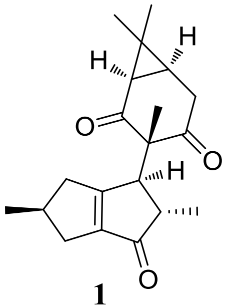

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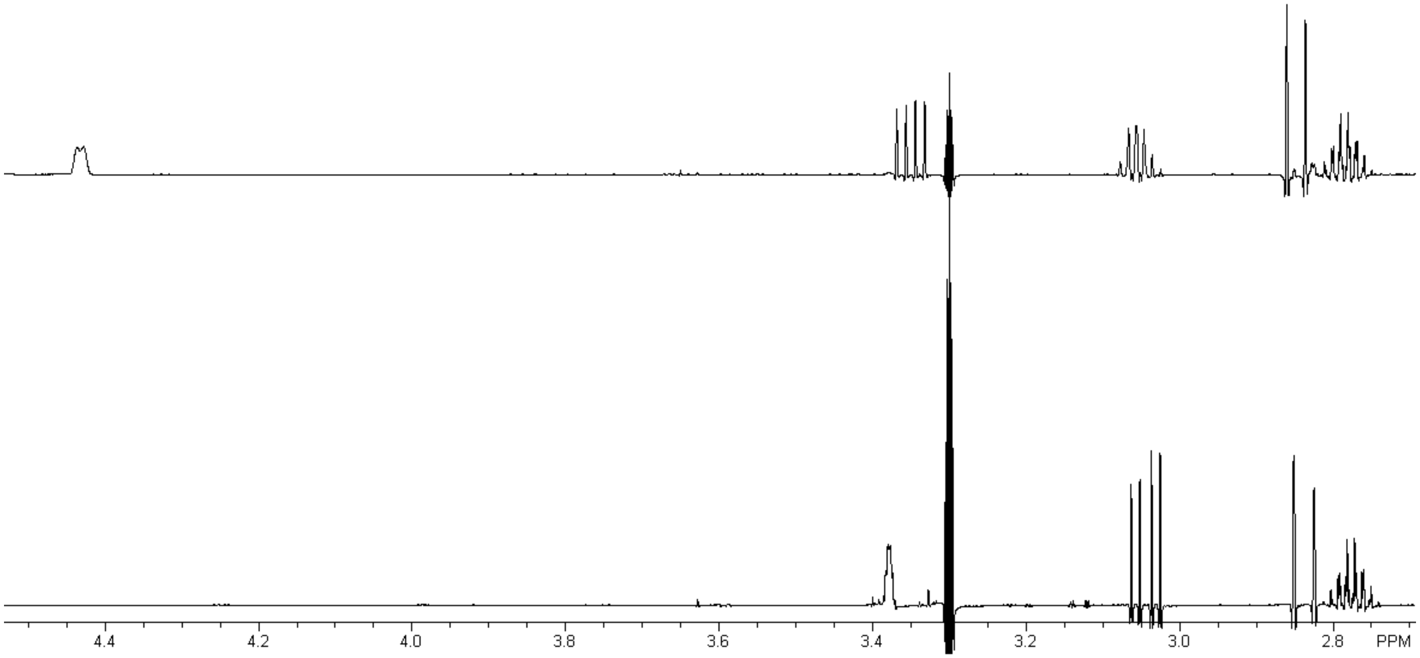

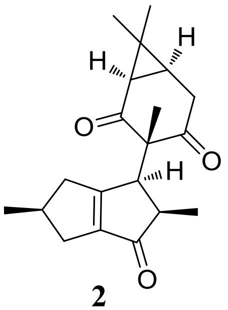

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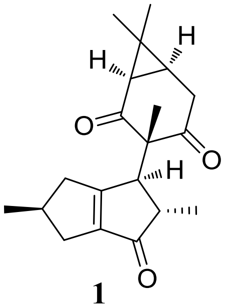

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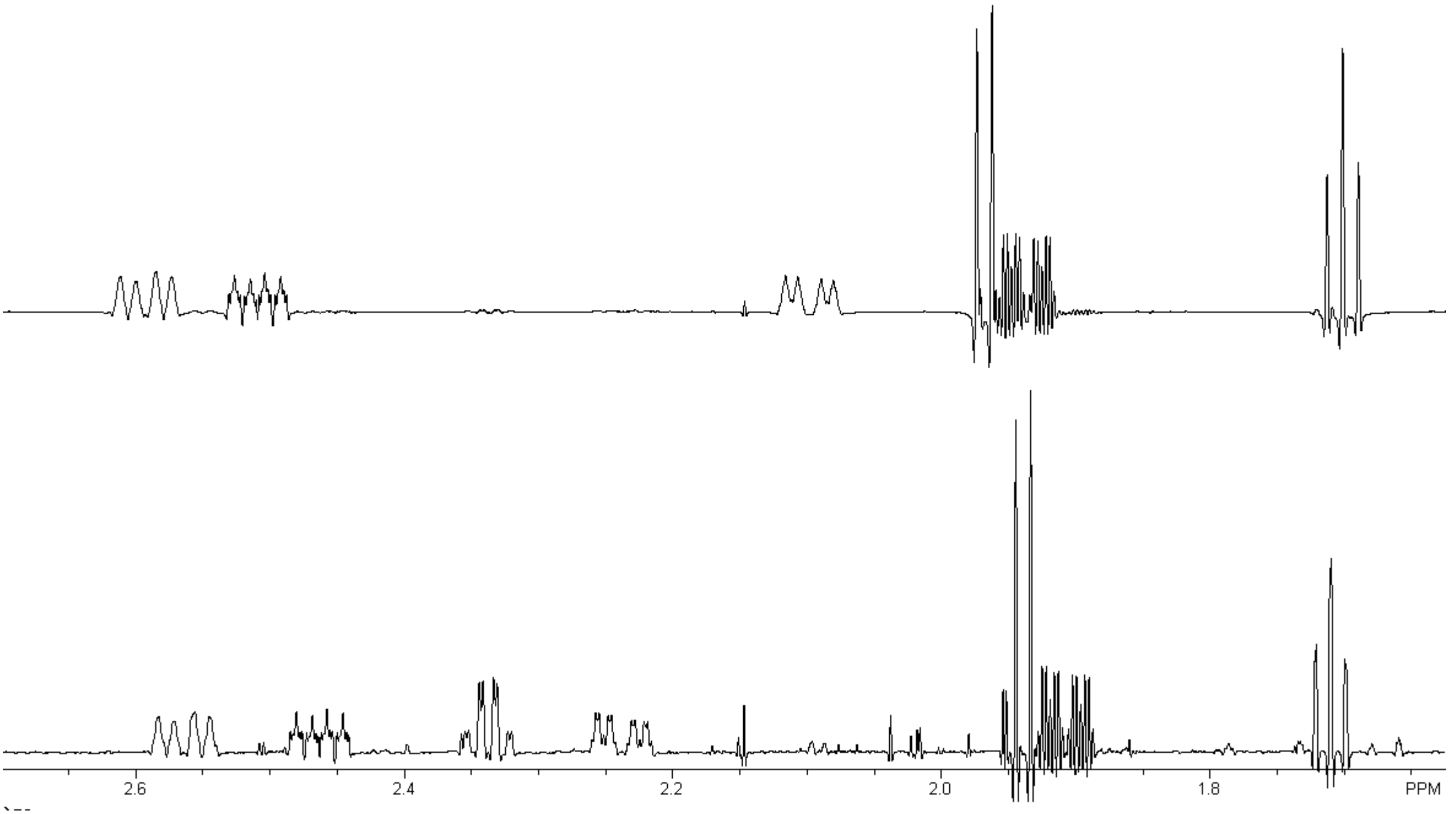

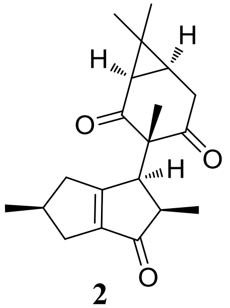

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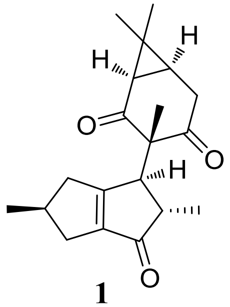

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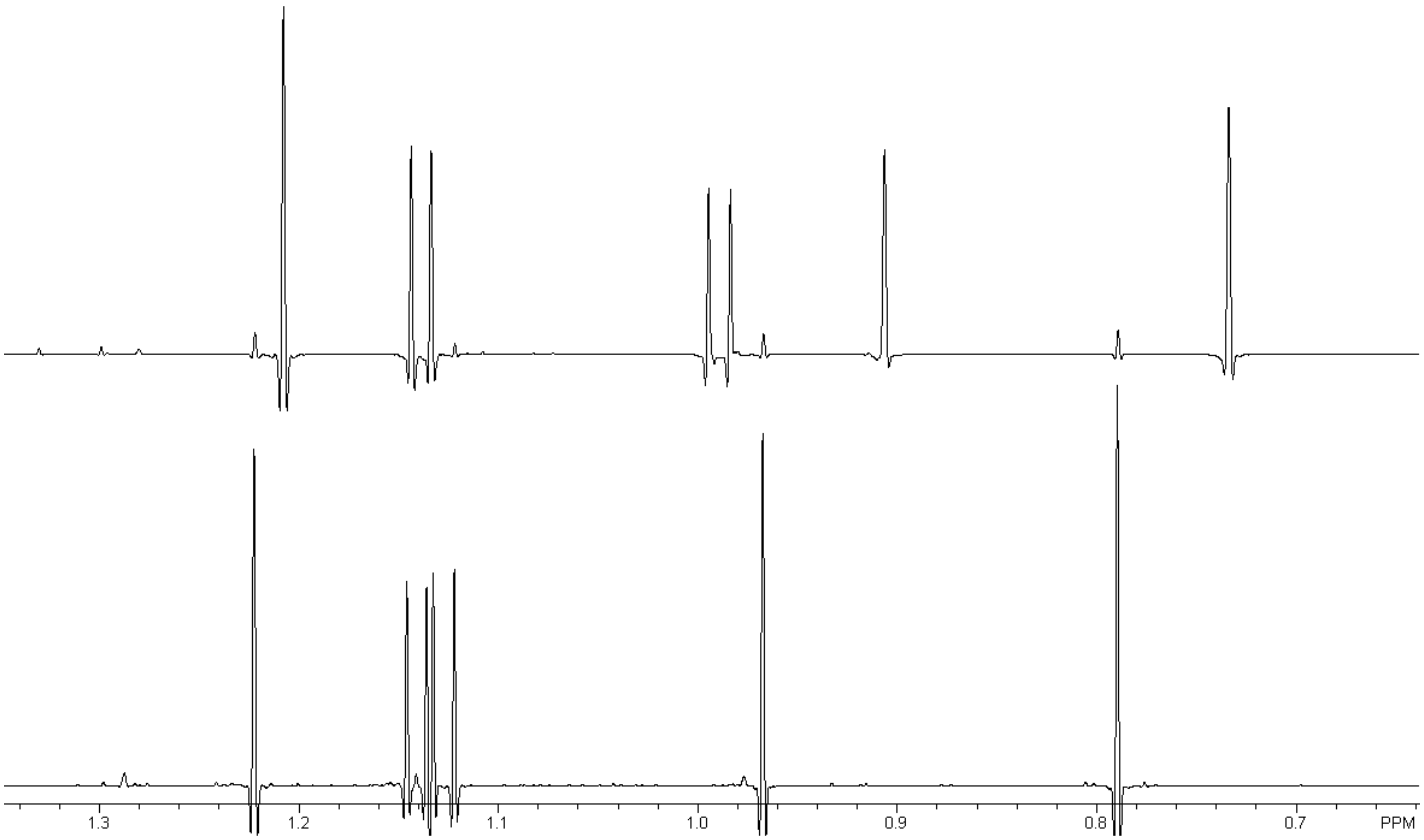


Figure S7. Comparison of the ^{1}H-NMR signals of the H-12 proton in compound **1** at 400 and 750 MHz and compound **2** at 750 MHz. Only in **1**, the highly coupled vicinal methylene protons, 2H-13, form an AB pair with very close chemical shifts (Δδ=0.0014ppm). Therefore, H-12 in **1** gives rise to a higher order resonance pattern with a ddd-like multiplicity that can be readily misinterpreted when working under first-order assumptions. In contrast, as the methylene protons, 2H-13, resonate as relatively distant AM/AX nuclei in **2**, H-12 gives rise to an apparent triplet (pseudo triplet; with two additional long-range couplings). In fact, as the 6-*epi* relationship between **1** and **2** does essentially not affect the geometry of the six-membered ring, its coupling patters have to be identical in both molecules – only the resonances are not, due to the higher order effects caused by the differences in ***relative*** chemical shifts.

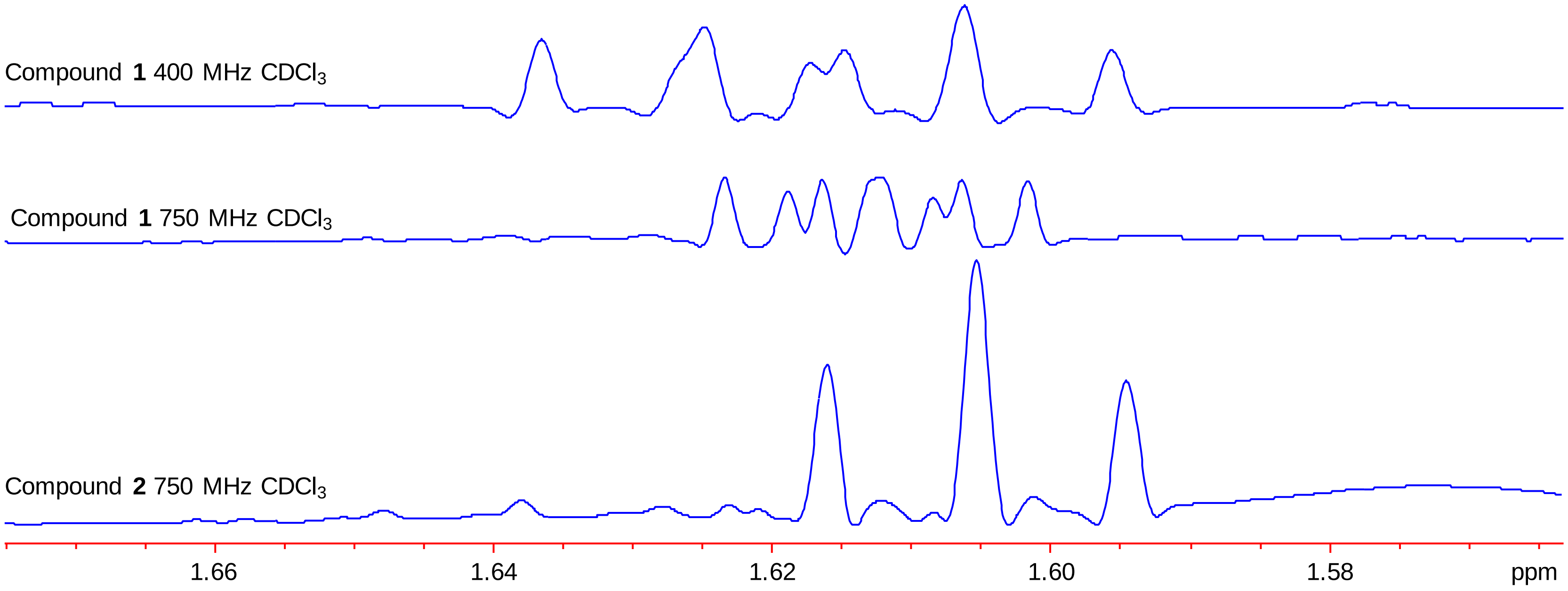
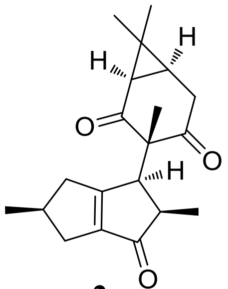


Figure S8. Comparison of the 100 MHz 1D ^{13}C-NMR spectra of compounds **1** and **2** in CD_3OD.



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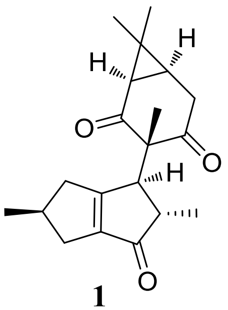

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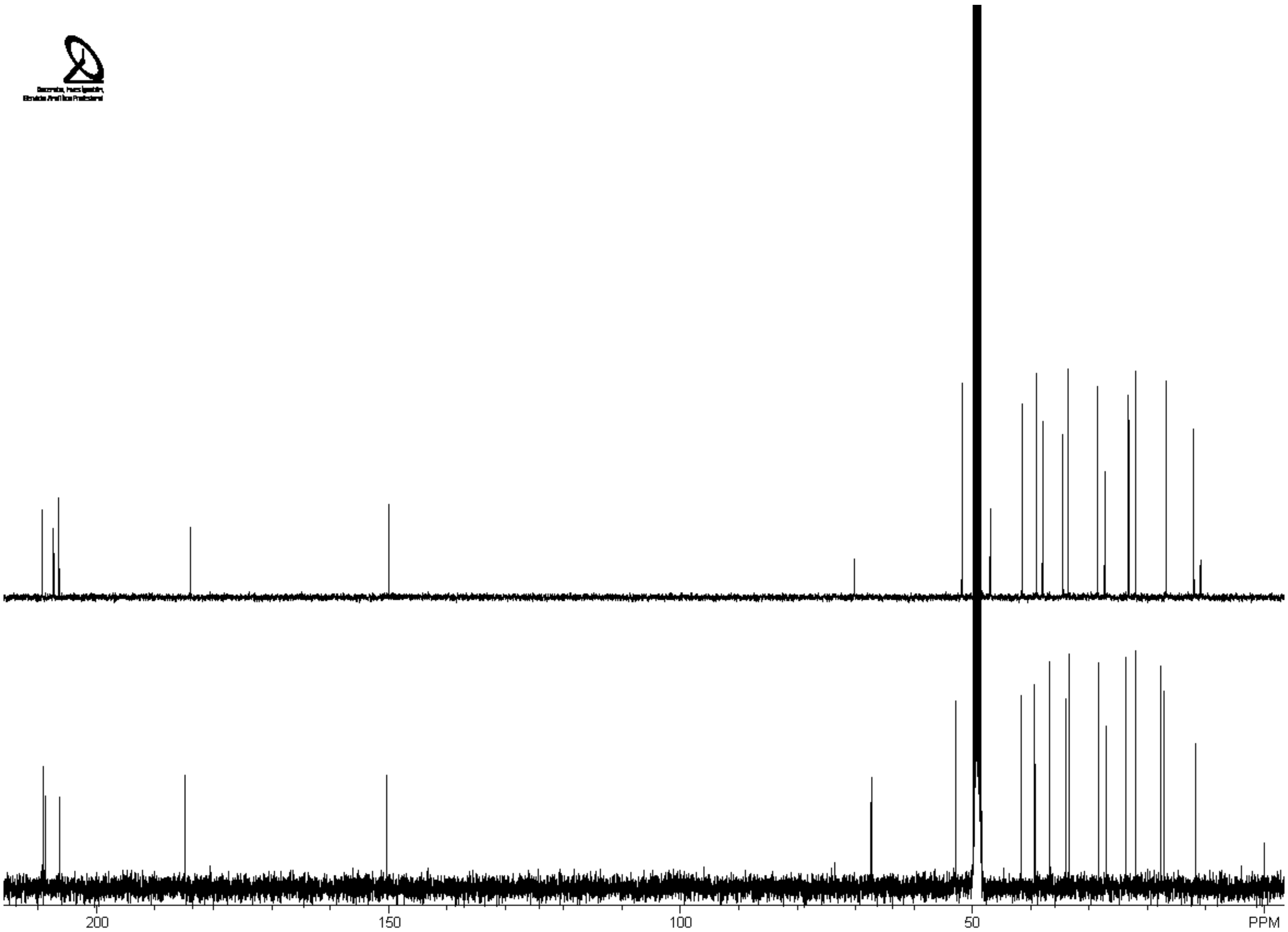

Figure S9. HSQC spectrum (400 MHz, CD_3OD) of 6-*epi*-Riolozatrione (**2**).

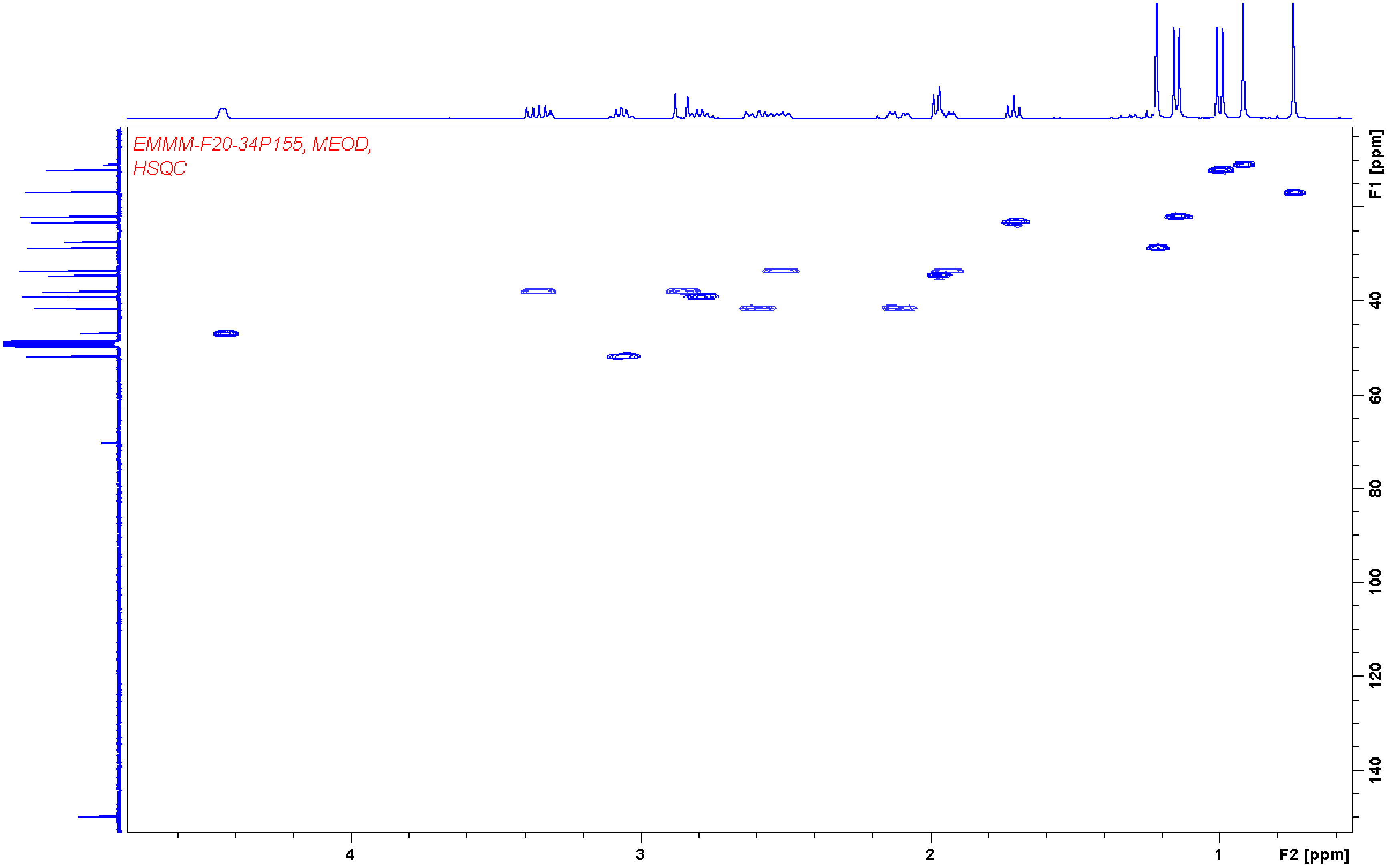

Figure S10. HMBC spectrum (400 MHz, CD_3OD) of 6-*epi*-Riolozatrione (**2**).

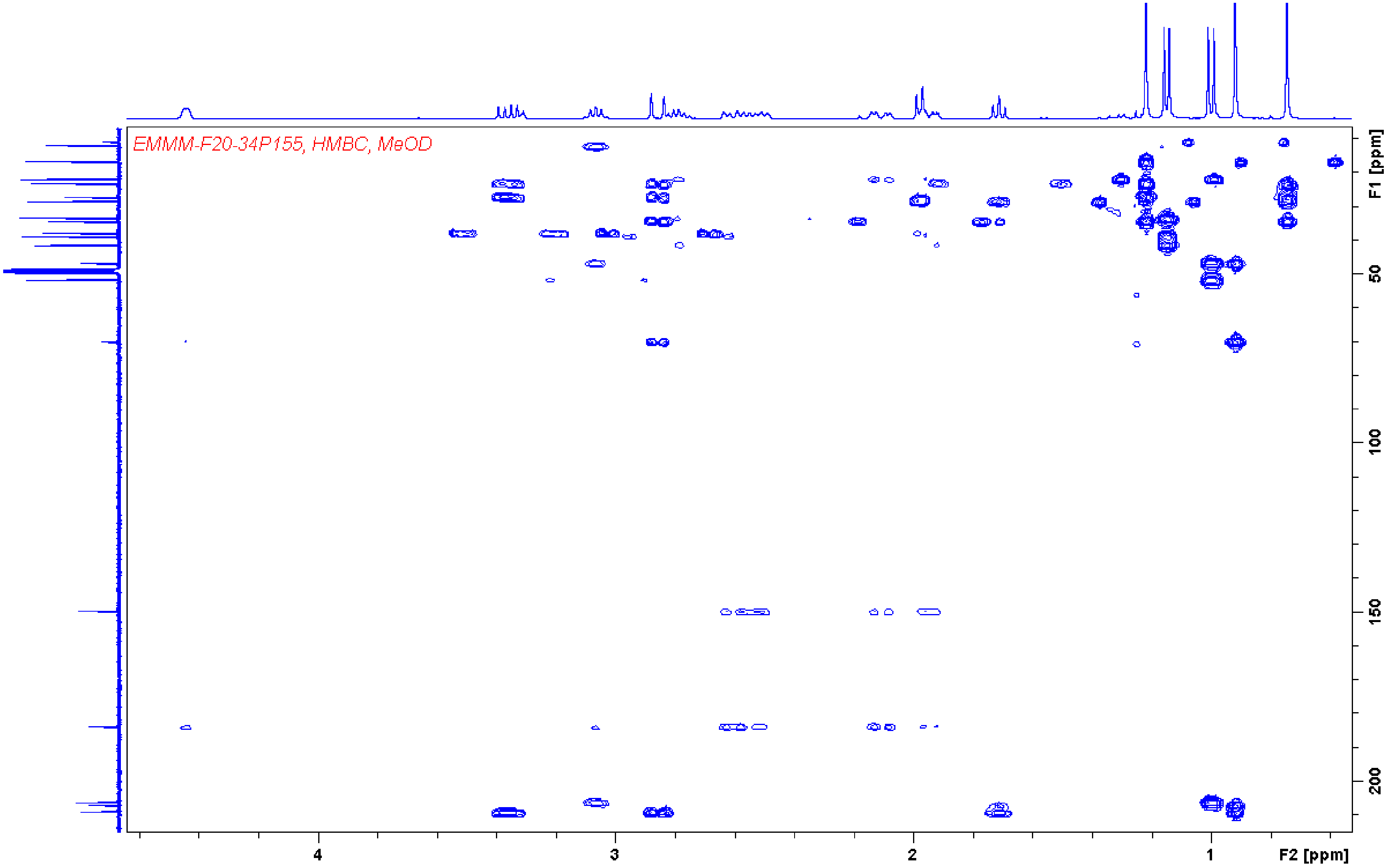

Figure S11. NOESY spectrum (400 MHz, CD_3OD) of 6-*epi*-Riolozatrione (**2**).

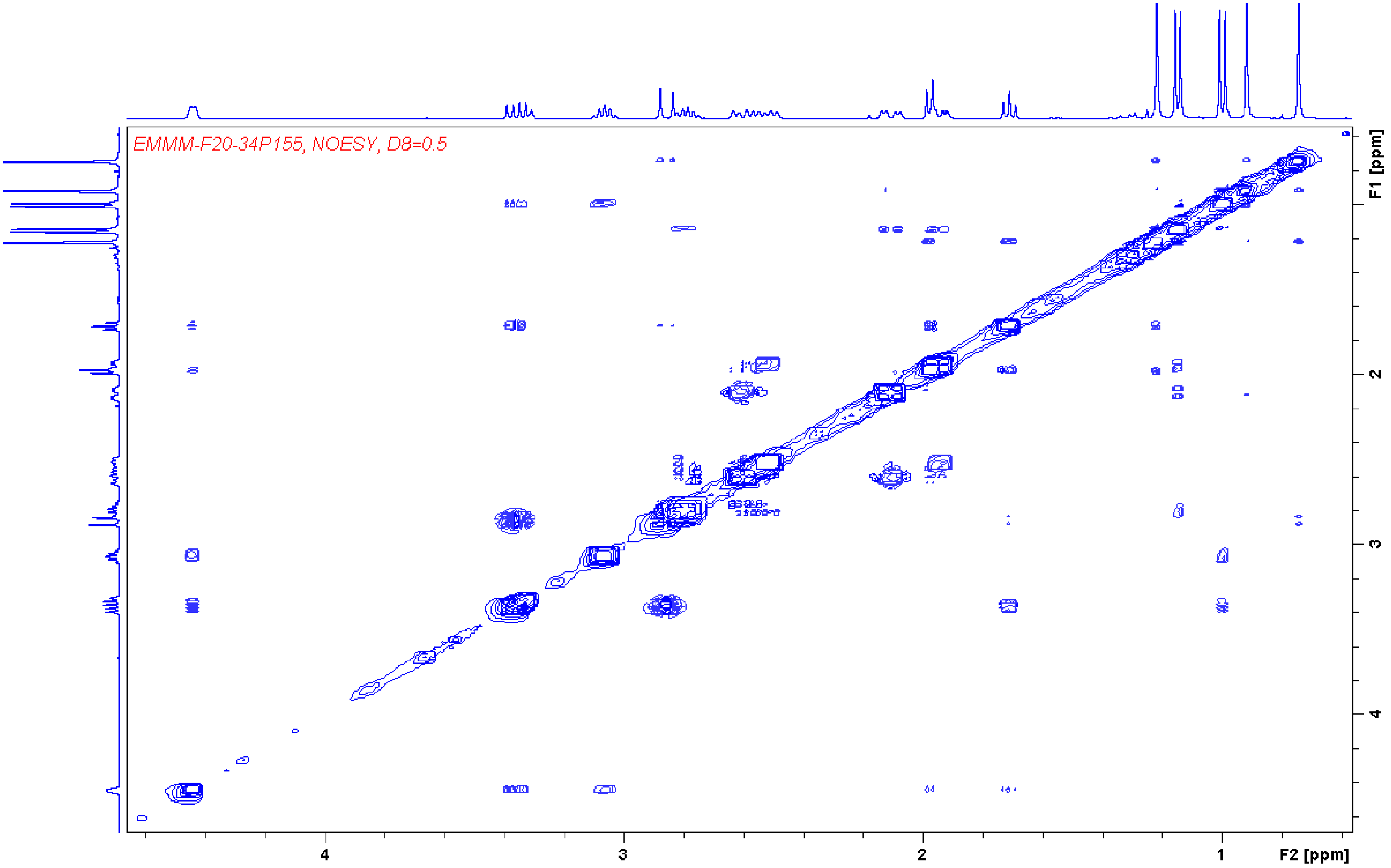

Figure S12. Calculated (red) vs. experimental (blue) and difference (green) 1D ^{1}H-NMR signal of H-1b in compound 1 in CD_3OD at 700 MHz.

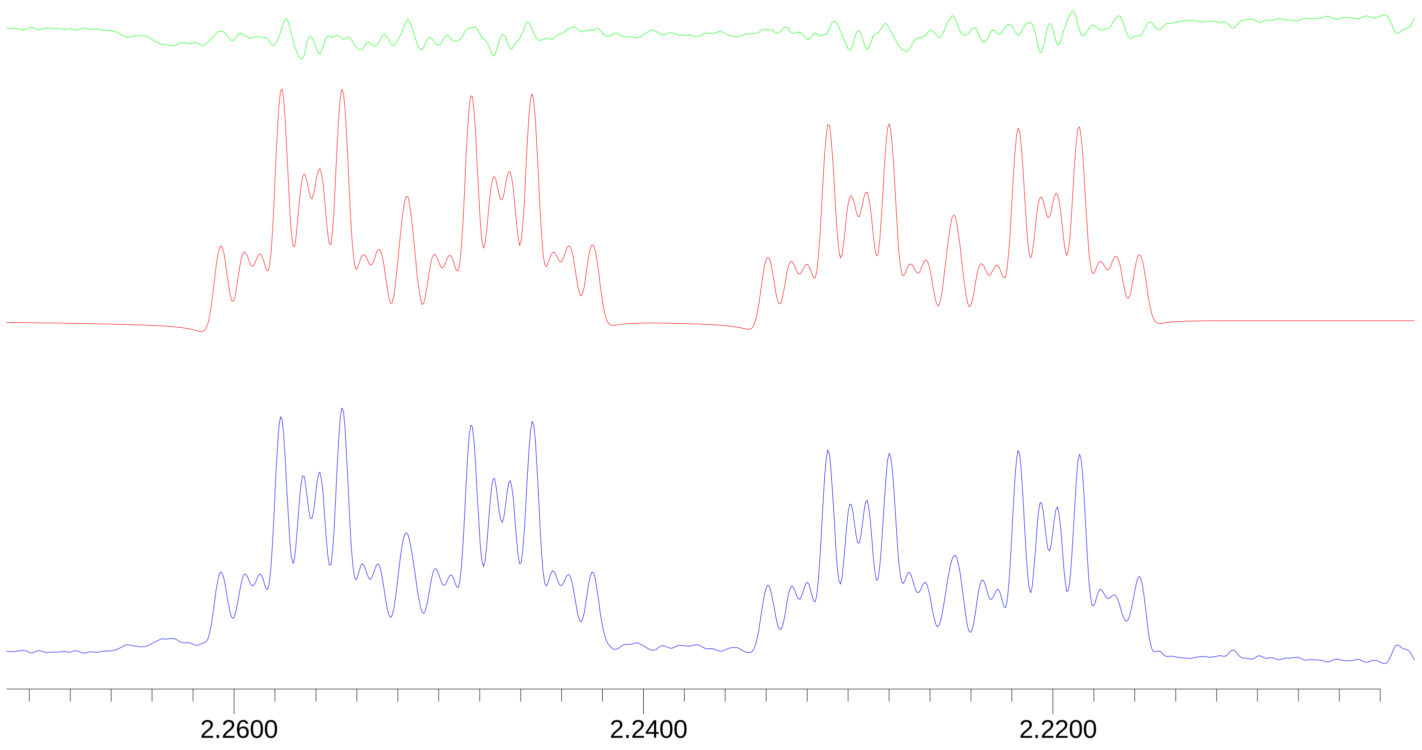

Figure S13. ^{1}H NMR HiFSA data for Riolozatrione (**1**) in CD$_3$OD (PERCH .pms file format)

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CHEMICAL SHIFTS(PPM): FIT-INDEX=  28.957
PROTON 2*SPIN=1 SPECIES=1H    POPULATION= 1.0000
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H12 /1      1.710480  1*1*1  STAT=Y  PRED= 1.558 RANGE= 0.411 WIDTH= 0.609 RESP= 1.0000 HSQC=C12
H15 /1      1.939020  1*1*1  STAT=Y  PRED= 1.832 RANGE= 0.462 WIDTH= 0.876 RESP= 1.0000 HSQC=C15
H6  /1      2.337510  1*1*1  STAT=Y  PRED= 2.872 RANGE= 0.468 WIDTH= 0.578 RESP= 1.0000 HSQC=C6
H1A /1      2.238770  1*1*1  STAT=Y  PRED= 1.678 RANGE= 0.451 WIDTH= 0.521 RESP= 1.0000 HSQC=C1
H1B /1      2.563580  1*1*1  STAT=Y  PRED= 2.328 RANGE= 0.444 WIDTH= 0.585 RESP= 1.0000 HSQC=C1
H2  /1      2.776340  1*1*1  STAT=Y  PRED= 2.460 RANGE= 0.441 WIDTH= 0.483 RESP= 1.0000 HSQC=C2
H3A /1      1.907940  1*1*1  STAT=Y  PRED= 2.069 RANGE= 0.391 WIDTH= 0.442 RESP= 1.0000 HSQC=C3
H3B /1      2.462910  1*1*1  STAT=Y  PRED= 2.460 RANGE= 0.370 WIDTH= 0.506 RESP= 1.0000 HSQC=C3
H19 /1      1.140890  1*1*3  STAT=Y  PRED= 1.058 RANGE= 0.264 WIDTH= 0.500 RESP= 1.0000 HSQC=C19
H13A/1      3.043140  1*1*1  STAT=Y  PRED= 3.063 RANGE= 0.407 WIDTH= 0.653 RESP= 1.0000 HSQC=C13
H13B/1      2.838660  1*1*1  STAT=Y  PRED= 2.343 RANGE= 0.416 WIDTH= 0.956 RESP= 1.0000 HSQC=C13
H16 /1      1.222410  1*1*3  STAT=Y  PRED= 1.221 RANGE= 0.216 WIDTH= 0.750 RESP= 1.0000 HSQC=C16
H17 /1      0.789750  1*1*3  STAT=Y  PRED= 0.965 RANGE= 0.332 WIDTH= 0.562 RESP= 1.0000 HSQC=C17
H18 /1      0.967460  1*1*3  STAT=Y  PRED= 1.183 RANGE= 0.392 WIDTH= 0.676 RESP= 1.0000 HSQC=C18
H20 /1      1.127430  1*1*3  STAT=Y  PRED= 1.173 RANGE= 0.269 WIDTH= 0.410 RESP= 1.0000 HSQC=C20

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J10_31     2.2395  J  H7   H3A   STAT=Y  PRED=  0.000 RANGE= 0.001
J10_32     2.8447  J  H7   H3B   STAT=Y  PRED=  0.000 RANGE= 0.001
J23_24     7.7901  J  H12  H15   STAT=Y  PRED=  10.333 RANGE= 2.000
J23_36     7.9276  J  H12  H13A  STAT=Y  PRED=  9.837 RANGE= 5.000
J23_37     0.9628  J  H12  H13B  STAT=Y  PRED=  1.118 RANGE= 5.000
J24_36    -0.2019  J  H15  H13A  STAT=Y  PRED=  0.000 RANGE= 0.001
J24_37    -0.5000  J  H15  H13B  STAT=Y  PRED=  0.000 RANGE= 0.001
J27_47     7.4637  J  H6   H20   STAT=Y  PRED=  7.032 RANGE= 2.237
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J27_29     0.7459  J  H6   H1B   STAT=Y  PRED=  0.000 RANGE= 0.001
J27_31     0.2028  J  H6   H3A   STAT=Y  PRED=  0.000 RANGE= 0.001
J27_32     0.0884  J  H6   H3B   STAT=Y  PRED=  0.000 RANGE= 0.001
J28_29   -18.7214  J  H1A  H1B   STAT=Y  PRED= -15.891 RANGE= 2.632
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J28_31     2.0396  J  H1A  H3A   STAT=Y  PRED=  1.737 RANGE= 1.000
J28_32     2.0349  J  H1A  H3B   STAT=Y  PRED=  2.066 RANGE= 1.000
J29_30     8.2098  J  H1B  H2    STAT=Y  PRED=  7.227 RANGE= 4.500
J29_31     2.0738  J  H1B  H3A   STAT=Y  PRED=  2.072 RANGE= 1.000
J29_32     1.0952  J  H1B  H3B   STAT=Y  PRED=  1.709 RANGE= 1.763
J30_33     6.9495  J  H2   H19   STAT=Y  PRED=  7.051 RANGE= 1.000
J30_31     6.4032  J  H2   H3A   STAT=Y  PRED=  3.938 RANGE= 2.611
J30_32     8.4003  J  H2   H3B   STAT=Y  PRED=  10.316 RANGE= 2.853
J31_32   -15.9028  J  H3A  H3B   STAT=Y  PRED= -16.751 RANGE= 3.272
J36_37   -18.5145  J  H13A H13B  STAT=Y  PRED= -16.154 RANGE= 1.303

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    0.00100000 = Diagonalization criterium (not used)
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    0.00000000 = Right frequency limit(ppm)
         0.410 = Default line-width(Hz)
  0.0000000000 = Data-point resolution(Hz)
         0.000 = Gaussian contribution%
         0.000 = Dispersion contribution%
    0.00000000 = Decoupling frequency (for DORES only)

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

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Figure S14. ^{1}H NMR HiFSA data for 6-*epi*-Riolozatrione (**2**) in CD$_3$OD (PERCH .pms file format)

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H13A/1      3.349960  1*1*1  STAT=Y  PRED= 3.077 RANGE= 0.424 WIDTH= 1.410 RESP= 1.0000 HSQC=C13
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H16 /1      0.733900  1*1*3  STAT=Y  PRED= 0.881 RANGE= 0.351 WIDTH= 0.971 RESP= 1.0000 HSQC=C16
H18 /1      1.207750  1*1*3  STAT=Y  PRED= 1.255 RANGE= 0.414 WIDTH= 0.486 RESP= 1.0000 HSQC=C18
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J10_44    -0.4145  J  H7A  H18   STAT=Y  PRED=  0.000 RANGE= 0.001
J23_24     7.9358  J  H12A H15A  STAT=Y  PRED=  10.333 RANGE= 2.000
J23_37     0.6424  J  H12A H13B  STAT=Y  PRED=  0.269 RANGE= 5.000
J23_36     8.4397  J  H12A H13A  STAT=Y  PRED=  8.850 RANGE= 5.000
J27_47     7.7129  J  H6A  H20   STAT=Y  PRED=  7.032 RANGE= 2.237
J27_28     0.9992  J  H6A  H1A   STAT=Y  PRED=  0.000 RANGE= 0.001
J27_29     0.9352  J  H6A  H1B   STAT=Y  PRED=  0.000 RANGE= 0.001
J27_32     0.2720  J  H6A  H3B   STAT=Y  PRED=  0.000 RANGE= 0.001
J27_30     0.0029  J  H6A  H2A   STAT=Y  PRED=  0.000 RANGE= 0.001
J28_29   -18.5844  J  H1A  H1B   STAT=Y  PRED= -15.884 RANGE= 2.632
J28_30     6.3365  J  H1A  H2A   STAT=Y  PRED=  7.062 RANGE= 4.500
J28_31     1.9488  J  H1A  H3A   STAT=Y  PRED=  1.716 RANGE= 1.758
J28_32     2.0035  J  H1A  H3B   STAT=Y  PRED=  2.072 RANGE= 1.000
J29_30     8.2174  J  H1B  H2A   STAT=Y  PRED=  7.210 RANGE= 4.500
J29_31     2.0716  J  H1B  H3A   STAT=Y  PRED=  2.069 RANGE= 1.000
J29_32     1.1656  J  H1B  H3B   STAT=Y  PRED=  1.750 RANGE= 1.000
J30_33     6.9555  J  H2A  H19   STAT=Y  PRED=  7.051 RANGE= 1.000
J30_31     6.3205  J  H2A  H3A   STAT=Y  PRED=  7.100 RANGE= 2.288
J30_32     8.3159  J  H2A  H3B   STAT=Y  PRED=  10.313 RANGE= 2.855
J31_32   -15.8538  J  H3A  H3B   STAT=Y  PRED= -16.750 RANGE= 3.273
J36_37   -16.9872  J  H13A H13B  STAT=Y  PRED= -16.158 RANGE= 1.302

CONTROL PARAMETERS:
       SOLVENT = None
     REFERENCE = TMS
    0.00000000 = CONCENTRATION (vol%)
       298.000 = TEMPERATURE (vol%, def=1.0%)
  699.95430000 = FIELD(1H,MHz), used to transform shifts to ppms
    0.00100000 = Minimum line-intensity
    0.00100000 = Diagonalization criterium (not used)
    0.00000000 = Left frequency limit(ppm)
    0.00000000 = Right frequency limit(ppm)
         0.376 = Default line-width(Hz)
  0.0000000000 = Data-point resolution(Hz)
         0.000 = Gaussian contribution%
         0.000 = Dispersion contribution%
    0.00000000 = Decoupling frequency (for DORES only)

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

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Figure S15. ^{1}H NMR HiFSA data for Riolozatrione (**1**) in CDCl$_3$ (PERCH .pms file format)

```
ACTIVE SPECIES:1H
CHEMICAL SHIFTS(PPM):
PROTON    2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.80740
 H7     / 1     3.126458  1*1*1  STAT=Y  PRED= 3.125 RANGE= 0.073 WIDTH(Y)= 1.324 RESP(Y)= 1.0000
 H12    / 1     1.614077  1*1*1  STAT=Y  PRED= 1.614 RANGE= 0.073 WIDTH(Y)= 0.892 RESP(Y)= 1.0000
 H15    / 1     1.883196  1*1*1  STAT=Y  PRED= 1.883 RANGE= 0.073 WIDTH(Y)= 0.646 RESP(Y)= 1.0000
 H6     / 1     2.456355  1*1*1  STAT=Y  PRED= 2.457 RANGE= 0.073 WIDTH(Y)= 1.023 RESP(Y)= 1.0000
 H1A    / 1     2.310340  1*1*1  STAT=Y  PRED= 2.310 RANGE= 0.073 WIDTH(Y)= 0.878 RESP(Y)= 1.0000
 H1B    / 1     2.485253  1*1*1  STAT=Y  PRED= 2.483 RANGE= 0.073 WIDTH(Y)= 0.726 RESP(Y)= 1.0000
 H2     / 1     2.753404  1*1*1  STAT=Y  PRED= 2.755 RANGE= 0.073 WIDTH(Y)= 0.940 RESP(Y)= 1.0000
 H3A    / 1     1.961866  1*1*1  STAT=Y  PRED= 1.961 RANGE= 0.073 WIDTH(Y)= 0.907 RESP(Y)= 1.0000
 H3B    / 1     2.494908  1*1*1  STAT=Y  PRED= 2.497 RANGE= 0.073 WIDTH(Y)= 0.916 RESP(Y)= 1.0000
 H19    / 1     1.153539  1*1*3  STAT=Y  PRED= 1.155 RANGE= 0.073 WIDTH(Y)= 0.886 RESP(Y)= 1.0000
 H13A   / 1     2.882158  1*1*1  STAT=Y  PRED= 2.888 RANGE= 0.073 WIDTH(Y)= 0.928 RESP(Y)= 1.0000
 H13B   / 1     2.884841  1*1*1  STAT=Y  PRED= 2.878 RANGE= 0.073 WIDTH(Y)= 1.124 RESP(Y)= 1.0000
 H16    / 1     1.235937  1*1*3  STAT=Y  PRED= 1.235 RANGE= 0.073 WIDTH(Y)= 1.143 RESP(Y)= 1.0000
 H17    / 1     0.852886  1*1*3  STAT=Y  PRED= 0.853 RANGE= 0.073 WIDTH(Y)= 0.933 RESP(Y)= 1.0000
 H18    / 1     1.088124  1*1*3  STAT=Y  PRED= 1.089 RANGE= 0.073 WIDTH(Y)= 1.031 RESP(Y)= 1.0000
 H20    / 1     1.157132  1*1*3  STAT=Y  PRED= 1.157 RANGE= 0.073 WIDTH(Y)= 0.846 RESP(Y)= 1.0000

COUPLING CONSTANTS(HZ):
 J10_27      2.0096   J H7      H6        STAT=Y  PRED= 1.896 RANGE= 0.100
 J10_28      1.3779   J H7      H1A       STAT=Y  PRED= 1.357 RANGE= 0.100
 J10_29      1.5871   J H7      H1B       STAT=Y  PRED= 1.687 RANGE= 0.100
 J10_31      2.2919   J H7      H3A       STAT=Y  PRED= 2.240 RANGE= 0.100
 J10_32      2.8463   J H7      H3B       STAT=Y  PRED= 2.845 RANGE= 0.100
 J23_24      7.6821   J H12     H15       STAT=Y  PRED= 7.790 RANGE= 0.100
 J23_36      8.0127   J H12     H13A      STAT=Y  PRED= 7.928 RANGE= 0.100
 J23_37      0.6452   J H12     H13B      STAT=Y  PRED= 0.963 RANGE= 0.100
 J24_36     -0.4748   J H15     H13A      STAT=Y  PRED= -0.202 RANGE= 0.100
 J24_37     -0.1206   J H15     H13B      STAT=Y  PRED= -0.500 RANGE= 0.100
 J27_28      0.7631   J H6      H1A       STAT=Y  PRED= 0.775 RANGE= 0.100
 J27_29      0.6335   J H6      H1B       STAT=Y  PRED= 0.746 RANGE= 0.100
 J27_31      0.0080   J H6      H3A       STAT=Y  PRED= 0.203 RANGE= 0.100
 J27_32      0.0673   J H6      H3B       STAT=Y  PRED= 0.088 RANGE= 0.100
 J27_47      7.4599   J H6      H20       STAT=Y  PRED= 7.464 RANGE= 0.100
 J28_29    -18.5611   J H1A     H1B       STAT=Y  PRED= -18.721 RANGE= 0.100
 J28_30      6.6499   J H1A     H2        STAT=Y  PRED= 6.495 RANGE= 0.100
 J28_31      2.0453   J H1A     H3A       STAT=Y  PRED= 2.040 RANGE= 0.100
 J28_32      2.0472   J H1A     H3B       STAT=Y  PRED= 2.035 RANGE= 0.100
 J29_30      8.2769   J H1B     H2        STAT=Y  PRED= 8.210 RANGE= 0.100
 J29_31      2.1368   J H1B     H3A       STAT=Y  PRED= 2.072 RANGE= 1.000
 J29_32      1.0197   J H1B     H3B       STAT=Y  PRED= 1.095 RANGE= 0.100
 J30_31      6.6044   J H2      H3A       STAT=Y  PRED= 6.403 RANGE= 0.100
 J30_32      8.4073   J H2      H3B       STAT=Y  PRED= 8.400 RANGE= 0.100
 J30_33      6.9716   J H2      H19       STAT=Y  PRED= 6.949 RANGE= 0.100
 J31_32    -16.0398   J H3A     H3B       STAT=Y  PRED= -15.903 RANGE= 0.100
 J36_37    -18.1640   J H13A    H13B      STAT=Y  PRED= -18.515 RANGE= 0.100

CONTROL PARAMETERS:
       Solvent =  none (def. 99% enriched)
     REFERENCE = TMS
         1.000 =  Concentration (vol%, def=1.0%)
    0.00100000 =  Minimum line-intensity
    0.00100000 =  Diagonalization criterium (not in use)
  699.95432200 =  FIELD(1H,MHz), used to transform shifts to ppms
   16.23558651 =  Left frequency (ppm)
   -3.90528483 =  Right frequency (ppm)
         0.000 =  Acquisition time (s, for QMTLS)
         0.397 =  Line-width (for modes D, P & T, 0=use defaults)
   0.053778627 =  Data-point resolution (Hz)
        52.609 =  GAUSSIAN (%, 0=use default from INF)
         0.000 =  Dispersion contribution (%, 0=use default from INF)
    0.00000000 =  Decoupling frequency (for DORES)

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

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Figure S16. ^{1}H NMR HiFSA data for 6-*epi*-Riolozatrione (**2**) in $CDCl_3$ (PERCH .pms file format)

```
ACTIVE SPECIES:1H
CHEMICAL SHIFTS(PPM):
PROTON    2*SPIN= 1 SPECIES=1H    POPULATION(Y)=   0.91072
 H7A  / 1     4.219272  1*1*1  STAT=Y  PRED= 4.222 RANGE= 0.073 WIDTH(Y)= 3.500 RESP(Y)= 1.0000
 H12A / 1     1.607877  1*1*1  STAT=Y  PRED= 1.607 RANGE= 0.073 WIDTH(Y)= 0.629 RESP(Y)= 1.0000
 H15A / 1     1.864763  1*1*1  STAT=Y  PRED= 1.862 RANGE= 0.073 WIDTH(Y)= 0.946 RESP(Y)= 1.0000
 H6A  / 1     2.921293  1*1*1  STAT=Y  PRED= 2.920 RANGE= 0.073 WIDTH(Y)= 0.718 RESP(Y)= 1.0000
 H1A  / 1     2.174499  1*1*1  STAT=Y  PRED= 2.172 RANGE= 0.073 WIDTH(Y)= 3.107 RESP(Y)= 1.0000
 H1B  / 1     2.479418  1*1*1  STAT=Y  PRED= 2.481 RANGE= 0.073 WIDTH(Y)= 1.775 RESP(Y)= 1.0000
 H2A  / 1     2.757998  1*1*1  STAT=Y  PRED= 2.757 RANGE= 0.073 WIDTH(Y)= 0.554 RESP(Y)= 1.0000
 H3A  / 1     2.002126  1*1*1  STAT=Y  PRED= 2.002 RANGE= 0.073 WIDTH(Y)= 0.576 RESP(Y)= 1.0000
 H3B  / 1     2.540613  1*1*1  STAT=Y  PRED= 2.541 RANGE= 0.073 WIDTH(Y)= 0.605 RESP(Y)= 1.0000
 H19B / 1     1.155959  1*1*3  STAT=Y  PRED= 1.156 RANGE= 0.073 WIDTH(Y)= 0.643 RESP(Y)= 1.0000
 H13A / 1     3.121516  1*1*1  STAT=Y  PRED= 3.123 RANGE= 0.073 WIDTH(Y)= 1.498 RESP(Y)= 1.0000
 H13B / 1     2.931317  1*1*1  STAT=Y  PRED= 2.929 RANGE= 0.073 WIDTH(Y)= 1.868 RESP(Y)= 1.0000
 H17B / 1     1.019603  1*1*3  STAT=Y  PRED= 1.019 RANGE= 0.073 WIDTH(Y)= 2.914 RESP(Y)= 1.0000
 H16B / 1     0.804109  1*1*3  STAT=Y  PRED= 0.804 RANGE= 0.073 WIDTH(Y)= 2.037 RESP(Y)= 1.0000
 H18B / 1     1.226542  1*1*3  STAT=Y  PRED= 1.225 RANGE= 0.073 WIDTH(Y)= 0.780 RESP(Y)= 1.0000
 H20B / 1     1.070224  1*1*3  STAT=Y  PRED= 1.069 RANGE= 0.073 WIDTH(Y)= 0.619 RESP(Y)= 1.0000

COUPLING CONSTANTS(HZ):
 J10_27      6.3191   J H7A   H6A     STAT=Y  PRED= 7.604 RANGE= 3.320
 J48         1.4989   J H7A   H1A     STAT=Y  PRED= -0.500 RANGE= 1.000
 J49         1.5066   J H7A   H1B     STAT=Y  PRED= -0.500 RANGE= 1.000
 J45         2.1803   J H7A   H3A     STAT=Y  PRED= 2.000 RANGE= 1.000
 J46         2.8238   J H7A   H3B     STAT=Y  PRED= 2.000 RANGE= 1.000
 20         -0.3510   J H7A   H18B    STAT=Y
 J23_24      7.8141   J H12A  H15A    STAT=Y  PRED= 9.000 RANGE= 2.000
 J23_36      8.3722   J H12A  H13A    STAT=Y  PRED= 8.821 RANGE= 5.000
 J23_37      0.6381   J H12A  H13B    STAT=Y  PRED= 0.280 RANGE= 5.000
 18          0.8346   J H6A   H1A     STAT=Y  PRED= 0.280 RANGE= 5.000
 19          0.8728   J H6A   H1B     STAT=Y  PRED= 0.280 RANGE= 5.000
 J27_47      7.7524   J H6A   H20B    STAT=Y  PRED= 7.032 RANGE= 2.230
 J28_29    -18.4677   J H1A   H1B     STAT=Y  PRED= -15.926 RANGE= 2.560
 J28_30      6.5099   J H1A   H2A     STAT=Y  PRED= 7.071 RANGE= 4.500
 J28_31      2.1374   J H1A   H3A     STAT=Y  PRED= 1.716 RANGE= 1.750
 J28_32      2.0492   J H1A   H3B     STAT=Y  PRED= 2.072 RANGE= 1.000
 J29_30      8.2393   J H1B   H2A     STAT=Y  PRED= 7.215 RANGE= 4.500
 J29_31      2.2020   J H1B   H3A     STAT=Y  PRED= 2.069 RANGE= 1.000
 J29_32      1.1195   J H1B   H3B     STAT=Y  PRED= 1.749 RANGE= 1.000
 J30_31      6.4856   J H2A   H3A     STAT=Y  PRED= 7.096 RANGE= 2.280
 J30_32      8.3419   J H2A   H3B     STAT=Y  PRED= 10.031 RANGE= 3.200
 J30_33      6.9456   J H2A   H19B    STAT=Y  PRED= 7.056 RANGE= 1.000
 J31_32    -16.0054   J H3A   H3B     STAT=Y  PRED= -16.802 RANGE= 3.250
 J36_37    -16.9517   J H13A  H13B    STAT=Y  PRED= -15.509 RANGE= 1.330

CONTROL PARAMETERS:
       Solvent =  none (def. 99% enriched)
     REFERENCE = TMS
         1.000 =  Concentration (vol%, def=1.0%)
    0.00100000 =  Minimum line-intensity
    0.00100000 =  Diagonalization criterium (not in use)
  699.95432200 =  FIELD(1H,MHz), used to transform shifts to ppms
   16.23496007 =  Left frequency (ppm)
   -3.90591196 =  Right frequency (ppm)
         0.000 =  Acquisition time (s, for QMTLS)
         0.495 =  Line-width (for modes D, P & T, 0=use defaults)
   0.053778627 =  Data-point resolution (Hz)
       142.439 =  GAUSSIAN (%, 0=use default from INF)
         0.000 =  Dispersion contribution (%, 0=use default from INF)
    0.00000000 =  Decoupling frequency (for DORES)

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

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Figure S17. Full ^{1}H NMR δ and *J*-correlation maps, termed Quantum Interaction and Linkage Tables (QuILTs), of riolozatrione (**1**) and 6-*epi*-riolozatrione (**2**) were achieved by HiFSA processing of the 700 MHz spectra in $CDCl_3$. Multiplicities within parentheses are due to couplings of ≤1 Hz. Couplings with absolute value of ≤0.10 Hz are given as "*ø*".

δ **1**	**M**	**H**	1b(β)	1a(α)	2	3b(β)	3a(α)	6	7	11	12	13a(α)	13b(β)	16	17	18	19	20
2.3103	ddddd(d)	1b(β)	d	2	3	4	4	5	4	7	8	7	7	9	9	6	4	6
2.4853	ddddd(d)	1a(α)	-18.56	d	3	4	4	5	4	7	8	7	7	9	9	6	4	6
2.7534	ddqdd	2	6.65	8.28	d	3	3	6	5	8	9	8	8	10	10	7	3	7
1.9619	ddddd	3b(β)	2.05	2.14	6.60	d	2	5	5	8	9	8	8	10	10	7	4	6
2.4949	ddddd	3a(α)	2.05	1.02	8.41	-16.04	d	5	5	8	9	8	8	10	10	7	4	6
2.4564	qd(dd)	6	0.76	0.63	Ø	Ø	Ø	d	3	6	7	6	6	8	8	5	7	3
3.1265	ddddd	7	1.38	1.59	Ø	2.29	2.85	2.01	d	5	6	5	5	7	7	4	6	4
1.8832	d(dd)	11	Ø	Ø	Ø	Ø	Ø	Ø	Ø	d	3	4	4	4	4	5	9	7
1.6141	dd(d)	12	Ø	Ø	Ø	Ø	Ø	Ø	Ø	7.68	d	3	3	4	4	6	10	8
2.8822	dd(d)	13a(α)	Ø	Ø	Ø	Ø	Ø	Ø	Ø	-0.47	8.01	d	2	5	5	5	9	7
2.8848	d(dd)	13b(β)	Ø	Ø	Ø	Ø	Ø	Ø	Ø	-0.12	0.65	-18.16	d	5	5	5	9	7
1.2359	s	16	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	d	4	7	11	9
0.8529	s	17	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	d	7	11	9
1.0881	s	18	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	d	8	6
1.1535	d	19	Ø	Ø	6.972	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	d	8
1.1571	d	20	Ø	Ø	Ø	Ø	Ø	7.46	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	d

δ **2**	M	**H**	1b(β)	1a(α)	2	3b(β)	3a(α)	6	7	11	12	13a(α)	13b(β)	16	17	18	19	20
2.1745	ddddd(d)	1b(β)	d	2	3	4	4	5	4	7	8	7	7	9	9	6	4	6
2.4794	ddddd(d)	1a(α)	-18.47	d	3	4	4	5	4	7	8	7	7	9	9	6	4	6
2.7580	ddqdd	2	6.51	8.24	d	3	3	6	5	8	9	8	8	10	10	7	3	7
2.0021	ddddd	3b(β)	2.14	2.20	6.486	d	2	5	5	8	9	8	8	10	10	7	4	6
2.5406	ddddd	3a(α)	2.05	1.12	8.34	-16.01	d	5	5	8	9	8	8	10	10	7	4	6
2.9213	qd(dd)	6	0.83	0.87	Ø	Ø	Ø	d	3	6	7	6	6	8	8	5	7	3
4.2193	ddddd(d)	7	1.50	1.51	Ø	2.18	2.82	6.32	d	5	6	5	5	7	7	4	6	4
1.8648	d	11	Ø	Ø	Ø	Ø	Ø	Ø	Ø	d	3	4	4	4	4	5	9	7
1.6079	dd(d)	12	Ø	Ø	Ø	Ø	Ø	Ø	Ø	7.81	d	3	3	4	4	6	10	8
3.1215	dd	13a(α)	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	8.37	d	2	5	5	5	9	7
2.9313	d(d)	13b(β)	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	0.64	-16.95	d	5	5	5	9	7
1.2265	s	16	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	d	4	7	11	9
0.8041	s	17	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	d	7	11	9
1.0196	(d)	18	Ø	Ø	Ø	Ø	Ø	Ø	-0.35	Ø	Ø	Ø	Ø	Ø	Ø	d	8	6
1.1560	d	19	Ø	Ø	6.95	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	d	8
1.0702	d	20	Ø	Ø	Ø	Ø	Ø	7.75	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	d

Figure S18. Calculated (red) vs. experimental (blue) and difference (green) 1D ^{1}H-NMR signals in compounds **1** and **2** in CDCl$_3$ at 700 MHz.

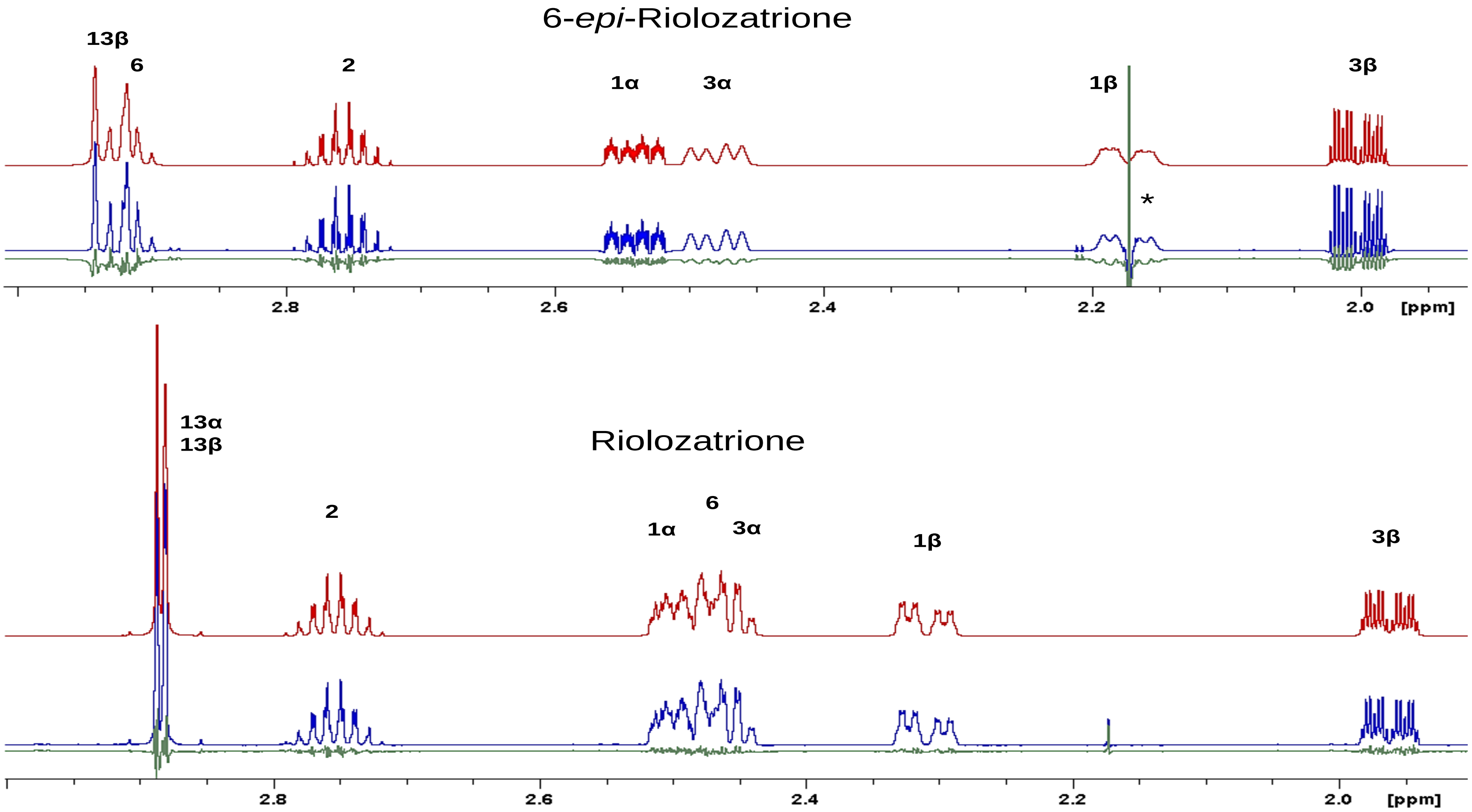

Figure S19. Experimental and calculated IR and VCD spectra at the B3PW91/DGDZVP level of theory for **3** (left) and **4** (right).