Supplementary Information

Citrifolin A: A New Alkylresorcinol Glucoside Isolated from the Leaves of *Eugenia citrifolia*

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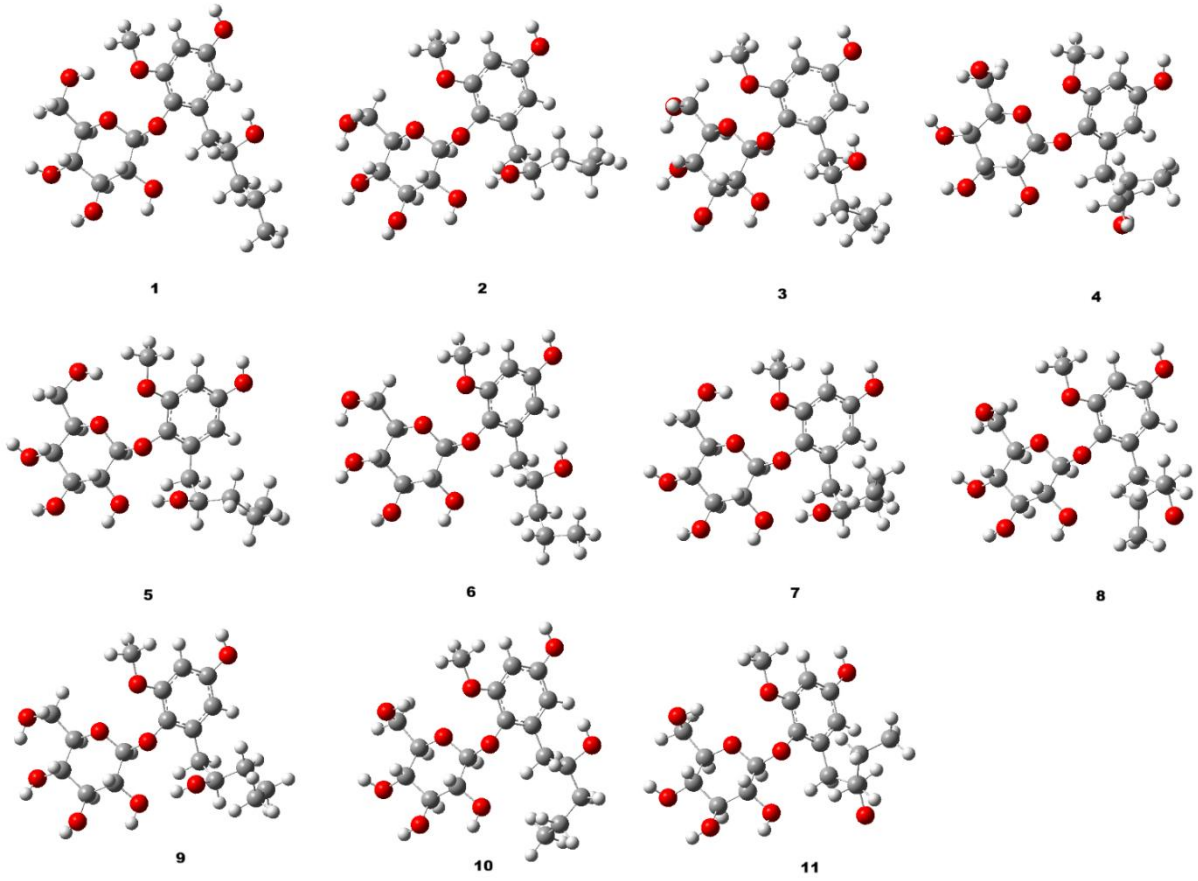

Figure S1. Set of 11 optimized conformers identified for the 2'*R* stereoisomer of citrifolin A. Conformational sampling was performed with the MMFF94 force field in Avogadro, and final structures were refined by DFT optimization at the B3LYP/6-31G(d) level of theory in MeOH (SMD model).

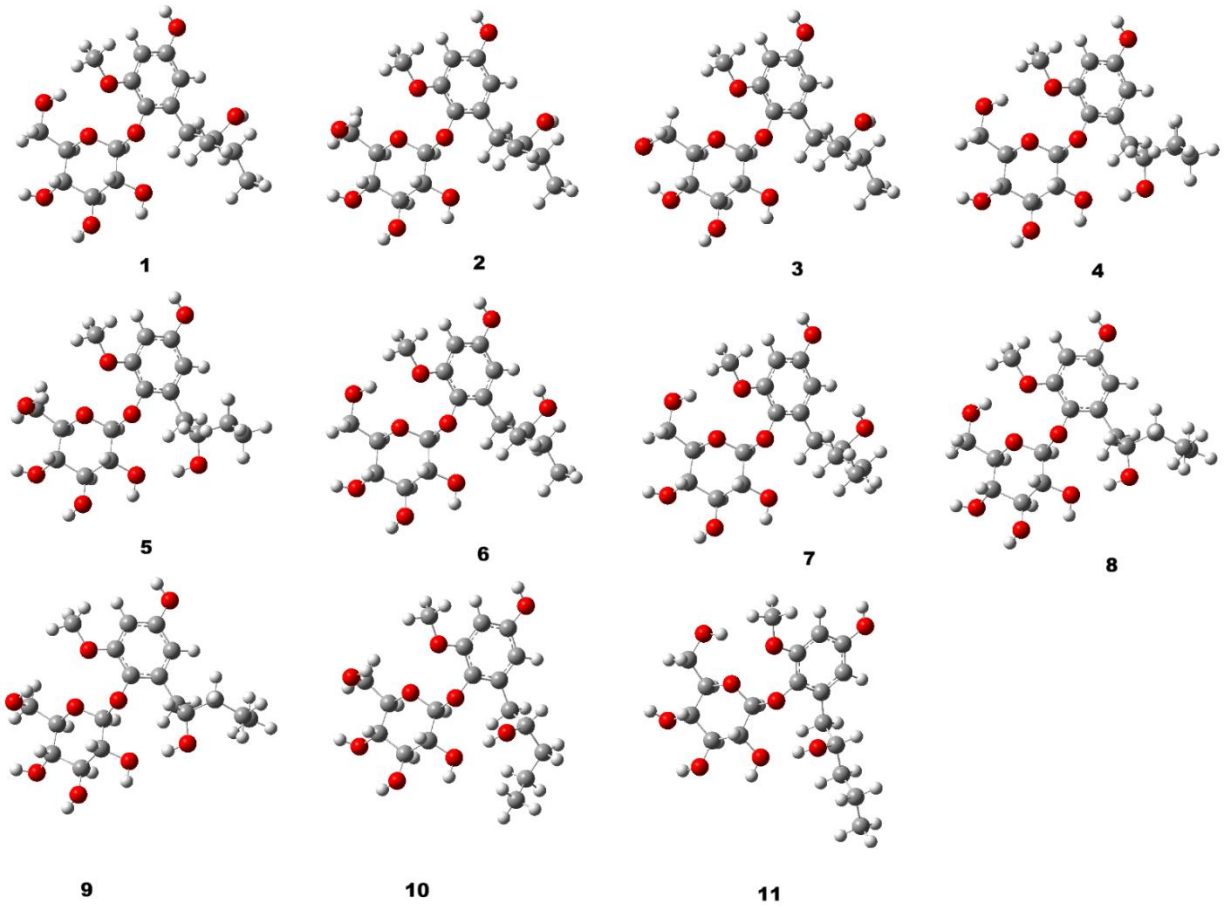

Figure S2. Set of 11 optimized conformers identified for the 2'*S* stereoisomer of citrifolin A. Conformational sampling was performed with the MMFF94 force field in Avogadro, and final structures were refined by DFT optimization at the B3LYP/6-31G(d) level of theory in MeOH (SMD model).

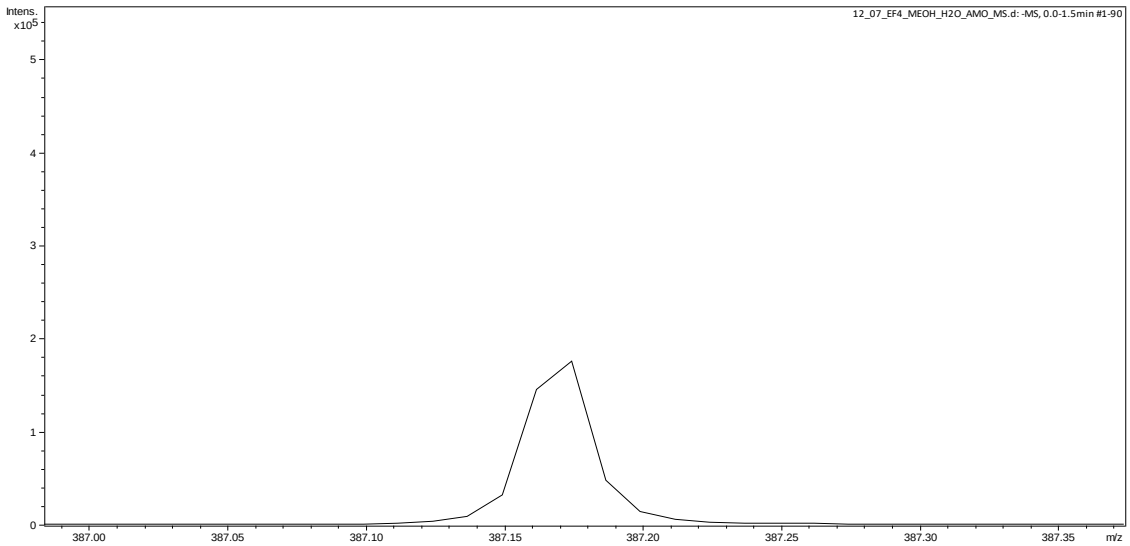

Figure S3. HRESIMS spectrum of compound **1**, *m/z* 387.1680 $[M - H]^-$ (calcd. for $C_{18}H_{27}O_9^-$, 387.1661, $\Delta_{m/z\ theoretical}$ = + 4.91 ppm).

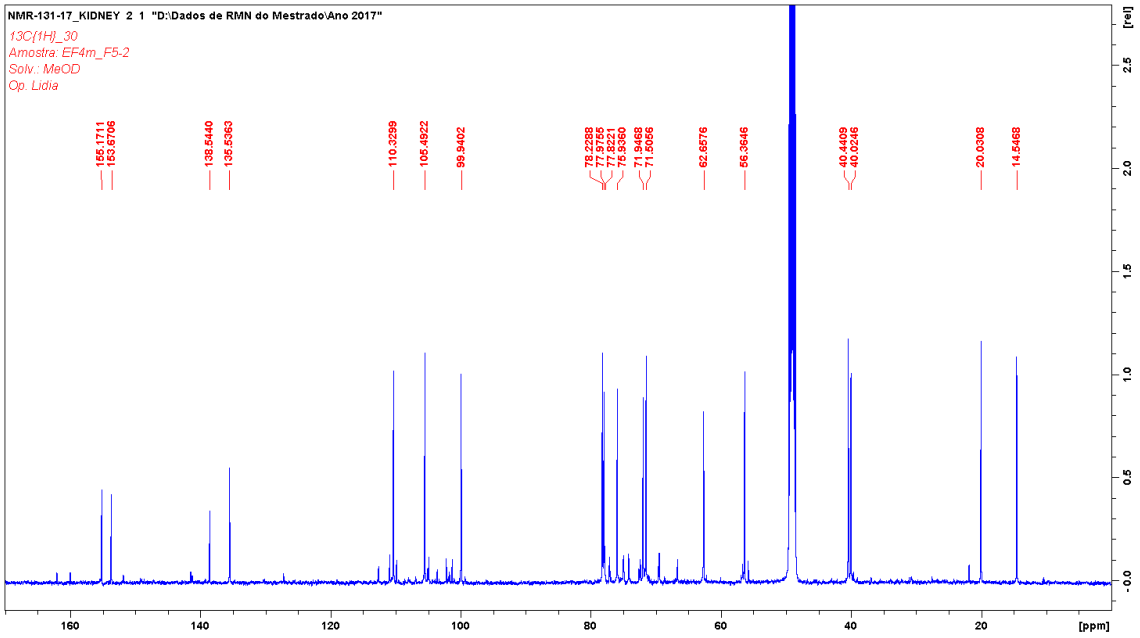

Figure S4. ^{13}C NMR spectrum of compound **1** (11.7 T, CD_3OD, TMS).

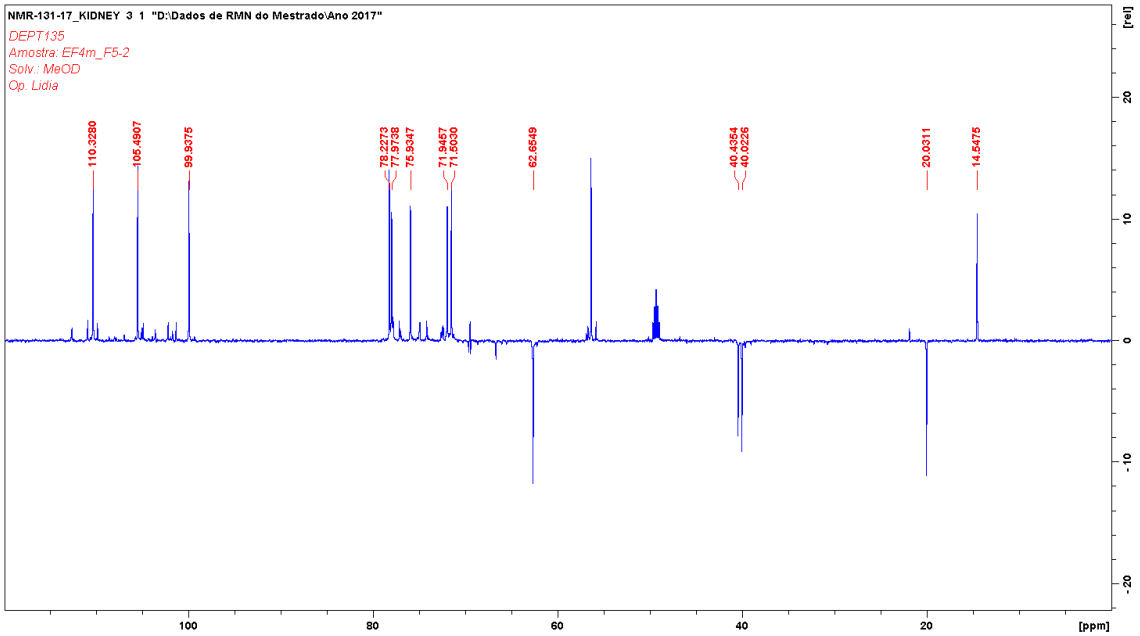

Figure S5. DEPT135 spectrum of compound **1** (11.7 T, CD_3OD, TMS).

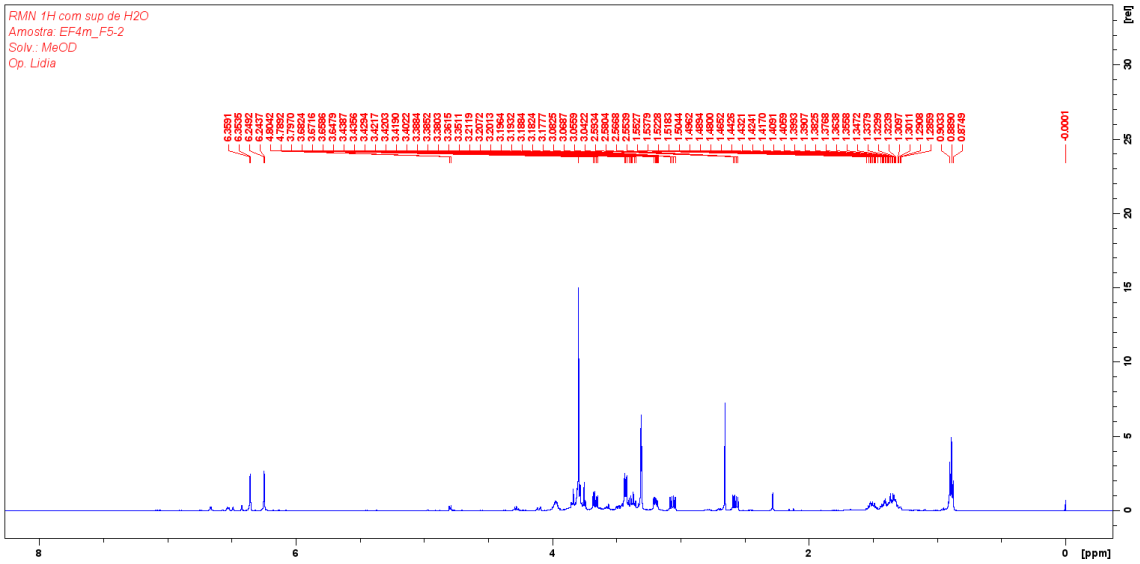

Figure S6. ^{1}H NMR spectrum of compound **1** (11.7 T, CD_3OD, TMS).

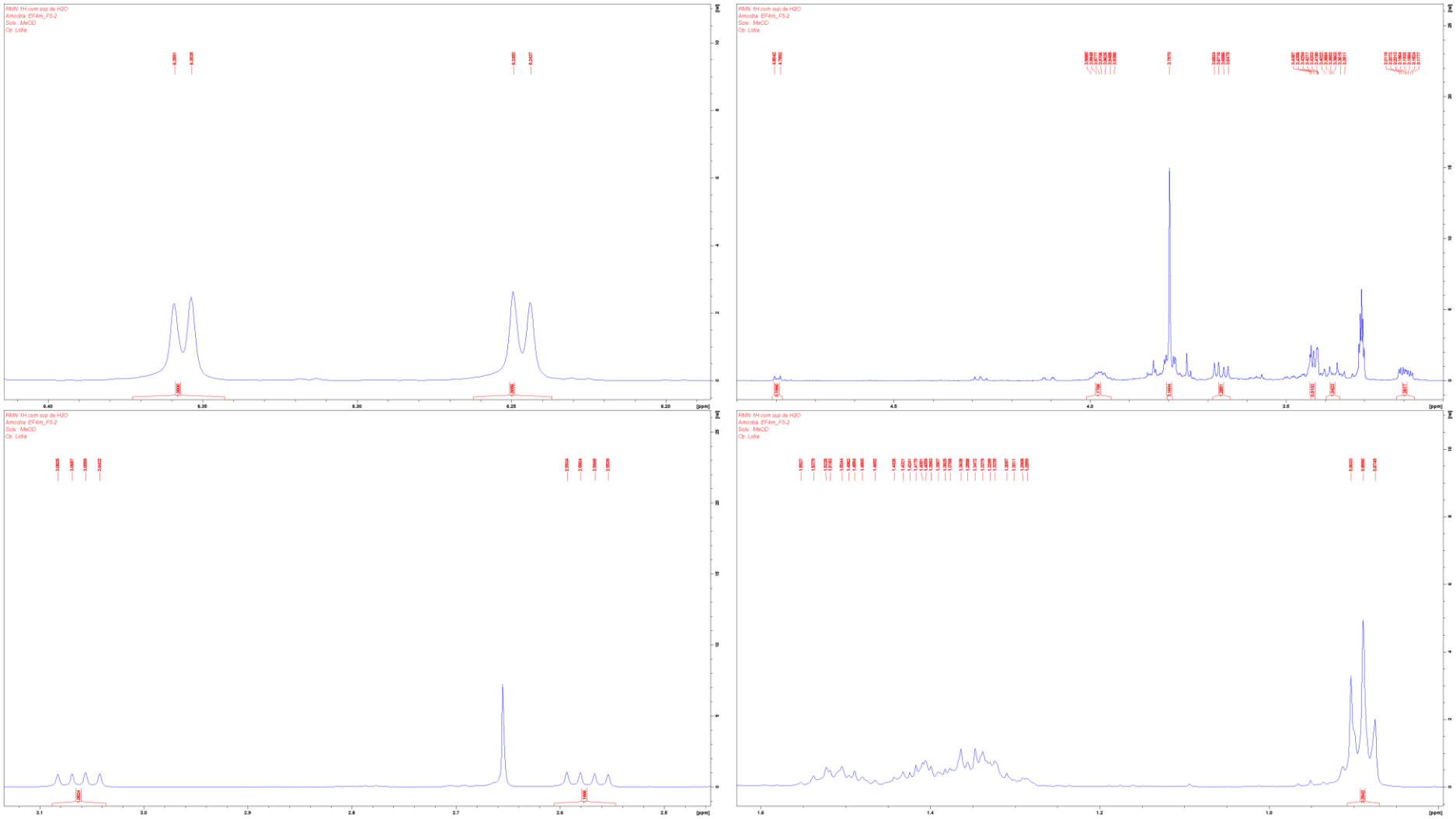

Figure S7. Enlargements of ^{1}H NMR spectrum of compound **1** (11.7 T, CD_3OD, TMS).

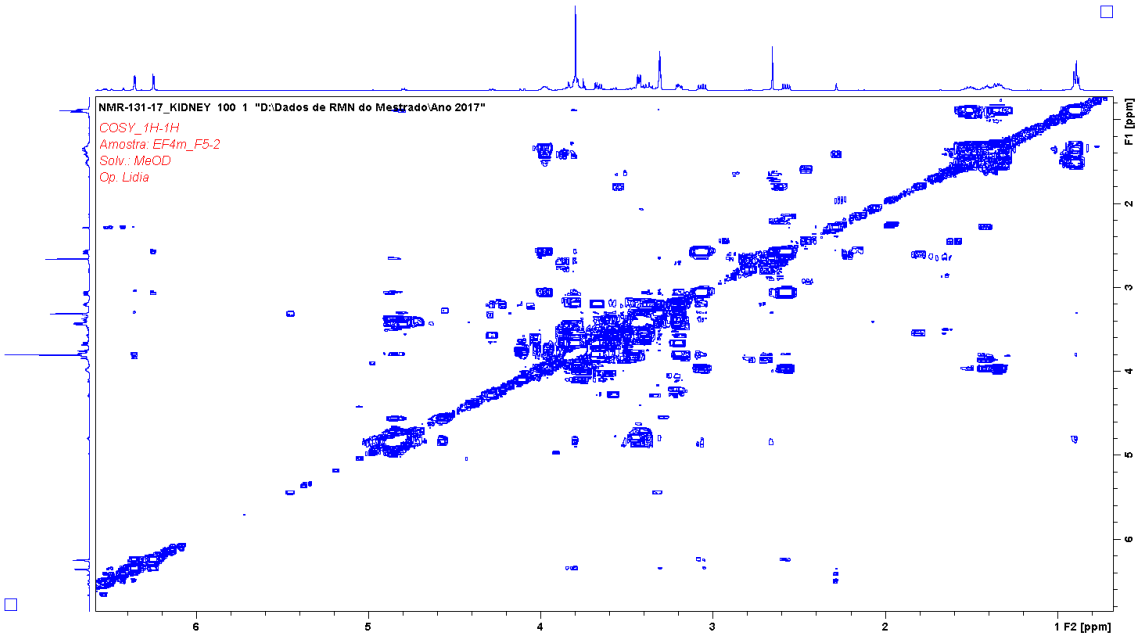

Figure S8. ^{1}H-^{1}H COSY spectrum of compound **1** (11.7 T, CD_3OD, TMS).

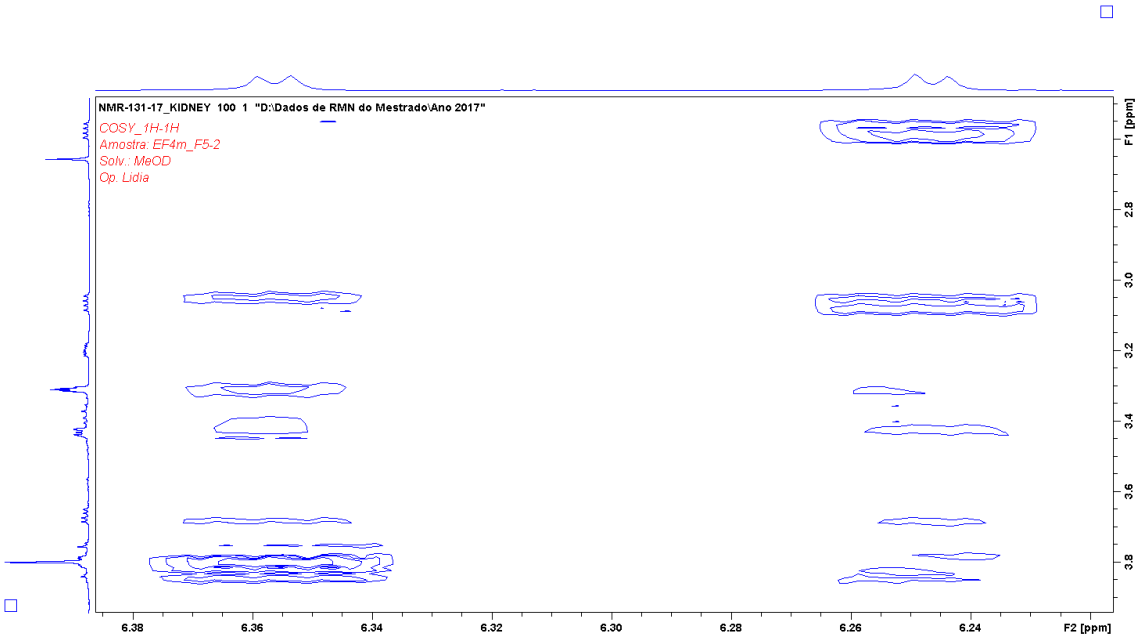

Figure S9. First enlargement of ^{1}H-^{1}H COSY spectrum of compound **1** (11.7 T, CD_3OD, TMS).

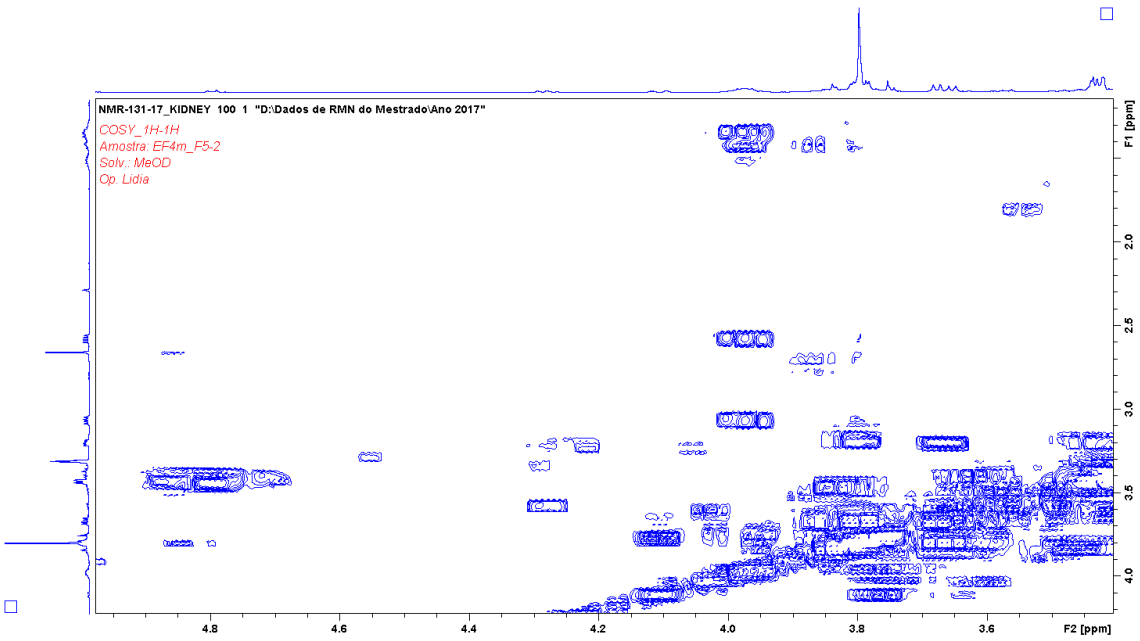

Figure S10. Second enlargement of ^{1}H-^{1}H COSY spectrum of compound **1** (11.7 T, CD_3OD, TMS).

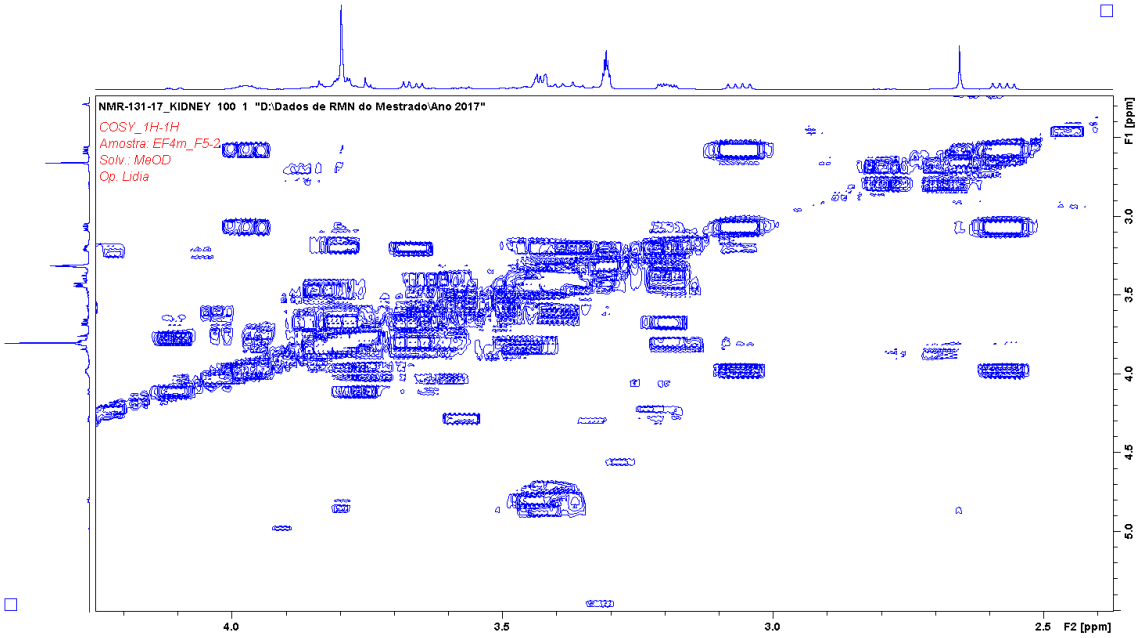

Figure S11. Third enlargement of ^{1}H-^{1}H COSY spectrum of compound **1** (11.7 T, CD_3OD, TMS).

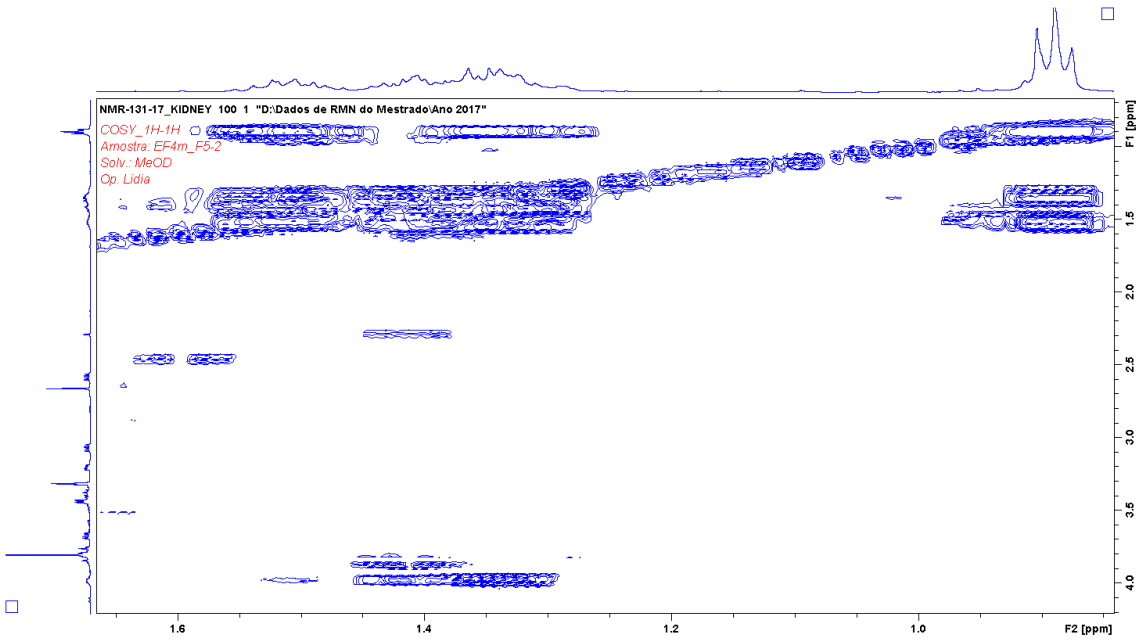

Figure S12. Fourth enlargement of ^{1}H-^{1}H COSY spectrum of compound **1** (11.7 T, CD_3OD, TMS).

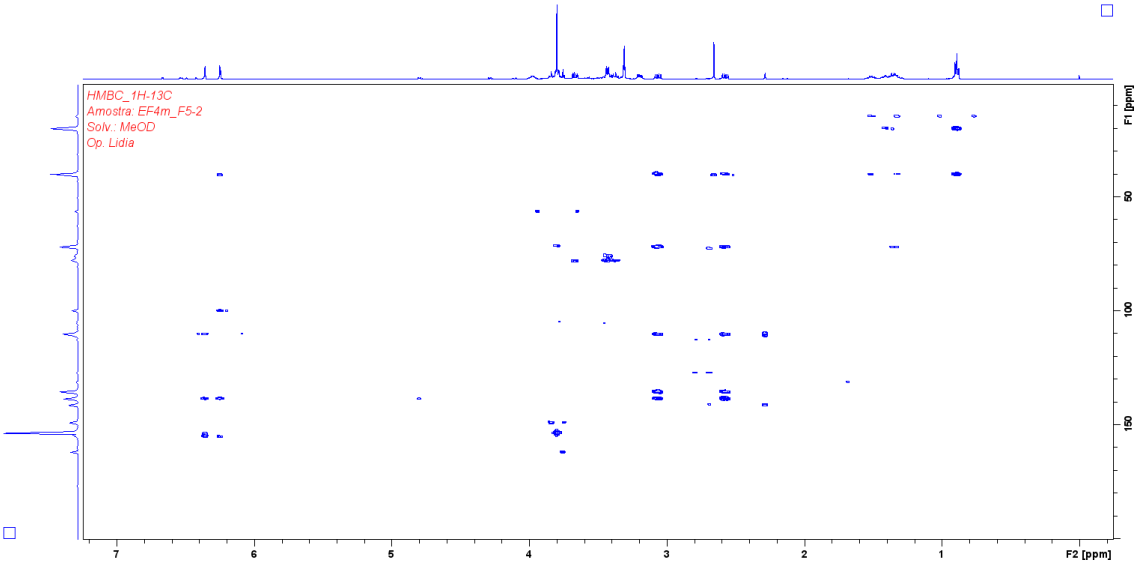

Figure S13. ^{1}H-^{13}C HMBC spectrum of compound **1** (11.7 T, CD_3OD, TMS).

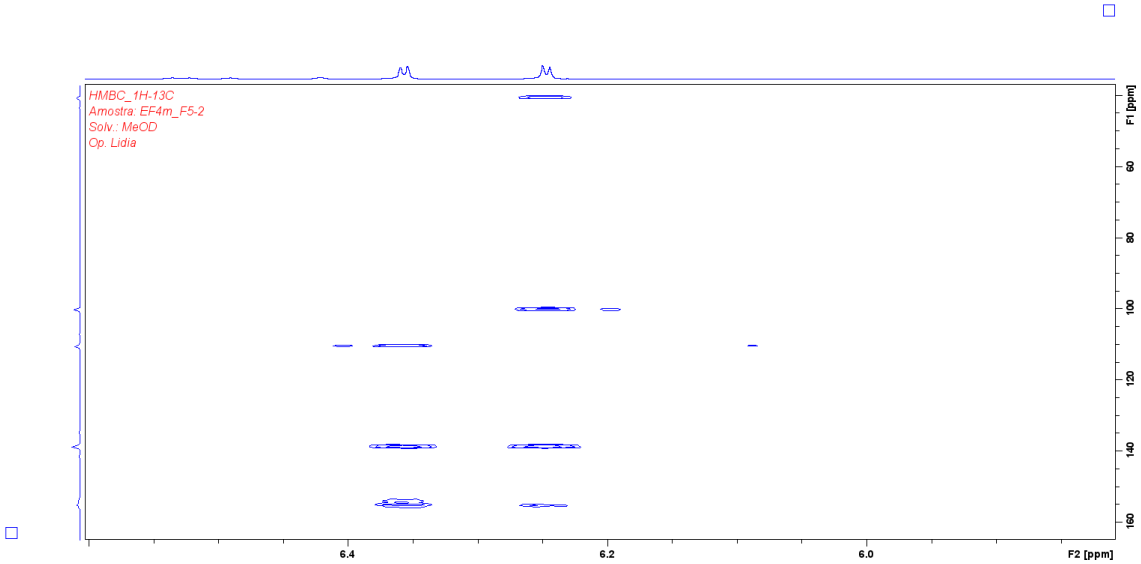

Figure S14. First enlargement of ^{1}H-^{13}C HMBC spectrum of compound **1** (11.7 T, CD_3OD, TMS).

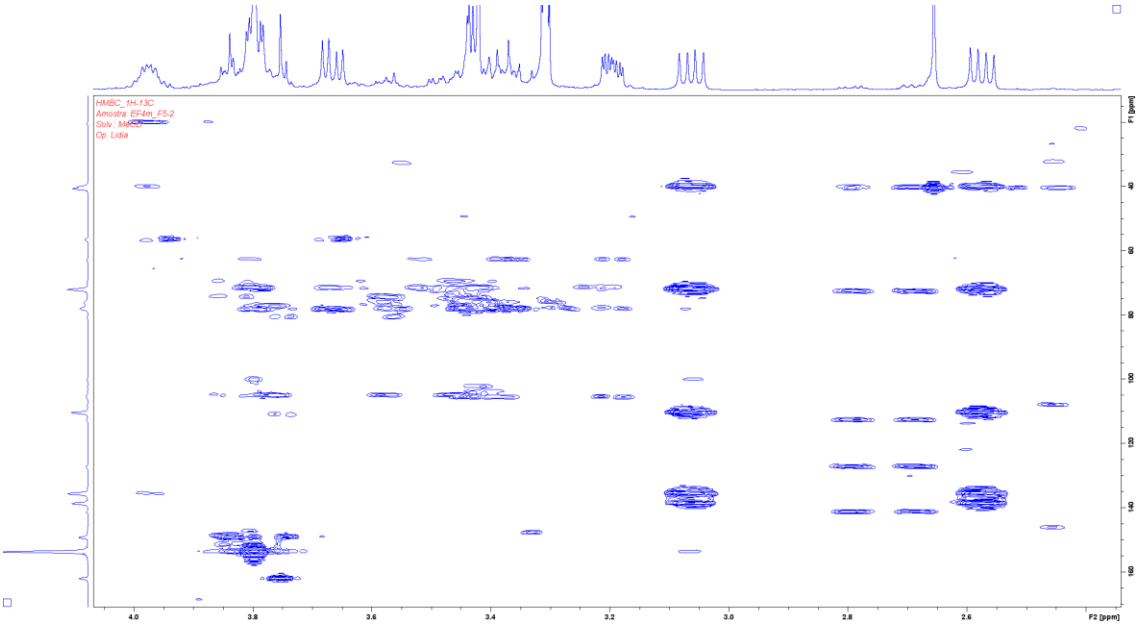

Figure S15. Second enlargement of ^{1}H-^{13}C HMBC spectrum of compound **1** (11.7 T, CD_3OD, TMS).

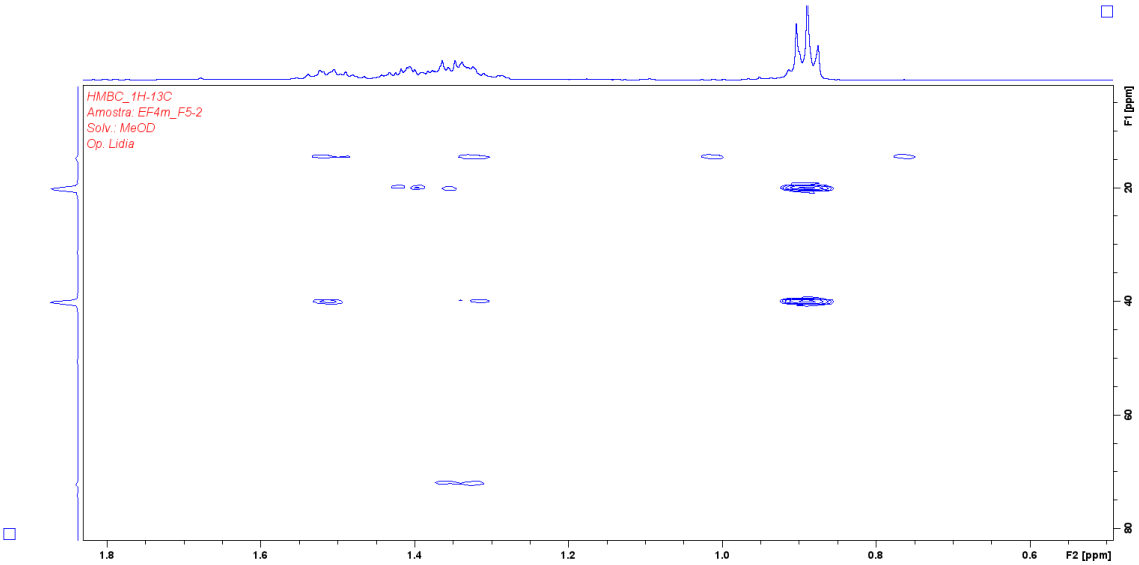

Figure S16. Third enlargement of ^{1}H-^{13}C HMBC spectrum of compound **1** (11.7 T, CD_3OD, TMS).

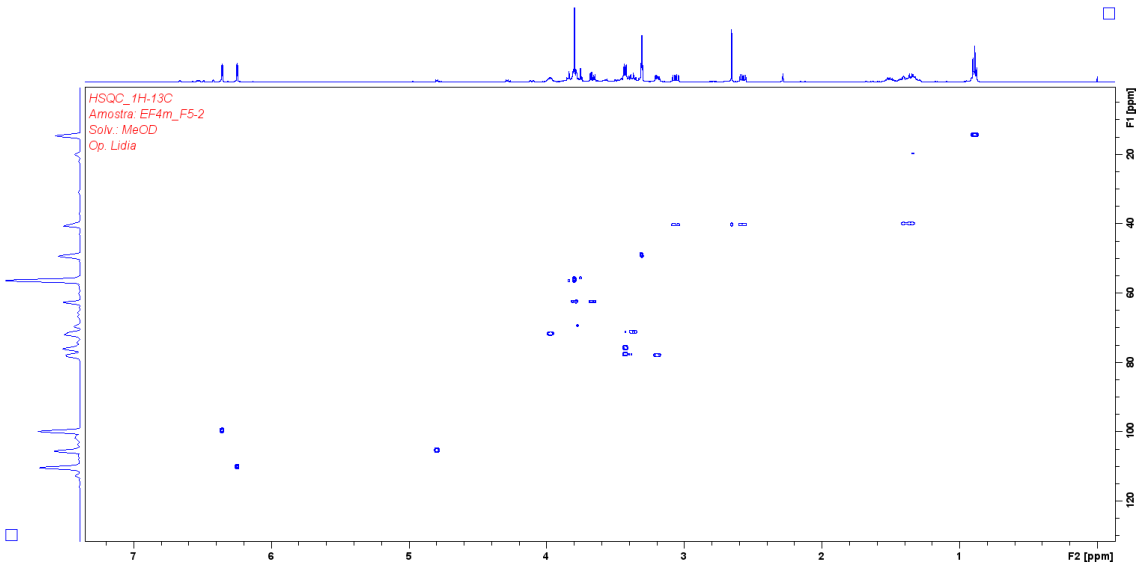

Figure S17. ^{1}H-^{13}C HSQC spectrum of compound **1** (11.7 T, CD_3OD, TMS).

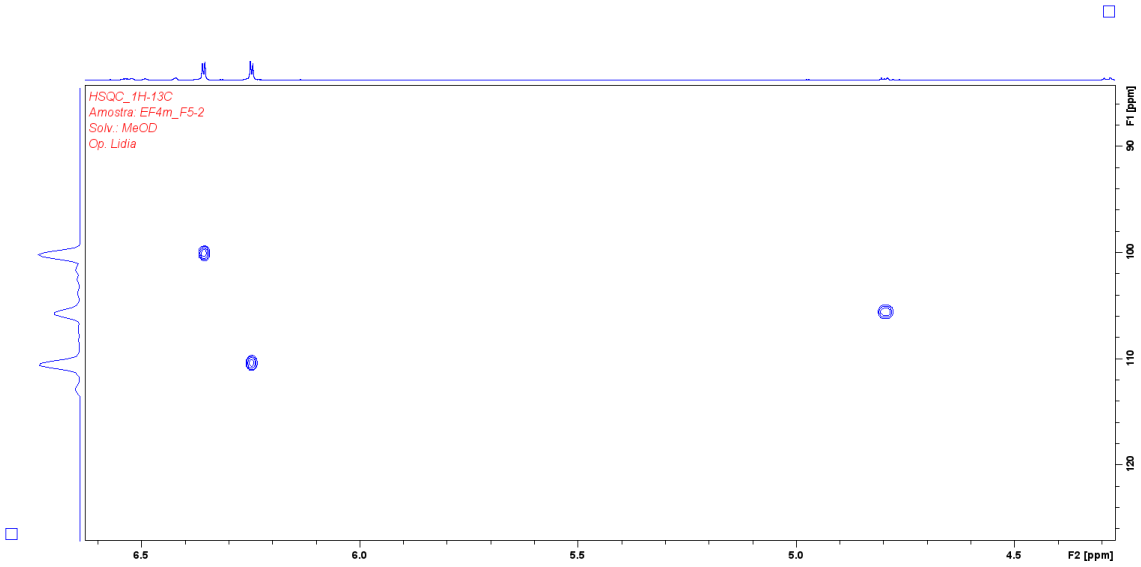

Figure S18. First enlargement of ^{1}H-^{13}C HSQC spectrum of compound **1** (11.7 T, CD_3OD, TMS).

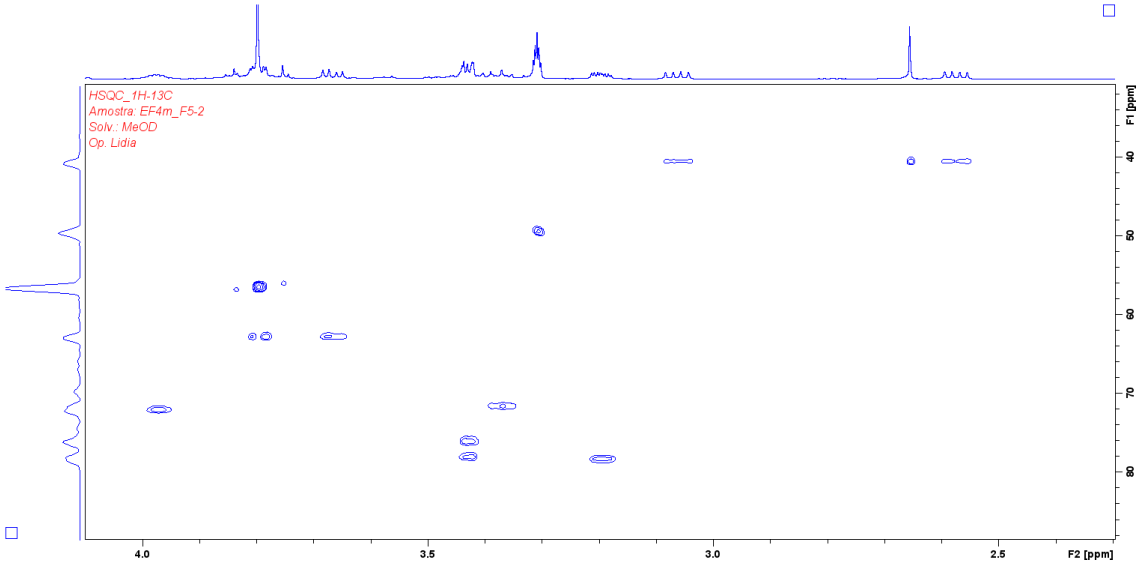

Figure S19. Second enlargement of ^{1}H-^{13}C HSQC spectrum of compound **1** (11.7 T, CD_3OD, TMS).

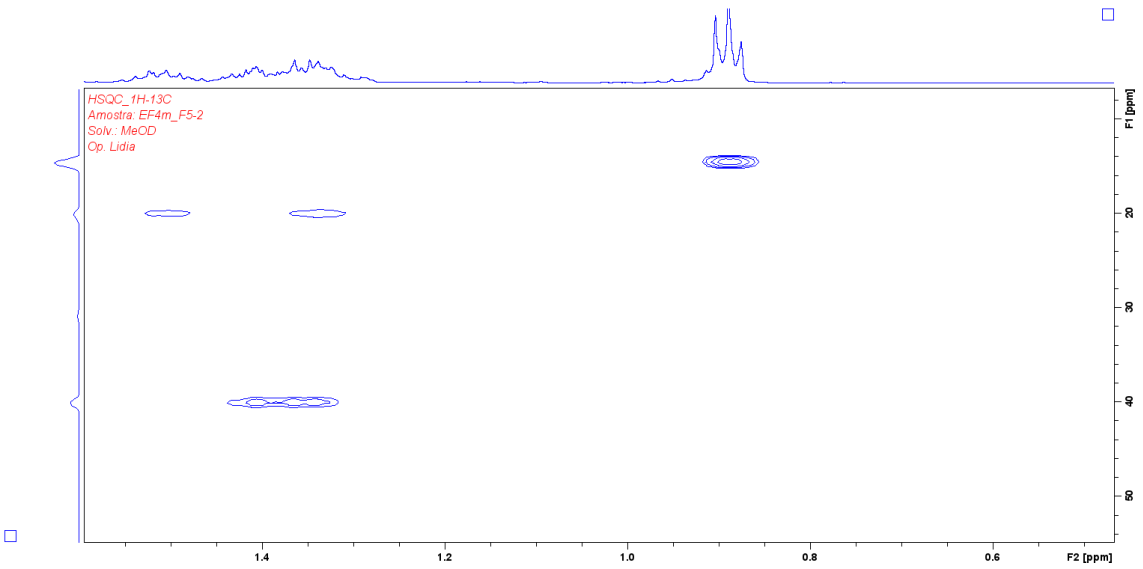

Figure S20. Third enlargement of ^{1}H-^{13}C HSQC spectrum of compound **1** (11.7 T, CD_3OD, TMS).

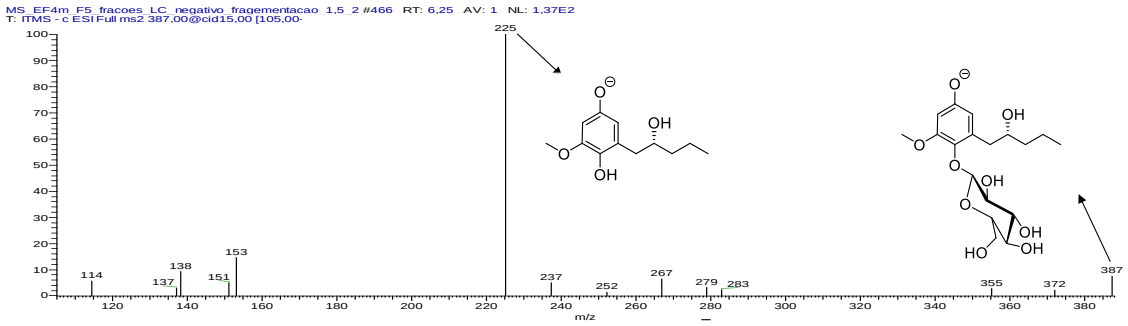

Figure S21. Fragmentation pattern MS^2-ESI (–) of citrifolin A.

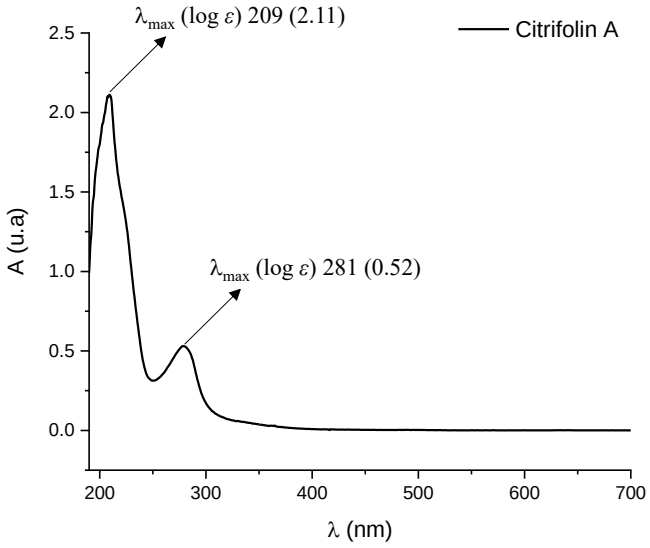

Figure S22. UV-Vis spectrum of citrifolin A in MeOH (190-700 nm).

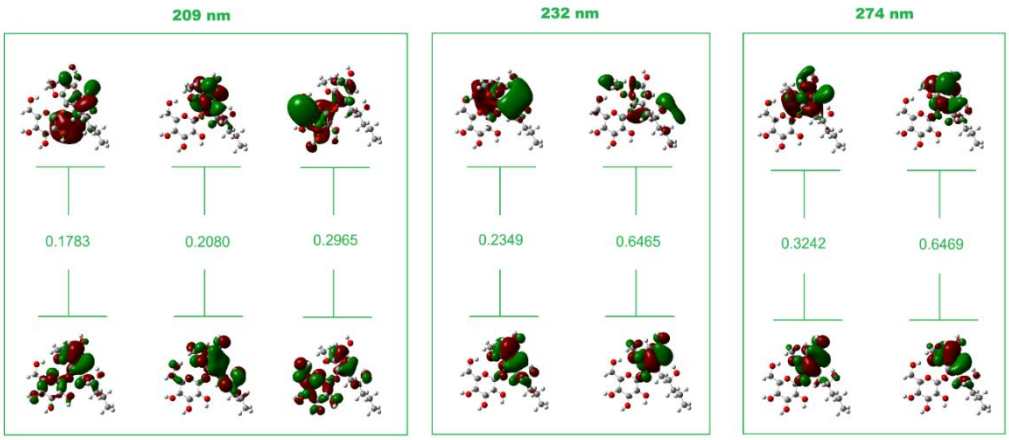

Figure S23. Natural transition orbitals on a hole-electron model for 2'*R* citrofolin A. The values presented between the orbitals refer to the occupation number of each transition pair.

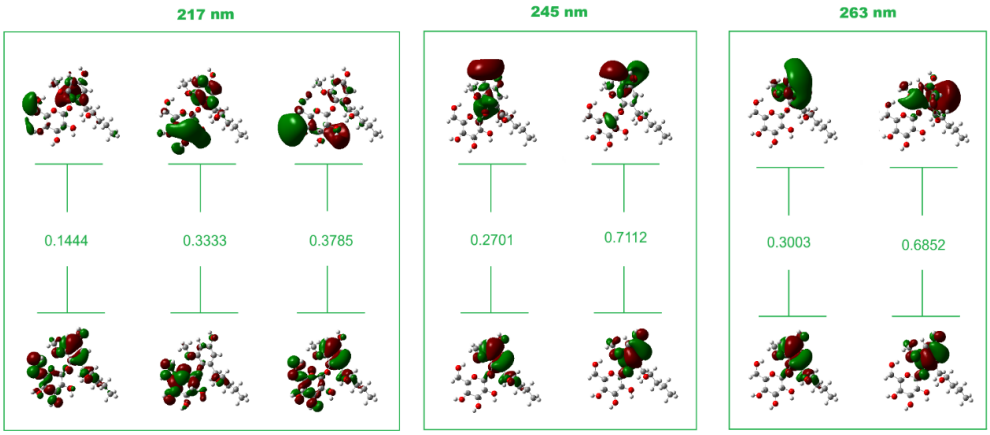

Figure S24. Natural transition orbitals on a hole-electron model for 2'*S* citrofolin A. The values presented between the orbitals refer to the occupation number of each transition pair.

Table S1. Relative energies and Boltzmann weights for the 11 conformers obtained for the 2'*R* stereoisomer of citrifolin A. Calculations were performed at the chosen DFT level, and populations were derived from Boltzmann statistics at 298 K

Conformer	Energy / a.u.	Boltzmann weight / %
2'*R* conformer 1	–1379.46267782	96.7896
2'*R* conformer 2	–1379.45608555	0.0899
2'*R* conformer 3	–1379.45478623	0.0227
2'*R* conformer 4	–1379.45734452	0.3409
2'*R* conformer 5	–1379.45803248	0.7065
2'*R* conformer 6	–1379.45746511	0.3874
2'*R* conformer 7	–1379.45561585	0.0546
2'*R* conformer 8	–1379.45702467	0.2430
2'*R* conformer 9	–1379.45789703	0.6121
2'*R* conformer 10	–1379.45752281	0.4118
2'*R* conformer 11	–1379.45734598	0.3415

Table S2. Relative energies and Boltzmann weights for the 11 conformers obtained for the 2'*S* stereoisomer of citrifolin A. Calculations were performed at the chosen DFT level, and populations were derived from Boltzmann statistics at 298 K

Conformer	Energy / a.u.	Boltzmann weight / %
2'*S* conformer 1	–1379.45962782	1.2093
2'*S* conformer 2	–1379.45970978	1.3189
2'*S* conformer 3	–1379.45830305	0.2973
2'*S* conformer 4	–1379.4613087	7.1727
2'*S* conformer 5	–1379.46131286	7.2043
2'*S* conformer 6	–1379.45944227	0.9954
2'*S* conformer 7	–1379.46103364	5.3599
2'*S* conformer 8	–1379.45612907	0.2732
2'*S* conformer 9	–1379.45607525	0.2081
2'*S* conformer 10	–1379.45836777	0.3184
2'*S* conformer 11	–1379.46353825	76.0678