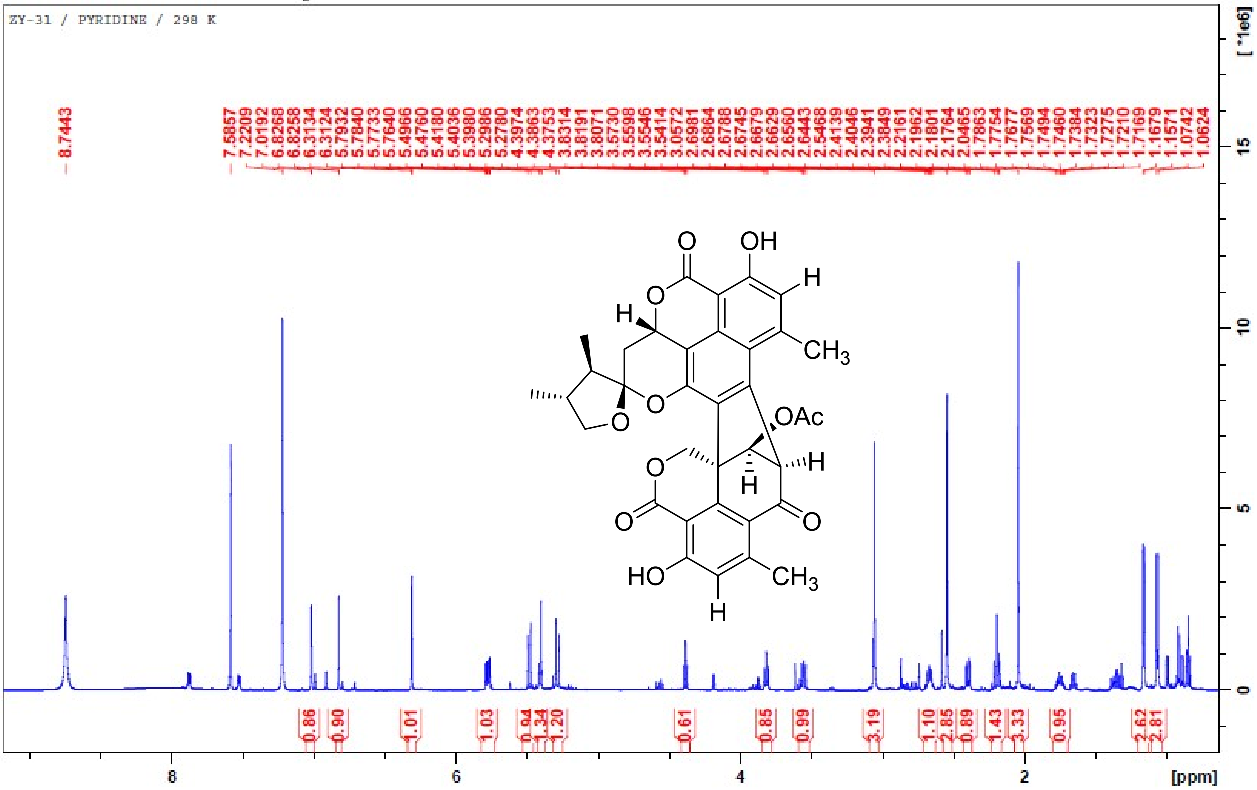
Supporting Information

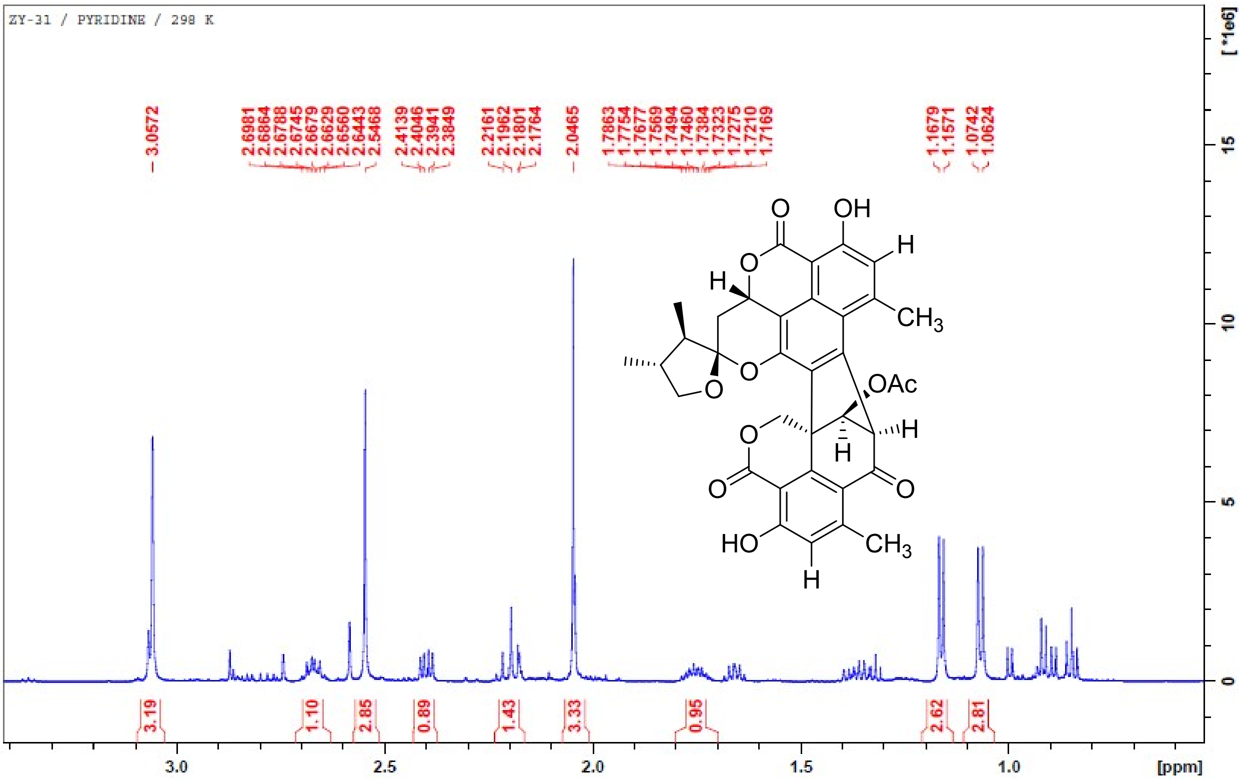
Talaroketals A and B, Unusual Bis(oxaphenalenone) Spiro and Fused Ketals from the Soil Fungus *Talaromyces stipitatus* ATCC 10500

Yi Zang,[a] Grégory Genta-Jouve,[b] Pascal Retailleau,[c] Alexandre Escargueil,[d] Stéphane Mann,[a] Bastien Nay,*[a] Soizic Prado*[a]

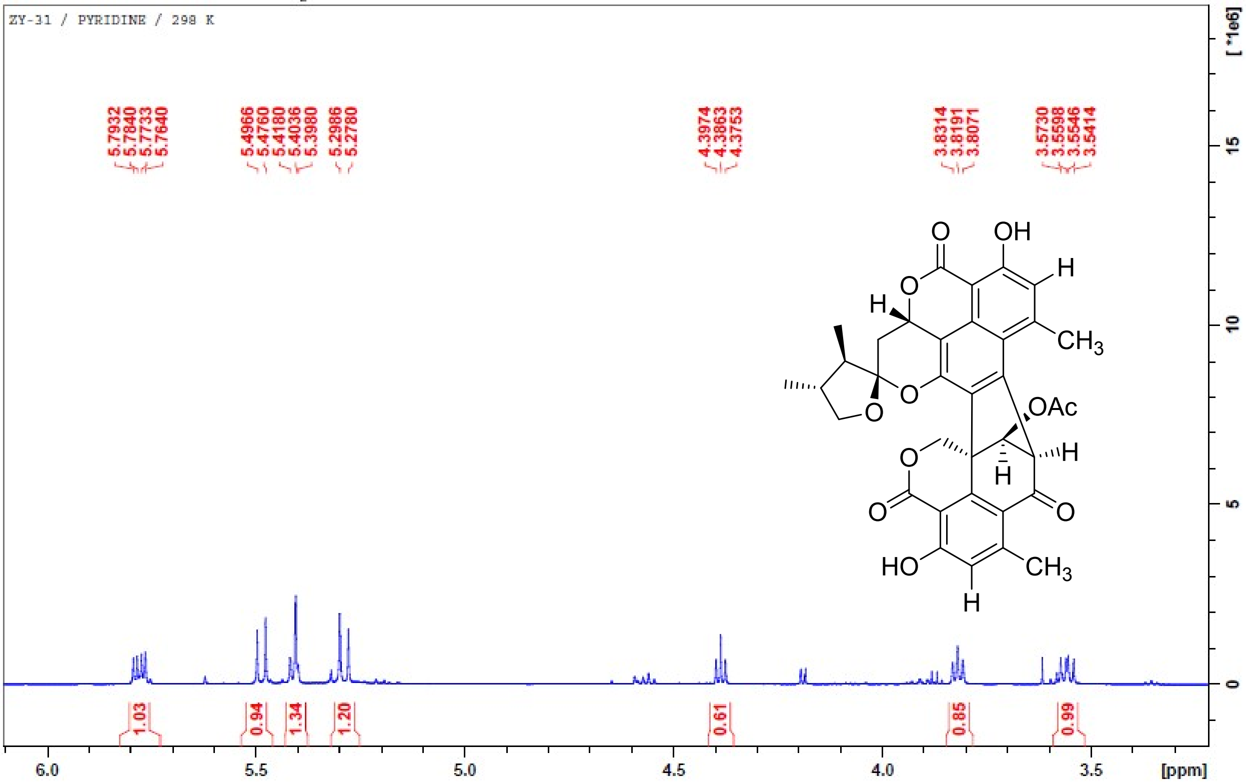
S1. ^{1}H NMR spectrum of talaroketal A (**2**) in C_5D_5N.



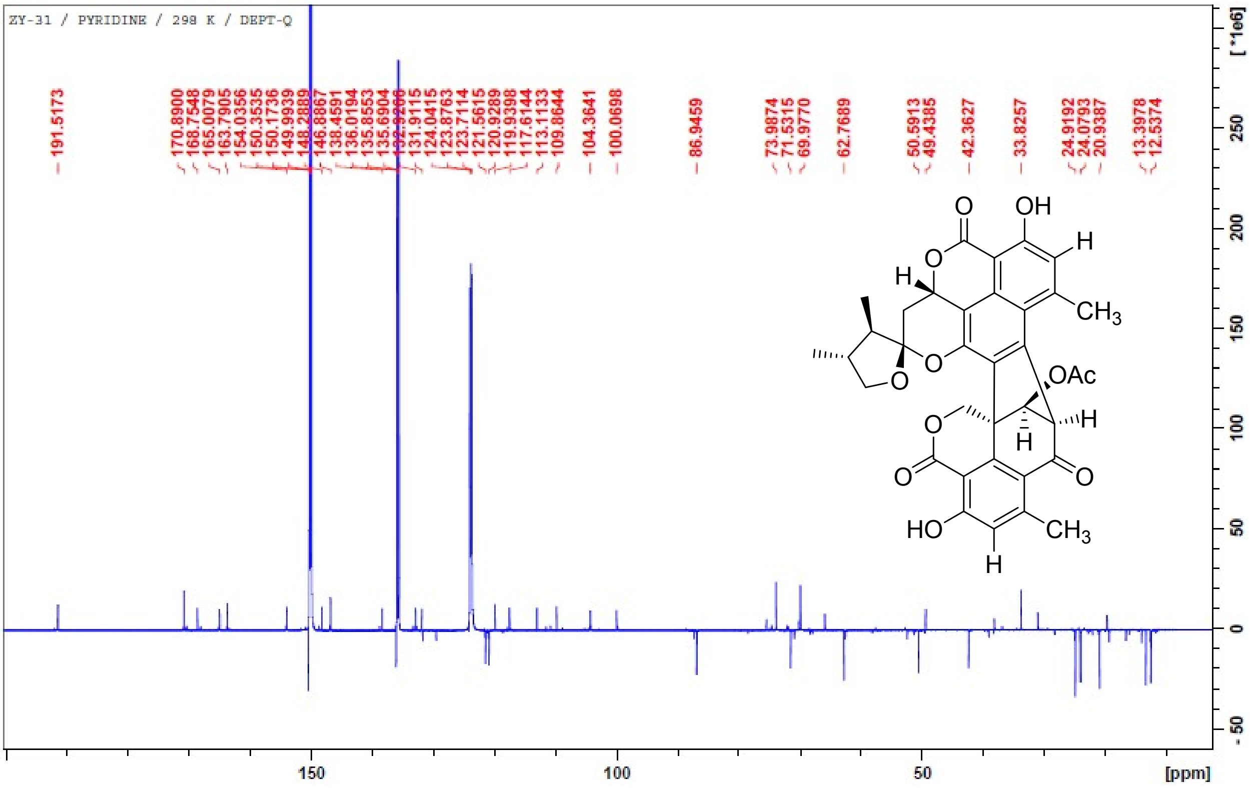
S2. ^{1}H NMR spectrum of talaroketal A (**2**)-Enlargement-1 in C_5D_5N.



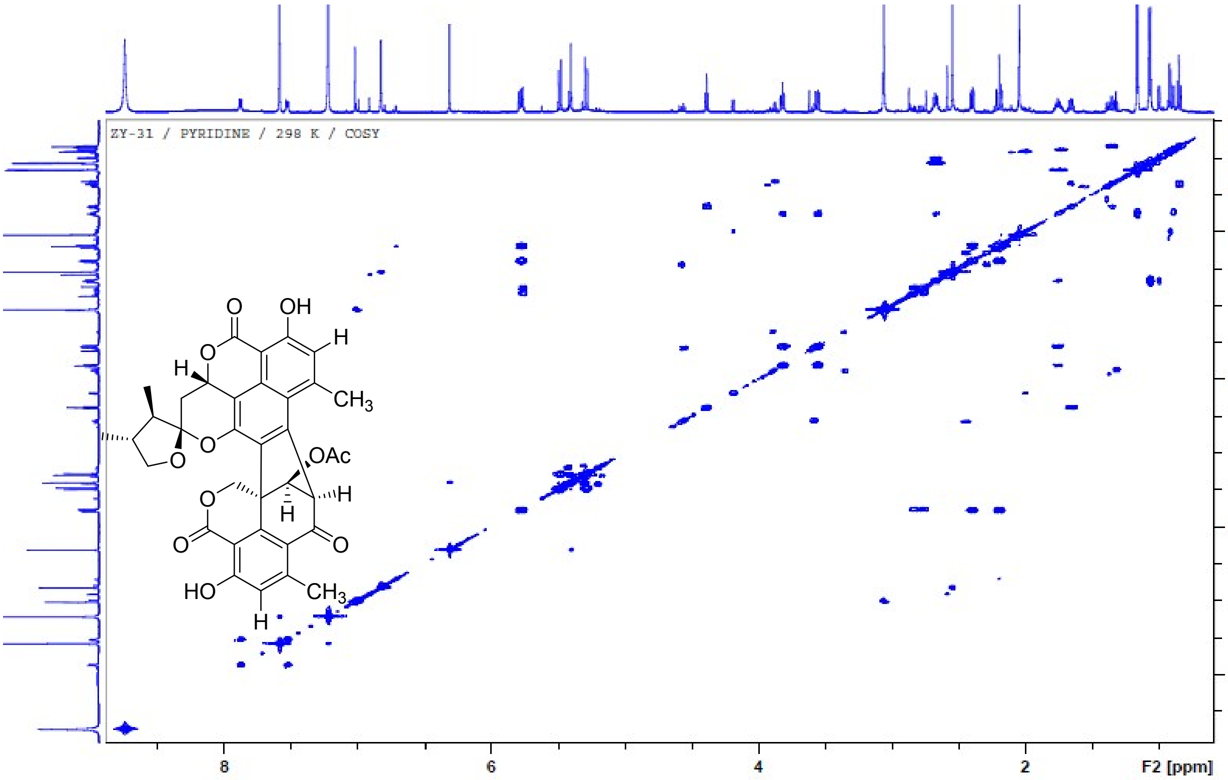
S3. ^{1}H NMR spectrum of talaroketal A (**2**)-Enlargement-2 in C_5D_5N.



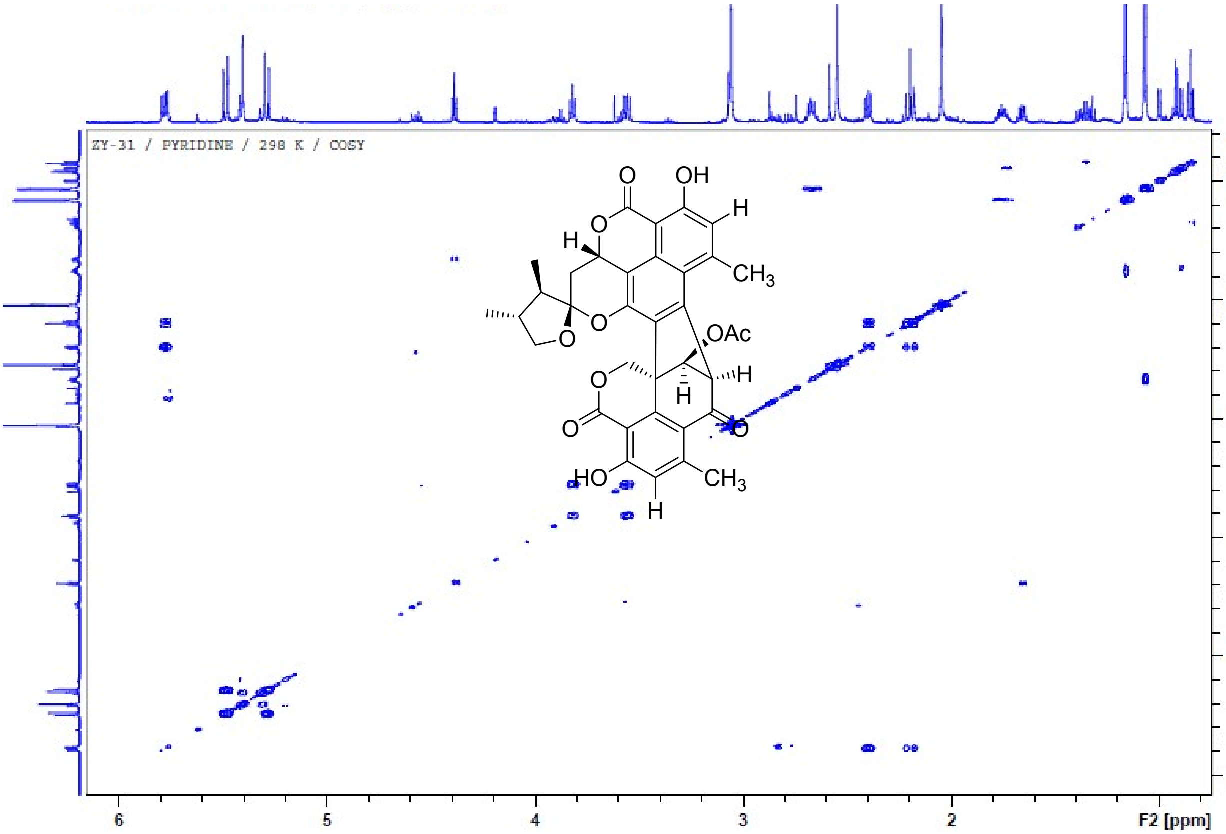
S4. DEPT-Q spectrum of talaroketal A (**2**) in C_5D_5N.



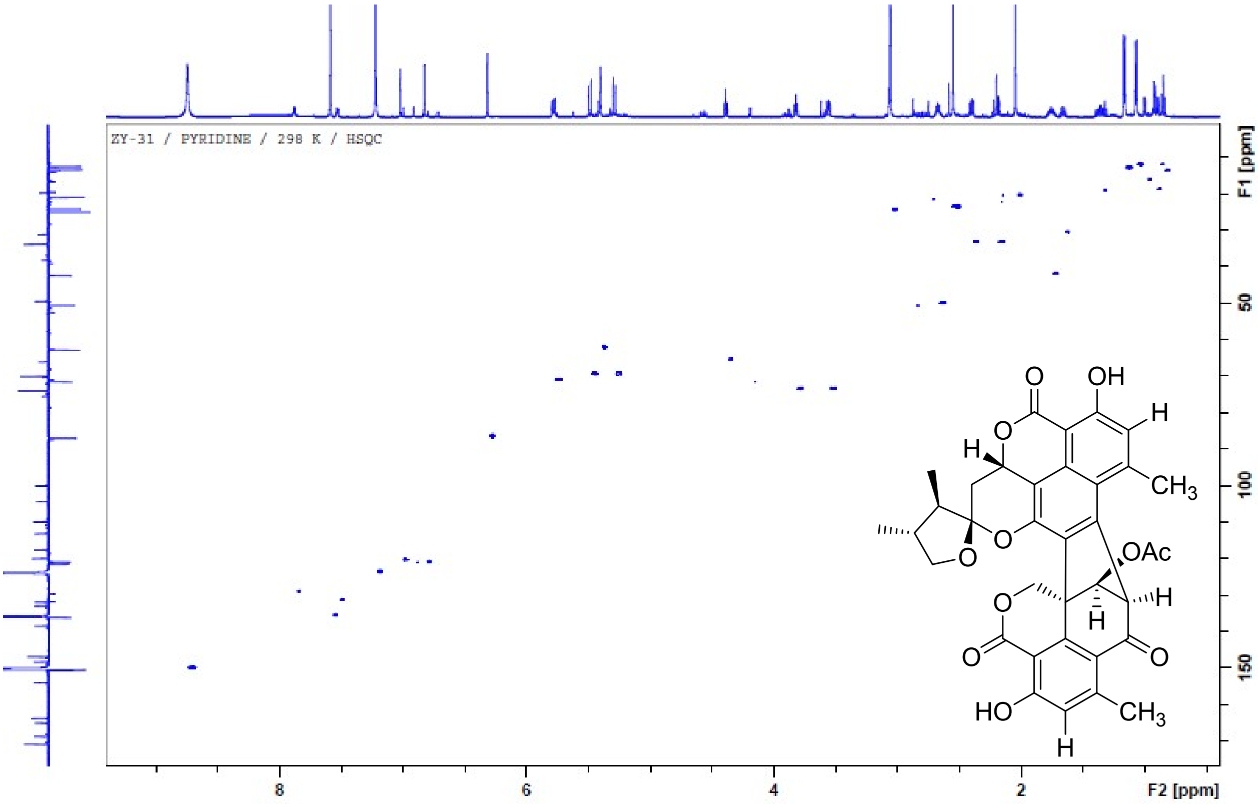
S5. ^{1}H-^{1}H COSY spectrum of talaroketal A (**2**) in C_5D_5N.



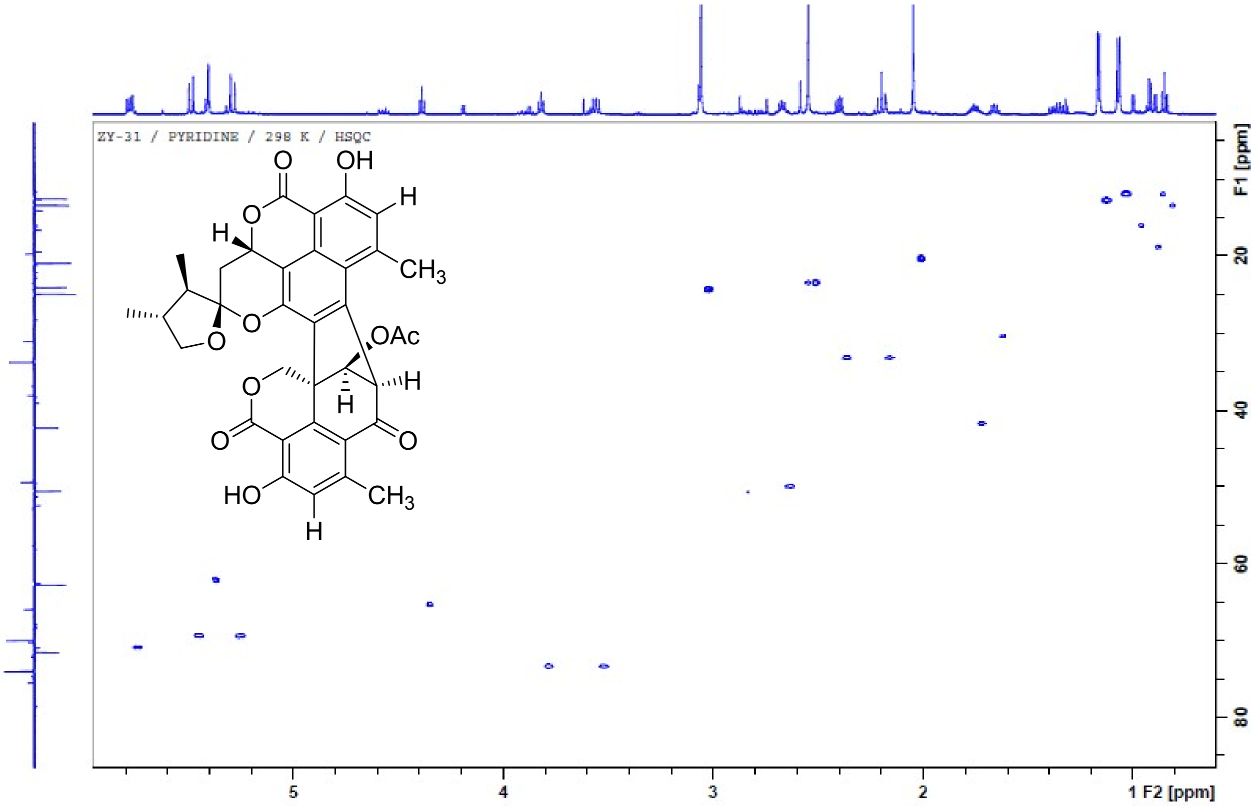
S6. ^{1}H-^{1}H COSY spectrum of talaroketal A (**2**)-Enlargement in C_5D_5N.



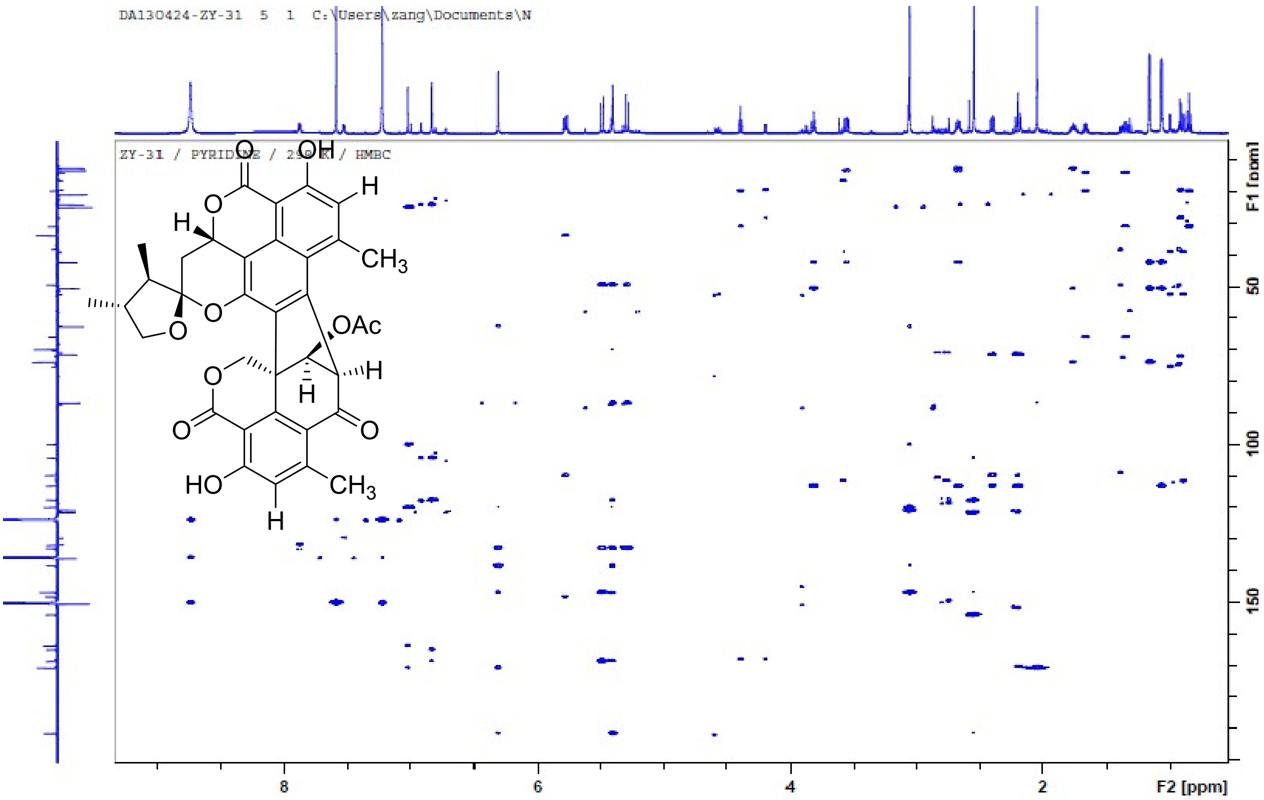
S7. HSQC spectrum of talaroketal A (**2**) in C_5D_5N.



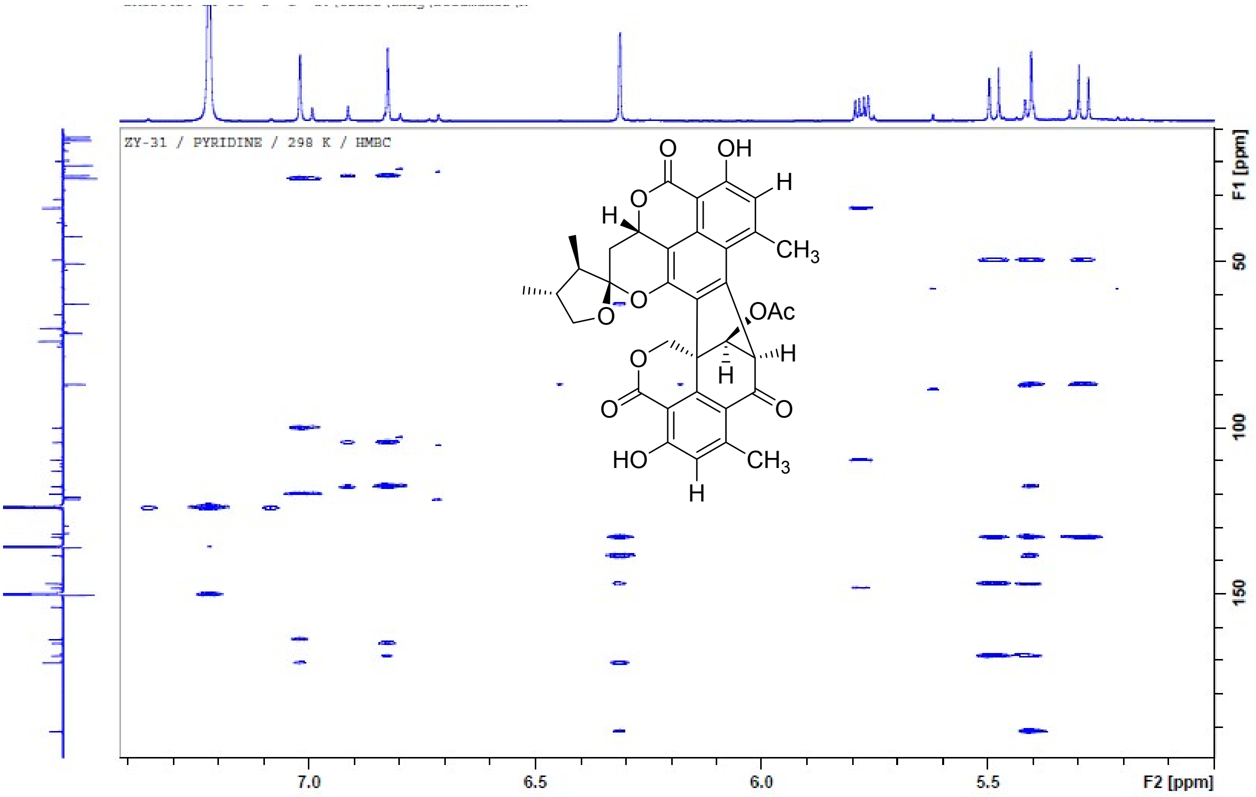
S8. HSQC spectrum of talaroketal A (**2**)-Enlargement in C_5D_5N.



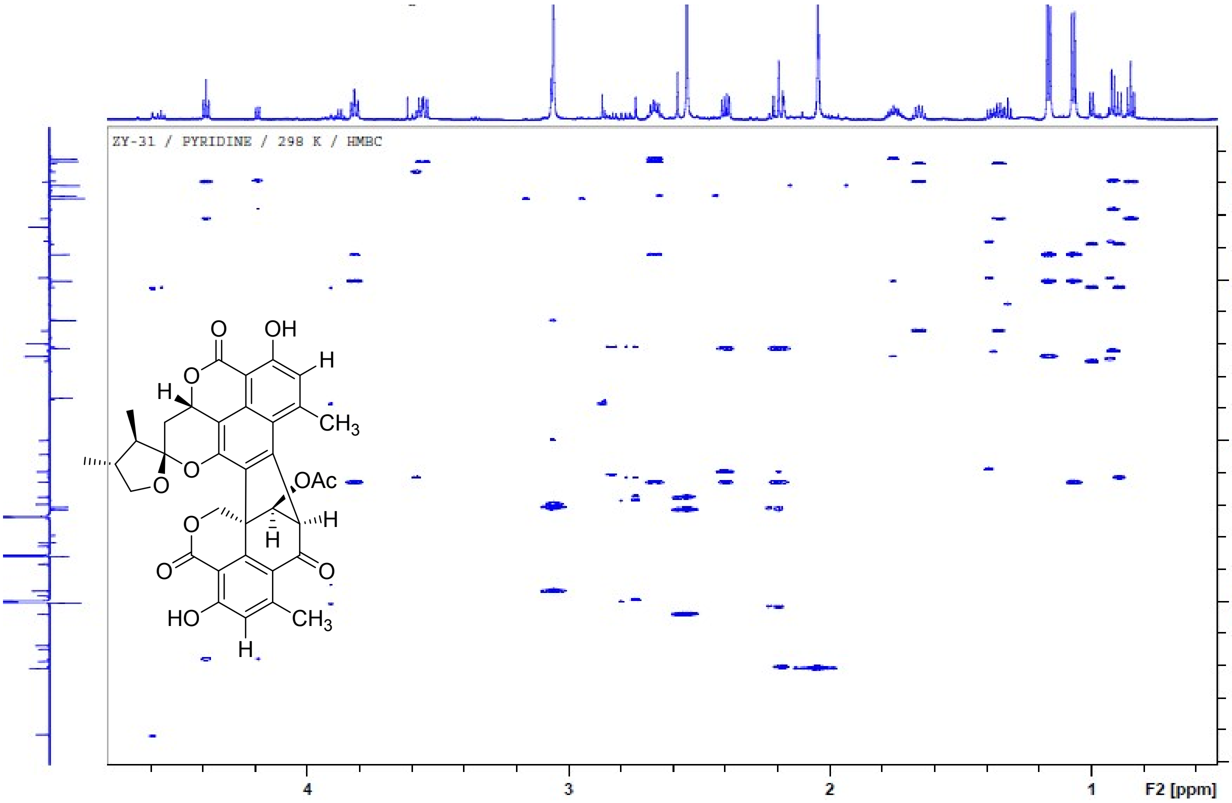
S9. HMBC spectrum of talaroketal A (**2**)-in C_5D_5N.



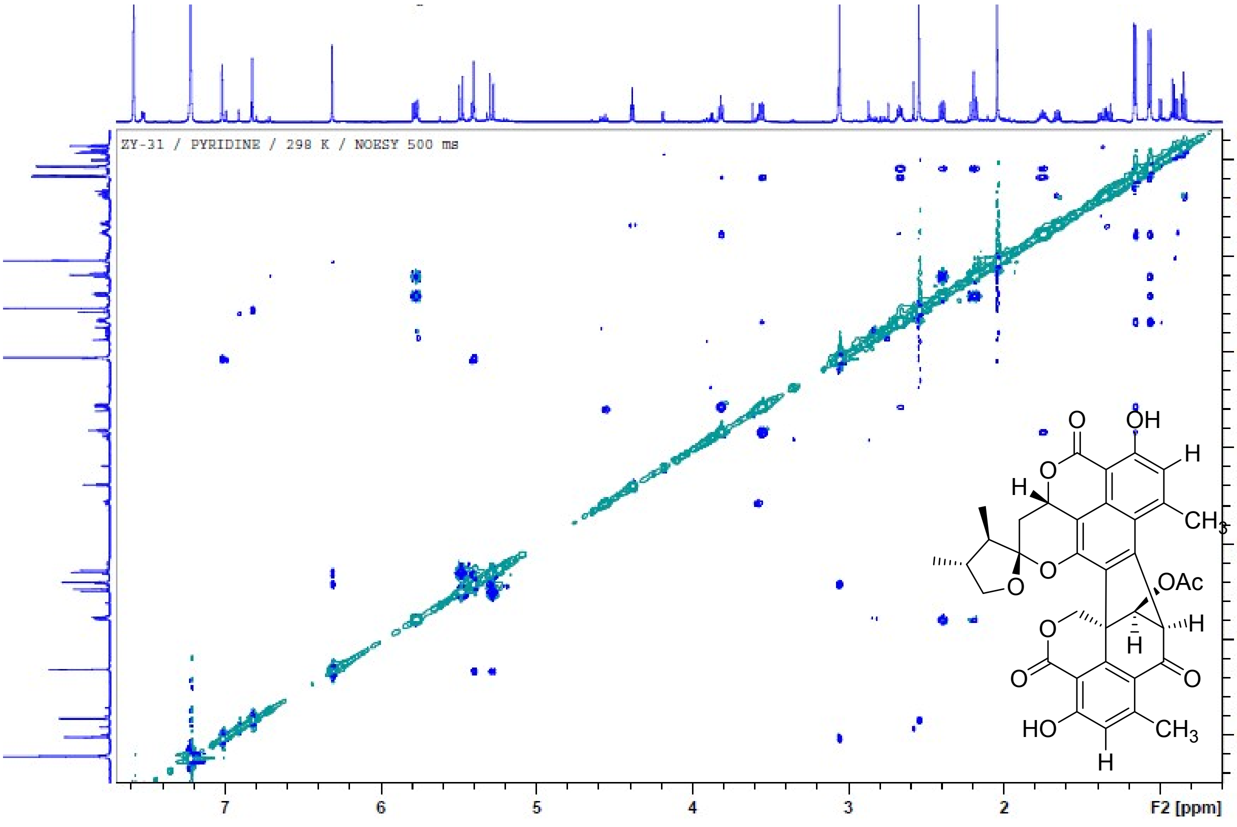
S10. HMBC spectrum of talaroketal A (**2**)-Enlargement-1 in C_5D_5N.



S11. HMBC spectrum of Talaroketal A (**2**)-Enlargement-2 in C_5D_5N.



S12. NOESY spectrum of talaroketal A (**2**) in C_5D_5N.



S13. (+) ESI-MS spectrum of talaroketal A (**2**)

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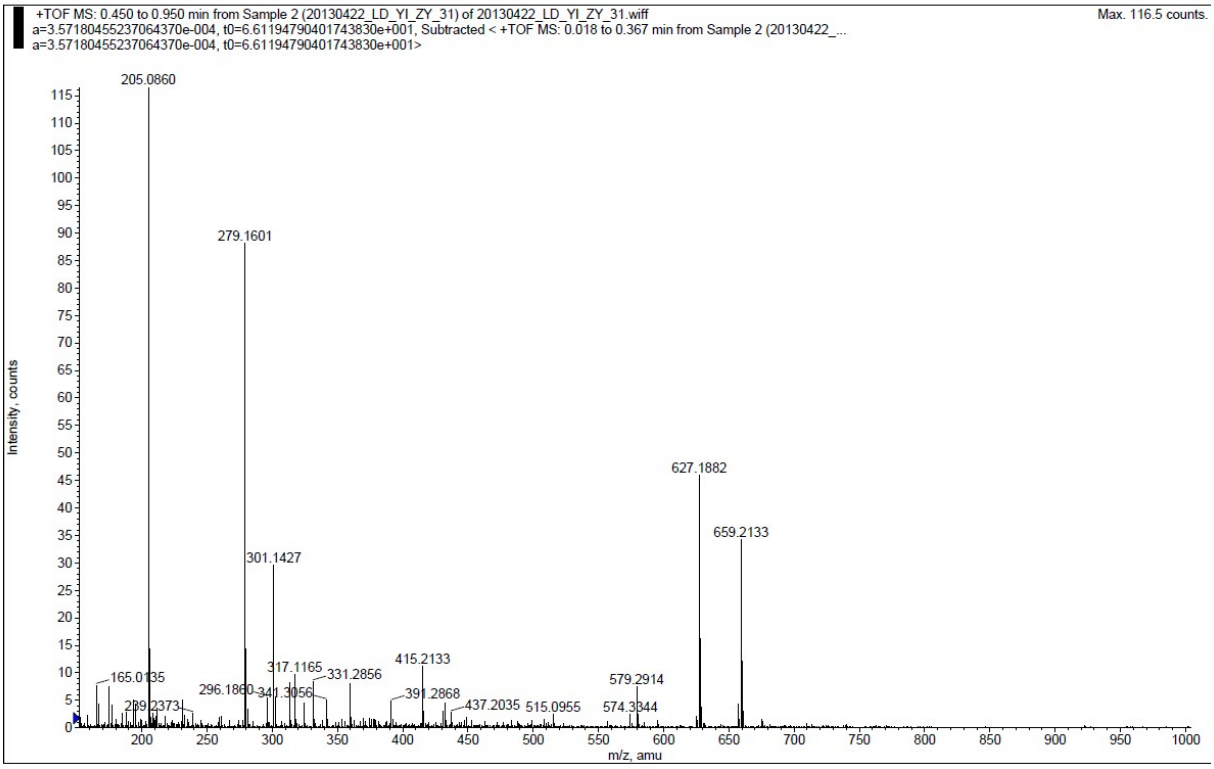

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a=3.57180455237064370e-004, t0=6.61194790401743830e+001>
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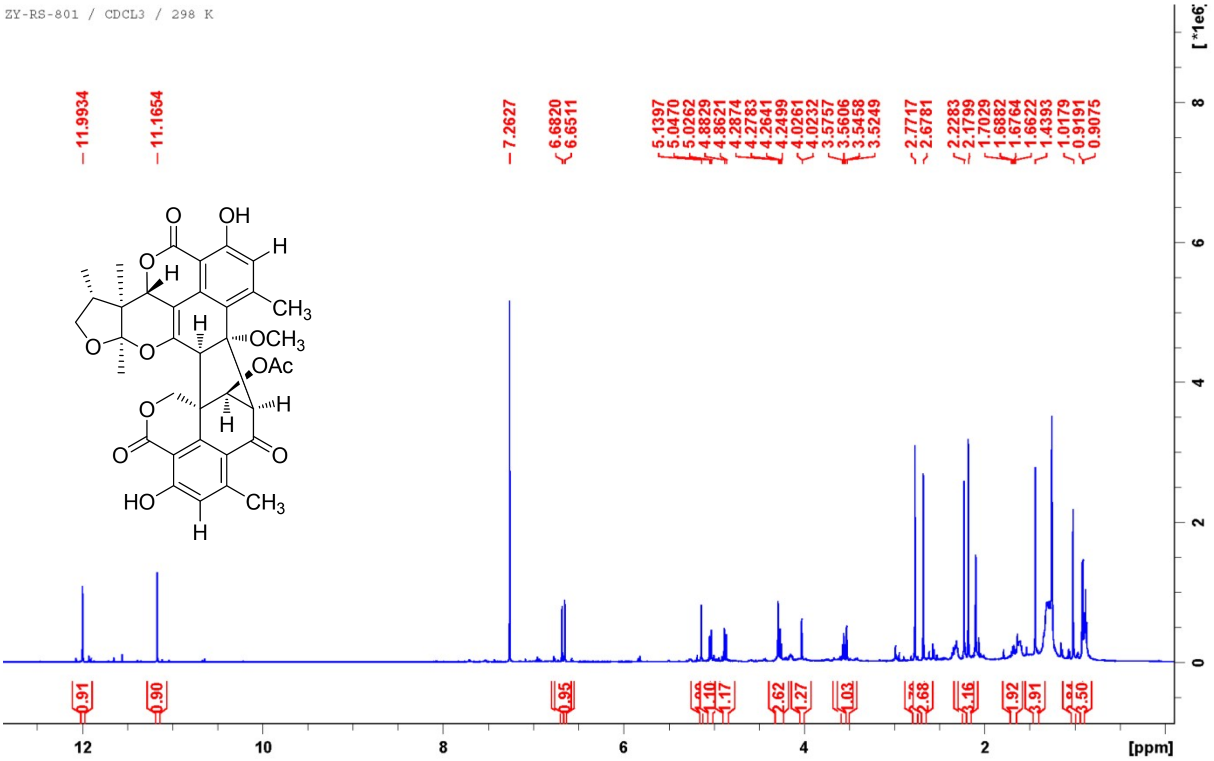
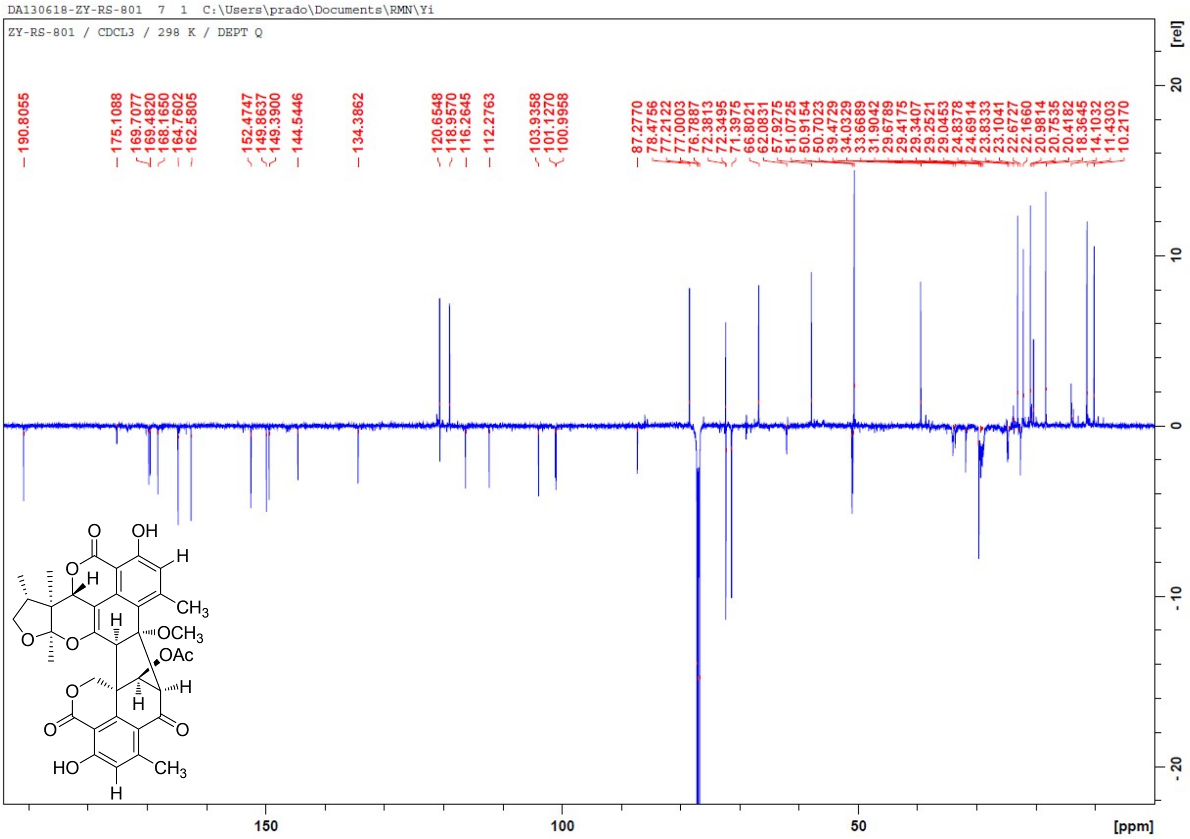
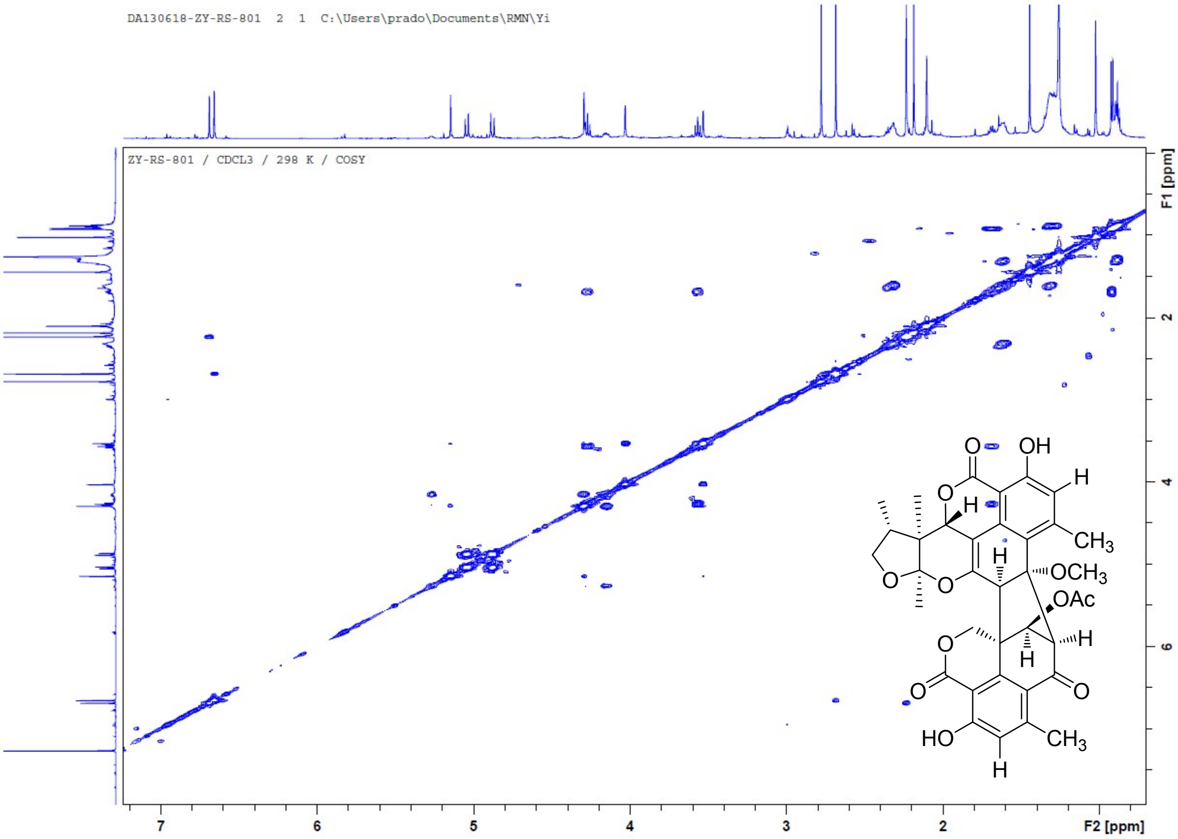
S14. ^{1}H-NMR spectrum of talaroketal B (**3**) in $CDCl_3$.



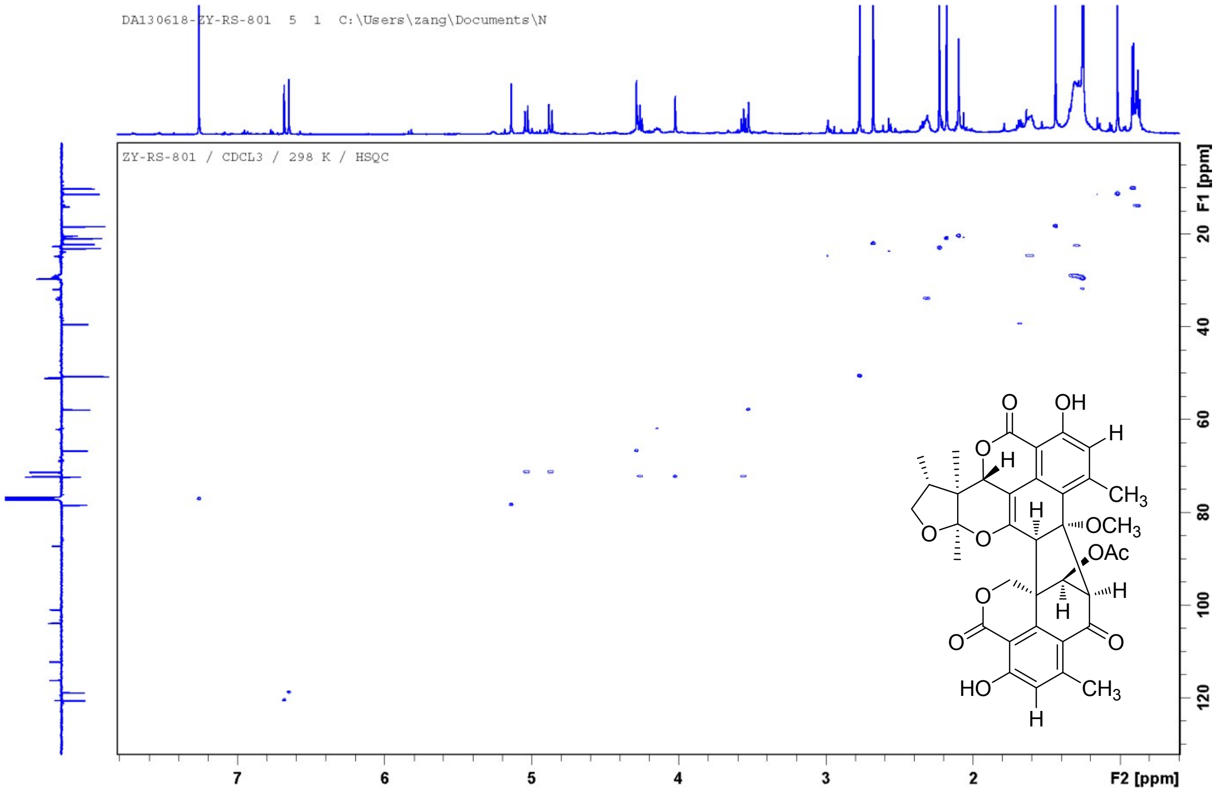
S15. DEPT-Q spectrum of talaroketal B (**3**) in $CDCl_3$.



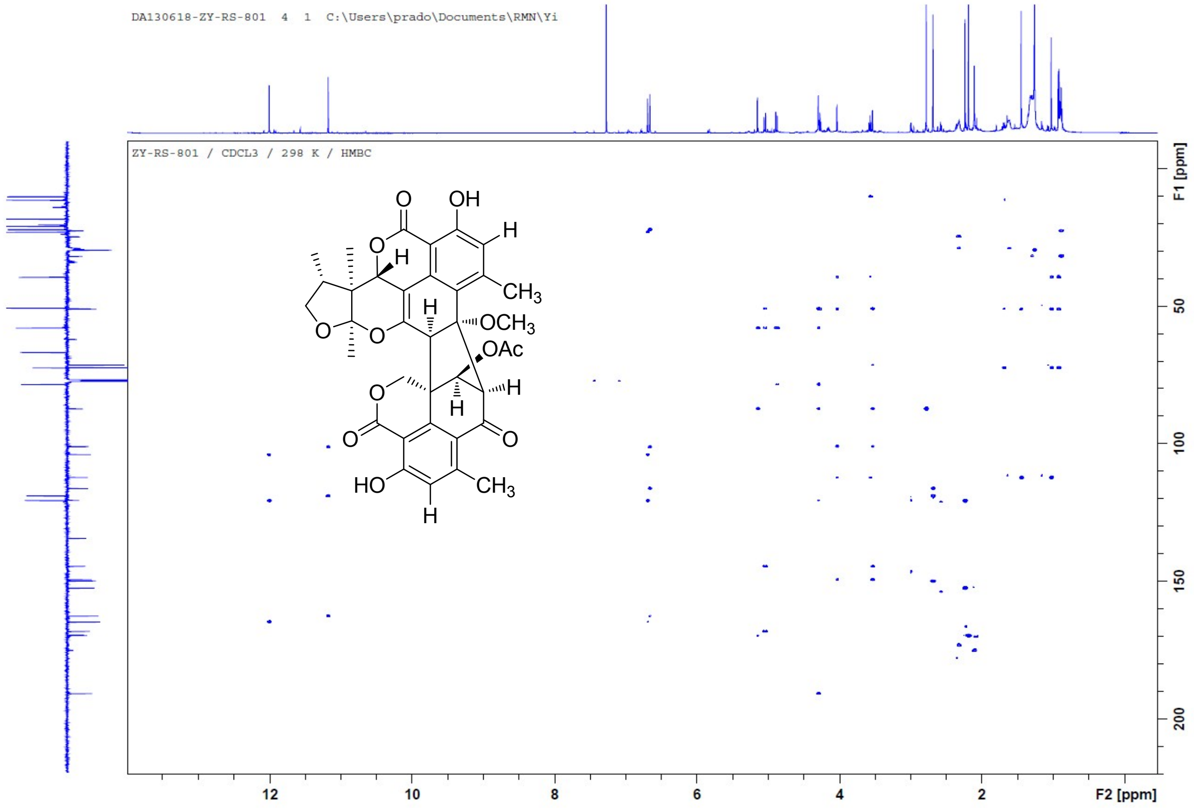
S16. ^{1}H-^{1}H COSY spectrum of talaroketal B (**3**) in CDCl$_3$.



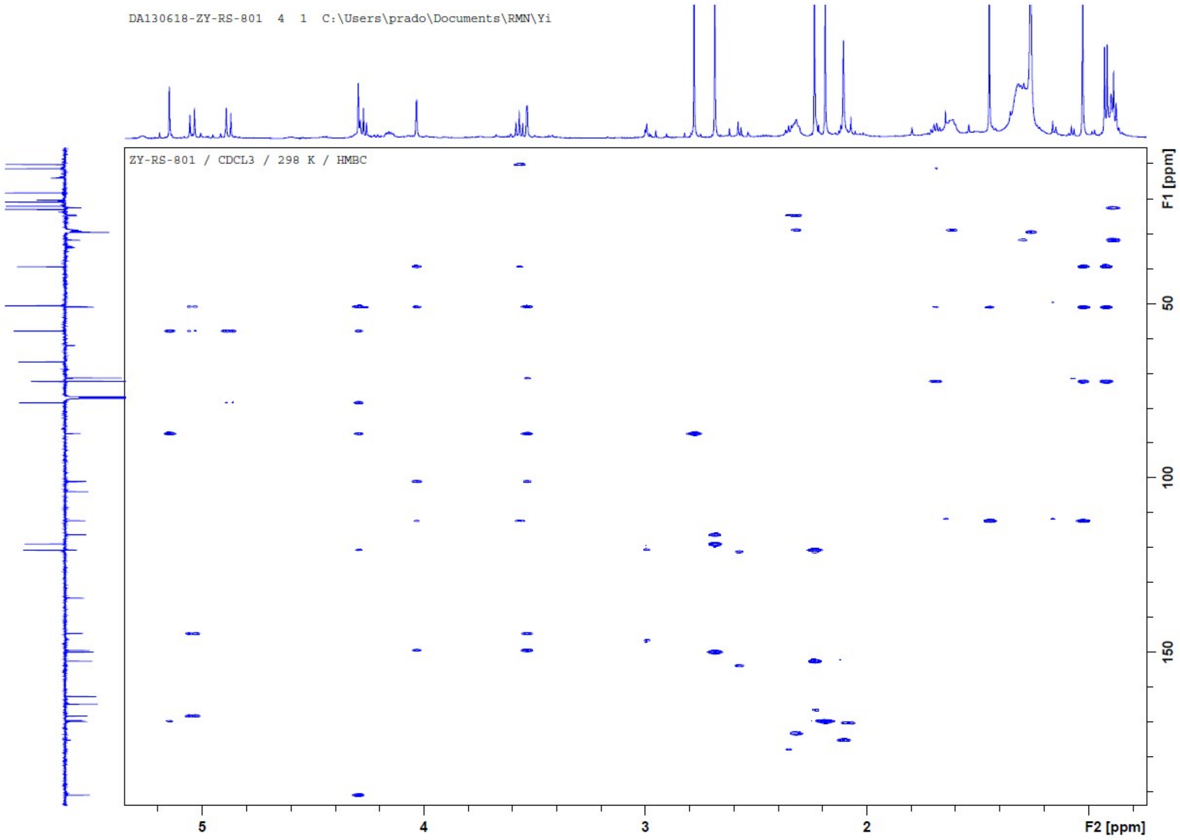
S17. HSQC spectrum of talaroketal B (**3**) in $CDCl_3$.



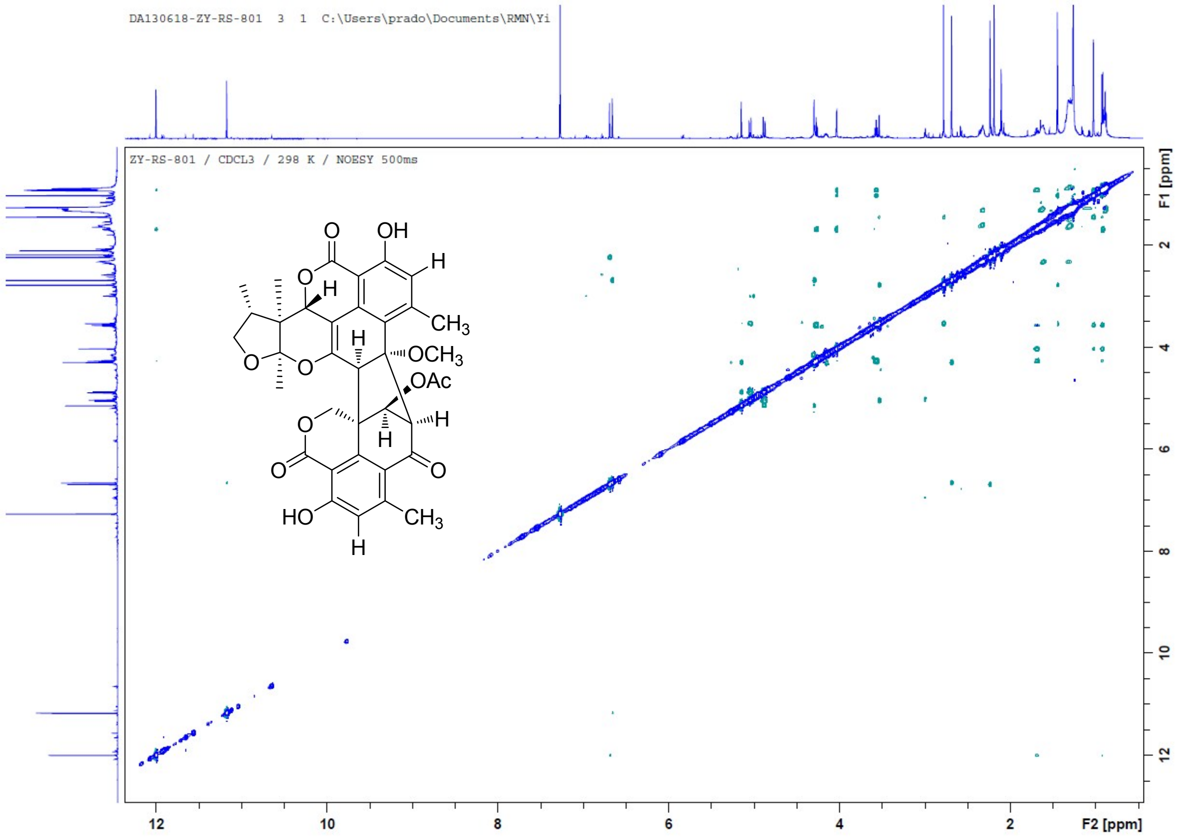
S18. HMBC spectrum of talaroketal B (**3**) in $CDCl_3$.



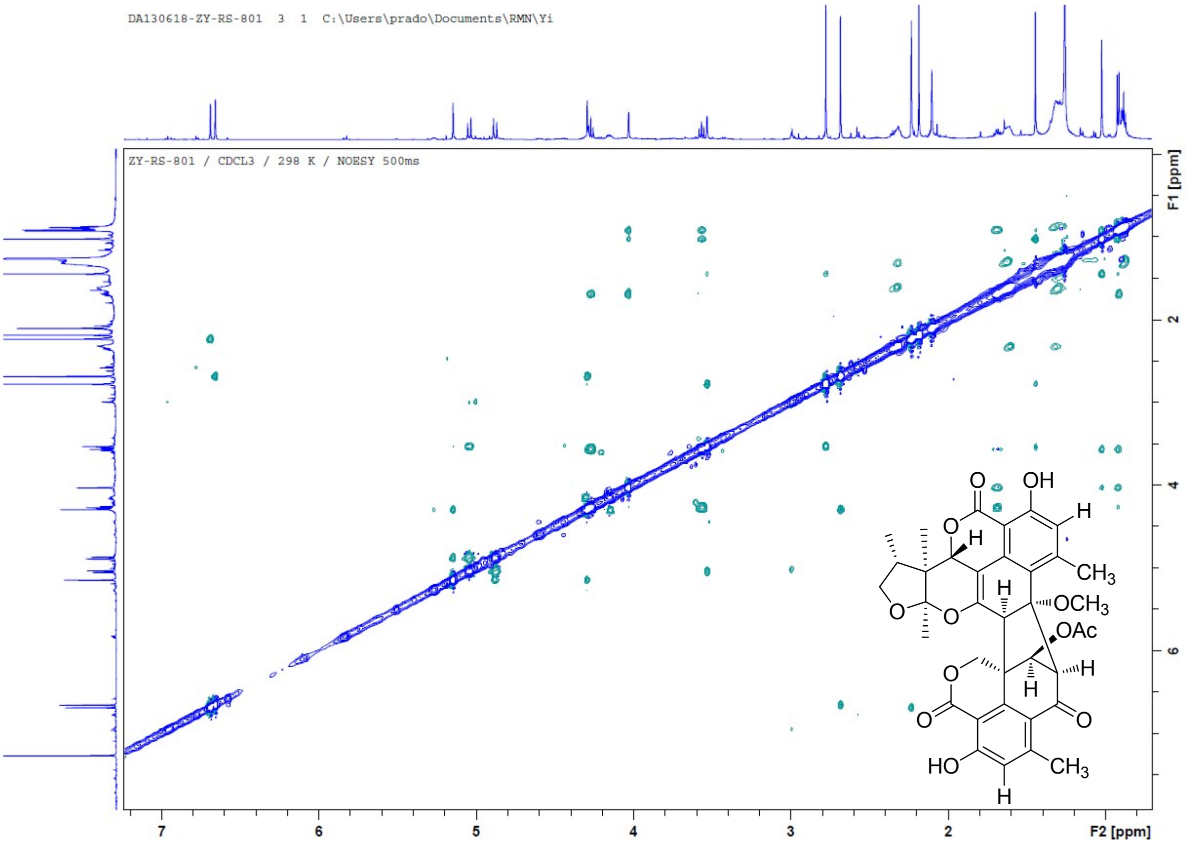
S19. HMBC spectrum of talaroketal B (**3**)-Enlargement in $CDCl_3$.



S20. NOESY spectrum of talaroketal B (**3**) in CDCl$_3$.



S21. NOESY spectrum of talaroketal B (**3**)-Enlargment in CDCl$_3$.



S22. (+) ESI-MS spectrum of talaroketal B (**3**)

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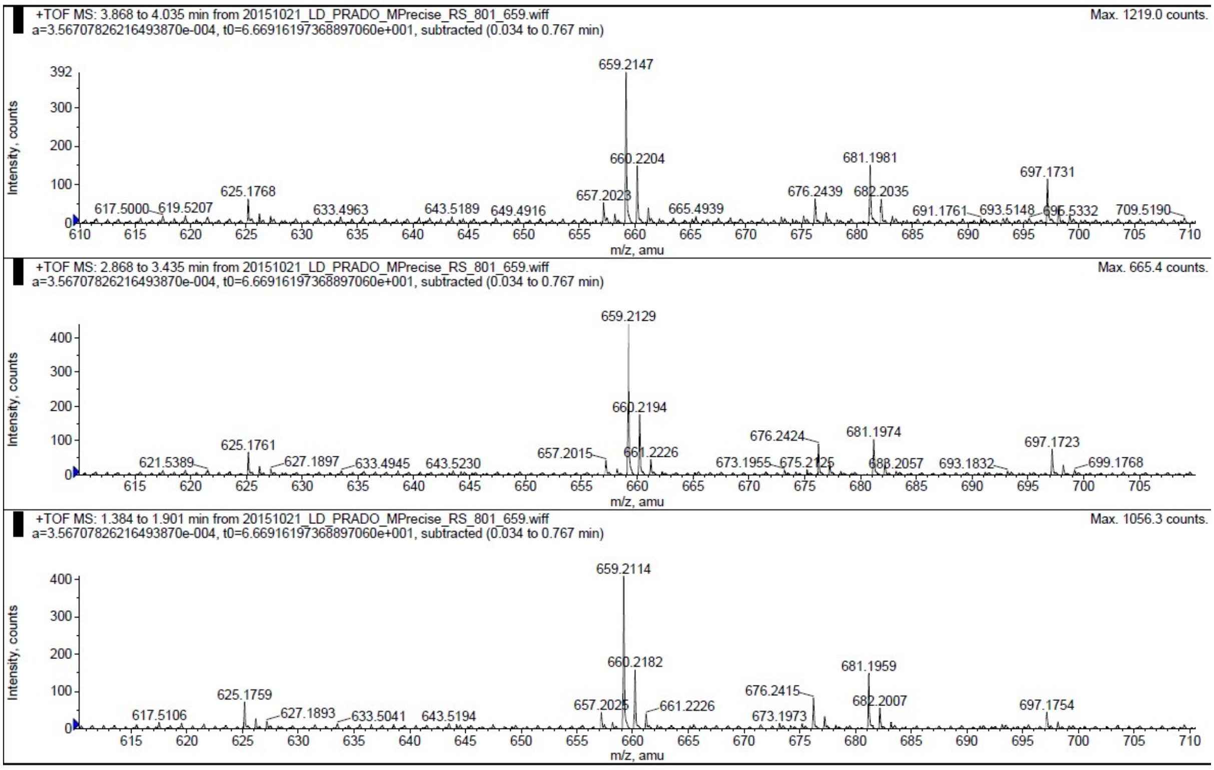
post PM test



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•Initials : PK

Analyst Version: QS

Determination of the absolute configuration of 2 and 3

All the calculations were carried out using the Gaussian 09 program using the B3LYP method. For compound **2**, the coordinates obtained from the X-ray diffraction were used for the rotational strengths calculation at the 6-311g level of theory (nstates = 20). For compound **3**, a geometry optimization (6-311+g(d,p) was performed followed by a frequency calculation at the same level of theory in order to check that no imaginary frequencies were present (indicating a minimum on the potential energy surface). Calculation of the rotational strengths were then realized for 15 excited states at the 6-311+g(d,p) level.

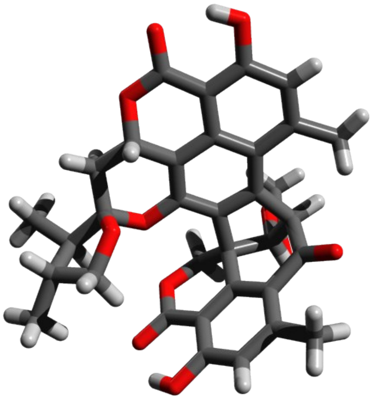

Figure 1: conformation of 2 used for the DFT calculations.

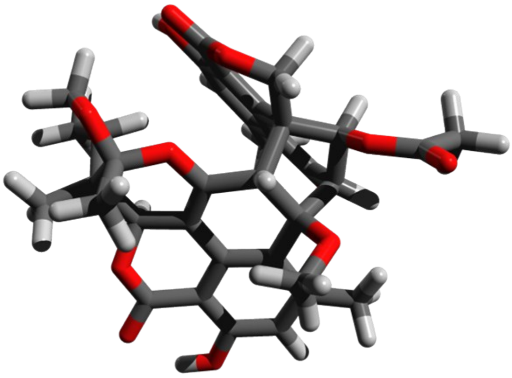

Figure 2: conformation of 3 used for the DFT calculations**.**

Cartesian coordinates of 2:

O	11.22100	0.57800	0.62600
O	8.82800	4.22100	2.09200
O	10.48000	2.68800	2.42900

O	10.32300	5.13600	5.78100
O	9.91200	5.44400	7.91700
O	8.76500	3.63300	9.37700
H	9.01600	4.41400	9.19700
O	11.40600	1.61000	4.27900
O	11.98900	3.36600	3.04300
C	9.62300	4.96500	0.02700
O	10.07700	1.07100	1.16400
O	7.56900	0.57100	1.38300
H	8.33000	0.82200	1.63300
O	6.75300	1.68900	4.54800
C	10.19400	4.10900	2.22100
C	8.47800	4.25000	0.70000
H	7.62900	4.74100	0.56300
H	8.37800	3.33200	0.34300
H	14.18400	3.03100	4.34400
H	9.53500	5.94500	0.20100
C	10.82700	4.42300	0.84200
H	11.13900	3.56800	0.42800
C	10.66600	4.86900	3.38300
H	10.57200	5.84000	3.21300
H	11.62200	4.67300	3.54900
C	9.84000	4.47200	4.59000
H	8.90500	4.78700	4.42900
C	9.79700	3.00500	4.71500
C	10.08800	2.19100	3.63300
C	9.37200	2.45900	5.93100
C	9.27700	3.35700	7.03500
C	9.81800	4.68300	6.94200
C	8.81800	2.86300	8.24000
C	8.41400	1.51900	8.36300
H	8.02000	1.22100	9.17400
C	8.57700	0.65600	7.36300
C	9.09100	1.08200	6.06500
C	9.37600	0.26700	4.93300
C	9.91300	0.83000	3.77700
C	10.09700	0.25300	2.71100
C	10.15400	1.56000	3.60700
H	9.94100	2.39600	3.10200
C	9.07600	1.18100	4.64500
H	9.12500	1.75000	5.46600
C	7.72100	1.30700	3.92900
C	7.66300	0.85500	2.51200
C	8.83100	0.37100	1.91800
C	6.46300	0.89800	1.73500

C	6.48200	0.39400	0.46200
H	5.67500	0.36900	0.04000
C	7.64600	0.08000	0.11100
C	8.84900	0.11000	0.59200
C	10.07400	0.58000	0.02300
C	11.33200	0.22200	1.83300
H	12.08800	0.12600	2.37000
H	11.55400	1.15100	1.57300
C	9.70300	4.74100	1.50500
H	9.85000	3.79000	1.68900
H	10.44500	5.26400	1.87400
H	8.86300	5.02700	1.92100
C	11.99900	5.42100	0.86300
H	11.68100	6.29100	1.18200
H	12.36200	5.51700	0.04200
H	12.69900	5.08900	1.46300
C	8.22300	0.80700	7.62400
H	9.04200	1.34600	7.62200
H	7.61900	1.12800	6.92200
H	7.78200	0.88700	8.49600
C	5.15200	1.41500	2.26100
H	4.51600	1.50500	1.52100
H	4.79600	0.78700	2.92400
H	5.29100	2.28900	2.68100
C	12.21400	2.56200	3.93700
C	13.45700	2.56800	4.81100
H	13.26200	3.03100	5.65300
H	13.72700	1.64500	5.00100

Cartesian coordinates of 3 :

C	0.78700	2.61960	1.07250
C	0.86740	1.20610	0.91990
C	2.09880	0.58670	0.59770
C	3.23280	1.41680	0.32430
C	3.09910	2.80640	0.36940
C	1.91450	3.41940	0.75250
C	0.46660	3.17400	1.69980
O	1.47330	2.32730	2.02750
C	0.35780	0.40780	1.20400
C	0.34700	0.93360	1.32500
C	0.88860	1.75550	1.01450
C	2.19480	0.95620	0.62200
O	1.91590	4.77120	0.81890
O	0.54110	4.33380	2.06490
C	4.62400	0.90580	0.02600

C	0.68390	2.81520	0.12790
C	0.09680	4.17980	0.32510
C	2.11890	3.01510	0.66390
C	0.18820	2.22590	1.25660
C	0.35220	1.24840	2.11680
C	1.78570	0.89870	1.91420
C	2.55860	1.54800	0.77830
O	1.26280	4.12890	0.52720
C	2.07510	3.62800	0.43100
C	1.53070	2.64220	1.40630
C	2.32760	2.08130	2.42290
C	1.78710	1.11640	3.27830
C	0.45740	0.69060	3.14360
O	3.25210	3.94900	0.44500
O	2.38290	0.18450	2.70460
O	3.61540	2.46020	2.57070
C	0.06130	0.35220	4.10130
H	3.62390	1.44650	1.03200
C	1.66820	1.17830	1.29910
H	2.12110	3.57290	1.62850
H	1.12520	2.32740	1.93880
C	2.92090	0.35000	1.74950
C	2.50510	0.98010	2.43490
O	1.47660	1.58300	1.71180
C	3.67660	0.29430	0.58400
C	4.44870	1.38670	1.31760
O	3.62490	1.84970	2.37600
C	4.55410	0.59810	0.30300
C	3.87420	1.23480	2.61790
C	2.04710	0.80770	3.89340
H	1.88580	1.55410	0.27410
O	2.89050	3.70510	0.26310
O	4.75950	4.65840	0.99790
C	4.15010	4.17720	0.05630
C	4.79650	4.17210	1.30380
O	3.23230	1.36610	1.51890
C	3.12160	0.80600	2.81810
H	3.95900	3.43160	0.15420
H	1.14800	5.32680	0.97990
H	4.77290	0.17560	0.11490
H	5.33010	1.34590	0.76200
H	4.92990	1.22740	0.99190
H	0.26780	4.91420	0.49490
H	0.60850	4.57470	1.22800
H	2.41270	0.69300	4.05500

H -	4.18500	2.08360	3.25660
H -	0.71870	0.67820	4.82190
H	0.90410	0.05950	4.69440
H	0.39310	1.24960	3.53760
H	2.93370	0.78470	0.07700
H	4.74050	2.20000	0.62380
H	5.38070	0.98620	1.76770
H	5.03180	0.02110	1.09170
H	3.94170	1.37890	0.79840
H	5.35910	1.08660	0.28370
H	4.76280	0.69370	2.99510
H	4.21890	2.11770	2.03990
H	3.34470	1.62320	3.51270
H	1.17800	0.11920	3.95730
H	1.74660	1.79360	4.30750
H	2.86770	0.41560	4.52850
H	4.18240	4.76490	2.01290
H	5.80810	4.62880	1.25350
H	4.90880	3.14090	1.68820
H	3.52090	1.53730	3.54980
H	2.07540	0.58920	3.12760
H	3.72810	0.12110	2.88340

X-ray crystallographic data of talaroketal A (2). A colorless cobbledstone-like crystal of talaroketal A (obtained from CH_2Cl_2/C_6H_{12}) (**2**) having approximate dimensions of 0.38 × 0.25 × 0.09 mm was mounted in a nylon loop. The crystallographic data were collected on a Rigaku diffractometer constituted by a MM007 HF copper rotating-anode generator, equipped with Osmic CMF confocal optics, and a Rapid II curved image plate. The crystal-to-detector distance was 127.40 mm. The data were collected at a temperature of 193 K to a maximum 2θ value of 136.5° based on a triclinic unit cell. A total of six sweeps of oscillation images were therefore collected using approx 180°-ω oscillations in 5.0° steps. Diffraction pattern showed split reflections but only one domain could be reasonably indexed and R_{int} value circa 0.08 tended to indicate that partial overlaps could be ignored, as post-verified by the TWIN/BASF value in SHELXL-2014[1] and the TWINROTMAT option in PLATON1. An empirical absorption correction (done using Fs_ABSCOR)[2] was applied which resulted in transmission factors ranging from 0.62 to 0.92. The data were also corrected for Lorentz and polarization effects. The structure was solved by direct methods (SHELXS-97)[3] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model as defined in SHELXL-2014/7.[1] Two molecules of interest occupy the noncentrosymmetric triclinic unit cell. The acetyl group in position 9′ of one monomer displays large anisotropic displacement parameters for the terminal carbonyl O and methyl C atoms despite application of soft restraints (SAME, RIGU sd by default, and ISOR sd 0.02 instructions in SHELXL-2014) and a sphere of contacts from vicinal molecules including the second acetyl group in position x−1, y+1, z. 'Anti-bumping' restraints help also to avoid steric clashes with methyl hydrogens constrained by AFIX 33. This unusual behaviour may be related to the possible unsolved twinning problem. Regards to the absolute configuration determination, which is rendered difficult by the absence of strong anomalous scatterers, the relatively poor quality of the data and the low coverage of Bijvoet pairs measured (69%) due to the triclinic cell and the diffractometer set-up limitation, several approaches reasonably converge to claim the proposed enantiomer: 1*S*, 10*R*, 11*R*, 13*S*, 8′*R*, 9′*S*, 9′a*S*.

References :

1. (a) Sheldrick, G. M., A short history of SHELX. *Acta crystallographica. Section A, Foundations of crystallography* 2008, *64* (Pt 1), 112-22; (b) Sheldrick, G. M., Crystal structure refinement with SHELXL. *Acta Crystallogr. C* 2015, *71* (Pt 1), 3-8.
2. Spek, A. L., Structure validation in chemical crystallography. *Acta Crystallogr. D,* 2009,

65 (Pt 2), 148-55.

3. Rigaku, *Crystal clear-SM expert.* Rigaku Corporation, Tokyo, Japan, 2001.