Structure and Absolute Configuration of Diterpenoids from *Hymenaea stigonocarpa*

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Raman optical activity (ROA) calculations

All DFT and Time-Dependent DFT (TDDFT) calculations were carried out at 298 K in DMSO solution using the Polarizable Continuum Model (PCM) incorporated in Gaussian 09 software.[1] The 4*R*,5*S*,8*R*,9*S* and 5*S*,8*S*,9*R*,10*S* configurations were arbitrarily chosen for the calculations of **1** and **2**, respectively. Conformational analysis was carried out at the molecular mechanics level of theory with the Monte Carlos algorithm using the MMFF force field implemented in Spartan 08 software package (Wavefunction, Irvine, CA, USA). A total number of 54 conformers for **1** and 44 conformers for **2** with relative energy within 10 kcal/mol of the lowest-energy conformer were identified and further geometry optimized at the B3LYP/6-31G(d) level. The 10 conformers identified within an energy window of 1.5 kcal/mol for **1** and the 5 conformers identified within an energy window of 1.2 kcal/mol for **2**, corresponding to more than 90% of the total Boltzmann distribution, were selected for Raman and ROA spectral calculations. ROA calculations were carried out using the so-called "one-step" approach[2] at the B3LYP/PCM/TZVP level in DMSO. The incident light frequency was 532 nm. The Boltzmann factor for each conformer was calculated based on Gibbs free energy obtained at the B3LYP/PCM/TZVP level in DMSO. Each spectrum was plotted as a sum of Lorentzian bands with half-widths of 10 cm^{-1}. The calculated wavenumbers were multiplied with a scaling factor of 0.98 and the spectra were plotted using Origin software (OriginLab, Northampton, MA, USA). As the Boltzmann population predicted for each conformer of **1** and **2** was very similar, simple averages of the four lowest-energy conformers of **1** and the two lowest-energy conformers of **2** were used in the composite Raman and ROA spectra (Figures S30 and S31).

T1. Complete assignments of ^{1}H and ^{13}C NMR chemical shifts for **2**

(+)-(5*S*,8S,9*R*,10*S*)-labd-13-en-8*β*-ol-15-oic acid (2)(400 /100 MHz, $CDCl_3$)				**MARSAIOLI, DE FREITAS LEITÃO FILHO & DE PAIVA CAMPELLO , 1975 (100 MHz $CDCl_3$)**	**IMAMURA *et al.*, 1977 (25 MHz, $CDCl_3$)**
Position	**δ_C, type**	**δ_H (*J* in Hz)**	**HMBC**	**δ_H (*J* in Hz)**	**δ (ppm)**
1a	39.8, CH_2	1.67, m			39.8
1b		0.97, m			
2a	18.4, CH_2	1.63, m			18.2
2b		1.46, m			
3a	41.9, CH_2	1.41, m			41.9
3b		1.18, m			
4	33.2, C				33.1
5	56.1, CH	0.92, m	7, 9, 10, 18, 19, 20		56.1
6a	23.5, CH_2	1.61, m			23.5
6b		1.44, m			
7	44.6, CH_2	1.90, m 1.42, m	5, 8, 9, 17		44.7
8	74.4, C				74.4
9	61.3, CH	1.09, bt (3.5)	1, 5, 7, 8, 12, 17, 20		61.3
10	39.2, C				39.2
11a	20.5, CH_2	1.65, m			20.5
11b		1.29, m			
12a	44.5, CH_2	2.33, m	9, 13, 14, 16, 17		44.5
12b		2.24, m			
13	163.9, C				163.9
14	114.6, CH	5.71, bs	12, 15, 16	5.66, m	114.7
15	171.6, C				171.5
16	19.4, CH_3	2.18, s	12, 13, 14, 15	2.16, d (1.0)	19.4
17	24.0, CH_3	1.17, s	7, 8, 9	1.13, s	24.0
18	21.5, CH_3	0.80, s	3, 4, 5, 19	0.86, s	21.5
19	33.4, CH_3	0.88, s	3, 4, 5, 18	0.95, s	33.3
20	15.4, CH_3	0.79, s	1, 5, 9, 10	0.83, s	15.4

T2. Complete assignments of ^{1}H and ^{13}C NMR chemical shifts for **3**

(+)-(5*S,9*S**,10*S**)-labd-7,13-dien-15-oic acid (3) (400/100 MHz, $CDCl_3$)**				**MARSAIOLI, DE FREITAS LEITÃO FILHO & DE PAIVA CAMPELLO, 1975 (100 MHz $CDCl_3$)**	**IMAMURA *et al.*, 1977 (25 MHz, $CDCl_3$)**
Position	**δ_C, type**	**δ_H (*J* in Hz)**	**HMBC**	**δ_H (*J* in Hz)**	**δ (ppm)**
1a	39.2, CH_2	1.85, m			39.2
1b		0.97, m			
2a	18.8, CH_2	1.56, m			18.8
2b		1.47, m			
3a	42.2, CH_2	1.42, m			42.3
3b		1.18, m			
4	33.0, C				33.0
5	50.1, CH	1.19, m	6, 7, 9, 10, 19, 20		50.2
6a	23.8, CH_2	2.00, m	5, 10		23.8
6b		1.88, m			
7	122.8, CH	5.42, bs	5, 6, 9, 17	5.36, m	122.7
8	134.6, C				134.4
9	54.4, CH	1.65, m			54.5
10	36.8, C				36.9
11a	25.3, CH_2	1.63, m	8, 13		**22.1***
11b		1.36, m			
12a	43.6, CH_2	2.40, m	9, 11, 13, 14, 16		43.6
12b		2.13, m			
13	163.6, C				163.2
14	115.0, CH	5.71, bd (0.9)	12, 15, 16	5.63, m	115.2
15	171.9, C				172.2
16	19.3, CH_3	2.20, bd (0.9)	12, 13, 14, 15	2.15, d (1.0)	19.3
17	22.2, CH_3	1.71, bs	6, 7, 8, 9	1.65, s	**25.3***
18	33.1, CH_3	0.87, s	3, 4, 5, 19	0.85, s	33.1
19	21.8, CH_3	0.89, s	3, 4, 5	0.86, s	21.8
20	13.6, CH_3	0.77, s	1, 5, 9, 10	0.75, s	13.6

*Reversed δ_C values

T3. NMR chemical shifts for **4** and comparison with literature

(+)-(5*S,9*S**,10*S**)-labd-7-en-15-oic acid (4) (400 MHz, $CDCl_3$)**		**GARCÍA-SÁNCHEZ *et al*., 2000 (300 MHz, $CDCl_3$)**
Position	**δ_H (*J* in Hz)**	**δ_H (*J* in Hz)**
1a		1.83, m
1b		0.94, m
2a		1.52, m
2b		1.46, m
3a		1.40, m
3b		1.16, m
4		
5		1.17, m
6a		1.93, m
6b		1.89, m
7	5.39, m	5.38, bs
8		
9		1.57, m
10		
11a		1.49, m
11b		1.13, m
12a		1.56, m
12b		1.18, m
13		1.94, m
14a		2.39, dd (14.9, 5.8)
14b		2.14, dd (14.9, 8.3)
15		
16	1.00, d (6.7)	0.99, d (6.6)
17	1.66, m	1.65, bs
18	0.86, s	0.85, s
19	0.88, s	0.87, s
20	0.76, s	0.75, s

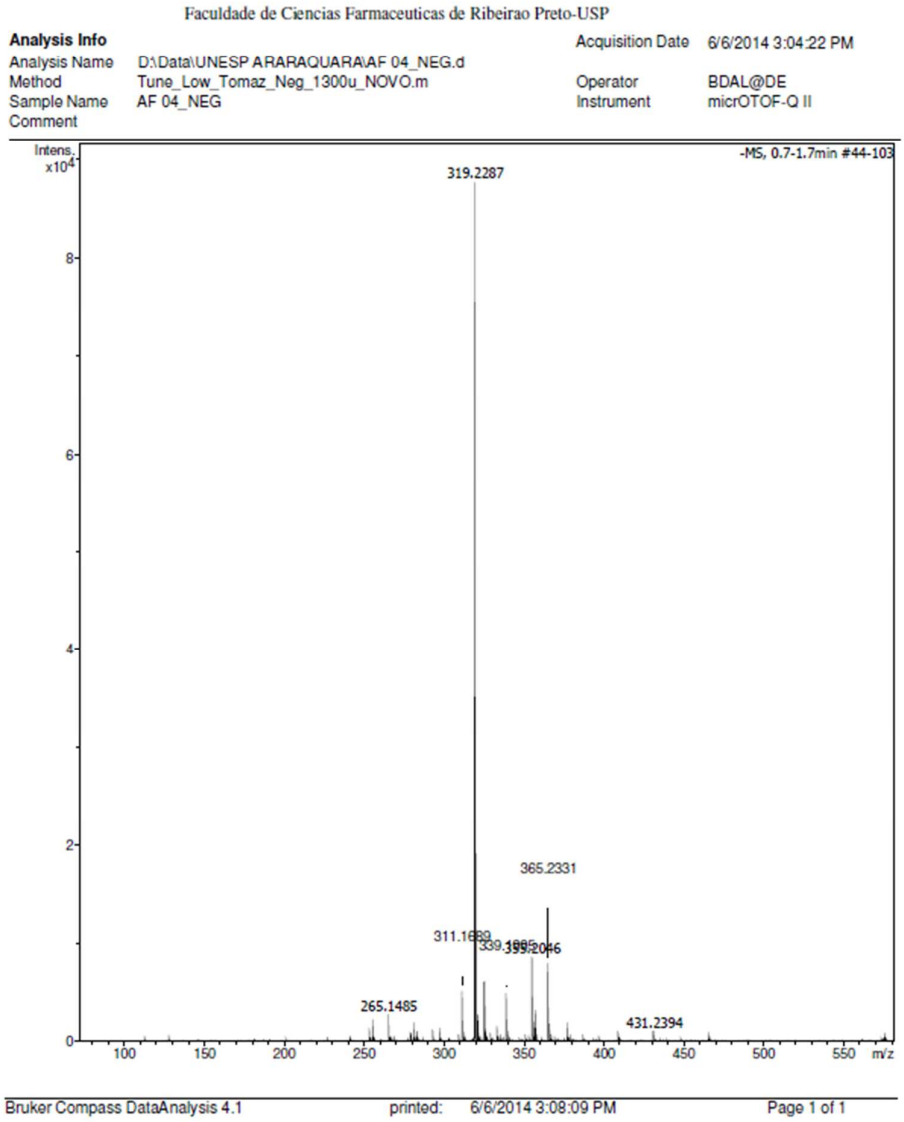
T4. NMR chemical shifts for **5** and comparison with literature

***p*-hydroxybenzoic acid (5) (400 MHz, CD_3OD)**		**(MIRANDA *et al.*, 2014) (300 MHz, CD_3OD)**
Position	**δ_H (*J* in Hz)**	**δ_H (*J* in Hz)**
1		
2		
3, 7	6.77, d (8.3)	6.82 (d. 8.9)
4, 6	7.85, d (8.3)	7.89 (d, 8.9)
5		
5-OH		

T5. NMR chemical shifts for **6** and comparison with literature

	4′,5,7-trihydroxy-3′,5′-dimethoxyflavone (6) (500/125 MHz, DMSO-d_6)		**KUWABARA *et al.*, 2003 (400/100 MHz, DMSO-d_6)**	
Position	**δ_C, type**	**δ_H (*J* in Hz)**	**δ_C, type**	**δ_H (*J* in Hz)**
2	163.5		163.6	
3	103.5	6.96, s	103.5	6.97, s
4	181.6		181.7	
5	157.4		157.3	
6	99.0	6.17, d (2.1)	98.8	6.21, d (2.0)
7	165.0		165,1	
8	94.3	6.52, d (2.1)	94,1	6.56, d (2.0)
9	161.4		161,3	
10	103.5		103,6	
1’	120.3		120,3	
2’,6’	104.4	7.31, s	104,3	7.32 (s)
3’,5’	148.2		148,1	
4’	140.0		139,8	
3’,5’-OCH_3	56.3	3.88, s	56,3	3.89, s

S1. HRESIMS spectrum of compound **1** (negative ion mode)



S2. HRESIMS spectrum of compound **1** (positive ion mode)

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Analysis Info

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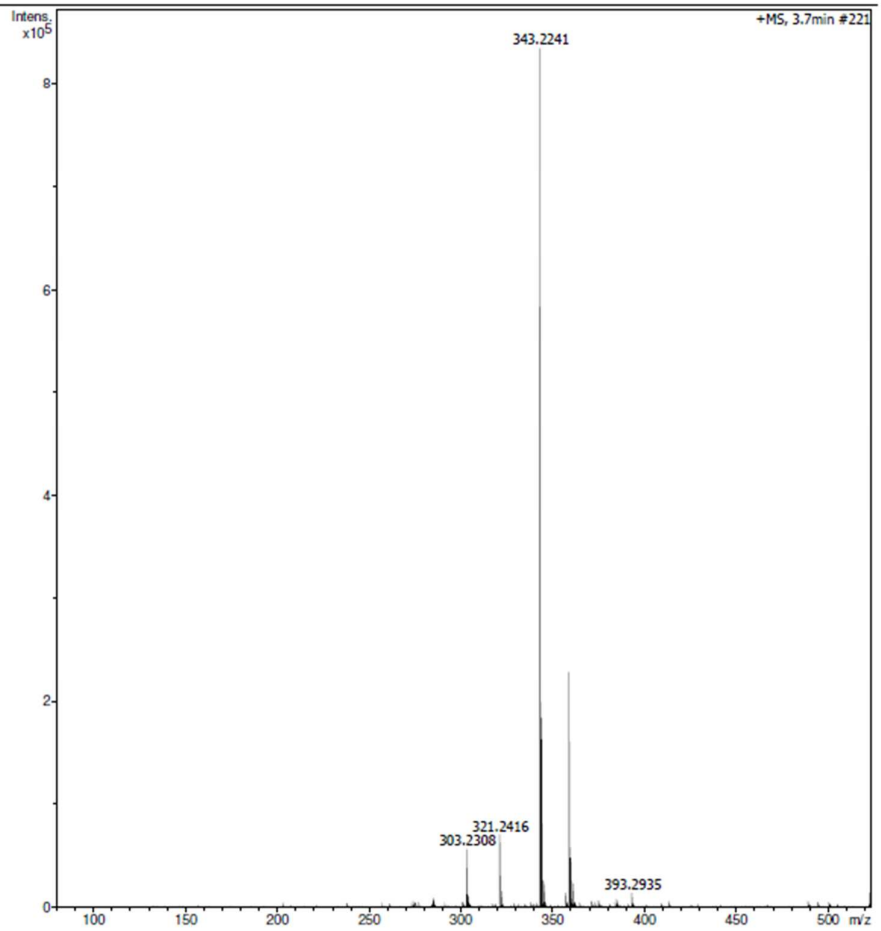

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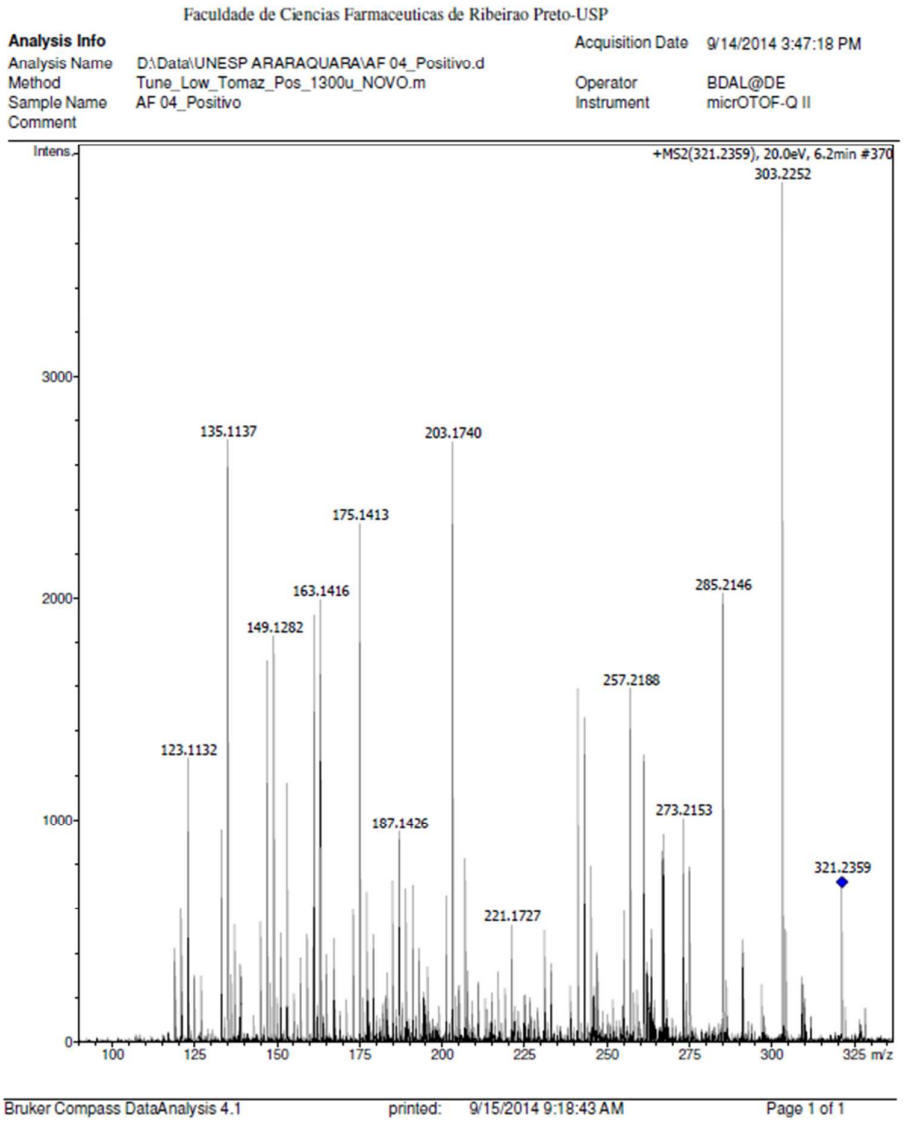
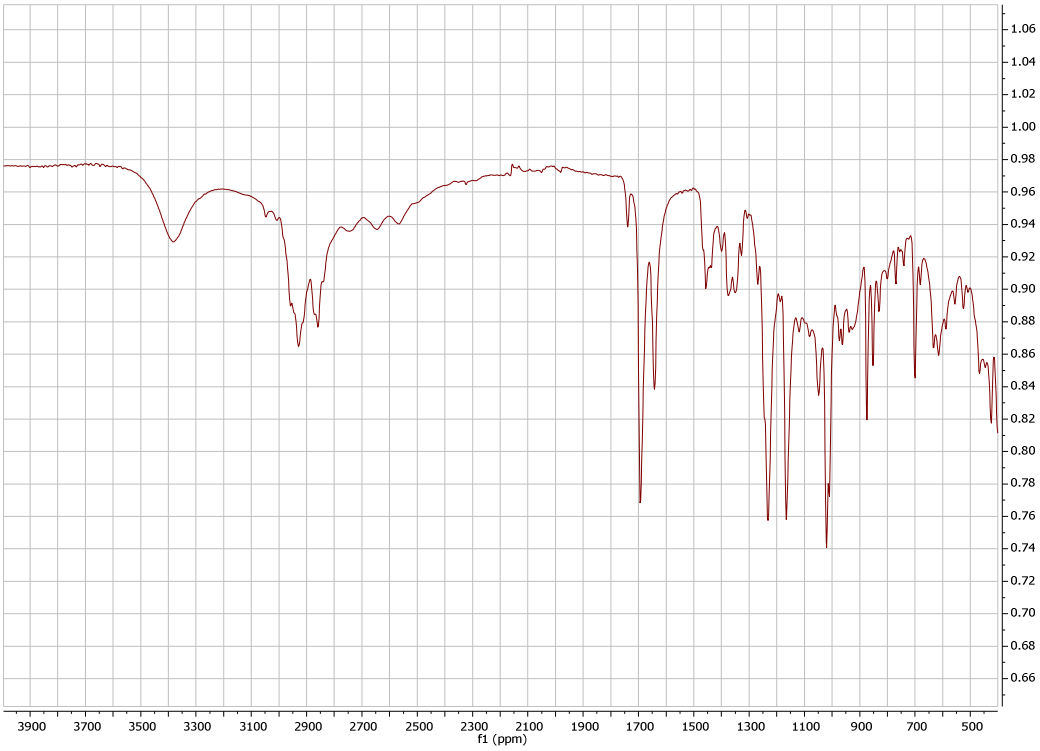
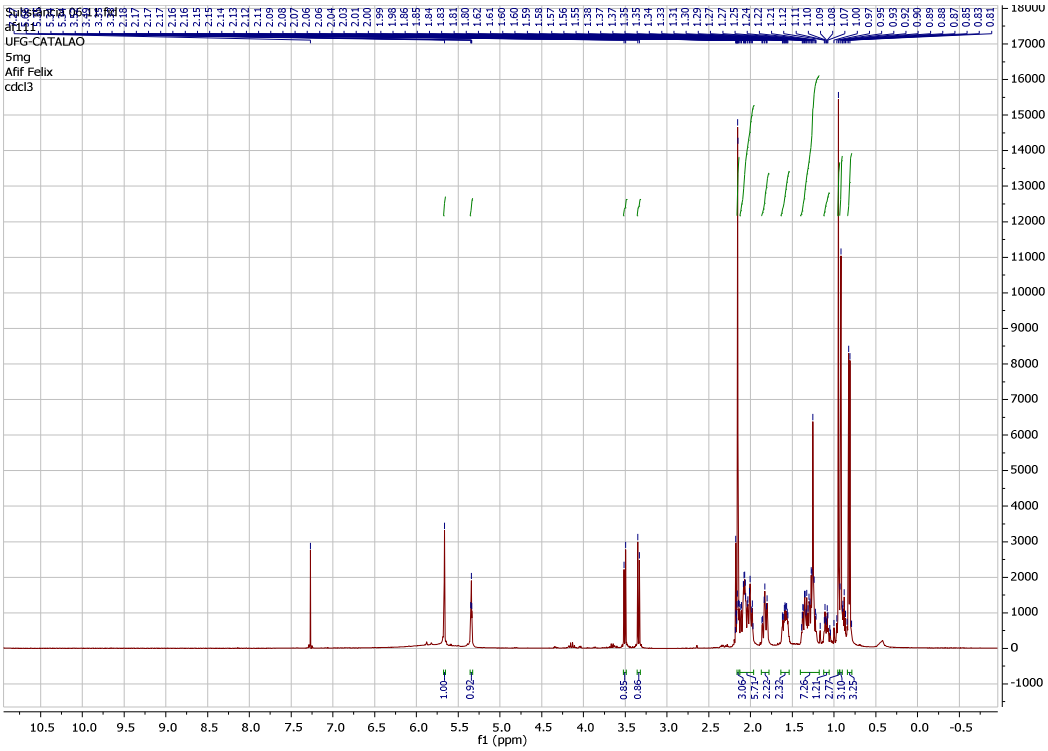
S3. MS-MS spectrum of compound **1** (positive ion mode)



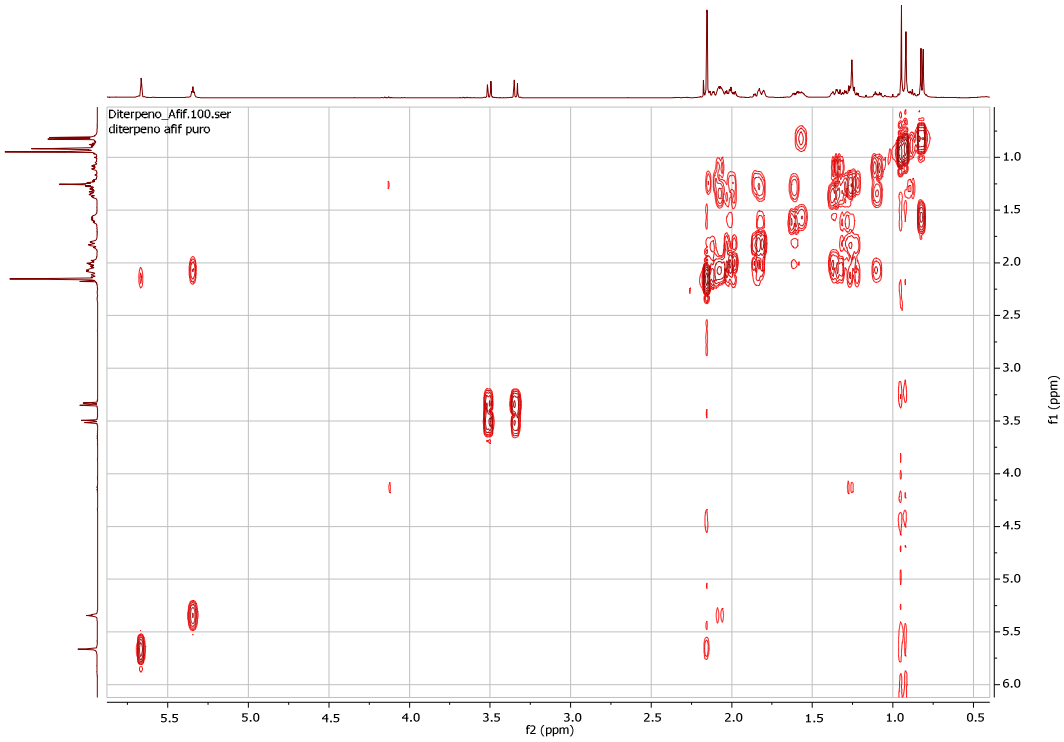
S4. IR spectrum of compound **1**



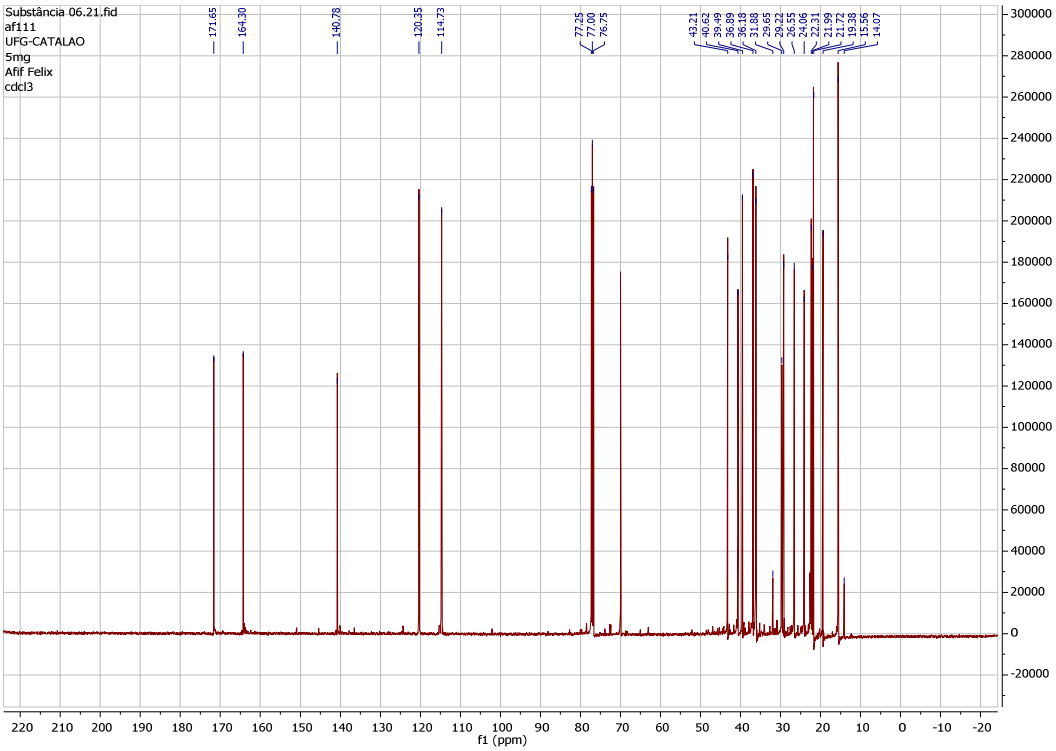
S5. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1**



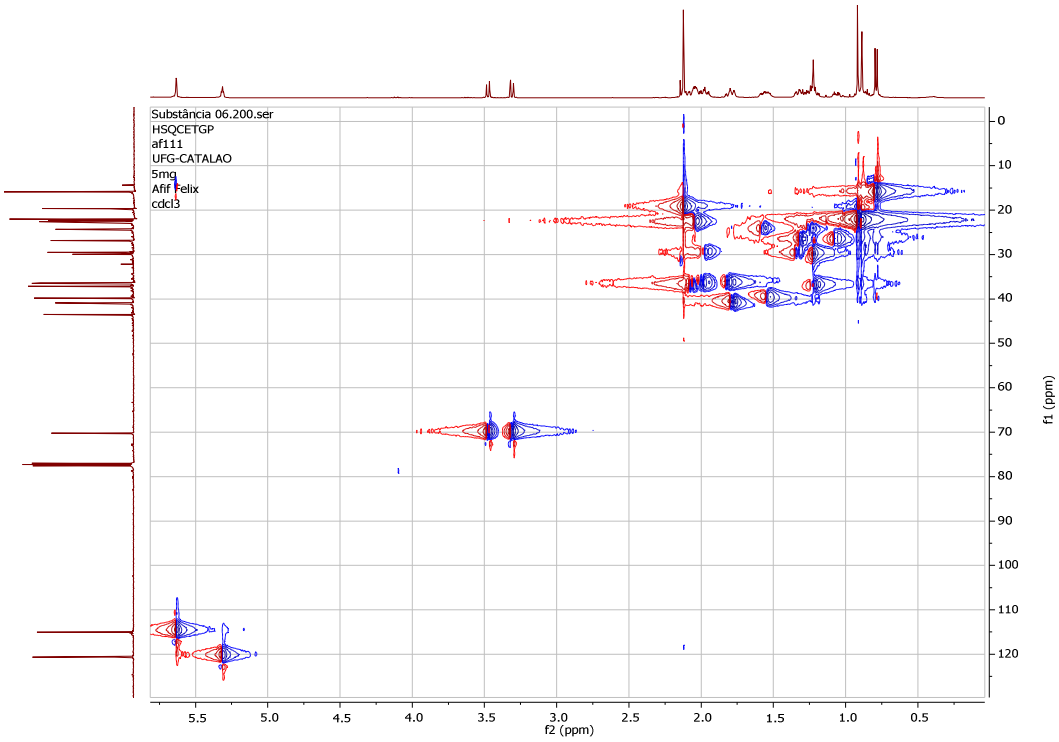
S6. COSY (600 MHz, $CDCl_3$) spectrum of compound **1**



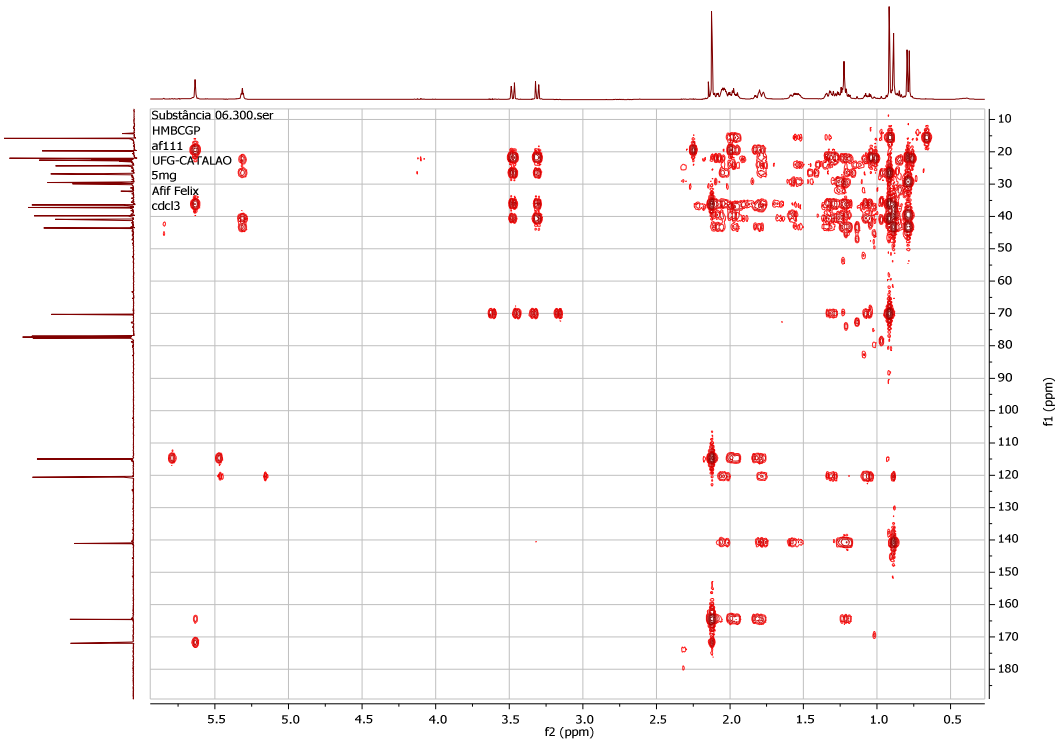
S7. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **1**



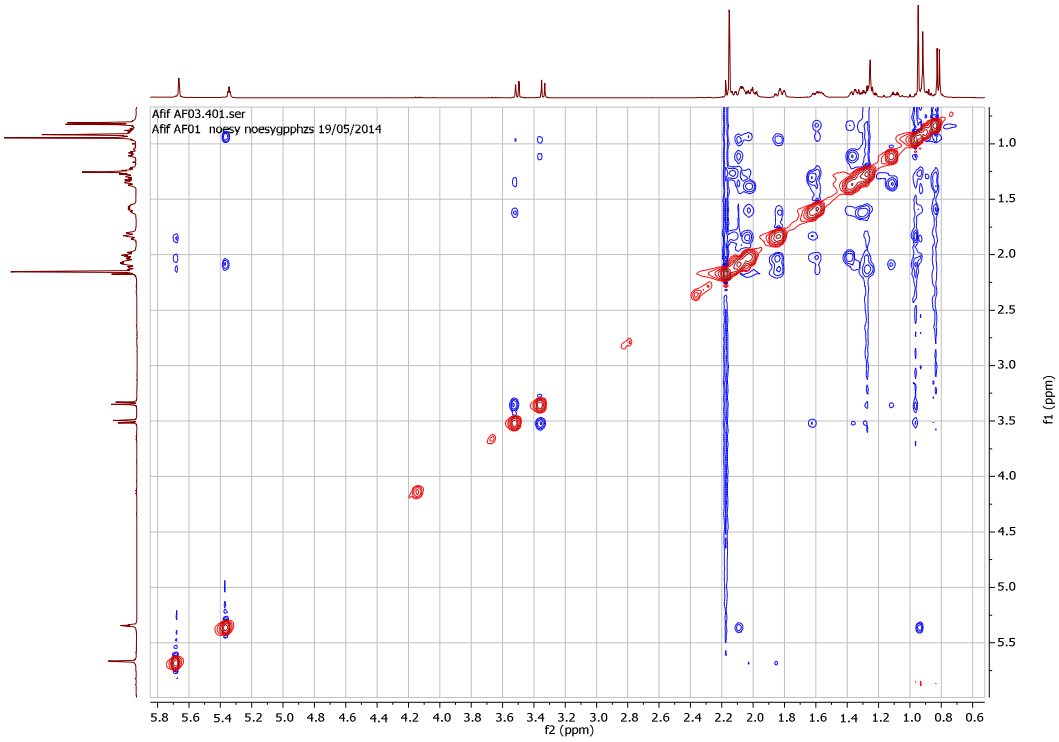
S8. HSQC (400 MHz, $CDCl_3$) spectrum of compound **1**



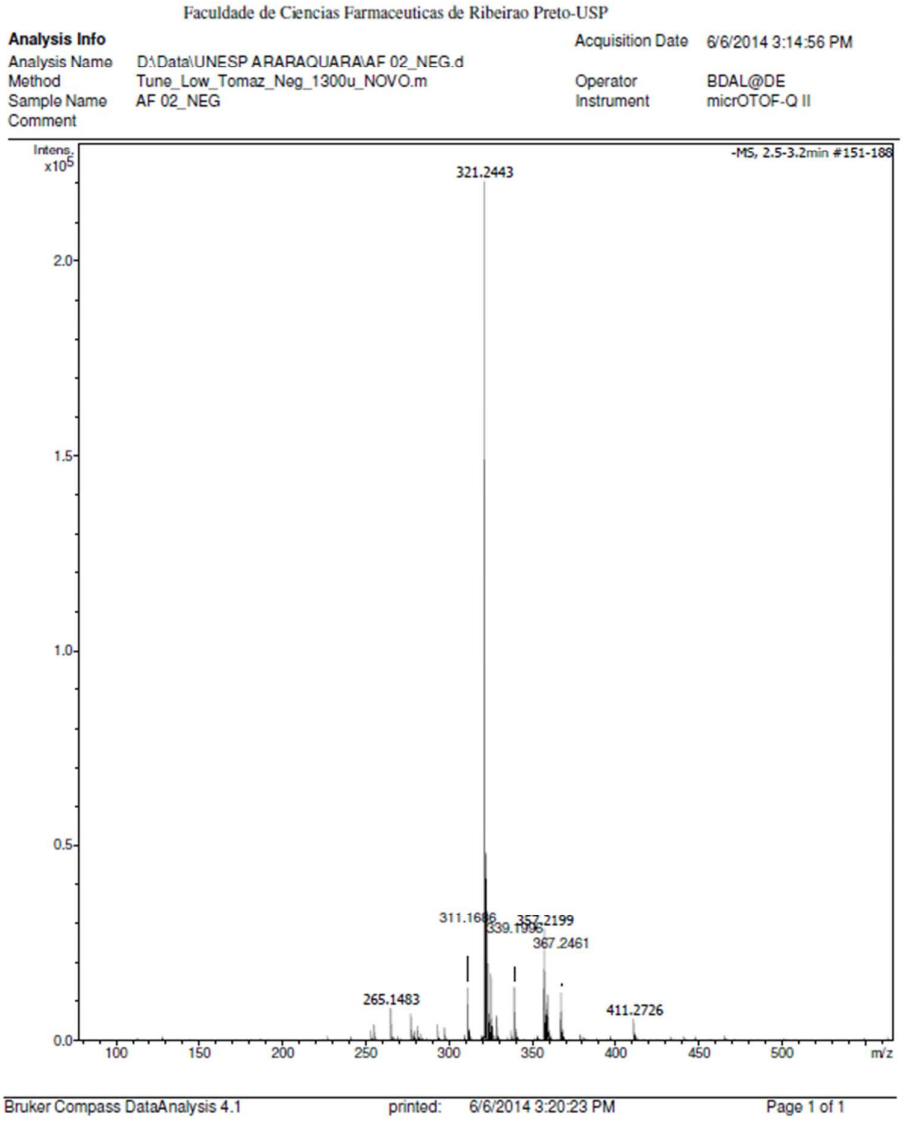
S9. HMBC (400 MHz, $CDCl_3$) spectrum of compound **1**



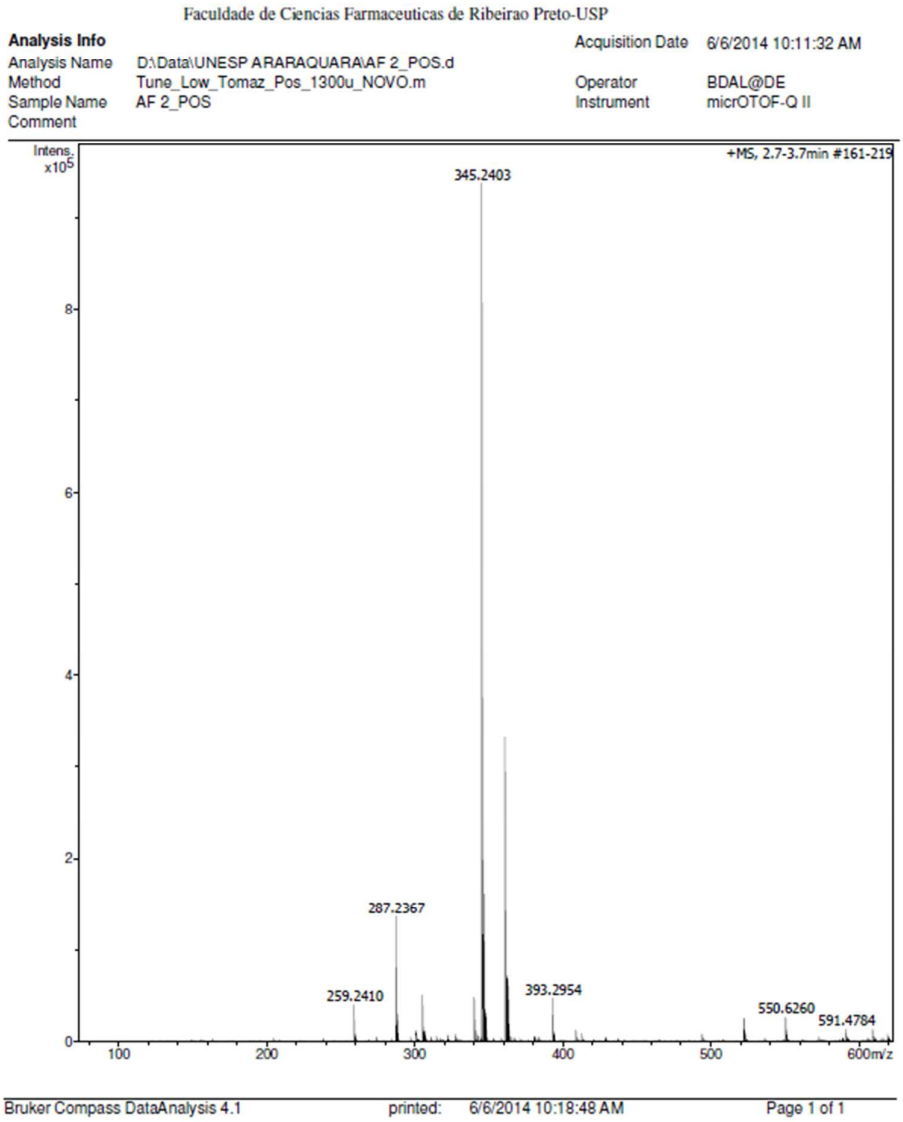
S10. NOESY (600 MHz, $CDCl_3$) spectrum of compound **1**



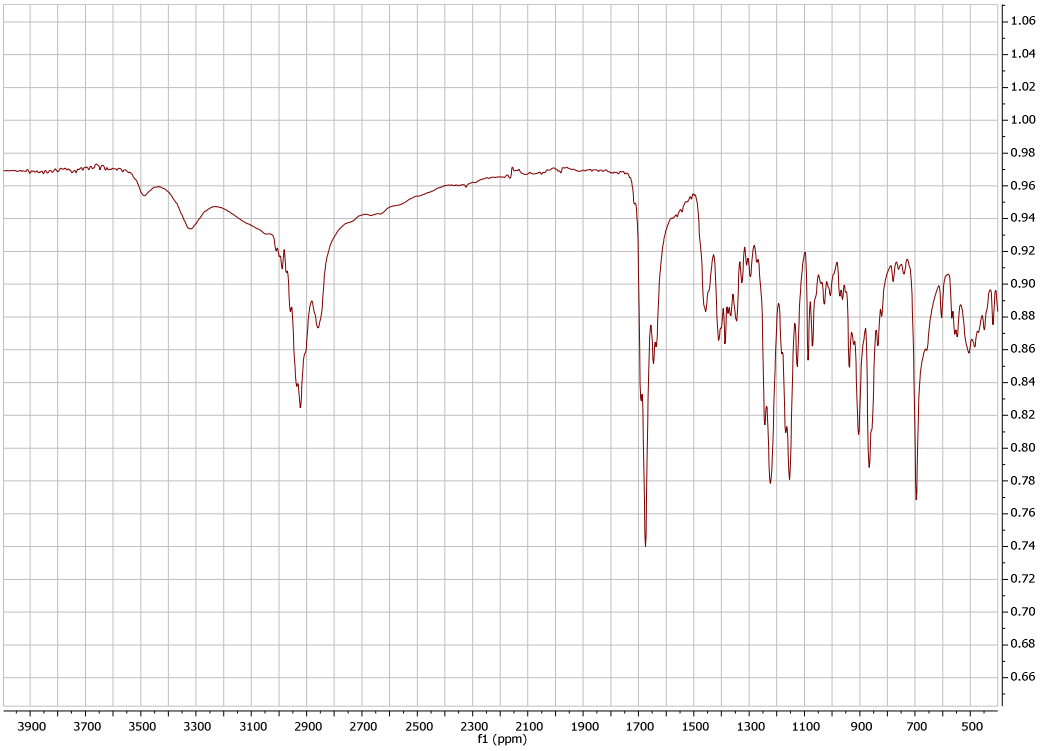
S11. HRESIMS spectrum of compound **2** (negative ion mode)



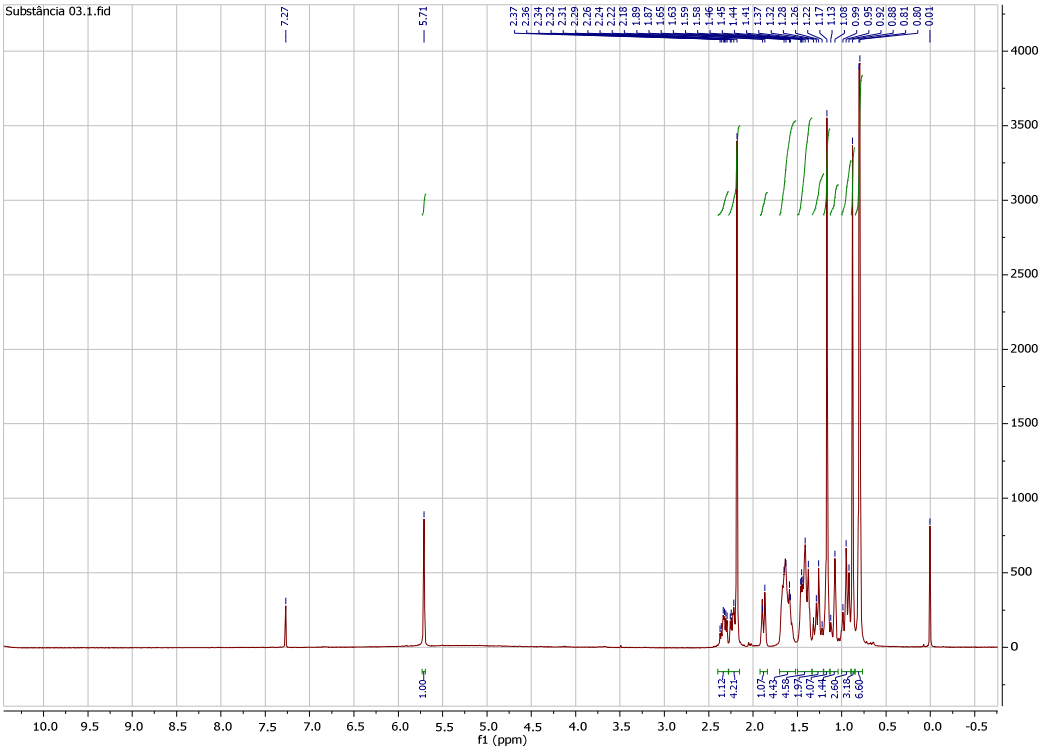
S12. HRESIMS spectrum of compound **2** (positive ion mode)



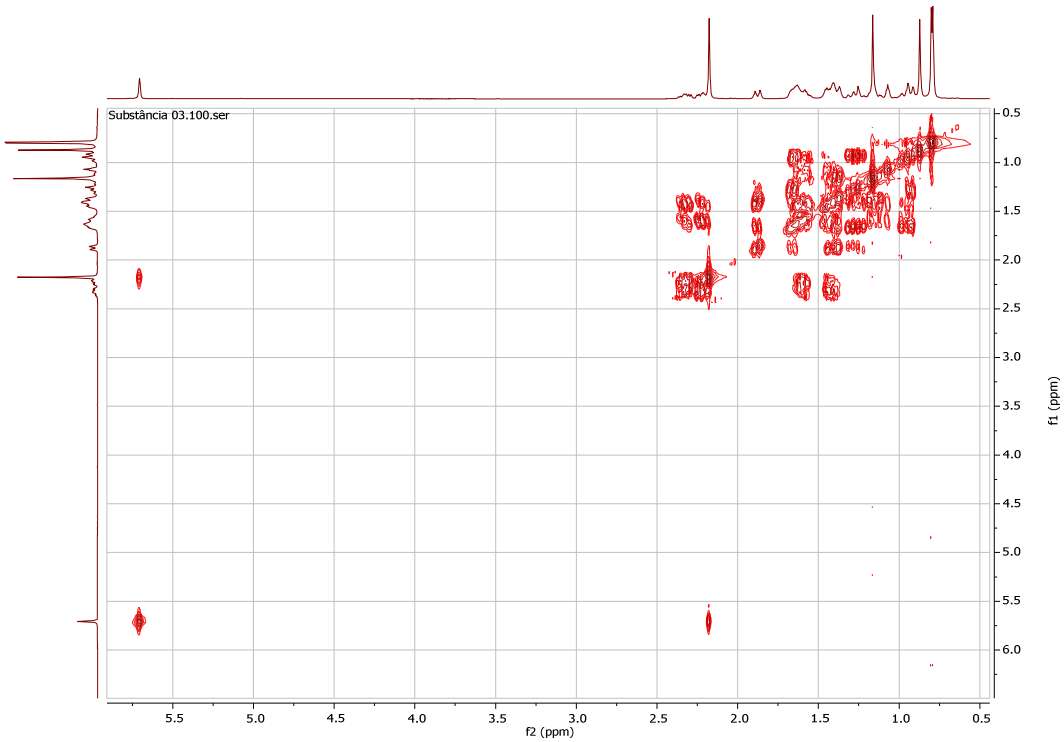
S13. IR spectrum of compound **2**



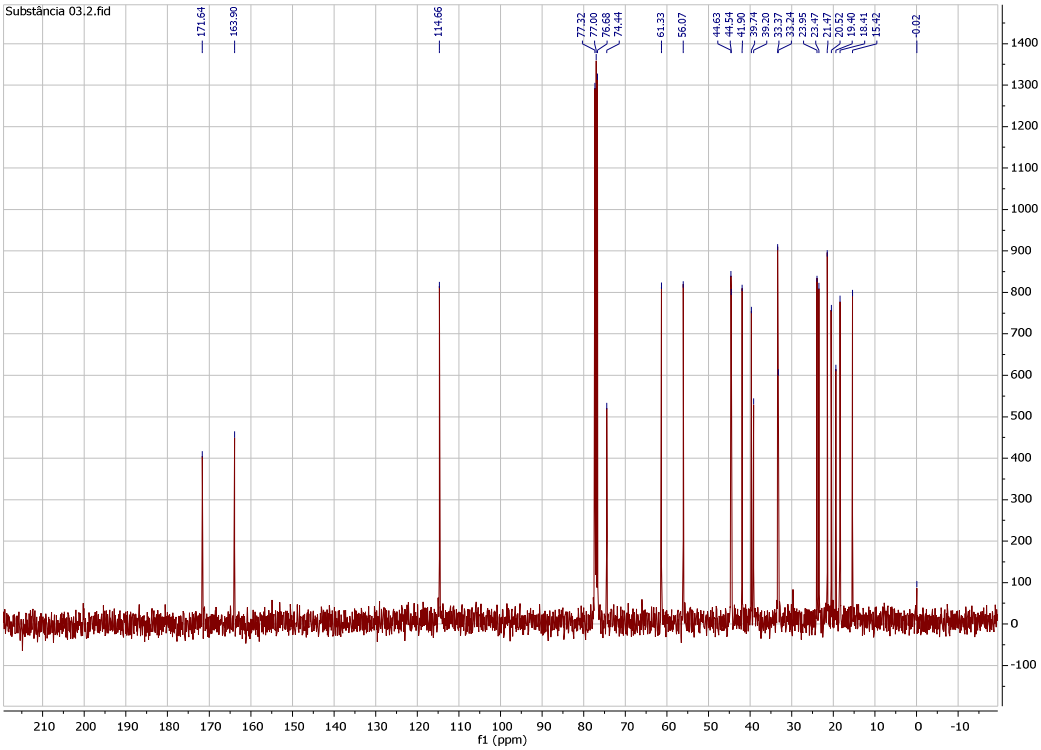
S14. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **2**



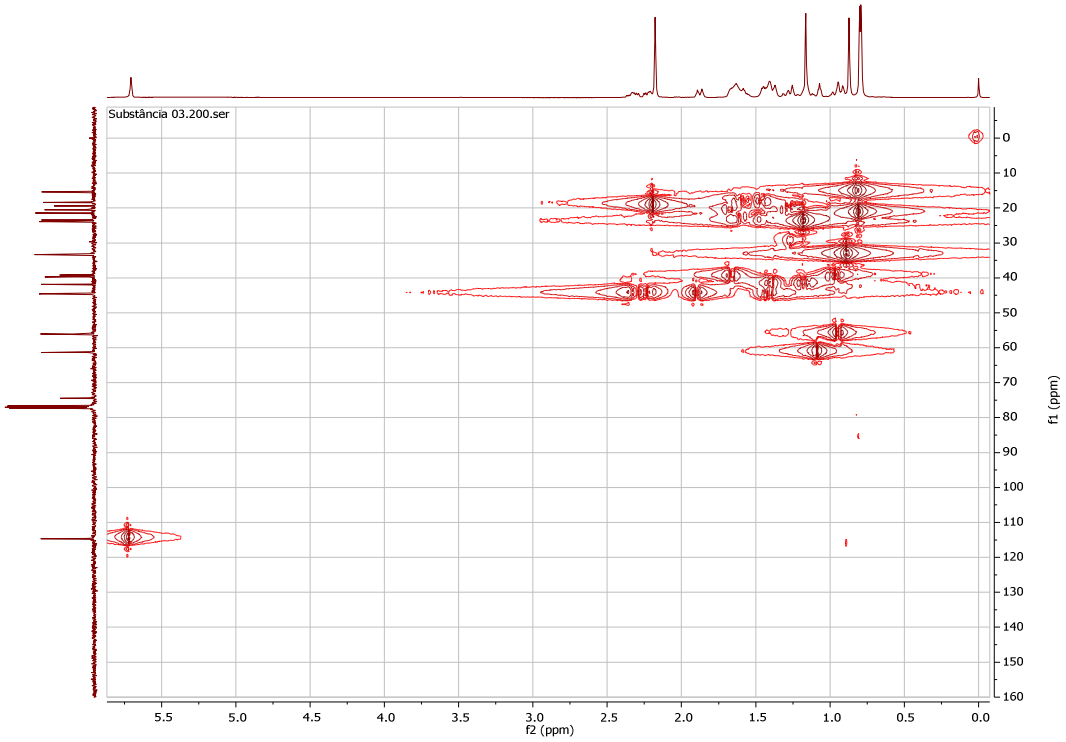
S15. COSY (600 MHz, $CDCl_3$) spectrum of compound **2**



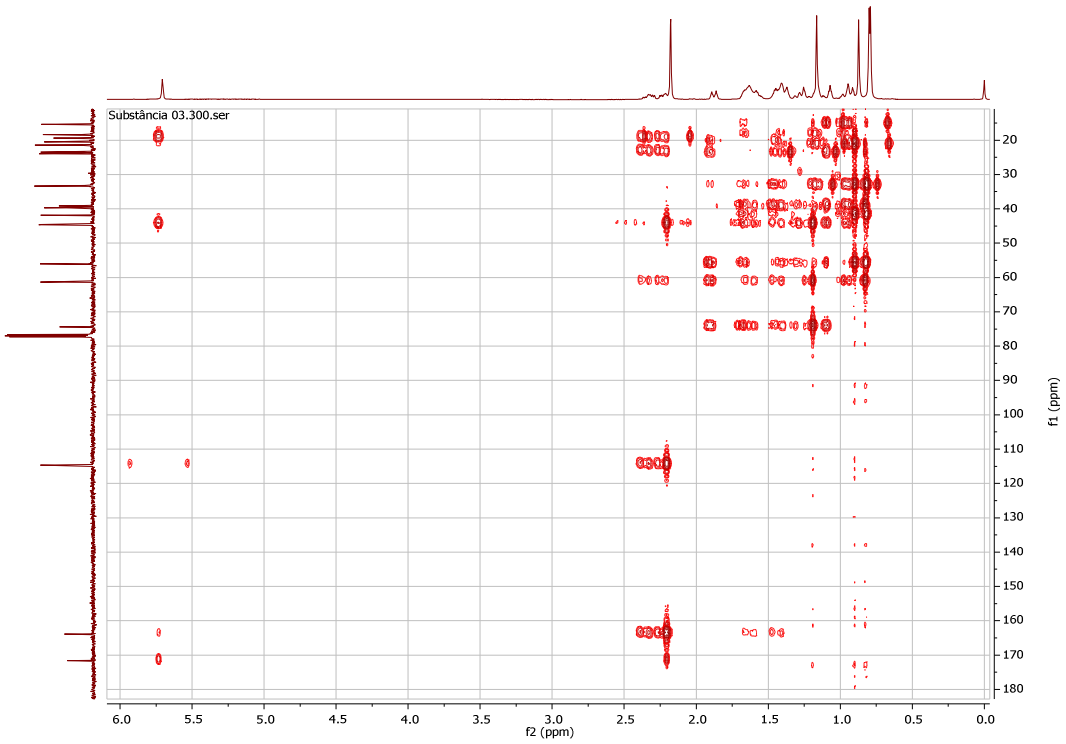
S16. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **2**



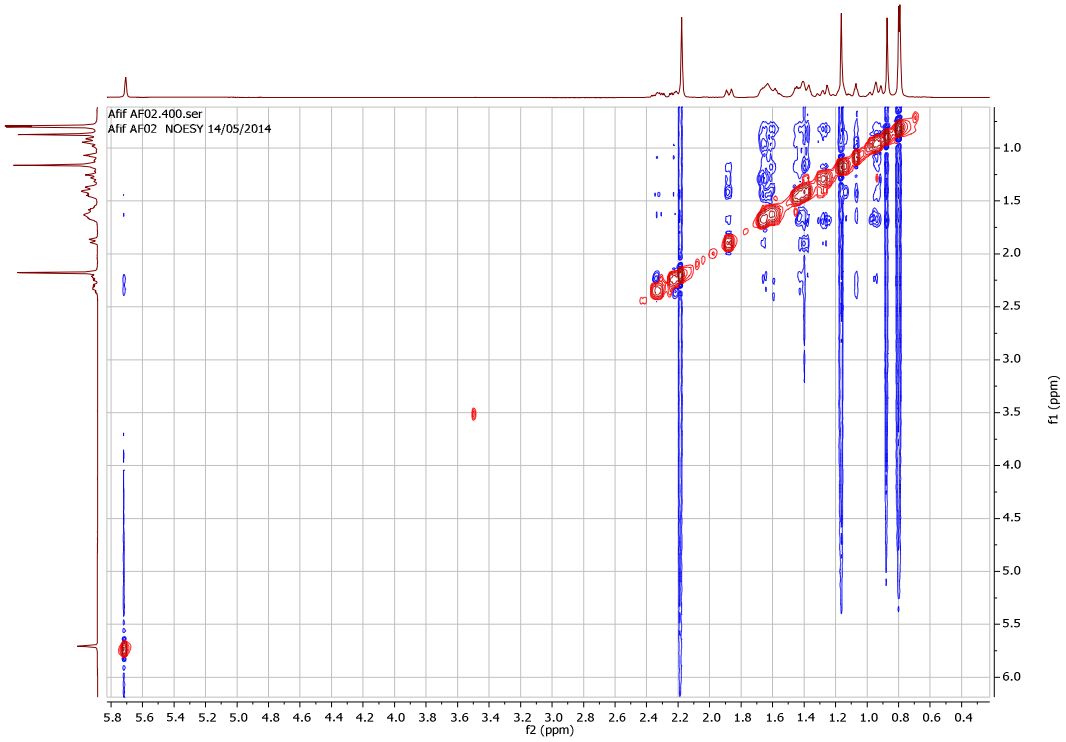
S17. HSQC (400 MHz, $CDCl_3$) spectrum of compound **2**



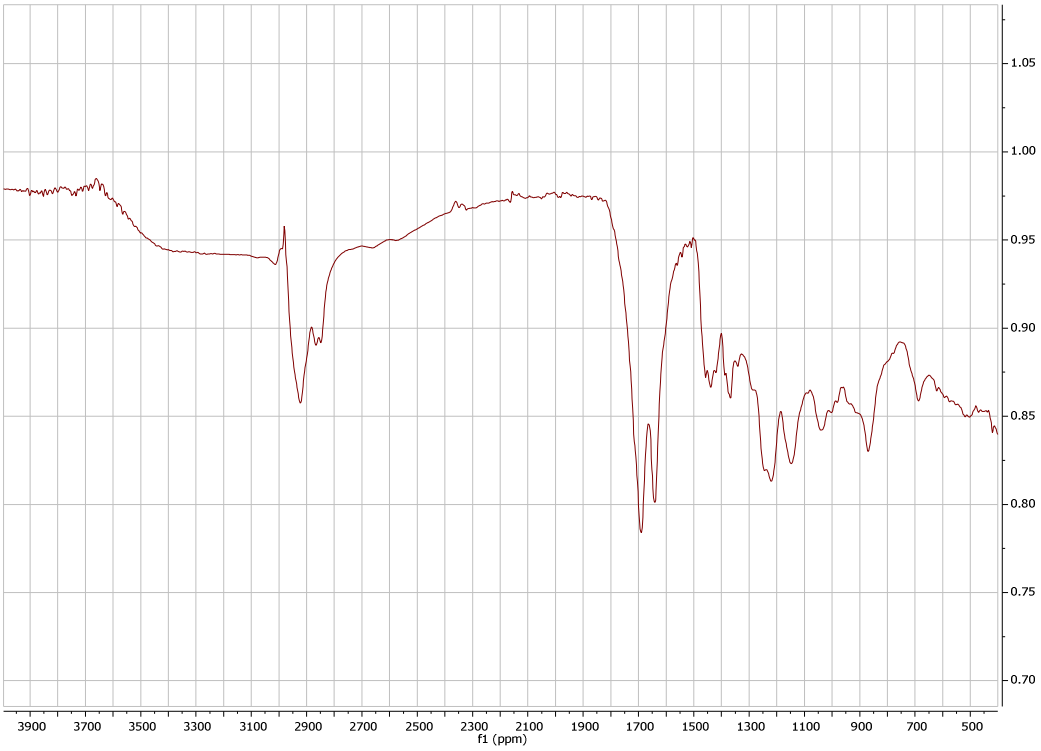
S18. HMBC (400 MHz, $CDCl_3$) spectrum of compound **2**



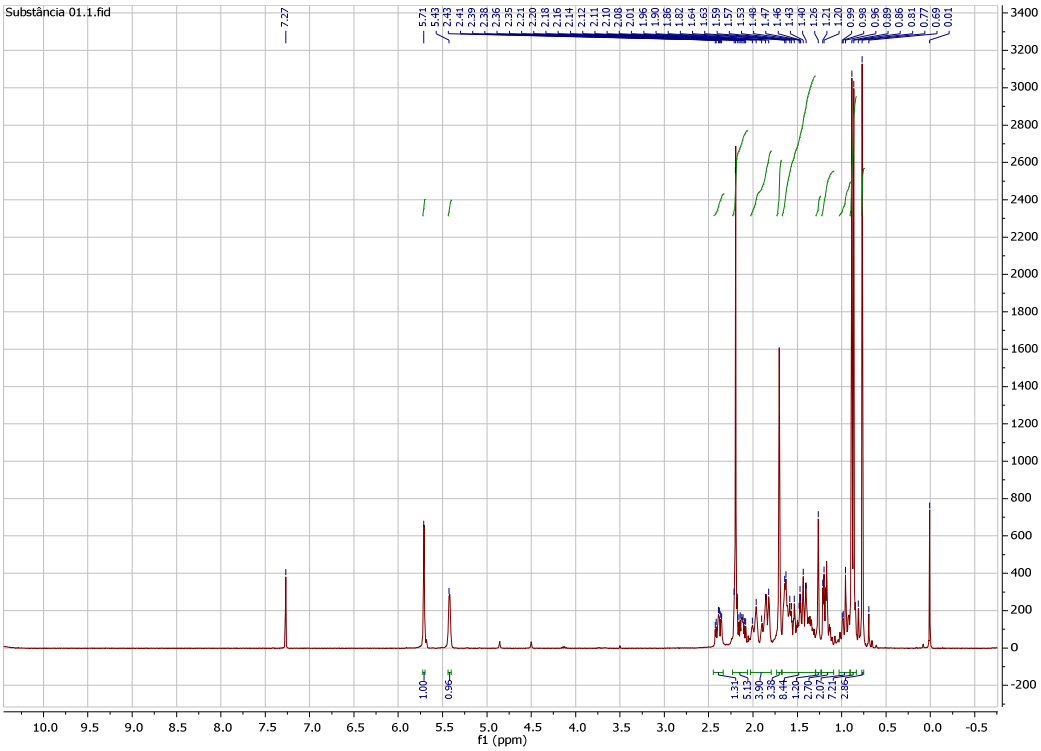
S19. NOESY (600 MHz, $CDCl_3$) spectrum of compound **2**



S20. IR spectrum of compound **3**



S21. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3**



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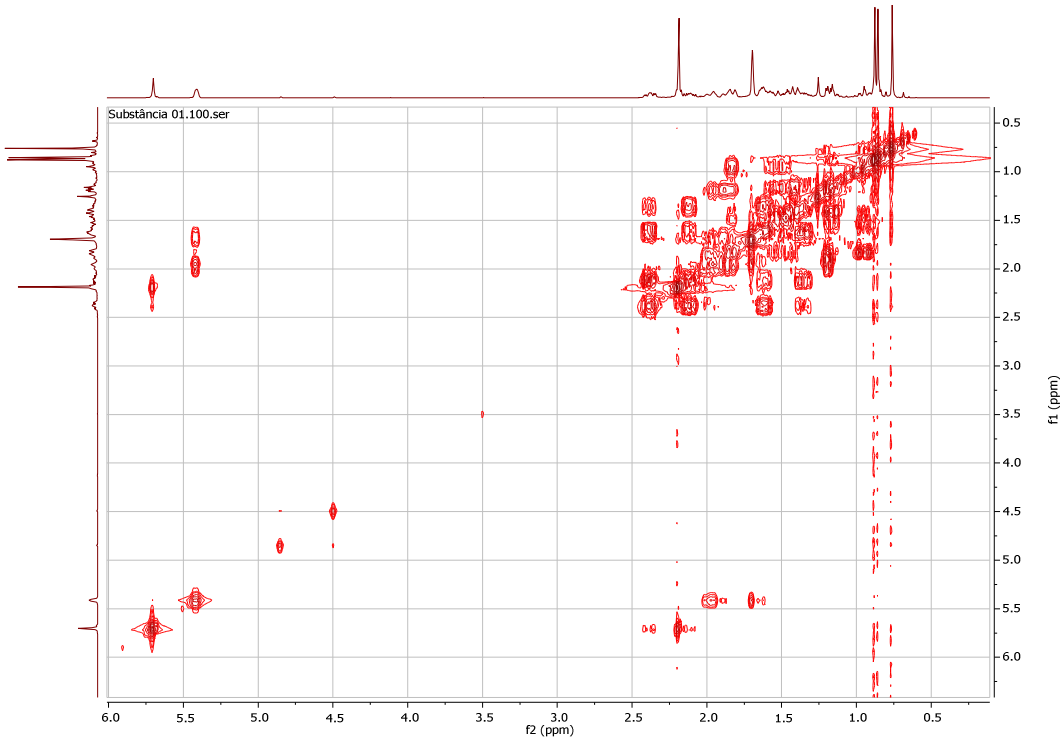
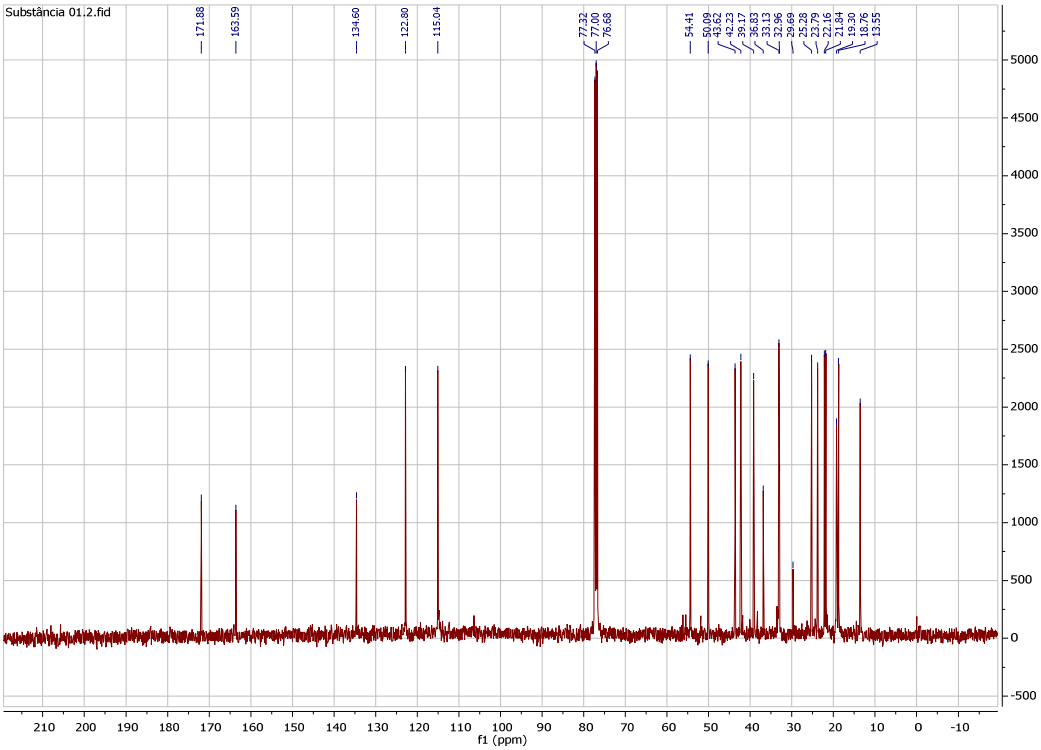
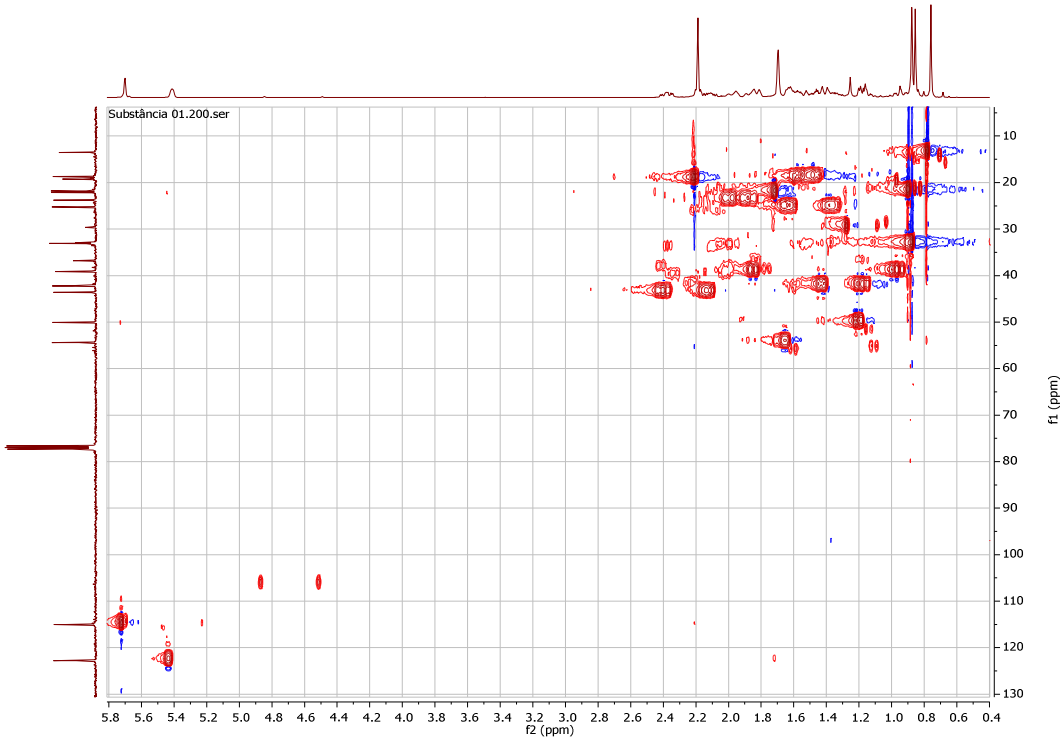


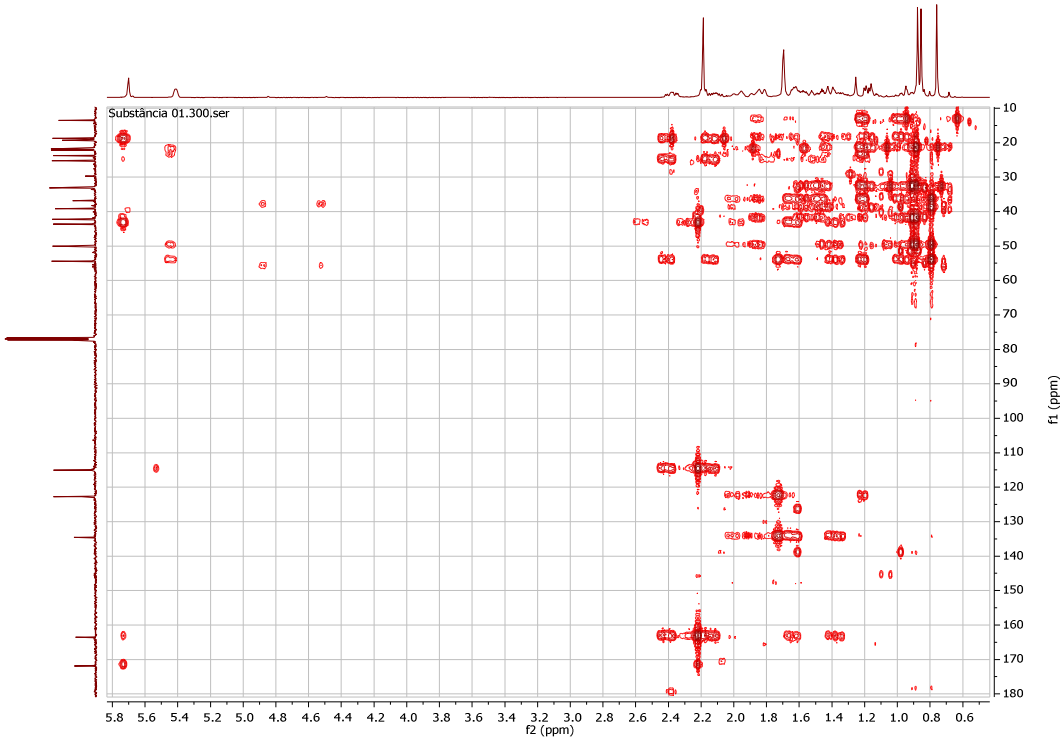
S23. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3**



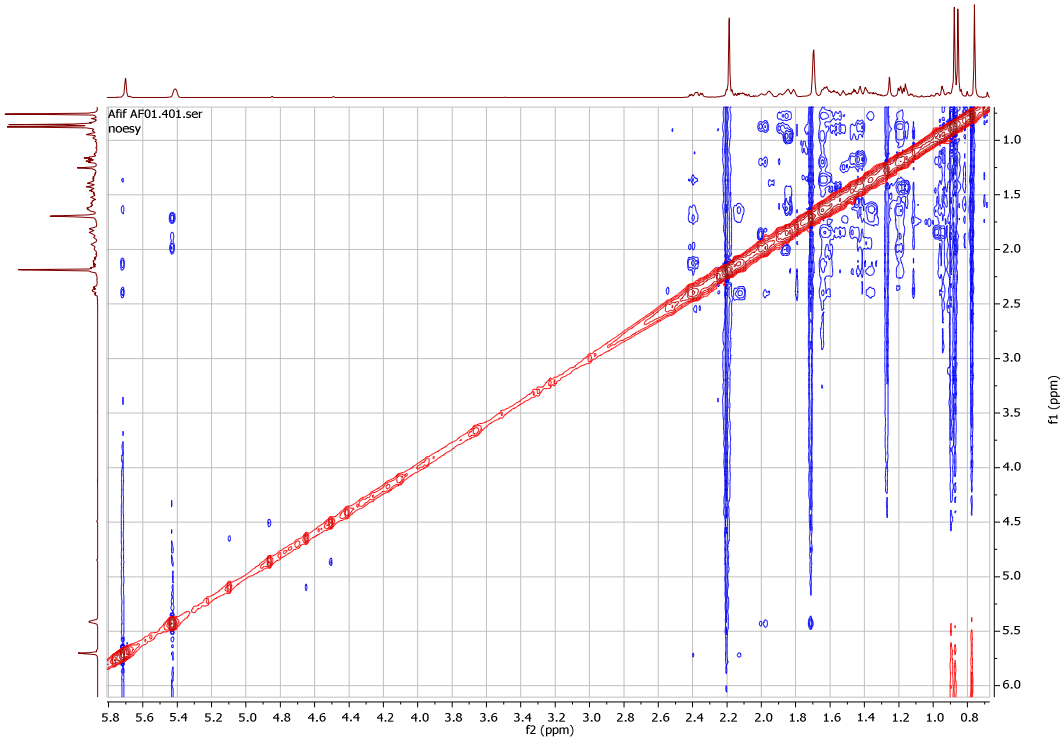
S24. HSQC (400 MHz, $CDCl_3$) spectrum of compound **3**



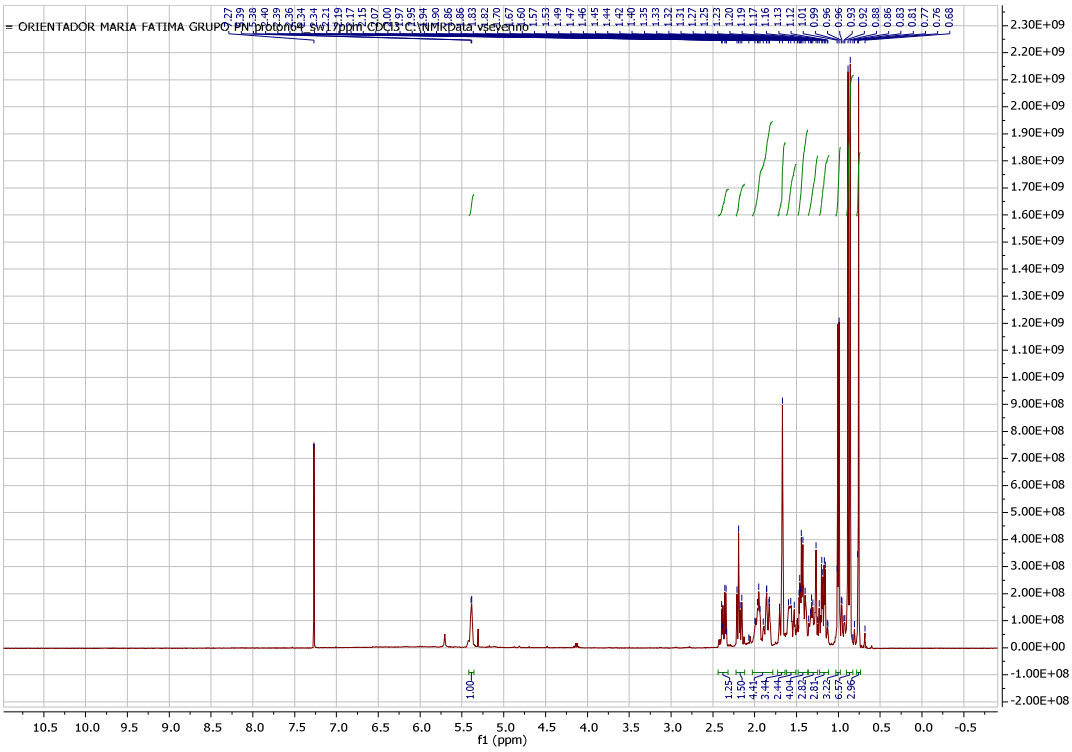
S25. HMBC (400 MHz, $CDCl_3$) spectrum of compound **3**



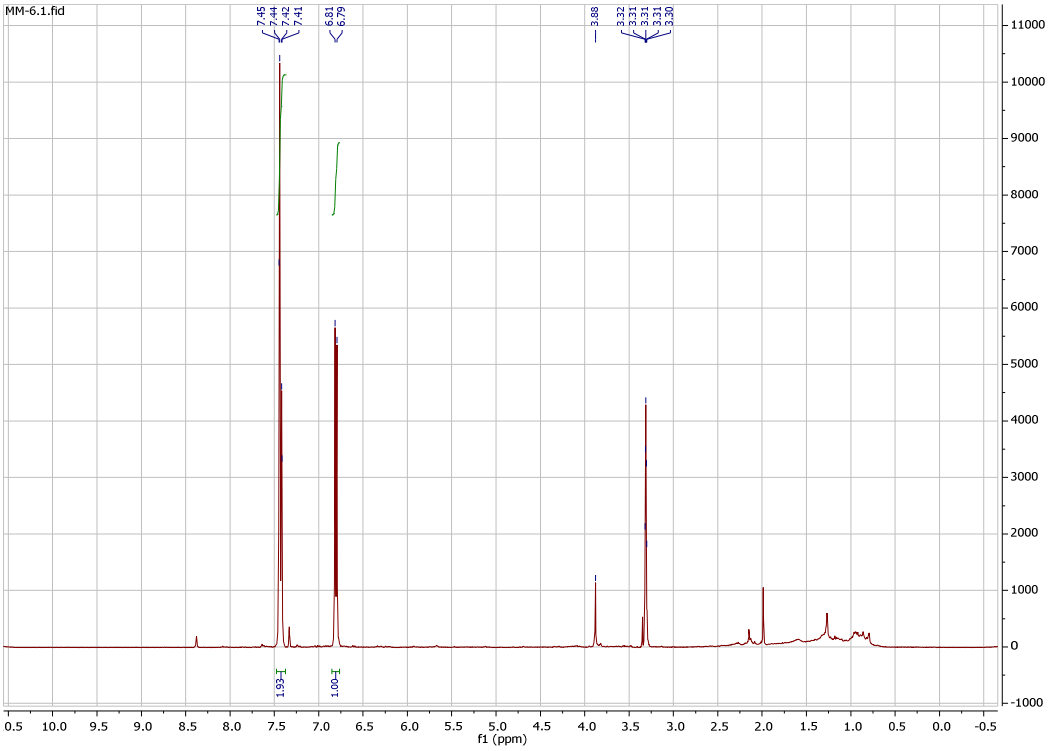
S26. NOESY (600 MHz, $CDCl_3$) spectrum of compound **3**



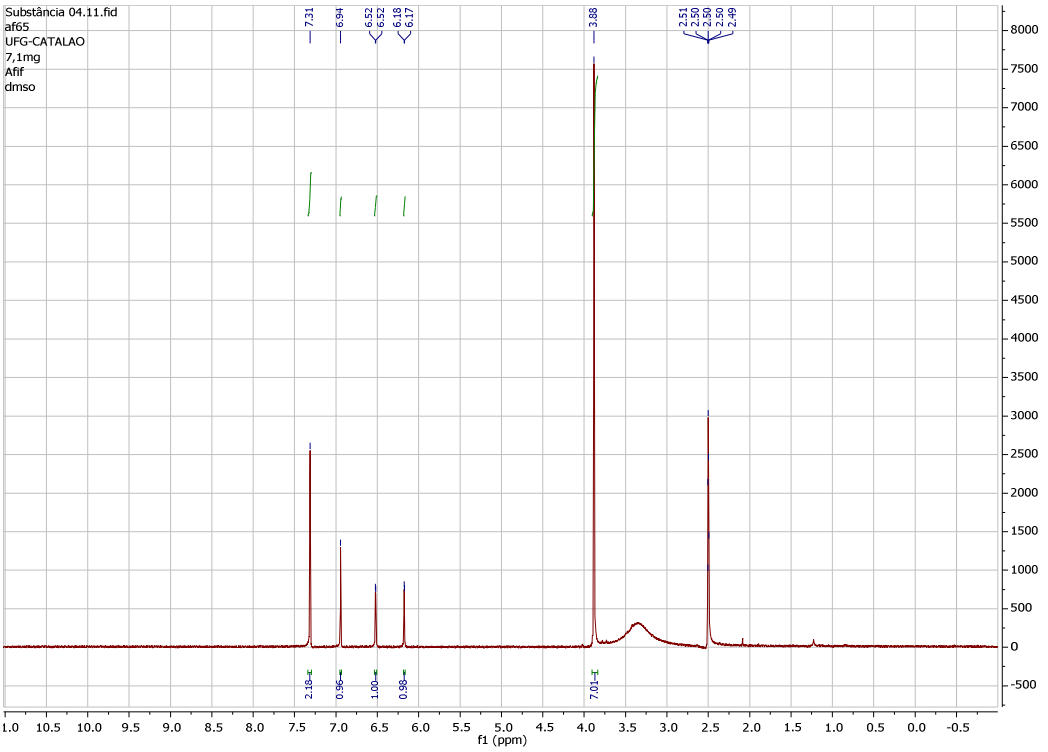
S27. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4**



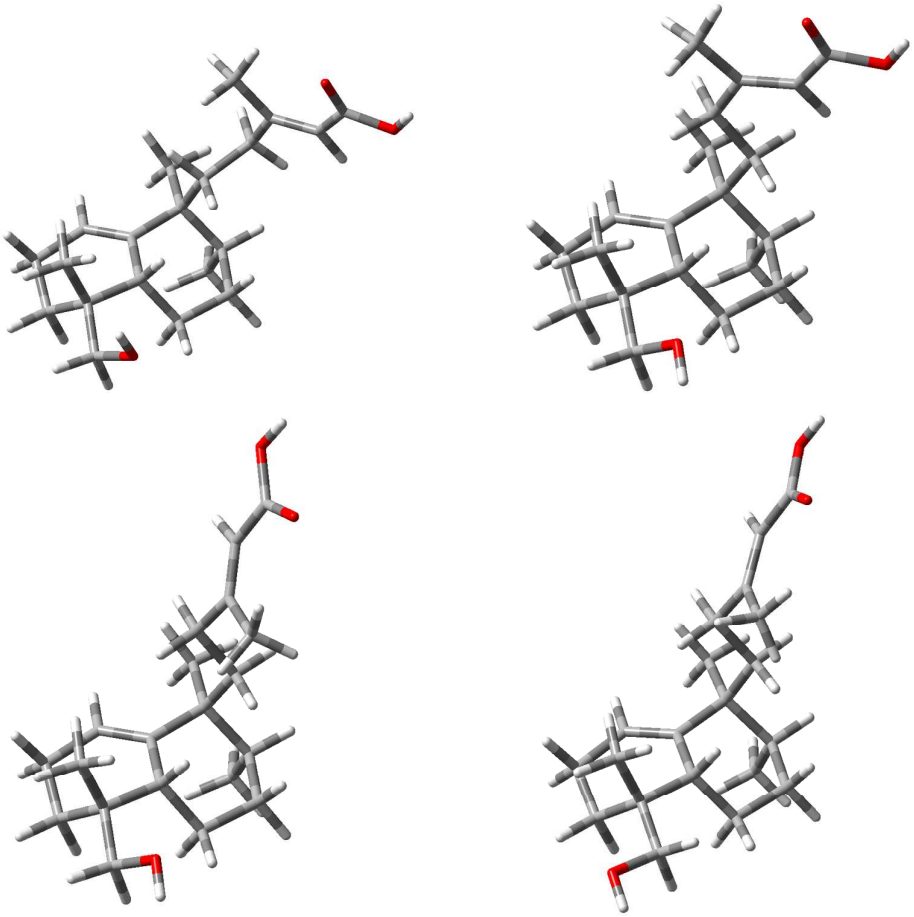
S28. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5**



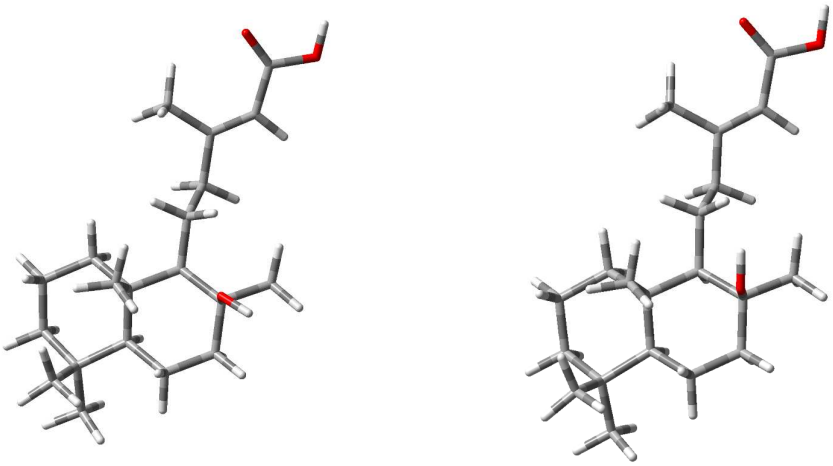
S29. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6**



S30. Structure of the four lowest-energy conformers of (4*R*,5*S*,8*R*,9*S*)-**1** at the B3LYP/PCM(DMSO)/TZVP level used for Raman and ROA calculations



S31. Structure of the two lowest-energy conformers of (5*S*,8*S*,9*R*,10*S*)-**2** at the B3LYP/PCM(DMSO)/TZVP level used for Raman and ROA calculations



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