Electronic Supplementary Information

Two rare meroterpenoidal rotamers from *Ganoderma applanatum*

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1. The ^{13}C NMR calculation of 1 and **2**

Computational Methods

The CONFLEX 7 searches based on molecular mechanics with MMFF94S force fields were performed for model compounds of 3'*R*,6'*R*,7'*S*,10'*S*,11'*R* and 3'*R*,6'*R*,7'*S*,10'*R*,11'*S*. All of the predominant conformers (90%) were optimized by DFT calculation at B3LYP/6-311 G (d, p) level with the PCM in MeOH. All the above calculations were carried out with the Gaussian 09 package of programs. Under the circumstances, the calculation of their ^{13}C NMR chemical shifts at MPW1PW91-SCRF/6-311+G (2d, p) level with the PCM in MeOH was performed. Boltzmann averaging over all accessible conformers according to

$$\overline{\sigma}^x = \frac{\sum_{\text{confSi}} \sigma_i^x g_i \exp(-E_i/RT)}{\sum_{\text{confSi}} g_i \exp(-E_i/RT)}$$

Where $\overline{\sigma}^x$ is the Boltzmann-averaged calculated shielding constant for portion *x*, σ_i^x is the shielding constant for portion *x* in conformer *i*, and *Ei* is the potential energy of conformer *i* (relative to the global minimum) kJ mol^{-1}, obtained from a single-point solvent calculation on the pas-phase structures as discussed previously. *R* is the molar gas constant (8.3145 J K^{-1} mol^{-1}), g_i is the degeneracy of conformer *i*, and the temperature *T* was taken as 298.15 K.

Chemical shifts were then calculated according to

$$\delta_{\text{calc}}^x = \frac{\sigma_{\text{ref}} - \overline{\sigma}^x}{1 - 10^{-6}\sigma_{\text{ref}}}$$

Where δ^x_{calc} is the calculated chemical shift for portion *x* (in ppm), $\overline{\sigma}^x$ is the shielding constant for carbon *x* as calculated above (again in ppm) and σ_{ref} is the shielding constant for the carbon in tetramethylsilane (TMS). This last value was obtained by minimizing TMS in MeOH at the MPW1PW91-SCRF/6-311+G (2d, p) level and calculating the shielding constant for this structure again at the MPW1PW91-SCRF/6-311+G (2d, p) level; the value obtained was σ_{ref} = 188.0549 ppm.

The parameters a and b of the linear regression $\delta_{calcd} = a\delta_{exptl} + b$; the correlation coefficient, R^2; the mean absolute error (MAE) defined as $\Sigma n\ |\delta_{calcd} - \delta_{exptl}|/n$; the corrected mean absolute error (CMAE), defined as $\Sigma n\ |\delta_{corr} - \delta_{exptl}|/n$, where δ_{corr} =

(δ_{calcd} – b)/a and therefore corrects for systematic errors were presented.

Table S1. Comparison of MPW1PW91-SCRF/6-311+G (2d, p) calculated chemical shifts of (3′*R*,6′*R*,7′*S*,10′*S*,11′*R*)-**1** and (3′*R*,6′*R*,7′*S*,10′*R*,11′*S*)-**1** with the ^{13}C NMR experimental data (δ in ppm) of **1** in MeOH.

	1	(3′*R*,6′*R*,7′*S*,10′*S*,11′*R*)-**1**		(3′*R*,6′*R*,7′*S*,10′*R*,11′*S*)-**1**	
No.	δ_{exptl}	δ_{corr}	$\Delta\delta_C$[a]	δ_{corr}	$\Delta\delta_C$[a]
1	156.4	157.8	1.4	161.5	5.1
2	120.0	119.3	0.7	121.8	1.8
3	115.3	115.3	0.0	118.2	2.9
4	150.8	148.8	2.0	152.4	1.6
5	126.5	125.5	1.0	128.5	2.0
6	119.9	118.8	1.1	121.3	1.4
1′	205.1	206.3	1.2	211.4	6.3
2′	45.4	42.6	2.8	44.5	0.9
3′	54.3	56.5	2.2	57.9	3.6
4′	35.8	32.0	3.8	32.2	3.6
5′	31.5	34.5	3.0	36.3	4.8
6′	74.7	78.9	4.2	81.4	6.7
7′	55.6	62.5	6.9	65.1	9.5
8′	68.9	67.4	1.5	68.5	0.4
9′	185	186.2	1.2	191.3	6.3
10′	106.8	104.2	2.6	107.2	0.4
11′	77.8	77.2	0.6	77.7	0.1
12′	67.7	65.7	2.0	66.9	0.8
13′	62.2	60.3	1.9	61.1	1.1
CMAE			2.1		3.1

[a]$\Delta\delta_C = |\delta_{corr} - \delta_{exptl}|$

Table S2. Comparison of MPW1PW91-SCRF/6-311+G (2d, p) calculated chemical shifts of (3′*R*,6′*R*,7′*S*,10′*S*,11′*R*)-**2** and (3′*R*,6′*R*,7′*S*,10′*R*,11′*S*)-**2** with the ^{13}C NMR experimental data (δ in ppm) of **2** in MeOH.

	2	(3′*R*,6′*R*,7′*S*,10′*S*,11′*R*)-**2**		(3′*R*,6′*R*,7′*S*,10′*R*,11′*S*)-**2**	
No.	δ_{exptl}	δ_{corr}	$\Delta\delta_C$[a]	δ_{corr}	$\Delta\delta_C$[a]
1	156.4	157.8	1.4	157.7	1.3
2	120.1	119.3	0.8	118.9	1.2
3	115.3	115.4	0.1	115.5	0.2
4	150.8	148.8	2.0	148.8	2.0
5	126.3	125.6	0.7	125.5	0.8
6	119.9	118.9	1.0	118.5	1.4
1′	205.1	206.2	1.1	206.3	1.2
2′	45.3	42.7	2.6	43.6	1.7
3′	54.5	56.7	2.2	56.6	2.1
4′	35.6	32.2	3.4	31.6	4.0
5′	31.9	34.7	2.8	35.6	3.7
6′	74.9	79.0	4.1	79.5	4.6
7′	55.5	62.7	7.2	63.7	8.2
8′	68.8	67.5	1.3	67.0	1.8
9′	185	186.1	1.1	186.8	1.8
10′	106.8	104.3	2.5	104.8	2.0
11′	78.2	77.3	0.9	76.0	2.2
12′	67.6	65.8	1.8	65.5	2.1
13′	63.6	60.4	3.2	59.8	3.8
CMAE			2.1		2.4

[a] $\Delta\delta_C = |\delta_{corr} - \delta_{exptl}|$

2. HPLC peak areas of a mixture of (–)-1 and (–)-2 at varied temperatures

Table S3. HPLC peak areas of a mixture of (–)-**1** and (–)-**2** at varied temperatures

Temperature	(–)-**1**	(–)-**2**	Proportion
15 °C	11233	4312	2.6:1
30 °C	11665	4477	2.6:1
45 °C	11598	4530	2.6:1

3. Supplementary Figures

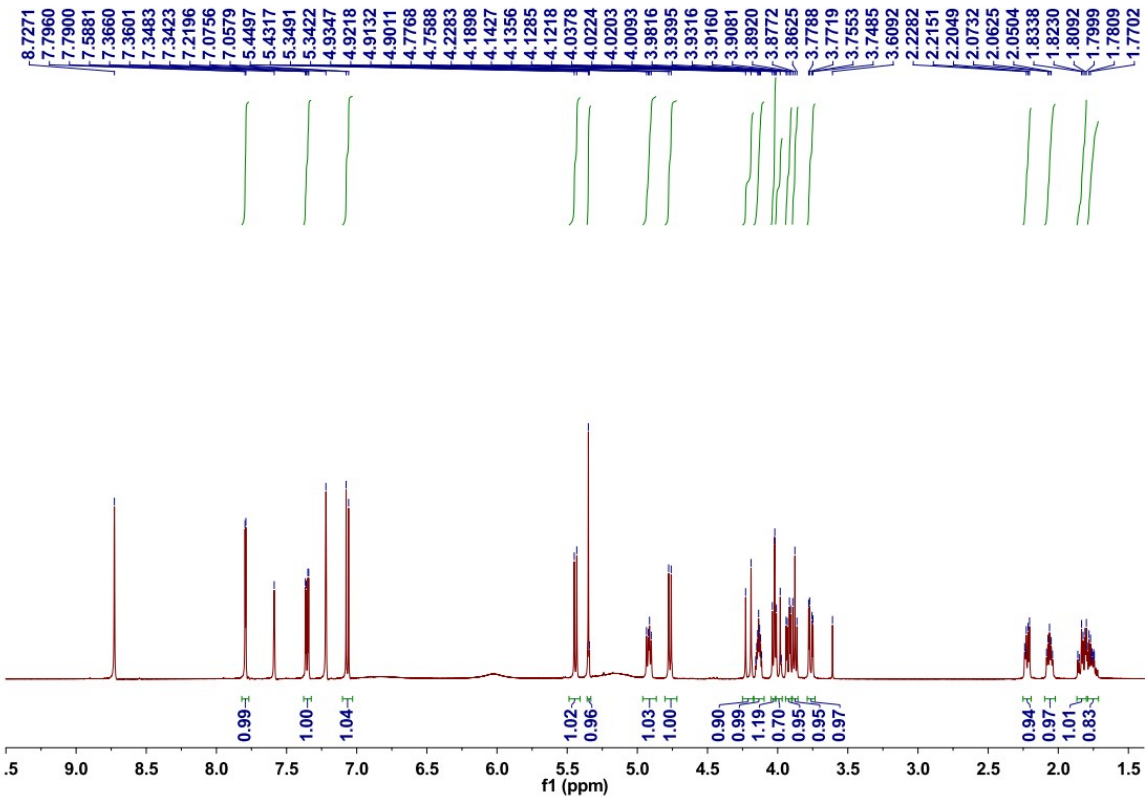


Figure S1. ^{1}H NMR spectrum of **1** in pyridine-d_5

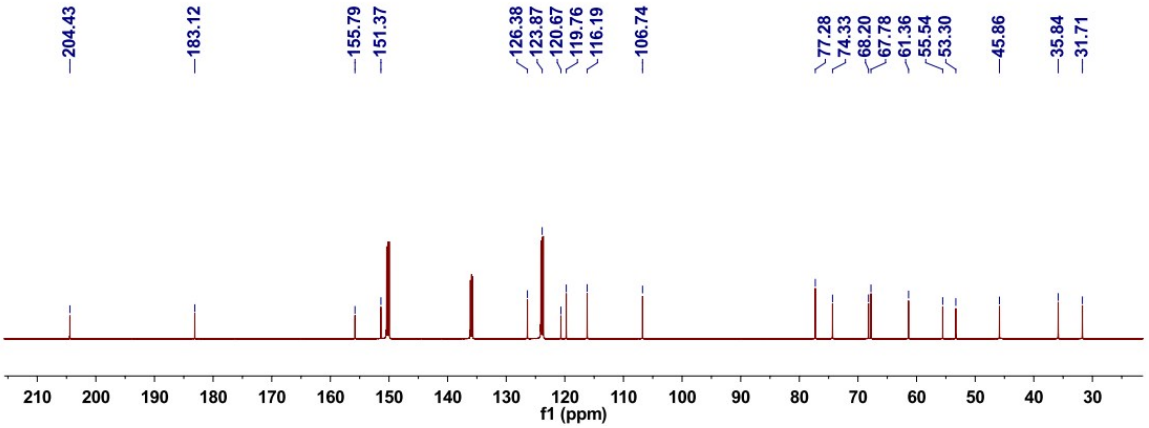


Figure S2. ^{13}C NMR spectrum of **1** in pyridine-d_5

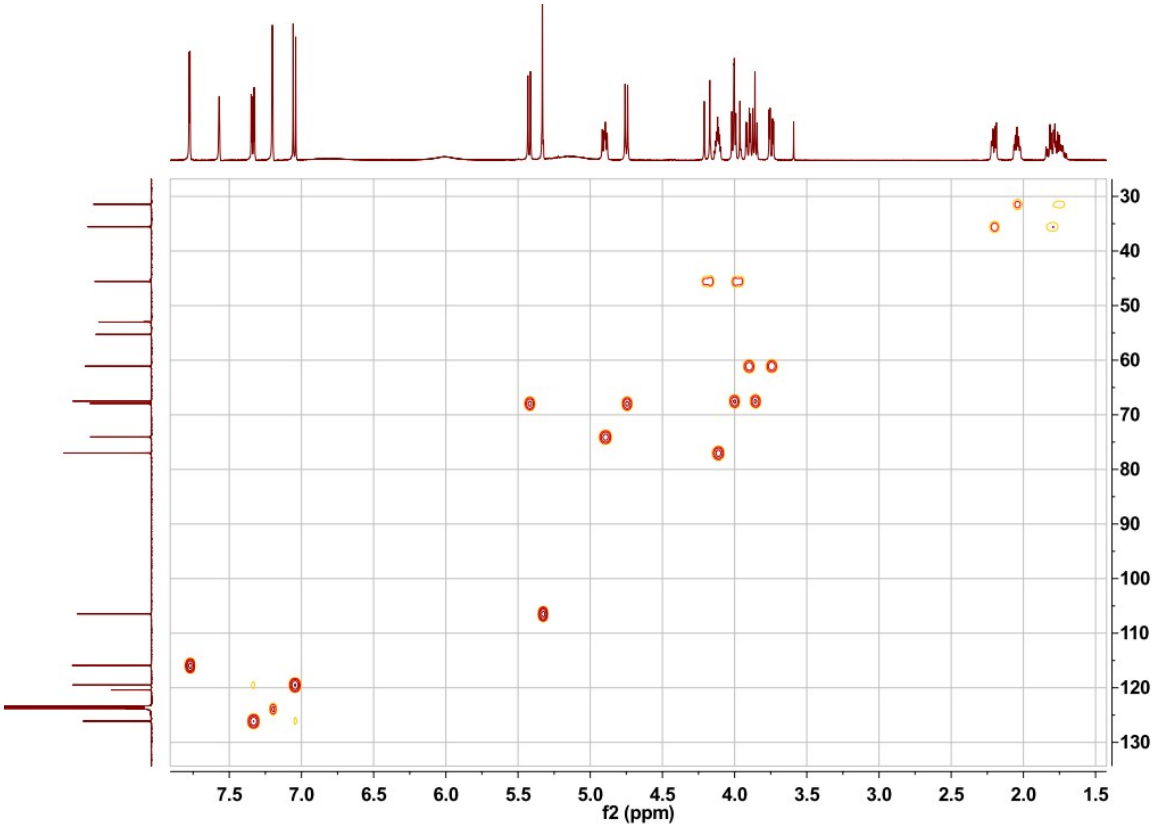


Figure S3. HSQC spectrum of **1** in pyridine-d_5

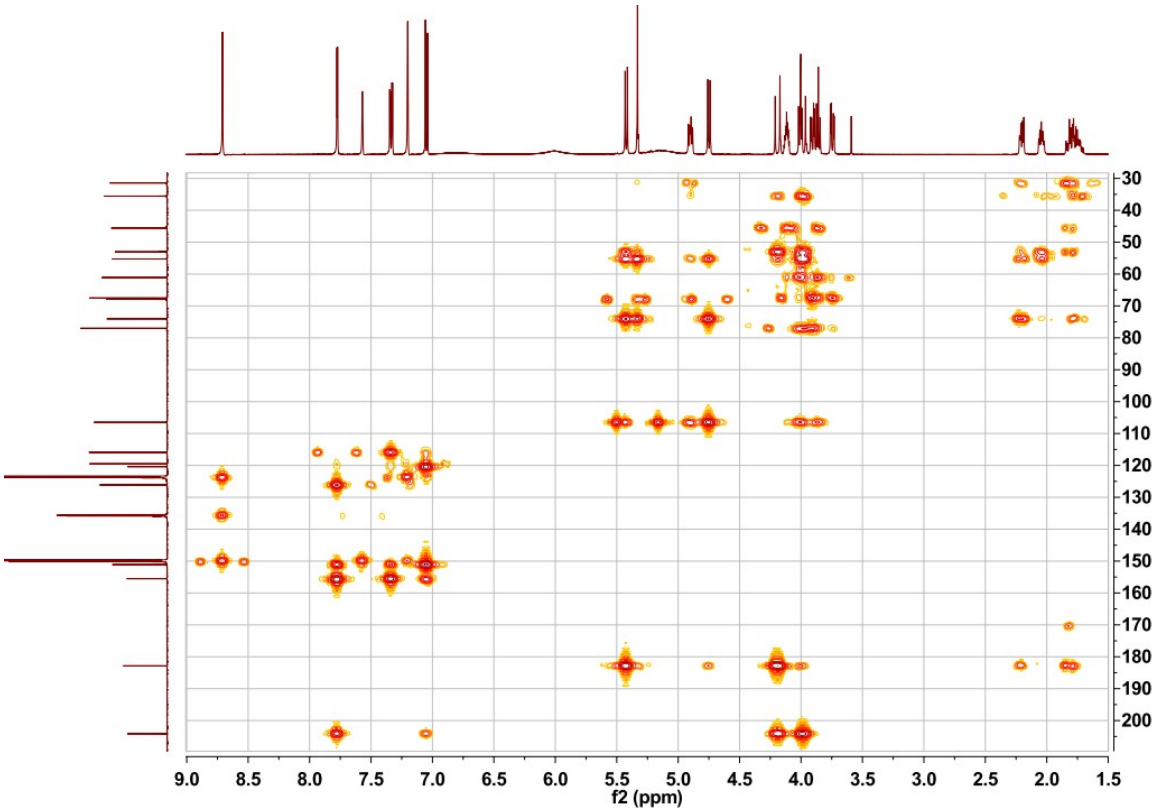


Figure S4. HMBC spectrum of **1** in pyridine-d_5

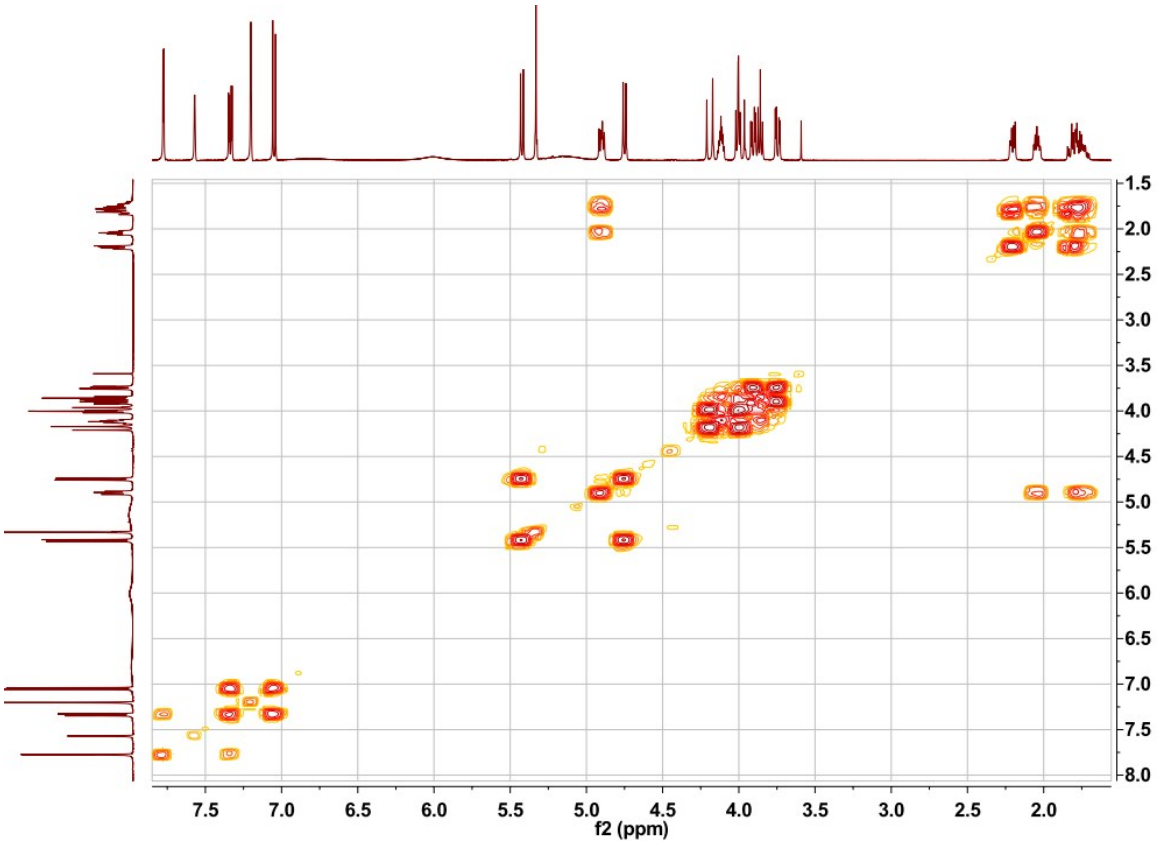


Figure S5. ^{1}H-^{1}H COSY spectrum of **1** in pyridine-d_5

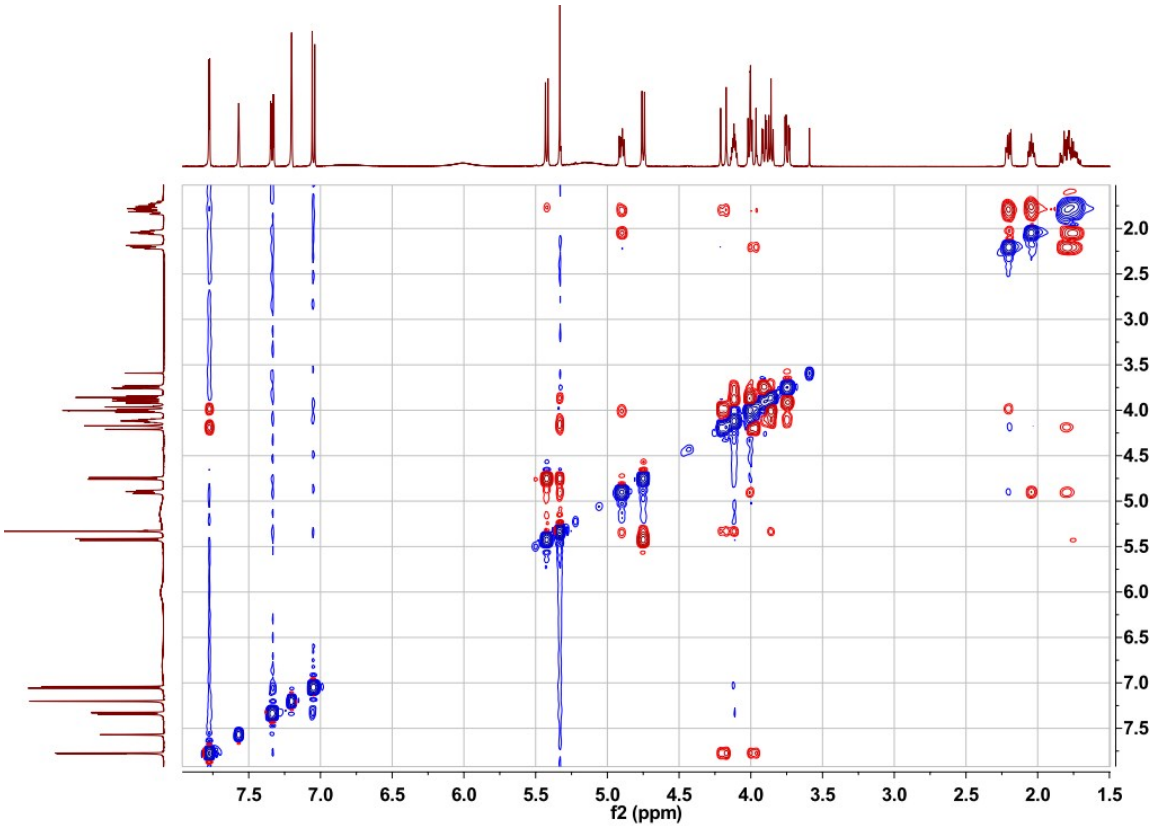


Figure S6. ROESY spectrum of **1** in pyridine-d_5

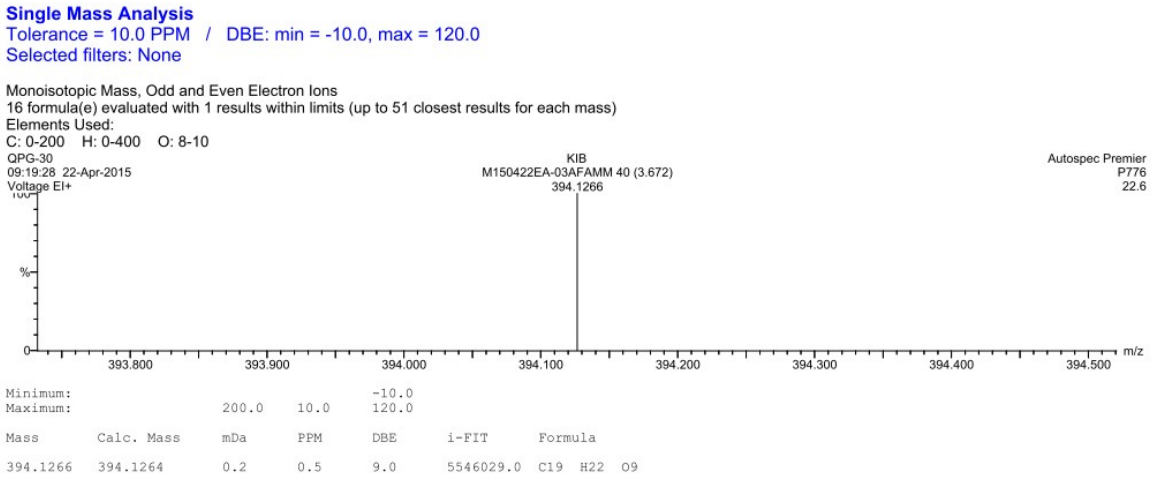


Figure S7. HREIMS spectrum of **1**

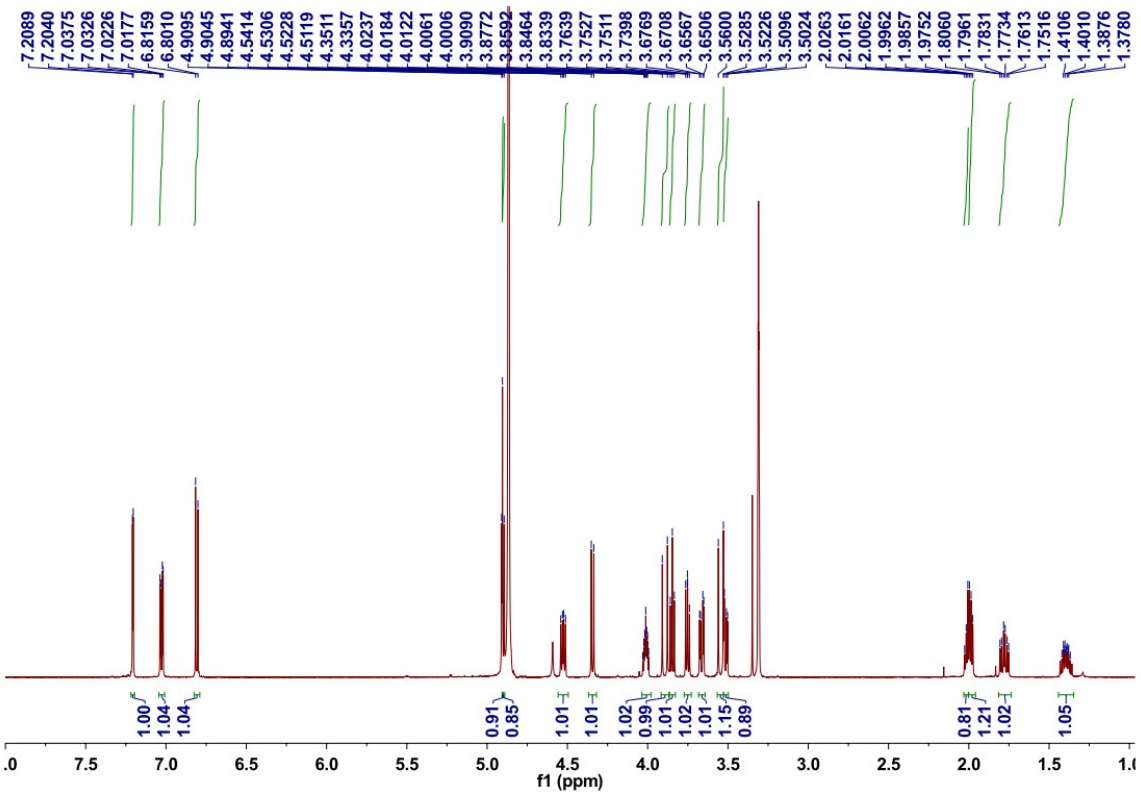


Figure S8. ^{1}H NMR spectrum of **1** in methanol-d_4

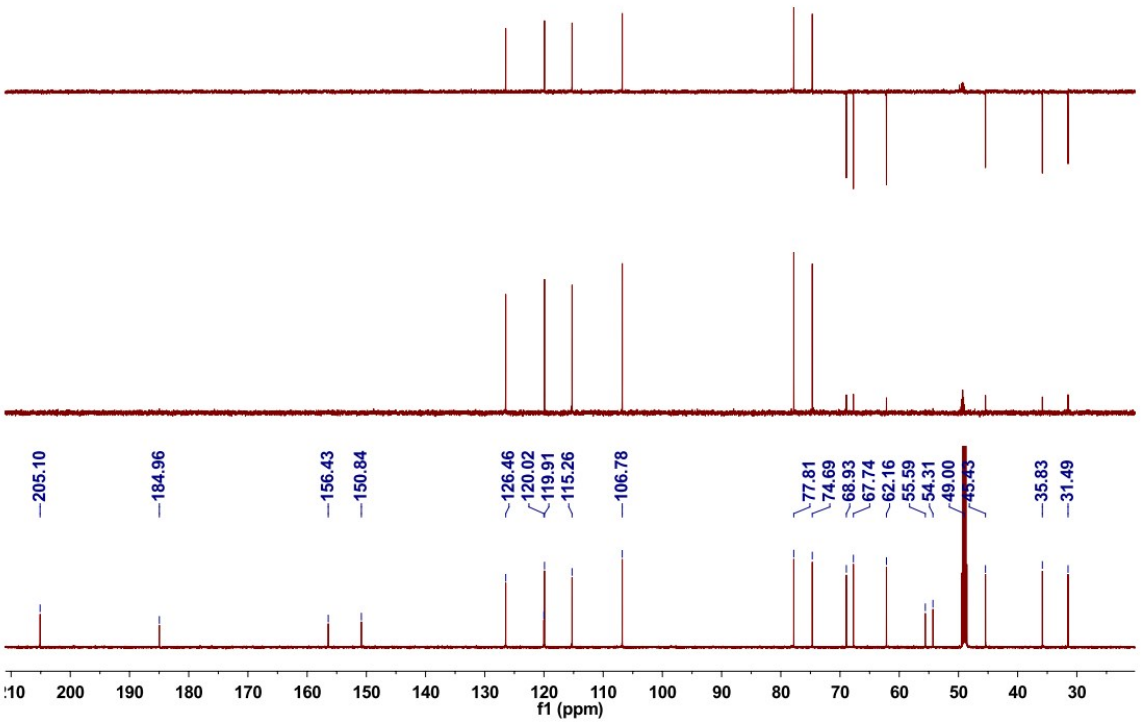


Figure S9. ^{13}C NMR and DEPT spectra of **1** in methanol-d_4

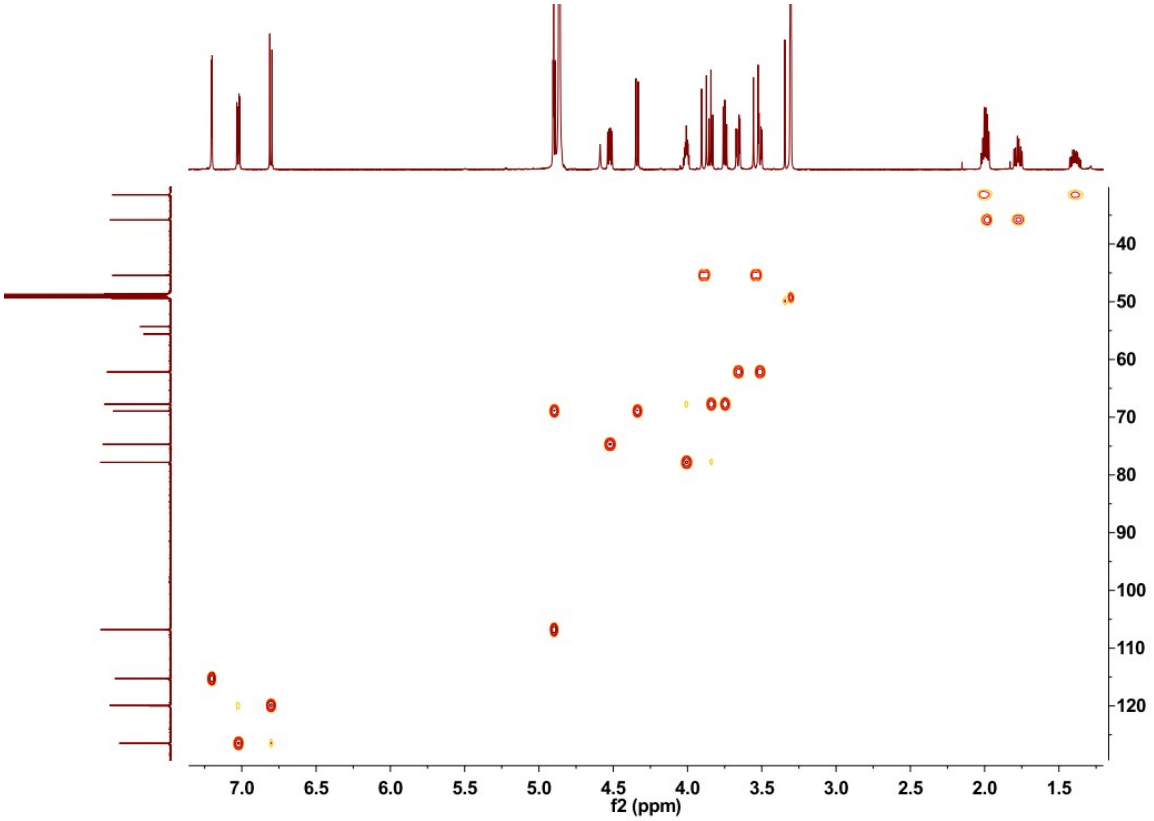


Figure S10. HSQC spectrum of **1** in methanol-d_4

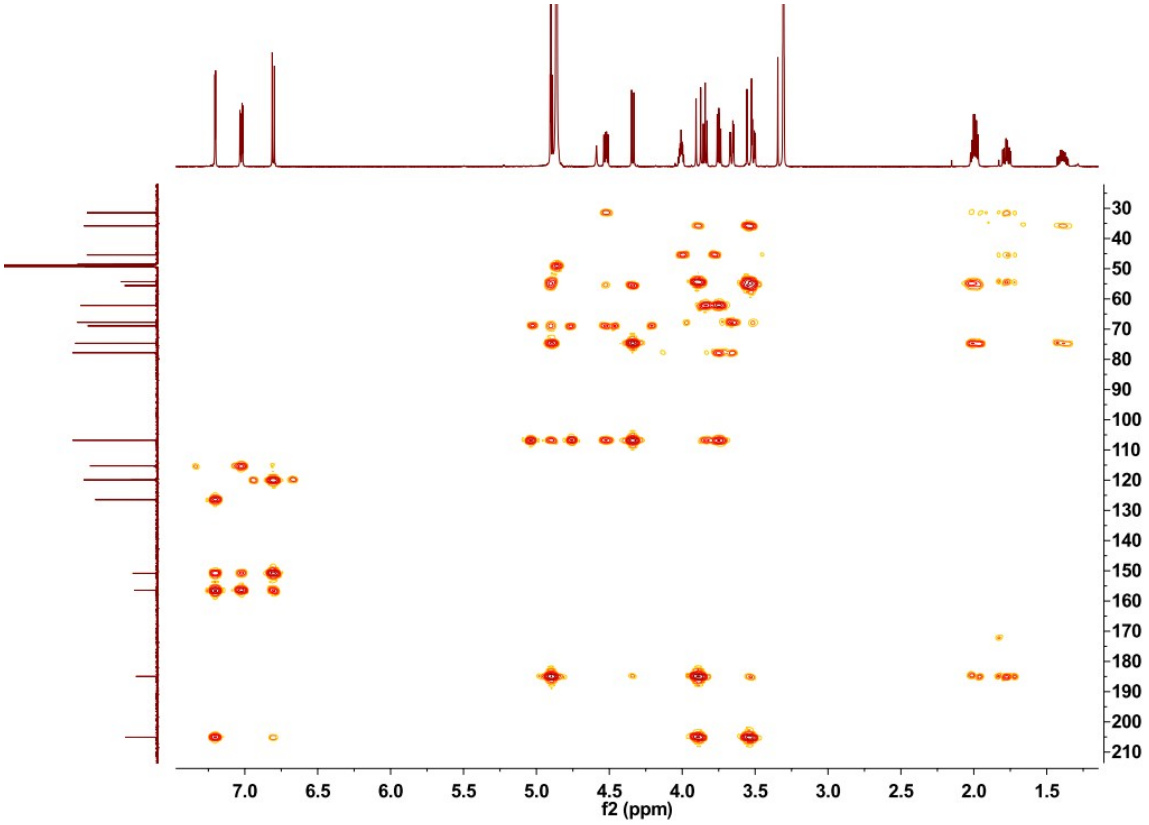


Figure S11. HMBC spectrum of **1** in methanol-d_4

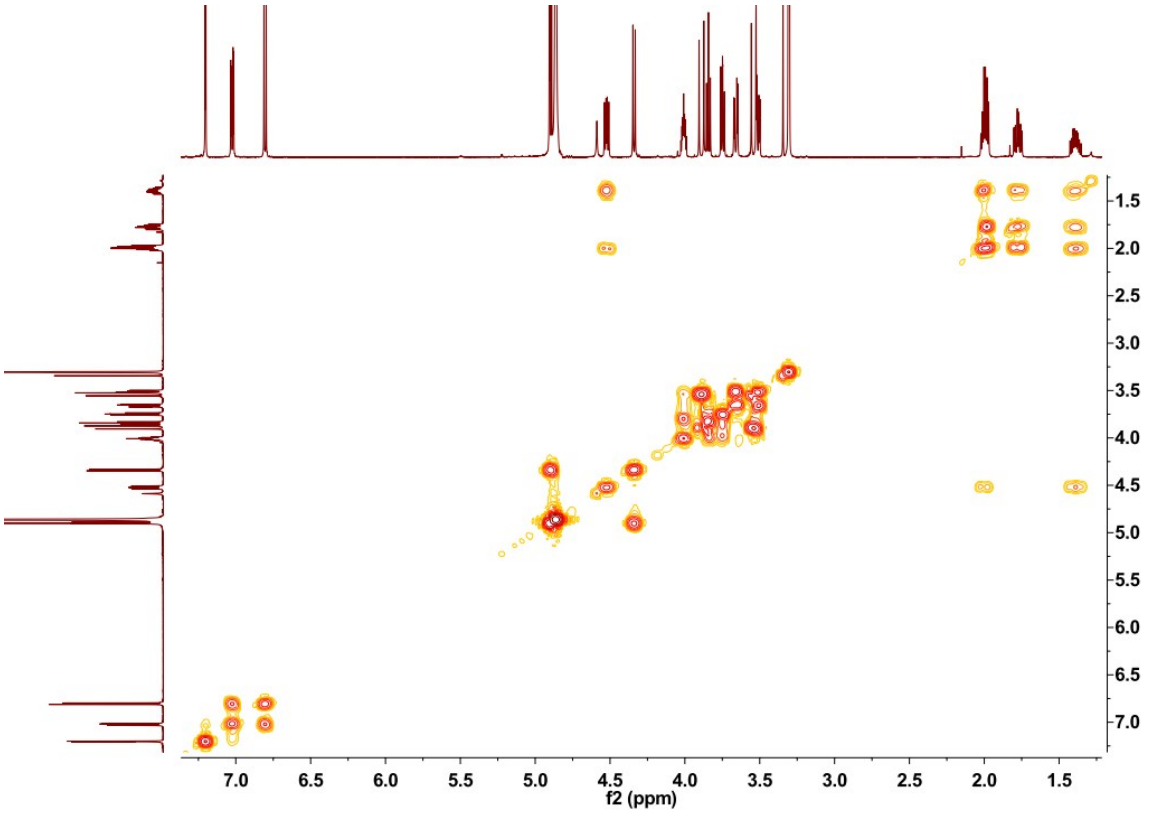


Figure S12. ^{1}H-^{1}H COSY spectrum of **1** in methanol-d_4

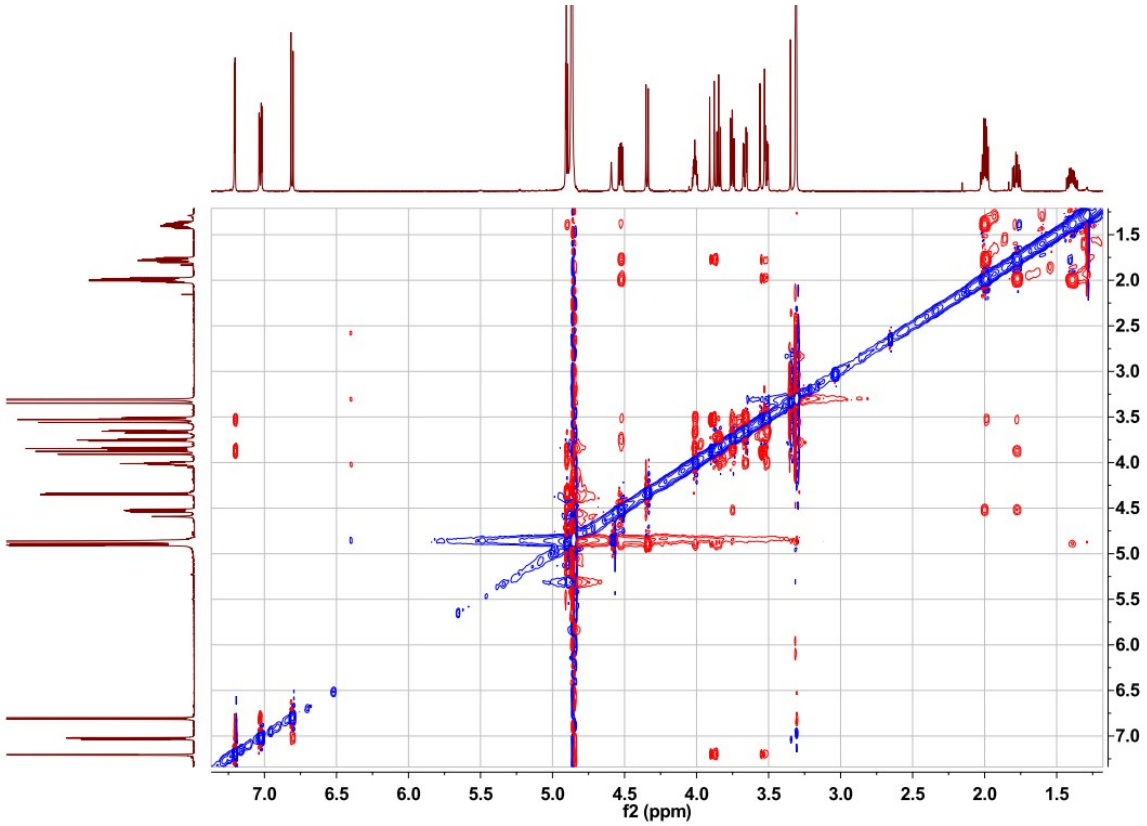


Figure S13. ROESY spectrum of **1** in methanol-d_4

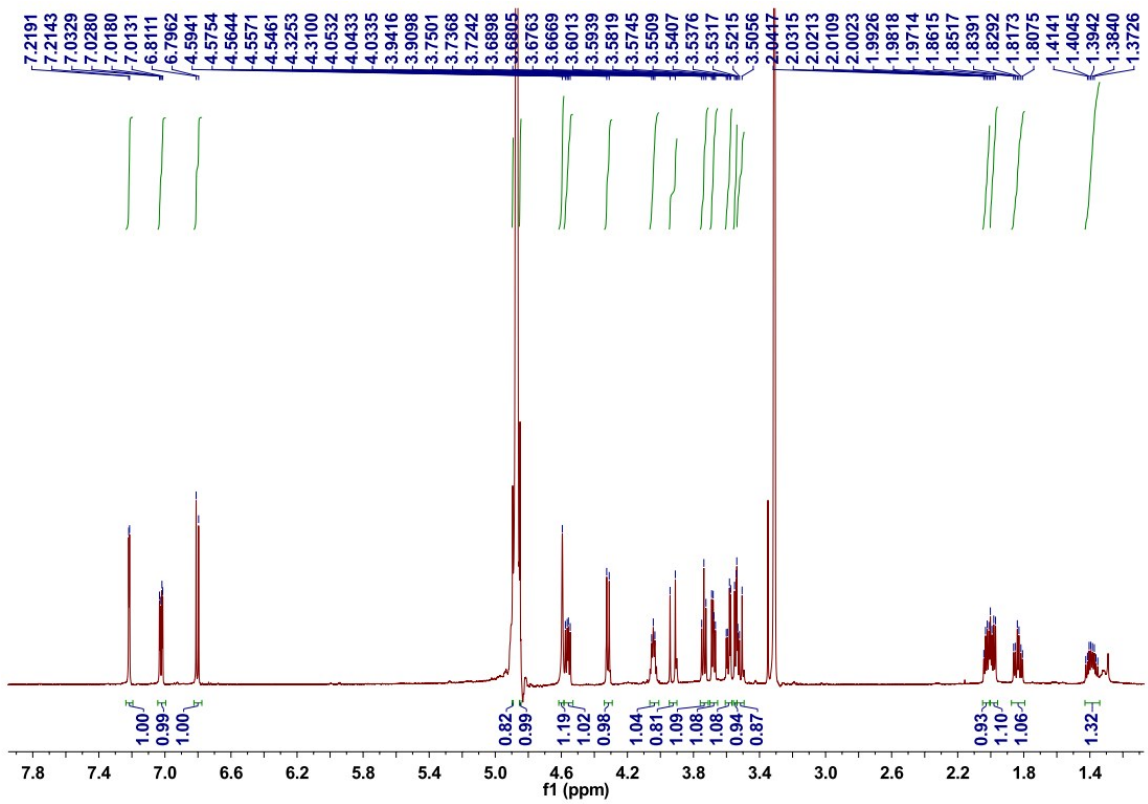


Figure S14. ^{1}H NMR spectrum of **2** in methanol-d_4

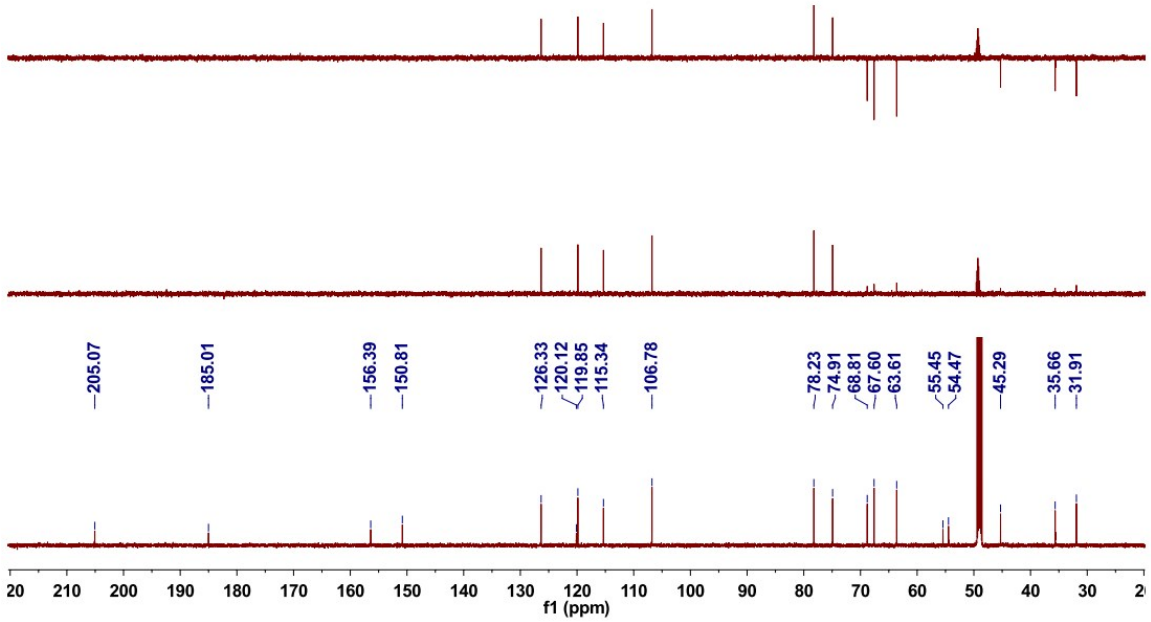


Figure S15. ^{13}C NMR and DEPT spectra of **2** in methanol-d_4

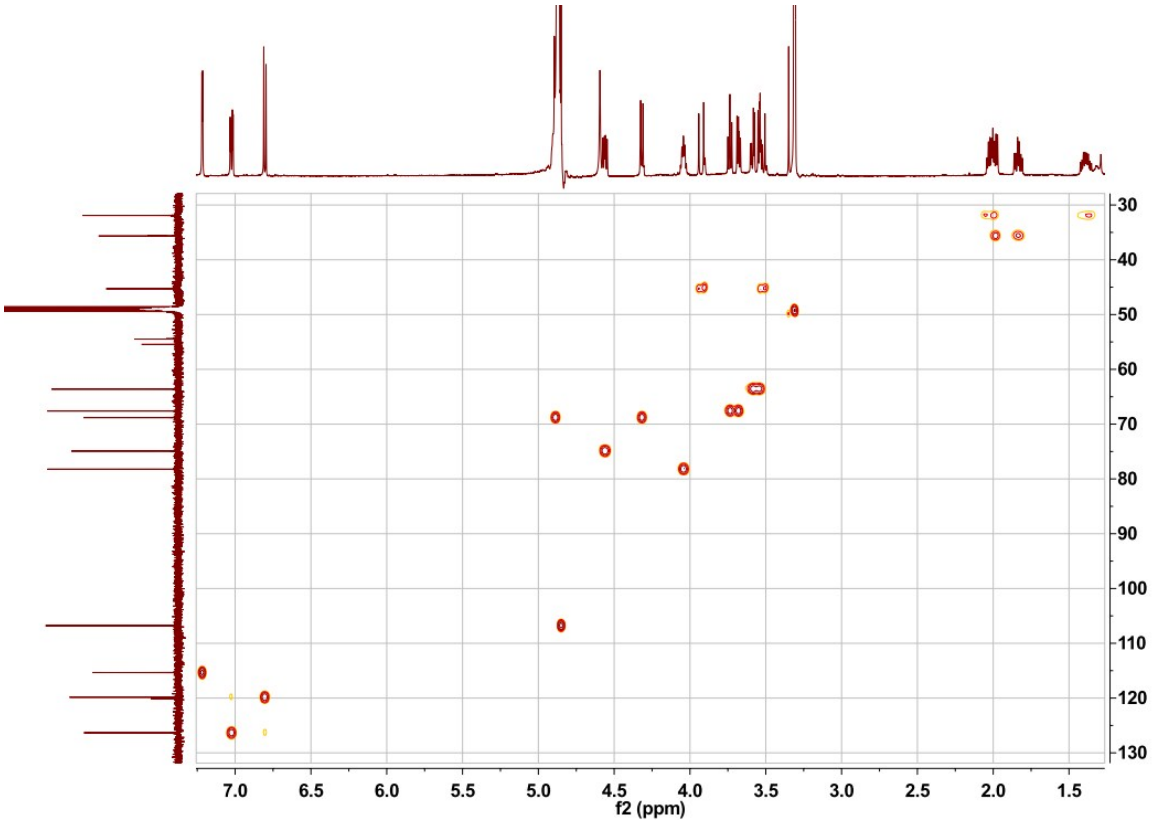


Figure S16. HSQC spectrum of **2** in methanol-d_4

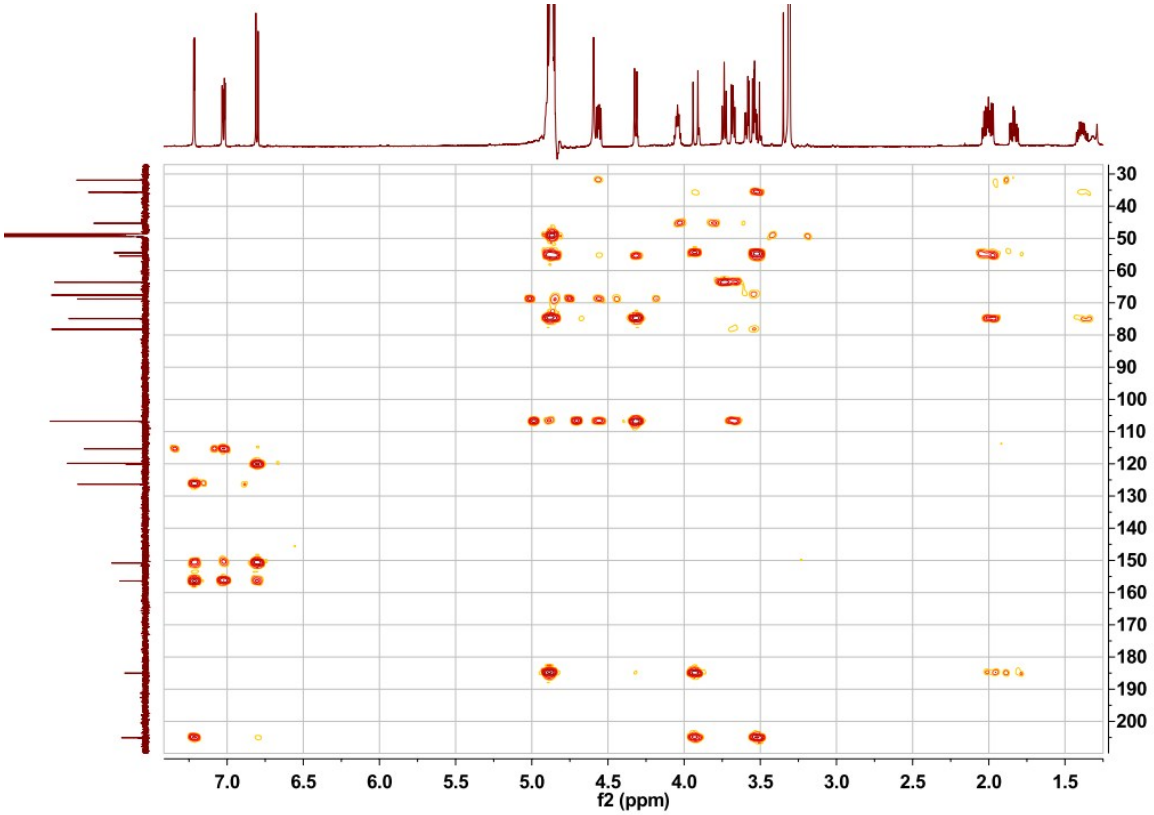


Figure S17. HMBC spectrum of **2** in methanol-d_4

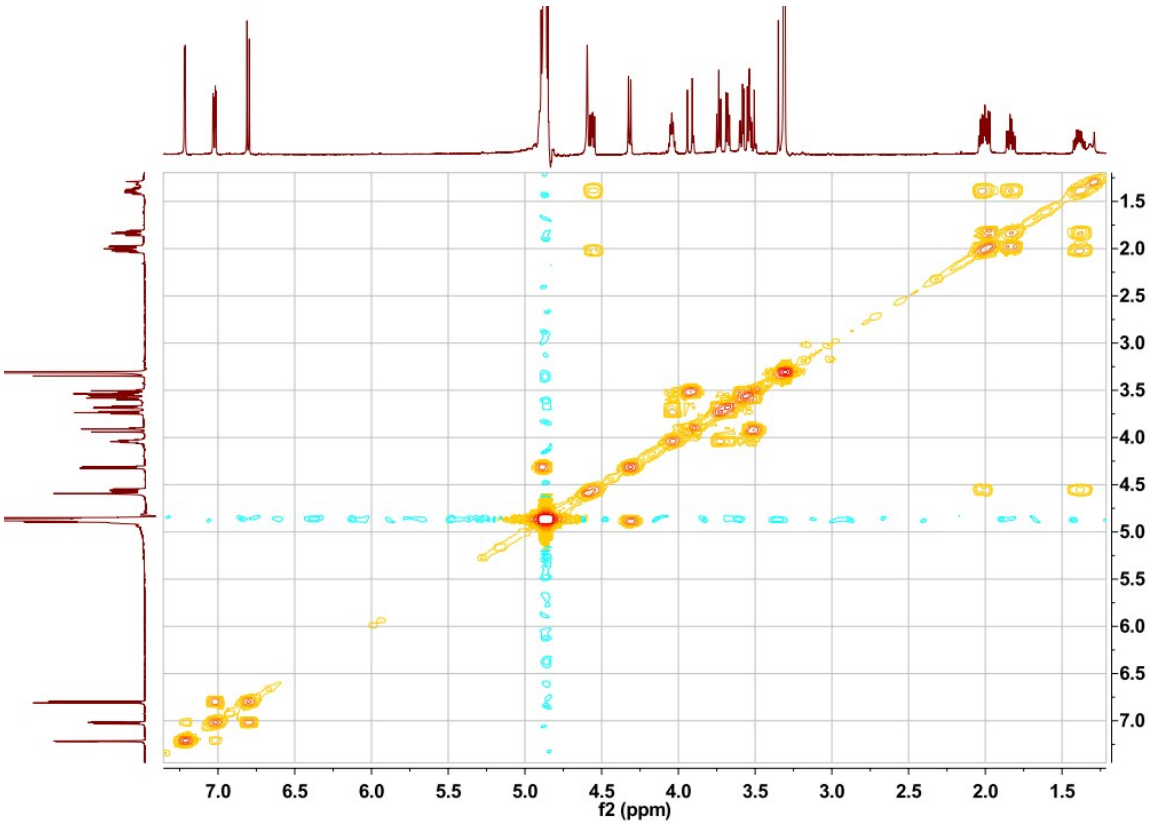


Figure S18. ^{1}H-^{1}H COSY spectrum of **2** in methanol-d_4

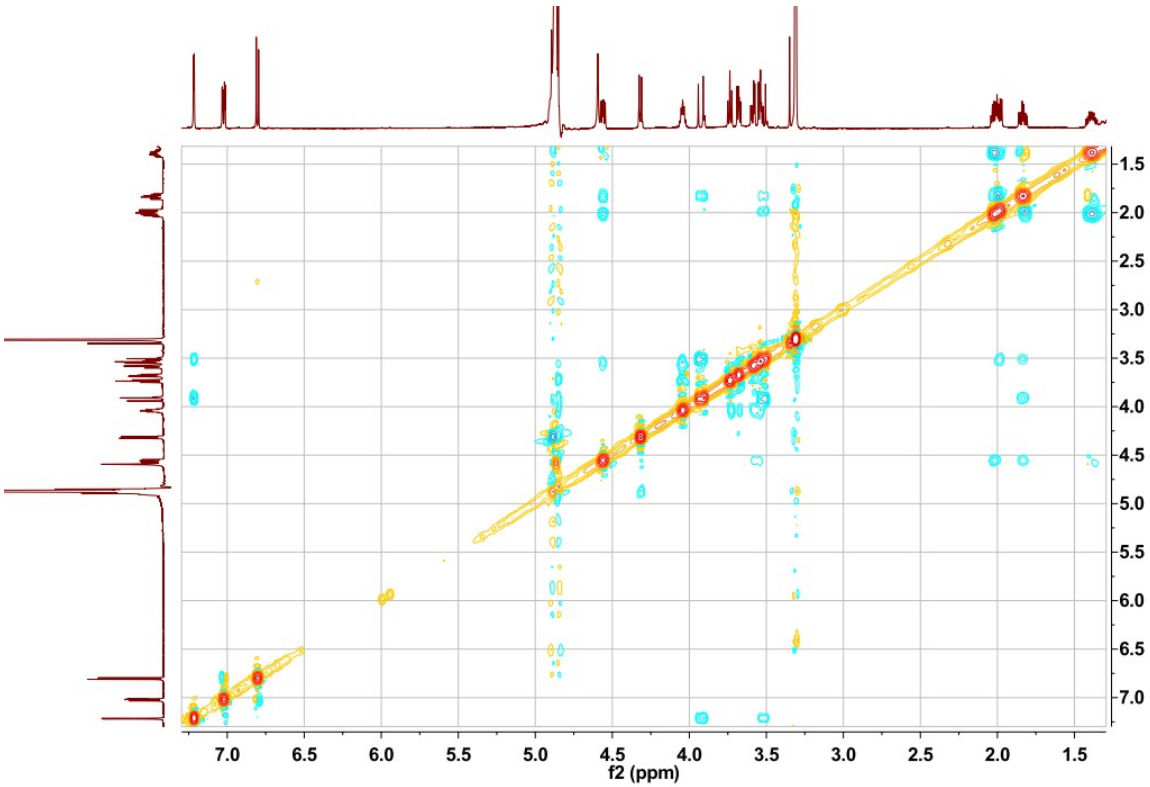
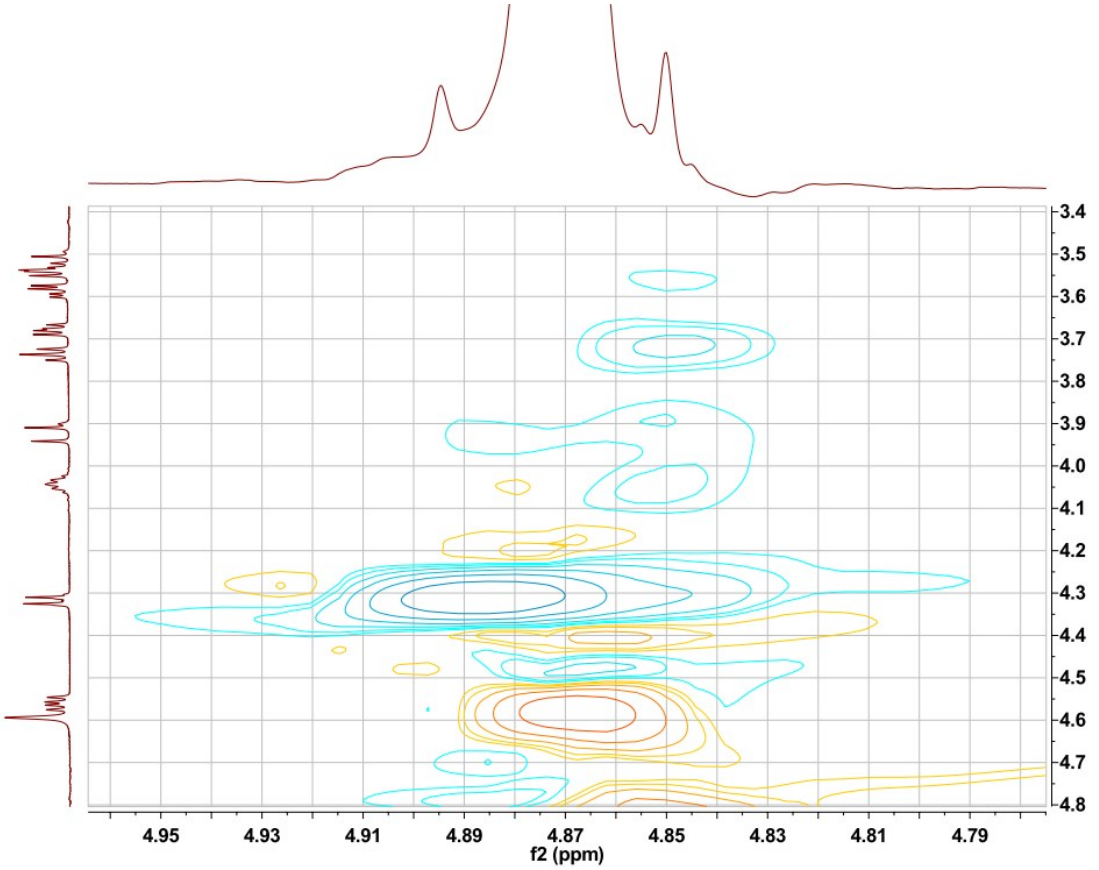
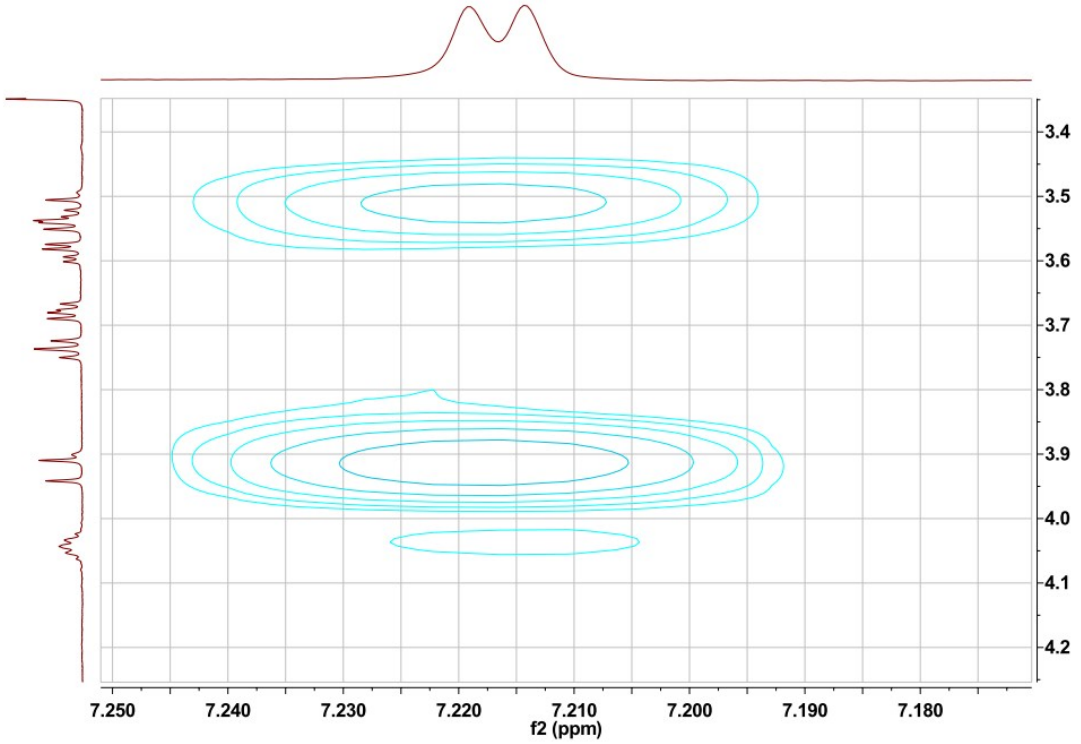


Figure S19. ROESY spectrum of **2** in methanol-d_4



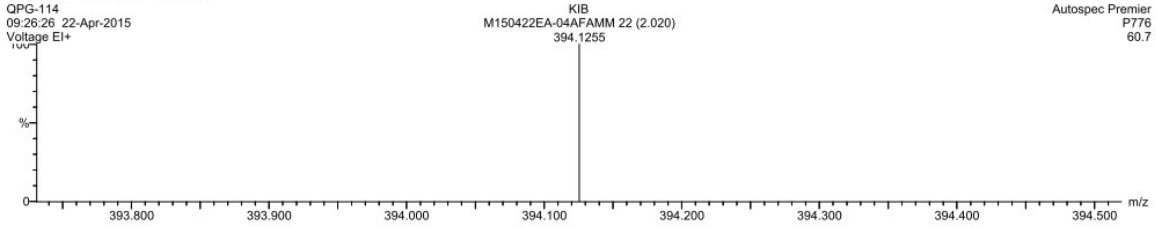
Enlarged ROESY spectrum of **2** (middle-field region) in methanol-d_4



Enlarged ROESY spectrum of **2** (H-3/H-11′) in methanol-d_4

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -10.0, max = 120.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
16 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)
Elements Used:
C: 0-200 H: 0-400 O: 8-10



Minimum:				-10.0		
Maximum:		200.0	10.0	120.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
394.1255	394.1264	-0.9	-2.3	9.0	5546044.5	C19 H22 O9

Figure S20. HREIMS spectrum of **2**