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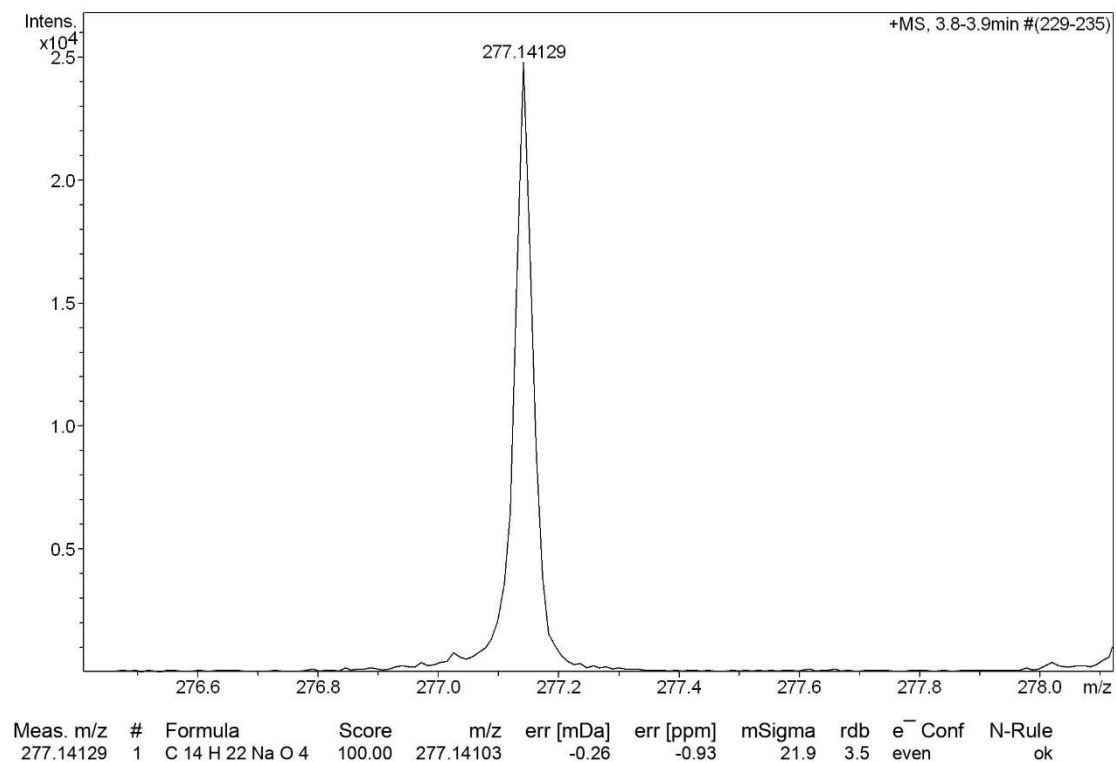


Figure S1. HRESI-MS spectrum of compound 1.

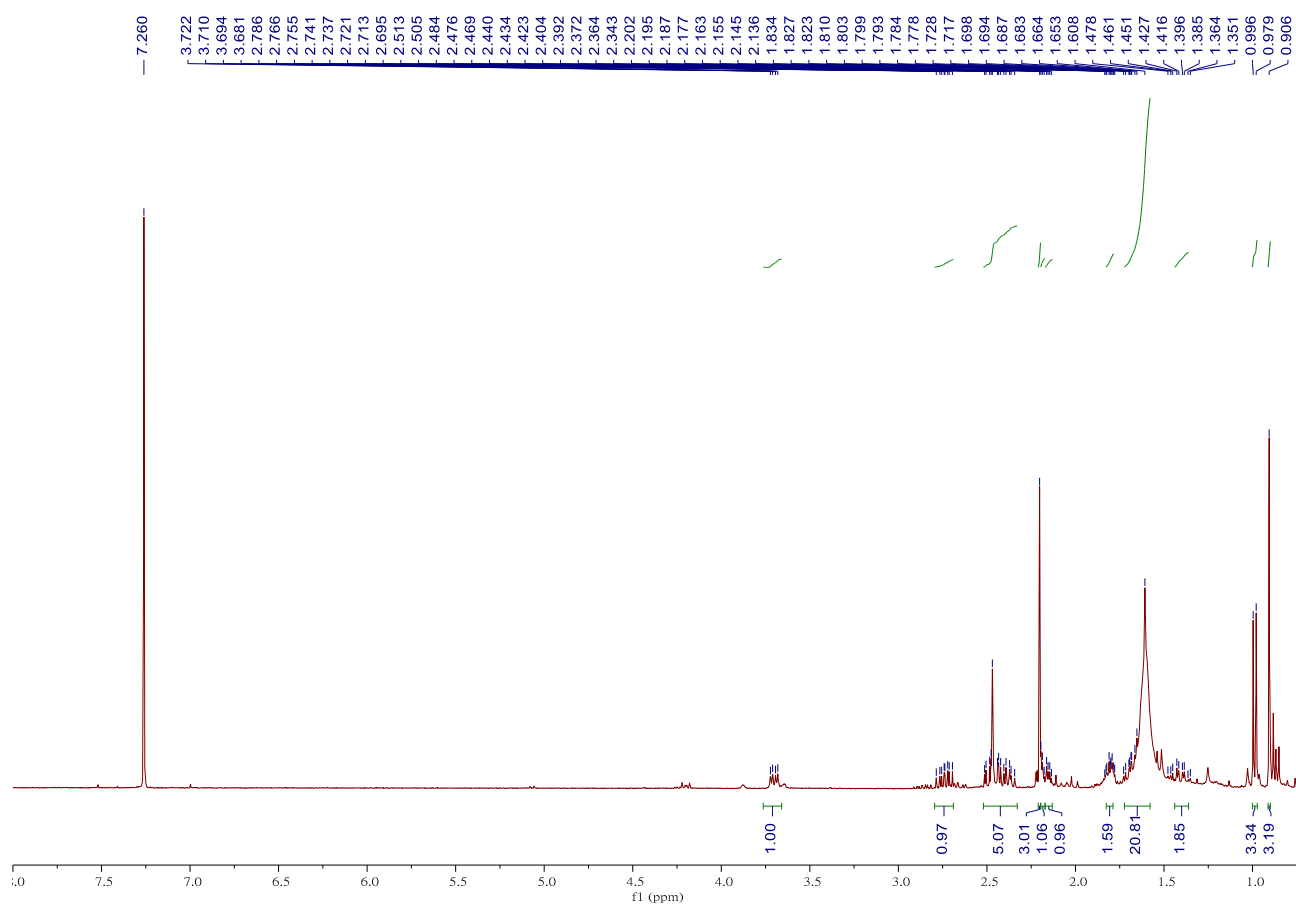


Figure S2. ¹H-NMR spectrum (400 MHz, CDCl₃) of compound 1.

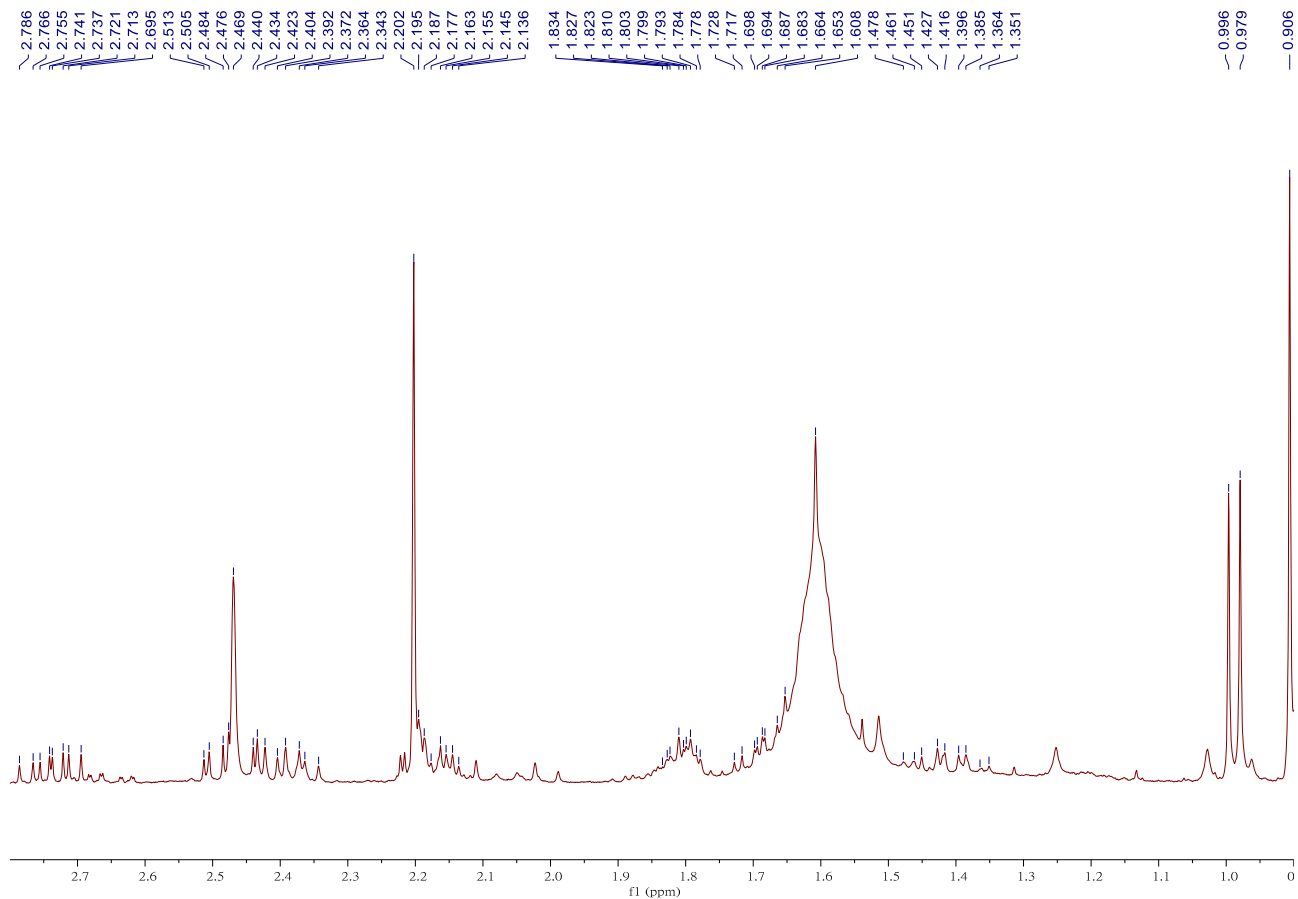


Figure S3. Expanded $^1\text{H-NMR}$ spectrum (0.90~2.80 ppm) of compound **1**.

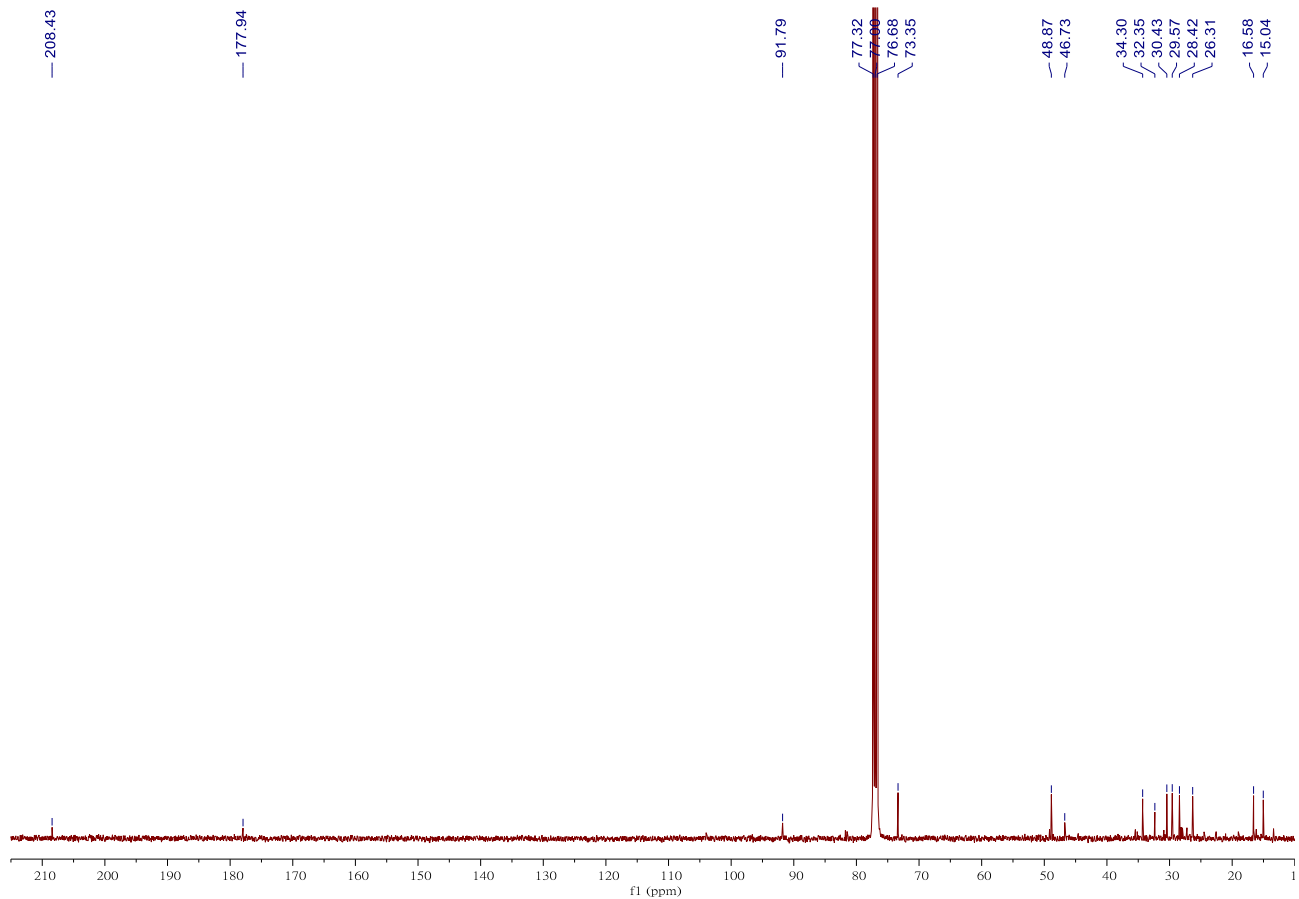


Figure S4. $^{13}\text{C-NMR}$ spectrum (100 MHz, CDCl_3) of compound **1**.

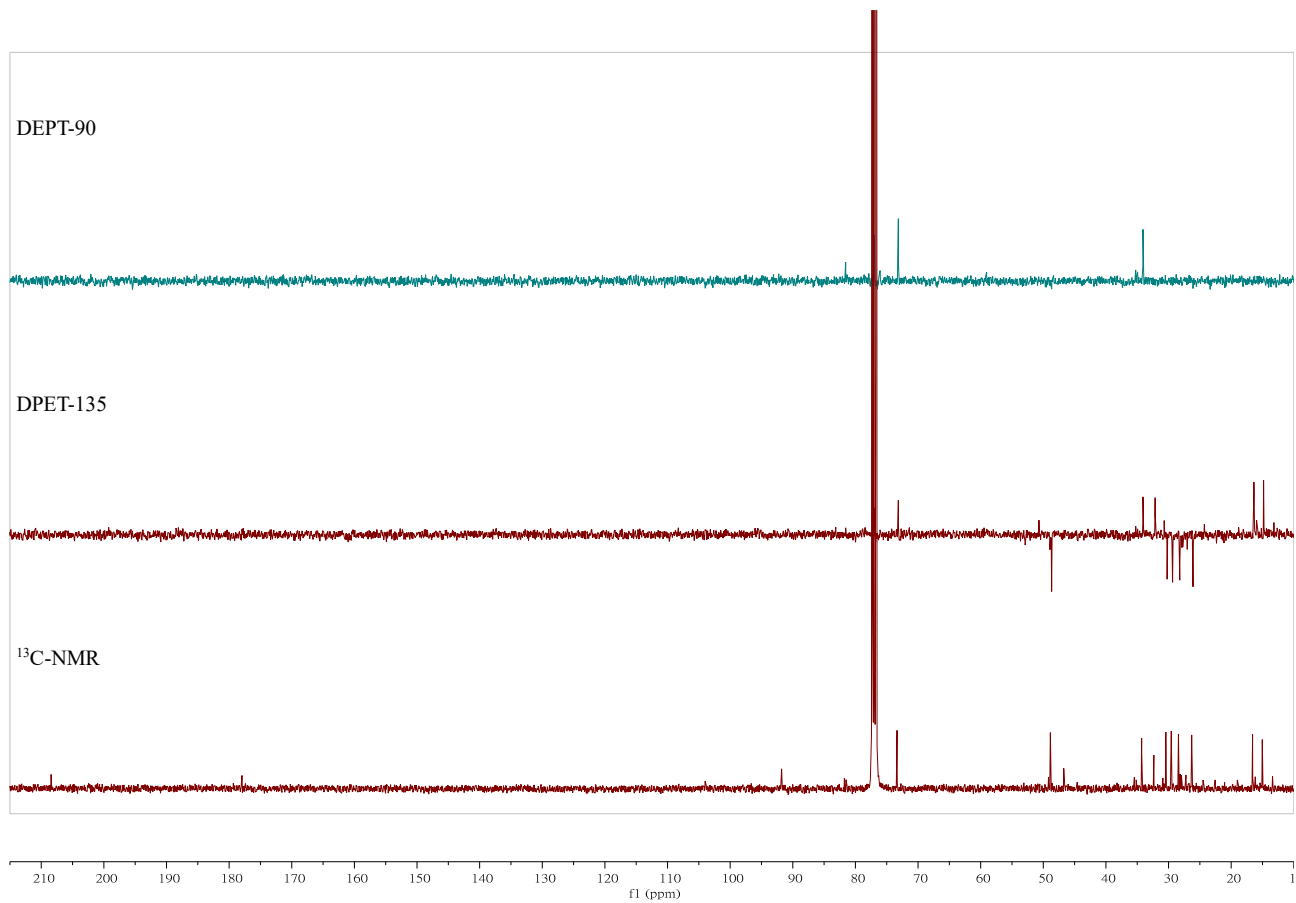


Figure S5. DEPT spectrum of compound **1**.

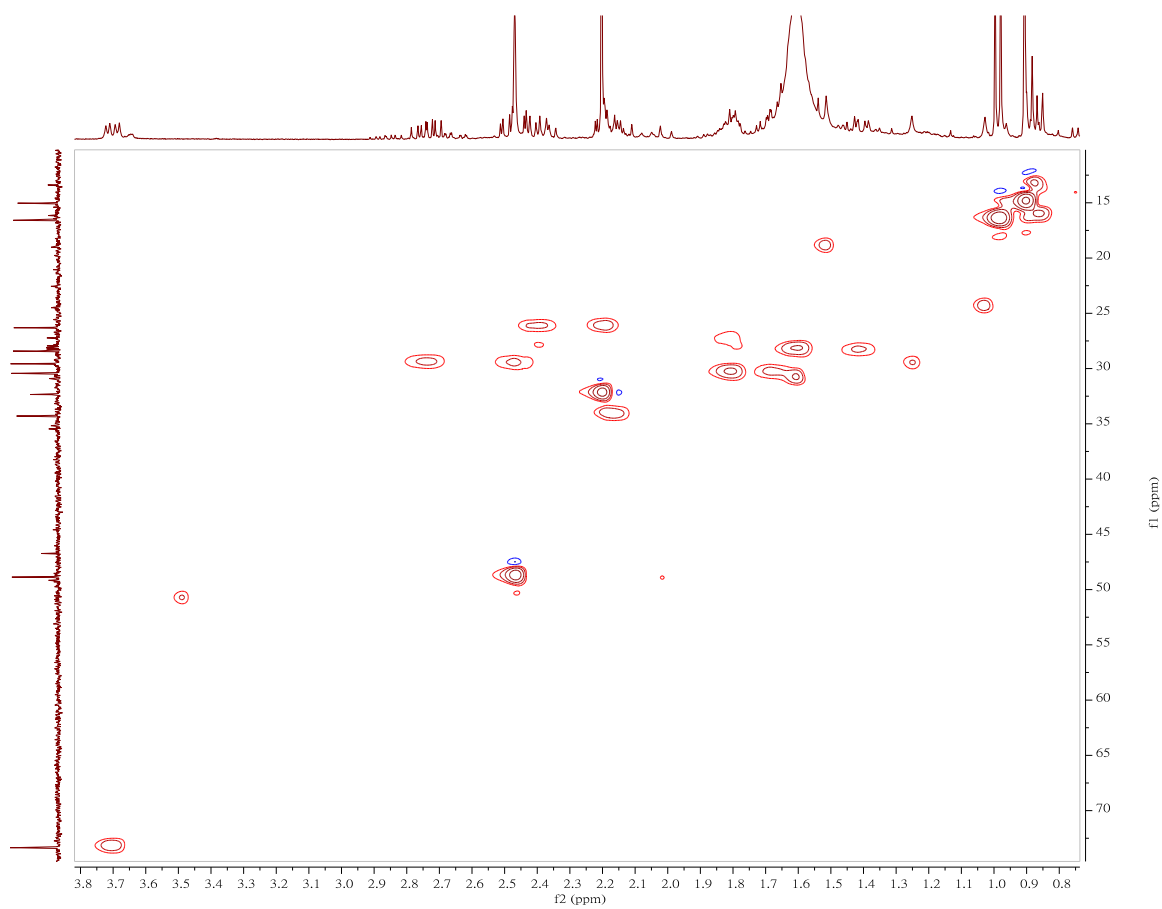


Figure S6. HSQC spectrum of compound **1**.

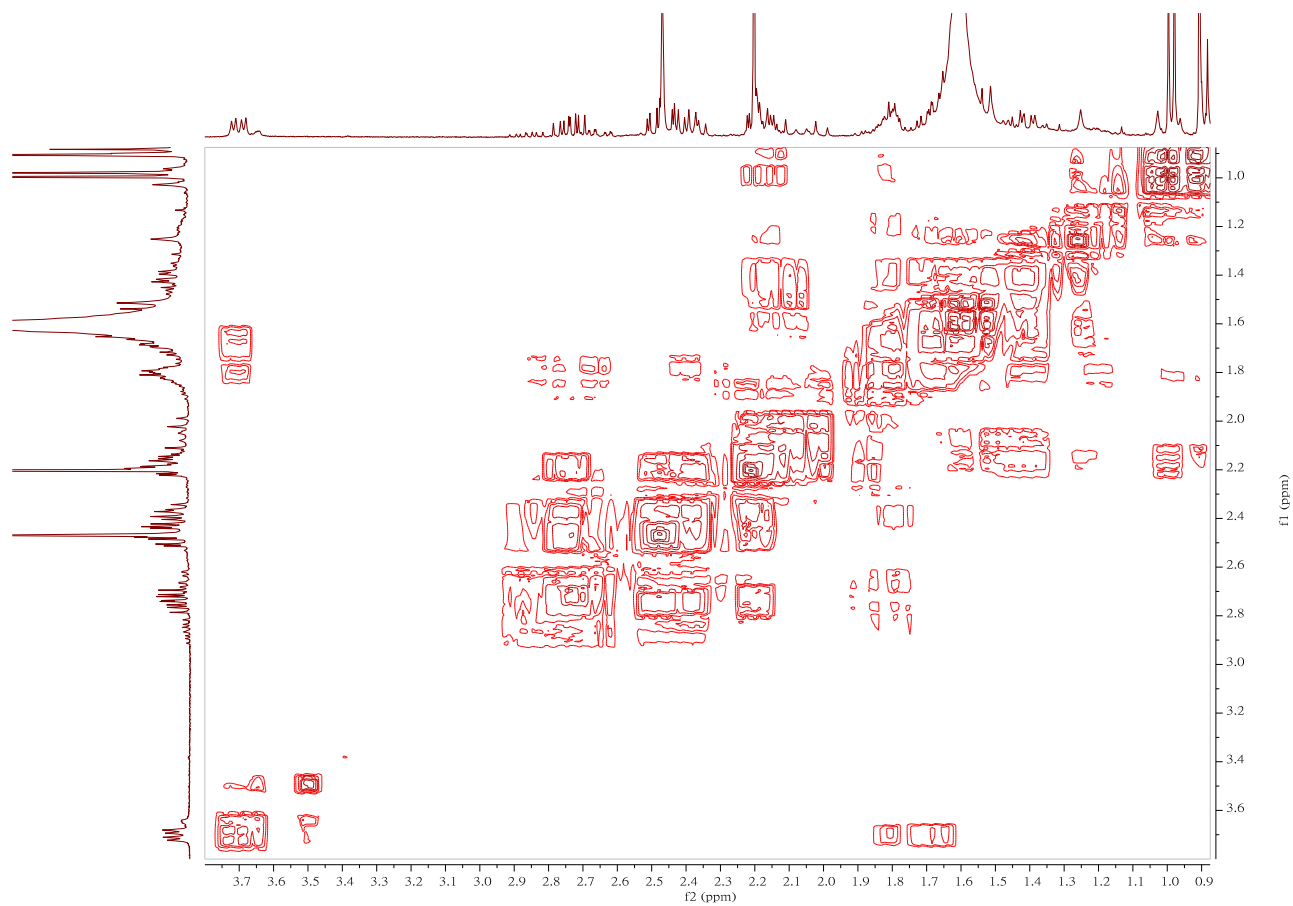


Figure S7. ^1H - ^1H COSY spectrum of compound **1**.

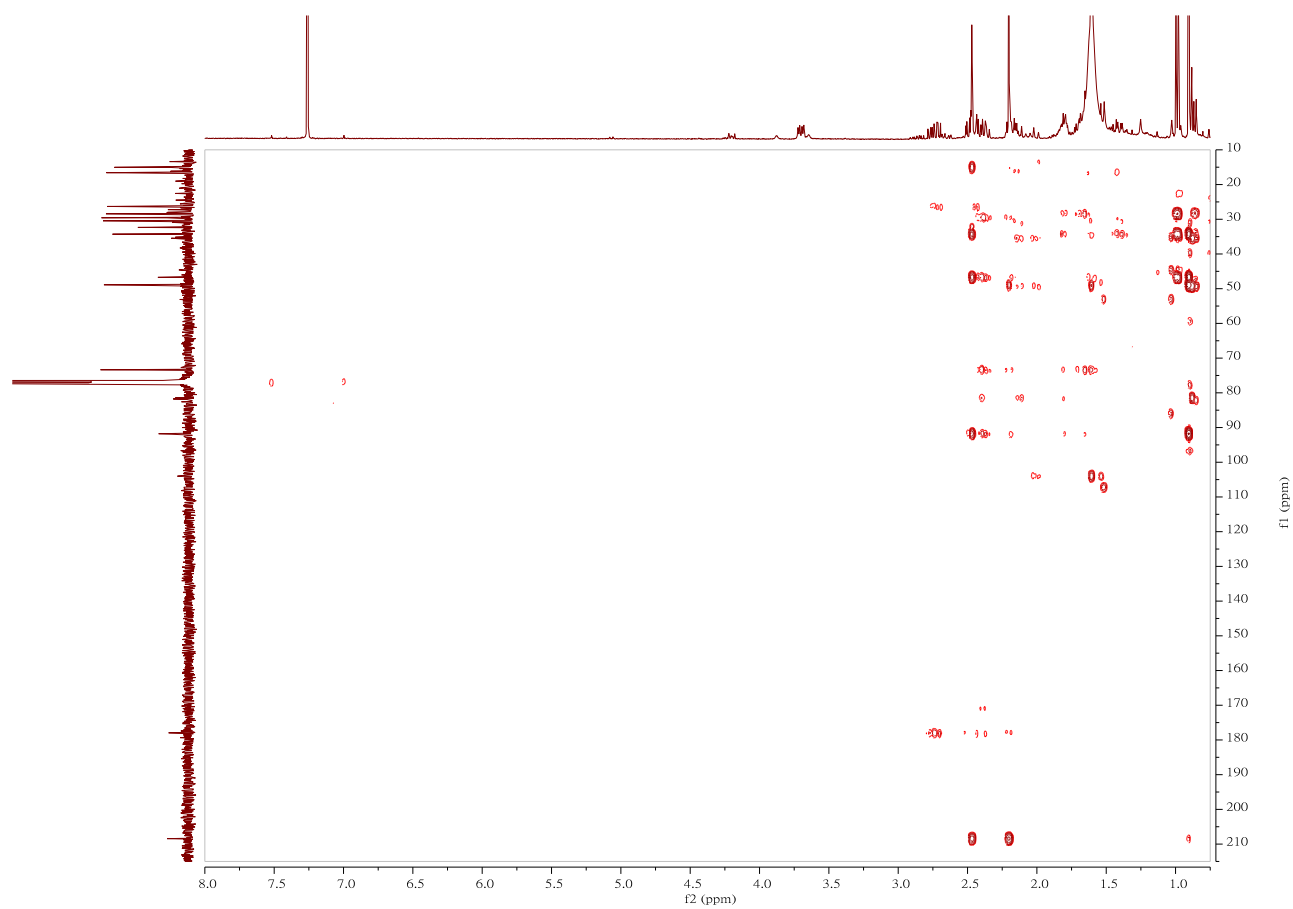


Figure S8. HMBC spectrum of compound **1**.

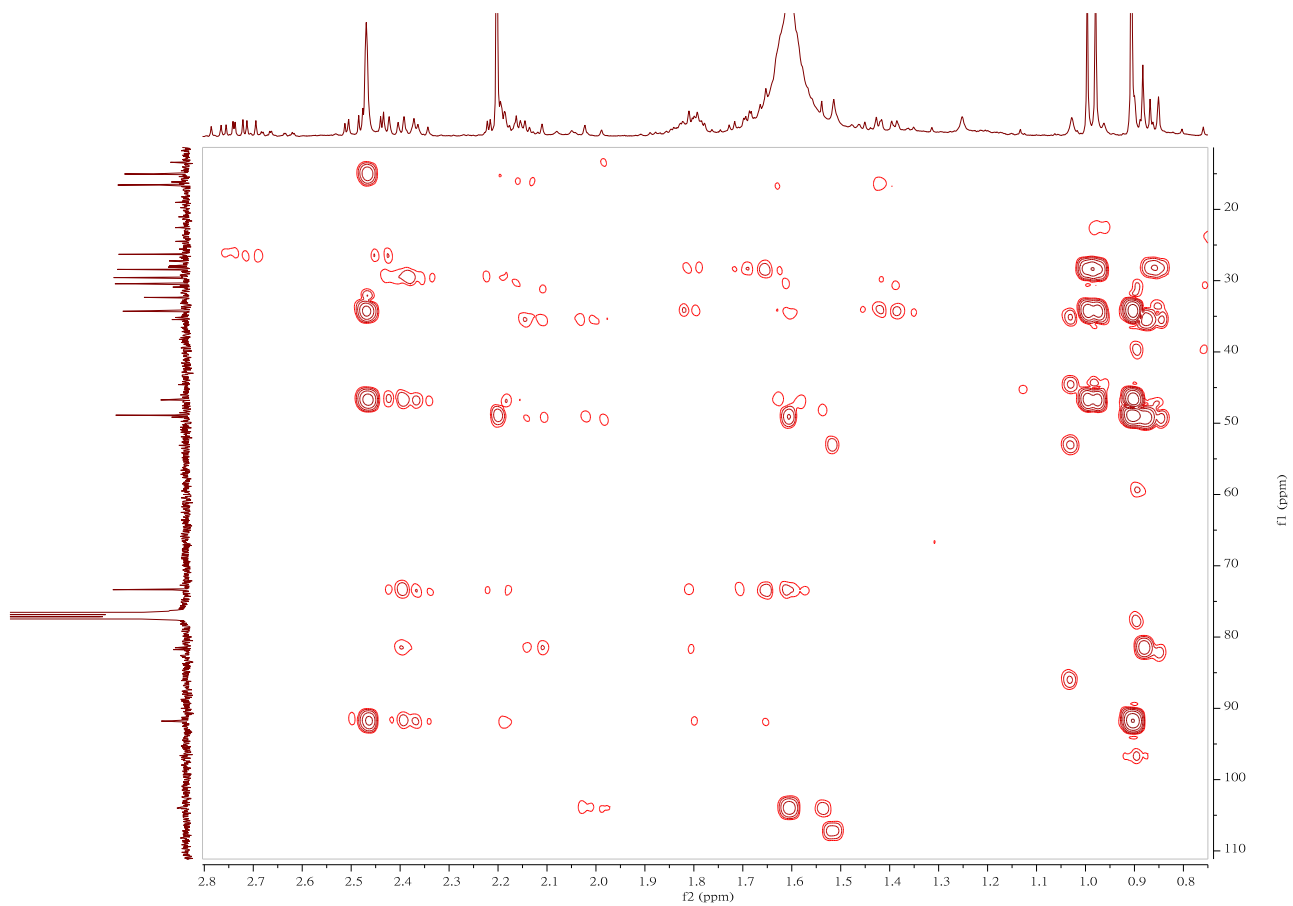


Figure S9. Expanded HMBC spectrum of compound **1**.

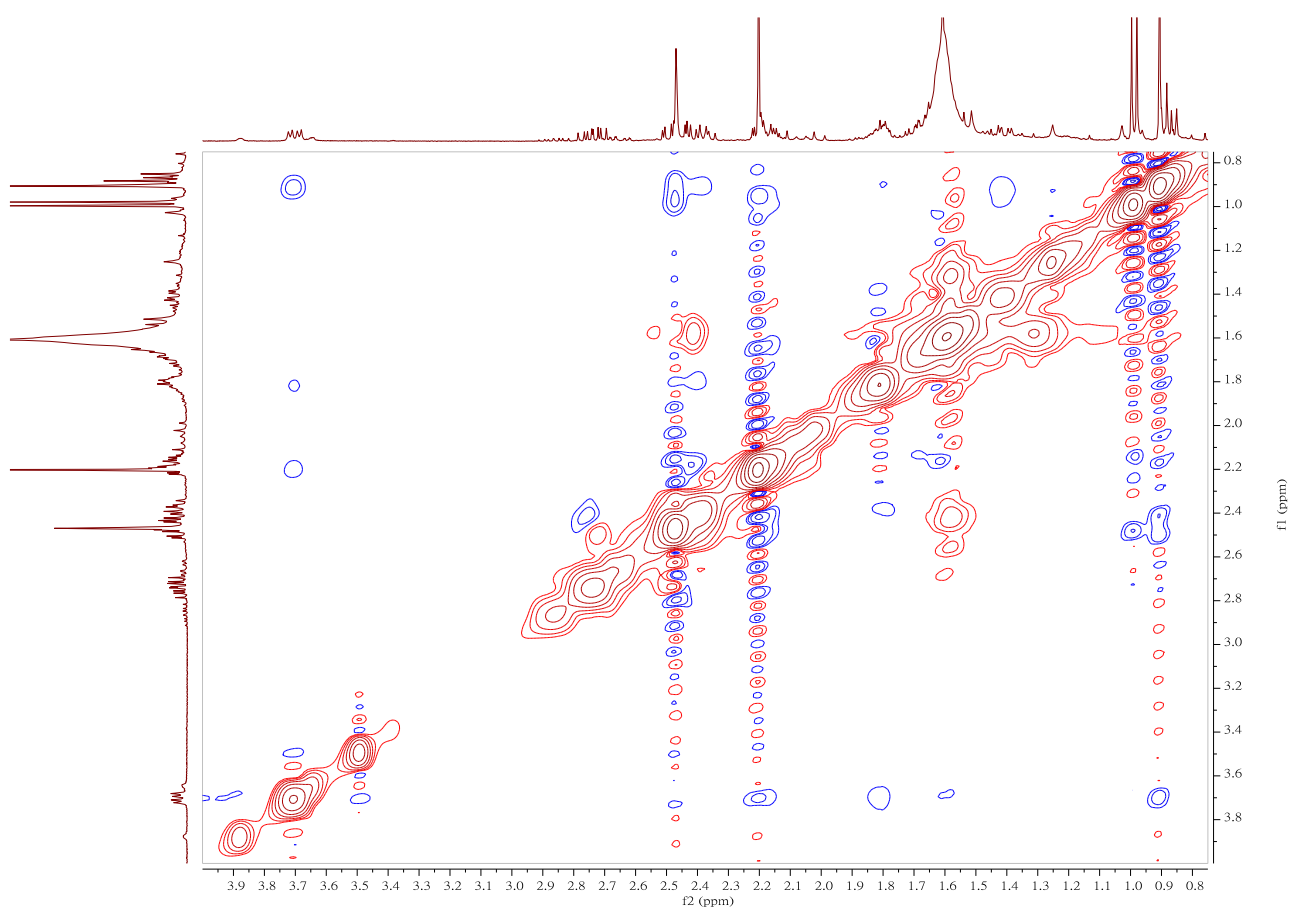


Figure S10. NOESY spectrum of compound **1**.

Functional	Solvent?	Basis Set	Type of Data					
mPW1PW91	PCM	6-311+G(d,p)	Shielding Tensors					
Nuclei	sp27	DP4+		0.00,00%		0.00%		
		Experimental	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5	
a	232.4	24.4	23.8					
x	177.9	0.9	2.3					
	51.8	52.2	91.6					
	73.4	109.9	111.8					
	49.9	138.8	139.2					
	49.7	134.1	135.5					
	34.3	147.6	146.8					
	50.4	156.0	156.5					
	32.3	151.7	151.3					
	29.5	153.9	154.4					
	28.4	156.4	156.0					
	26.3	155.57	160.31					
	15	172.73	171.14					
	16.5	169.17	169.64					
	3.7	22.96	22.74					
H	1.81	30.12	28.99					
H	1.69	30.14	30.17					
H	1.61	30.27	31.29					
H	1.41	30.26	31.07					
H	2.17	29.79	28.47					
H	2.74	29.02	29.18					
H	2.47	29.51	29.43					
H	2.37	29.33	29.59					
H	2.19	29.57	29.70					
H	2.47	29.38	29.30					
H	2.47	29.728004	28.222938					
H	2.3	29.3461387	29.4924026					
H	0.99	30.6851046	30.67451077					
H	0.91	30.7998508	30.6181446					

1	Functional	Solvent?	Basis Set	Type of Data						
2	mPW1PW91	PCM	6-311+G(d,p)	Shielding Tensors						
3										
4				Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5	Isomer 6	
5	sDP4+ (H data)			-	-	-	-	-	-	
6	sDP4+ (C data)			-	-	-	-	-	-	
7	sDP4+ (all data)			-	-	-	-	-	-	
8	uDP4+ (H data)			-	-	-	-	-	-	
9	uDP4+ (C data)			-	-	-	-	-	-	
10	uDP4+ (all data)			-	-	-	-	-	-	
11	DP4+ (H data)			-	-	-	-	-	-	
12	DP4+ (C data)			-	-	-	-	-	-	
13	DP4+ (all data)			-	-	-	-	-	-	

Isomer 1: 1-1*S*,4*S*,5*R*,6*R*; Isomer 2: 1-1*R*,4*S*,5*R*,6*R*.

Figure S11. DP4+ analysis result of 1-1*S*,4*S*,5*R*,6*R* and 1-1*R*,4*S*,5*R*,6*R*.

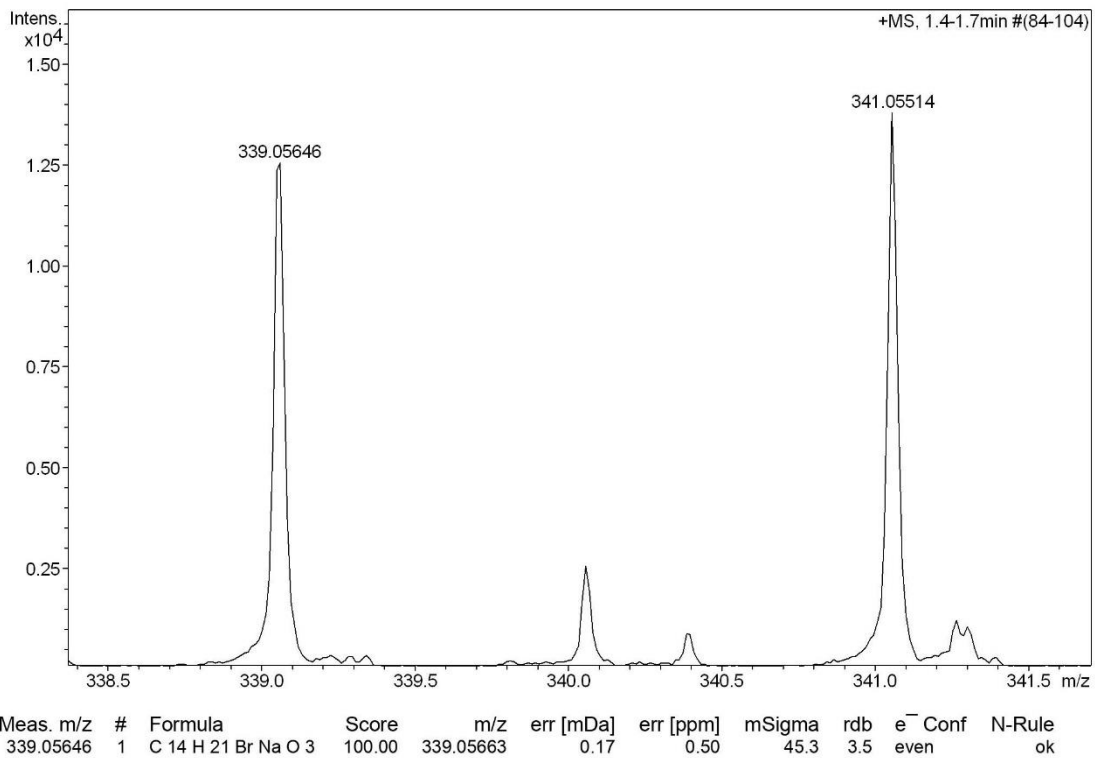


Figure S12. HRESI-MS spectrum of compound **2**.

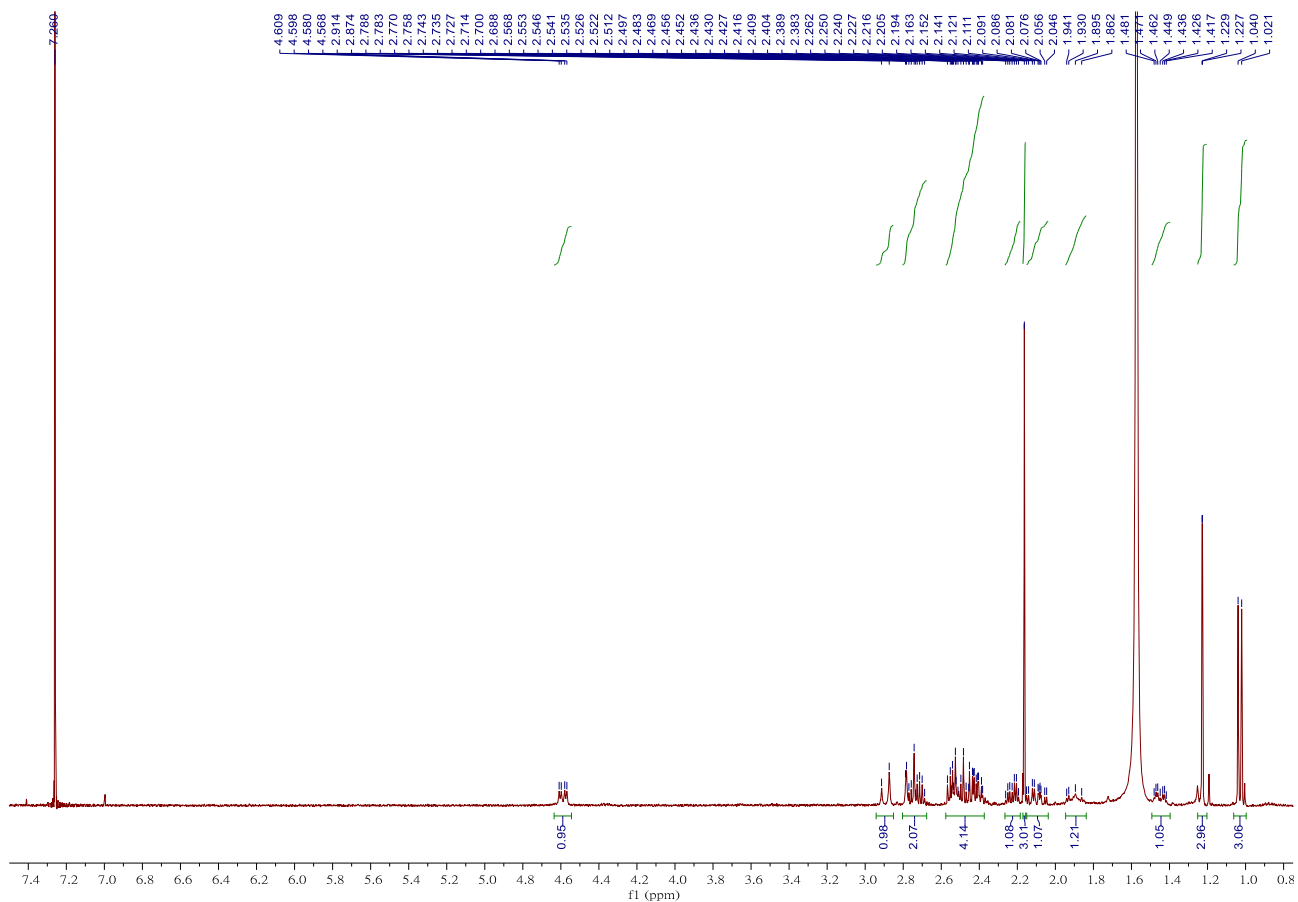


Figure S13. ¹H-NMR spectrum (400 MHz, CDCl₃) of compound **2**.

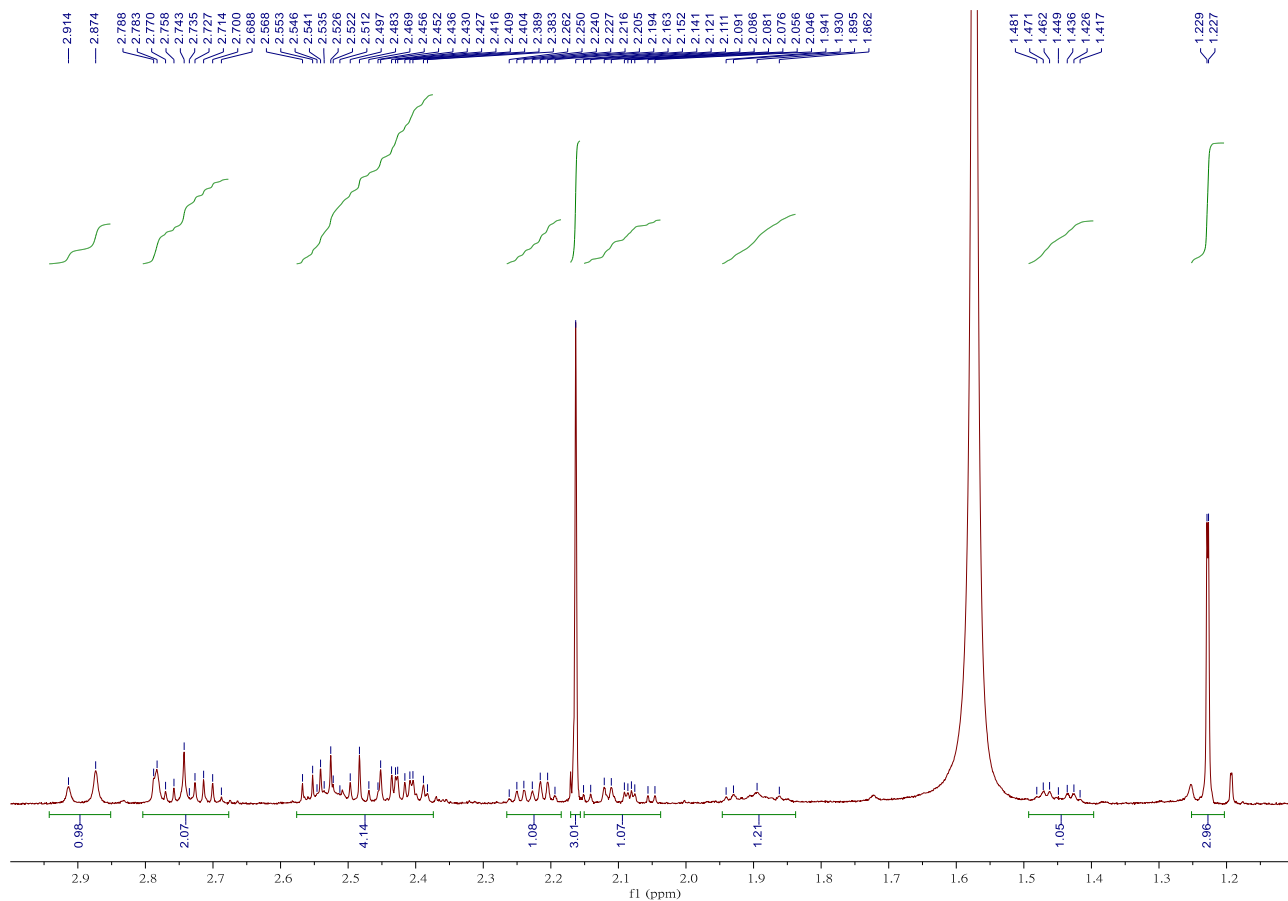


Figure S14. Expanded ^1H -NMR spectrum (1.10~3.00 ppm) of compound **2**.

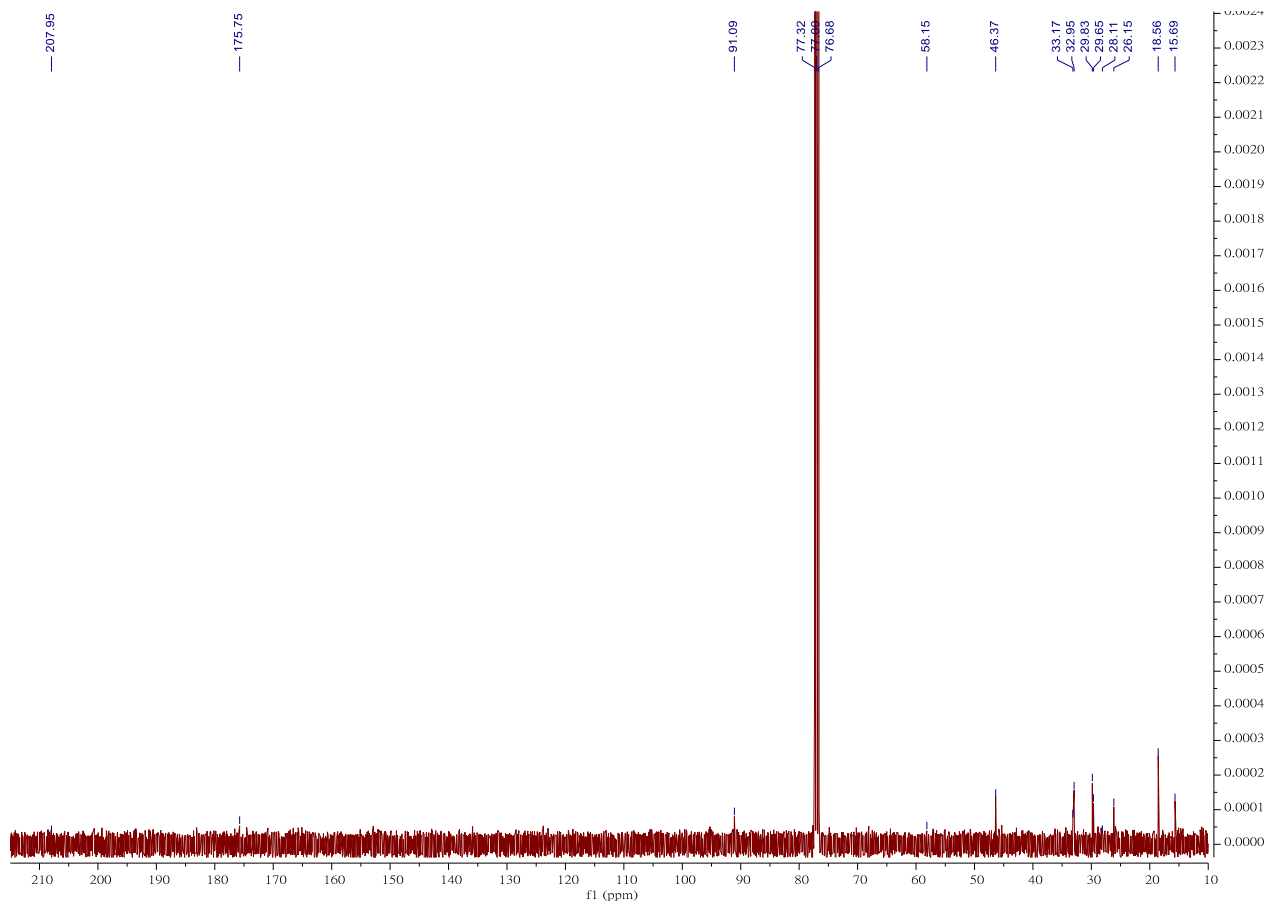


Figure S15. ^{13}C -NMR spectrum (100 MHz, CDCl_3) of compound **2**.

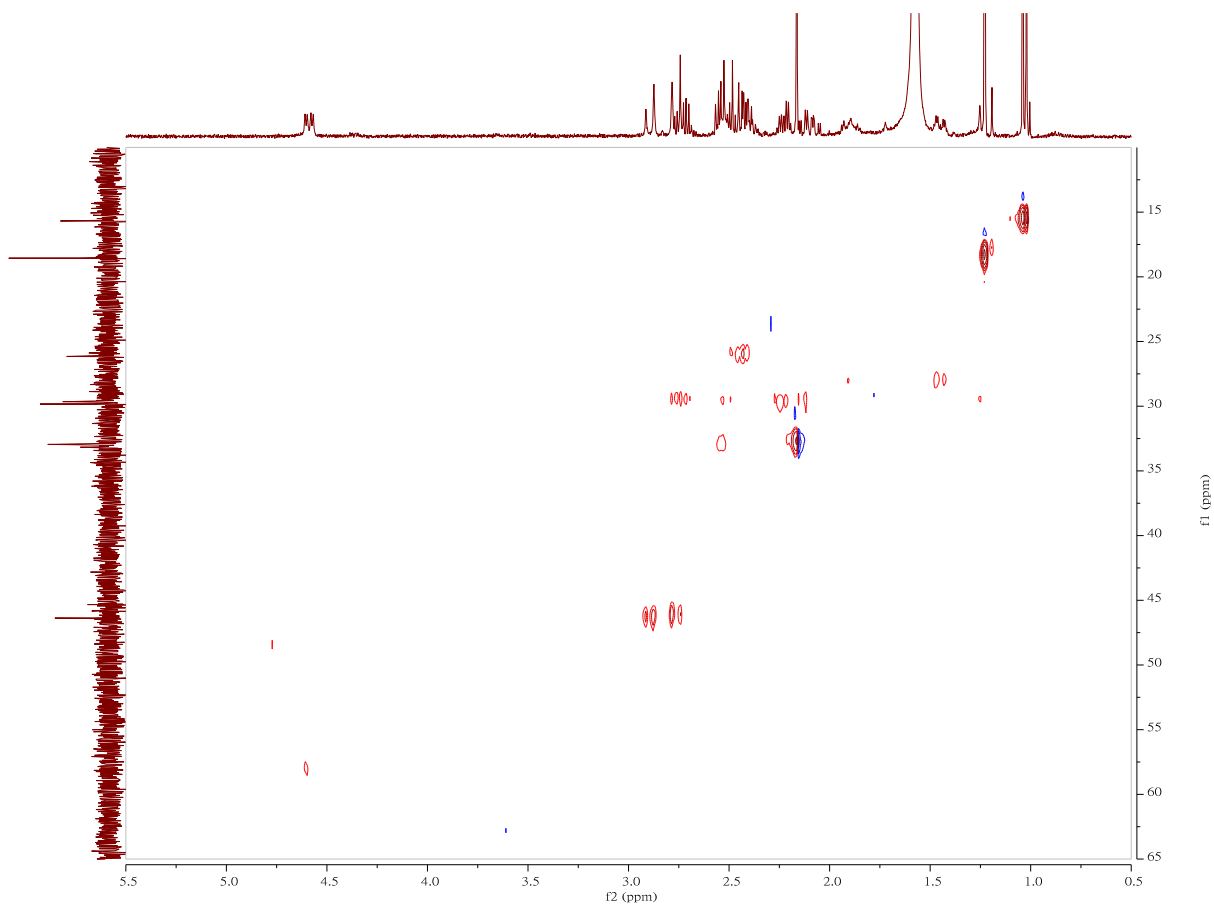


Figure S16. HSQC spectrum of compound 2.

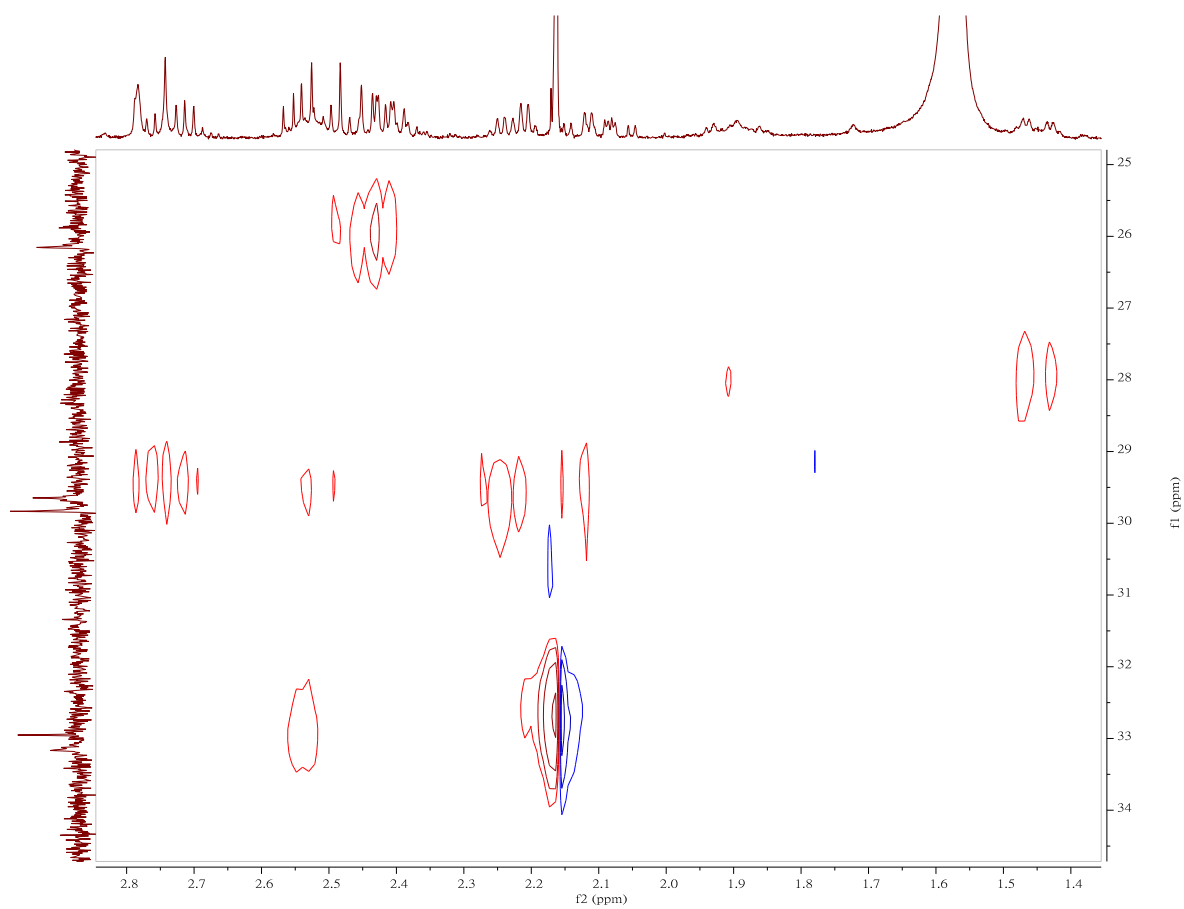


Figure S17. Expanded HSQC spectrum of compound 2.

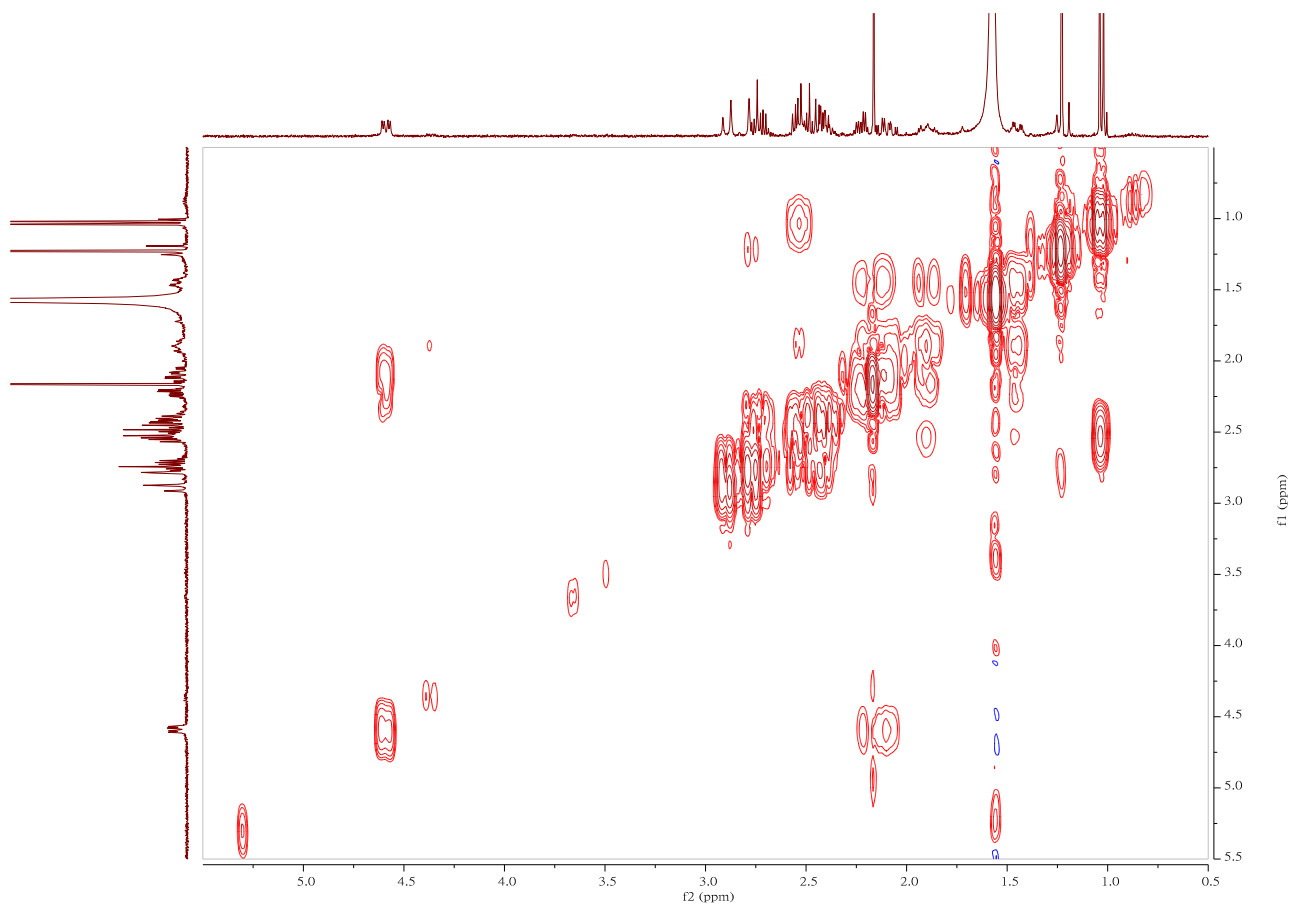


Figure S18. ^1H - ^1H COSY spectrum of compound 2.

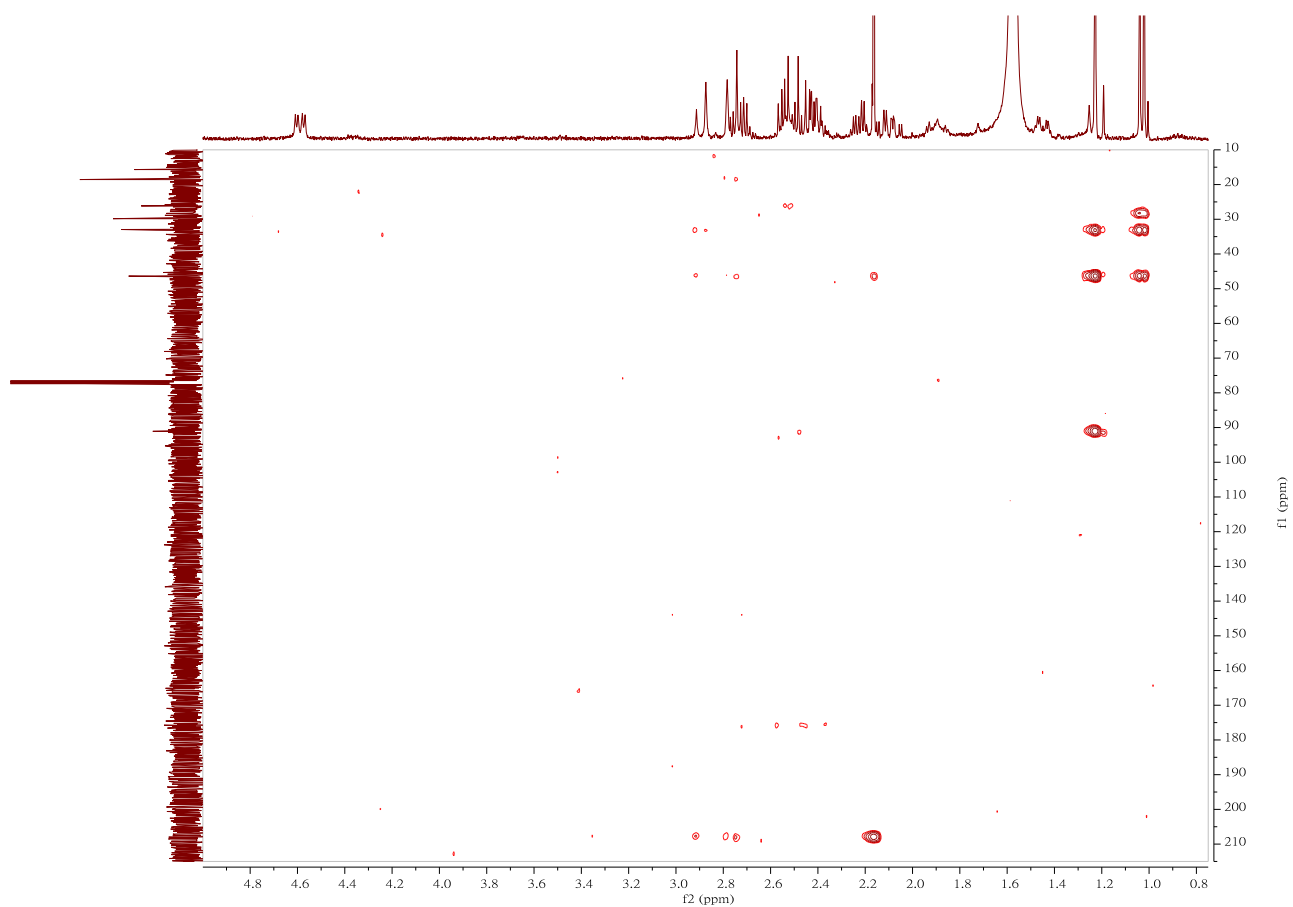


Figure S19. HMBC spectrum of compound 2.

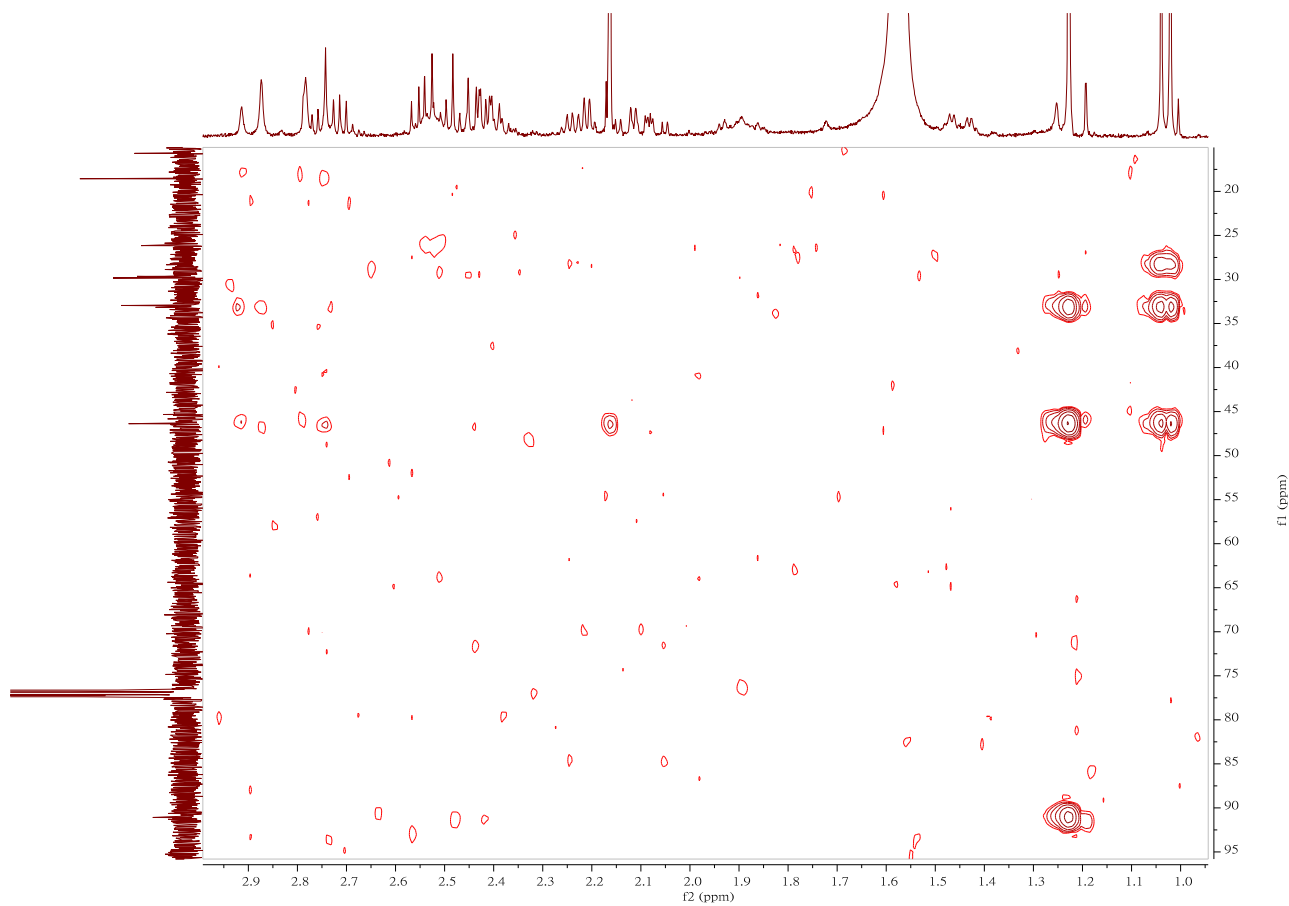


Figure S20. Expanded HMBC spectrum of compound **2**.

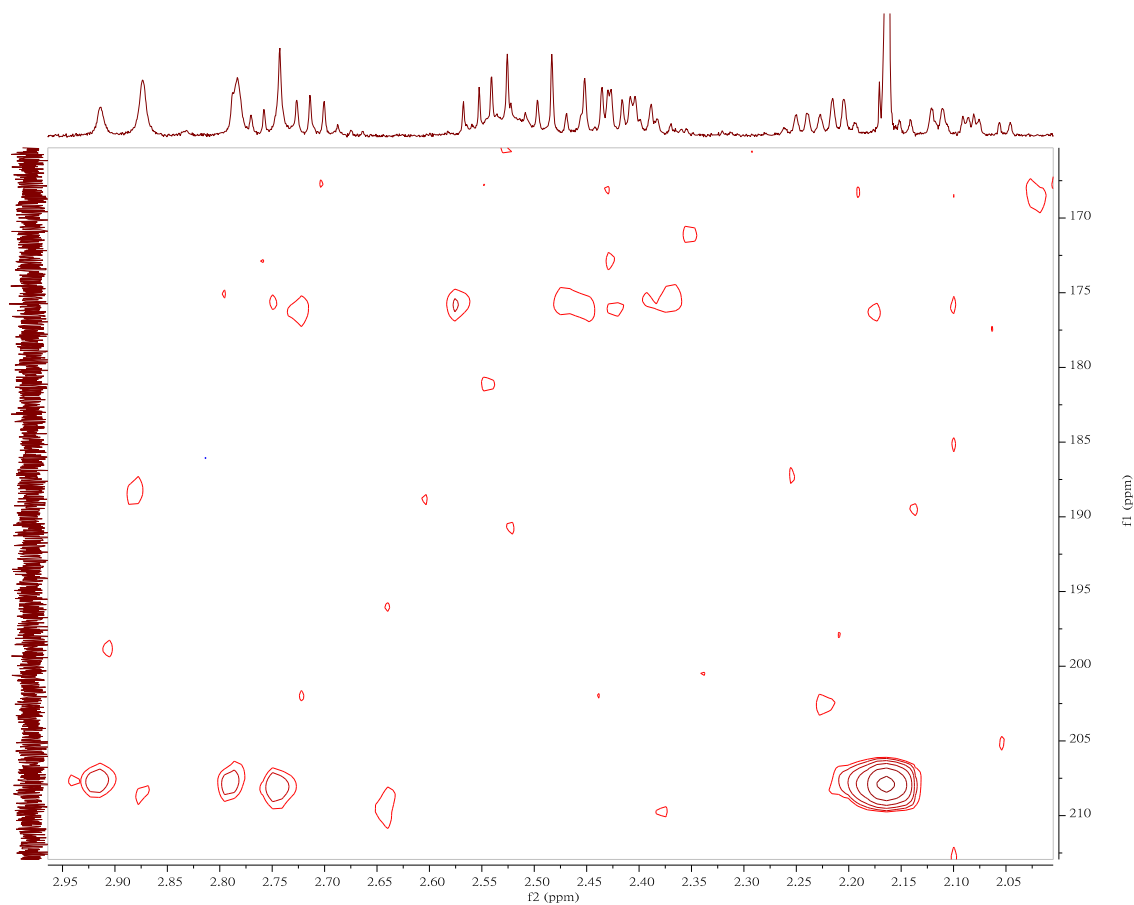


Figure S21. Expanded HMBC spectrum of compound **2**.

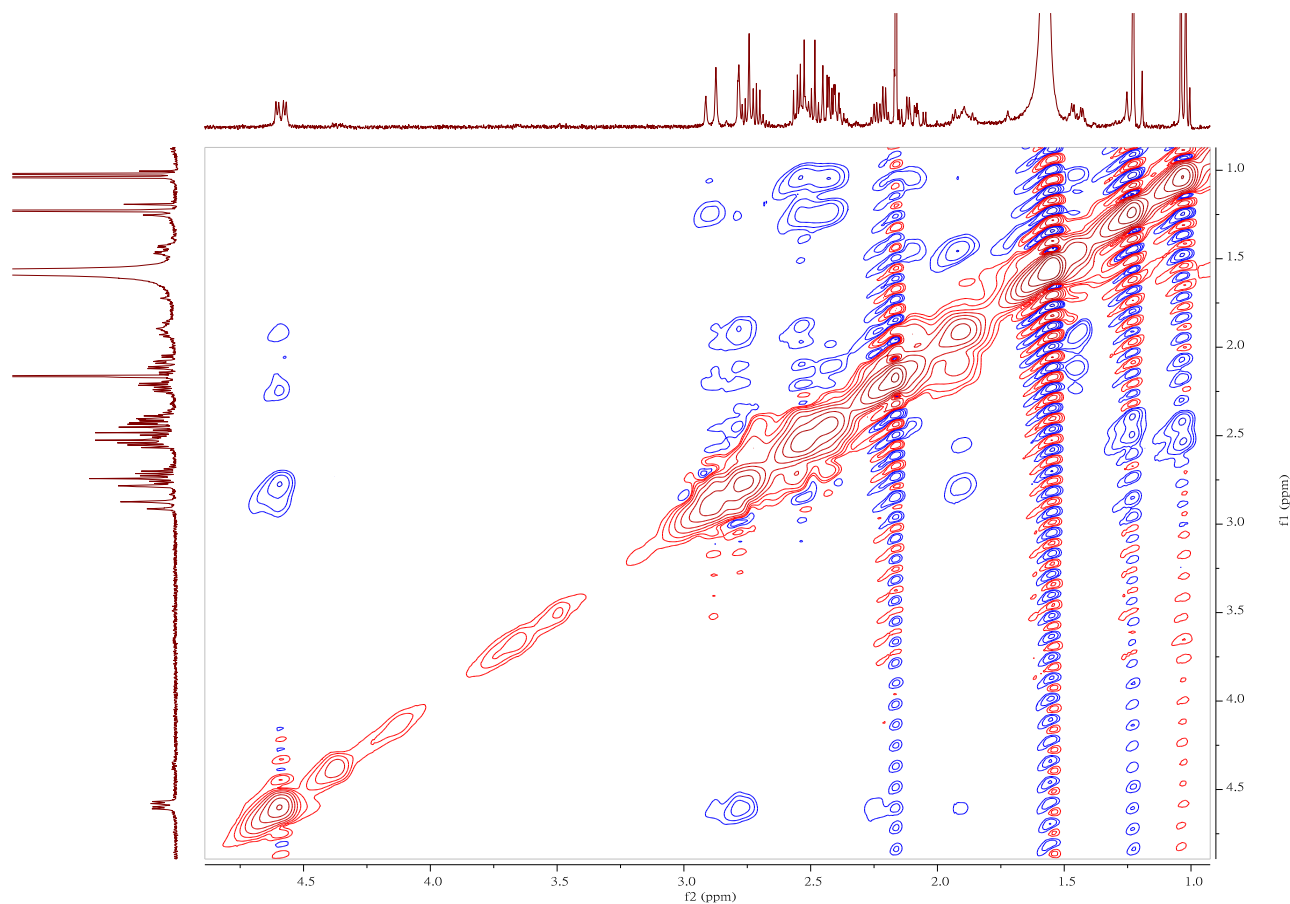


Figure S22. NOESY spectrum of compound **2**.

Functional	Solvent?	Basis Set	Type of Data
mPW1PW91	PCM	6-311+G(d,p)	Shielding Tensors
Isomer 1	Isomer 2	Isomer 3	Isomer 4
Isomer 5			

Isomer	DP4+	0.00%	0.00%
C	207.9	-33.9	-32.4
C	155.8	3.2	3.9
C	91.1	91.8	94.9
C	58.2	108.8	114.1
C	46.4	131.9	137.7
C	46.4	136.4	122.4
C	33.2	147.8	146.6
C	29.7	153.6	155.0
C	33	152.5	152.8
C	29.7	153.8	150.1
C	28.1	156.1	155.0
C	26.2	157.94	149.55
C	18.6	167.10	170.20
C	15.7	170.92	167.10
H	4.59	26.77	27.21
H	2.28	29.67	29.64
H	2.08	29.64	29.21
H	1.89	29.68	30.62
H	1.45	30.37	30.17
H	2.56	29.28	29.68
H	2.74	29.07	29.22
H	2.53	29.34	29.35
H	2.48	29.49	29.39
H	2.41	29.49	29.98
H	2.89	28.81	28.36
H	2.76	29.196066	29.9302849
H	2.16	29.397153	29.4102052
H	1.03	30.7940061	30.6952398
H	1.28	30.6472398	30.7480349

Functional	Solvent?	Basis Set	Type of Data
mPW1PW91	PCM	6-311+G(d,p)	Shielding Tensors
	Isomer 1	Isomer 2	Isomer 3
	Isomer 4	Isomer 5	Isomer 6
sDP4+ (H data)	100.00%	0.00%	-
sDP4+ (C data)	99.98%	0.02%	-
sDP4+ (all data)	100.00%	0.00%	-
uDP4+ (H data)	100.00%	0.00%	-
uDP4+ (C data)	99.91%	0.09%	-
uDP4+ (all data)	100.00%	0.00%	-
DP4+ (H data)	100.00%	0.00%	-
DP4+ (C data)	100.00%	0.00%	-
DP4+ (all data)	100.00%	0.00%	-

Isomer 1: **2-1R,4S,5R,6R**; Isomer 2: **2-1S,4S,5R,6R**.

Figure S23. DP4+ analysis result of **2-1R,4S,5R,6R** and **2-1S,4S,5R,6R**.

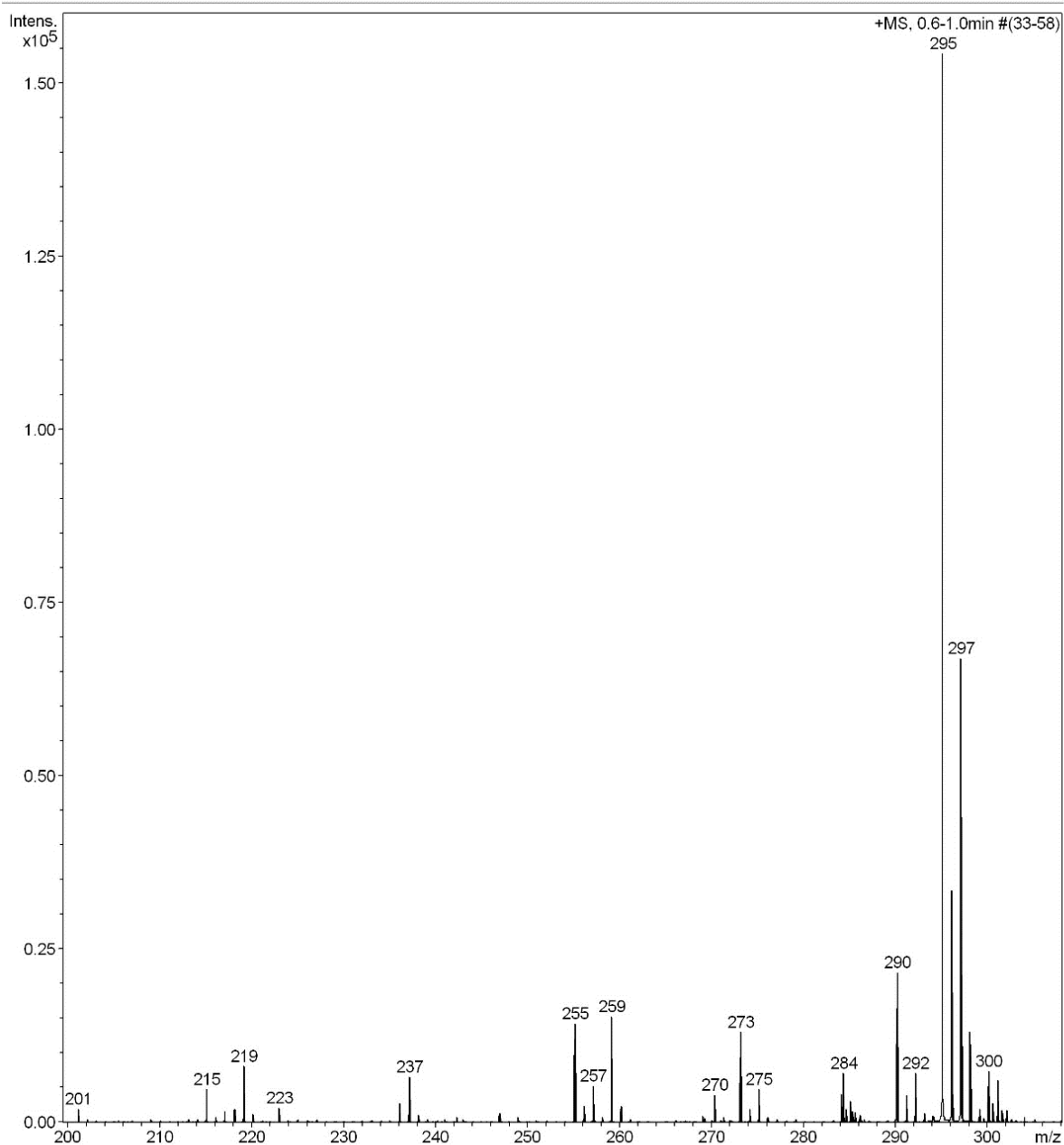


Figure S24. ESI-MS spectrum of compound **3**.

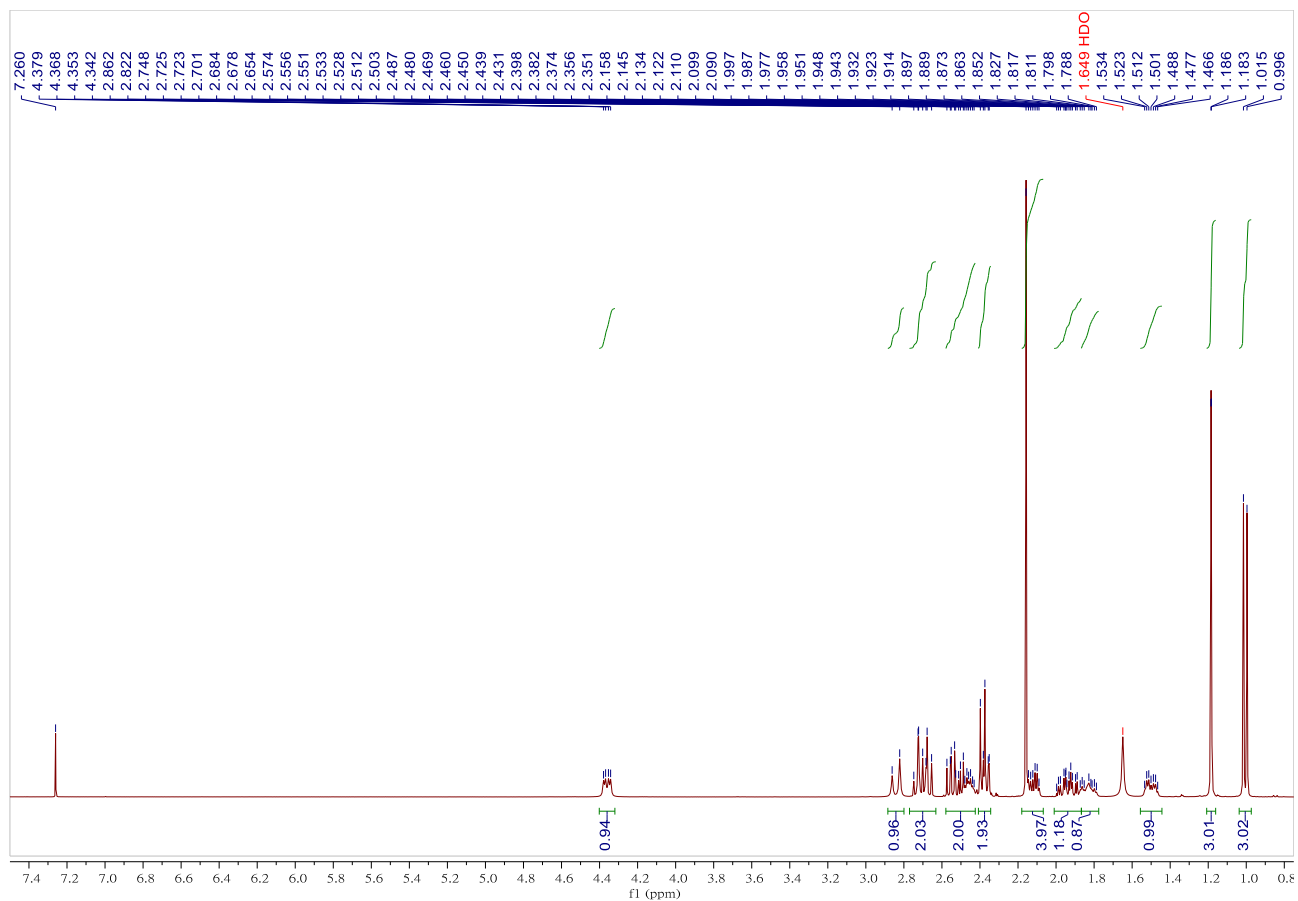


Figure S25. ^1H -NMR spectrum (400 MHz, CDCl_3) of compound **3**.

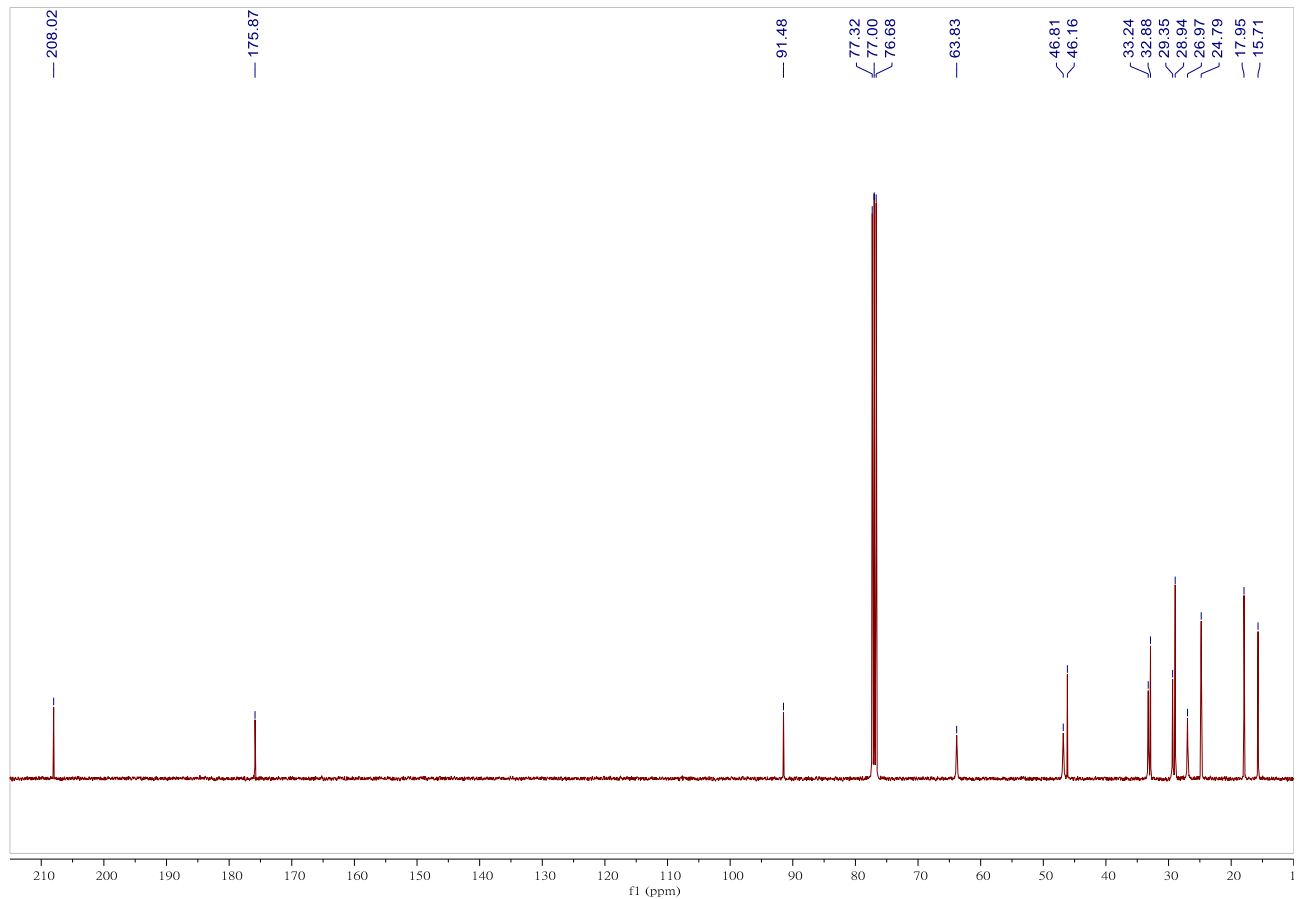


Figure S26. ^{13}C -NMR spectrum (100 MHz, CDCl_3) of compound **3**.

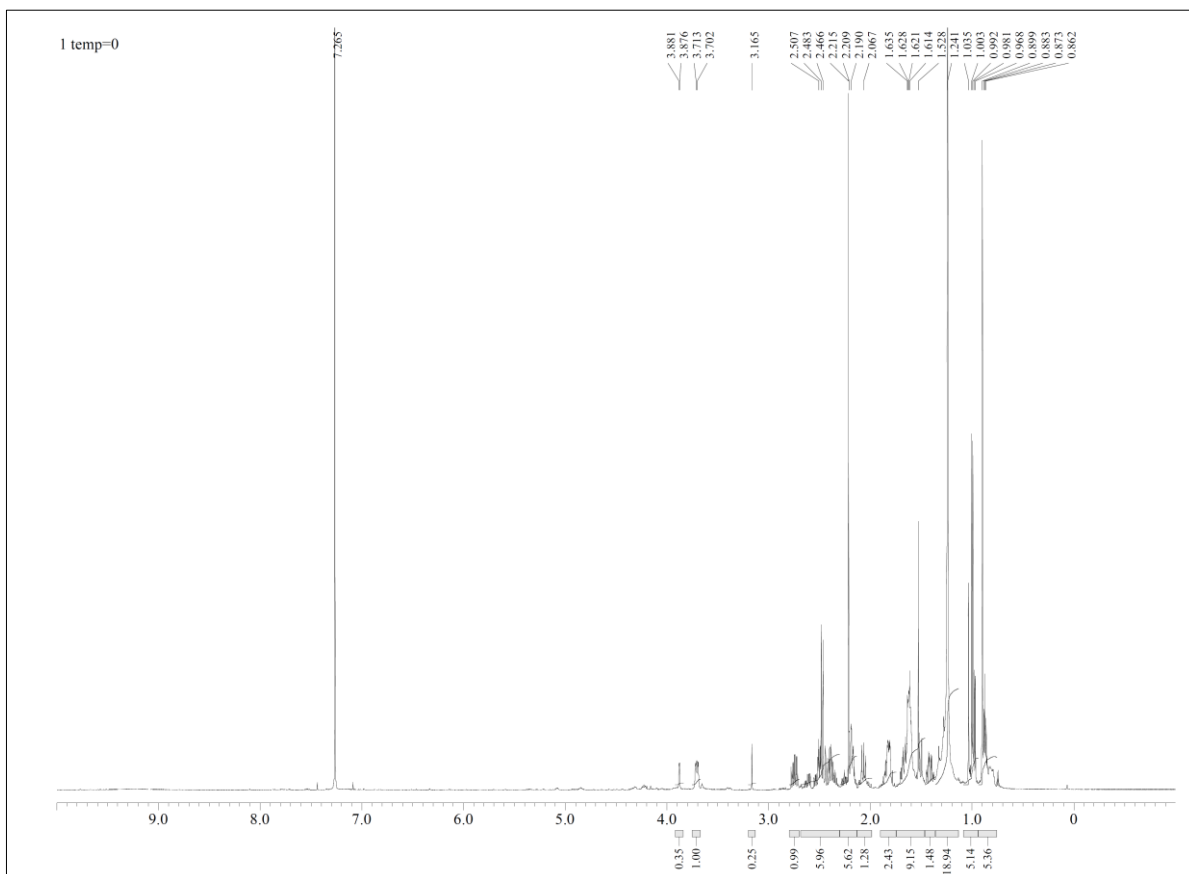


Figure S27. The ^1H -NMR spectrum of **1** at 0°C .

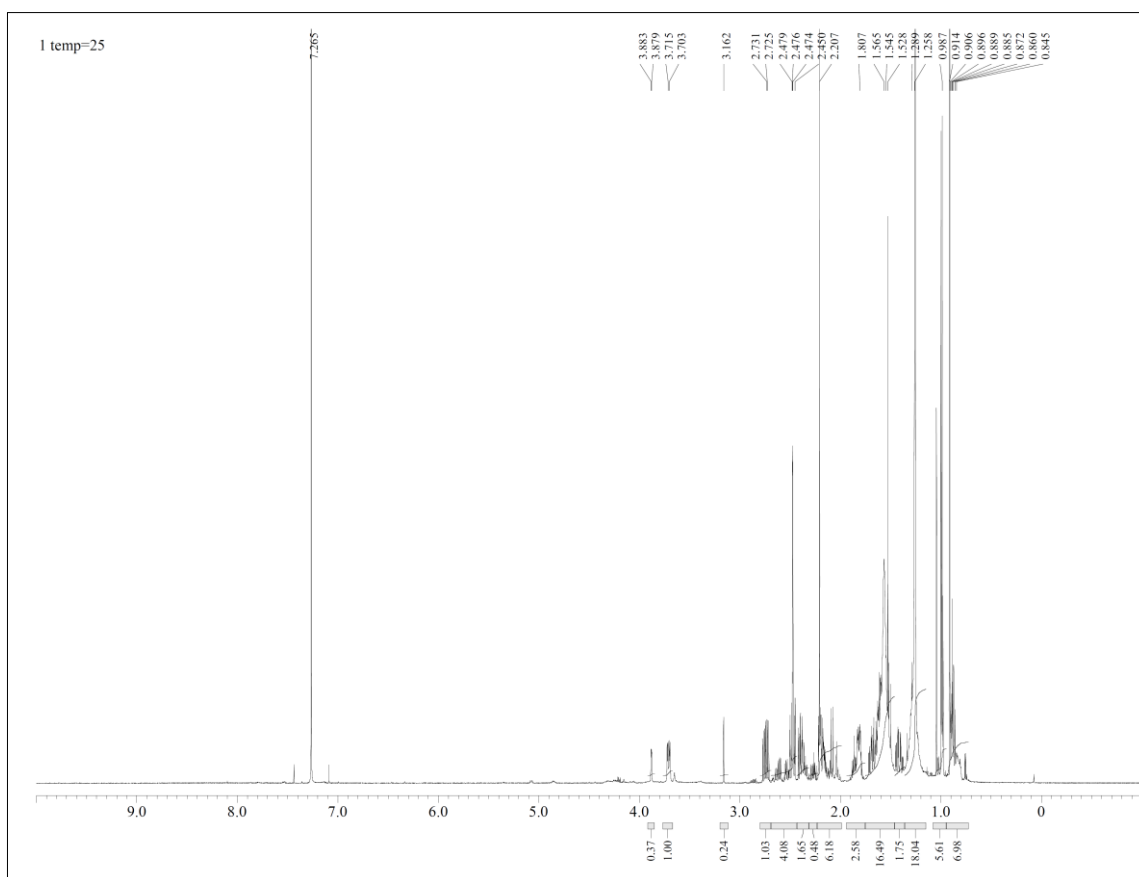


Figure S28. The ^1H -NMR spectrum of **1** at 25°C .

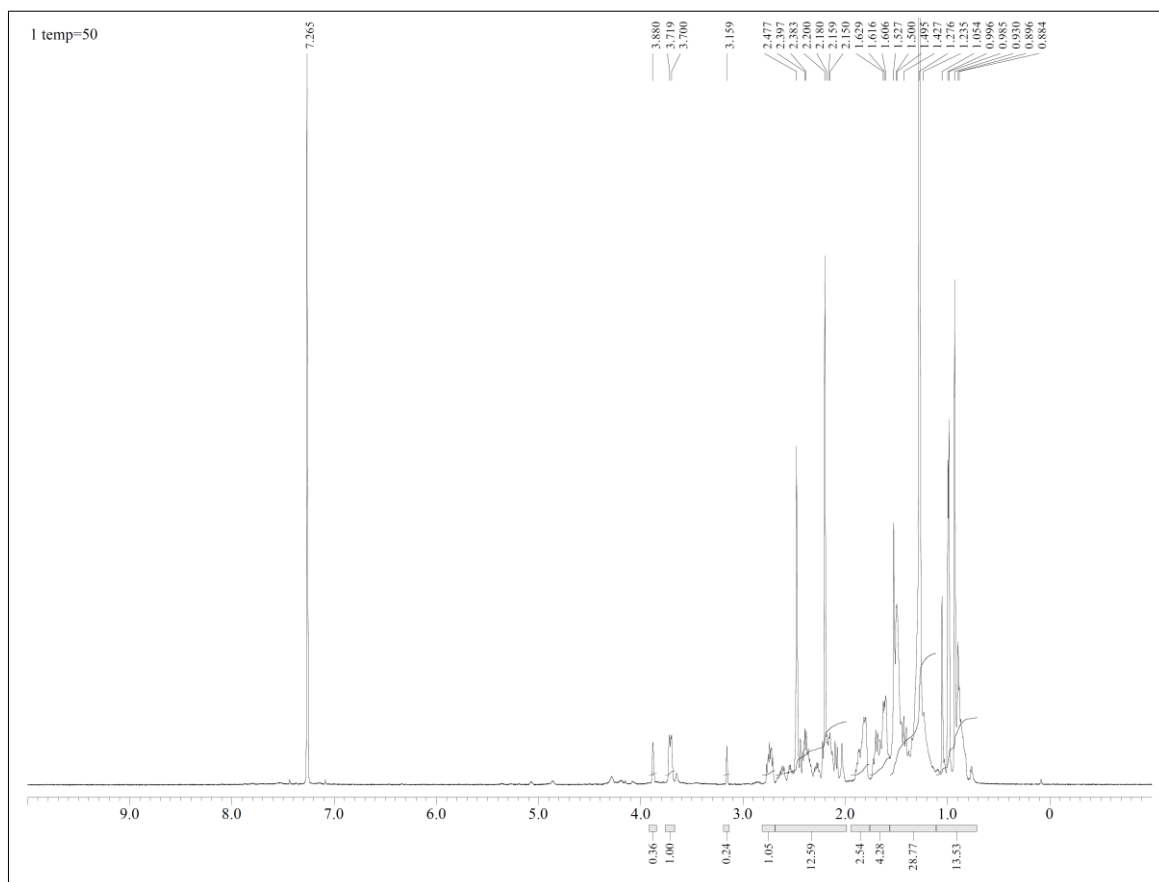


Figure S29. The ^1H -NMR spectrum of **1** at 50°C.

Table S1. DP4+ analysis results of compounds **1** and **2**.

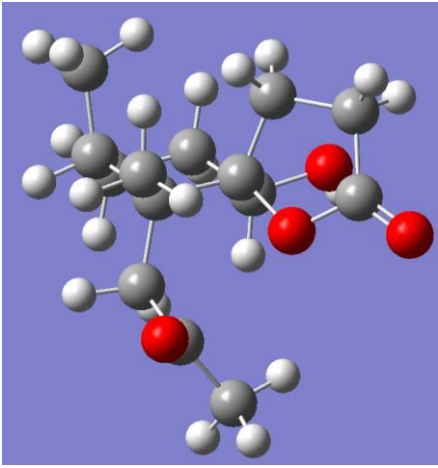
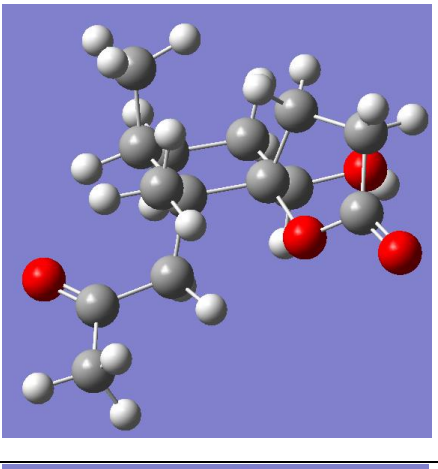
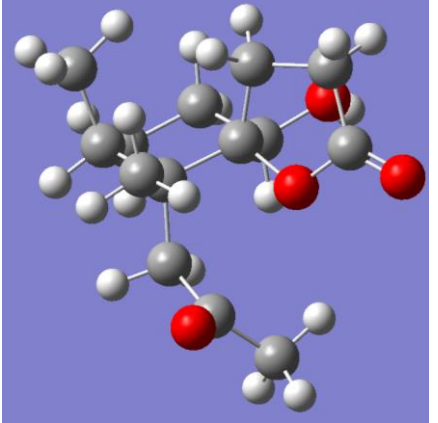
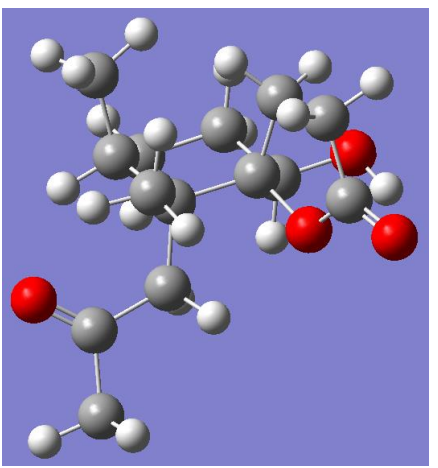
Compound	1		2	
	Diastereomer 1 1-1 <i>S</i> ,4 <i>S</i> ,5 <i>R</i> ,6 <i>R</i>	Diastereomer 2 1-1 <i>R</i> ,4 <i>S</i> ,5 <i>R</i> ,6 <i>R</i>	Diastereomer 1 2-1 <i>R</i> ,4 <i>S</i> ,5 <i>R</i> ,6 <i>R</i>	Diastereomer 2 2-1 <i>S</i> ,4 <i>S</i> ,5 <i>R</i> ,6 <i>R</i>
sDP4+ (H data)	99.79%	0.21%	100.00%	0.00%
sDP4+ (C data)	78.90%	21.10%	99.98%	0.02%
sDP4+ (All data)	99.94%	0.06%	100.00%	0.00%
uDP4+ (H data)	99.45%	0.55%	100.00%	0.00%
uDP4+ (C data)	95.89%	4.11%	99.91%	0.09%
uDP4+ (All data)	99.98%	0.02%	100.00%	0.00%
DP4+ (H data)	100.00%	0.00%	100.00%	0.00%
DP4+ (C data)	98.87%	1.13%	100.00%	0.00%
DP4+ (All data)	100.00%	0.00%	100.00%	0.00%

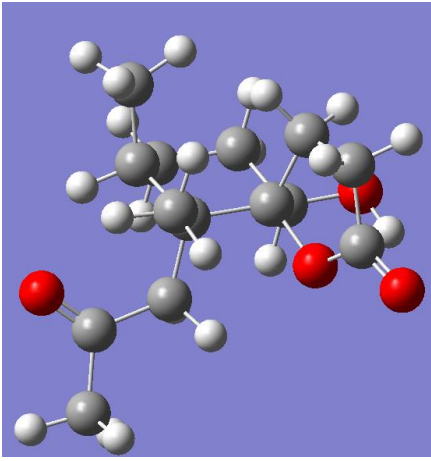
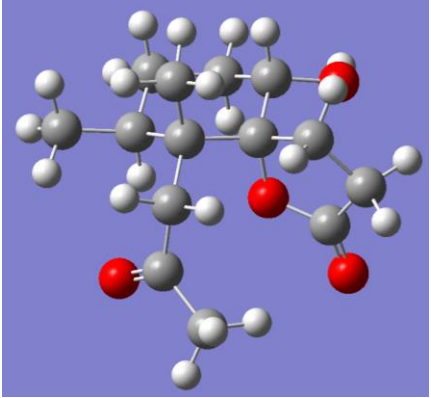
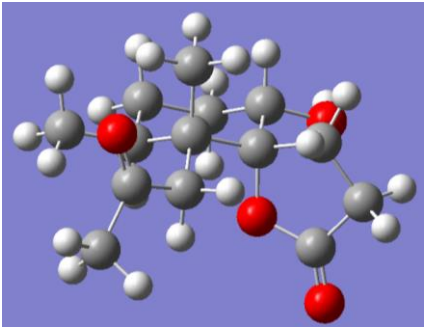
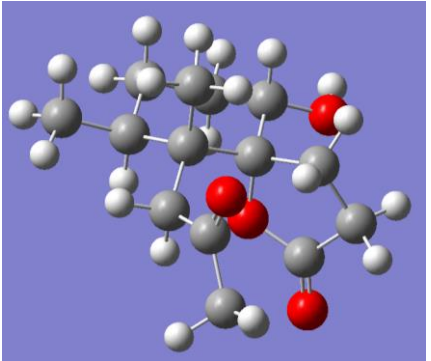
Table S2. Experimental and calculated specific optical rotation values of compounds **1** and **2**.

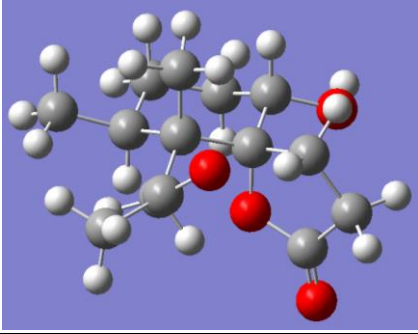
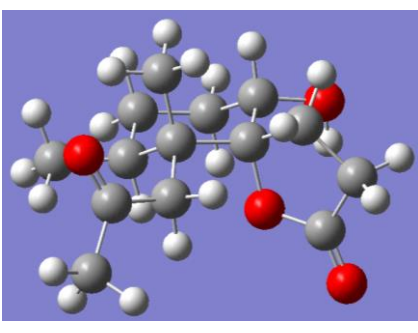
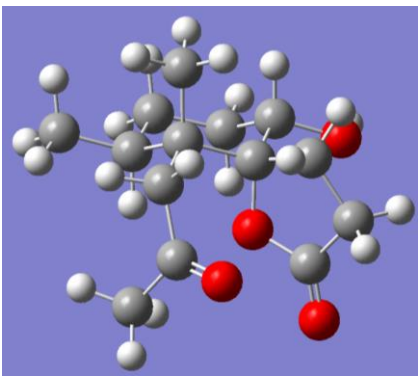
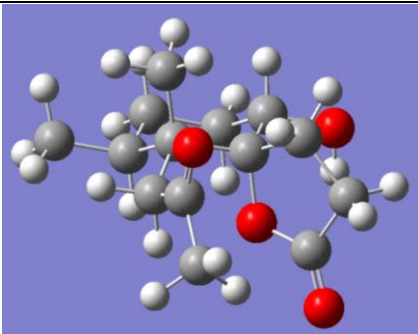
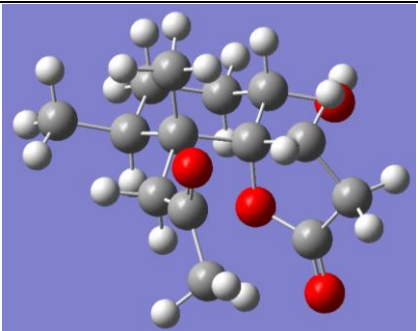
	Cald. value ^a	Exp. value
Exp. 1 ^b		185
Cald. 1 -1 <i>S</i> ,4 <i>S</i> ,5 <i>R</i> ,6 <i>R</i>	66	
Cald. 1 -1 <i>R</i> ,4 <i>R</i> ,5 <i>S</i> ,6 <i>S</i>	-66	
Exp. 2 ^c		44
Cald. 2 -1 <i>R</i> ,4 <i>S</i> ,5 <i>R</i> ,6 <i>R</i>	12	
Cald. 2 -1 <i>S</i> ,4 <i>R</i> ,5 <i>S</i> ,6 <i>S</i>	-12	

^a Solvent phase in CHCl₃; ^b[α]_D²⁵ (*c* 0.001, CHCl₃); ^c[α]_D²² (*c* 0.015, CHCl₃)

Table S3. Optimized conformational search results of **1**.

	3D structures of 1-1R,4S,5R,6R	Relative energy (KJ/mol)	Boltzmann distribution
1		0.000000	32.96%
2		0.305770	19.67%
3		0.312200	19.46%
4		0.508900	13.96%

5		0.508980	13.95%
	3D structures of 1-1 <i>S</i> ,4 <i>S</i> ,5 <i>R</i> ,6 <i>R</i>	Relative energy (KJ/mol)	Boltzmann distribution
1		0.000000	15.57%
2		0.030420	14.79%
3		0.135140	12.39%

4		0.211430	10.89%
5		0.278060	9.73%
6		0.315970	9.13%
7		0.365190	8.40%
8		0.473250	7.00%

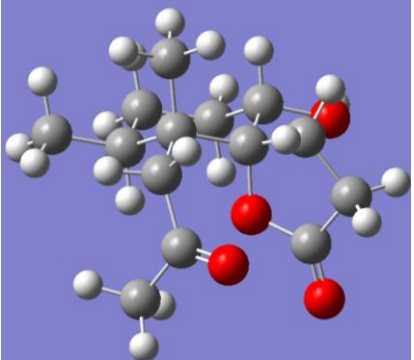
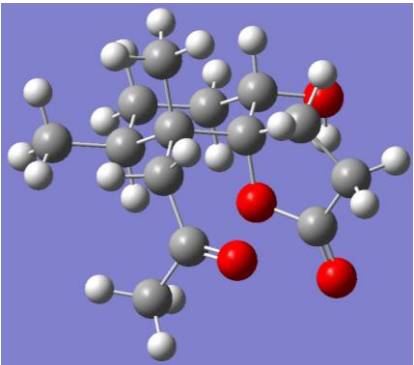
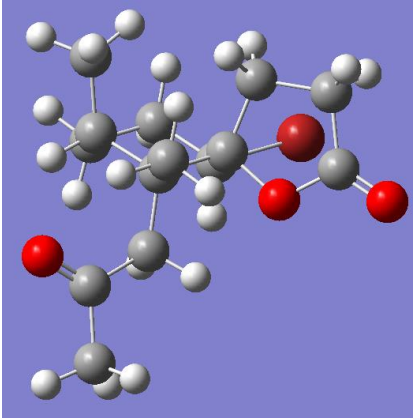
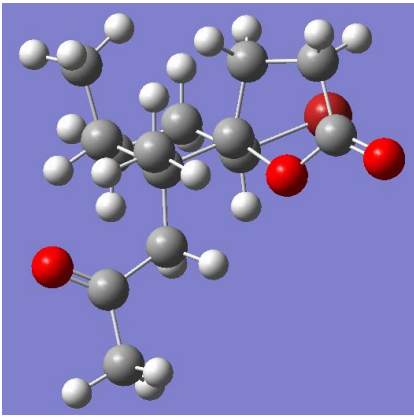
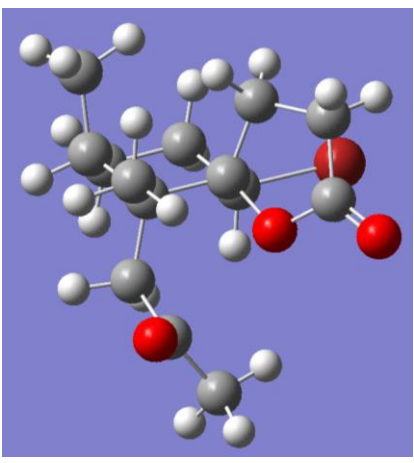
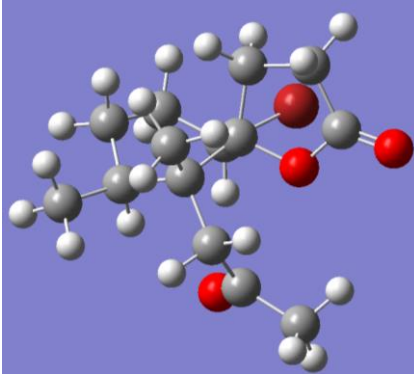
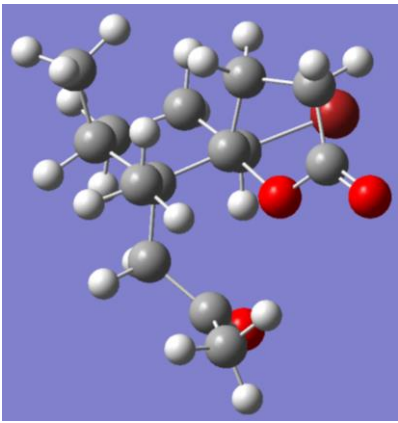
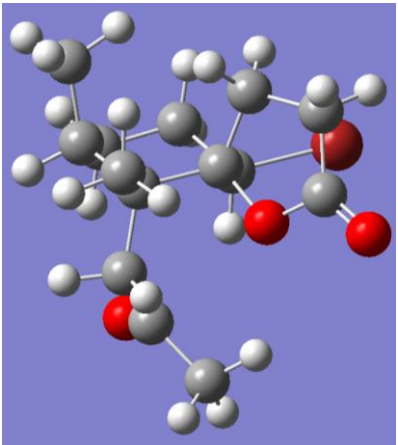
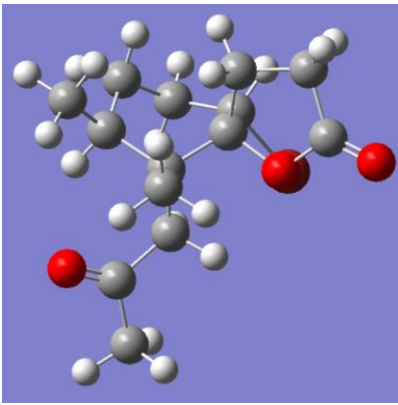
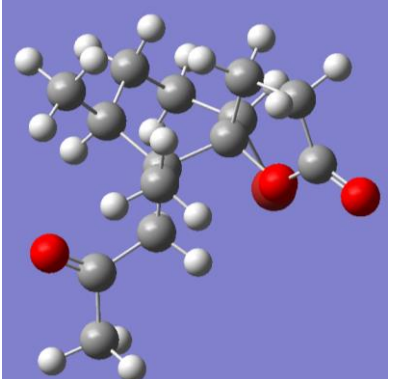
9		0.539540	6.26%
10		0.581580	5.83%

Table S4. Optimized conformational search results of **2**.

	3D structures of 2-1R,4S,5R,6R	Relative energy (KJ/mol)	Boltzmann distribution
1		0.000000	21.27%
2		0.001030	21.23%
3		0.107180	17.75%
4		0.158220	16.28%

5		0.303900	12.73%
6		0.404970	10.73%
3D structures of 2-1 <i>S</i> ,4 <i>S</i> ,5 <i>R</i> ,6 <i>R</i>		Relative energy (KJ/mol)	Boltzmann distribution
1		0.000000	23.94%
2		0.012130	23.45%


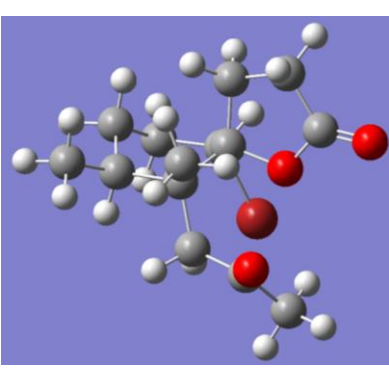
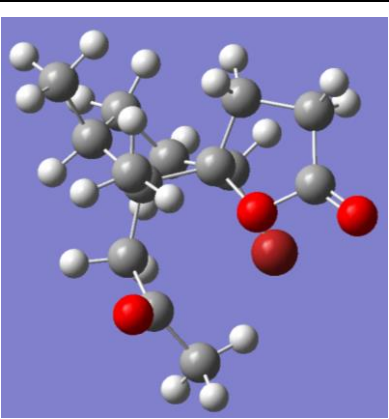
3		0.013190	23.41%
4		0.263030	15.35%
5		0.324280	13.84%

Table S5. X-ray crystallographic data of compound **3**.

Identification code	ic21528	
Empirical formula	C ₁₄ H ₂₁ ClO ₃	
Formula weight	272.76	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	a = 8.2367(2) Å	α = 90°.
	b = 9.9002(3) Å	β = 90°.
	c = 17.2237(5) Å	γ = 90°.
Volume	1404.51(7) Å ³	
Z	4	
Density (calculated)	1.290 Mg/m ³	
Absorption coefficient	0.270 mm ⁻¹	
F(000)	584	
Crystal size	0.599 x 0.512 x 0.081 mm ³	
Theta range for data collection	2.365 to 29.988°.	
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -24 ≤ l ≤ 24	
Reflections collected	39483	
Independent reflections	4100 [R(int) = 0.0666]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9705 and 0.6668	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4100 / 0 / 172	
Goodness-of-fit on F ²	1.159	
Final R indices [I > 2σ(I)]	R1 = 0.0460, wR2 = 0.1060	
R indices (all data)	R1 = 0.0621, wR2 = 0.1248	
Absolute structure parameter	-0.04(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.228 and -0.382 e.Å ⁻³	