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Figure S1.   HRESI-MS spectrum of compound **1**.

Figure S2. ^{1}H-NMR spectrum (400 MHz, CDCl$_3$) of compound **1**.

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

Figure S4. ^{13}C-NMR spectrum (100 MHz, CDCl₃) of compound **1**.
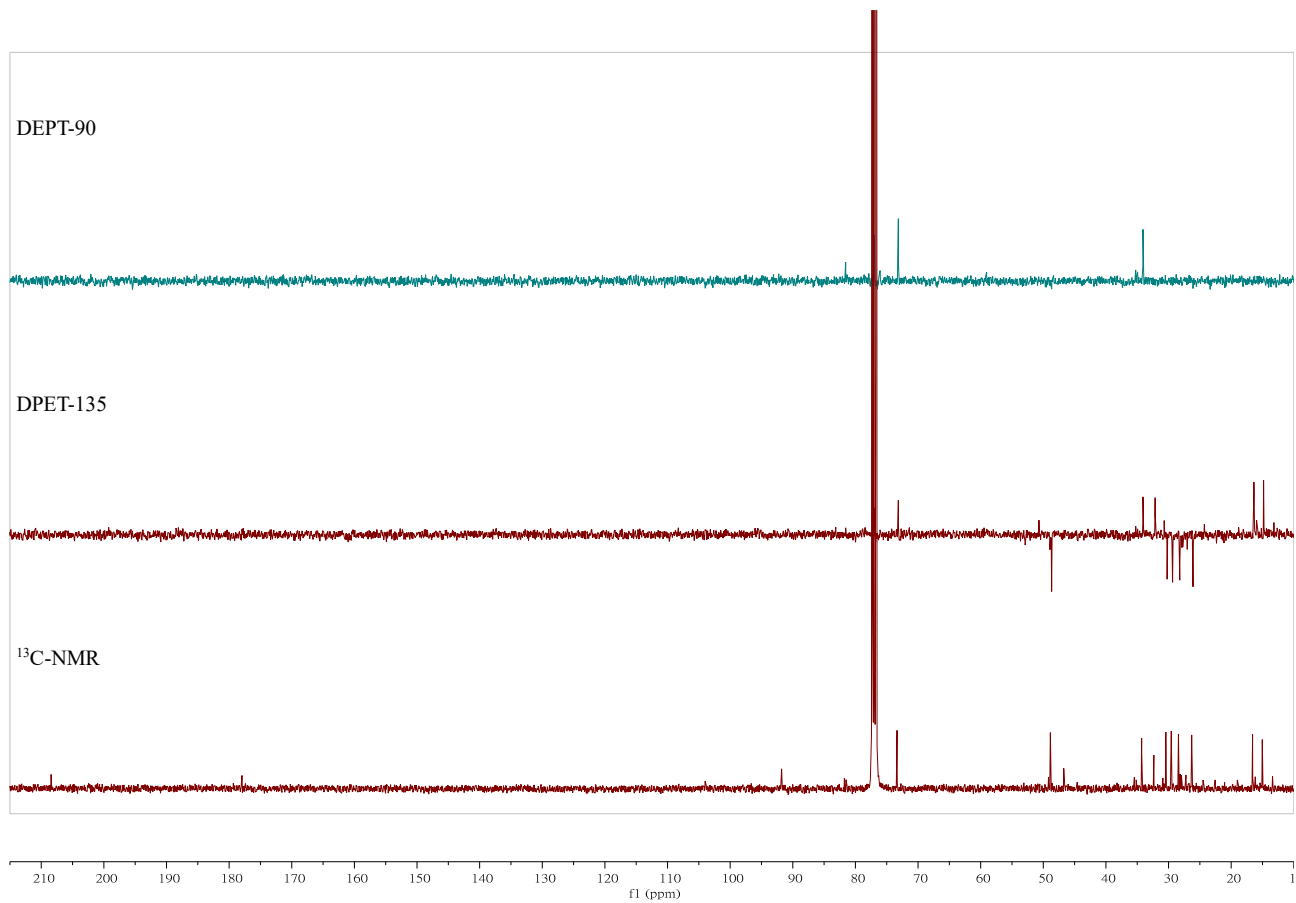
Figure S5. DEPT spectrum of compound **1**.
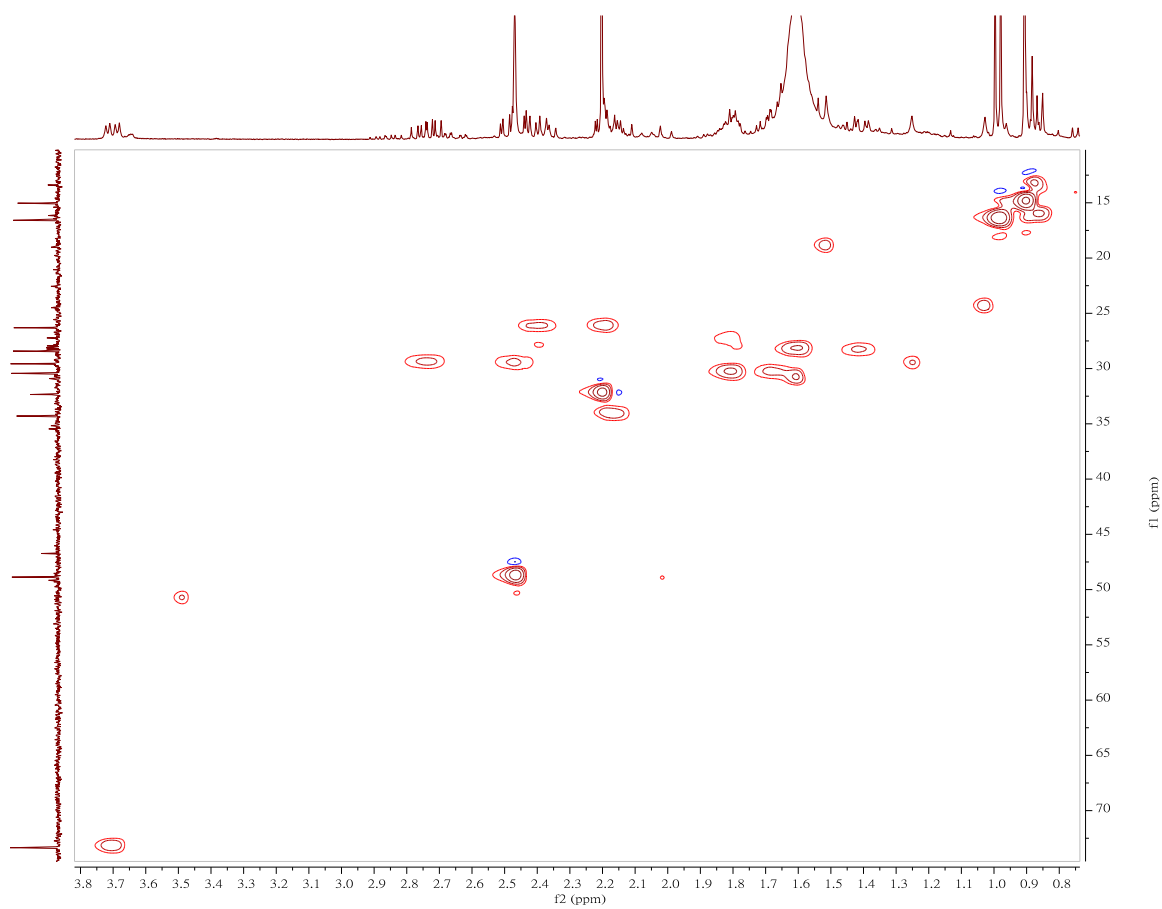
Figure S6. HSQC spectrum of compound **1**.
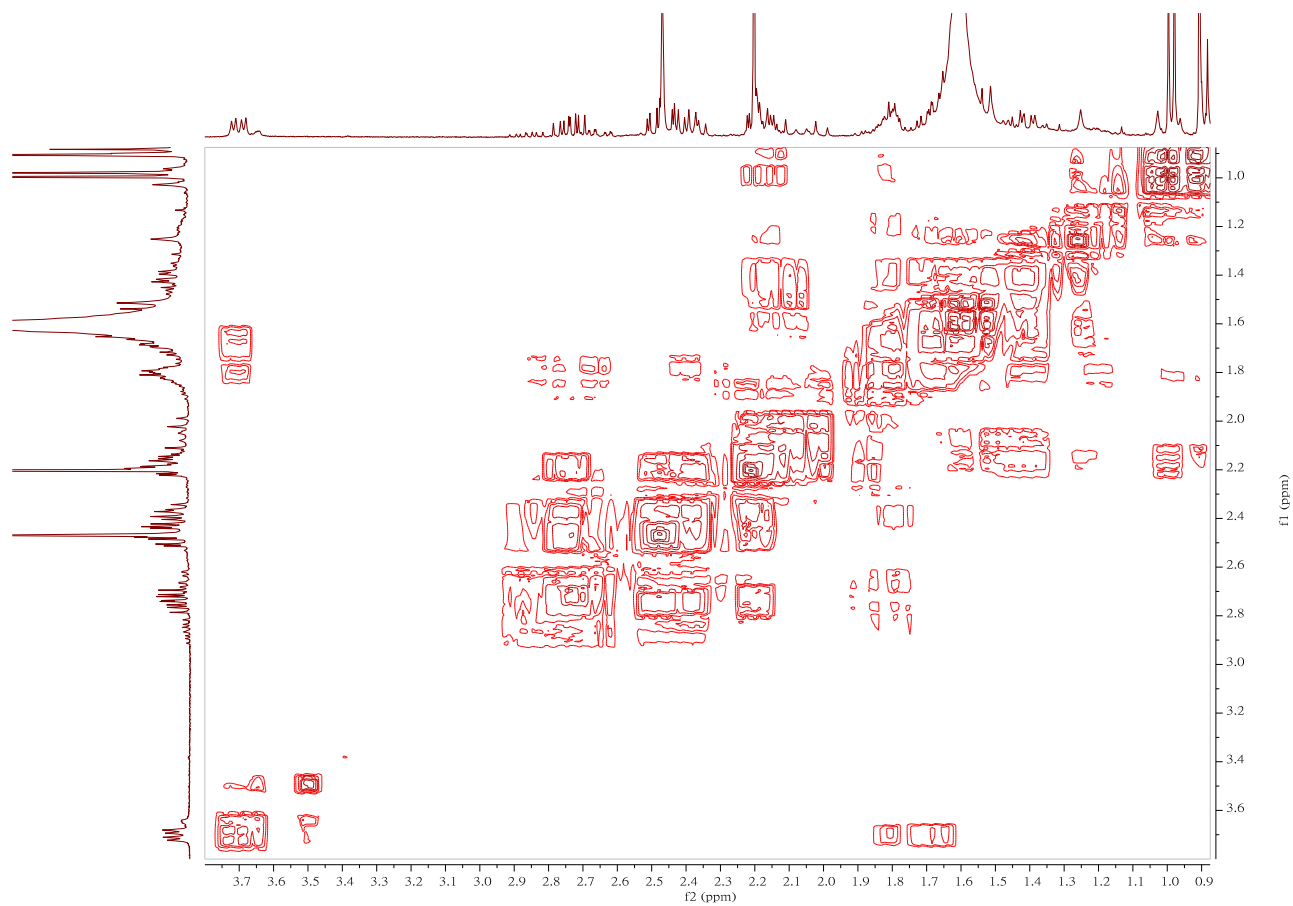
Figure S7. ^{1}H-^{1}H COSY spectrum of compound **1**.
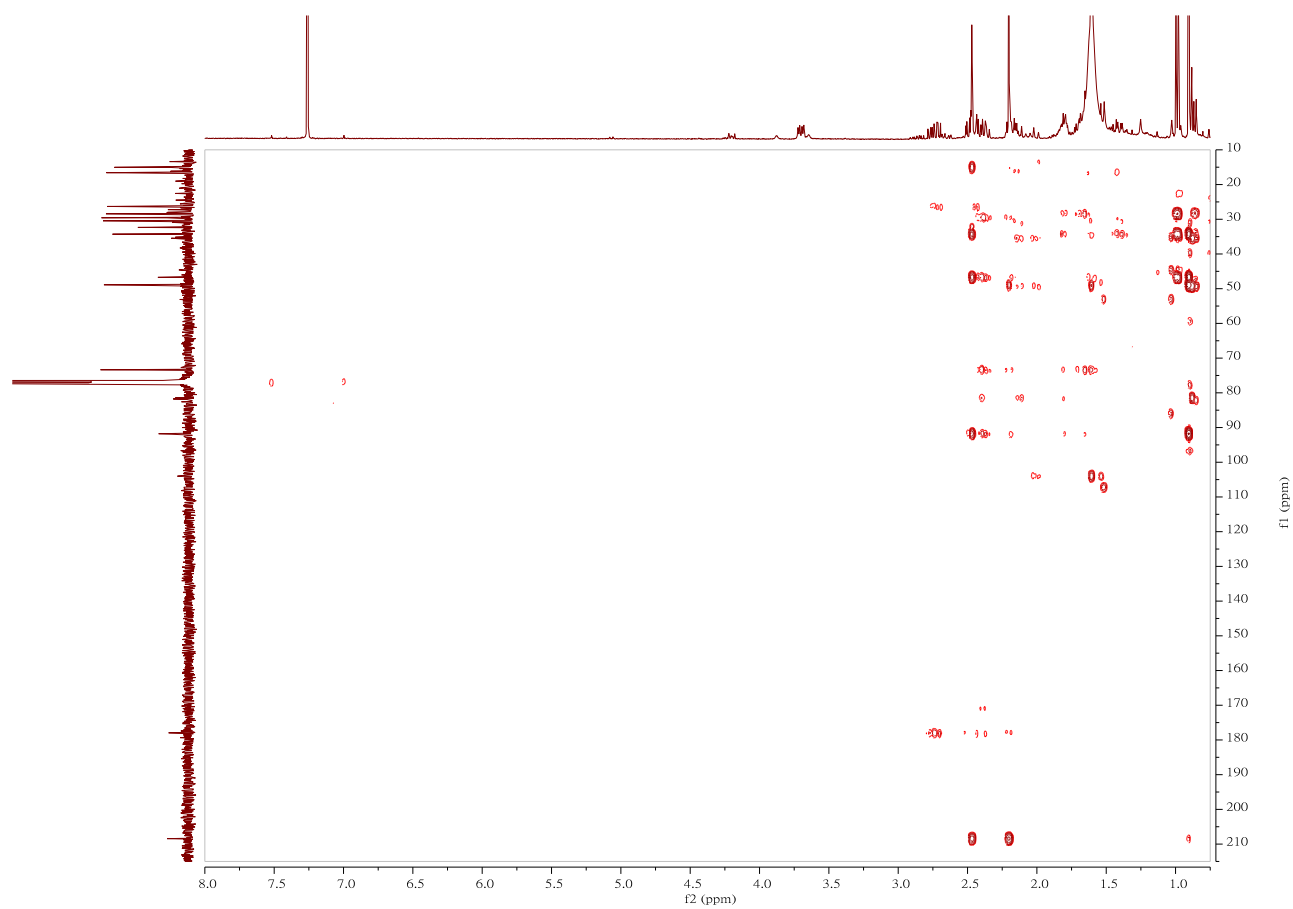
Figure S8. HMBC spectrum of compound **1**.
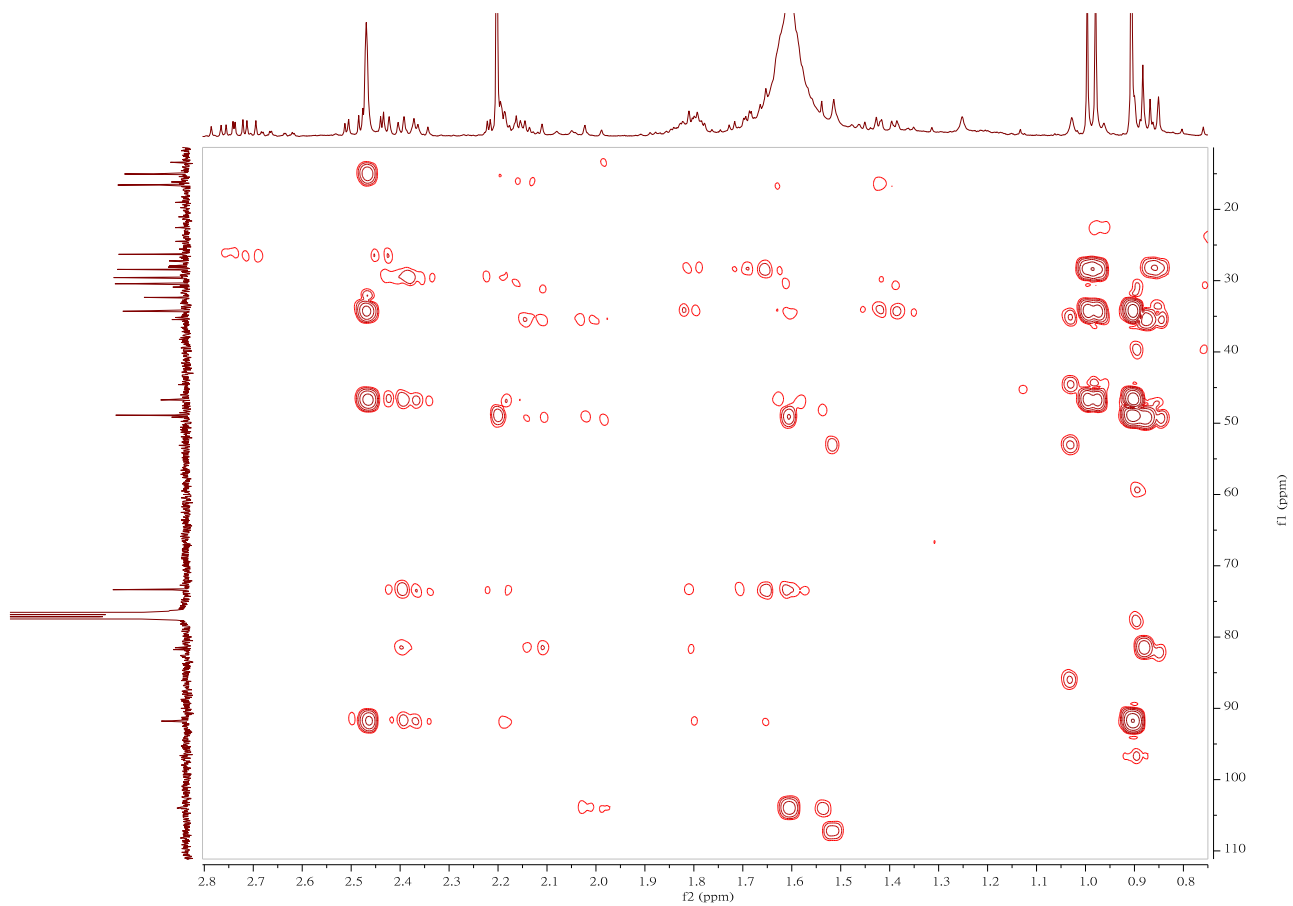
Figure S9. Expanded HMBC spectrum of compound **1**.
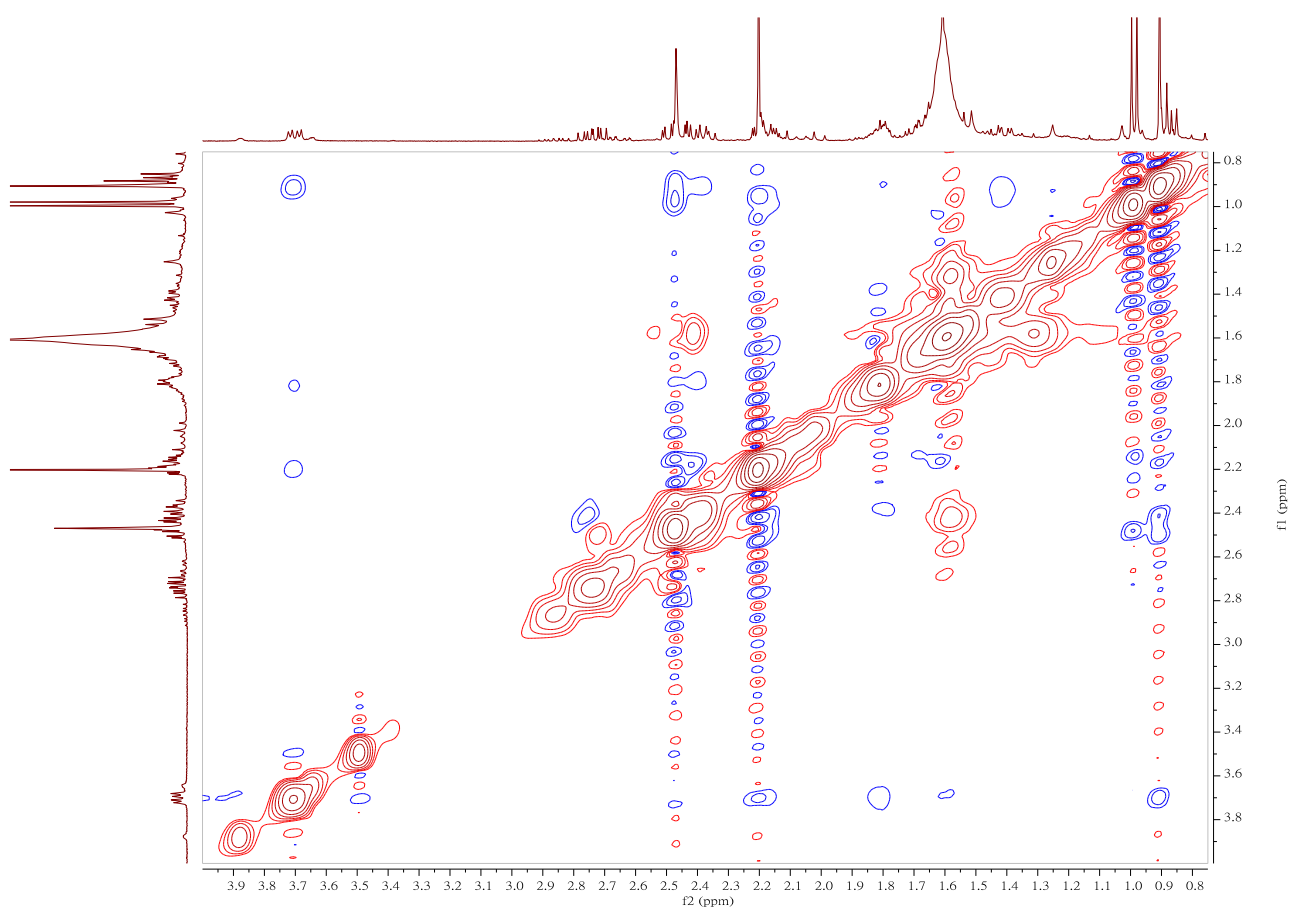
Figure S10. NOESY spectrum of compound **1**.

Functional	Solvent?		Basis Set	Type of Data	
mPW1PW91	PCM		6-311+G(d,p)	Shielding Tensors	

	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5	Isomer 6
sDP4+ (H data)	99.79%	0.21%	-	-	-	-
sDP4+ (C data)	78.90%	21.10%	-	-	-	-
sDP4+ (all data)	99.94%	0.06%	-	-	-	-
uDP4+ (H data)	99.45%	0.55%	-	-	-	-
uDP4+ (C data)	95.89%	4.11%	-	-	-	-
uDP4+ (all data)	99.98%	0.02%	-	-	-	-
DP4+ (H data)	100.00%	0.00%	-	-	-	-
DP4+ (C data)	98.87%	1.13%	-	-	-	-
DP4+ (all data)	100.00%	0.00%	-	-	-	-

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*.

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
339.05646	1	C 14 H 21 Br Na O 3	100.00	339.05663	0.17	0.50	45.3	3.5	even	ok
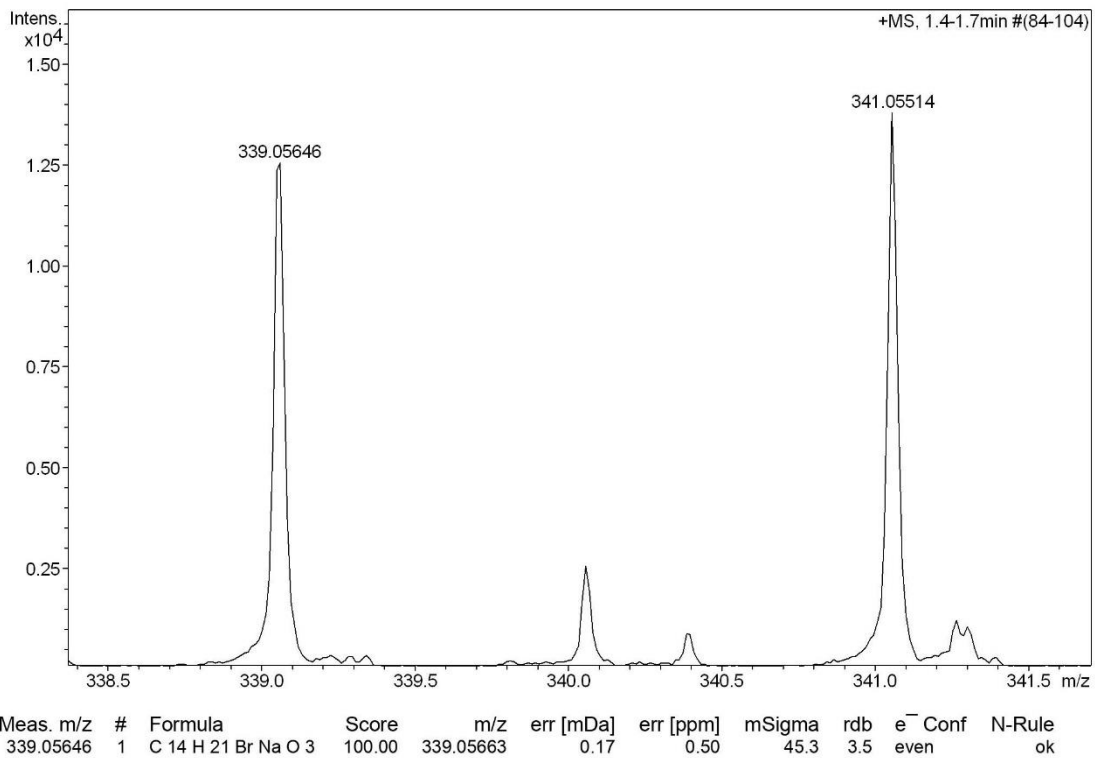
Figure S12. HRESI-MS spectrum of compound **2**.
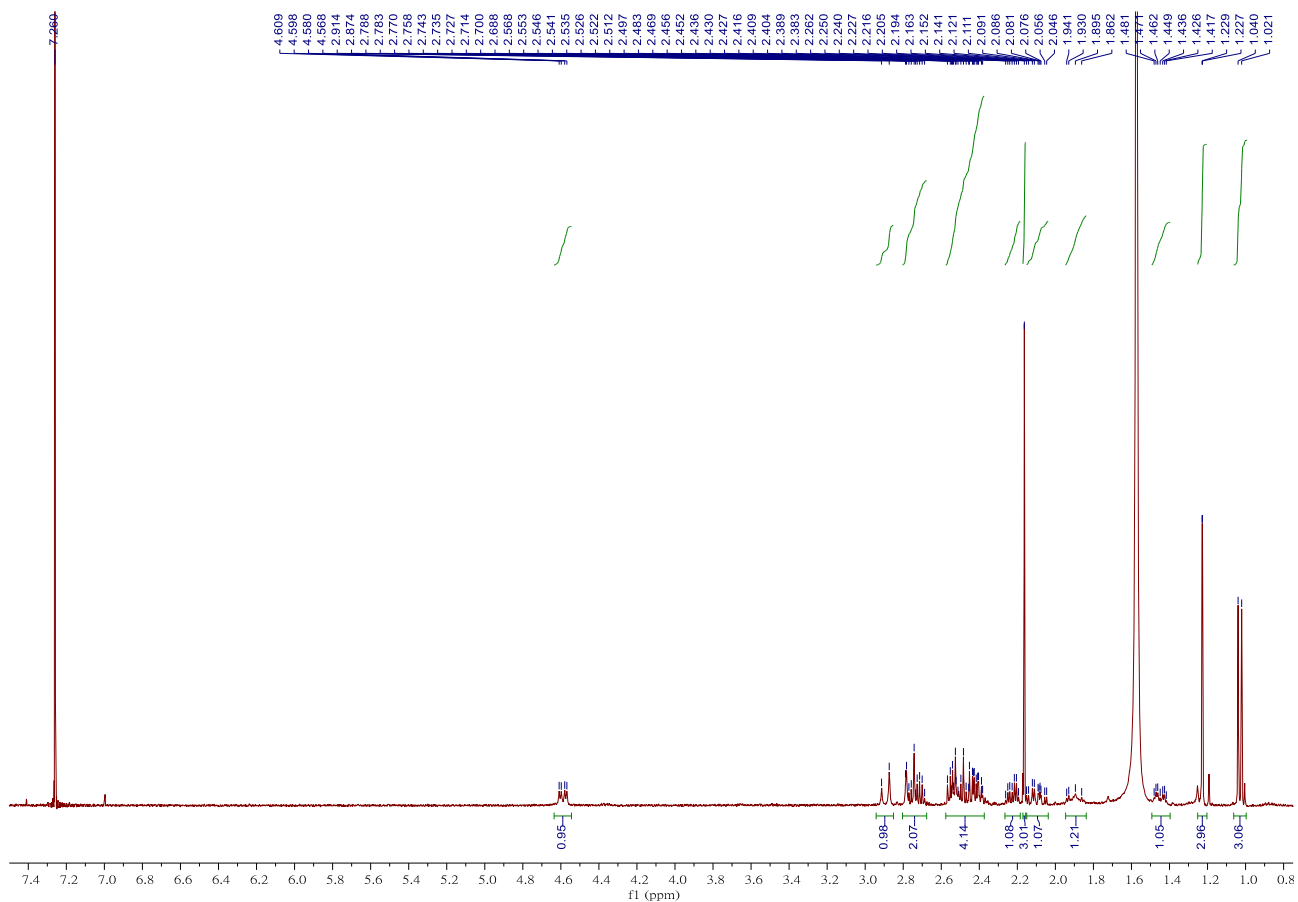
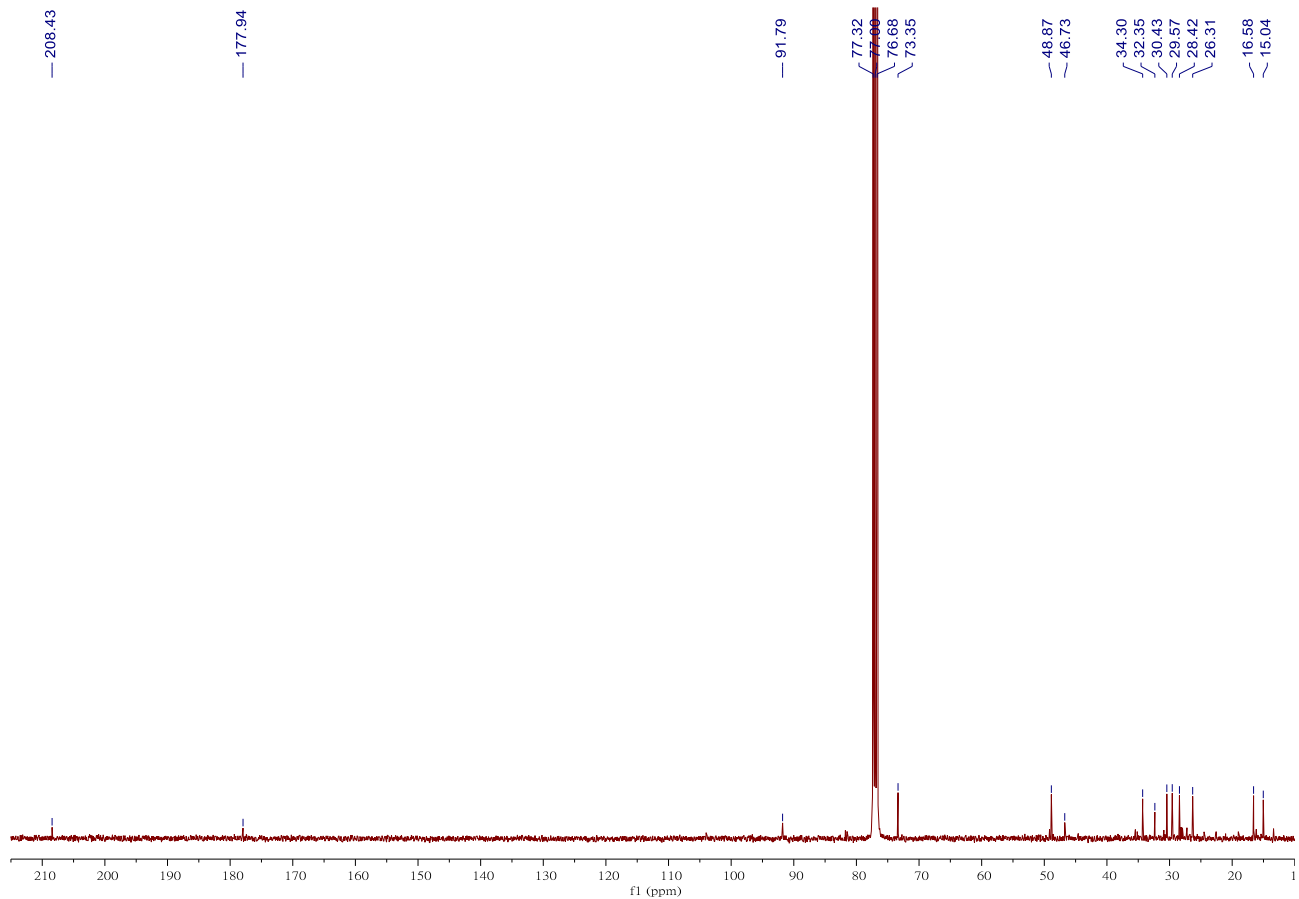**Figure S13.** ^{1}H-NMR spectrum (400 MHz, CDCl$_3$) of compound **2**.
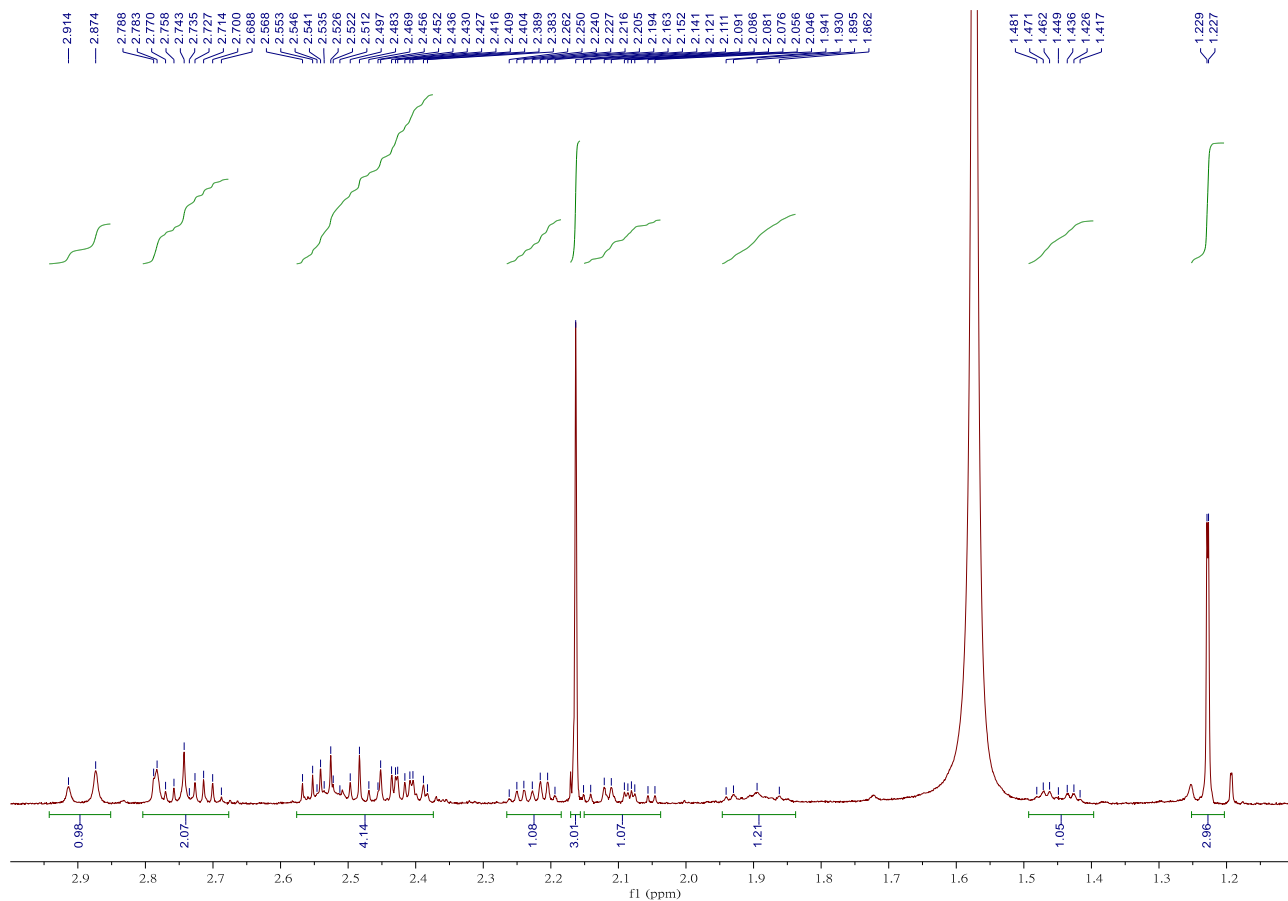
Figure S14. Expanded ^{1}H-NMR spectrum (1.10~3.00 ppm) of compound **2**.

Figure S15. ^{13}C-NMR spectrum (100 MHz, CDCl$_3$) of compound **2**.
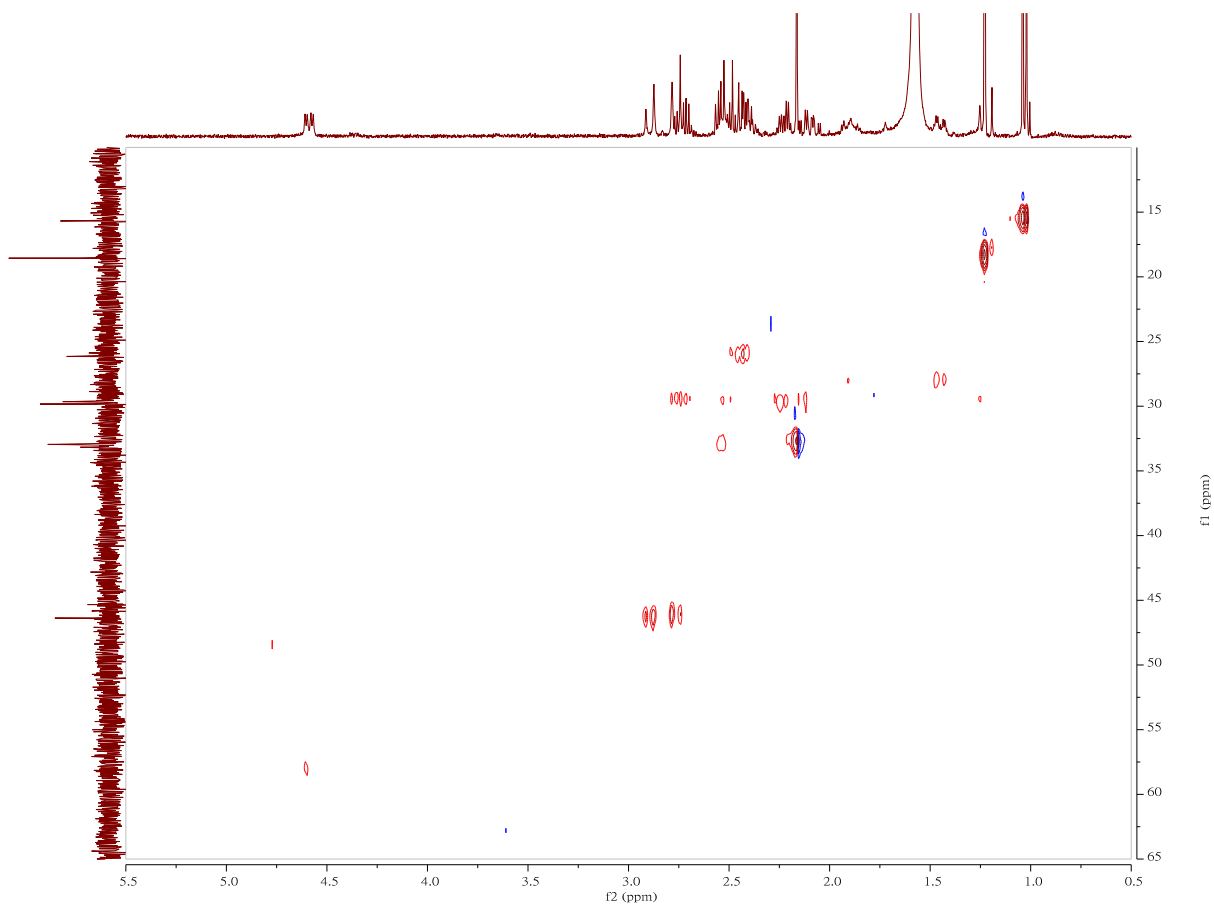
Figure S16. HSQC spectrum of compound **2**.
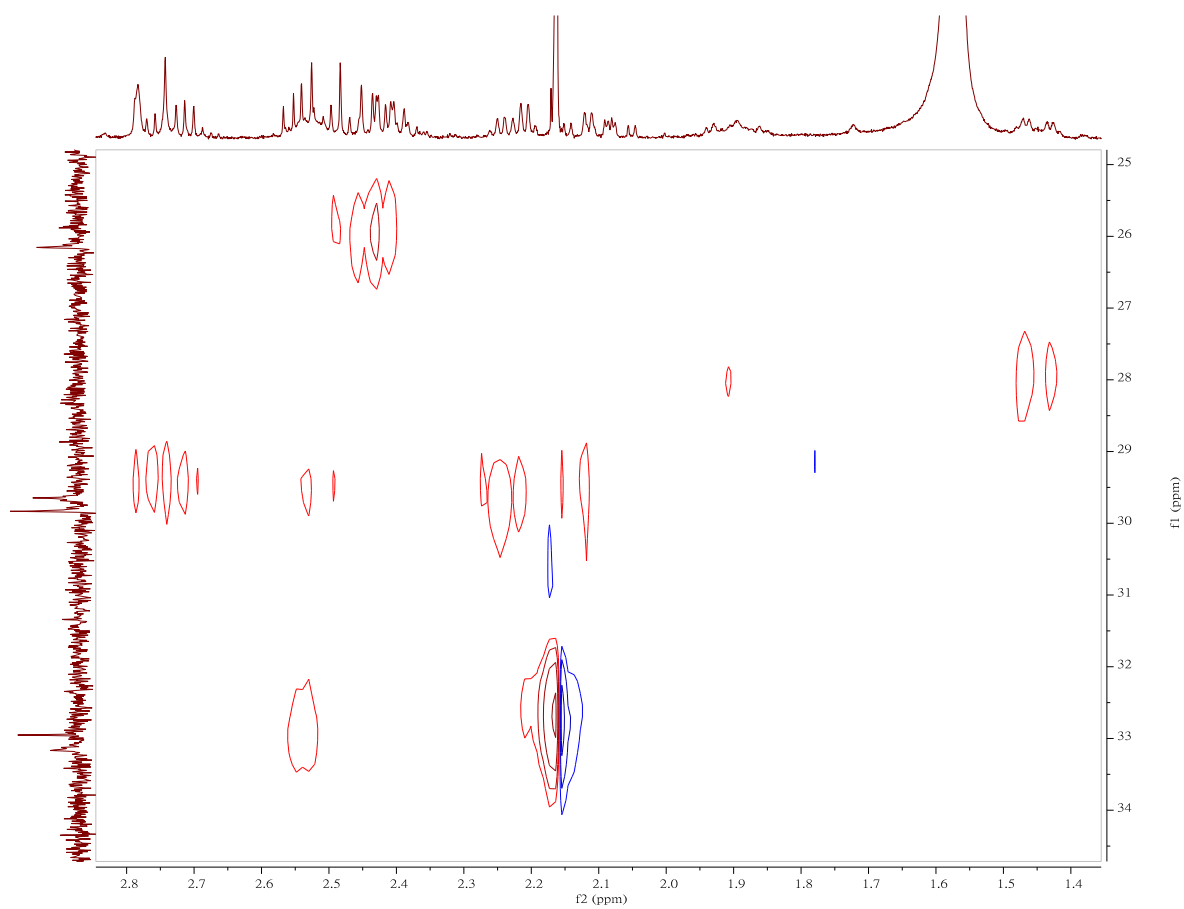
Figure S17. Expanded HSQC spectrum of compound **2**.
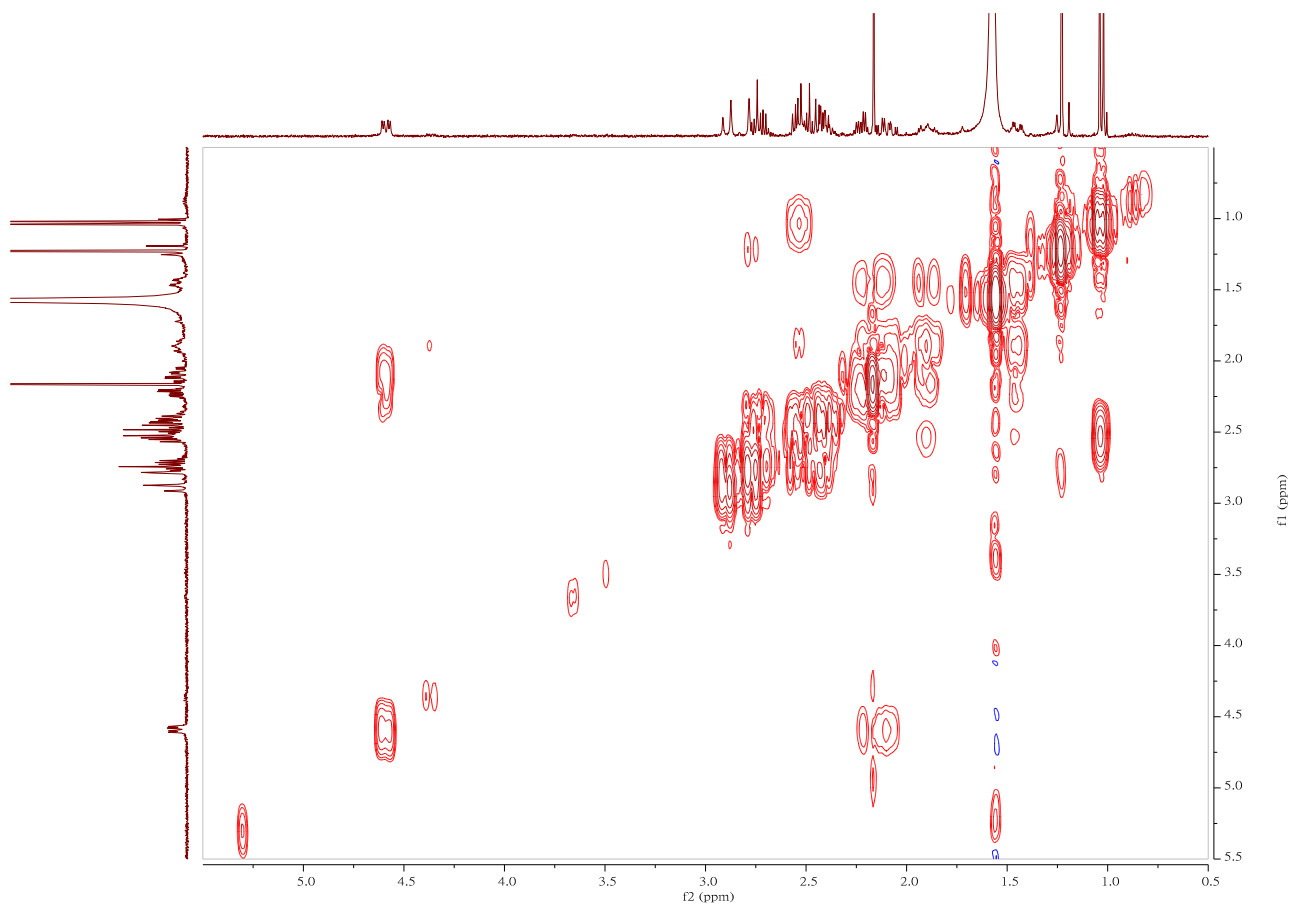
Figure S18. ^{1}H-^{1}H COSY spectrum of compound **2**.
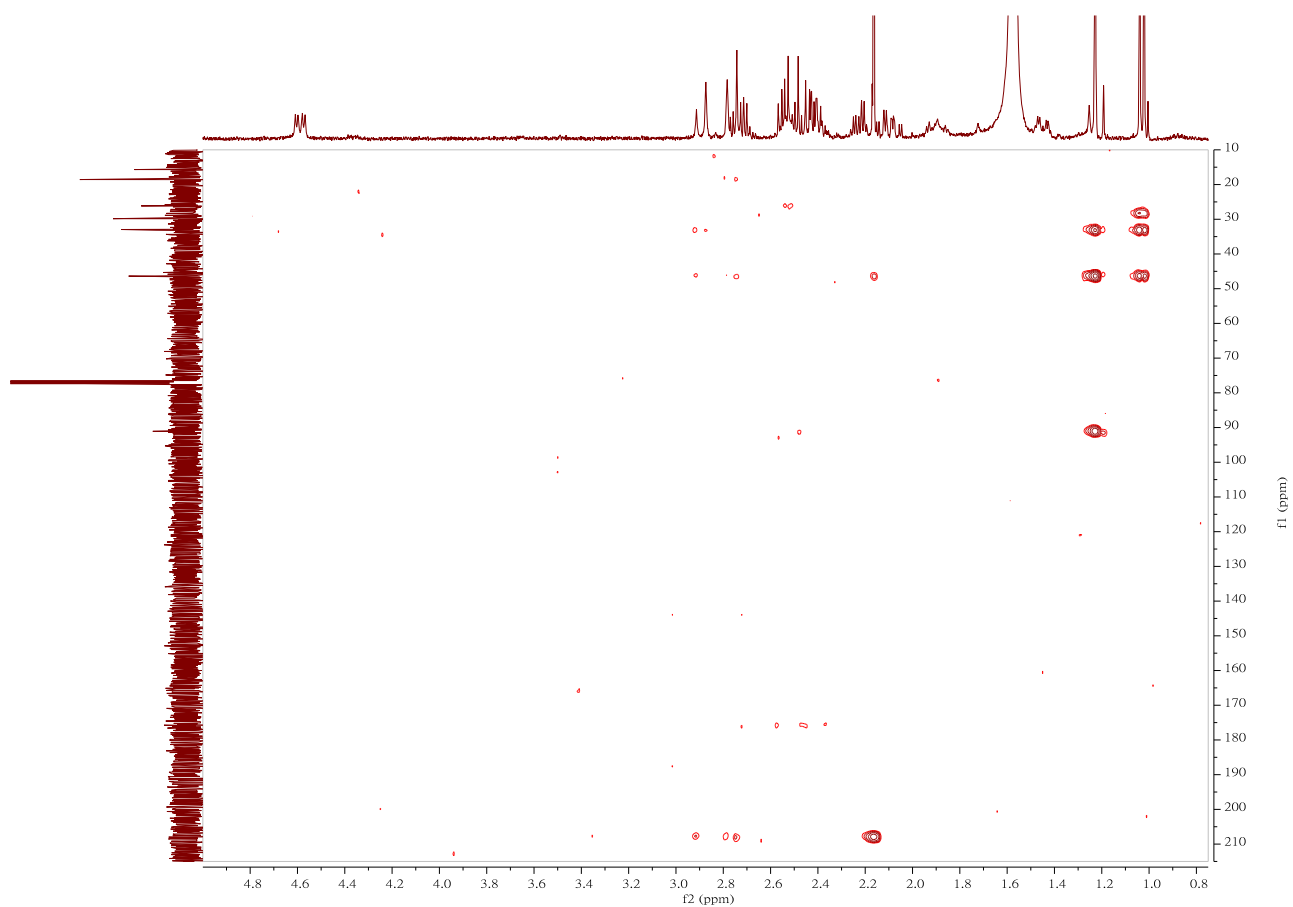
Figure S19. HMBC spectrum of compound **2**.
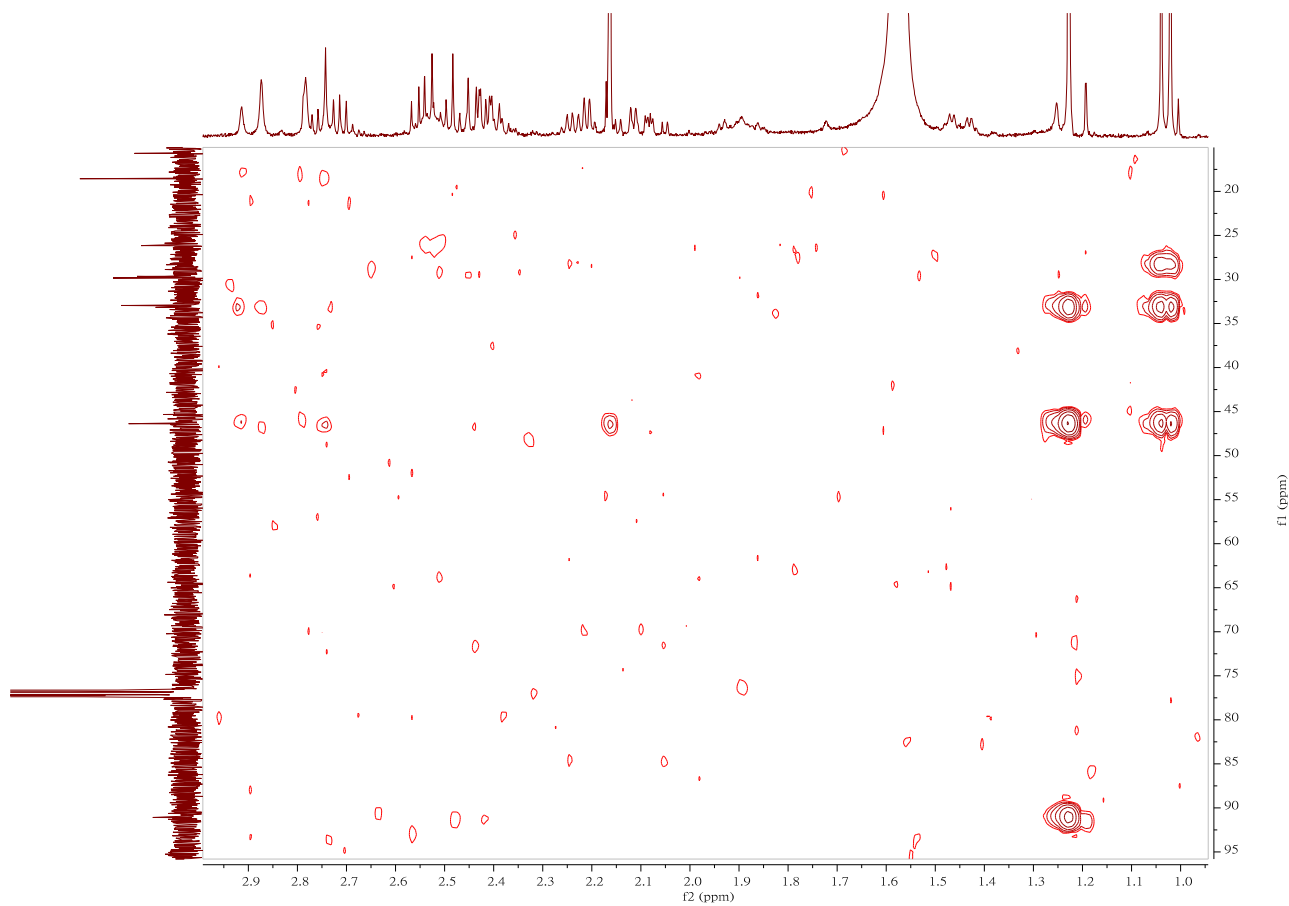
**Figure S20.** Expanded HMBC spectrum of compound **2**.
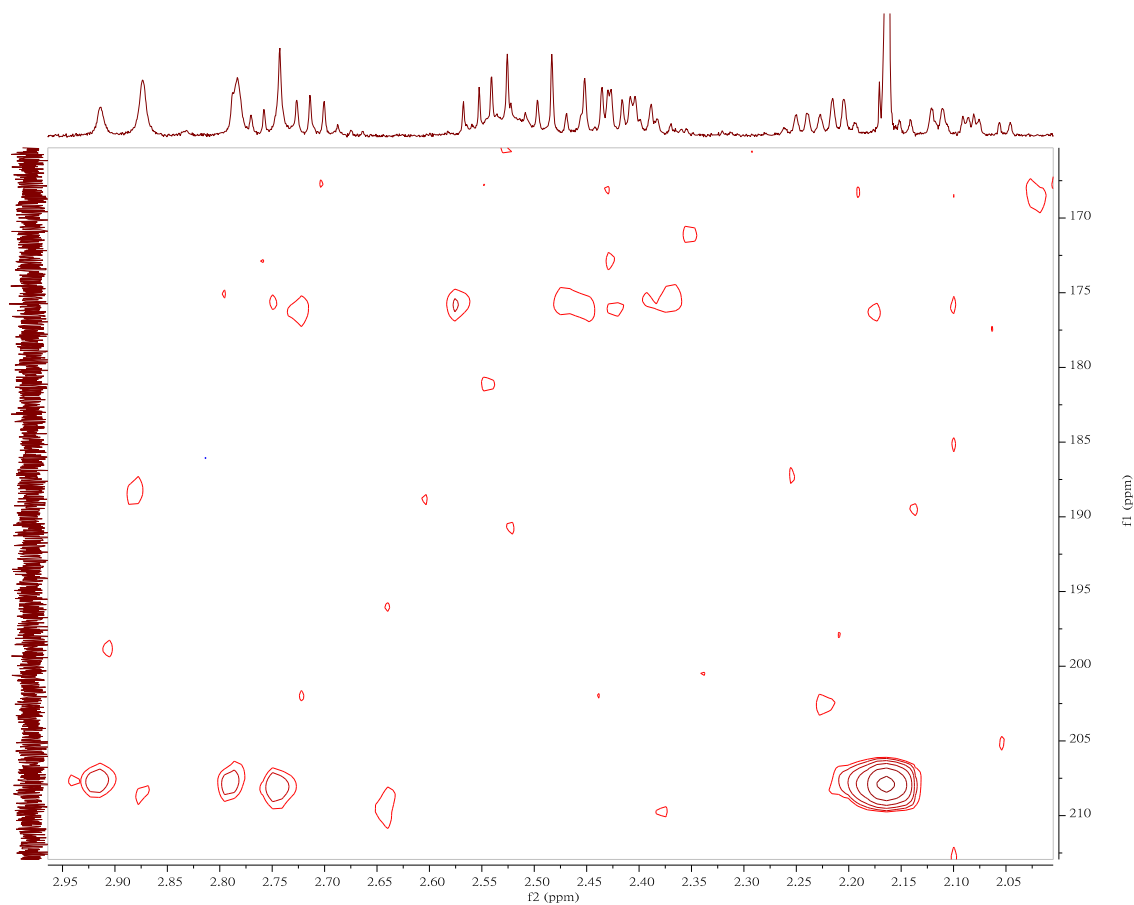
Figure S21. Expanded HMBC spectrum of compound **2**.
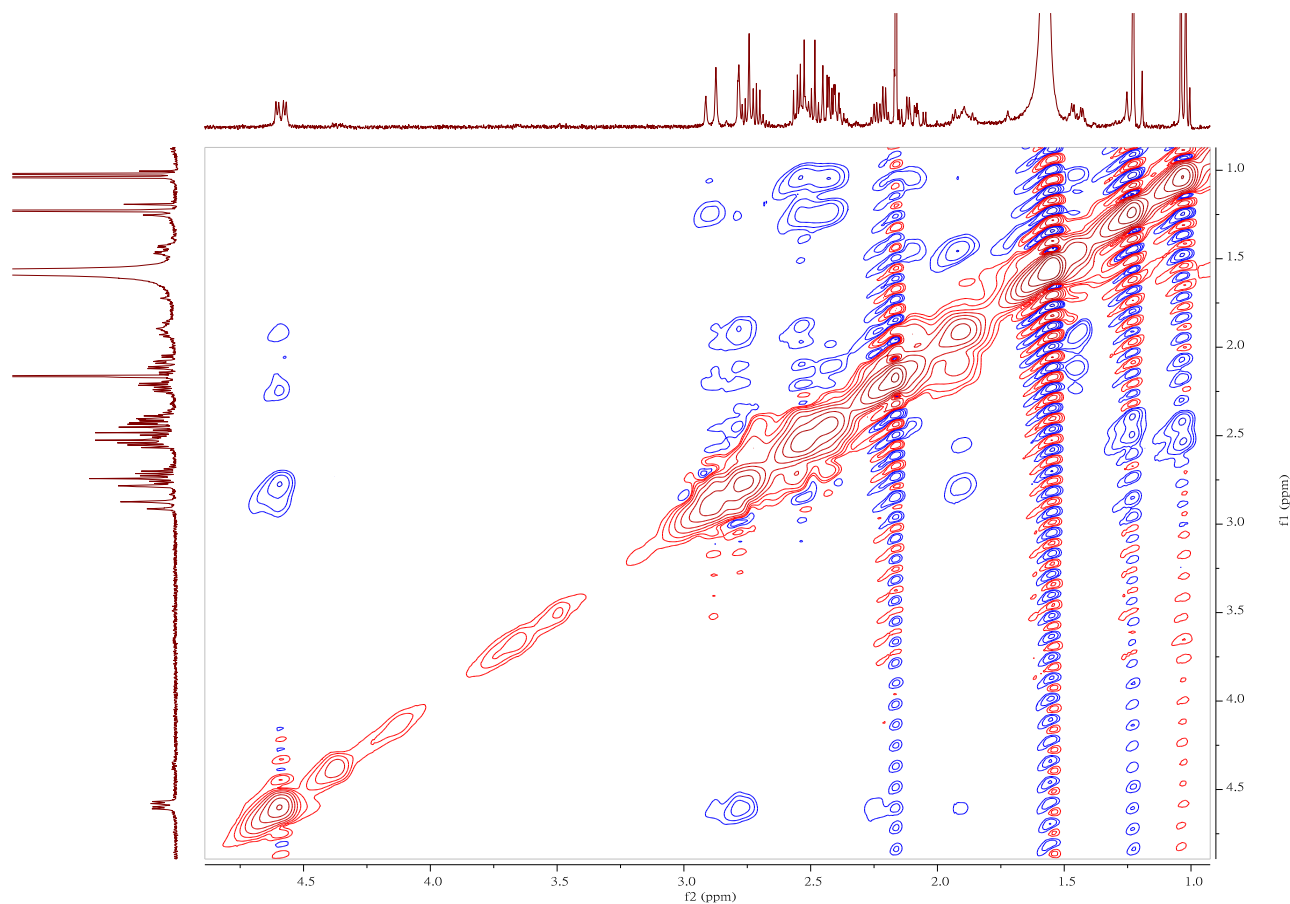
Figure S22. NOESY spectrum of compound **2**.

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

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

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

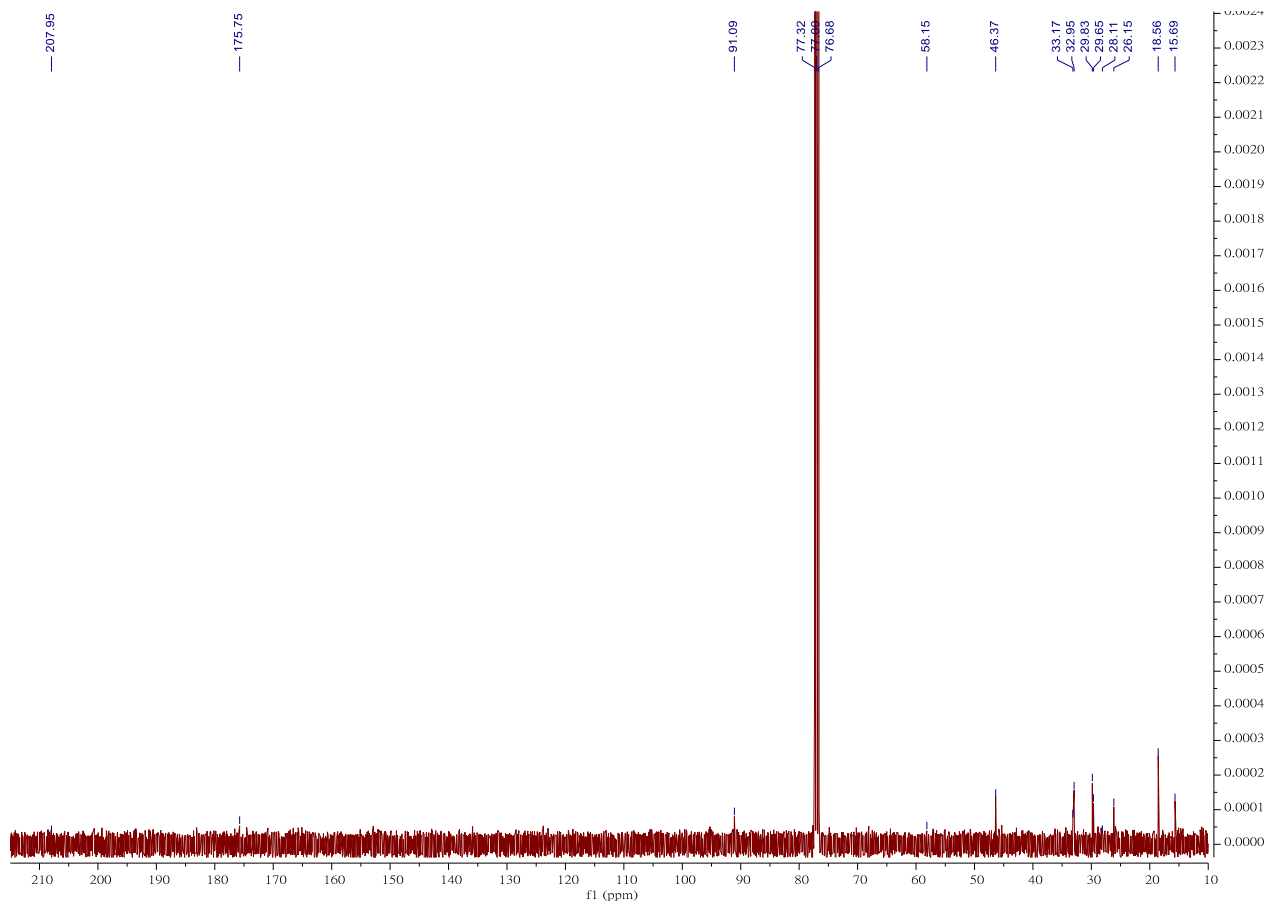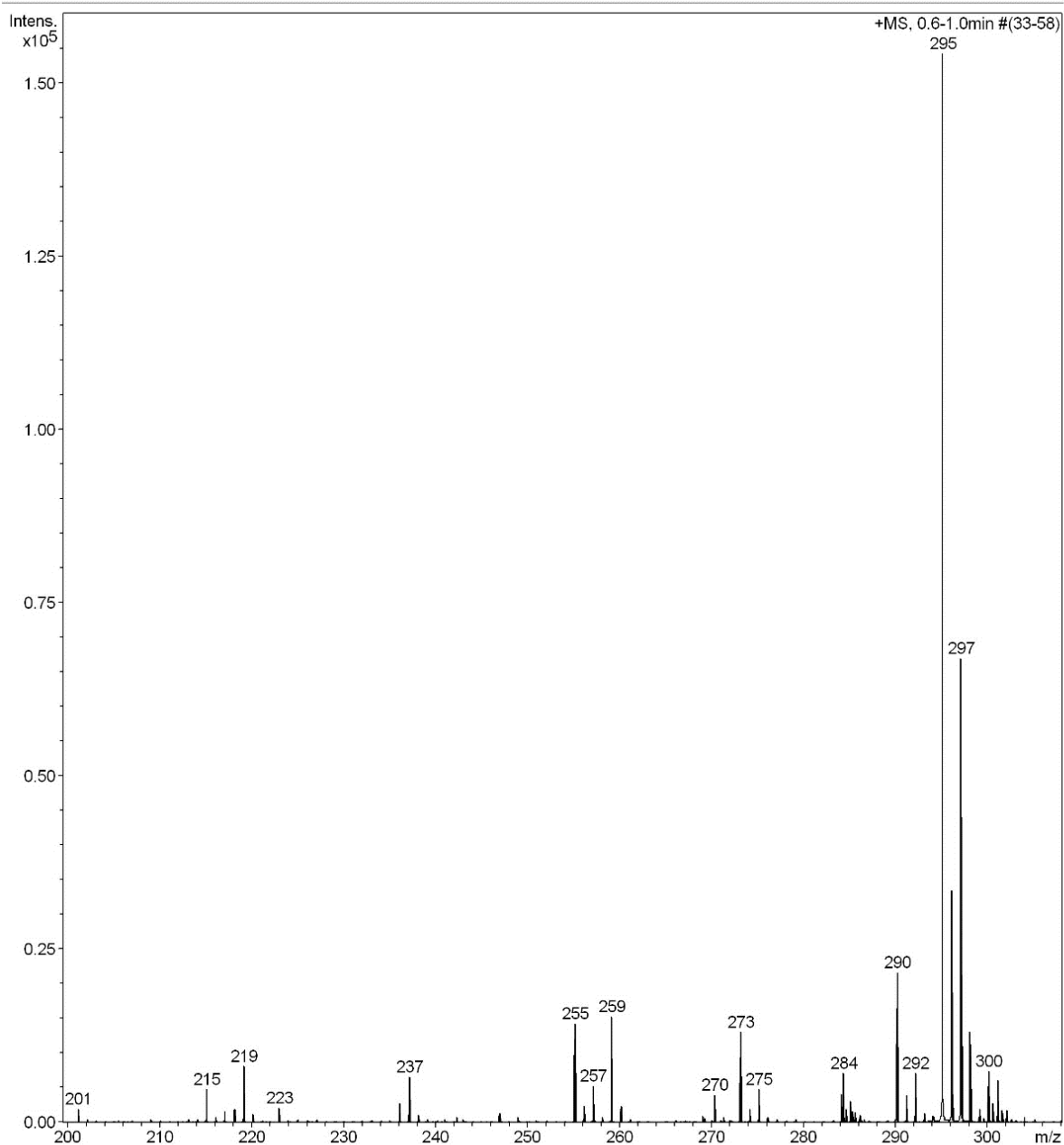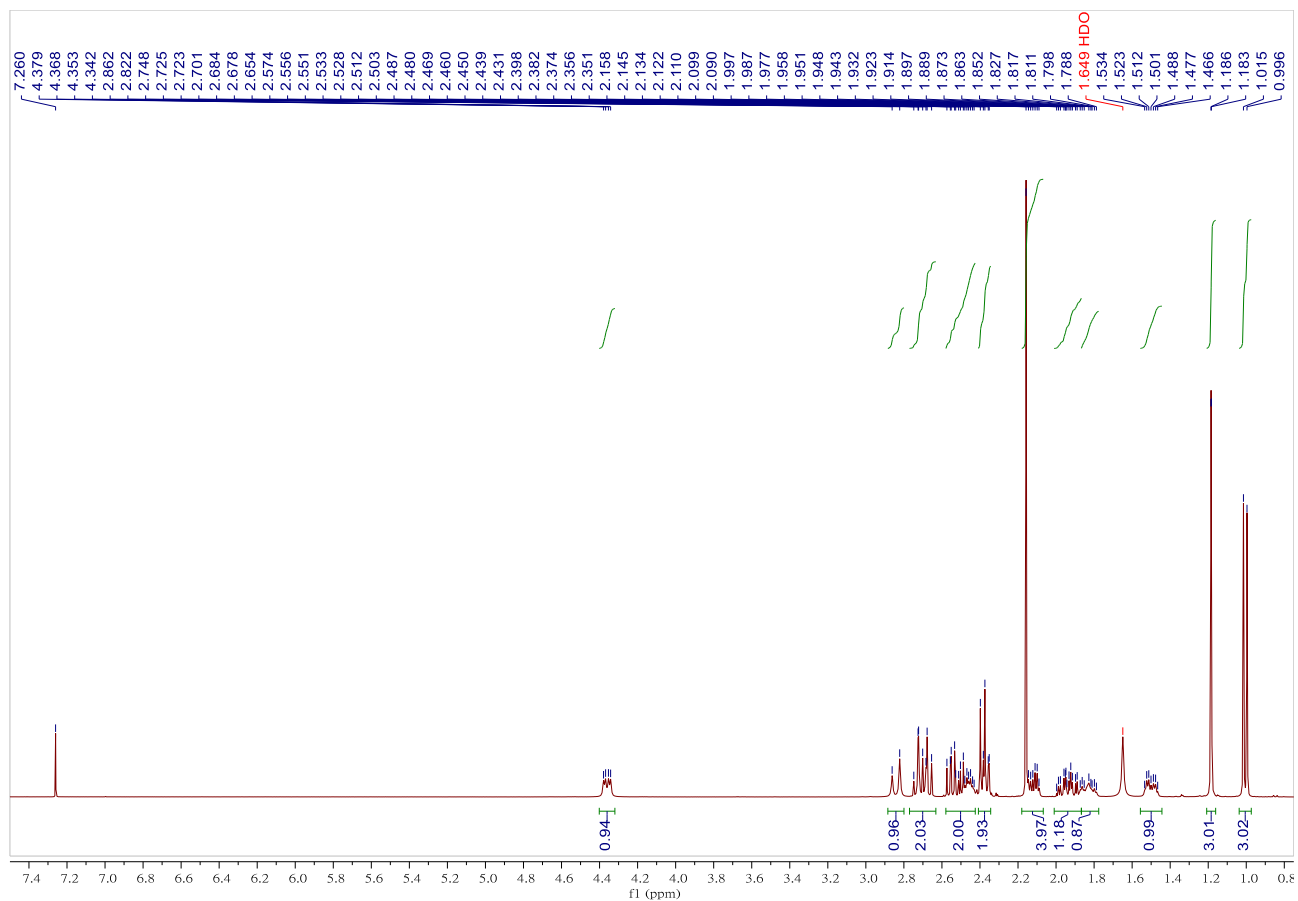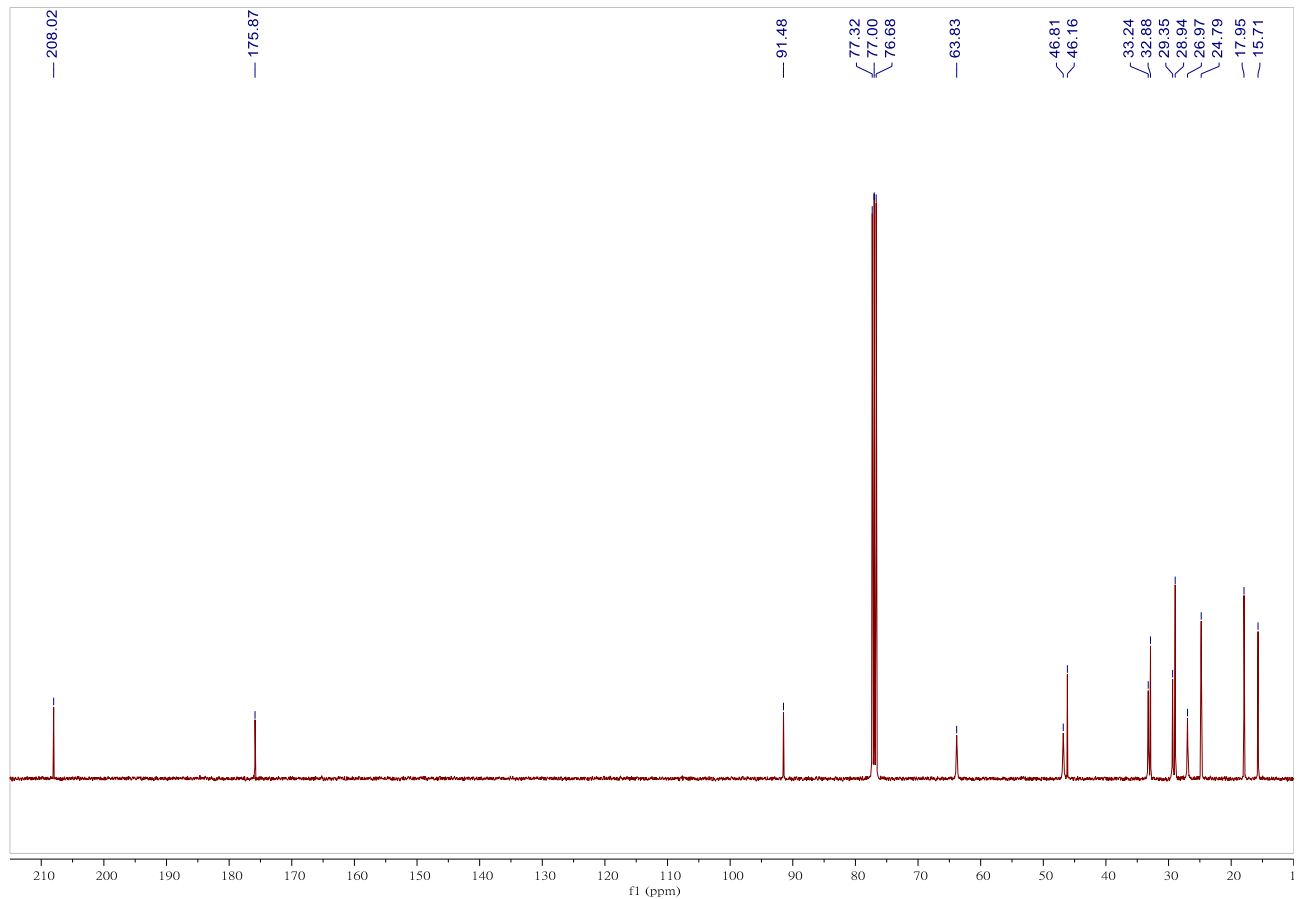**Figure S25.** ^{1}H-NMR spectrum (400 MHz, CDCl$_3$) of compound **3**.

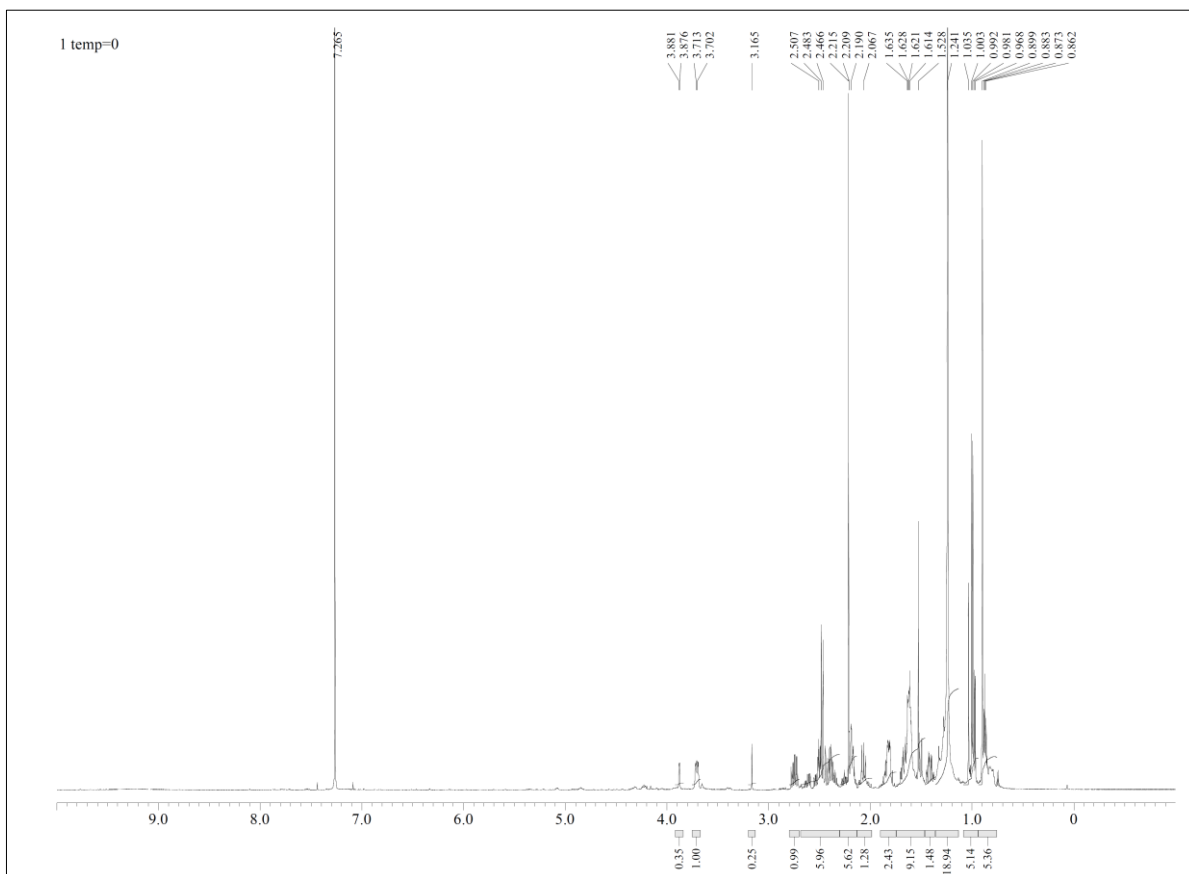**Figure S26.** ^{13}C-NMR spectrum (100 MHz, CDCl$_3$) of compound **3**.

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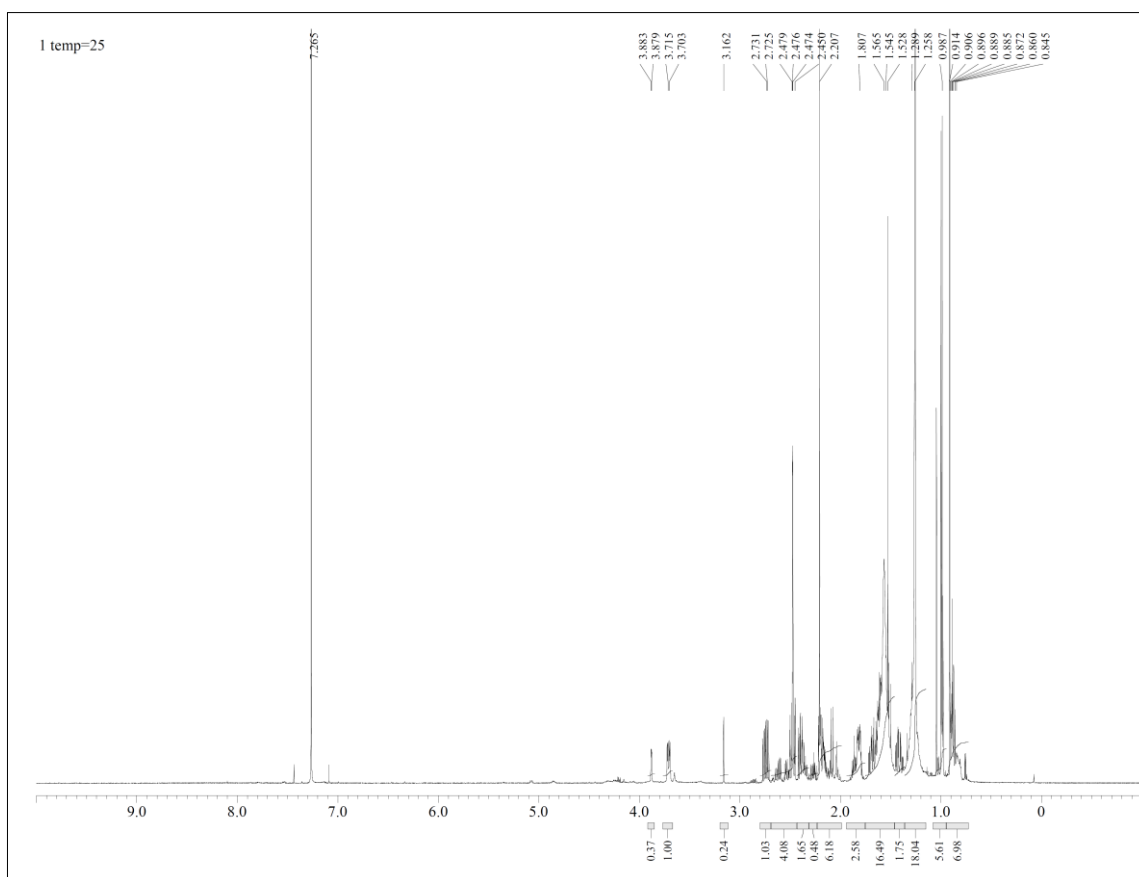

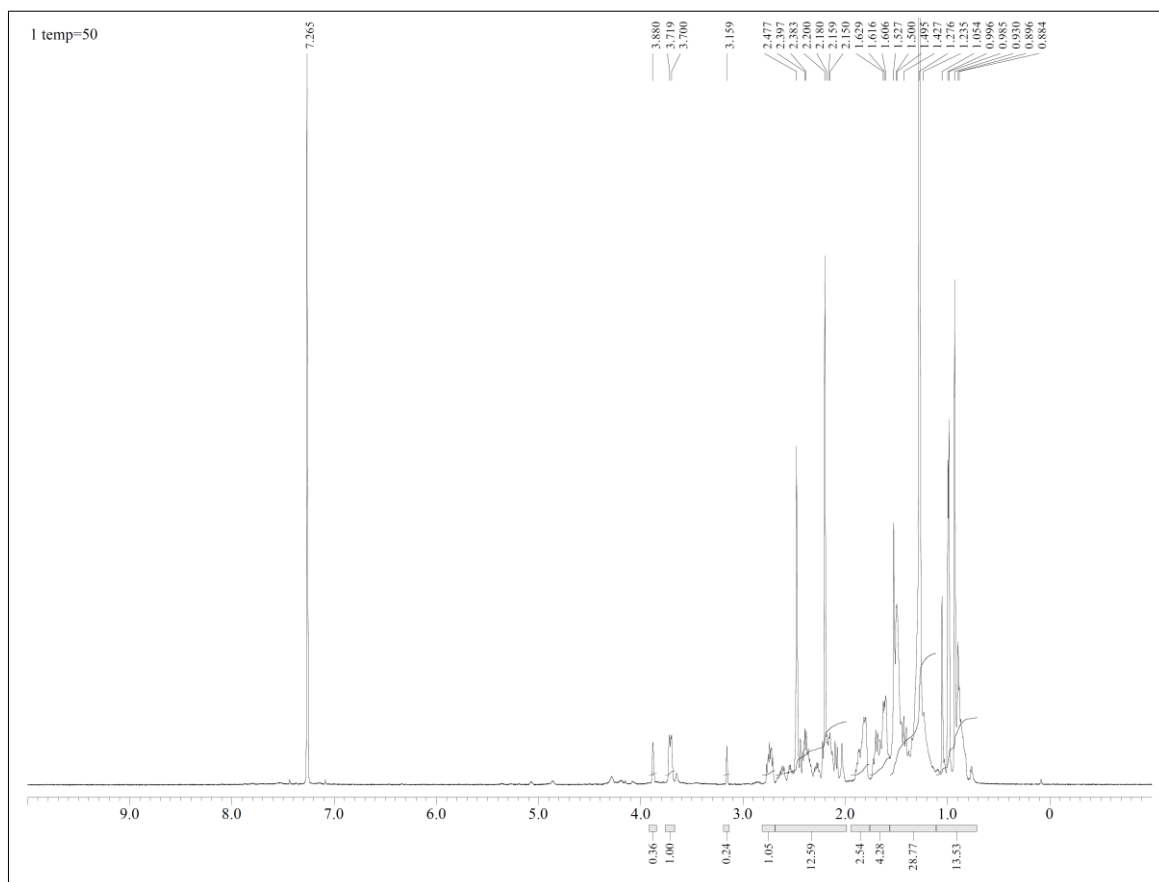**Figure S28.** The ^{1}H-NMR spectrum of **1** at 25°C.

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

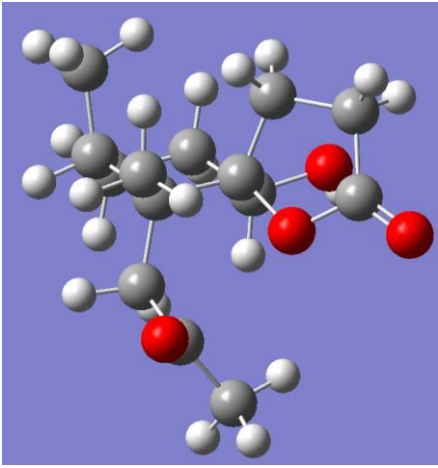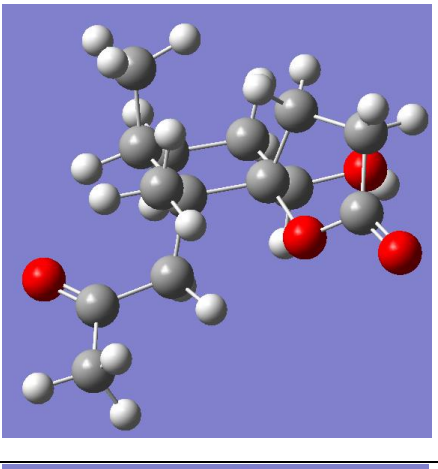**Table S1.**   DP4+ analysis results of compounds **1** and **2**.
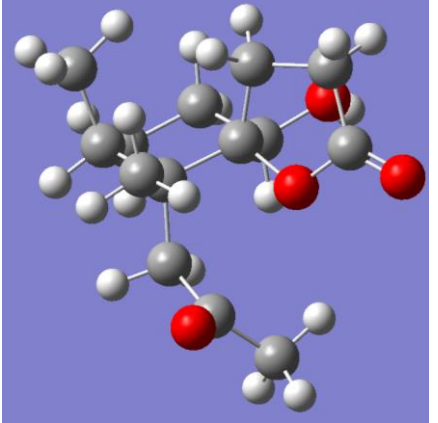
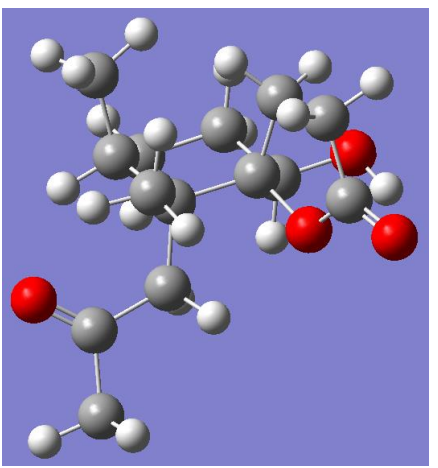| Compound	**1**		**2**	
Configuration	Diastereomer 1 1-1*S*,4*S*,5*R*,6*R*	Diastereomer 2 1-1*R*,4*S*,5*R*,6*R*	Diastereomer 1 2-1*R*,4*S*,5*R*,6*R*	Diastereomer 2 2-1*S*,4*S*,5*R*,6*R*
sDP4+ (H data)	99.79%	0.21%	100.00%	0.00%
sDP4+ (C data)	78.90%	21.10%	99.98%	0.02%
sDP4+ (All data)	**99.94%**	0.06%	**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%
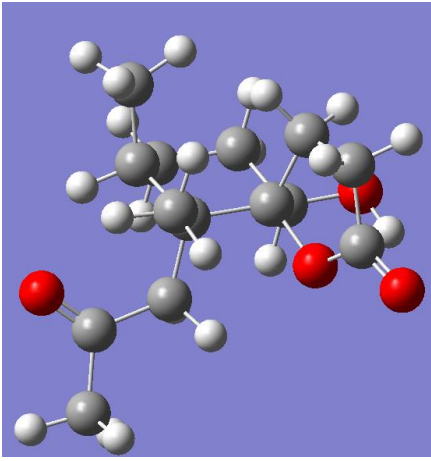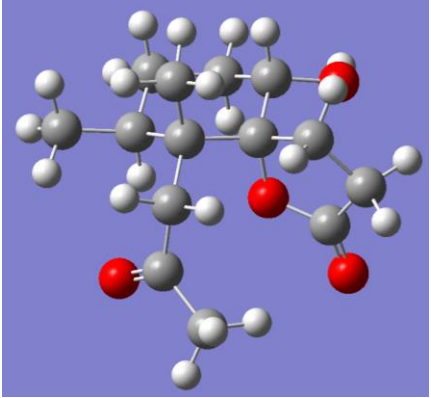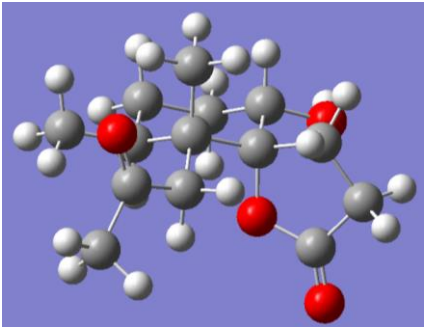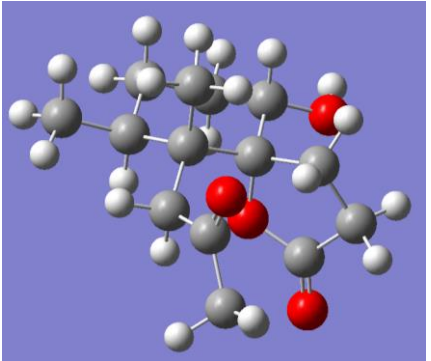
Table S2.   Experimental and calculated specific optical rotation values of compounds **1** and **2**.
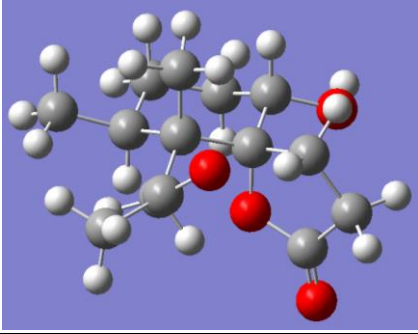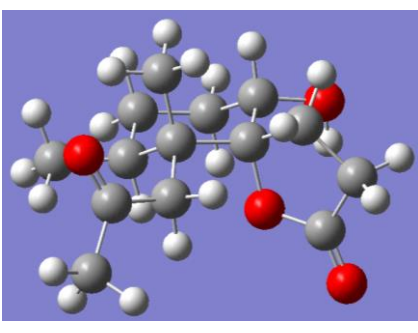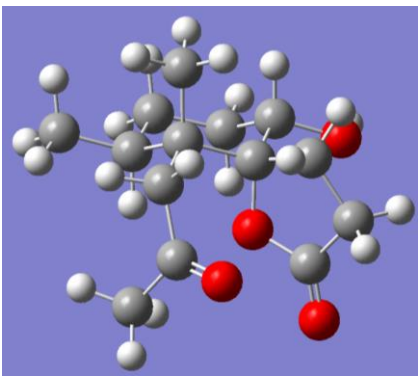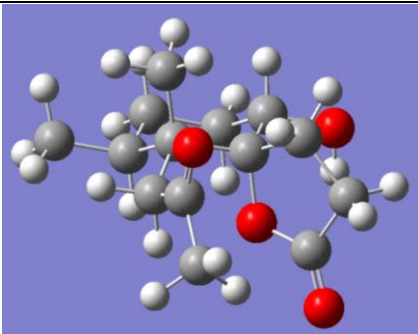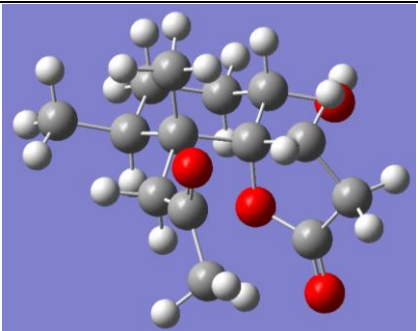
	Cald. value [a]	Exp. value
Exp. **1** [b]		185
Cald. **1**-1*S*,4*S*,5*R*,6*R*	66	
Cald. **1**-1*R*,4*R*,5*S*,6*S*	-66	
Exp. **2** [c]		44
Cald. **2**-1*R*,4*S*,5*R*,6*R*	12	
Cald. **2**-1*S*,4*R*,5*S*,6*S*	-12	

[a] Solvent phase in CHCl$_3$; [b] $[\alpha]_D^{25}$ (*c* 0.001, CHCl$_3$); [c] $[\alpha]_D^{22}$ (*c* 0.015, CHCl$_3$)

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

	3D structures of **1**-1*R*,4*S*,5*R*,6*R*	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%

	3D structures of **1**-1*S*,4*S*,5*R*,6*R*	Relative energy (KJ/mol)	Boltzmann distribution
5		0.508980	13.95%
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%
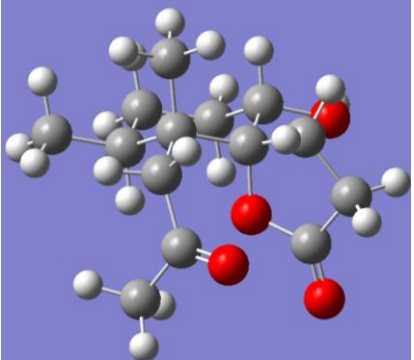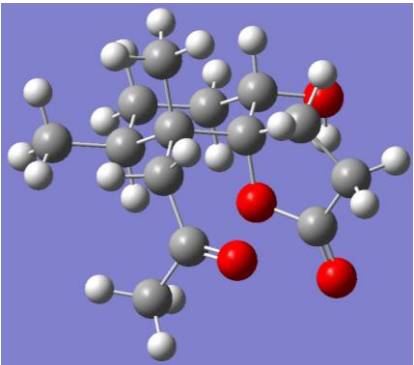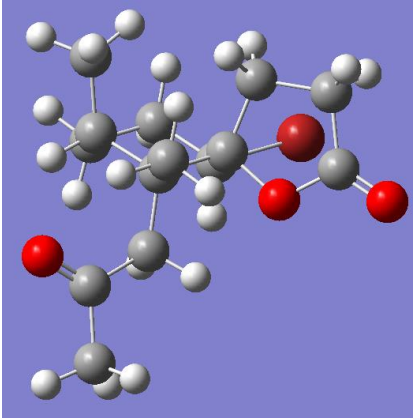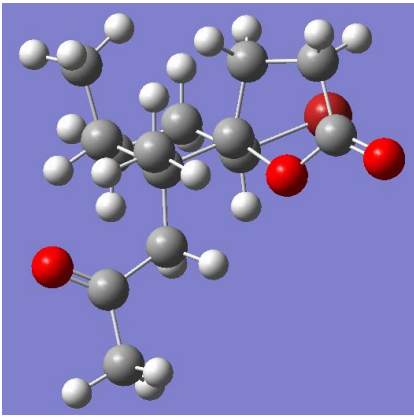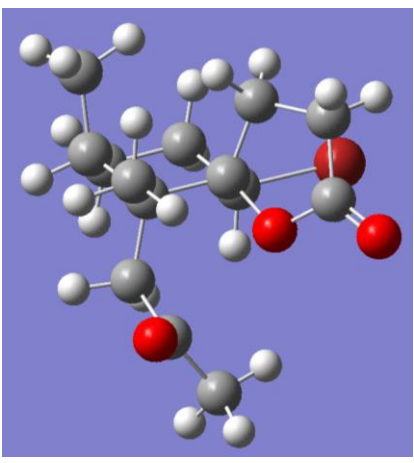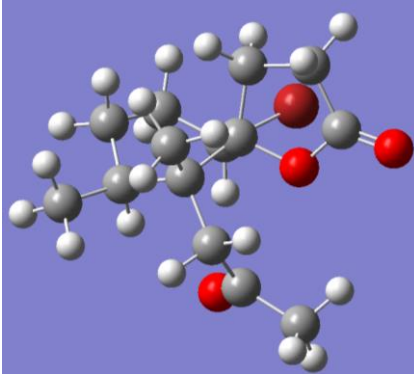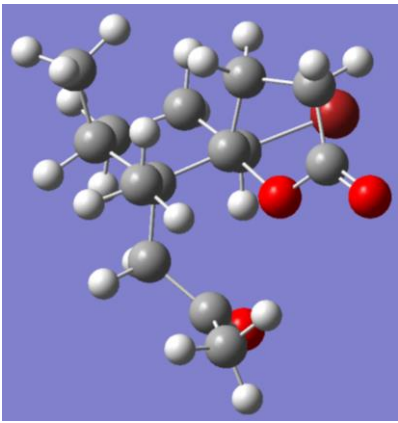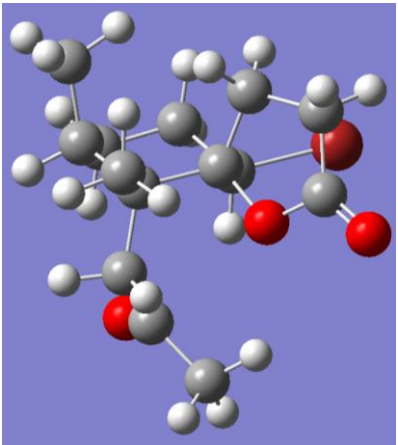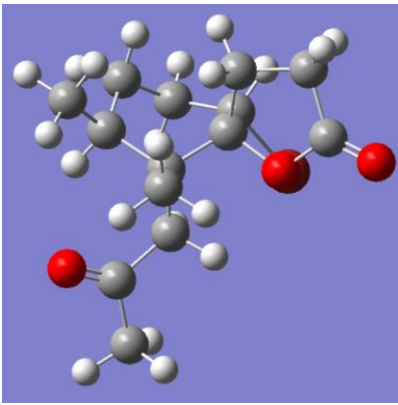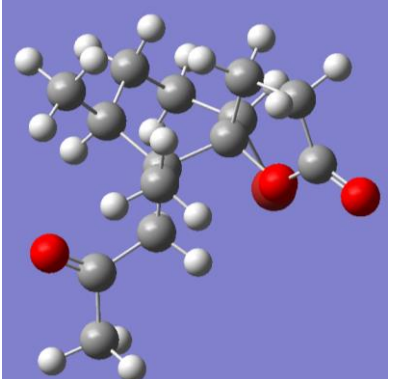
| 9 | | 0.539540 | 6.26% |
| 10 | | 0.581580 | 5.83% |

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

	3D structures of **2**-1*R*,4*S*,5*R*,6*R*	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%

		Relative energy (KJ/mol)	Boltzmann distribution
5		0.303900	12.73%
6		0.404970	10.73%
	3D structures of **2**-1*S*,4*S*,5*R*,6*R*	Relative energy (KJ/mol)	Boltzmann distribution
1		0.000000	23.94%
2		0.012130	23.45%
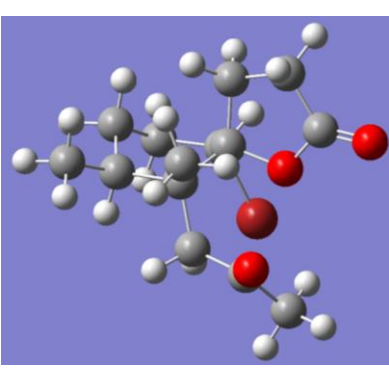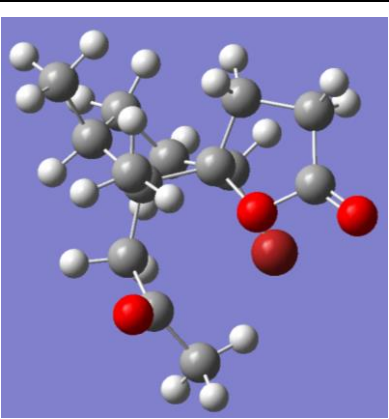
3		0.013190	23.41%
4		0.263030	15.35%
5		0.324280	13.84%

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

Identification code	ic21528
Empirical formula	C14 H21 Cl O3
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>2sigma(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}