Supporting Information

Lignans and [11]-chaetoglobosins from *Pseudeurotium bakeri* and their immunosuppressive activity

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Contents of Supporting Information

Computational details

Conformational search was done using Molecular Merck force field (MMFF) embedded in Spartan'14 software (Wavefunction Inc., Irvine, CA, USA). Density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations were performed with Gaussian09 RevD.01.[1] Double-hybrid (DH) DFT calculations were conducted with ORCA 4.2.1 program package using RIJCOSX approximation, tight SCF criteria, and grid 6 integrity.[2]

For conformational analysis, conformers of compounds **1** and **2** each within an 8 kcal/mol energy window from MMFF conformational search were subjected to geometry optimizations followed by frequency calculations using DFT method at the B3LYP[3]-GD3BJ[4,5]/Def2-SVP[6] level of theory with the solvation model PCM for MeOH. The optimized low-energy conformers (ΔG < 4.0 kcal/mol) were subjected to single point calculations using the DH-DFT method at the PWPB95[7]-D3BJ/def2-QZVPP[8] level with the SMD[9] solvent model for MeOH to obtain more accurate electronic energies. The TDDFT calculations were carried out using PBE1PBE (PBE0) [10], TPSSh[11], and M06-2X[12] functionals in combination with the TZVP basis set[13] and the PCM model for MeOH. The results were visualized and exported using the SpecDis program.[14] The calculated ECD spectra was generated as a sum of Gaussian curve using rotatory strengths computed in the dipole-velocity gauge from ECD data of the individual conformers. Boltzmann distributions of the conformers in equilibrium population were estimated from the relative Gibbs free energies (ΔG) at 298.15K.

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Preparation of the acetonide derivative 4a

A mixture of compound **4** (4.5 mg), cat. *p*-TsOH and 2,2-dimethoxypropane (1.5 mL) was stirred at room temperature for 2 h. Saturated aqueous NaHCO3 (10 mL) was added, the reaction mixture was then extracted with EtOAc (10 mL × 3). The organic layer was collected and concentrated in vacuum, then the crude mixture was subjected to semi-HPLC to obtain **4a** (3.2 mg). ^{1}H NMR data (600 MHz, CD_3OD) of **4a**: δ_H 7.10 (1H, br s, H-2'), 7.75 (1H, d, J = 7.8, H-5'), 7.07 (1H, t, J = 7.8, H-6'), 7.12 (1H, t, J = 7.8, H-7'), 7.52 (1H, d, J = 7.8, H-8'), 5.94 (1H, dd, J = 15.3, 10.3, H-13), 5.10 (1H, dd, J = 15.3, 11.3, H-14), 2.91(1H, dd, J = 14.5, 4.6, H-10a), 2.76 (1H, dd, J = 14.5, 6.9, H-10b), 4.63 (1H, s, H-11b), 3.43 (1H, m, H-3), 2.36 (1H, t, J = 7.2, H-6), 3.33 (1H, overlapped, H-7), 3.33 (1H, overlapped, H-4), 3.89 (1H, t, J = 7.5, H-19), 3.50 (1H, t, J = 7.6, H-18), 3.69 (1H, dd, J = 7.0, 4.5, H-20a), 1.39 (1H, m, H-20b), 1.30 (3H, d, J = 7.3 Hz, H_3-12), 0.98 (3H, d, J = 6., H_3-22), 1.30 (3H, s, H_3-24), 1.28 (3H, s, H_3-25).

$Mo_2(OAc)_4$-ICD ***experiment of 4***

A sample of **4** (0.5 mg) was dissolved in a dry DMSO (1 mL) solution of the $Mo_2(OAc)_4$ (1.5 mg) and the ECD spectrum was recorded at once. The ECD spectrum was recorded every 10 min until stationary. The inherent CD of **4** was subtracted to give the induced ECD of the Mo-complex. The observed Cotton effect at about 310 nm (band IV) was correlated to the absolute configuration of 18, 19-diol moiety.

Preparation of (S)- and (R)-MTPA Esters of Compounds 5 and 6

Two samples of compound **5** (each 1.5 mg), together with cat. 4-N,N-dimethylaminopyridine were added into 100 μL of anhydrous pyridine. After dissolving completely, 4 μL of (R)- and (S)-α-methoxy-α-(trifluoromethyl) phenylacetyl chloride (MTPA-Cl) were added, respectively. The mixtures were kept at room temperature overnight, and then 1 mL of CH_3OH was added respectively to quench the reactions. The mixtures were then purified by semipreparative RP-HPLC to obtain corresponding (S)- and (R)-MTPA esters of **5**. Meanwhile, (*S*)- and (*R*)-MTPA esters of **6** were also prepared and purified (**6a** and **6b**) with the same manner. ^{1}H NMR data (600 MHz) can be seen in Table S1 and S2.

Table S1. ^{1}H (600 MHz) data for the (*S*)- and (*R*)-MTPA esters of **5**.

Position	**(*S*)-MTPA ester**[a]	**(*R*)-MTPA ester**[a]	$\Delta\delta^{S-R}$
	δ_H (*J* in Hz)	δ_H (*J* in Hz)	
3	3.75, tt (6.4, 2.3)	3.74, tt (6.3, 2.2)	- 0.01
4	2.65, m	2.51, m	+ 0.14
6	2.65, m	2.53, m	+ 0.12
8	2.50, dd (11.6, 9.9)	2.52, dd (11.5, 9.7)	- 0.02
10a	2.98, dd (14.6, 4.8)	2.99, dd (14.5, 4.8)	- 0.01
10b	2.67, dd (14.6, 8.0)	2.69, dd (14.5, 8.2)	- 0.02
11a	5.05, s	5.02, s	+ 0.03
11b	5.00, s	4.93, s	+ 0.07
12	1.28, d (7.4)	1.21, d (7.4)	+ 0.07
13	5.78, ddd (15.5, 9.9, 1.5)	5.92, ddd (15.3, 9.9, 1.6)	- 0.14
14	5.19, ddd (15.5, 9.7, 1.7)	5.15 ddd (15.3, 9.8, 3.2)	+ 0.04
15a	1.86, m	1.80, m	+ 0.06
15b	1.52, m	1.56, m	- 0.04
16	1.62, overlapped	1.55, m	+ 0.07
17a	1.78, dd (16.0, .0)	1.76, dd (16.1, 2.1)	+ 0.02
17b	1.62, overlapped	1.50, m	+ 0.12
19	3.45, ddd (10.4, 5.8, 1.9)	3.56, ddd (10.4, 5.4, 2.1)	- 0.11
20a	3.91, dd (19.8, 2.3)	3.97, dd (19.9, 2.2)	- 0.06
20b	1.95, dd (19.2, 5.3)	1.97, dd (19.2, 5.6)	- 0.02
22	0.88, d (6.7)	0.66, d (6.6)	+ 0.22
23	3.43, s	3.46, s	- 0.03

[a]In $CDCl_3$

Table S2. ^{1}H (600 MHz) data for the (*S*)- and (*R*)-MTPA esters of **6**.

Position	(*S*)-MTPA ester[a]	(*R*)-MTPA ester[a]	$\Delta\delta^{S-R}$
	δ_H (*J* in Hz)	δ_H (*J* in Hz)	
3	3.43, m	3.43, m	0
4	2.77, dd (14.5, 8.2)	2.79, dd (14.5, 8.1)	- 0.02
5	2.53, m	2.54, m	- 0.01
7	5.21, dd (9.5, 5.5)	5.13, dd (10.5, 4.8)	+ 0.08
8	2.79, m	2.77, m	+ 0.02
10a	2.92, dd (14.5, 3.7)	2.94, dd (14.5, 3.7)	- 0.02
10b	2.63, dd (14.5, 8.0)	2.65, dd (14.5, 8.0)	- 0.02
11	1.31, d (7.2)	1.31, d (7.2)	0
12	1.75, s	1.75, s	0
13	6.04, ddd (15.2, 10.1, 1.7)	6.02, ddd (15.3, 9.9, 1.6)	+ 0.02
14	5.16, ddd (15.2, 10.1, 4.3)	5.14 ddd (15.3, 9.9, 4.2)	+ 0.02
15a	2.03, ddt (13.3, 3.8, 1.5)	1.97, ddt (12.8, 4.1, 1.9)	+ 0.06
15b	1.90, dt (15.6, 1.7)	1.84, dt (15.9, 1.6)	+ 0.06
16	1.74, m	1.69, m	+ 0.05
17a	1.71, m	1.63, overlapped	+ 0.08
17b	1.65, m	1.57, m	+ 0.08
19	3.46, ddd (10.3, 6.0, 1.8)	3.52, ddd (10.5, 5.7, 1.9)	- 0.06
20a	4.01, dd (18.8, 2.3)	4.06, dd (19.0, 2.0)	- 0.05
20b	1.58, m	1.63, overlapped	- 0.05
22	0.93, d (6.5)	0.67, d (6.5)	+ 0.26
23	3.53, s	3.61, s	- 0.08

[a]In $CDCl_3$

Table S3. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) data of **1** in CD_3OD.

NO.	δ_H, (mult, *J* in Hz)	^{1}H-^{1}H COSY	δ_C	HMBC
1			142.9	
2	6.17, overlapped		110.6	4, 6
3			157.6	
4	5.98, t (2.3)		100.9	2, 6
5			157.6	
6	6.17, overlapped		110.6	2, 4
7a	3.43, d (13.2)		46.7	1, 2, 6
7b	2.82, d (13.2)			1, 2, 6
8			79.7	
9	1.60, s		25.4	7, 8, 6'
1'			138.5	
2'	5.87, d (2.3)		107.2	4', 6'
3'			155.4	
4'	6.11, d (2.3)		102.3	2', 6'
5'			150.5	
6'			119.5	
7'a	2.24, m		38.7	1', 2', 6'
7'b	2.17, m			1', 2', 6'
8'	3.80, dt d (12.1, 6.1, 2.7)	7'a, 7'b, 9'-Me	65.7	1', 8
9'	1.25, d (6.1)	8'	22.1	7', 8'

Table S4. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) data of **2** in CD_3OD.

NO.	δ_H, (mult, *J* in Hz)	^{1}H-^{1}H COSY	δ_C	HMBC
1			142.5	
2	6.16, overlapped		110.8	4, 6
3			158.5	
4	6.07, t (2.1)		101.2	2, 6
5			158.5	
6	6.16, overlapped		110.8	2, 4
7a	3.12, overlapped		42.8	1, 2, 6
7b	3.12, overlapped			1, 2, 6
8			78.9	
9	1.37, s		26.4	7, 8, 6'
1'			137.6	
2'	5.99, d (2.2)		107.5	4', 6'
3'			156.0	
4'	6.13, d (2.2)		102.7	2', 6'
5'			155.8	
6'			121.6	
7'a	2.42, overlapped		38.7	1', 2', 6'
7'b	2.42, overlapped			1', 2', 6'
8'	3.89, dt (7.7, 5.8)	7'a, 7'b, 9'-Me	65.7	1', 8
9'	1.22, d (6.1)	8'	21.4	7', 8'

Table S5. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) data of **3** in $CDCl_3$

NO.	δ_H, (mult, *J* in Hz)	^{1}H-^{1}H COSY	δ_C	HMBC
1			170.9	
3	3.50, m	4, 10a, 10b	53.9	3', 9
4	3.15, overlapped	3, 5	43.7	1, 6, 9, 21
5	2.89, m	4, 11-Me	35.2	
6			146.6	
7	4.27, dd (12.3, 2.2)	8	76.4	
8	2.21, m	7, 13	51.2	6, 9, 21
9			59.7	
10a	3.15, overlapped	3	35.5	2', 3', 4'
10b	2.67, m	3		2', 3', 4'
11	1.36, d (6.6)	5	15.1	6
12	5.37, s		115.2	5, 6, 7
	5.28, s			5, 6, 7
13	2.64, m	8, 14, 19	39.9	7
14	3.78, ddd (11.4, 9.2, 4.1)	13, 15*α*, 15*β*	86.0	
15*α*	2.16, overlapped	14, 16	42.7	
15*β*	1.48, q (11.8)	14, 16		
16	1.86, d (7.4)	15*α*, 15*β*, 17a, 17b, 22-Me	27.4	
17a	2.57, overlapped	16	52.8	18, 19
17b	2.47, m	16		18, 19
18			212.5	
19	2.57, overlapped	13, 20	56.4	18
20	5.12, dd (9.5, 2.0)	19	74.7	18, 21
21			202.0	
22	1.06, d (6.8)	16	24.4	15, 16, 17
2'	6.87, s		122.8	3', 4', 9'
3'			111.2	
4'			127.3	
5'	7.50, d (7.8)	6'	118.4	7', 9'
6'	7.13, t (7.8)	5'	119.7	4', 8'
7'	7.22, t (7.8)	8'	122.5	5', 9'
8'	7.41, d (7.8)	7'	111.9	4', 6'
9'			136.6	
2-NH	6.87, br s			
1'-NH	8.58, br s			

Table S6. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) data of **4** in CD_3OD.

NO.	δ_H, (mult, *J* in Hz)	^{1}H-^{1}H COSY	δ_C	HMBC
1			176.6	
3	3.73, t (7.1)	4, 10a, 10b	60.3	
4	3.41, d (2.24)	3	51.3	1, 9, 21
5			151.2	
6	2.30, t (7.2)	7, 12-Me	47.6	4, 5
7	3.28, m	6, 8	75.0	
8	2.08, m	7, 13	55.7	9, 21
9			66.4	
10a	2.91, dd (14.4, 4.8)	3	32.7	2', 3', 4'
10b	2.78, dd (14.4, 6.7)	3		2', 3', 4'
11	4.81, s		114.9	4, 5, 6
	4.70, s			4, 5, 6
12	1.26, d (7.4)	6	22.2	5, 6, 7
13	5.84, dd (15.2, 9.7)	8, 14	129.9	7, 15
14	5.08, ddd (15.2, 10.4, 4.3)	13, 15*α*, 15*β*	135.8	8
15*α*	2.02, overlapped	14, 16	43.4	
15*β*	1.54, m	14, 16		
16	1.65, overlapped	15*α*, 15*β*, 17a, 17b, 22-Me	28.9	
17a	1.65, overlapped	16, 18	38.8	
17b	1.42, overlapped	16, 18		
18	3.45, m	17, 19	73.9	
19	3.63, overlapped	18, 20a, 20b	69.8	21
20a	3.63, overlapped	19	45.0	18, 21
20b	1.42, overlapped	19		18, 21
21			211.4	
22	1.00, d (6.3)	16	25.9	15*α*, 15*β*, 16, 17a, 17b
2'	7.04, s		125.3	3', 4', 9'
3'			110.3	
4'			129.0	
5'	7.52, d (8.1)	6'	119.4	7', 9'
6'	7.01, t (8.1)	5'	120.0	4', 8'
7'	7.08, t (8.1)	8'	122.4	5', 9'
8'	7.32, d (8.1)	7'	112.5	4', 6'
9'			138.0	

Table S7. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) data of **5** in $CDCl_3$.

NO.	δ_H, (mult, *J* in Hz)	^{1}H-^{1}H COSY	δ_C	HMBC
1			175.0	
3	3.76, m	4, 10a, 10b	58.1	
4	3.28, overlapped	3	51.3	1, 9, 21
5			148.7	
6	2.43 t (7.2)	7, 12-Me	45.3	
7	3.36, m	6, 8	73.6	
8	2.26, t (10.7)	7, 13	55.1	14
9			64.8	
10a	2.97, dd (14.5, 4.5)	3	32.4	2', 3', 4'
10b	2.70, dd (14.5, 7.6)	3		2', 3', 4'
11	5.04, s		115.2	4, 5, 6
	4.99, s			4, 5, 6
12	1.28, d (7.3)	6	21.9	5, 6, 7
13	5.85, dd (15.4, 10.7)	8, 14	126.7	7
14	5.27, ddd (15.4, 10.8, 4.5)	13, 15*α*, 15*β*	138.0	8, 16
15*α*	2.00, overlapped	14, 16	41.8	13
15*β*	1.69, overlapped	14, 16	28.1	13
16	1.52, m	15*α*, 15*β*, 17a, 17b,	28.1	
17a	1.67, m	16, 18	36.5	
17b	1.61, m	16, 18		
18	3.65, m	17, 19	73.0	
19	3.28, overlapped	18, 20a, 20b	78.9	18, 21
20a	3.78, dd (17.7, 3.8)	19	42.9	18, 21
20b	1.69, overlapped	19		18, 21
21			210.1	
22	1.03, d (6.5)	16	25.2	15*α*, 15*β*, 16, 17a, 17b
23	3.43, s		58.4	19
2'	6.99, d (2.3)		123.3	3', 4', 9'
3'			110.5	
4'			127.2	
5'	7.50, d (7.8)	6'	118.4	7', 9'
6'	7.14, t (7.8)	5'	120.1	4', 8'
7'	7.20, t (7.8)	8'	122.6	5', 9'
8'	7.36, d (7.8)	7'	111.7	4', 6'
9'			136.4	
2-NH	6.32, br s			
1'-NH	8.42, br s			

Table S8. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) data of **6** in $CDCl_3$.

NO.	δ_H, (mult, *J* in Hz)	^{1}H-^{1}H COSY	δ_C	HMBC
1			175.6	
3	3.43, dd (6.9, 3.7)	4, 10a, 10b	53.7	
4	2.71, m	3, 5	51.4	1, 9, 21
5	2.53, m	4, 11-Me	35.5	9
6			139.8	
7	5.48, s	8	125.5	
8	2.85, dt (10.2, 4.0)	7, 13	49.8	1, 9, 14
9			68.9	
10a	2.92, dd (14.6, 3.7)	3	33.7	2', 3', 4'
10b	2.66, dd (14.6, 6.9)	3		2', 3', 4'
11	1.30, d (7.2)		13.7	6
12	1.75, s	6	20.1	5, 6, 7
13	5.95, dd (15.3, 10.2)	8, 14	130.0	7, 15
14	5.11, ddd (15.3, 11.0, 4.3)	13, 15*α*, 15*β*	133.5	8, 16
15*α*	1.99, m	14, 16	41.8	
15*β*	1.65, overlapped	14, 16		
16	1.55, overlapped	15*α*, 15*β*, 17a, 17b,	28.1	
17a	1.65, overlapped	16, 18	36.5	18, 19
17b	1.55, overlapped	16, 18		18, 19
18	3.73, overlapped	17, 19	73.6	
19	3.24, dt (7.9, 3.8)	18, 20a, 20b	78.8	21
20a	3.73, overlapped	19	42.4	18, 21
20b	1.38, m	19		18, 21
21			212.3	
22	1.02, d (6.3)	16	25.3	15*α*, 15*β*, 16, 17a, 17b
23	3.35		58.1	19
2'	6.97, br d (2.3)		123.6	3', 4', 9'
3'			110.5	
4'			127.5	
5'	7.50, d (7.8)	6'	118.5	7', 9'
6'	7.14, t (7.8)	5'	120.0	4', 8'
7'	7.19, t (7.8)	8'	122.4	5', 9'
8'	7.35, d (7.8)	7'	111.7	4', 6'
9'			136.4	
2-NH	6.16, br s			
1'-NH	8.60, br s			

Table S9. Cytotoxicity of Compounds **1**–**6** against seven Human Cancer Cell Lines and one Normal Human Cell Line.

Compounds	IC_{50} (μM) ± SD [a]							
	MCF-7	Hela	HCT-116	HT-29	HepG2	A549	A427	LO2[b]
1	>50	>50	>50	>50	>50	>50	>50	>50
2	>50	38.8 ± 1.7	40.3 ± 0.1	46.6 ± 0.4	42.3 ± 2.2	>50	>50	>50
3	48.7 ± 1.1	46.6 ± 1.9	49.3 ± 0.6	>50	>50	>50	40.8 ± 0.5	>50
4	>50	>50	41.1 ± 1.3	>50	>50	>50	>50	>50
5	17.5 ± 1.0	17.9 ± 1.3	10.3 ± 1.0	24.6 ± 0.3	>50	19.9 ± 1.9	>50	>50
6	18.8 ± 1.4	15.7 ± 0.8	20.9 ± 1.0	25.0 ± 1.5	14.7 ± 1.3	17.6 ± 1.3	>50	45.0 ± 1.0
Doxorubicin hydrochloride	2.8 ± 1.0	1.3 ± 1.1	1.5 ± 1.6	1.7 ± 1.8	0.1 ± 1.0	0.2 ± 0.7	1.45 ± 1.0	1.6 ± 0.7

Doxorubicin hydrochloride was applied as a positive control.

[a]Values based on three individual experiments.

[b]The normal human liver cell line.

Figure S1. ^{1}H NMR (400 MHz, CD_3OD) spectrum of **1.**

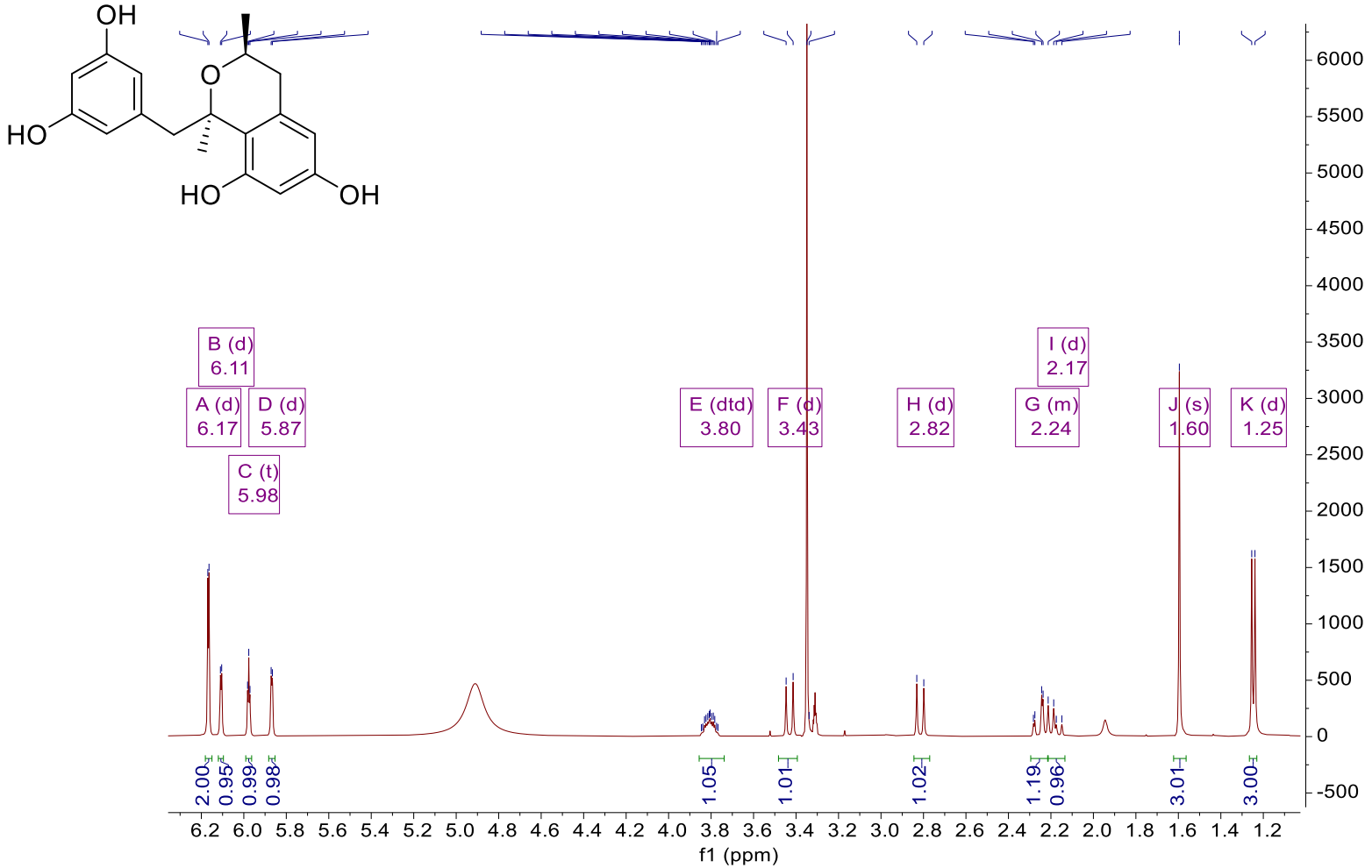

Figure S2. ^{13}C NMR (100 MHz, CD_3OD) spectrum of **1**.

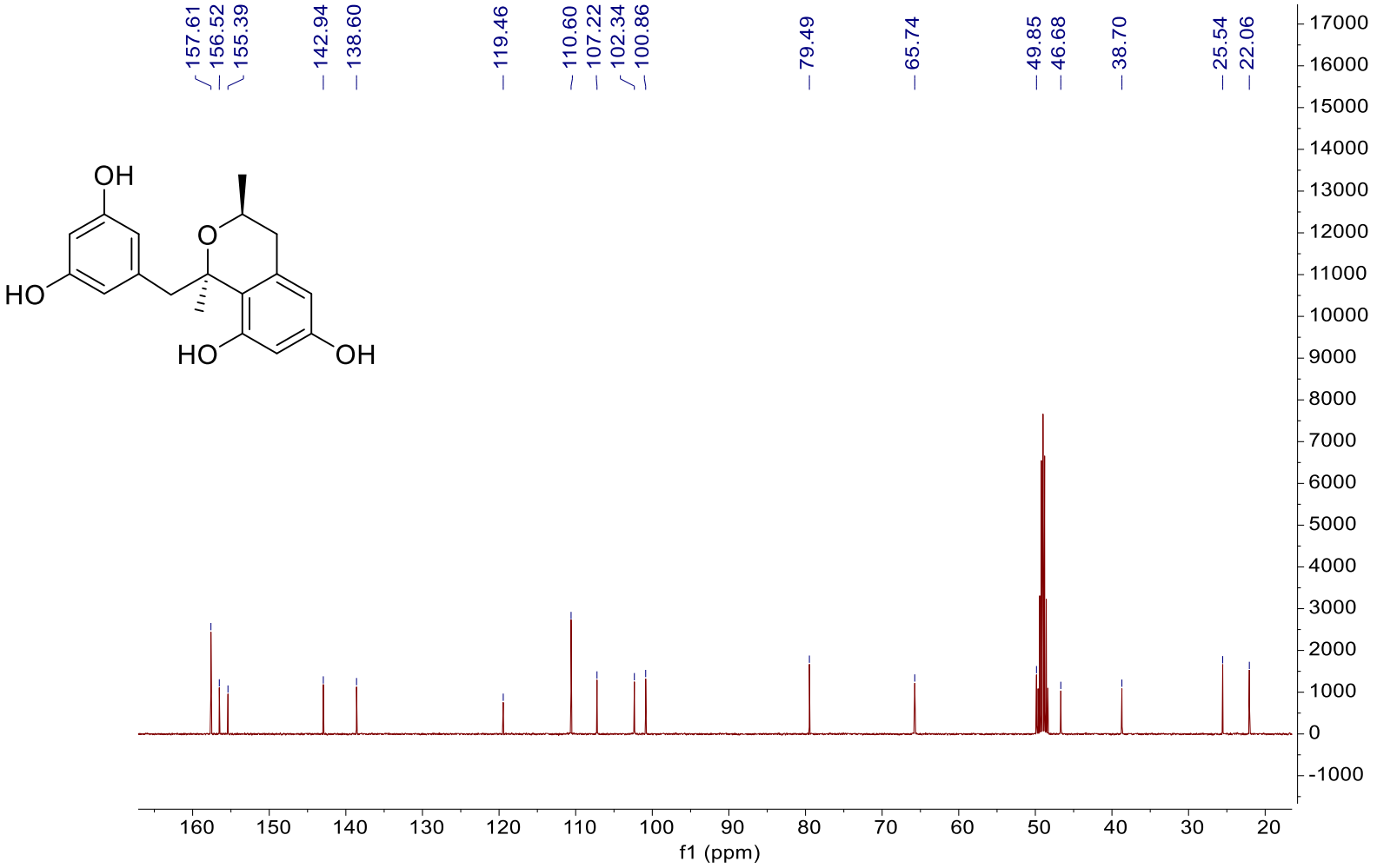

Figure S3. DEPT-135 (100 MHz, CD_3OD) spectrum of **1**.

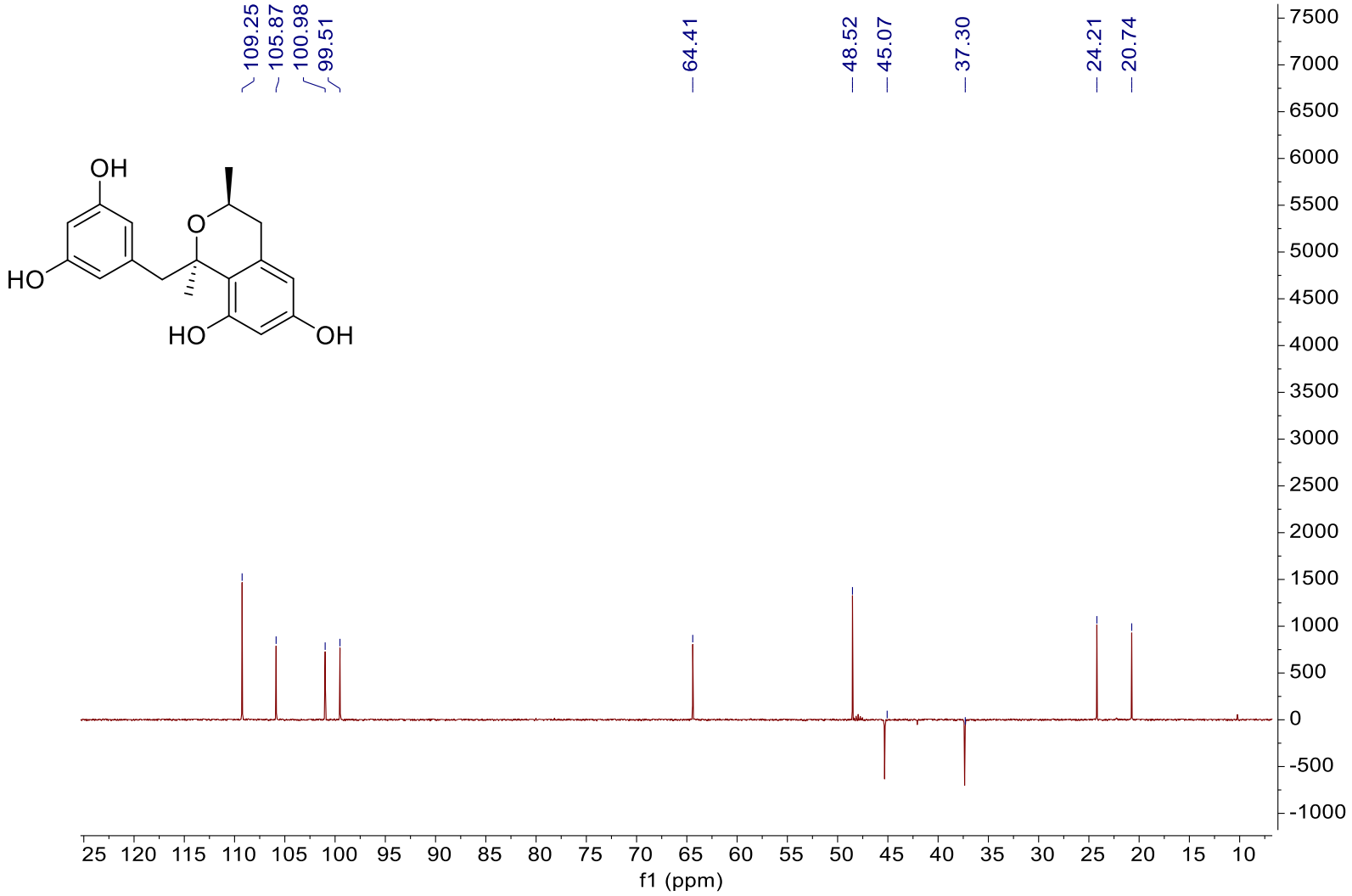

Figure S4. HSQC spectrum of **1** in CD_3OD.

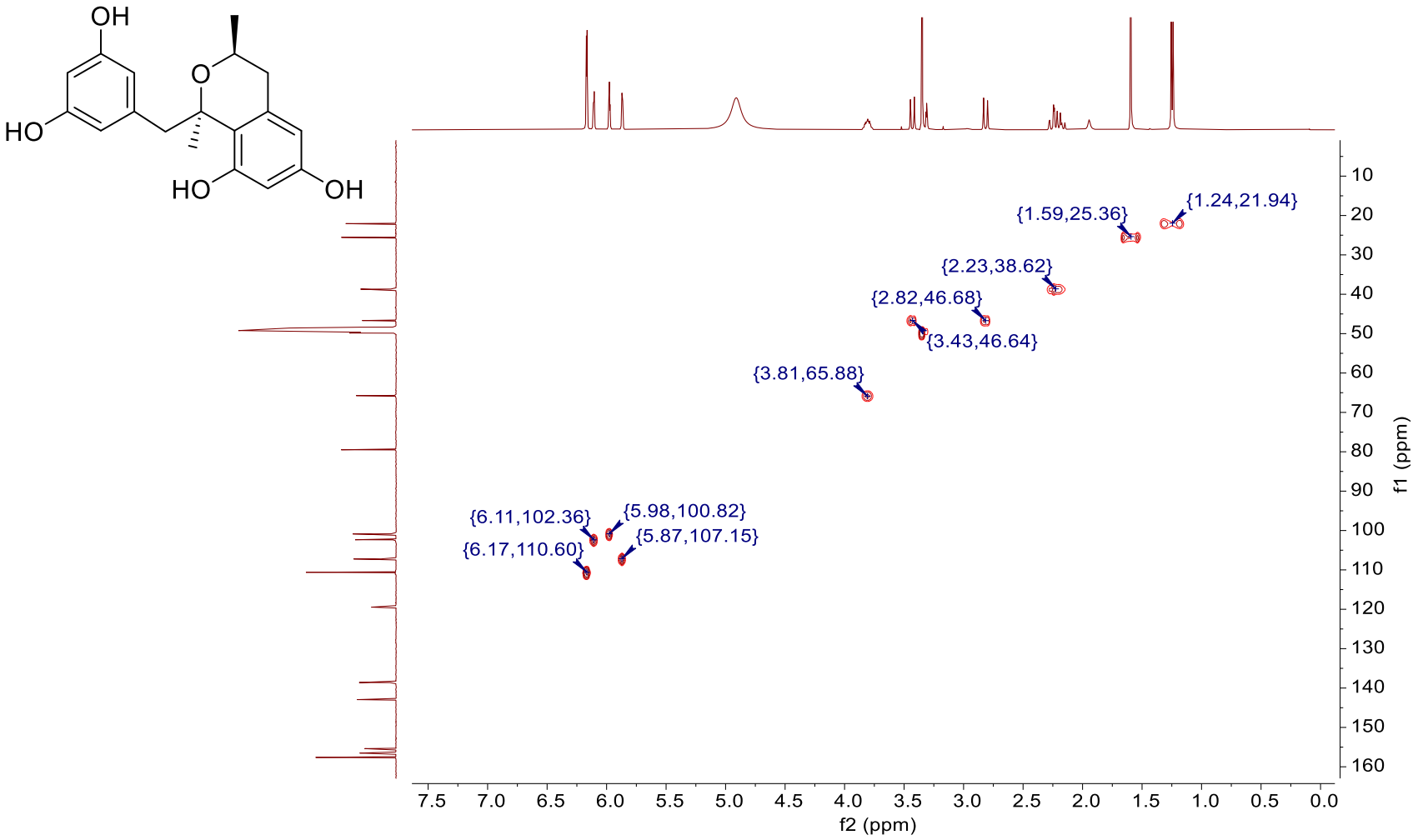

Figure S5. HMBC spectrum of **1** in CD_3OD.

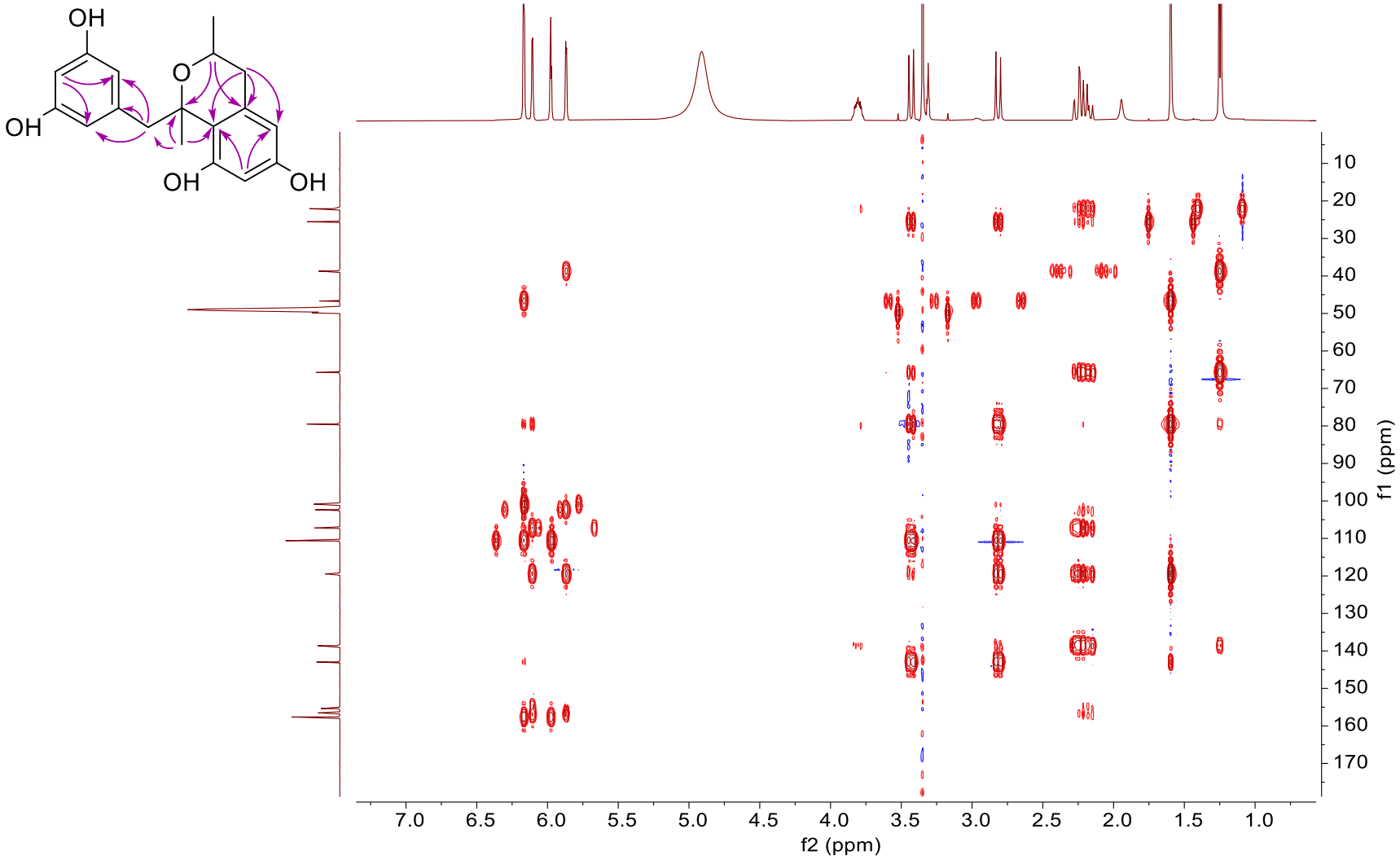

Figure S6. ^{1}H–^{1}H COSY spectrum of **1** in CD_3OD.

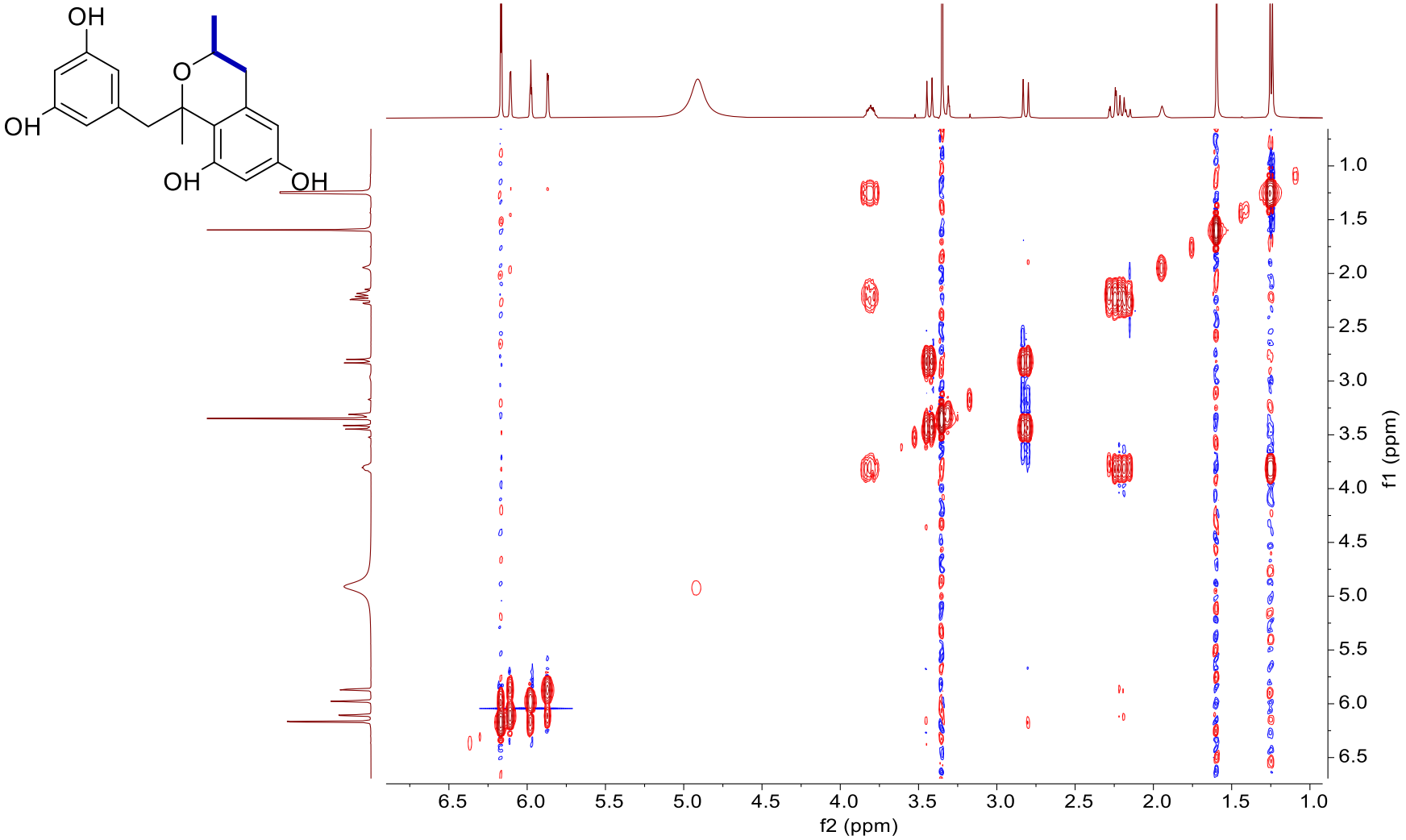

Figure S7. NOESY spectrum of **1** in CD_3OD.

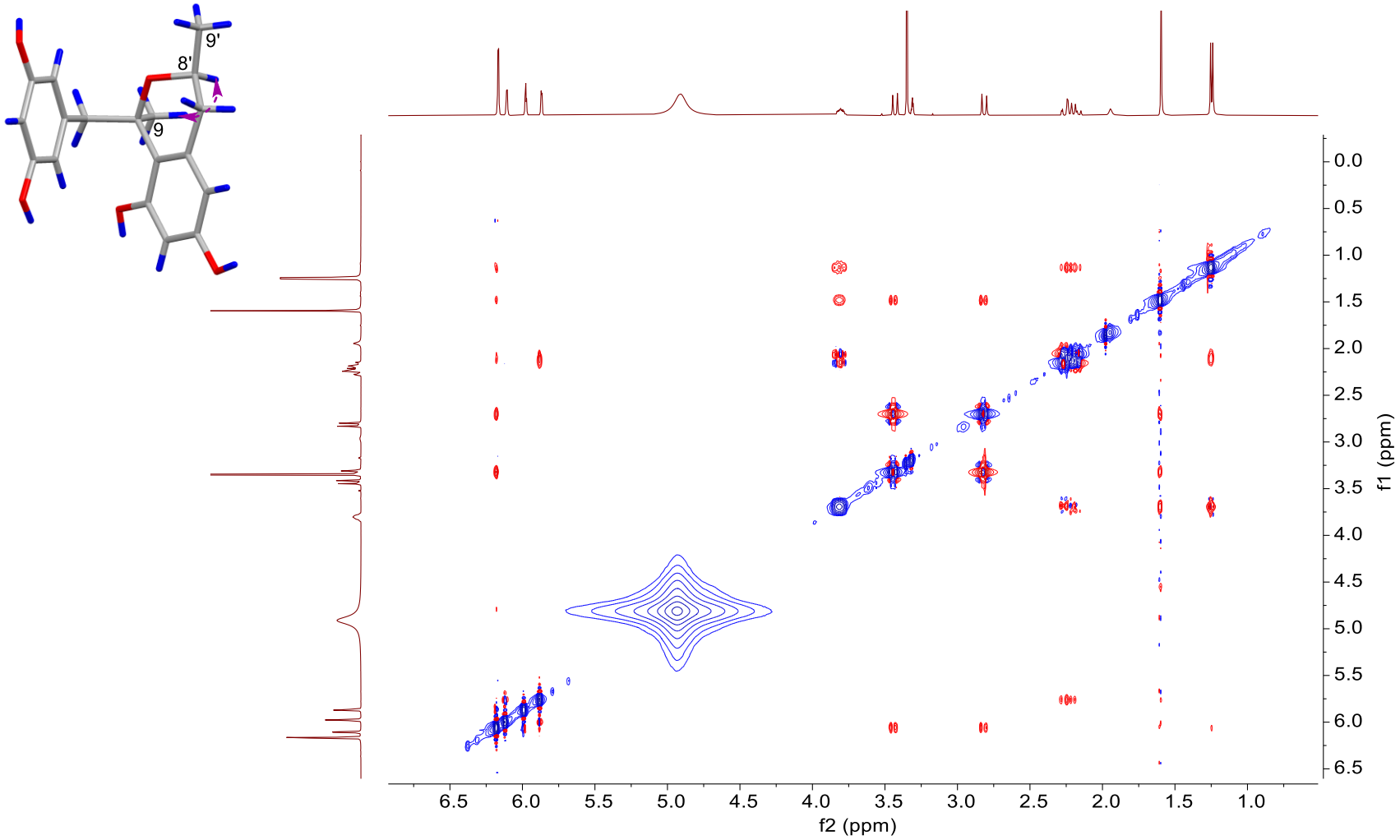

Figure S8. HRESIMS (+) spectrum of **1**.

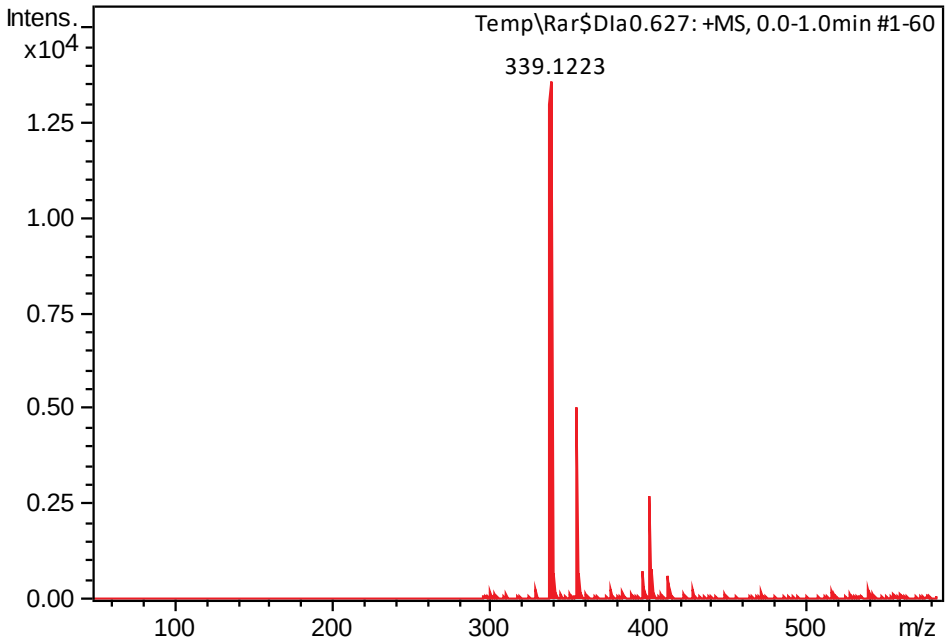

Figure S9. UV spectrum of **1**.

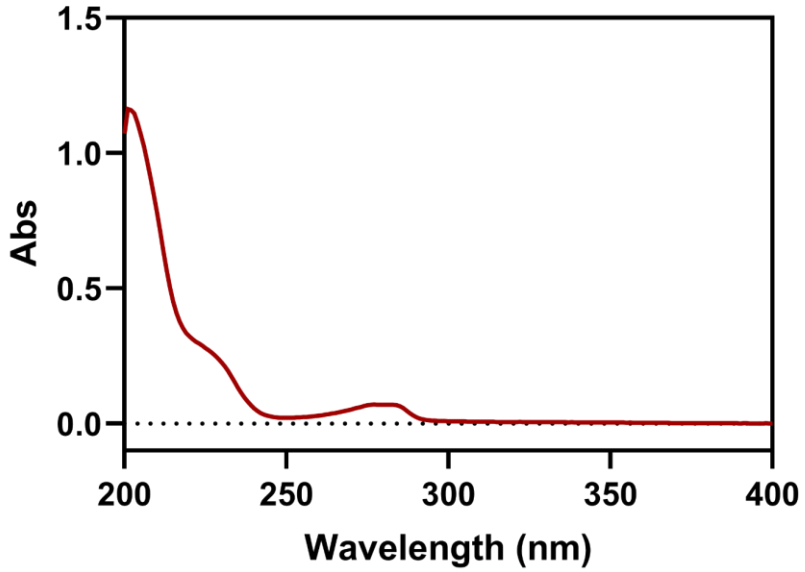

Figure S10. IR spectrum of **1**.

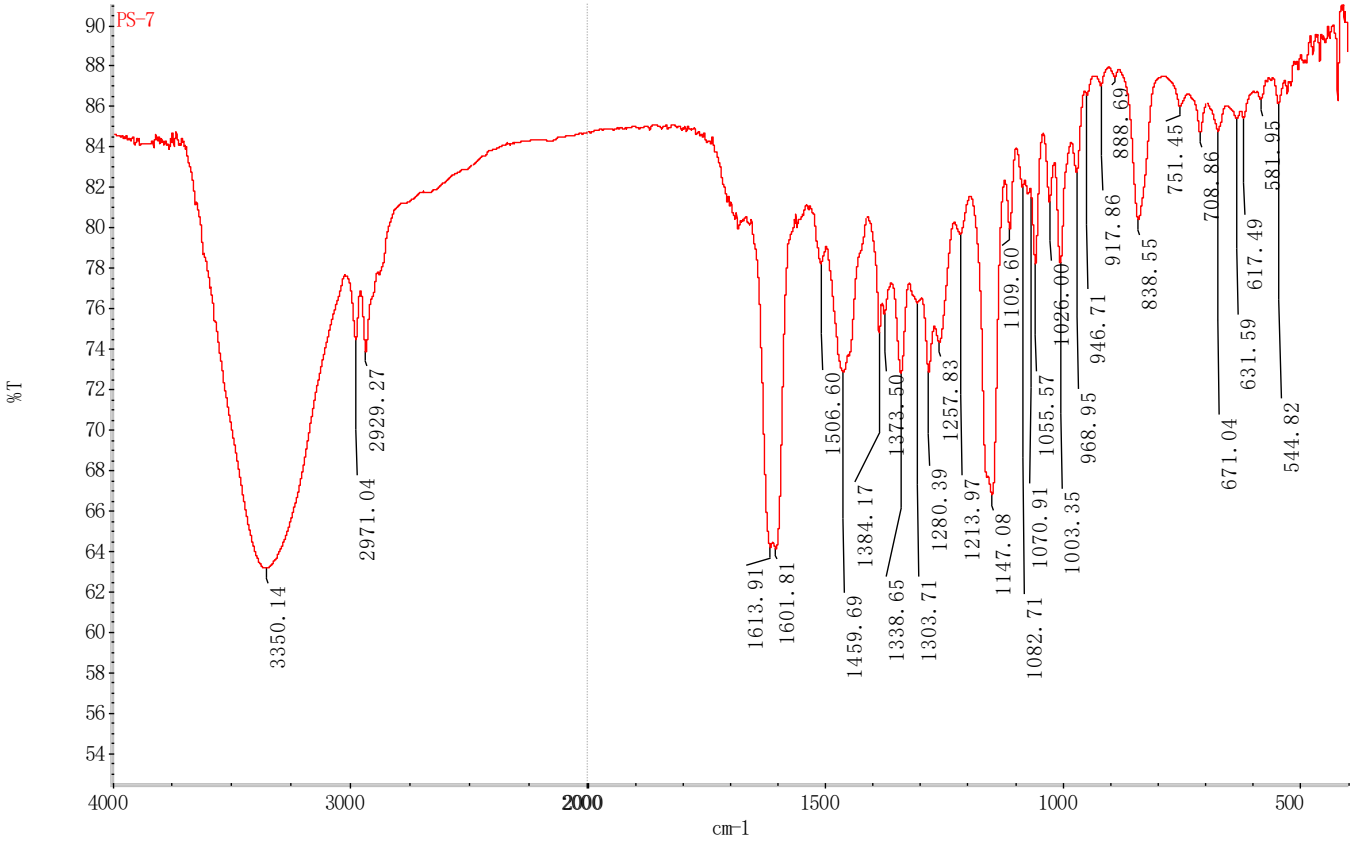

Figure S11. ECD spectrum of **1**.

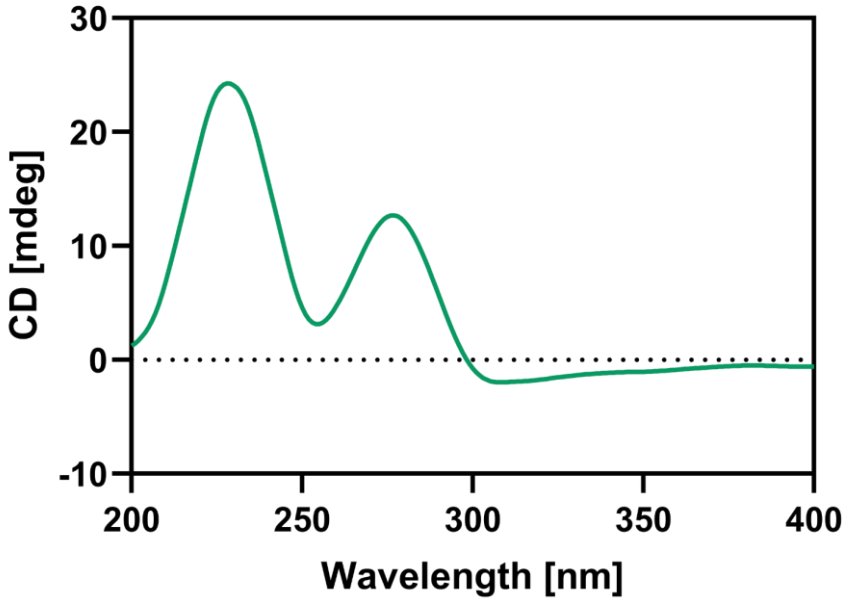

Figure S12. ^{1}H NMR (400 MHz, CD_3OD) spectrum of **2**.

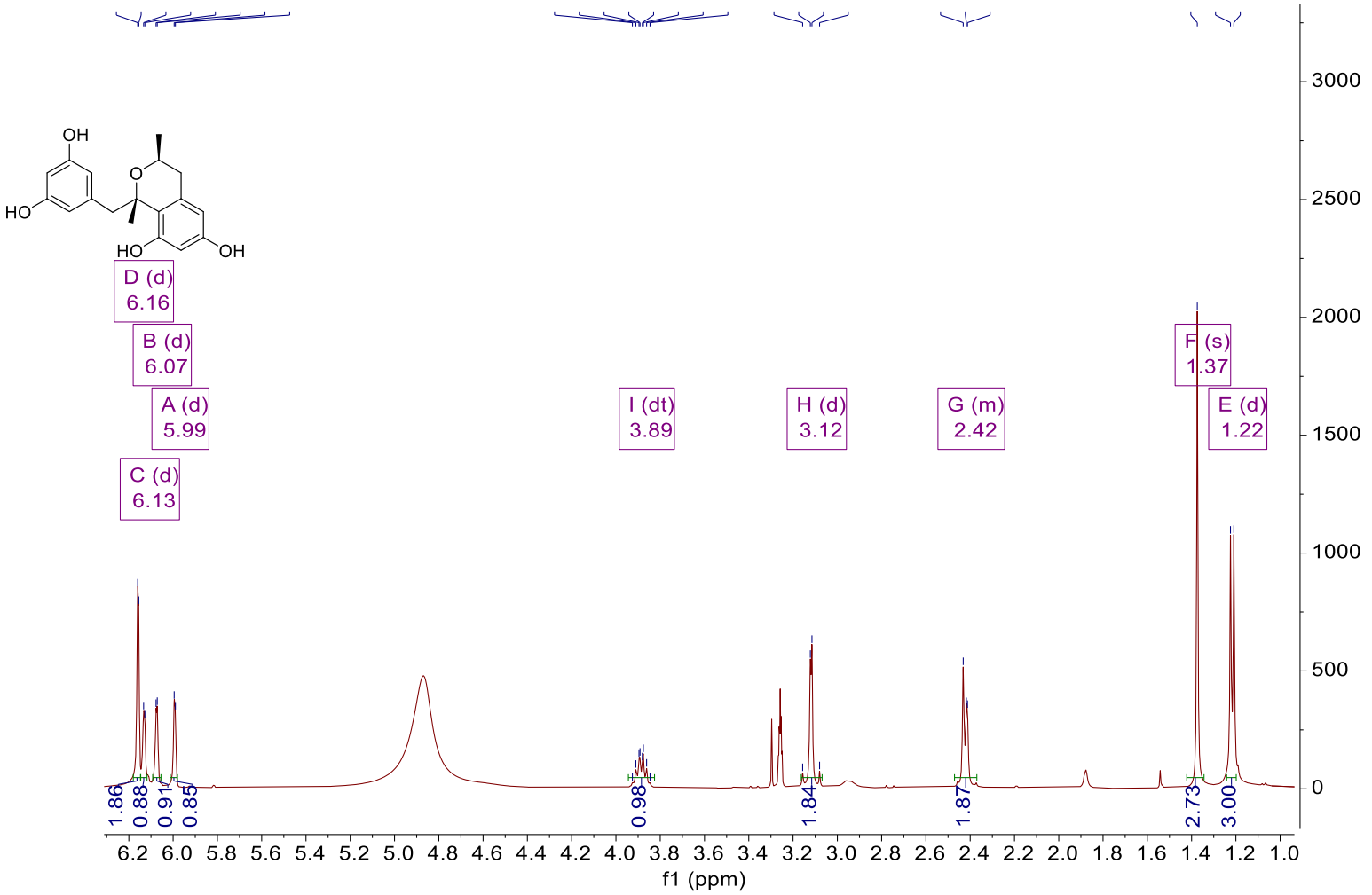

Figure S13. ^{13}C NMR (100 MHz, CD_3OD) spectrum of **2**.

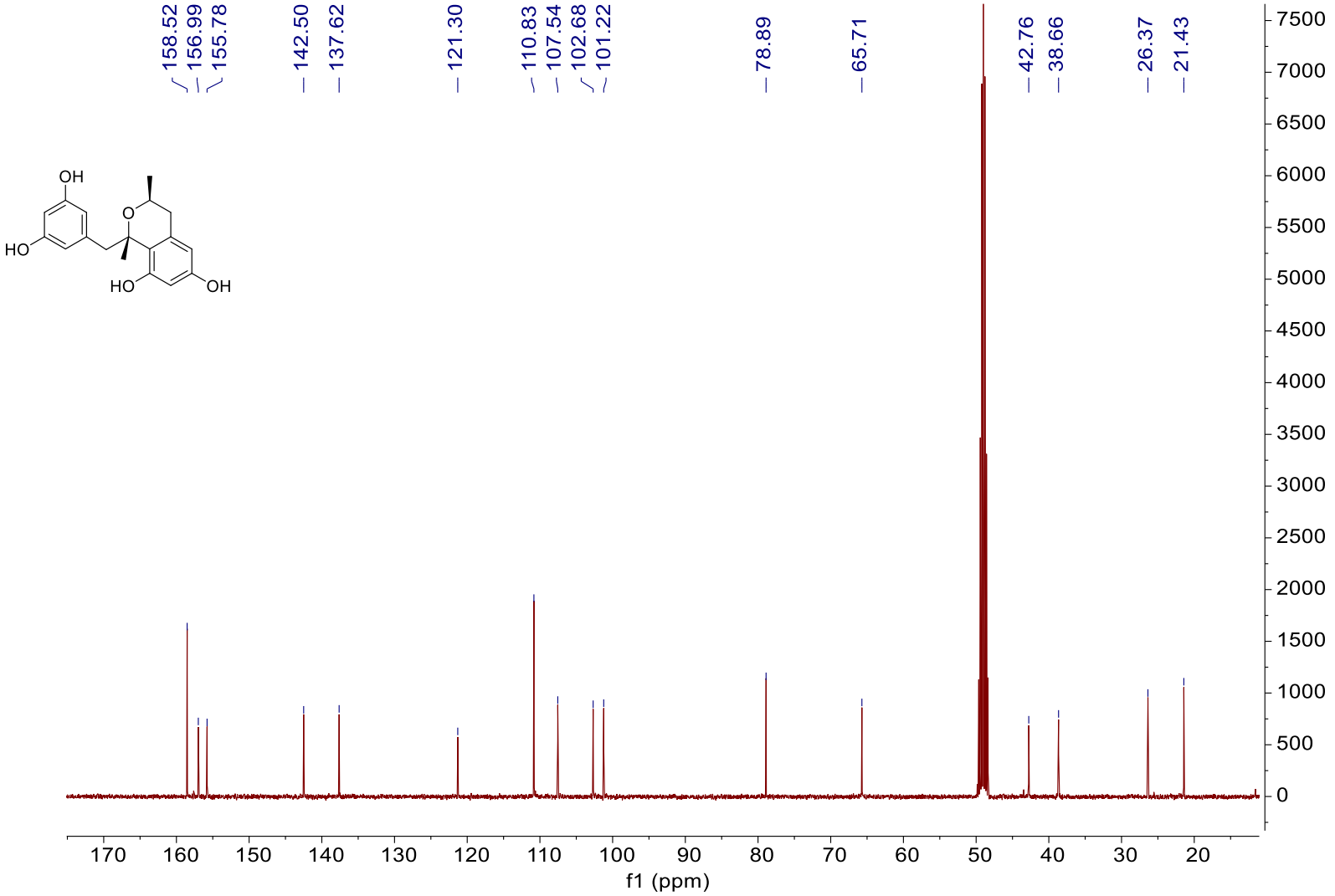

Figure S14. DEPT-135 (100 MHz, CD_3OD) spectrum of **2**.

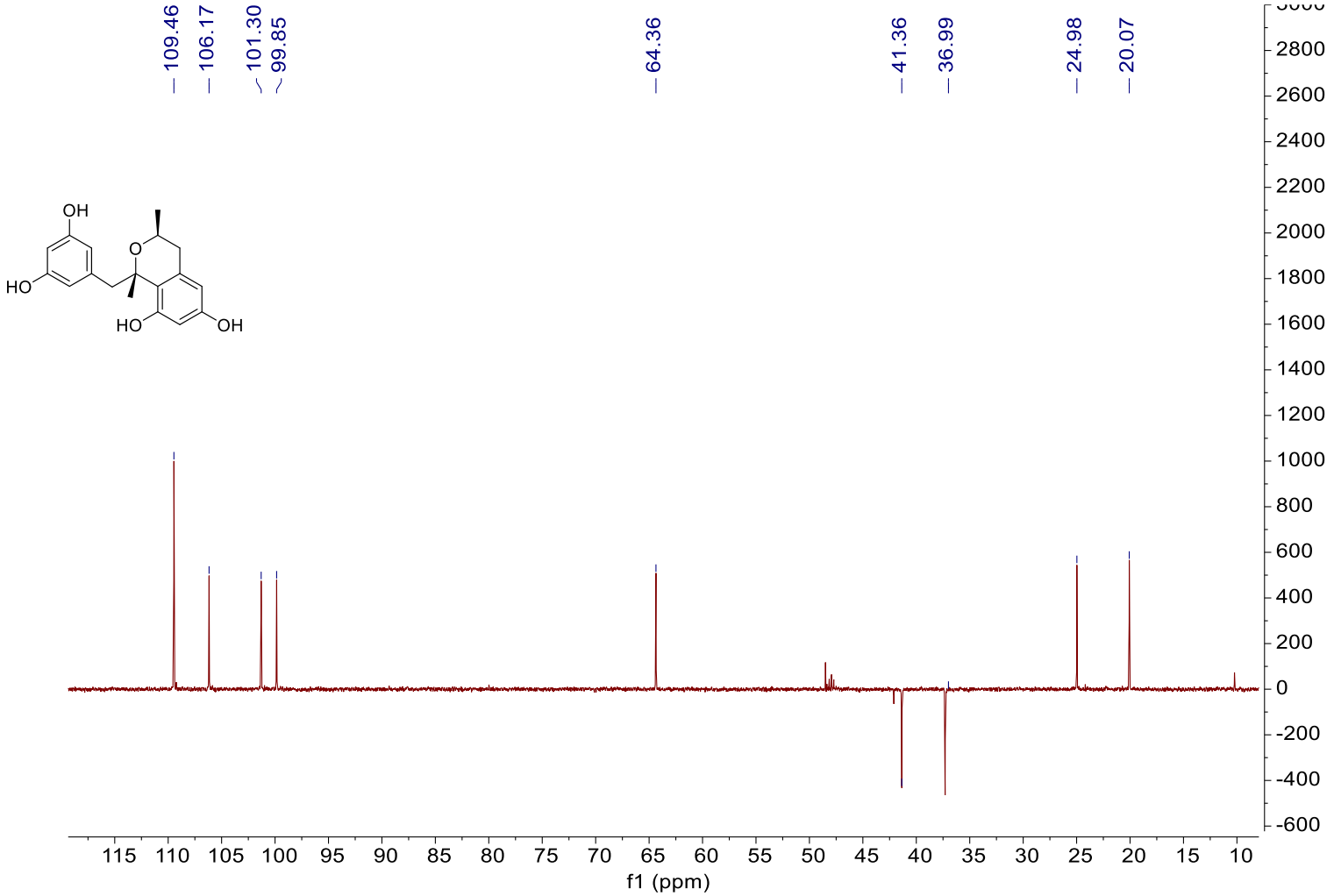

Figure S15. HSQC spectrum of **2** in CD_3OD.

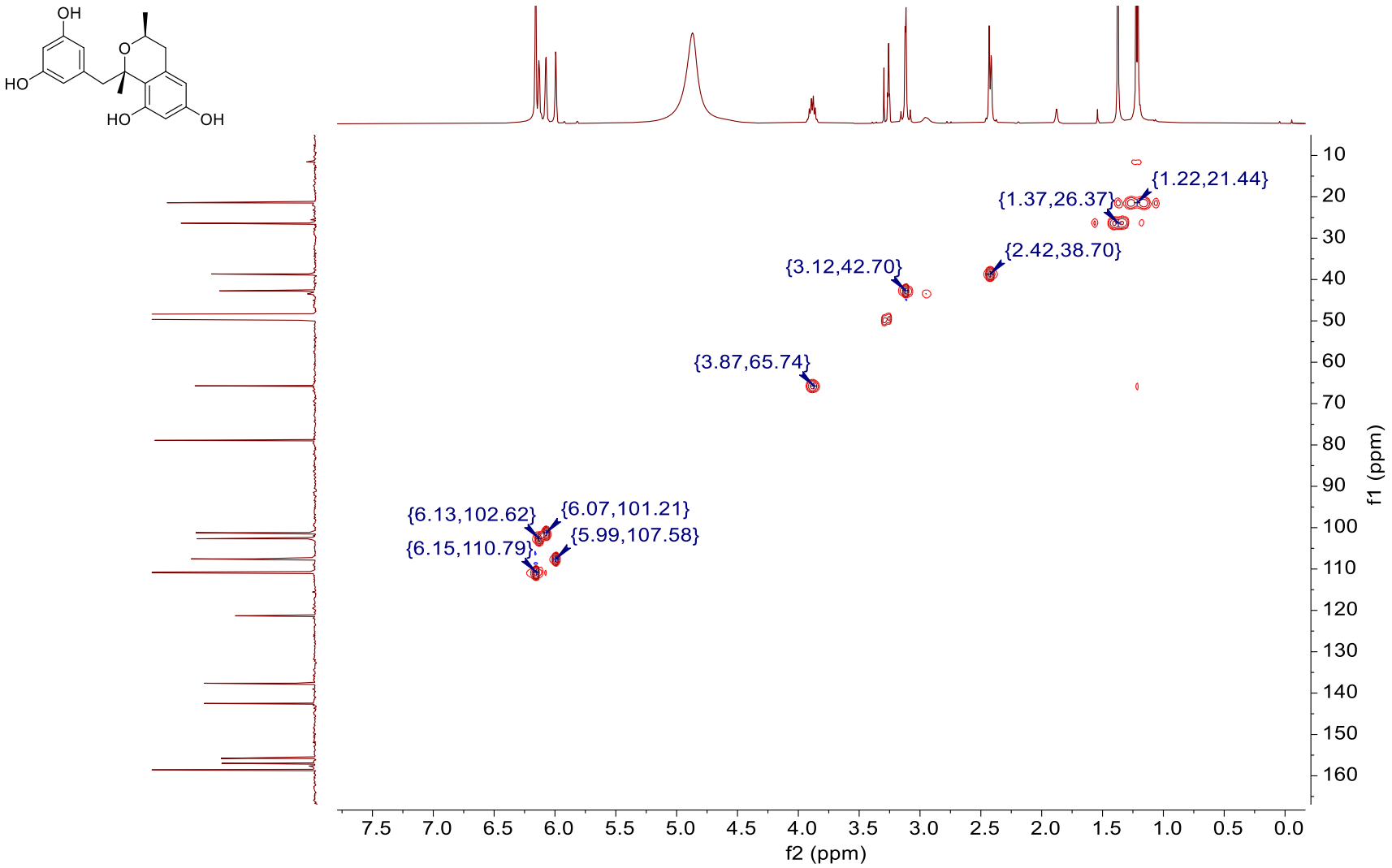

Figure S16. HMBC spectrum of **2** in CD_3OD.

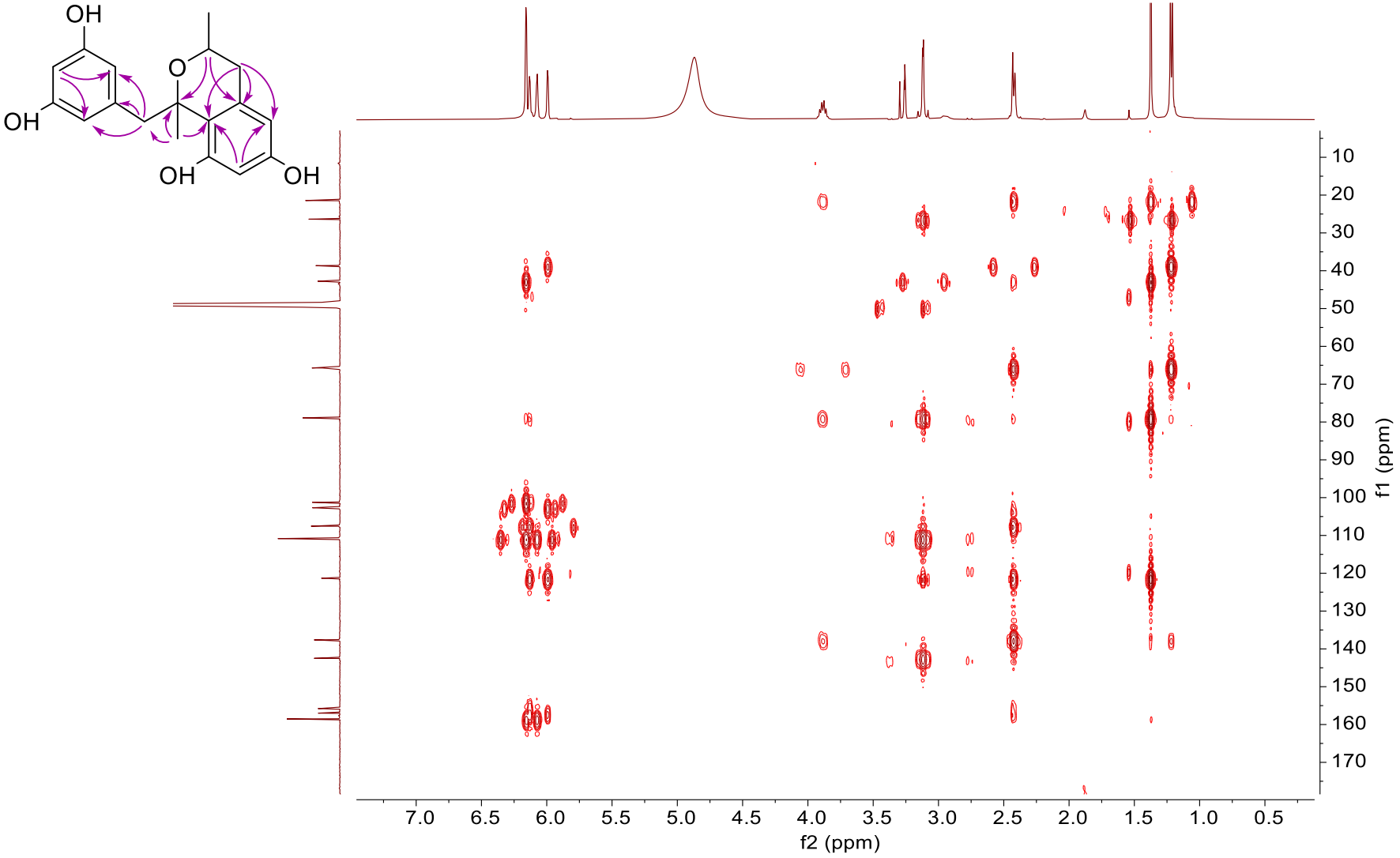

Figure S17. ^{1}H–^{1}H COSY spectrum of **2** in CD_3OD.

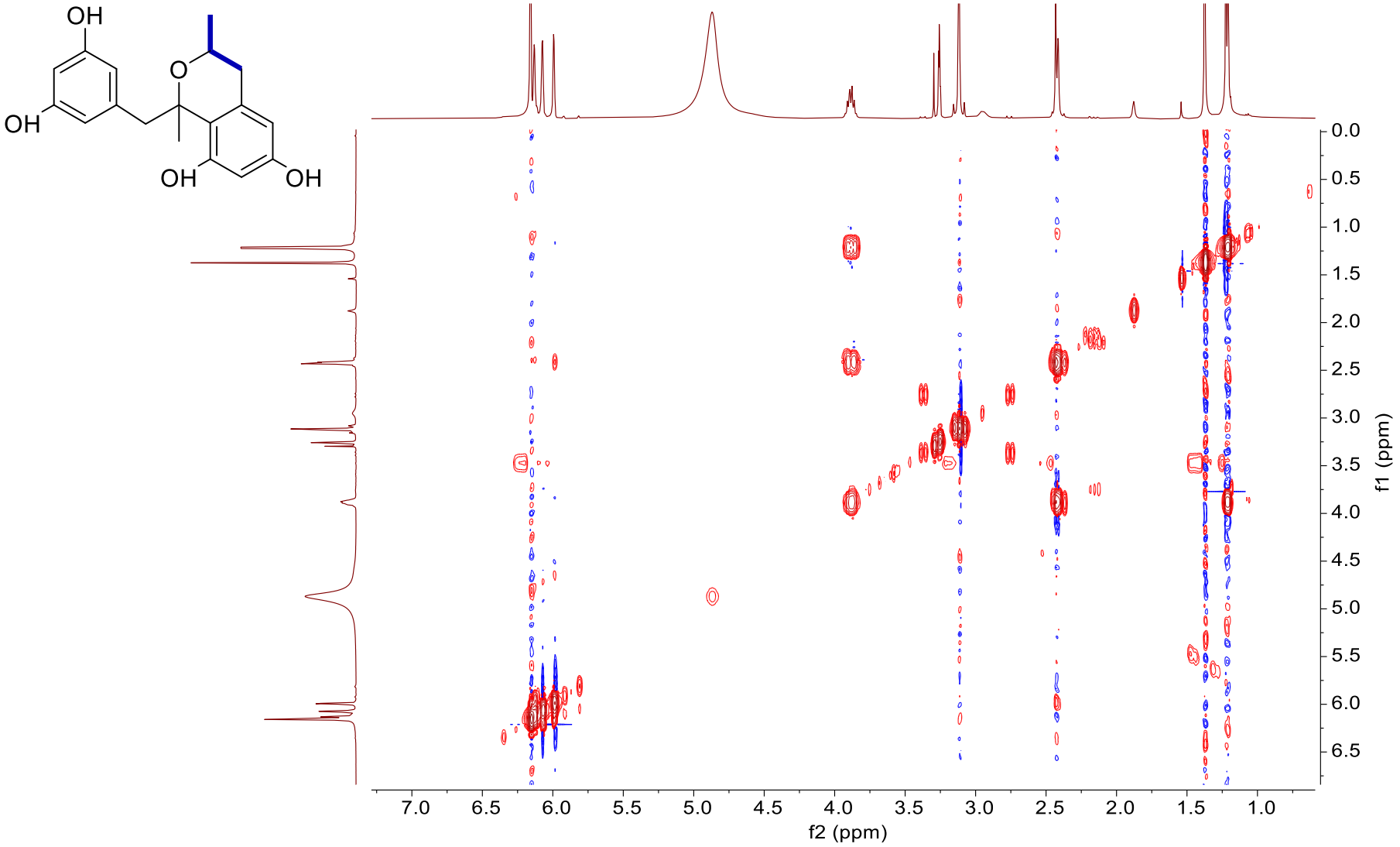

Figure S18. NOESY spectrum of **2** in CD_3OD.

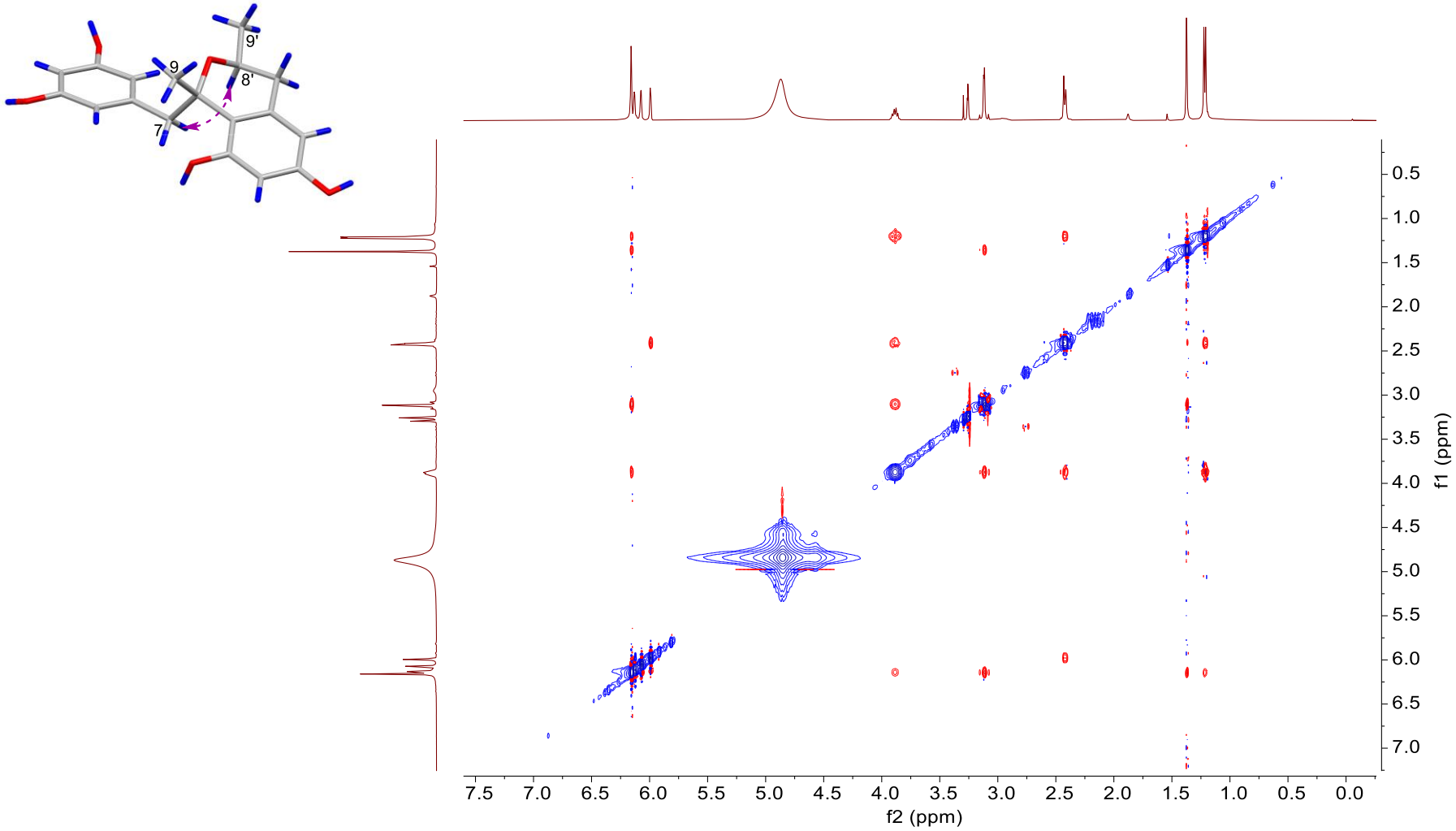

Figure S19. HRESIMS (+) spectrum of **2**.

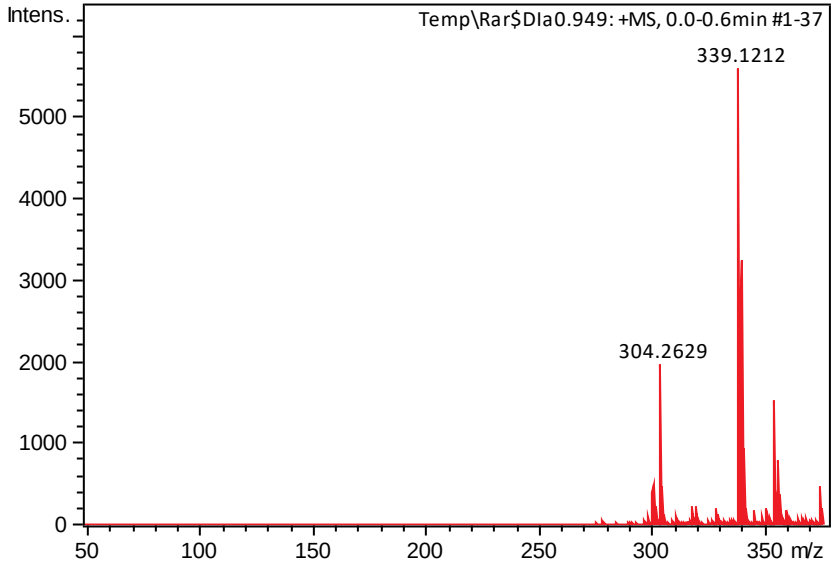

Figure S20. UV spectrum of **2**.

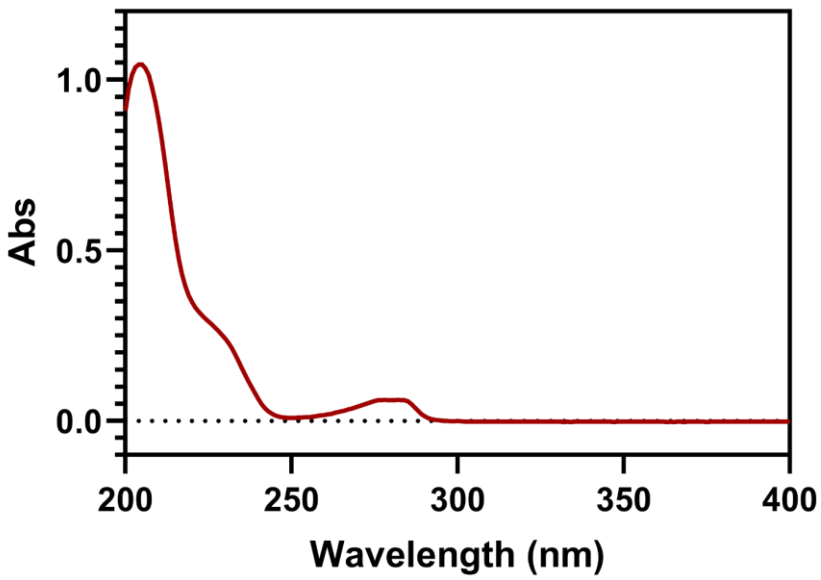

Figure S21. IR spectrum of **2**.

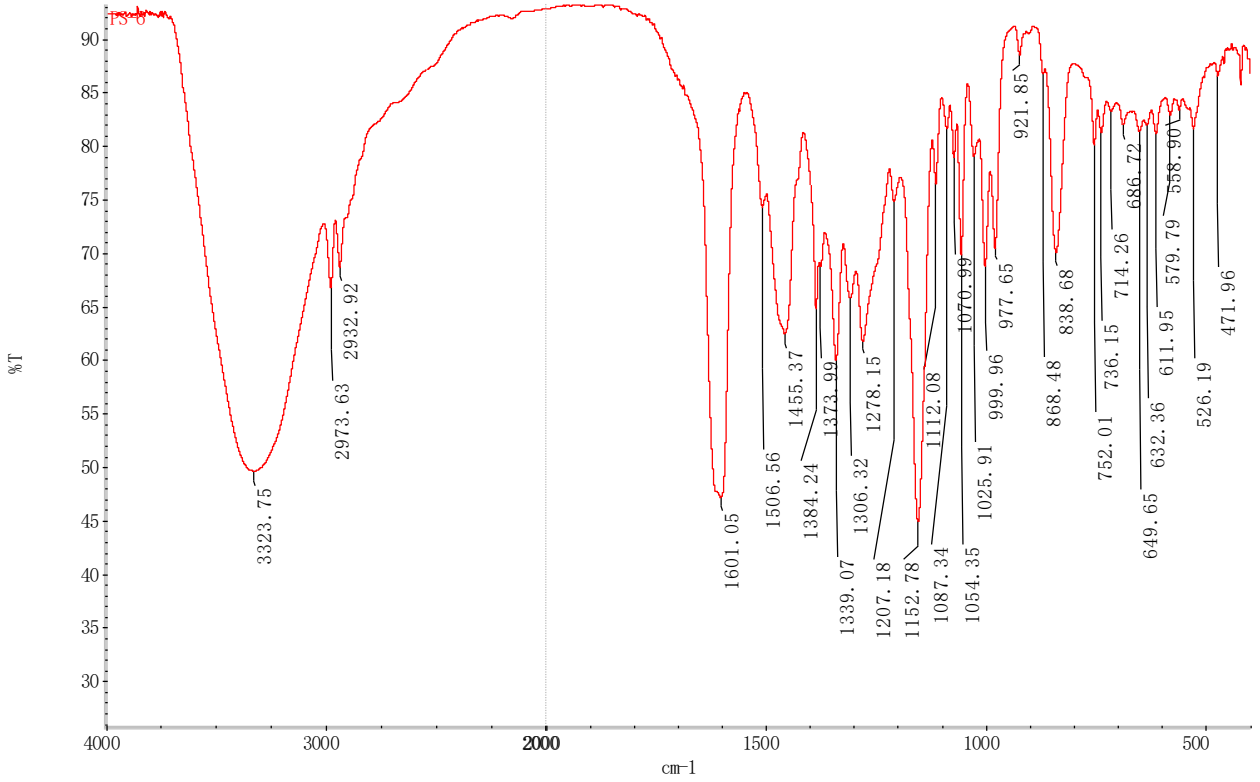

Figure S22. ECD spectrum of **2**.

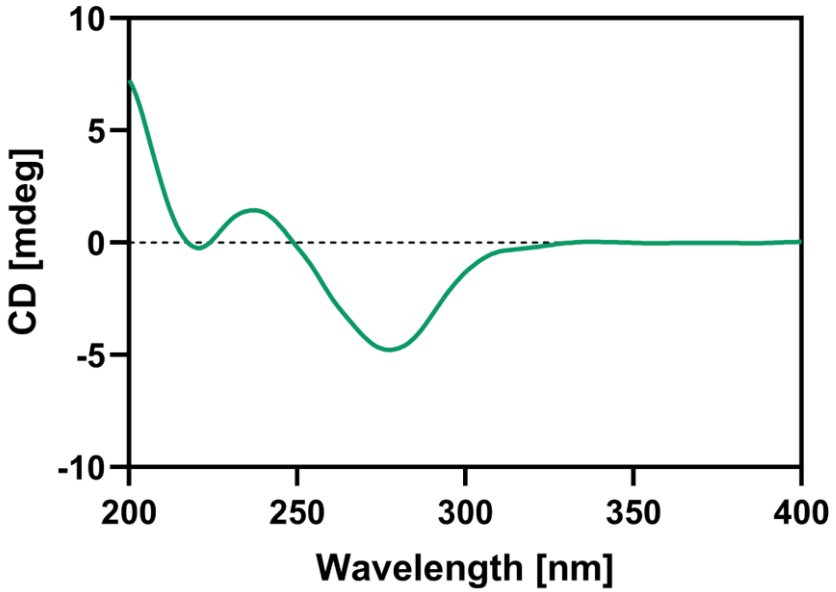

Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3**.

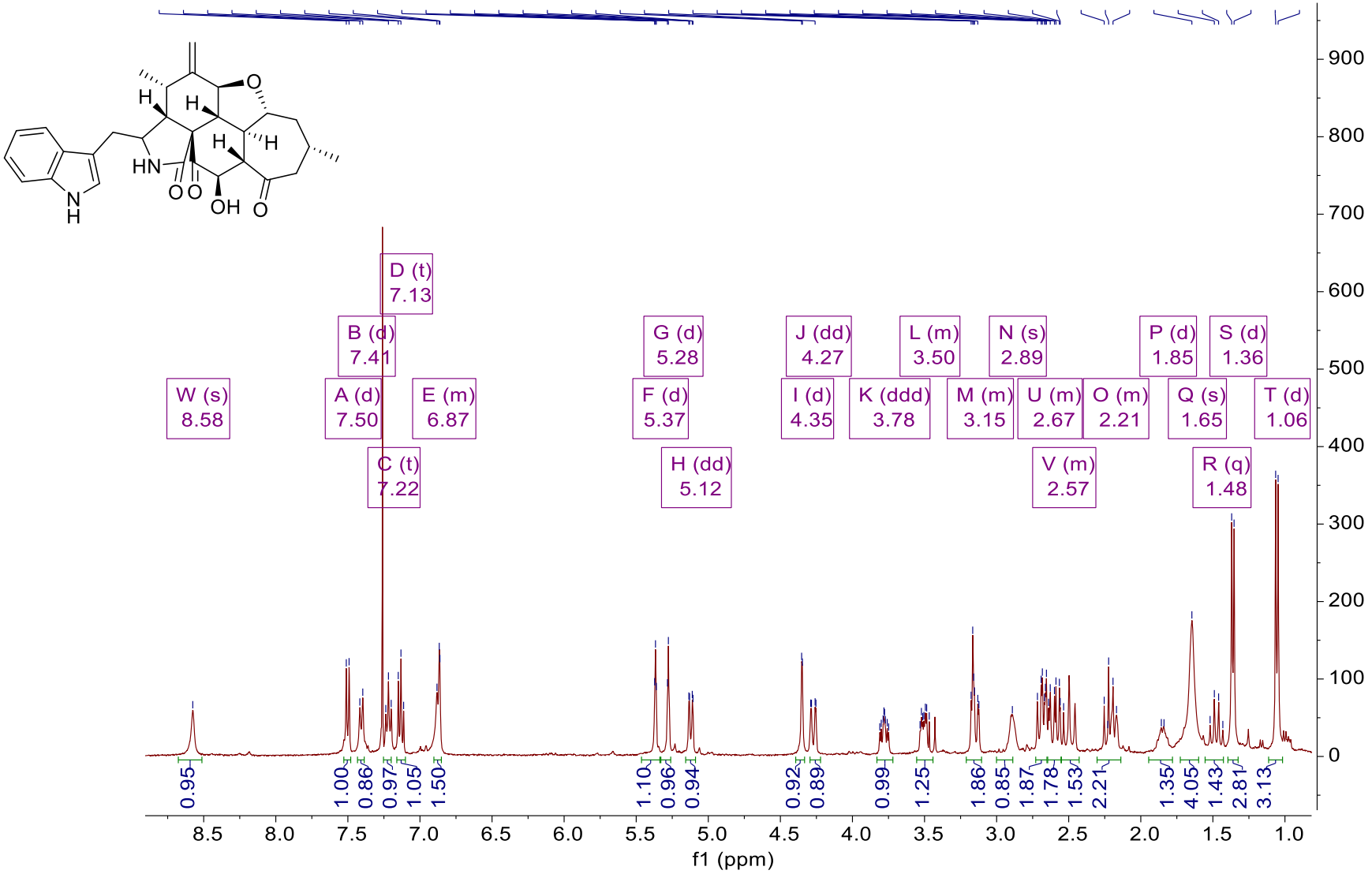

Figure S24. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3**.

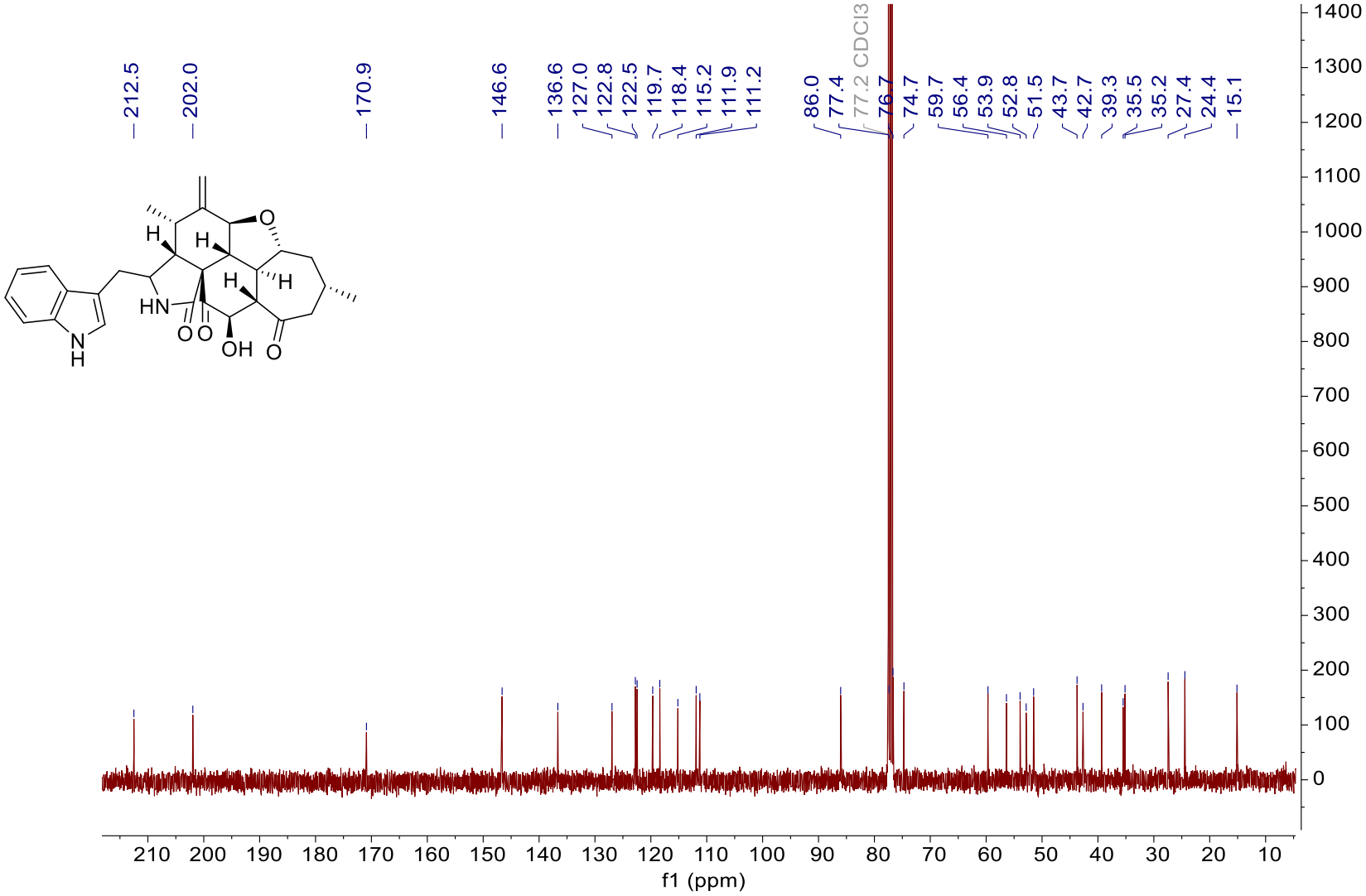

Figure S25. DEPT-135 (100 MHz, $CDCl_3$) spectrum of **3**.

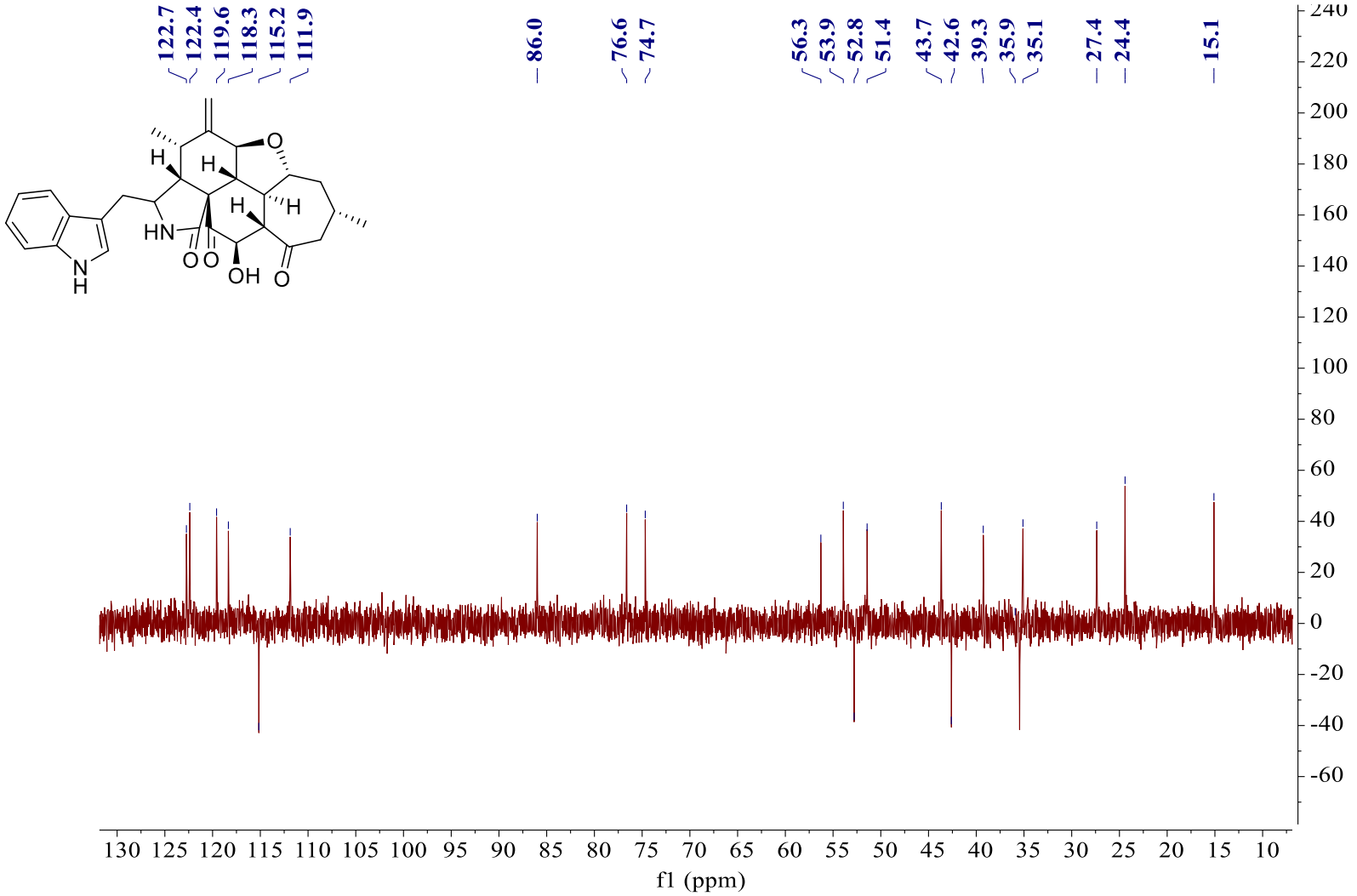

Figure S26. HSQC spectrum of **3** in $CDCl_3$.

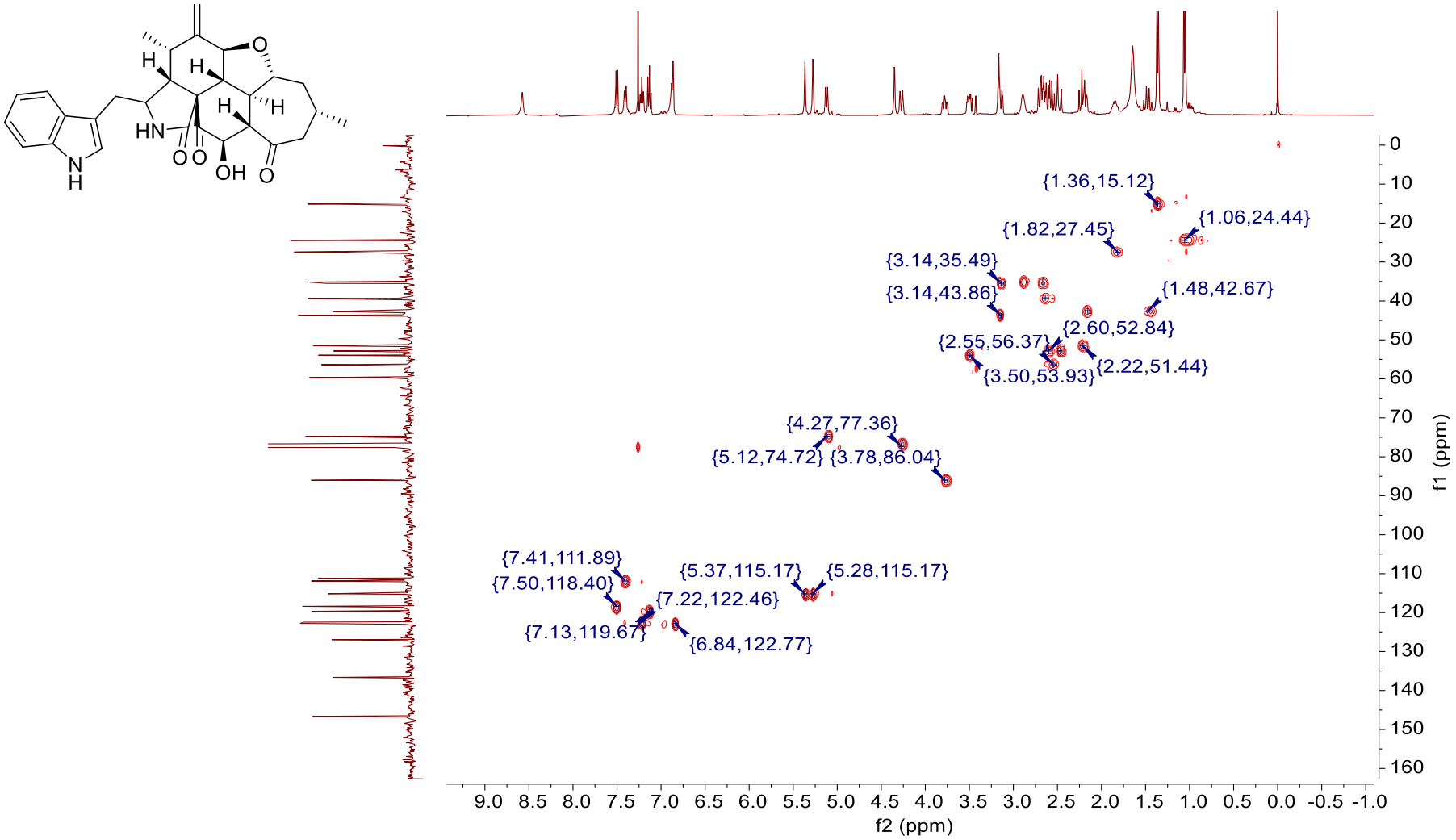

Figure S27. HMBC spectrum of **3** in $CDCl_3$.

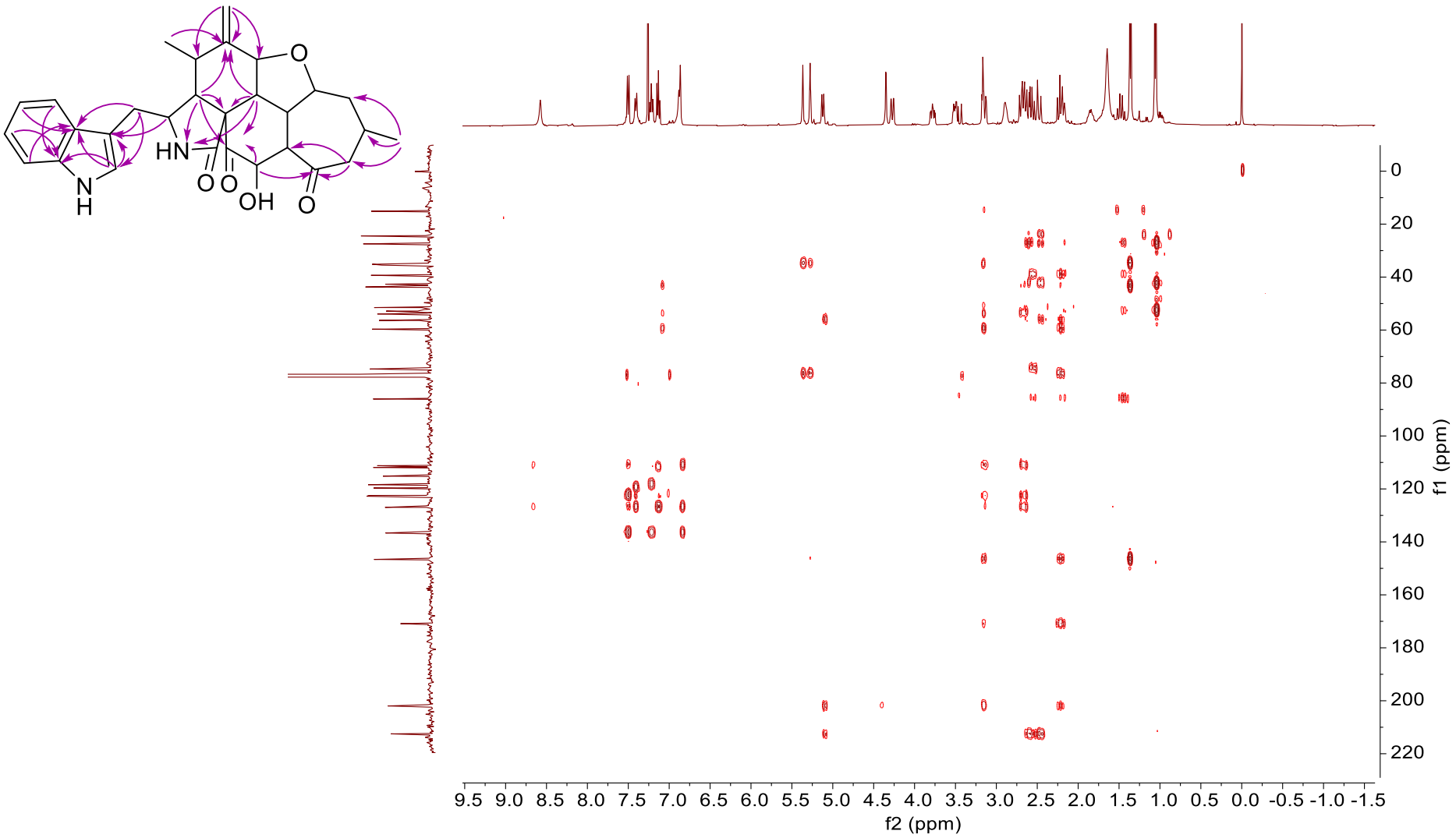

Figure S28. ^{1}H–^{1}H COSY spectrum of **3** in $CDCl_3$.

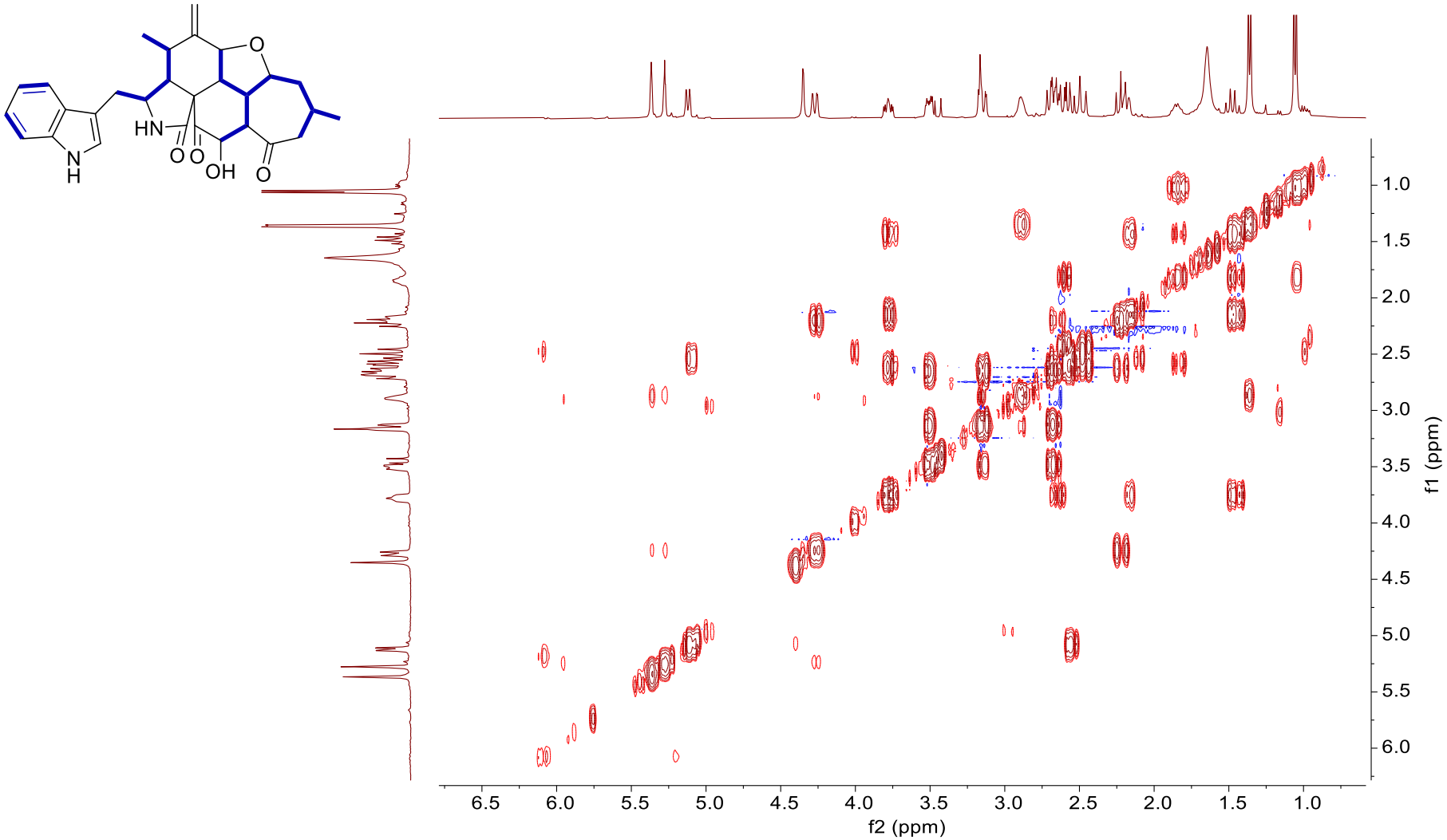

Figure S29. NOESY spectrum of **3** in $CDCl_3$.

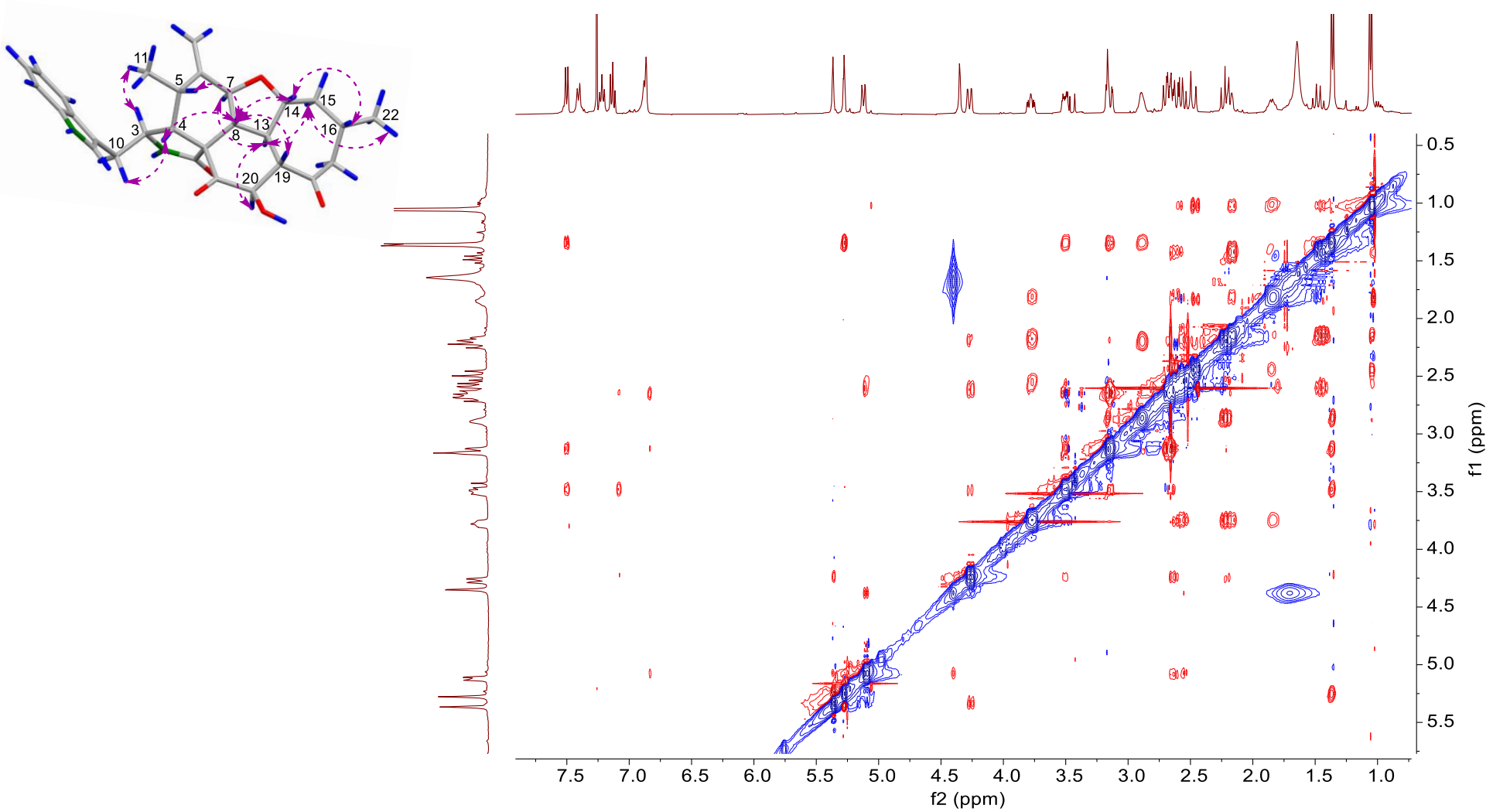

Figure S30. HRESIMS (+) spectrum of **3**.

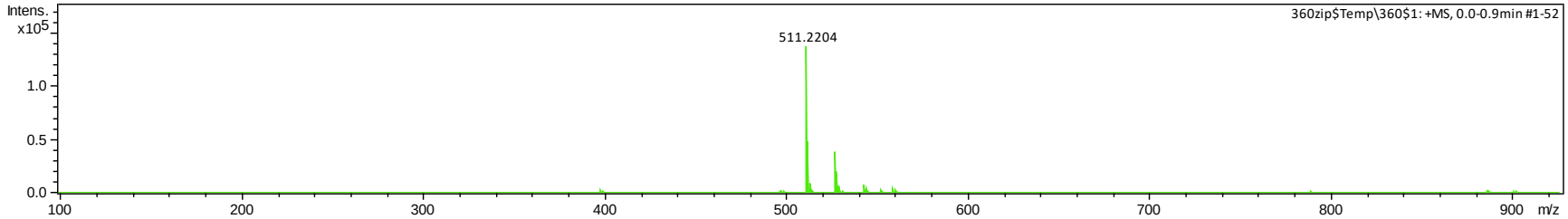

Figure S31. UV spectrum of **3**.

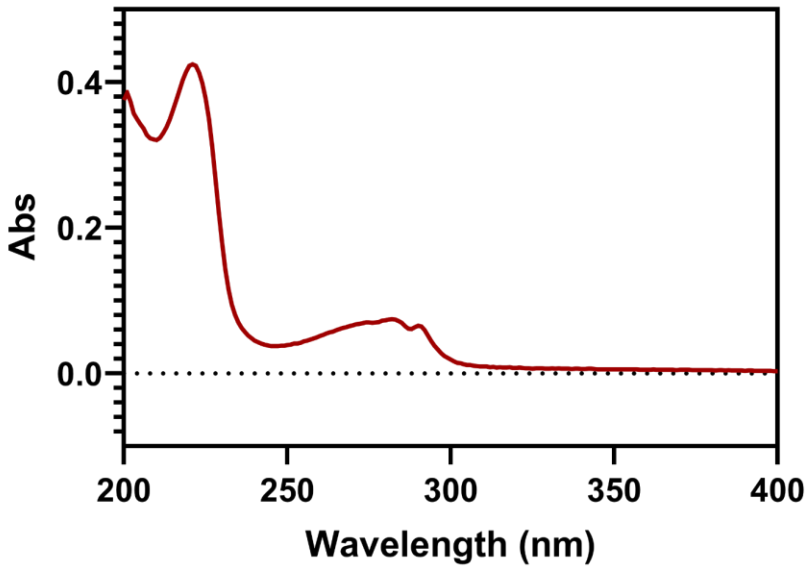

Figure S32. IR spectrum of **3**.

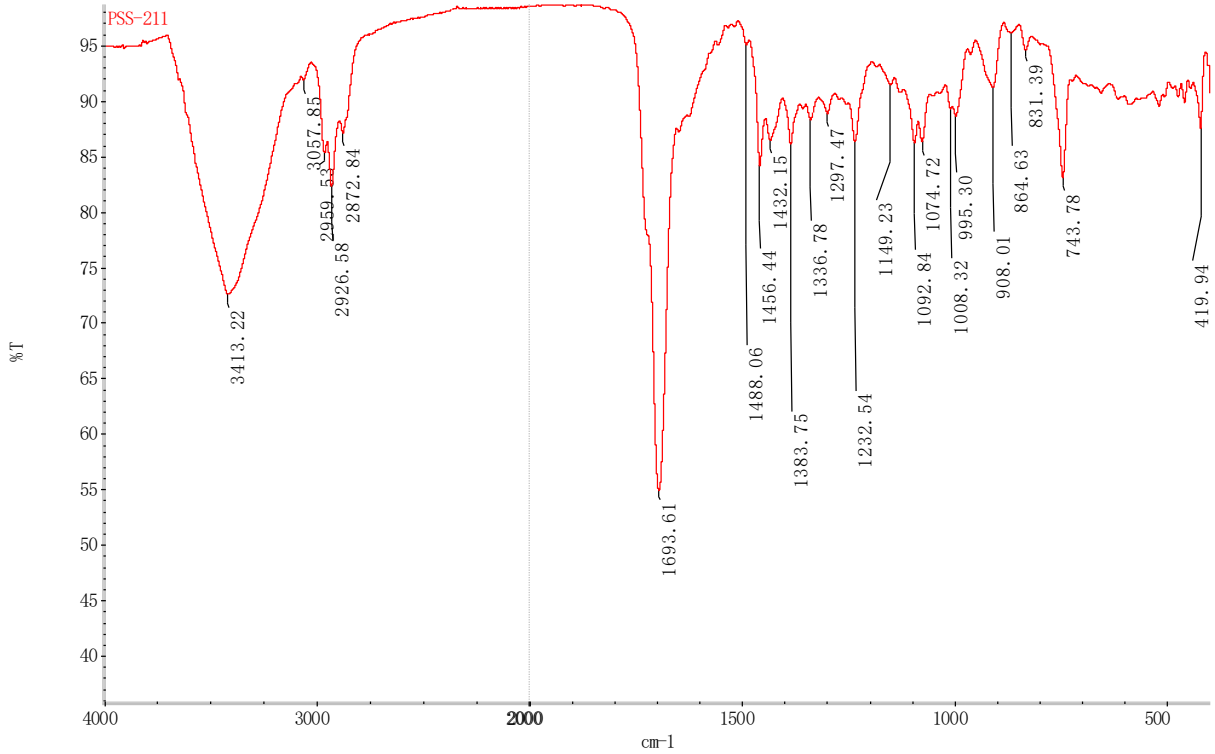

Figure S33. ECD spectrum of **3**.

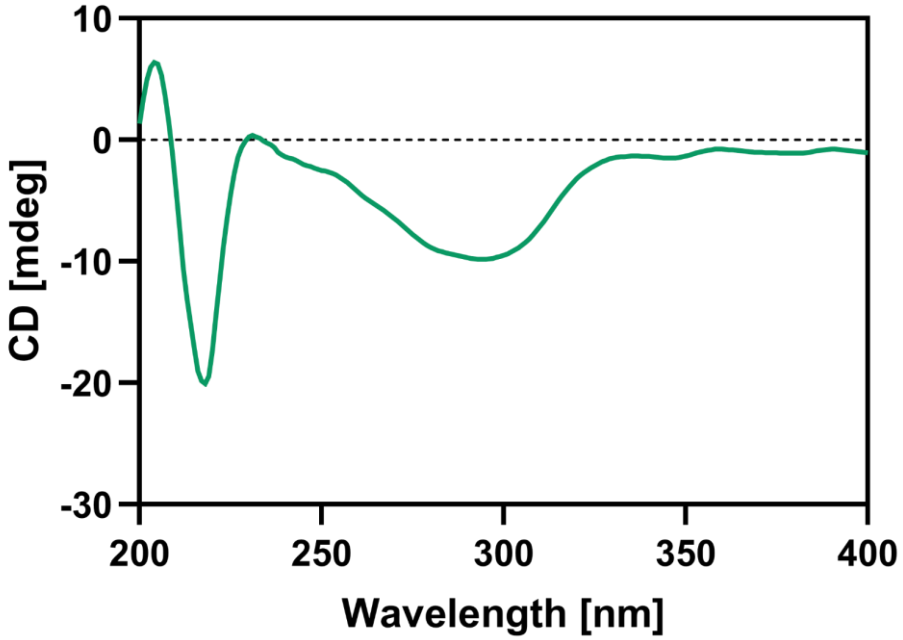

Figure S34. ^{1}H NMR (400 MHz, CD_3OD) spectrum of **4**.

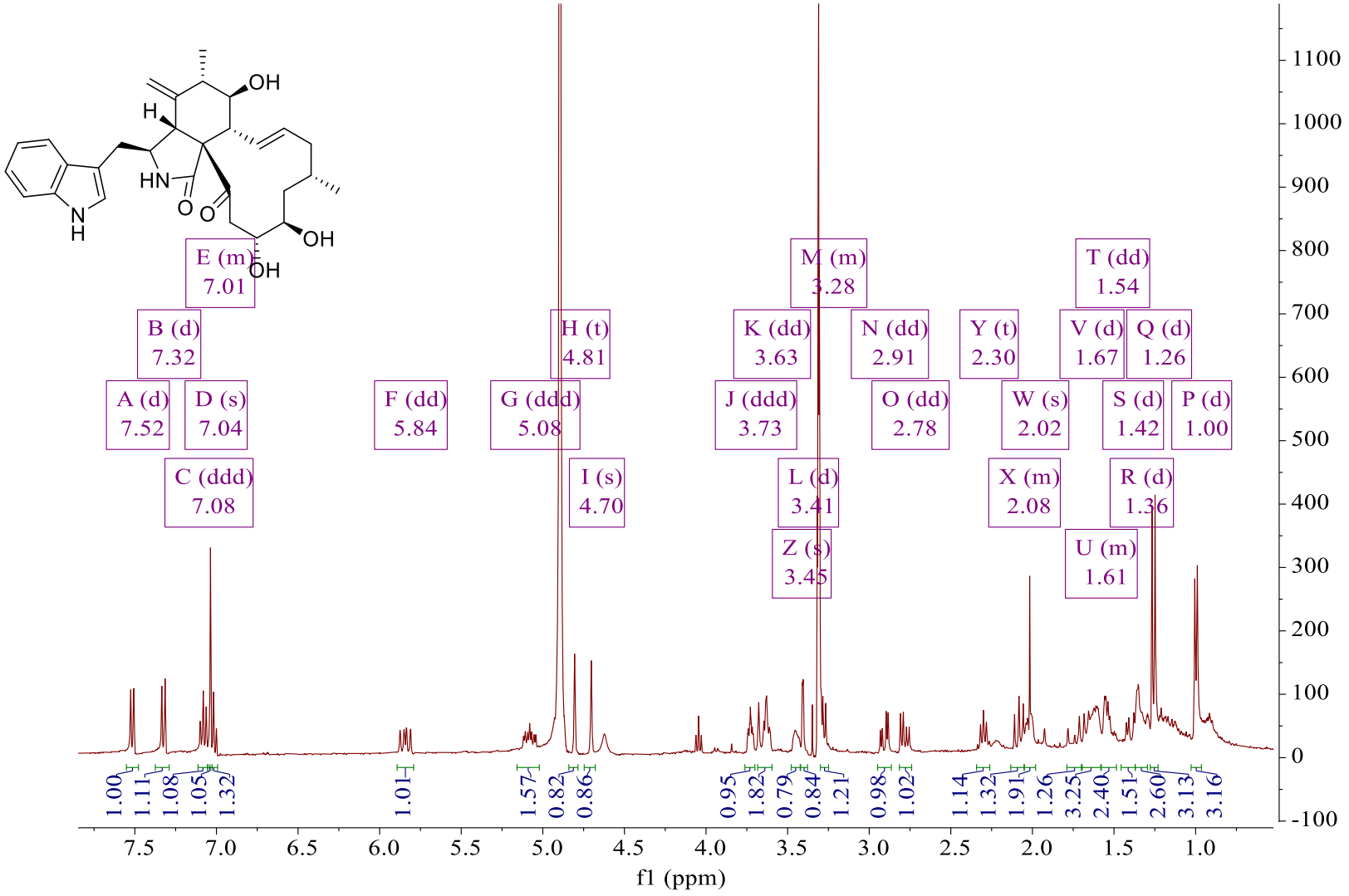

Figure S35. ^{13}C NMR (100 MHz, CD_3OD) spectrum of **4**.

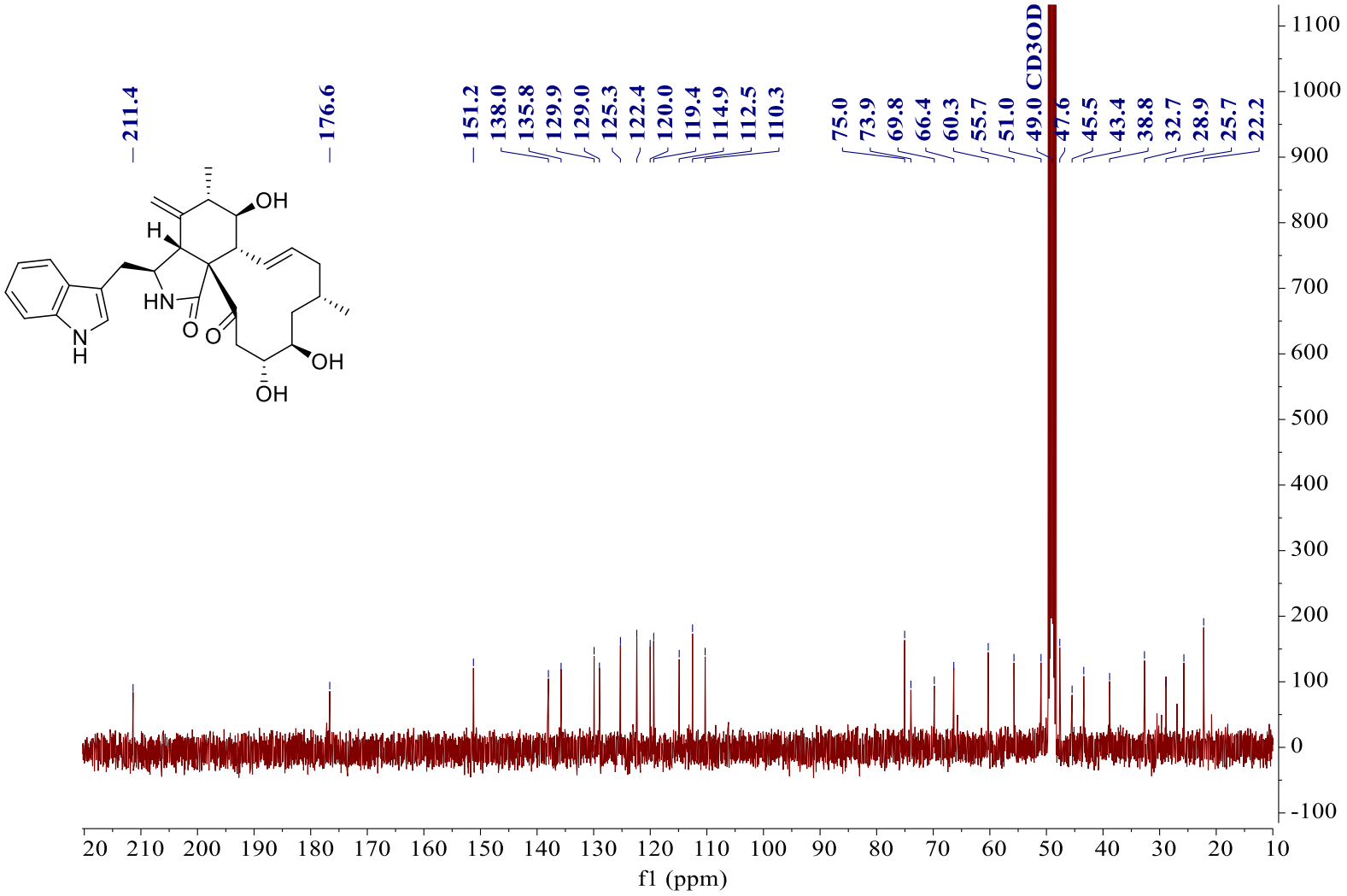

Figure S36. DEPT-135 (100 MHz, CD_3OD) spectrum of **4**.

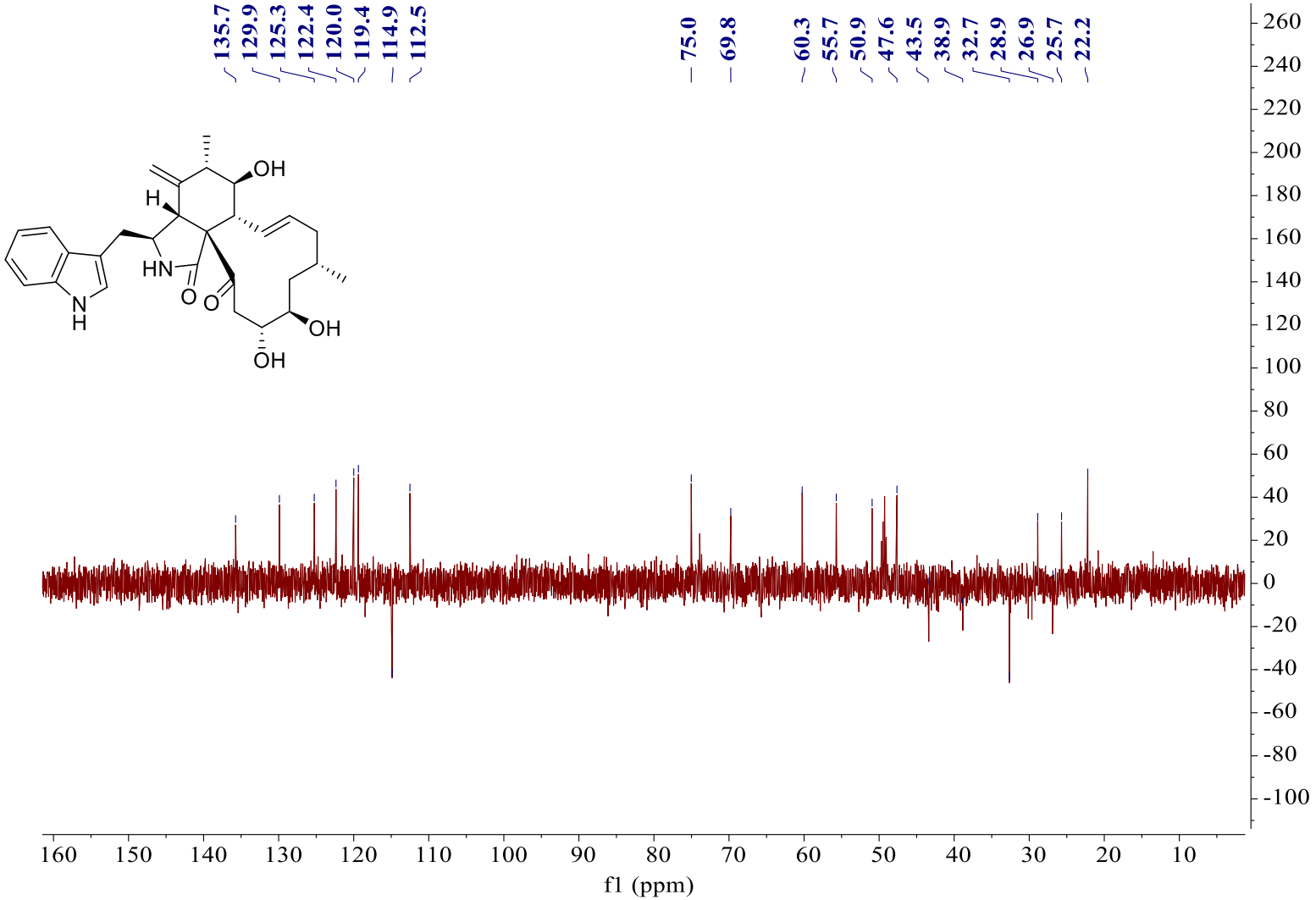

Figure S37. HSQC spectrum of **4** in CD_3OD.

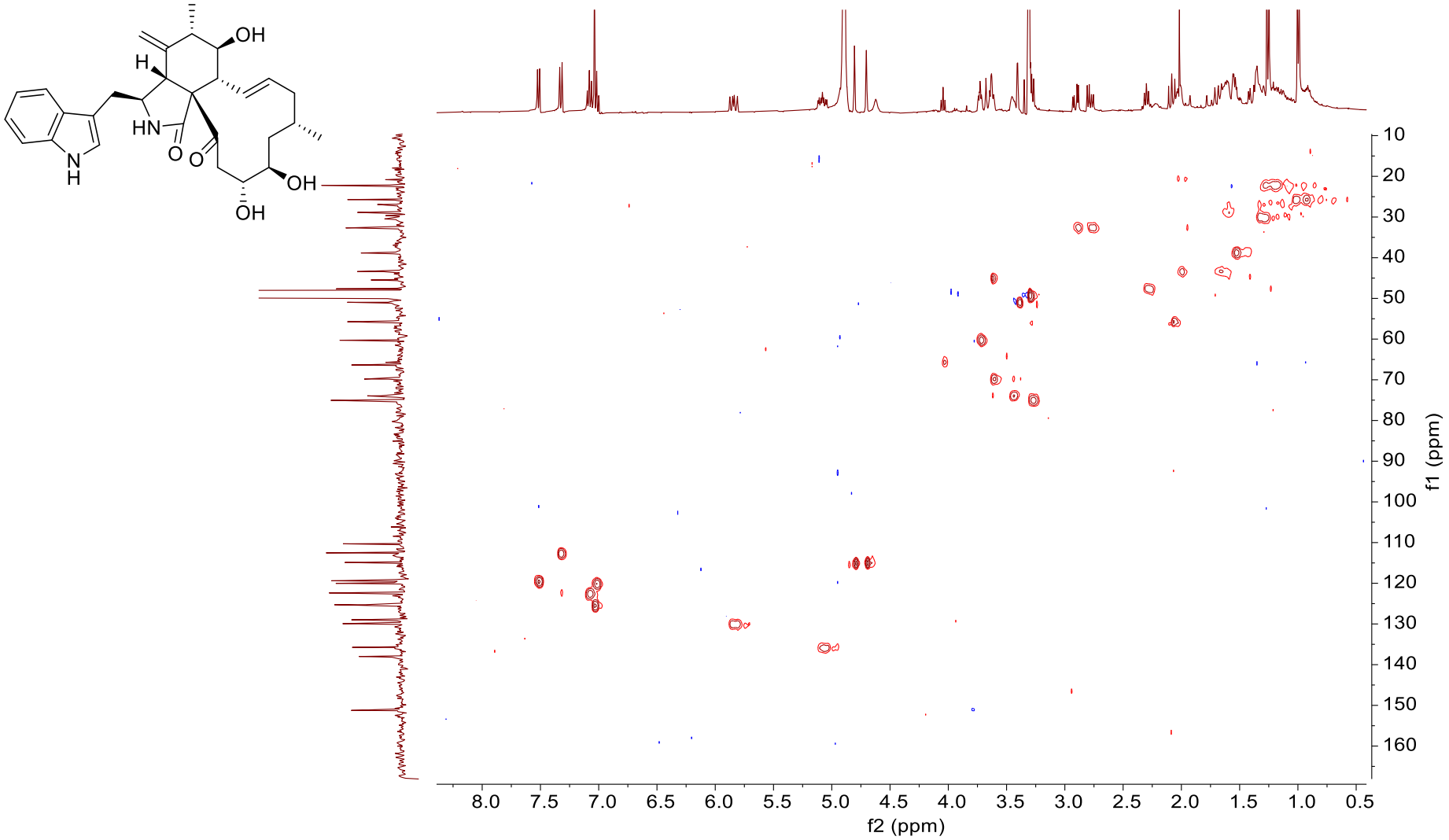

Figure S38. HMBC spectrum of **4** in CD_3OD.

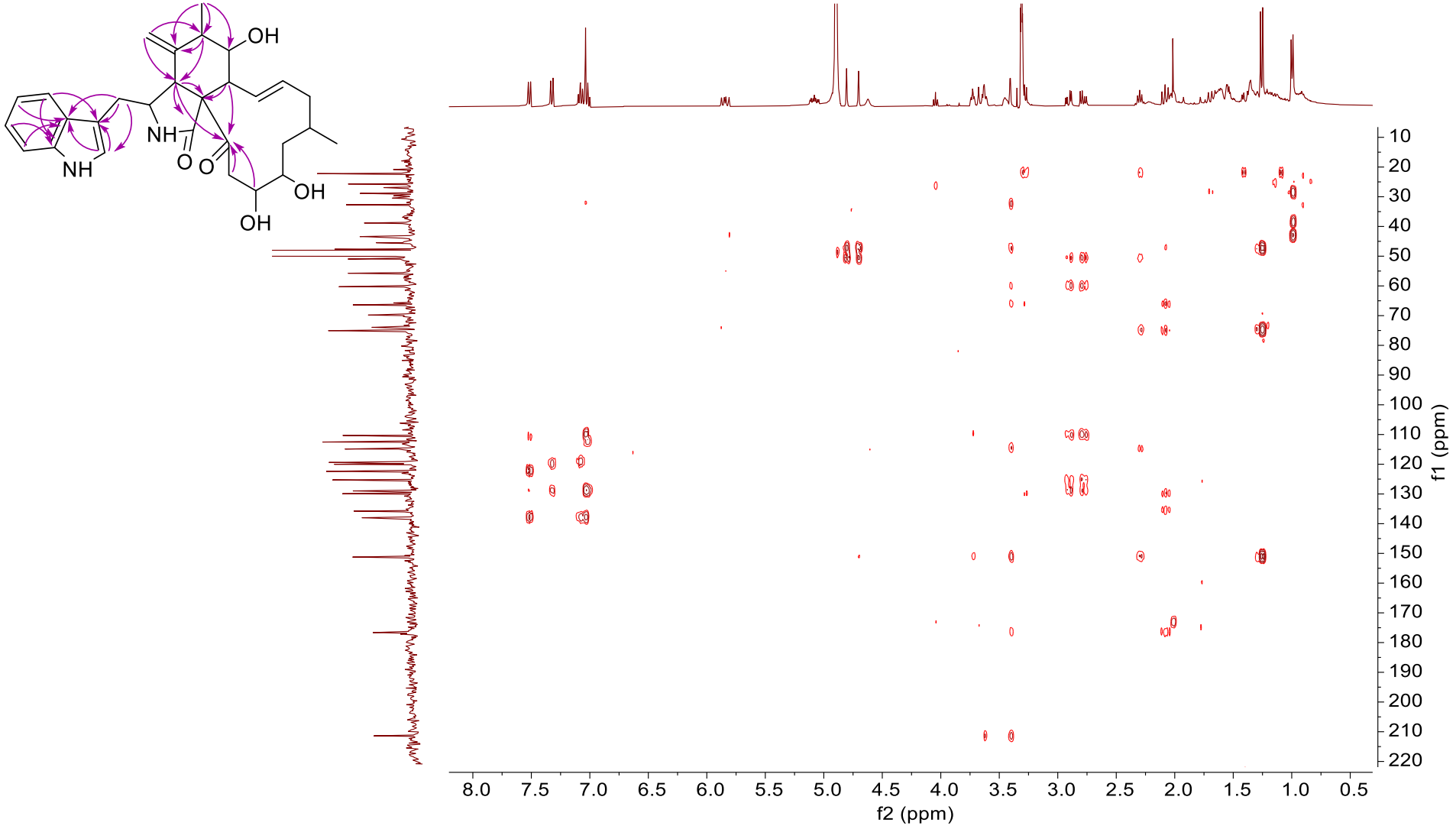

Figure S39. ^{1}H–^{1}H COSY spectrum of **4** in CD_3OD.

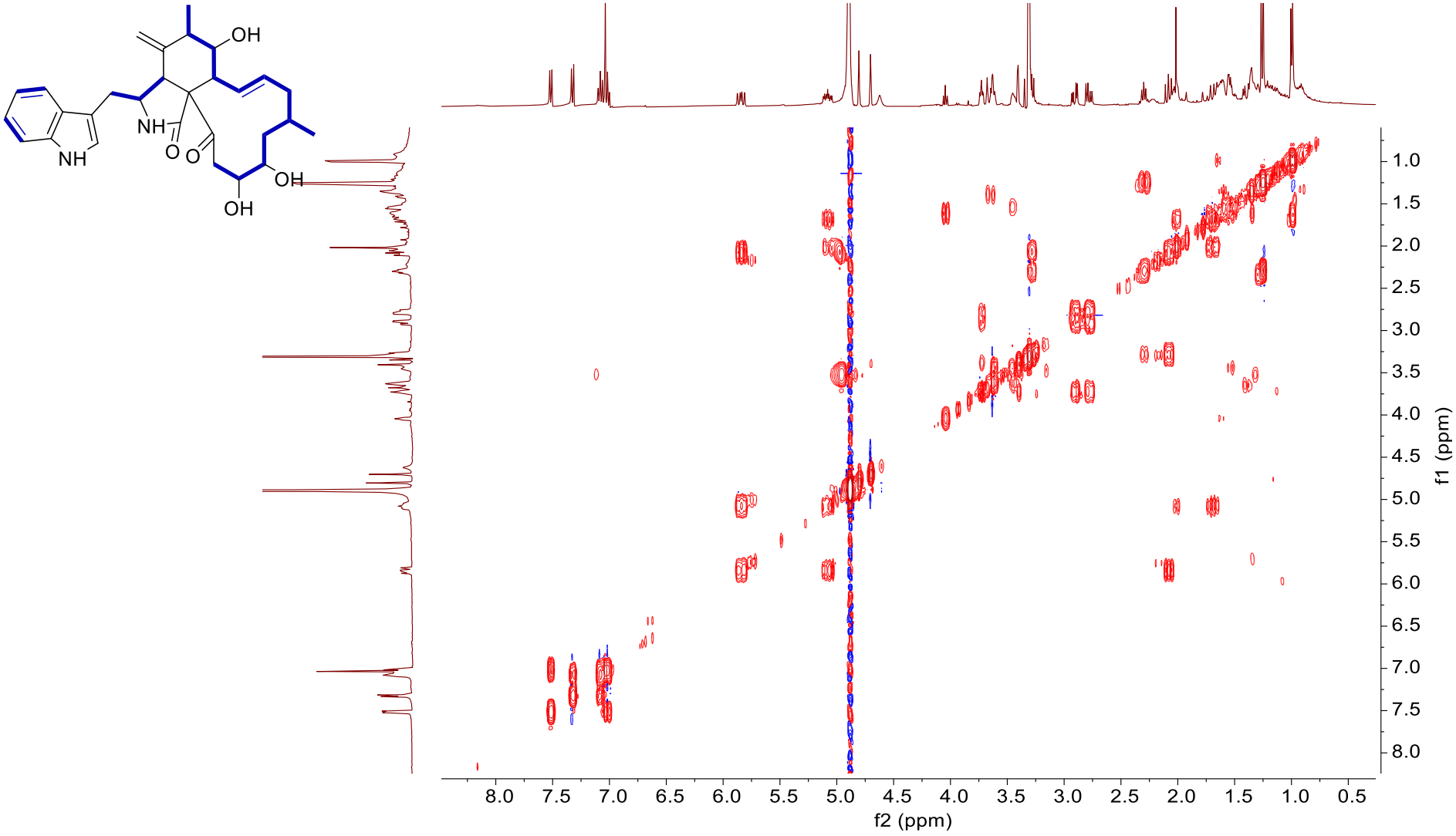

Figure S40. NOESY spectrum of **4** in CD_3OD.

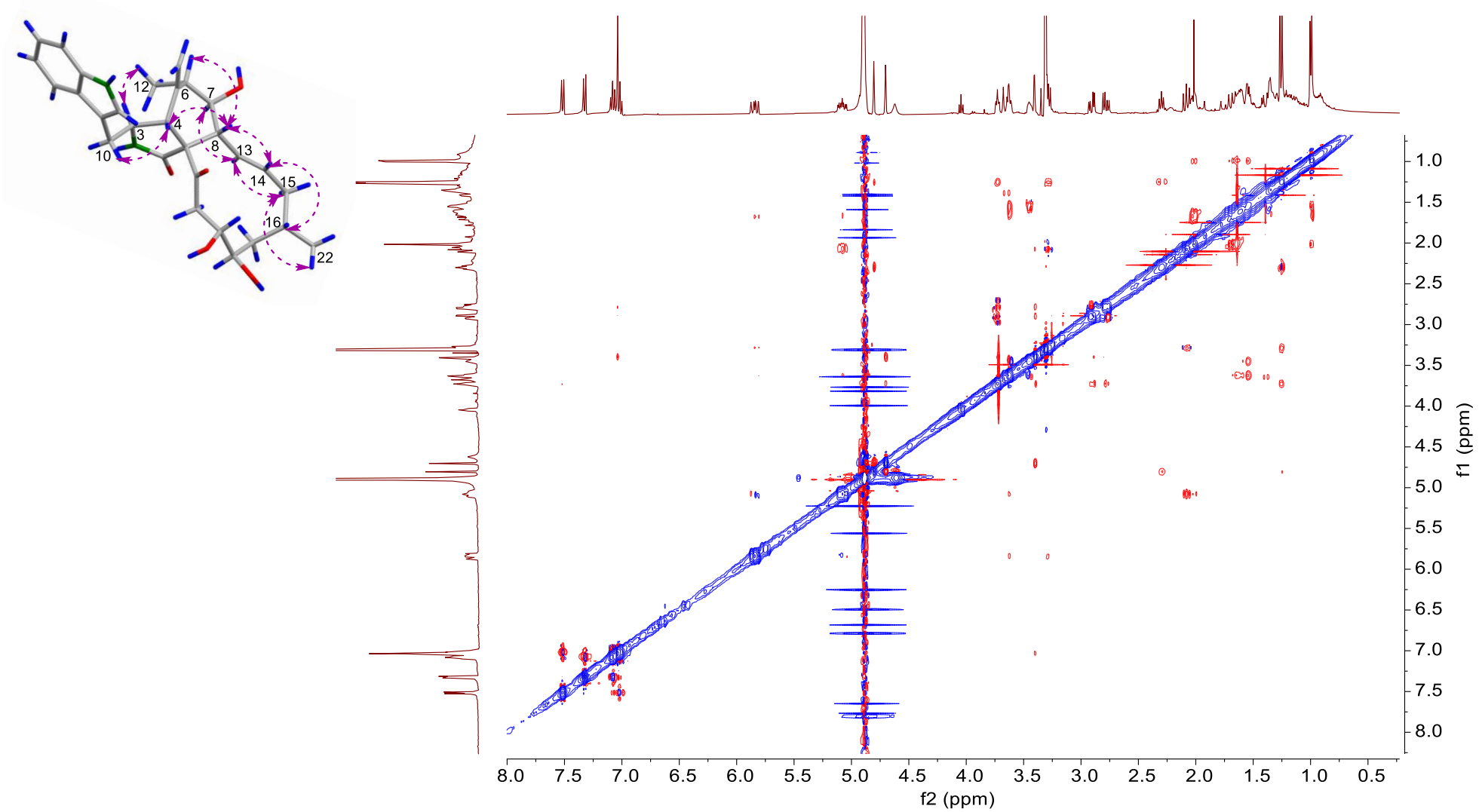

Figure S41. HRESIMS (+) spectrum of **4**.

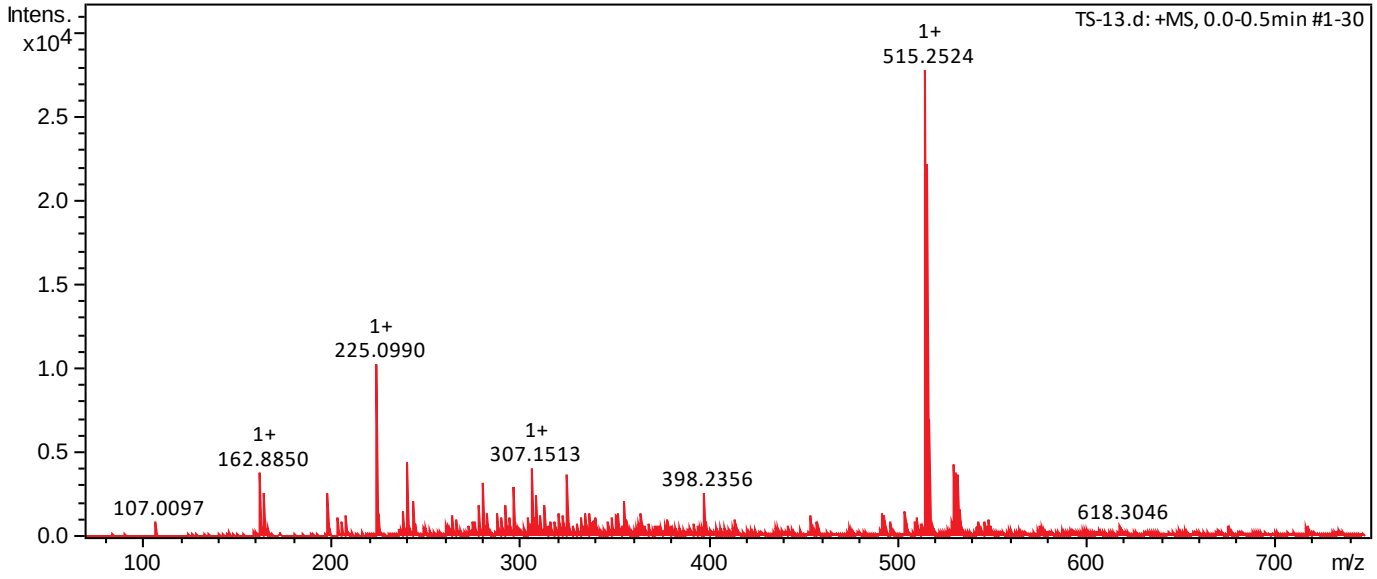

Figure S42. UV spectrum of **4**.

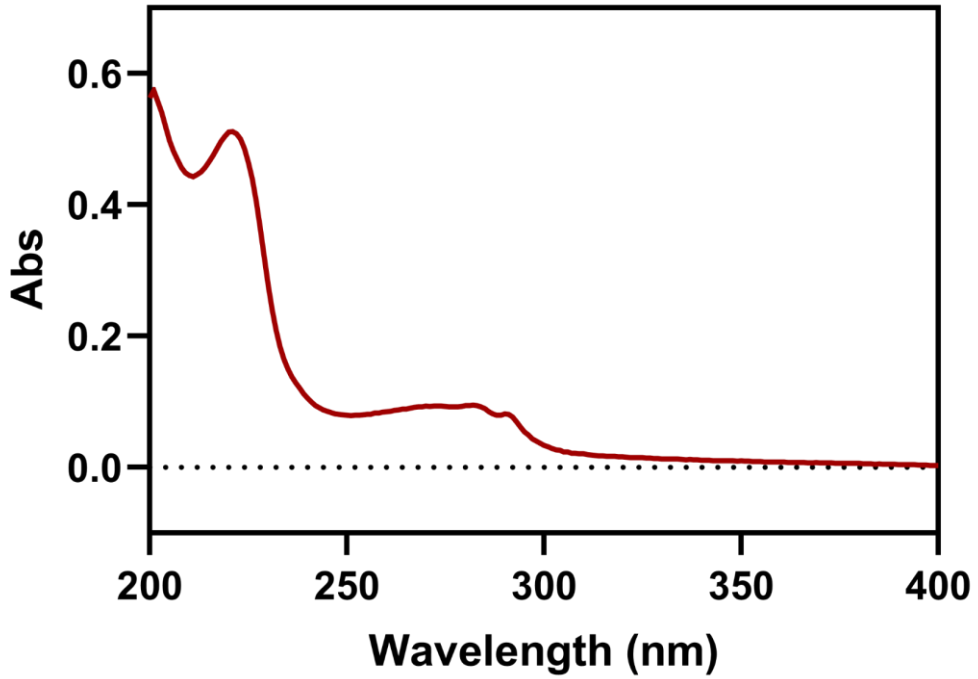

Figure S43. IR spectrum of **4**.

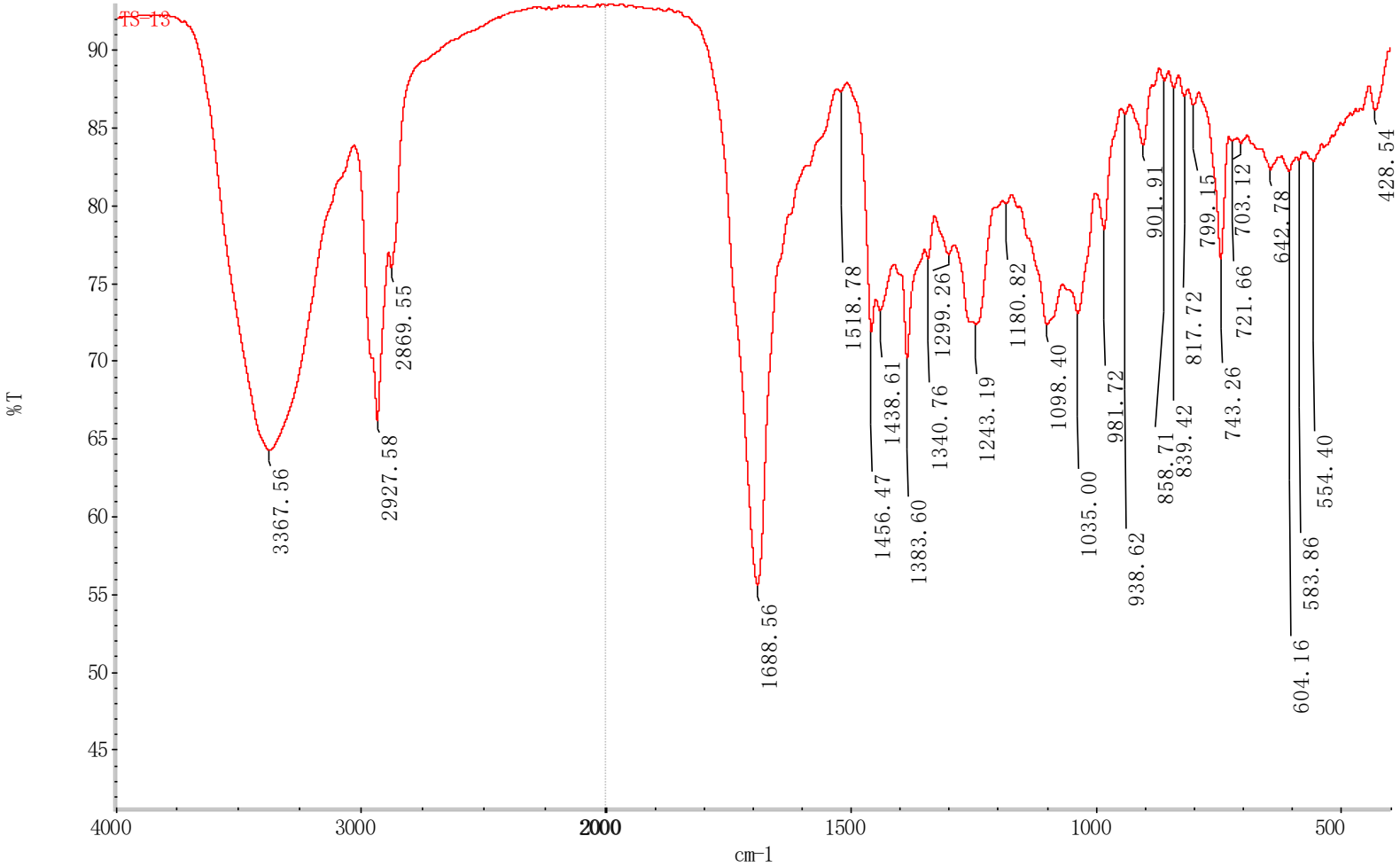

Figure S44. ECD spectrum of **4**.

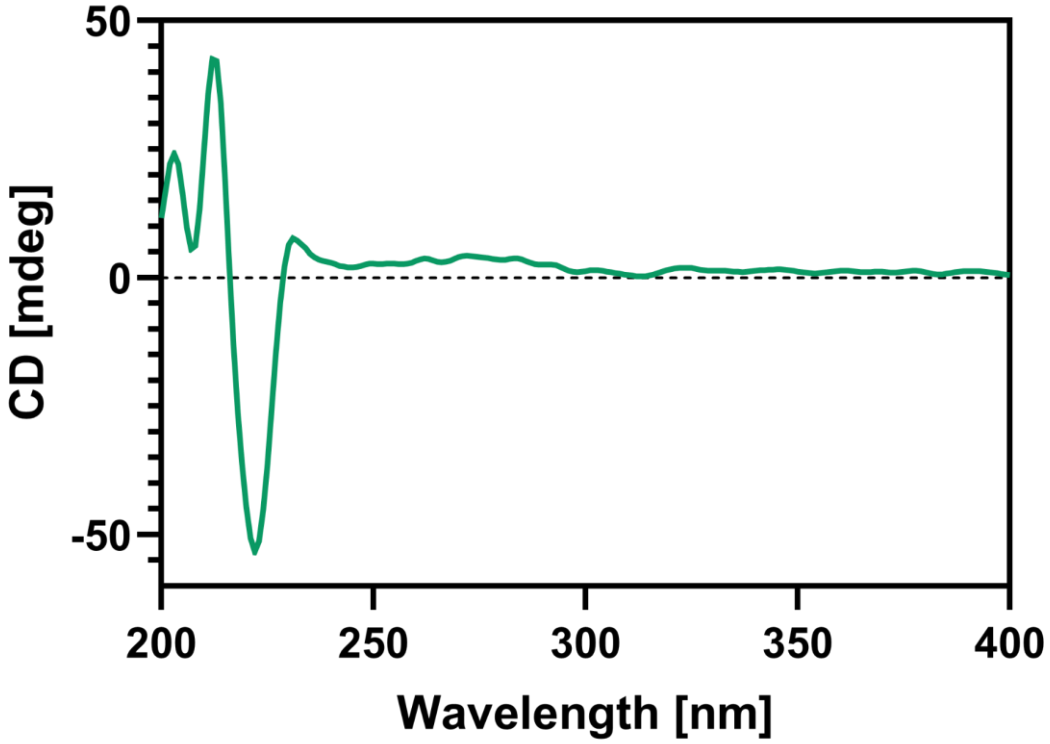

Figure S45. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5**.

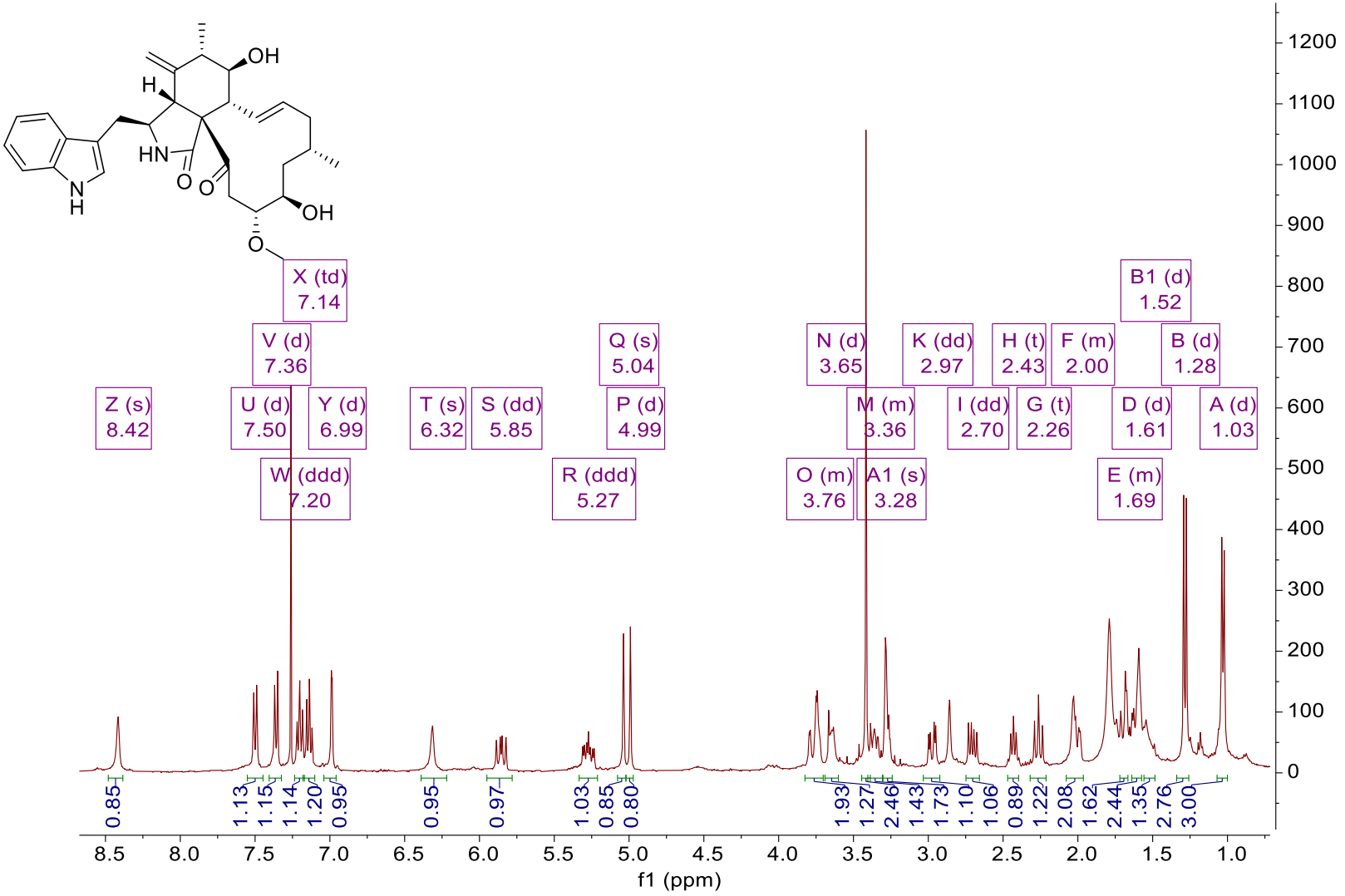

Figure S46. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5**.

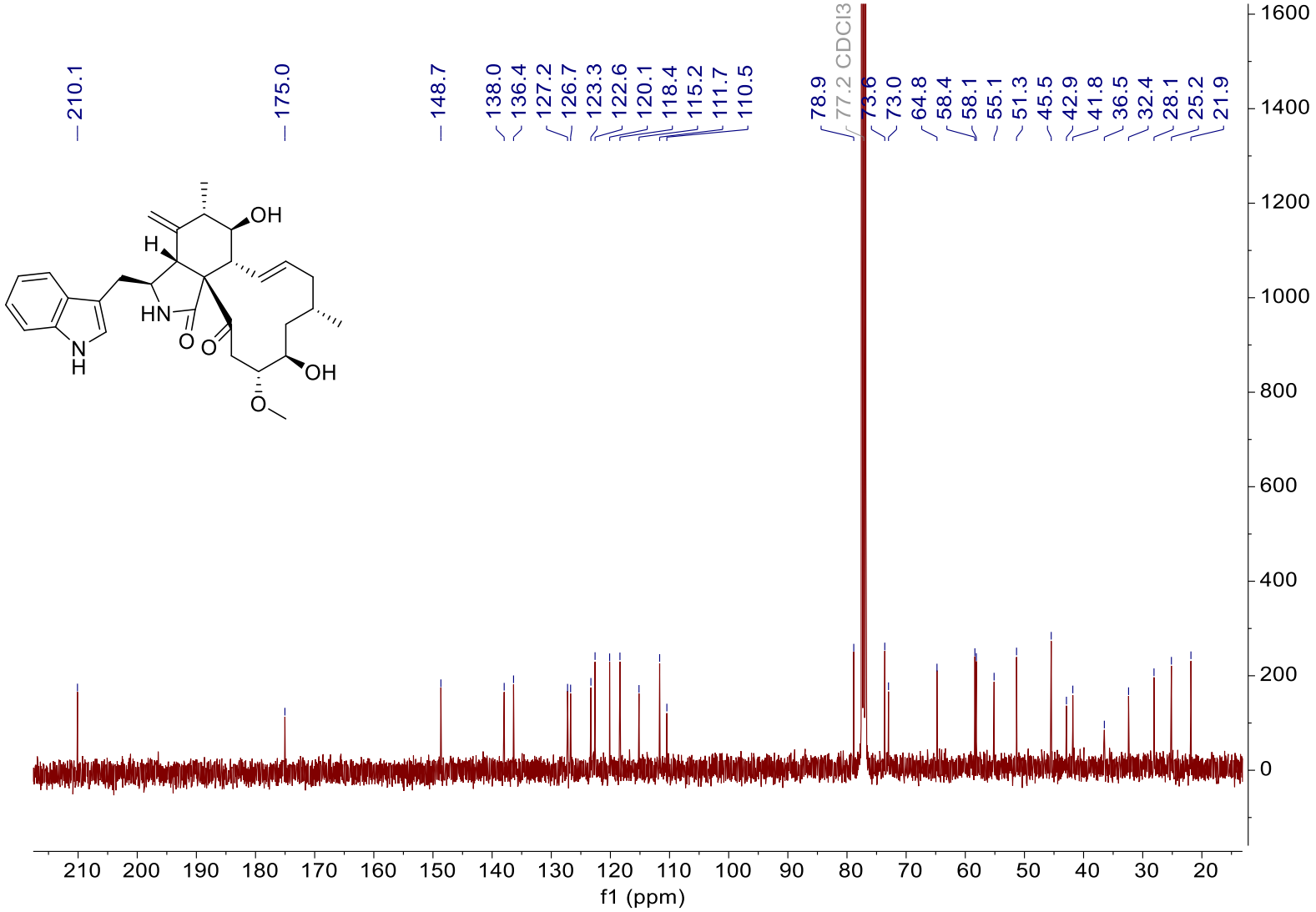

Figure S47. DEPT-135 (100 MHz, $CDCl_3$) spectrum of **5**.

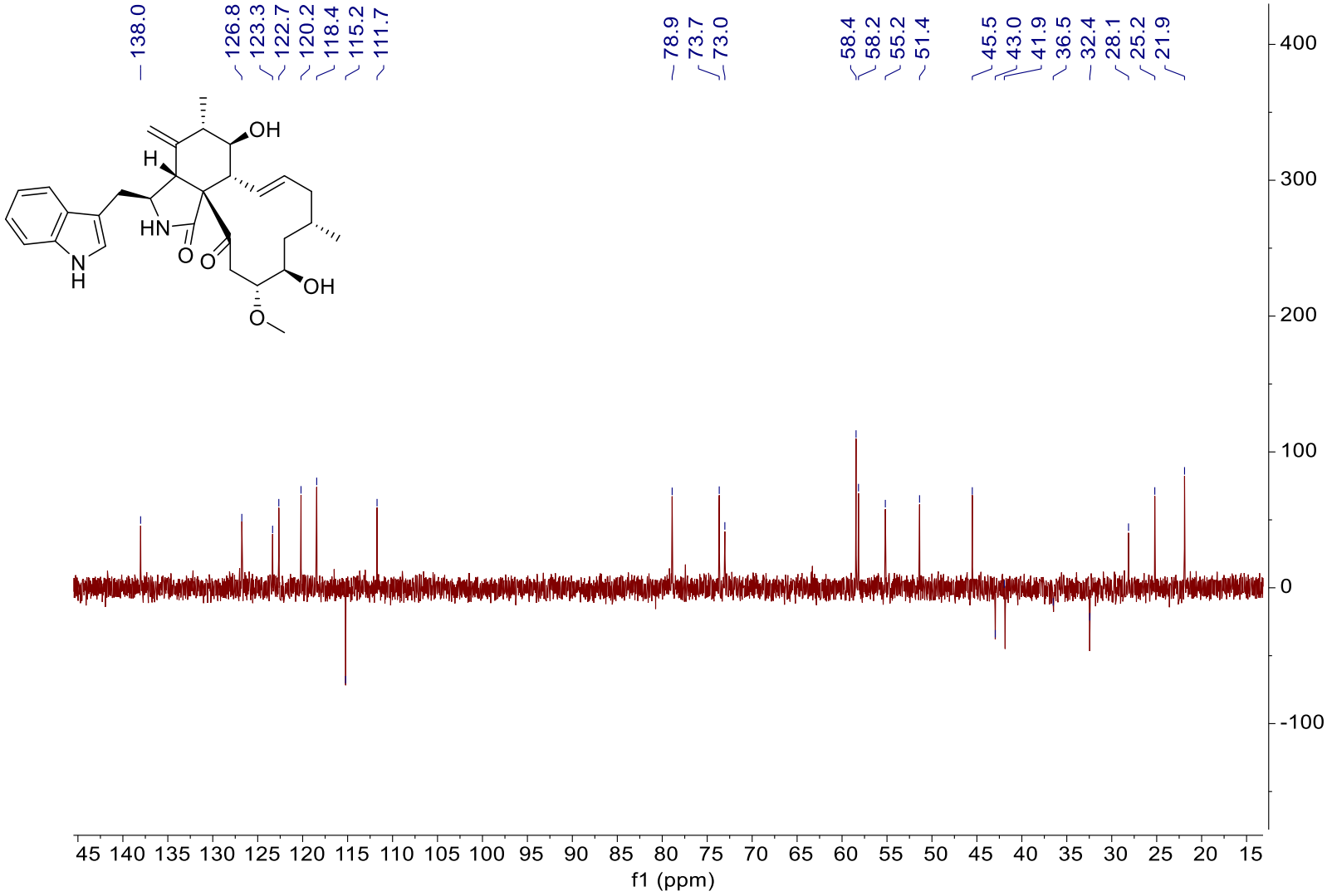

Figure S48. HSQC spectrum of **5** in $CDCl_3$.

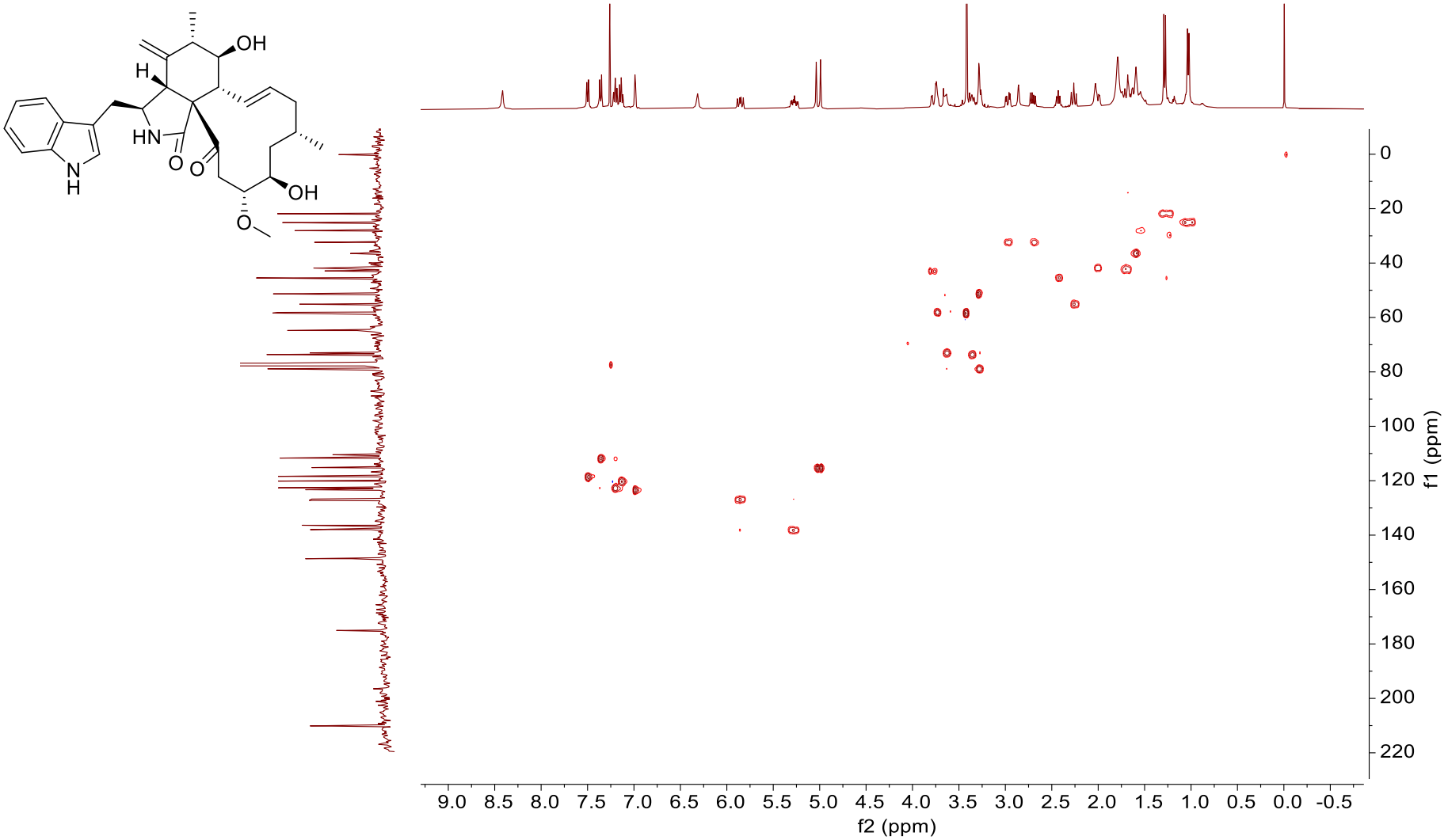

Figure S49. HMBC spectrum of **5** in $CDCl_3$.

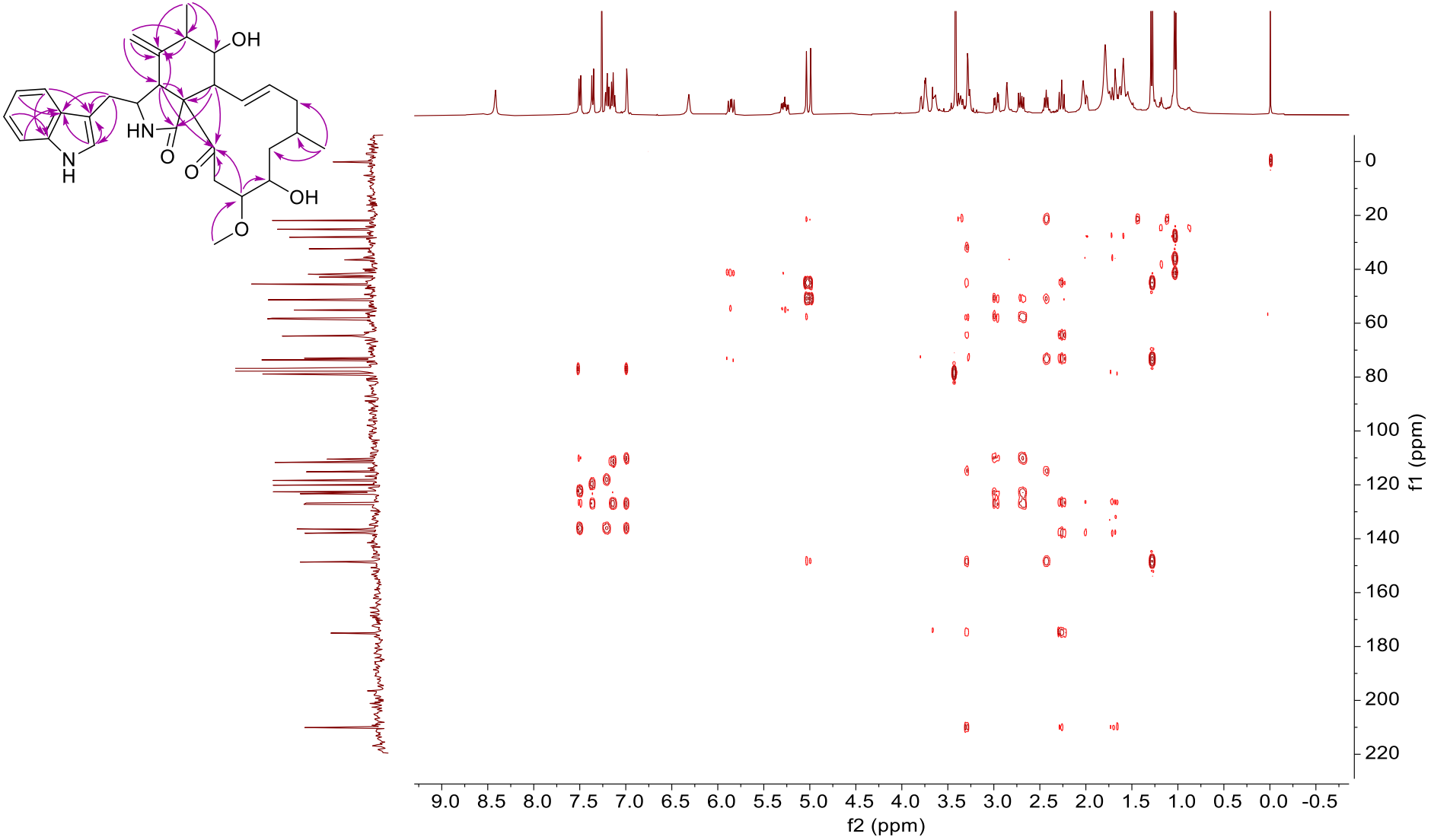

Figure S50. ^{1}H–^{1}H COSY spectrum of **5** in $CDCl_3$.

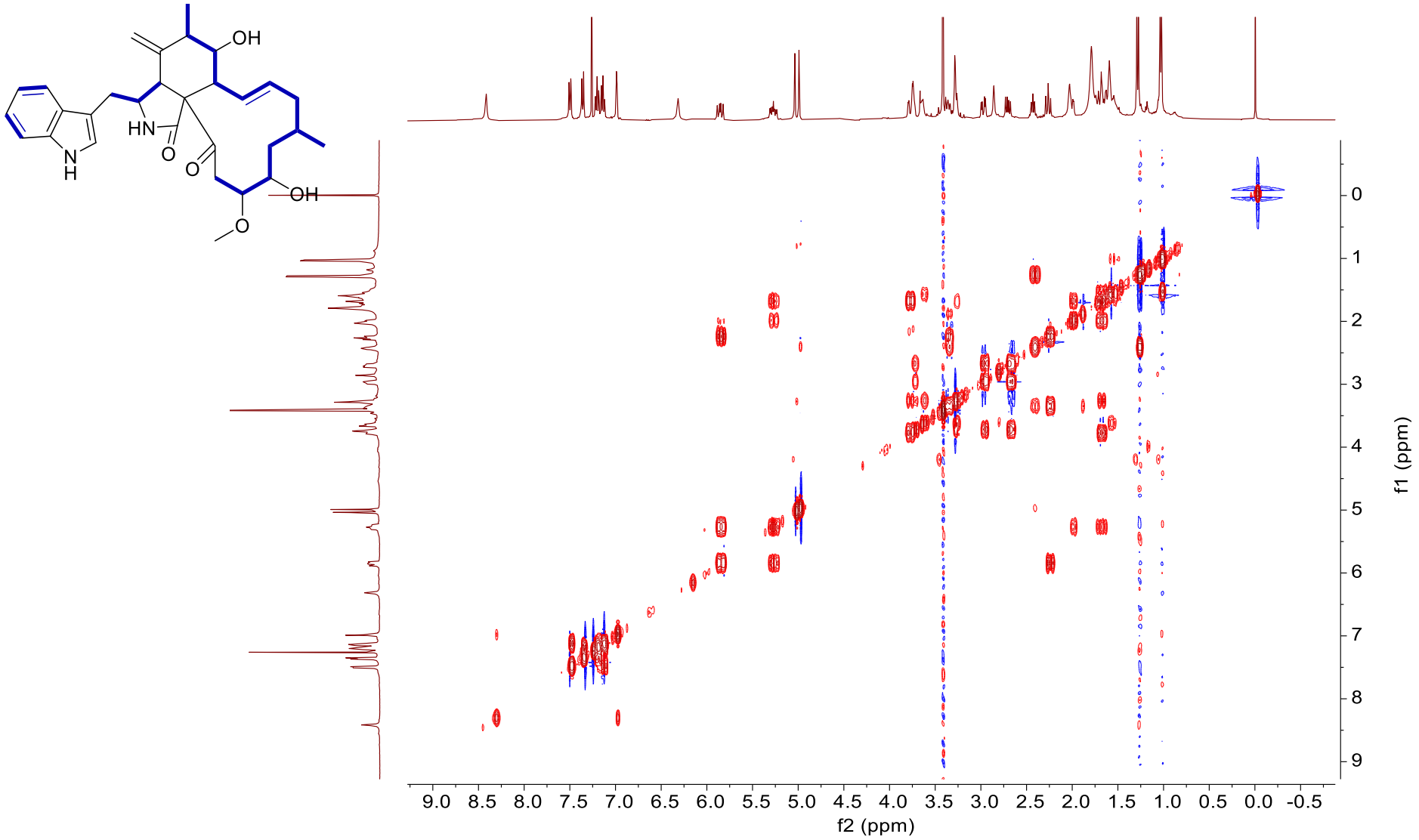

Figure S51. NOESY spectrum of **5** in $CDCl_3$.

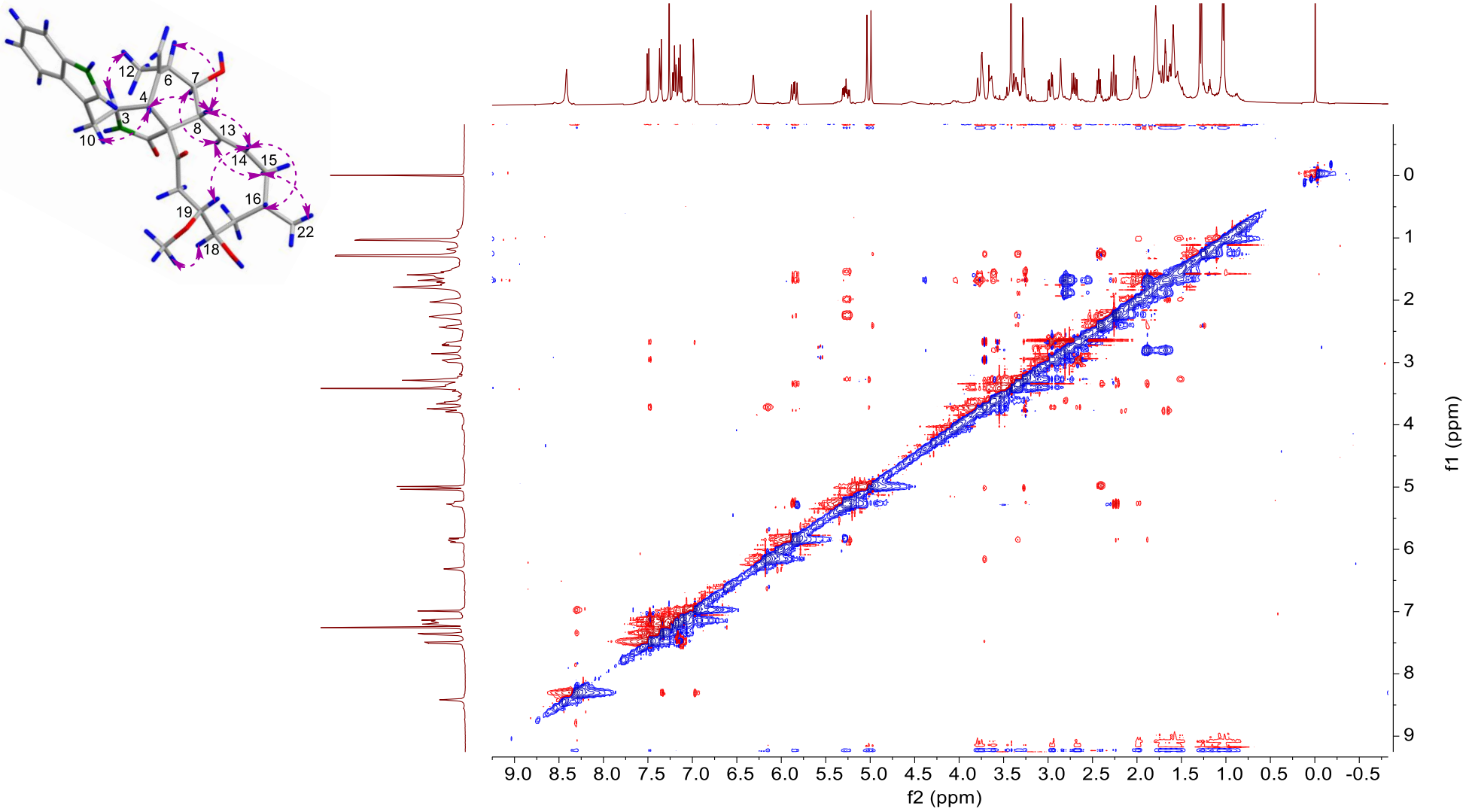

Figure S52. HRESIMS (+) spectrum of **5**.

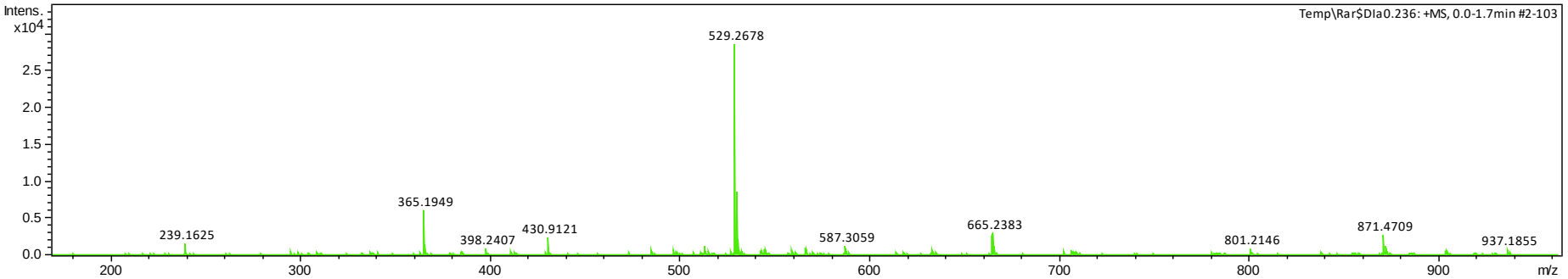

Figure S53. UV spectrum of **5**.

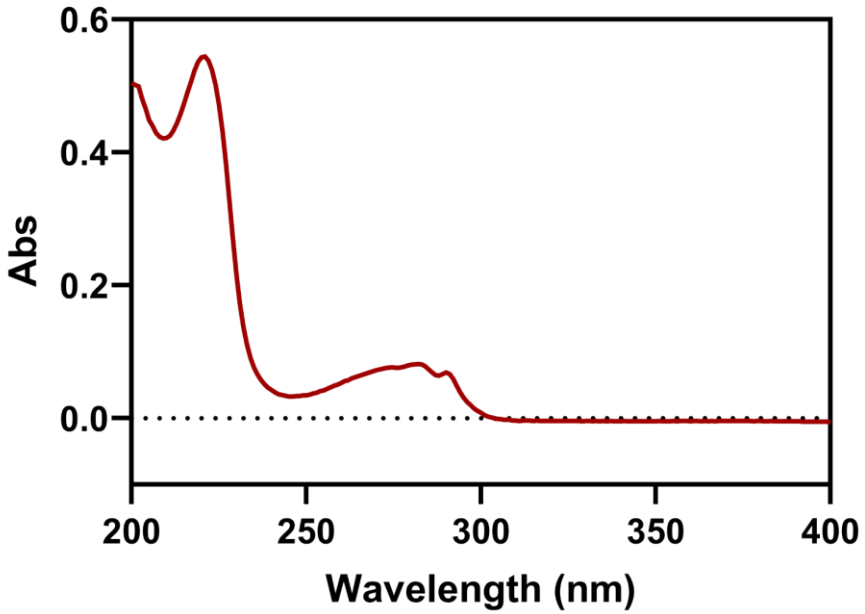

Figure S54. IR spectrum of **5**.

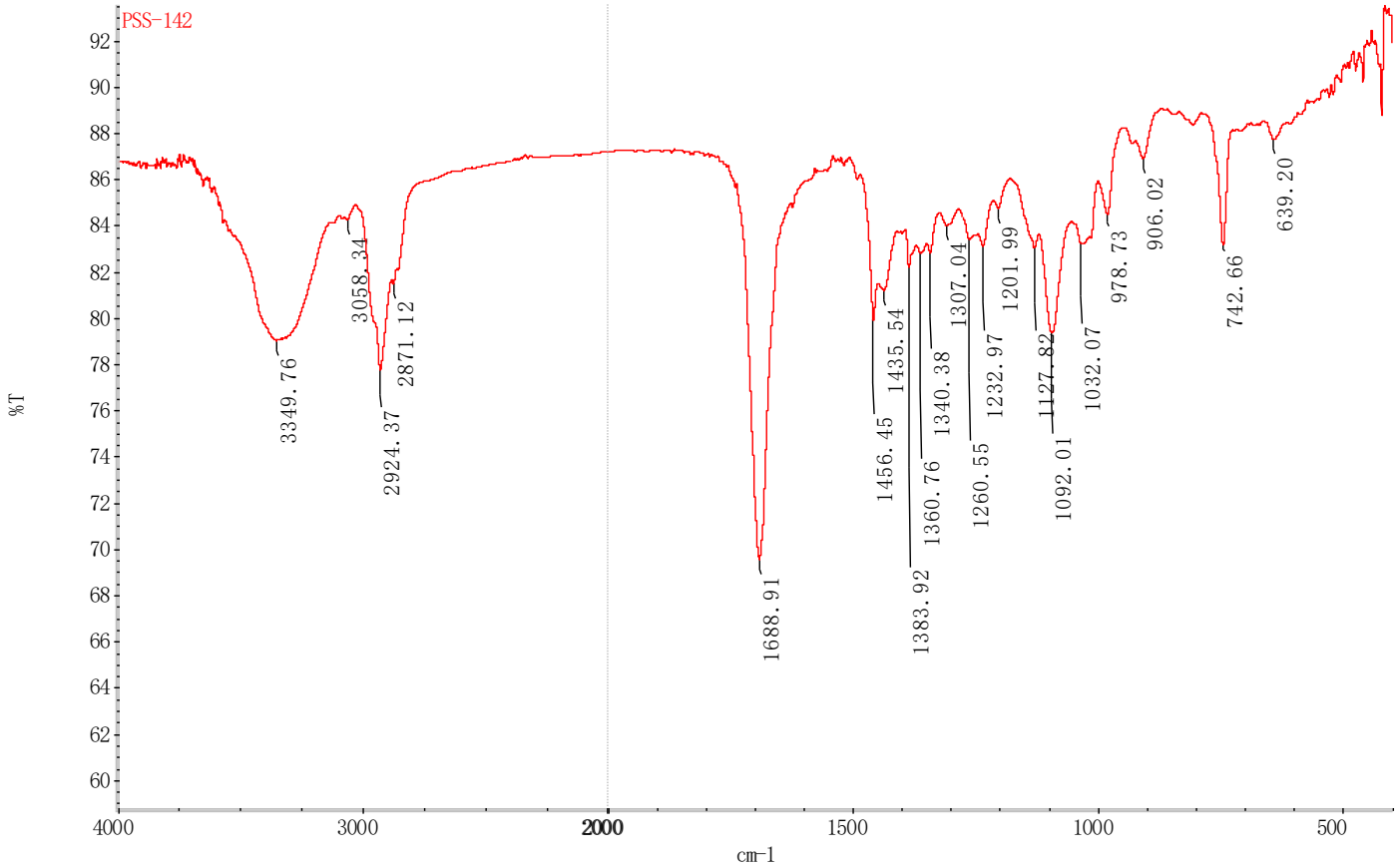

Figure S55. ECD spectrum of **5**.

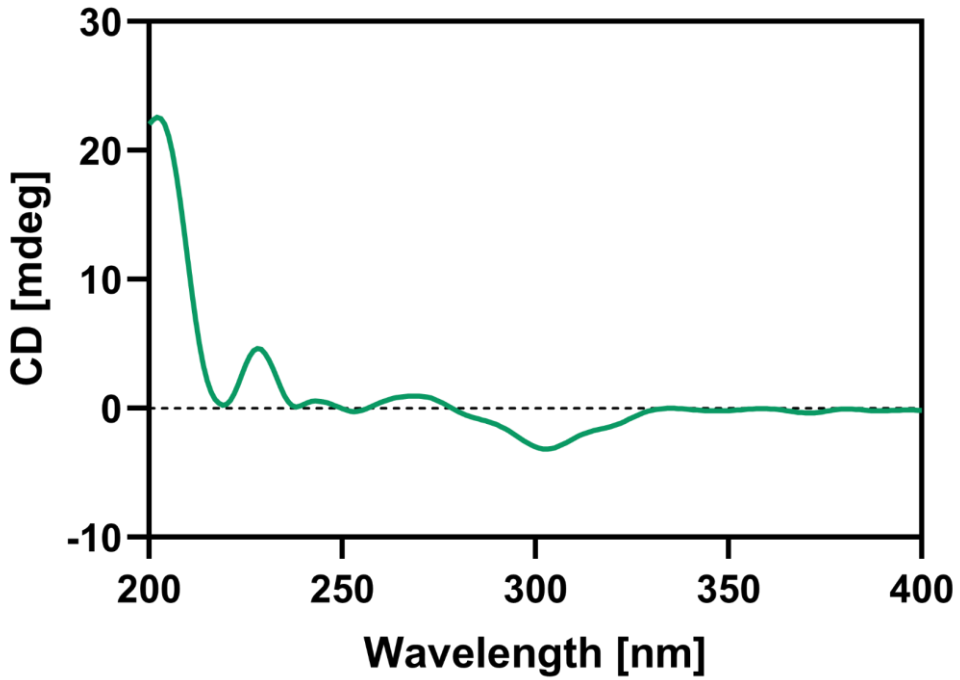

Figure S56. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6**.

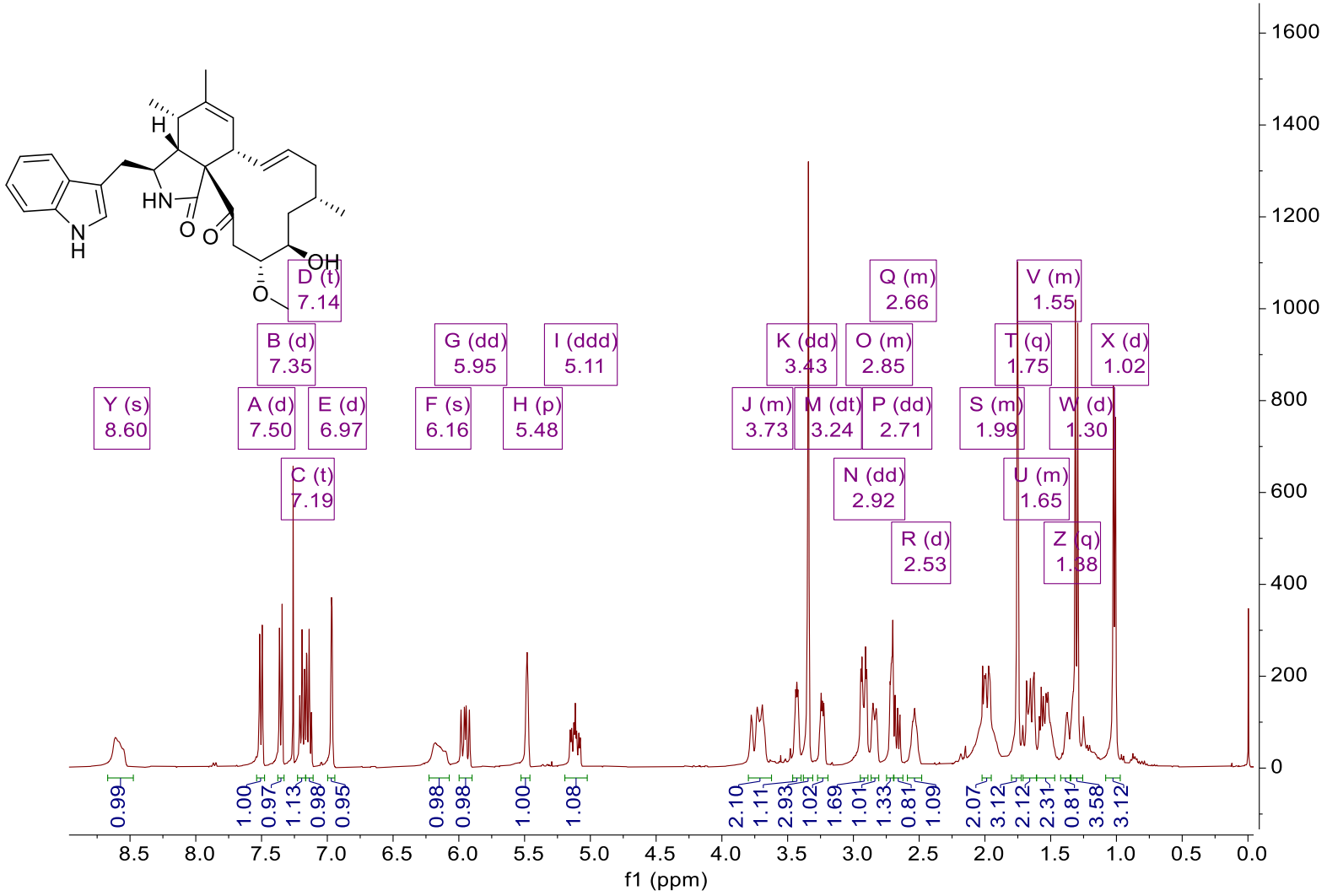

Figure S57. ^{13}C NMR (100 MHz, CD_3OD) spectrum of **6**.

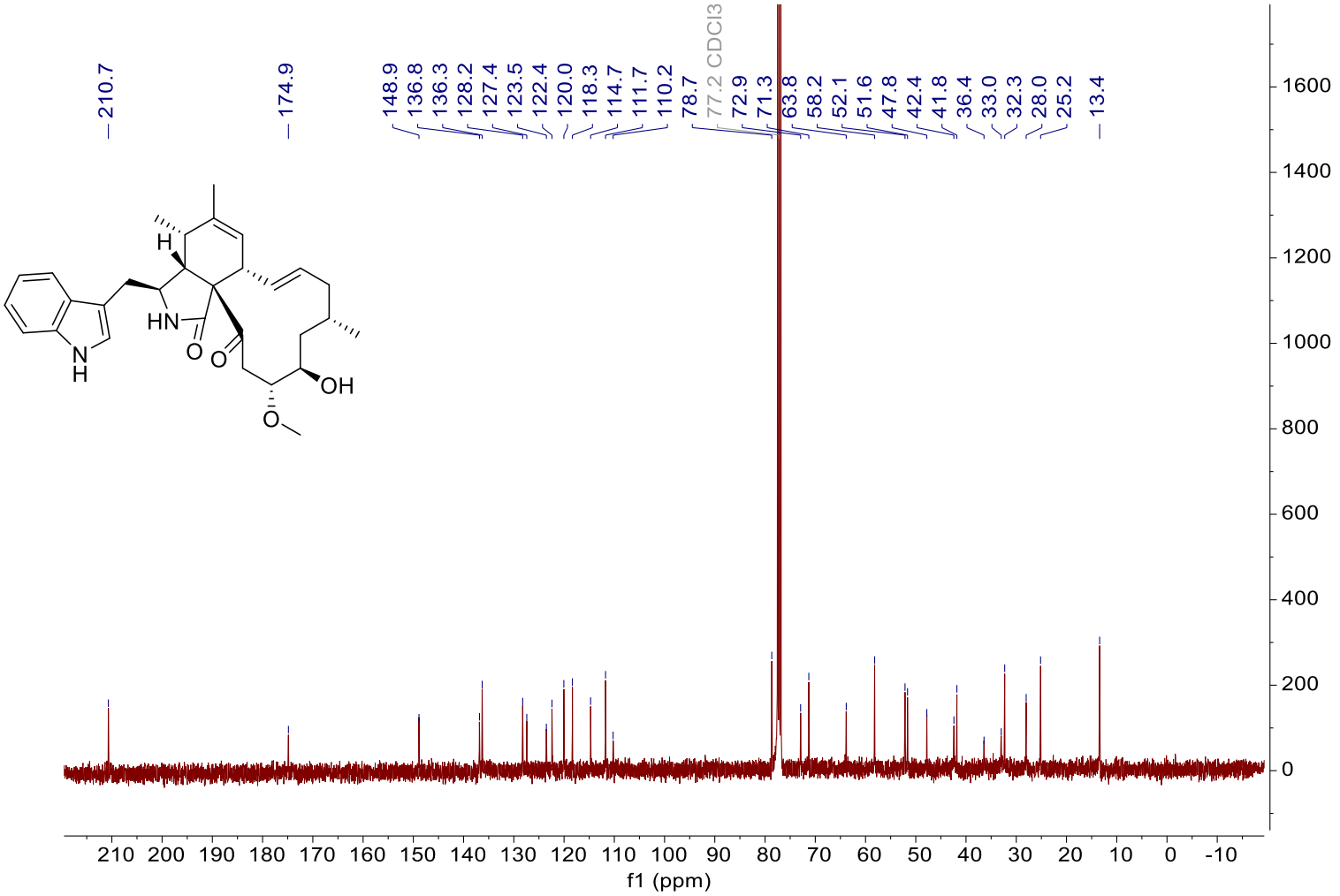

Figure S58. DEPT-135 (100 MHz, CD_3OD) spectrum of **6**.

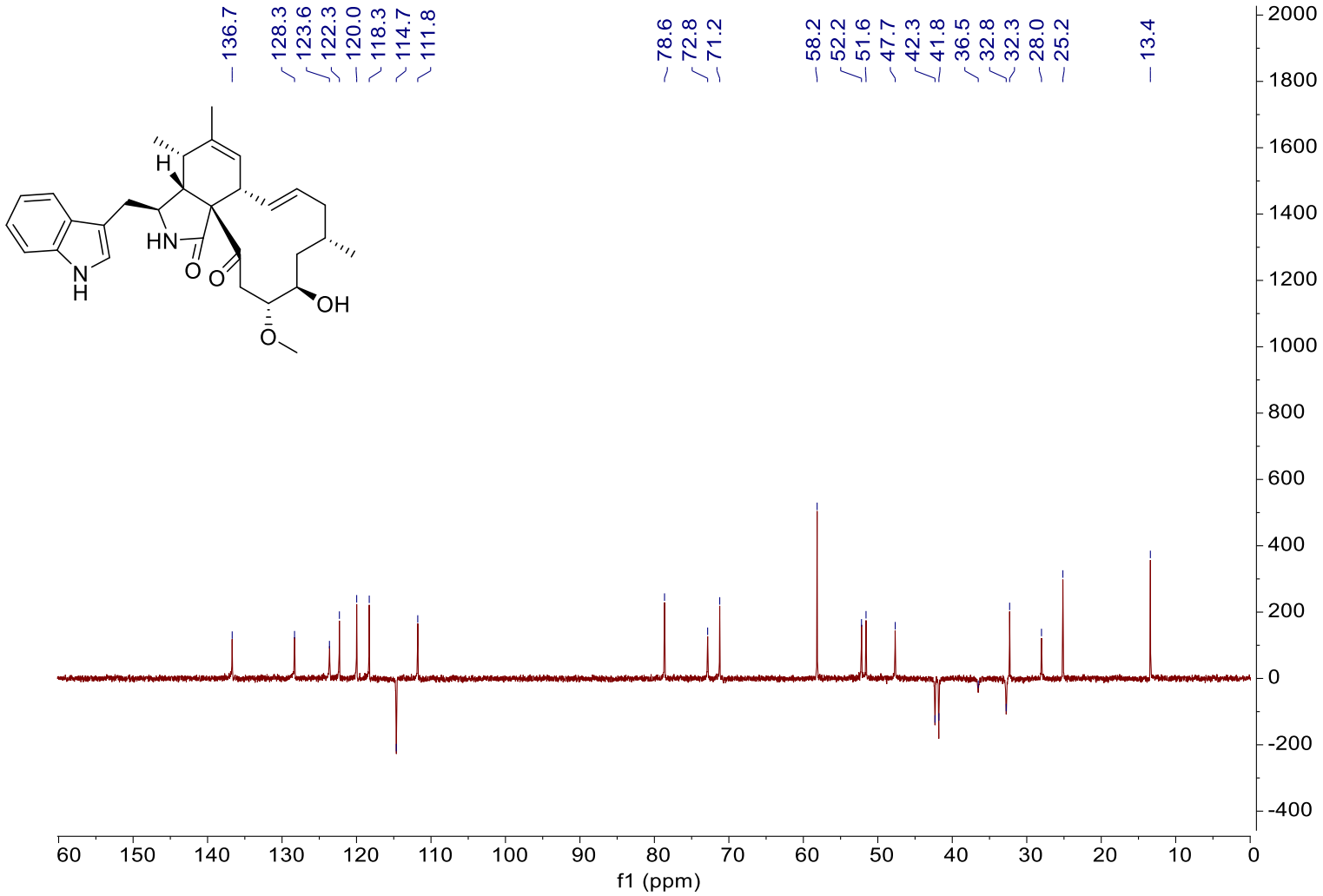

Figure S59. HSQC spectrum of **6** in CD_3OD.

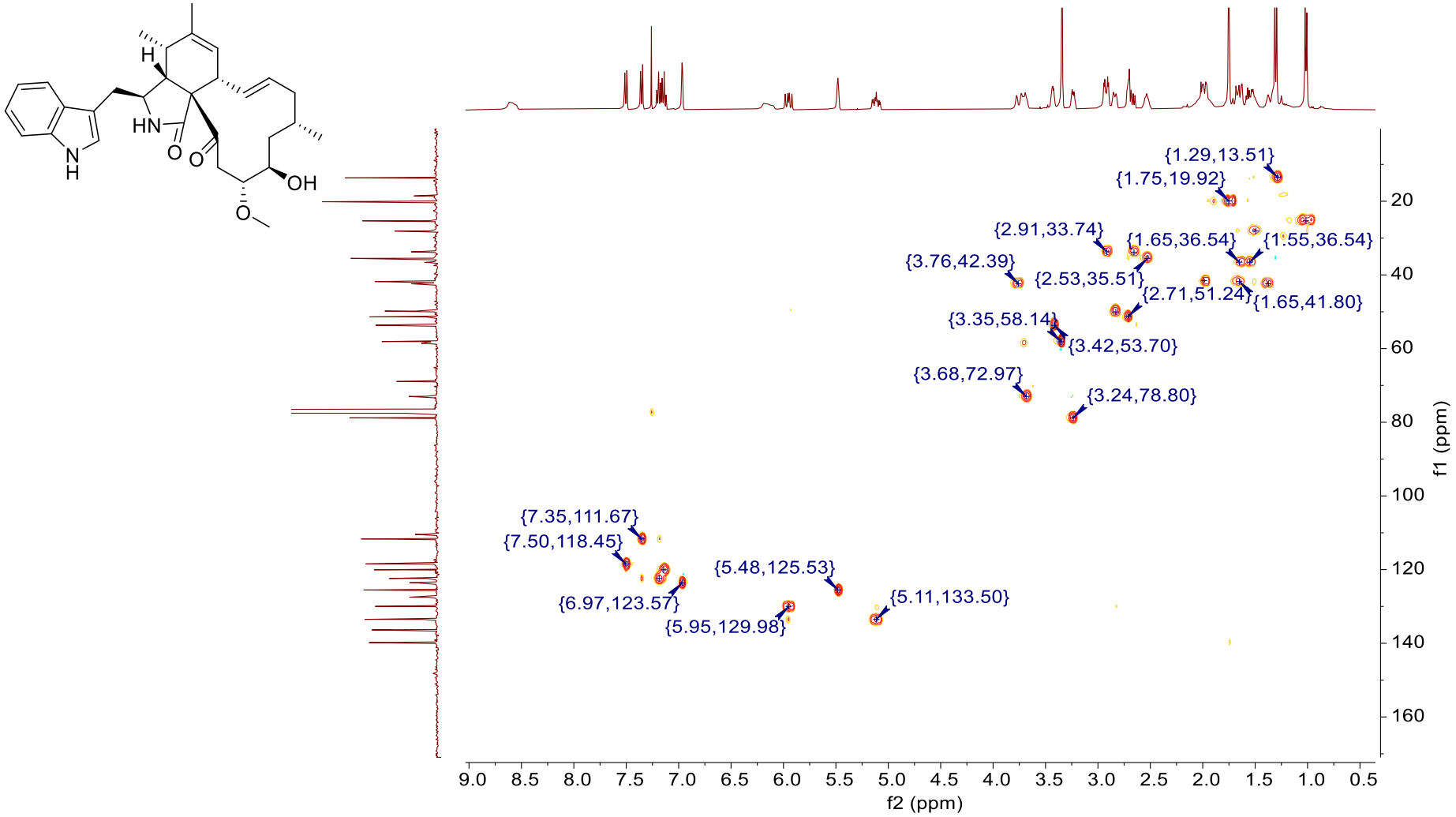

Figure S60. HMBC spectrum of **6** in CD_3OD.

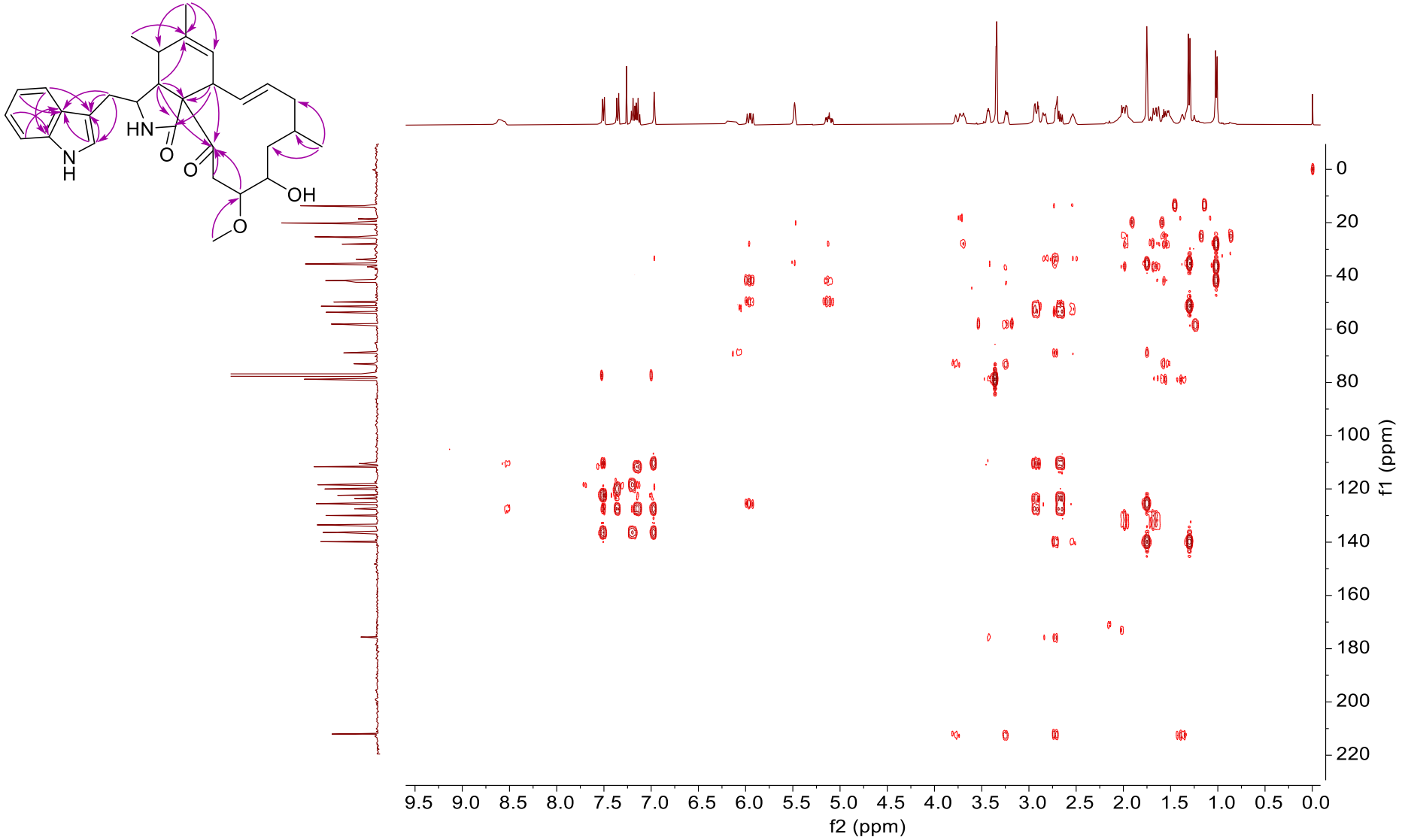

Figure S61. ^{1}H–^{1}H COSY spectrum of **6** in CD_3OD.

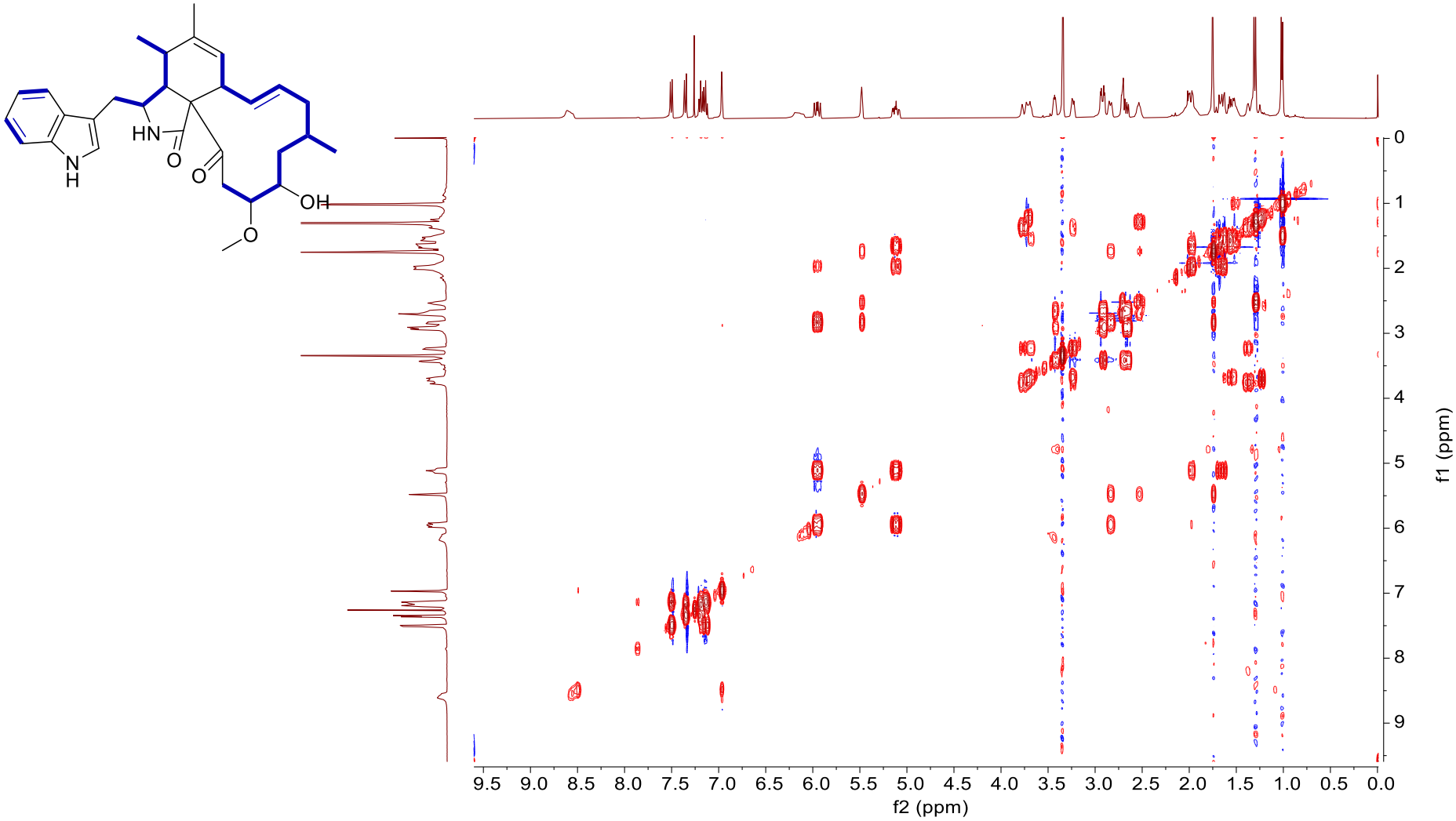

Figure S62. NOESY spectrum of **6** in CD_3OD.

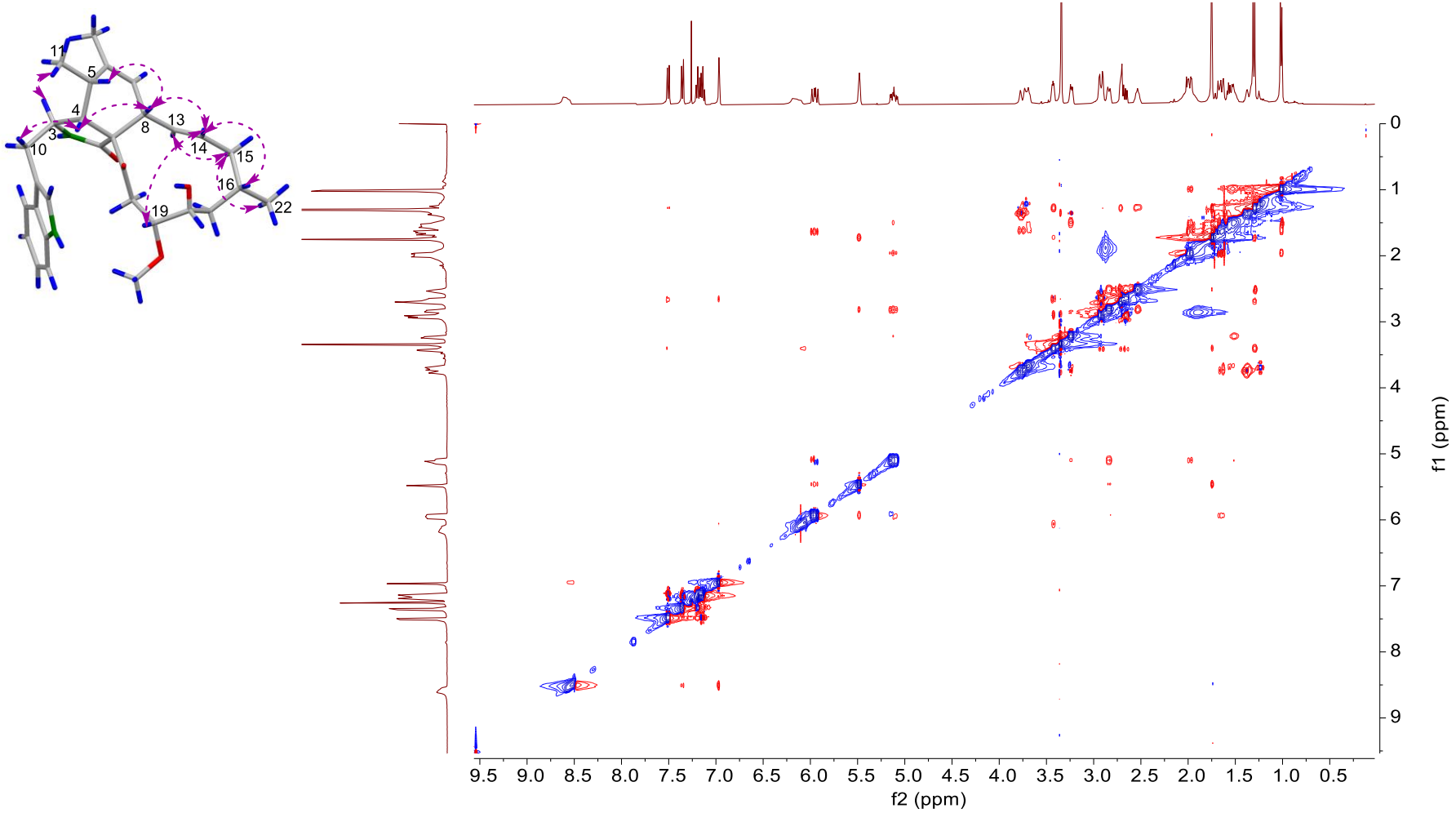

Figure S63. HRESIMS (+) spectrum of **6**.

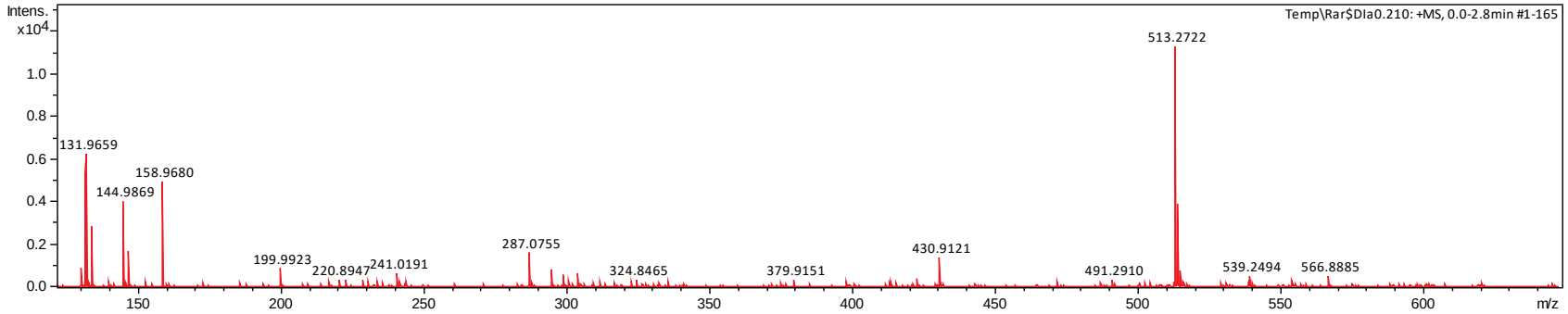

Figure S64. UV spectrum of **6**.

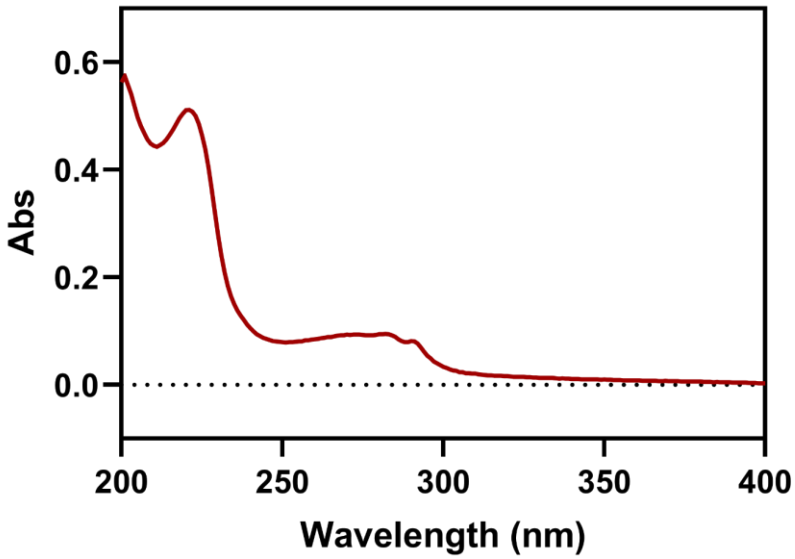

Figure S65. IR spectrum of **6**.

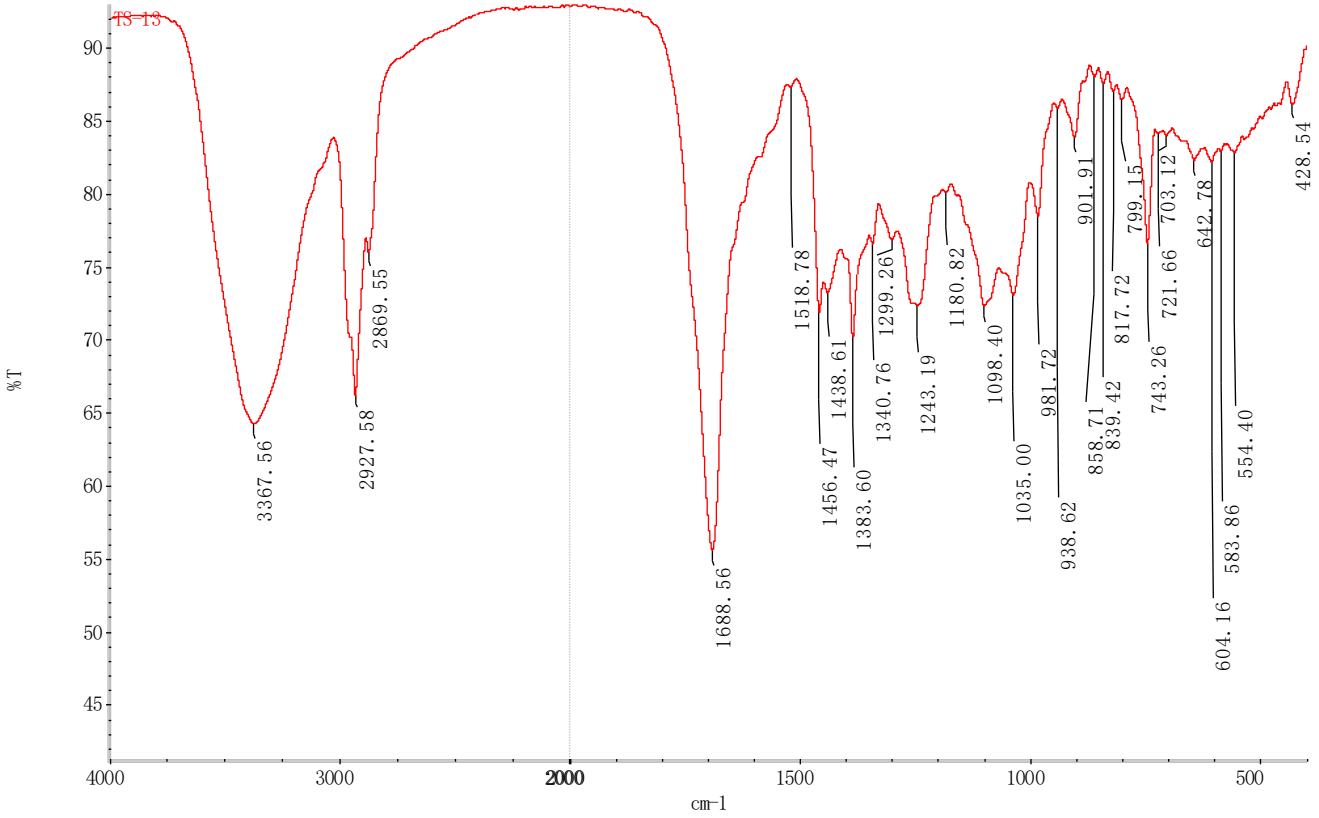

Figure S66. ECD spectrum of **6**.

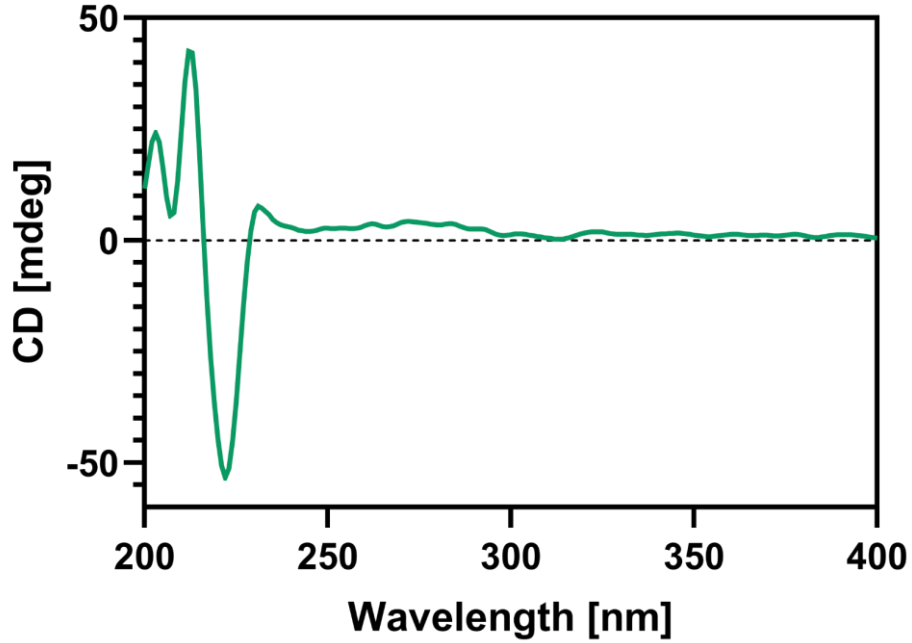

Figure S67. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4a**.

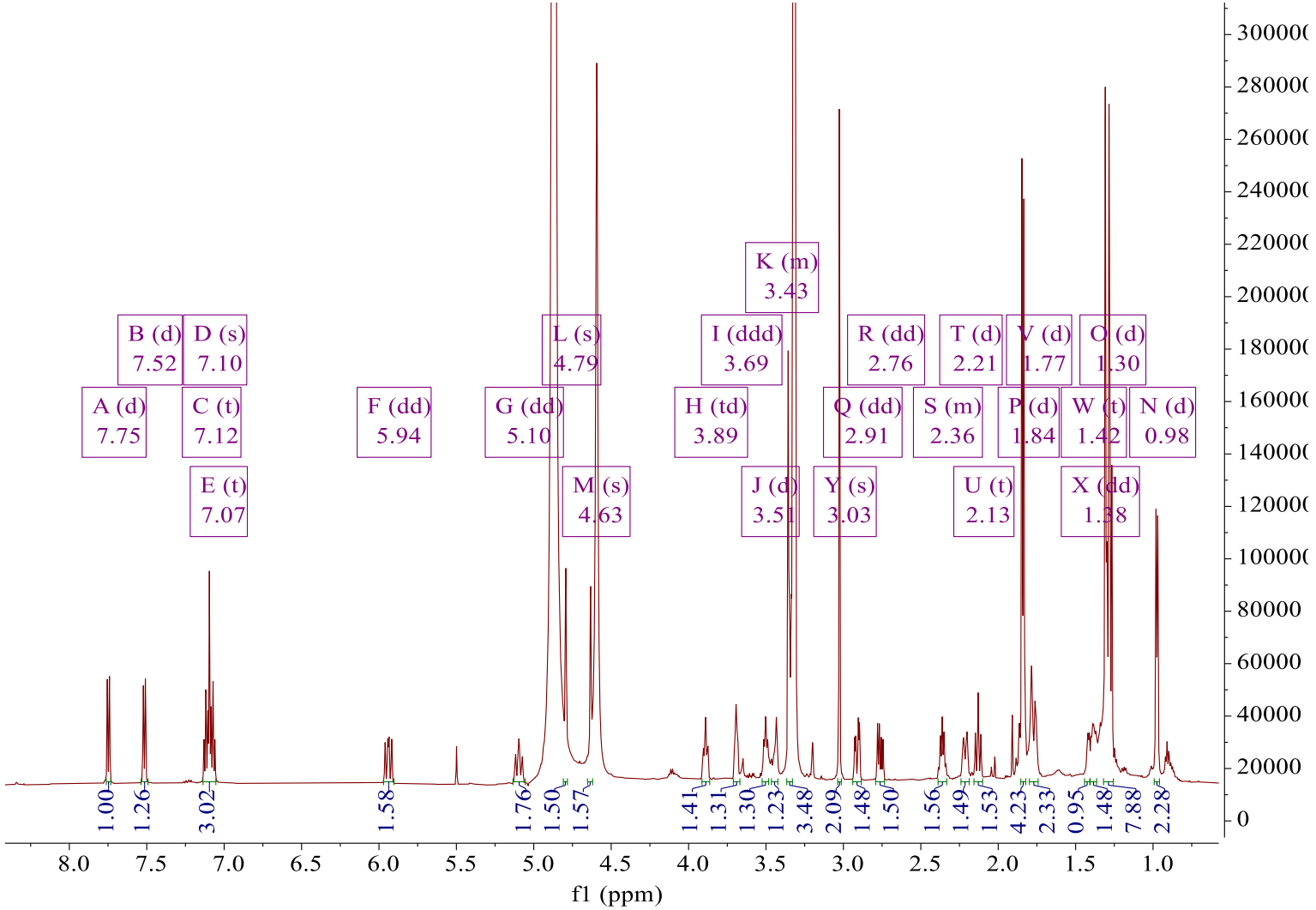

Figure S68. NOESY spectrum of **4a** in $CDCl_3$.

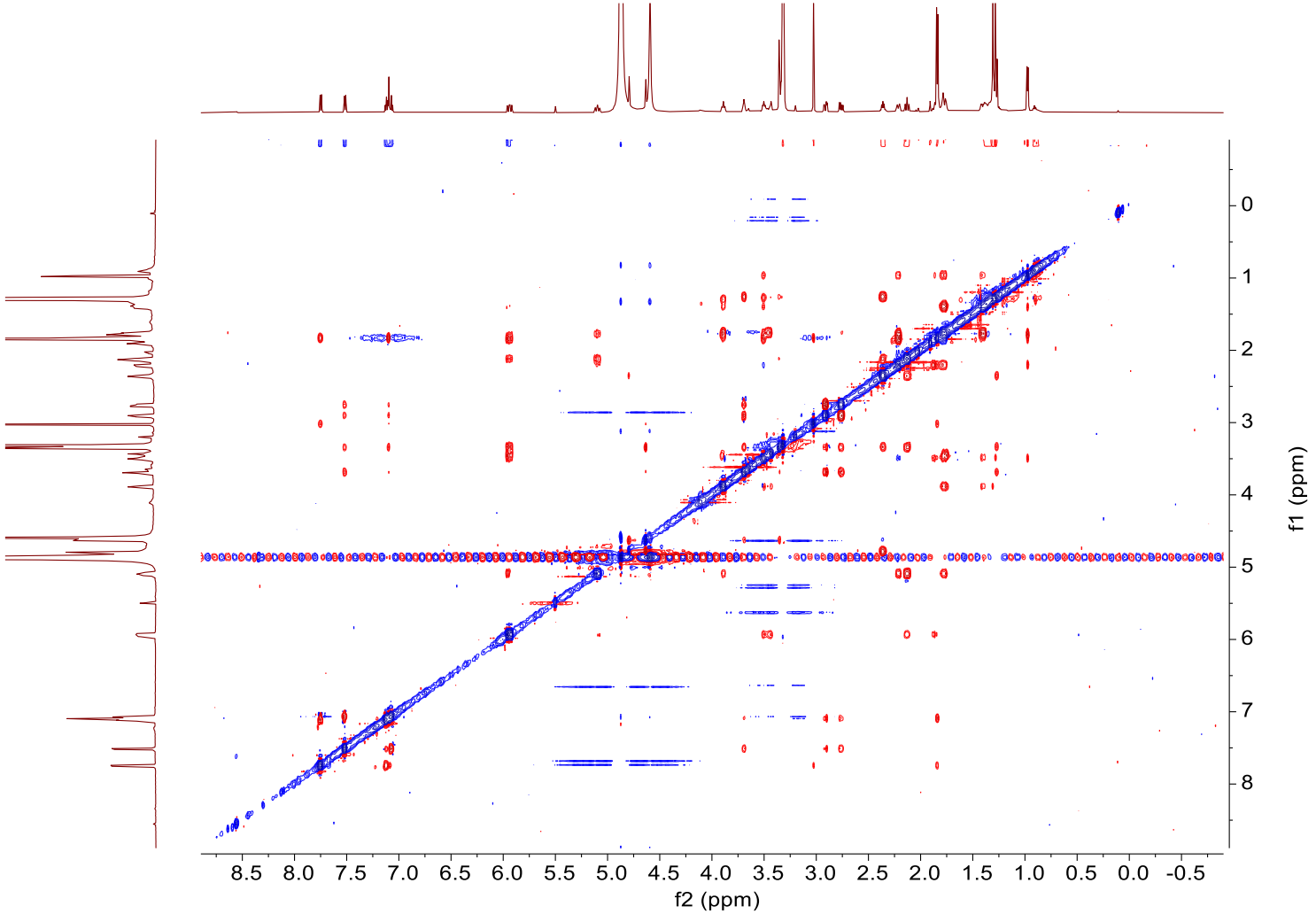

Figure S69. Enlarged NOESY spectrum of **4a** in $CDCl_3$.

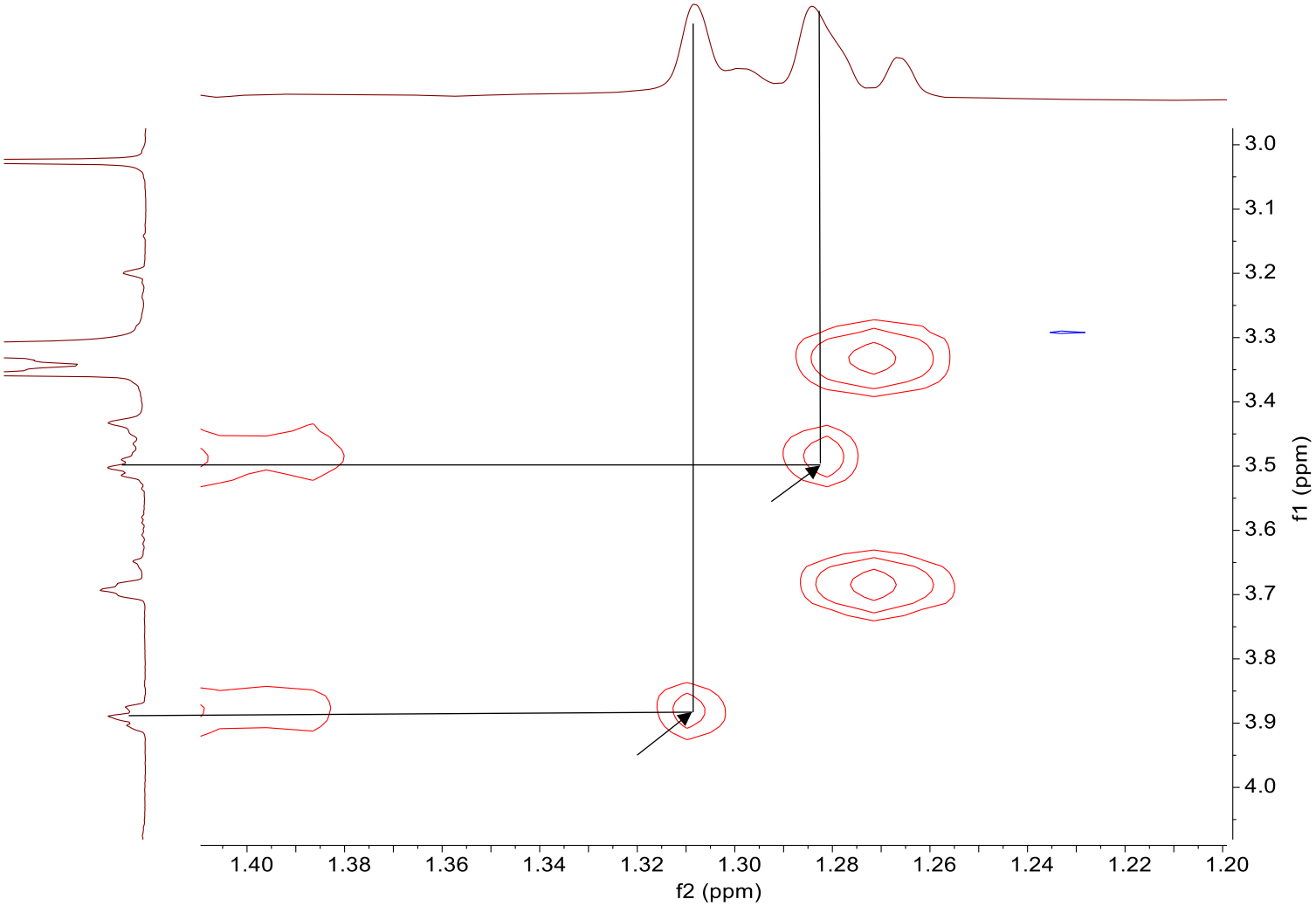

Figure S70. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of *R*-MTPA esters of **5**.

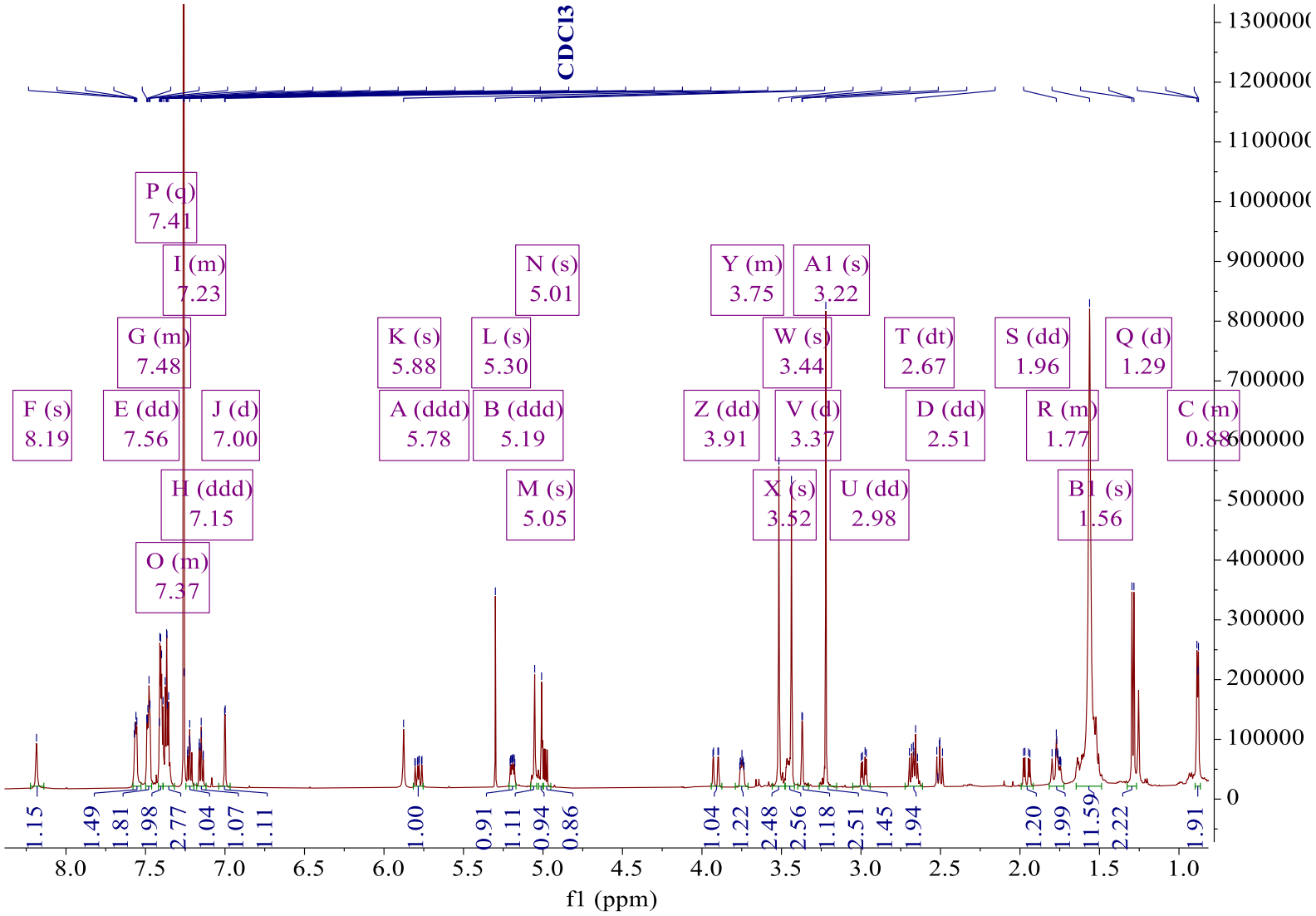

Figure S71. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of *S*-MTPA esters of **5**.

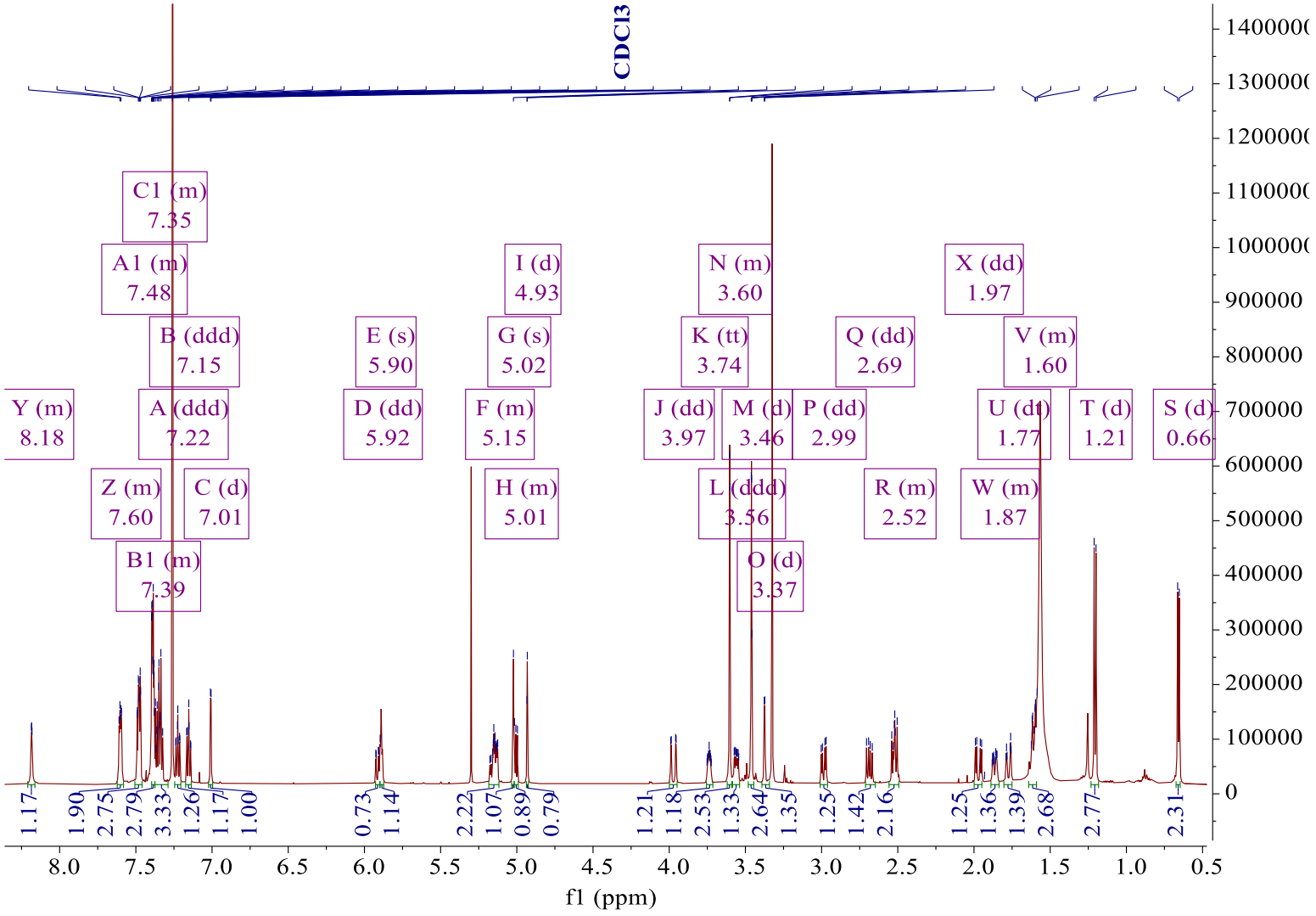

Figure S72. ^{1}H NMR (600 MHz, CD_3OD) spectrum of *S*-MTPA esters of **6**.

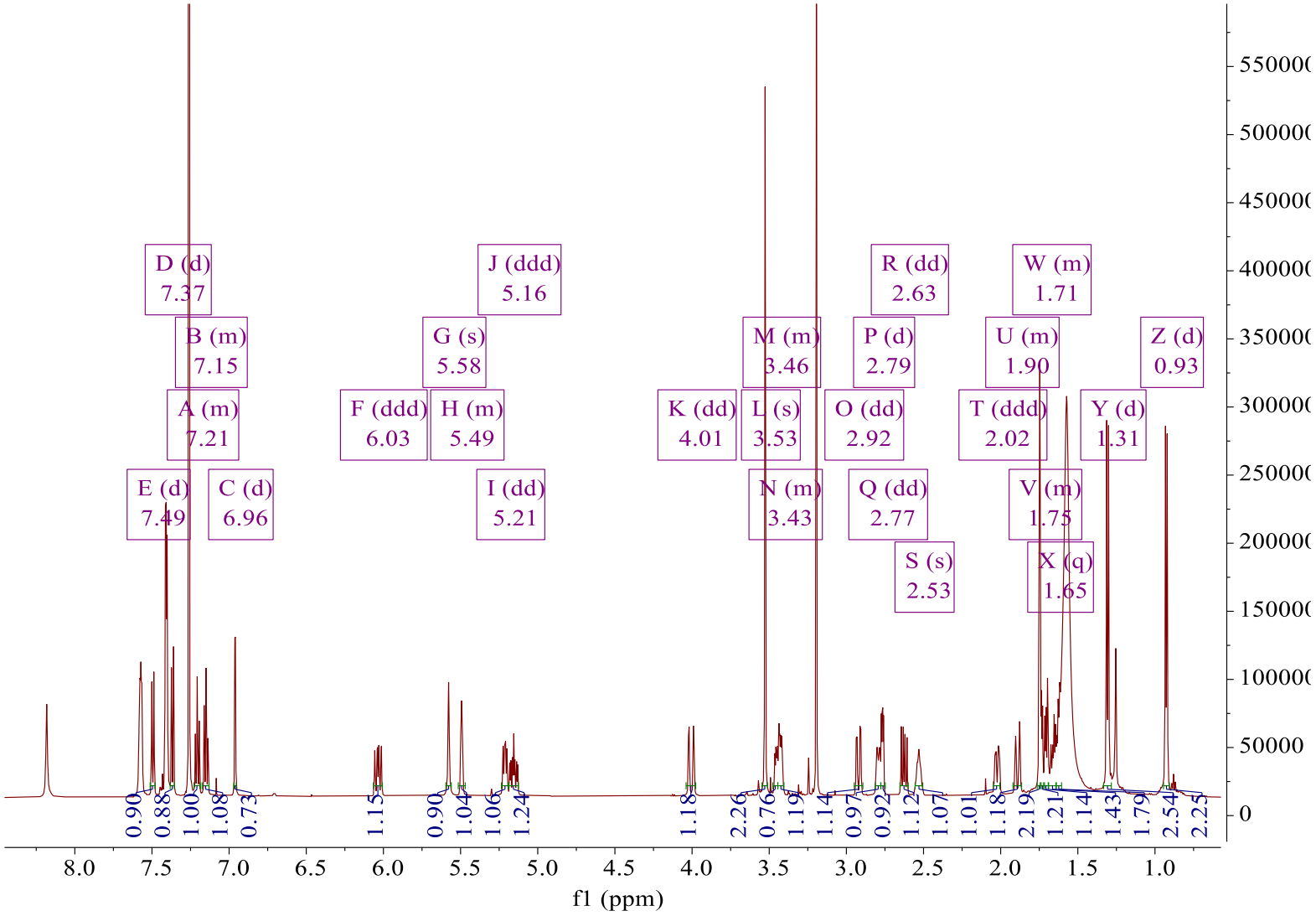

Figure S73. ^{1}H NMR (600 MHz, CD_3OD) spectrum of *R*-MTPA esters of **6**.