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Supporting Information

Hyperispirones A and B, spiro-bridged polycyclic polyprenylated acylphloroglucinols with anti-angiogenesis activity from *Hypericum beanii*

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Contents

Table S1. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR Assignments for 2 (in methanol-d_4, J in Hz) [a]

No	δ_H	δ_C
1		198.6, C
2		117.7, C
3		177.8, C
4		26.2, C
5		213.1, C
6		65.5, C
7	2.11, m	28.4, CH_2
8	2.65, m	46.7, CH
9		78.2, C
10a	1.83, m	41.5, CH_2
10b	1.86, m	
11a	1.77, m	26.9, CH_2
11b	2.01, m	
12		97.3, C
13		71.9, C
14a	1.69, m	44.2, CH_2
14b	2.10, m	
15	1.12, s	24.9, CH_3
16	1.23, s	27.6, CH_3
17a	2.52, m	39.6, CH_2
17b	2.61, m	
18	5.01, m	120.6, CH
19		136.8, C
20	1.75, s	26.2, CH_3
21	1.54, s	18.0, CH_3
22a	2.50, m	39.3, CH_2
22b	2.61, m	
23	5.00, m	120.1, CH
24		137.0, C
25	1.72, s	26.3, CH_3
26	1.49, s	18.1, CH_3
27		196.1, C
28		138.6, C
29 (33)	7.93, m	130.5, CH
30 (32)	7.48, m	129.7, CH
31	7.60, m	134.8, CH

[a] "m" means overlapped or multiplet with other signals.

Quantum chemical calculations

The random conformational searches were performed by SYBYL-X 2.1.1 program using MMFF94s molecular force field, with an energy cutoff of 10 kcal mol^{-1} to the global minima. 35 conformers were obtained and were subsequently optimized by using Gaussion09 software at B3LYP/6-31+G(d) level in gas phase. Frequency calculation was performed at the same level to exclude imaginary frequencies. The optimized stable conformers with an energy window of 3 kcal/mol were selected for further NMR and/or ECD calculations. The NMR computations were performed at mPW1PW91/6-31+G(d,p) level with chloroform as the solvent. The ECD curves were predicted at CAM-B3LYP/6-31+G(d) level in methanol.[1] The overall NMR and ECD data were weighted by Boltzmann distribution, and were subsequently compared with the experimental ones, respectively.

References:

[1] Gaussian 09, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

Table S2. Cartesian coordinate of dominant conformer of **1** at B3LYP/6-31+G(d) level

Standard orientation					
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.144368	0.121454	-1.316263
2	6	0	-0.882026	-0.585009	-0.055228
3	6	0	-2.15806	0.14555	-0.634899
4	6	0	-3.524617	-0.367004	-0.082345
5	6	0	-3.525215	-1.898929	-0.152795
6	6	0	-2.397422	-2.590757	0.334315
7	6	0	-1.202692	-1.827756	0.754757
8	6	0	-4.628111	-2.65657	-0.559951
9	6	0	-4.607897	-4.050972	-0.48572
10	6	0	-3.493546	-4.721931	0.022244
11	6	0	-2.391389	-3.987074	0.444115
12	6	0	-4.649092	0.253223	-0.933427
13	6	0	-3.751916	0.034947	1.400235
14	6	0	0.024245	0.481464	0.658381
15	6	0	-1.865073	1.650843	-0.419084
16	6	0	-0.35064	1.759476	-0.164534
17	8	0	-0.237987	0.64886	2.025153
18	6	0	0.062177	3.093459	0.51017
19	6	0	-0.43377	4.320502	-0.209831
20	6	0	-1.18453	5.316277	0.287768
21	6	0	-1.570029	6.490807	-0.580434
22	6	0	-1.6985	5.39725	1.704491
23	6	0	2.25123	-0.199552	-2.303261
24	6	0	3.559233	-0.649877	-1.617059
25	6	0	3.262311	-1.59872	-0.432207
26	6	0	2.316352	-0.994826	0.682186
27	6	0	1.494687	0.210859	0.204047
28	6	0	4.544132	-2.060055	0.326168
29	6	0	4.216918	-1.922741	1.821028
30	6	0	3.253735	-0.719891	1.903164
31	6	0	4.487157	-1.297703	-2.652632
32	1	0	1.638557	-1.796259	0.989332
33	6	0	2.542138	-0.626069	3.249839
34	1	0	2.758074	-2.465312	-0.874452
35	8	0	3.96544	0.510297	1.761167
36	6	0	0.021793	-0.936598	-1.263462
37	6	0	0.439117	1.486618	-1.464156
38	8	0	-0.486201	-2.192724	1.685512
39	8	0	0.553719	2.230718	-2.41362
40	1	0	2.086418	1.109089	0.400443
41	8	0	-0.113079	-1.871764	-2.017223
42	8	0	4.228261	0.498814	-1.0426
43	1	0	-2.19359	-0.058294	-1.711978
44	1	0	-5.518646	-2.165234	-0.934834
45	1	0	-5.47374	-4.615128	-0.820451
46	1	0	-3.486912	-5.805547	0.085658

47	1	0	-1.508399	-4.473785	0.845007
48	1	0	-4.60612	-0.087563	-1.972932
49	1	0	-5.636781	0.006418	-0.532264
50	1	0	-4.566082	1.343722	-0.931642
51	1	0	-4.600767	-0.519698	1.810706
52	1	0	-2.877839	-0.16913	2.024894
53	1	0	-3.979266	1.101013	1.491343
54	1	0	-2.17431	2.263654	-1.268859
55	1	0	-2.381742	2.034165	0.464534
56	1	0	-0.107006	-0.221146	2.436549
57	1	0	-0.300569	3.050253	1.539466
58	1	0	1.15803	3.132632	0.57462
59	1	0	-0.125826	4.389549	-1.251402
60	1	0	-1.193036	7.432891	-0.160262
61	1	0	-1.179899	6.392426	-1.596863
62	1	0	-2.661616	6.595746	-0.641724
63	1	0	-2.791763	5.498312	1.713597
64	1	0	-1.436205	4.531111	2.314108
65	1	0	-1.303509	6.290407	2.206224
66	1	0	2.447942	0.674958	-2.935494
67	1	0	1.902486	-0.996585	-2.968351
68	1	0	5.380222	-1.401061	0.074557
69	1	0	4.84203	-3.075958	0.051645
70	1	0	5.101127	-1.758786	2.443688
71	1	0	3.707306	-2.822429	2.188429
72	1	0	4.045021	-2.211074	-3.06179
73	1	0	5.454731	-1.546293	-2.211007
74	1	0	4.661234	-0.611202	-3.490164
75	1	0	1.938496	-1.518505	3.442355
76	1	0	1.900667	0.257651	3.281157
77	1	0	3.283062	-0.52862	4.049304
78	1	0	4.269482	0.589924	0.840155
79	1	0	4.417117	1.135909	-1.744157

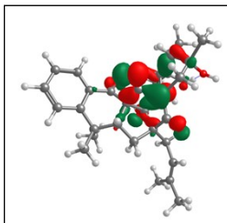
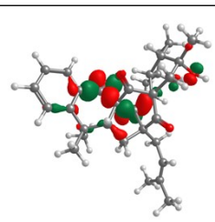
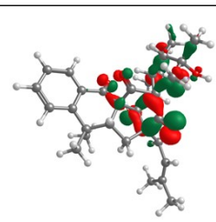
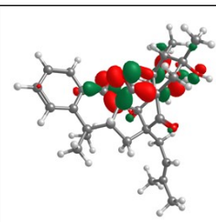
Table S3. Calculated and experimental ^{13}C NMR data of **1**

No.	δ_{exp}	δ_{cal}	δ_{scal}	$\Delta\delta$	NO.	δ_{exp}	δ_{cal}	δ_{scal}	$\Delta\delta$
1	89.3	93.16	91.6	-2.31	18	53.1	52.32	50.1	2.98
2	71.9	77.77	76.0	-4.08	19	37.0	42.61	40.3	-3.26
3	204.4	204.71	204.9	-0.53	20	28.3	32.91	30.4	-2.11
4	71.4	75.07	73.2	-1.83	21	26.1	25.22	22.6	3.50
5	209.4	210.40	210.7	-1.30	22	29.3	33.34	30.8	-1.54
6	66.3	68.90	67.0	-0.66	23	119.6	120.19	119.1	0.53
7	46.2	49.41	47.2	-0.97	24	135.1	136.00	135.1	-0.03
8	46.5	50.25	48.0	-1.52	25	18.1	19.01	16.3	1.81
9	78.7	81.11	79.4	-0.67	26	26.1	28.00	25.4	0.69
10	41.2	43.84	41.5	-0.31	27	199.5	200.78	200.9	-1.44
11	23.2	25.97	23.4	-0.15	28	136.2	133.97	133.1	3.14
12	45.9	49.50	47.3	-1.36	29	150.2	149.95	149.3	0.90
13	72.1	75.30	73.5	-1.36	30	123.5	123.74	122.7	0.83
14	31.5	33.90	31.4	0.09	31	133.9	133.19	132.3	1.63
15	28.7	28.45	25.9	2.82	32	127.1	124.52	123.5	3.63
16	25.4	25.31	22.7	2.72	33	126.5	127.01	126.0	0.50
17	37.0	39.80	37.4	-0.40					

Table S4. Key transitions and their related rotatory and oscillator strengths of dominant conformer of **1** at the CAM-B3LYP/6-31+g(d) level

HOMO is 143					
No.	**Energy (cm-1)**	**Wavelength (nm)**	**R(length)**	**Osc. Strength**	**Major contribs**
1	32730.78528	305.5227644	-11.6126	0.001	H-6->LUMO (11%), H-4->LUMO (10%), H-2->L+1 (36%)
2	32949.36153	303.4960174	-26.3209	0.0087	H-6->LUMO (29%), H-4->LUMO (12%), H-2->L+1 (17%)
3	35168.99932	284.3413288	11.8983	0.0018	H-7->L+1 (19%), H-5->L+1 (18%), H-4->L+1 (18%), H-2->L+4 (14%)
4	38083.08047	262.5838004	-1.1296	0.0596	H-1->LUMO (74%)
5	40340.62632	247.8890615	53.1191	0.2865	H-3->LUMO (72%)
6	43082.10483	232.1149359	5.7887	0.006	HOMO->L+1 (68%)
7	43395.04794	230.4410405	-16.518	0.0183	H-4->LUMO (16%), H-2->LUMO (36%), HOMO->L+1 (15%)
8	46305.09632	215.9589504	2.2448	0.0055	H-7->LUMO (10%), H-7->L+1 (16%), H-5->L+1 (13%), H-3->L+1 (13%), H-1->L+1 (17%)
9	46660.78683	214.312717	-5.4492	0.0162	HOMO->LUMO (74%)
10	47823.83831	209.1007404	12.2749	0.0152	H-6->LUMO (13%), H-5->LUMO (14%), H-2->L+4 (11%)
11	48027.09003	208.2158214	4.7844	0.0063	H-7->LUMO (10%), H-6->L+1 (13%), H-2->L+1 (15%), H-1->L+1 (18%)
12	48806.22161	204.8919107	19.4056	0.0115	H-7->L+1 (20%), H-1->L+1 (26%)
13	48919.13923	204.4189689	-0.7745	0.0015	H-7->LUMO (21%), H-6->L+1 (35%)
14	49618.42192	201.5380501	-23.2668	0.1057	H-3->L+1 (18%), H-3->L+2 (12%), H-1->L+2 (19%)
15	50502.40557	198.0103697	-1.9601	0.0118	H-7->L+1 (13%), H-4->LUMO (13%), H-2->LUMO (21%)
16	50776.63408	196.9409785	-6.0957	0.0022	HOMO->L+3 (19%), HOMO->L+5 (15%), HOMO->L+7 (28%), HOMO-

					>L+9 (13%)
17	51353.32049	194.7293749	34.1537	0.2268	H-3->L+1 (46%), H-1->L+2 (15%)
18	51671.10294	193.5317698	0.6037	0.001	H-6->L+1 (10%), H-5->LUMO (21%), H-5->L+1 (13%), H-4->LUMO (11%), H-4->L+1 (16%)
19	51961.46253	192.4503182	79.8594	0.3696	H-3->L+2 (37%), H-1->L+2 (24%)
20	52911.58365	188.9945322	-11.3767	0.0271	H-5->LUMO (20%), H-5->L+1 (14%), H-4->LUMO (13%)
21	53190.65148	188.0029614	23.8646	0.0228	H-13->LUMO (32%), H-12->LUMO (26%)
22	53615.70567	186.512513	-85.0435	0.1233	H-5->L+4 (11%), H-4->L+4 (12%), HOMO->L+4 (12%)
23	53747.17404	186.0562937	-40.28	0.0485	H-12->LUMO (10%), H-11->LUMO (18%), H-7->LUMO (14%)
24	54344.02432	184.0128722	4.0679	0.1286	H-8->L+1 (43%)
25	54448.06984	183.6612396	14.5084	0.131	H-8->L+1 (15%)
26	54699.71482	182.8163096	24.5536	0.0242	H-11->L+1 (28%), H-9->L+1 (22%)
27	55062.66431	181.6112628	-5.853	0.0074	HOMO->L+4 (43%)
28	56277.33528	177.6914267	5.7095	0.0026	HOMO->L+6 (28%)
29	56340.24653	177.4930111	-8.1627	0.0042	H-1->L+3 (14%), H-1->L+7 (15%)
30	56450.74449	177.1455822	6.1116	0.0011	H-10->L+1 (11%), H-6->L+2 (10%), H-1->L+7 (11%)
31	56537.85236	176.872654	-2.7233	0.0195	H-10->L+1 (30%), H-6->L+2 (14%), H-4->L+2 (12%)
32	56602.37672	176.6710266	-3.5506	0.0305	H-10->L+1 (12%), H-2->L+3 (22%)
33	57048.40132	175.2897499	49.9318	0.0593	H-12->LUMO (10%), H-11->LUMO (13%)
34	57321.82327	174.4536274	-21.7236	0.1802	
35	57504.10457	173.9006298	17.5768	0.0398	H-3->L+3 (11%)
36	57671.06134	173.3971903	-34	0.0144	H-3->L+3 (15%), H-3->L+7 (16%)
37	57951.74228	172.557366	17.9614	0.0351	H-4->L+3 (20%)
38	58095.30897	172.1309376	-105.3054	0.1044	H-1->L+4 (22%)
39	58369.53747	171.3222416	-18.9242	0.0173	H-8->LUMO (48%)
40	58697.80512	170.3641214	154.0169	0.0289	
41	58733.29352	170.2611824	-130.9198	0.2581	HOMO->L+2 (10%)
42	58916.38138	169.7320807	-64.1962	0.0362	
43	58988.97127	169.523214	14.7067	0.0113	H-16->LUMO (12%)
44	59176.89846	168.9848617	-2.936	0.0537	
45	59652.76557	167.6368213	15.5195	0.0149	H-2->L+2 (12%), HOMO->L+2 (22%), HOMO->L+3 (12%)
46	59864.88938	167.042821	66.7736	0.1449	
47	59937.47928	166.8405165	28.5632	0.0387	H-12->L+1 (34%)
48	60027.00682	166.5916815	-6.7275	0.0659	
49	60100.40328	166.3882346	-34.8792	0.0289	H-9->LUMO (30%)
50	60416.57261	165.517499	-5.0761	0.0117	H-10->LUMO (56%)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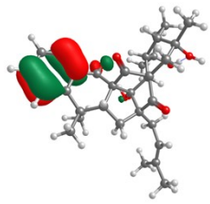
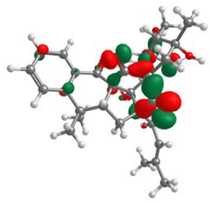
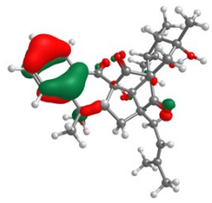
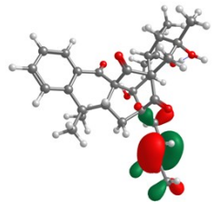
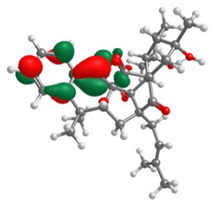
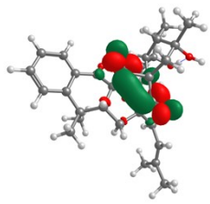
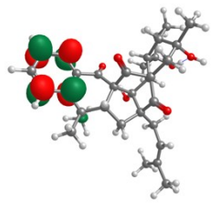
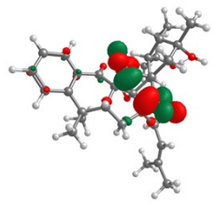
			
140	**141**	**142**	**143(HOMO)**
			
144 (LUMO)	**145**	**146**	**148**

Key molecular orbitals involved in important transitions regarding the ECD spectrum of dominant conformer of **1**.

Figure S1. ^{1}H NMR spectrum of compound **1** in chloroform-*d*

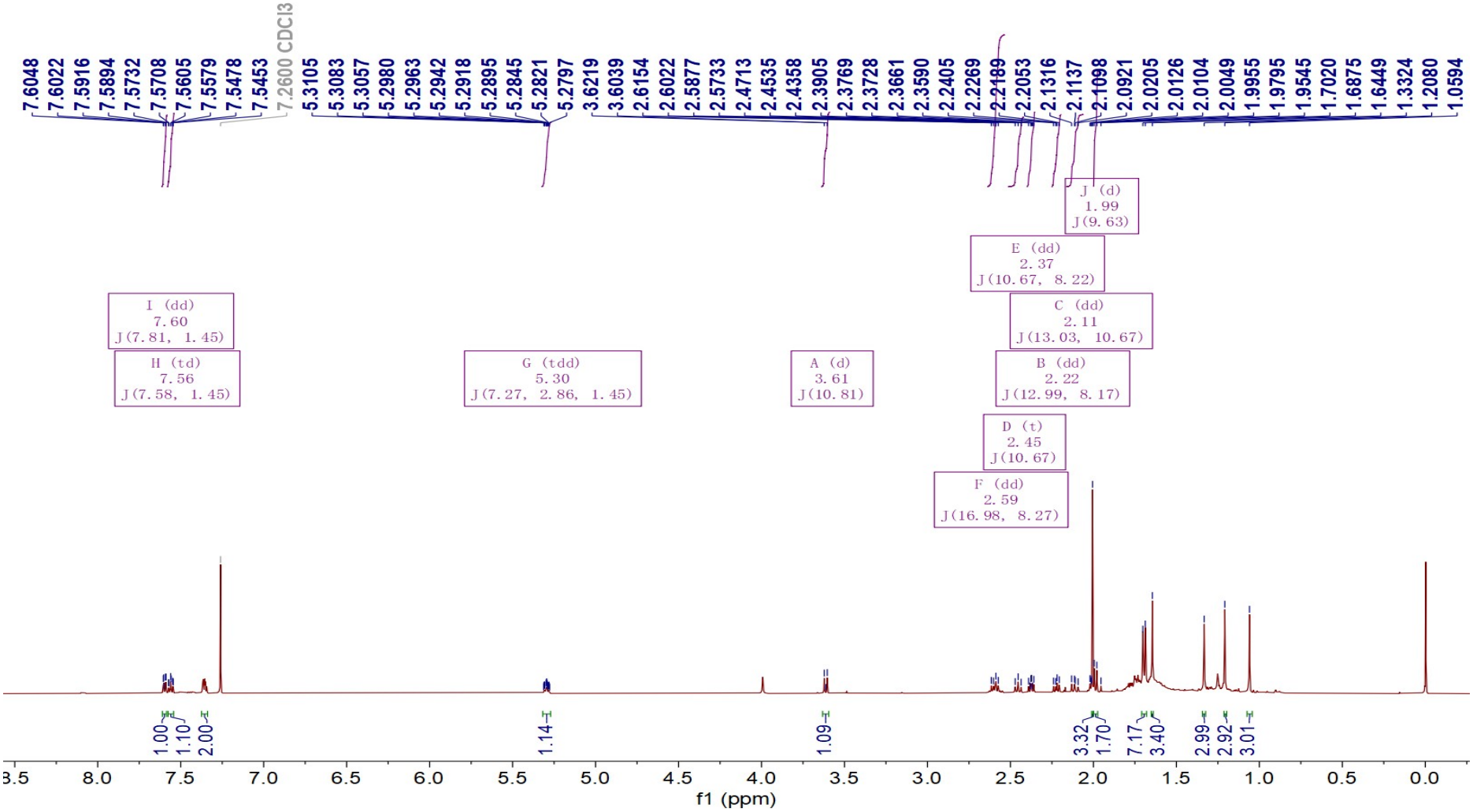


Figure S2. ^{13}C NMR spectrum of compound **1** in chloroform-*d*

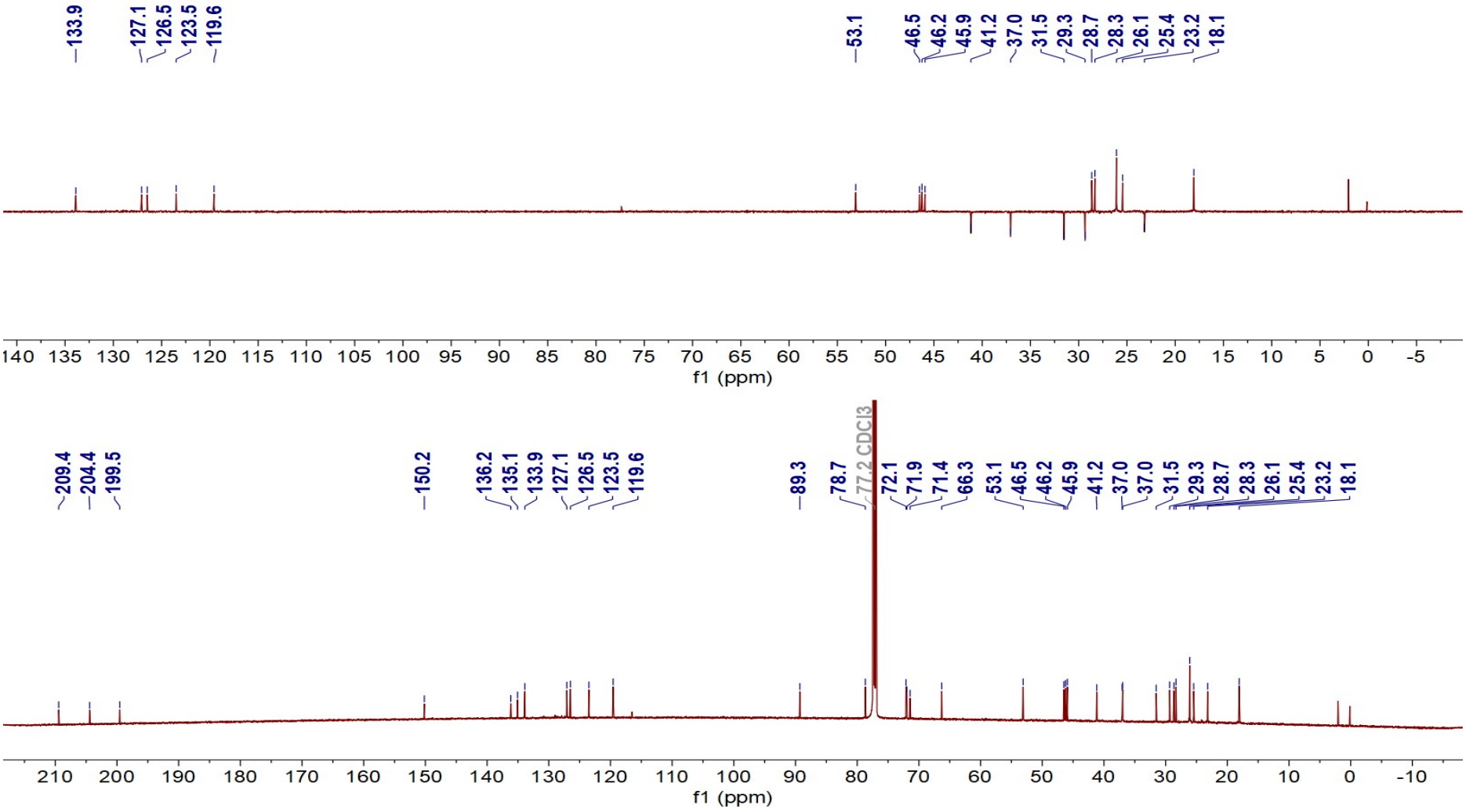


Figure S3. HSQC spectrum of compound **1** in chloroform-*d*

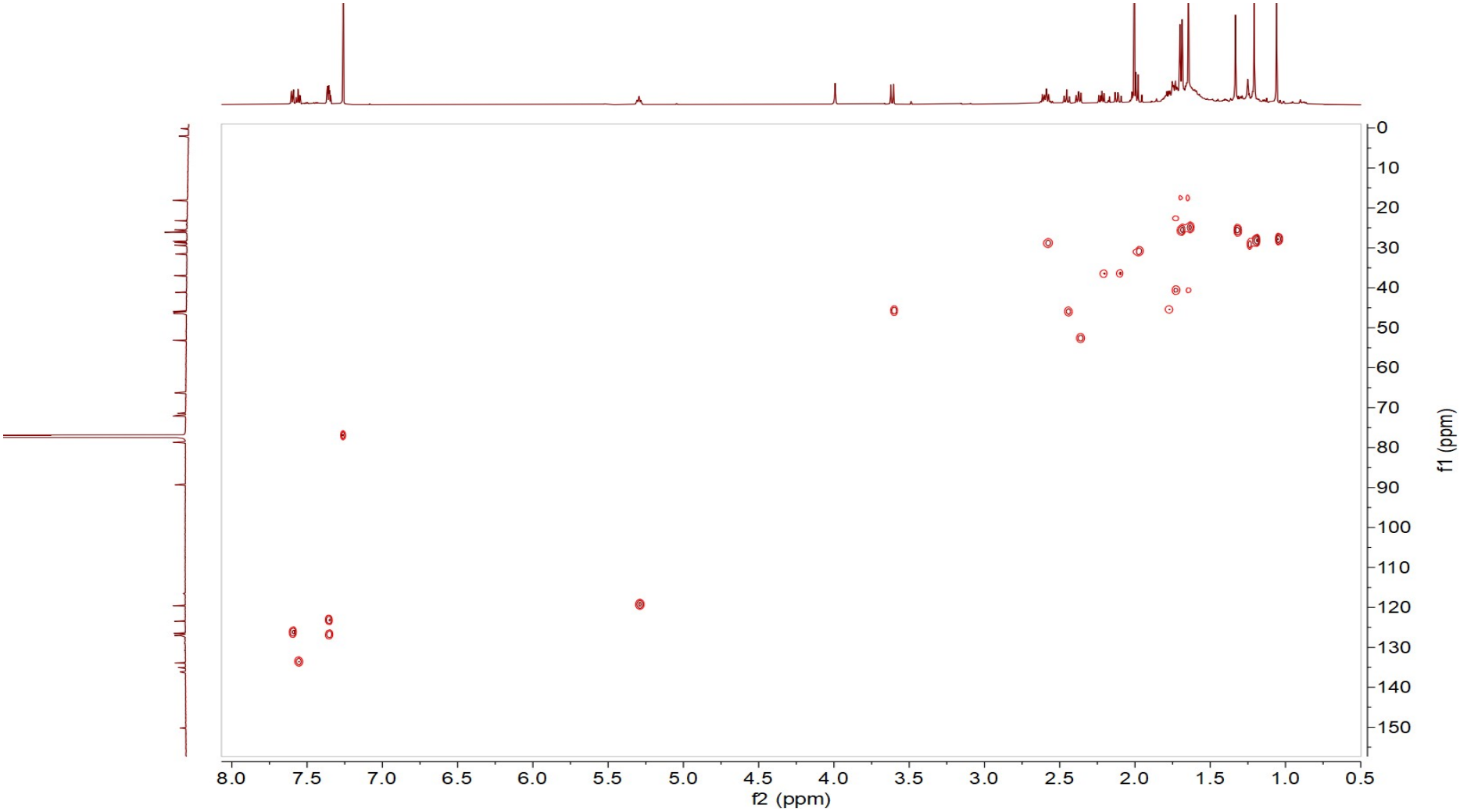


Figure S4. HMBC spectrum of compound **1** in chloroform-*d*

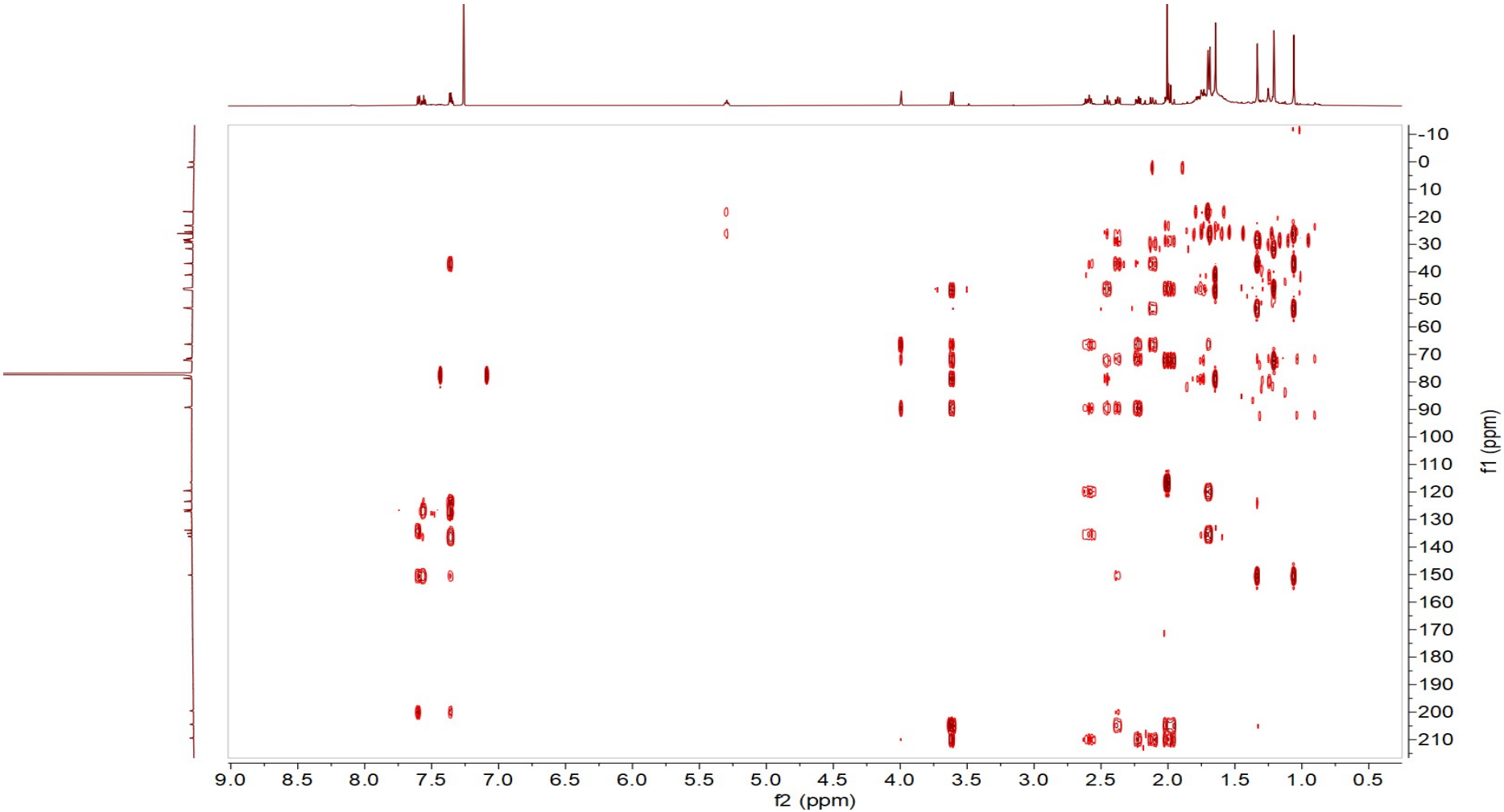


Figure S5. ^{1}H–^{1}H COSY spectrum of compound **1** in chloroform-*d*

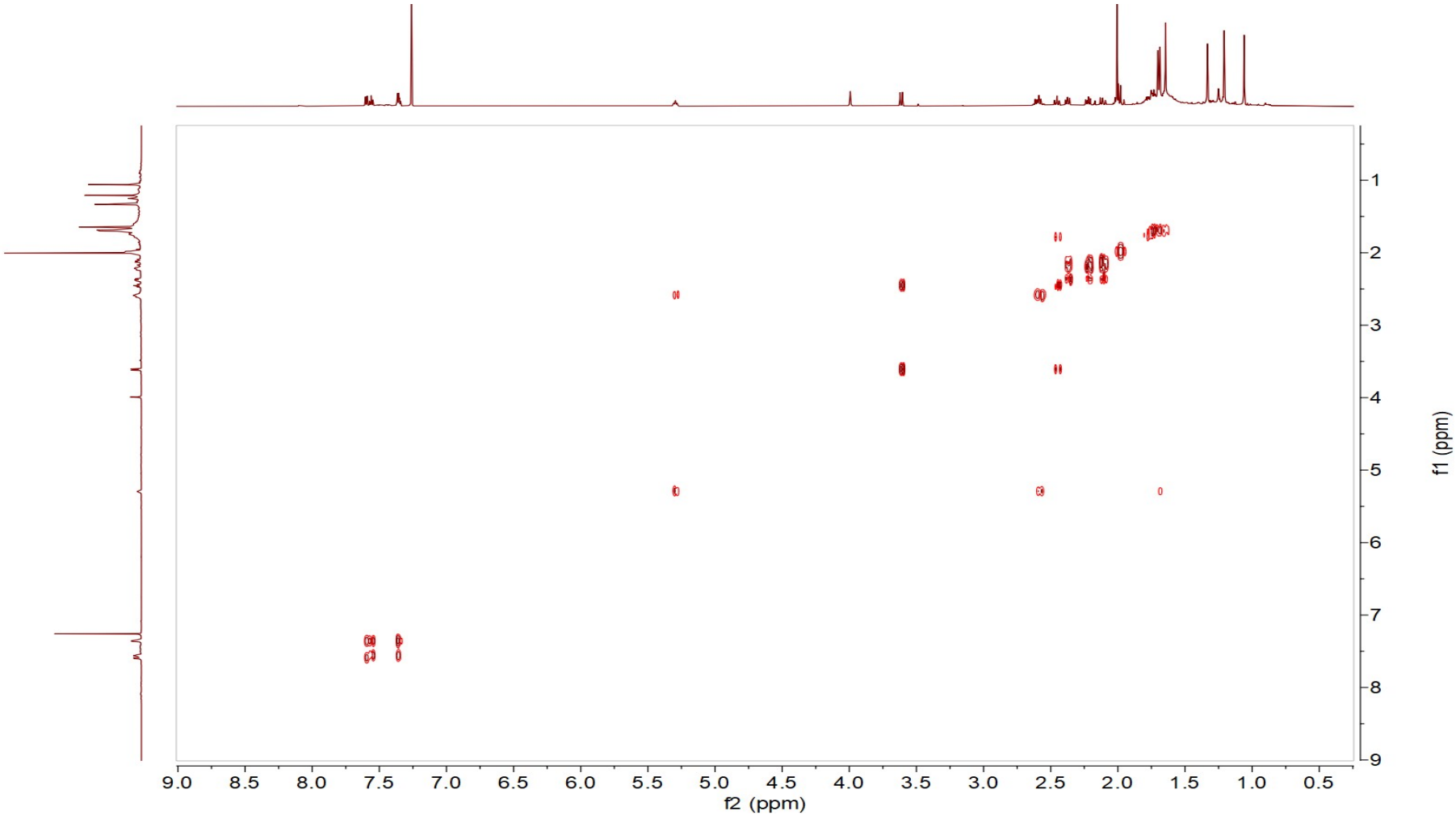


Figure S6. ROESY spectrum of compound **1** in chloroform-*d*

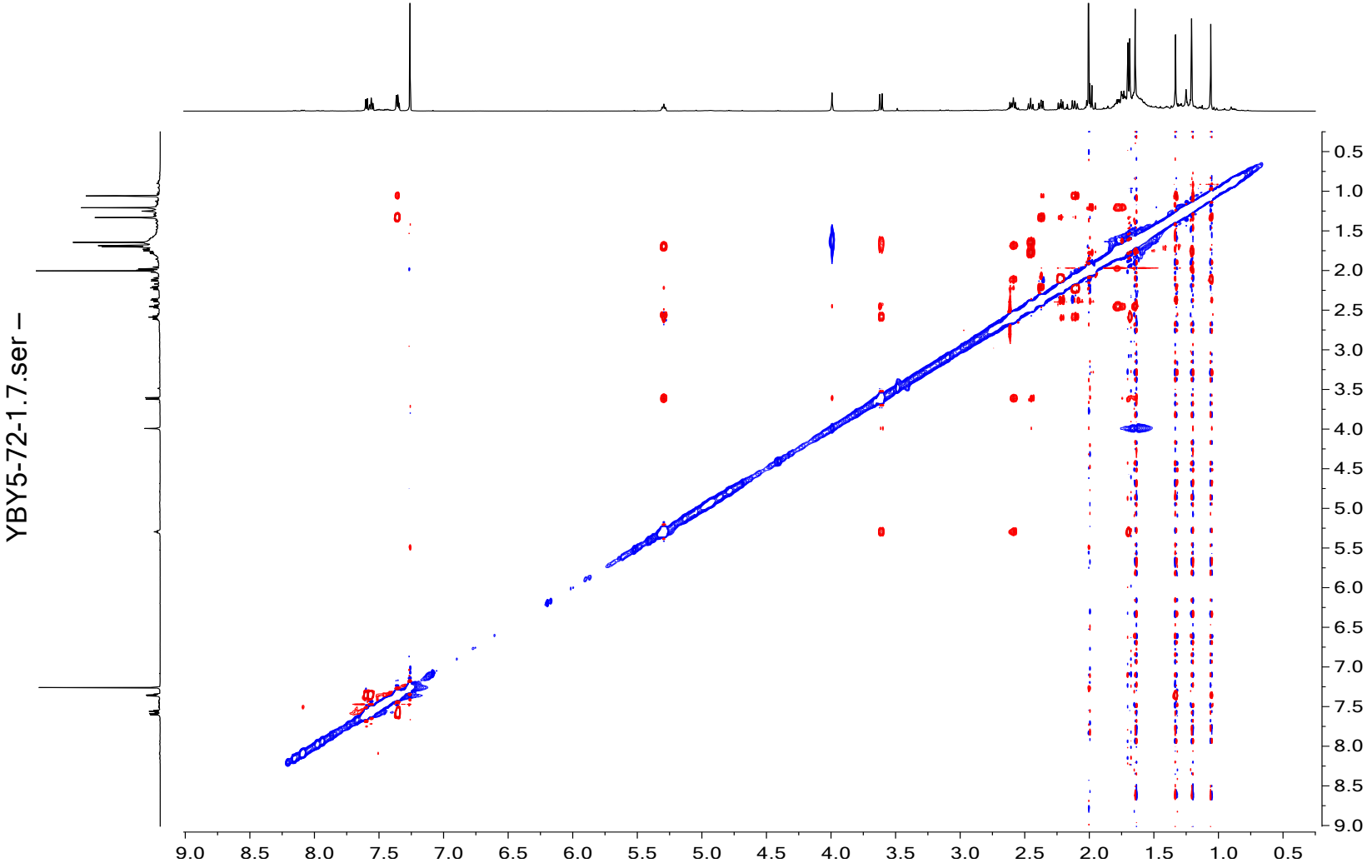


Figure S7. HRESIMS spectrum of compound **1**

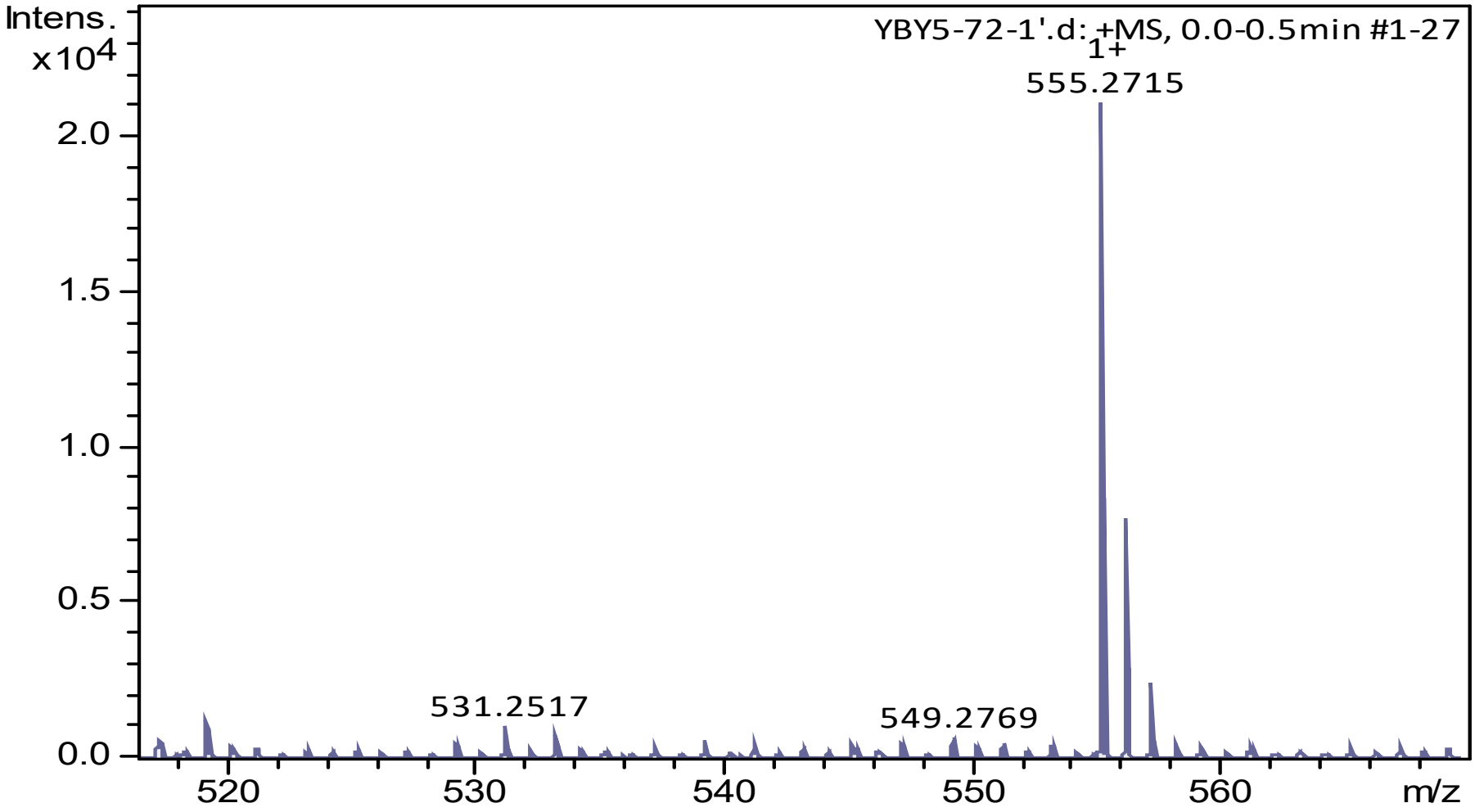


Figure S8. UV spectrum of compound **1**

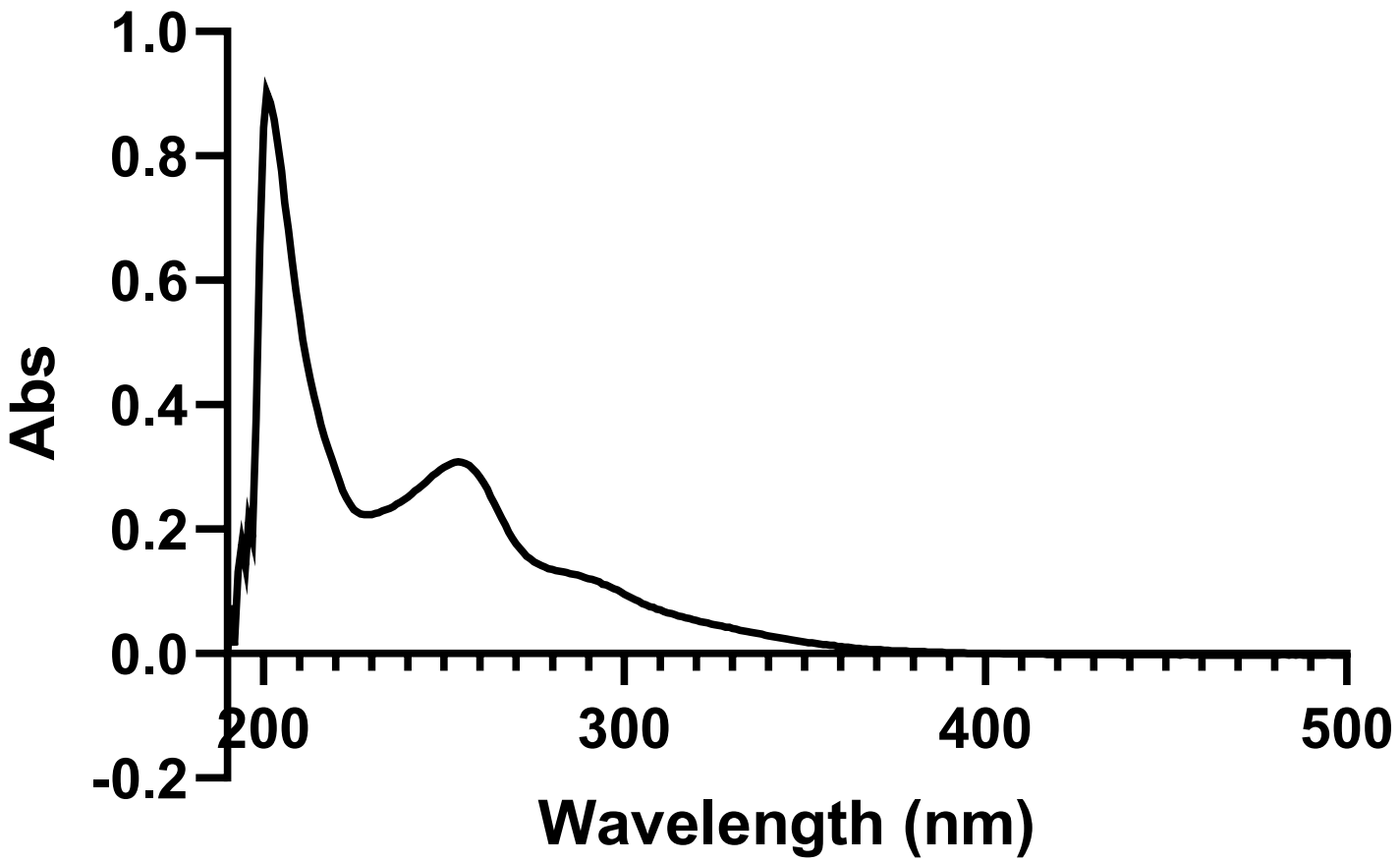


Figure S9. IR spectrum of compound **1**

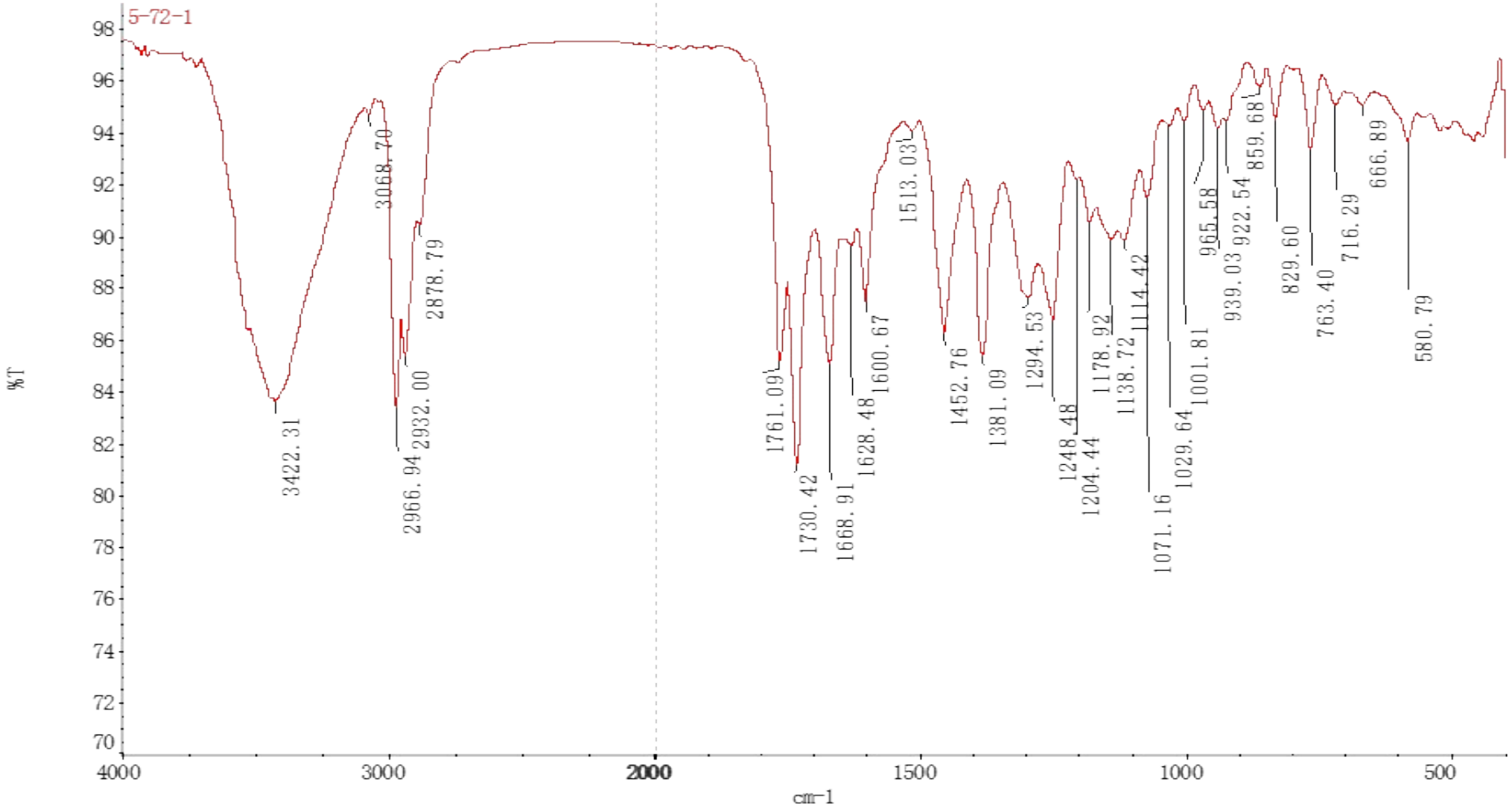


Figure S10. ^{1}H NMR spectrum of compound **2** in methanol-d_4

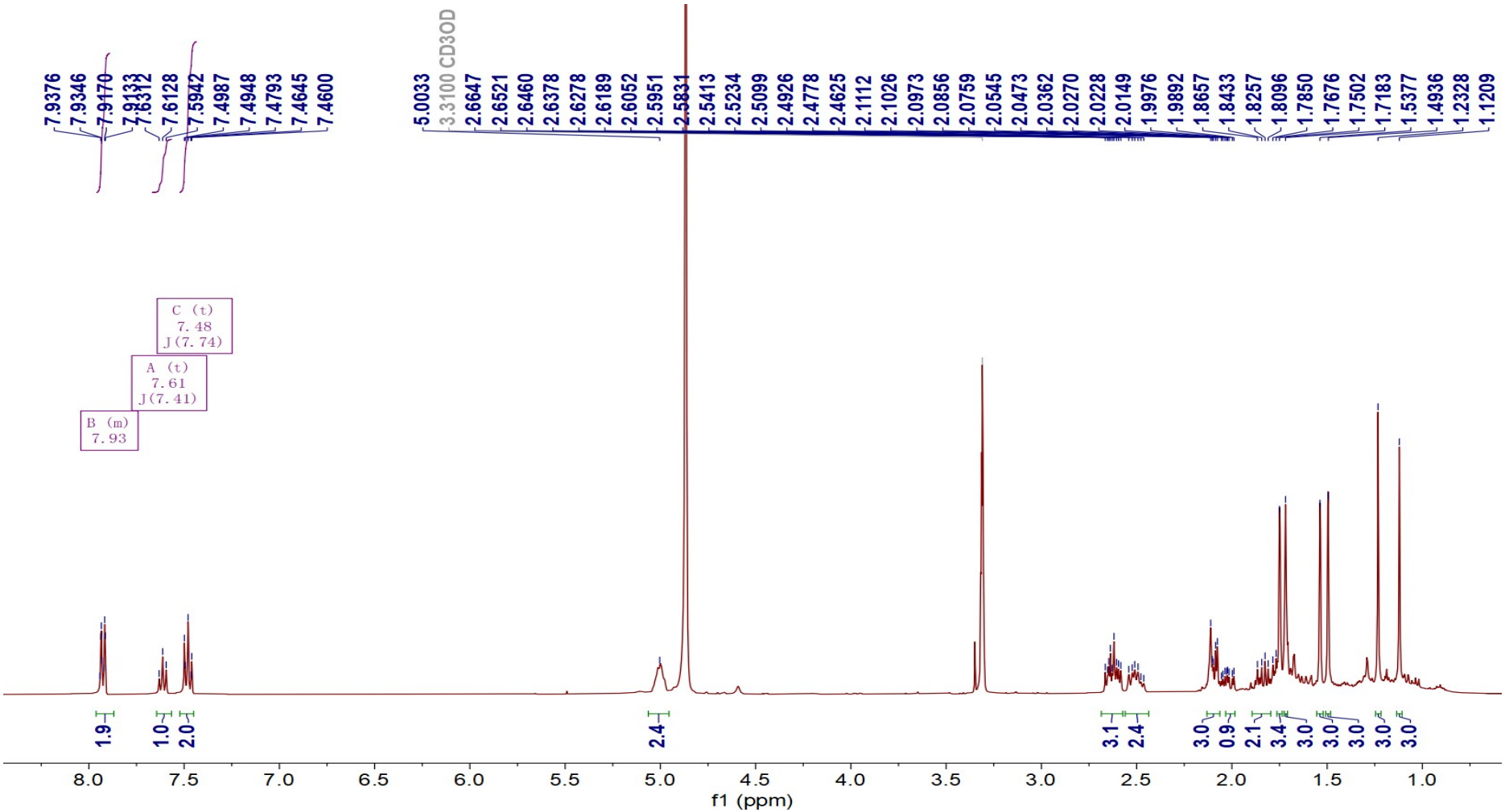


Figure S11. ^{13}C NMR spectrum of compound **2** in methanol-d_4

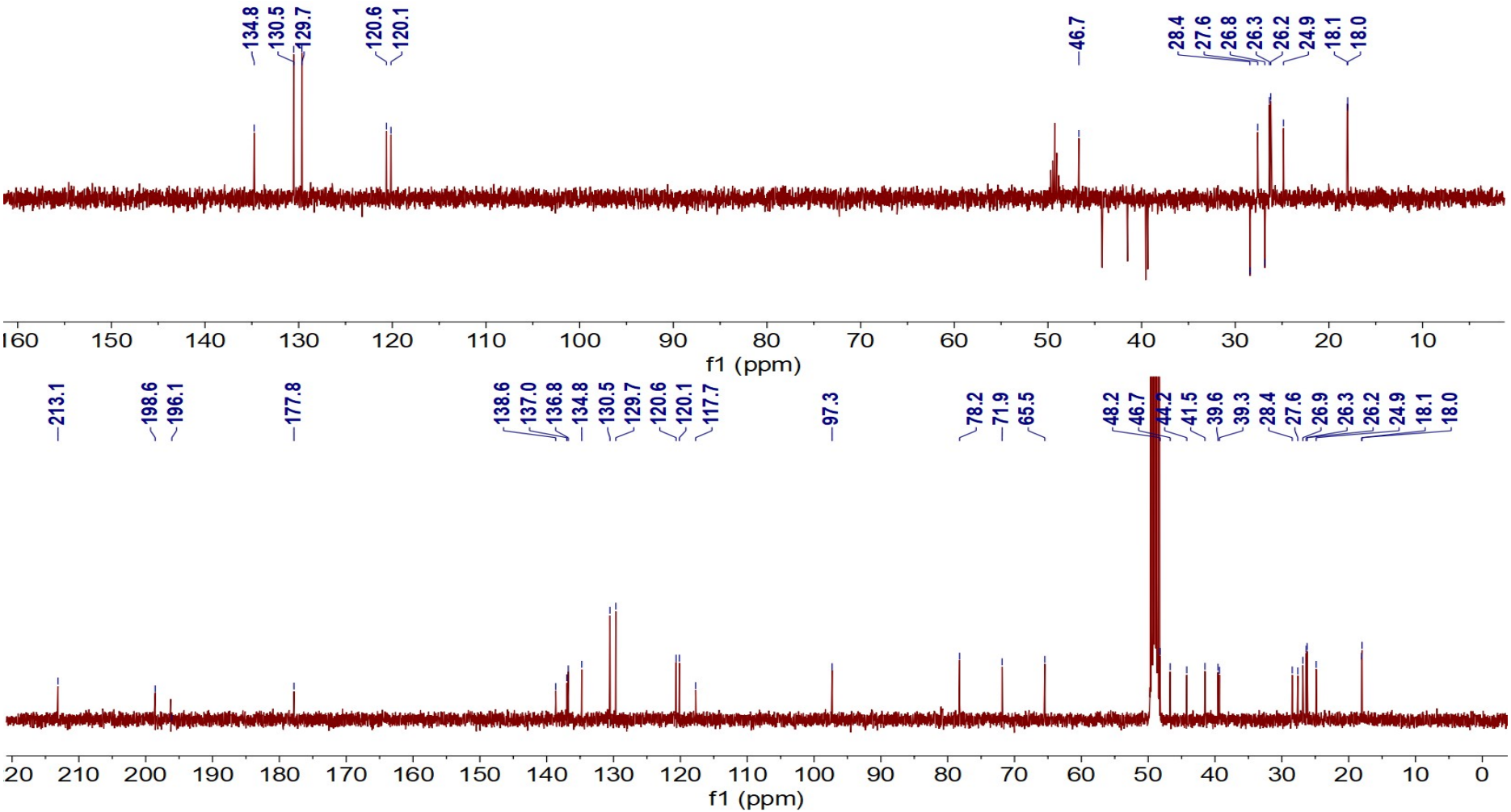


Figure S12. HSQC spectrum of compound **2** in methanol-d_4

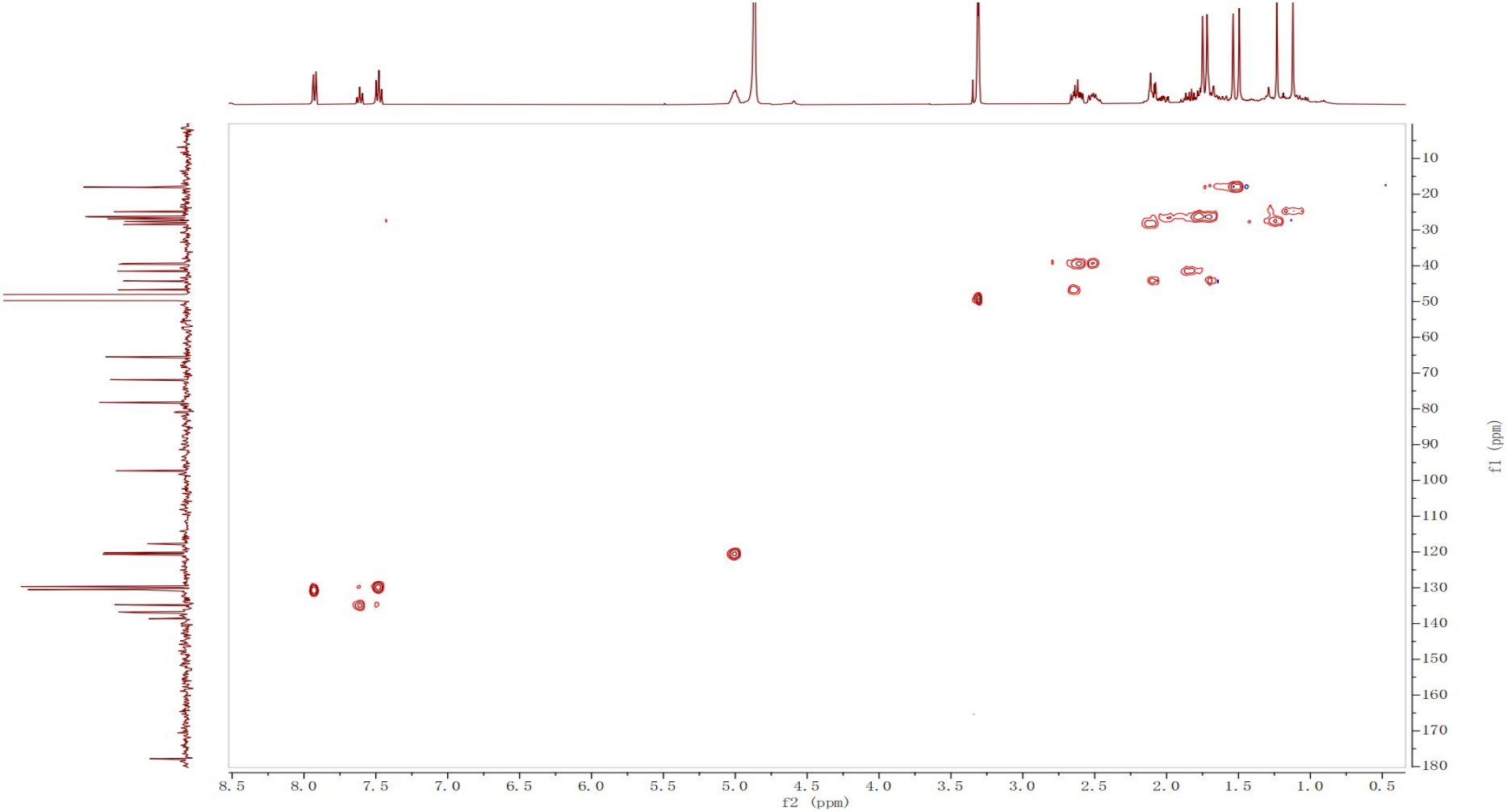


Figure S13. HMBC spectrum of compound **2** in methanol-d_4

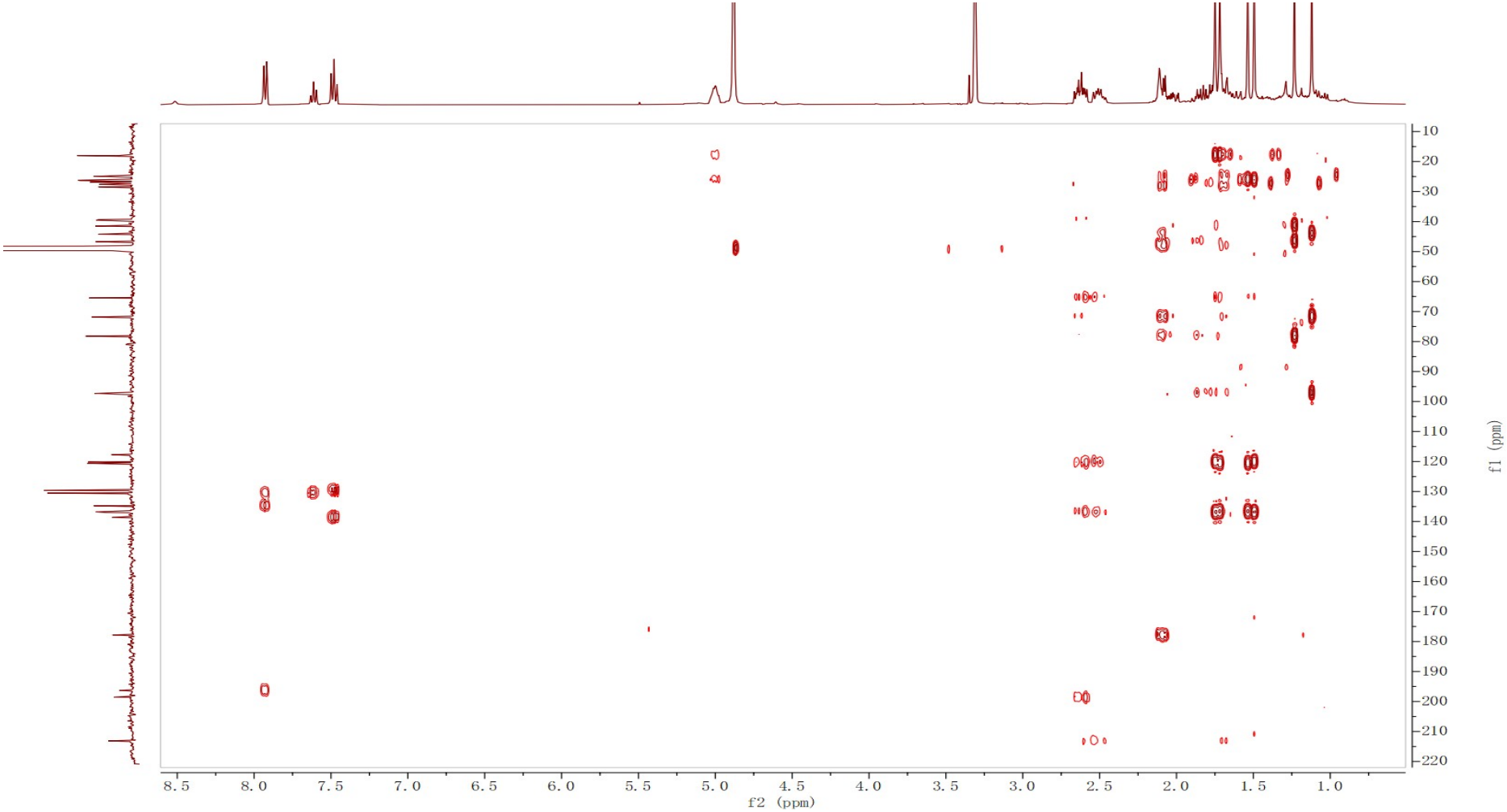


Figure S14. ^{1}H–^{1}H COSY spectrum of compound **2** in methanol-d_4

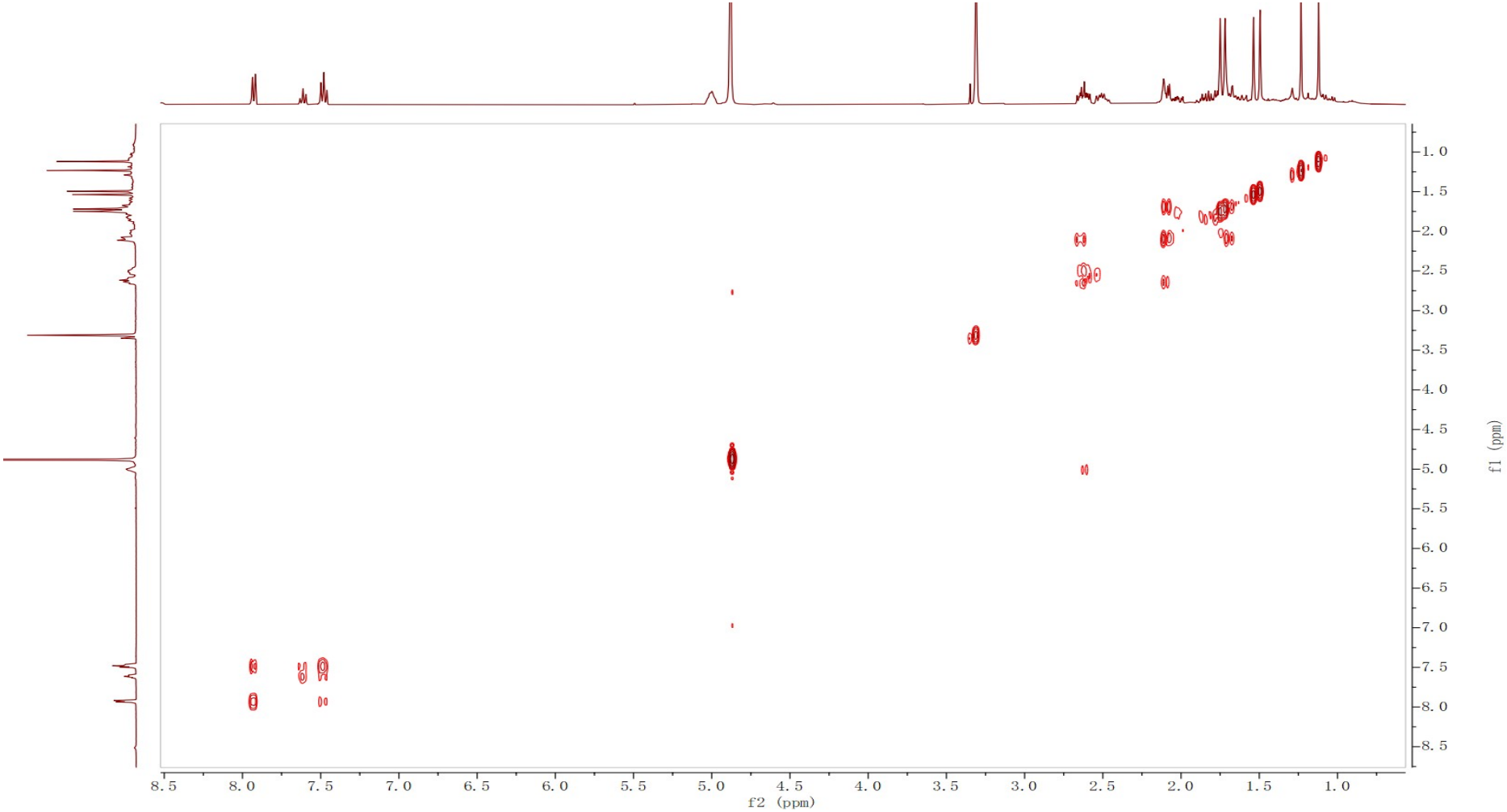


Figure S15. NOESY spectrum of compound **2** in methanol-d_4

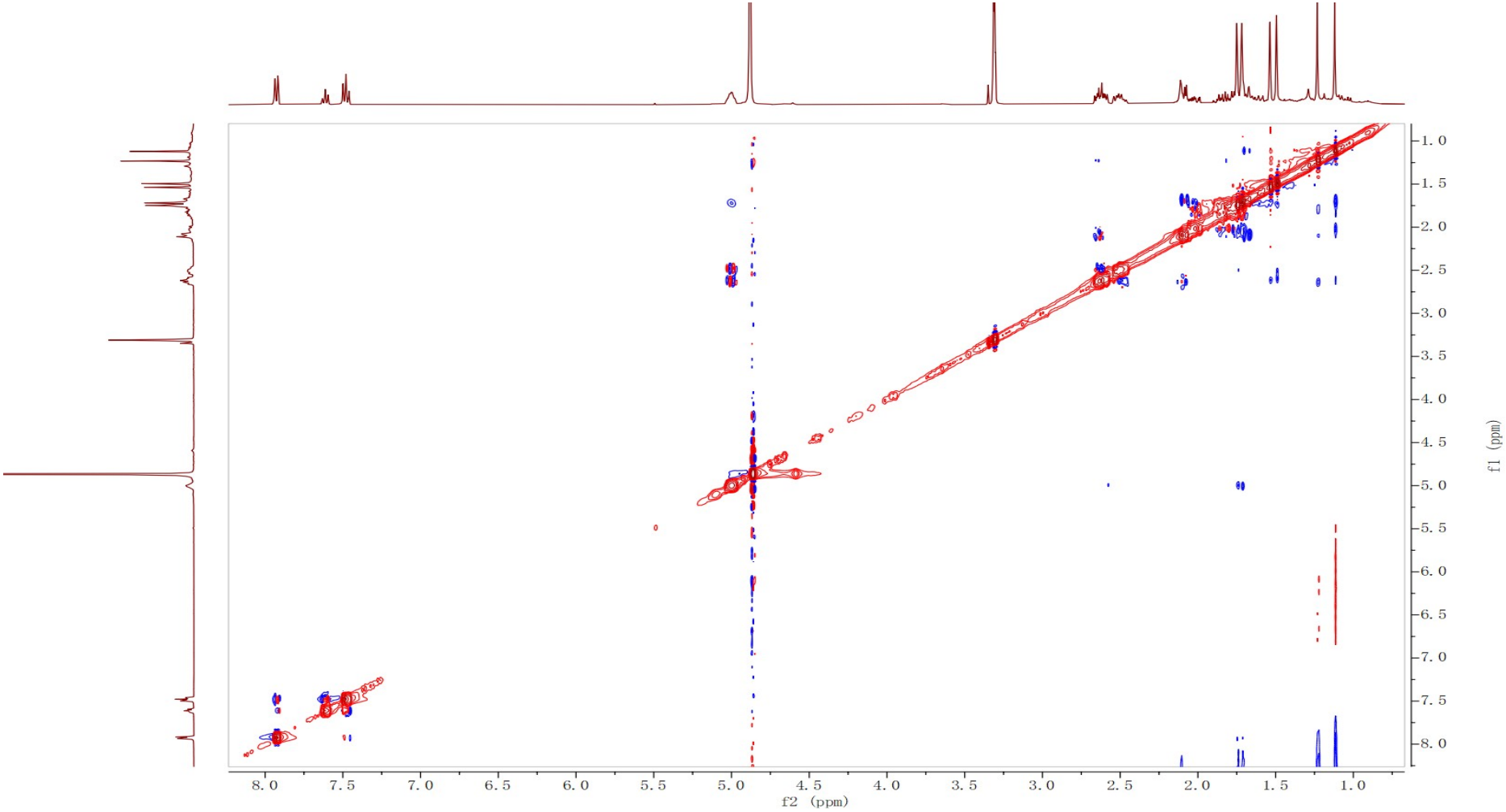


Figure S16. HRESIMS spectrum of compound **2**

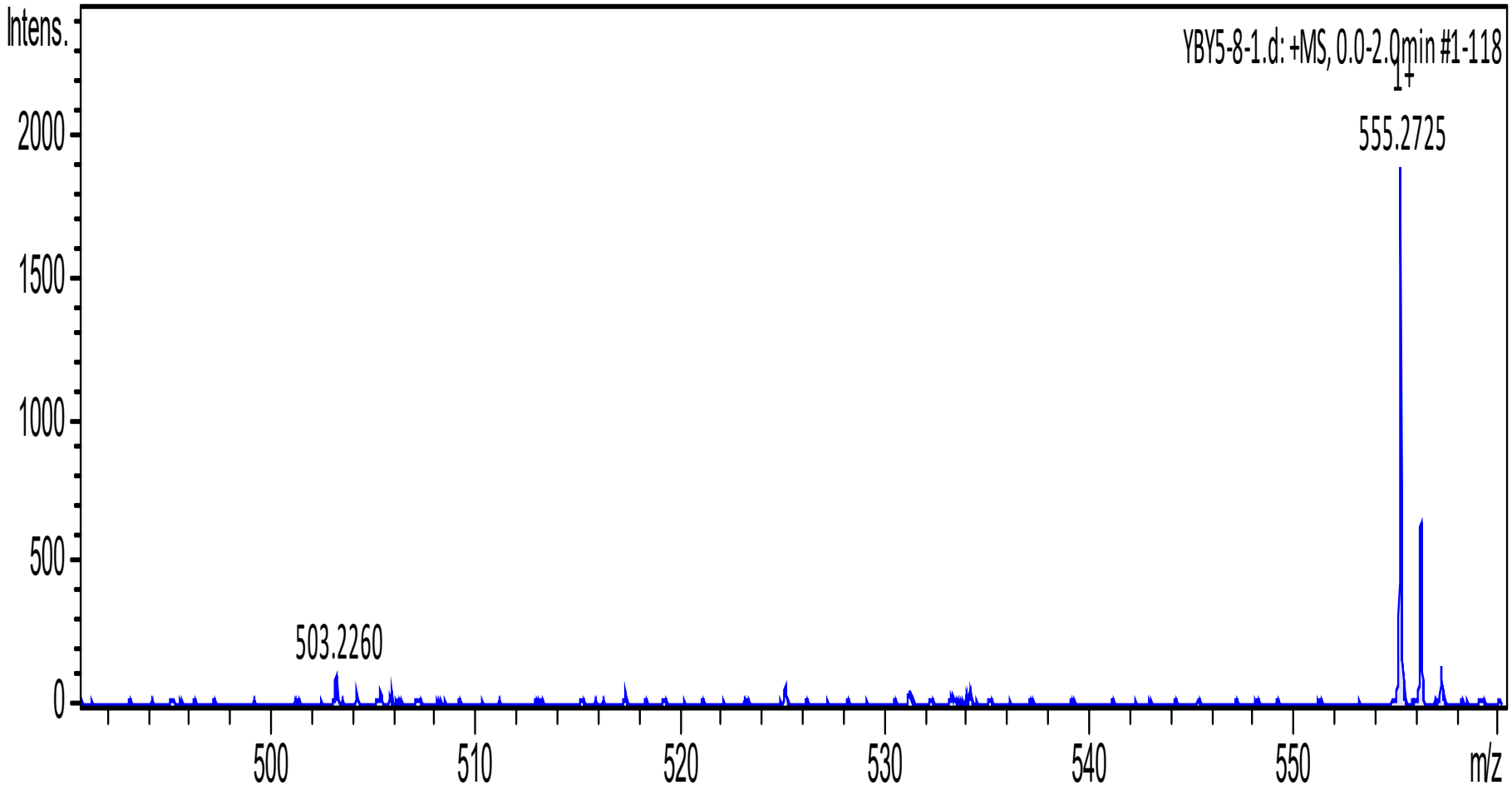


Figure S17. UV spectrum of compound **2**

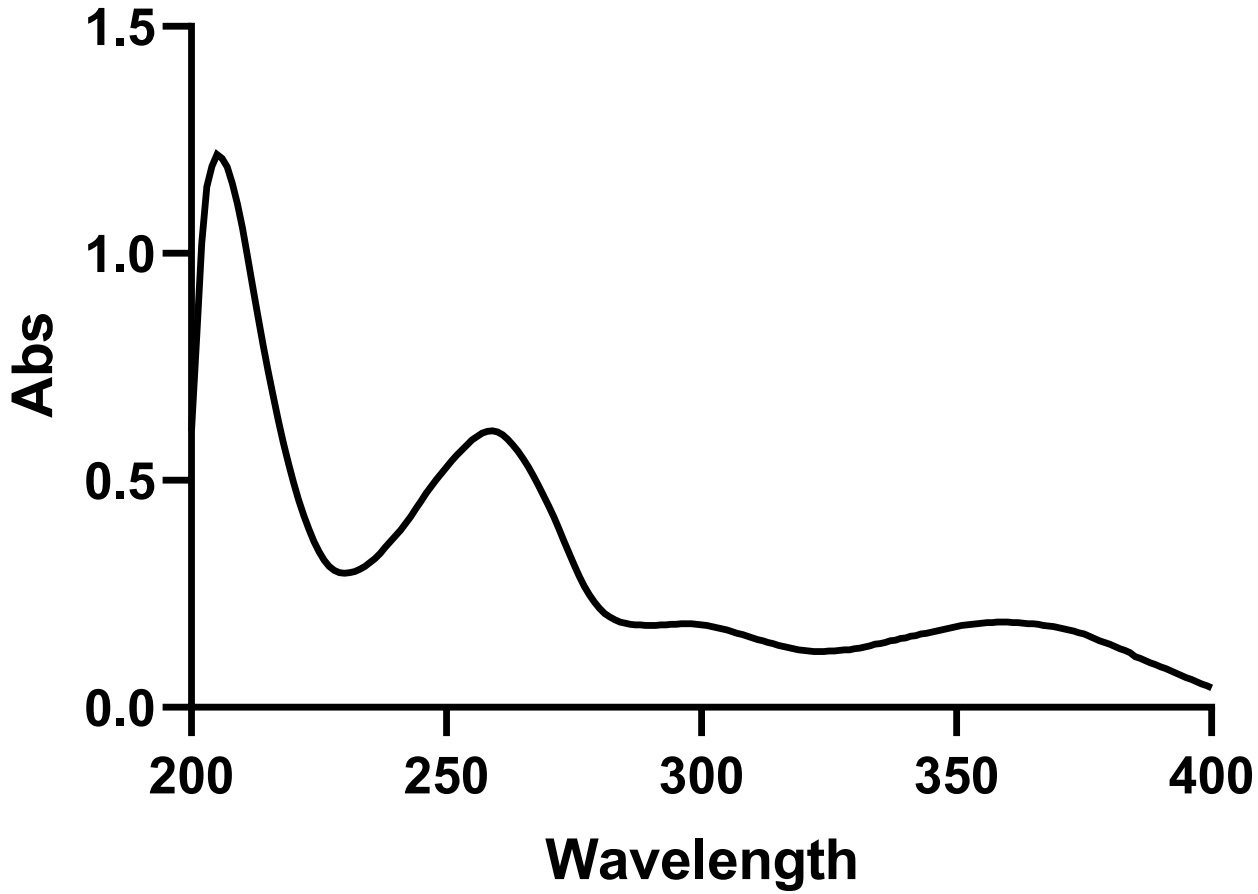


Figure S18. IR spectrum of compound **2**