Fischeriana A, a meroterpenoid with an unusual 6/6/5/5/5/6/6 heptacyclic carbon skeleton from the roots of *Euphorbia fischeriana*

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Supporting information

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EXPERIMENTAL SECTION

X-ray crystal structure analysis

Crystallographic data of **1** was obtained from an Agilent Gemini E X-ray single crystal diffractometer, equipped with an Oxford Cryostream cooler. The structure was determined by direct methods using SHELXS-9732 and refined anisotropically by full-matrix least-squares on F2 using SHELXL-97. The absolute configuration of **1** was confirmed by refinement of the Flack parameters. This crystallographic data can be obtained via email (deposit@ccdc.cam.ac.uk) or by sending a request to Director, CCDC (12 Union Road, Cambridge CB2 1EZ, UK, fax: + 44(0)1223−336033).

Crystal data for **1**, $C_{27}H_{30}O_8 \cdot 2(CH_4O)$, M = 570.61, crystal size 0.25 × 0.23 × 0.11 mm^3, orthorhombic, a = 11.8058(8) Å, b = 12.6003(11) Å, c = 19.4463(12) Å, α = 90°, β = 90°, γ = 90°, V = 2892.7(3) $Å^3$, T = 108.2 K, space group $P2_12_12_1$ (no. 19), Z = 4, μ(CuKa) = 0.809 mm^{-1}, D_{calcd} = 1.310 mg/m^3, F(000) = 1216, 20698 reflections measured, 5559 independent reflections (R_{int} = 0.0381). The final R^1 values were 0.0373 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0944 ($I > 2\sigma(I)$). The final R^1 values were 0.0398 (all data). The final $wR(F^2)$ values were 0.0973 (all data). The goodness of fit on F^2 was 1.024. Flack parameter = -0.02(13).

ECD Calculation.

In general, conformational analyses of **1** was carried out via systematic searching in the Discovery Studio (version 16.1.0.15350) using the MMFF94 force field. Conformers with Boltzmann distribution over 1% are chosen as the beginning for ECD calculations. Ground-state geometries are optimized at the B3LYP and cam-B3LYP/6-31G(d) level in methanol by the Gaussian 09 program (Gaussian Inc., Wallingford, CT, USA).[1] All quantum computations are performed on an IBM cluster machine located at the High Performance Computing Center of Peking Union Medical College. The energies, oscillator strengths, and rotational strengths (velocity) of the first 120 electronic excitations are calculated using the TD-DFT methodology at the B3LYP and cam-B3LYP/6-31G (d) level in methanol. The ECD spectra are simulated by the overlapping Gaussian function (half the bandwidth at 1/e peak height, 28 eV).[2]

The number of imaginary frequencies is zero.

Cartesian coordinate of low-energy optimized conformers of 1 optimized: [method: B3LYP/6-31G (d)]

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.539288	0.555941	1.808846
2	1	0	4.577340	4.569992	-0.298072
3	1	0	6.787469	1.131450	1.493505
4	6	0	4.573230	0.754216	-0.040164
5	1	0	1.518950	2.956091	-1.089548
6	8	0	0.717806	-2.309421	2.701068
7	1	0	1.477377	0.350226	2.026185
8	6	0	-3.668238	-1.150158	-0.979267
9	1	0	-3.260951	-0.825489	-1.942251
10	1	0	-0.746828	-1.205282	-1.956291
11	1	0	5.617453	2.650096	0.145701
12	6	0	2.240582	0.960031	-0.715024
13	1	0	-2.699162	-3.087523	-1.131356
14	1	0	-5.685523	2.925211	0.556716
15	8	0	-0.897610	-2.686584	1.090424

16	6	0	-3.594983	2.806250	1.041838
17	6	0	0.717489	-0.808645	-0.342661
18	1	0	-3.314036	3.412767	0.175945
19	1	0	7.548289	-0.331291	0.853009
20	1	0	-5.952222	2.110114	-1.881126
21	6	0	-6.309024	0.278665	-0.106858
22	1	0	-4.247150	2.442574	-1.810666
23	1	0	-1.560568	2.299246	1.525985
24	6	0	-4.959776	1.032675	-0.263926
25	6	0	3.339408	0.152828	-0.351327
26	1	0	-4.656979	-1.569788	-1.191309
27	8	0	5.593159	-0.097498	0.300273
28	1	0	4.014765	-1.950607	-0.587664
29	8	0	2.161421	-4.051594	-0.996968
30	8	0	1.007166	0.422384	-1.036903
31	6	0	0.048118	-0.537284	1.064203
32	1	0	-6.476860	-0.435805	-0.918824
33	6	0	3.584147	2.924647	-0.475324
34	8	0	3.669022	4.287658	-0.547532
35	6	0	-1.450444	-1.800513	0.077092
36	6	0	-4.979312	1.646583	-1.675507
37	8	0	0.181801	-2.948987	-1.344751
38	6	0	1.476056	-3.044503	-0.934055
39	6	0	1.890615	-1.717387	-0.467201
40	6	0	-4.952494	2.149698	0.812401
41	1	0	-1.936966	-0.673917	1.837921
42	6	0	-1.748730	1.367937	-0.963816
43	1	0	-4.817192	0.891064	-2.450212
44	1	0	-2.355403	2.189742	-1.336727
45	1	0	-3.677955	3.506420	1.882157
46	1	0	-4.051190	-0.421379	0.971153
47	6	0	0.044103	-1.922343	1.759620
48	1	0	-3.347143	-2.731951	0.449711
49	1	0	-1.606074	0.697502	-1.810431
50	1	0	-6.353769	-0.268897	0.841414
51	6	0	-2.809476	-2.281344	-0.394712
52	6	0	-1.478827	-0.483517	0.848987
53	6	0	4.683805	2.149876	-0.093837
54	1	0	7.266556	1.023955	-0.247491
55	1	0	-7.154062	0.978481	-0.118240
56	6	0	-0.369729	-1.648804	-1.033431
57	6	0	-2.511273	1.776854	1.365665
58	6	0	3.160296	-1.301997	-0.424871
59	1	0	-0.796123	1.840223	-0.712690

60	1	0	-2.768008	1.311522	2.327059
61	6	0	6.858769	0.483570	0.612707
62	6	0	-3.772031	0.040489	0.007268
63	1	0	-5.281934	1.727500	1.771917
64	6	0	-2.350213	0.683032	0.271435
65	6	0	2.364841	2.341239	-0.794424

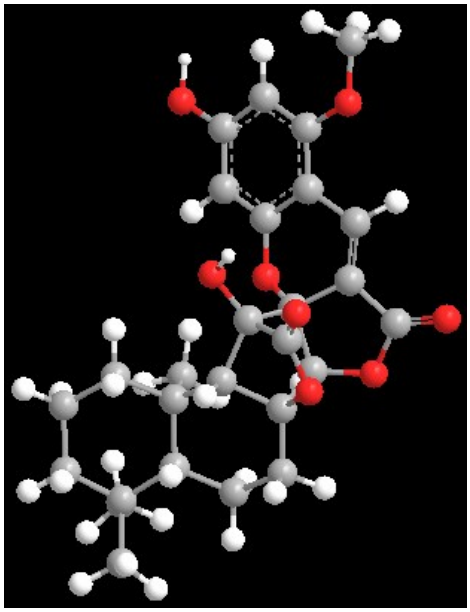
Sum of electronic and thermal Free Energies= -1648.239105 (Hartree/Particle).

References

(1) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Rev. C 01; Gaussian, Inc., Wallingford CT, 2009.

(2) Stephens, P. J.; Harada, N. ECD cotton effect approximated by the Gaussian curve and other methods. Chirality, 2010, 22, 229–233.

Table S1. The 3D conformers of (5*R*,8*S*,9*R*,10*R*,11*R*,13*R*,14*S*)-**1**

No.	Conformers	Population (%)
1		100

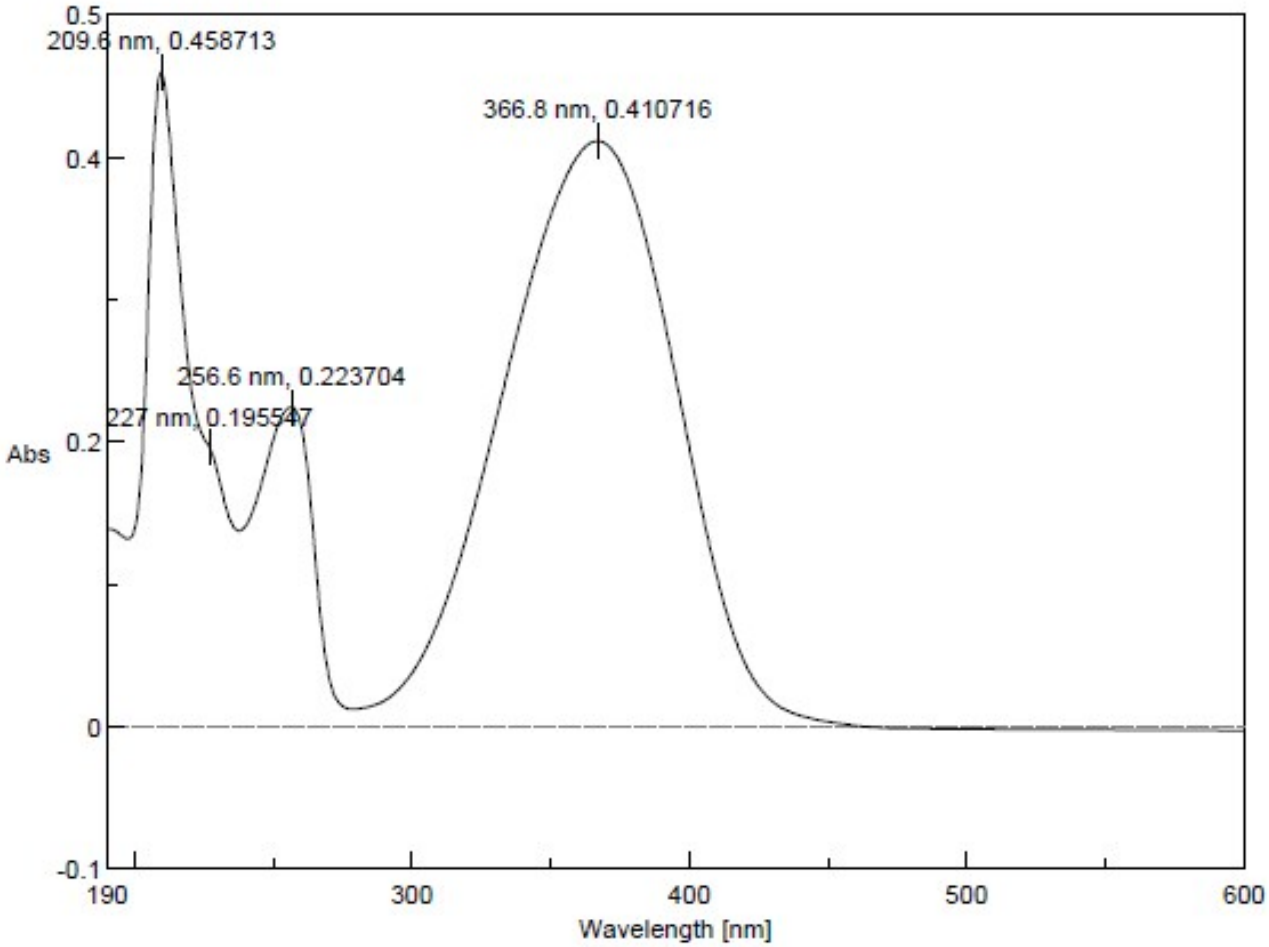


Figure S1. UV spectrum of **1**

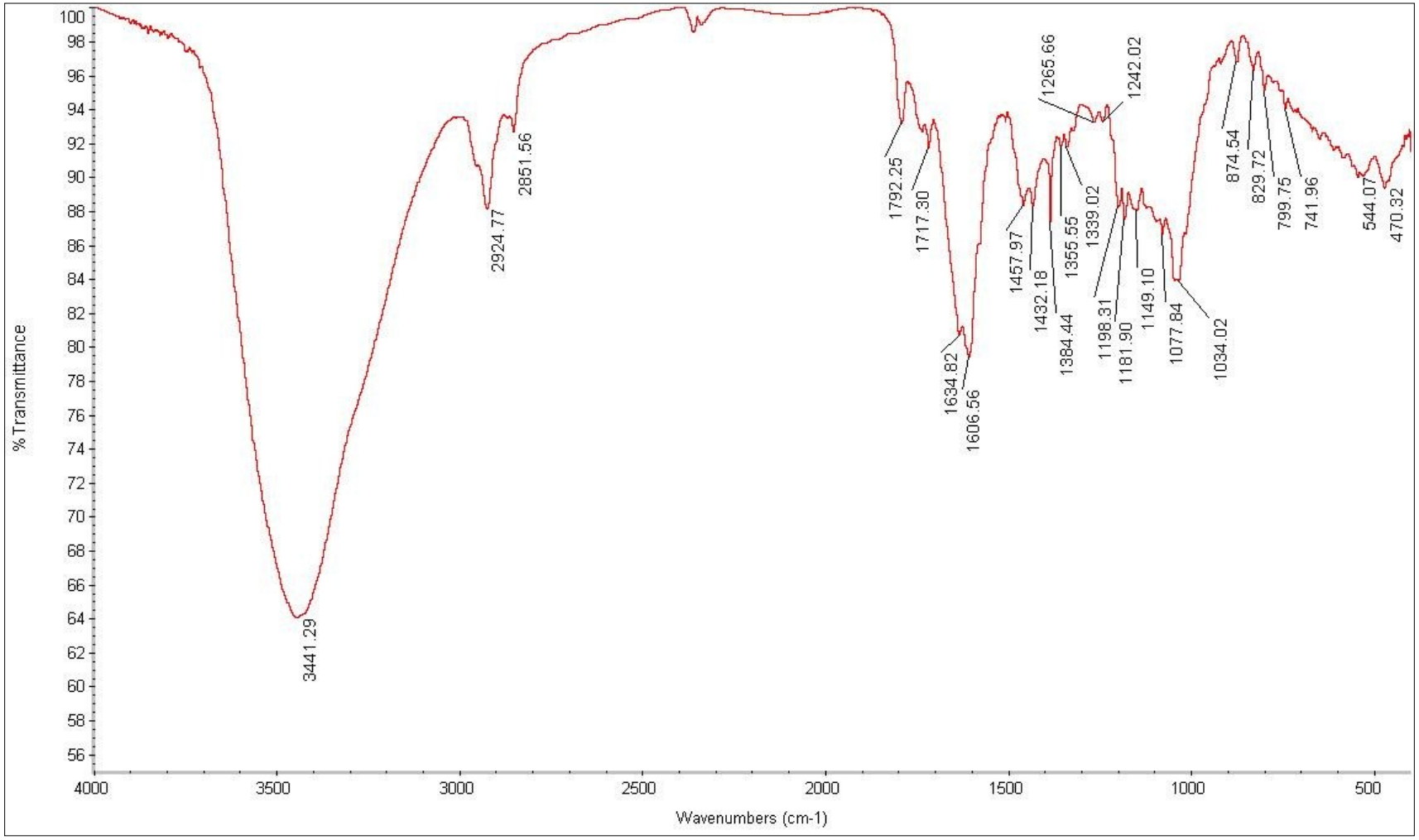
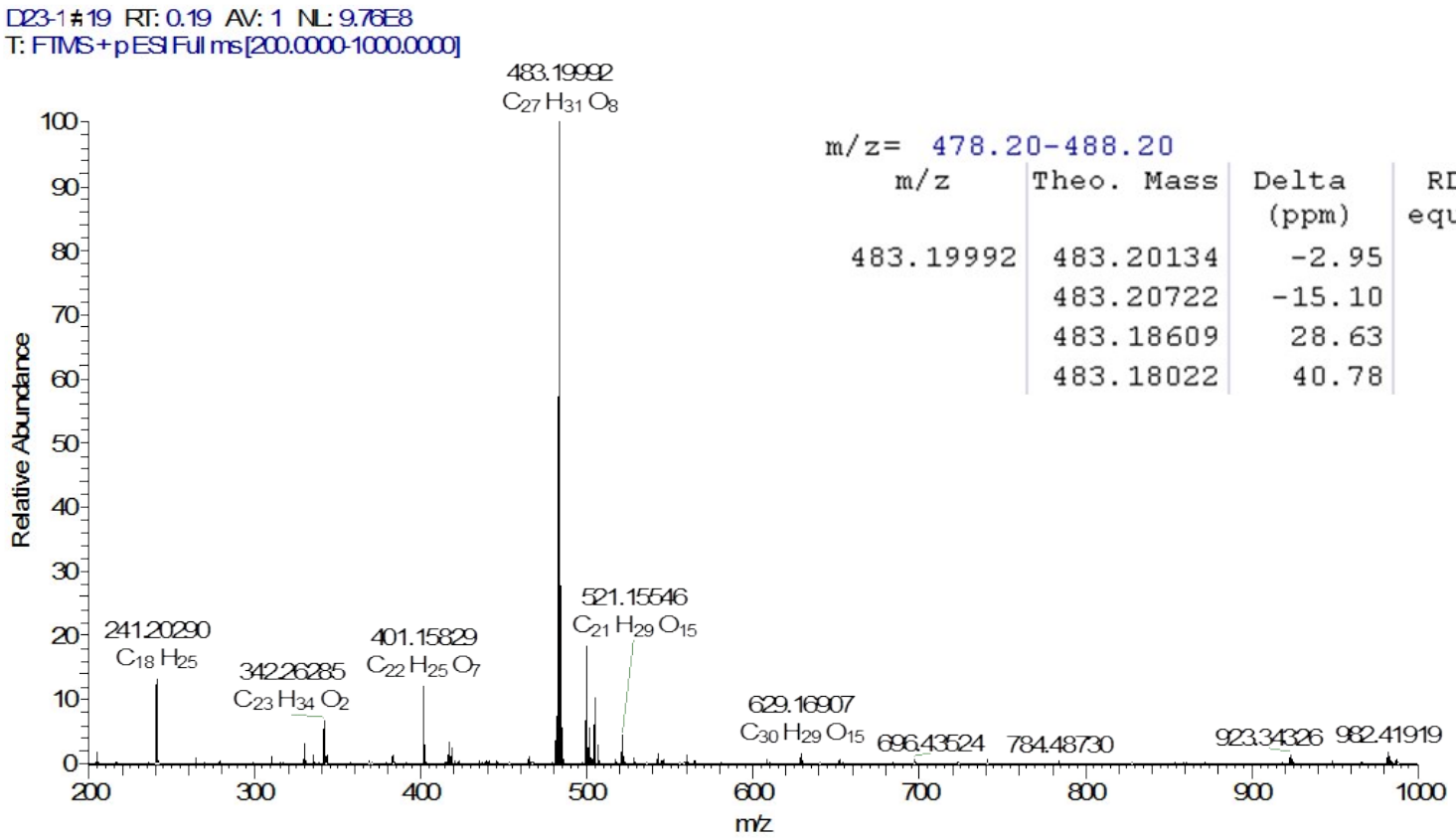


Figure S2. IRspectrum of **1**



m/z= 478.20-488.20

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
483.19992	483.20134	-2.95	12.5	$C_{27}H_{31}O_8$
	483.20722	-15.10	3.5	$C_{20}H_{35}O_{13}$
	483.18609	28.63	8.5	$C_{23}H_{31}O_{11}$
	483.18022	40.78	17.5	$C_{30}H_{27}O_6$

Figure S3. HRESIMS spectrum of **1**

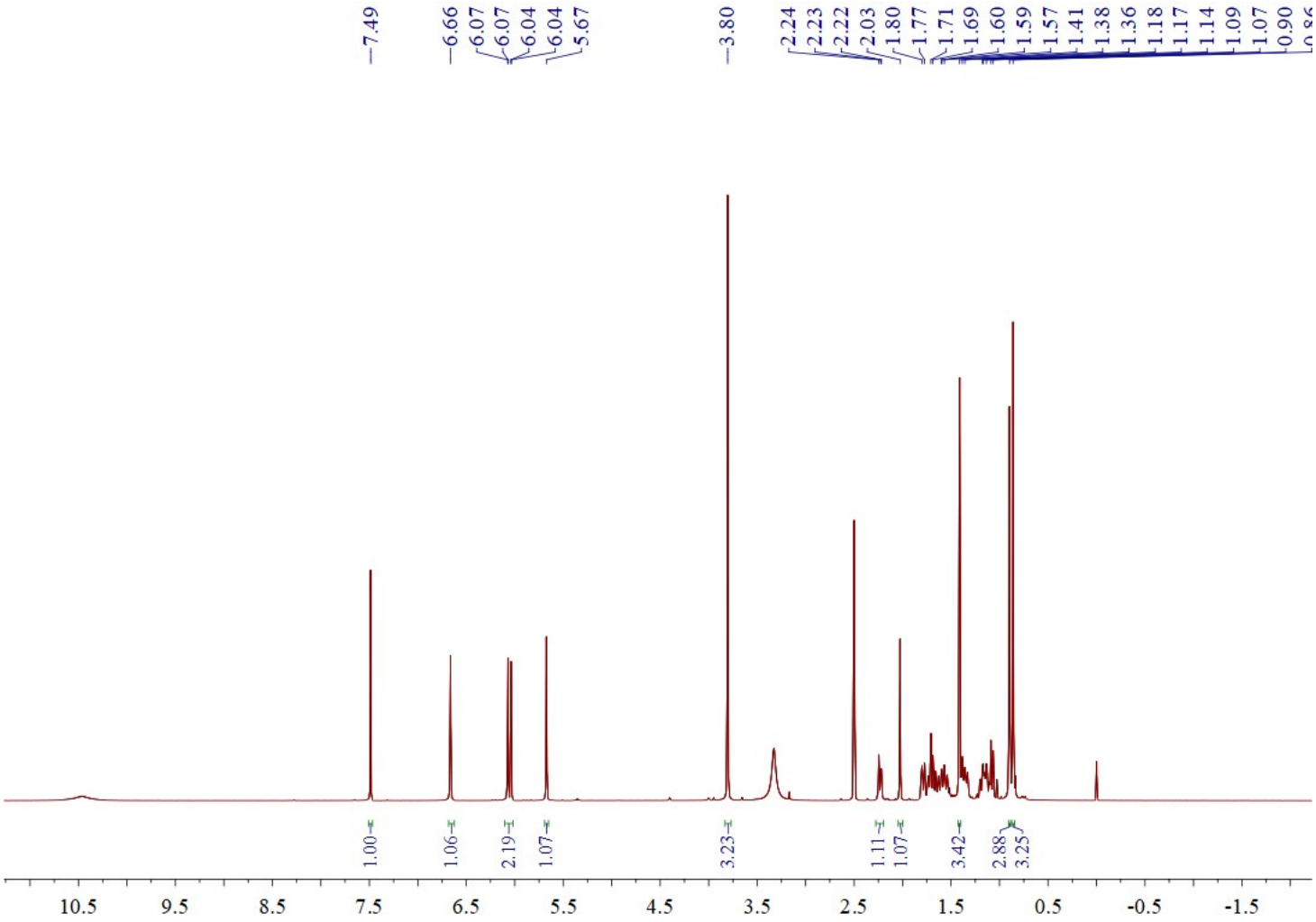


Figure S4. ^{1}H NMR spectrum of **1** in DMSO-d_6 (500 MHz).

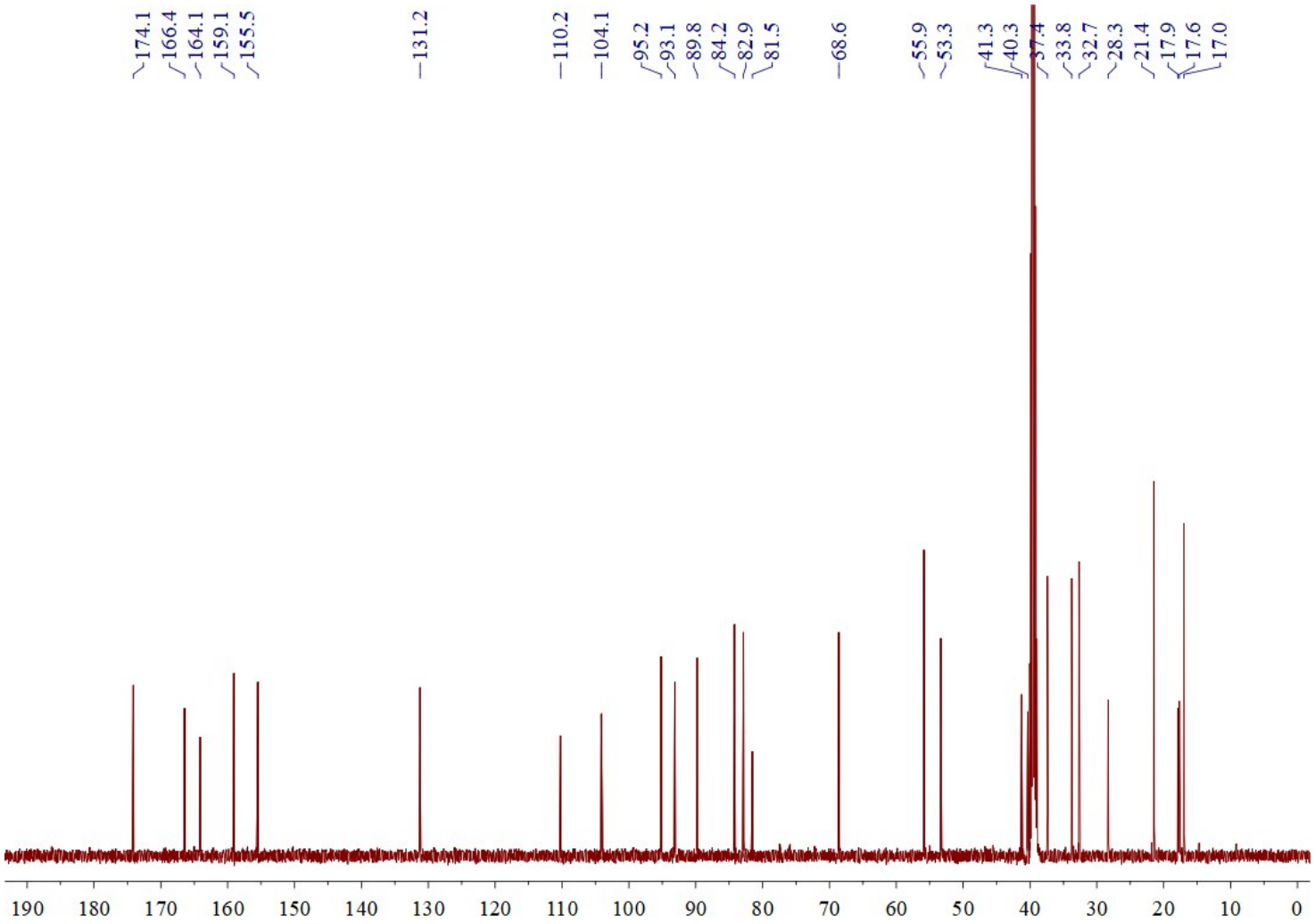


Figure S5. ^{13}C NMR spectrum of **1** in DMSO-d_6 (125 MHz).

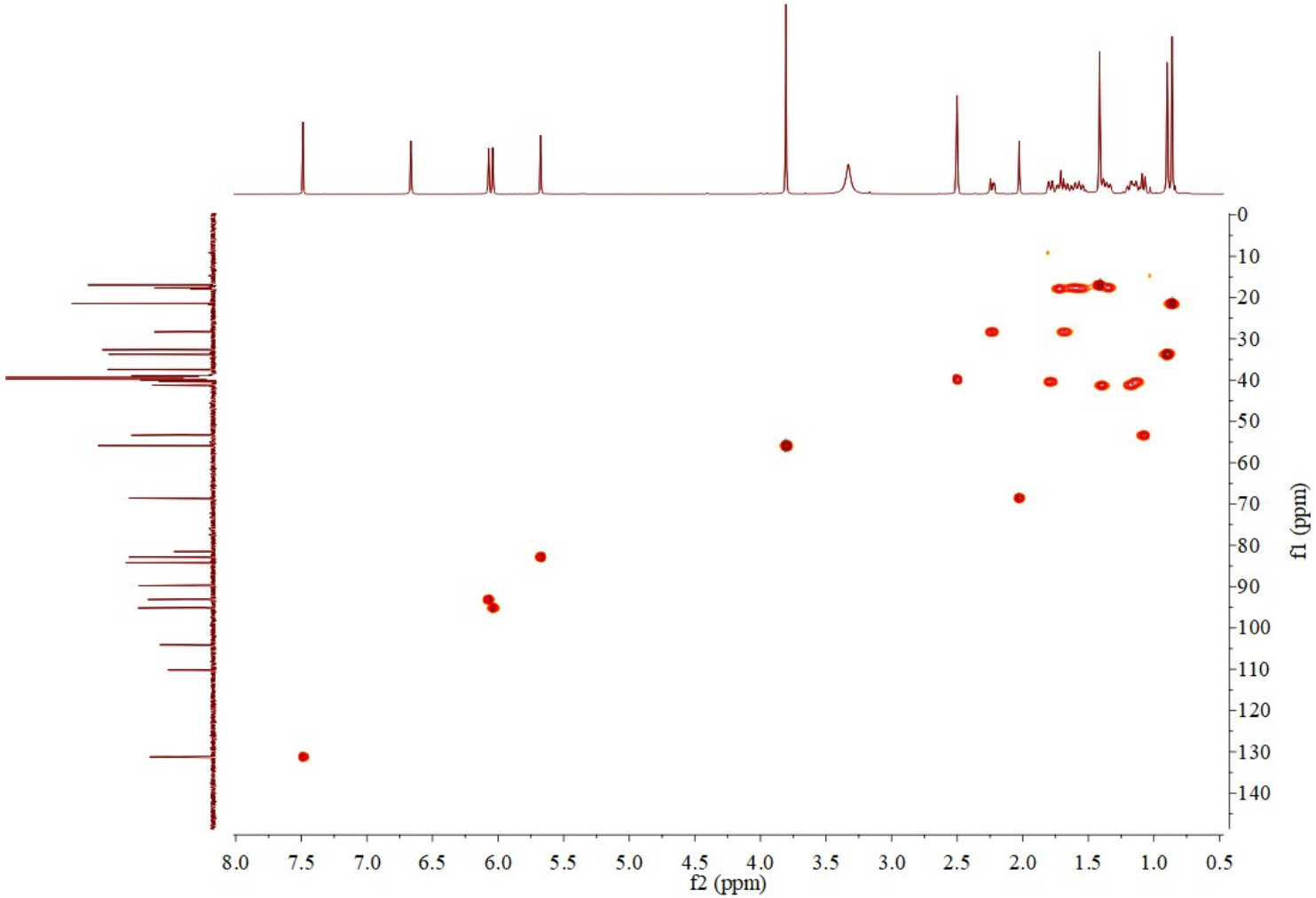


Figure S6. HSQC spectrum of **1** in DMSO-d_6 (500 MHz).

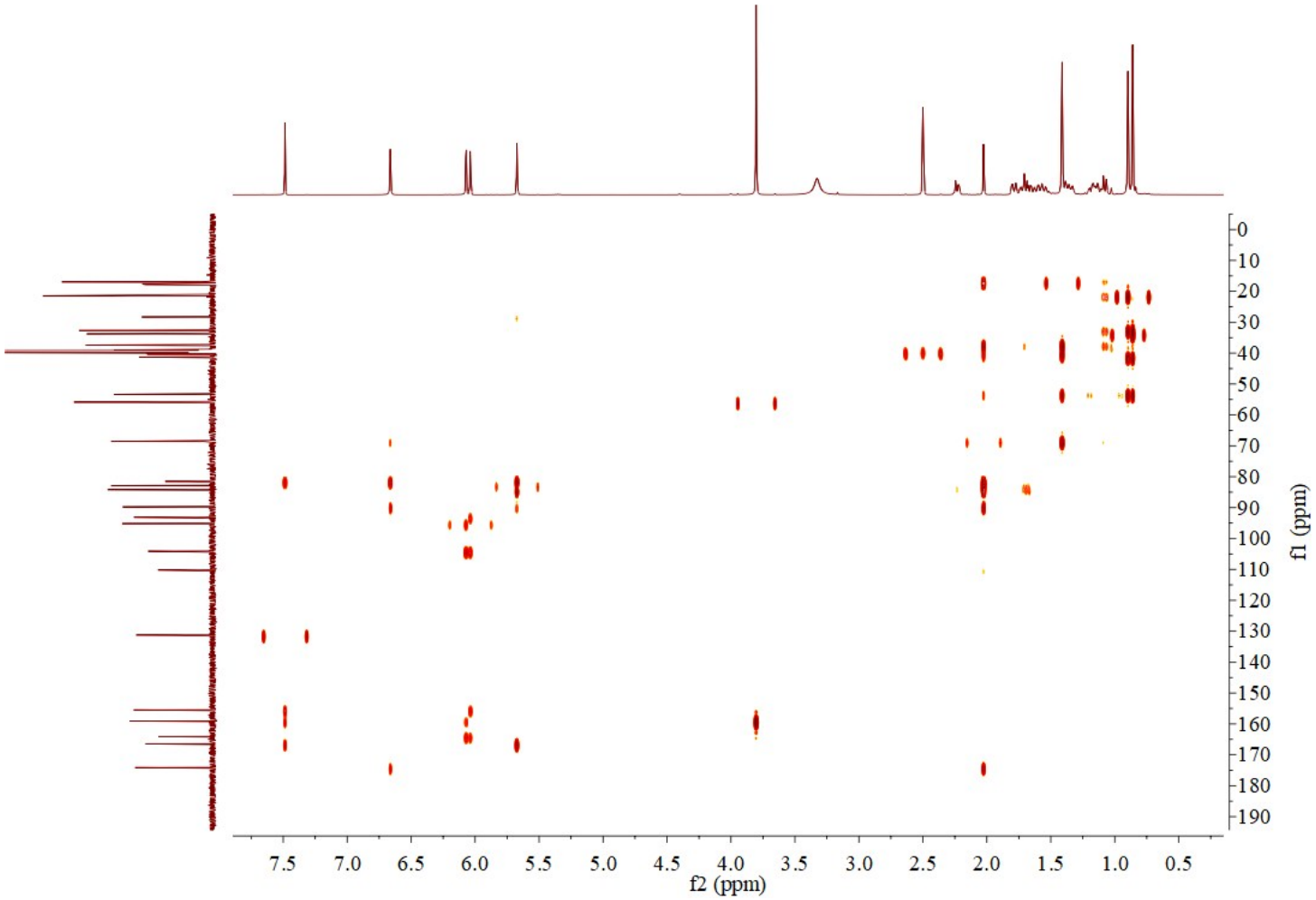


Figure S7. HMBC spectrum of **1** in DMSO-d_6 (500 MHz).

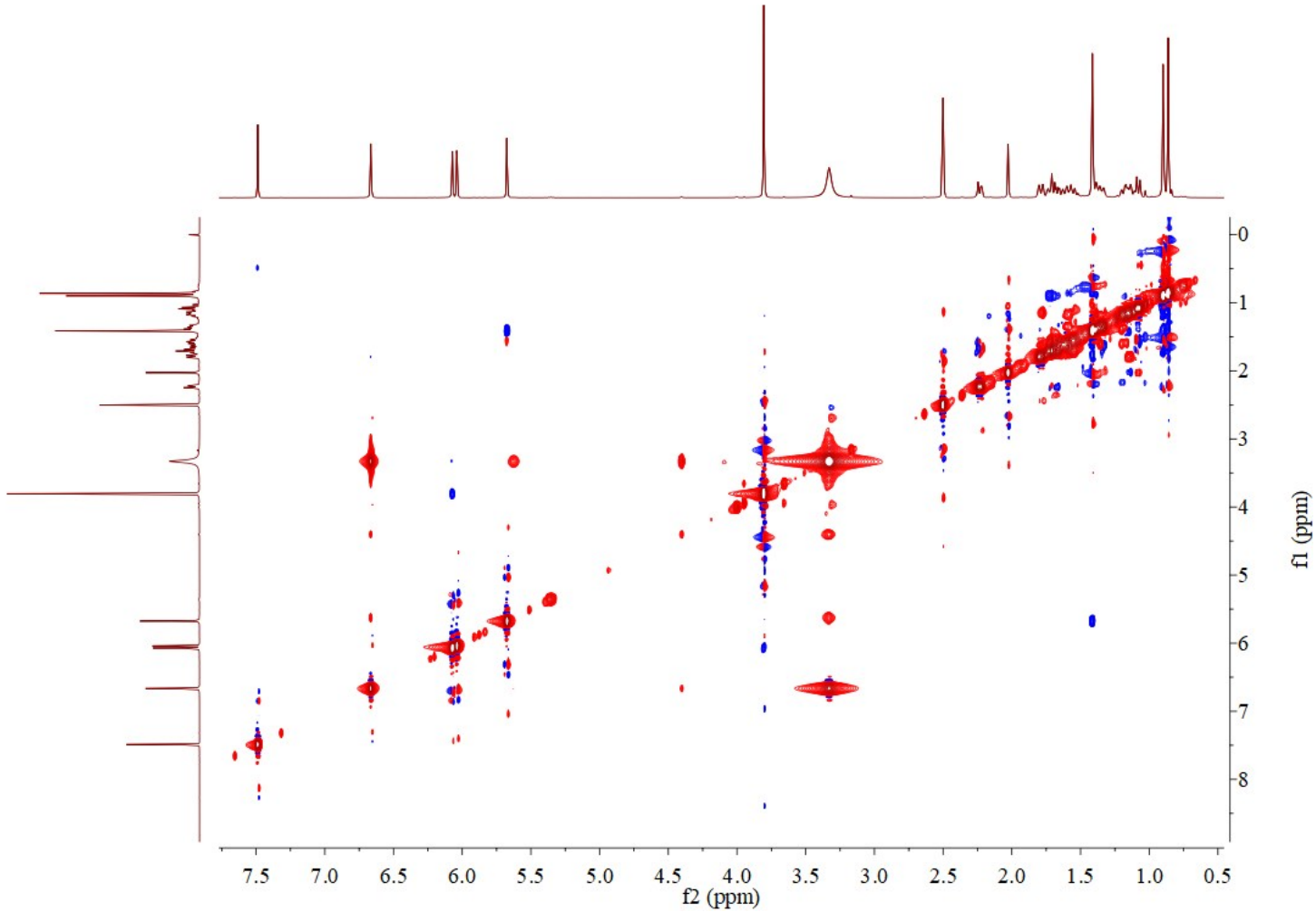


Figure S8. NOESY spectrum of **1** in DMSO-d_6 (500 MHz).

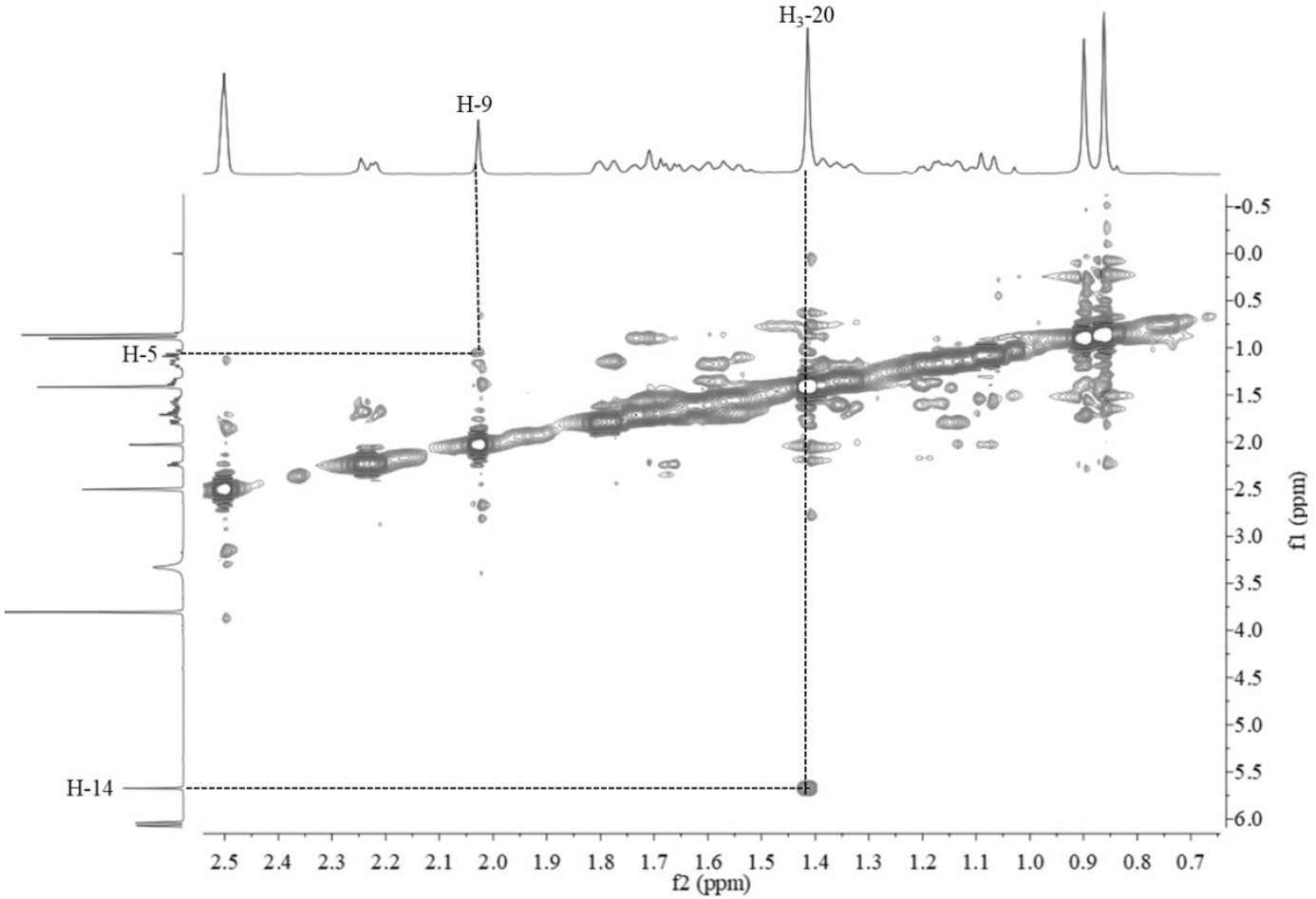


Figure S9. The expansion for NOESY spectrum of **1** in DMSO-d_6 (500 MHz).

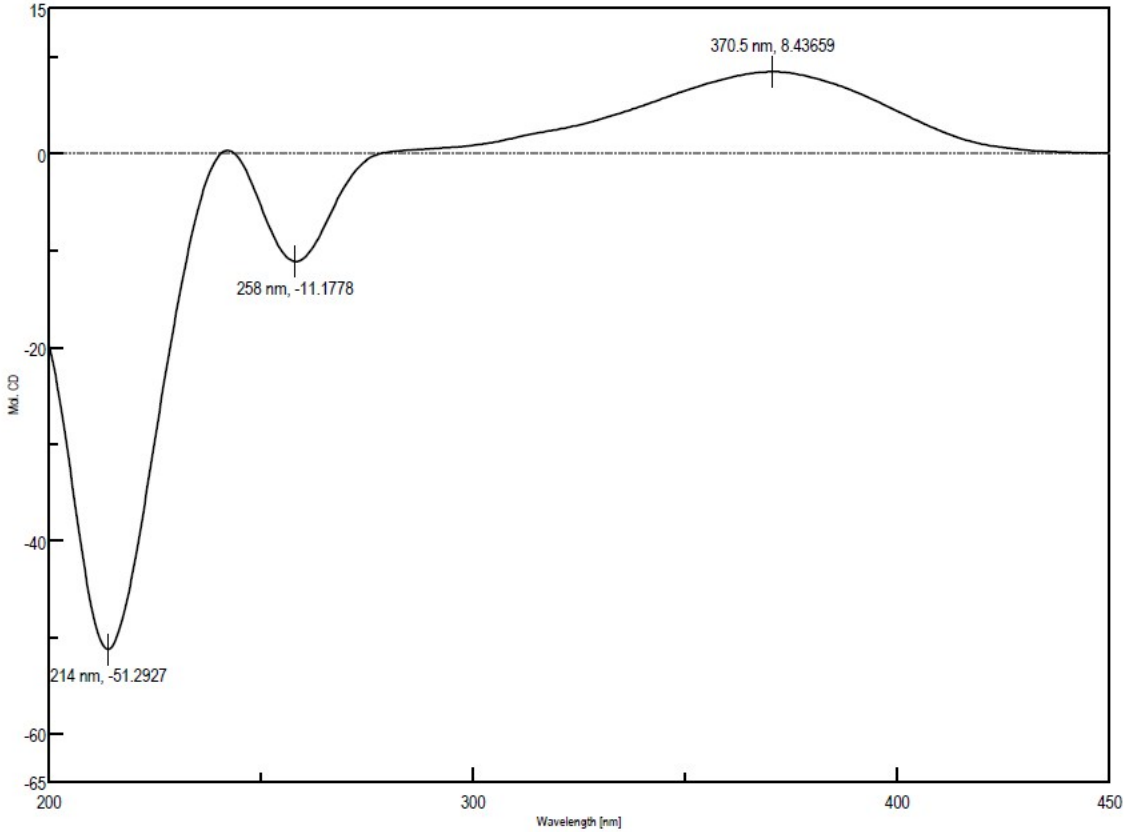


Figure S10. ECD spectrum of **1** in MeOH.