Supporting Information

Ochrasperfloroid, an Ochratoxin-Ergosteroid Heterodimer with Inhibition of IL-6 and NO Production from *Aspergillus flocculosus* 16D-1

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Computational Details.

Methods

Monte Carlo (MCMM) conformational search was carried out by means of the Macromodel 9.9.223[1] software using Merck Molecular Force Field (MMFF) applying a 21 kJ/mol energy window. Conformational analysis of model **I** afforded 276 conformers, which were reclustered excluding the different orientations of the C-22 alkanol side chain. The resulting 6 geometries were subjected to geometry optimization using B3LYP/6-31G(d) with polarizable continuum model (PCM) for DMSO level of theory (Gaussian 09[2]). After dereplication, the resulting 6 reoptimized conformers were submitted to calculate NMR chemical shifts at B3LYP/6-311+G(2d,p) level using PCM model for DMSO (Gaussian 09). Boltzmann distribution was estimated from the B3LYP/6-31G(d) relative thermal free energies (ΔG) in the PCM model for DMSO. The MOLEKEL[3] software package was used for visualization of the results.

Empirical scaling of computed ^{13}C NMR chemical shifts

Computed chemical shifts were scaled empirically[4] according to

$$\delta^{x}_{\text{scaled}} = \frac{\delta^{x}_{\text{calcd}} - \text{intercept}}{\text{slope}},$$

where $\delta^{x}_{\text{calcd}}$ is the calculated chemical shift x (in ppm) relative to tetramethylsilane (TMS), which is calculated at the same level of theory, and slope and intercept are the slope and intercept resulting from a regression calculation on a plot of δ_{calcd} against $\delta_{\text{exptl.}}$

References

(1) MacroModel, Schrödinger LLC, **2012**. http://www.schrodinger.com/productpage/14/11/.

(2) M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al. *Gaussian 09, Revision B.01*, **2010**, Gaussian, Inc., Wallingford CT.

(3) U. Varetto, MOLEKEL 5.4., **2009**, Swiss National Supercomputing Centre: Manno, Switzerland.

(4) G. Barone, L. Gomez-Paloma, D. Duca, A. Silvestri, R. Riccio, G. Bifulco, *Chem Eur J*. **2002**, *8*, 3233−3239.

Results

Figure S1. Conformations of low-energy conformers of model **I** calculated at B3LYP/6-31G(d) level of theory in DMSO (PCM).

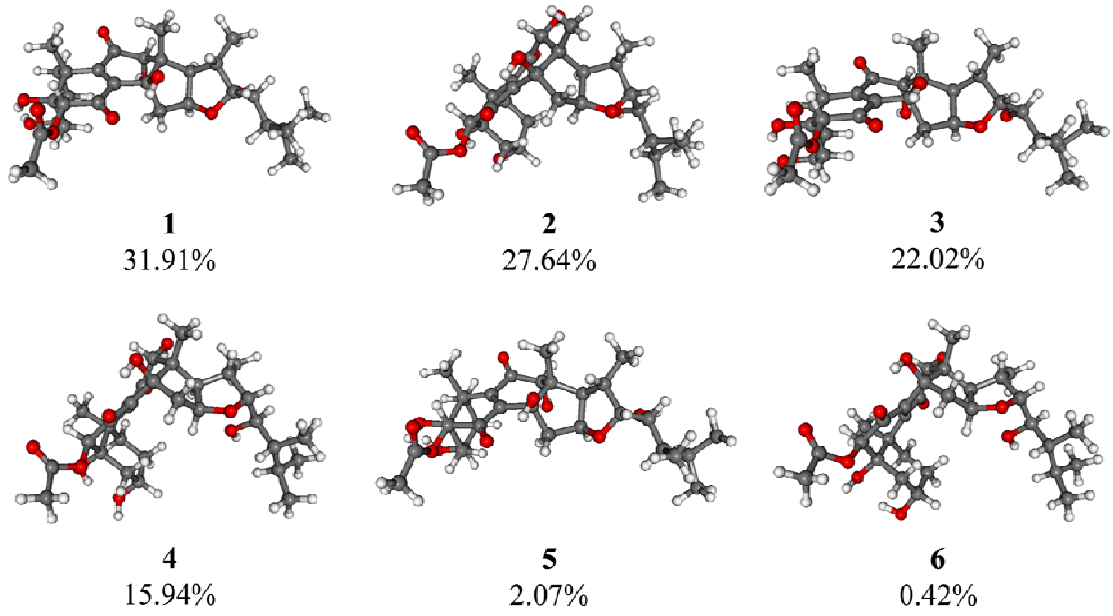

Table S1. Cartesian Coordinates, Gibbs Free Energies (B3LYP/6-31G(d)), and Equilibrium Populations of Low-energy Conformers of Model **I** in DMSO (PCM).

Conformation **1**

ΔG = 0.00 kcal/mol P (%) = 31.91%

1	C	0.05089300	0.10883400	-0.84044500
2	C	0.77574500	-1.23016600	-1.18993500
3	C	0.74260500	0.59596000	0.46466600
4	C	2.17507600	0.03979900	0.43473000
5	C	2.24419900	-1.02552400	-0.69472100
6	C	0.64250100	-1.59482900	-2.68204700
7	O	0.32465100	1.00528500	-1.92206400
8	O	3.11305300	1.07924100	0.09976000
9	C	4.07389700	0.57064700	-0.83066100
10	C	3.27172800	-0.43370400	-1.69565600
11	C	4.10717200	-1.46211000	-2.46269500
12	C	5.33682600	0.03517300	-0.13234000
13	C	6.00859900	1.08959100	0.78702000
14	C	7.17988400	0.48617900	1.61528300
15	O	4.96151000	-1.13933500	0.60589800
16	C	6.42451500	2.34072500	-0.00945900
17	C	7.59537000	1.40703400	2.77445200
18	C	8.40575100	0.09681600	0.77145900

19	C	0.12654300	-2.38665200	-0.40029900
20	C	-1.36777900	-2.45270700	-0.69585100
21	C	-2.14470100	-1.18440700	-0.47216200
22	C	-1.46755900	-0.01364700	-0.63604900
23	O	0.28652300	-2.21633500	1.01349500
24	O	-1.89079400	-3.48466500	-1.09288500
25	C	-3.65460000	-1.27724700	-0.21617400
26	C	-4.17709500	0.05210000	0.46094500
27	C	-3.71695700	1.23848800	-0.39287000
28	C	-2.20231700	1.28008800	-0.56040000
29	O	-1.63219300	2.36475400	-0.64324400
30	C	-4.03392900	-2.45422900	0.72833300
31	C	-3.51451900	-2.29530100	2.16161900
32	C	-4.01122700	-0.99584300	2.79998000
33	C	-3.66668400	0.20370600	1.91766500
34	O	-5.60018200	0.08238200	0.44521900
35	C	-4.35715000	-1.52054300	-1.57933000
36	O	-5.44932400	-0.98780600	2.95264200
37	O	-4.14865600	2.46439900	0.20392500
38	C	-4.64865800	3.42188400	-0.61704200
39	O	-4.77539700	3.28207100	-1.81574200
40	C	-5.01528500	4.65306600	0.16931900
41	H	0.21336000	0.20685100	1.33713900
42	H	0.73954400	1.68759800	0.52255100
43	H	2.45254100	-0.38372100	1.40440100
44	H	2.63457900	-1.96892500	-0.30513600
45	H	1.10090600	-0.83882600	-3.31797900
46	H	1.12074200	-2.55917000	-2.88479300
47	H	-0.40737700	-1.67639700	-2.98499100
48	H	-0.04717100	1.86256600	-1.64189600
49	H	4.38672700	1.41832800	-1.44934100
50	H	2.72761200	0.18503300	-2.41561000
51	H	4.63861300	-2.12757700	-1.77545800
52	H	4.84764400	-0.96908400	-3.10469800
53	H	3.47474500	-2.07788600	-3.11034100
54	H	6.04247900	-0.24394500	-0.92996600
55	H	5.23752600	1.38794500	1.50959900
56	H	6.78952900	-0.42844400	2.08203100
57	H	5.76216000	-1.66051200	0.76733100
58	H	7.02545500	3.02019900	0.60331000
59	H	7.01968800	2.08161000	-0.89386300
60	H	5.55205300	2.90564200	-0.35148300
61	H	8.32758200	0.90614000	3.41899600

62	H	6.73273900	1.67910600	3.39466200
63	H	8.05782600	2.33485700	2.41729200
64	H	9.15943300	-0.39565400	1.39709100
65	H	8.87796200	0.97770700	0.32067500
66	H	8.15202600	-0.59465400	-0.04106900
67	H	0.57421000	-3.33431700	-0.72050900
68	H	0.16344600	-3.08432700	1.43032100
69	H	-4.16365900	1.16541100	-1.39032300
70	H	-3.68894000	-3.39529500	0.30013200
71	H	-5.12827700	-2.50381000	0.74829300
72	H	-2.41592700	-2.28712700	2.17729700
73	H	-3.82551900	-3.15383600	2.77151200
74	H	-3.55225600	-0.86301600	3.78887400
75	H	-4.10595200	1.11245800	2.33976400
76	H	-2.57954600	0.33132700	1.93704300
77	H	-5.89533200	-0.34057900	1.27854400
78	H	-4.06964100	-0.78483700	-2.33725800
79	H	-4.08353900	-2.50853500	-1.95614000
80	H	-5.44038200	-1.47388800	-1.44398300
81	H	-5.72331200	-1.82835200	3.35507500
82	H	-5.47910300	5.38634600	-0.49079000
83	H	-4.11505300	5.08169700	0.62205300
84	H	-5.70072900	4.39287400	0.98161000

Conformation **2**

ΔG = 0.08 kcal/mol P (%) = 27.64%

1	C	0.50394300	2.01716700	-1.12799400
2	C	-0.55878900	2.70875700	-0.19834900
3	C	-0.37320700	1.13916900	-2.05711000
4	C	-1.44285600	0.55744900	-1.13422800
5	C	-1.67362700	1.61278200	-0.01633400
6	C	-1.05898900	4.01417500	-0.84084900
7	O	1.23709300	3.01660100	-1.83330900
8	O	-2.68989500	0.36477500	-1.81410200
9	C	-3.75701500	0.78683300	-0.95083500
10	C	-3.16603000	1.99502600	-0.17773800
11	C	-3.87606600	2.38514400	1.12041200
12	C	-4.31465700	-0.37176600	-0.10607400
13	C	-4.78941400	-1.57265500	-0.96633100
14	C	-5.18925300	-2.79803800	-0.09406000
15	O	-3.28889900	-0.76589600	0.82139600
16	C	-5.89917200	-1.15159700	-1.94806200
17	C	-5.29389800	-4.08447400	-0.92976600

18	C	-6.47043300	-2.58692900	0.73085300
19	C	0.11216800	3.06280100	1.14210000
20	C	0.64915900	1.80382100	1.80878400
21	C	1.54098600	0.92490200	0.98447900
22	C	1.51632100	1.13323000	-0.36346900
23	O	-0.76679700	3.73048400	2.01940600
24	O	0.37068100	1.60639300	2.98645600
25	C	2.53471000	-0.01805200	1.68702000
26	C	3.08168800	-1.10203900	0.67226000
27	C	3.61142500	-0.38033000	-0.56688500
28	C	2.57208700	0.51702500	-1.22271600
29	O	2.66842100	0.77238800	-2.41945000
30	C	1.94202600	-0.80502900	2.89313500
31	C	0.86096900	-1.82157000	2.51310700
32	C	1.37548400	-2.83849000	1.49108200
33	C	1.98877700	-2.13066700	0.28271000
34	O	4.20115200	-1.77612100	1.23657400
35	C	3.68539800	0.86702600	2.23832000
36	O	2.42157200	-3.67169100	2.04283200
37	O	4.07098400	-1.32635500	-1.53664400
38	C	5.31029000	-1.14100800	-2.06001200
39	O	6.04391200	-0.22732400	-1.74623800
40	C	5.62518200	-2.21888500	-3.06323100
41	H	0.19467600	0.38822600	-2.60985900
42	H	-0.84977900	1.80458500	-2.78540200
43	H	-1.12276300	-0.40083500	-0.70810400
44	H	-1.56695100	1.13384200	0.96006600
45	H	-1.49107800	3.84727500	-1.83167300
46	H	-1.81992200	4.47387900	-0.20562800
47	H	-0.23292300	4.72000400	-0.95473200
48	H	1.81159000	2.52433800	-2.44964300
49	H	-4.56569100	1.12706500	-1.60520400
50	H	-3.23993000	2.83888600	-0.87088600
51	H	-3.84521700	1.56645100	1.84623200
52	H	-4.92584000	2.64481200	0.93765900
53	H	-3.38395200	3.25188700	1.57236100
54	H	-5.17452700	0.03229400	0.44968900
55	H	-3.91514500	-1.88150000	-1.55453800
56	H	-4.36064600	-2.96080500	0.60839300
57	H	-3.71298100	-1.22284200	1.56295000
58	H	-6.33605200	-2.02090300	-2.44971000
59	H	-6.71370900	-0.62128100	-1.43939200
60	H	-5.51235700	-0.49207700	-2.73084000

61	H	-5.44752100	-4.95344200	-0.27883000
62	H	-4.37932400	-4.25709800	-1.50990300
63	H	-6.13547900	-4.05158500	-1.63186400
64	H	-6.65178500	-3.45036600	1.38165700
65	H	-7.34873500	-2.47288200	0.08454000
66	H	-6.41453600	-1.69948300	1.37273300
67	H	0.98337600	3.70505300	0.92566400
68	H	-0.70129600	3.24596100	2.86712200
69	H	4.45928700	0.25220700	-0.28069000
70	H	1.56274600	-0.11361600	3.64179100
71	H	2.78454100	-1.33744500	3.34853200
72	H	-0.01741300	-1.31689600	2.08942100
73	H	0.50799400	-2.34469900	3.41214000
74	H	0.55336700	-3.48430100	1.15494800
75	H	2.43847400	-2.86848300	-0.38826200
76	H	1.17771900	-1.64543100	-0.26950300
77	H	3.84821800	-2.56400600	1.70115500
78	H	4.12359100	1.51754500	1.47506800
79	H	3.30614700	1.50802500	3.04054200
80	H	4.47326400	0.22884400	2.64475400
81	H	2.13379000	-3.99728100	2.91140800
82	H	6.63329500	-2.07526200	-3.45250500
83	H	4.90191200	-2.18316800	-3.88432700
84	H	5.54251800	-3.20418200	-2.59401200

Conformation **3**

ΔG = 0.22 kcal/mol P (%) = 22.02%

1	C	0.05427000	0.10048600	-0.84045300
2	C	0.77838400	-1.24142900	-1.18115600
3	C	0.74291500	0.59452300	0.46366100
4	C	2.17370700	0.03281300	0.44501400
5	C	2.24557500	-1.03412800	-0.68360700
6	C	0.64912200	-1.61275300	-2.67186700
7	O	0.33167700	0.99046900	-1.92652900
8	O	3.11888500	1.06730800	0.11582700
9	C	4.08294200	0.55362000	-0.80847900
10	C	3.27104100	-0.43504400	-1.68243800
11	C	4.09055600	-1.44483700	-2.49133000
12	C	5.33043900	0.00343400	-0.08880700
13	C	5.99200500	1.02961800	0.86021400
14	C	7.28661700	0.45126100	1.50299000
15	O	4.99984200	-1.14916400	0.71016200
16	C	6.21543900	2.39476100	0.18545900

17	C	7.66145700	1.19930200	2.79255600
18	C	8.48781800	0.40144000	0.54361200
19	C	0.12633700	-2.39327300	-0.38714700
20	C	-1.36735600	-2.45885500	-0.68684800
21	C	-2.14322600	-1.18889400	-0.47060700
22	C	-1.46470000	-0.01957400	-0.63908000
23	O	0.28360400	-2.21482500	1.02562400
24	O	-1.89021400	-3.49169000	-1.08152100
25	C	-3.65369000	-1.27734100	-0.21775300
26	C	-4.17183800	0.05526000	0.45601600
27	C	-3.71283200	1.23768200	-0.40260500
28	C	-2.19792500	1.27557800	-0.57121000
29	O	-1.62637200	2.35891800	-0.66099100
30	C	-4.04177500	-2.45142700	0.72753700
31	C	-3.53598300	-2.29155600	2.16634400
32	C	-4.02792200	-0.99017200	2.79480300
33	C	-3.65974400	0.20729900	1.91167500
34	O	-5.59507500	0.08623400	0.44715600
35	C	-4.35350000	-1.52025600	-1.58252900
36	O	-5.46793500	-1.09591300	2.93828100
37	O	-4.14166300	2.46644600	0.19055300
38	C	-4.63516400	3.42433000	-0.63413000
39	O	-4.75964400	3.28204600	-1.83272700
40	C	-4.99802300	4.65913700	0.14828600
41	H	0.20841100	0.21471100	1.33702300
42	H	0.74417600	1.68654400	0.51274200
43	H	2.44142500	-0.39258600	1.41606300
44	H	2.63306800	-1.97899100	-0.29180100
45	H	1.11118000	-0.86060000	-3.30982100
46	H	1.12487500	-2.57953700	-2.86872900
47	H	-0.40002800	-1.69253400	-2.97752100
48	H	-0.04127800	1.84944500	-1.65289700
49	H	4.40950400	1.39798900	-1.42599900
50	H	2.72253400	0.19930100	-2.38498600
51	H	4.60281100	-2.17561500	-1.85418600
52	H	4.85185700	-0.93928800	-3.09726900
53	H	3.45175000	-2.01128000	-3.17572500
54	H	6.05608900	-0.28092100	-0.86497000
55	H	5.27050300	1.17659600	1.67542900
56	H	7.04561400	-0.58005900	1.78680200
57	H	5.12527300	-1.94211900	0.16904900
58	H	6.80835100	3.05500200	0.82724000
59	H	6.74825100	2.29926000	-0.76849400

60	H	5.26587400	2.90112100	-0.01089900
61	H	8.52386700	0.72656100	3.27822200
62	H	6.83103800	1.19735500	3.50918900
63	H	7.93142900	2.24467100	2.59716800
64	H	9.33213400	-0.11328300	1.01774100
65	H	8.82963900	1.40697100	0.27002500
66	H	8.25684900	-0.13566500	-0.38393500
67	H	0.57362700	-3.34316600	-0.70136100
68	H	0.15556600	-3.07947700	1.44791300
69	H	-4.16075400	1.16222100	-1.39933900
70	H	-3.69133000	-3.39313500	0.30493600
71	H	-5.13599900	-2.50363900	0.73684500
72	H	-2.43790600	-2.28736100	2.18915000
73	H	-3.86704400	-3.13875400	2.77731200
74	H	-3.58418100	-0.86338300	3.78973000
75	H	-4.08186200	1.12860000	2.32658300
76	H	-2.57018000	0.32040800	1.93149300
77	H	-5.88269200	-0.36315700	1.27017000
78	H	-4.05799900	-0.78982400	-2.34247000
79	H	-4.08608200	-2.51177300	-1.95464600
80	H	-5.43685100	-1.46531900	-1.45098700
81	H	-5.75576700	-0.39189700	3.54303000
82	H	-5.45809600	5.39233100	-0.51452800
83	H	-4.09665600	5.08557100	0.60085100
84	H	-5.68551700	4.40404700	0.96045900

Conformation **4**

ΔG = 0.41 kcal/mol P (%) = 15.94%

1	C	0.50446800	2.01574800	-1.13257100
2	C	-0.55899200	2.70965000	-0.20553100
3	C	-0.37194500	1.13465600	-2.05942800
4	C	-1.44148000	0.55502800	-1.13511900
5	C	-1.67266600	1.61307700	-0.01987900
6	C	-1.06043400	4.01223800	-0.85276100
7	O	1.23763000	3.01332900	-1.84053800
8	O	-2.68847100	0.36026700	-1.81447900
9	C	-3.75573900	0.78322500	-0.95178300
10	C	-3.16554600	1.99343600	-0.18119600
11	C	-3.87512800	2.38512300	1.11674400
12	C	-4.31215000	-0.37416200	-0.10455800
13	C	-4.78700300	-1.57676100	-0.96239300
14	C	-5.18499300	-2.80104900	-0.08777000
15	O	-3.28537000	-0.76613000	0.82267500

16	C	-5.89816900	-1.15802600	-1.94353600
17	C	-5.28929900	-4.08892000	-0.92130200
18	C	-6.46562000	-2.58968700	0.73792600
19	C	0.11149900	3.06925100	1.13379400
20	C	0.64826000	1.81257000	1.80492100
21	C	1.54143100	0.93180800	0.98417500
22	C	1.51681100	1.13476300	-0.36462500
23	O	-0.76786900	3.73981200	2.00850300
24	O	0.36708900	1.61777900	2.98237800
25	C	2.53686400	-0.00756300	1.68863100
26	C	3.07717800	-1.09826100	0.67751700
27	C	3.60966400	-0.38448000	-0.56418200
28	C	2.57217200	0.51467800	-1.22156500
29	O	2.66978300	0.76727600	-2.41879700
30	C	1.95069900	-0.78693200	2.90317700
31	C	0.87211500	-1.81240400	2.53729100
32	C	1.38272500	-2.83070500	1.52069800
33	C	1.97905200	-2.12421000	0.29753400
34	O	4.19155700	-1.77848800	1.24489700
35	C	3.69129400	0.88006300	2.22824400
36	O	2.39142100	-3.63497100	2.18564800
37	O	4.06332200	-1.33619500	-1.53138700
38	C	5.29642300	-1.14939900	-2.06898000
39	O	6.03103500	-0.23281300	-1.76630300
40	C	5.60302200	-2.22967100	-3.07222500
41	H	0.19651300	0.38238200	-2.60975400
42	H	-0.84866500	1.79764900	-2.78981500
43	H	-1.12106800	-0.40204300	-0.70645500
44	H	-1.56479400	1.13661800	0.95759900
45	H	-1.49279900	3.84128700	-1.84278100
46	H	-1.82147100	4.47376500	-0.21899300
47	H	-0.23493900	4.71825200	-0.96958800
48	H	1.81311500	2.51935700	-2.45458300
49	H	-4.56482100	1.12151400	-1.60665100
50	H	-3.24075500	2.83600800	-0.87575800
51	H	-3.84300800	1.56773800	1.84398400
52	H	-4.92527000	2.64350400	0.93428200
53	H	-3.38348700	3.25311200	1.56682000
54	H	-5.17177100	0.03038000	0.45122500
55	H	-3.91317500	-1.88592100	-1.55110400
56	H	-4.35562300	-2.96189700	0.61421500
57	H	-3.70858100	-1.22095400	1.56603200
58	H	-6.33502400	-2.02841600	-2.44333300

59	H	-6.71249700	-0.62749800	-1.43475400
60	H	-5.51276400	-0.49944000	-2.72779800
61	H	-5.44164200	-4.95696800	-0.26884200
62	H	-4.37508600	-4.26172600	-1.50196800
63	H	-6.13151000	-4.05785500	-1.62272900
64	H	-6.64556000	-3.45213400	1.39042800
65	H	-7.34462100	-2.47760300	0.09221800
66	H	-6.40995300	-1.70105500	1.37817900
67	H	0.98238300	3.71112000	0.91516000
68	H	-0.70464900	3.25645200	2.85707900
69	H	4.46084700	0.24542500	-0.28212000
70	H	1.56876600	-0.08963600	3.64511700
71	H	2.79608300	-1.30967800	3.36403000
72	H	-0.00851100	-1.31231800	2.11396800
73	H	0.53727900	-2.33922500	3.43798500
74	H	0.56403100	-3.48747700	1.20279800
75	H	2.41976500	-2.85763900	-0.38575500
76	H	1.16201000	-1.63696400	-0.24567600
77	H	3.82585300	-2.54373300	1.73822100
78	H	4.12281300	1.52918700	1.46000400
79	H	3.31780500	1.52275200	3.03186700
80	H	4.48291400	0.24365100	2.63026900
81	H	2.54902500	-4.42156000	1.63746000
82	H	6.60953600	-2.08952400	-3.46687000
83	H	4.87588000	-2.19196800	-3.88987300
84	H	5.51933300	-3.21434400	-2.60199400

Conformation **5**

ΔG = 1.61 kcal/mol P (%) = 2.07%

1	C	0.03622800	0.14301600	-0.79858600
2	C	0.75749900	-1.17128800	-1.23524200
3	C	0.73776800	0.54972400	0.52815800
4	C	2.17143500	0.00139500	0.44836900
5	C	2.23071100	-0.99451800	-0.74326700
6	C	0.60771500	-1.44662100	-2.74463900
7	O	0.30112800	1.10513000	-1.82473900
8	O	3.10116400	1.06277000	0.16419600
9	C	4.05505100	0.61254400	-0.80299300
10	C	3.24804100	-0.34318200	-1.71729100
11	C	4.07896500	-1.32380800	-2.54900800
12	C	5.32608300	0.04254400	-0.14788000
13	C	6.00340100	1.04608700	0.82291000
14	C	7.17696600	0.39830700	1.61375200

15	O	4.95991800	-1.17299000	0.52546200
16	C	6.41841100	2.33613300	0.09068100
17	C	7.60436500	1.26039800	2.81301300
18	C	8.39539200	0.04377600	0.74418100
19	C	0.11779800	-2.37272000	-0.50812600
20	C	-1.38168800	-2.42638600	-0.78128900
21	C	-2.15746500	-1.17103100	-0.48774000
22	C	-1.48059800	0.00706700	-0.59457100
23	O	0.29926500	-2.28804100	0.91041000
24	O	-1.90932200	-3.44284400	-1.21034100
25	C	-3.66713700	-1.29216600	-0.21513200
26	C	-4.17443200	0.01977600	0.47970100
27	C	-3.73195800	1.21982300	-0.36494500
28	C	-2.21433400	1.29669800	-0.45208900
29	O	-1.64827200	2.38401500	-0.42162300
30	C	-4.00759100	-2.49009700	0.72122700
31	C	-3.47318200	-2.33724800	2.14866300
32	C	-4.01709200	-1.06298800	2.80873900
33	C	-3.67734400	0.15822000	1.94199600
34	O	-5.61326500	-0.03710100	0.48413500
35	C	-4.38352300	-1.53256400	-1.57346900
36	O	-5.42310800	-1.15868500	3.06173000
37	O	-4.26079400	2.41282800	0.22213600
38	C	-4.55136400	3.44872900	-0.62068200
39	O	-4.43706500	3.37549200	-1.82372500
40	C	-5.02412900	4.64536000	0.15913900
41	H	0.21800400	0.10487500	1.37922300
42	H	0.73235200	1.63553300	0.65479700
43	H	2.46191800	-0.47800300	1.38765600
44	H	2.62524300	-1.95889700	-0.41403800
45	H	1.05404800	-0.65103300	-3.33966100
46	H	1.08852800	-2.39411700	-3.01048100
47	H	-0.44557400	-1.51656300	-3.03886000
48	H	-0.03977600	1.95100800	-1.48054600
49	H	4.35904100	1.49588000	-1.37433200
50	H	2.69649500	0.31399100	-2.39621200
51	H	4.61817500	-2.02589800	-1.90566500
52	H	4.81237700	-0.79291700	-3.16850900
53	H	3.44198100	-1.90338500	-3.22502000
54	H	6.02516200	-0.18874900	-0.96636500
55	H	5.23611600	1.30788900	1.56352000
56	H	6.78479700	-0.53570500	2.03867300
57	H	5.76478900	-1.69542400	0.66001300

58	H	7.02167600	2.98268500	0.73589400
59	H	7.01082700	2.12227600	-0.80755200
60	H	5.54573300	2.91885000	-0.21946800
61	H	8.33576700	0.72425500	3.42949400
62	H	6.74657100	1.50884700	3.44961700
63	H	8.07206300	2.20073900	2.49798000
64	H	9.15150500	-0.47965600	1.34107500
65	H	8.86783700	0.94277000	0.33095500
66	H	8.13336400	-0.60874600	-0.09748300
67	H	0.55966100	-3.29938900	-0.89191700
68	H	0.16657700	-3.17642500	1.27889400
69	H	-4.12483000	1.12915800	-1.38256700
70	H	-3.64738800	-3.41442500	0.26939700
71	H	-5.10015700	-2.56830100	0.75636000
72	H	-2.37446500	-2.29935300	2.14478400
73	H	-3.76306800	-3.20679500	2.74960600
74	H	-3.55107100	-0.93418800	3.79234200
75	H	-4.12664600	1.05771700	2.37676500
76	H	-2.59200500	0.30602800	1.96254300
77	H	-5.92648000	0.84937400	0.73784000
78	H	-4.13772300	-0.77153100	-2.32051600
79	H	-4.07301900	-2.50014700	-1.97190400
80	H	-5.46590000	-1.53749100	-1.42712900
81	H	-5.86239700	-0.94126400	2.21846900
82	H	-5.34079100	5.42930500	-0.52901700
83	H	-4.20908100	5.01574400	0.78980600
84	H	-5.85137300	4.36703200	0.81893700

Conformation **6**

ΔG = 2.55 kcal/mol P (%) = 0.42%

1	C	-0.56319600	-2.00624500	-1.03154800
2	C	0.48825000	-2.69433600	-0.08651100
3	C	0.33062200	-1.19124400	-2.00163800
4	C	1.42628700	-0.60711700	-1.11145600
5	C	1.63456200	-1.62406900	0.04588700
6	C	0.94489800	-4.03602800	-0.68509600
7	O	-1.33510500	-3.00641900	-1.69255000
8	O	2.67243600	-0.48080100	-1.80803400
9	C	3.73322200	-0.89530400	-0.93313800
10	C	3.11448900	-2.05455400	-0.10867100
11	C	3.82298200	-2.41289400	1.19937800
12	C	4.32562700	0.28114200	-0.13817100
13	C	4.82858200	1.43321300	-1.04745700

14	C	5.26570700	2.68110400	-0.22628500
15	O	3.31518500	0.73929500	0.77667000
16	C	5.92229700	0.94293900	-2.01489800
17	C	5.40482500	3.92895700	-1.11389900
18	C	6.54269200	2.46710800	0.60442600
19	C	-0.17987600	-2.97637800	1.26921100
20	C	-0.68047200	-1.68439100	1.90214800
21	C	-1.52348300	-0.78569200	1.04679700
22	C	-1.53534500	-1.06085000	-0.28978500
23	O	0.68782300	-3.63952800	2.16088200
24	O	-0.44166700	-1.49054200	3.08890400
25	C	-2.42639000	0.25776300	1.73536000
26	C	-3.03540200	1.22660800	0.65944700
27	C	-3.65378400	0.38607800	-0.45894000
28	C	-2.60082100	-0.46477500	-1.15273600
29	O	-2.69720300	-0.70854700	-2.34960700
30	C	-1.67916500	1.13938100	2.78594900
31	C	-0.64410400	2.10080700	2.19524400
32	C	-1.28592600	3.04576400	1.17141300
33	C	-1.99834000	2.22692600	0.08579500
34	O	-4.08128100	1.96946700	1.31275900
35	C	-3.53564000	-0.52460000	2.49346700
36	O	-2.17185300	3.97997400	1.79763800
37	O	-4.28883200	1.25643300	-1.39991600
38	C	-5.40964700	0.78722500	-2.02873600
39	O	-5.90711400	-0.28762700	-1.77955900
40	C	-5.90575600	1.78864000	-3.03549300
41	H	-0.22011500	-0.44621600	-2.57885500
42	H	0.77891700	-1.89986300	-2.70675900
43	H	1.13958000	0.37690900	-0.72246300
44	H	1.54704000	-1.10505700	1.00383400
45	H	1.37323900	-3.91770800	-1.68445900
46	H	1.69766600	-4.49453600	-0.03937200
47	H	0.09796200	-4.72133500	-0.76685300
48	H	-1.88180400	-2.52732100	-2.34226500
49	H	4.52880900	-1.28323700	-1.57687500
50	H	3.15950400	-2.92691300	-0.76820400
51	H	3.81971300	-1.56597600	1.89273000
52	H	4.86396000	-2.70799600	1.02017800
53	H	3.31087800	-3.24752800	1.68796300
54	H	5.17698000	-0.12331300	0.43025800
55	H	3.96038000	1.74225200	-1.64450800
56	H	4.44421100	2.89617800	0.47039600

57	H	3.75406400	1.21636900	1.49657900
58	H	6.38066300	1.77922600	-2.55216000
59	H	6.72408900	0.41127500	-1.48772300
60	H	5.51451900	0.26346200	-2.76947000
61	H	5.58377300	4.81906000	-0.49901300
62	H	4.49442900	4.10334500	-1.70004800
63	H	6.24396000	3.84393900	-1.81454900
64	H	6.75100700	3.35120700	1.21834300
65	H	7.41536200	2.30062500	-0.03815200
66	H	6.46301000	1.60919400	1.28291100
67	H	-1.07450800	-3.59731900	1.08389500
68	H	0.59554700	-3.16524500	3.01159900
69	H	-4.41008100	-0.29186600	-0.04914700
70	H	-1.22380300	0.49853700	3.53732500
71	H	-2.45161700	1.72642900	3.29639100
72	H	0.17403000	1.54653100	1.71441100
73	H	-0.19516600	2.69498600	2.99956100
74	H	-0.50789200	3.65424300	0.69651000
75	H	-2.51519800	2.89950200	-0.60736800
76	H	-1.23946700	1.69574000	-0.49908700
77	H	-4.58201000	2.42228100	0.61090900
78	H	-4.07496700	-1.22711400	1.85061400
79	H	-3.08236500	-1.09991300	3.30519200
80	H	-4.25605800	0.17348300	2.92390000
81	H	-3.01188300	3.50345900	1.93325500
82	H	-6.85002700	1.44542500	-3.45846200
83	H	-5.16429700	1.90230800	-3.83330500
84	H	-6.03730400	2.76782000	-2.56553100

Table S2. Comparison of Experimental ^{13}C NMR Chemical Shifts of Moiety **B** in **1** and Calculated ^{13}C NMR Chemical Shifts of Model **I** (B3LYP/6-311+G(2d,p)/PCM(DMSO))[a]

Nucleus #	Exptl	Calcd[b]	Nucleus #	Exptl	Calcd[b]
1	23.1	24.4	13	54.7	54.7
2	29.2	30.5	14	80.7	82.5
3	64.4	68.3	15	49.6	47.3
4	31.8	31.0	16	85	83.0
5	75.1	76.0	17	58.7	57.4
6	78.5	75.2	18	15.14	14.7
7	193.7	196.0	19	22.7	21.1
8	145.5	142.6	20	38.7	40.5
9	146.8	149.4	21	15.08	12.8
10	**44.2**	**48.6**	22	81.6	82.2
11	202.5	200.7		CMAE[c]	1.9
12	82.1	79.8		RMSD[d]	2.2
				largest outlier[e]	$\Delta\delta = 4.4$

[a] Since our conformational search disregarding the orientations of the C-22 alkanol side chain, this NMR chemical shifts comparison did not include the chemical shifts of the C-22 alkanol side chain. [b] See computational details. [c] CMAE = corrected mean absolute error, computed as $(1/n)\sum_i^n |\delta_{calcd} - \delta_{exptl}|$, where δ_{calcd} refers to the scaled calculated chemical shifts here. [d] RMSD = root-mean-square deviation. [e] Largest outlier is highlighted in bold text.

Figure S2. ^{1}H-NMR spectrum of **1** in DMSO-d_6.

Figure S3. ^{13}C-NMR spectrum of **1** in DMSO-d_6.

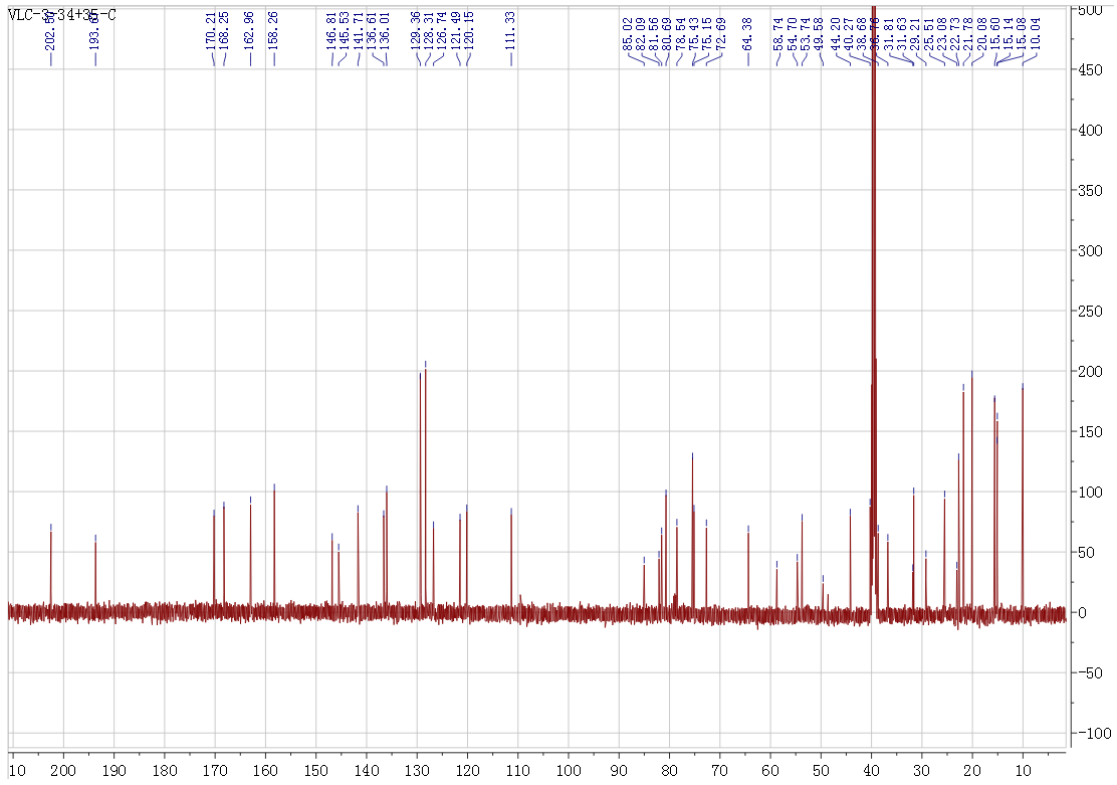

Figure S4. DEPT135 spectrum of **1** in DMSO-d_6.

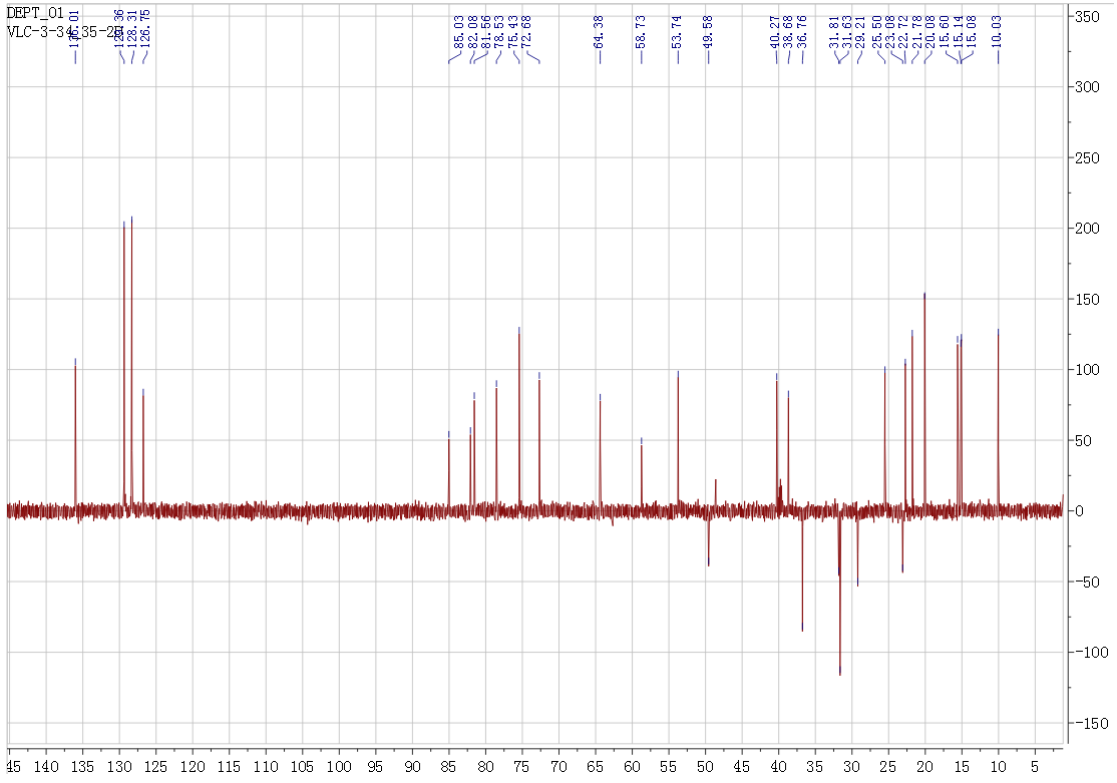

Figure S5. ^{1}H-^{1}H COSY spectrum of **1** in DMSO-d_6.

Figure S6. HSQC spectrum of **1** in DMSO-d_6.

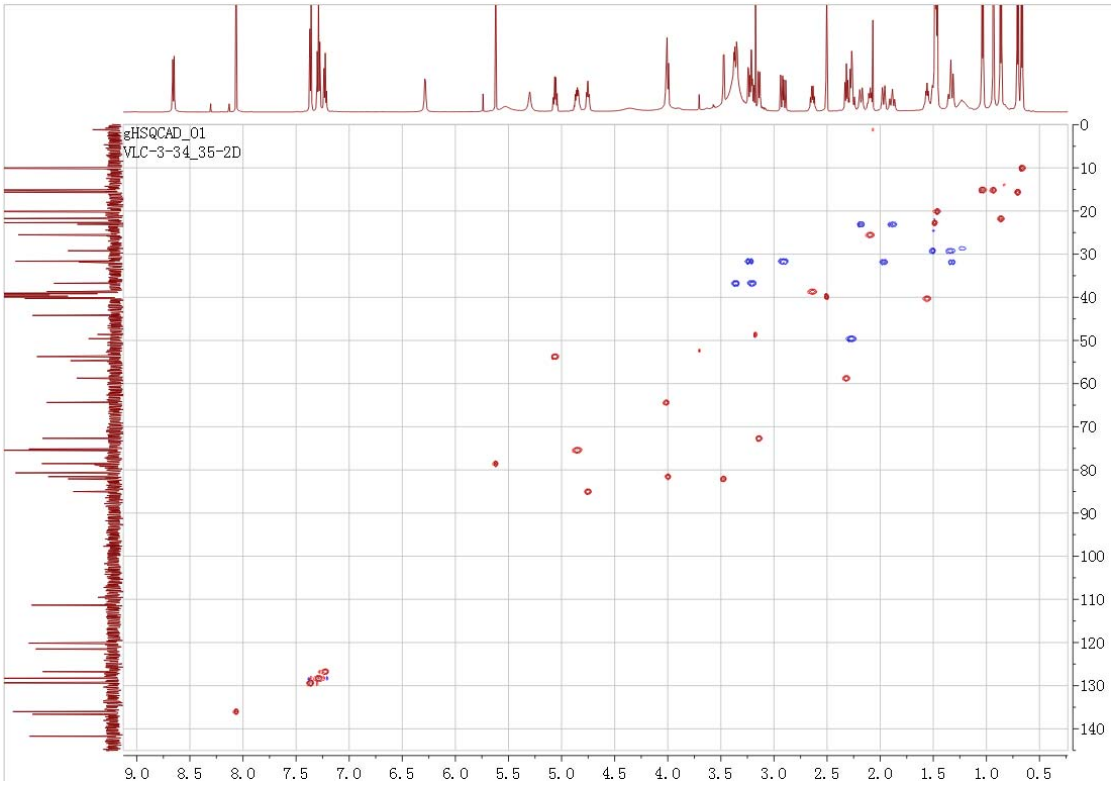

Figure S7. HMBC spectrum of **1** in DMSO-d_6.

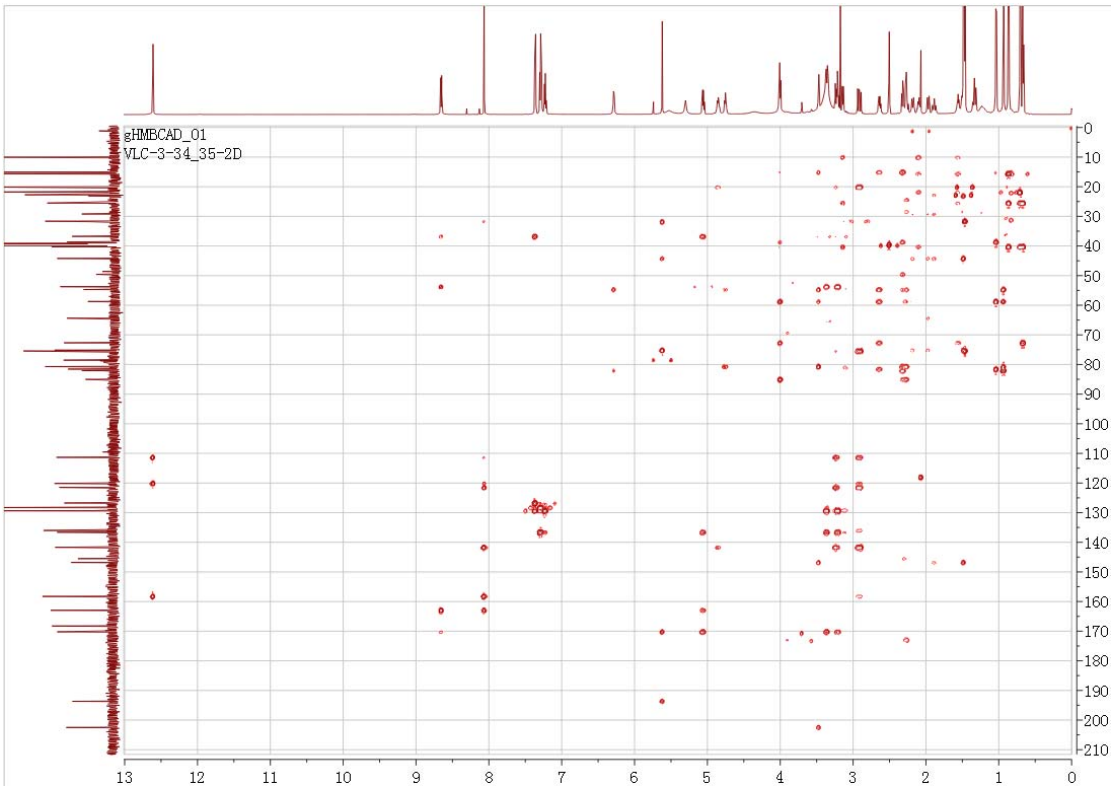

Figure S8. ROESY spectrum of **1** in DMSO-d_6.

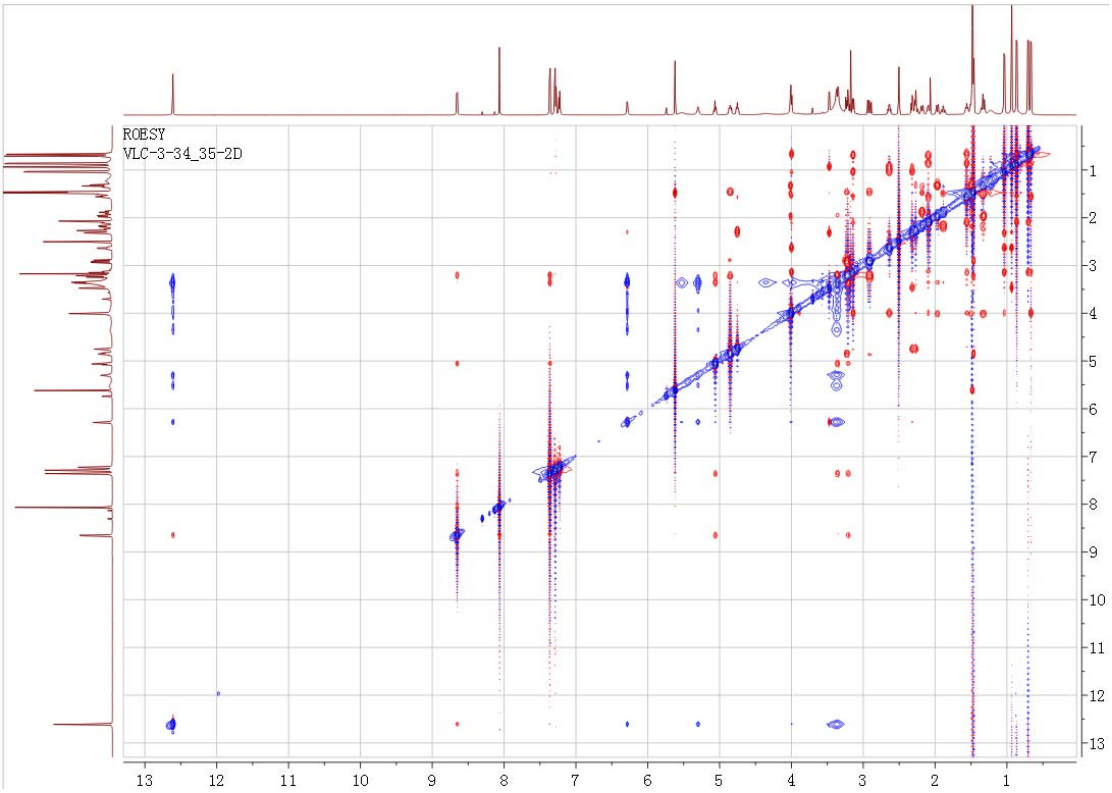

Figure S9. HRESIMS of **1**.

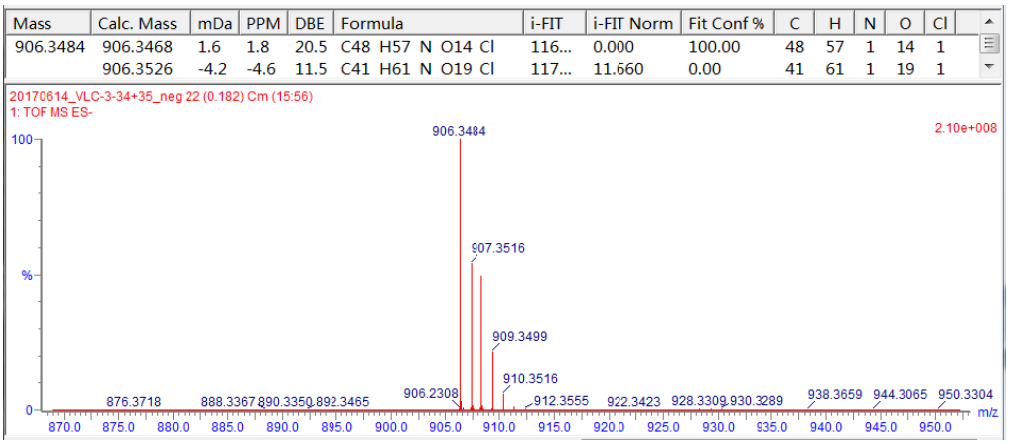

Figure S10. HRESIMS/MS of **1** (**a**) positive ion mode; (**b**) negative ion mode.

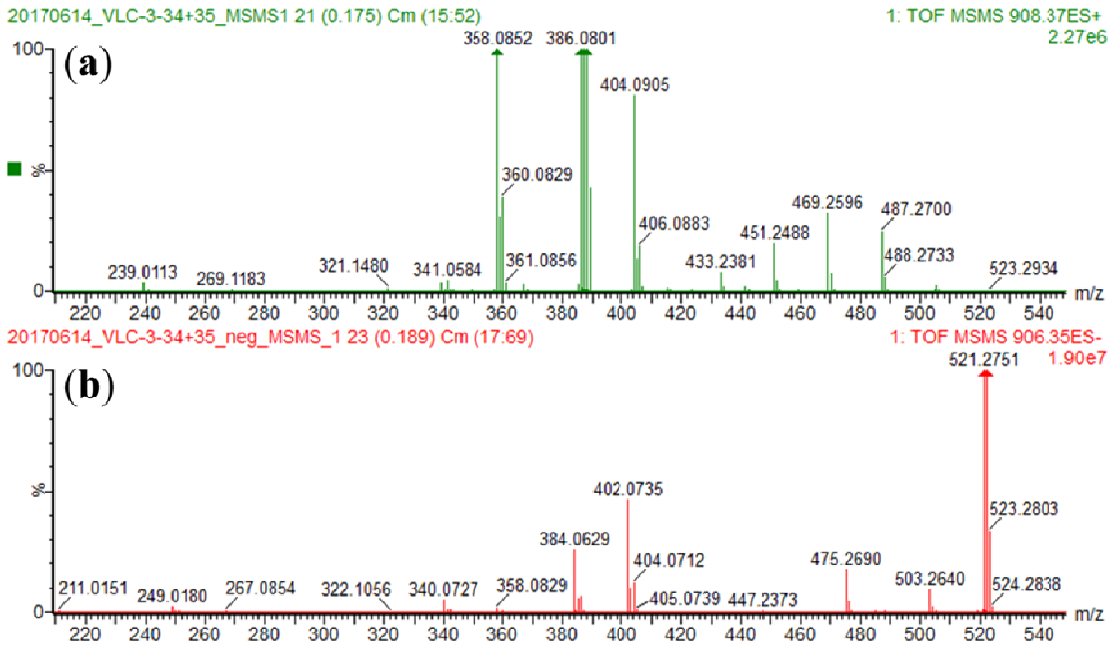

Figure S11. UV spectrum of **1** in MeOH.

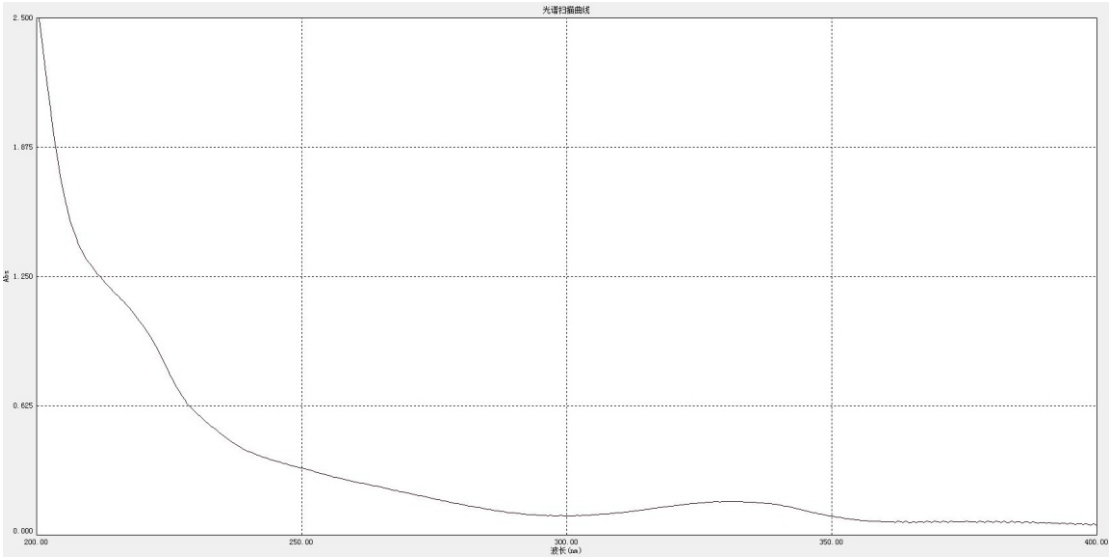

Figure S12. IR spectrum of **1**.

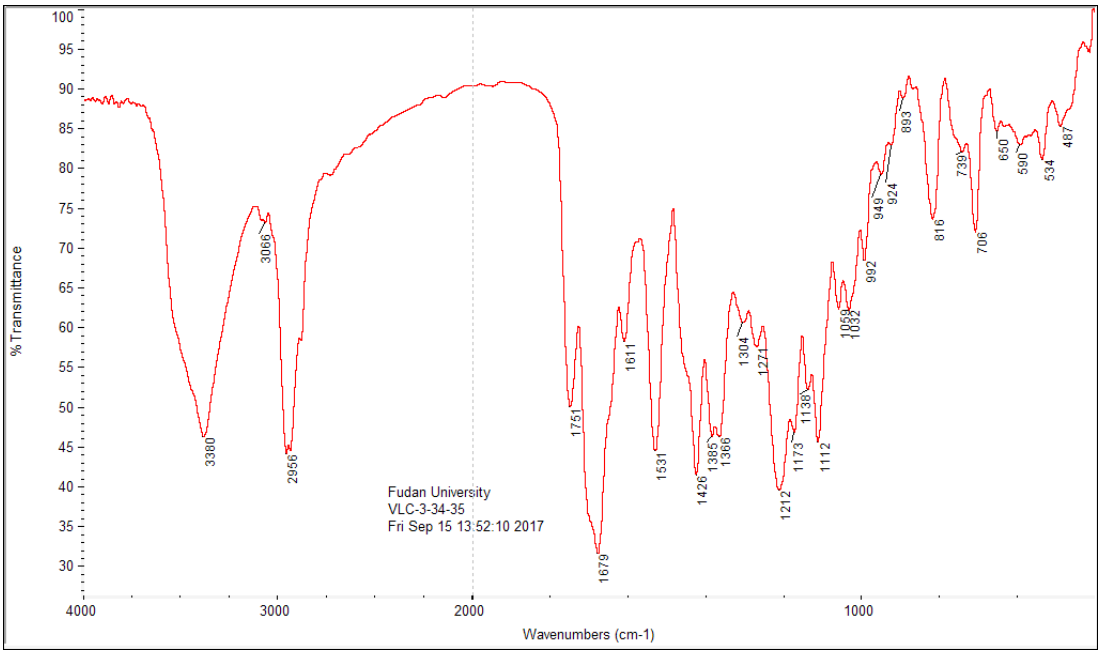

Figure S13. ECD spectrum of **1** in MeOH.

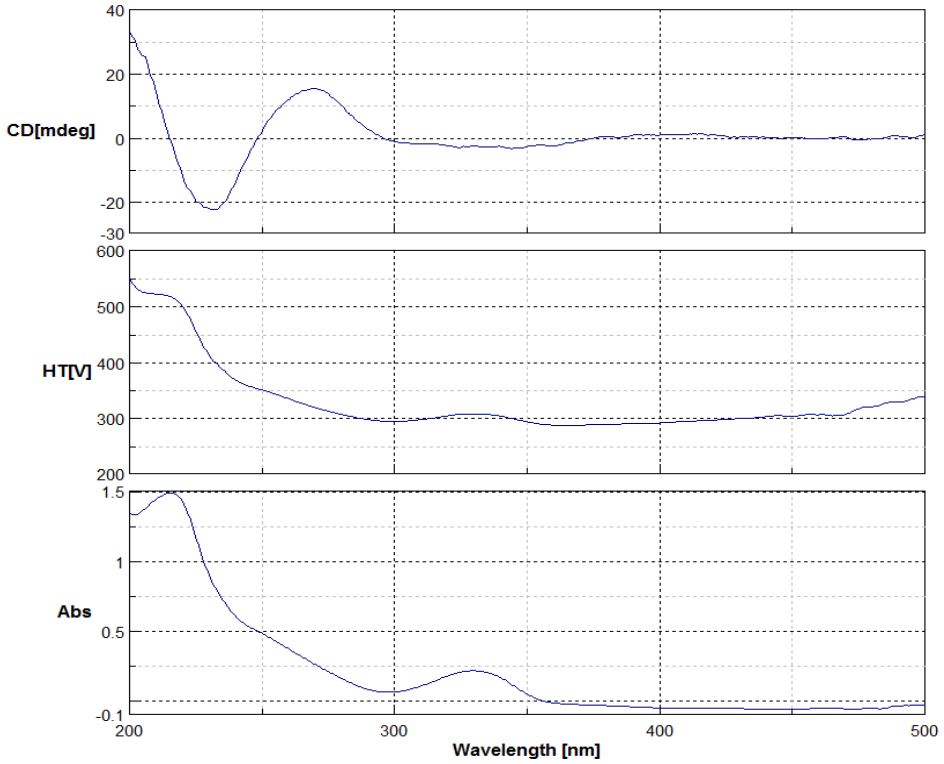

Figure S14. ^{1}H-NMR spectrum of **2** in DMSO-d_6 + 1% TFA.

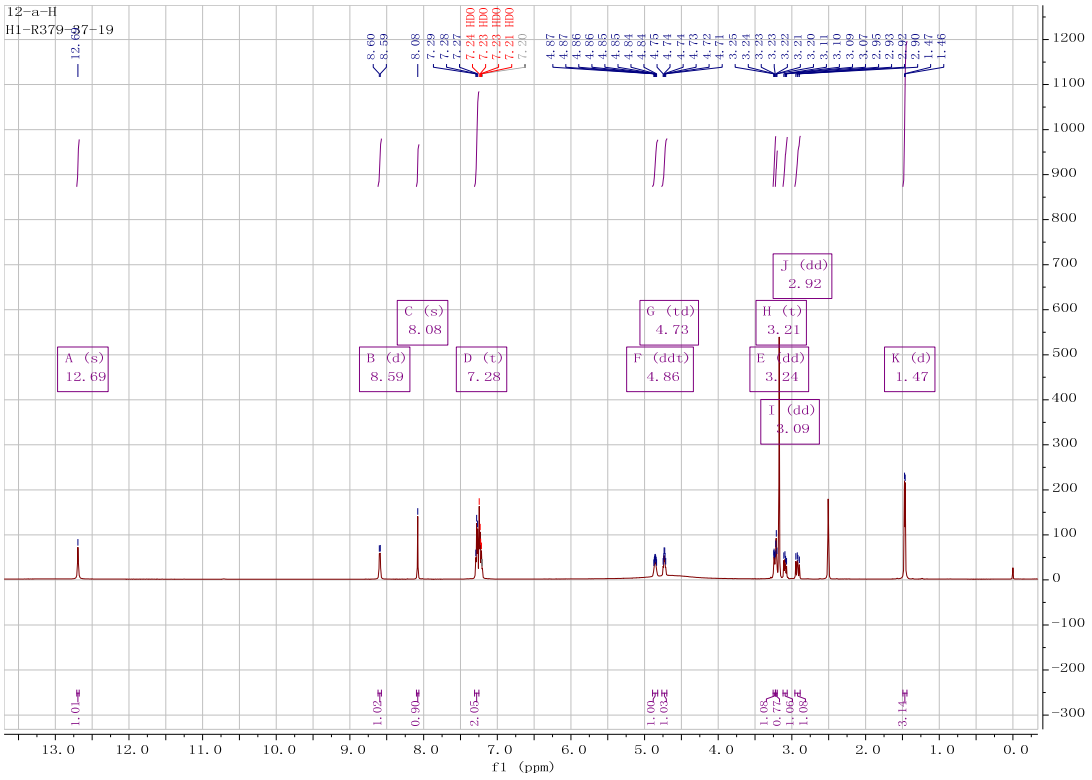

Figure S15. ^{13}C-NMR spectrum of **2** in DMSO-d_6 + 1% TFA.

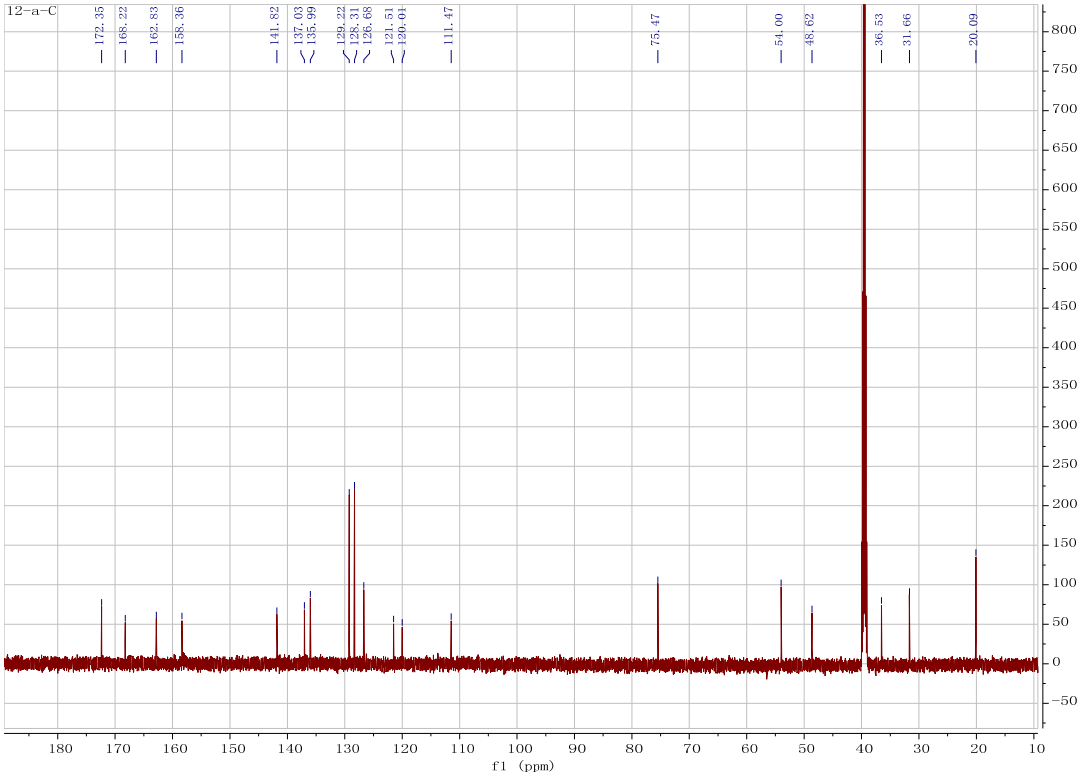

Table S3. ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR Data of **2** in DMSO-d_6 + 1% TFA

Position	δ_C, type	δ_H (J in Hz)	Position	δ_C, type	δ_H (J in Hz)
1	162.8, C		13	54.0, CH	4.86, ddt (9.7, 6.2, 3.4)
3	75.5, CH	4.73, td (7.7, 4.8)	14	36.5, CH_2	3.09, dd (13.8, 8.2)
4	31.7, CH_2	3.21[a], m			3.23[a], m
		2.92, dd (17.2, 11.7)	15	136.0, C	
5	121.5, C		16	129.2, CH	7.18–7.31, m
6	137.0, CH	8.08, s	17	128.3, CH	7.18–7.31, m
7	120.0, C		18	126.7, CH	7.18–7.31, m
8	158.4, C		19	128.3, CH	7.18–7.31, m
9	111.5, C		20	129.2, CH	7.18–7.31, m
10	141.8, C		21	20.1, CH_3	1.47, d (6.3)
11	168.2, C		22	172.3, C	
12-NH		8.59, d (7.4)	8-OH		12.69, s

[a] Overlapped with other signals.