Electronic Supplementary Information

Ervaoffines E−G, Three Iboga-Type Alkaloids Featuring Ring C Cleavage and Rearrangement from *Ervatamia officinalis*

Zhi-Wen Liu,‡[a] Ben-Qin Tang,‡[b] Qing-Hua Zhang,[a] Wen-Jing Wang,[a] Xiao-Jun Huang,[a] Jian Zhang,[a] Lei Shi,[a] Xiao-Qi Zhang,*[a] and Wen-Cai Ye*[a]

[a] Institute of Traditional Chinese Medicine & Natural Products, and Guangdong Province Key Laboratory of Pharmacodynamic Constituents of TCM and New Drugs Research, Jinan University, Guangzhou 510632, People's Republic of China

[b] Department of Medical Science, Shunde Polytechnic, Foshan 528333, People's Republic of China

List of Supplementary Information

1. Calculated and experimental ECD spectra of 1-3

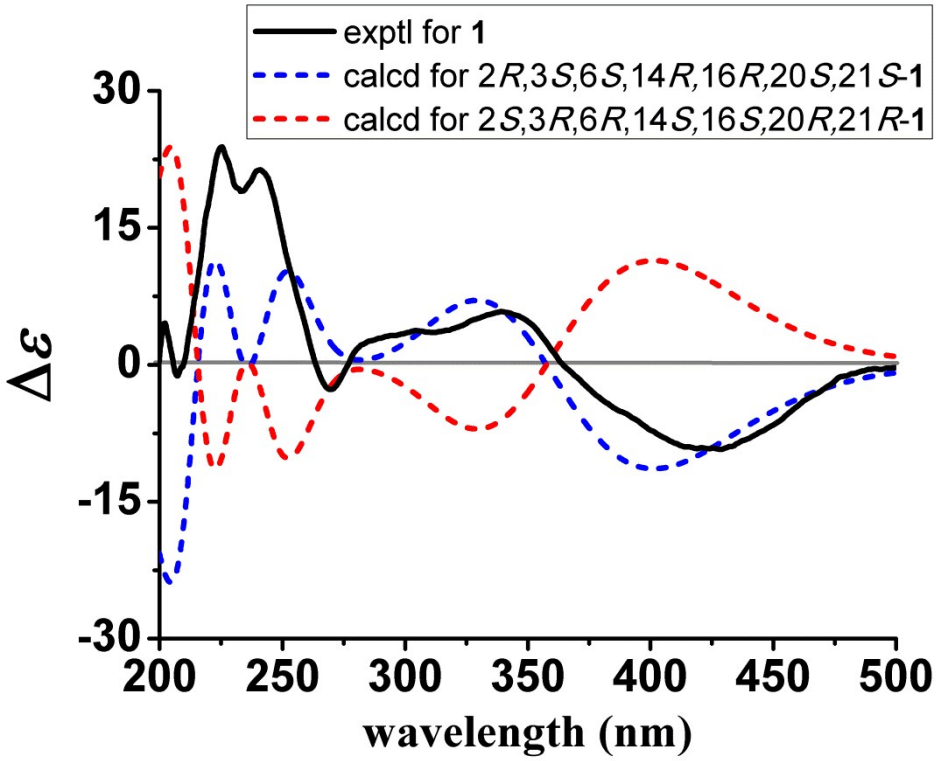


Figure S1. Calculated and experimental ECD spectra of **1**

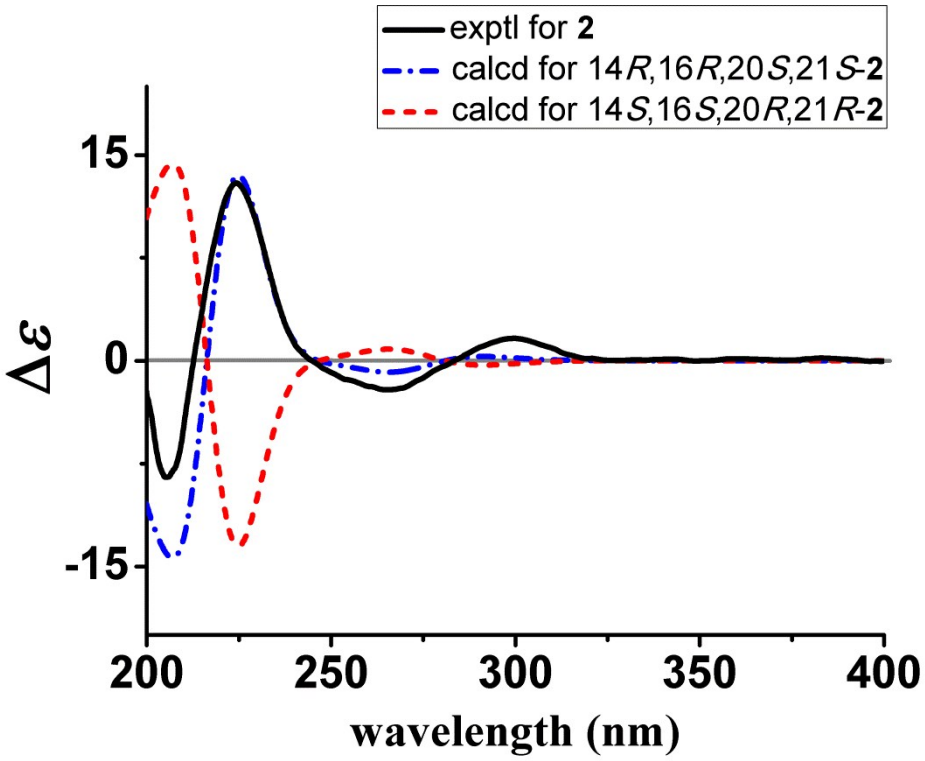


Figure S2. Calculated and experimental ECD spectra of **2**

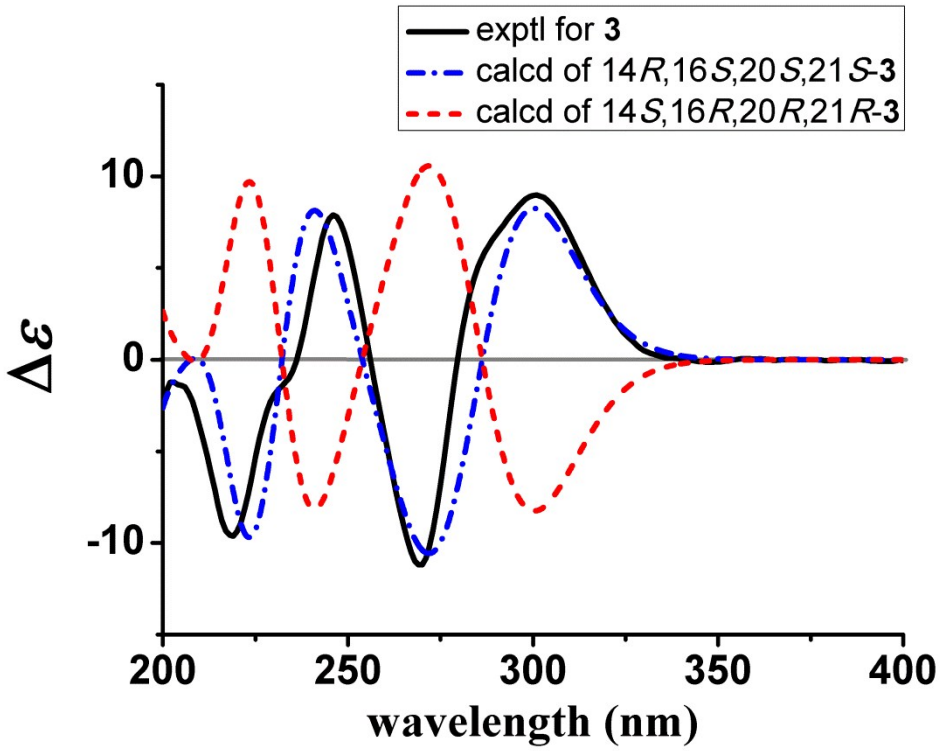


Figure S3. Calculated and experimental ECD spectra of **3**

2. Calculation details for 1–3

The Conformational analysis of **1**–**3** were performed in Sybyl 8.1 software using MMFF94s force field, which afforded 5, 3 and 8 selected conformers for **1**, **2** and **3** respectively, with an energy cutoff of 10 kcal mol^{-1} to the global minima. All of the obtained conformers were optimized using the B3LYP/6-31+G(d) level in gas phase by using Gaussian09 software [1]. TDDFT ECD calculations for the optimized conformers were performed at the CAM-B3LYP/6-31+G(d) level. The overall calculated ECD curves of all the compounds were weighted by Boltzmann distribution after a UV correction of 15, 18 and 18 nm, respectively. The ECD curves were produced by SpecDis 1.64 software [2].

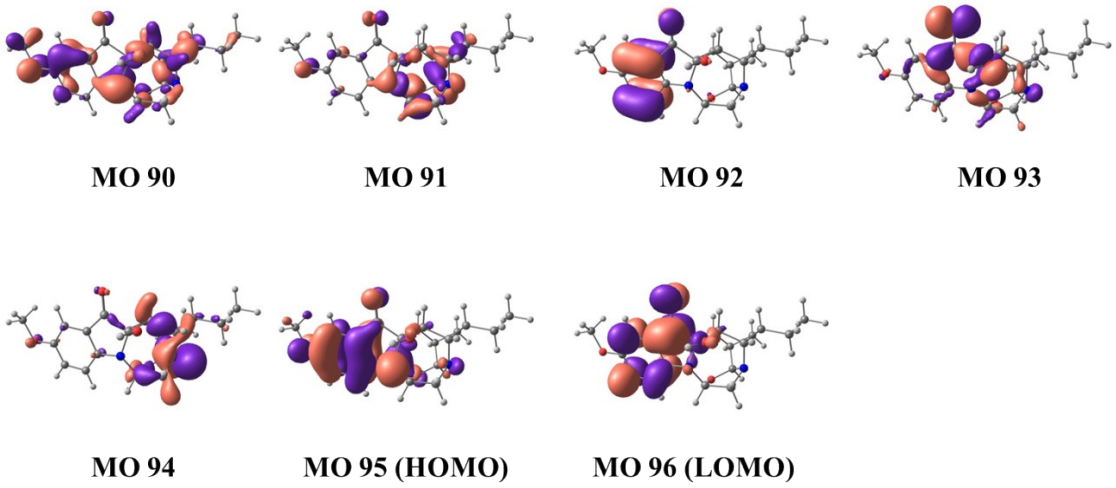


Figure S4. Key molecular orbitals involved in important transitions regarding the ECD spectra of predominant conformer **1a** in methods at the CAM-B3LYP/6-31+G(d) level

Table S1. Selected key transitions and their related rotatory and oscillator strengths of conformer of **1a** at the B3LYP/6-31+G(d) level in methods

HOMO is 95					
No.	**Energy (cm^{-1})**	**Wavelength (nm)**	**R (length)**	**Osc. Strength**	**Major contribs**
1	26088.18	383.3153	-16.814	0.0831	HOMO->LUMO (97%)
2	31072.72	321.8257	8.9828	0.0016	H-2->LUMO (77%)
3	39090.74	255.8151	2.285	0.0042	H-1->LUMO (79%)
4	40470.76	247.0920	-7.1527	0.0147	H-3->LUMO (44%), H-1->LUMO (11%), HOMO->L+2 (26%)
5	43705.87	228.8022	63.1853	0.3034	H-3->LUMO (27%), HOMO->L+1 (43%), HOMO->L+2 (12%)
6	44735.04	223.5384	-81.918	0.4549	H-3->LUMO (19%), HOMO->L+1 (22%), HOMO->L+2 (23%), HOMO->L+4 (15%)
7	45680.33	218.9126	10.265	0.0277	H-5->LUMO (48%), H-4->LUMO (24%)
8	48339.56	206.8699	57.2521	0.0736	H-1->L+1 (16%), HOMO->L+3 (33%)
9	49171.12	203.3714	11.0145	0.0559	H-4->LUMO (20%), HOMO->L+5 (19%)
10	49417.93	202.3557	-25.149	0.0525	H-5->LUMO (22%), H-4->LUMO (38%)
11	49551.01	201.8122	-17.157	0.0087	H-1->L+1 (14%), HOMO->L+3 (24%), HOMO->L+4 (18%), HOMO->L+7 (20%)
12	50605.19	197.6082	-10.5027	0.0752	H-5->LUMO (10%), HOMO->L+9 (12%), HOMO->L+14 (31%)
13	51290.76	194.9669	11.2054	0.1428	HOMO->L+9 (10%), HOMO->L+11 (10%)
14	51569.03	193.9148	-19.8949	0.0172	H-9->LUMO (36%), H-7->LUMO (22%)
15	51723.08	193.3373	-4.2465	0.0131	HOMO->L+6 (18%), HOMO->L+8 (26%)
16	53420.08	187.1955	-12.2715	0.0258	H-1->L+3 (12%), HOMO->L+7 (20%)
17	53929.02	185.4289	17.3107	0.0094	H-1->L+2 (36%), HOMO->L+10 (13%)
18	54061.30	184.9752	2.555	0.0047	H-1->L+1 (14%), HOMO->L+1 (10%), HOMO->L+6 (13%), HOMO->L+11 (11%)
19	54525.07	183.4019	11.6212	0.0024	H-7->LUMO (43%), H-6->LUMO (20%)
20	54842.85	182.3392	-2.5947	0.0046	H-1->L+3 (16%), HOMO->L+10 (11%)
21	55104.99	181.4718	-0.5312	0.0032	H-6->LUMO (25%), H-1->L+2 (10%)
22	55233.23	181.0504	-6.4975	0.0102	HOMO->L+12 (17%)
23	55275.98	180.9104	-6.1284	0.0155	H-6->LUMO (17%)
24	55741.36	179.4000	-20.1155	0.007	H-1->L+2 (12%), H-1->L+4 (22%), HOMO->L+15 (12%)
25	56068.02	178.3548	-4.2975	0.0068	H-1->L+4 (13%), HOMO->L+15 (10%)
26	56190.62	177.9657	-1.166	0.0003	H-13->LUMO (19%), H-1->L+5 (12%)
27	56455.97	177.1292	8.508	0.0803	H-3->L+2 (20%), H-2->L+1 (15%)
28	56826.99	175.9727	27.3246	0.1128	H-3->L+2 (17%), HOMO->L+12 (13%)
29	57381.10	174.2734	-0.3992	0.0375	HOMO->L+10 (16%), HOMO->L+12 (10%)
30	58038.44	172.2996	-1.2056	0.0023	HOMO->L+12 (12%)
31	58229.60	171.7340	-11.2539	0.014	HOMO->L+13 (17%)

32	58441.72	171.1106	0.4297	0.0009	H-2->L+2 (24%)
33	58725.63	170.2834	-3.5627	0.0106	H-3->L+1 (16%), H-1->L+9 (17%)
34	58950.66	169.6334	0.4294	0.0055	H-3->L+1 (15%)
35	59092.62	169.2259	1.802	0.0017	HOMO->L+6 (12%)
36	59718.51	167.4523	36.0434	0.0432	H-11->LUMO (18%), H-8->LUMO (35%)
37	60082.27	166.4385	-12.8379	0.0099	H-1->L+10 (17%), HOMO->L+19 (10%)
38	60108.88	166.3648	-10.7525	0.0056	H-1->L+3 (13%), H-1->L+11 (13%)
39	60314.56	165.7975	5.8199	0.0011	H-4->L+1 (17%), H-1->L+9 (23%)
40	60719.45	164.6919	-11.9985	0.0063	H-4->L+1 (11%), H-4->L+2 (10%)
41	60876.73	164.2664	-57.1652	0.1024	H-14->LUMO (30%), H-8->LUMO (12%)
42	61159.83	163.5060	-0.61	0.0069	H-1->L+6 (13%), H-1->L+10 (16%)
43	61391.31	162.8895	-6.6029	0.0059	
44	61629.25	162.2606	0.0723	0.0132	
45	61742.97	161.9617	28.5753	0.0107	H-5->L+2 (12%)
46	62079.31	161.0843	0.4709	0.0004	HOMO->L+19 (11%)
47	62120.44	160.9776	8.2866	0.0144	HOMO->L+18 (10%)
48	62326.12	160.4464	48.7261	0.0394	HOMO->L+18 (15%)
49	62500.33	159.9991	21.6671	0.0339	H-17->LUMO (12%), H-16->LUMO (10%), H-13->LUMO (15%)
50	62874.58	159.0468	-18.8051	0.0193	H-3->L+3 (12%)

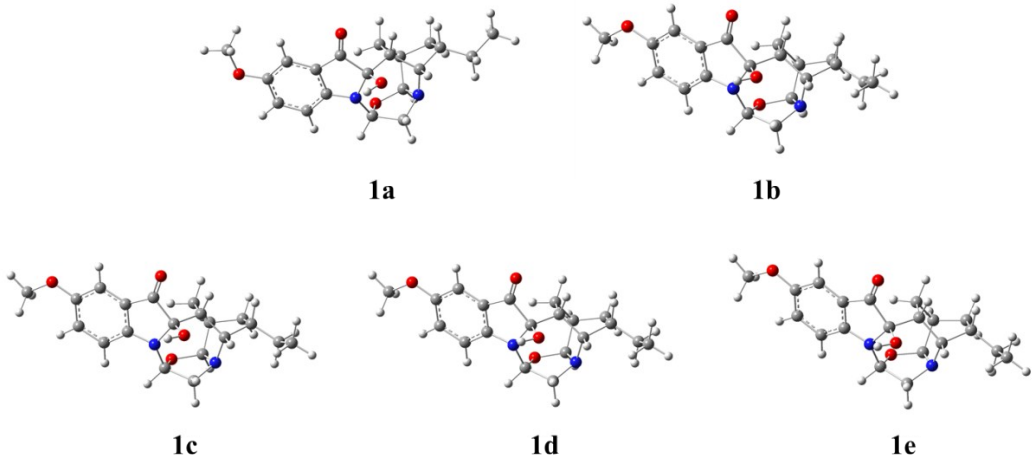


Figure S5. Optimized geometries of predominant conformers of **1** in the gas phase at the B3LYP/6-31+G(d) level.

Table S2. Standard orientation of **1a**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.168137	-0.980392	0.10465
2	6	0	-2.506941	-0.346958	0.566886
3	6	0	-0.934572	-0.56995	-1.381711
4	6	0	-1.99137	0.476698	-1.792484
5	6	0	-3.631726	-0.829979	-0.380899
6	6	0	-3.397777	-0.155608	-1.766915
7	1	0	-2.728457	-0.641313	1.595059
8	1	0	-1.762507	0.880203	-2.785344
9	6	0	1.865027	0.69319	0.467507
10	7	0	0.5576	0.71904	0.957572
11	6	0	0.025836	-0.657445	1.031402
12	6	0	-0.273915	1.899274	0.808616
13	6	0	-1.632512	1.782351	1.51631
14	7	0	-2.48356	1.132637	0.518586
15	8	0	-0.653364	2.154679	-0.547829
16	6	0	-1.990419	1.621833	-0.772171
17	8	0	-0.396488	-0.982293	2.351962
18	6	0	1.267037	-1.532942	0.636177
19	6	0	2.349427	-0.616051	0.311682
20	6	0	3.661646	-0.893942	-0.104158
21	6	0	4.496325	0.181188	-0.391529
22	6	0	4.003972	1.501672	-0.266682
23	6	0	2.707587	1.774367	0.150452
24	8	0	1.256231	-2.753975	0.644793
25	6	0	-5.036225	-0.576716	0.190546
26	6	0	-6.163606	-1.17251	-0.662885
27	1	0	-3.510759	-1.917892	-0.489324
28	8	0	5.796119	0.08212	-0.812048
29	6	0	6.345413	-1.218798	-0.974187
30	1	0	-1.268315	-2.069294	0.183119
31	1	0	0.06614	-0.15656	-1.532472
32	1	0	-1.017858	-1.445883	-2.035095
33	1	0	-4.152449	0.623596	-1.943115
34	1	0	-3.498772	-0.8801	-2.583582
35	1	0	0.309388	2.761753	1.139484
36	1	0	-2.006687	2.793637	1.718805
37	1	0	-1.60516	1.215782	2.447005
38	1	0	-2.590601	2.472328	-1.122893
39	1	0	0.372044	-0.948688	2.945197
40	1	0	3.975609	-1.927367	-0.200099

41	1	0	4.677637	2.31643	-0.516979
42	1	0	2.3674	2.802399	0.212112
43	1	0	-5.08898	-1.007452	1.200954
44	1	0	-5.183282	0.504914	0.307023
45	1	0	-6.051414	-2.260017	-0.765815
46	1	0	-7.143053	-0.981579	-0.20817
47	1	0	-6.181282	-0.744244	-1.672573
48	1	0	7.373379	-1.068352	-1.308114
49	1	0	6.345234	-1.771989	-0.025501
50	1	0	5.794051	-1.791996	-1.731456

Table S3. Standard orientation of **1b**

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	-1.303498	0.904656	0.36052
2	6	0	-2.612178	0.315435	-0.226289
3	6	0	-0.941671	0.09002	1.640718
4	6	0	-1.879058	-1.131097	1.746734
5	6	0	-3.710051	0.377349	0.865646
6	6	0	-3.330117	-0.660135	1.96483
7	1	0	-2.911577	0.881856	-1.108553
8	1	0	-1.555619	-1.792716	2.557975
9	6	0	1.833439	-0.282889	-0.623054
10	7	0	0.498375	-0.272328	-1.052139
11	6	0	-0.144777	0.997011	-0.656977
12	6	0	-0.226106	-1.518756	-1.231608
13	6	0	-1.634986	-1.332951	-1.814439
14	7	0	-2.466378	-1.100766	-0.632981
15	8	0	-0.486644	-2.203769	-0.004127
16	6	0	-1.846612	-1.9057	0.423472
17	8	0	-0.659583	1.690059	-1.791857
18	6	0	1.040146	1.812919	-0.029271
19	6	0	2.221697	0.954822	-0.073599
20	6	0	3.52474	1.207649	0.351314
21	6	0	4.470636	0.184994	0.249726
22	6	0	4.08335	-1.066305	-0.268396
23	6	0	2.774926	-1.313217	-0.701656
24	8	0	0.936879	2.970805	0.337007
25	6	0	-5.135545	0.155288	0.327861
26	6	0	-5.675946	1.293152	-0.54813
27	1	0	-3.671752	1.386073	1.300551
28	8	0	5.735531	0.482442	0.687022

29	6	0	6.732838	-0.527168	0.625793
30	1	0	-1.498168	1.950408	0.624556
31	1	0	0.097362	-0.248581	1.622186
32	1	0	-1.055379	0.714859	2.533569
33	1	0	-4.009871	-1.522355	1.920463
34	1	0	-3.437907	-0.226382	2.966483
35	1	0	0.400281	-2.178703	-1.836311
36	1	0	-1.937111	-2.267936	-2.301618
37	1	0	-1.718671	-0.513123	-2.527763
38	1	0	-2.346898	-2.878913	0.516312
39	1	0	0.055099	1.779118	-2.443727
40	1	0	3.799749	2.171038	0.769849
41	1	0	4.802761	-1.874948	-0.337075
42	1	0	2.519894	-2.298232	-1.077458
43	1	0	-5.156876	-0.79088	-0.228338
44	1	0	-5.806279	0.026529	1.189491
45	1	0	-5.078244	1.436002	-1.456081
46	1	0	-6.704825	1.085295	-0.865888
47	1	0	-5.682683	2.246062	-0.002593
48	1	0	6.910184	-0.853346	-0.407991
49	1	0	7.641967	-0.07124	1.021167
50	1	0	6.463739	-1.394981	1.243104

Table S4. Standard orientation of **1c**

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	-1.237124	1.102833	0.238879
2	6	0	-2.585093	0.545754	-0.295196
3	6	0	-0.930843	0.381802	1.588416
4	6	0	-1.935874	-0.772335	1.795786
5	6	0	-3.653994	0.781951	0.802273
6	6	0	-3.361849	-0.20922	1.965753
7	1	0	-2.867175	1.055099	-1.219742
8	1	0	-1.646514	-1.379567	2.660916
9	6	0	1.817898	-0.354946	-0.597759
10	7	0	0.490933	-0.307409	-1.037485
11	6	0	-0.078135	1.02981	-0.780497
12	6	0	-0.305657	-1.516336	-1.126993
13	6	0	-1.697787	-1.285113	-1.734183
14	7	0	-2.515414	-0.905256	-0.581173
15	8	0	-0.615956	-2.082897	0.150781
16	6	0	-1.952654	-1.65632	0.542976

17	8	0	-0.566312	1.627582	-1.97793
18	6	0	1.156477	1.83854	-0.24535
19	6	0	2.27772	0.90697	-0.169038
20	6	0	3.589238	1.119724	0.254393
21	6	0	4.468488	0.035348	0.272193
22	6	0	4.008834	-1.236168	-0.125729
23	6	0	2.693362	-1.445105	-0.554582
24	8	0	1.114929	3.028214	0.017866
25	6	0	-5.119235	0.783768	0.315722
26	6	0	-5.65691	-0.484958	-0.360684
27	1	0	-3.474438	1.798674	1.179023
28	8	0	5.744989	0.295559	0.700405
29	6	0	6.677155	-0.774338	0.755839
30	1	0	-1.361855	2.178595	0.408321
31	1	0	0.087867	-0.014676	1.610412
32	1	0	-1.011737	1.088214	2.422594
33	1	0	-3.457935	0.295171	2.935086
34	1	0	-4.085174	-1.035246	1.969043
35	1	0	0.28032	-2.26302	-1.668233
36	1	0	-2.059327	-2.235607	-2.146563
37	1	0	-1.72468	-0.521912	-2.511808
38	1	0	-2.51617	-2.583636	0.715335
39	1	0	0.173036	1.735511	-2.598869
40	1	0	3.919416	2.1024	0.577443
41	1	0	4.677405	-2.089694	-0.097698
42	1	0	2.377414	-2.445238	-0.831212
43	1	0	-5.750355	1.015399	1.187144
44	1	0	-5.244633	1.630503	-0.37498
45	1	0	-5.55971	-1.368083	0.281384
46	1	0	-6.722763	-0.36032	-0.590249
47	1	0	-5.128865	-0.704035	-1.292843
48	1	0	7.60828	-0.336865	1.120161
49	1	0	6.347787	-1.558471	1.451134
50	1	0	6.84587	-1.212166	-0.237488

Table S5. Standard orientation of **1d**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.237123	1.102832	0.238881
2	6	0	-2.585093	0.545755	-0.295194
3	6	0	-0.930841	0.381798	1.588416
4	6	0	-1.935872	-0.772339	1.795785

5	6	0	-3.653993	0.781949	0.802277
6	6	0	-3.361846	-0.209225	1.965755
7	1	0	-2.867176	1.055102	-1.219738
8	1	0	-1.646511	-1.379573	2.660913
9	6	0	1.817898	-0.354944	-0.597762
10	7	0	0.490933	-0.307407	-1.037488
11	6	0	-0.078135	1.029812	-0.780496
12	6	0	-0.305657	-1.516333	-1.126997
13	6	0	-1.697788	-1.285109	-1.734186
14	7	0	-2.515414	-0.905254	-0.581174
15	8	0	-0.615955	-2.082897	0.150775
16	6	0	-1.952653	-1.656321	0.542973
17	8	0	-0.566315	1.627587	-1.977927
18	6	0	1.156477	1.83854	-0.245348
19	6	0	2.277719	0.906971	-0.169039
20	6	0	3.589238	1.119724	0.254393
21	6	0	4.468488	0.035348	0.27219
22	6	0	4.008834	-1.236167	-0.125735
23	6	0	2.693361	-1.445103	-0.554587
24	8	0	1.114929	3.028214	0.01787
25	6	0	-5.119234	0.783766	0.315727
26	6	0	-5.65691	-0.484958	-0.360682
27	1	0	-3.474437	1.798671	1.179028
28	8	0	5.74499	0.295559	0.700401
29	6	0	6.67715	-0.774342	0.755851
30	1	0	-1.361854	2.178594	0.408326
31	1	0	0.087869	-0.014679	1.610411
32	1	0	-1.011734	1.088208	2.422596
33	1	0	-4.085172	-1.035251	1.969043
34	1	0	-3.457932	0.295164	2.935088
35	1	0	0.280319	-2.263016	-1.668239
36	1	0	-2.059328	-2.235602	-2.146567
37	1	0	-1.724682	-0.521907	-2.511809
38	1	0	-2.516168	-2.583638	0.71533
39	1	0	0.173033	1.735519	-2.598866
40	1	0	3.919416	2.102399	0.577444
41	1	0	4.677405	-2.089693	-0.097706
42	1	0	2.377414	-2.445235	-0.83122
43	1	0	-5.750354	1.015395	1.18715
44	1	0	-5.244633	1.630503	-0.374973
45	1	0	-5.559707	-1.368085	0.281383
46	1	0	-6.722763	-0.36032	-0.590244
47	1	0	-5.128867	-0.704032	-1.292843
48	1	0	7.608274	-0.336872	1.12018

49	1	0	6.347772	-1.55847	1.451147
50	1	0	6.845873	-1.212177	-0.237471

Table S6. Standard orientation of **1e**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.260316	0.999826	-0.07952
2	6	0	2.553911	0.365565	0.495595
3	6	0	0.982866	0.343388	-1.466242
4	6	0	1.953212	-0.838094	-1.672988
5	6	0	3.701323	0.579645	-0.521595
6	6	0	3.402357	-0.31846	-1.760434
7	1	0	2.807522	0.827293	1.45236
8	1	0	1.684604	-1.399908	-2.57479
9	6	0	-1.884913	-0.360958	0.570978
10	7	0	-0.576824	-0.383192	1.066777
11	6	0	0.053896	0.939011	0.884556
12	6	0	0.16565	-1.627344	1.142689
13	6	0	1.536786	-1.481485	1.820119
14	7	0	2.421629	-1.091701	0.721354
15	8	0	0.510588	-2.157264	-0.142186
16	6	0	1.879362	-1.772428	-0.458262
17	8	0	0.508723	1.474159	2.123856
18	6	0	-1.123182	1.814568	0.325839
19	6	0	-2.276219	0.932793	0.170189
20	6	0	-3.559207	1.213306	-0.298769
21	6	0	-4.478898	0.166989	-0.392009
22	6	0	-4.086926	-1.135278	-0.022198
23	6	0	-2.799987	-1.412243	0.452296
24	8	0	-1.022944	3.009383	0.105358
25	6	0	5.088848	0.329059	0.091304
26	6	0	6.249872	0.67242	-0.851156
27	1	0	3.661446	1.634858	-0.8294
28	8	0	-5.72481	0.493562	-0.862723
29	6	0	-6.693917	-0.535714	-0.997258
30	1	0	1.440458	2.074356	-0.20145
31	1	0	-0.048206	-0.011351	-1.545325
32	1	0	1.126442	1.075967	-2.268761
33	1	0	4.095486	-1.170821	-1.789657
34	1	0	3.546254	0.234688	-2.696067
35	1	0	-0.474776	-2.368503	1.626783
36	1	0	1.839157	-2.462116	2.208293

37	1	0	1.560616	-0.751313	2.62892
38	1	0	2.412756	-2.714338	-0.645169
39	1	0	-0.252711	1.580367	2.717812
40	1	0	-3.836482	2.219184	-0.59939
41	1	0	-4.786706	-1.959423	-0.10877
42	1	0	-2.535723	-2.433378	0.705314
43	1	0	5.183654	0.931378	1.006445
44	1	0	5.154736	-0.721336	0.40357
45	1	0	6.216338	1.727182	-1.154739
46	1	0	7.2161	0.498636	-0.362488
47	1	0	6.229993	0.064199	-1.763912
48	1	0	-6.922962	-1.000956	-0.028808
49	1	0	-7.590619	-0.049049	-1.384785
50	1	0	-6.364357	-1.307479	-1.706144

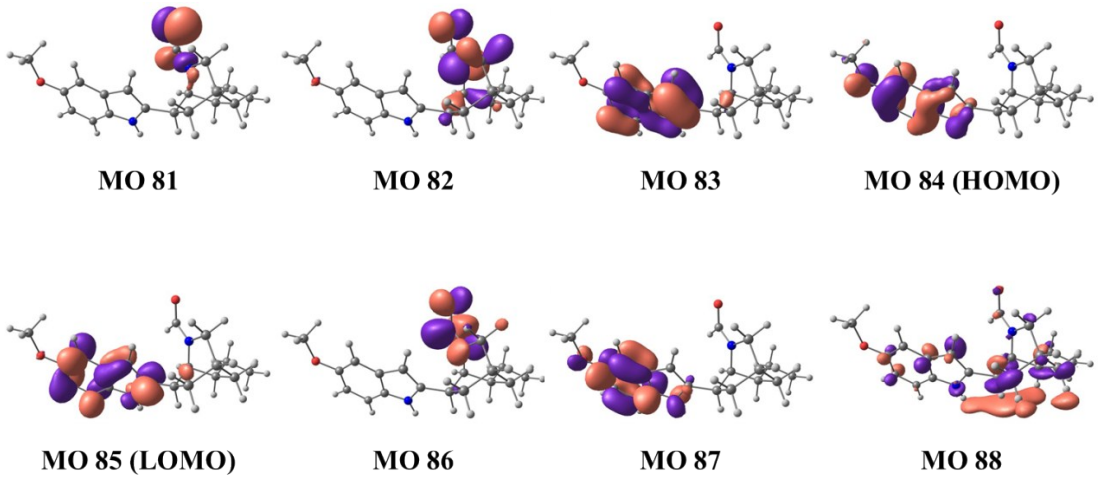


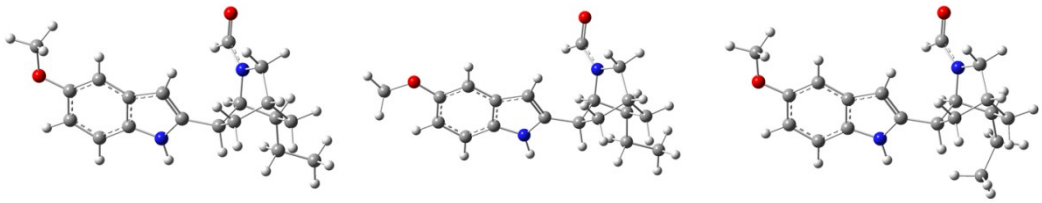
Figure S6. Key molecular orbitals involved in important transitions regarding the ECD spectra of predominant conformer **2a** in methods at the CAM-B3LYP/6-31+G(d) level

Table S7. Selected key transitions and their related rotatory and oscillator strengths of conformer of **2a** at the B3LYP/6-31+G(d) level in methods

HOMO is 84					
No.	**Energy (cm^{-1})**	**Wavelength (nm)**	**R(length)**	**Osc. Strength**	**Major contribs**
1	36253.26	275.8373	4.3751	0.0819	HOMO->LUMO (89%)
2	38810.86	257.6598	-10.0622	0.2414	H-1->LUMO (89%)
3	43884.12	227.8728	-1.0544	0.0011	H-3->L+1 (91%)

4	44923.78	222.5993	-1.6975	0.0022	H-1->L+1 (32%), HOMO->L+1 (60%)
5	45006.05	222.1924	10.1475	0.0225	H-2->LUMO (78%), HOMO->L+1 (16%)
6	45205.27	221.2132	9.6457	0.028	H-2->LUMO (13%), H-1->L+1 (63%), HOMO->L+1 (22%)
7	47046.64	212.5550	-1.6529	0.0012	H-3->LUMO (94%)
8	48109.69	207.8583	16.8523	0.1393	H-1->L+2 (54%), H-1->L+3 (10%), HOMO->L+2 (10%), HOMO->L+3 (12%)
9	48912.22	204.4479	-37.5428	0.1842	H-1->L+2 (10%), H-1->L+3 (16%), HOMO->L+2 (32%), HOMO->L+3 (33%)
10	49941.39	200.2347	-27.5021	0.2341	H-1->L+3 (10%), HOMO->L+2 (27%), HOMO->L+3 (43%)
11	50505.98	197.9964	54.5175	0.3951	H-1->L+2 (15%), H-1->L+3 (55%), HOMO->L+2 (13%)
12	51862.61	192.8171	-2.99	0.0143	H-4->LUMO (21%), HOMO->L+4 (55%)
13	52416.72	190.7788	-42.7043	0.1984	H-4->LUMO (20%), H-1->L+4 (26%), HOMO->L+4 (25%)
14	53724.96	186.1332	1.097	0.0032	HOMO->L+5 (74%)
15	54043.55	185.0359	-2.584	0.0035	H-1->L+5 (81%)
16	55203.39	181.1483	36.822	0.2122	H-2->L+1 (74%)
17	55651.83	179.6886	-5.4288	0.0872	H-5->LUMO (61%), H-1->L+4 (25%)
18	56005.11	178.5551	0.1424	0.0235	H-2->L+2 (73%), H-2->L+3 (13%)
19	57002.82	175.4299	-11.9376	0.0068	H-2->L+3 (27%), HOMO->L+6 (19%), HOMO->L+8 (25%)
20	57116.55	175.0806	3.4766	0.0072	H-2->L+2 (10%), H-2->L+3 (44%), HOMO->L+6 (13%), HOMO->L+8 (16%)
21	57645.65	173.4736	0.4359	0.005	H-1->L+6 (75%)
22	57700.50	173.3087	7.044	0.0447	H-5->LUMO (20%), H-4->LUMO (24%), H-1->L+4 (20%), H-1->L+6 (13%)
23	57889.23	172.7437	0.2284	0.0069	H-3->L+2 (97%)
24	58101.36	172.1130	10.4694	0.008	HOMO->L+6 (54%), HOMO->L+8 (24%)
25	59440.25	168.2362	-1.4295	0.0002	H-8->LUMO (14%), H-7->LUMO (31%), H-6->LUMO (28%), H-1->L+7 (11%)
26	59544.29	167.9422	0.2194	0.0018	H-1->L+7 (19%), HOMO->L+7 (53%)
27	59603.17	167.7763	-0.7868	0.0002	H-1->L+7 (23%), H-1->L+8 (18%), H-1->L+9 (10%), HOMO->L+7 (29%)
28	59671.73	167.5835	-11.0494	0.0251	H-3->L+3 (87%)
29	59803.20	167.2151	1.7171	0.003	H-1->L+7 (32%), H-1->L+8 (51%)
30	60424.25	165.4965	1.6813	0.0075	HOMO->L+10 (81%)
31	60670.25	164.8254	-0.0149	0.0036	H-2->L+4 (94%)
32	61259.04	163.2412	-1.3345	0.0015	H-4->L+1 (99%)
33	61992.20	161.3106	-1.8295	0.0037	HOMO->L+8 (15%), HOMO->L+9 (61%)
34	62112.38	160.9985	1.3724	0.0044	H-2->L+5 (79%)
35	62372.09	160.3281	-2.1162	0.0023	H-1->L+9 (65%)
36	62634.22	159.6571	6.4741	0.0122	H-8->LUMO (25%), H-6->LUMO (45%), H-1->L+9

					(10%)
37	62794.73	159.2490	-3.4098	0.0129	H-3->L+4 (94%)
38	63134.29	158.3925	-2.21	0.001	H-1->L+10 (82%)
39	63182.68	158.2712	3.0852	0.0118	H-8->LUMO (41%), H-7->LUMO (36%)
40	63572.25	157.3013	4.6962	0.0012	HOMO->L+11 (41%), HOMO->L+13 (42%)
41	63748.08	156.8675	1.6616	0.0684	H-9->LUMO (13%), H-4->L+2 (55%)
42	64246.54	155.6504	-9.3295	0.0228	H-9->LUMO (57%)
43	64326.39	155.4572	1.7541	0.0022	H-1->L+11 (77%)
44	64589.32	154.8243	0.9001	0.0051	H-3->L+5 (90%)
45	64906.30	154.0682	-1.6473	0.0002	HOMO->L+11 (52%), HOMO->L+13 (33%)
46	65007.12	153.8293	-7.2691	0.0058	H-2->L+6 (14%), H-2->L+7 (59%), H-2->L+9 (12%)
47	65060.36	153.7034	5.5455	0.0014	H-11->LUMO (57%), H-9->LUMO (17%)
48	65224.89	153.3157	2.3171	0.002	H-5->L+1 (85%)
49	65332.17	153.0640	3.8965	0.0007	H-2->L+6 (68%), H-2->L+7 (10%)
50	65874.17	151.8046	0.4319	0.021	H-5->L+2 (74%), H-4->L+3 (16%)



2a **2b** **2c**

Figure S7. Optimized geometries of predominant conformers of **2** in the gas phase at the B3LYP/6-31+G(d) level

Table S8. Standard orientation of **2a**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.061243	0.465642	0.639747
2	6	0	-0.145495	-0.561242	0.538553
3	6	0	1.347056	-0.584344	0.704598
4	6	0	2.106322	-0.043108	-0.54855
5	7	0	2.01267	1.419361	-0.57111
6	6	0	-2.355435	-0.063939	0.31165
7	6	0	-2.171198	-1.435912	0.0008

8	7	0	-0.818532	-1.705417	0.130758
9	6	0	-3.649493	0.496309	0.255194
10	6	0	-4.713735	-0.327047	-0.102445
11	6	0	-4.511163	-1.696831	-0.401982
12	6	0	-3.244895	-2.262431	-0.353143
13	6	0	1.86799	0.220889	1.939316
14	6	0	3.119677	1.030389	1.543266
15	6	0	4.157313	0.090536	0.891533
16	6	0	3.61068	-0.417056	-0.479224
17	6	0	2.694856	2.109868	0.534088
18	6	0	3.901703	-1.903006	-0.750178
19	6	0	5.398184	-2.204788	-0.914484
20	6	0	1.336065	2.125604	-1.512594
21	1	0	1.653784	-0.426849	-1.469456
22	1	0	3.547792	1.516949	2.42794
23	1	0	0.854992	1.485232	-2.275196
24	8	0	1.252094	3.350022	-1.537038
25	8	0	-6.018602	0.091019	-0.199057
26	6	0	-6.310752	1.45129	0.065097
27	1	0	-0.835511	1.487906	0.911768
28	1	0	1.643737	-1.63585	0.821028
29	1	0	-0.391033	-2.611973	0.013152
30	1	0	-3.793651	1.546117	0.485556
31	1	0	-5.375659	-2.294223	-0.675283
32	1	0	-3.103263	-3.314478	-0.58887
33	1	0	1.08895	0.900052	2.30231
34	1	0	2.098276	-0.464927	2.763473
35	1	0	5.114111	0.609052	0.75871
36	1	0	4.348259	-0.756141	1.565972
37	1	0	4.093249	0.157056	-1.28347
38	1	0	3.556913	2.674171	0.151371
39	1	0	2.006909	2.83643	0.982787
40	1	0	3.373797	-2.211477	-1.664809
41	1	0	3.500064	-2.522565	0.064659
42	1	0	5.563494	-3.26818	-1.122955
43	1	0	5.963597	-1.953399	-0.009409
44	1	0	5.826626	-1.63093	-1.745745
45	1	0	-7.387632	1.562155	-0.079768
46	1	0	-6.053536	1.726013	1.098039
47	1	0	-5.779776	2.118993	-0.628025

Table S9. Standard orientation of **2b**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.965897	0.644819	0.689091
2	6	0	-0.117549	-0.434613	0.567467
3	6	0	1.373931	-0.553033	0.703013
4	6	0	2.149051	-0.070408	-0.565619
5	7	0	2.164048	1.3934	-0.600534
6	6	0	-2.297613	0.194409	0.383447
7	6	0	-2.203082	-1.194	0.0842
8	7	0	-0.868397	-1.544581	0.202638
9	6	0	-3.55156	0.821804	0.338287
10	6	0	-4.676514	0.067549	0.005833
11	6	0	-4.567018	-1.311694	-0.284137
12	6	0	-3.326296	-1.951521	-0.245763
13	6	0	1.969795	0.218199	1.925137
14	6	0	3.267325	0.937699	1.504323
15	6	0	4.228502	-0.0728	0.840593
16	6	0	3.623592	-0.549714	-0.517748
17	6	0	2.901481	2.039971	0.496557
18	6	0	3.805952	-2.053238	-0.785963
19	6	0	5.272216	-2.454632	-1.001071
20	6	0	1.446852	2.137628	-1.481714
21	1	0	1.658319	-0.424918	-1.478016
22	1	0	3.741506	1.397045	2.3794
23	1	0	0.903177	1.525262	-2.225839
24	8	0	1.399457	3.363337	-1.481957
25	8	0	-5.868957	0.752876	-0.015056
26	6	0	-7.052745	0.053312	-0.350146
27	1	0	-0.673944	1.652944	0.952037
28	1	0	1.599788	-1.621079	0.81708
29	1	0	-0.497222	-2.476792	0.091921
30	1	0	-3.669391	1.879759	0.554491
31	1	0	-5.44433	-1.89436	-0.540805
32	1	0	-3.254793	-3.012853	-0.471797
33	1	0	1.245264	0.951701	2.294178
34	1	0	2.165013	-0.478442	2.749099
35	1	0	5.21352	0.382784	0.686724
36	1	0	4.377196	-0.926982	1.515801
37	1	0	4.13007	-0.015783	-1.333758
38	1	0	2.265102	2.810516	0.946114
39	1	0	3.795688	2.544551	0.105424
40	1	0	3.227254	-2.330086	-1.679326

41	1	0	3.394587	-2.640829	0.047046
42	1	0	5.359299	-3.528068	-1.205429
43	1	0	5.885517	-2.235369	-0.119022
44	1	0	5.706913	-1.915705	-1.852318
45	1	0	-7.859395	0.787994	-0.304595
46	1	0	-7.003387	-0.365001	-1.365541
47	1	0	-7.26185	-0.756147	0.36377

Table S10. Standard orientation of **2c**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.955785	0.49456	0.651564
2	6	0	-0.048319	-0.533642	0.50604
3	6	0	1.447374	-0.569574	0.643602
4	6	0	2.181107	-0.001665	-0.616786
5	7	0	2.095313	1.462425	-0.576123
6	6	0	-2.257326	-0.01729	0.324949
7	6	0	-2.088039	-1.382365	-0.018179
8	7	0	-0.735494	-1.664978	0.084589
9	6	0	-3.54785	0.554394	0.294786
10	6	0	-4.622181	-0.253336	-0.066802
11	6	0	-4.434155	-1.618107	-0.398012
12	6	0	-3.171631	-2.193322	-0.377711
13	6	0	1.991904	0.20624	1.884371
14	6	0	3.265173	0.979768	1.488774
15	6	0	4.251435	0.012065	0.795152
16	6	0	3.696048	-0.352423	-0.611584
17	6	0	2.85346	2.097379	0.513935
18	6	0	4.108101	-1.744911	-1.139333
19	6	0	3.596259	-3.005362	-0.425891
20	6	0	1.386325	2.213336	-1.456453
21	1	0	1.697715	-0.347868	-1.53641
22	1	0	3.725308	1.430095	2.375889
23	1	0	0.859483	1.606759	-2.216129
24	8	0	1.320965	3.438446	-1.431685
25	8	0	-5.926433	0.174621	-0.137247
26	6	0	-6.204211	1.532067	0.166235
27	1	0	-0.720166	1.509668	0.942387
28	1	0	1.740095	-1.620149	0.737264
29	1	0	-0.326783	-2.583222	-0.008163
30	1	0	-3.680929	1.599985	0.549378
31	1	0	-5.307582	-2.201673	-0.672214

32	1	0	-3.038942	-3.240808	-0.638077
33	1	0	1.235568	0.90502	2.25778
34	1	0	2.204345	-0.495065	2.70031
35	1	0	5.245254	0.46691	0.700285
36	1	0	4.374139	-0.883539	1.419168
37	1	0	4.138279	0.353346	-1.327272
38	1	0	3.725083	2.632141	0.110436
39	1	0	2.215976	2.843107	1.001825
40	1	0	5.207384	-1.767977	-1.129439
41	1	0	3.821635	-1.805196	-2.199115
42	1	0	4.107173	-3.89019	-0.823662
43	1	0	2.522557	-3.161677	-0.5814
44	1	0	3.78304	-2.982204	0.654486
45	1	0	-7.28212	1.651711	0.040393
46	1	0	-5.928784	1.776011	1.20158
47	1	0	-5.678865	2.211283	-0.519056

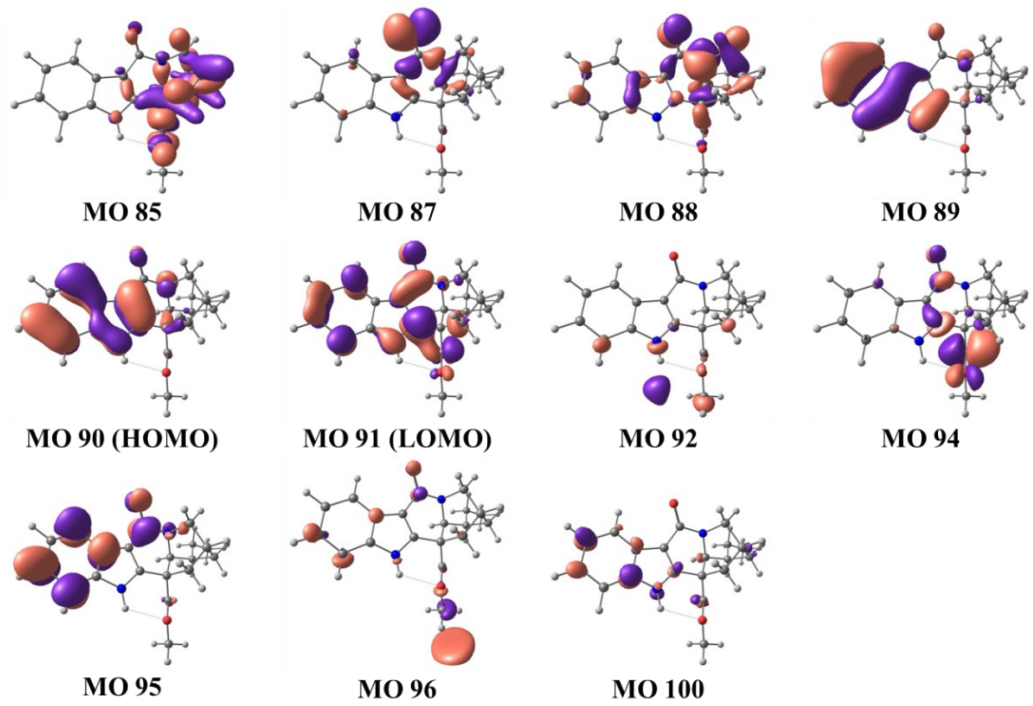


Figure S8. Key molecular orbitals involved in important transitions regarding the ECD spectra of predominant conformer **3d** in methods at the CAM-B3LYP/6-31+G(d) level

Table S11. Selected key transitions and their related rotatory and oscillator strengths of conformer of **3d** at the B3LYP/6-31+G(d) level in methods

HOMO is 90					
No.	**Energy (cm^{-1})**	**Wavelength (nm)**	**R(length)**	**Osc. Strength**	**Major contribs**
1	36658.15	272.7906	40.0188	0.0451	HOMO->LUMO (68%)
2	38754.40	258.0352	-43.9868	0.0112	H-3->LUMO (45%), H-3->L+4 (18%)
3	40445.76	247.2447	-5.729	0.0526	H-1->LUMO (50%)
4	42049.20	237.8167	12.38	0.123	H-2->LUMO (45%), HOMO->L+4 (13%)
5	44029.30	227.1215	-9.2358	0.0085	HOMO->L+1 (56%), HOMO->L+4 (16%)
6	44694.72	223.7401	11.8034	0.0952	H-2->LUMO (13%), HOMO->L+1 (15%), HOMO->L+4 (29%), HOMO->L+5 (14%)
7	44773.76	223.3451	30.3177	0.1224	H-5->L+3 (10%), HOMO->L+3 (51%)
8	46269.93	216.1231	9.9111	0.0108	H-5->L+3 (23%), H-2->L+3 (12%), HOMO->L+3 (27%)
9	47329.75	211.2836	-21.177	0.287	H-1->LUMO (21%), H-1->L+1 (11%), H-1->L+4 (26%)
10	47895.95	208.7859	-23.8443	0.1178	H-1->L+1 (51%), H-1->L+5 (15%)
11	49030.78	203.9535	0.2118	0.0138	HOMO->L+2 (50%), HOMO->L+9 (16%)
12	50020.43	199.9183	-74.1422	0.3621	H-1->L+4 (21%), HOMO->L+6 (12%), HOMO->L+9 (25%), HOMO->L+10 (12%)
13	50392.26	198.4432	68.014	0.0788	HOMO->L+5 (22%), HOMO->L+8 (23%), HOMO->L+10 (17%)
14	51035.89	195.9405	-0.7711	0.0344	H-2->L+1 (11%), H-2->L+3 (21%), H-1->L+3 (20%)
15	51616.61	193.7361	11.0174	0.0085	H-2->L+1 (12%), H-2->L+2 (11%), H-2->L+3 (12%), H-1->L+3 (18%)
16	52448.98	190.6615	-4.9705	0.017	H-1->L+3 (12%), HOMO->L+6 (13%), HOMO->L+11 (11%)
17	52642.56	189.9604	-9.2657	0.0686	H-2->L+3 (20%), H-1->L+3 (29%)
18	52974.86	188.7688	-6.538	0.0741	H-1->L+8 (24%), H-1->L+9 (18%)
19	53119.24	188.2557	12.8866	0.0842	H-4->LUMO (13%), H-1->L+10 (18%)
20	53315.23	187.5637	-22.9672	0.016	H-1->L+8 (13%), HOMO->L+5 (11%), HOMO->L+8 (10%)
21	53826.59	185.7818	42.8472	0.0626	H-4->LUMO (31%), H-3->LUMO (10%), H-1->L+9 (10%), H-1->L+10 (10%)
22	54341.98	184.0198	-6.2051	0.0043	H-4->LUMO (10%), H-1->L+2 (21%)
23	54566.20	183.2636	4.8202	0.0068	H-4->LUMO (13%), H-2->L+4 (19%)
24	54820.27	182.4143	-3.6463	0.005	H-2->L+1 (21%), HOMO->L+6 (11%)
25	55420.35	180.4391	5.8399	0.0094	HOMO->L+13 (28%)
26	55527.62	180.0905	-2.4619	0.0104	H-3->LUMO (11%), H-3->L+4 (13%), H-2->L+4 (14%), HOMO->L+13 (15%)
27	55928.48	178.7998	-4.9974	0.0159	HOMO->L+7 (11%), HOMO->L+11 (10%)

28	56358.38	177.4359	-2.4215	0.0068	HOMO->L+7 (27%)
29	56885.06	175.7931	3.733	0.0048	H-2->L+1 (13%), H-2->L+2 (12%)
30	57152.04	174.9719	9.286	0.0191	H-1->L+11 (12%)
31	57330.28	174.4279	-8.2683	0.0073	H-3->L+1 (21%)
32	57448.85	174.0679	-16.6521	0.0224	H-1->L+5 (13%)
33	57693.24	173.3305	0.8487	0.004	
34	58148.94	171.9722	-14.0925	0.0065	H-2->L+2 (16%), HOMO->L+16 (21%)
35	58267.51	171.6222	0.179	0.0015	H-2->L+9 (18%), H-1->L+13 (14%)
36	58771.61	170.1502	7.7552	0.0078	H-1->L+13 (39%)
37	58895.82	169.7913	9.6501	0.0037	H-2->L+12 (13%), HOMO->L+6 (14%), HOMO->L+12 (12%)
38	59173.27	168.9952	0.2304	0.0031	H-2->L+5 (10%), HOMO->L+15 (11%), HOMO->L+16 (21%)
39	59668.50	167.5926	-47.7968	0.0517	H-6->LUMO (17%), H-5->LUMO (15%), H-3->L+3 (16%)
40	59807.23	167.2039	2.7147	0.013	HOMO->L+14 (23%)
41	60217.77	166.0639	7.0709	0.0058	H-5->LUMO (25%), H-3->L+3 (40%)
42	60455.70	165.4104	-25.4674	0.0339	
43	60575.08	165.0844	5.7898	0.0143	H-2->L+9 (12%)
44	60699.29	164.7466	-9.5975	0.0174	H-4->L+1 (10%), H-1->L+7 (10%)
45	60892.86	164.2229	-8.3357	0.0057	H-2->L+10 (12%)
46	60942.87	164.0881	-8.3158	0.0416	H-4->L+4 (18%)
47	61353.41	162.9901	-24.3933	0.0303	H-2->L+11 (23%)
48	61388.89	162.8959	3.7193	0.0046	H-1->L+7 (28%), H-1->L+16 (23%)
49	61580.05	162.3903	45.0472	0.0362	H-4->L+4 (15%), HOMO->L+18 (11%)
50	61721.20	162.0189	17.0875	0.0017	H-6->LUMO (15%)

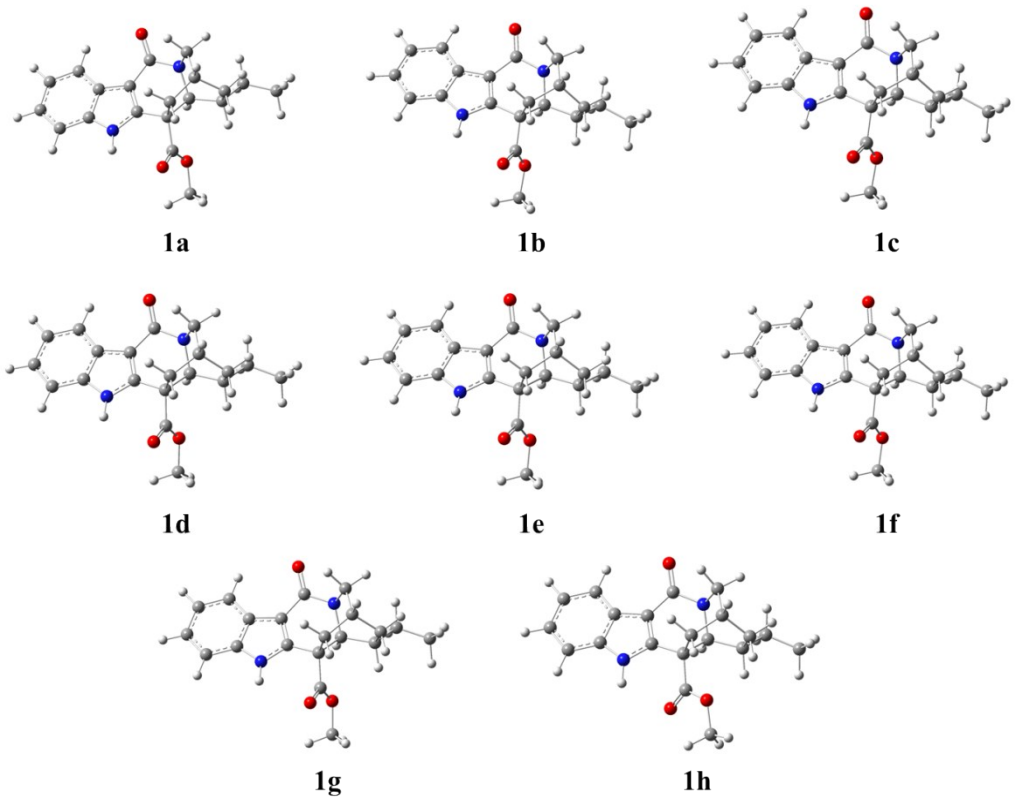


Figure S9. Optimized geometries of predominant conformers of **3** in the gas phase at the B3LYP/6-31+G(d) level

Table S12. Standard orientation of **3a**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.216539	-0.887416	-0.665929
2	6	0	5.46525	0.464827	-0.311109
3	6	0	4.441286	1.318322	0.06428
4	6	0	3.138375	0.78761	0.078242
5	6	0	2.870626	-0.577779	-0.281356
6	6	0	3.937529	-1.416275	-0.654581
7	7	0	1.905372	1.400788	0.413973
8	6	0	0.900209	0.452404	0.259717
9	6	0	1.453033	-0.766666	-0.153306
10	6	0	-0.575764	0.640838	0.488079
11	6	0	-1.289045	-0.388786	-0.482545
12	7	0	-0.809319	-1.762253	-0.132448
13	6	0	-2.834195	-0.311229	-0.325785
14	6	0	-3.516967	-1.307065	-1.280936

15	6	0	-5.012433	-1.038956	-1.423588
16	6	0	-0.957519	0.250028	1.94431
17	6	0	-1.941709	-0.942281	1.938688
18	6	0	-3.208451	-0.547595	1.155099
19	6	0	-1.307057	-2.165487	1.228246
20	1	0	-2.200756	-1.212014	2.985654
21	1	0	-0.997625	-0.165962	-1.537194
22	1	0	-3.153956	0.721446	-0.618046
23	6	0	0.642355	-1.977015	-0.274709
24	8	0	1.049604	-3.102979	-0.434586
25	6	0	-0.910087	2.106839	0.235572
26	8	0	-0.453357	3.057326	0.836097
27	8	0	-1.77379	2.270195	-0.811086
28	6	0	-2.126483	3.639451	-1.162138
29	1	0	6.061111	-1.51356	-0.951399
30	1	0	6.491622	0.829424	-0.337776
31	1	0	4.628655	2.351868	0.336987
32	1	0	3.733396	-2.454691	-0.920947
33	1	0	1.775376	2.354593	0.723203
34	1	0	-3.033431	-1.257258	-2.277368
35	1	0	-3.342862	-2.3458	-0.933312
36	1	0	-5.532563	-1.104754	-0.46161
37	1	0	-5.208993	-0.043163	-1.836115
38	1	0	-5.477898	-1.769072	-2.096347
39	1	0	-0.048483	-0.013747	2.518978
40	1	0	-1.404929	1.109048	2.478274
41	1	0	-3.973563	-1.340283	1.246413
42	1	0	-3.666458	0.358972	1.586081
43	1	0	-2.064544	-2.965619	1.07281
44	1	0	-0.497874	-2.611237	1.840758
45	1	0	-1.226837	4.179327	-1.473324
46	1	0	-2.826347	3.493976	-1.992396
47	1	0	-2.59802	4.129811	-0.30491

Table S13. Standard orientation of **3b**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.220848	-0.893256	-0.338277
2	6	0	5.437074	0.497723	-0.251534
3	6	0	4.374125	1.383879	-0.083817
4	6	0	3.090865	0.83654	-0.011636

5	6	0	2.850937	-0.558592	-0.116462
6	6	0	3.938534	-1.432816	-0.270323
7	7	0	1.860263	1.467206	0.177397
8	6	0	0.863548	0.530127	0.136878
9	6	0	1.41937	-0.726547	-0.035778
10	6	0	-0.622594	0.75942	0.306063
11	6	0	-1.24478	-0.399077	-0.580848
12	7	0	-0.80661	-1.668246	0.029858
13	6	0	-2.782147	-0.2895	-0.64728
14	6	0	-3.454453	-1.227787	-1.680018
15	6	0	-3.443893	-2.741812	-1.429644
16	6	0	-1.142563	0.464344	1.772581
17	6	0	-2.19145	-0.680234	1.771412
18	6	0	-3.347127	-0.362798	0.803414
19	6	0	-1.530043	-1.98444	1.288205
20	1	0	-2.573195	-0.81634	2.790922
21	1	0	-0.821746	-0.33684	-1.587444
22	1	0	-2.978447	0.717321	-1.0346
23	6	0	0.588301	-1.918932	0.101073
24	8	0	1.014685	-3.034472	0.383598
25	6	0	-0.99669	2.141989	-0.224748
26	8	0	-0.372195	2.734779	-1.088395
27	8	0	-2.109897	2.654541	0.337045
28	6	0	-2.541365	3.936357	-0.164167
29	1	0	6.074306	-1.555479	-0.45858
30	1	0	6.450252	0.886471	-0.310745
31	1	0	4.540462	2.455637	-0.00825
32	1	0	3.772208	-2.503651	-0.329773
33	1	0	1.696172	2.454571	0.033041
34	1	0	-4.499199	-0.896508	-1.773557
35	1	0	-2.990856	-1.028952	-2.657337
36	1	0	-2.426524	-3.138122	-1.368386
37	1	0	-3.970078	-3.008117	-0.505228
38	1	0	-3.961076	-3.253817	-2.250177
39	1	0	-0.291899	0.183385	2.402979
40	1	0	-1.583084	1.366229	2.203743
41	1	0	-4.110617	-1.145988	0.884675
42	1	0	-3.828158	0.582822	1.077286
43	1	0	-2.279767	-2.768229	1.128163
44	1	0	-0.806929	-2.370623	2.012874
45	1	0	-3.442025	4.175878	0.401303
46	1	0	-1.766589	4.688663	0.003246
47	1	0	-2.758525	3.872659	-1.233484

Table S14. Standard orientation of **3c**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.304028	-0.787341	-0.48366
2	6	0	5.481569	0.607215	-0.369639
3	6	0	4.398276	1.456726	-0.150844
4	6	0	3.134179	0.869517	-0.05557
5	6	0	2.932541	-0.529635	-0.186924
6	6	0	4.040741	-1.366761	-0.392487
7	7	0	1.891767	1.458579	0.18169
8	6	0	0.922452	0.49328	0.145946
9	6	0	1.509479	-0.742193	-0.071864
10	6	0	-0.565202	0.670321	0.361517
11	6	0	-1.171115	-0.475864	-0.545255
12	7	0	-0.68452	-1.751681	0.012902
13	6	0	-2.712204	-0.454618	-0.579761
14	6	0	-3.273484	-1.554293	-1.504617
15	6	0	-4.766234	-1.380264	-1.812297
16	6	0	-1.031536	0.306827	1.831029
17	6	0	-2.05785	-0.857531	1.814188
18	6	0	-3.239033	-0.52203	0.885942
19	6	0	-1.388837	-2.133451	1.262888
20	1	0	-2.41244	-1.036991	2.836717
21	1	0	-0.774633	-0.369778	-1.558827
22	1	0	-3.00188	0.507299	-1.022428
23	6	0	0.716917	-1.962173	0.058096
24	8	0	1.182187	-3.06874	0.3136
25	6	0	-1.002082	2.05606	-0.108142
26	8	0	-0.397932	2.723787	-0.930829
27	8	0	-2.148232	2.480337	0.459497
28	6	0	-2.638386	3.763362	0.018567
29	1	0	6.172811	-1.420514	-0.643994
30	1	0	6.480702	1.02763	-0.448096
31	1	0	4.535051	2.531007	-0.054502
32	1	0	3.90453	-2.440484	-0.473059
33	1	0	1.692468	2.443391	0.066664
34	1	0	-2.711072	-1.541664	-2.448601
35	1	0	-3.096354	-2.541911	-1.061875
36	1	0	-5.379229	-1.410075	-0.903148
37	1	0	-4.959232	-0.421302	-2.311038
38	1	0	-5.123667	-2.17709	-2.474895
39	1	0	-0.155237	0.019649	2.421994
40	1	0	-1.476843	1.181135	2.311987

41	1	0	-4.00549	-1.300813	0.9826
42	1	0	-3.702965	0.424483	1.182206
43	1	0	-2.136726	-2.914943	1.075431
44	1	0	-0.653059	-2.549342	1.957216
45	1	0	-1.905956	4.544159	0.238015
46	1	0	-2.837013	3.745235	-1.056005
47	1	0	-3.557994	3.926652	0.580676

Table S15. Standard orientation of **3d**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.089208	-1.313105	-0.511915
2	6	0	5.400989	0.05591	-0.373318
3	6	0	4.402831	1.005497	-0.164328
4	6	0	3.084995	0.544421	-0.100809
5	6	0	2.748837	-0.82808	-0.248112
6	6	0	3.774357	-1.766413	-0.449421
7	7	0	1.900105	1.248347	0.105236
8	6	0	0.844836	0.376228	0.085941
9	6	0	1.312561	-0.908617	-0.136013
10	6	0	-0.623335	0.701625	0.272474
11	6	0	-1.349331	-0.420902	-0.534014
12	7	0	-0.957068	-1.703233	0.092148
13	6	0	-2.886742	-0.278786	-0.528711
14	6	0	-3.560644	-1.398601	-1.347476
15	6	0	-5.041839	-1.12283	-1.6369
16	6	0	-1.102444	0.534336	1.775348
17	6	0	-2.190331	-0.565609	1.869634
18	6	0	-3.370063	-0.203071	0.951003
19	6	0	-1.628588	-1.924103	1.397986
20	1	0	-2.524125	-0.648486	2.911736
21	1	0	-0.989935	-0.418667	-1.565987
22	1	0	-3.108686	0.664838	-1.035602
23	6	0	0.414004	-2.044888	0.081275
24	8	0	0.794885	-3.171381	0.385319
25	6	0	-0.886853	2.100958	-0.286704
26	8	0	-1.469272	2.362626	-1.316602
27	8	0	-0.341638	3.061878	0.507594
28	6	0	-0.539614	4.425885	0.073084
29	1	0	5.894507	-2.026209	-0.667563
30	1	0	6.437969	0.37661	-0.427467

31	1	0	4.643299	2.060138	-0.05381
32	1	0	3.535257	-2.820719	-0.544587
33	1	0	1.819514	2.235702	0.304883
34	1	0	-3.025995	-1.507426	-2.301241
35	1	0	-3.454217	-2.360115	-0.830223
36	1	0	-5.629629	-1.026045	-0.715415
37	1	0	-5.166331	-0.193991	-2.208421
38	1	0	-5.484217	-1.937046	-2.222946
39	1	0	-0.244222	0.282328	2.407724
40	1	0	-1.506345	1.479976	2.151451
41	1	0	-4.197645	-0.901868	1.124911
42	1	0	-3.749835	0.797748	1.195931
43	1	0	-2.437126	-2.661843	1.31077
44	1	0	-0.894908	-2.331126	2.100741
45	1	0	-1.607218	4.651905	0.018175
46	1	0	-0.053813	5.04227	0.829881
47	1	0	-0.08635	4.582124	-0.909259

Table S16. Standard orientation of **3e**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.070317	-0.947659	0.669061
2	6	0	-5.331052	0.385215	0.288122
3	6	0	-4.300796	1.237917	-0.103998
4	6	0	-3.004242	0.71708	-0.101756
5	6	0	-2.718577	-0.619706	0.28745
6	6	0	-3.775715	-1.460636	0.671388
7	7	0	-1.797289	1.321325	-0.452819
8	6	0	-0.780331	0.420381	-0.292531
9	6	0	-1.288774	-0.782302	0.166985
10	6	0	0.687283	0.642358	-0.58634
11	6	0	1.40636	-0.351658	0.379264
12	7	0	0.944348	-1.706316	0.007342
13	6	0	2.945643	-0.268165	0.278849
14	6	0	3.665819	-1.252577	1.224216
15	6	0	3.394213	-1.029713	2.717055
16	6	0	1.074531	0.197629	-2.052037
17	6	0	2.120329	-0.943574	-2.000263
18	6	0	3.35339	-0.46918	-1.212315
19	6	0	1.541874	-2.175532	-1.270397
20	1	0	2.400585	-1.222215	-3.023721

21	1	0	1.087759	-0.153758	1.403503
22	1	0	3.22283	0.742566	0.600192
23	6	0	-0.440928	-1.976961	0.130748
24	8	0	-0.87481	-3.122172	0.055479
25	6	0	0.959763	2.128134	-0.345024
26	8	0	0.756311	2.994779	-1.176337
27	8	0	1.35923	2.393921	0.911275
28	6	0	1.534017	3.786918	1.247009
29	1	0	-5.899408	-1.586236	0.962475
30	1	0	-6.353289	0.754029	0.296269
31	1	0	-4.501571	2.263674	-0.403455
32	1	0	-3.576769	-2.489715	0.952847
33	1	0	-1.687688	2.253495	-0.831045
34	1	0	3.400915	-2.282894	0.956752
35	1	0	4.744642	-1.150833	1.038892
36	1	0	4.022162	-1.691031	3.325651
37	1	0	3.614911	0.004307	3.013969
38	1	0	2.351702	-1.240746	2.980205
39	1	0	1.477247	1.053578	-2.602504
40	1	0	0.177881	-0.131526	-2.588221
41	1	0	4.15399	-1.215844	-1.290287
42	1	0	3.746497	0.460209	-1.645043
43	1	0	2.329748	-2.918372	-1.089989
44	1	0	0.760947	-2.669412	-1.856801
45	1	0	1.86354	3.79101	2.285825
46	1	0	2.285725	4.242033	0.597471
47	1	0	0.587434	4.32259	1.139097

Table S17. Standard orientation of **3f**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.304065	-0.78723	-0.483712
2	6	0	5.481596	0.607313	-0.36947
3	6	0	4.398311	1.456779	-0.150471
4	6	0	3.134211	0.869541	-0.055317
5	6	0	2.932572	-0.529568	-0.187001
6	6	0	4.040779	-1.366665	-0.392636
7	7	0	1.891786	1.458584	0.182066
8	6	0	0.922458	0.493295	0.145938
9	6	0	1.509483	-0.742138	-0.072059
10	6	0	-0.565176	0.670332	0.361572

11	6	0	-1.171158	-0.475848	-0.545221
12	7	0	-0.6845	-1.751687	0.012808
13	6	0	-2.712246	-0.454573	-0.579578
14	6	0	-3.273617	-1.554097	-1.504553
15	6	0	-4.766466	-1.380221	-1.811851
16	6	0	-1.03144	0.306892	1.831046
17	6	0	-2.057627	-0.857588	1.814304
18	6	0	-3.238935	-0.522201	0.886189
19	6	0	-1.388568	-2.133464	1.262948
20	1	0	-2.412098	-1.037097	2.836874
21	1	0	-0.774735	-0.369689	-1.558817
22	1	0	-3.001991	0.507423	-1.022026
23	6	0	0.716957	-1.962158	0.057767
24	8	0	1.182292	-3.068763	0.312997
25	6	0	-1.002102	2.055995	-0.108322
26	8	0	-0.398265	2.723527	-0.931357
27	8	0	-2.148155	2.480349	0.459567
28	6	0	-2.63861	3.763111	0.01831
29	1	0	6.17283	-1.420327	-0.64445
30	1	0	6.480718	1.027739	-0.448015
31	1	0	4.535065	2.531044	-0.053953
32	1	0	3.904569	-2.440374	-0.473392
33	1	0	1.692506	2.443396	0.06702
34	1	0	-2.711427	-1.54119	-2.448672
35	1	0	-3.09625	-2.541784	-1.062064
36	1	0	-5.379296	-1.410745	-0.902618
37	1	0	-4.959773	-0.420999	-2.309968
38	1	0	-5.123818	-2.176723	-2.474882
39	1	0	-0.155101	0.019916	2.422058
40	1	0	-1.47692	1.181151	2.311945
41	1	0	-4.005283	-1.301094	0.982838
42	1	0	-3.702966	0.424236	1.18253
43	1	0	-0.652647	-2.549205	1.957223
44	1	0	-2.136385	-2.915052	1.075617
45	1	0	-3.557953	3.926593	0.580807
46	1	0	-1.906139	4.544078	0.237028
47	1	0	-2.837795	3.744487	-1.056157

Table S18. Standard orientation of **3g**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.070378	-0.947376	0.669433
2	6	0	-5.331111	0.385387	0.288096
3	6	0	-4.300891	1.23799	-0.104246
4	6	0	-3.00433	0.71716	-0.101888
5	6	0	-2.718677	-0.619558	0.287564
6	6	0	-3.775805	-1.460397	0.671742
7	7	0	-1.79736	1.32138	-0.452855
8	6	0	-0.780383	0.420495	-0.292355
9	6	0	-1.288887	-0.782194	0.167111
10	6	0	0.687194	0.642447	-0.586151
11	6	0	1.406303	-0.351756	0.379259
12	7	0	0.94417	-1.706336	0.007175
13	6	0	2.945578	-0.26841	0.278747
14	6	0	3.665707	-1.253116	1.223872
15	6	0	3.394392	-1.030385	2.716784
16	6	0	1.074356	0.197857	-2.051971
17	6	0	2.12009	-0.943409	-2.000411
18	6	0	3.353222	-0.469151	-1.212476
19	6	0	1.541577	-2.175403	-1.270676
20	1	0	2.400249	-1.221923	-3.023925
21	1	0	1.087792	-0.153979	1.403549
22	1	0	3.222913	0.742188	0.600331
23	6	0	-0.441107	-1.976922	0.130662
24	8	0	-0.875064	-3.122075	0.055231
25	6	0	0.959879	2.128165	-0.344723
26	8	0	0.755924	2.994933	-1.17581
27	8	0	1.360198	2.39376	0.911313
28	6	0	1.535249	3.786737	1.247121
29	1	0	-5.899476	-1.585853	0.963043
30	1	0	-6.353354	0.754187	0.29612
31	1	0	-4.501606	2.263789	-0.403604
32	1	0	-3.576857	-2.489429	0.953364
33	1	0	-1.687587	2.253701	-0.830664
34	1	0	3.400576	-2.283361	0.956351
35	1	0	4.744513	-1.151566	1.038345
36	1	0	3.615176	0.003593	3.013783
37	1	0	2.351916	-1.241423	2.980051
38	1	0	4.022427	-1.691794	3.325191
39	1	0	0.177642	-0.131242	-2.588086
40	1	0	1.477003	1.053853	-2.602405

41	1	0	4.153851	-1.215757	-1.290638
42	1	0	3.746242	0.460323	-1.645105
43	1	0	0.760568	-2.669155	-1.857073
44	1	0	2.329405	-2.918332	-1.090439
45	1	0	2.286927	4.241747	0.597476
46	1	0	0.588737	4.322554	1.139386
47	1	0	1.864961	3.790684	2.285874

Table S19. Standard orientation of **3h**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.304014	-0.787528	-0.483396
2	6	0	5.481591	0.607057	-0.369635
3	6	0	4.398251	1.456569	-0.150972
4	6	0	3.134115	0.869418	-0.05578
5	6	0	2.932479	-0.529726	-0.187067
6	6	0	4.040668	-1.366887	-0.392448
7	7	0	1.891725	1.458503	0.182193
8	6	0	0.922402	0.493091	0.145903
9	6	0	1.509413	-0.742323	-0.071982
10	6	0	-0.565258	0.670171	0.361316
11	6	0	-1.171261	-0.475949	-0.545395
12	7	0	-0.684683	-1.751749	0.012822
13	6	0	-2.712365	-0.454492	-0.579738
14	6	0	-3.273933	-1.554166	-1.504458
15	6	0	-4.766669	-1.379874	-1.812079
16	6	0	-1.031536	0.306828	1.830892
17	6	0	-2.057863	-0.857537	1.814162
18	6	0	-3.239049	-0.521713	0.885995
19	6	0	-1.38897	-2.133458	1.262834
20	1	0	-2.412511	-1.03688	2.836712
21	1	0	-0.774813	-0.369979	-1.559026
22	1	0	-3.001971	0.50744	-1.022479
23	6	0	0.716792	-1.962327	0.057919
24	8	0	1.181942	-3.068862	0.313638
25	6	0	-1.001713	2.056063	-0.108062
26	8	0	-0.397516	2.723377	-0.931154
27	8	0	-2.147653	2.480672	0.459582
28	6	0	-2.63753	3.763813	0.018744
29	1	0	6.17278	-1.420762	-0.643592
30	1	0	6.480732	1.027425	-0.448303

31	1	0	4.535115	2.530774	-0.053971
32	1	0	3.904447	-2.44062	-0.472982
33	1	0	1.691986	2.443055	0.065471
34	1	0	-2.711558	-1.541753	-2.448487
35	1	0	-3.096954	-2.541783	-1.061624
36	1	0	-5.124383	-2.176847	-2.474346
37	1	0	-5.379604	-1.409154	-0.902878
38	1	0	-4.959396	-0.421053	-2.31118
39	1	0	-0.155167	0.019933	2.4219
40	1	0	-1.476987	1.181193	2.311667
41	1	0	-3.702481	0.425042	1.182328
42	1	0	-4.005915	-1.300084	0.982716
43	1	0	-2.136861	-2.914946	1.075297
44	1	0	-0.653268	-2.549356	1.957274
45	1	0	-1.904831	4.544391	0.23809
46	1	0	-2.836335	3.745741	-1.055799
47	1	0	-3.556987	3.927273	0.581061

[1] Gaussian 09, Revision A.02, 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, J. A.; Jr., 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.; J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, 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, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; Gaussian, Inc., Wallingford CT, **2009**.

[2] Bruhn, T.; Schaumlöffel, A.; Hemberger, Y.; Bringmann, G.; SpecDis version 1.60,
University of Wuerzburg, Germany, **2012**.

3. Single-crystal X-ray diffraction data and structures of 2 and 4

The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXL-97 package software[3]. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as deposition number CCDC 1528868 for **2** and CCDC 1524395 for **4**.

X-ray crystallographic data of 2. Colorless blocks; $C_{19}H_{24}N_2O_2$ (fw = 312.40); Orthorhombic, space group $P2_12_12_1$; a = 7.00418(8) Å, b = 15.07922(14) Å, c = 15.68796(17) Å, α = 90°, β = 90°, γ = 90°; V = 1656.93(3) Å^3, T = 100.01 (10) K, Z = 4, D_c = 1.252 g/cm^3, F(000) = 672. A total of 15731 reflections were collected in the range 4.07 ≤ θ ≤ 73.68, of which 3249 unique reflections with $I > 2\sigma(I)$ were collected for the analysis. Final R = 0.0302 and R_w =0.0769, and the goodness of fit on F^2 was equal to 1.044; Flack parameter = −0.00(7).

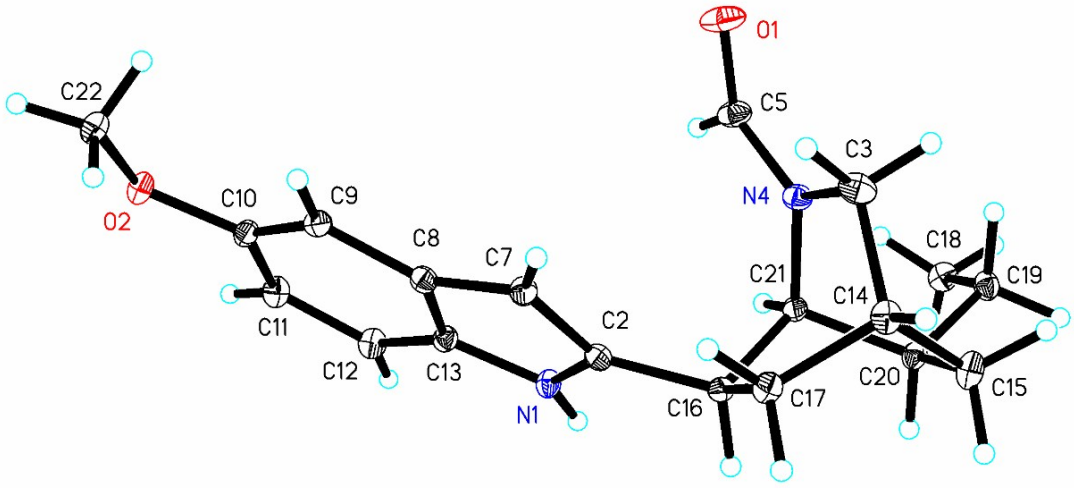


Figure S10. X-ray ORTEP drawing of **2**

X-ray crystallographic data of 4. Colorless blocks; $C_{20}H_{24}N_2O_2$ (fw = 324.41); Orthorhombic, space group $P2_12_12_1$; a = 8.75070(10) Å, b = 14.3787(2) Å, c = 27.3576(4) Å, α = 90°, β = 90°, γ = 90°; V = 3442.23(8) Å^3, T = 173(2) K, Z = 8, D_c = 1.252 g/cm^3, F(000) = 1392. A total of 27736 reflections were collected in the range 3.47 ≤ θ ≤ 62.68, of which 5506 unique reflections with $I > 2\sigma(I)$ were collected for the analysis. Final R = 0.0291 and R_w =0.0737, and the goodness of fit on F^2 was equal to 1.092; Flack parameter = −0.03(7).

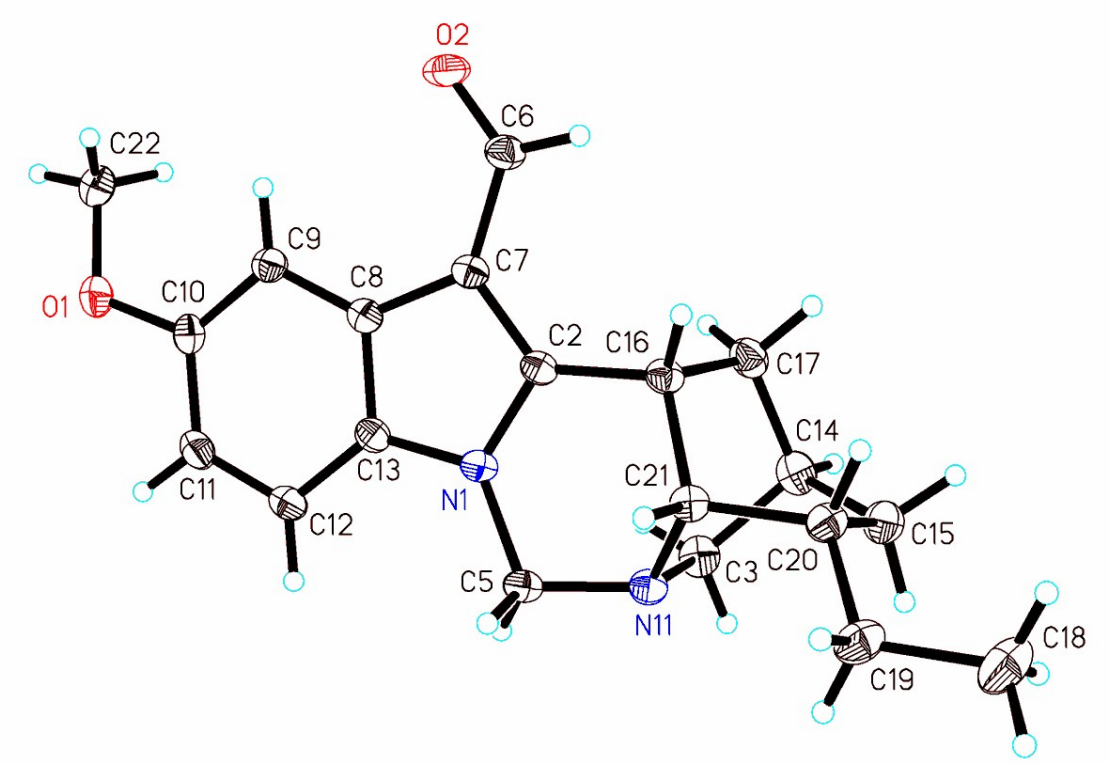


Figure S11. X-ray ORTEP drawing of **4**

[3] Sheldrick, G. M. *Acta Cryst*. **2008**, *64*, 112.

4. 1D and 2D NMR data of 1−3

Table S20. 1D and 2D NMR Data of **1**[a]

no.		δ_H[b]	δ_C[b]	^{1}H-^{1}H COSY[b]	HMBC[b]	NOESY[c]
2			92.4			
3		4.81 d (4.0)	96.3	H-14	C-6, 15, 17, 21	H-5*α*, 15*α*
5	*α*	3.19 dd (12.7, 5.5)	54.5		C-13, 21	H-3
	β	3.92 d (12.7)			C-3, 21	H-21, OH
6		5.83 d (5.5)	81.6		C-2, 3, 13	H-12
7			203.4			
8			120.9			
9		7.02 d (2.7)	105.8		C-7, 11, 13	
10			155.0			
11		7.26 dd (8.9, 2.7)	129.1	H-12	C-9, 13	
12		7.17 d (8.9)	113.0	H-11	C-8, 10	H-6
13			157.1			
14		1.79 m	31.4	H-3, 15*β*, 17*β*	C-20	
15	*α*	1.06	30.8		C-3, 17, 19	H-3, 19b
	β	1.90 m		H-14, 20	C-3, 17, 21	H-20
16		2.18 m	43.3	H-17, 21	C-7, 14, 20	H-20, OH
17	*α*	1.06	19.9		C-2, 15	
	β	1.14 m		H-14	C-2, 3, 15	
18		0.96 t (7.3)	12.1	H-19	C-20	H-21
19	a	1.59 m	28.6	H-18, 20	C-15, 21	H-21
	b	1.47		H-18	C-15, 21	H-15*β*
20		1.48	40.5	H-15*β*, 19a, 21	C-18	H-16, 15*β*
21		3.30	55.3	H-16, 20	C-2, 3, 5, 15, 19	H-5*β*, 18, OH
22(OCH_3)		3.78 s	56.3		C-10	
OH[c]		6.39 br s[c]			C-7,16[c]	H-5*β*, 16, 21

[a]Measured at 600 (^{1}H) and 150 (^{13}C) MHz. δ in ppm, J in Hz. Overlapped signals are reported without designating multiplicity. [b]Measured in CD_3OD. [c]Measured in DMSO-d_6.

Table S21 1D and 2D NMR data of **2**[a]

no.		δ_H	δ_C	^{1}H-^{1}H COSY	HMBC	NOESY
2			143.4			
3	a	3.47 d (12.4)	48.4		C-15	H-7, 17*β*
	b	3.25 d (12.4)		H-14	C-17	H-15*β*
5		7.53 s	164.8		C-21	H-21
7		6.14 s	99.9		C-9, 13	H-3a, 9, 17*β*
8			133.2			
9		6.95 d (2.4)	103.0		C-7, 11, 13	H-7, 22
10			155.2			
11		6.68 dd (8.7, 2.4)	111.9	H-12	C-9	
12		7.15 d (8.7)	112.2	H-11	C-10	
13			130.2			
14		2.13 m	27.1	H-3, 15*β*, 17*β*		
15	*α*	2.05 m	32.9	H-20	C-19	H-15*β*, 20
	β	1.28		H-14		H-3b
16		3.30	39.6	H-17	C-2, 7, 20	H-17*α*, 20, 21
17	*α*	2.18 m	31.1	H-16		H-16
	β	2.00 m		H-16		H-3a, 7
18		0.97 t (7.4)	11.7	H-19	C-20	H-20, 21
19	a	1.34 m	29.4	H-18, 20	C-21	H-21
	b	1.27		H-18, 20		
20		1.92 m	40.7	H- 15*α*, 19, 21		H-15*α*, 16, 18
21		3.57 br s	57.4	H-20	C-2, 3, 5, 17, 19	H-5, 18, 19
22 (OCH_3)		3.77 s	56.3		C-10	H-9

[a]Measured at 600 (^{1}H) and 150 (^{13}C) MHz in CD_3OD. δ in ppm, J in Hz. Overlapped signals are reported without designating multiplicity.

Table S22. 1D and 2D NMR Data of **3**[a]

no		δ_H	δ_C	^{1}H-^{1}H COSY	HMBC	NOESY
2			157.3			
3	a	3.35 dt (12.0, 3.0)	53.2	H-14	C-6, 15, 17	H-17*β*
	b	3.32 br d		H-14	C-6, 15, 17	H-15*β*, 19
6			179.0			
7			105.6			
8			126.3			
9		7.85 dd (8.0, 2.2)	121.3	H-10	C-7, 11, 13	
10		7.19	123.2	H-9, 11	C-8, 12	
11		7.17	124.0	H-10, 12	C-9, 13	
12		7.36 dd (8.0, 2.2)	113.0	H-11	C-8, 10	
13			137.9			
14		2.22 br s	32.8	H-3, 15*β*, 17		
15	*α*	1.91 td (13.0, 11.0)	30.7	H-14, 20	C-3	H-17*α*
	β	1.40 m		H-14	C-17	H-3b, 19
16			49.1			
17	*α*	1.79 dt (14.0, 2.0)	34.5	H-14	C-3, 22	H-15*α*, 20
	β	2.78 m		H-14	C-2, 15, 22	H-15*β*
18		0.98 t (7.4)	12.3	H-19	C-20	
19	a	1.70 m	29.3	H-18, 20	C-15, 21	
	b	1.56 m		H-18	C-15, 21	
20		1.75 m	36.4	H-15*α*, 19a, 21		H-18
21		4.17 d (2.6)	59.7	H-20	C-2, 3, 15, 17	
22(*C*OOCH$_3$)			174.0			
23(COO*CH$_3$*)		3.85 s	53.5		C-21	

[a]Measured at 600 (^{1}H) and 150 (^{13}C) MHz in CD$_3$OD. δ in ppm, J in Hz. Overlapped signals are reported without designating multiplicity.

5. ^{1}H-^{1}H COSY, key HMBC and NOESY correlations of 3

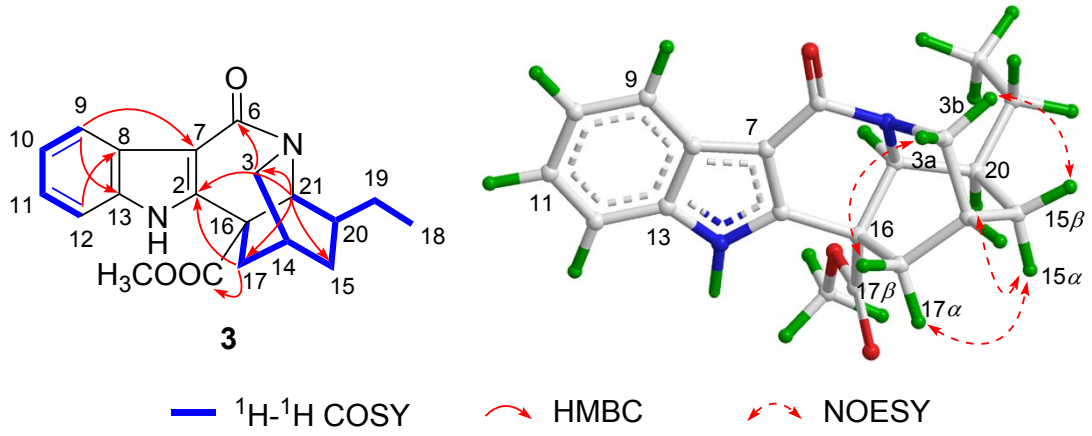


Figure S12. ^{1}H-^{1}H COSY, key HMBC and NOESY correlations of **3**

6. Structure characterization of compounds 4–9

Lirofolines A (4). Colorless blocks ($CHCl_3$/MeOH); mp 185−186 °C; $[\alpha]_D^{25}$ = −37.5 (*c* = 0.93, MeOH) UV (MeOH) λ_{max} (log ε) 216 (4.25), 257 (4.03), 277 (3.88), 307 (3.84) nm; IR (KBr) ν_{max} 3450, 2929, 2861, 1725, 1646, 1580, 1515, 1483, 1455, 1399, 1364, 1315, 1263, 1243, 1225, 1191, 1152, 1122, 1086, 1039, 917, 894, 857, 802, 757, 709, 660, 598 cm^{-1}; ESIMS *m/z* 325 $[M + H]^+$; ^1H NMR (600 MHz, CD_3OD) δ 2.70 (1H, dd, *J* = 10.1, 2.0 Hz, H-3α), 3.26 (1H, dd, *J* = 10.1, 2.9 Hz, H-3β), 4.87 (1H, d, *J* = 12.0 Hz, H-5α), 4.91 (1H, d, *J* = 12.0 Hz, H-5β), 10.1 (1H, s, H-6), 7.73 (1H, d, *J* = 2.5 Hz, H-9), 6.86 (1H, dd, *J* = 8.8, 2.5 Hz, H-11), 7.12 (1H, d, *J* = 8.8 Hz, H-12), 1.79 (1H, m, H-14), 1.17 (1H, m, H-15β), 1.88 (1H, m, H-15α), 3.53 (1H, d, *J* = 11.5 Hz, H-16), 1.69 (1H, m, H-17α), 2.18 (1H, t, *J* = 12.0 Hz, H-17β), 0.96 (1H, t, *J* = 7.4 Hz, H-18), 1.59 (2H, m, H-19), 1.72 (1H, m, H-20), 2.83 (1H, br s, H-21), 3.88 (3H, s, H-22); ^{13}C NMR (150 MHz, CD_3OD) δ 154.3 (C-2), 53.5 (C-3), 67.1 (C-5), 182.9 (C-6), 111.7 (C-7), 127.0 (C-8), 103.0 (C-9), 156.8 (C-10), 112.7 (C-11), 109.8 (C-12), 129.8 (C-13), 25.4 (C-14), 31.1 (C-15), 29.6 (C-16), 33.4 (C-17), 11.7 (C-18), 27.3 (C-19), 37.8 (C-20), 51.5 (C-21), 55.8 (C-22).

Lirofolines B (5). Yellow oil; $[\alpha]_D^{25}$ = −27.4 (*c* = 0.82, MeOH); UV (MeOH) λ_{max} (log ε) 218 (4.19), 255 (3.97), 306 (3.77) nm; IR (KBr) ν_{max} 3420, 2953, 2929, 2860, 1626, 1579, 1487, 1455, 1405, 1374, 1311, 1233, 1193, 1154, 1083, 1051, 994, 943, 857, 824, 798 cm^{-1}; ESIMS *m/z* 355 $[M + H]^+$; ^1H NMR (600 MHz, CD_3OD) δ 2.66 (1H, dd, *J* = 11.0, 2.6 Hz, H-3α), 3.26 (1H, dd, *J* = 11.0, 2.8 Hz, H-3β), 4.91 (1H, d, *J* = 12.0 Hz, H-5α), 4.97 (1H, d, *J* = 12.0 Hz, H-5β), 7.36 (1H, d, *J* = 2.5 Hz, H-9), 6.90

(1H, dd, J = 8.7, 2.3 Hz, H-11), 7.16 (1H, d, J = 8.7 Hz, H-12), 1.80 (1H, m, H-14), 1.17 (1H, m, H-15β), 1.89 (1H, m, H-15α), 3.66 (1H, d, J = 11.3 Hz, H-16), 1.58 (1H, m, H-17α), 2.28 (1H, m, H-17β), 0.96 (1H, t, J = 7.5 Hz, H-18), 1.60 (2H, m, H-19), 1.73 (1H, m, H-20), 2.81 (1H, br s, H-21), 4.73 (dd, J = 10.0, 7.1 Hz, H-22a), 4.78 (dd, J = 10.0, 7.1 Hz, H-22b), 3.90 (3H, s, H-23); ^{13}C NMR (150 MHz, CD_3OD) δ 152.7 (C-2), 53.5 (C-3), 67.2 (C-5), 192.5 (C-6), 108.0 (C-7), 126.8 (C-8), 103.8 (C-9), 156.6 (C-10), 111.6 (C-11), 110.1 (C-12), 129.8 (C-13), 25.4 (C-14), 31.2 (C-15), 31.8 (C-16), 32.4 (C-17), 11.7 (C-18), 27.3 (C-19), 37.8 (C-20), 51.9 (C-21), 67.0 (C-22), 55.9 (C-23).

6-Oxo-ibogaine (6). Yellow oil; $[\alpha]$ = +7.4 (c = 0.54, MeOH); UV (MeOH) λ_{max} (log ε) 215 (4.18), 250 (3.90), 303 (3.53) nm; IR (KBr) ν_{max} 3138, 2930, 2870, 1595, 1575, 1457, 1434, 1359, 1271, 1192, 1144, 1026, 959, 868, 806, 671, 608 cm^{-1}; ESIMS m/z 325 $[M+H]^+$; ^{1}H NMR (400 MHz, CD_3OD) δ 2.94 (1H, m, H-3a), 3.11 (1H, m, H-3b), 3.63 (1H, d, J = 18.1 Hz, H-5β), 3.82 (1H, d, J = 18.1 Hz, H-5α), 7.92 (1H, d, J = 2.5 Hz, H-9), 6.84 (1H, dd, J = 8.7, 2.5 Hz, H-11), 7.22 (1H, d, J = 8.7 Hz, H-12), 1.87 (1H, m, H-14), 1.22 (1H, m, H-15β), 1.83 (1H, m, H-15α), 3.50 (1H, m, H-16), 1.64 (1H, overlapped, H-17α), 2.21 (1H, m, H-17β), 0.98 (1H, t, J = 7.2 Hz, H-18), 1.53 (1H, m, H-19a), 1.60 (1H, overlapped, H-19b), 1.62 (1H, overlapped, H-20), 3.07 (1H, br s, H-21), 3.84 (3H, s, H-22); ^{13}C NMR (100 MHz, CD_3OD) δ 156.5 (C-2), 53.9 (C-3), 67.3 (C-5), 202.7 (C-6), 114.2 (C-7), 129.9 (C-8), 105.8 (C-9), 157.6 (C-10), 113.6 (C-11), 112.3 (C-12), 132.4 (C-13), 28.5 (C-14), 32.5 (C-15), 43.3 (C-16), 34.1 (C-17), 12.0 (C-18), 28.0 (C-19), 42.3 (C-20), 56.3 (C-21), 56.1 (C-22).

8-Oxo-ibogaine lactam (7). Yellow oil; $[\alpha]_D^{25}$ = −24.7 (*c* = 1.07, MeOH); UV (MeOH) λ_{max} (log ε) 213 (4.22), 252 (3.93), 278 (3.71), 305 (3.63) nm; IR (KBr) ν_{max} 3248, 2955, 2929, 2873, 1661, 1609, 1482, 1442, 1400, 1358, 1307, 1270, 1200, 1154, 1067, 1034 cm^{-1}; ESIMS *m/z* 339 $[M + H]^+$, 337 $[M - H]^-$; ^1H NMR (600 MHz, Pyridine-d_6) δ 4.03 (1H, d, *J* = 17.7 Hz, H-5α), 5.64 (1H, d, *J* = 17.7 Hz, H-5β), 8.62 (1H, d, *J* = 2.2 Hz, H-9), 7.14 (1H, dd, *J* = 8.8, 2.2 Hz, H-11), 7.39 (1H, d, *J* = 8.8 Hz, H-12), 2.67 (1H, m, H-14), 1.25 (1H, m, H-15β), 1.78 (1H, m, H-15α), 3.59 (1H, d, *J* = 10.0 Hz, H-16), 1.90 (1H, m, H-17α), 2.16 (1H, m, H-17β), 0.84 (1H, t, *J* = 7.3 Hz, H-18), 1.19 (1H, m, H-19a), 1.39 (1H, m, H-19b), 1.56 (1H, m, H-20), 3.94 (1H, br s, H-21), 3.82 (3H, s, H-22); ^{13}C NMR (150 MHz, Pyridine-d_6) δ 151.1 (C-2), 175.2 (C-3), 56.2 (C-5), 194.7 (C-6), 112.6 (C-7), 131.9 (C-8), 105.3 (C-9), 156.9 (C-10), 113.5 (C-11), 112.1 (C-12), 129.7 (C-13), 38.5 (C-14), 30.7 (C-15), 42.2 (C-16), 33.1 (C-17), 11.4 (C-18), 27.6 (C-19), 37.7 (C-20), 60.1 (C-21), 55.6 (C-22).

Coronaridine (8). Yellow oil; $[\alpha]_D^{25}$ = −85.2 (*c* = 0.78, MeOH); UV (MeOH) λ_{max} (log ε) 242 (3.92), 284 (3.83) nm; IR (KBr) ν_{max} 3378, 3054, 2953, 2928, 2857, 1709, 1649, 1558, 1488, 1459, 1434, 1370, 1344, 1327, 1251, 1194, 1170, 1136, 1077, 1007, 980, 741, 717 cm^{-1}; ESIMS *m/z* 339 $[M + H]^+$; ^1H NMR (400 MHz, $CDCl_3$) δ 2.84 (1H, m, H-3a), 2.94 (1H, m, H-3b), 3.04 (1H, m, H-5β), 3.20 (1H, m, H-5α), 3.25 (1H, m, H-6β), 3.43 (1H, m, H-6α), 7.15 (1H, d, *J* = 7.6 Hz, H-9), 7.11 (1H, t, *J* = 7.6 H-10), 7.17 (1H, t, *J* = 7.6 Hz, H-11), 7.27 (1H, d, *J* = 7.6 Hz, H-12), 1.91 (1H, m, H-14), 1.16 (1H, m, H-15β), 1.77 (1H, m, H-15α), 1.95 (1H, m, H-17β), 2.62 (1H, m, H-17α), 0.94 (1H, t, *J* = 7.4 Hz, H-18), 1.48 (1H, m, H-19a), 1.61 (1H, m, H-19b), 1.38

(1H, m, H-20), 3.60 (1H, br s, H-21), 3.74 (3H, s, H-23), 7.87 (1H, br s, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6 (C-2), 51.6 (C-3), 53.1 (C-5), 22.1 (C-6), 110.3 (C-7), 128.8 (C-8), 118.4 (C-9), 119.2 (C-10), 121.9 (C-11), 110.3 (C-12), 135.5 (C-13), 27.4 (C-14), 32.0 (C-15), 55.1 (C-16), 36.5 (C-17), 11.6 (C-18), 26.7 (C-19), 39.1 (C-20), 57.4 (C-21), 175.7 (C-22), 52.5 (C-23).

5-Oxocoronaridine (9). Yellow oil; $[\alpha]$ = −68.5 (c = 0.67, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ε) 242 (4.40), 283 (4.41) nm; IR (KBr) ν_{max} 254, 2968, 2942, 2869, 1740, 1633, 1539, 1483, 1457, 1340, 1243, 1199, 1150, 1085, 742 cm^{-1}; HRESIMS *m/z*: 353.1866 $[M+H]^+$ (calcd for $C_{21}H_{25}N_2O_3$, 353.1860); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.14 (1H, m, H-3a), 3.61 (1H, m, H-3b), 3.76 (1H, d, J = 15.5 Hz, H-6β), 4.10 (1H, d, J = 15.5 Hz, H-6α), 7.55 (1H, d, J = 7.8 Hz, H-9), 7.12 (1H, t, J = 7.8 Hz, H-10), 7.17 (1H, t, J = 7.8 Hz, H-11), 7.26 (1H, d, J = 7.8 Hz, H-12), 2.16 (1H, m, H-14), 1.34 (1H, m, H-15β), 1.79 (1H, m, H-15α), 1.65 (1H, dt, J = 13.8, 2.0 Hz, H-17β), 2.91 (1H, dt, J = 13.8, 2.0 Hz, H-17α), 0.99 (1H, t, J = 7.4 Hz, H-18), 1.48 (1H, m, H-19a), 1.59 (1H, m, H-19b), 1.83 (1H, m, H-20), 4.53 (1H, br s, H-21), 3.70 (3H, s, H-23); 7.91 (1H, br s, NH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 136.3 (C-2), 48.2 (C-3), 175.4 (C-5), 32.5 (C-6), 103.7 (C-7), 127.6 (C-8), 118.6 (C-9), 120.0 (C-10), 122.5 (C-11), 110.7 (C-12), 135.1 (C-13), 27.8 (C-14), 29.8 (C-15), 50.3 (C-16), 34.4 (C-17), 11.9 (C-18), 28.5 (C-19), 35.4 (C-20), 52.9 (C-21), 174.0 (C-22), 53.0 (C-23).

7. Spectra of physico-chemical properties of 1–9

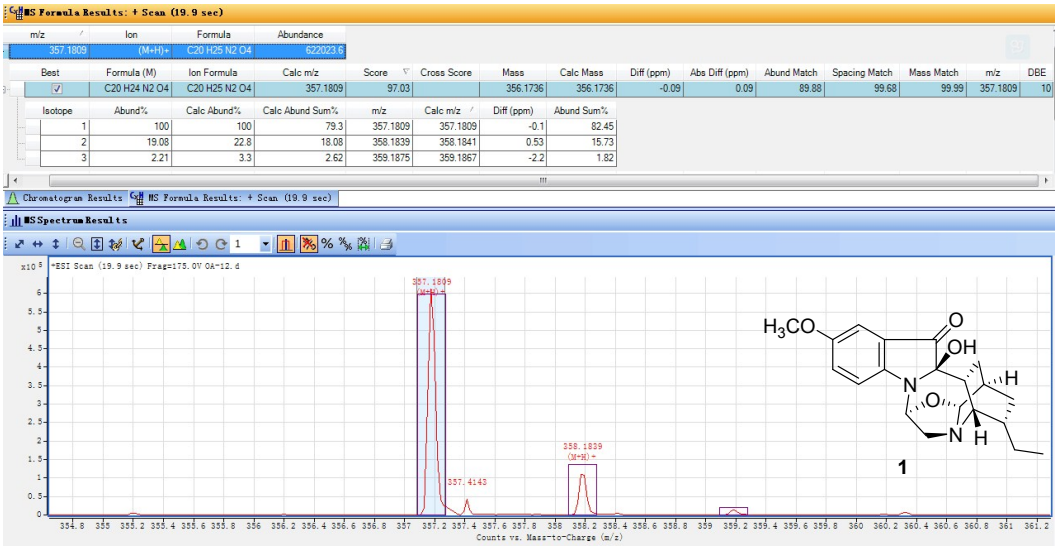


Figure S13. HR-ESI-MS spectrum of **1**

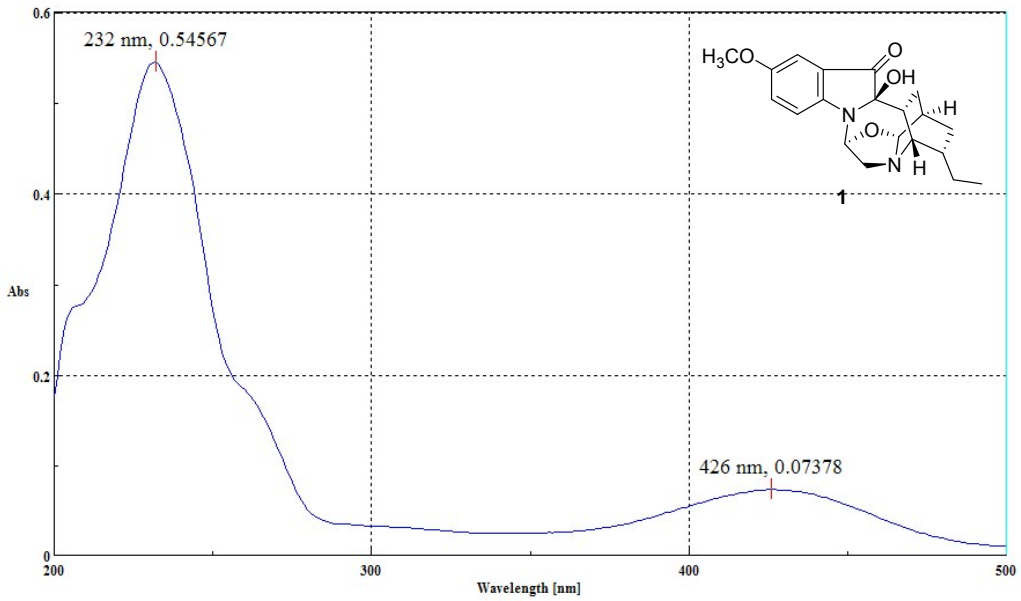


Figure S14. UV spectrum of **1** (MeOH)

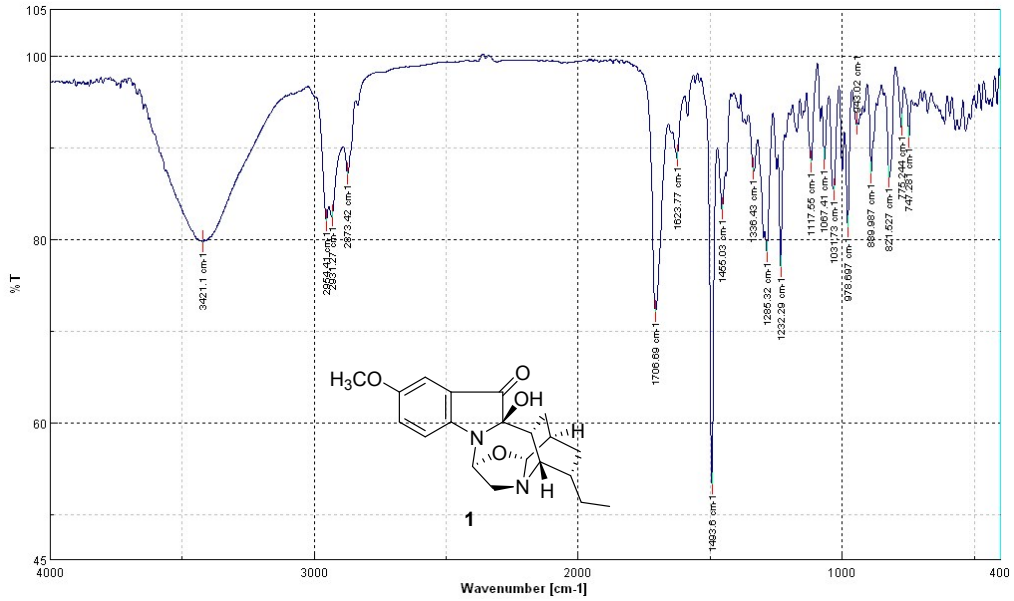


Figure S15. IR spectrum of **1** (KBr)

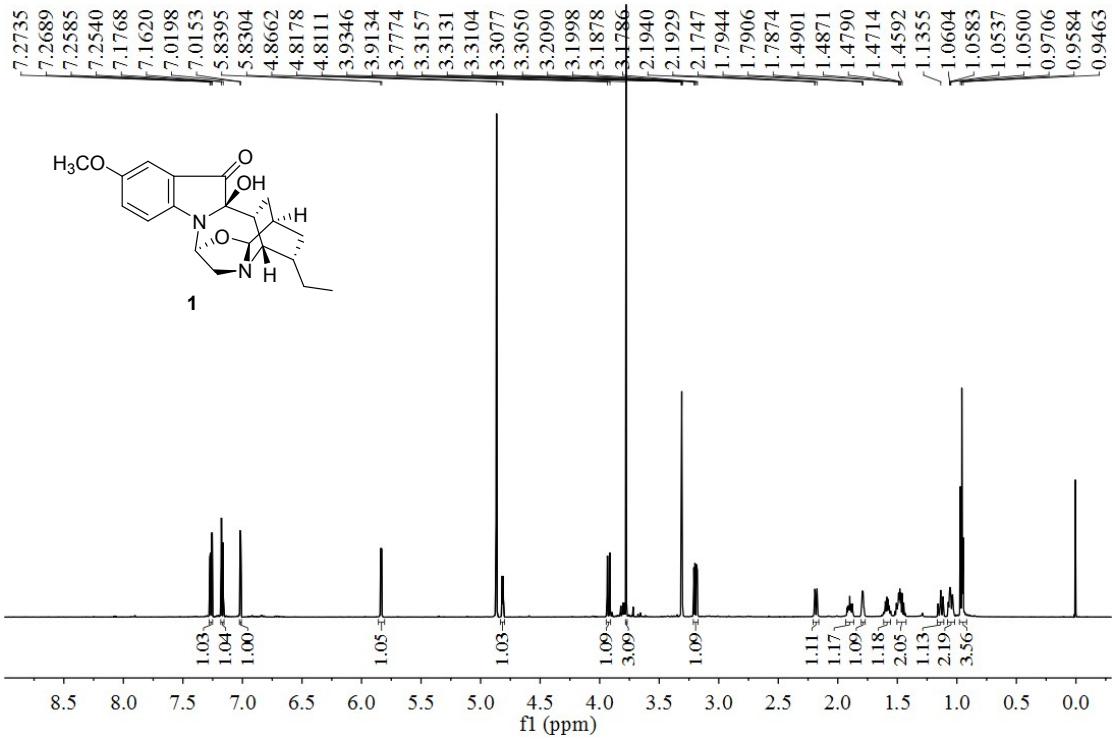


Figure S16. ^{1}H NMR spectrum of **1** (CD_3OD)

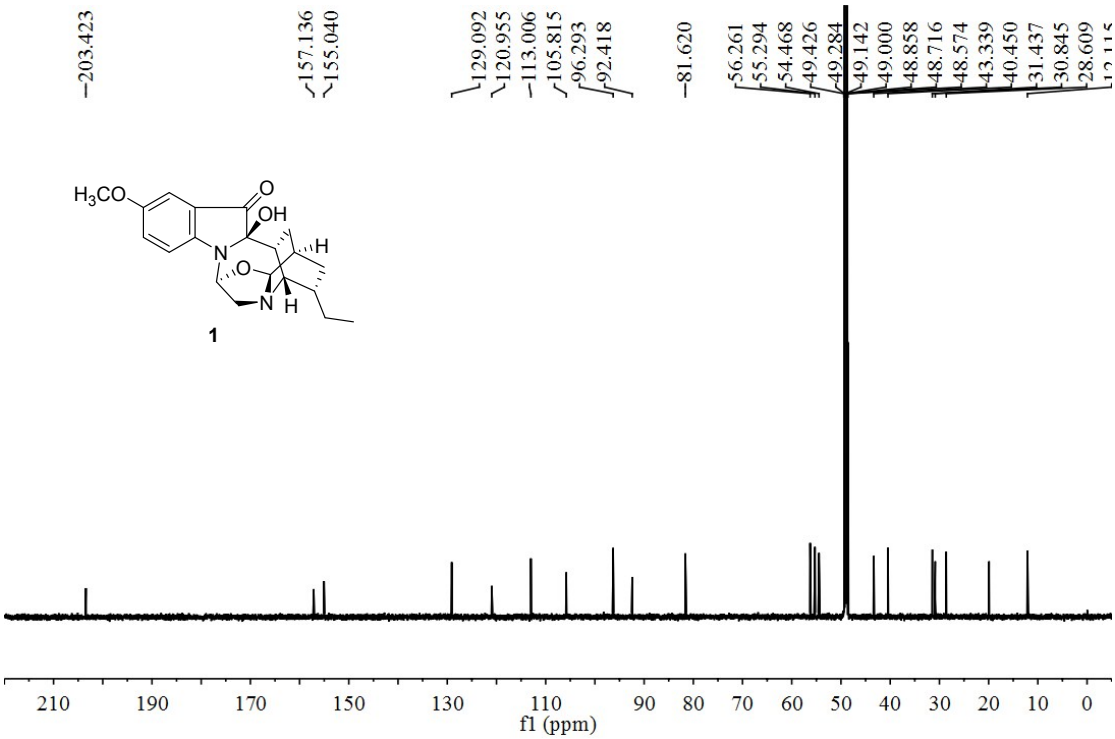


Figure S17. ^{13}C NMR spectrum of **1** (CD_3OD)

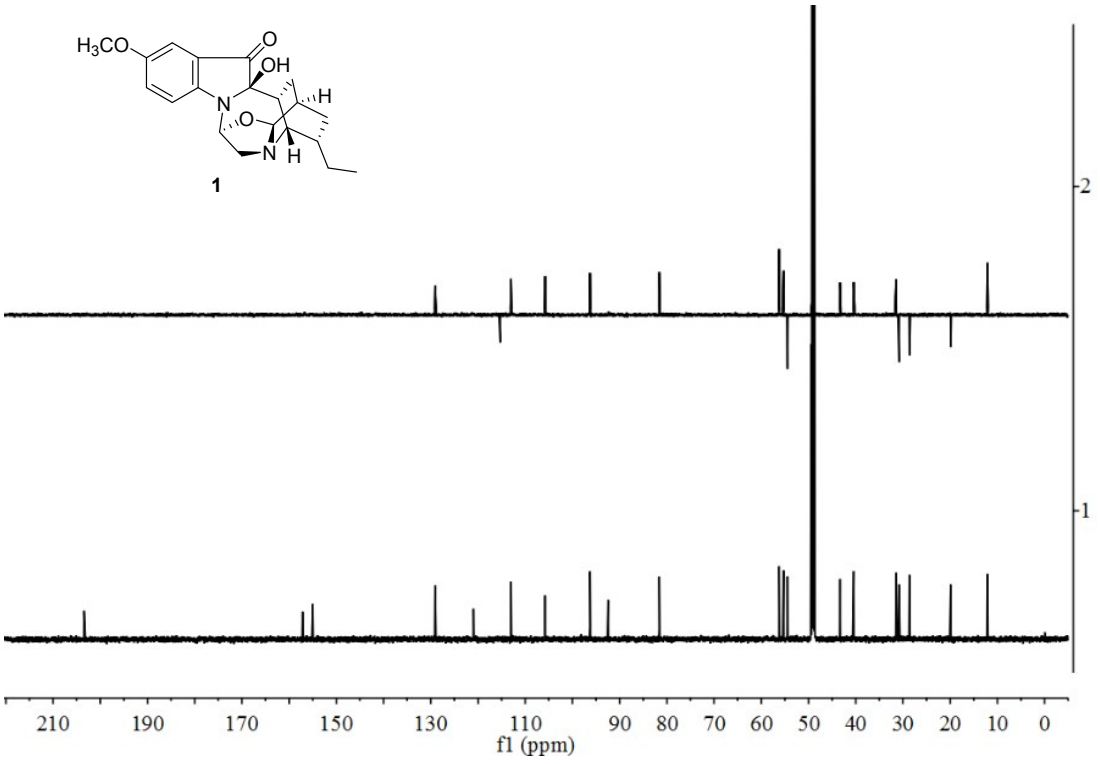


Figure S18. DEPT135 and ^{13}C NMR spectra of **1** (CD_3OD)

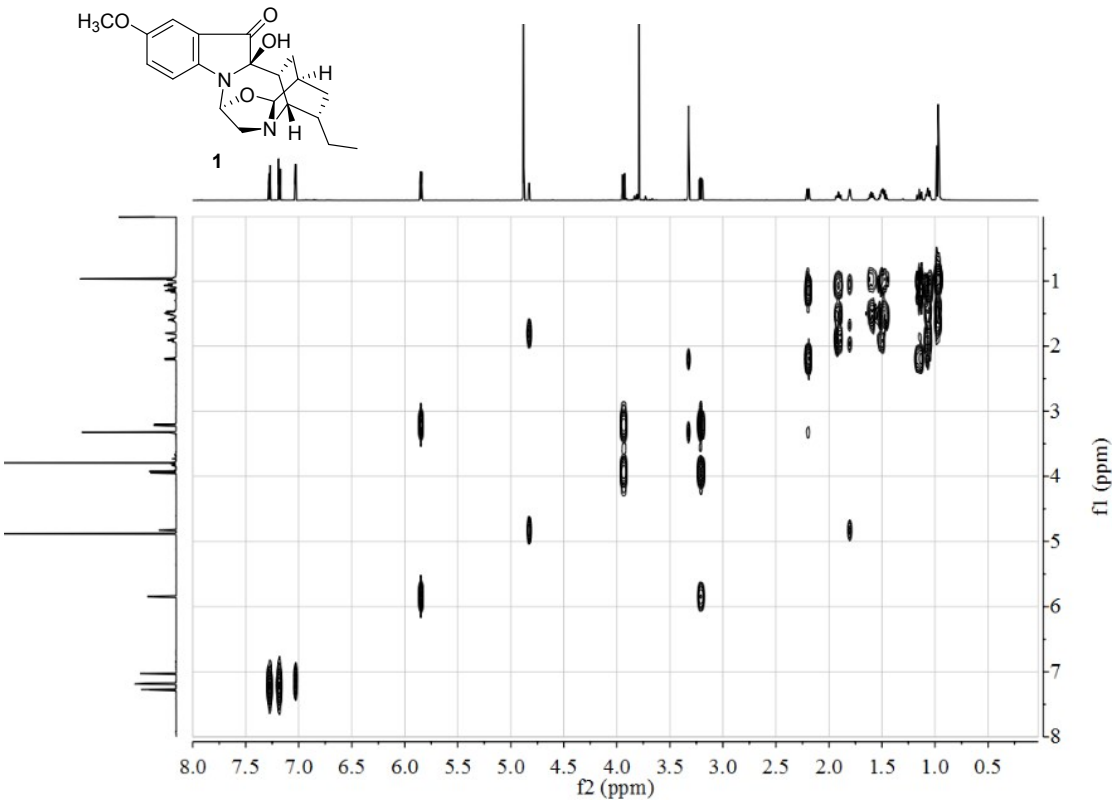


Figure S19. ^{1}H-^{1}H COSY spectrum of **1** (CD_3OD)

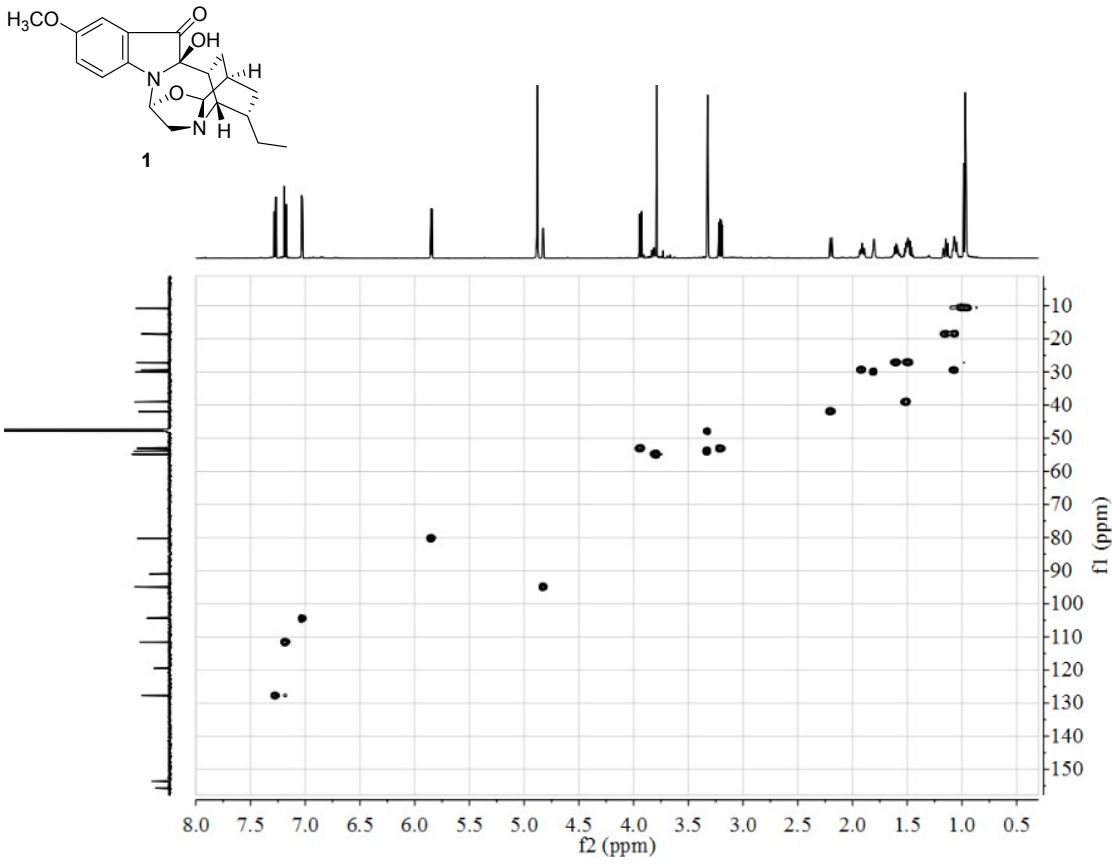


Figure S20. HSQC spectrum of **1** (CD_3OD)

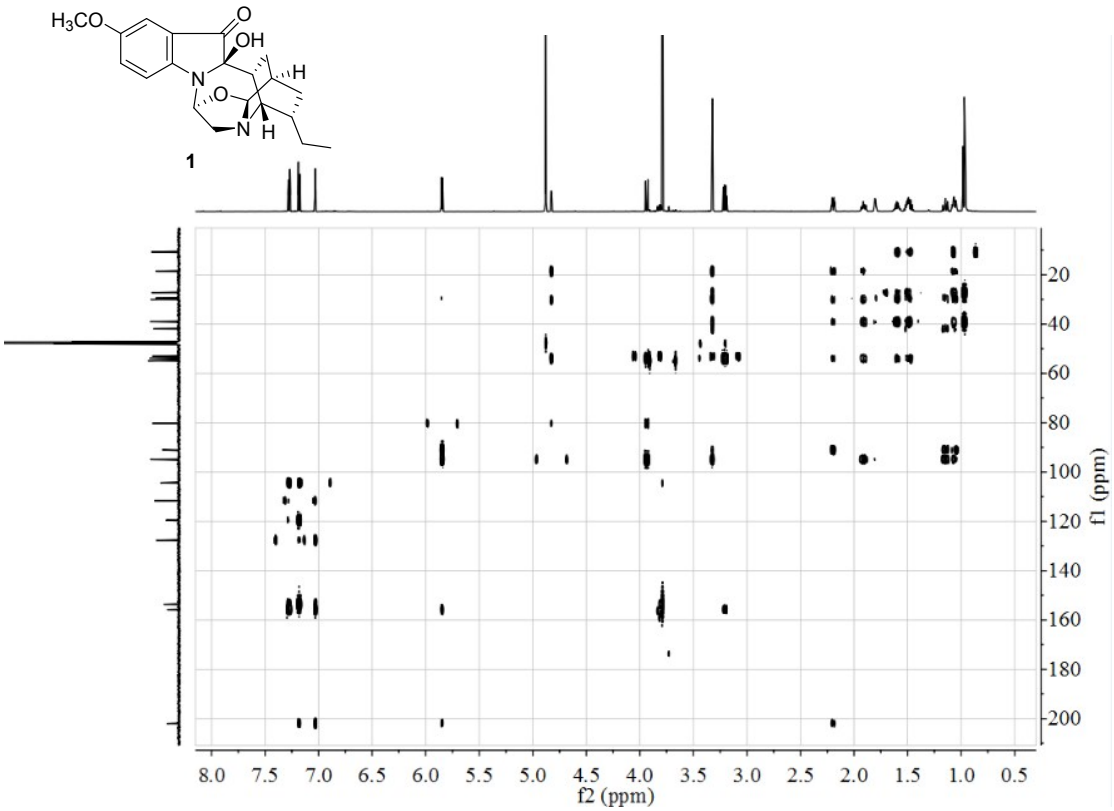


Figure S21. HMBC spectrum of **1** (CD_3OD)

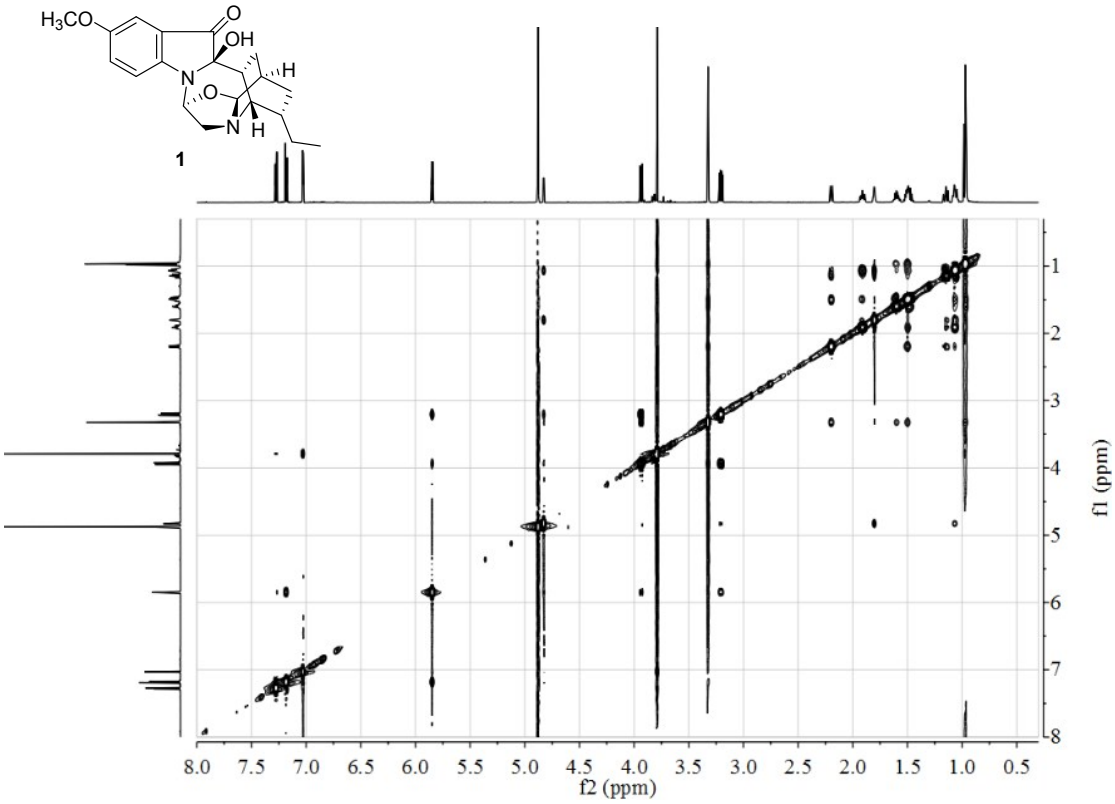


Figure S22. NOESY spectrum of **1** (CD_3OD)

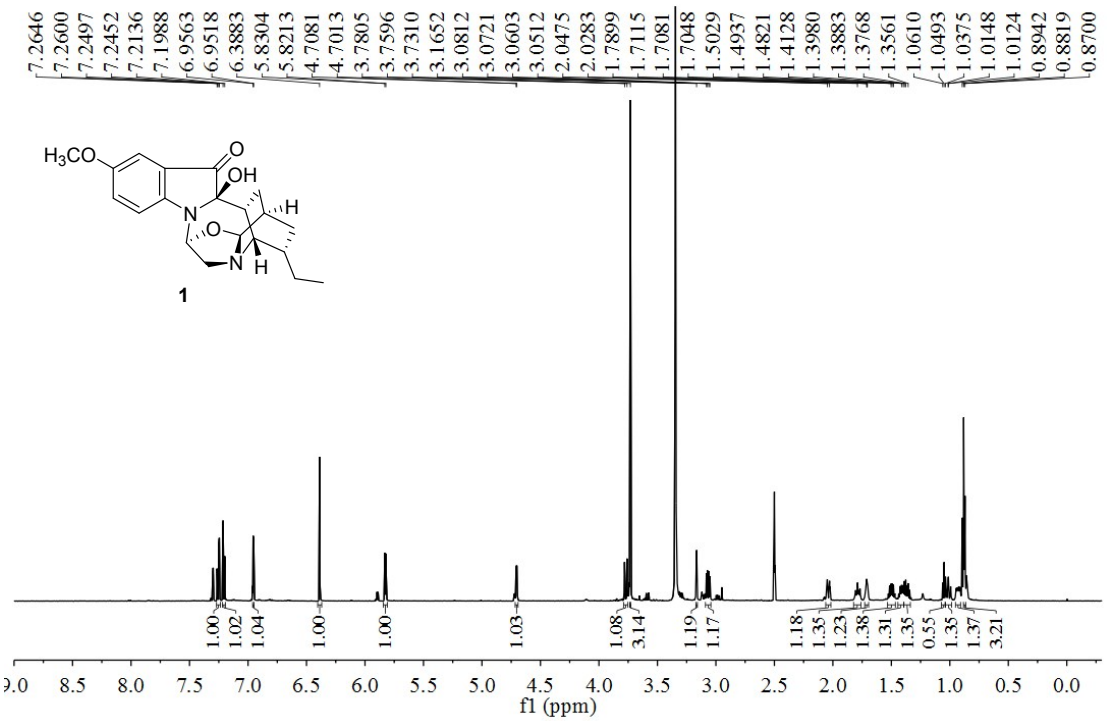


Figure S23. ^{1}H NMR spectrum of **1** (DMSO-d_6)

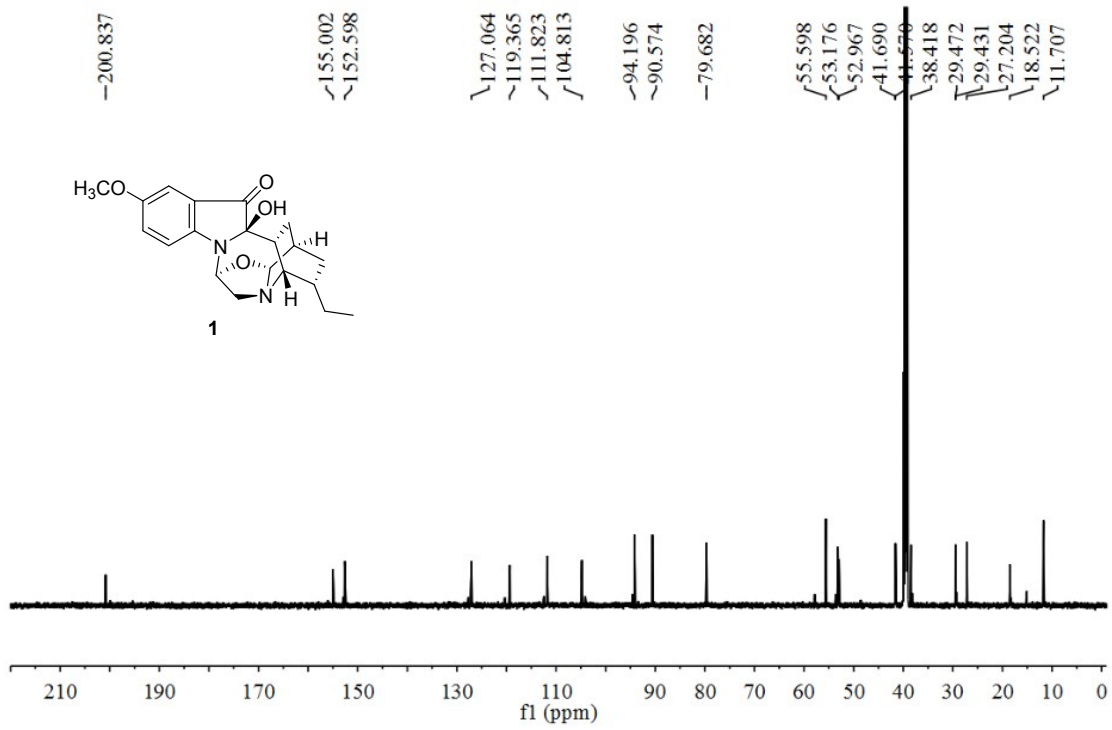


Figure S24. ^{13}C NMR spectrum of **1** (DMSO-d_6)

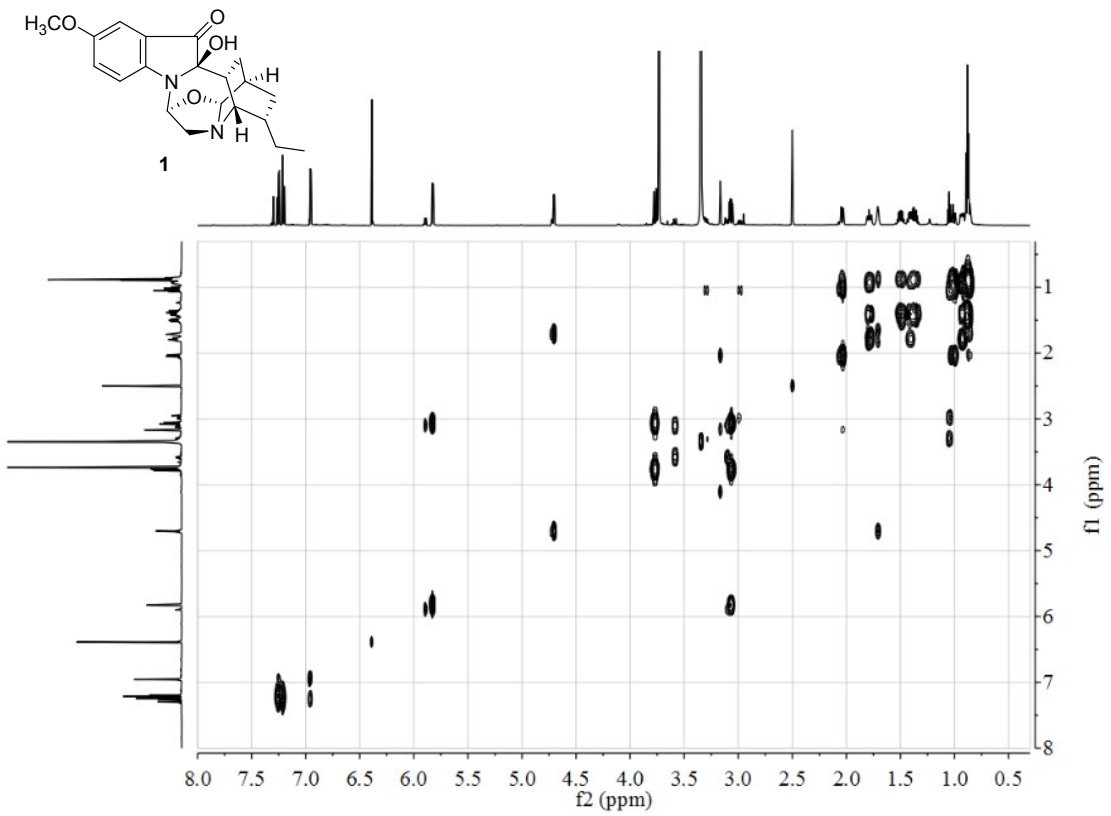


Figure S25. ^{1}H-^{1}H COSY spectrum of **1** (DMSO-d_6)

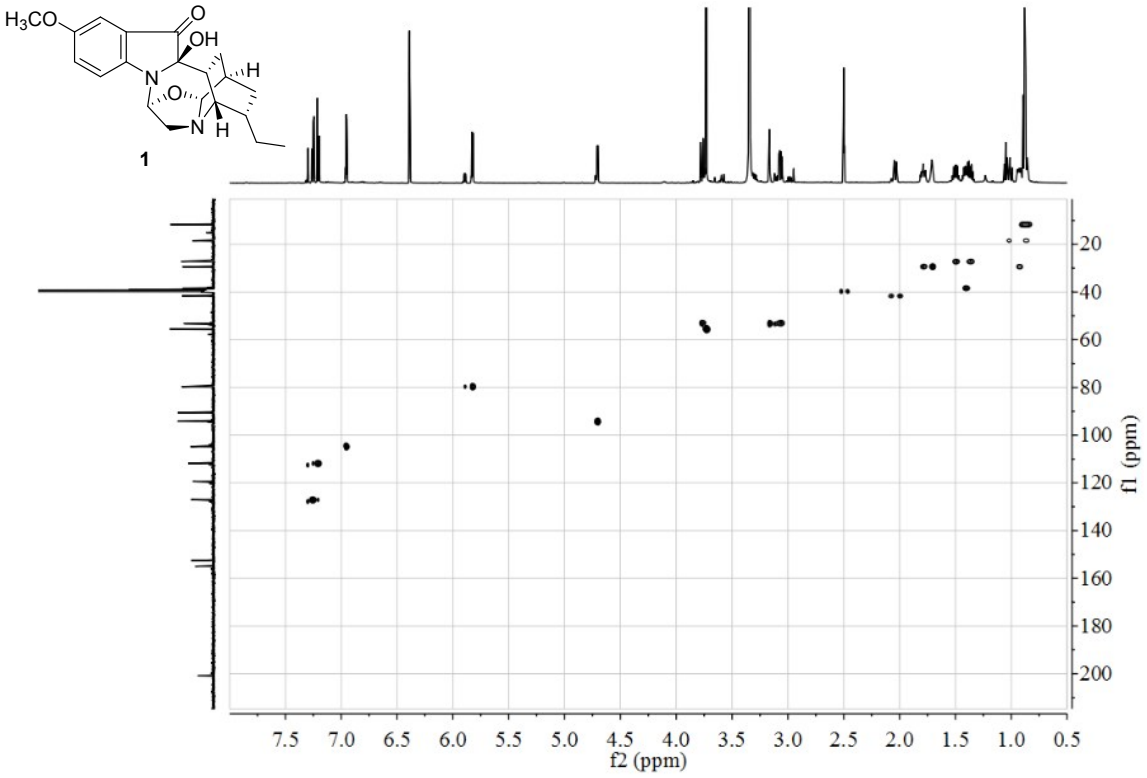


Figure S26. HSQC spectrum of **1** (DMSO-d_6)

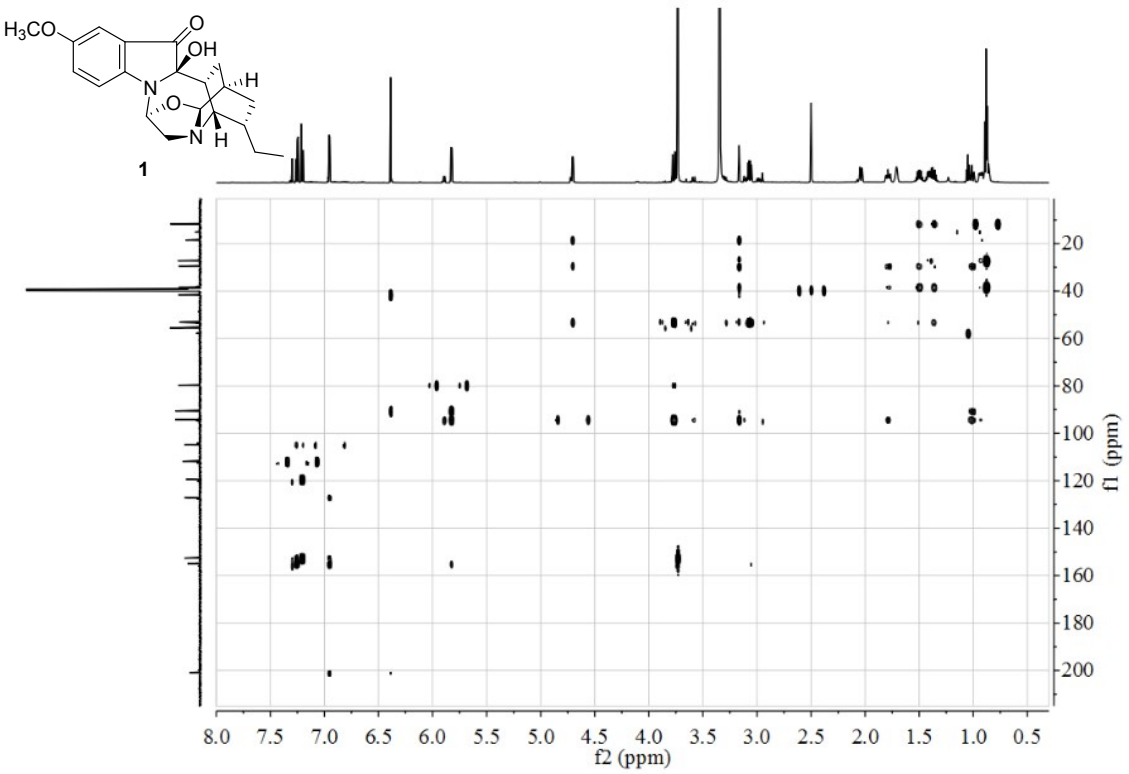


Figure S27. HMBC spectrum of **1** (DMSO-d_6)

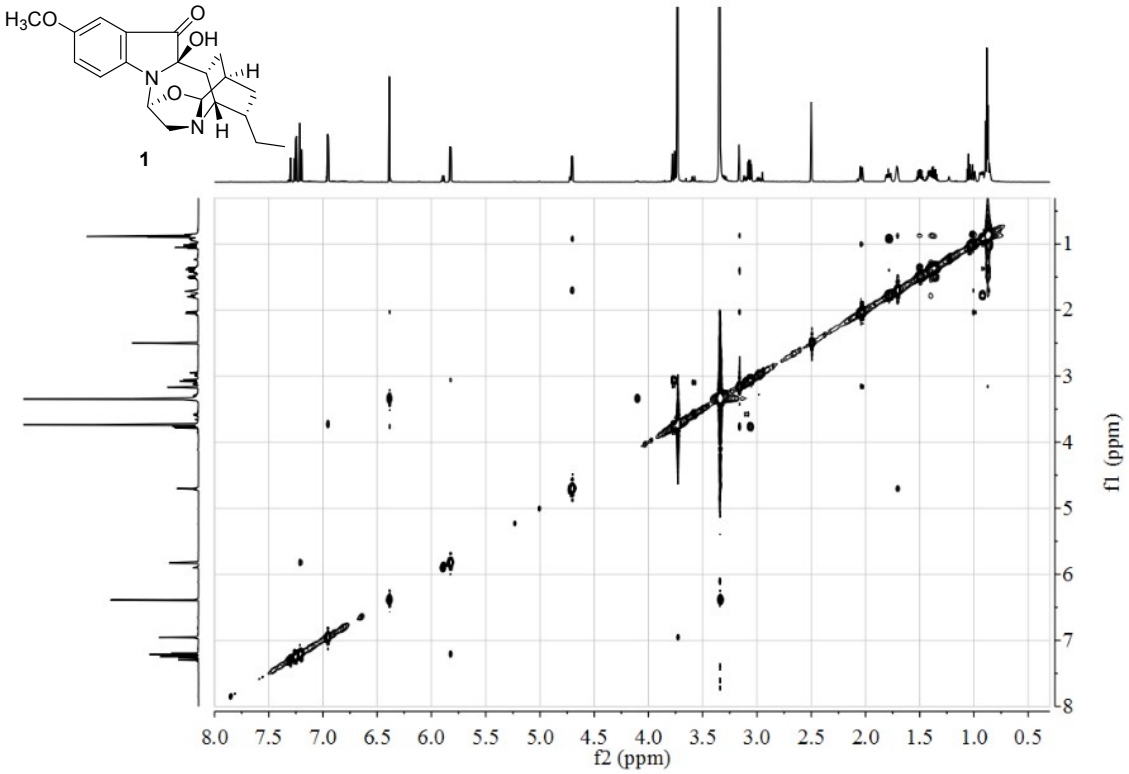


Figure S28. NOESY spectrum of **1** (DMSO-d_6)

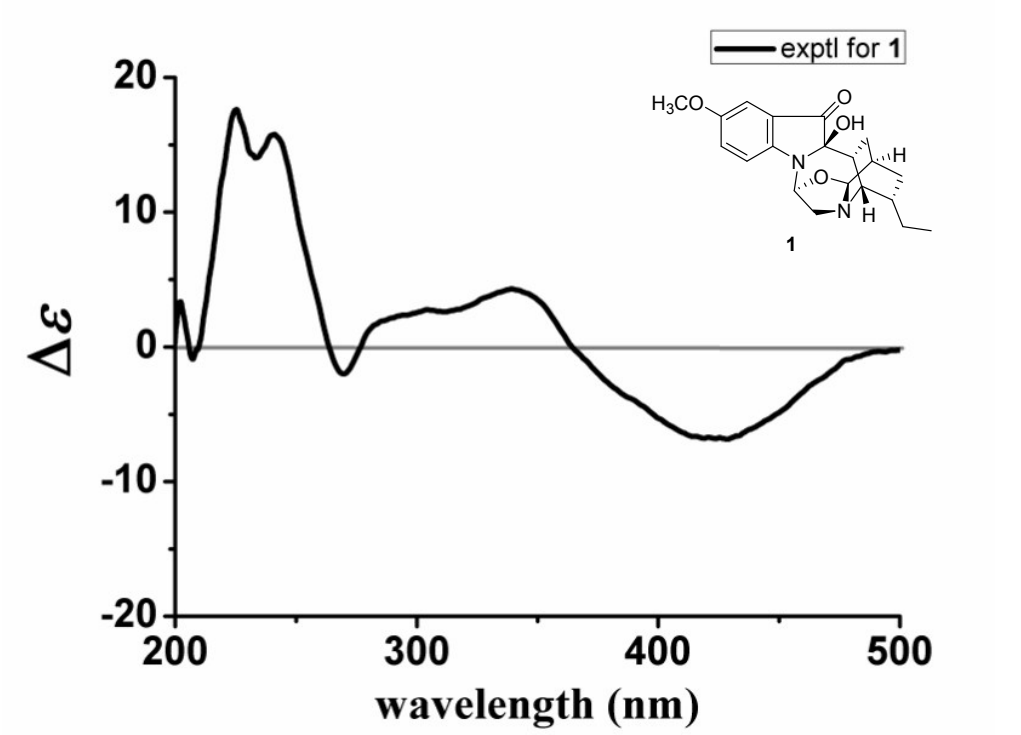


Figure S29. ECD spectrum of **1** (MeOH)

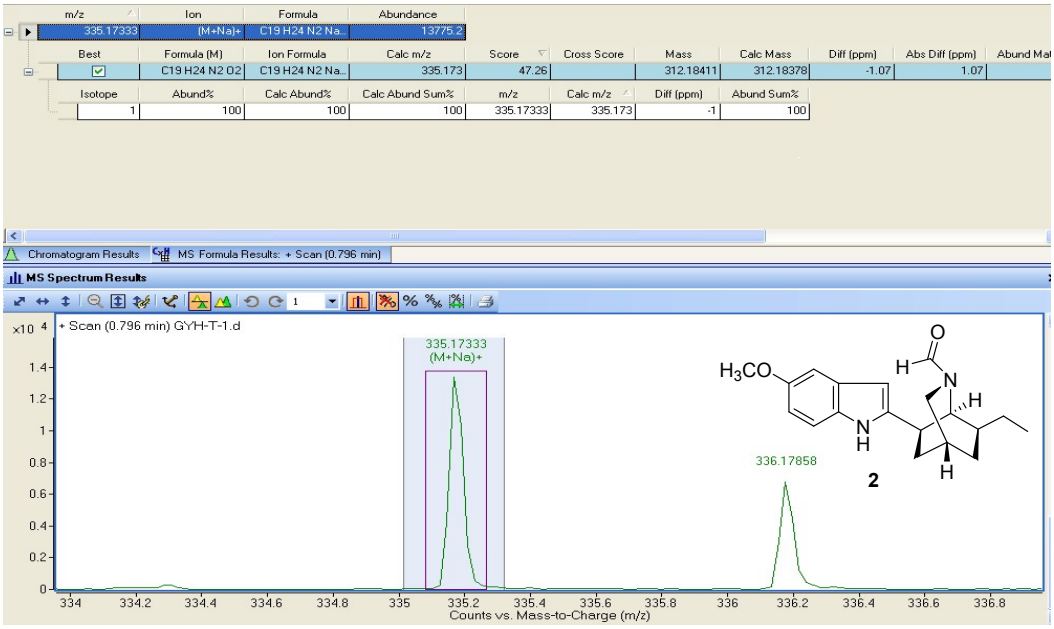


Figure S30. HR-ESI-MS spectrum of **2**

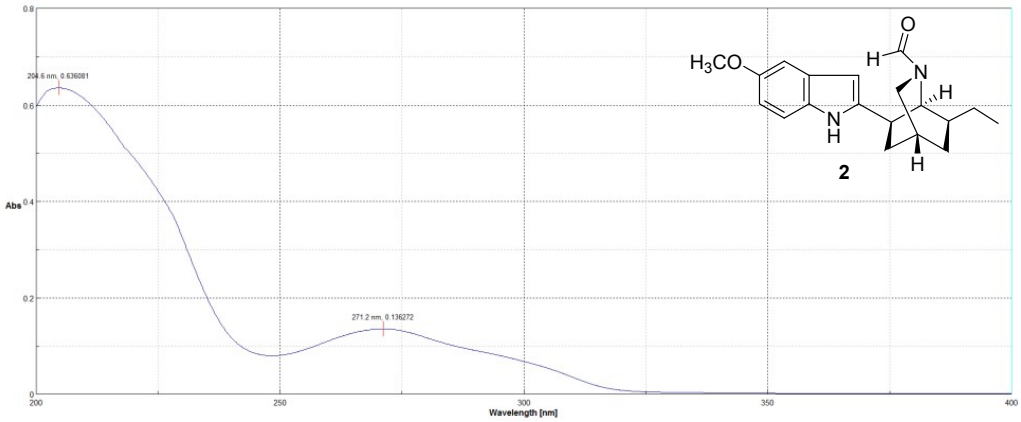


Figure S31. UV spectrum of **2** (MeOH)

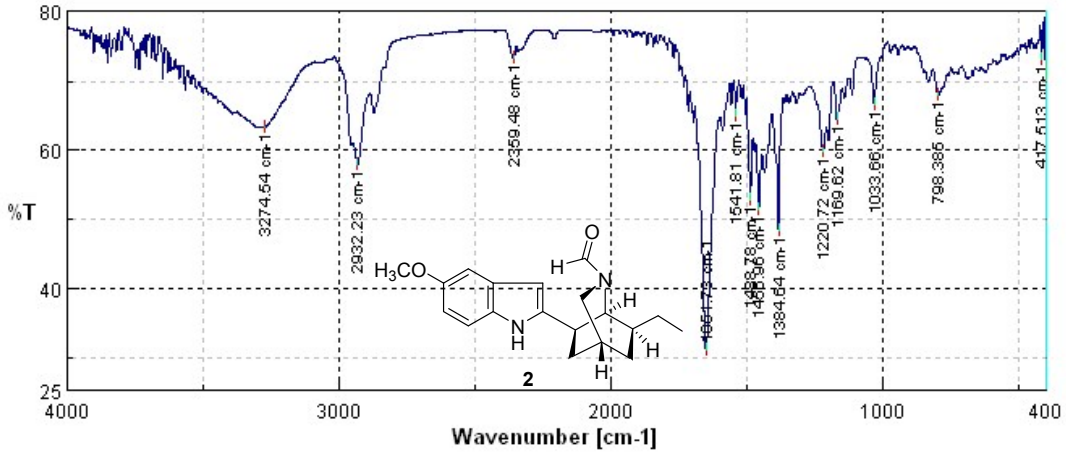


Figure S32. IR spectrum of **2** (KBr)

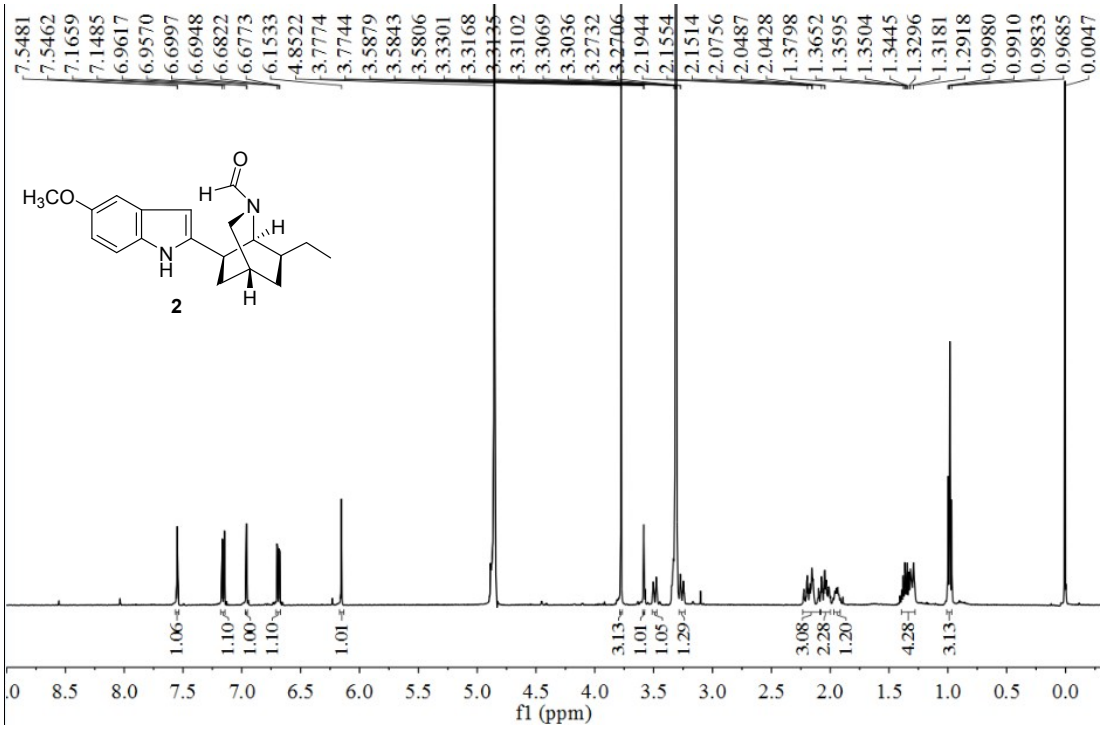


Figure S33. ^{1}H NMR spectrum of **2** (CD_3OD)

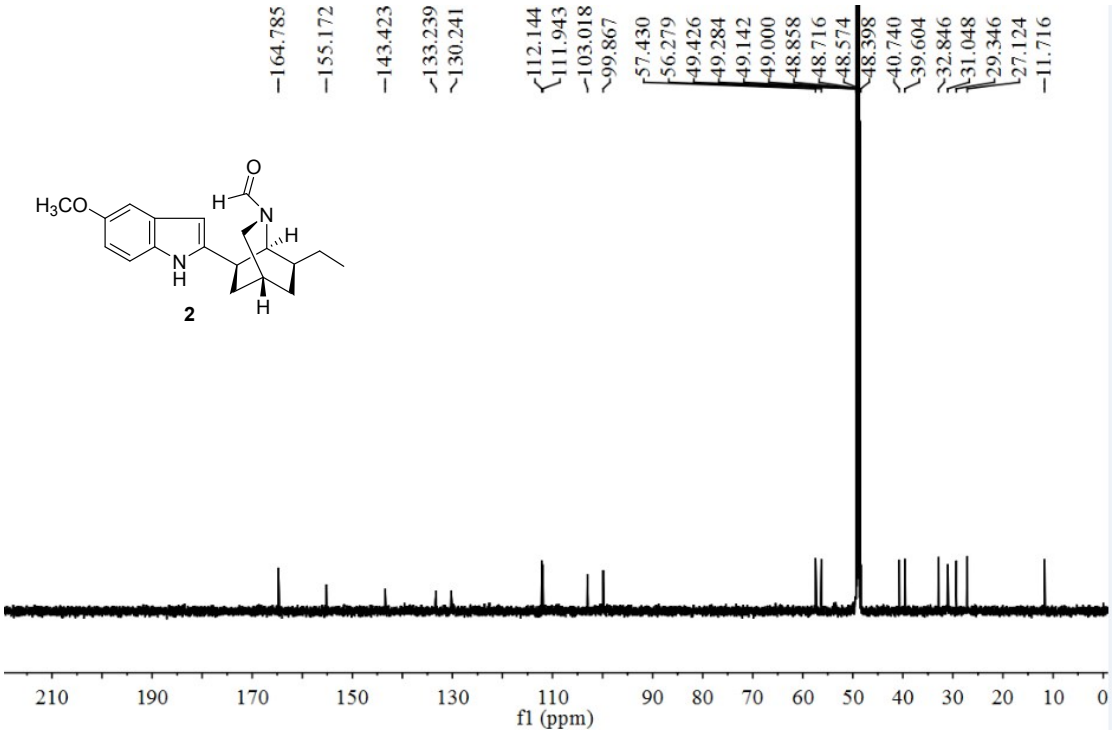


Figure S34. ^{13}C NMR spectrum of **2** (CD_3OD)

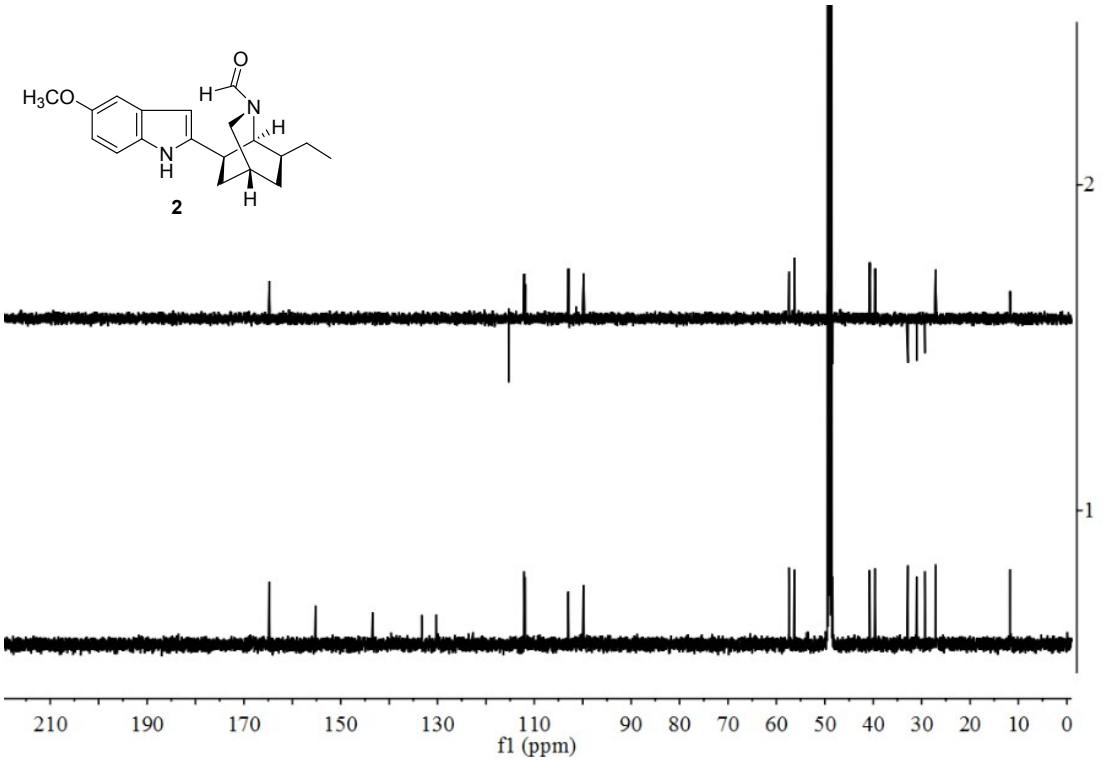


Figure S35. DEPT135 and ^{13}C NMR spectra of **2** (CD_3OD)

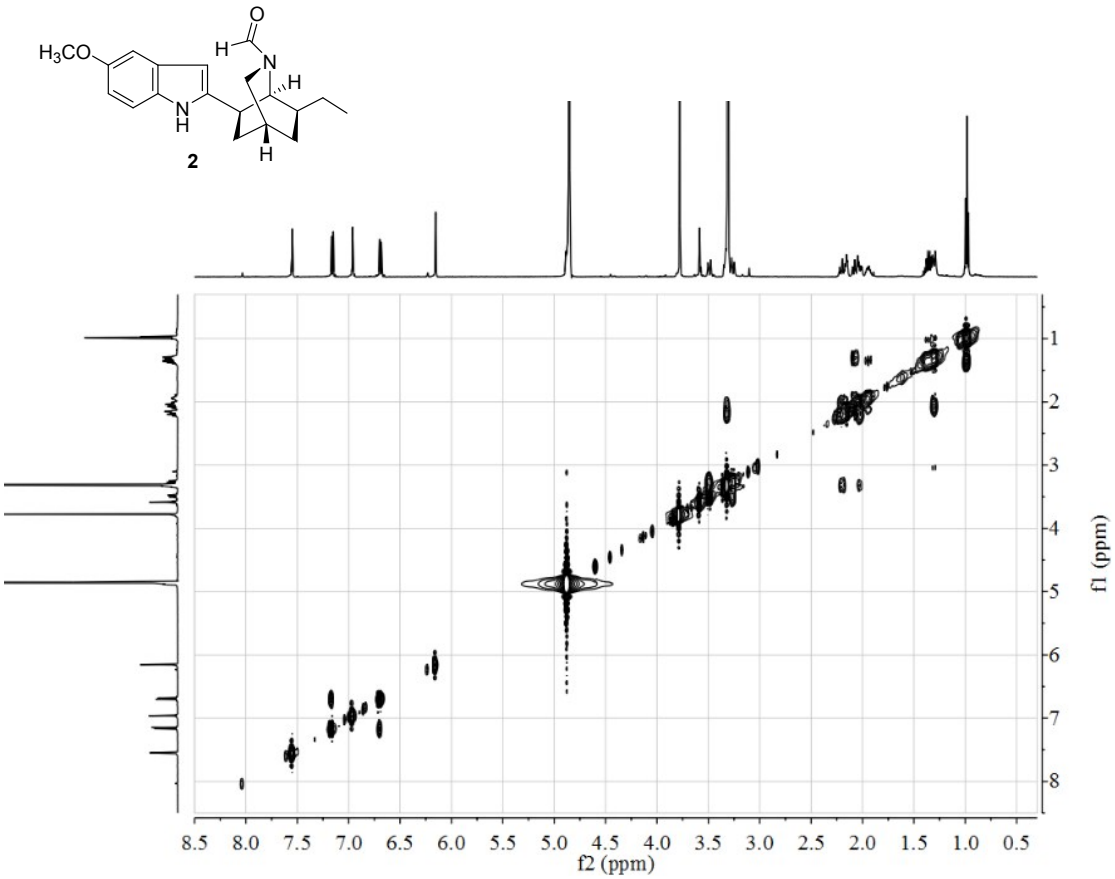


Figure S36. ^{1}H-^{1}H COSY spectrum of **2** (CD_3OD)

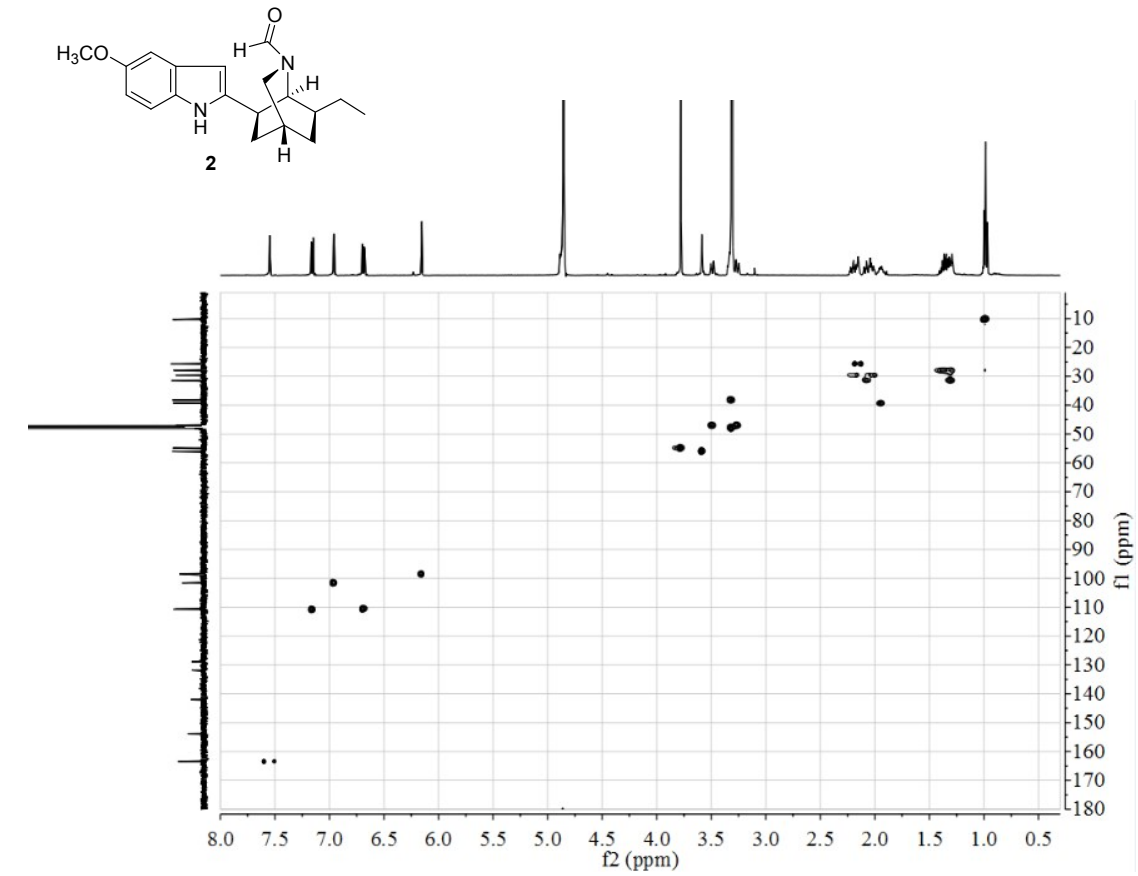


Figure S37. HSQC spectrum of **2** (CD_3OD)

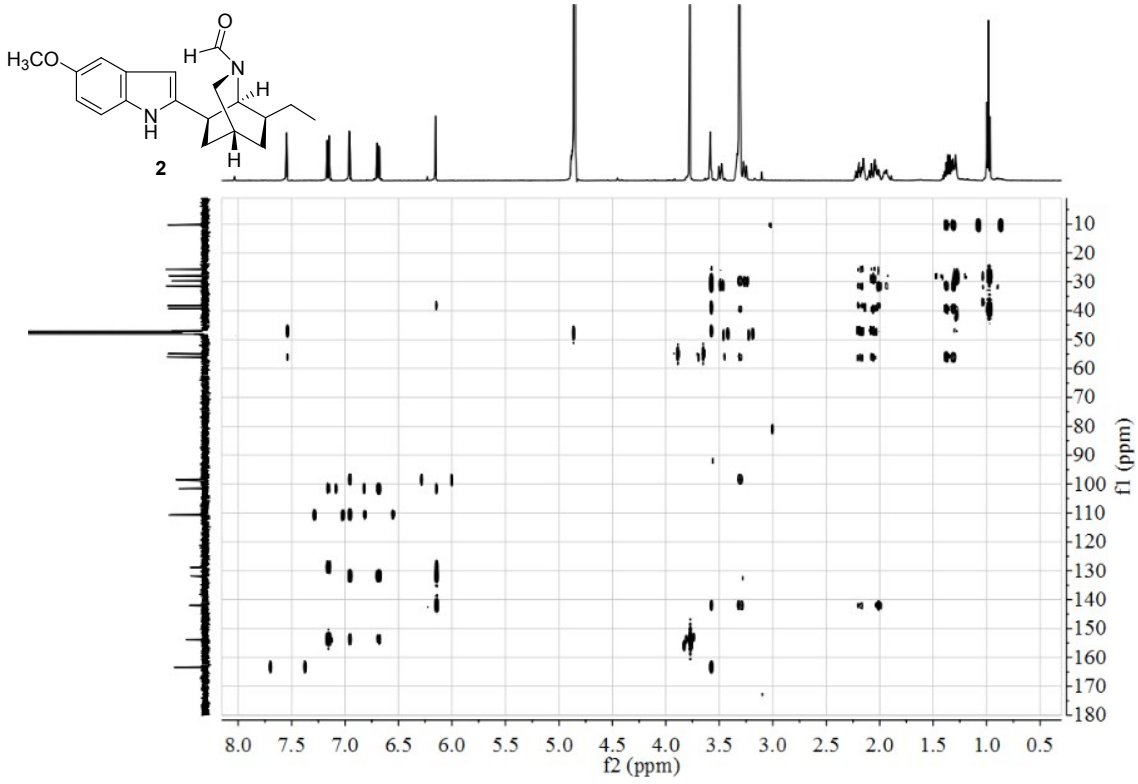


Figure S38. HMBC spectrum of **2** (CD_3OD)

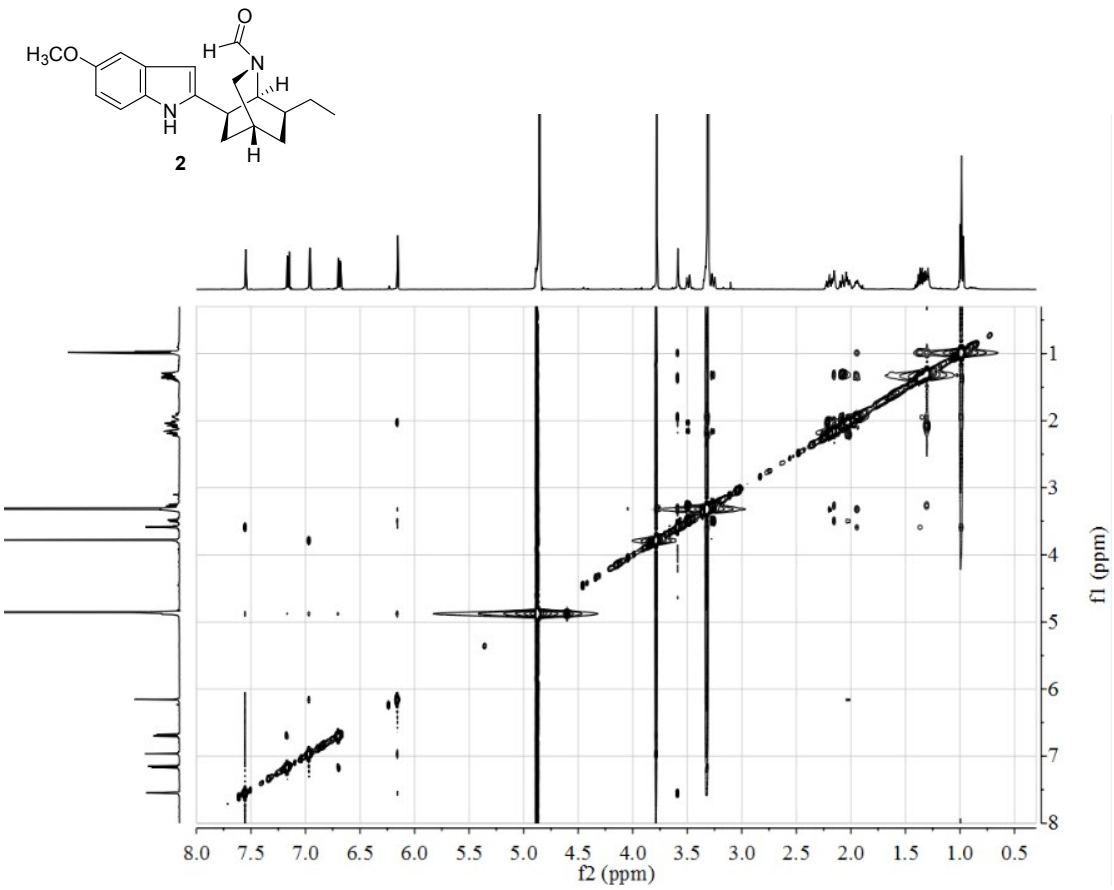


Figure S39. NOESY spectrum of **2** (CD_3OD)

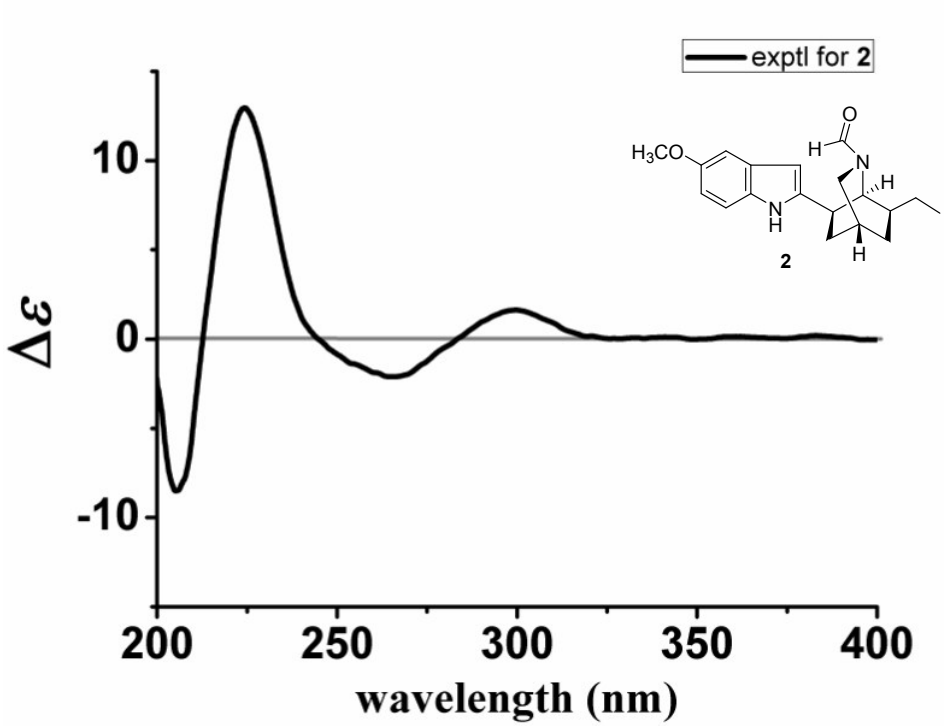


Figure S40. ECD spectrum of **2** (MeOH)

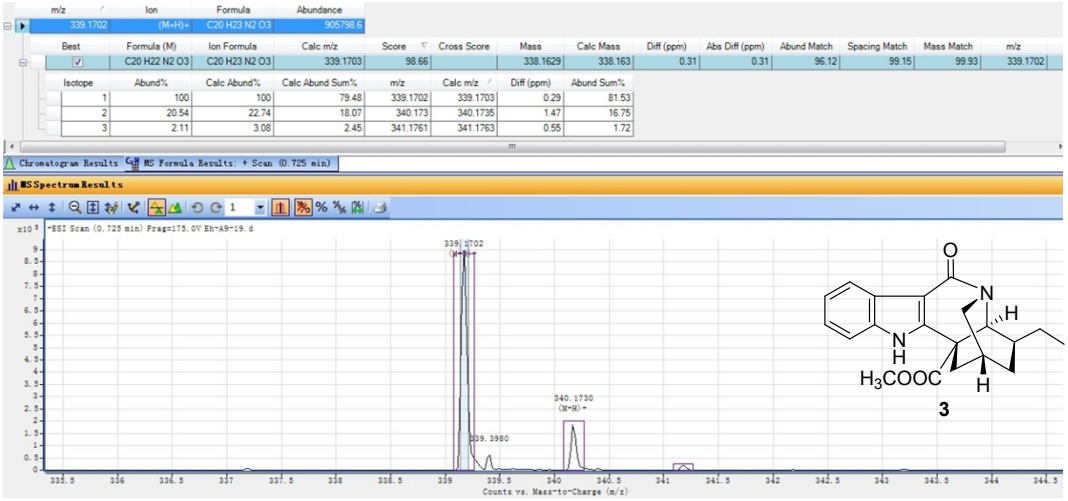


Figure S41. HR-ESI-MS spectrum of **3**

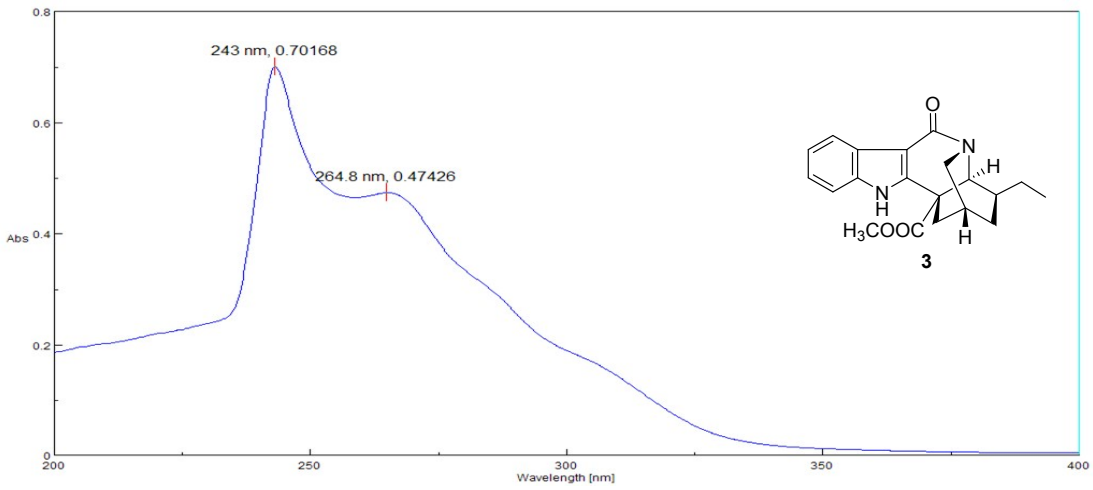


Figure S42. UV spectrum of **3** ($CHCl_3$)

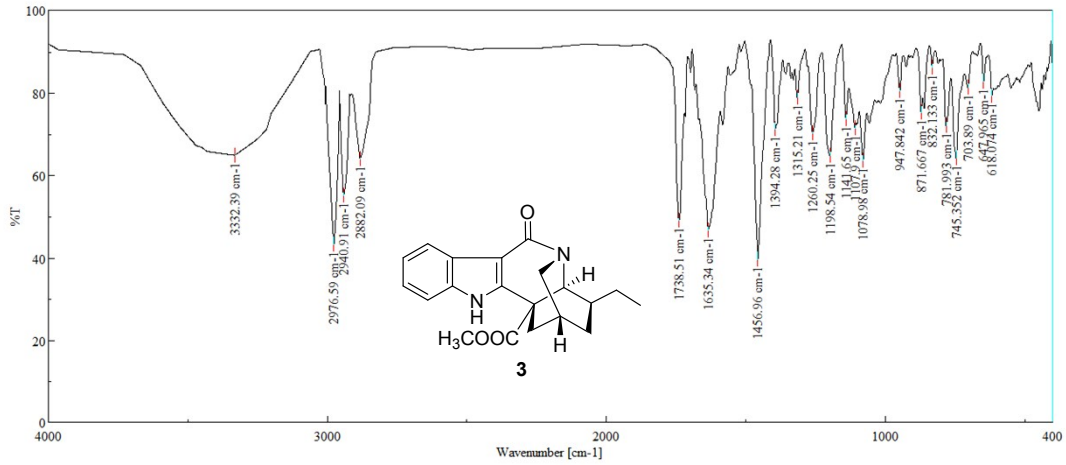


Figure S43. IR spectrum of **3** (KBr)

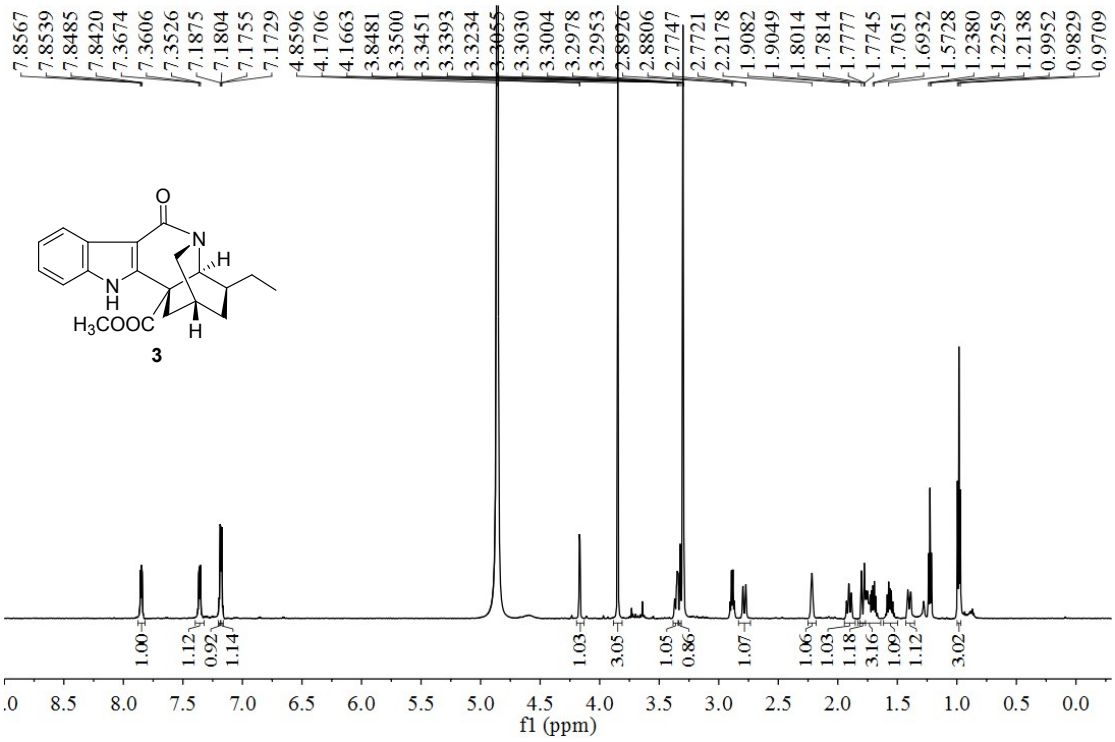


Figure S44. ^{1}H NMR spectrum of **3** (CD_3OD)

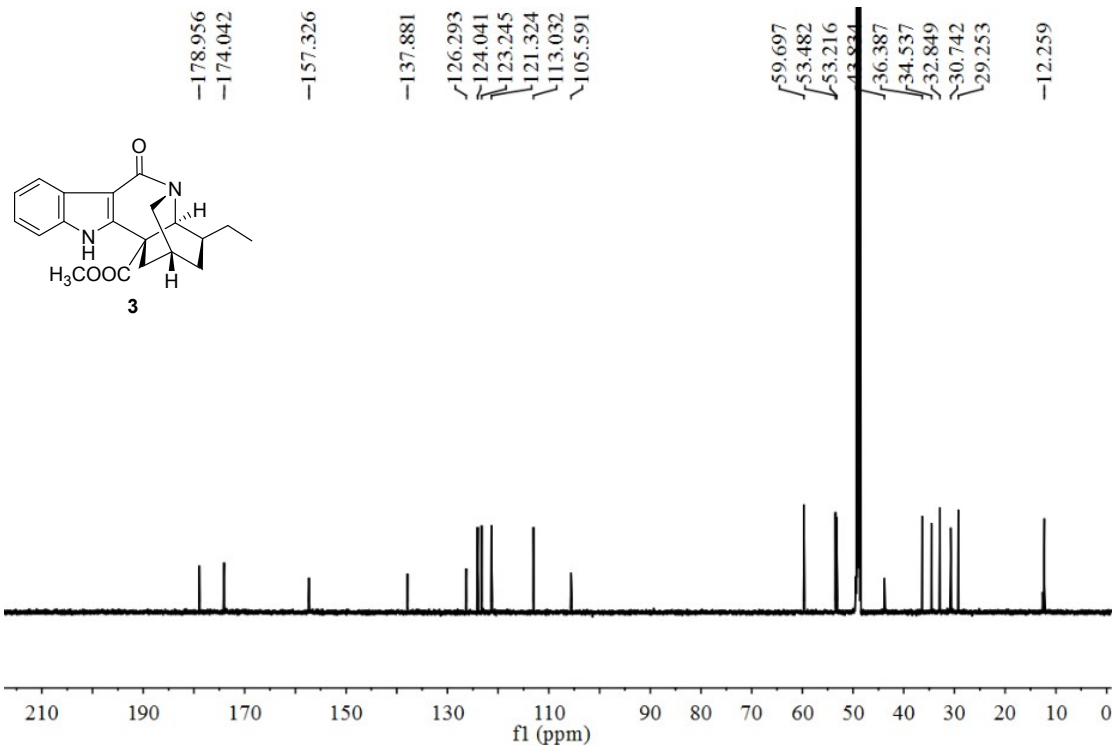


Figure S45. ^{13}C NMR spectrum of **3** (CD_3OD)

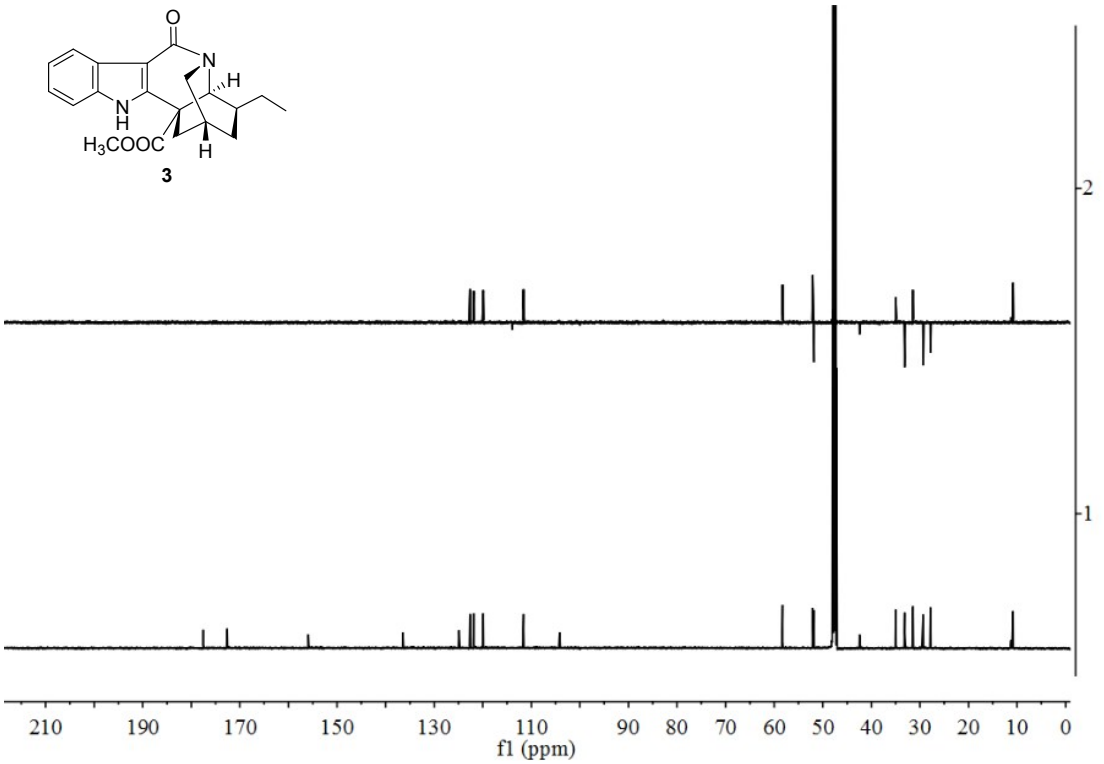


Figure S46. DEPT-135 and ^{13}C NMR spectra of **3** (CD_3OD)

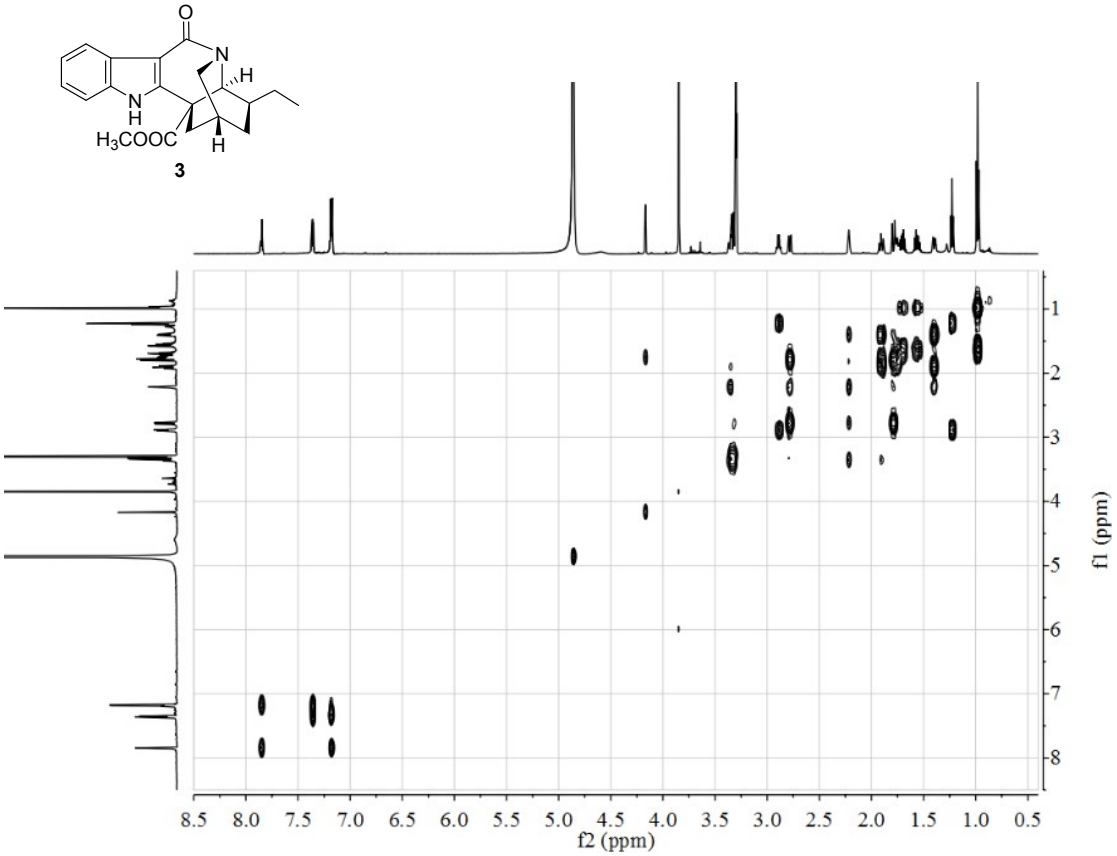


Figure S47. ^{1}H-^{1}H COSY spectrum of **3** (CD_3OD)

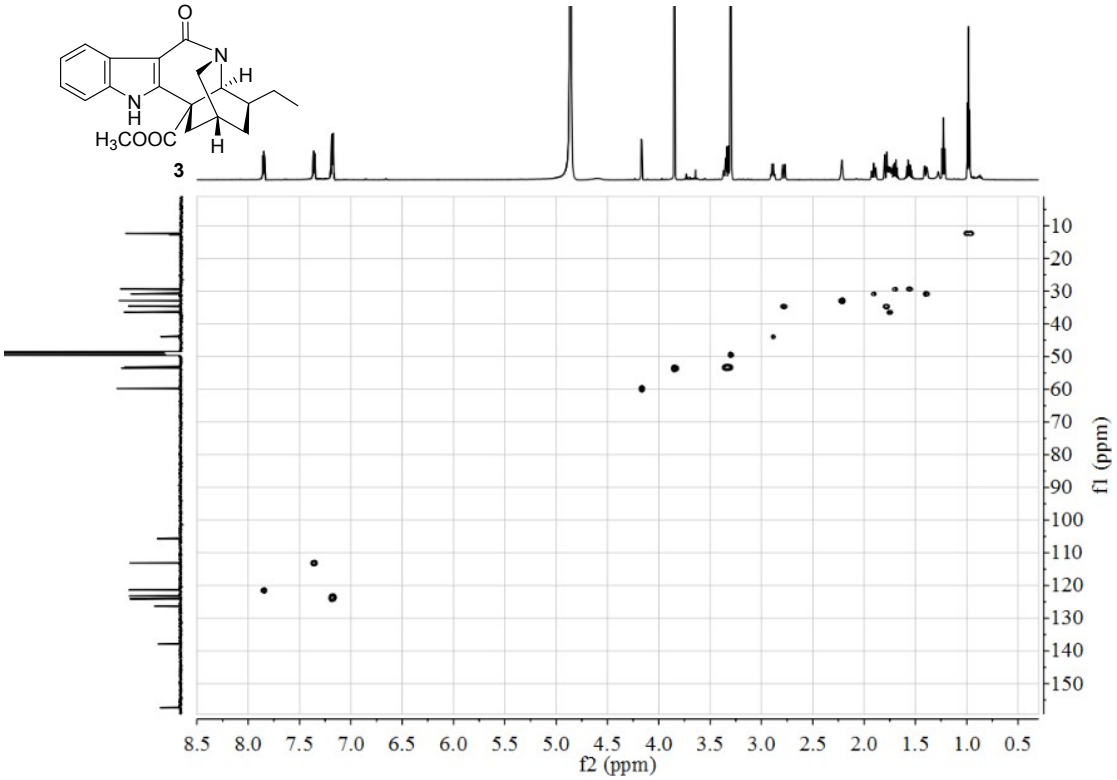


Figure S48. HSQC spectrum of **3** (CD_3OD)

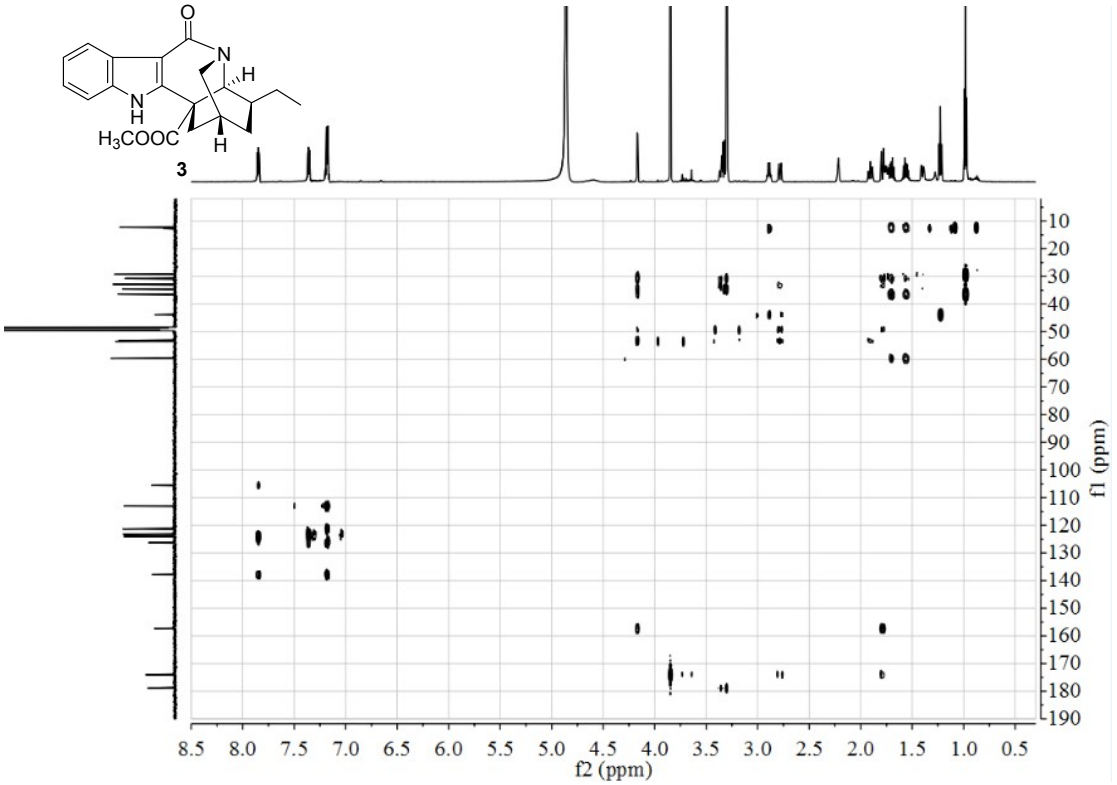


Figure S49. HMBC spectrum of **3** (CD_3OD)

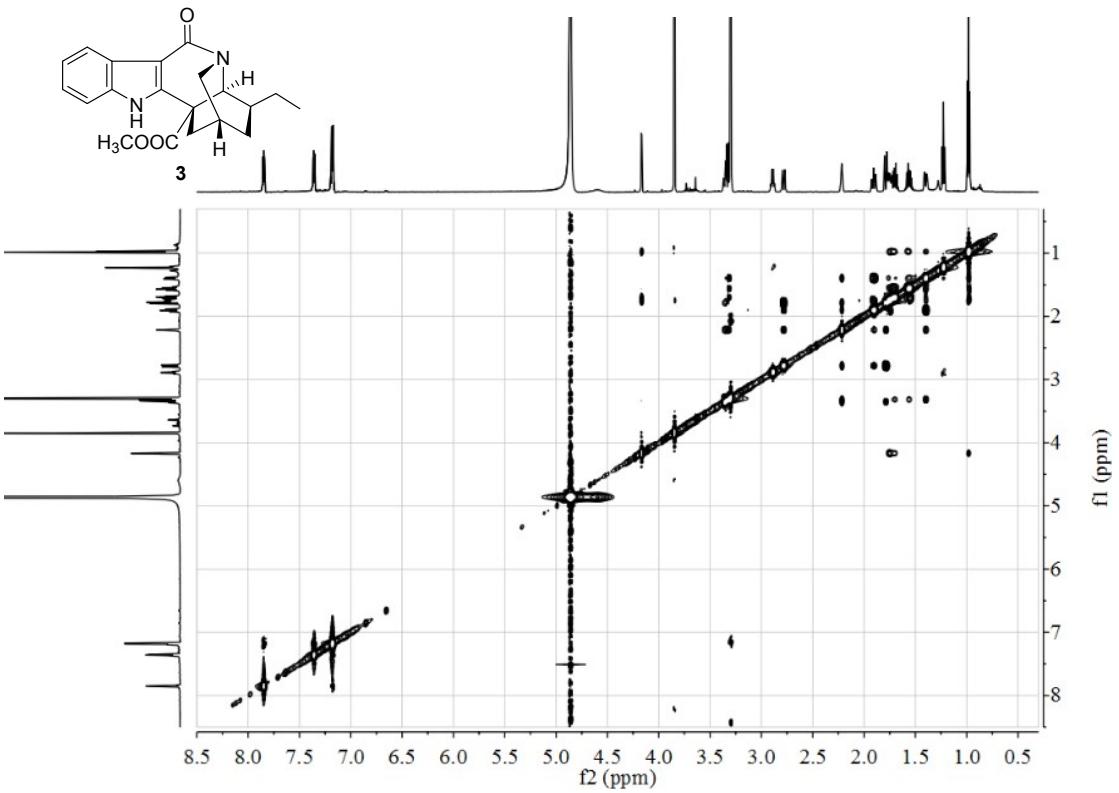


Figure S50. NOESY spectrum of **3** (CD_3OD)

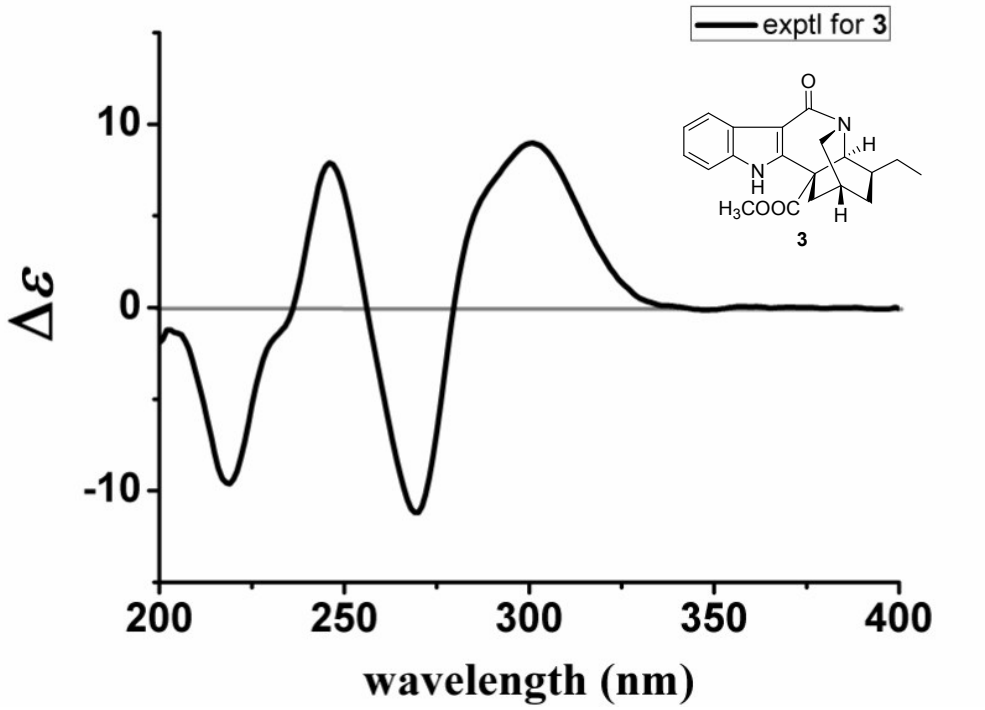


Figure S51. ECD spectrum of **3** (MeCN)

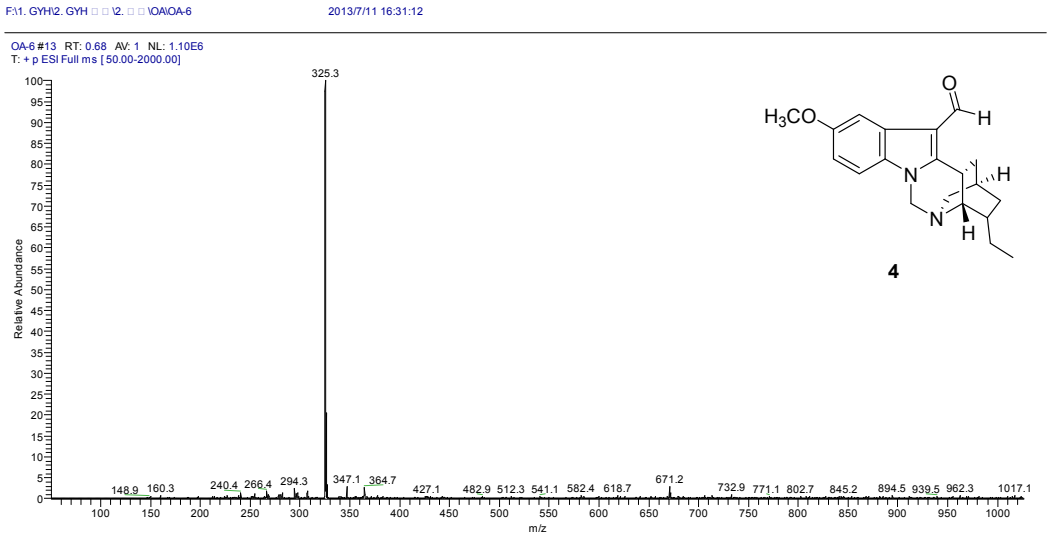


Figure S52. ESI-MS spectrum of **4**

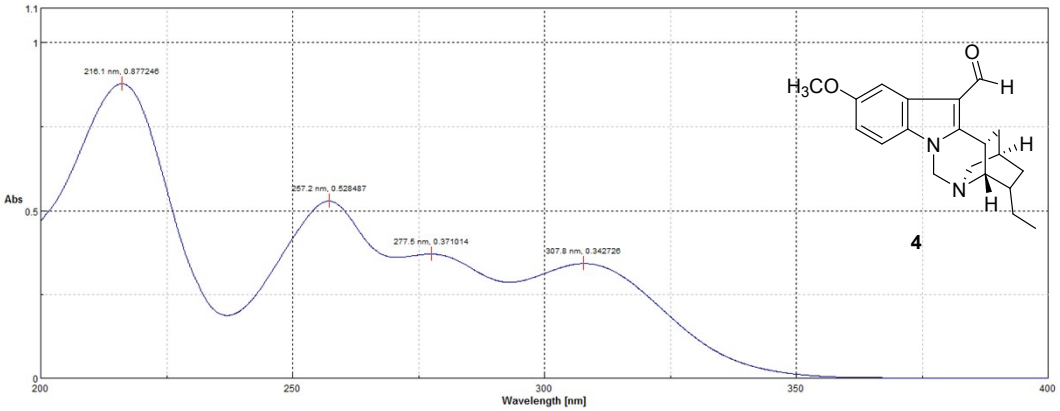


Figure S53. UV spectrum of **4** (MeOH)

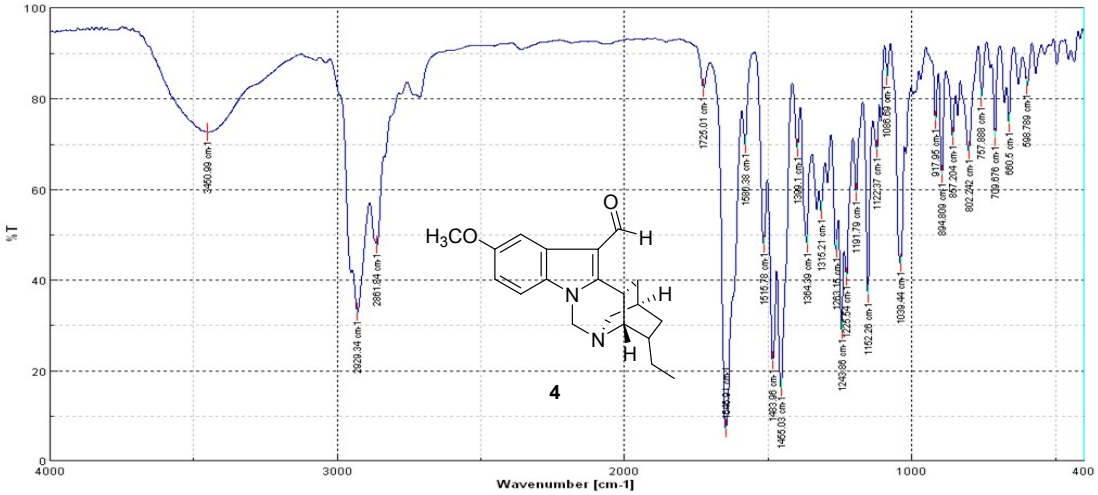


Figure S54. IR spectrum of **4** (KBr)

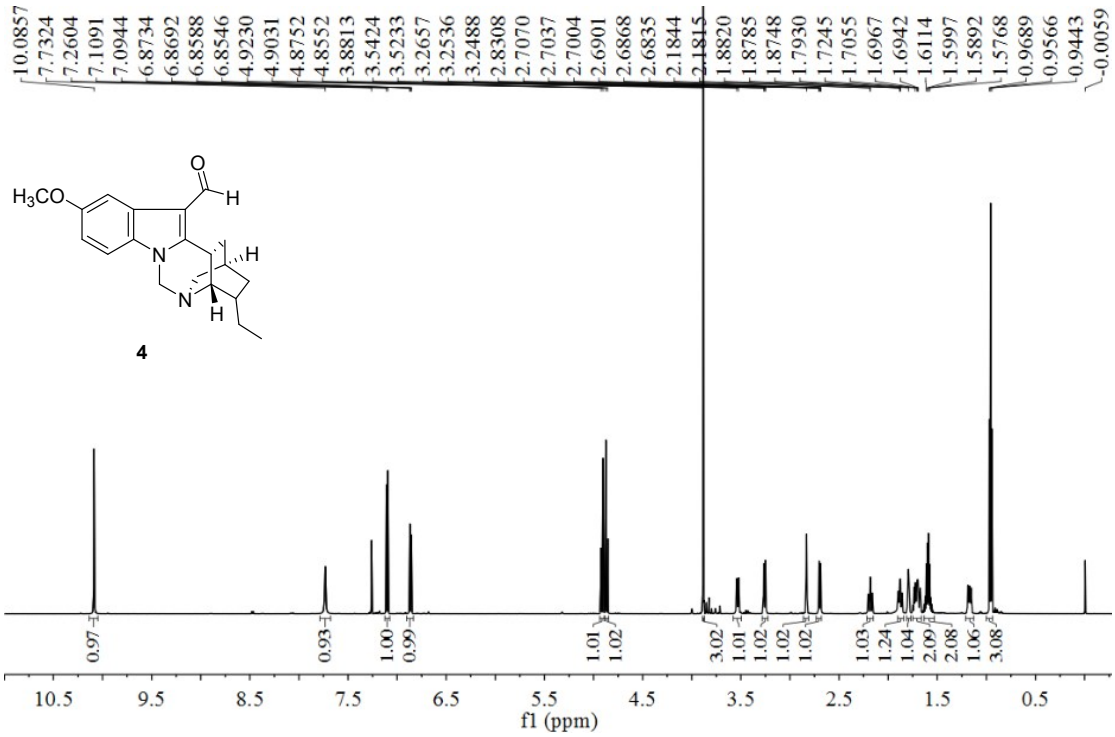


Figure S55. ^{1}H NMR spectrum of **4** ($CDCl_3$)

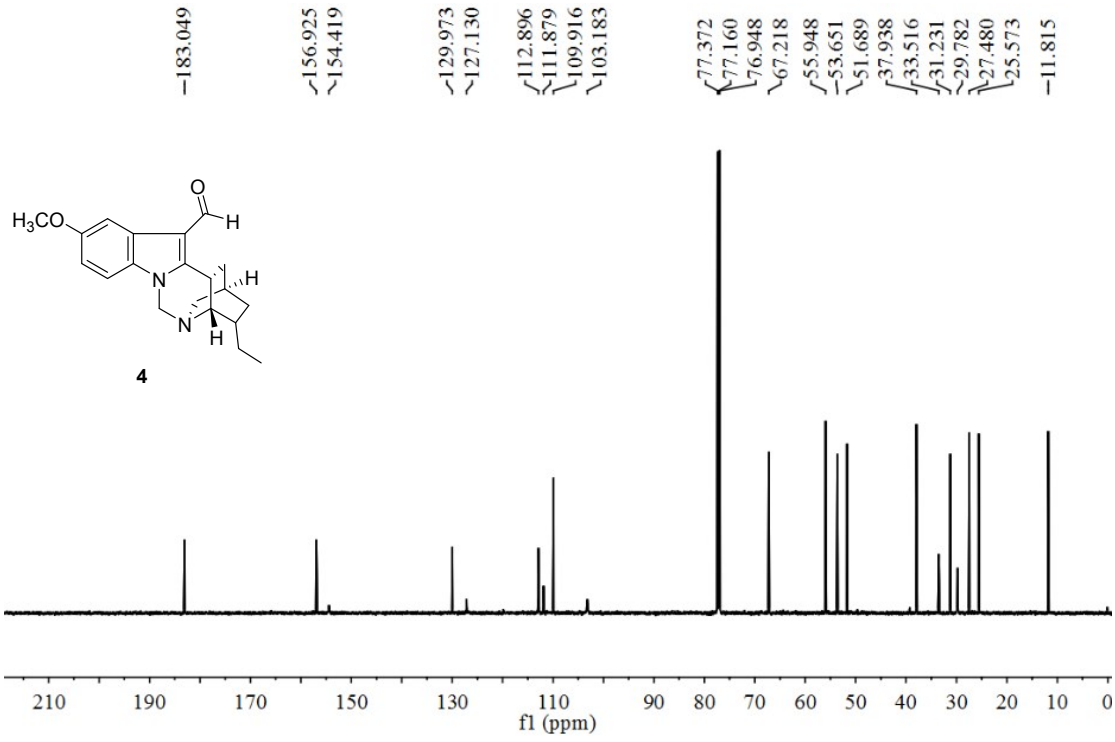


Figure S56. ^{13}C NMR spectrum of **4** ($CDCl_3$)

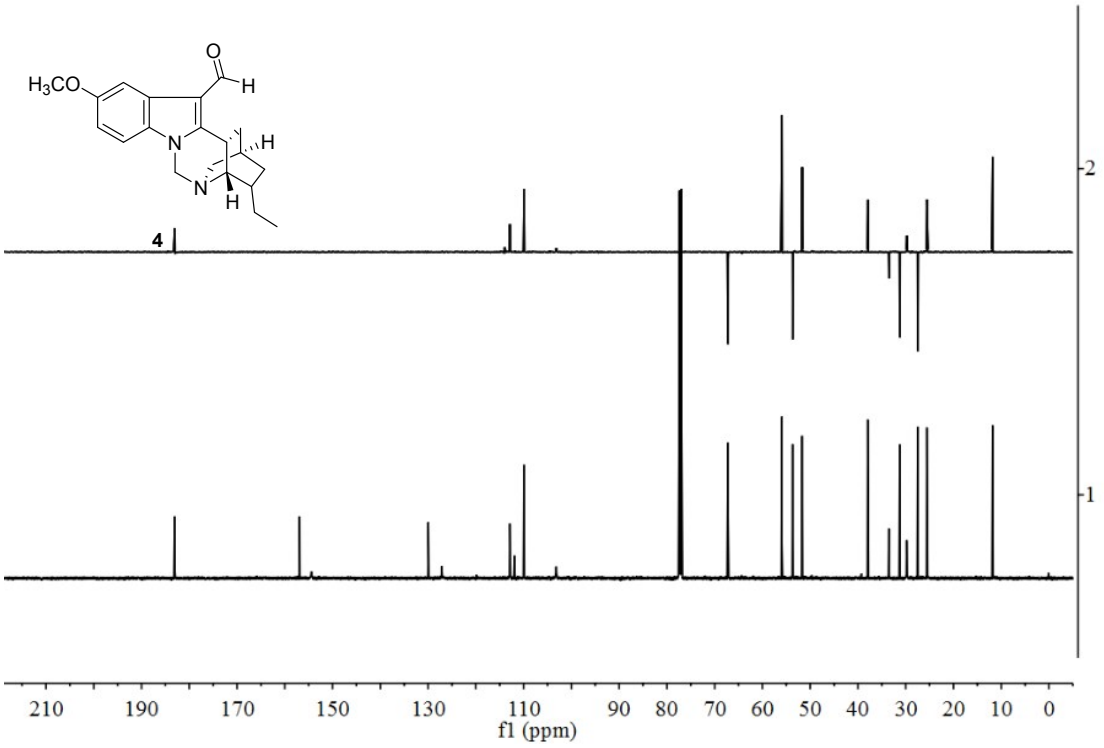


Figure S57. DEPT-135 and ^{13}C NMR spectra of **4** ($CDCl_3$)

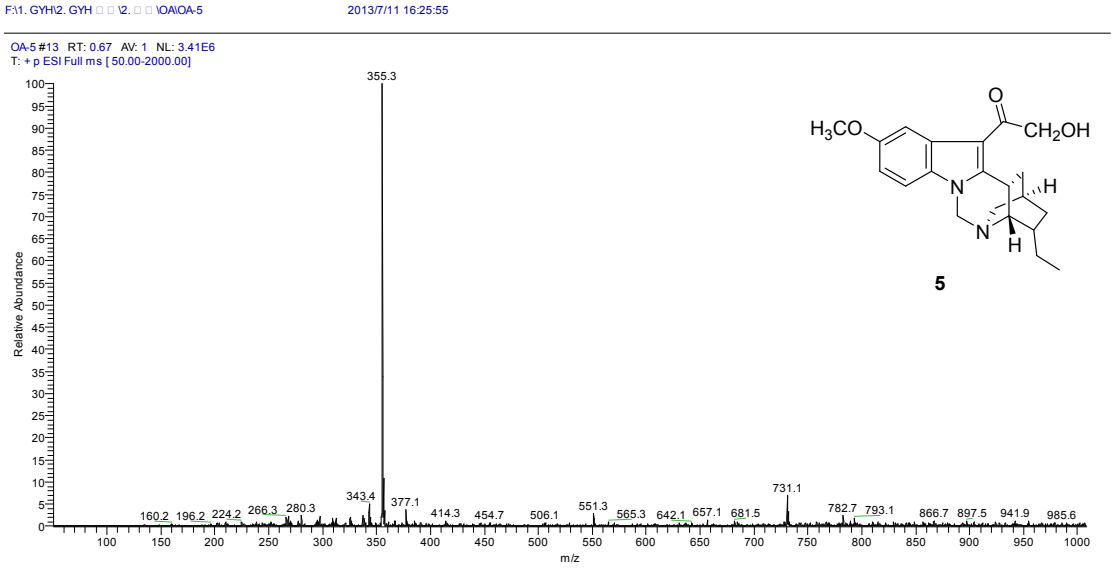


Figure S58. ESI-MS spectrum of **5**

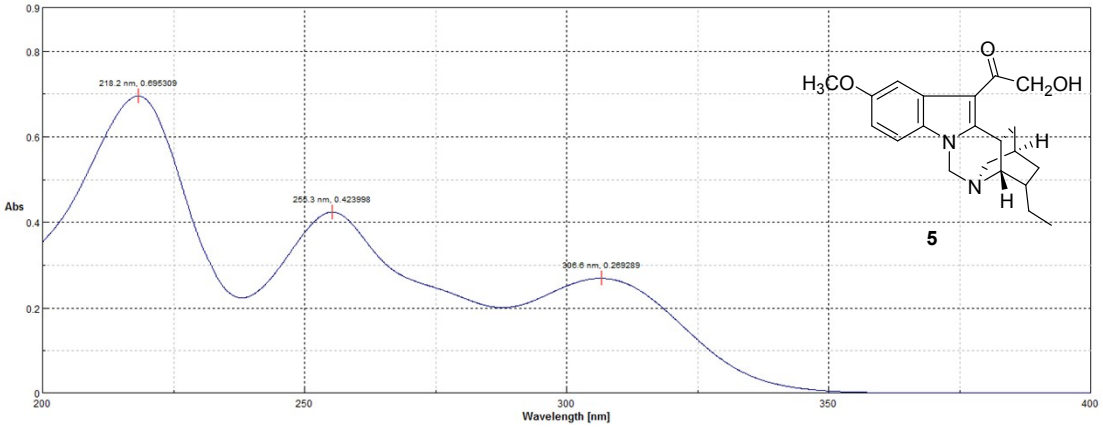


Figure S59. UV spectrum of **5** (MeOH)

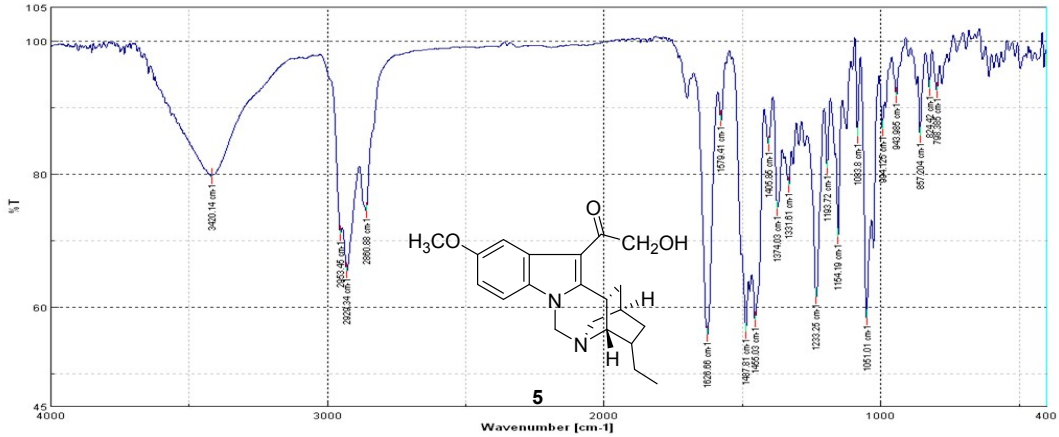


Figure S60. IR spectrum of **5** (KBr)

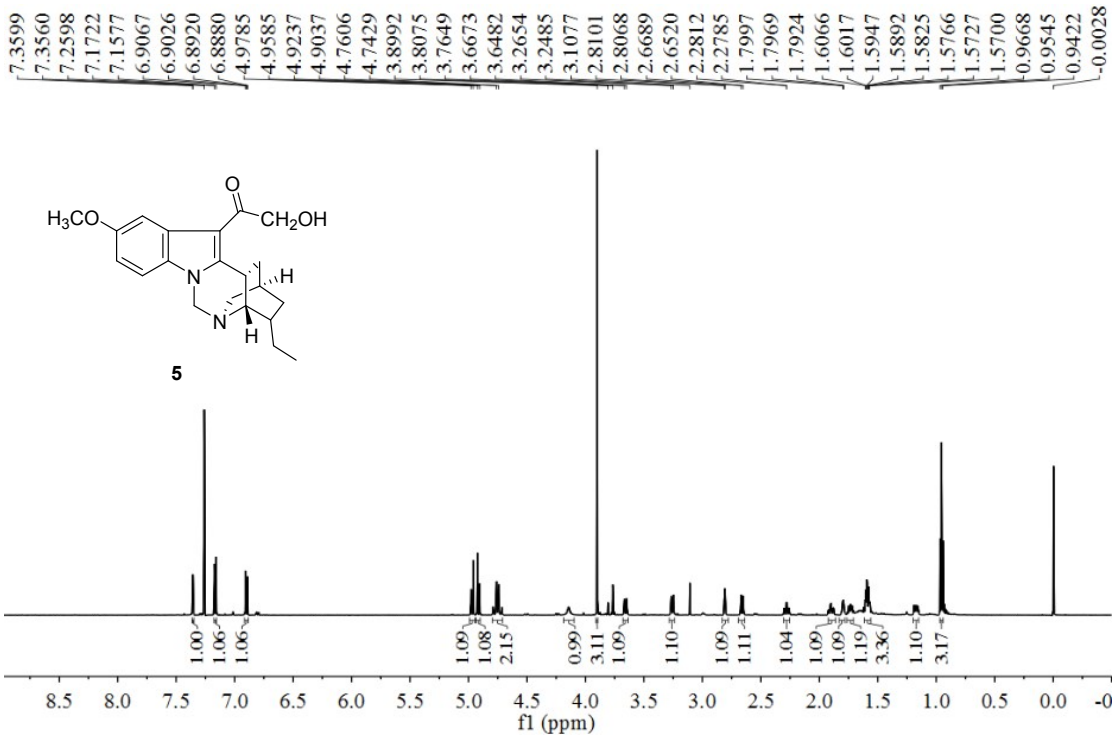


Figure S61. ^{1}H NMR spectrum of **5** ($CDCl_3$)

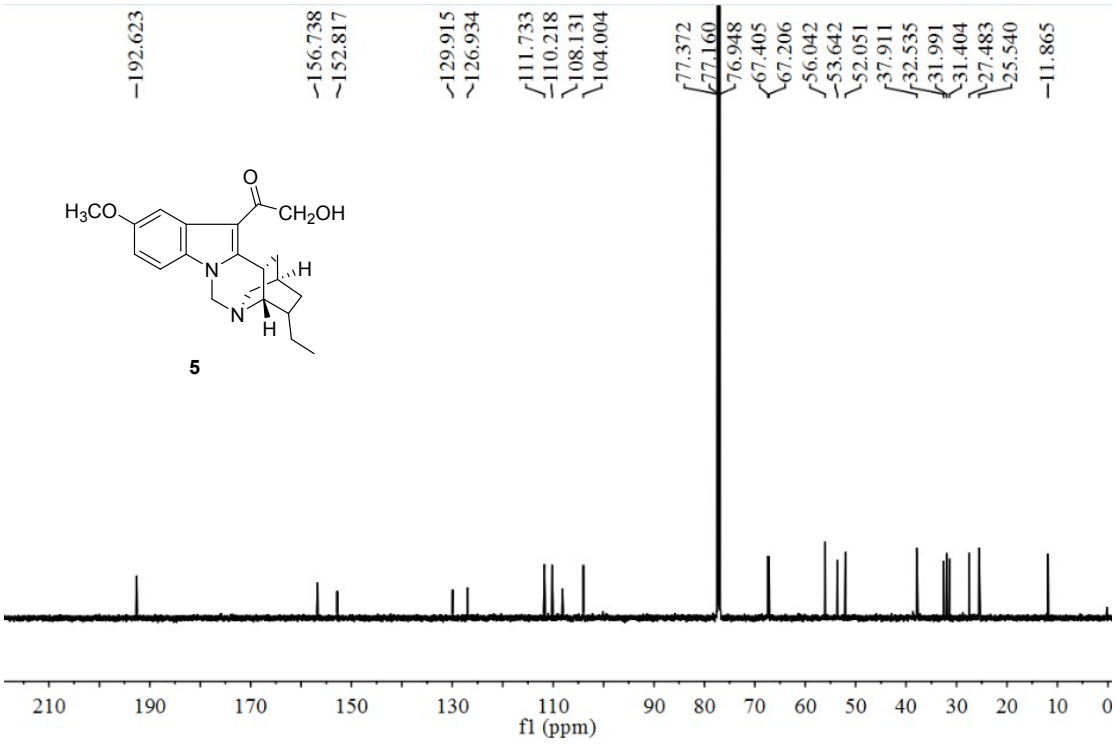


Figure S62. ^{13}C NMR spectrum of **5** ($CDCl_3$)

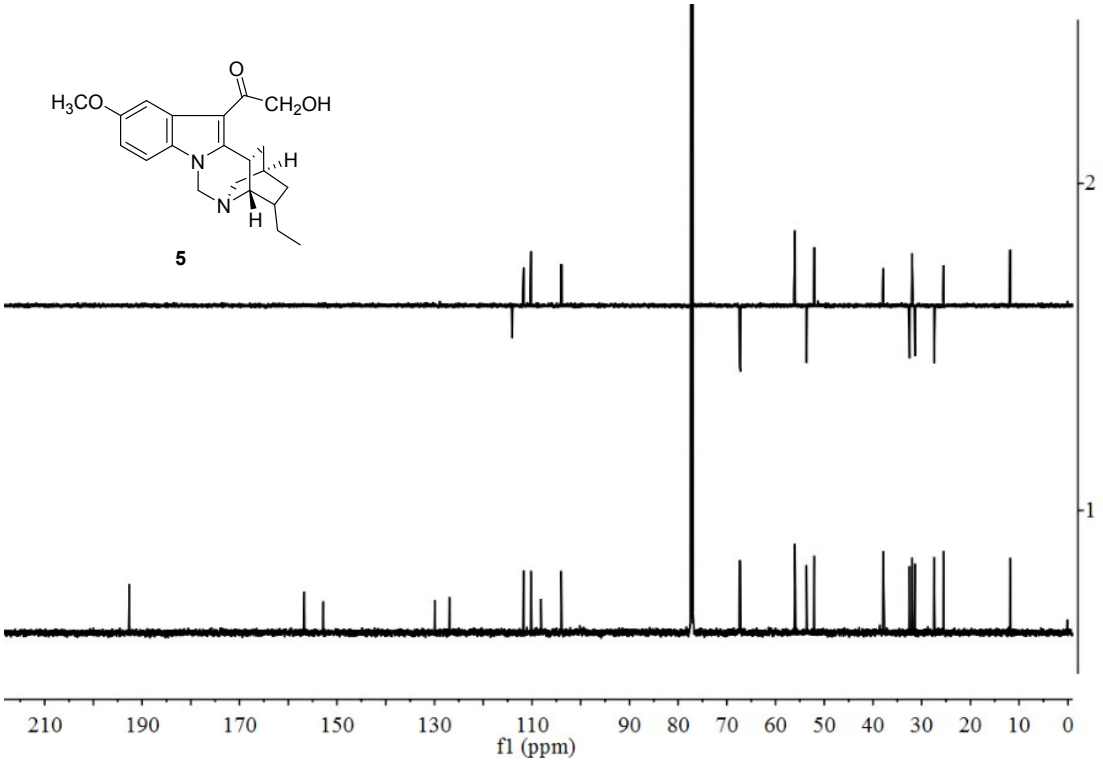


Figure S63. DEPT-135 and ^{13}C NMR spectra of **5** ($CDCl_3$)

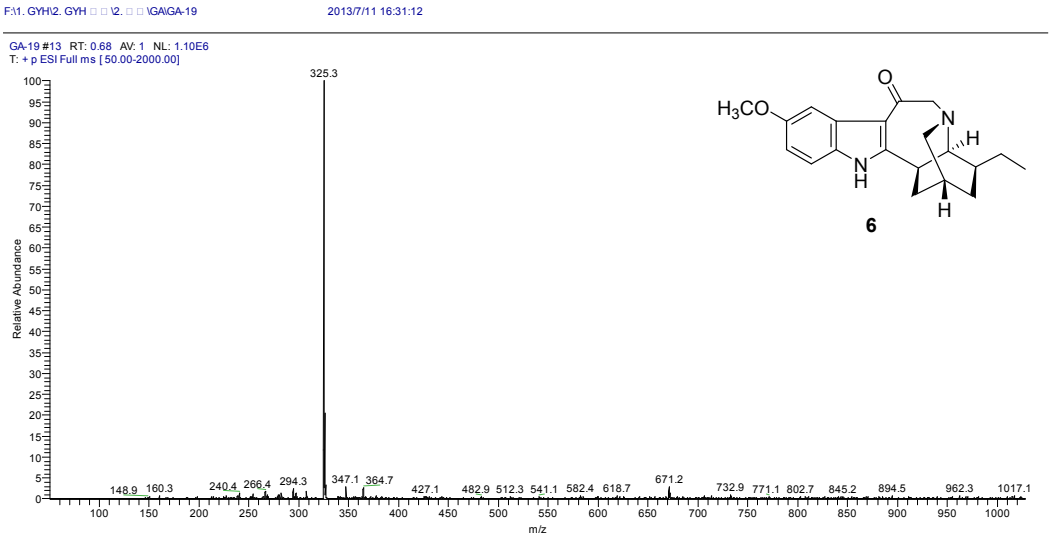


Figure S64. ESI-MS spectrum of **6**

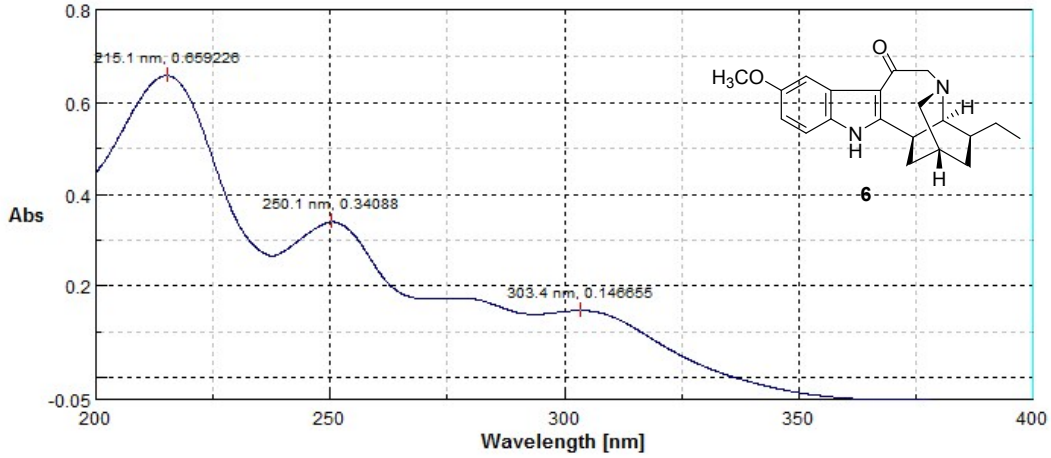


Figure S65. UV spectrum of **6** (MeOH)

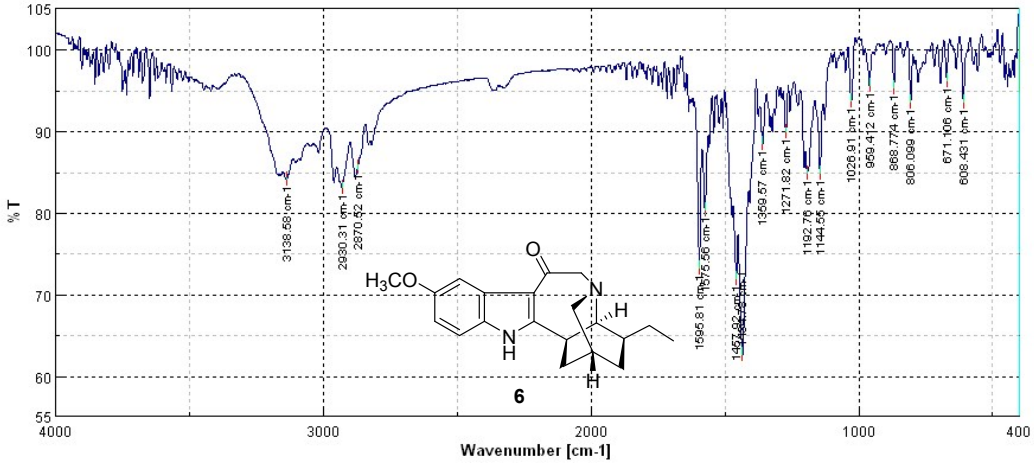


Figure S66. IR spectrum of **6** (KBr)

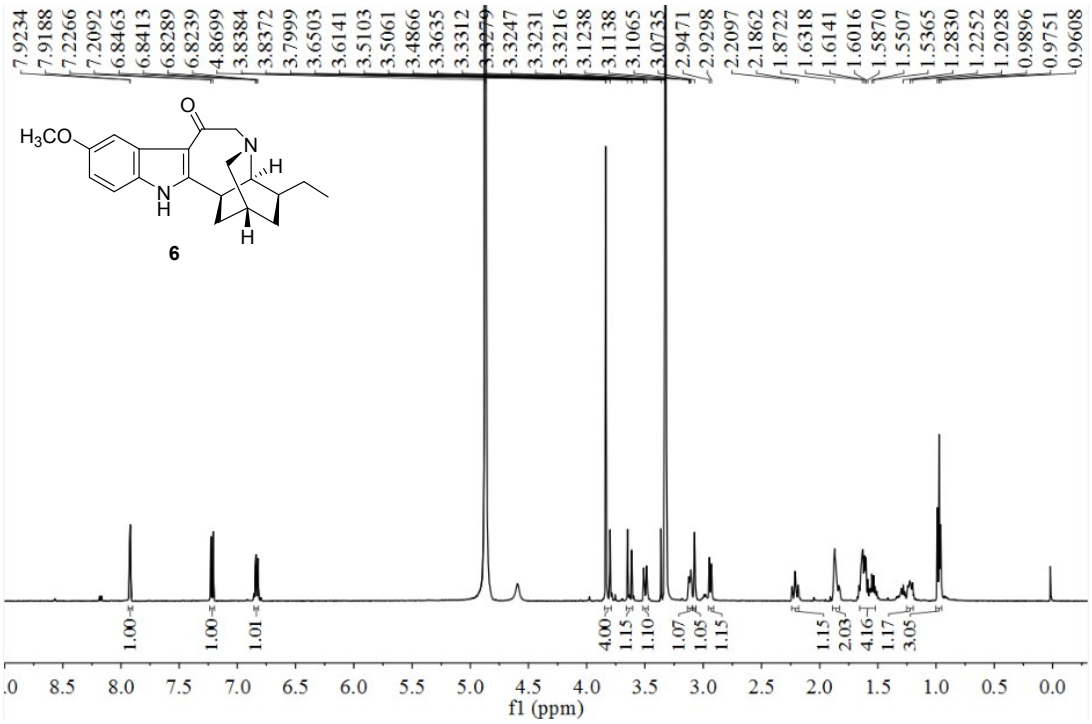


Figure S67. ^{1}H NMR spectrum of **6** (CD_3OD)

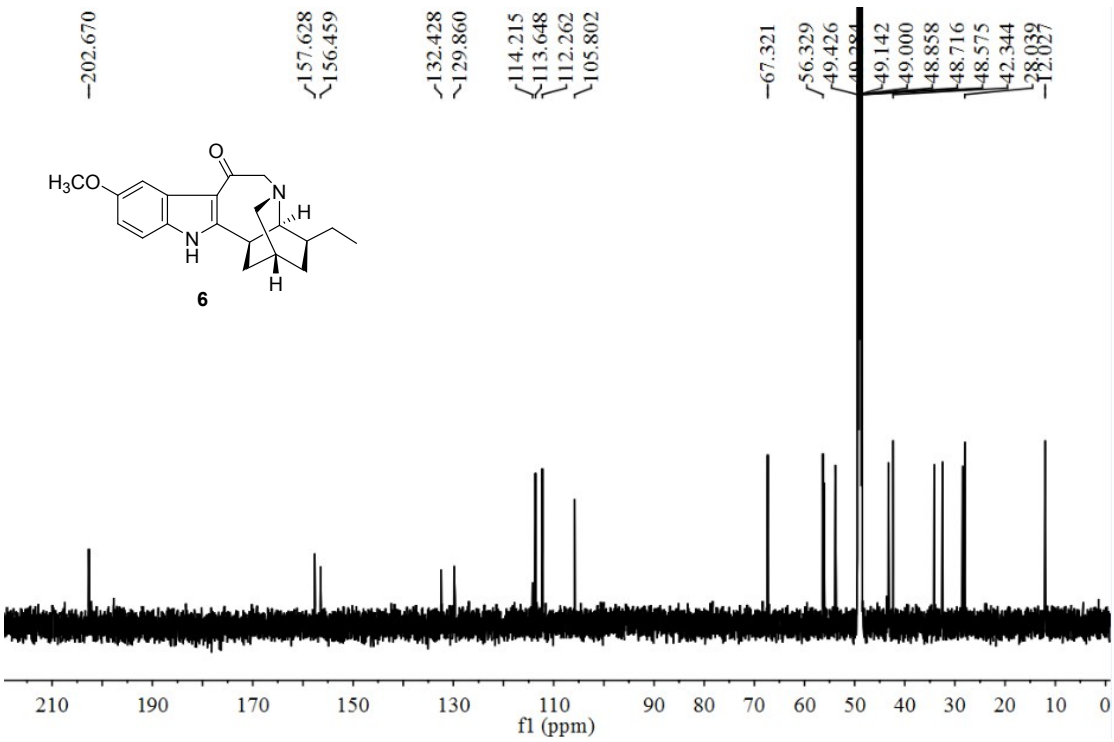


Figure S68. ^{13}C NMR spectrum of **6** (CD_3OD)

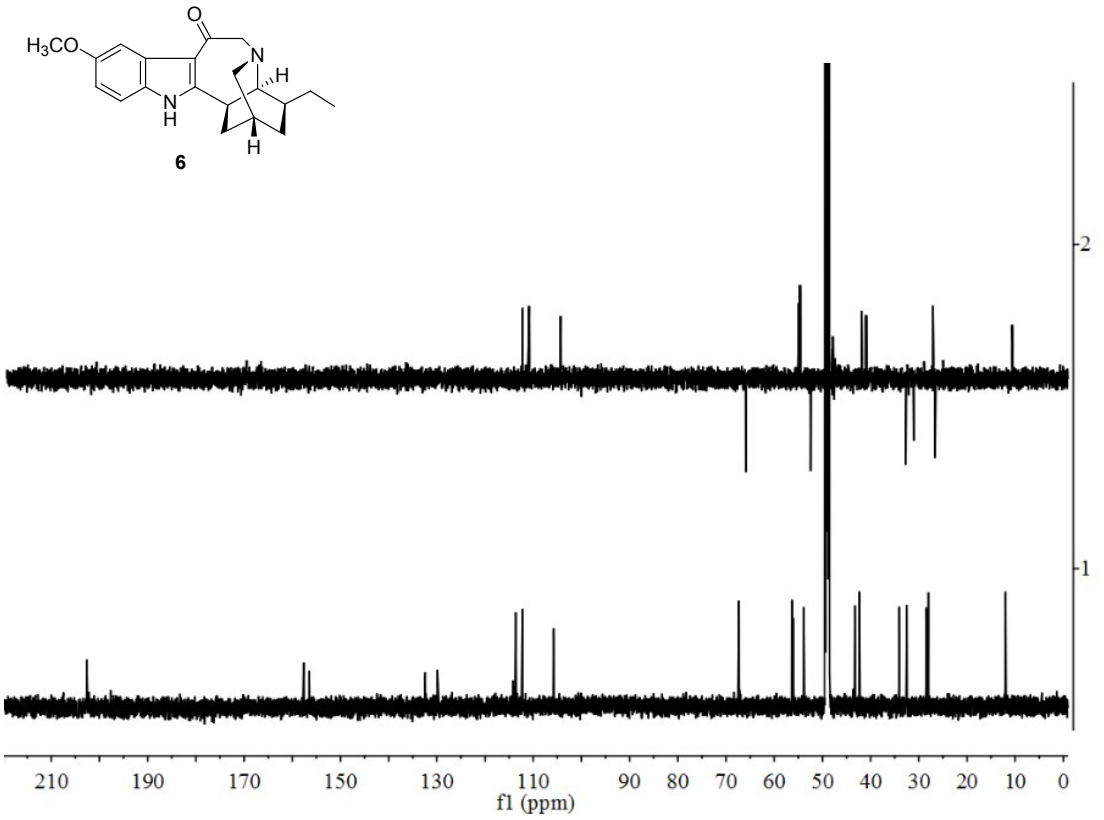


Figure S69. DEPT-135 and ^{13}C NMR spectra of **6** (CD_3OD)

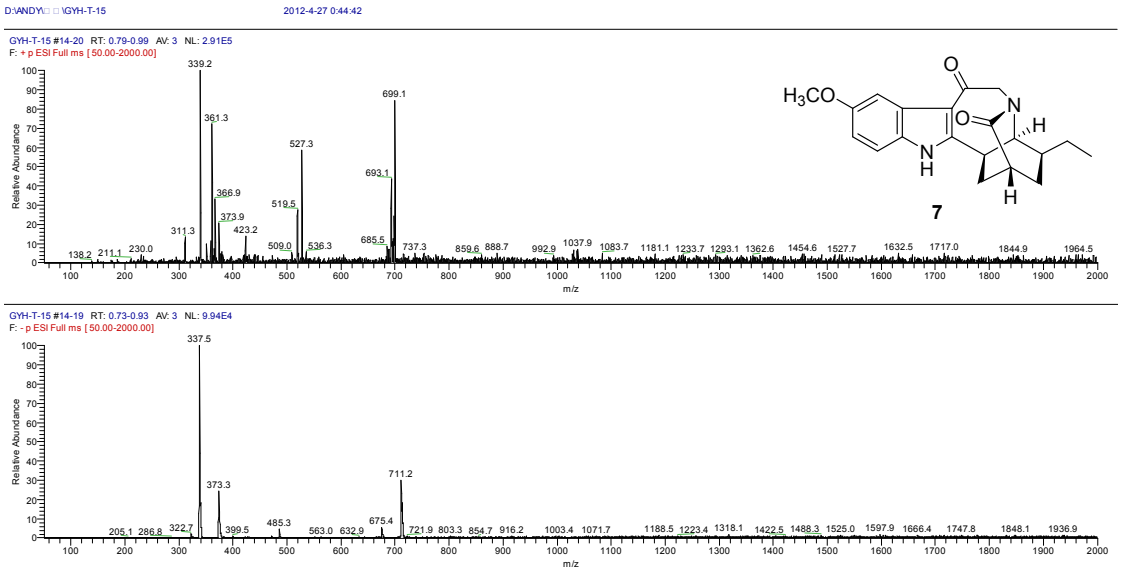


Figure S70. ESI-MS spectrum of **7**

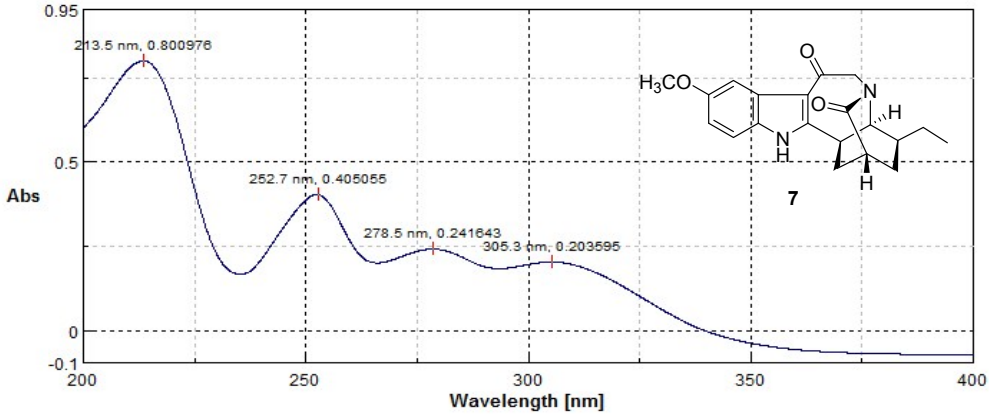


Figure S71. UV spectrum of **7** (MeOH)

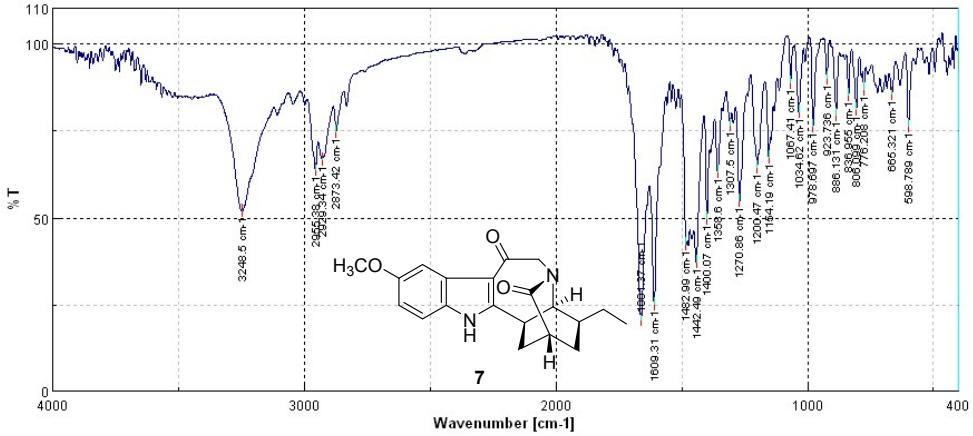


Figure S72. IR spectrum of **7** (KBr)

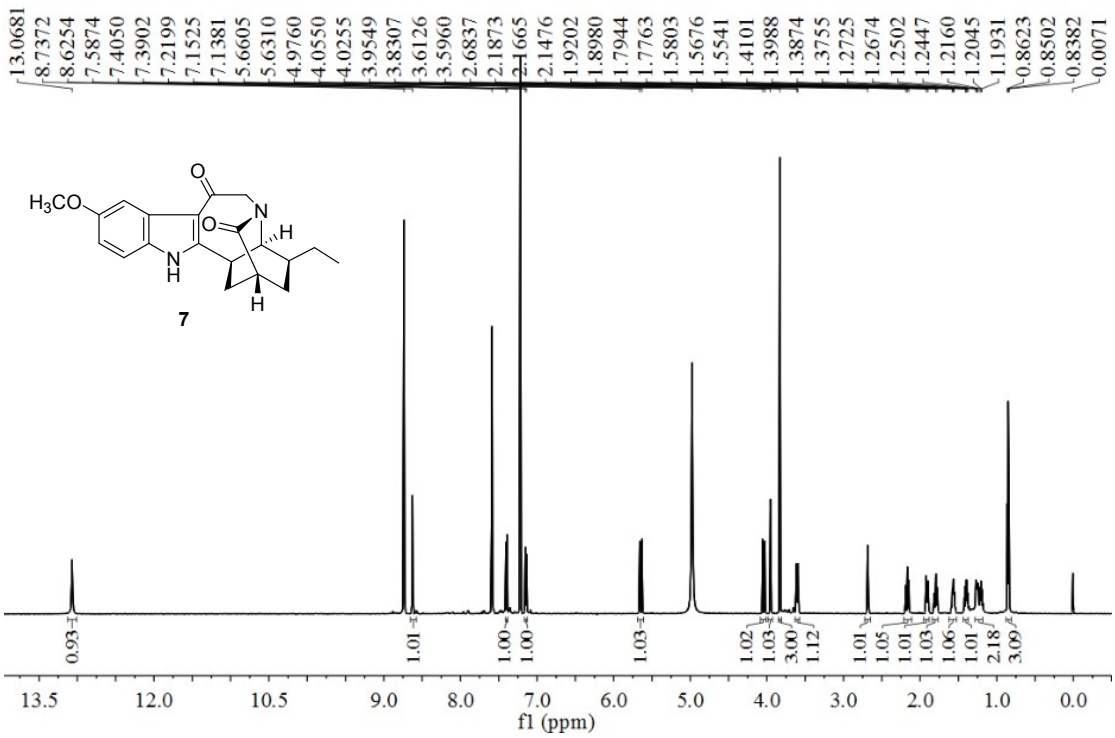


Figure S73. ^{1}H NMR spectrum of **7** (Pyridine-d_5)

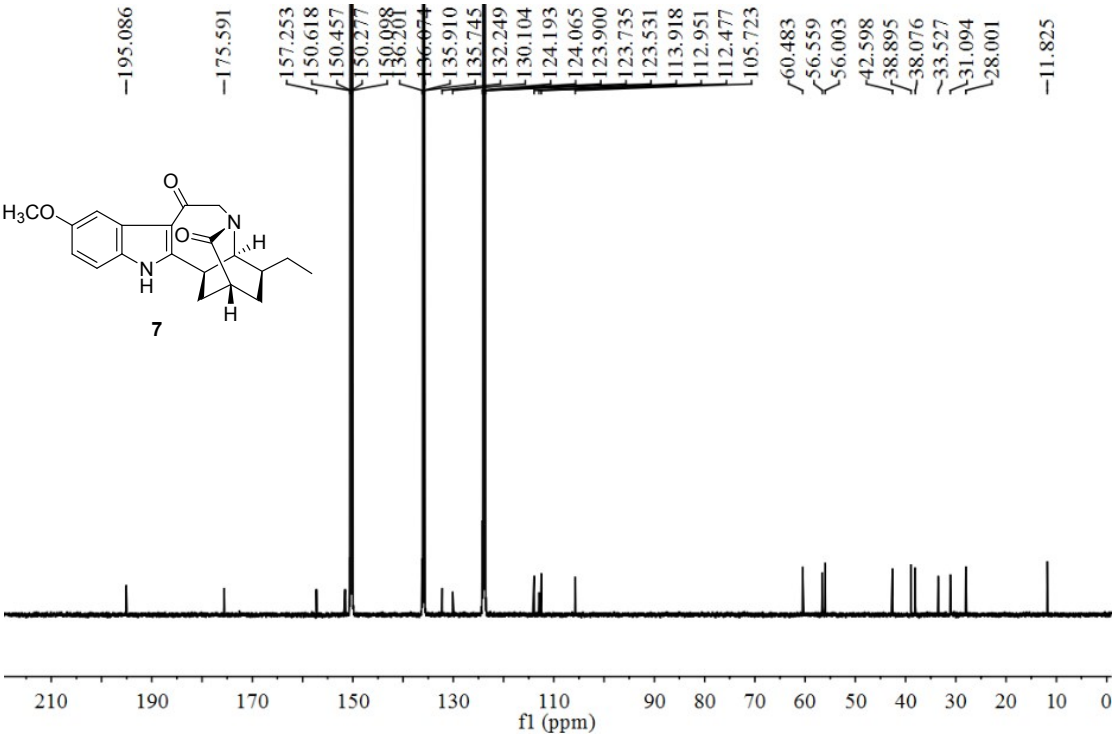


Figure S74. ^{13}C NMR spectrum of **7** (Pyridine-d_5)

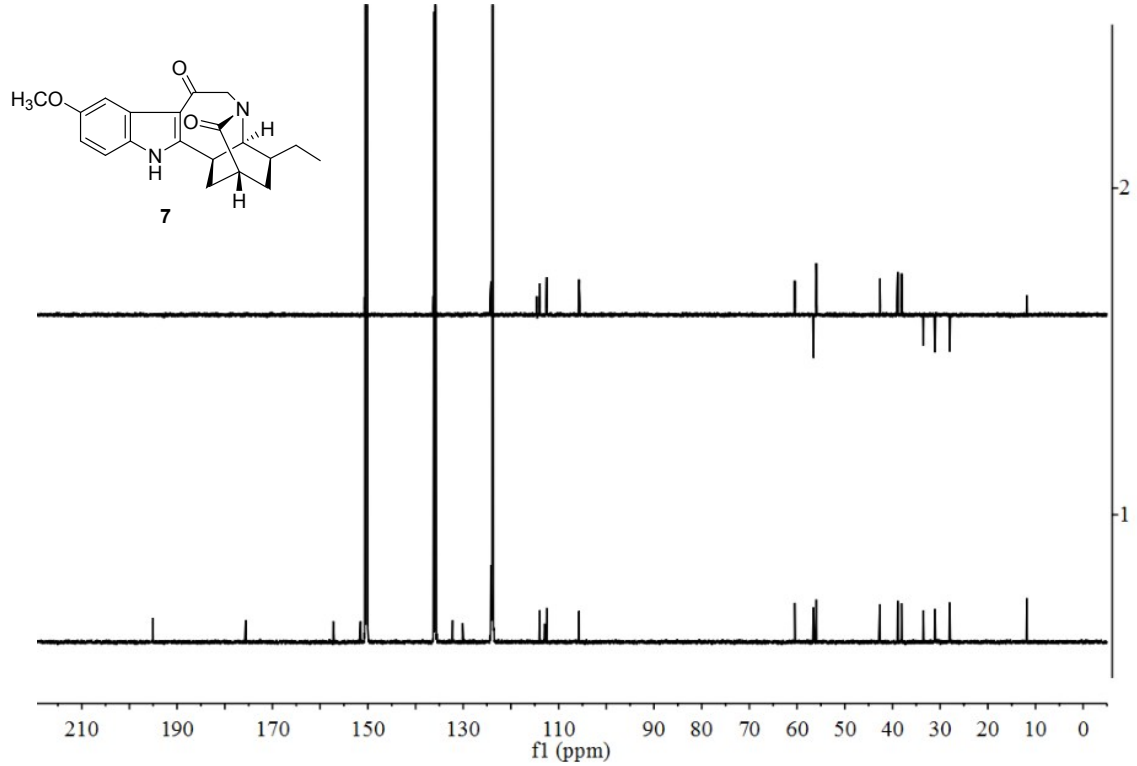


Figure S75. DEPT-135 and ^{13}C NMR spectra of **7** (Pyridine-d_5)

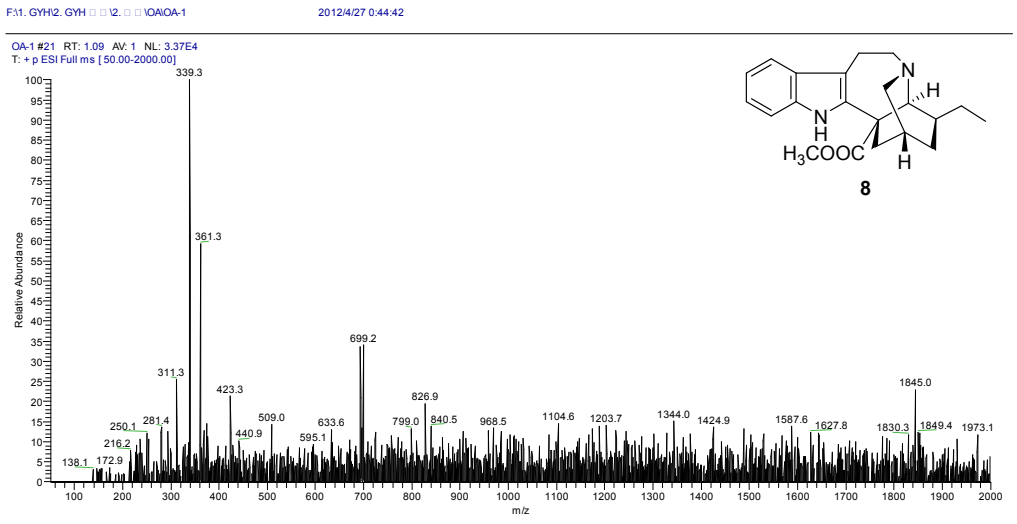


Figure S76. ESI-MS spectrum of **8**

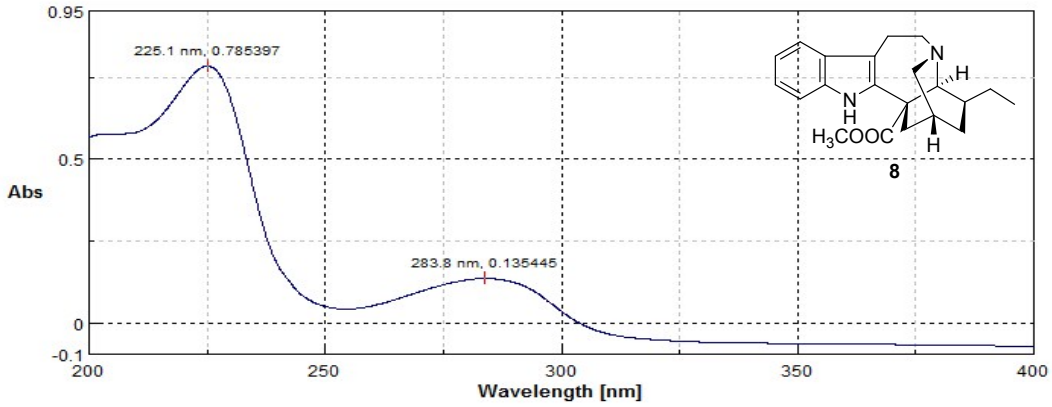


Figure S77. UV spectrum of **8** (MeOH)

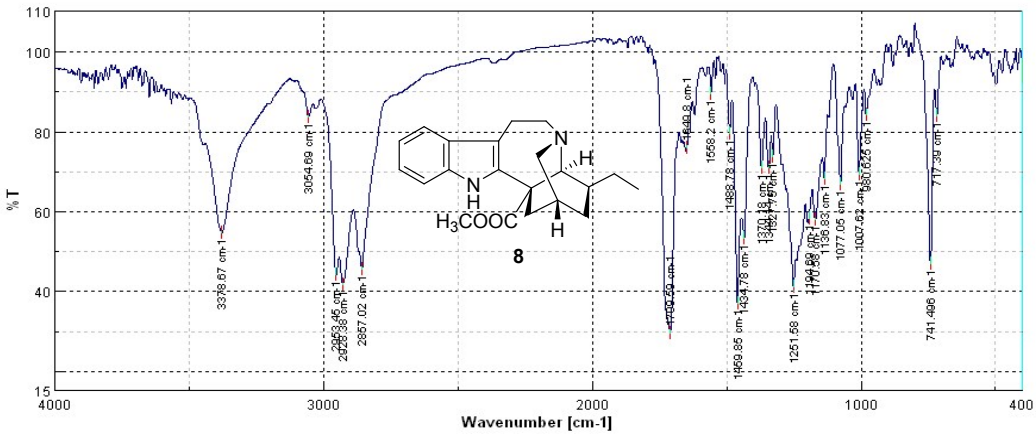


Figure S78. IR spectrum of **8** (KBr)

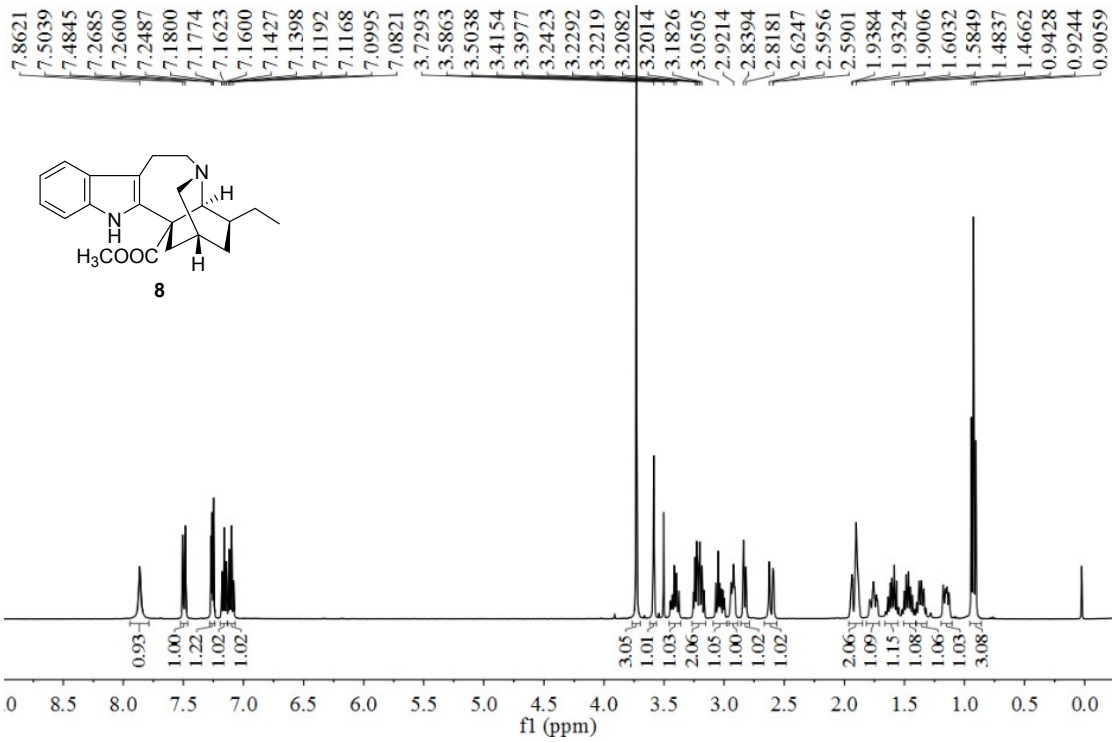


Figure S79. ^{1}H NMR spectrum of **8** ($CDCl_3$)

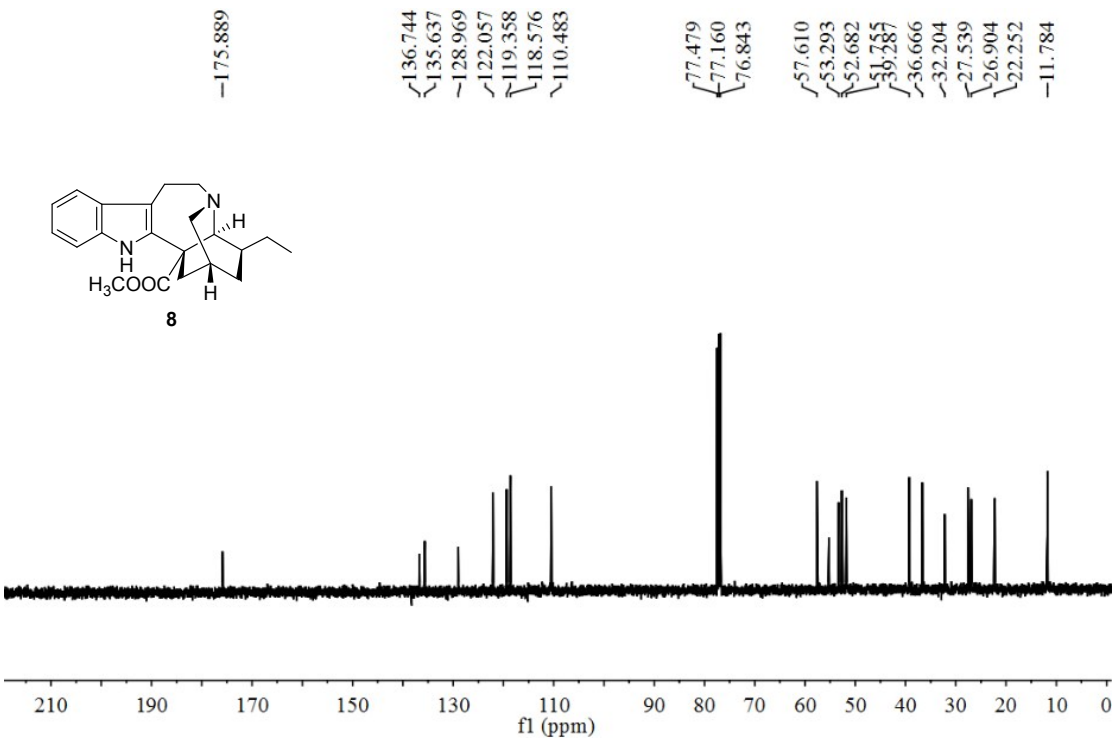


Figure S80. ^{13}C NMR spectrum of **8** ($CDCl_3$)

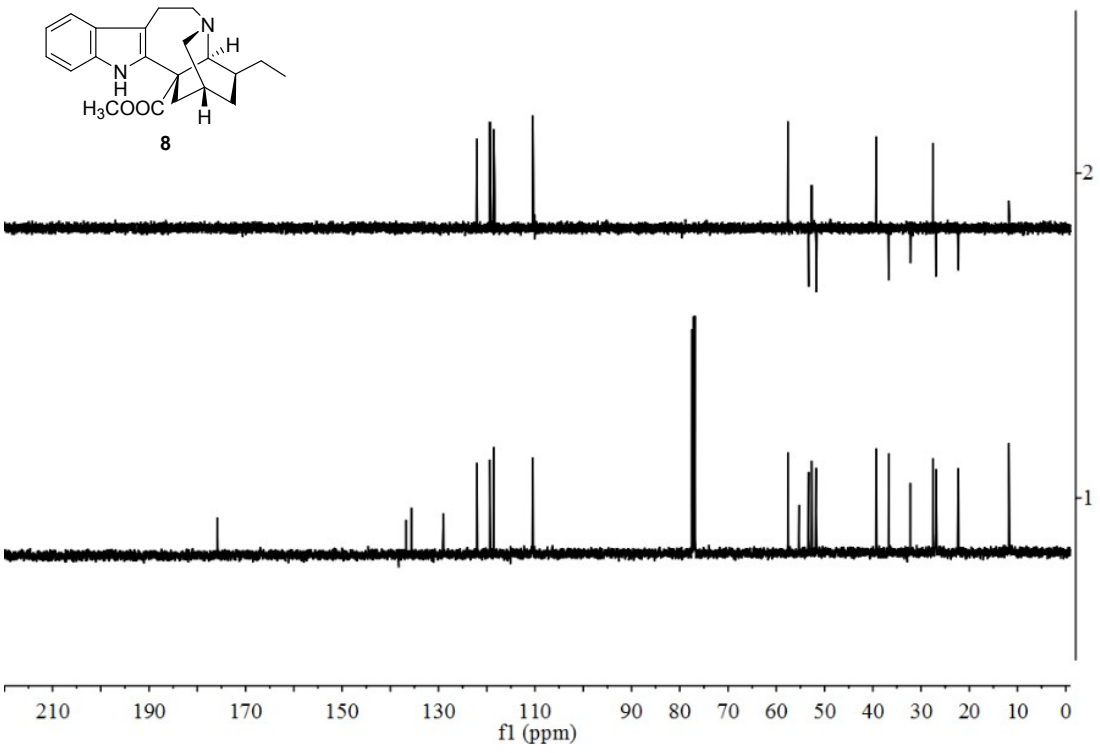


Figure S81. DEPT-135 and ^{13}C NMR spectra of **8** ($CDCl_3$)

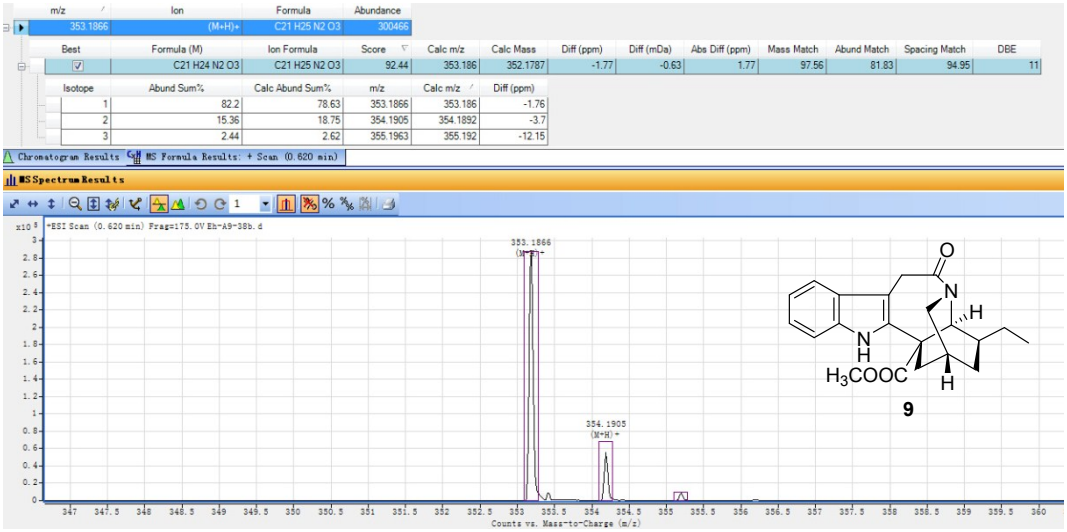


Figure S82. HRESIMS spectrum of **9**

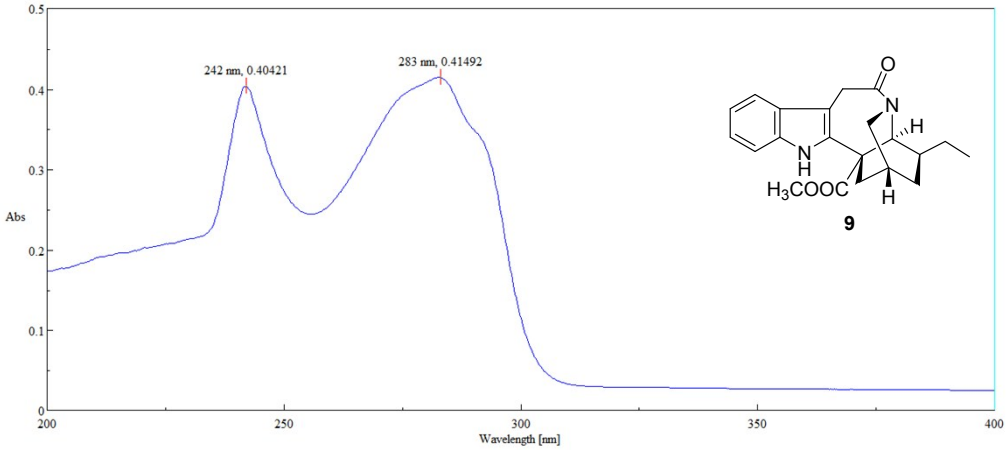


Figure S83. UV spectrum of **9** ($CHCl_3$)

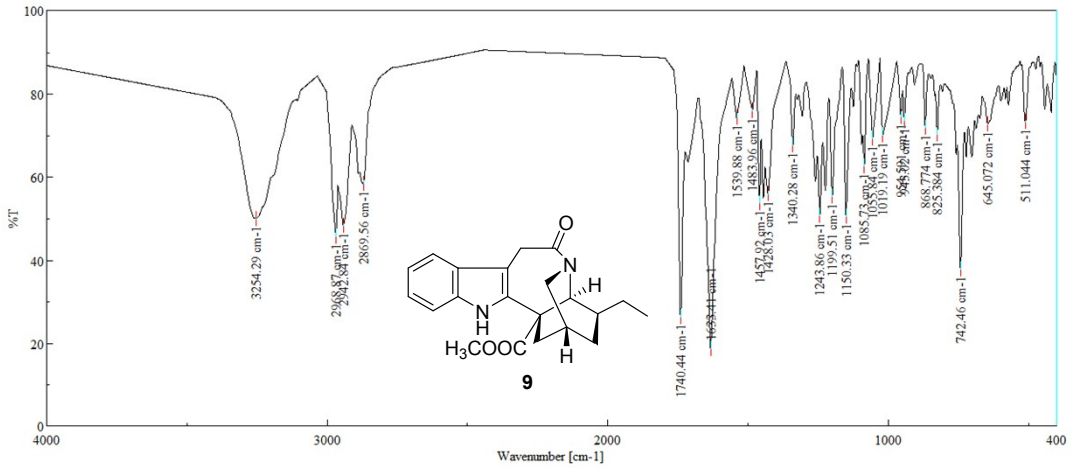


Figure S84. IR spectrum of **9** (KBr)

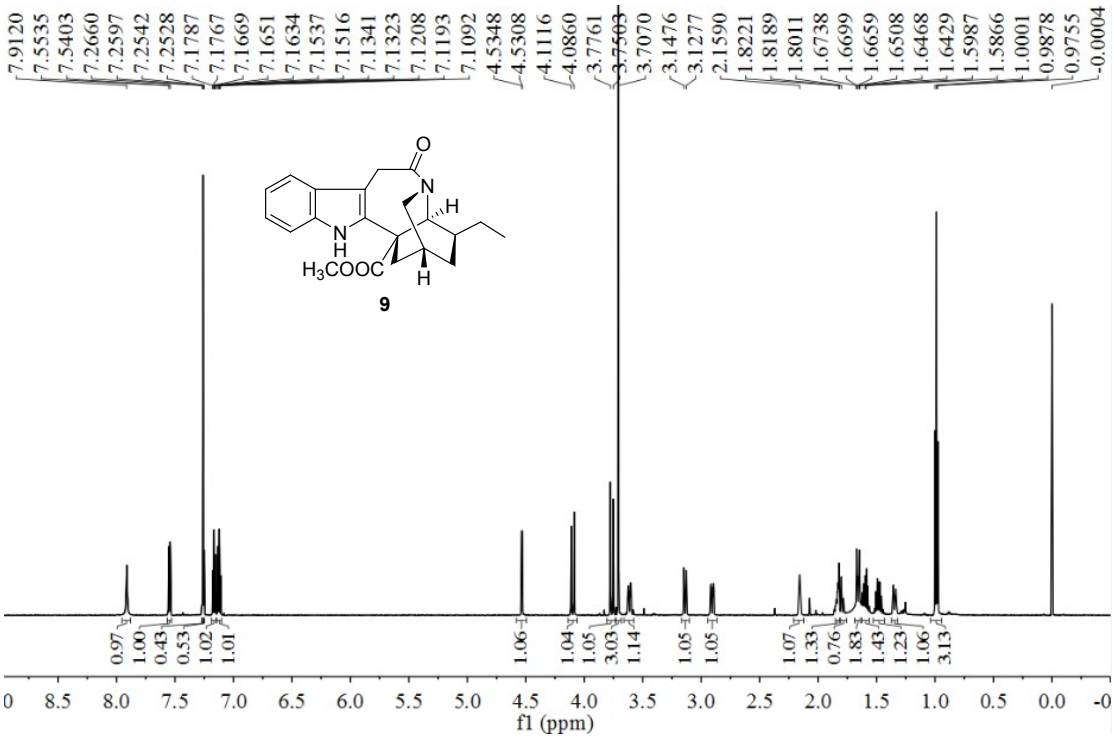


Figure S85. ^{1}H NMR spectrum of **9** ($CDCl_3$)

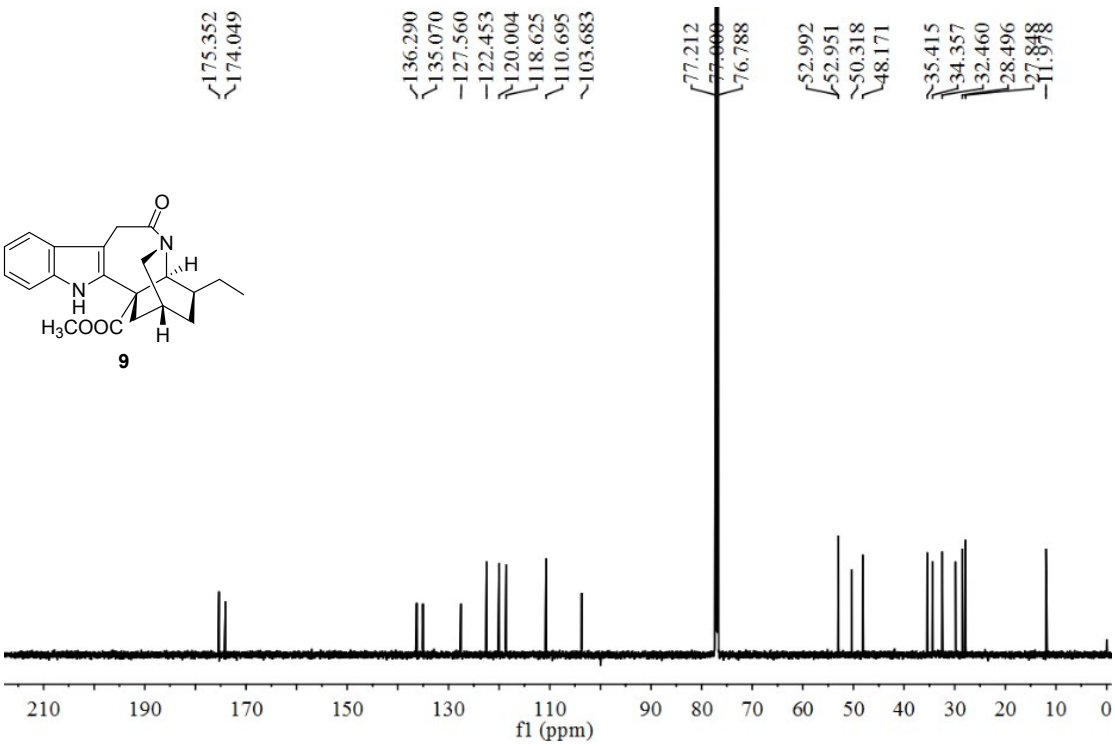


Figure S86. ^{13}C NMR spectrum of **9** ($CDCl_3$)

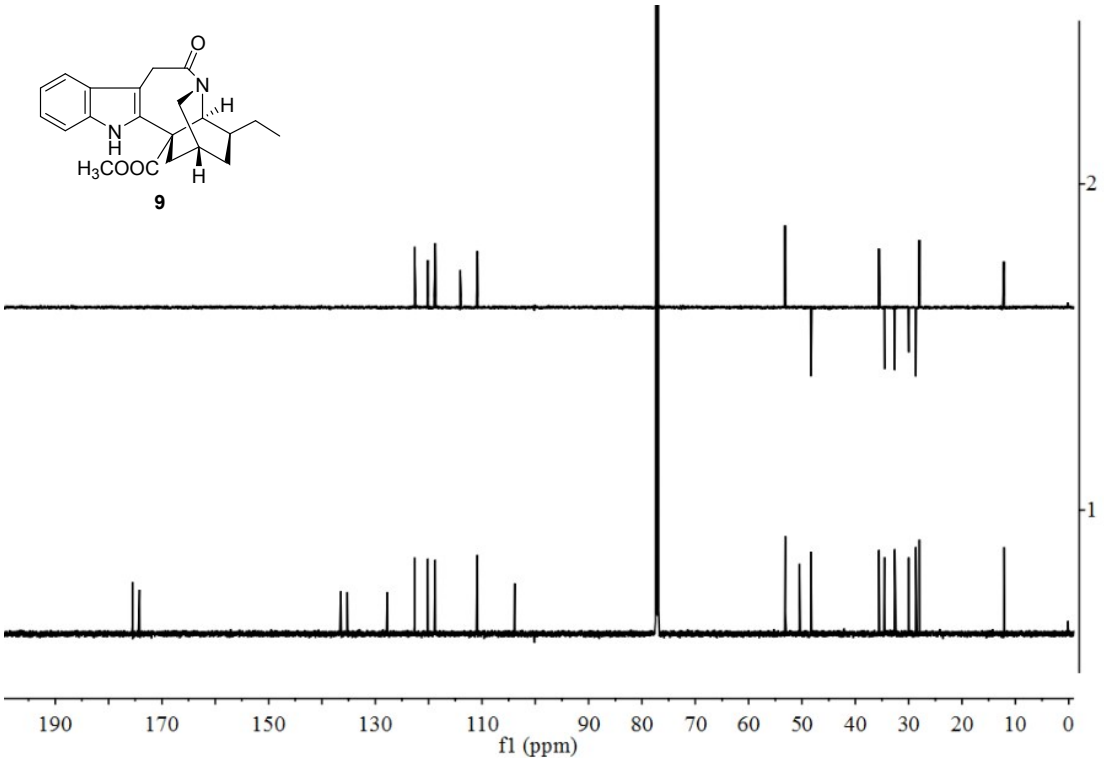


Figure S87. DEPT-135 and ^{13}C NMR spectra of **9** ($CDCl_3$)