Supporting Information for

Polycyclic pyrroloindoline-containing natural product with unprecedented hexahydro-2a,4a-diazapentaleno[1,6-ab]indene core from *Alstonia scholaris*

Guanqun Zhan,[§] Fuxin Zhang,[§] Kailing Yang, Tao Yang, Ruixi Zhou, Xueqing Ma, Nan Wang, Zengjun Guo[*]

School of Pharmacy, Health Science Center, Xi'an Jiaotong University, Xi'an 710061, P. R. China

List of Supplementary Data

1. Computational calculations section

1.1 Conformational analysis and structure optimization

Conformational analysis was performed using OpenBabel with genetic algorithm at MMFF94 force field for the configurations of the calculated compounds.[1] The conformers of each configuration were then optimized with the software package Gaussian 09 at the M062X/6-31G(d) level.[2] Room-temperature equilibrium populations were calculated according to Boltzmann distribution law:

$$\frac{N_i}{N} = \frac{g_i e^{-\frac{E_i}{k_B T}}}{\sum g_i e^{-\frac{E_i}{k_B T}}}$$

where N_i is the number of conformer *i* with energy E_i and degeneracy g_i at temperature *T*, and k_B is Boltzmann constant.

Table S1 Energies of molecule **1a** at M062X/6-31G(d) level.

Conformers	Energy（Hartree）	Population (%)
1a-1	−1113.678594	1.17
1a-2	−1113.679985	5.13
1a-3	−1113.678694	1.30
1a-4	−1113.678897	1.62
1a-5	−1113.679382	2.71
1a-7	−1113.679557	3.26
1a-9	−1113.680908	13.65
1a-10	−1113.679105	2.02
1a-11	−1113.67987	4.54
1a-15	−1113.679609	3.44
1a-16	−1113.681264	19.89
1a-19	−1113.681154	17.70
1a-20	−1113.679073	1.95
1a-24	−1113.679291	2.46

1 O'Boyle, N. M.; Banck, M.; James, C. A.; Morley, C.; Vandermeersch, T.; Hutchison, G. R. *J. Cheminformatics* 2011, 3, 33.

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

1a-29	−1113.678973	1.76
1a-32	−1113.681137	17.4

Table S2 Energies of molecule **1b** at M062X/6-31G(d) level.

Conformers	**Energy（Hartree）**	**Population (%)**
1b-1	−1113.631503	2.91
1b-2	−1113.633912	37.43
1b-3	−1113.631791	3.95
1b-13	−1113.631641	3.37
1b-15	−1113.633863	35.51
1b-18	−1113.631841	4.16
1b-20	−1113.631794	3.96
1b-28	−1113.631301	2.35
1b-45	−1113.631298	2.34
1b-47	−1113.631808	4.02

Table S3 Energies of molecule **1c** at M062X/6-31G(d) level.

Conformers	**Energy（Hartree）**	**Population (%)**
1c-1	−1113.630746	3.62
1c-2	−1113.630745	3.61
1c-3	−1113.631325	6.68
1c-4	−1113.630164	1.95
1c-5	−1113.630631	3.20
1c-6	−1113.630011	1.66
1c-7	−1113.629986	1.62
1c-9	−1113.63063	3.20
1c-10	−1113.630622	3.17
1c-11	−1113.632036	14.19
1c-12	−1113.631144	5.51
1c-16	−1113.632093	15.08
1c-18	−1113.631937	12.78
1c-19	−1113.631713	10.08
1c-20	−1113.631999	13.65

Table S4 Energies of molecule **1d** at M062X/6-31G(d) level.

Conformers	**Energy（Hartree）**	**Population (%)**
1d-1	−1113.675	12.69

1d-3	−1113.672	1.23
1d-4	−113.673	1.67
1d-5	−113.674	4.50
1d-6	−113.674	11.08
1d-7	−113.675	23.77
1d-10	−113.674	5.18
1d-11	−113.674	9.90
1d-12	−113.674	4.98
1d-16	−113.674	11.20
1d-19	−113.674	10.38
1d-23	−113.673	3.41

1.2 NMR calculation

NMR calculations were carried out by Gaussian 09 following the protocol adapted from Michael *et al*.[3] The theoretical calculation of NMR was conducted using the Gauge-Including Atomic Orbitals (GIAO) method at mPW1PW91/6-31G(d) by the SMD model. Finally, the calculated NMR chemical shift values were averaged according to Boltzmann distribution for each conformer and fitting to the experimental values by linear regression. DP4+ probability analysis was performed according to the reported methods.[4]

3. Michael, W. L.; Matthew, R. S.; Dean, J. T. *Chem. Rev.* **2012**, *112*, 1839−1862.
4 Grimblat, N.; Zanardi, M.M.; Sarotti, A.M. *J. Org. Chem*. **2015**, 80, 12526−12534.

Table S5 Experimental and calculated ^{13}C NMR of **1a**

No.	$\delta_{exptl.}$	$\delta_{calcd\text{-}1a\text{-}1}$	$\delta_{calcd\text{-}1a\text{-}2}$	$\delta_{calcd\text{-}1a\text{-}3}$	$\delta_{calcd\text{-}1a\text{-}4}$	$\delta_{calcd\text{-}1a\text{-}5}$	$\delta_{calcd\text{-}1a\text{-}7}$	$\delta_{calcd\text{-}1a\text{-}9}$	$\delta_{calcd\text{-}1a\text{-}10}$	$\delta_{calcd\text{-}1a\text{-}11}$	$\delta_{calcd\text{-}1a\text{-}15}$	$\delta_{calcd\text{-}1a\text{-}16}$	$\delta_{calcd\text{-}1a\text{-}19}$	$\delta_{calcd\text{-}1a\text{-}20}$	$\delta_{calcd\text{-}1a\text{-}24}$	$\delta_{calcd\text{-}1a\text{-}29}$	$\delta_{calcd\text{-}1a\text{-}32}$	$\delta_{calcd\text{-}weighted}$	δ_{calcd}	$\Delta\delta_{exptl\text{-}calcd}$
2	95.1	103.6451	103.3428	103.6405	104.0296	103.5745	103.5434	103.7728	104.158	103.2757	104.2365	103.5788	104.3599	103.3259	104.5107	104.1253	104.5602	103.958	93.6	1.5
4	56.6	143.176	142.5934	143.3169	142.5346	142.9238	142.8791	142.9232	141.7771	140.995	142.2207	137.5833	141.7144	142.0518	142.7495	141.5591	141.2018	141.1509	54.6	2.0
5	42.3	149.8044	152.7057	149.7687	152.7018	149.8301	149.6911	152.4025	152.9272	151.2885	152.94	153.9642	153.0327	152.1424	149.9103	153.1368	153.3623	152.7144	42.5	-0.2
6	88.1	106.9968	107.5144	107.0349	107.6005	106.9434	106.8814	107.2229	107.5424	107.6474	107.7299	109.8806	107.5604	107.1615	106.9906	107.8383	107.7097	107.9403	89.4	-1.3
7	135.6	65.9537	64.8866	65.8597	64.6189	66.029	66.0827	64.4475	64.8382	64.1852	64.69	65.2626	64.9549	64.0123	65.9205	64.8294	64.9443	64.98212	134.5	1.1
8	125.5	74.1449	74.5209	74.1476	74.4838	74.1325	74.112	74.6155	74.4235	76.4413	74.4512	73.5634	74.471	74.7132	74.037	74.3488	74.1765	74.31254	124.7	0.8
9	123.5	78.67	78.582	78.6915	78.4171	78.7007	78.7386	78.2044	78.4263	78.5149	78.4904	78.1164	78.4473	78.4549	78.4729	78.5576	78.4631	78.38649	120.4	3.1
10	131.5	69.398	68.8441	69.4334	68.9549	69.3524	69.354	68.8485	68.9217	69.4277	68.9126	68.8615	68.8995	69.0756	69.386	68.9523	68.8863	68.96181	130.3	1.2
11	113.4	88.2036	87.9724	88.2788	87.578	88.4077	88.475	87.4893	87.6091	87.5935	87.6075	86.8665	87.5999	87.6844	87.7749	87.7134	87.6785	87.54578	110.8	2.6
12	152.9	47.1527	47.3535	47.1909	47.2481	47.2368	47.2295	47.1781	47.0616	46.6498	47.1512	48.7121	47.1315	47.5816	46.8966	47.2908	47.3221	47.48895	152.8	0.1
13	99.8	100.4838	99.9143	100.4293	99.9621	100.464	100.438	100.1416	99.4652	99.9298	99.9988	97.8844	99.6516	100.9143	99.8767	99.5085	99.3287	99.44526	98.3	1.5
14	67.1	128.3856	127.5542	128.2216	125.9184	127.2715	127.1194	125.1117	129.9627	127.6312	129.773	129.2527	128.7447	128.3219	126.8309	129.9143	128.7482	128.1144	68.3	-1.2
15	43.6	151.1639	151.7383	151.2977	153.3103	151.6581	151.747	153.1904	151.984	154.919	151.6002	153.3641	153.502	152.7246	152.7249	151.1248	151.1608	152.66	42.5	1.1
16	212.5	-8.1175	-8.3641	-8.0067	-12.0473	-7.8334	-7.7647	-12.8728	-9.4152	-11.7999	-9.6719	-12.8308	-12.0792	-10.2501	-11.0524	-9.6396	-10.3953	-11.2447	214.4	-1.9
17	44.1	152.0618	152.072	152.0178	146.6397	154.6682	154.695	148.4279	149.7662	149.0842	150.5661	152.9728	152.7884	150.8376	148.4702	151.1013	149.71	151.1728	44.1	0
18	24.6	169.764	170.4684	169.6204	168.753	170.9662	170.9477	168.7677	168.9337	167.207	169.723	167.4022	168.2867	170.39	173.841	175.8377	176.2198	170.1943	24.1	0.6
19	32.7	162.5495	163.5064	162.5979	162.4659	165.2158	165.2457	161.7975	162.177	163.3183	162.6483	165.9218	165.6283	165.3981	161.0469	162.7448	162.0306	163.8336	30.8	1.9
20	23.7	169.329	171.3639	169.2514	169.3683	171.4043	171.3781	169.6848	169.4976	170.23	169.3865	174.026	173.897	171.636	172.4786	173.9695	174.9775	172.5807	21.6	2.1
21	14.4	178.7505	178.6348	178.8018	178.625	178.6277	178.6308	178.3862	178.6252	178.4482	178.6649	178.5056	178.3785	177.8857	177.9244	181.4952	179.6468	178.7196	15.2	-0.8
OCH_3-13	56.2	139.7379	139.7982	139.6854	139.5896	139.1504	139.1997	139.3135	140.0451	139.5849	139.8227	141.154	139.9798	139.3754	139.6931	140.1802	140.1355	140.042	55.8	0.4

Table S6 Experimental and calculated ^{13}C NMR of **1b**

No.	$\delta_{exptl.}$	$\delta_{calcd\text{-}1b\text{-}1}$	$\delta_{calcd\text{-}1b\text{-}2}$	$\delta_{calcd\text{-}1b\text{-}3}$	$\delta_{calcd\text{-}1b\text{-}13}$	$\delta_{calcd\text{-}1b\text{-}15}$	$\delta_{calcd\text{-}1b\text{-}18}$	$\delta_{calcd\text{-}1a\text{-}20}$	$\delta_{calcd\text{-}1b\text{-}28}$	$\delta_{calcd\text{-}1b\text{-}45}$	$\delta_{calcd\text{-}1b\text{-}47}$	$\delta_{calcd\text{-}weighted}$	δ_{calcd}	$\Delta\delta_{exptl\text{-}calcd}$
2	95.1	96.5596	97.2456	97.3698	97.2528	97.5001	96.7698	96.9898	97.3424	96.7478	96.9434	97.26971	100.6	-5.5
4	56.6	134.0472	134.428	134.1978	134.1905	134.17	131.4149	133.9853	134.2091	134.1056	133.9093	134.1318	62.0	-5.4
5	42.3	163.1208	163.1566	162.8913	162.9075	163.0393	163.3667	163.0067	163.1666	163.0351	162.9908	163.0886	31.6	10.7

6	88.1	104.4844	104.6163	104.4335	104.4043	104.5832	104.864	104.5446	104.7088	104.553	104.5996	104.5938	92.9	-4.8
7	135.6	59.6605	59.9326	59.9654	60.0061	60.1094	59.084	59.8479	59.9674	60.0019	59.8084	59.95003	139.7	-4.1
8	125.5	74.5909	74.5486	74.6776	74.7187	74.7369	75.2436	74.7318	74.6051	74.6419	74.7261	74.67434	124.3	1.2
9	123.5	75.8426	76.1767	76.3564	76.2424	76.2873	75.5795	76.1293	76.0393	76.0082	76.1021	76.17867	122.7	0.8
10	131.5	69.5397	69.5131	69.5036	69.4965	69.3551	69.5604	69.4846	69.4871	69.4631	69.4839	69.45472	129.8	1.7
11	113.4	78.6046	79.3181	79.3797	79.1309	79.4156	77.8375	79.0115	79.0892	79.0145	78.9571	79.22735	119.5	-6.1
12	152.9	43.604	43.8985	43.9019	43.8279	43.9449	42.5465	43.813	43.9431	43.6631	43.812	43.8366	156.6	-3.7
13	99.8	99.7426	100.4986	99.5273	99.2305	99.9458	100.0271	100.1169	100.8443	99.9089	100.1599	100.1452	97.6	2.2
14	67.1	120.9839	123.3105	123.4237	123.2959	123.5907	123.332	122.788	123.3228	121.9435	122.776	123.2733	73.3	-6.2
15	43.6	148.1745	148.6294	150.6511	150.5795	146.7494	145.3157	147.2509	147.1286	148.1997	147.2788	147.8021	47.6	-4.0
16	212.5	-10.1986	-10.8879	-11.4322	-11.4513	-9.4135	-10.7309	-9.8494	-11.0808	-9.9334	-9.8182	-10.2763	213.4	-0.9
17	44.1	151.4523	151.2356	150.6164	150.3814	152.7078	151.7406	152.0104	154.1594	149.9725	152.0601	151.8354	43.4	0.7
18	24.6	170.035	166.4613	166.2938	166.1028	175.1834	170.8958	173.2529	174.6989	171.6677	173.2617	170.686	23.6	1.0
19	32.7	163.9333	163.5638	163.8814	164.2485	162.254	161.3645	161.1682	162.522	164.2385	161.1516	162.853	31.8	0.9
20	23.7	171.3084	169.4266	169.2849	169.2314	174.9903	168.3369	170.7013	174.9825	171.1202	170.6584	171.6697	22.6	1.1
21	14.4	178.6388	178.9477	178.5898	178.5112	181.1391	178.3097	178.4924	180.4298	180.4931	178.5197	179.6972	14.2	0.2
OCH_3-13	56.2	141.0284	141.1564	141.2915	141.2721	140.6017	140.7886	141.2363	140.3453	141.1986	141.2044	140.9367	54.8	1.4

Table S7 Experimental and calculated ^{13}C NMR of **1c**

No.	$\delta_{exptl.}$	$\delta_{calcd\text{-}1c\text{-}1}$	$\delta_{calcd\text{-}1c\text{-}2}$	$\delta_{calcd\text{-}1c\text{-}3}$	$\delta_{calcd\text{-}1c\text{-}4}$	$\delta_{calcd\text{-}1b\text{-}15}$	$\delta_{calcd\text{-}1c\text{-}5}$	$\delta_{calcd\text{-}1c\text{-}6}$	$\delta_{calcd\text{-}1c\text{-}7}$	$\delta_{calcd\text{-}1c\text{-}9}$	$\delta_{calcd\text{-}1c\text{-}10}$	$\delta_{calcd\text{-}1c\text{-}12}$	$\delta_{calcd\text{-}1c\text{-}16}$	$\delta_{calcd\text{-}1c\text{-}18}$	$\delta_{calcd\text{-}1c\text{-}19}$	$\delta_{calcd\text{-}1c\text{-}20}$	$\delta_{calcd\text{-}weighted}$	δ_{calcd}	$\Delta\delta_{exptl\text{-}calcd}$
2	95.1	94.8994	94.9239	94.8493	94.726	95.083	94.7618	94.7722	94.9291	94.9358	95.2504	95.1817	95.3179	95.2211	95.2008	95.2826	95.14946	102.8	-7.7
4	56.6	139.5006	139.4436	139.5496	139.4447	139.4737	139.3784	139.5406	139.4443	139.4576	139.4647	139.5502	139.5513	139.7705	139.5788	139.7907	139.5826	56.2	0.4
5	42.3	160.8454	160.8506	160.8083	160.6788	160.7022	160.7406	161.0112	161.0315	160.9049	160.8942	160.8924	160.6976	160.9475	160.9474	160.9838	160.8735	33.9	8.4
6	88.1	110.2248	110.0808	110.132	110.1439	110.2911	110.1958	110.0852	110.1089	110.1436	110.2076	110.3988	109.6731	110.3444	110.388	110.4219	110.1875	87.1	1.0
7	135.6	56.6148	56.678	56.6507	56.6366	56.6171	56.6637	56.6335	56.709	56.7056	56.7692	56.6729	56.8859	56.5815	56.6334	56.5698	56.68445	143.2	-7.6
8	125.5	74.3677	74.3881	74.3134	74.466	74.2274	74.2879	74.247	74.2126	74.3639	74.215	74.2791	74.215	74.4838	74.4217	74.4162	74.3312	124.7	0.8
9	123.5	75.3772	75.354	75.4388	75.3767	75.3874	75.3282	75.3879	75.3236	75.4372	75.4346	75.3946	75.3518	75.3666	75.3964	75.3358	75.38054	123.6	-0.1
10	131.5	70.8121	70.7047	70.7704	70.6717	70.8353	70.6862	70.7253	70.6922	70.674	70.7644	70.8491	70.6857	70.8506	70.8072	70.8595	70.77884	128.4	3.1
11	113.4	76.521	76.6102	76.5128	76.5074	76.3705	76.5617	76.6428	76.7925	76.5907	76.5055	76.3742	76.5509	76.1129	76.3247	76.0767	76.39377	122.5	-9.1
12	152.9	47.672	47.6658	47.7183	47.7422	47.6408	47.7756	47.7788	47.5675	47.6484	47.3734	47.4475	47.2966	47.3173	47.3568	47.3552	47.4429	152.9	0.0
13	99.8	101.2855	101.2404	101.2957	101.0987	101.5495	100.8425	101.2448	101.222	101.288	101.0447	101.4	100.51	101.0457	101.5005	101.0342	101.0913	96.6	3.2
14	67.1	128.855	128.7711	128.803	128.5992	129.6401	128.0926	128.8447	128.996	128.9453	129.8666	130.2544	129.7716	130.7946	130.5388	130.7682	129.9008	66.4	0.7
15	43.6	154.7903	154.746	154.1341	154.6462	154.2467	154.7302	154.6776	154.1744	154.2456	149.1481	152.3963	156.1388	153.1734	153.9307	153.0519	153.4251	41.7	1.9

16	212.5	-9.8817	-9.8669	-9.9648	-10.3105	-10.9876	-10.5416	-10.037	-9.7718	-10.0003	-13.5499	-9.9789	-11.2685	-8.7111	-9.0903	-8.7681	-10.2978	213.4	-0.9
17	44.1	150.1718	150.1282	151.3809	151.5539	149.9405	151.2867	150.0429	151.5553	150.9139	153.288	153.0041	150.8224	152.2687	156.5978	152.2071	152.2447	43.0	1.1
18	24.6	168.9487	168.9123	169.906	170.2723	163.5926	170.1934	171.3575	173.6339	172.3461	164.2293	169.2315	169.7085	172.4052	171.7067	172.3226	169.8238	24.5	0.1
19	32.7	162.4268	162.4863	162.6788	163.8205	160.6224	163.8911	164.3444	161.5275	164.6058	163.5144	162.465	165.6442	161.0049	167.2673	160.989	163.2625	31.4	1.3
20	23.7	169.4406	169.4283	169.4161	171.6554	169.6634	171.7286	171.2542	170.7566	171.0348	169.5171	169.7489	171.6716	169.2893	173.3725	169.3197	170.3736	24.0	-0.3
21	14.4	178.7273	178.7649	178.7261	178.7311	178.8994	178.7567	180.8538	178.5461	180.828	179.1933	178.8252	181.3962	178.6762	178.313	178.6787	179.249	14.6	-0.2
OCH_3-13	56.2	135.9939	136.007	136.014	135.9367	135.172	135.9117	135.9002	136.0839	136.0346	135.6292	134.7275	135.591	134.3308	135.0551	134.3124	135.2506	60.8	-4.6

Table S8 Experimental and calculated ^{13}C NMR of **1d**

No.	$\delta_{exptl.}$	$\delta_{calcd\text{-}1d\text{-}1}$	$\delta_{calcd\text{-}1d\text{-}3}$	$\delta_{calcd\text{-}1d\text{-}4}$	$\delta_{calcd\text{-}1d\text{-}5}$	$\delta_{calcd\text{-}1d\text{-}6}$	$\delta_{calcd\text{-}1d\text{-}7}$	$\delta_{calcd\text{-}1d\text{-}10}$	$\delta_{calcd\text{-}1d\text{-}11}$	$\delta_{calcd\text{-}1d\text{-}12}$	$\delta_{calcd\text{-}1d\text{-}16}$	$\delta_{calcd\text{-}1d\text{-}19}$	$\delta_{calcd\text{-}1d\text{-}23}$	$\delta_{calcd\text{-}weighted}$	δ_{calcd}	$\Delta\delta_{exptl\text{-}calcd}$
2	95.1	100.914	101.1236	100.9651	100.6559	100.4888	101.1253	100.8296	100.9175	101.2924	100.8862	101.0346	99.4829	100.8743	96.8	-1.7
4	56.6	148.1289	148.2173	148.2618	147.977	148.0189	148.4031	148.1384	148.2058	148.3442	148.1021	148.3447	149.5884	148.2515	47.1	9.5
5	42.3	152.6669	149.6294	152.5997	152.655	152.6695	152.6481	152.7122	152.74	152.7222	152.6897	152.8578	150.5943	152.5725	42.6	-0.3
6	88.1	108.097	107.702	108.045	108.2286	108.1362	108.018	108.2114	108.2253	107.9775	108.0946	108.1521	108.6686	108.1096	89.2	-1.1
7	135.6	61.8811	63.2634	61.7483	61.8321	62.0265	62.0153	61.7118	62.0141	62.0809	62.0617	61.8575	61.7761	61.96405	137.6	-2.0
8	125.5	75.1542	74.4567	75.0479	74.9863	74.9992	75.0807	75.0254	75.0255	75.0504	75.013	75.0666	76.8245	75.1016	123.9	1.6

9	123.5	79.5443	79.7103	79.4654	79.5424	79.6085	79.5127	79.5002	79.6164	79.6254	79.653	79.4325	79.0076	79.52775	119.2	4.3
10	131.5	70.2306	70.5806	70.1947	70.0745	70.13	70.1644	70.1932	70.1447	70.207	70.2426	70.11	70.8895	70.19305	129.0	2.5
11	113.4	83.455	83.9685	83.6172	83.8498	83.7532	83.5072	83.5414	83.7807	83.511	83.6835	83.516	82.6252	83.56203	115.0	-1.6
12	152.9	50.3548	50.6418	50.4089	50.6527	50.6405	50.4729	50.408	50.632	50.5442	50.6222	50.4033	50.9339	50.52169	149.6	3.3
13	99.8	103.8421	103.3128	103.9607	104.0037	104.1339	103.8205	104.0207	103.9828	103.698	104.0314	103.5248	103.5231	103.855	93.7	6.1
14	67.1	132.0671	131.712	131.7338	131.7926	131.4699	132.008	132.0516	131.6668	132.1433	131.9393	131.8779	130.006	131.8105	64.4	2.7
15	43.6	153.3977	155.3819	153.5515	152.7244	153.5138	153.0891	153.6226	152.4872	153.5163	153.5792	152.3889	152.8257	153.1421	42.0	1.6
16	212.5	-10.266	-11.9001	-12.5046	-11.5347	-10.1837	-10.0994	-10.0455	-10.0437	-10.51	-9.9254	-10.4542	-9.2212	-10.2553	213.4	-0.9
17	44.1	151.5502	150.5238	150.0038	150.4287	150.3746	152.8448	151.3455	152.2577	151.3184	151.3597	152.9318	158.2518	152.0221	43.2	0.9
18	24.6	168.8304	166.291	164.0375	163.3405	168.8844	169.7837	171.4664	172.6419	171.3479	168.7653	172.4834	169.48	169.7211	24.6	0.0
19	32.7	162.2997	163.6831	160.5768	160.6451	162.3942	162.664	164.3628	161.5732	164.3867	162.491	164.6691	165.5603	162.8118	31.9	0.8
20	23.7	169.6189	169.3985	169.524	169.5847	169.5347	169.3935	171.1669	170.2762	171.1612	169.3116	171.2474	172.1389	169.9758	24.4	-0.7
21	14.4	178.7553	179.0143	178.8452	178.8678	178.8373	178.7547	180.7528	178.5401	180.8546	178.7932	180.9289	178.2295	179.1548	14.7	-0.3
OCH3-13	56.2	135.3489	133.3458	135.4552	133.6718	135.3239	135.3889	135.3564	135.2612	135.3787	135.3336	134.9568	137.7642	135.2769	60.8	-4.6

Table S9. Related parameters of ^{13}C NMR calculations and $DP4^+$ analysis for four potential isomers of **1**

Configuration	DP4+(%)	R^2	RMSE
1a	100	0.9994	1.50
1b	0.00	0.9944	4.10
1c	0.00	0.9945	4.00
1d	0.00	0.9964	3.23

1.3 ECD calculation

The theoretical calculations were carried out using Gaussian 09.[2] Firstly, conformers were optimized using density functional theory method and at B3LYP/6-31G (d) and filtered by Boltzmann-based population. The remaining conformers were finally calculated to obtain the ECD spectrum. The ECD calculation was conducted using Time-dependent Density functional theory (TD-DFT) at CAM-B3LYP/6-31G (d) level. Rotatory strengths for a total of 70 excited states were calculated. The ECD spectrum was simulated in SpecDis1.70 by overlapping Gaussian functions for each transition according to the following equation.[5]

$$\Delta\varepsilon(E) = \frac{1}{2.297\times10^{-39}} \times \frac{1}{\sqrt{2\pi\sigma}} \sum_{i}^{A} \Delta E_i R_i e^{-\left(\frac{E-E_i}{2\sigma}\right)^2}$$

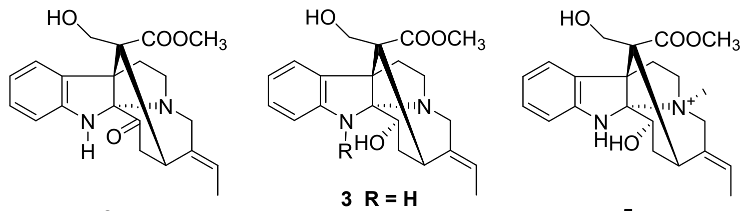
where σ represents the width of the band at 1/*e* height, and ΔE_i and R_i are the excitation energies and rotatory strengths for transition *i*, respectively.

Table S10 Anti-inflammatory activity of compounds **1-5** on NO production in LPS-induced RAW264.7 mouse macrophages and the cell survival rates.

Compounds	**Inhibition (%)**	**Survival rates (%) of RAW 264.7 at 200 μM**	
		LPS (0 μg/mL)	**LPS (1 μg/mL)**
1	41.29 ± 2.80	97.36 ± 4.13	97.68 ± 3.97
2	17.73 ± 2.80	94.85 ± 3.87	95.12 ± 4.75
3	10.91 ± 2.26	93.77 ± 3.94	95.12 ± 4.58
4	5.16 ± 1.66	98.12 ± 4.81	96.73 ± 3.79
5	13.96 ± 1.71	97.86 ± 3.45	96.24 ± 4.35
L-NMMA[b]	IC_{50} = 33.74±2.13	92.43 ± 3.53	94.48 ± 2.47

[b] NG-Monomethyl-*L*-arginine (*L*-NMMA) was used as a positive control.

5 Bruhn, T.; Schaumloeffel, A.; Hemberger, Y.; Bringmann, G. *Chirality* **2013**, *25*, 243−249.



2 | 3 R = H | 4 R = CHO | 5

Figure S1 The isolated known PiNPs from *Alstonia scholaris*

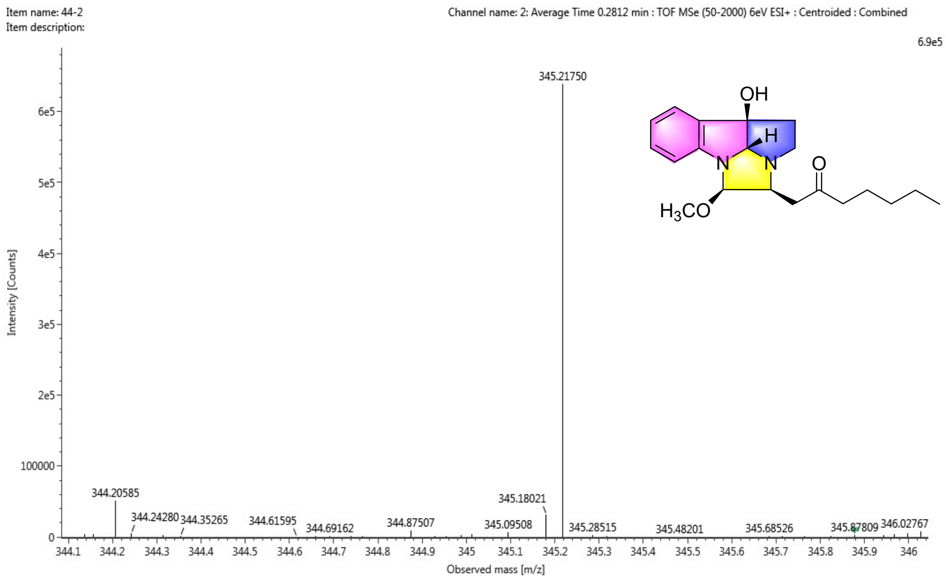


Figure S2. (+)-HR-ESI-MS spectrum of **1**

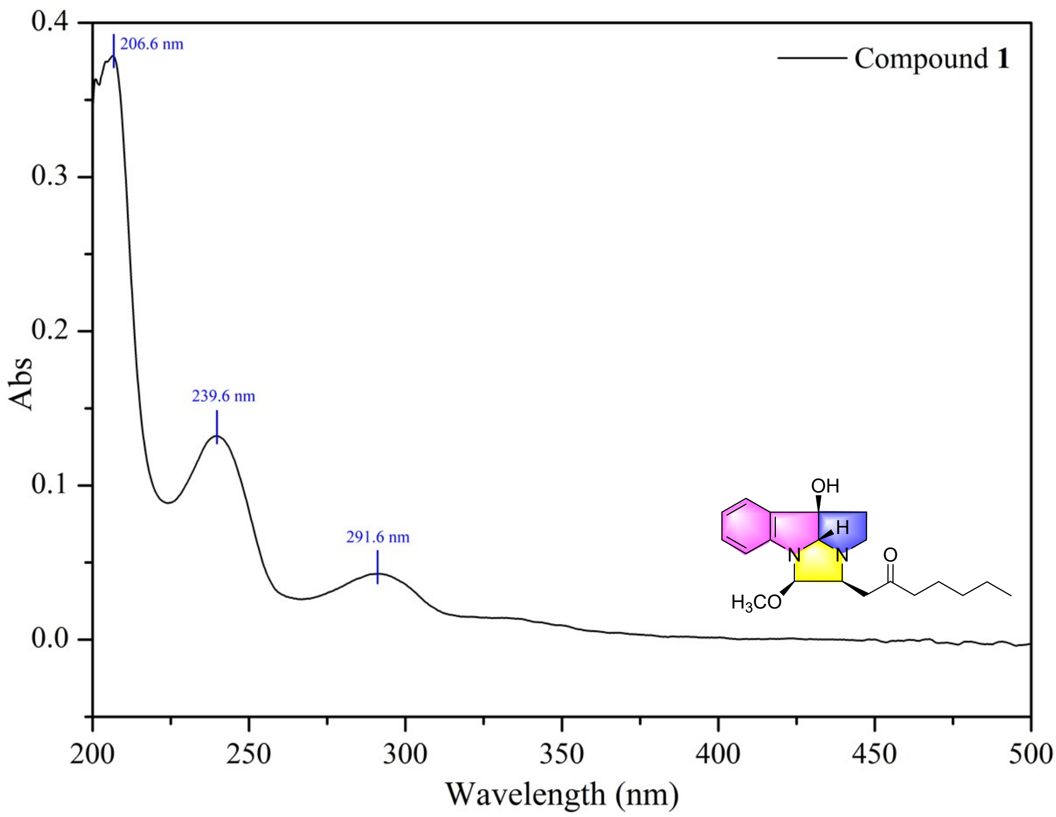


Figure S3. UV spectrum of **1** in MeOH

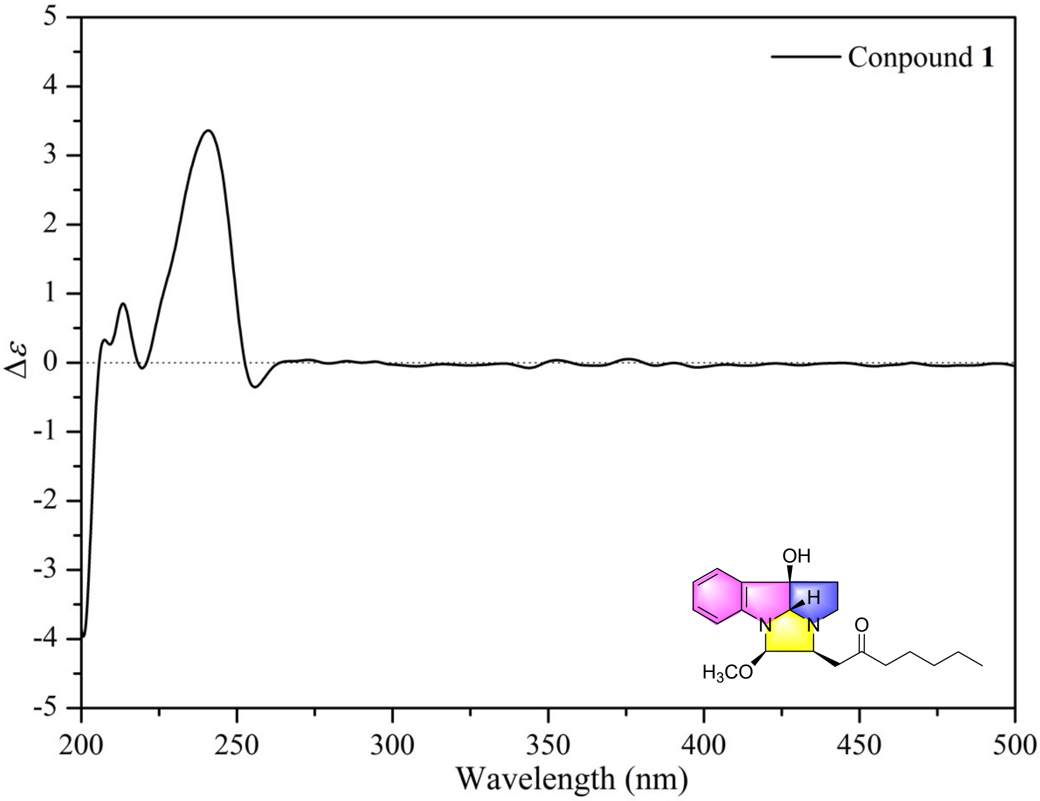


Figure S4. ECD spectrum of **1** in MeOH

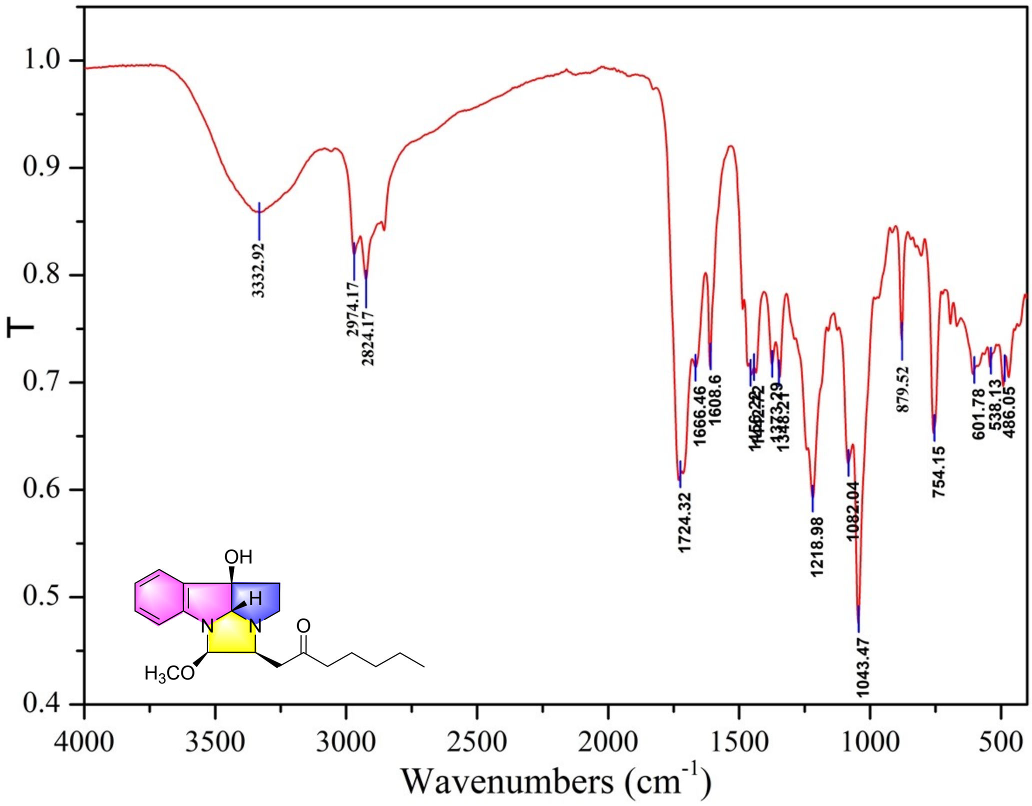


Figure S5. IR spectrum of **1**

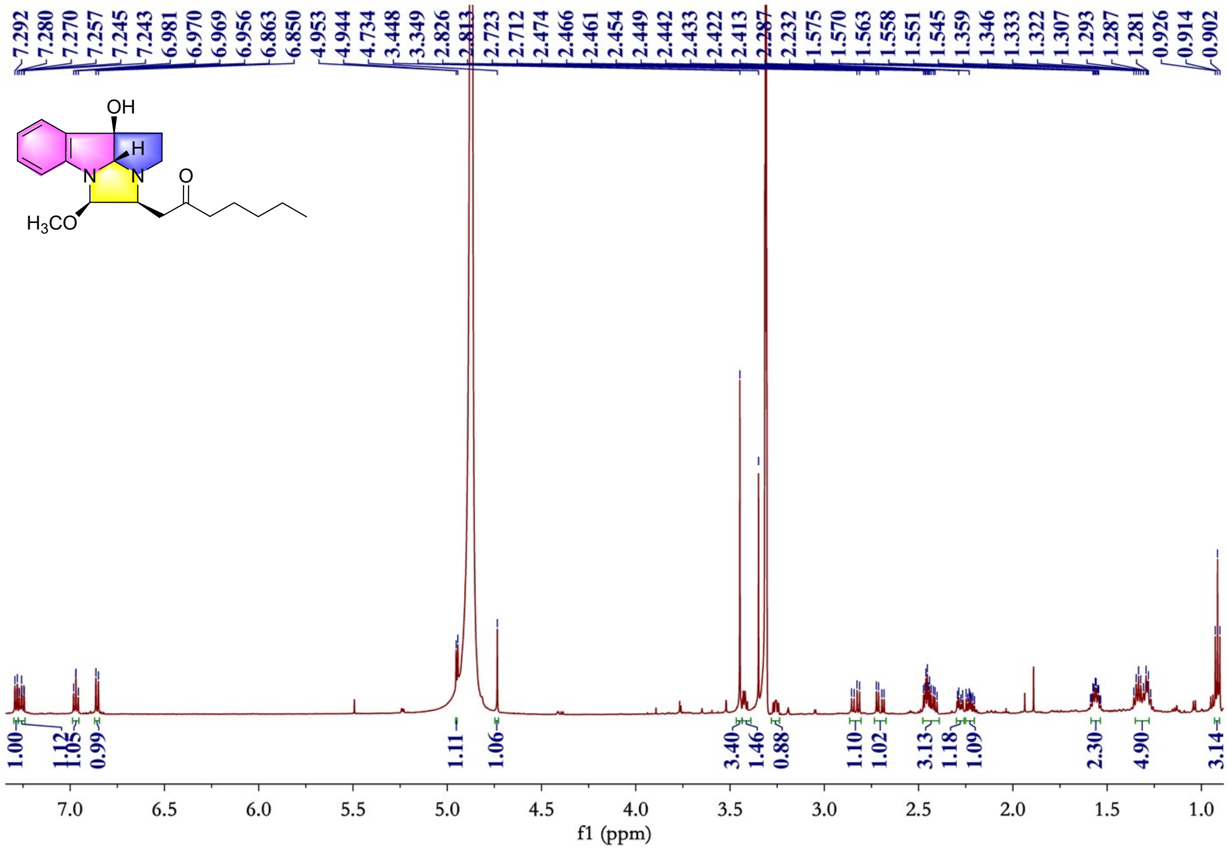


Figure S6. ^{1}H NMR (600 MHz) spectrum of **1** in CD_3OD

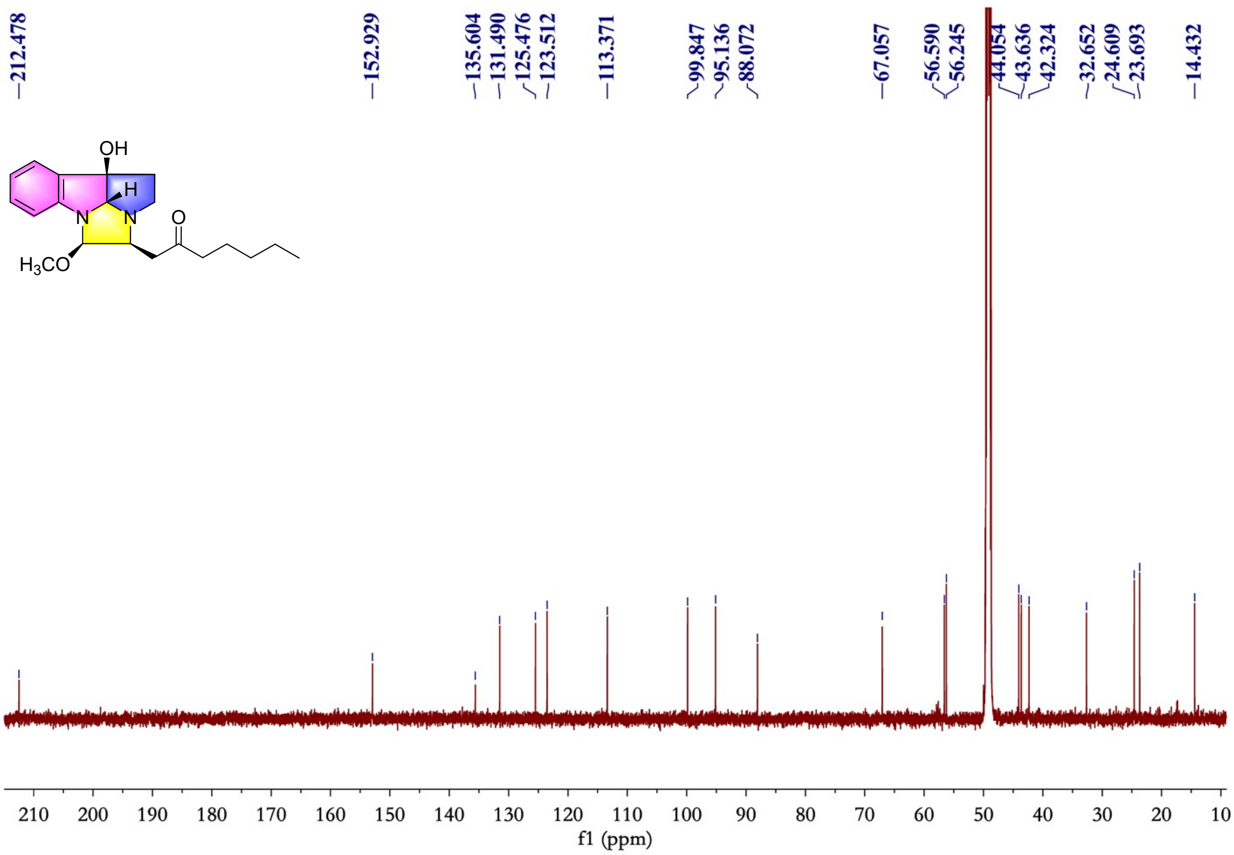


Figure S7. ^{13}C NMR (150 MHz) spectrumof **1** in CD_3OD

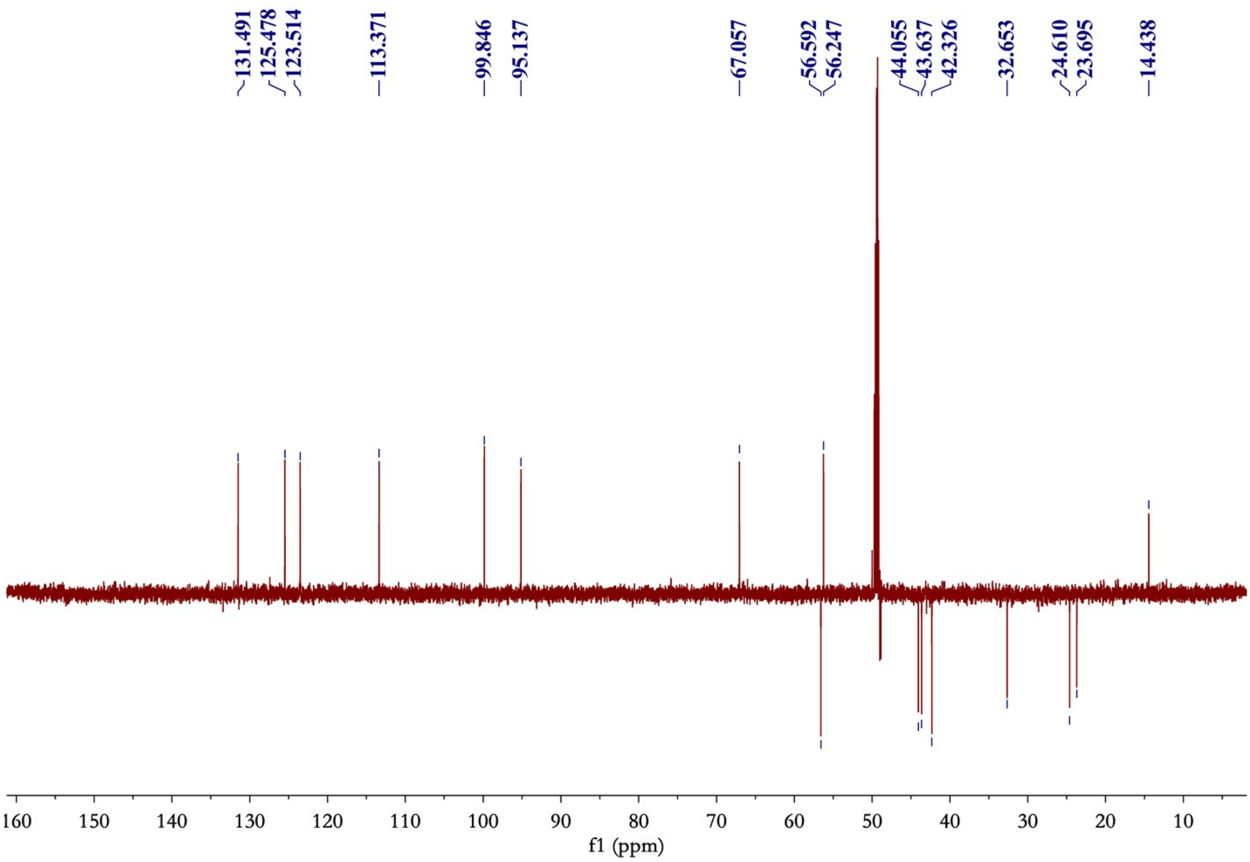


Figure S8. DEPT 135 spectrum of **1** in CD_3OD

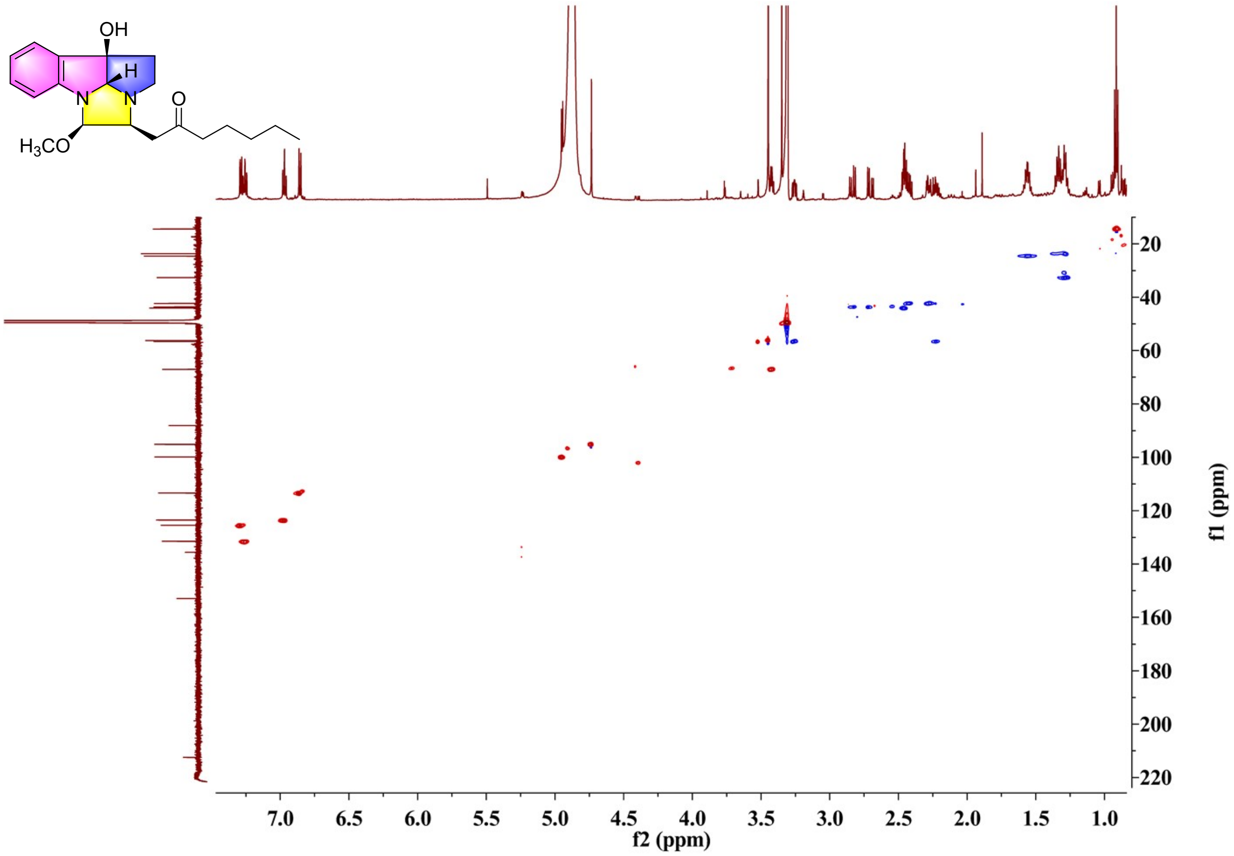


Figure S9. HSQC spectrum of **1** in CD_3OD

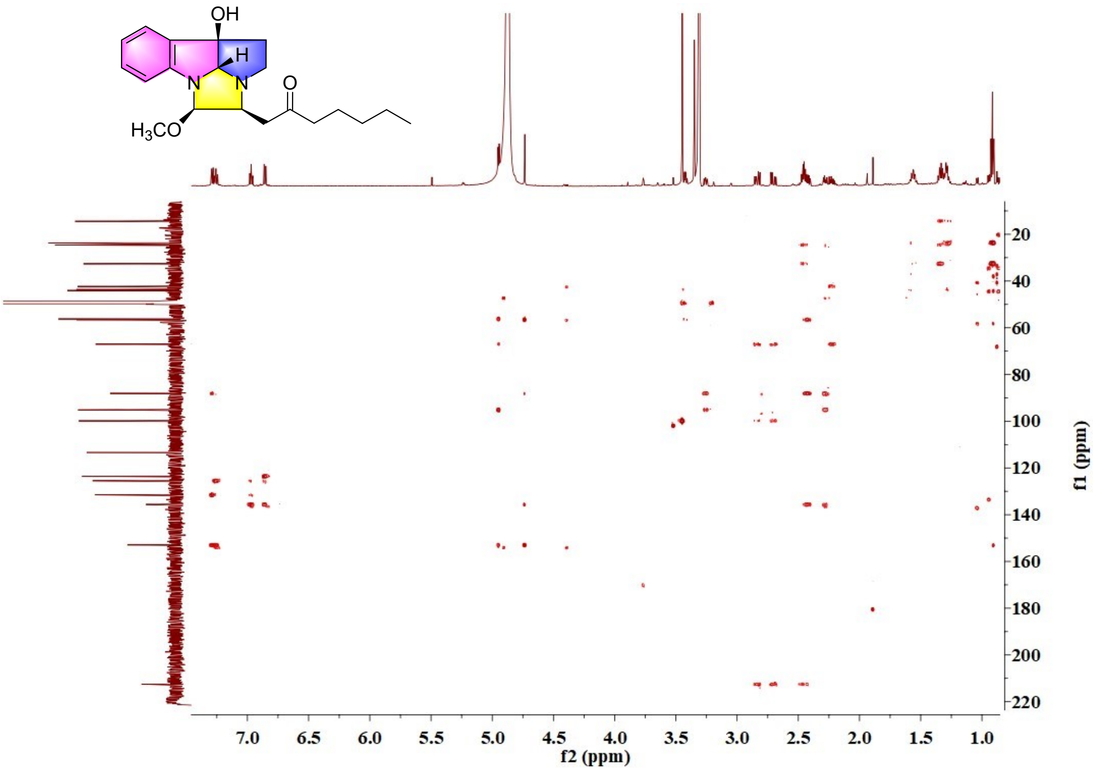


Figure S10. HMBC spectrum of **1** in CD_3OD

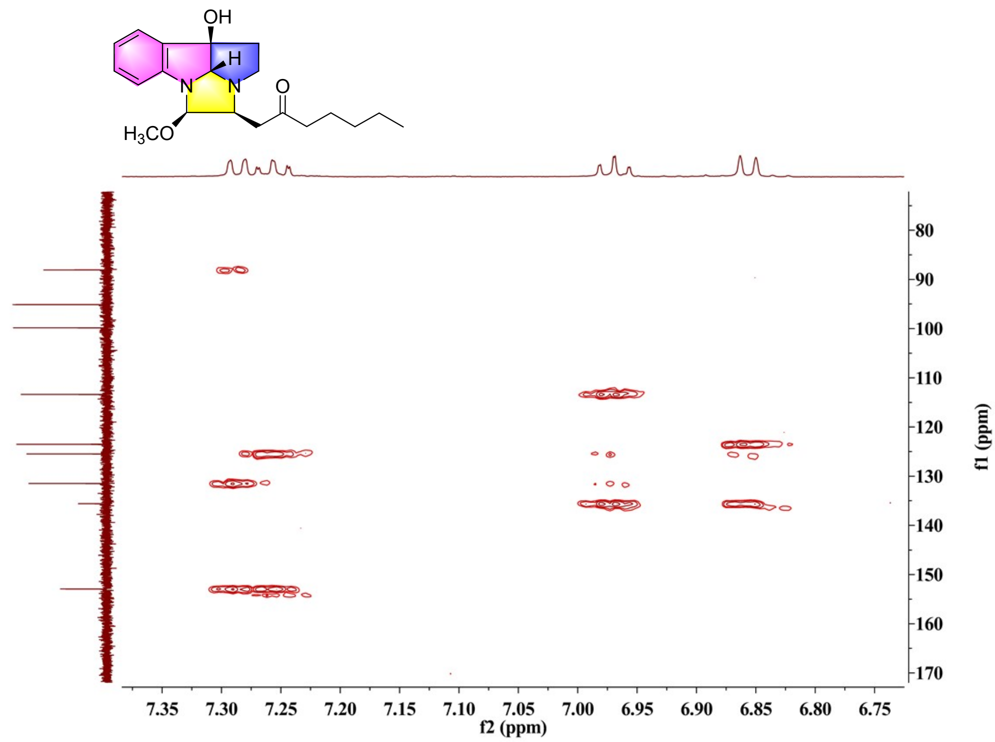


Figure S11. Locally amplified HMBC spectrum (from 6.75 to 7.35) of **1** in CD_3OD

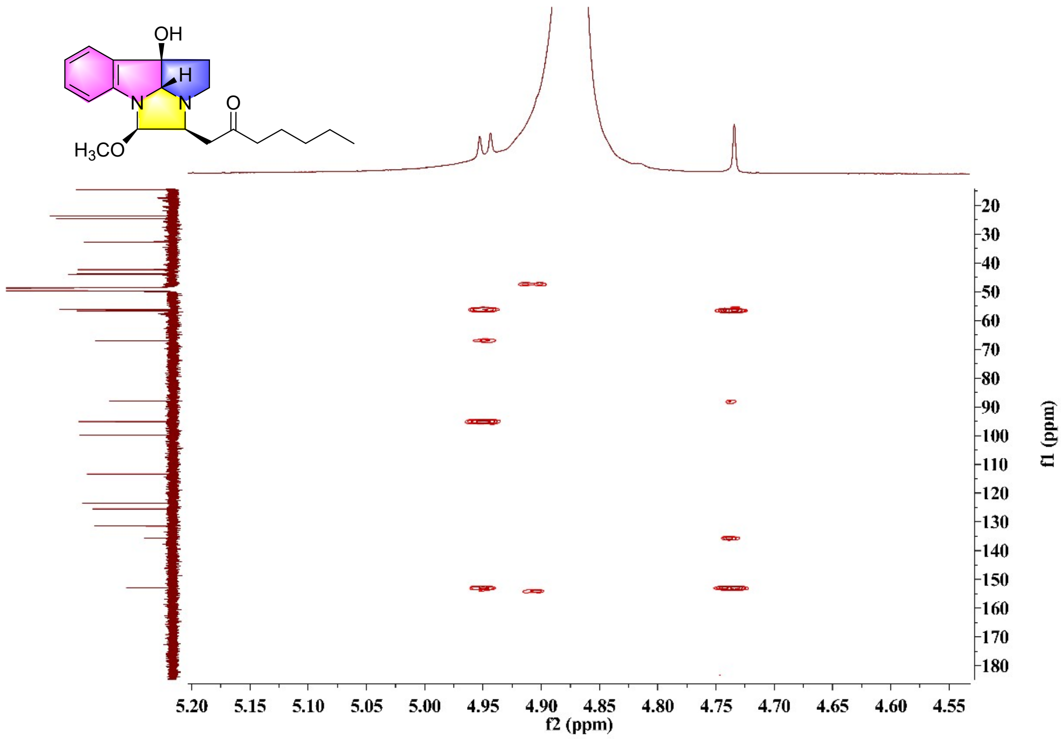


Figure S12. Locally amplified HMBC spectrum (from 4.55 to 5.20) of **1** in CD_3OD

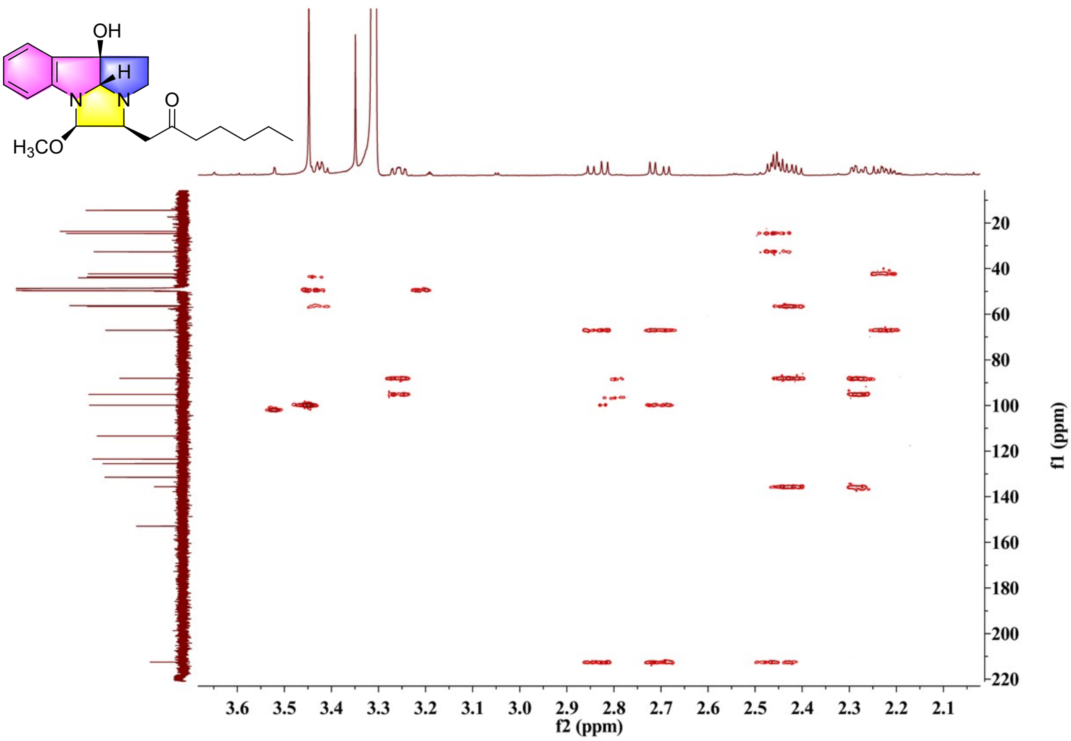


Figure S13. Locally amplified HMBC spectrum (from 2.10 to 3.60) of **1** in CD_3OD

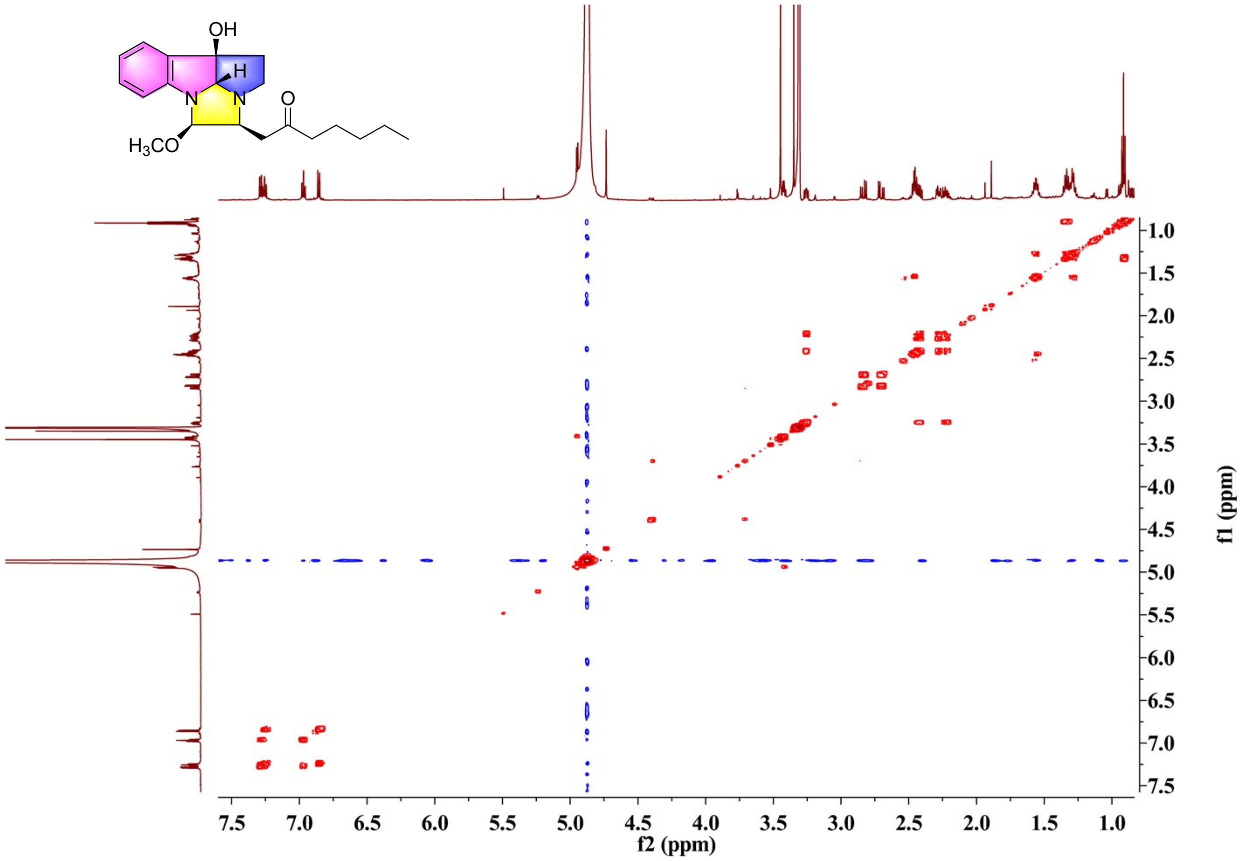


Figure S14. $^1H-^1H$ COSY spectrum of **1** in CD_3OD

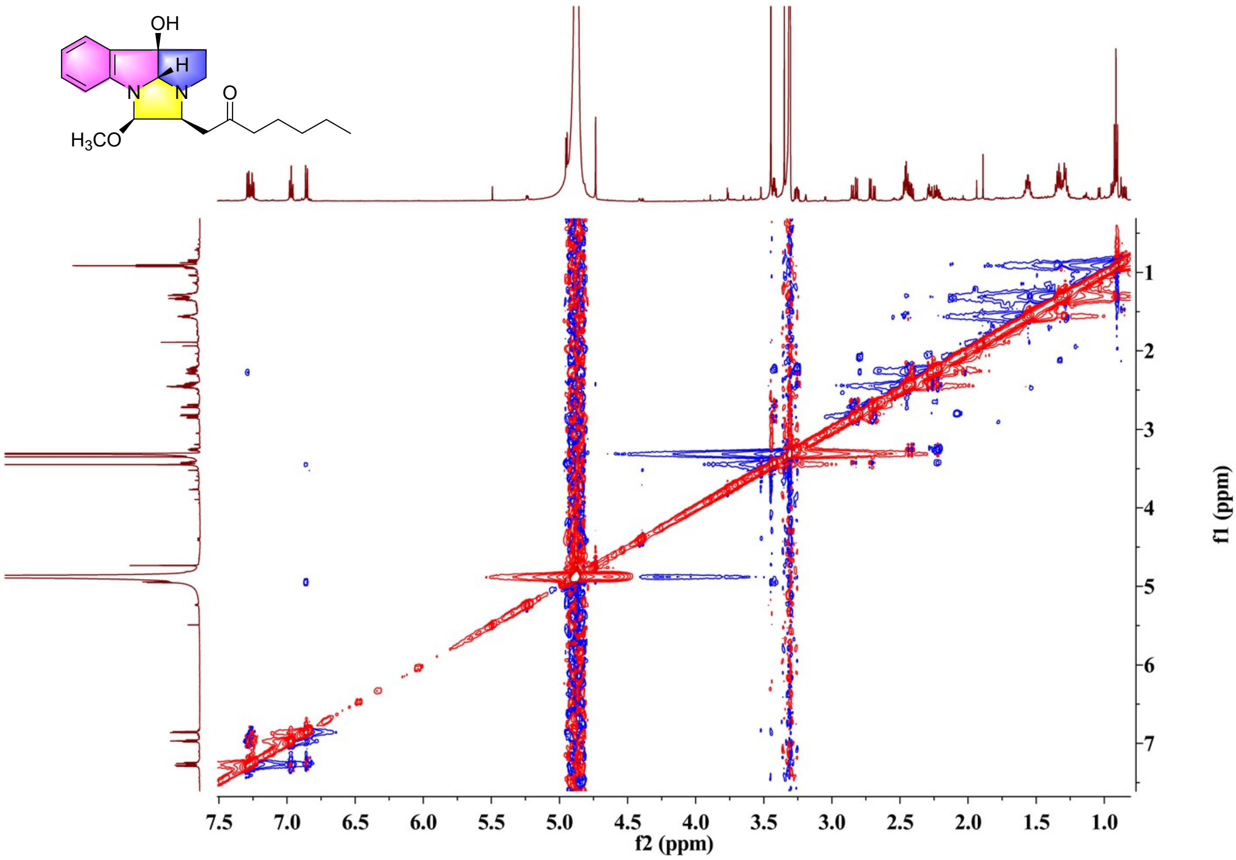


Figure S15. NOESY spectrum of **1** in CD_3OD

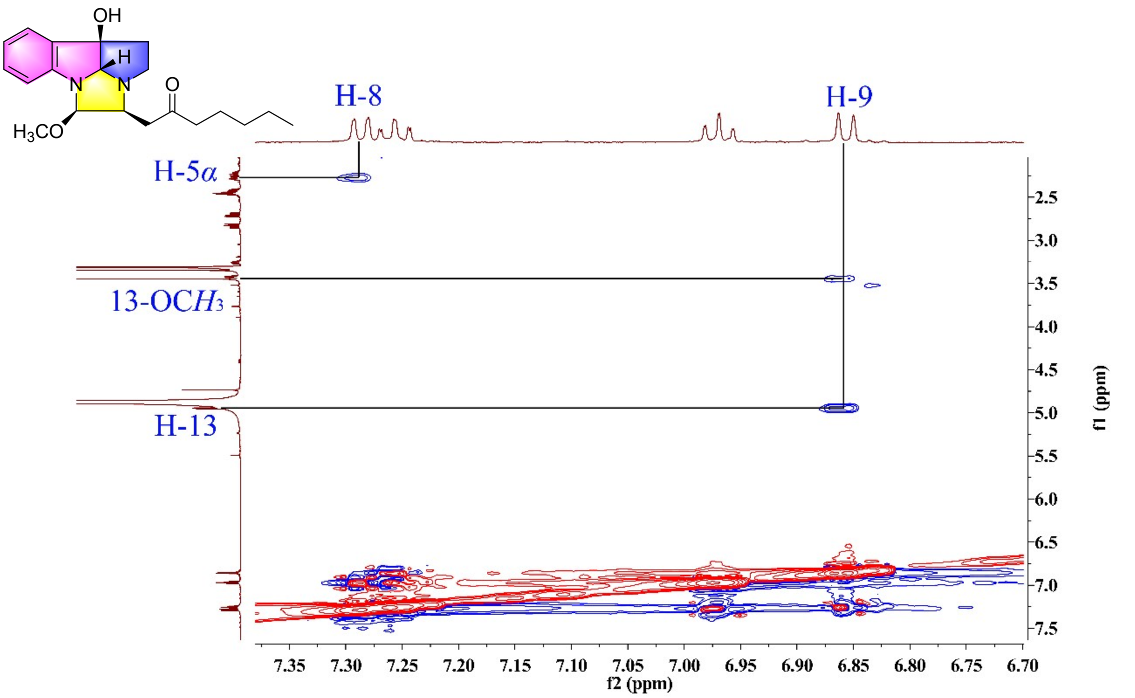


Figure S16. Locally amplified NOESY spectrum (from 6.70 to 7.35) of **1** in CD_3OD

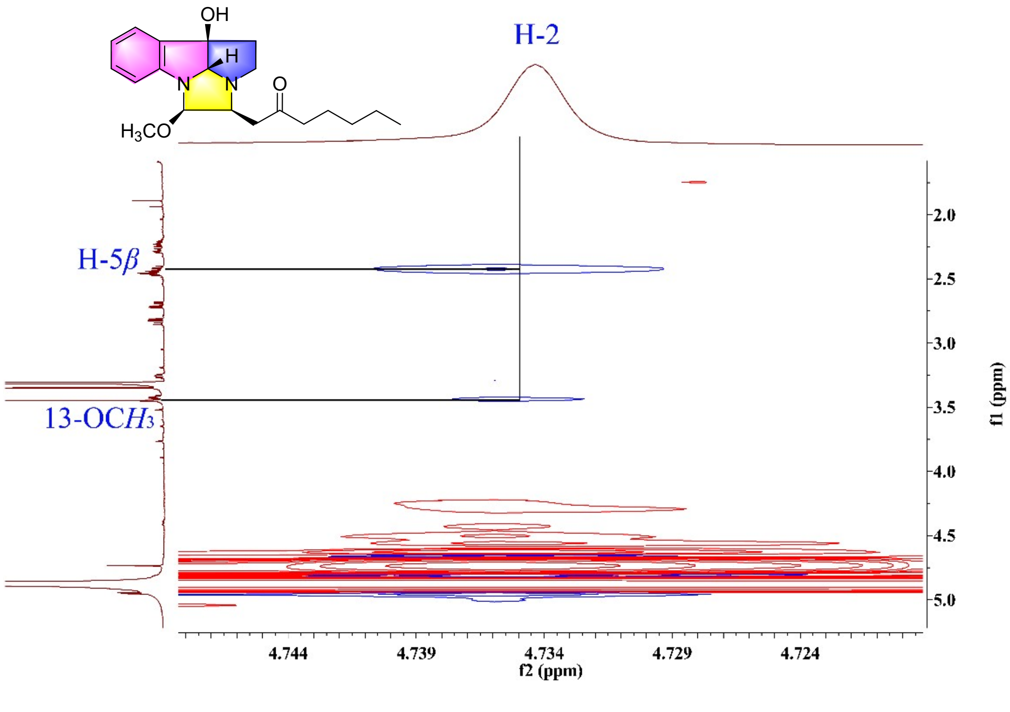


Figure S17. Locally amplified NOESY spectrum (from 4.72 to 4.74) of **1** in CD_3OD

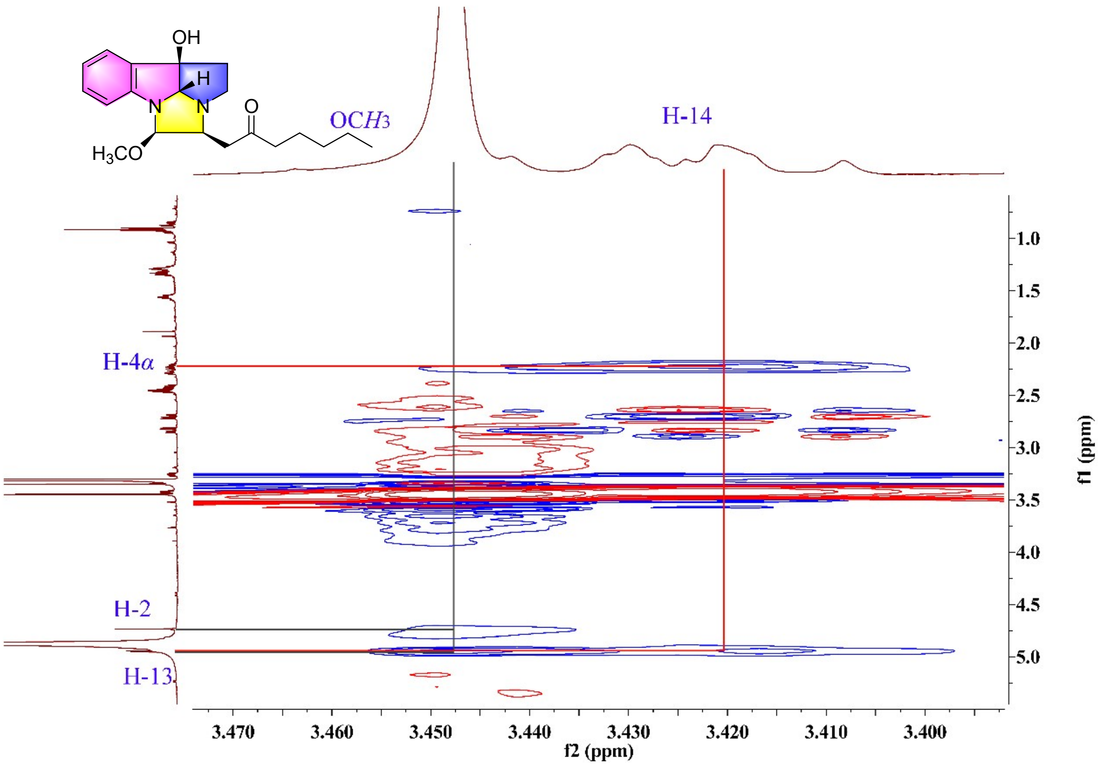


Figure S18. Locally amplified NOESY spectrum (from 3.40 to 3.47) of **1** in CD_3OD

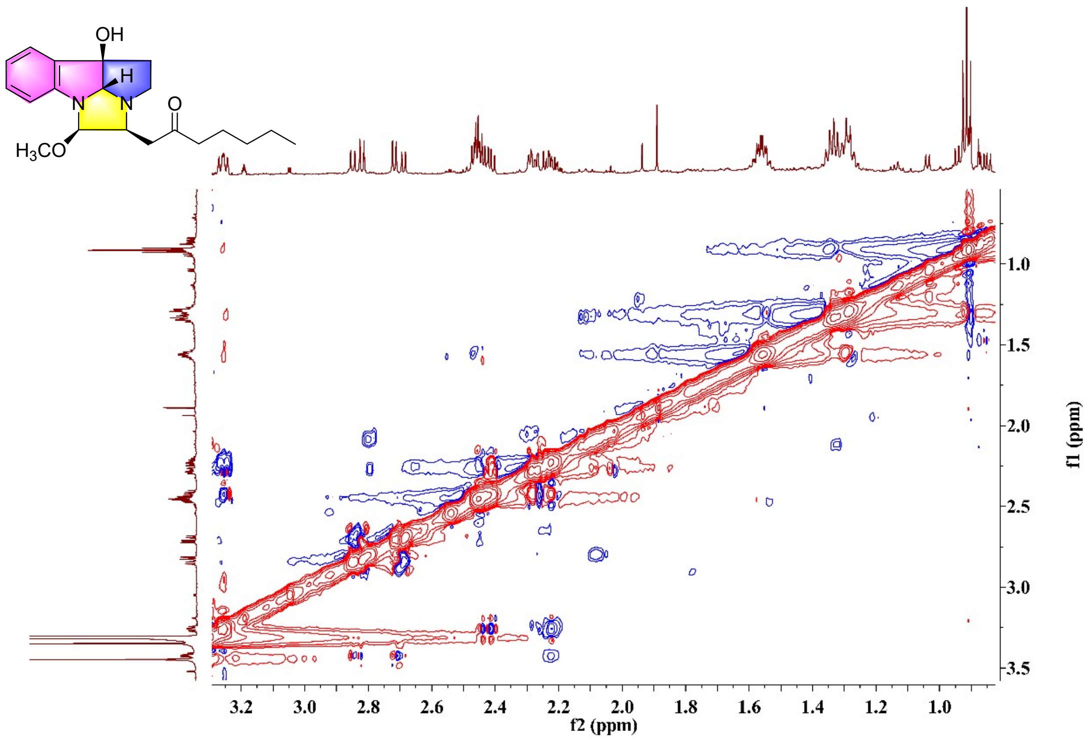


Figure S19. Locally amplified NOESY spectrum (from 0.90 to 3.22) of **1** in CD_3OD