Supporting Information

Analgesic monoterpene indole alkaloids from *Gelsemium elegans* stems

JIN Pengfei[1], ZHENG Guijuan[1], HUANG Lang[1], YUAN Xinghua[1], MA Xiaomin[1], ZHAN Guanqun[1], ABUDUREXITI Adila[2*], YAO Guangmin[1,2*]

[1]*Hubei Key Laboratory of Natural Medicinal Chemistry and Resource Evaluation, School of Pharmacy, Tongji Medical College, Huazhong University of Science and Technology, Wuhan 430030, China;*

[2]*Laboratory of Xinjiang Native Medicinal and Edible Plant Resource Chemistry, College of Chemistry and Environmental Science, Kashi University, Kashgar 844007, China*

[*Corresponding authors] E-mail: gyap@mail.hust.edu.cn (YAO Guangmin); aji_228@163.com (ABUDUREXITI Adila).

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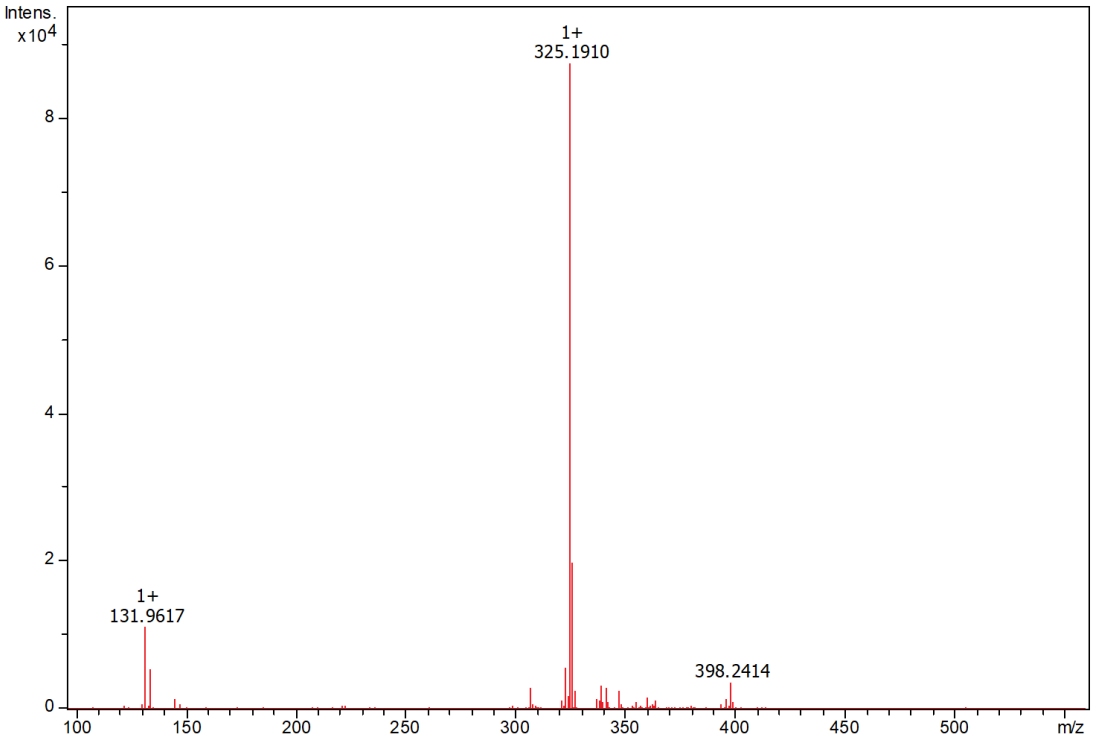

Figure S1. (+)-HR-ESI-MS spectrum of **1**.

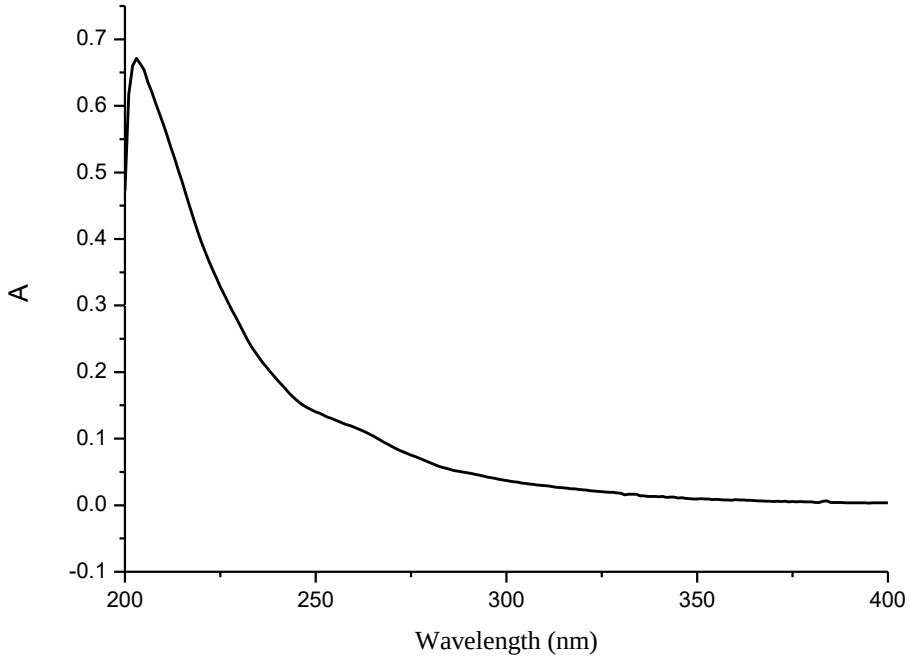

Figure S2. UV spectrum of **1** in MeOH.

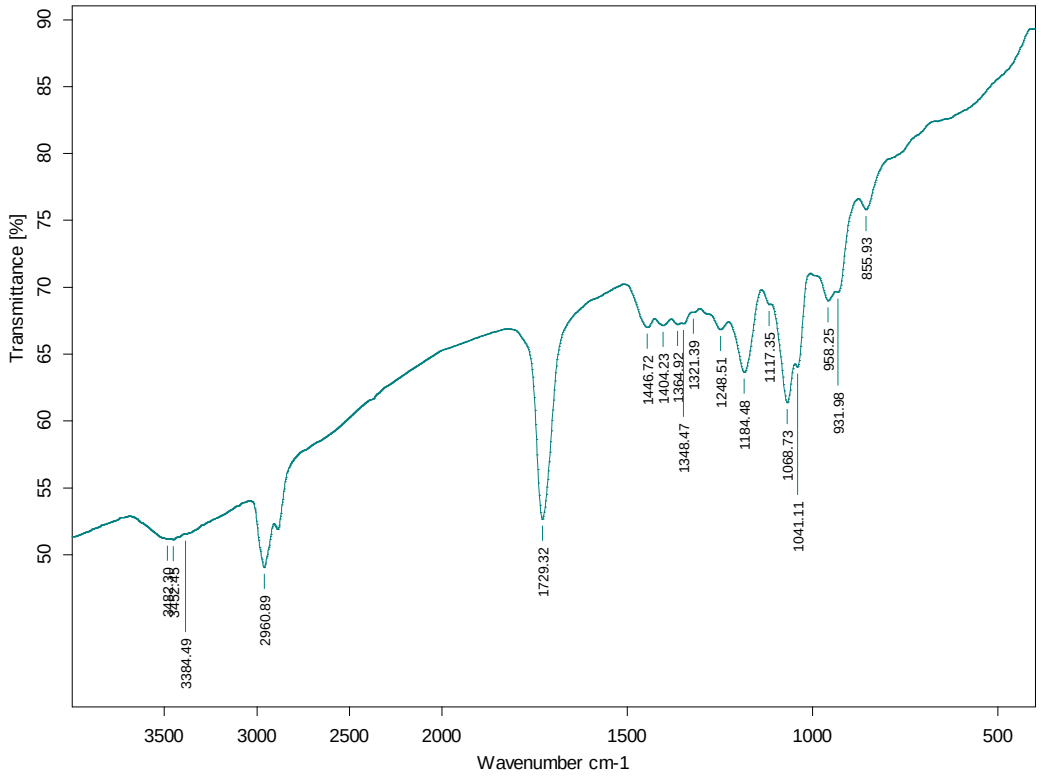

Figure S3. IR spectrum of **1** (IR).

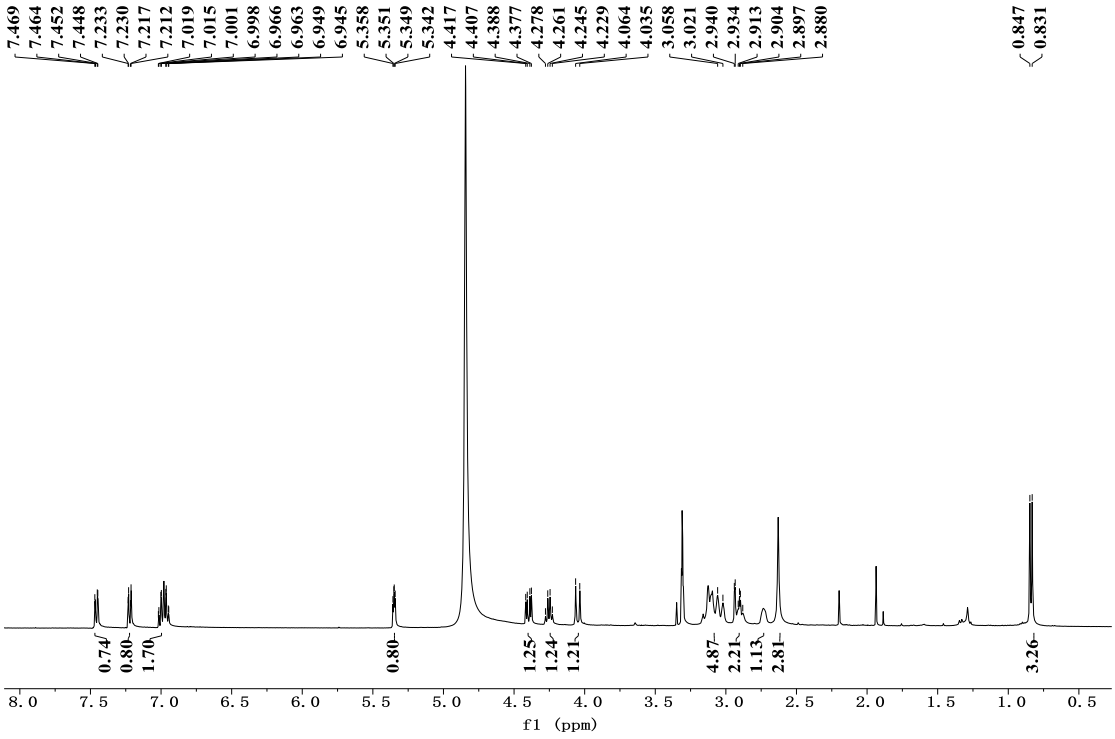

Figure S4. ^{1}H NMR (400 MHz, methanol-d_4) spectrum of **1**.

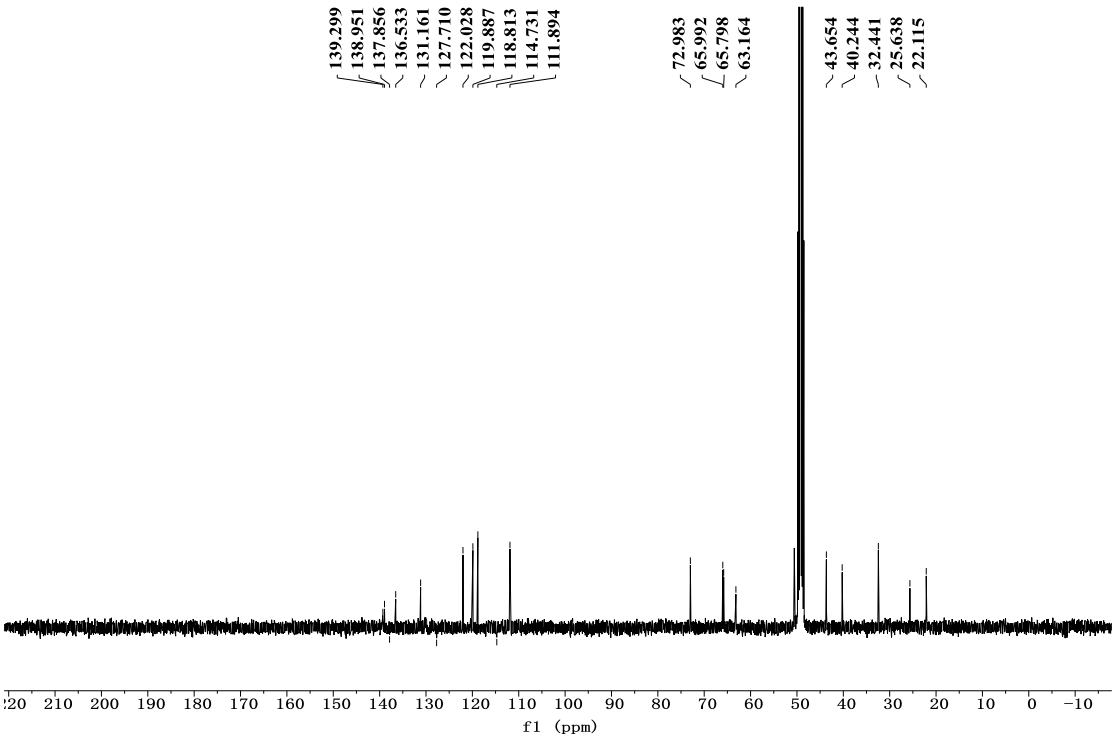

Figure S5. ^{13}C NMR (100 MHz, methanol-d_4) spectrum of **1**.

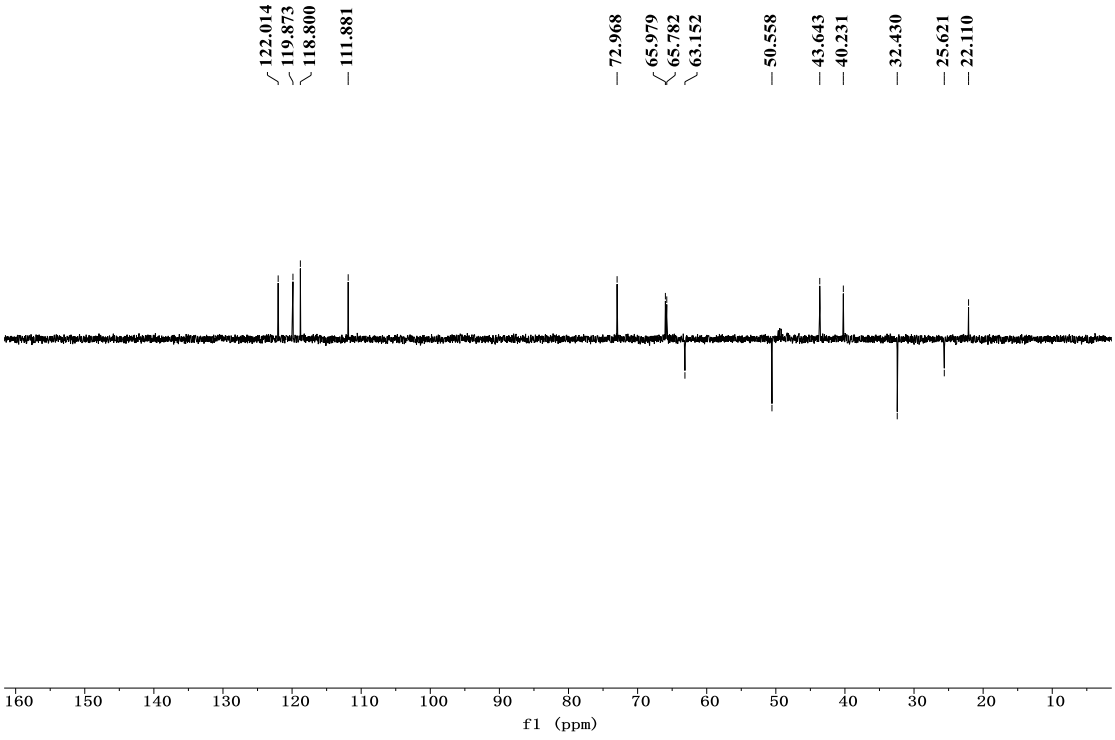

Figure S6. DEPT 135° NMR (100 MHz, methanol-d_4) spectrum of **1**.

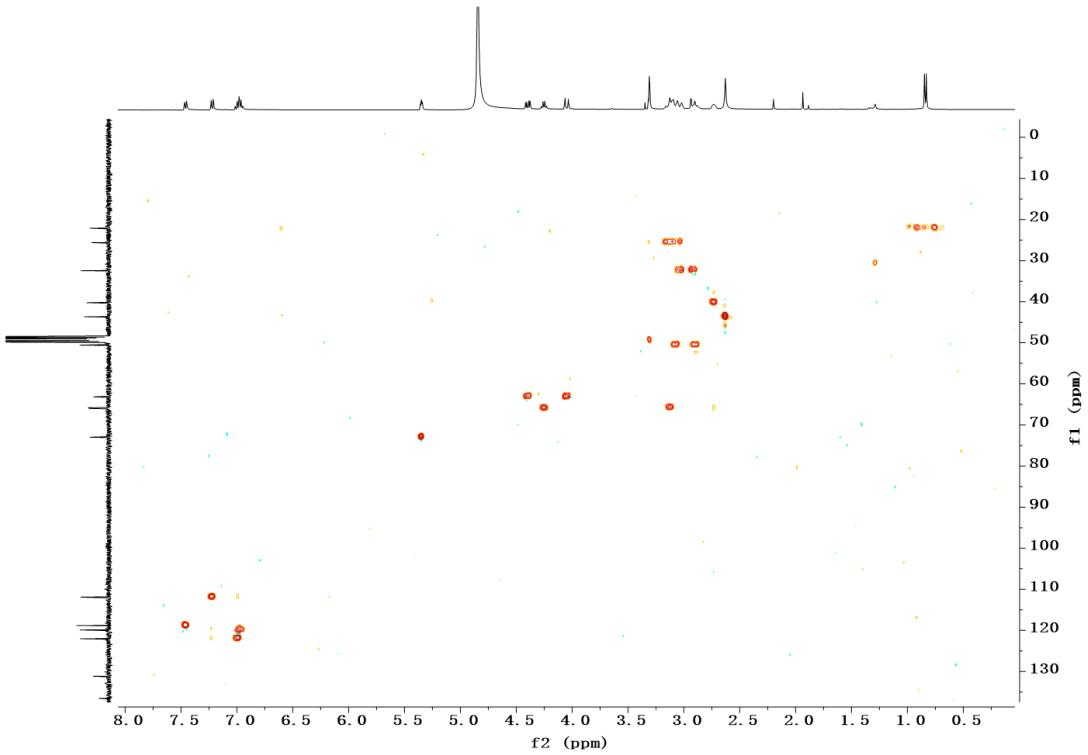

Figure S7. HMQC spectrum of **1** (^{1}H: 400 MHz, ^{13}C: 100 MHz, methanol-d_4).

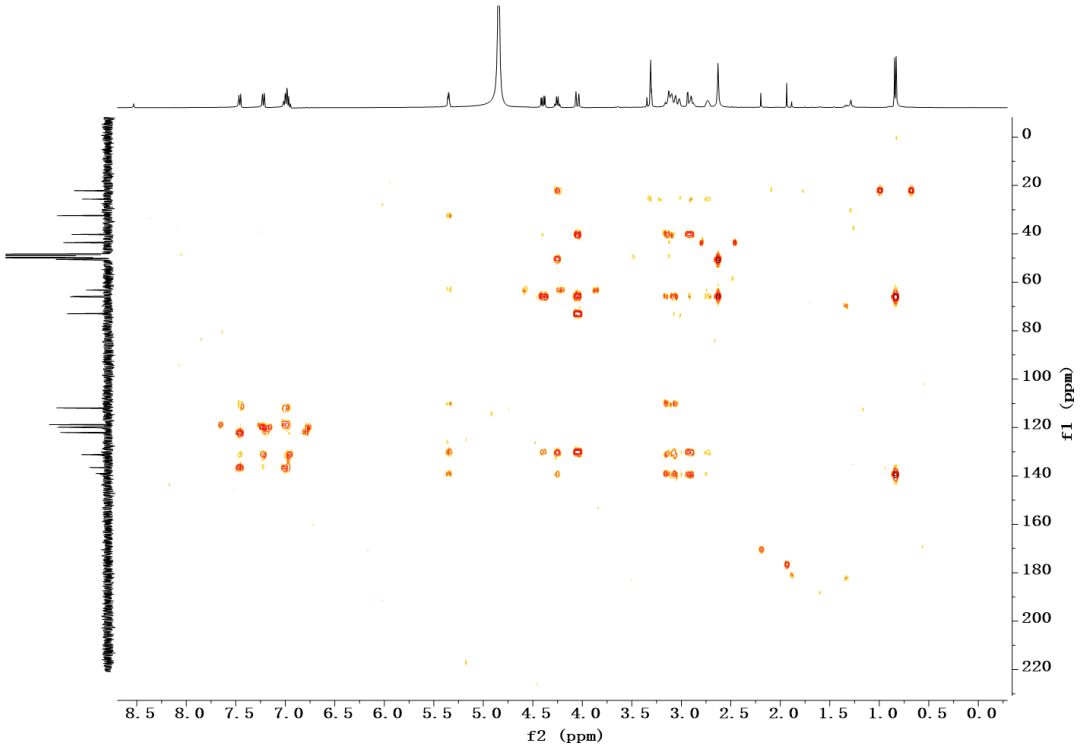

Figure S8. HMBC spectrum of **1** (^{1}H: 400 MHz, ^{13}C: 100 MHz, methanol-d_4).

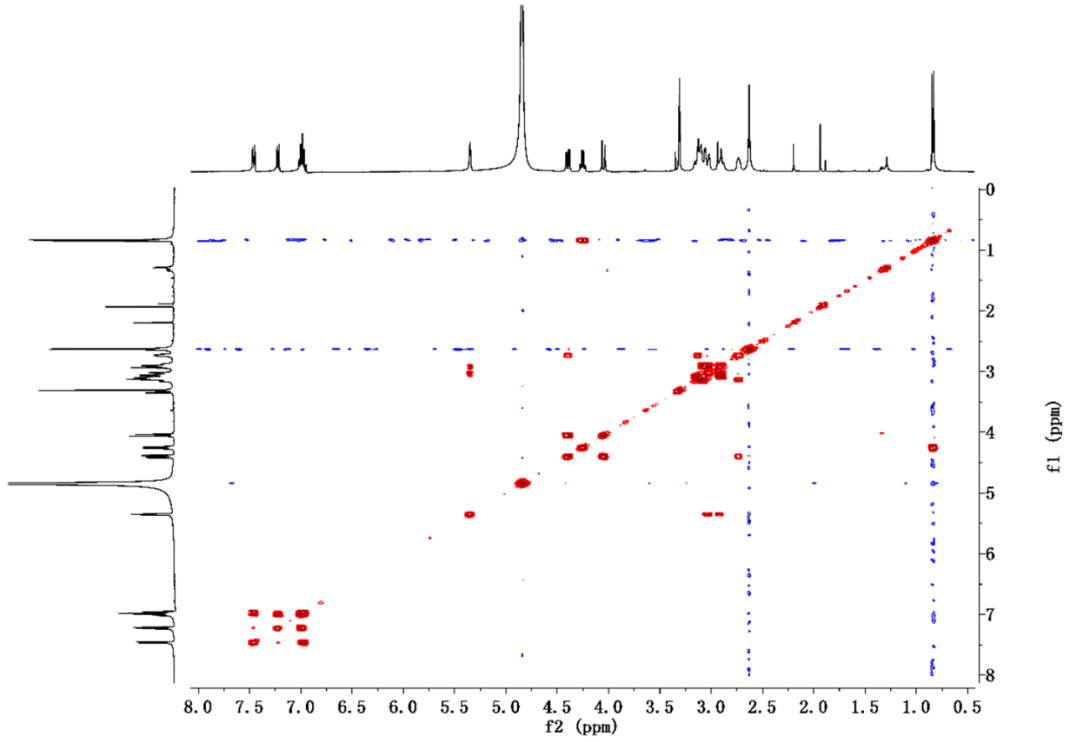

Figure S9. ^{1}H-^{1}H COSY (400 MHz, methanol-d_4) spectrum of **1**.

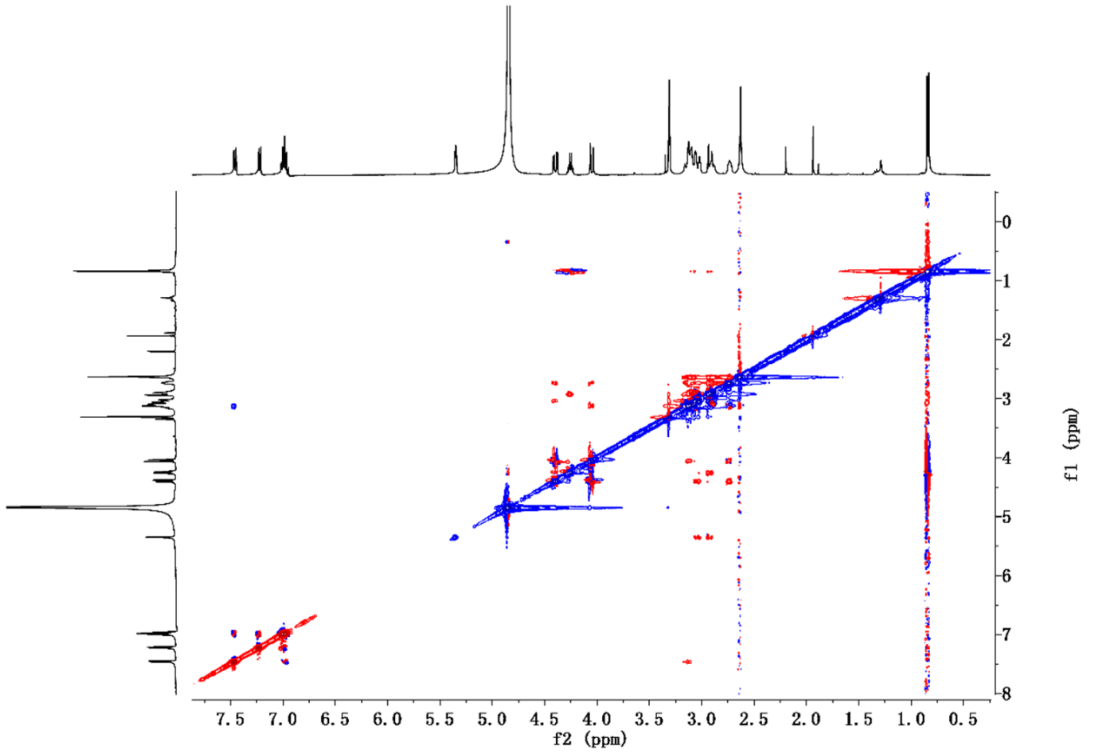

Figure S10. NOESY (400 MHz, methanol-d_4) spectrum of **1**.

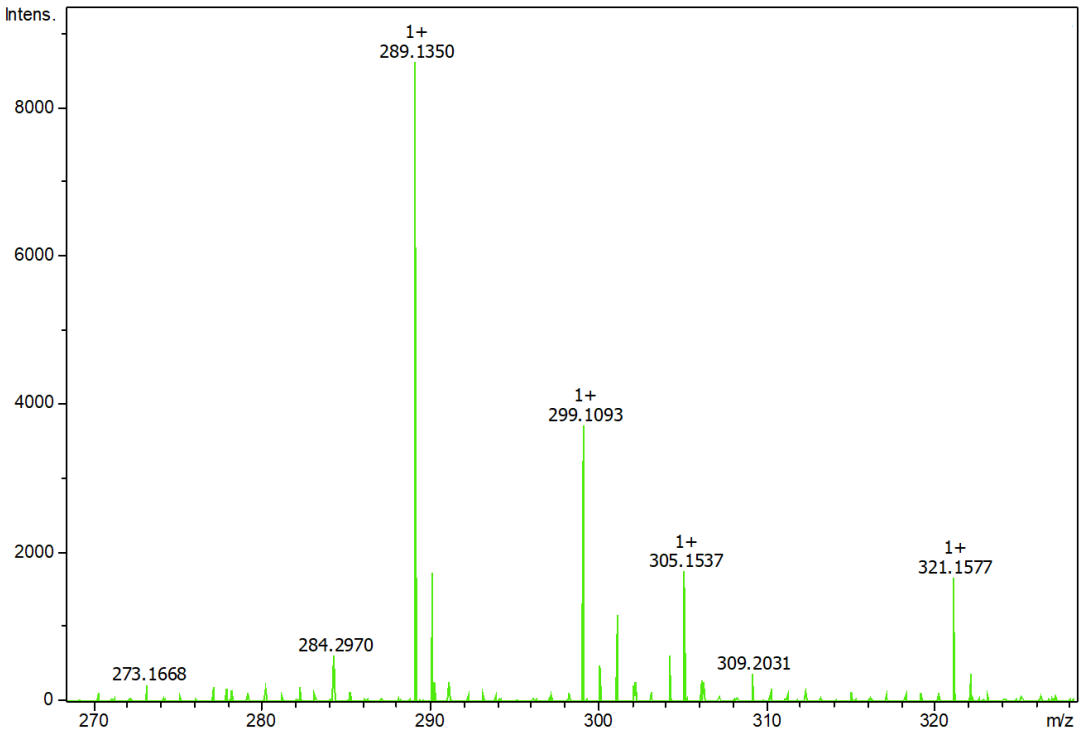

Figure S11. (+)-HR-ESI-MS spectrum of **2**.

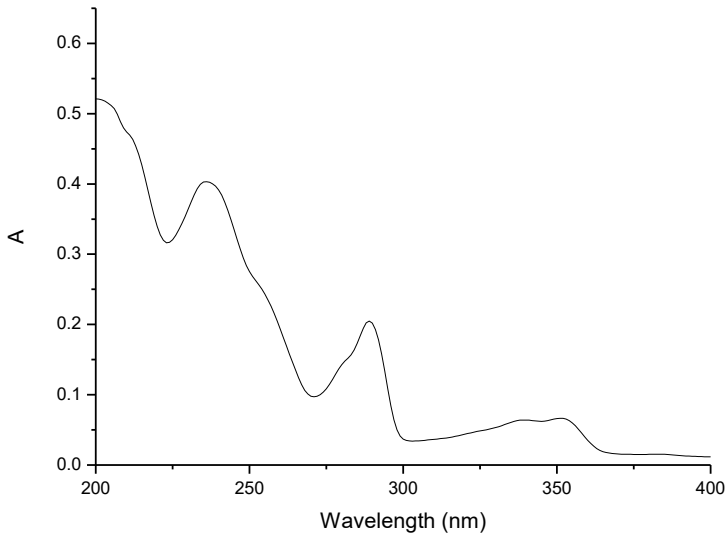

Figure S12. UV spectrum of **2** in MeOH.

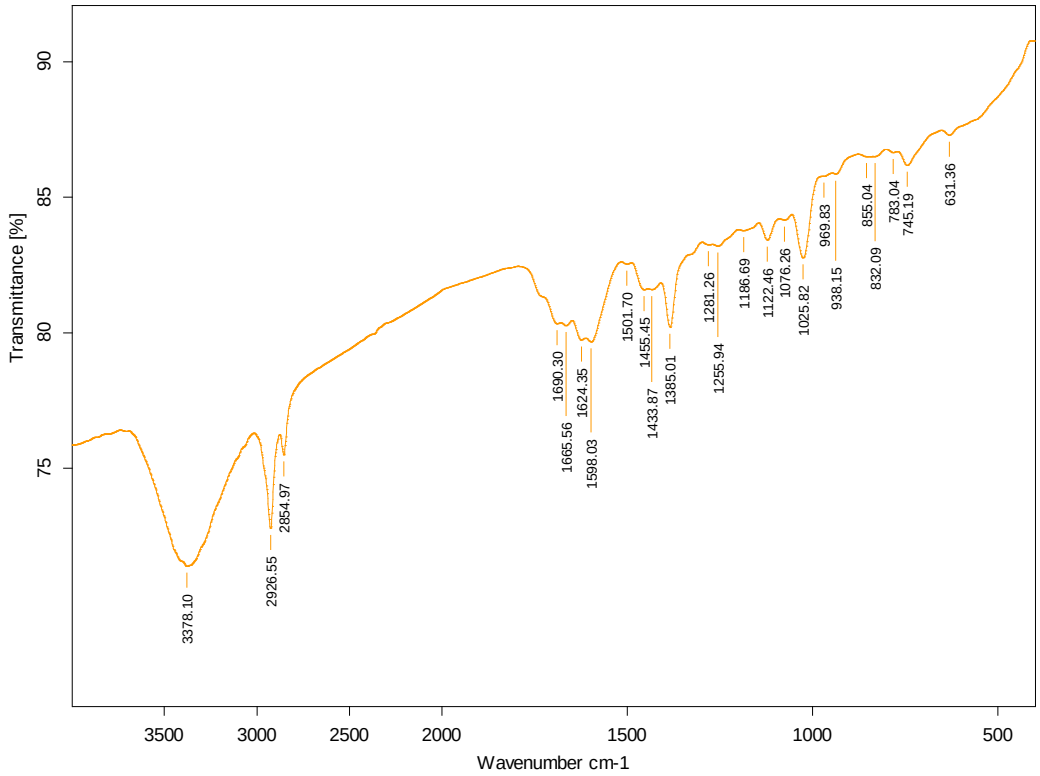

Figure S13. IR spectrum of **2** (IR).

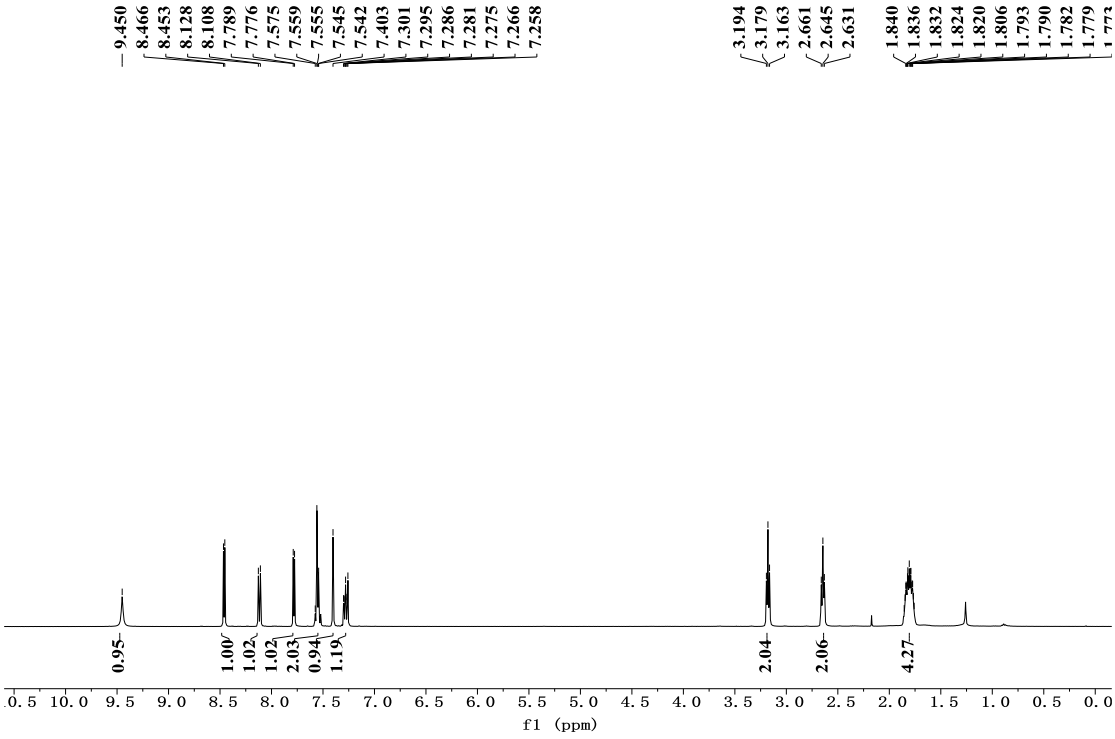

Figure S14. ^{1}H NMR (400 MHz, chloroform-*d*) spectrum of **2**.

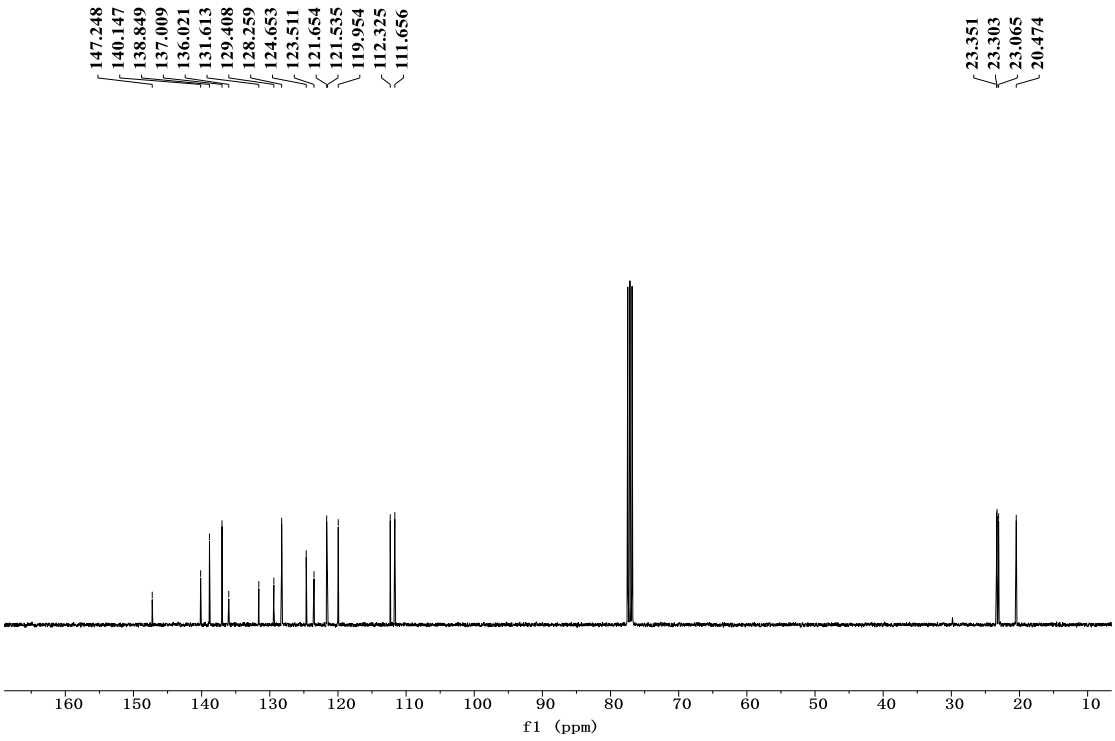

Figure S15. ^{13}C NMR (100 MHz, chloroform-*d*) spectrum of **2**.

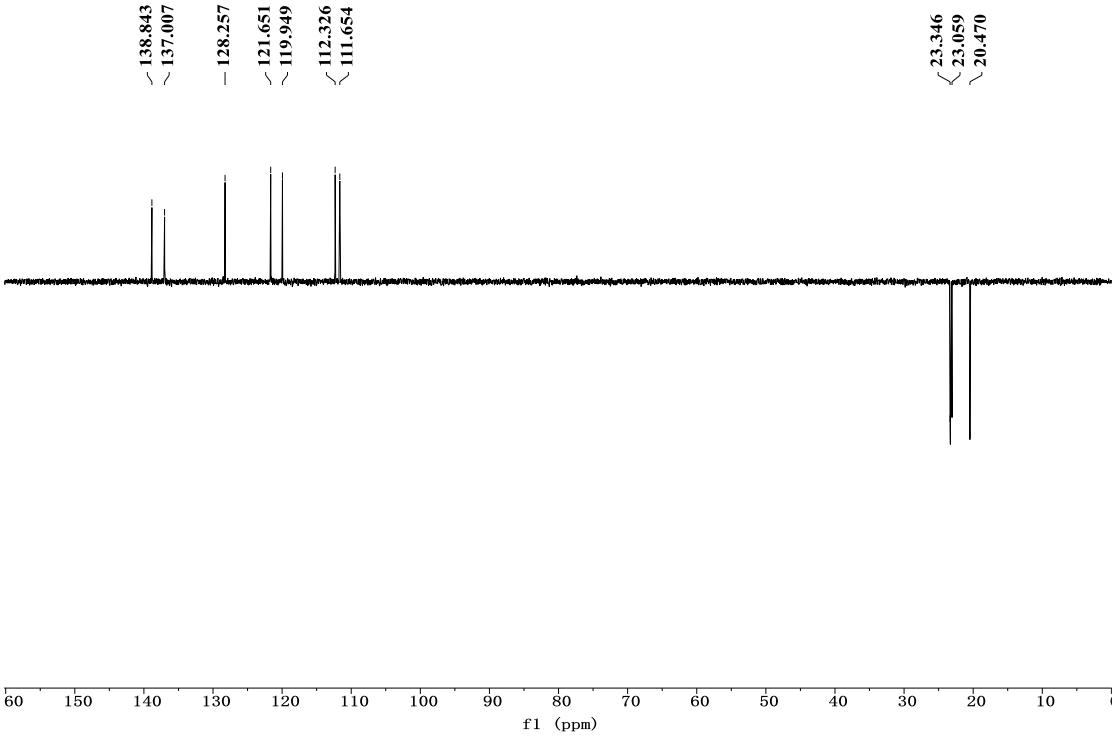

Figure S16. DEPT 135° NMR (100 MHz, chloroform-*d*) spectrum of **2**.

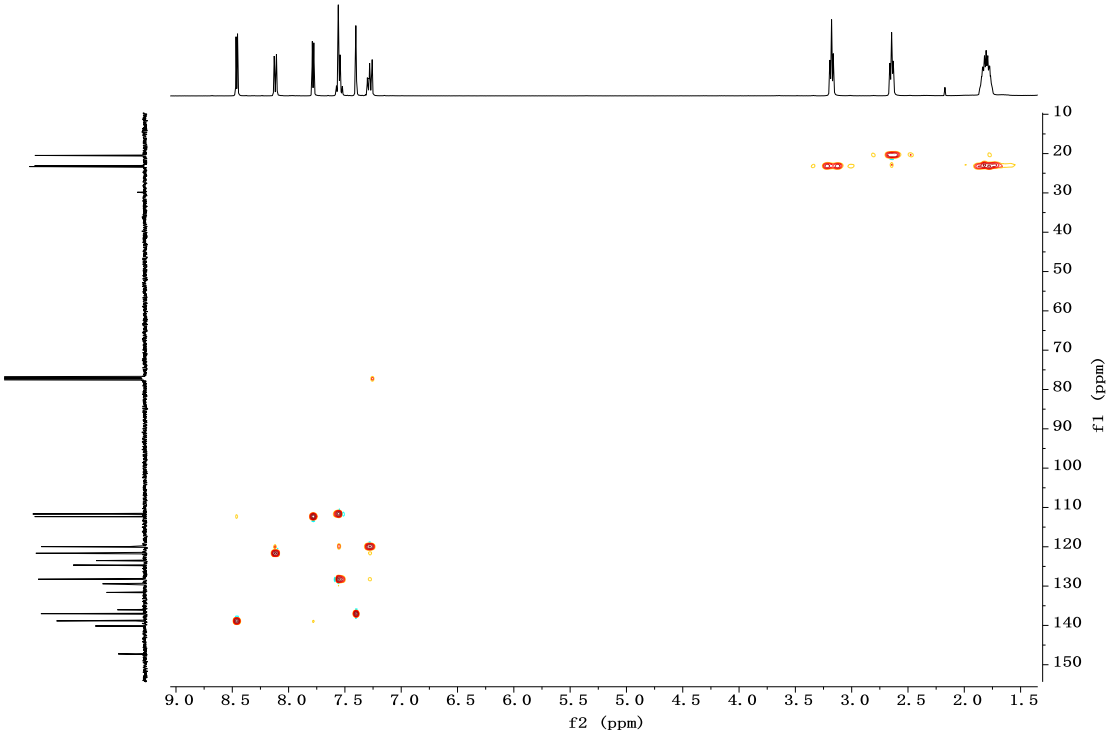

Figure S17. HMQC spectrum of **2** (^{1}H: 400 MHz, ^{13}C: 100 MHz, chloroform-*d*).

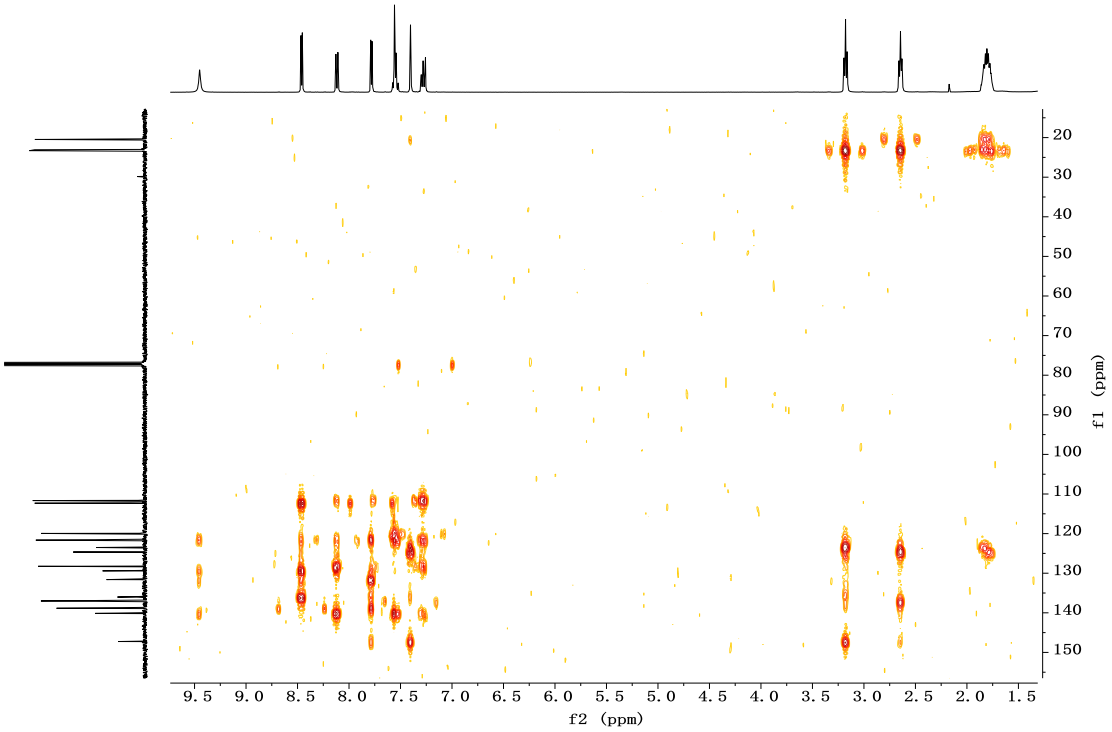

Figure S18. HMBC spectrum of **2** (^{1}H: 400 MHz, ^{13}C: 100 MHz, chloroform-*d*).

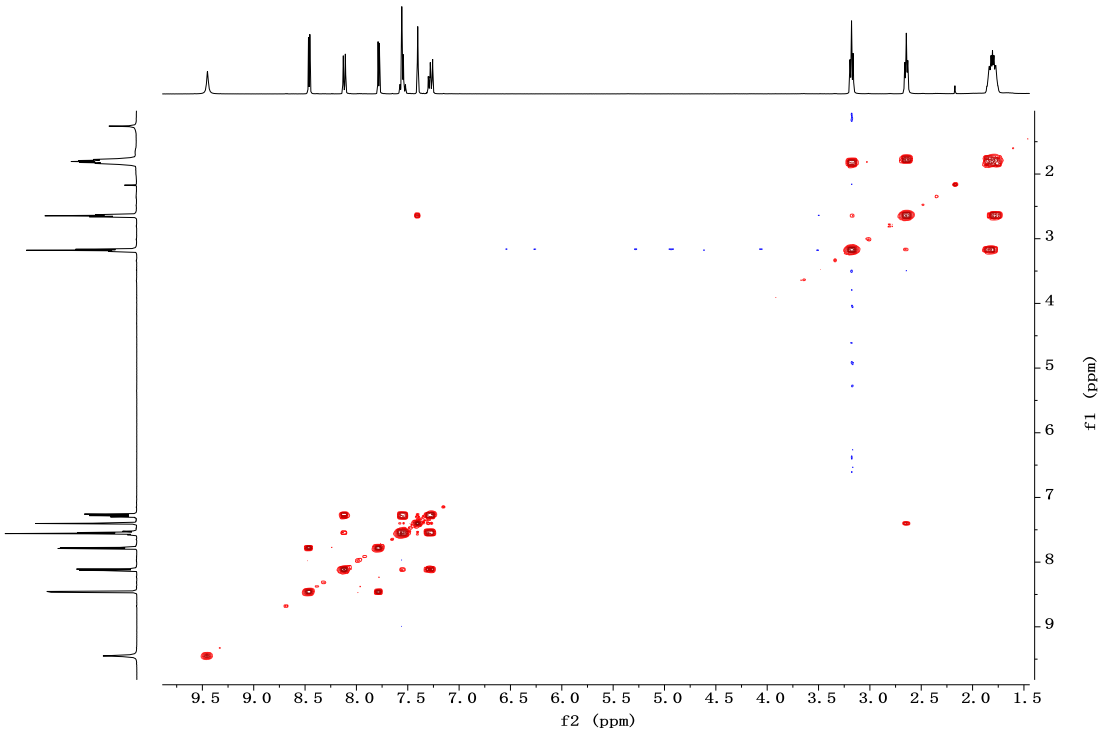

Figure S19. ^{1}H-^{1}H COSY (400 MHz, chloroform-*d*) spectrum of **2**.

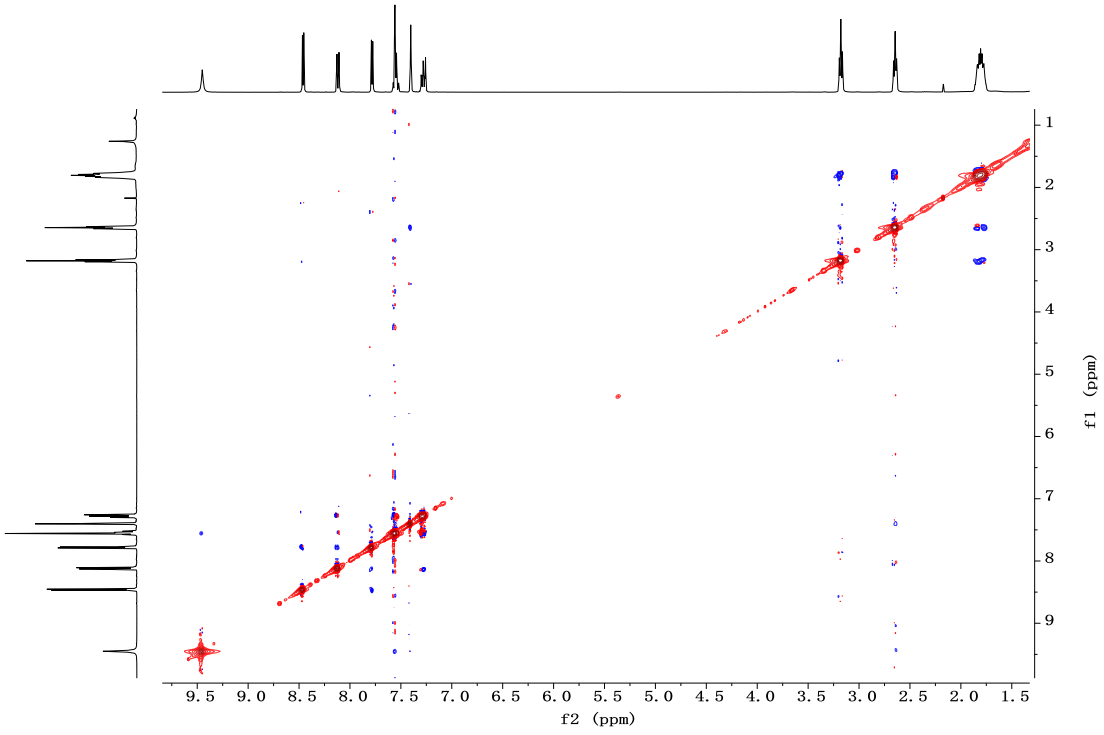

Figure S20. NOESY (400 MHz, chloroform-*d*) spectrum of **2**.

Table S1. Important thermodynamic parameters (a.u.) and Boltzmann distributions of the optimized 19*S**-**1** at B3LYP/6-31G (d) level in methanol.

Conformation	Gibbs free energies (Hartree)	Boltzmann distribution
1	-1036.12	94.16%
2	-1036.11	0.97%
3	-1036.12	4.86%

Table S2. Optimized coordinate of 19*S**-**1** at B3LYP/6-31G (d) level in methanol

Conformation 1							
Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	-0.70728	-1.43699	-0.85572	H	C	-4.14219	0.847123
C	-0.9289	-1.08975	0.458824	H	C	-4.61257	0.877903
C	0.50301	-2.06979	-1.49181	H	C	-3.88443	0.298239
N	1.216853	0.709386	1.862231	H	H	0.060232	-2.49863
C	1.339737	-0.75355	1.701924	H	H	-0.59411	-1.09862
C	-0.06418	-1.41204	1.651024	H	H	2.370585	-1.46691
C	1.513042	-0.97617	-1.93343	H	H	1.045531	-0.33745
C	1.917729	-0.21312	-0.69979	H	H	3.131541	1.469373
C	1.840196	1.106117	-0.46568	H	H	1.750157	2.569688
C	2.055109	1.527463	0.972163	H	H	3.152394	-2.76273
C	2.258717	-1.09256	0.492341	H	H	2.355053	-3.21756
C	2.269718	-2.57215	0.094003	H	H	1.139653	1.686666
O	1.090845	-3.00576	-0.58412	H	H	2.052665	3.997267
C	1.395558	2.164108	-1.44998	H	H	3.337679	2.776343
C	2.462704	3.224328	-1.72388	H	H	2.783452	3.707067
H	0.197337	-2.65182	-2.37362	H	H	2.31539	0.988001
H	3.283871	-0.85789	0.818864	H	H	0.590915	0.579899
H	1.845739	-1.17622	2.589098	H	H	1.059572	2.199814
C	1.309573	1.135682	3.247717	H	H	-0.37073	2.201162
O	0.25339	2.865312	-0.94282	H	H	-1.86264	-1.16063
C	-2.67167	-0.31501	-0.85061	H	H	-2.58799	0.218483
C	-2.17985	-0.36926	0.483309	H	H	-4.73292	1.314851
N	-1.74335	-0.95536	-1.64629	H	H	-5.55773	1.365757
C	-2.93904	0.231911	1.5034	H	H	-4.24403	0.324628
Conformation 2							
Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	-0.4159	-1.57404	-0.68509	C	-4.02998	0.406718	1.363307
C	-0.59838	-1.09145	0.594481	C	-4.5863	0.200207	0.084021
C	0.836706	-2.07651	-1.35605	C	-3.84465	-0.38672	-0.93465
N	1.774515	1.071575	1.845392	H	0.612014	-2.17787	1.967622

C	1.747117	-0.37828	1.668692	H	-0.14364	-0.75908	2.646254
C	0.371883	-1.12899	1.752088	H	2.556457	-1.26725	-2.41454
C	1.638459	-0.88001	-1.95303	H	1.047376	-0.42294	-2.74928
C	1.902843	0.05035	-0.79508	H	1.901114	2.846158	0.767774
C	1.37465	1.275485	-0.6272	H	0.26301	2.227451	0.881807
C	1.313986	1.913639	0.743676	H	3.605249	-2.26618	-0.61634
C	2.553222	-0.66482	0.387662	H	3.041054	-2.69424	1.001791
C	2.767805	-2.15346	0.089333	H	0.68846	1.477266	-2.65377
O	1.613888	-2.82269	-0.41783	H	0.763634	3.915797	-2.81564
C	0.661708	2.057894	-1.7216	H	2.353853	3.280583	-2.32596
C	1.312553	3.411933	-2.01351	H	1.28883	4.059717	-1.13182
H	0.57264	-2.7724	-2.16635	H	1.651792	2.602707	3.258299
H	3.551383	-0.23834	0.561782	H	1.783282	0.969553	3.934493
H	2.324858	-0.77692	2.516635	H	0.229323	1.542923	3.270639
C	1.327853	1.561825	3.132239	H	-1.12925	1.509787	-1.12015
O	-0.69925	2.343085	-1.376	H	-1.72022	-1.71066	-2.36488
C	-2.52883	-0.76141	-0.64171	H	-2.31403	0.190186	2.643015
C	-1.94625	-0.57374	0.643338	H	-4.63567	0.87208	2.13609
N	-1.56383	-1.34933	-1.43576	H	-5.61006	0.507465	-0.11027
C	-2.72557	0.026563	1.650398	H	-4.27092	-0.54581	-1.92188
Conformation 3							
Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	0.562719	0.239098	1.568877	C	4.251368	-0.84934	-0.95593
C	0.855547	-0.8615	0.79377	C	4.679462	0.401359	-0.4658
C	-0.70328	0.593294	2.304638	C	3.870059	1.157797	0.374788
N	-1.14771	-1.50382	-1.5449	H	-0.18103	-2.58023	1.547203
C	-1.35154	-1.90263	-0.13714	H	0.585671	-2.81123	-0.00927
C	0.009251	-2.09094	0.58364	H	-2.56365	1.645636	1.98706
C	-1.66922	1.397018	1.395998	H	-1.21034	2.338205	1.090265
C	-1.99666	0.524882	0.210236	H	-3.04629	-0.68981	-2.14446
C	-1.86453	0.797818	-1.09699	H	-1.62918	-0.12847	-3.02844
C	-1.98016	-0.39378	-2.02349	H	-3.35143	-0.59272	2.432686
C	-2.32802	-0.91636	0.564868	H	-2.51933	-2.15088	2.352371
C	-2.43406	-1.09225	2.083468	H	-2.00923	2.162869	-2.71906
O	-1.31018	-0.60134	2.810555	H	0.202888	3.217199	-2.49102
C	-1.50844	2.12824	-1.73452	H	0.381787	1.446317	-2.56747
C	-0.00324	2.27709	-1.9684	H	0.529276	2.278039	-1.01314
H	-0.4567	1.202141	3.186736	H	-2.15056	-3.11872	-2.55361
H	-3.32713	-1.15122	0.16445	H	-0.44598	-3.39311	-2.12054
H	-1.85121	-2.88853	-0.10852	H	-0.8454	-2.30627	-3.45702
C	-1.15811	-2.63263	-2.45837	H	-2.85405	3.13397	-0.74709
O	-1.91777	3.264022	-0.96737	H	1.669826	2.000855	2.036629
C	2.62022	0.630812	0.713611	H	2.69196	-2.33287	-1.0003

C	2.167329	-0.63071	0.23854	H	4.906502	-1.4141	-1.61397
N	1.615561	1.142753	1.509303	H	5.656648	0.782118	-0.75042
C	3.009316	-1.36841	-0.61202	H	4.197405	2.123618	0.75186

Table S3. Important thermodynamic parameters (a.u.) and Boltzmann distributions of the optimized 19*R**-**1** at B3LYP/6-31G (d) level in methanol.

Conformation	Gibbs free energies (Hartree)	Boltzmann distribution
1	-1036.12	77.60%
2	-1036.11	13.05%
3	-1036.12	9.34%

Table S4. Optimized coordinate of 19*R**-**1** at B3LYP/6-31G (d) level in methanol

Conformation 1							
Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	1.230997	1.059339	-0.53507	C	4.911764	-1.54913	0.344563
C	1.497625	0.158738	0.485476	C	5.344982	-0.92928	-0.84573
C	-0.09777	1.712232	-0.37745	C	4.540072	-0.01261	-1.51205
N	-1.56287	-1.27772	1.258866	H	0.932299	0.741149	2.4612
C	-0.98592	-0.04428	1.827363	H	0.925281	-0.98047	2.206432
C	0.626721	-0.03352	1.742831	H	-1.70354	2.870111	-1.33521
C	-1.41436	1.822916	-1.19641	H	-1.3829	1.335187	-2.17348
C	-2.26515	1.013742	-0.18139	H	-3.65816	-0.80932	1.495868
C	-2.87604	-0.15264	-0.44229	H	-3.27231	-2.10308	0.369087
C	-2.93358	-1.12415	0.717932	H	-1.91297	3.356747	1.341695
C	-1.84095	1.202789	1.30173	H	-0.78431	2.677461	2.529139
C	-1.16486	2.567469	1.505273	H	-3.27015	0.188697	-2.51905
O	-0.06628	2.762979	0.597736	H	-2.68897	-2.08578	-3.32726
C	-3.26551	-0.65669	-1.81513	H	-1.31173	-1.33937	-2.47419
C	-2.32559	-1.73438	-2.35589	H	-2.27926	-2.59139	-1.6773
H	-0.39683	0.843513	0.152485	H	-2.07276	-2.27556	3.093859
H	-2.7469	1.210187	1.92026	H	-0.43612	-2.58134	2.467223
H	-1.14604	-0.035	2.923726	H	-1.82702	-3.31593	1.665711
C	-1.47502	-2.40969	2.170124	H	-5.18352	-0.57621	-1.4374
O	-4.57409	-1.24938	-1.78031	H	2.339301	1.693905	-2.241
C	3.288463	0.276022	-0.95934	H	3.346786	-1.75136	1.807646
C	2.821705	-0.34648	0.239691	H	5.56661	-2.25973	0.841755
N	2.303227	1.142437	-1.39799	H	6.324928	-1.17043	-1.24849
C	3.666337	-1.26567	0.889025	H	4.875223	0.467733	-2.42803
Conformation 2							
Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	1.222486	1.025898	-0.59604	C	4.891699	-1.53269	0.461704

C	1.482632	0.19162	0.481246	C	5.331693	-0.99051	-0.76351
C	-0.10526	1.690913	-0.48709	C	4.532103	-0.11566	-1.48984
N	-1.58529	-1.18458	1.345804	H	0.913184	0.90485	2.411324
C	-1.00628	0.084896	1.826446	H	0.90045	-0.83077	2.271864
C	0.606972	0.084658	1.745695	H	-1.70899	2.785509	-1.5201
C	-1.41986	1.749125	-1.3157	H	-1.38601	1.203395	-2.26164
C	-2.27378	1.005477	-0.25578	H	-3.6852	-0.69951	1.524173
C	-2.88377	-0.17405	-0.44083	H	-3.28547	-2.06681	0.495006
C	-2.95148	-1.06625	0.77989	H	-1.92781	3.444559	1.108133
C	-1.85741	1.292802	1.213391	H	-0.80734	2.845738	2.345956
C	-1.18166	2.667848	1.329343	H	-3.30417	0.031355	-2.52643
O	-0.07592	2.802388	0.418016	H	-2.5012	-2.24484	-3.21269
C	-3.23542	-0.77511	-1.78119	H	-1.2149	-1.33287	-2.40068
C	-2.19461	-1.80033	-2.25572	H	-2.07883	-2.60537	-1.5238
H	-0.40848	0.859924	0.097833	H	-2.12756	-2.03639	3.24391
H	-2.767	1.341141	1.824521	H	-0.48252	-2.39421	2.668899
H	-1.16781	0.171658	2.919074	H	-1.86449	-3.18485	1.905076
C	-1.5161	-2.24309	2.342829	H	-4.71602	-1.86553	-2.45097
O	-4.52278	-1.3904	-1.62765	H	2.341851	1.552476	-2.33144
C	3.279154	0.210871	-0.96181	H	3.320638	-1.63697	1.92838
C	2.805818	-0.33262	0.272718	H	5.542349	-2.21232	1.005562
N	2.297823	1.049408	-1.45907	H	6.312681	-1.25902	-1.14596
C	3.645104	-1.21148	0.982065	H	4.872413	0.305121	-2.43286
Conformation 3							
Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	-1.10298	-0.91851	0.699318	C	-4.99989	0.792266	-1.03733
C	-1.47	0.376624	0.363167	C	-5.34469	-0.5744	-0.99311
C	0.265746	-0.98274	1.283225	C	-4.44996	-1.52559	-0.51676
N	1.439849	1.869111	-0.75399	H	-0.91472	1.912885	1.740609
C	0.947143	1.814037	0.638028	H	-1.04386	2.458223	0.0928
C	-0.65548	1.638522	0.70781	H	1.982991	-2.25106	1.813141
C	1.608921	-1.68709	0.952128	H	1.575087	-2.33233	0.073984
C	2.366035	-0.37146	0.628263	H	3.549202	2.033117	-0.31562
C	2.909045	-0.05766	-0.56129	H	3.118421	1.571172	-1.95996
C	2.845742	1.417285	-0.91053	H	2.143673	-0.06358	3.413472
C	1.913946	0.850689	1.476005	H	0.94248	1.241393	3.399373
C	1.335681	0.393304	2.823547	H	3.680289	-0.4762	-2.5046
O	0.273466	-0.55963	2.653634	H	4.415479	-2.80512	-2.11121
C	3.243384	-1.04785	-1.66972	H	5.206511	-1.66633	-0.99538
C	4.250122	-2.12345	-1.27029	H	3.890802	-2.70727	-0.41781
H	0.482922	-0.11139	0.717492	H	1.799688	3.985586	-0.87637
H	2.797447	1.458415	1.706798	H	0.16964	3.442559	-1.33759
H	1.080559	2.806338	1.112209	H	1.528637	3.136674	-2.42182

C	1.229353	3.173221	-1.36876	H	1.369775	-1.06616	-2.23754
O	2.072037	-1.73228	-2.15339	H	-2.09618	-2.79591	0.549148
C	-3.19873	-1.08004	-0.07967	H	-3.50439	2.289817	-0.64821
C	-2.82038	0.297735	-0.12575	H	-5.72411	1.510563	-1.41226
N	-2.13723	-1.79366	0.447801	H	-6.32679	-0.88968	-1.33474
C	-3.75453	1.232464	-0.60922	H	-4.71682	-2.57885	-0.47911

Table S5 DP4+ probability of ^{13}C NMR chemical shift of compound **1**.

Functional	Solvent?	Basis Set	Type of Data
mPW1PW91	PCM	6-311G(d,p)	Shielding Tensors

	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5	Isomer 6
sDP4+ (H data)	-	-	-	-	-	-
sDP4+ (C data)	100.00%	0.00%	-	-	-	-
sDP4+ (all data)	100.00%	0.00%	-	-	-	-
uDP4+ (H data)	-	-	-	-	-	-
uDP4+ (C data)	100.00%	0.00%	-	-	-	-
uDP4+ (all data)	100.00%	0.00%	-	-	-	-
DP4+ (H data)	-	-	-	-	-	-
DP4+ (C data)	100.00%	0.00%	-	-	-	-
DP4+ (all data)	100.00%	0.00%	-	-	-	-