Supplementary Materials

Brasilterpenes A-E, bergamotane sesquiterpenoid derivatives with hypoglycemic activity from the deep sea-derived fungus *Paraconiothyrium brasiliense* HDN15-135

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Contents

Figure S1 HPLC analysis of the crude extract of HDN15-135

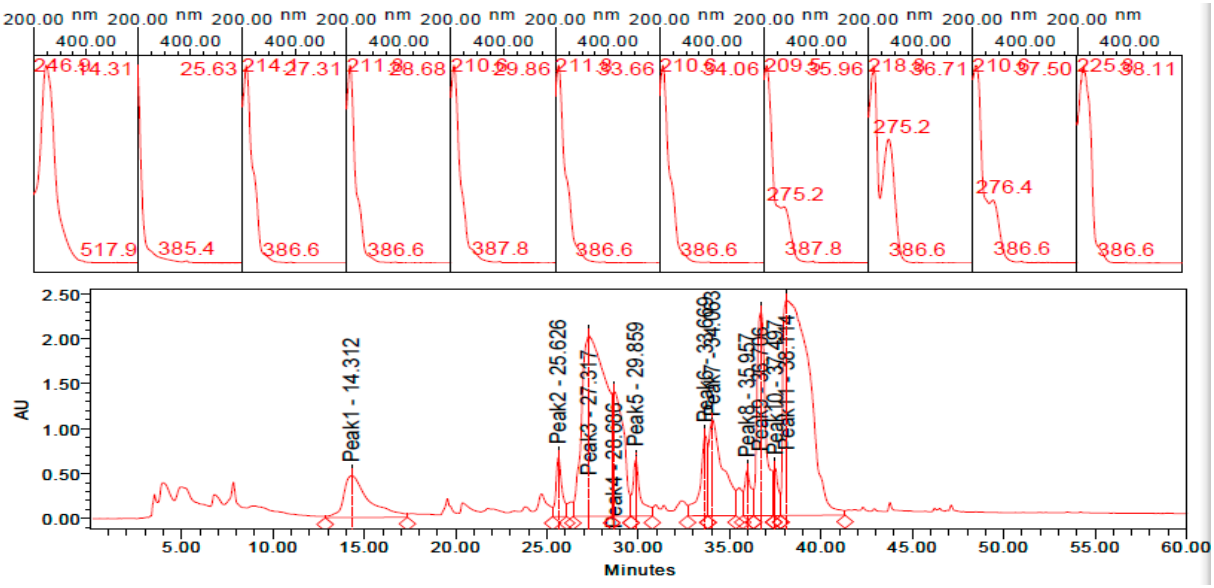
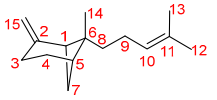
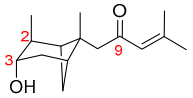


Figure S2 Structures of reported bergamotane sesquiterpenoids

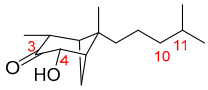
Type I bicyclo[3.1.1]heptan [1-9]



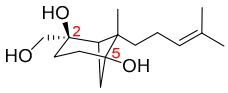
1-1 beta-bergamotene [1]



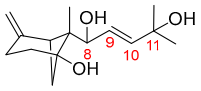
1-2 tanavulgarol [2]



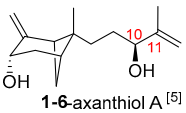
1-3 3beta-hydroxy-2-oxo1,2,12,1 3-tetrahydro-bergamotene [3]



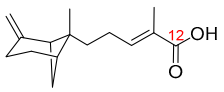
1-4 beta-trans-2beta,5,15-trihydroxybergamot-10-ene [4]



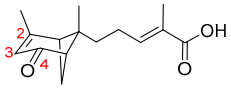
1-5 *E*-beta-trans-5,8,11-trihydroxybergamot-9-ene [4]



1-6-axanthiol A [5]



1-7 (+)-(E)-endo-beta-bergamotenoic acid [6]



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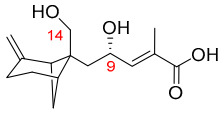

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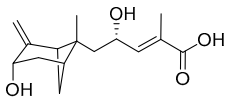
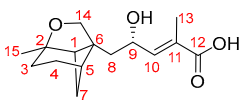


1-10 donacinoic acid B [9]

Type II tricyclo[4.3.0.0^{4,7}]nonane [9-14]



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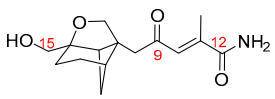

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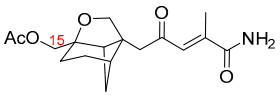
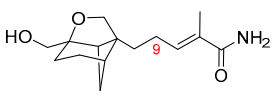


2-3 brasilamide D [10]



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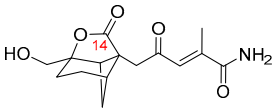

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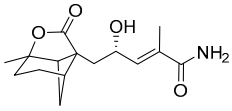

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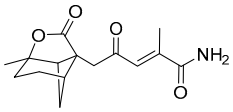

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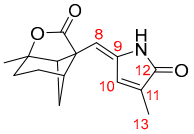

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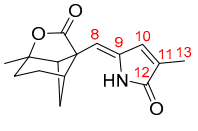

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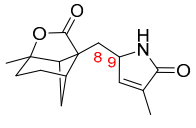
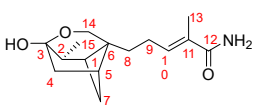


2-10 dihydroampullicin [14]

Type III tricyclo[3.3.1.$0^{2,7}$]nonane [10, 11]



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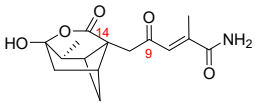

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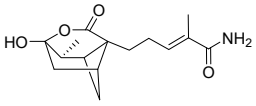

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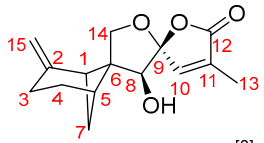
Type IV 6/4/5/5 tetracyclic skeleton [8, 9, 15-17]



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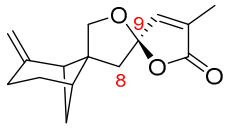

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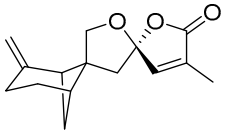

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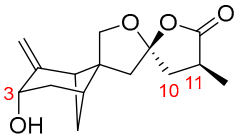
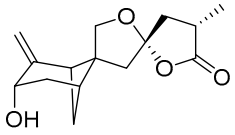


4-4 expansolide C [15]



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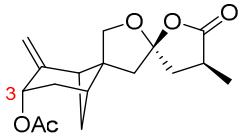

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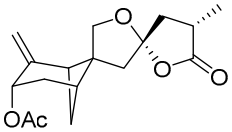
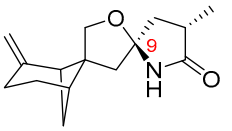


4-7 expansolide B [16]



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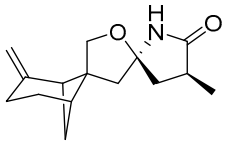

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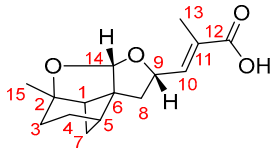
Type V 5/6/4/5 tetracyclic skeleton [9]



5-1 donacinoic acid A [9]

References

[1] Kulkarni, K. S.; Paknikar, S. K.; Vaidya, A. S.; Kelkar, G. R.; Bates, R. B.; Bhattacharyya, S. C. Structure of *β*-bergamotene. *Tetrahedron Lett.* **1963**, *4*, 505-511. https://doi.org/10.1016/S0040-4039(01)90662-8.

[2] Chandra, A.; Misra, L. N.; Thakur, R. S. Tanavulgarol, an oxygenated sesquiterpene with an uncommon skeleton from *Tanacetum vulgare*. *Phytochemistry* **1987**, *26*, 3077-3078. https://doi.org/10.1016/S0031-9422(00)84600-2.

[3] Misra, L. N.; Ahmad, A. An oxygenated tetrahydrobergamotene from the essential oil of *Dracocephalum nutans*. *Planta Med.* **1992**, *58*, 478-479. https://doi.org/10.1055/s-2006-961524.

[4] Wang, Y.; Li, D. H.; Li, Z. L.; Sun, Y. J.; Hua, H. M.; Liu, T.; Bai, J. Terpenoids from the marine-derived fungus *Aspergillus fumigatus* YK-7. *Molecules* **2016**, *21*, 31. https://doi.org/10.3390/molecules21010031.

[5] Yin, H.; Jiang, N.; Guo, C.; Gao, J.-M. A new bergamotane sesquiterpenoid from the rhizomes of *Amomum villosum* var. *xanthioides*. *Nat. Prod. Res.* **2021**, *35*, 377-383. https://doi.org/10.1080/14786419.2019.1633649.

[6] Breeden, D. C.; Young, T. E.; Coates, R. M.; Juvik, J. A. Identification and bioassay of kairomones for *Helicoverpa zea*. *J. Chem. Ecol.* **1996**, *22*, 513-539. https://doi.org/10.1007/BF02033653.

[7] Liu, M.; Hu, Z. X.; Luo, Y. Q.; Zhou, M.; Wang, W. G.; Li, X. N.; Du, X.; Pu, J. X.; Sun, H. D. Two new compounds from *Schisandra propinqua* var. *propinqua*. *Nat. Prod. Bioprospect.* **2017**, *7*, 257-262. https://doi.org/10.1007/s13659-017-0129-7.

[8] Oh, H.; Gloer, J. B.; Shearer, C. A. Massarinolins A-C: new bioactive sesquiterpenoids from the aquatic fungus *Massarina tunicata*. *J. Nat. Prod.* **1999**, *62*, 497-501. https://doi.org/10.1021/np980447+.

[9] Zhao, Z. Z.; Zhao, K.; Chen, H. P.; Bai, X.; Zhang, L.; Liu, J. K. Terpenoids from the mushroom-associated fungus *Montagnula donacina*. *Phytochemistry* **2018**, *147*, 21-29. https://doi.org/10.1016/j.phytochem.2017.12.015.

[10] Liu, L.; Gao, H.; Chen, X.; Cai, X.; Yang, L.; Guo, L.; Yao, X.; Che, Y. Brasilamides A-D: sesquiterpenoids from the plant endophytic fungus *Paraconiothyrium brasiliense*. *Eur. J. Org. Chem.* **2010**, *2010*, 3302-3306. https://doi.org/10.1002/ejoc.201000284.

[11] Guo, Z.; Ren, F.; Che, Y.; Liu, G.; Liu, L. New bergamotane sesquiterpenoids from the plant endophytic fungus *Paraconiothyrium brasiliense*. *Molecules* **2015**, *20*, 14611-14620. https://doi.org/10.3390/molecules200814611.

[12] Kimura, Y.; Nakajima, H.; Hamasaki, T. Pinthunamide, a new tricyclic sesquiterpene amide produced by a fungus, *Ampullifernia* sp. *Tetrahedron Lett.* **1989**, *30*, 1267-1270. https://doi.org/10.1016/S0040-4039(00)72732-8.

[13] Kimura, Y.; Nakajima, H.; Hamasaki, T.; Matsumoto, T.; Matsuda, Y.; Tsuneda, A. Ampullicin and isoampullicin, new metabolites from an *Ampulliferina*-like fungus sp. No. 27. *Agric. Biol. Chem.* **1990**, *54*, 813-814. https://doi.org/10.1271/bbb1961.54.813.

[14] Kimura, Y.; Matsumoto, T.; Nakajima, H.; Hamasaki, T.; Matsuda, Y. Dihydroampullicin, a new plant growth regulators produced by the *Ampulliferina*-like fungus sp. No. 27. *Biosci. Biotechnol. Biochem.* **1993**, *57*, 687-688. https://doi.org/10.1271/bbb.57.687.

[15] Ying, Y. M.; Fang, C. A.; Yao, F. Q.; Yu, Y.; Shen, Y.; Hou, Z. N.; Wang, Z.; Zhang, W.; Shan, W. G.; Zhan, Z. J. Bergamotane sesquiterpenes with alpha-glucosidase inhibitory activity from the plant pathogenic fungus *Penicillium expansum*. *Chem. Biodivers.* **2017**, *14*, e1600184. https://doi.org/10.1002/cbdv.201600184.

[16] Massias, M.; Rebuffat, S.; Molho, L.; Chiaroni, A.; Riche, C.; Bodo, B. Expansolides A and B: tetracyclic sesquiterpene lactones from *Penicillium expansum*. *J. Am. Chem. Soc.* **1990**, *112*, 8112-8115. https://doi.org/10.1021/ja00178a039.

[17] Zhang, L. H.; Feng, B. M.; Chen, G.; Li, S. G.; Sun, Y.; Wu, H. H.; Bai, J.; Hua, H. M.; Wang, H. F.; Pei, Y. H. Sporulaminals A and B: a pair of unusual epimeric spiroaminal derivatives from a marine-derived fungus *Paraconiothyrium sporulosum* YK-03. *RSC Adv.* **2016**, *6*, 42361-42366. https://doi.org/10.1039/c6ra01401a.

Figure S3 HRESIMS spectrum of brasilterpene A (**1**)

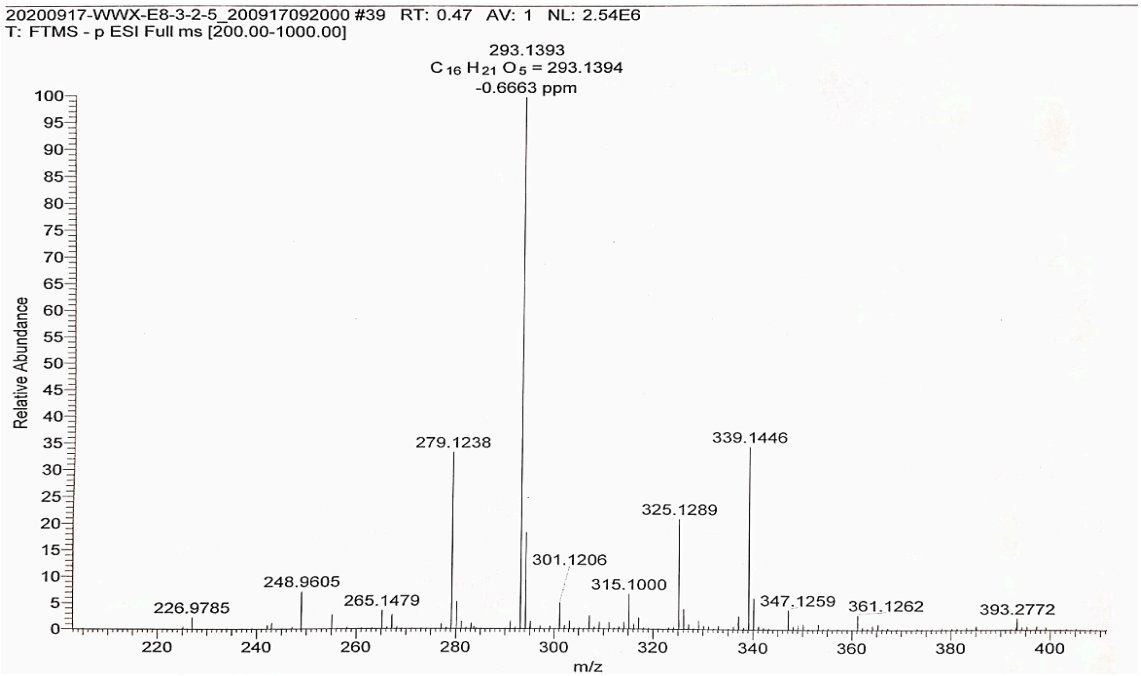


Figure S4 IR spectrum (KBr) of brasilterpene A (**1**)

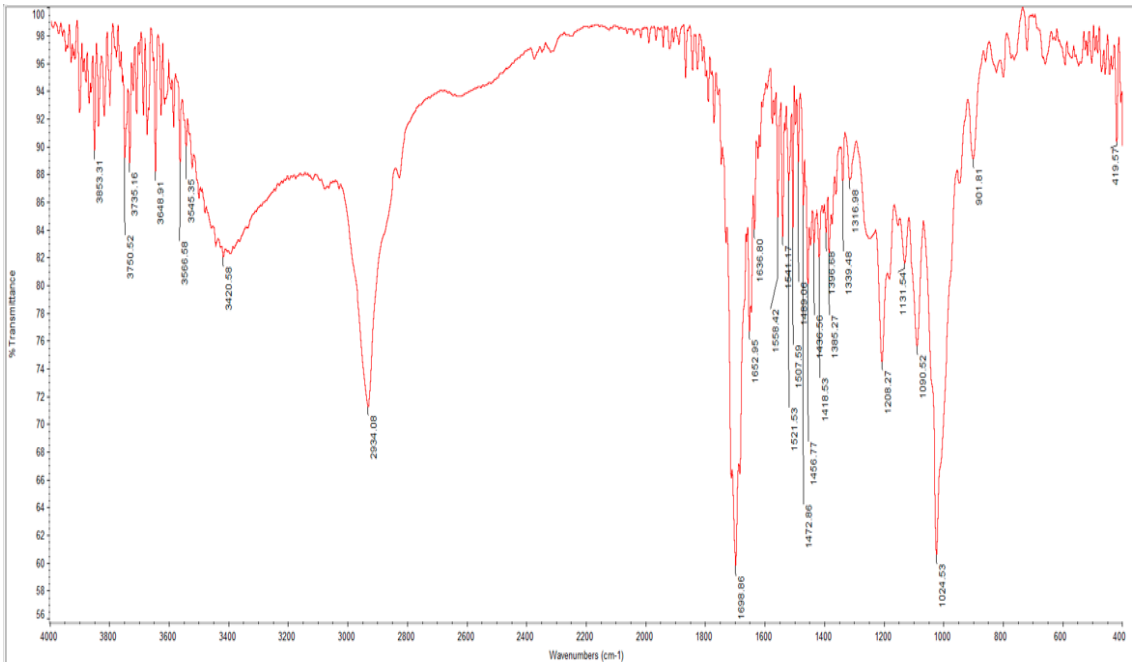


Figure S5 ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of brasilterpene A (**1**)

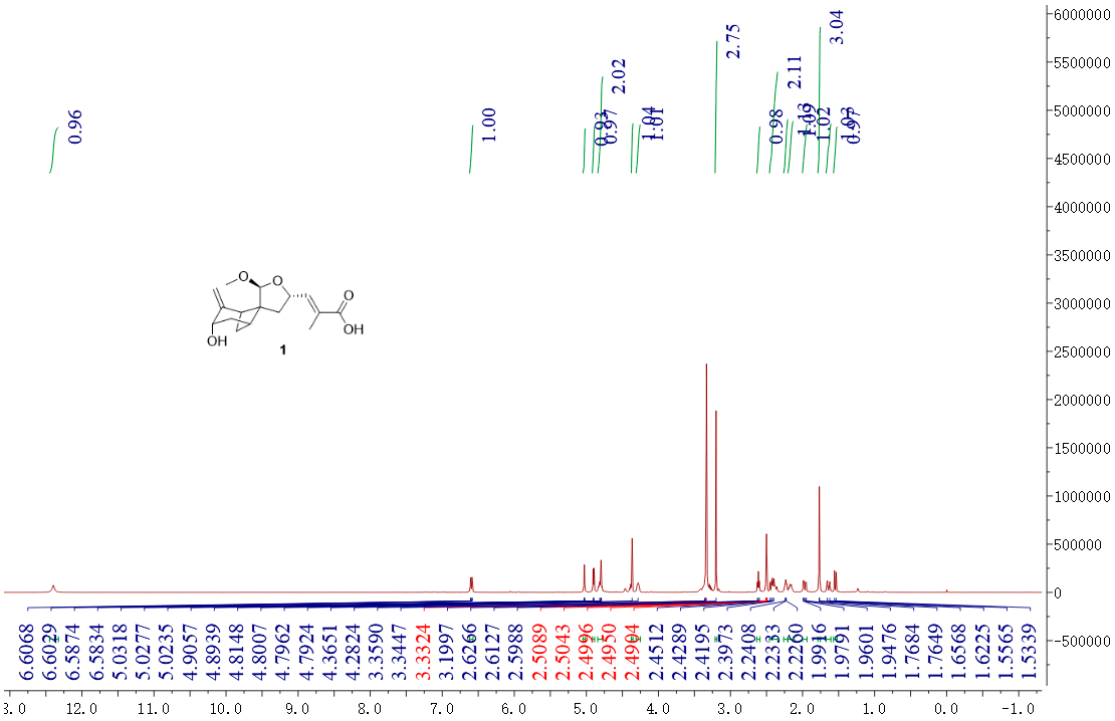


Figure S6 DEPTQ-NMR spectrum (DMSO-d_6, 100 MHz) of brasilterpene A (**1**)

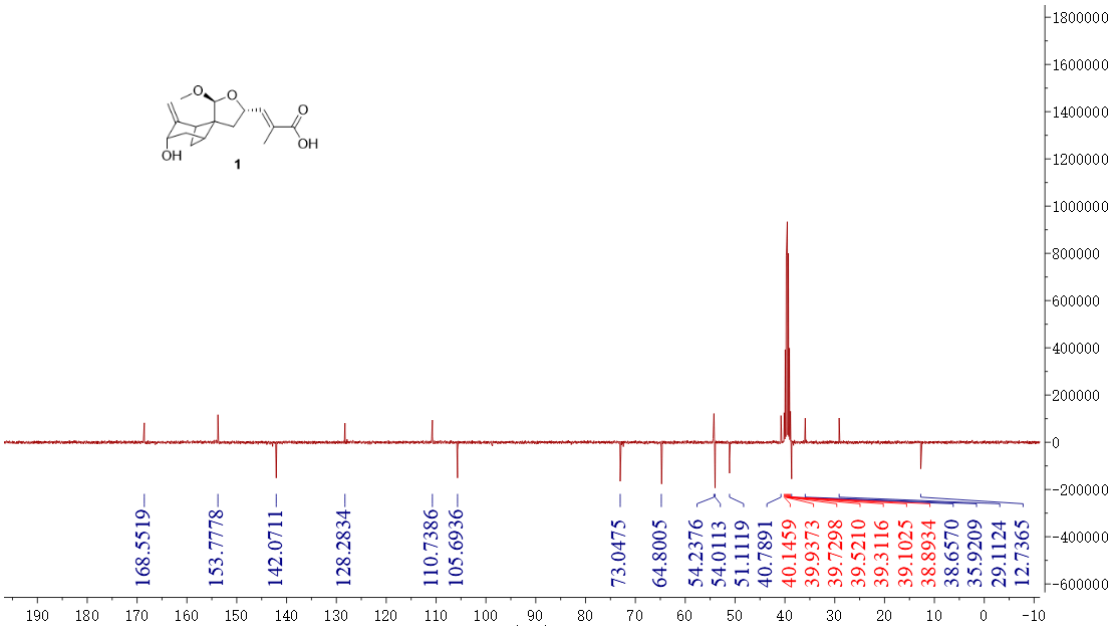


Figure S7 HSQC spectrum of brasilterpene A (**1**)

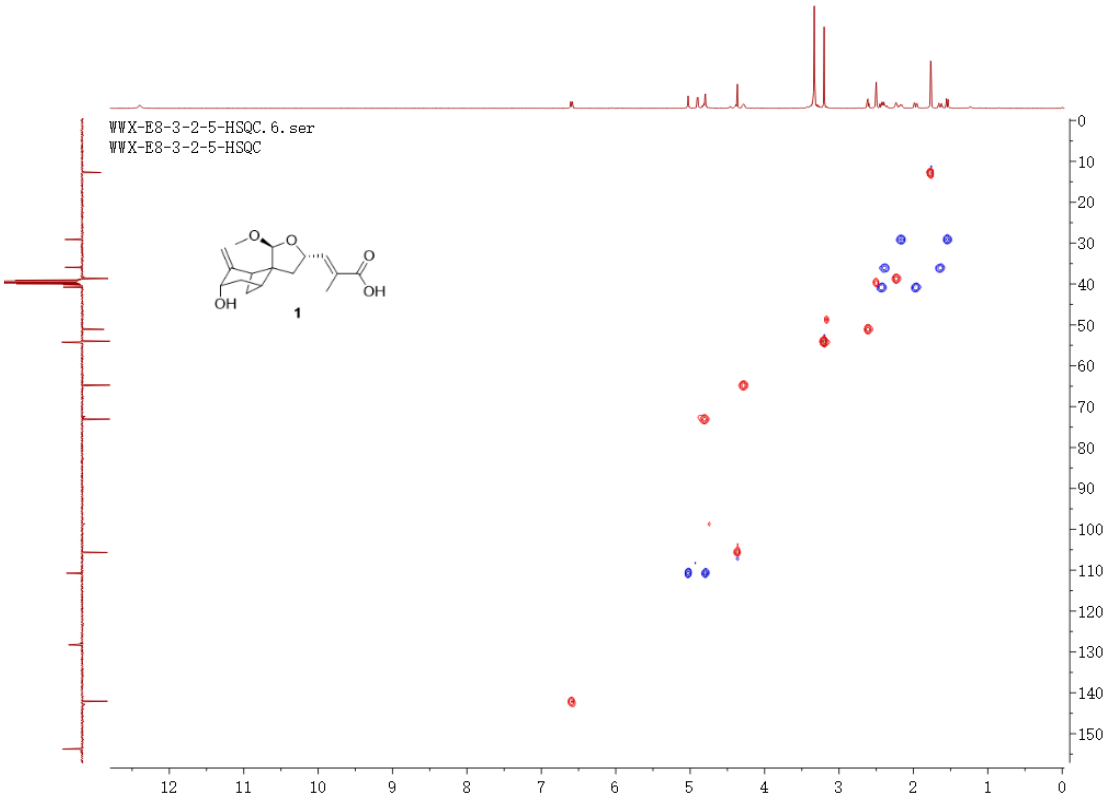


Figure S8 HMBC spectrum of brasilterpene A (**1**)

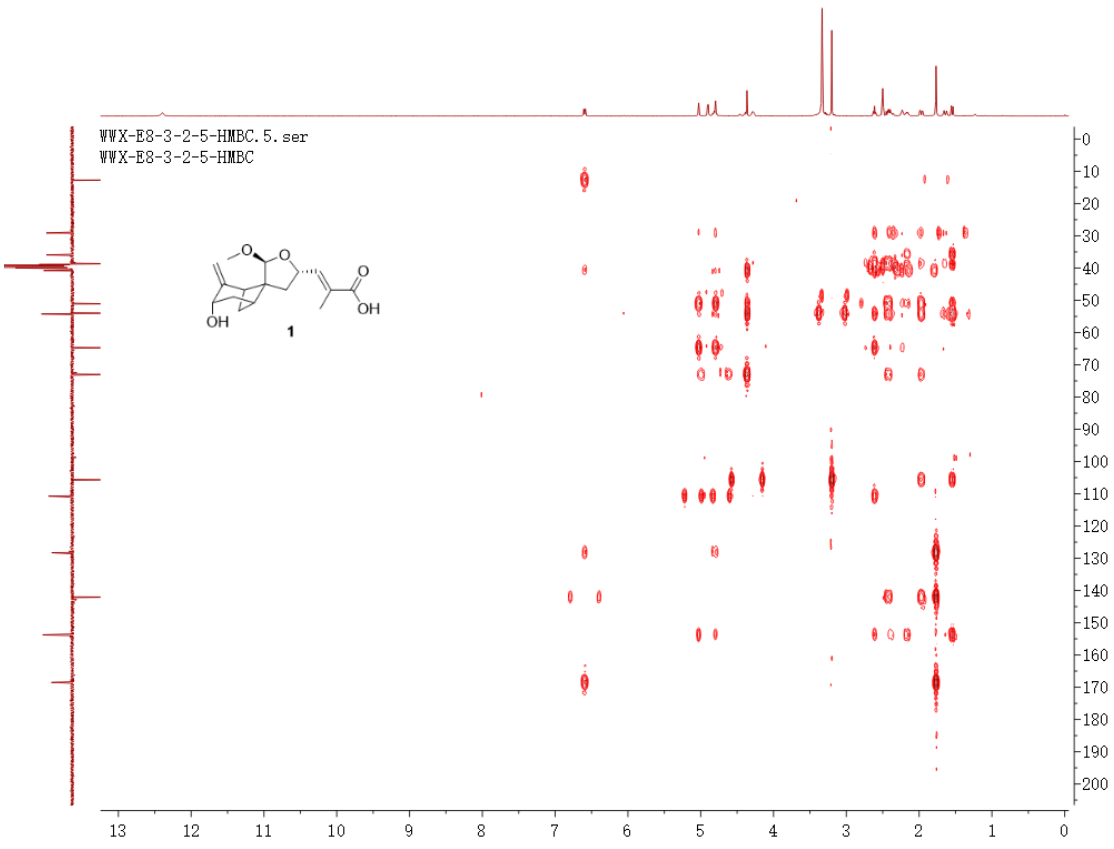


Figure S9 ^{1}H-^{1}H COSY spectrum of brasilterpene A (**1**)

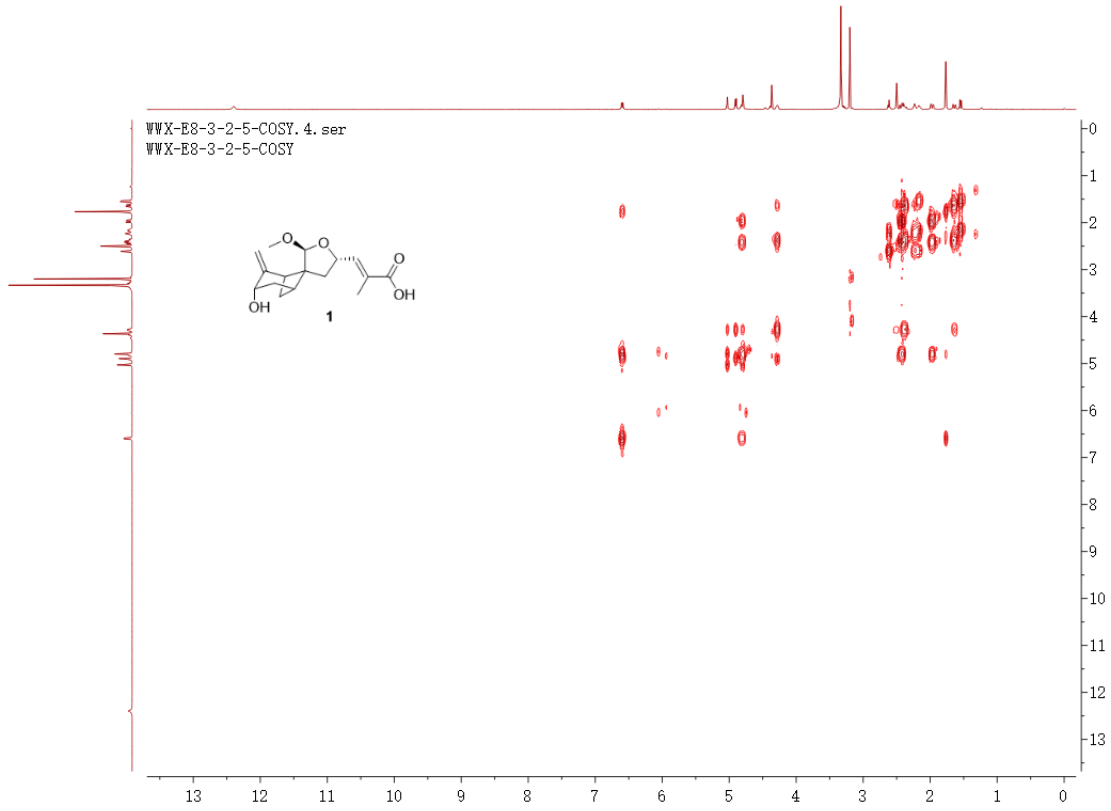


Figure S10 NOESY spectrum of brasilterpene A (**1**)

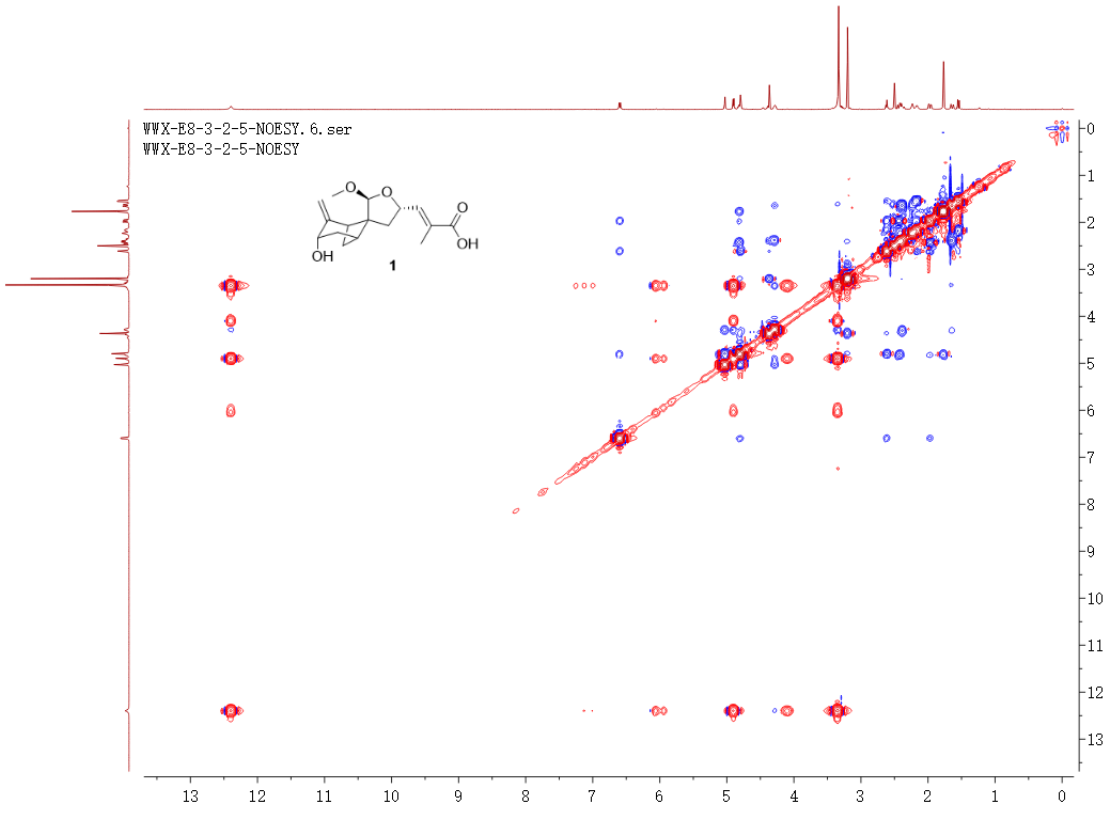


Figure S11 HRESIMS spectrum of brasilterpene B (**2**)

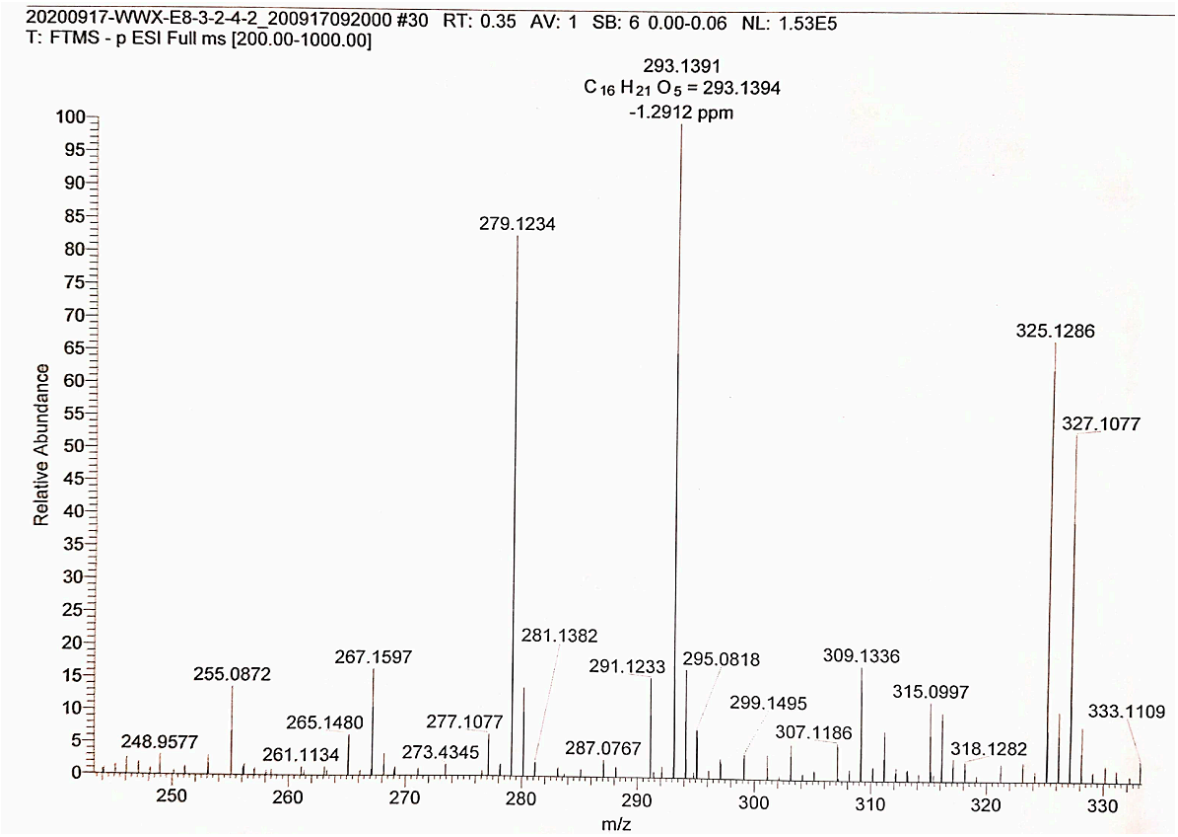


Figure S12 IR spectrum (KBr) of brasilterpene B (**2**)

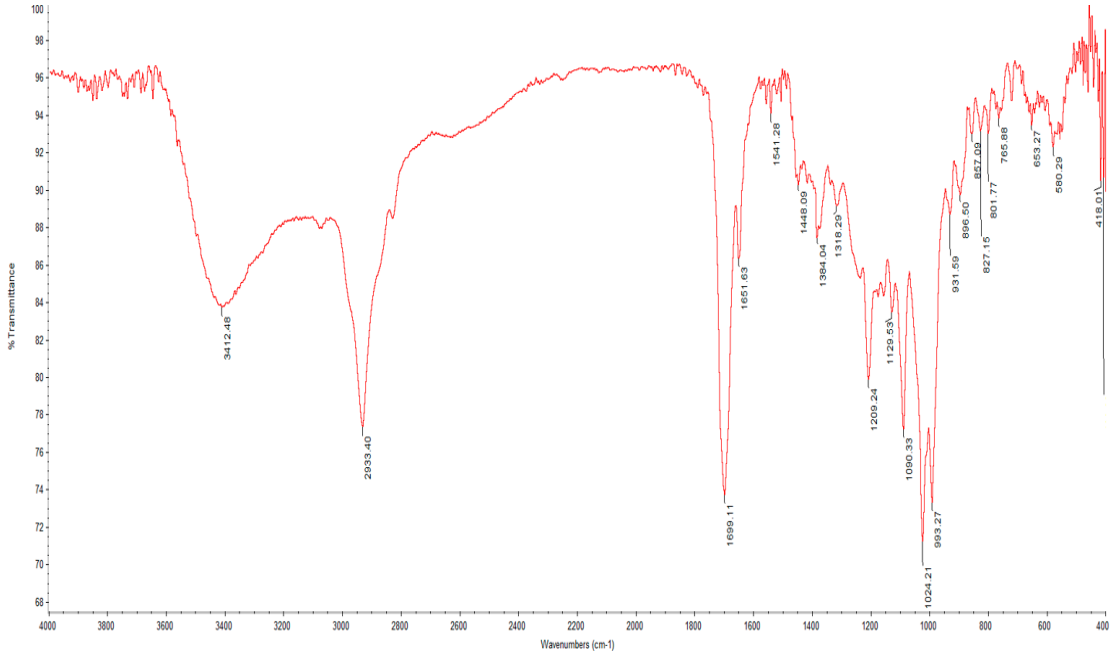


Figure S13 ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of brasilterpene B (**2**)

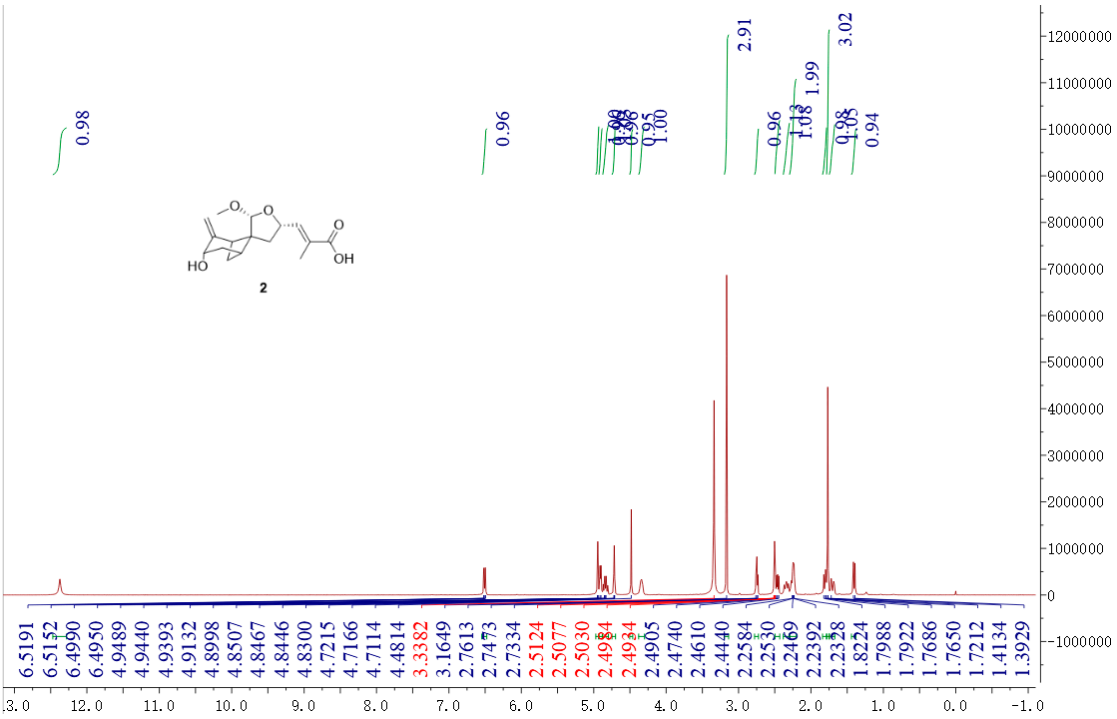


Figure S14 DEPTQ-NMR spectrum (DMSO-d_6, 125 MHz) of brasilterpene B (**2**)

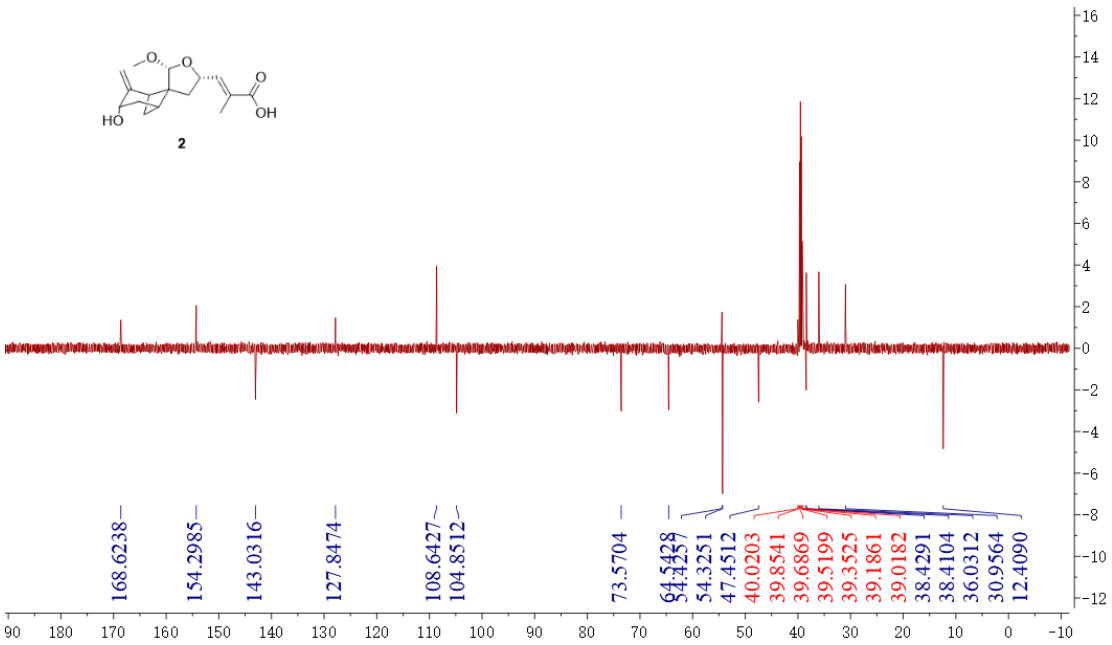


Figure S15 HSQC spectrum of brasilterpene B (**2**)

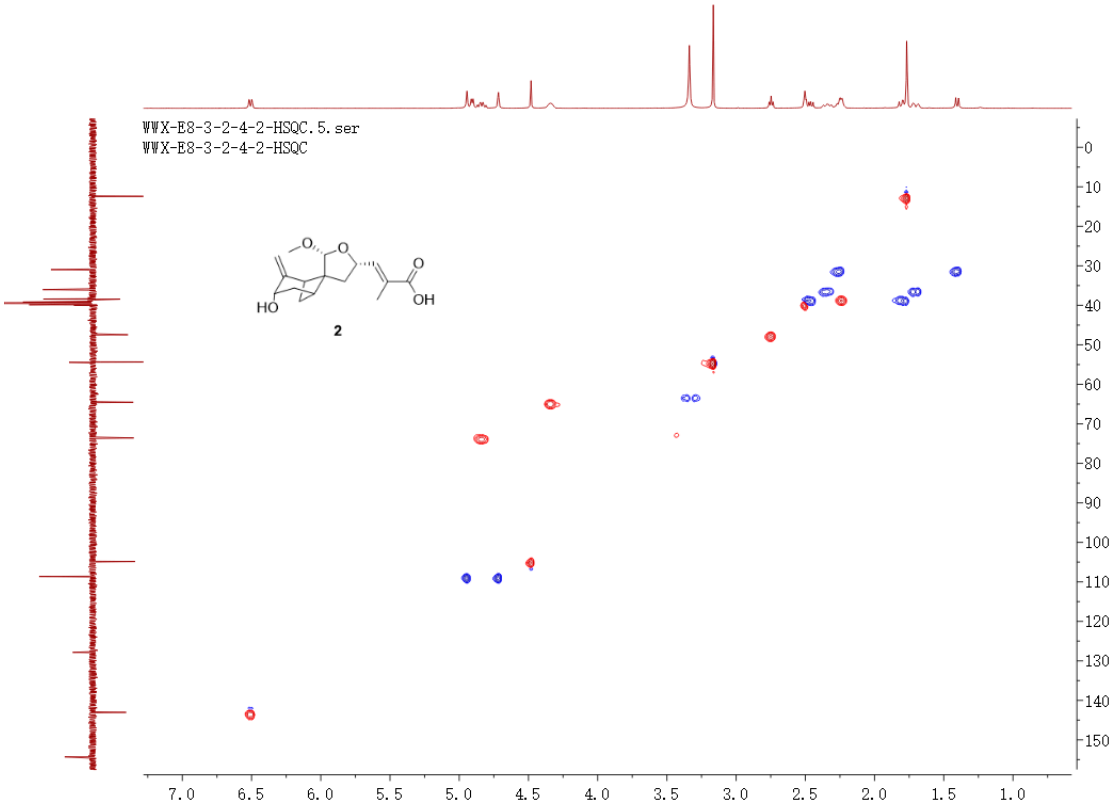


Figure S16 HMBC spectrum of brasilterpene B (**2**)

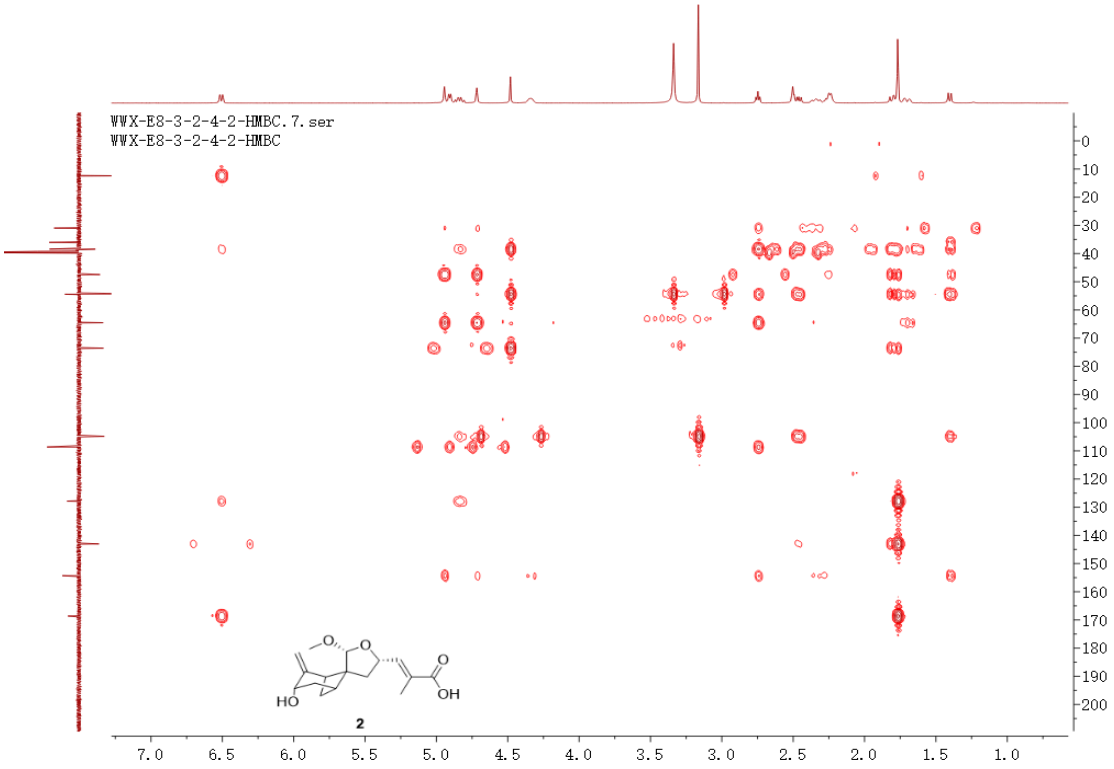


Figure S17 ^{1}H-^{1}H COSY spectrum of brasilterpene B (**2**)

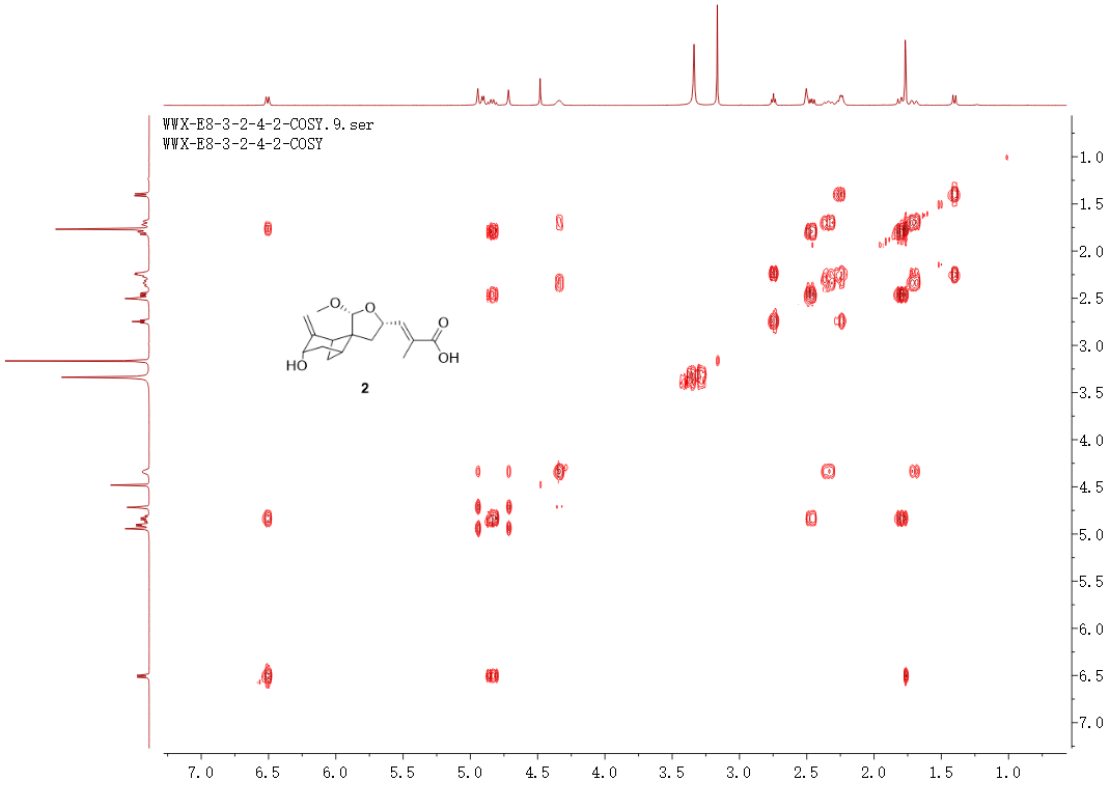


Figure S18 NOESY spectrum of brasilterpene B (**2**)

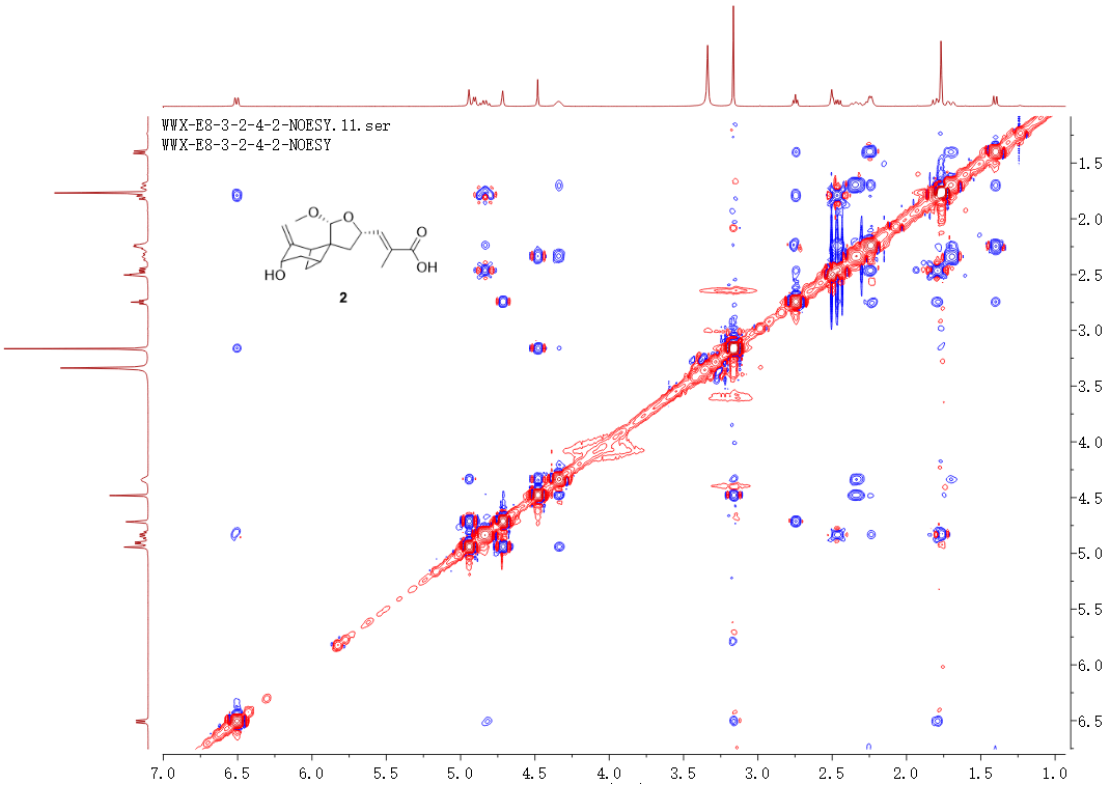


Figure S19 HRESIMS spectrum of brasilterpene C (**3**)

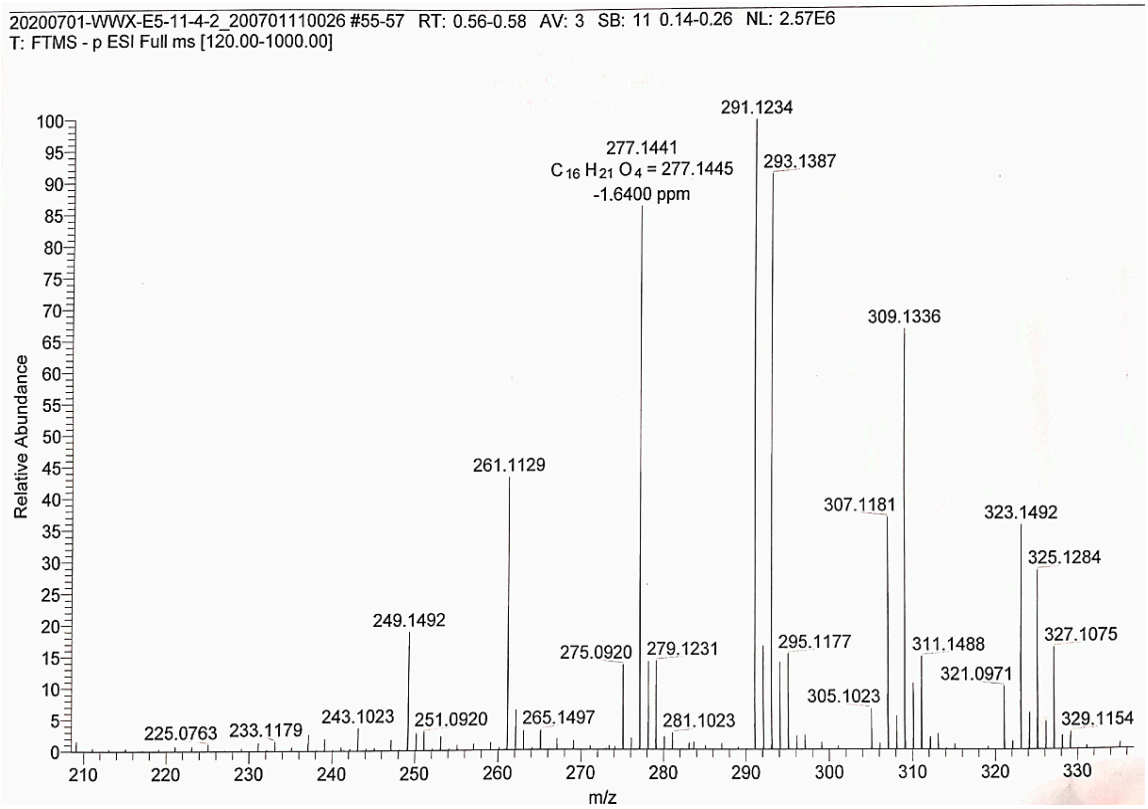


Figure S20 IR spectrum (KBr) of brasilterpene C (**3**)

Figure S21 ^{1}H NMR spectrum (DMSO-*d*$_6$, 500 MHz) of brasilterpene C (**3**)

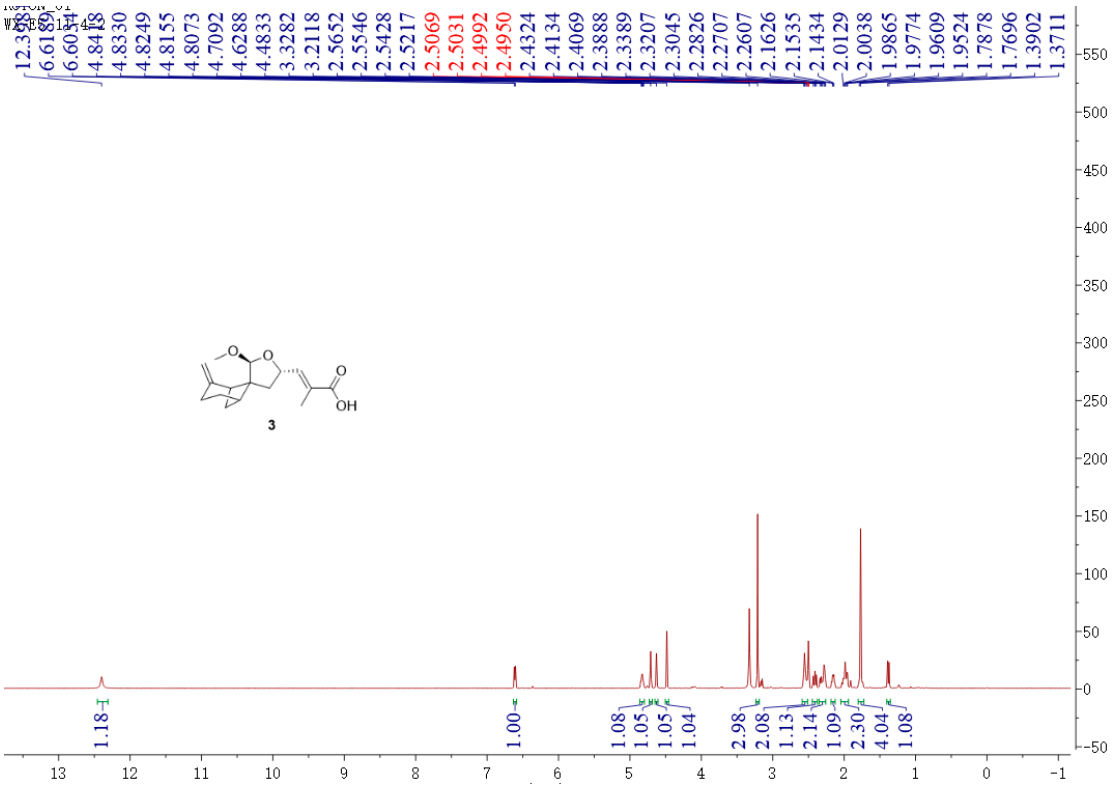


Figure S22 ^{13}C NMR spectrum (DMSO-*d*$_6$, 100 MHz) of brasilterpene C (**3**)

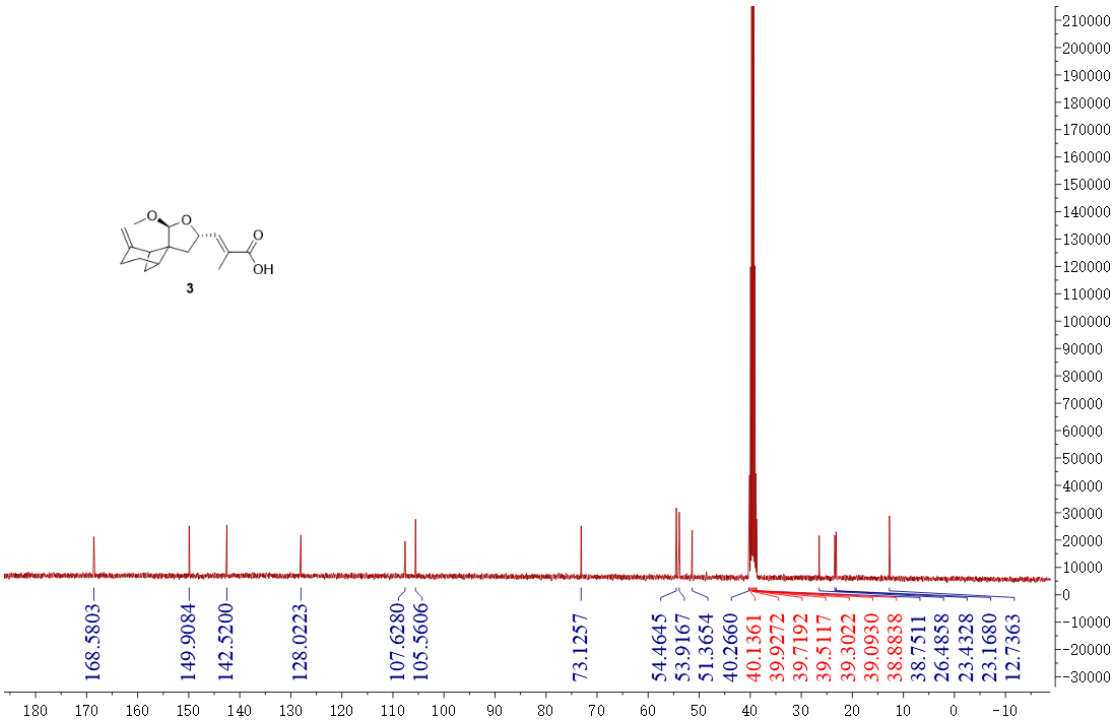


Figure S23 HSQC spectrum of brasilterpene C (**3**)

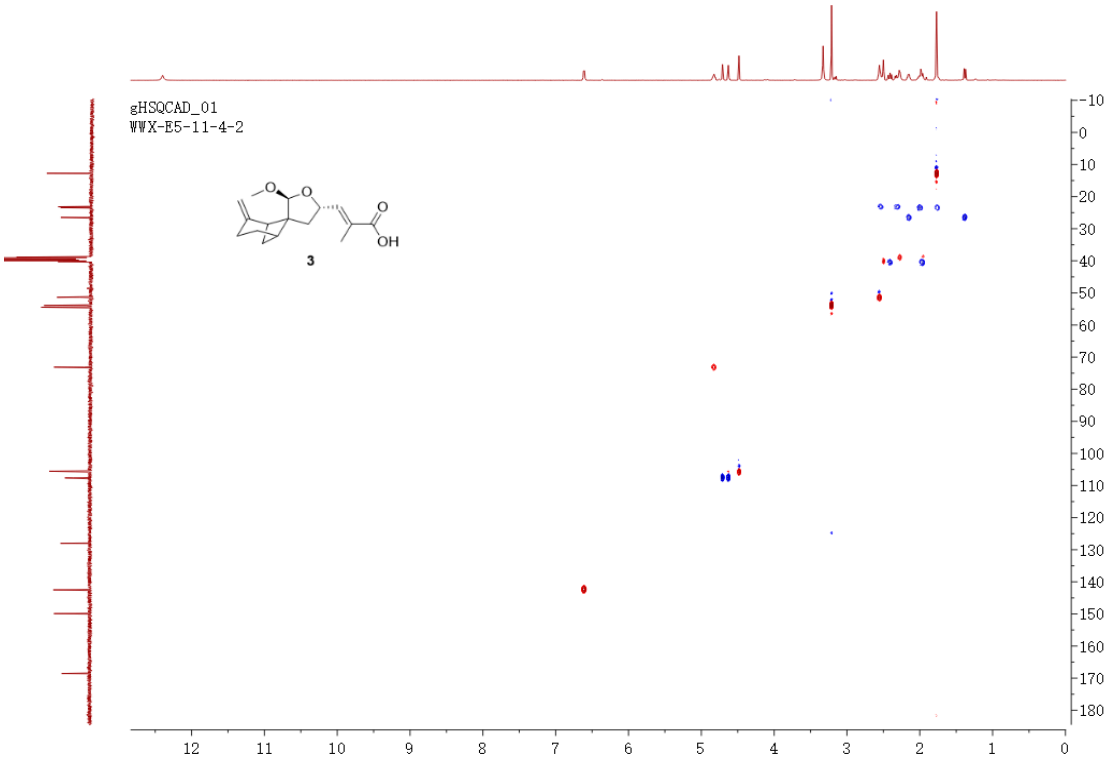


Figure S24 HMBC spectrum of brasilterpene C (**3**)

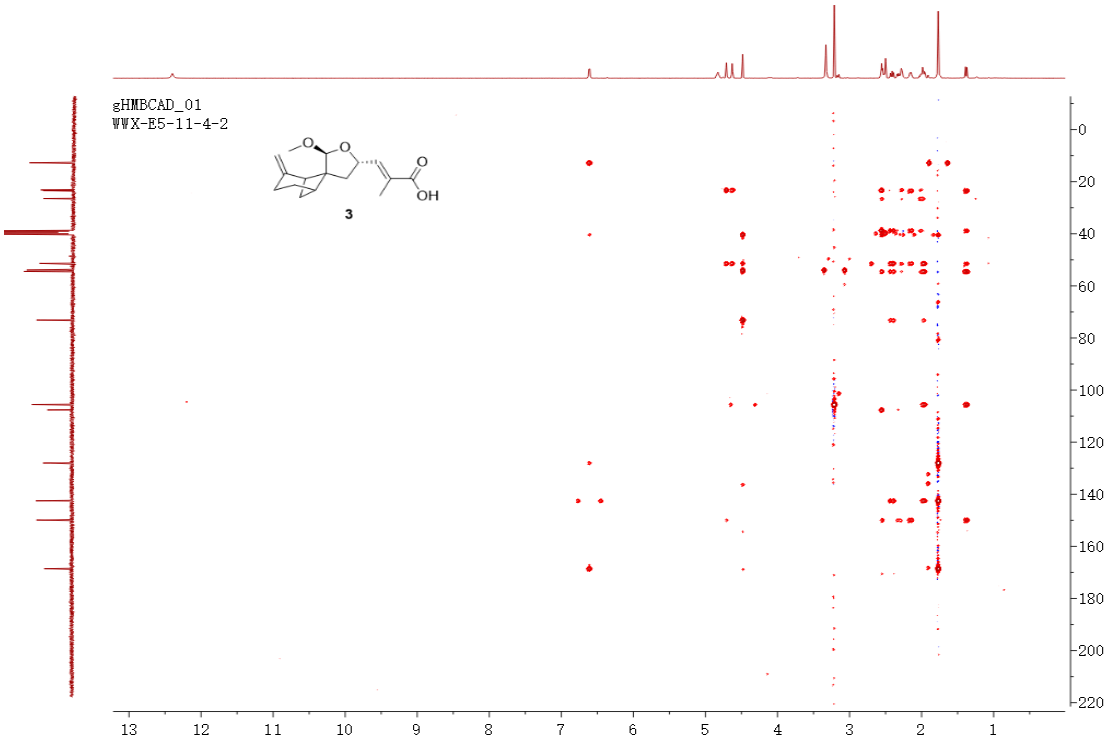


Figure S25 ^{1}H-^{1}H COSY spectrum of brasilterpene C (**3**)

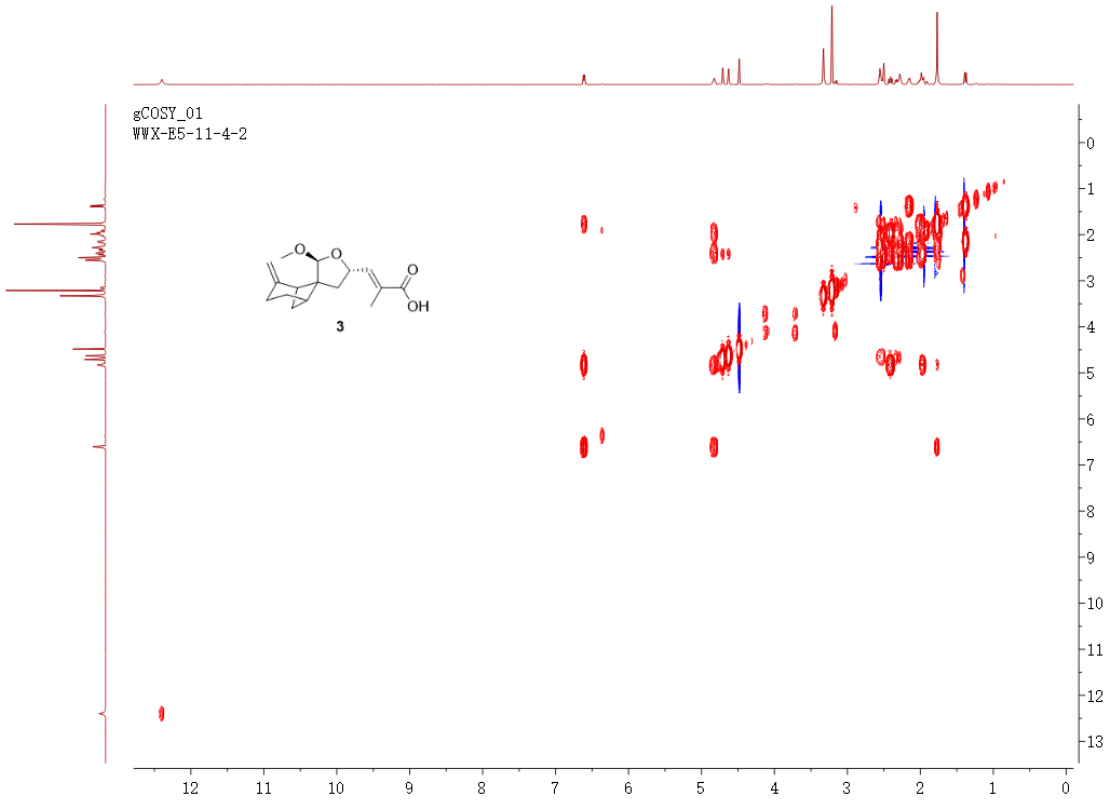


Figure S26 NOESY spectrum of brasilterpene C (**3**)

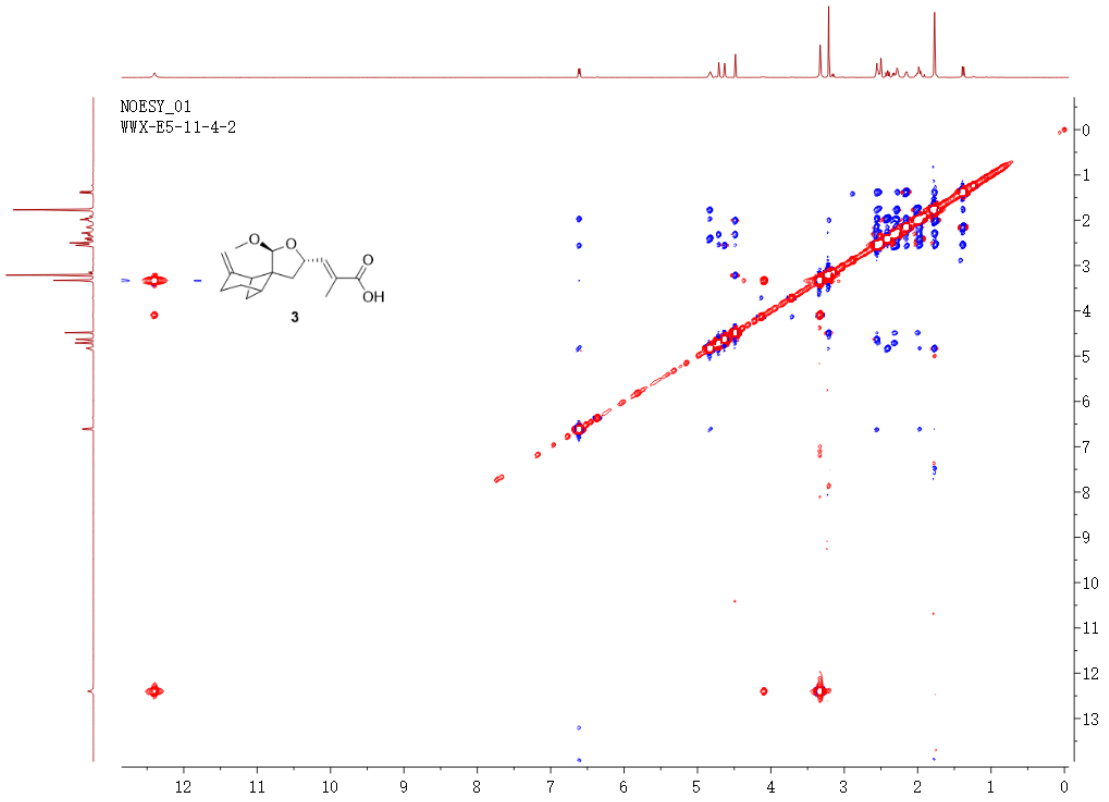


Figure S27 HRESIMS spectrum of brasilterpene D (**4**)

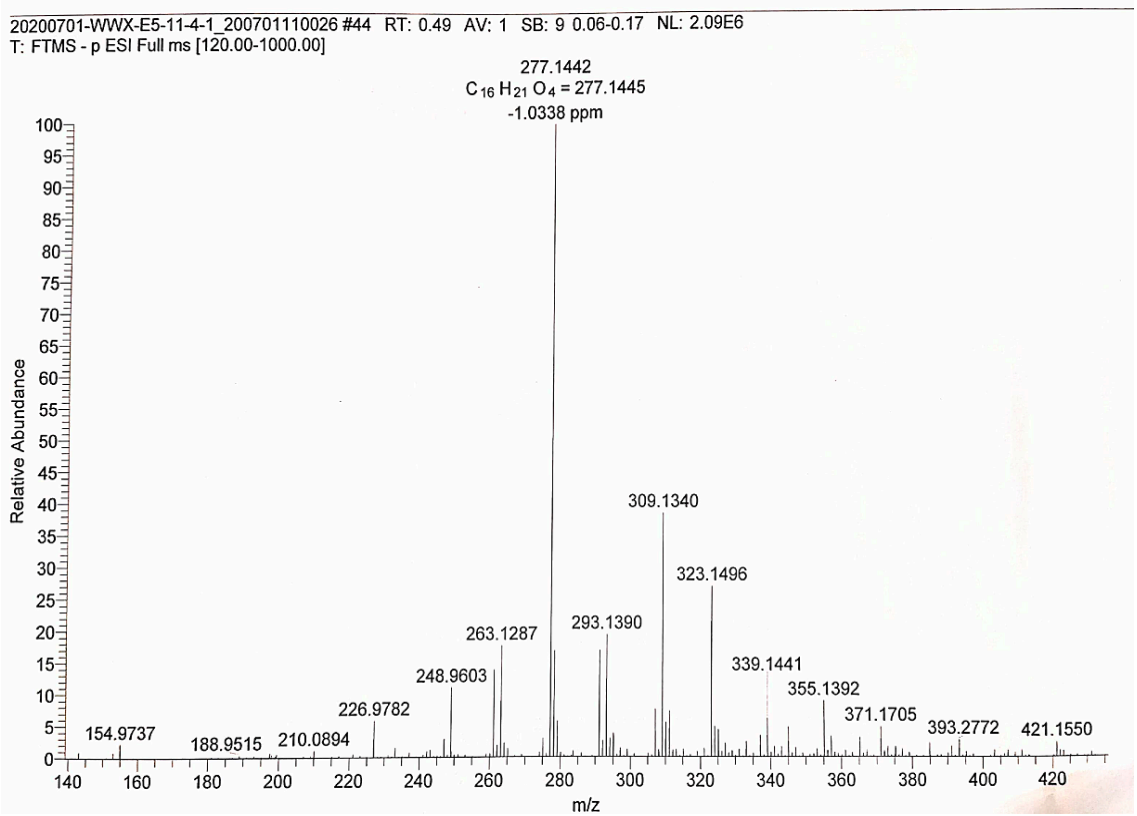


Figure S28 IR spectrum (KBr) of brasilterpene D (**4**)

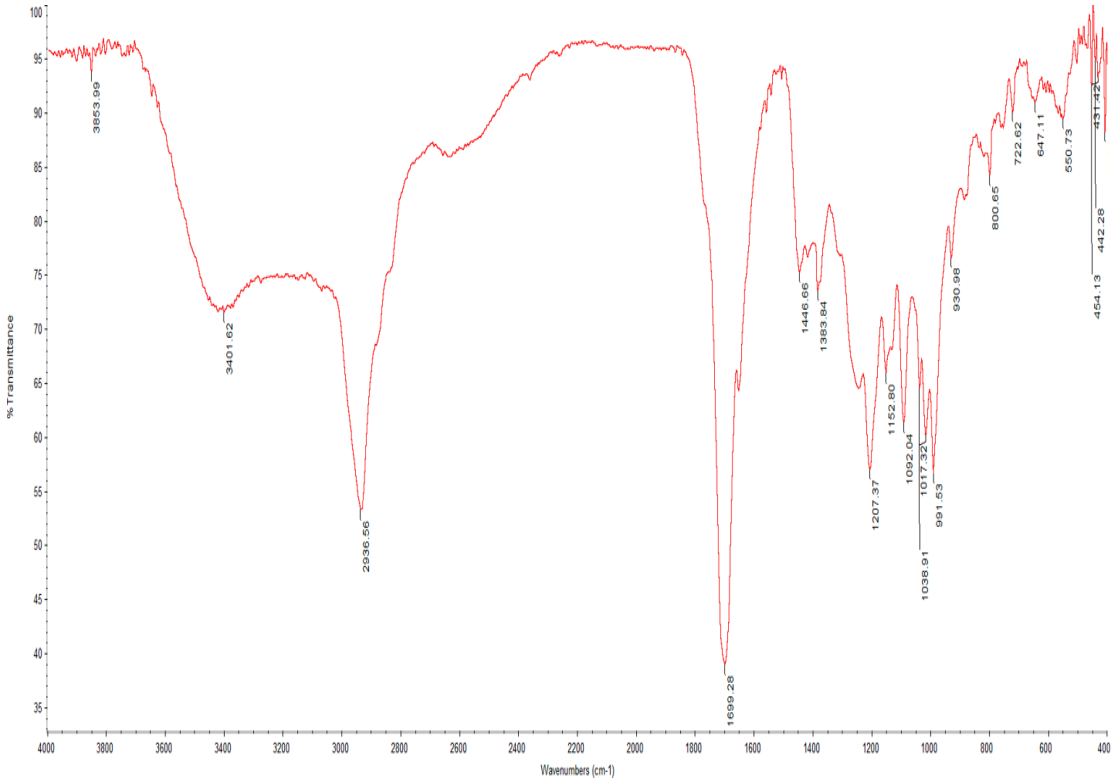


Figure S29 ^{1}H NMR spectrum (DMSO-*d*$_6$, 500 MHz) of brasilterpene D (4)

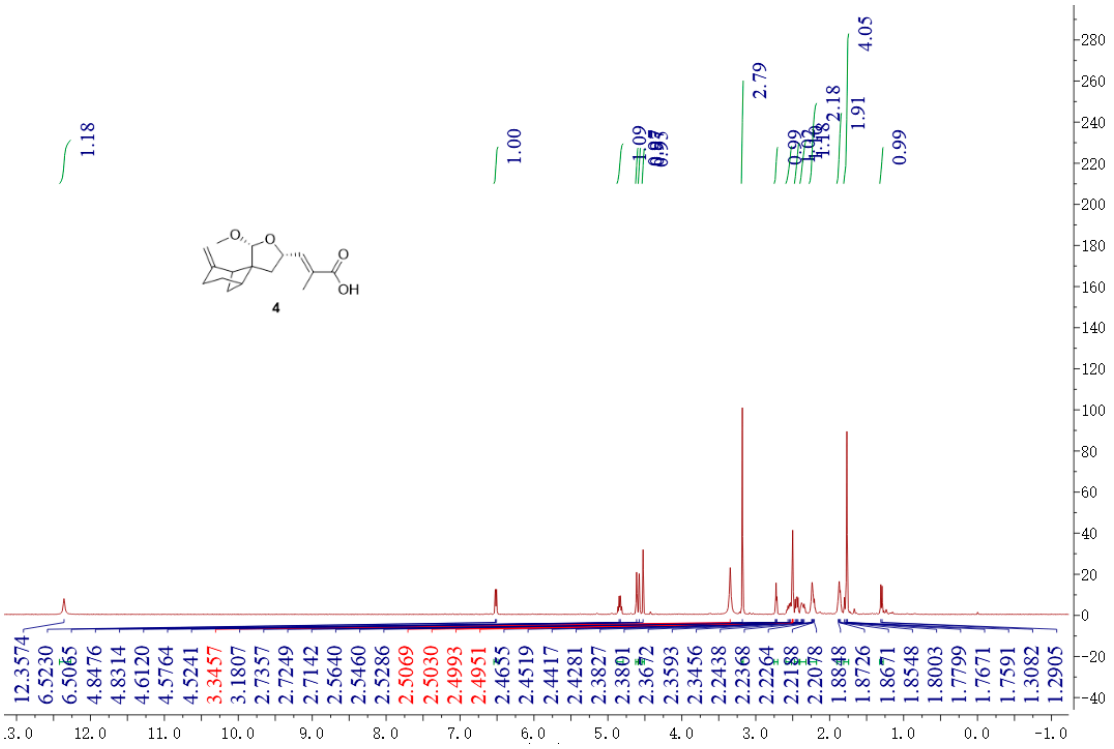


Figure S30 ^{13}C NMR spectrum (DMSO-d_6, 100 MHz) of brasilterpene D (**4**)

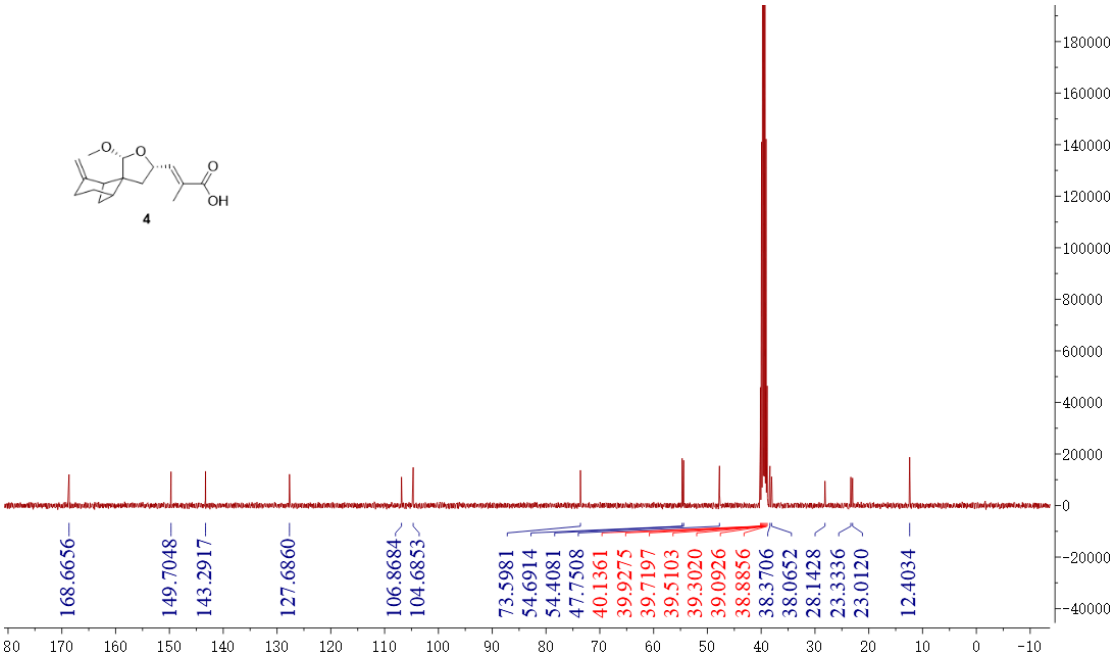


Figure S31 HSQC spectrum of brasilterpene D (**4**)

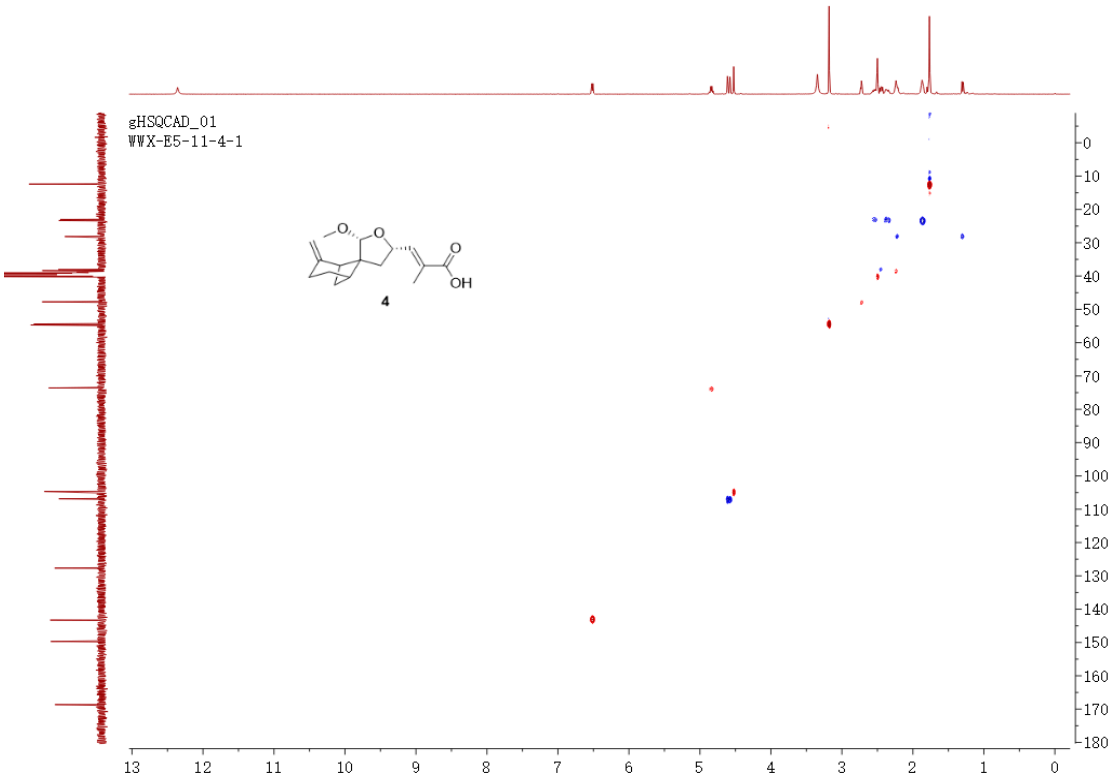


Figure S32 HMBC spectrum of brasilterpene D (**4**)

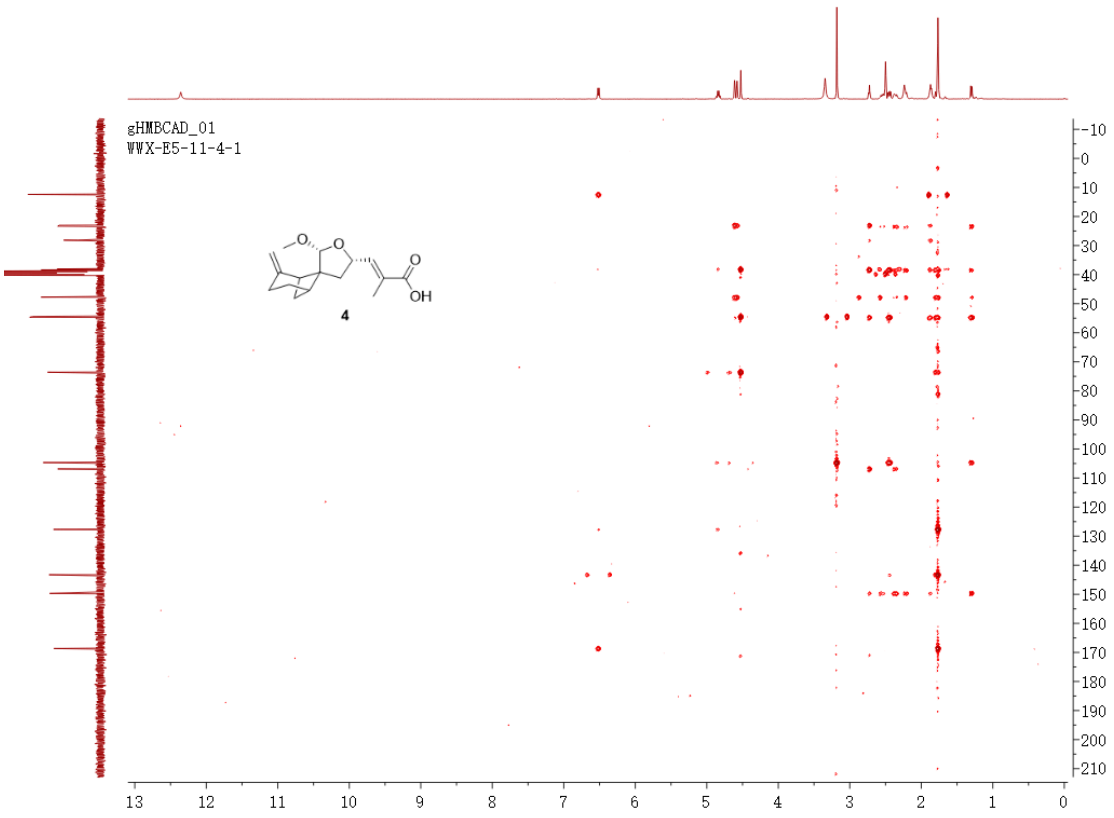


Figure S33 ^{1}H-^{1}H COSY spectrum of brasilterpene D (**4**)

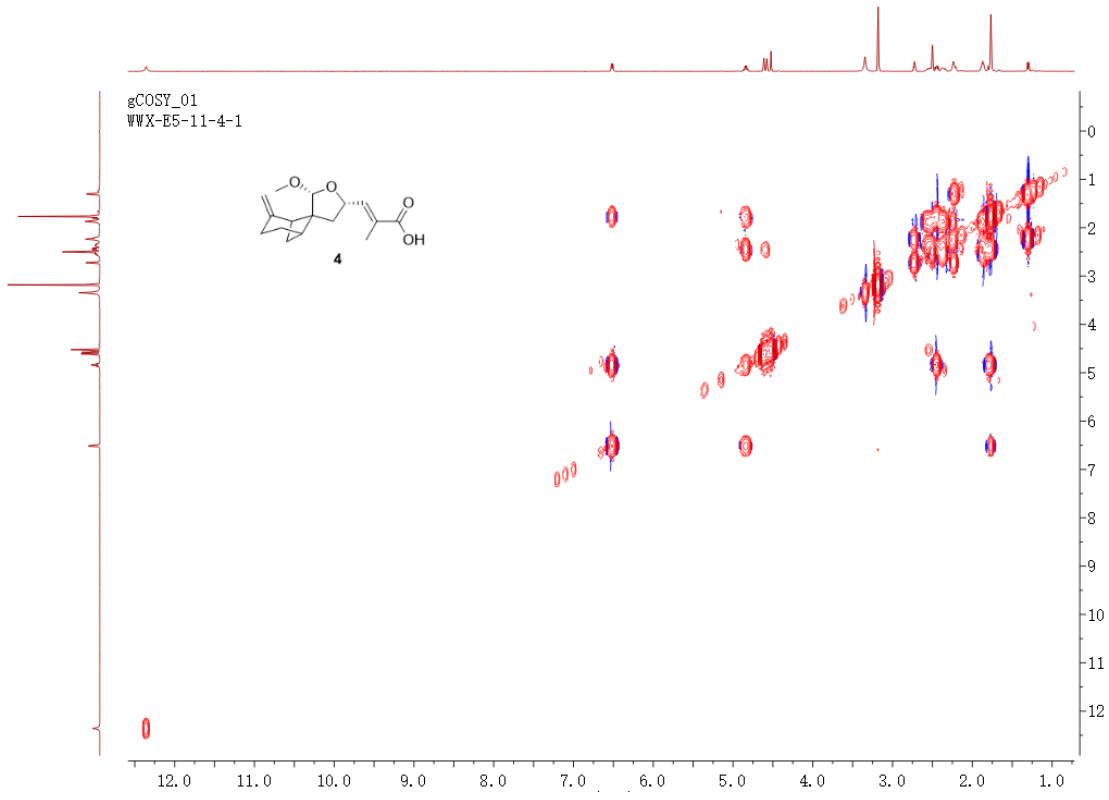


Figure S34 NOESY spectrum of brasilterpene D (**4**)

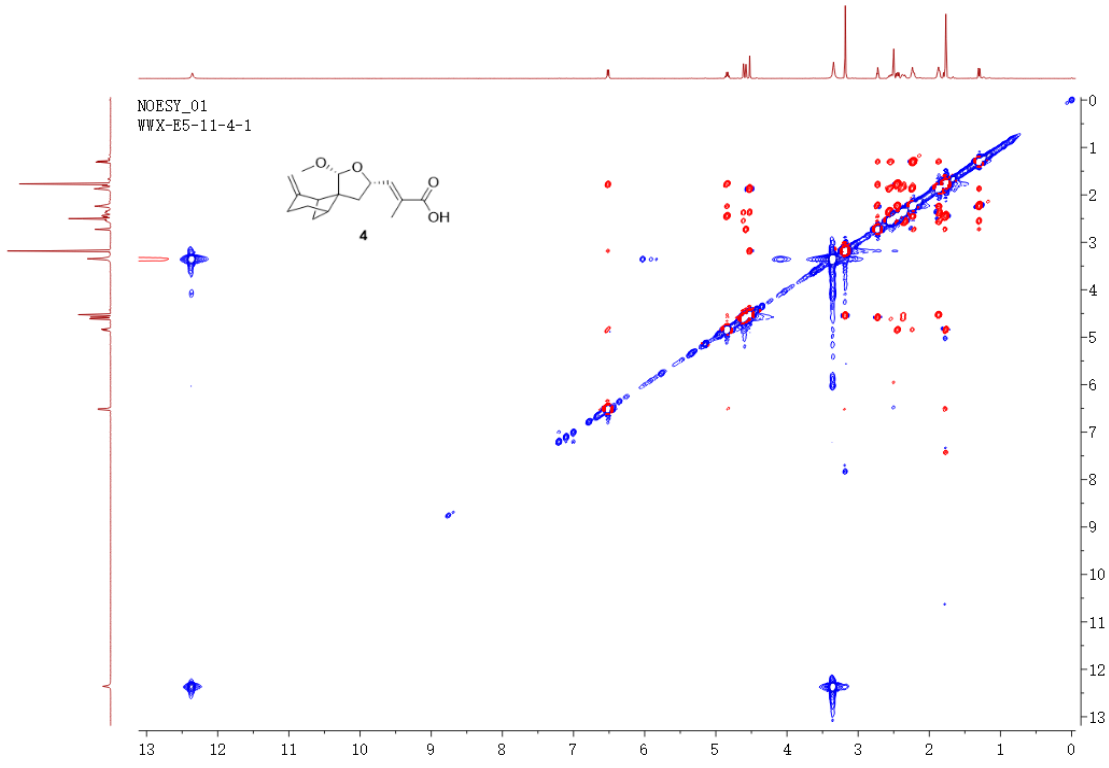


Figure S35 HRESIMS spectrum of brasilterpene E (**5**)

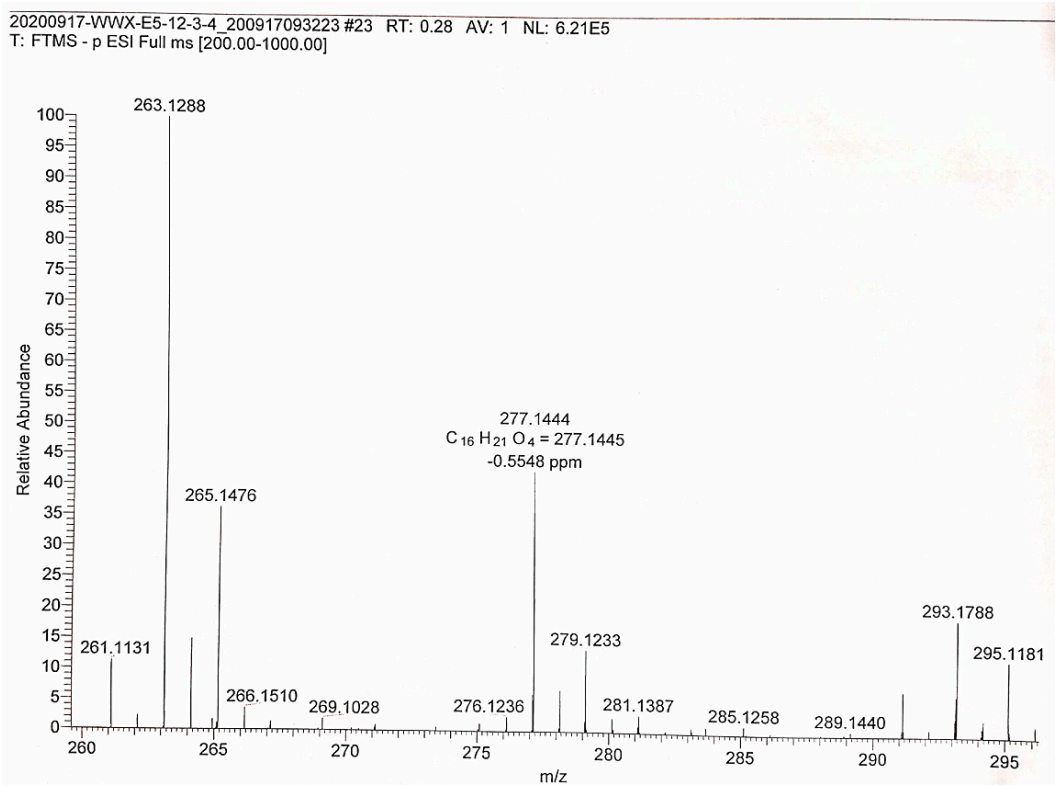


Figure S36 IR spectrum (KBr) of brasilterpene E (**5**)

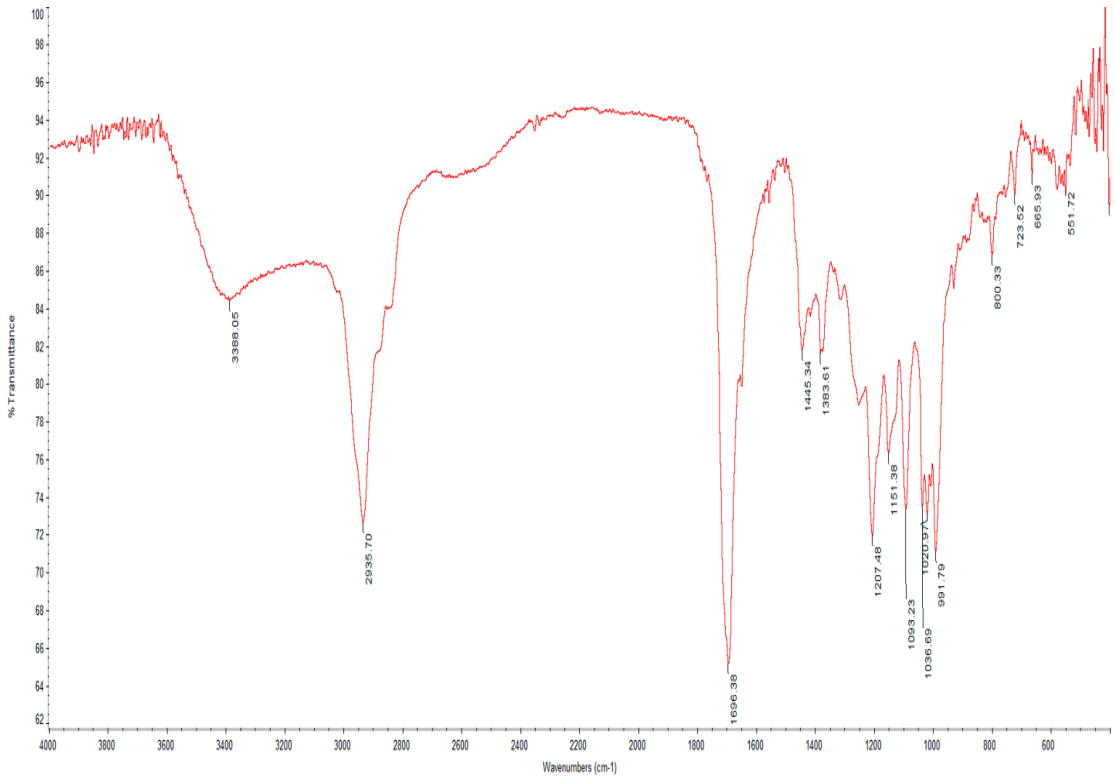


Figure S37 ^{1}H NMR spectrum (DMSO-d_6, 600 MHz) of brasilterpene E (**5**)

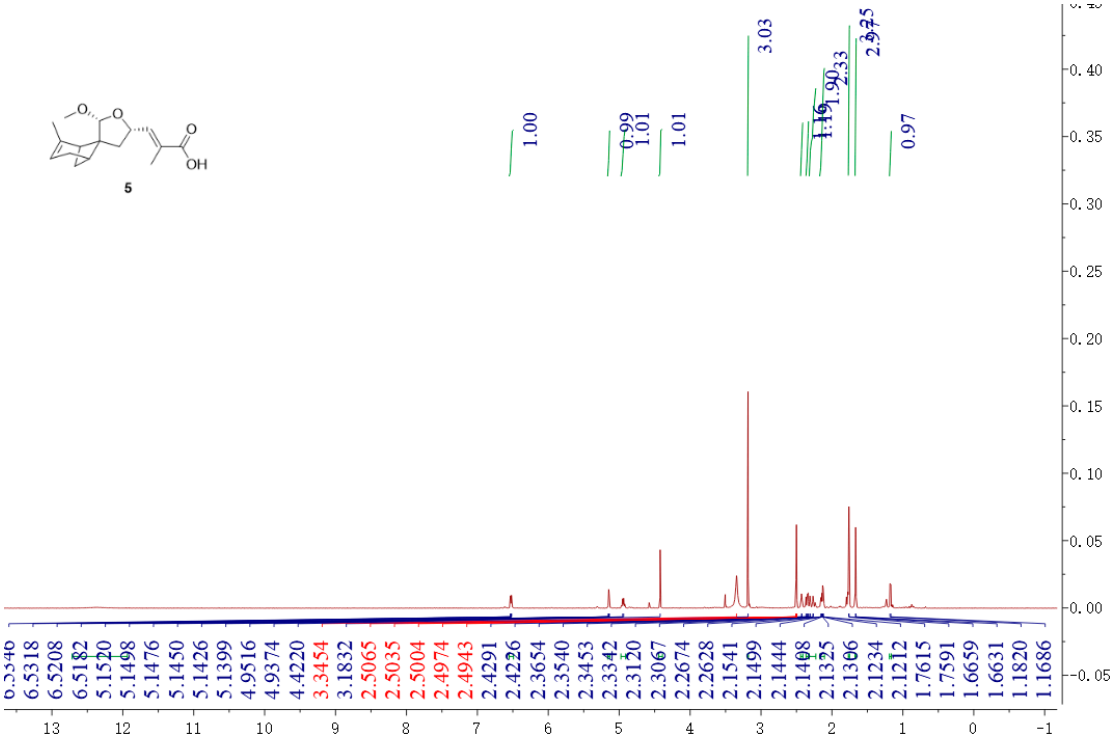


Figure S38 DEPTQ-NMR spectrum (DMSO-d_6, 100 MHz) of brasilterpene E (**5**)

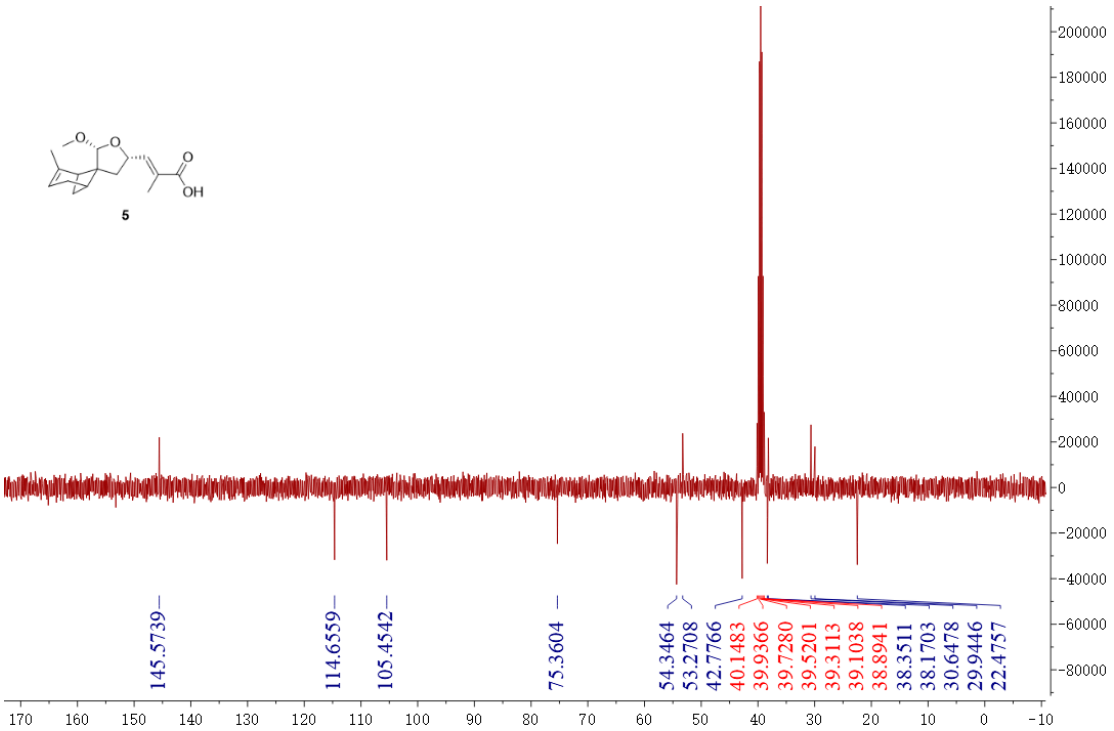


Figure S39 HSQC spectrum of brasilterpene E (**5**)

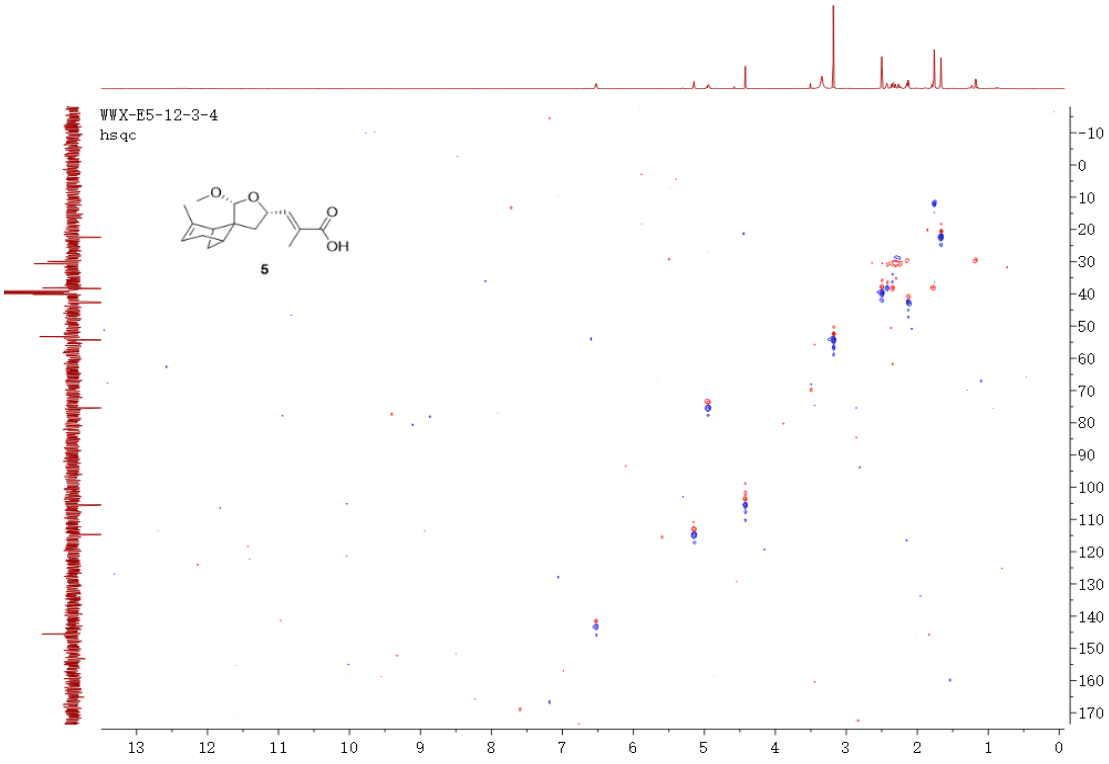


Figure S40 HMBC spectrum of brasilterpene E (**5**)

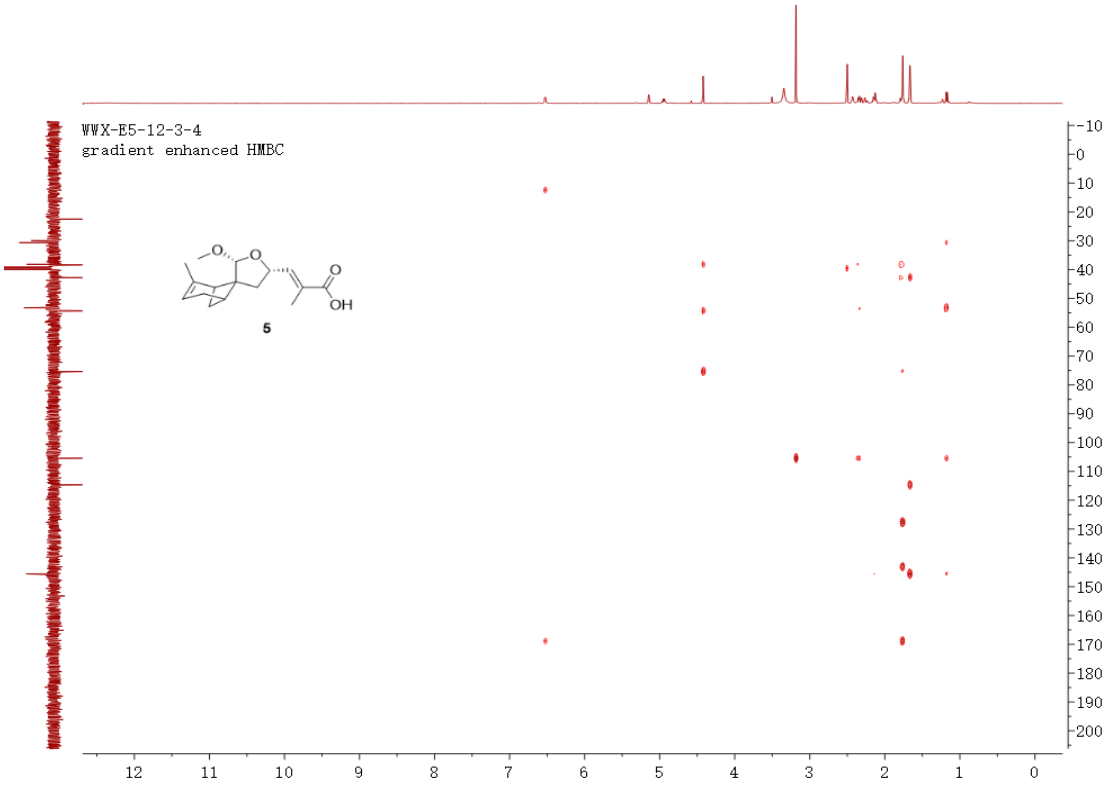


Figure S41 ^{1}H-^{1}H COSY spectrum of brasilterpene E (**5**)

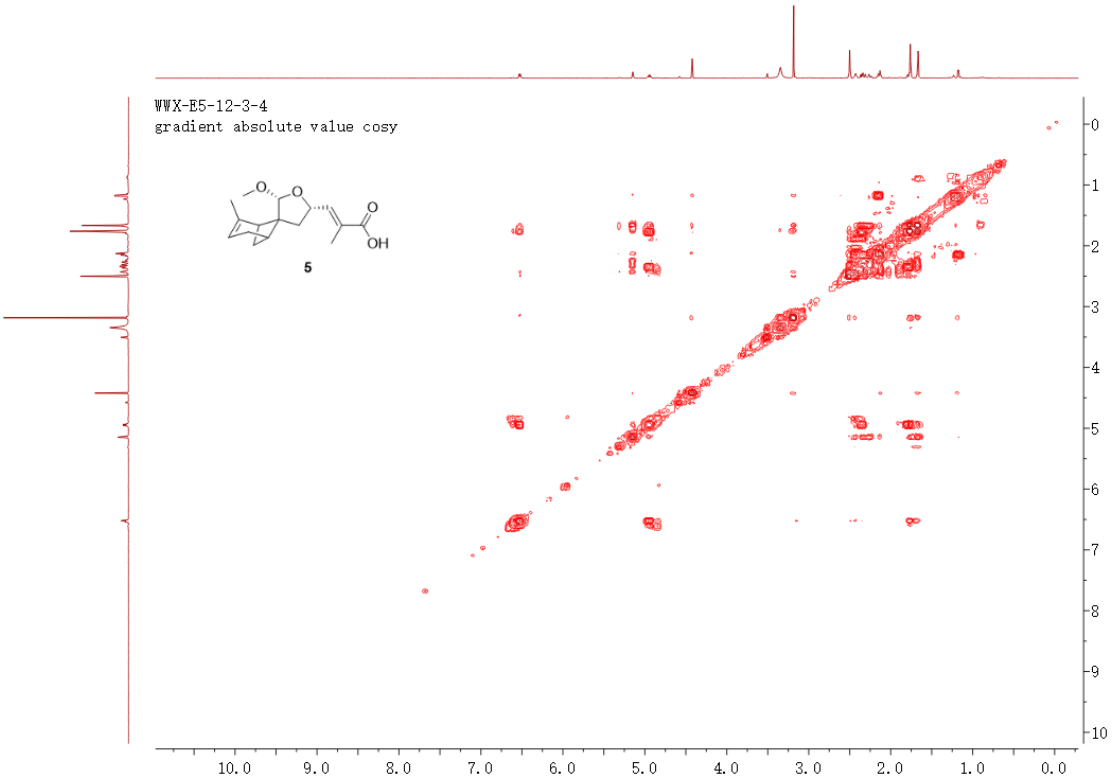


Figure S42 NOESY spectrum of brasilterpene E (**5**)

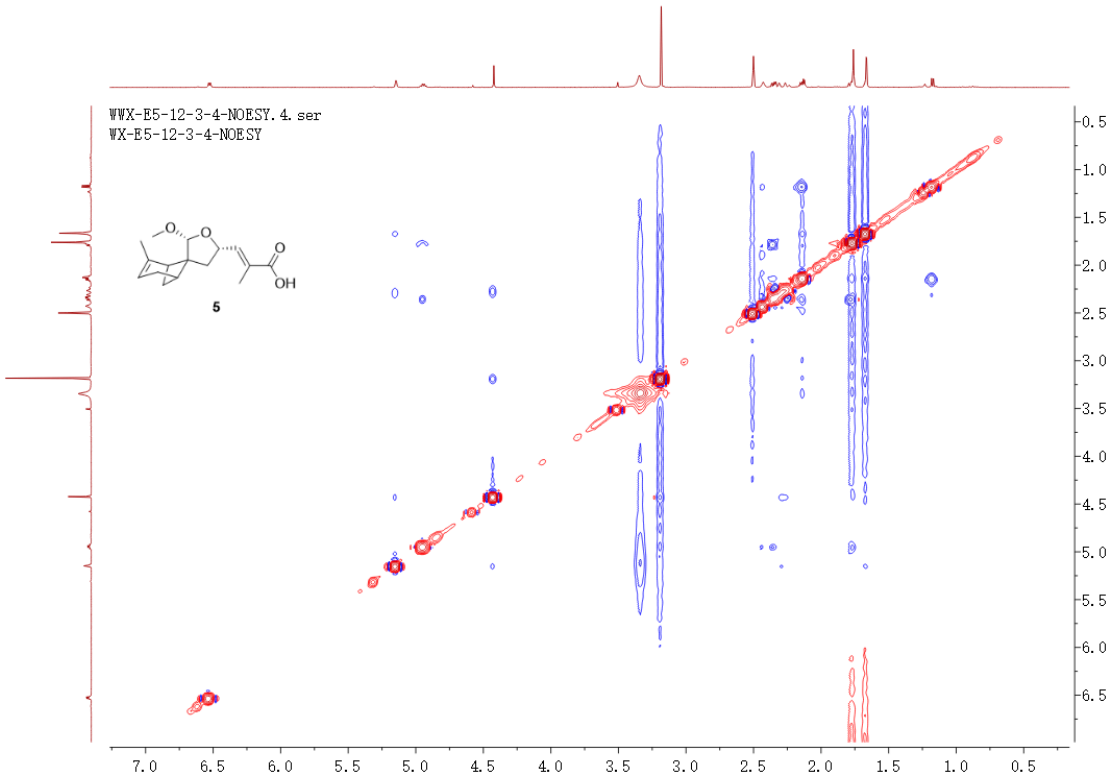
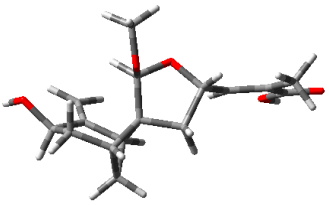
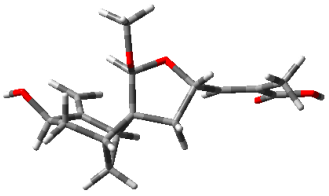


Figure S43 DFT-optimized structures for low-energy conformers of **1a** (1*S*,3*R*,5*R*,6*S*,9*S*,14*S*-**1**) at B3LYP/6-31+G(d) level in DMSO (PCM).

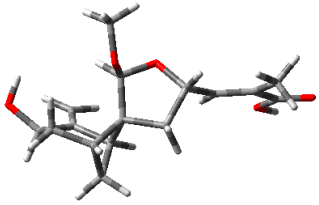
Conformer populations were calculated using the Gibbs free energy and Boltzmann population at 298 K estimated thereof.



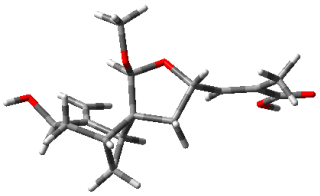
Conf. 1a-1 18.2%



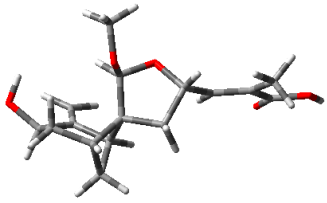
Conf. 1a-2 7.6%



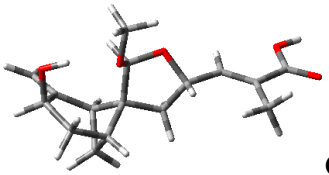
Conf. 1a-3 32.3%



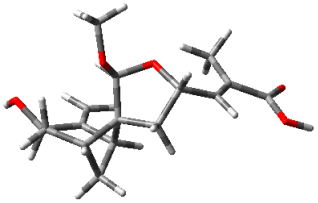
Conf. 1a-4 18.3%



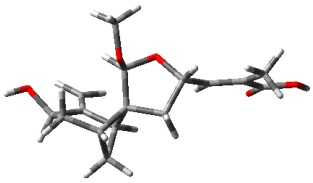
Conf. 1a-5 14.7%



Conf. 1a-6 0.2%



Conf. 1a-7 0.1%



Conf. 1a-8 8.6%

Table S1 Harmonic frequencies (cm**$^{-1}$) of compound **1a**.

Conformations	**Frequencies**		
	1	2	3
1a-1	19.0735	20.4381	46.8963
1a-2	19.4948	25.5870	48.7451
1a-3	18.9596	20.4157	50.4323
1a-4	19.3234	21.1288	51.8031
1a-5	18.8909	25.8729	51.0282
1a-6	20.7770	26.2576	48.7462
1a-7	17.3998	22.5128	55.2759
1a-8	20.1087	25.8532	52.0789

Table S2 Important thermodynamic parameters (a.u.) and Boltzmann distributions of the optimized compound **1a** at B3LYP/6-31G+(d) level of theory with PCM solvent model for DMSO.

Conformations	E+ZPE	G	%
1a-1	-998.681195	-998.732499	18.2%
1a-2	-998.680769	-998.731668	7.6%
1a-3	-998.681877	-998.733039	32.3%
1a-4	-998.681398	-998.732500	18.3%
1a-5	-998.681464	-998.732294	14.7%
1a-6	-998.677933	-998.728364	0.2%
1a-7	-998.676975	-998.727925	0.1%
1a-8	-998.681003	-998.731790	8.6%

E+ZPE, G: total energy with zero point energy (ZPE) and Gibbs free energy at B3LYP/6-31G+(d) level of theory with PCM solvent model for DMSO. %: Boltzmann distributions, using the relative Gibbs free energies as weighting factors.

Table S3 Cartesian coordinates of the low-energy re-optimized conformers of compound **1a** (1*S*,3*R*,5*R*,6*S*,9*S*,14*S*-**1**) calculated at B3LYP/6-31+G(d) level of theory with PCM solvent model for DMSO.

Conformer 1a-1		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z

1	C	-1.18068	-1.25636	1.99685
2	C	-2.55339	-0.64705	2.19793
3	C	-2.58844	0.88969	2.04016
4	C	-1.23468	1.45984	1.58704
5	C	-0.50818	0.69	0.41353
6	C	-0.09203	-0.31358	1.5682
7	C	-0.87564	-2.54167	2.23415
8	C	-0.08366	0.9451	2.49944
9	C	0.6513	1.41724	-0.26873
10	C	0.88581	0.58166	-1.52444
11	O	-0.31821	-0.15124	-1.7888
12	C	-1.29084	0.18441	-0.79233
13	O	-2.11544	1.25058	-1.26498
14	C	-3.07397	0.78761	-2.20575
15	C	1.98861	-0.42539	-1.36078
16	C	3.26016	-0.31453	-1.79705
17	C	4.23381	-1.41746	-1.58571
18	O	3.76483	-2.42782	-0.83462
19	C	3.83604	0.87653	-2.50538
20	O	5.3726	-1.44172	-2.01942
21	O	-3.44418	-1.20966	1.23664
22	H	-2.94147	-0.91116	3.18869
23	H	-3.37232	1.1948	1.33685
24	H	-2.84635	1.33999	3.00714
25	H	-1.27234	2.54888	1.47586
26	H	0.88732	-0.78892	1.45211
27	H	0.13096	-2.92687	2.09608
28	H	-1.62345	-3.24758	2.58237
29	H	0.83525	1.54148	2.46575
30	H	-0.32834	0.78456	3.55481
31	H	1.55081	1.53065	0.34423
32	H	0.33025	2.42466	-0.56322
33	H	1.06893	1.22782	-2.388
34	H	-1.89124	-0.7031	-0.58739
35	H	-3.66209	1.64462	-2.54495
36	H	-2.58257	0.3387	-3.07415
37	H	-3.7519	0.06603	-1.73955
38	H	1.68199	-1.33873	-0.85302
39	H	4.51717	-3.05377	-0.80192
40	H	4.76717	1.19585	-2.02415
41	H	4.05358	0.62861	-3.54946

42	H	3.16967	1.74282	-2.49695
43	H	-3.35488	-2.1755	1.29293

Conformer 1a-2		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z
1	C	-1.31627	-1.58881	1.70311
2	C	-2.63939	-0.93698	2.0496
3	C	-2.55465	0.59396	2.24198
4	C	-1.1576	1.14591	1.91477
5	C	-0.483	0.60556	0.59138
6	C	-0.15485	-0.6604	1.4879
7	C	-1.11272	-2.91395	1.64002
8	C	-0.05723	0.35277	2.6775
9	C	0.735	1.37463	0.07794
10	C	0.91332	0.82493	-1.33479
11	O	-0.34503	0.27631	-1.74833
12	C	-1.29432	0.44706	-0.68912
13	O	-2.03382	1.65126	-0.8976
14	C	-3.02273	1.4851	-1.9039
15	C	1.92281	-0.28452	-1.40865
16	C	3.1948	-0.20138	-1.84843
17	C	3.97861	-1.46204	-1.83552
18	O	5.15449	-1.33623	-2.47213
19	C	3.8826	1.04464	-2.31611
20	O	3.65308	-2.51905	-1.32501
21	O	-3.56405	-1.19839	0.9955
22	H	-3.05409	-1.38686	2.95931
23	H	-3.30758	1.10879	1.63351
24	H	-2.78408	0.83349	3.28808
25	H	-1.11049	2.23171	2.05111
26	H	0.78623	-1.17138	1.2606
27	H	-0.1374	-3.3338	1.40792
28	H	-1.91471	-3.62157	1.82647
29	H	0.90511	0.86913	2.7697
30	H	-0.32197	-0.02122	3.67223
31	H	1.63586	1.27766	0.69173
32	H	0.4954	2.44412	0.01917
33	H	1.16248	1.6306	-2.0315
34	H	-1.96061	-0.41681	-0.68412
35	H	-3.54231	2.4383	-2.03372

36	H	-2.56512	1.20681	-2.85798
37	H	-3.75536	0.73061	-1.60123
38	H	1.54485	-1.25527	-1.08603
39	H	5.55137	-2.22858	-2.39602
40	H	4.07301	0.99461	-3.39312
41	H	3.30157	1.94986	-2.12163
42	H	4.83916	1.17384	-1.79793
43	H	-3.54038	-2.1544	0.82333

Conformer 1a-3		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z
1	C	-1.00053	0.97991	2.23099
2	C	-0.39119	2.28381	2.70961
3	C	0.93417	2.61054	1.9856
4	C	1.58852	1.34483	1.40402
5	C	0.70361	0.56235	0.3492
6	C	-0.02451	-0.00033	1.64066
7	C	-2.30628	0.67247	2.24882
8	C	1.3815	0.10984	2.33015
9	C	1.39284	-0.48971	-0.51763
10	C	0.35203	-0.76809	-1.60141
11	O	-0.54223	0.35504	-1.6438
12	C	-0.09941	1.32865	-0.69642
13	O	0.77225	2.26913	-1.32614
14	C	0.07503	3.10613	-2.23882
15	C	-0.4824	-1.98344	-1.3148
16	C	-0.33315	-3.21454	-1.84547
17	C	-1.2653	-4.31466	-1.48383
18	O	-2.15234	-3.99017	-0.52852
19	C	0.74215	-3.62232	-2.80957
20	O	-1.25525	-5.43192	-1.97058
21	O	-1.30204	3.36009	2.5283
22	H	-0.19412	2.19675	3.78475
23	H	0.78141	3.35546	1.19584
24	H	1.6184	3.07851	2.70449
25	H	2.62253	1.52468	1.09186
26	H	-0.4075	-1.02381	1.57812
27	H	-2.68218	-0.27364	1.87058
28	H	-3.03749	1.36229	2.66239
29	H	2.0588	-0.72997	2.13586

30	H	1.39712	0.29228	3.40949
31	H	1.70969	-1.39185	0.01477
32	H	2.28765	-0.05542	-0.9815
33	H	0.82913	-0.83994	-2.58325
34	H	-0.96649	1.8526	-0.2846
35	H	0.79017	3.81232	-2.66932
36	H	-0.36169	2.51849	-3.05167
37	H	-0.70409	3.67436	-1.7215
38	H	-1.30005	-1.80524	-0.61791
39	H	-2.6768	-4.80973	-0.41701
40	H	0.31105	-3.82467	-3.79553
41	H	1.51828	-2.86249	-2.93126
42	H	1.2472	-4.52955	-2.45971
43	H	-1.62848	3.31093	1.61474

Conformer 1a-4		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z
1	C	-2.19149	-0.12839	1.38068
2	C	-2.419	1.06845	2.28135
3	C	-1.12574	1.86597	2.56724
4	C	0.13454	1.0521	2.23315
5	C	0.20952	0.52305	0.74451
6	C	-0.77076	-0.6014	1.28055
7	C	-3.13254	-0.72893	0.63637
8	C	-0.01995	-0.43977	2.6465
9	C	1.5591	0.02121	0.2373
10	C	1.33715	-0.0724	-1.27129
11	O	0.23409	0.78409	-1.60313
12	C	-0.23028	1.4205	-0.40868
13	O	0.41323	2.68859	-0.25417
14	C	-0.08039	3.63867	-1.18893
15	C	0.97272	-1.45692	-1.72597
16	C	1.79247	-2.36933	-2.28714
17	C	1.27265	-3.69408	-2.71648
18	O	-0.0097	-3.91469	-2.38286
19	C	3.26191	-2.18582	-2.52976
20	O	1.91789	-4.544	-3.30548
21	O	-3.37615	1.93249	1.67946
22	H	-2.83693	0.7083	3.22953
23	H	-1.1168	2.81531	2.01885

24	H	-1.11034	2.13685	3.63046
25	H	1.04531	1.54105	2.59443
26	H	-0.66317	-1.59435	0.83252
27	H	-2.90755	-1.56324	-0.02025
28	H	-4.16179	-0.38116	0.65972
29	H	0.92189	-0.99538	2.7237
30	H	-0.59208	-0.64266	3.55767
31	H	1.89816	-0.91987	0.68135
32	H	2.33162	0.77366	0.44098
33	H	2.21167	0.30107	-1.81222
34	H	-1.31337	1.55924	-0.46961
35	H	0.44245	4.58447	-1.02285
36	H	0.11215	3.31297	-2.21545
37	H	-1.15159	3.80485	-1.03888
38	H	-0.08024	-1.70261	-1.59457
39	H	-0.18738	-4.81012	-2.73695
40	H	3.46379	-2.1186	-3.60383
41	H	3.66506	-1.28777	-2.0548
42	H	3.82645	-3.03255	-2.1237
43	H	-3.54657	2.65114	2.3107

Conformer 1a-5		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z
1	C	-2.26785	-0.02308	1.42345
2	C	-2.50518	1.18209	2.31312
3	C	-1.22875	2.03269	2.49946
4	C	0.04427	1.21032	2.23198
5	C	0.14518	0.59358	0.77679
6	C	-0.8428	-0.49979	1.36288
7	C	-3.19556	-0.63986	0.67594
8	C	-0.10297	-0.25912	2.72627
9	C	1.50312	0.06337	0.32054
10	C	1.30643	-0.11709	-1.18412
11	O	0.20092	0.70916	-1.58017
12	C	-0.27363	1.41959	-0.43483
13	O	0.36541	2.69442	-0.34717
14	C	-0.06603	3.57269	-1.37778
15	C	0.95829	-1.52678	-1.56512
16	C	1.77947	-2.45385	-2.09868
17	C	1.17014	-3.77256	-2.40571

18	O	2.00383	-4.57108	-3.09184
19	C	3.24031	-2.27622	-2.37965
20	O	0.05262	-4.14864	-2.10008
21	O	-3.53991	2.0014	1.78462
22	H	-2.83739	0.82447	3.29501
23	H	-1.24769	2.92163	1.85806
24	H	-1.20925	2.41188	3.52894
25	H	0.94613	1.72851	2.57418
26	H	-0.73195	-1.51677	0.97366
27	H	-2.95607	-1.48978	0.04311
28	H	-4.23329	-0.31697	0.6927
29	H	0.84194	-0.8028	2.84177
30	H	-0.67924	-0.41745	3.64353
31	H	1.8347	-0.8509	0.82243
32	H	2.27278	0.82635	0.4936
33	H	2.18677	0.23373	-1.73048
34	H	-1.35539	1.55716	-0.51749
35	H	0.44258	4.53137	-1.24469
36	H	0.19632	3.17663	-2.36322
37	H	-1.14531	3.74135	-1.31261
38	H	-0.08734	-1.78965	-1.40125
39	H	1.47729	-5.38562	-3.23007
40	H	3.42364	-2.26946	-3.45905
41	H	3.64318	-1.34753	-1.96734
42	H	3.82016	-3.09075	-1.93188
43	H	-3.34989	2.13334	0.84119

Conformer 1a-6		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z
1	C	-2.95208	-0.28602	1.57667
2	C	-2.72501	1.03133	2.28879
3	C	-1.25562	1.28137	2.6946
4	C	-0.31581	0.21328	2.1133
5	C	-0.55789	-0.30862	0.62373
6	C	-1.73482	-1.12141	1.30394
7	C	-4.1565	-0.72684	1.18349
8	C	-0.8154	-1.19599	2.56257
9	C	0.60105	-1.15378	0.07396
10	C	1.18468	-0.23375	-0.98156
11	O	0.02307	0.31152	-1.61145

12	C	-0.91496	0.60444	-0.56319
13	O	-0.82127	1.9742	-0.17351
14	C	-1.06811	2.85294	-1.2693
15	C	1.9803	-0.96269	-2.01689
16	C	3.31764	-0.93116	-2.18978
17	C	3.95818	-1.69345	-3.29423
18	O	3.10914	-2.46273	-3.99496
19	C	4.29091	-0.17284	-1.33533
20	O	5.14533	-1.666	-3.56917
21	O	-3.16946	2.07894	1.4305
22	H	-3.35196	1.07457	3.18683
23	H	-0.92045	2.28194	2.39914
24	H	-1.17919	1.24964	3.78934
25	H	0.72906	0.42427	2.36658
26	H	-1.95516	-2.09295	0.84837
27	H	-4.29169	-1.67408	0.67195
28	H	-5.04637	-0.12834	1.36199
29	H	-0.06219	-1.99202	2.53356
30	H	-1.31348	-1.25859	3.53602
31	H	0.20474	-2.07073	-0.38101
32	H	1.35086	-1.43565	0.81977
33	H	1.73441	0.59823	-0.52923
34	H	-1.91894	0.3972	-0.94963
35	H	-1.08145	3.87662	-0.8853
36	H	-0.27149	2.77746	-2.015
37	H	-2.03978	2.63975	-1.72524
38	H	1.37116	-1.5563	-2.69812
39	H	3.68209	-2.88206	-4.66921
40	H	4.72754	0.65606	-1.90213
41	H	3.83736	0.24068	-0.43133
42	H	5.10227	-0.8299	-1.00281
43	H	-2.4307	2.27145	0.8233

Conformer 1a-7		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z
1	C	-1.71226	-0.07967	1.38357
2	C	-2.2423	1.33115	1.53836
3	C	-1.15172	2.38298	1.84269
4	C	0.26406	1.78531	1.79526
5	C	0.58106	0.83277	0.57504

6	C	-0.21885	-0.23614	1.43113
7	C	-2.48033	-1.17442	1.26929
8	C	0.35454	0.50985	2.68227
9	C	2.05092	0.49983	0.31921
10	C	1.99664	-0.17941	-1.04945
11	O	0.85604	0.34506	-1.72799
12	C	0.1163	1.18514	-0.8329
13	O	0.4474	2.55222	-1.07988
14	C	-0.1959	3.03968	-2.24878
15	C	1.94379	-1.68475	-0.93222
16	C	1.05848	-2.57368	-1.43398
17	C	1.20181	-4.02284	-1.12849
18	O	2.34038	-4.33722	-0.48628
19	C	-0.10954	-2.22992	-2.31187
20	O	0.39504	-4.89194	-1.40934
21	O	-2.89053	1.70541	0.32423
22	H	-2.99921	1.36527	2.33076
23	H	-1.21918	3.23048	1.15038
24	H	-1.3211	2.78912	2.84804
25	H	1.029	2.5401	2.00704
26	H	0.12161	-1.27216	1.33725
27	H	-2.05189	-2.16922	1.18074
28	H	-3.56414	-1.11028	1.2681
29	H	1.37077	0.21823	2.97102
30	H	-0.25692	0.49931	3.59082
31	H	2.52662	-0.11362	1.09022
32	H	2.62815	1.42995	0.23871
33	H	2.89112	0.07551	-1.62909
34	H	-0.94749	1.0107	-1.00163
35	H	0.10724	4.07953	-2.39788
36	H	0.10326	2.46168	-3.12829
37	H	-1.28327	3.01052	-2.12897
38	H	2.77091	-2.06937	-0.33453
39	H	2.27676	-5.30863	-0.37858
40	H	-0.91254	-1.77752	-1.72169
41	H	0.18412	-1.54633	-3.11448
42	H	-0.52592	-3.10957	-2.81355
43	H	-3.53293	1.0069	0.11574

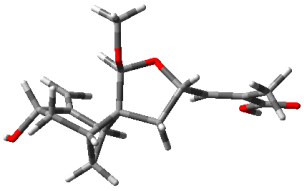
Conformer 1a-8	Standard Orientation (Ångstroms)

I	Atom	X	Y	Z
1	C	-2.23393	-0.45057	1.33805
2	C	-3.16276	0.74415	1.40681
3	C	-2.44569	2.08646	1.1341
4	C	-0.91957	1.95712	1.26219
5	C	-0.26436	0.85617	0.33459
6	C	-0.7706	-0.14044	1.45858
7	C	-2.61514	-1.71738	1.11418
8	C	-0.52021	1.04233	2.45537
9	C	1.24909	0.90301	0.13984
10	C	1.46592	-0.04263	-1.04033
11	O	0.2216	-0.15046	-1.74687
12	C	-0.74775	0.68155	-1.10227
13	O	-0.76792	1.97013	-1.72326
14	C	-1.37951	1.91858	-3.00522
15	C	1.85314	-1.43	-0.61633
16	C	3.08583	-1.97608	-0.64186
17	C	3.19074	-3.38473	-0.18521
18	O	4.40152	-3.91076	-0.43287
19	C	4.3456	-1.28194	-1.06078
20	O	2.3218	-4.04333	0.35765
21	O	-4.2124	0.57659	0.46053
22	H	-3.61056	0.77204	2.40788
23	H	-2.70796	2.48159	0.14559
24	H	-2.80766	2.82887	1.8565
25	H	-0.42294	2.93282	1.24016
26	H	-0.14418	-1.01768	1.6489
27	H	-1.90266	-2.53316	1.04091
28	H	-3.66511	-1.96501	0.98416
29	H	0.51782	1.151	2.79065
30	H	-1.15548	1.0875	3.34595
31	H	1.83655	0.63102	1.0223
32	H	1.55118	1.91695	-0.15192
33	H	2.1992	0.37579	-1.73589
34	H	-1.73429	0.21617	-1.1809
35	H	-1.36846	2.92621	-3.42953
36	H	-0.82551	1.25506	-3.67585
37	H	-2.42005	1.59006	-2.92178
38	H	1.01712	-2.04412	-0.27941
39	H	4.32326	-4.82753	-0.09653
40	H	4.71712	-1.69978	-2.00211

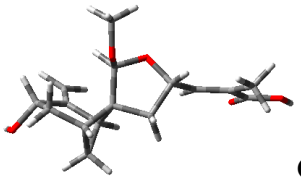
41	H	4.21182	-0.20643	-1.20277
42	H	5.12175	-1.3986	-0.29644
43	H	-4.82634	1.31946	0.58324

Figure S44 DFT-optimized structures for low-energy conformers of **1b** (1*S*,3*S*,5*R*,6*S*,9*S*,14*S*-**1**) at B3LYP/6-31+G(d) level in DMSO (PCM).

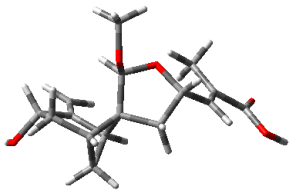
Conformer populations were calculated using the Gibbs free energy and Boltzmann population at 298 K estimated thereof.



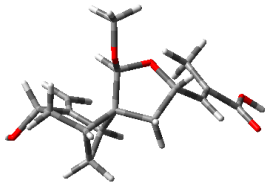
Conf. 1b-1 55.7%



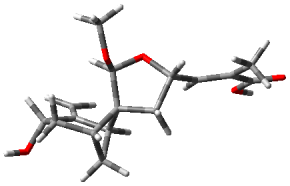
Conf. 1b-2 31.6%



Conf. 1b-3 1.55%



Conf. 1b-4 0.7%



Conf. 1b-5 10.4%

Table S4 Harmonic frequencies (cm**$^{-1}$) of compound **1b**.

Conformations	**Frequencies**		
	1	2	3
1b-1	21.7274	26.1484	51.5239
1b-2	22.0726	26.3038	51.6332
1b-3	11.3854	25.0126	56.9492

1b-4	12.5742	26.1711	57.0078
1b-5	20.2057	25.3751	51.0603

Table S5 Important thermodynamic parameters (a.u.) and Boltzmann distributions of the optimized compound **1b** at B3LYP/6-31G+(d) level of theory with PCM solvent model for DMSO.

Conformations	E+ZPE	G	%
1b-1	-998.681927	-998.732670	55.7%
1b-2	-998.681532	-998.732136	31.6%
1b-3	-998.677949	-998.729289	1.5%
1b-4	-998.677605	-998.728595	0.7%
1b-5	-998.680205	-998.731088	10.4%

E+ZPE, G: total energy with zero point energy (ZPE) and Gibbs free energy at B3LYP/6-31G+(d) level of theory with PCM solvent model for DMSO. %: Boltzmann distributions, using the relative Gibbs free energies as weighting factors

Table S6 Cartesian coordinates of the low-energy re-optimized conformers of compound **1b** (1*S*,3*S*,5*R*,6*S*,9*S*,14*S*-**1**) calculated at B3LYP/6-31+G(d) level of theory with PCM solvent model for DMSO.

Conformer 1b-1		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z
1	C	2.54326	-0.28775	-0.45061
2	C	3.47355	0.39018	0.5294
3	C	2.74563	1.42362	1.41713
4	C	1.41948	1.88673	0.77813
5	C	0.37884	0.72555	0.49251
6	C	1.28748	0.46869	-0.78289
7	C	2.72638	-1.51813	-0.95159
8	C	1.52448	2.0202	-0.77012
9	C	-1.06647	1.11706	0.19013
10	C	-1.80834	-0.21403	0.30836
11	O	-0.98943	-1.10142	1.08646
12	C	0.17552	-0.39095	1.51157
13	O	-0.05196	0.20649	2.78973
14	C	-0.13403	-0.76891	3.81987
15	C	-2.0365	-0.87835	-1.01915
16	C	-3.17689	-0.8834	-1.73951
17	C	-3.25631	-1.61807	-3.0293
18	O	-2.09009	-2.15101	-3.43042

19	C	-4.44626	-0.1762	-1.3645
20	O	-4.26212	-1.74137	-3.70648
21	O	4.48256	1.06743	-0.21679
22	H	3.98435	-0.34038	1.16644
23	H	3.38812	2.29541	1.58981
24	H	2.53364	0.9836	2.39812
25	H	1.00239	2.75855	1.29305
26	H	0.77729	0.10625	-1.68086
27	H	2.00641	-1.97572	-1.62471
28	H	3.60408	-2.10577	-0.69836
29	H	0.72753	2.61271	-1.23495
30	H	2.47026	2.39039	-1.17627
31	H	-1.22028	1.60888	-0.77533
32	H	-1.43185	1.80279	0.96518
33	H	-2.7493	-0.0824	0.85063
34	H	1.01919	-1.08403	1.5765
35	H	-0.97919	-1.44308	3.65258
36	H	0.79776	-1.339	3.88522
37	H	-0.28943	-0.25021	4.76975
38	H	-1.17242	-1.42388	-1.39535
39	H	-2.31975	-2.58808	-4.27618
40	H	-4.805	0.43656	-2.19899
41	H	-5.22445	-0.90301	-1.10939
42	H	-4.32464	0.49906	-0.51375
43	H	4.76649	0.46501	-0.92504

Conformer 1b-2		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z
1	C	2.48443	0.72767	-0.48921
2	C	3.24833	1.3309	0.66733
3	C	2.32509	1.74018	1.83619
4	C	0.86463	1.91889	1.37037
5	C	0.21513	0.63144	0.71149
6	C	1.02956	1.0963	-0.56888
7	C	2.99175	-0.1535	-1.36357
8	C	0.77107	2.55425	-0.04841
9	C	-1.30223	0.60214	0.53781
10	C	-1.575	-0.86497	0.20797
11	O	-0.4543	-1.63176	0.67517
12	C	0.4706	-0.74742	1.31207

13	O	0.19922	-0.68134	2.7138
14	C	0.53209	-1.89591	3.37208
15	C	-1.69695	-1.12255	-1.26606
16	C	-2.83247	-1.29542	-1.97253
17	C	-2.66927	-1.56202	-3.42402
18	O	-3.83085	-1.88421	-4.01609
19	C	-4.22593	-1.21655	-1.42793
20	O	-1.63362	-1.51188	-4.06337
21	O	3.91938	2.49659	0.1933
22	H	4.02037	0.64664	1.03635
23	H	2.67742	2.6747	2.28916
24	H	2.35818	0.97369	2.61865
25	H	0.24899	2.40044	2.13735
26	H	0.5729	0.88694	-1.54128
27	H	2.38797	-0.58584	-2.15731
28	H	4.02921	-0.47028	-1.30878
29	H	-0.21231	2.96744	-0.30242
30	H	1.5099	3.3199	-0.30221
31	H	-1.69523	1.29078	-0.21649
32	H	-1.78627	0.85309	1.49026
33	H	-2.45909	-1.22076	0.74508
34	H	1.48935	-1.11245	1.15297
35	H	-0.07147	-2.72477	2.99064
36	H	1.59721	-2.11789	3.25474
37	H	0.31922	-1.7762	4.43784
38	H	-0.74227	-1.19479	-1.78806
39	H	-3.57604	-2.03821	-4.9494
40	H	-4.7007	-2.20291	-1.44904
41	H	-4.26039	-0.85228	-0.39792
42	H	-4.83255	-0.524	-2.0217
43	H	4.29493	2.27593	-0.67596

Conformer 1b-3		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z
1	C	1.62992	-0.0037	-1.43887
2	C	3.01196	0.32763	-0.92357
3	C	2.97556	1.17759	0.36561
4	C	1.62111	1.8979	0.53313
5	C	0.36051	0.9387	0.58786
6	C	0.53143	0.91906	-0.99031

7	C	1.32829	-1.08169	-2.17735
8	C	1.0445	2.39318	-0.82636
9	C	-0.96021	1.51363	1.09425
10	C	-1.82215	0.25733	1.24683
11	O	-0.92618	-0.83189	1.48324
12	C	0.42208	-0.36904	1.37022
13	O	0.94931	-0.08781	2.6684
14	C	1.15458	-1.27433	3.42271
15	C	-2.68695	0.00826	0.03354
16	C	-2.90051	-1.12908	-0.66367
17	C	-3.7555	-1.11183	-1.88117
18	O	-4.37374	0.06144	-2.10019
19	C	-2.35293	-2.48117	-0.30931
20	O	-3.91627	-2.04565	-2.64752
21	O	3.69232	1.06998	-1.93352
22	H	3.59948	-0.57964	-0.74427
23	H	3.78163	1.92108	0.35321
24	H	3.14792	0.53487	1.23617
25	H	1.6565	2.65242	1.32598
26	H	-0.38566	0.83364	-1.58139
27	H	0.31073	-1.29255	-2.49523
28	H	2.09435	-1.78735	-2.48555
29	H	0.2555	3.14987	-0.74259
30	H	1.75973	2.76439	-1.56612
31	H	-1.41017	2.27518	0.45056
32	H	-0.80688	1.96956	2.08083
33	H	-2.48418	0.36271	2.1137
34	H	1.02967	-1.13984	0.88741
35	H	0.20874	-1.79667	3.59407
36	H	1.86496	-1.93455	2.91579
37	H	1.57441	-0.99416	4.39262
38	H	-3.19375	0.91406	-0.30058
39	H	-4.88695	-0.10296	-2.91812
40	H	-2.3496	-2.64573	0.77236
41	H	-2.9639	-3.29052	-0.72326
42	H	-1.33623	-2.59608	-0.69729
43	H	3.50657	0.63374	-2.78228

Conformer 1b-4		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z

1	C	1.7022	0.08531	-1.31632
2	C	3.03942	0.45281	-0.71455
3	C	2.89815	1.29888	0.57008
4	C	1.51705	1.98283	0.65099
5	C	0.2812	0.99069	0.624
6	C	0.55379	0.97908	-0.93989
7	C	1.47524	-1.00167	-2.06826
8	C	1.0163	2.46569	-0.7425
9	C	-1.08497	1.52786	1.04396
10	C	-1.92043	0.24791	1.13686
11	O	-1.01193	-0.81686	1.43136
12	C	0.32743	-0.31683	1.40771
13	O	0.76077	-0.02466	2.73784
14	C	0.94624	-1.20673	3.50405
15	C	-2.69021	-0.02371	-0.13305
16	C	-2.83525	-1.16749	-0.83565
17	C	-3.6197	-1.05979	-2.09096
18	O	-3.39133	-2.08779	-2.9246
19	C	-2.32314	-2.52148	-0.45013
20	O	-4.37512	-0.15654	-2.40297
21	O	3.76279	1.21467	-1.67898
22	H	3.63841	-0.43878	-0.49837
23	H	3.68337	2.06344	0.60951
24	H	3.03141	0.65911	1.44964
25	H	1.48149	2.73621	1.44489
26	H	-0.32044	0.87131	-1.58934
27	H	0.4849	-1.23935	-2.44733
28	H	2.27707	-1.68786	-2.325
29	H	0.20383	3.20117	-0.70923
30	H	1.76753	2.85719	-1.43455
31	H	-1.51238	2.2795	0.3738
32	H	-1.009	1.98383	2.03946
33	H	-2.64292	0.33241	1.95637
34	H	0.98643	-1.06951	0.96549
35	H	0.00472	-1.75297	3.61341
36	H	1.70461	-1.84811	3.04469
37	H	1.29468	-0.91756	4.49927
38	H	-3.1879	0.86905	-0.51797
39	H	-3.95575	-1.88303	-3.69862
40	H	-2.28712	-2.65564	0.63438
41	H	-2.98257	-3.31706	-0.81417

42	H	-1.32447	-2.6865	-0.86565
43	H	3.63559	0.78095	-2.53967

Conformer 1b-5		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z
1	C	1.97589	-0.42074	-1.62305
2	C	3.34627	-0.1341	-1.05833
3	C	3.28775	0.70223	0.2406
4	C	1.94385	1.44734	0.37737
5	C	0.66209	0.51448	0.37583
6	C	0.88343	0.51739	-1.19508
7	C	1.67666	-1.47295	-2.39871
8	C	1.42214	1.97714	-0.9908
9	C	-0.65849	1.11864	0.8491
10	C	-1.54627	-0.11131	1.03105
11	O	-0.68539	-1.25106	1.17881
12	C	0.67301	-0.80827	1.13561
13	O	1.15117	-0.55803	2.45957
14	C	1.29012	-1.7604	3.20445
15	C	-2.43062	-0.37843	-0.15313
16	C	-3.73969	-0.0764	-0.27408
17	C	-4.49089	-0.43605	-1.50551
18	O	-3.73078	-0.9707	-2.47541
19	C	-4.56694	0.63695	0.75488
20	O	-5.68641	-0.26772	-1.67272
21	O	4.06344	0.59034	-2.05469
22	H	3.8975	-1.06331	-0.87386
23	H	4.10769	1.42988	0.26424
24	H	3.42041	0.04486	1.10726
25	H	1.9699	2.18815	1.18344
26	H	-0.01719	0.46093	-1.81453
27	H	0.66898	-1.65225	-2.76114
28	H	2.44591	-2.17365	-2.70935
29	H	0.64717	2.74946	-0.91913
30	H	2.16902	2.34407	-1.70086
31	H	-1.09322	1.8649	0.17701
32	H	-0.51253	1.604	1.82253
33	H	-2.13368	-0.02802	1.95016
34	H	1.28998	-1.57901	0.66481
35	H	0.32266	-2.255	3.33154

36	H	1.99958	-2.43583	2.71663
37	H	1.67951	-1.50582	4.19393
38	H	-1.9301	-0.89329	-0.972
39	H	-4.36914	-1.14348	-3.19754
40	H	-3.97054	1.04943	1.5726
41	H	-5.09896	1.48084	0.30172
42	H	-5.3057	-0.04564	1.18757
43	H	4.97243	0.70045	-1.73083

Table S7 Calculated ^{1}H and ^{13}C NMR chemical shifts of compound **1a**.

Position	Type	Shielding tensors (calculated) [a]									Chemical shifts (ppm) (calculated)	Chemical shifts (ppm) (experimental) [b]
		1a-1	**1a-2**	**1a-3**	**1a-4**	**1a-5**	**1a-6**	**1a-7**	**1a-8**	**1a** (averaged)	**1a** (unscaled)	Brasilterpene A (**1**)
1	C	125.4239	125.5415	125.7861	125.5595	125.8964	123.1487	126.0792	125.6667	125.66054	58.30626	51.1
2	C	15.2609	15.2814	15.1319	18.3104	15.1342	12.082	14.6294	18.2888	16.011035	167.9558	153.8
3	C	109.7372	109.7596	108.7418	110.5339	108.7659	112.1642	110.4392	110.604	109.50122	74.46558	64.8
4	C	145.6046	145.6318	142.5551	142.7832	142.5691	140.4954	146.2924	142.8086	143.40976	40.55704	35.9
5	C	137.157	137.1378	136.7552	137.0139	136.749	134.0384	137.4473	136.9886	136.91856	47.04824	38.7
6	C	119.4322	119.3673	119.4518	119.4431	119.3804	122.1254	121.4862	119.4026	119.43455	64.53225	54.2
7	C	154.4205	154.4274	154.5381	154.2583	154.537	145.2376	154.4048	154.2429	154.41029	29.55651	29.1
8	C	138.3557	138.5902	138.2513	138.3947	138.4876	131.9963	138.9393	138.6483	138.37767	45.58913	40.8
9	C	103.8199	104.1436	103.8039	103.796	104.1304	103.6212	99.5351	104.1424	103.90154	80.06526	73.0
10	C	26.3189	25.7979	26.4523	26.3278	25.9359	28.7055	27.2426	25.8343	26.233146	157.7337	142.1
11	C	48.8347	48.6309	48.7763	48.8337	48.5797	46.4075	52.4568	48.6089	48.743062	135.2237	128.3
12	C	5.5818	5.8329	5.6114	5.5623	5.8495	6.1544	4.1953	5.816	5.6655228	178.3013	168.6
13	C	168.98	168.7373	168.9734	168.9844	168.7321	168.2854	169.2291	168.7463	168.90263	15.06417	12.7
14	C	70.6988	70.7011	70.7616	70.5488	70.7708	68.6866	70.7416	70.553	70.68539	113.2814	105.7
15	C	71.9598	71.965	70.4512	69.989	70.4418	63.3071	71.6801	69.943	70.696694	113.2701	110.7
16	C	126.7779	126.8001	126.8118	126.8016	126.8332	127.8321	126.8028	126.8315	126.81002	57.15678	54.0
1	H	28.9229	28.9162	28.9171	26.2931	28.9097	28.9603	29.1244	28.9338	28.439902	3.428998	2.61
3	H	26.9561	26.952	27.1632	26.856	27.1618	27.5008	26.969	26.852	27.02693	4.84197	4.28

4a	H	29.9663	29.9094	30.1471	29.9801	30.1341	29.49573	29.9375	29.9431	30.044455	1.824445	1.64
4b	H	29.48105	29.48675	29.3968	28.9394	29.4043	29.49573	29.4321	29.5039	29.346061	2.522839	2.38
5	H	29.48105	29.48675	29.4741	26.6039	29.4772	29.1733	29.5075	29.5039	28.954834	2.914066	2.23
7a	H	30.3533	30.3655	30.3432	27.1796	30.3555	30.975	30.3209	30.3762	29.775356	2.093544	1.55
7b	H	29.8698	29.9094	29.87597	26.6814	29.8655	29.5882	29.799	29.8327	29.288273	2.580627	2.17
8a	H	29.8698	29.9094	29.87597	28.3984	29.9312	29.89515	29.7054	29.9431	29.62136	2.24754	1.97
8b	H	29.2577	29.2827	29.2703	28.161	29.2956	29.49573	29.3235	29.2943	29.072836	2.796064	2.42
9	H	26.68777	26.72285	26.6901	28.789	26.6982	26.7931	26.5135	26.7052	27.07771	4.79119	4.81
10	H	24.5368	24.5057	24.5564	30.5027	24.5249	24.6917	24.5797	24.5007	25.625245	6.243655	6.60
13	H	30.1589	29.9094	30.0437	29.50045	29.9312	30.0079	30.3209	29.9431	29.930557	1.938343	1.77
13	H	30.0352	29.7595	29.87597	29.86437	29.7588	29.89515	28.6606	29.7537	29.864679	2.004221	1.77
13	H	29.8698	30.0418	30.1471	29.86437	30.046	30.1019	30.2414	30.0411	30.01306	1.85584	1.77
14	H	27.1863	27.1925	27.299	24.5303	27.3044	27.0488	27.1237	27.1869	26.75539	5.11351	4.37
15a	H	26.68777	26.6371	26.6901	30.3593	26.6982	26.46315	26.7508	26.5973	27.34815	4.52075	4.80
15b	H	26.68777	26.72285	26.3376	29.2675	26.3381	26.46315	26.6602	26.2974	26.962689	4.906211	5.03
16	H	28.3938	28.3968	28.3954	25.4785	28.399	28.3303	28.4392	28.4017	27.863805	4.005095	3.20
16	H	28.1628	28.1657	28.1723	30.033	28.1759	28.176	28.2241	28.1648	28.50965	3.35925	3.20
16	H	28.7907	28.7926	28.8325	30.159	28.8333	28.8594	28.7814	28.7901	29.060435	2.808465	3.20
3-OH	H	29.8698	29.9094	31.2024	29.86437	31.2042	27.9855	29.8797	30.5055	30.548603	1.320297	4.90
12-COOH	H	25.4851	25.3674	25.489	29.50045	25.3622	25.4467	25.5869	25.3639	26.18195	5.68695	12.40

[a] Calculated using the GIAO method at the B3LYP/6-311+G(d,p) level in DMSO (PCM). [b] Measured in DMSO-d_6 (400 and 100 MHz).

Table S8 Calculated ^{1}H and ^{13}C NMR chemical shifts of compound **1b**.

Position	Type	Shielding tensors (calculated) [a]						Chemical shifts (ppm) (calculated)	Chemical shifts (ppm) (experimental) [b]
		1b-1	**1b-2**	**1b-3**	**1b-4**	**1b-5**	**1b** (averaged)	**1b** (unscaled)	Brasilterpene A (**1**)
1	C	126.8673	126.9803	127.1546	127.0295	126.4992	126.8703	57.09645	51.1
2	C	14.5307	14.5615	14.2979	14.3107	17.6692	14.86201	169.1048	153.8
3	C	109.1947	109.1953	109.2252	109.2782	109.2818	109.2051	74.76175	64.8
4	C	146.2069	146.2703	146.3825	146.4152	141.7258	145.7646	38.2022	35.9
5	C	138.1753	138.1976	138.9825	138.9603	138.3587	138.2198	45.74704	38.7
6	C	119.9326	119.8808	122.1739	122.2038	120.3351	120.0097	63.95715	54.2
7	C	153.6784	153.6837	153.402	153.3337	153.8263	153.6886	30.27816	29.1
8	C	138.029	138.2677	138.9138	138.9603	138.1575	138.1384	45.82835	40.8
9	C	103.6849	103.9735	99.1035	98.6802	103.5881	103.6581	80.30872	73.0
10	C	26.3264	25.7646	26.7619	26.6285	26.2996	26.15496	157.8118	142.1
11	C	48.9163	48.7574	52.2765	51.7789	48.945	48.94226	135.0245	128.3
12	C	5.8509	5.9364	4.4983	4.2794	5.8397	5.844187	178.1226	168.6
13	C	168.909	168.6527	169.2185	169.2191	168.9243	168.8366	15.13015	12.7
14	C	70.5191	70.4922	70.6361	70.6643	70.4391	70.50515	113.4616	105.7
15	C	64.6031	64.5641	64.4498	64.4925	61.967	64.31309	119.6537	110.7
16	C	126.7121	126.7311	126.8201	126.8172	126.7146	126.7208179	57.24598	54.0
1	H	28.9706	28.9621	29.0822	29.0979	28.9378	28.96717	2.901732	2.61
3	H	27.3027	27.3054	27.32535	27.3292	27.2047	27.2939	4.575004	4.28
4a	H	29.9672	29.9662	29.9021	29.9076	30.05857	29.97495	1.893952	1.64
4b	H	29.4105	29.4134	29.4036	29.4065	29.2672	29.39636	2.472541	2.38

5	H	29.5511	29.5513	29.5679	29.5731	29.5348	29.54989	2.319011	2.23
7a	H	30.0433	30.0495	29.7994	29.7921	30.05857	30.04121	1.827686	1.55
7b	H	29.779	29.77775	29.6869	29.6787	29.747	29.7731	2.095796	2.17
8a	H	29.88015	29.8918	29.6301	29.6787	29.87105	29.87752	1.991377	1.97
8b	H	29.2737	29.2922	29.2559	29.2725	29.2672	29.27859	2.590312	2.42
9	H	26.7284	26.7465	26.55035	26.5403	26.7176	26.72885	5.140051	4.81
10	H	24.5327	24.5157	24.5461	24.5367	24.5153	24.52575	7.34315	6.60
13	H	30.1701	29.9662	28.6329	28.5494	29.87105	30.03869	1.830207	1.77
13	H	30.0433	29.77775	30.2284	30.15805	30.1651	29.97574	1.893163	1.77
13	H	29.88015	30.0495	30.3226	30.15805	30.05857	29.96118	1.907722	1.77
14	H	27.4065	27.4065	27.32535	27.3292	27.3811	27.40203	4.466874	4.37
15a	H	26.5707	26.5637	26.6891	26.6678	26.41525	26.55485	5.314048	4.80
15b	H	26.4806	26.4839	26.55035	26.5403	26.41525	26.47636	5.392539	5.03
16	H	28.1887	28.1955	28.2514	28.25	28.1825	28.19163	3.677271	3.20
16	H	28.8494	28.8504	28.8373	28.8362	28.8483	28.84932	3.019583	3.20
16	H	28.3926	28.3971	28.4479	28.4433	28.4006	28.39609	3.472813	3.20
3-OH	H	30.9158	30.9251	31.0301	31.0394	30.5954	30.88806	0.980837	4.90
12-COOH	H	25.5066	25.36	25.6084	25.4144	25.4969	25.46013	6.40877	12.40

[a] Calculated using the GIAO method at the B3LYP/6-311+G(d,p) level in DMSO (PCM). [b] Measured in DMSO-d_6 (400 and 100 MHz).

Figure S45 Correlation plots of experimental ^{13}C NMR chemical shifts of brasilterpene A (**1**) corresponding calculated ^{13}C NMR chemical shifts of **1a** and **1b**.

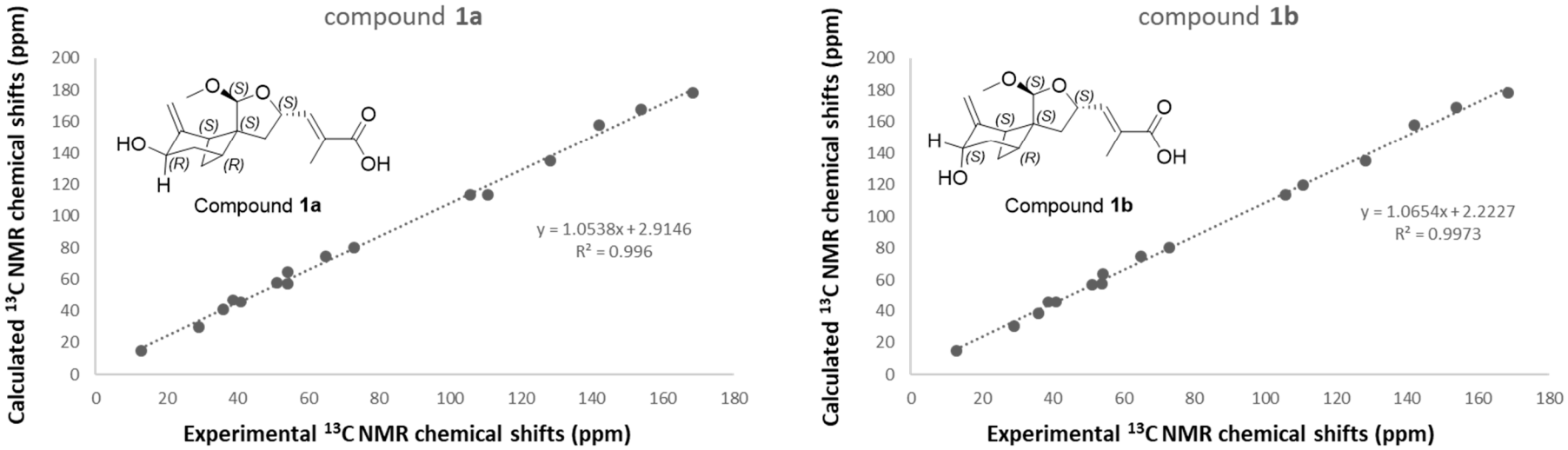


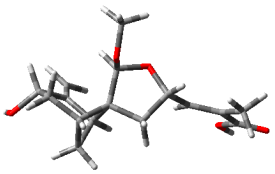
Table S9 DP4+ analysis using the calculated shielding tensors for compound **1a** and **1b**.

Functional	Solvent?		Basis Set		Type of Data	
B3LYP	PCM		6-311+G(d,p)		Shielding Tensors	
	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5	Isomer 6
sDP4+ (H data)	0.00%	100.00%	–	–	–	–
sDP4+ (C data)	0.89%	99.11%	–	–	–	–
sDP4+ (all data)	0.00%	100.00%	–	–	–	–
uDP4+ (H data)	0.00%	100.00%	–	–	–	–
uDP4+ (C data)	4.59%	95.41%	–	–	–	–
uDP4+ (all data)	0.00%	100.00%	–	–	–	–
DP4+ (H data)	0.00%	100.00%	–	–	–	–
DP4+ (C data)	0.04%	99.96%	–	–	–	–
DP4+ (all data)	0.00%	100.00%	–	–	–	–

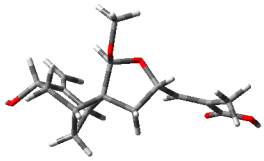
[a] sDP4+: scaled DP4+; [b] uDP4+: unscaled DP4+.

Figure S46 DFT-optimized structures for low-energy conformers of **1** (1*S*,3*S*,5*R*,6*S*,9*S*,14*S*-**1**) at B3LYP/6-31+G(d) level in MeOH (PCM).

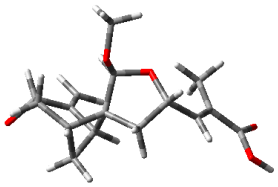
Conformer populations were calculated using the Gibbs free energy and Boltzmann population at 298 K estimated thereof.



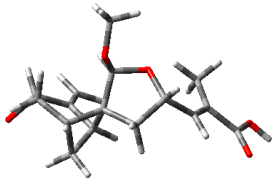
Conf. 1-1 56.0%



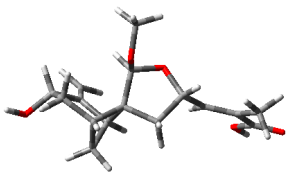
Conf. 1-2 31.8%



Conf. 1-3 1.5%



Conf. 1-4 0.7%



Conf. 1-5 9.9%

Table S10 Harmonic frequencies (cm**$^{-1}$) of compound **1**.

Conformations	**Frequencies**		
	1	2	3
1-1	21.6203	26.3272	51.6263
1-2	21.9977	26.2790	51.6923
1-3	11.6008	24.9585	56.8813
1-4	12.8130	26.3628	57.0150
1-5	20.1432	25.6184	51.2415

Table S11 Important thermodynamic parameters (a.u.) and Boltzmann distributions of the optimized compound **1** at B3LYP/6-31G+(d) level of theory with PCM solvent model for MeOH.

Conformations	E+ZPE	G	%
1-1	-998.681656	-998.732395	56.0%
1-2	-998.681260	-998.731860	31.8%
1-3	-998.677686	-998.728998	1.5%
1-4	-998.677348	-998.728302	0.7%
1-5	-998.679895	-998.730760	9.9%

E+ZPE, G: total energy with zero point energy (ZPE) and Gibbs free energy at B3LYP/6-31G+(d) level of theory with PCM solvent model for MeOH. %: Boltzmann distributions, using the relative Gibbs free energies as weighting factors

Table S12 Cartesian coordinates of the low-energy re-optimized conformers of compound **1** (1*S*,3*S*,5*R*,6*S*,9*S*,14*S*-**1**) calculated at B3LYP/6-31+G(d) level of theory with PCM solvent model for MeOH.

Conformer 1-1		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z
1	C	2.54326	-0.28775	-0.45061
2	C	3.47355	0.39018	0.5294
3	C	2.74563	1.42362	1.41713
4	C	1.41948	1.88673	0.77813
5	C	0.37884	0.72555	0.49251
6	C	1.28748	0.46869	-0.78289
7	C	2.72638	-1.51813	-0.95159
8	C	1.52448	2.0202	-0.77012
9	C	-1.06647	1.11706	0.19013
10	C	-1.80834	-0.21403	0.30836
11	O	-0.98943	-1.10142	1.08646
12	C	0.17552	-0.39095	1.51157

13	O	-0.05196	0.20649	2.78973
14	C	-0.13403	-0.76891	3.81987
15	C	-2.0365	-0.87835	-1.01915
16	C	-3.17689	-0.8834	-1.73951
17	C	-3.25631	-1.61807	-3.0293
18	O	-2.09009	-2.15101	-3.43042
19	C	-4.44626	-0.1762	-1.3645
20	O	-4.26212	-1.74137	-3.70648
21	O	4.48256	1.06743	-0.21679
22	H	3.98435	-0.34038	1.16644
23	H	3.38812	2.29541	1.58981
24	H	2.53364	0.9836	2.39812
25	H	1.00239	2.75855	1.29305
26	H	0.77729	0.10625	-1.68086
27	H	2.00641	-1.97572	-1.62471
28	H	3.60408	-2.10577	-0.69836
29	H	0.72753	2.61271	-1.23495
30	H	2.47026	2.39039	-1.17627
31	H	-1.22028	1.60888	-0.77533
32	H	-1.43185	1.80279	0.96518
33	H	-2.7493	-0.0824	0.85063
34	H	1.01919	-1.08403	1.5765
35	H	-0.97919	-1.44308	3.65258
36	H	0.79776	-1.339	3.88522
37	H	-0.28943	-0.25021	4.76975
38	H	-1.17242	-1.42388	-1.39535
39	H	-2.31975	-2.58808	-4.27618
40	H	-4.805	0.43656	-2.19899
41	H	-5.22445	-0.90301	-1.10939
42	H	-4.32464	0.49906	-0.51375
43	H	4.76649	0.46501	-0.92504

Conformer 1-2		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z
1	C	2.48443	0.72767	-0.48921
2	C	3.24833	1.3309	0.66733
3	C	2.32509	1.74018	1.83619
4	C	0.86463	1.91889	1.37037
5	C	0.21513	0.63144	0.71149
6	C	1.02956	1.0963	-0.56888

7	C	2.99175	-0.1535	-1.36357
8	C	0.77107	2.55425	-0.04841
9	C	-1.30223	0.60214	0.53781
10	C	-1.575	-0.86497	0.20797
11	O	-0.4543	-1.63176	0.67517
12	C	0.4706	-0.74742	1.31207
13	O	0.19922	-0.68134	2.7138
14	C	0.53209	-1.89591	3.37208
15	C	-1.69695	-1.12255	-1.26606
16	C	-2.83247	-1.29542	-1.97253
17	C	-2.66927	-1.56202	-3.42402
18	O	-3.83085	-1.88421	-4.01609
19	C	-4.22593	-1.21655	-1.42793
20	O	-1.63362	-1.51188	-4.06337
21	O	3.91938	2.49659	0.1933
22	H	4.02037	0.64664	1.03635
23	H	2.67742	2.6747	2.28916
24	H	2.35818	0.97369	2.61865
25	H	0.24899	2.40044	2.13735
26	H	0.5729	0.88694	-1.54128
27	H	2.38797	-0.58584	-2.15731
28	H	4.02921	-0.47028	-1.30878
29	H	-0.21231	2.96744	-0.30242
30	H	1.5099	3.3199	-0.30221
31	H	-1.69523	1.29078	-0.21649
32	H	-1.78627	0.85309	1.49026
33	H	-2.45909	-1.22076	0.74508
34	H	1.48935	-1.11245	1.15297
35	H	-0.07147	-2.72477	2.99064
36	H	1.59721	-2.11789	3.25474
37	H	0.31922	-1.7762	4.43784
38	H	-0.74227	-1.19479	-1.78806
39	H	-3.57604	-2.03821	-4.9494
40	H	-4.7007	-2.20291	-1.44904
41	H	-4.26039	-0.85228	-0.39792
42	H	-4.83255	-0.524	-2.0217
43	H	4.29493	2.27593	-0.67596

Conformer 1-3		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z

1	C	1.62992	-0.0037	-1.43887
2	C	3.01196	0.32763	-0.92357
3	C	2.97556	1.17759	0.36561
4	C	1.62111	1.8979	0.53313
5	C	0.36051	0.9387	0.58786
6	C	0.53143	0.91906	-0.99031
7	C	1.32829	-1.08169	-2.17735
8	C	1.0445	2.39318	-0.82636
9	C	-0.96021	1.51363	1.09425
10	C	-1.82215	0.25733	1.24683
11	O	-0.92618	-0.83189	1.48324
12	C	0.42208	-0.36904	1.37022
13	O	0.94931	-0.08781	2.6684
14	C	1.15458	-1.27433	3.42271
15	C	-2.68695	0.00826	0.03354
16	C	-2.90051	-1.12908	-0.66367
17	C	-3.7555	-1.11183	-1.88117
18	O	-4.37374	0.06144	-2.10019
19	C	-2.35293	-2.48117	-0.30931
20	O	-3.91627	-2.04565	-2.64752
21	O	3.69232	1.06998	-1.93352
22	H	3.59948	-0.57964	-0.74427
23	H	3.78163	1.92108	0.35321
24	H	3.14792	0.53487	1.23617
25	H	1.6565	2.65242	1.32598
26	H	-0.38566	0.83364	-1.58139
27	H	0.31073	-1.29255	-2.49523
28	H	2.09435	-1.78735	-2.48555
29	H	0.2555	3.14987	-0.74259
30	H	1.75973	2.76439	-1.56612
31	H	-1.41017	2.27518	0.45056
32	H	-0.80688	1.96956	2.08083
33	H	-2.48418	0.36271	2.1137
34	H	1.02967	-1.13984	0.88741
35	H	0.20874	-1.79667	3.59407
36	H	1.86496	-1.93455	2.91579
37	H	1.57441	-0.99416	4.39262
38	H	-3.19375	0.91406	-0.30058
39	H	-4.88695	-0.10296	-2.91812
40	H	-2.3496	-2.64573	0.77236
41	H	-2.9639	-3.29052	-0.72326

42	H	-1.33623	-2.59608	-0.69729
43	H	3.50657	0.63374	-2.78228

Conformer 1-4		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z
1	C	1.7022	0.08531	-1.31632
2	C	3.03942	0.45281	-0.71455
3	C	2.89815	1.29888	0.57008
4	C	1.51705	1.98283	0.65099
5	C	0.2812	0.99069	0.624
6	C	0.55379	0.97908	-0.93989
7	C	1.47524	-1.00167	-2.06826
8	C	1.0163	2.46569	-0.7425
9	C	-1.08497	1.52786	1.04396
10	C	-1.92043	0.24791	1.13686
11	O	-1.01193	-0.81686	1.43136
12	C	0.32743	-0.31683	1.40771
13	O	0.76077	-0.02466	2.73784
14	C	0.94624	-1.20673	3.50405
15	C	-2.69021	-0.02371	-0.13305
16	C	-2.83525	-1.16749	-0.83565
17	C	-3.6197	-1.05979	-2.09096
18	O	-3.39133	-2.08779	-2.9246
19	C	-2.32314	-2.52148	-0.45013
20	O	-4.37512	-0.15654	-2.40297
21	O	3.76279	1.21467	-1.67898
22	H	3.63841	-0.43878	-0.49837
23	H	3.68337	2.06344	0.60951
24	H	3.03141	0.65911	1.44964
25	H	1.48149	2.73621	1.44489
26	H	-0.32044	0.87131	-1.58934
27	H	0.4849	-1.23935	-2.44733
28	H	2.27707	-1.68786	-2.325
29	H	0.20383	3.20117	-0.70923
30	H	1.76753	2.85719	-1.43455
31	H	-1.51238	2.2795	0.3738
32	H	-1.009	1.98383	2.03946
33	H	-2.64292	0.33241	1.95637
34	H	0.98643	-1.06951	0.96549
35	H	0.00472	-1.75297	3.61341

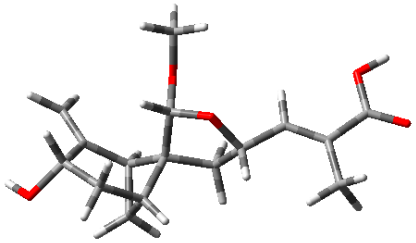
36	H	1.70461	-1.84811	3.04469
37	H	1.29468	-0.91756	4.49927
38	H	-3.1879	0.86905	-0.51797
39	H	-3.95575	-1.88303	-3.69862
40	H	-2.28712	-2.65564	0.63438
41	H	-2.98257	-3.31706	-0.81417
42	H	-1.32447	-2.6865	-0.86565
43	H	3.63559	0.78095	-2.53967

Conformer 1-5		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z
1	C	1.97589	-0.42074	-1.62305
2	C	3.34627	-0.1341	-1.05833
3	C	3.28775	0.70223	0.2406
4	C	1.94385	1.44734	0.37737
5	C	0.66209	0.51448	0.37583
6	C	0.88343	0.51739	-1.19508
7	C	1.67666	-1.47295	-2.39871
8	C	1.42214	1.97714	-0.9908
9	C	-0.65849	1.11864	0.8491
10	C	-1.54627	-0.11131	1.03105
11	O	-0.68539	-1.25106	1.17881
12	C	0.67301	-0.80827	1.13561
13	O	1.15117	-0.55803	2.45957
14	C	1.29012	-1.7604	3.20445
15	C	-2.43062	-0.37843	-0.15313
16	C	-3.73969	-0.0764	-0.27408
17	C	-4.49089	-0.43605	-1.50551
18	O	-3.73078	-0.9707	-2.47541
19	C	-4.56694	0.63695	0.75488
20	O	-5.68641	-0.26772	-1.67272
21	O	4.06344	0.59034	-2.05469
22	H	3.8975	-1.06331	-0.87386
23	H	4.10769	1.42988	0.26424
24	H	3.42041	0.04486	1.10726
25	H	1.9699	2.18815	1.18344
26	H	-0.01719	0.46093	-1.81453
27	H	0.66898	-1.65225	-2.76114
28	H	2.44591	-2.17365	-2.70935
29	H	0.64717	2.74946	-0.91913

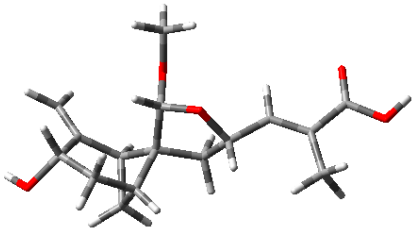
30	H	2.16902	2.34407	-1.70086
31	H	-1.09322	1.8649	0.17701
32	H	-0.51253	1.604	1.82253
33	H	-2.13368	-0.02802	1.95016
34	H	1.28998	-1.57901	0.66481
35	H	0.32266	-2.255	3.33154
36	H	1.99958	-2.43583	2.71663
37	H	1.67951	-1.50582	4.19393
38	H	-1.9301	-0.89329	-0.972
39	H	-4.36914	-1.14348	-3.19754
40	H	-3.97054	1.04943	1.5726
41	H	-5.09896	1.48084	0.30172
42	H	-5.3057	-0.04564	1.18757
43	H	4.97243	0.70045	-1.73083

Figure S47 DFT-optimized structures for low-energy conformers of **2** (1*S*,3*S*,5*R*,6*S*,9*S*,14*R*-**2**) at B3LYP/6-31+G(d) level in MeOH (PCM).

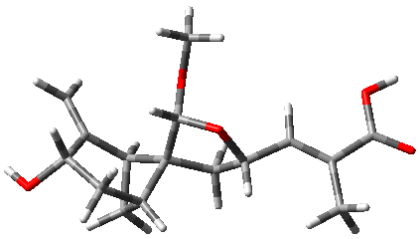
Conformer populations were calculated using the Gibbs free energy and Boltzmann population at 298 K estimated thereof.



Conf. 2-1 41.06%



Conf. 2-2 17.8%



Conf. 2-3 41.1%

Table S13 Harmonic frequencies (cm**$^{-1}$) of compound **2**.

Conformations	**Frequencies**		
	1	2	3

2-1	24.2970	30.1406	44.1924
2-2	26.0256	31.5825	45.6885
2-3	24.3081	30.1579	44.1860

Table S14 Important thermodynamic parameters (a.u.) and Boltzmann distributions of the optimized compound **2** at B3LYP/6-31G+(d) level of theory with PCM solvent model for MeOH.

Conformations	E+ZPE	G	%
2-1	-998.681458	-998.732066	41.06%
2-2	-998.680987	-998.731277	17.8%
2-3	-998.681460	-998.732068	41.1%

E+ZPE, G: total energy with zero point energy (ZPE) and Gibbs free energy at B3LYP/6-31G+(d) level of theory with PCM solvent model for MeOH. %: Boltzmann distributions, using the relative Gibbs free energies as weighting factors

Table S15 Cartesian coordinates of the low-energy re-optimized conformers of compound **2** (1*S*,3*S*,5*R*,6*S*,9*S*,14*R*-**2**) calculated at B3LYP/6-31+G(d) level of theory with PCM solvent model for MeOH.

Conformer 2-1		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z
1	C	-2.8643	-1.04166	1.18018
2	C	-3.53072	0.29667	1.39856
3	C	-2.52396	1.46831	1.38414
4	C	-1.0846	0.97936	1.64231
5	C	-0.53777	-0.12361	0.63567
6	C	-1.39963	-1.1073	1.5227
7	C	-3.46246	-2.10815	0.62986
8	C	-1.03947	-0.15565	2.71447
9	C	0.98136	-0.27652	0.63025
10	C	1.37851	0.69522	-0.4795
11	O	0.26231	0.7916	-1.38326
12	C	-0.8153	0.0098	-0.85847
13	O	-0.80037	-1.29597	-1.43872
14	C	-1.16054	-1.26602	-2.81256
15	C	2.56942	0.23525	-1.26157
16	C	3.81707	0.74657	-1.2332
17	C	4.88627	0.1869	-2.1019
18	O	4.50727	-0.881	-2.8226
19	C	4.27698	1.87972	-0.36348

20	O	6.02377	0.61827	-2.18005
21	O	-4.16951	0.26957	2.67322
22	H	-4.31297	0.48061	0.6538
23	H	-2.55782	1.98034	0.41597
24	H	-2.79537	2.21114	2.14409
25	H	-0.4034	1.81709	1.82629
26	H	-1.00825	-2.12503	1.62249
27	H	-2.92221	-3.03375	0.44987
28	H	-4.50596	-2.08111	0.33124
29	H	-0.05461	-0.33746	3.16074
30	H	-1.7522	-0.08921	3.54164
31	H	1.2541	-1.30962	0.37943
32	H	1.47587	-0.02531	1.57334
33	H	1.51258	1.7005	-0.06963
34	H	-1.76526	0.50256	-1.08382
35	H	-1.15092	-2.29192	-3.19058
36	H	-2.16926	-0.86062	-2.93757
37	H	-0.4421	-0.67847	-3.39174
38	H	2.35077	-0.59969	-1.92736
39	H	5.31272	-1.11602	-3.32684
40	H	4.50331	2.75942	-0.97498
41	H	3.53843	2.17346	0.3862
42	H	5.18216	1.59834	0.18615
43	H	-4.60396	-0.59658	2.75521

Conformer 2-2		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z
1	C	-2.03801	-1.91195	1.76271
2	C	-3.15745	-0.91866	1.97015
3	C	-2.72323	0.53327	1.67027
4	C	-1.18944	0.6848	1.71544
5	C	-0.37182	-0.26309	0.73481
6	C	-0.64265	-1.35274	1.84677
7	C	-2.21502	-3.19792	1.42658
8	C	-0.5547	-0.16335	2.8633
9	C	1.06529	0.18352	0.47621
10	C	0.8935	1.04688	-0.77244
11	O	-0.27259	0.5682	-1.46702
12	C	-0.86287	-0.48067	-0.69302
13	O	-0.38858	-1.75068	-1.14405

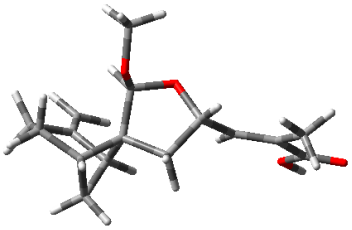
14	C	-0.88397	-2.0705	-2.43649
15	C	2.05767	0.96033	-1.70915
16	C	2.97602	1.91227	-1.9707
17	C	4.01786	1.56479	-2.9707
18	O	4.80374	2.61208	-3.27157
19	C	3.04569	3.26709	-1.33466
20	O	4.19585	0.48121	-3.49734
21	O	-3.56643	-0.99207	3.33436
22	H	-4.03299	-1.16921	1.36099
23	H	-3.08183	0.83527	0.67988
24	H	-3.17618	1.22188	2.3939
25	H	-0.88976	1.73816	1.69824
26	H	0.13719	-2.11142	1.96988
27	H	-1.37242	-3.85847	1.24014
28	H	-3.20782	-3.62281	1.31441
29	H	0.4663	0.12103	3.14413
30	H	-1.1242	-0.24983	3.79323
31	H	1.7006	-0.68959	0.27965
32	H	1.52786	0.75031	1.28976
33	H	0.66432	2.07775	-0.4874
34	H	-1.95111	-0.43757	-0.79237
35	H	-0.50691	-3.05922	-2.7117
36	H	-1.97767	-2.10611	-2.43189
37	H	-0.53197	-1.34847	-3.17915
38	H	2.12546	0.00484	-2.23264
39	H	5.42459	2.2439	-3.93398
40	H	4.04408	3.44671	-0.92089
41	H	2.82802	4.04669	-2.07205
42	H	2.34259	3.38805	-0.50703
43	H	-3.59699	-1.93473	3.57143

Conformer 2-3		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z
1	C	-2.50094	-1.01324	1.72152
2	C	-3.18668	0.31302	1.95297
3	C	-2.21475	1.50877	1.84354
4	C	-0.74883	1.06266	2.01539
5	C	-0.24131	-0.05086	0.99982
6	C	-1.01532	-1.03361	1.96549
7	C	-3.10612	-2.10799	1.23845

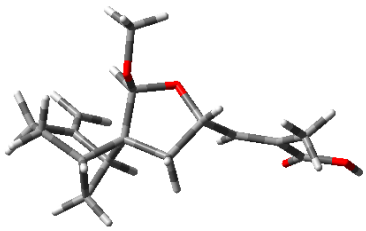
8	C	-0.60179	-0.04391	3.10792
9	C	1.2764	-0.16597	0.89213
10	C	1.57358	0.80221	-0.25634
11	O	0.40545	0.82326	-1.08999
12	C	-0.61907	0.03719	-0.47438
13	O	-0.61874	-1.28323	-1.01961
14	C	-1.08671	-1.30112	-2.36031
15	C	2.80719	0.42455	-1.02877
16	C	3.07952	0.62008	-2.33674
17	C	4.34731	0.11574	-2.92781
18	O	5.18666	-0.43884	-2.03618
19	C	2.20587	1.36199	-3.30582
20	O	4.6528	0.17896	-4.10615
21	O	-3.73816	0.30195	3.26801
22	H	-4.02145	0.45861	1.25843
23	H	-2.32688	1.99552	0.86827
24	H	-2.45453	2.26328	2.60263
25	H	-0.0796	1.92155	2.13397
26	H	-0.59105	-2.03839	2.06207
27	H	-2.55461	-3.02397	1.04398
28	H	-4.16766	-2.11469	1.01069
29	H	0.41521	-0.18973	3.49079
30	H	-1.25914	0.02514	3.97955
31	H	1.55625	-1.19493	0.63167
32	H	1.82692	0.10814	1.79706
33	H	1.70358	1.8138	0.1468
34	H	-1.59101	0.50756	-0.64794
35	H	-1.0745	-2.33603	-2.71282
36	H	-2.11459	-0.92953	-2.41394
37	H	-0.43644	-0.708	-3.00942
38	H	3.55589	-0.07759	-0.41668
39	H	5.94911	-0.71219	-2.5865
40	H	1.5968	0.66055	-3.88412
41	H	1.54703	2.08007	-2.81002
42	H	2.80682	1.95186	-4.00704
43	H	-4.1425	-0.57265	3.39943

Figure S48 DFT-optimized structures for low-energy conformers of **3** (1*S*,5*S*,6*S*,9*S*,14*S*-**3**) at B3LYP/6-31+G(d) level in MeOH (PCM).

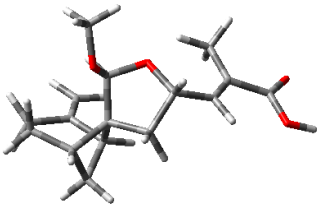
Conformer populations were calculated using the Gibbs free energy and Boltzmann population at 298 K estimated thereof.



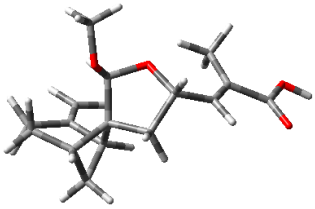
Conf. 3-1 67.8%



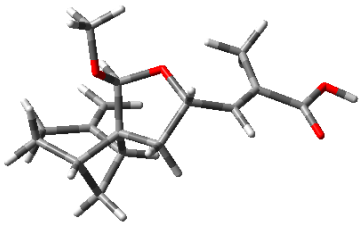
Conf. 3-2 31.0%



Conf. 3-3 0.6%



Conf. 3-4 0.3%



Conf. 3-5 0.3%

Table S16 Harmonic frequencies (cm**$^{-1}$) of compound **3**.

Conformations	**Frequencies**		
	1	2	3
3-1	18.3149	25.0466	51.3692
3-2	20.0477	26.5908	51.5991
3-3	15.1774	26.5726	63.4862
3-4	16.3926	29.8734	61.5577
3-5	16.4050	29.8643	61.5653

Table S17 Important thermodynamic parameters (a.u.) and Boltzmann distributions of the optimized compound **3** at B3LYP/6-31G+(d) level of theory with PCM solvent model for MeOH.

Conformations	E+ZPE	G	%
3-1	-923.467275	-923.517014	67.8%
3-2	-923.466815	-923.516276	31.0%
3-3	-923.463038	-923.512484	0.6%
3-4	-923.462759	-923.511969	0.3%
3-5	-923.462760	-923.511969	0.3%

E+ZPE, G: total energy with zero point energy (ZPE) and Gibbs free energy at B3LYP/6-31G+(d) level of theory with PCM solvent model for MeOH. %: Boltzmann distributions, using the relative Gibbs free energies as weighting factors.

Table S18 Cartesian coordinates of the low-energy re-optimized conformers of compound **3** (1*S*,5*S*,6*S*,9*S*,14*S*-**3**) calculated at B3LYP/6-31+G(d) level of theory with PCM solvent model for MeOH.

Conformer 3-1		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z
1	C	-1.34455	-0.13987	-2.35161
2	C	-2.41803	-1.19532	-2.46456
3	C	-2.35301	-2.2104	-1.30476
4	C	-0.94359	-2.27269	-0.68661
5	C	-0.43159	-0.90299	-0.07601
6	C	-0.11644	-0.54851	-1.58948
7	C	-1.45599	1.11007	-2.81904
8	C	0.17235	-2.08347	-1.75752
9	C	0.78446	-0.93895	0.84702
10	C	0.76404	0.44985	1.485
11	O	-0.566	0.97401	1.34659
12	C	-1.38413	-0.0184	0.72139
13	O	-2.01661	-0.82658	1.71749
14	C	-3.02227	-0.10571	2.41618
15	C	1.69123	1.41953	0.80977
16	C	2.91616	1.79834	1.22867
17	C	3.70434	2.79902	0.46246
18	O	3.13555	3.17686	-0.69438
19	C	3.61681	1.28008	2.45033
20	O	4.78186	3.25485	0.80416
21	H	-2.26453	-1.73341	-3.40885

22	H	-3.41928	-0.75239	-2.51269
23	H	-2.63929	-3.20003	-1.68024
24	H	-3.08742	-1.94827	-0.53492
25	H	-0.82025	-3.14133	-0.03162
26	H	0.75292	0.09044	-1.77293
27	H	-0.66625	1.84431	-2.68801
28	H	-2.34599	1.43381	-3.35057
29	H	1.17231	-2.40326	-1.44192
30	H	-0.00874	-2.52246	-2.74389
31	H	1.7332	-1.17011	0.35288
32	H	0.63231	-1.69567	1.62718
33	H	0.97573	0.38297	2.55623
34	H	-2.14546	0.47209	0.10803
35	H	-3.4758	-0.77695	3.15051
36	H	-2.59234	0.74805	2.94824
37	H	-3.80283	0.23158	1.72736
38	H	1.28434	1.86	-0.09934
39	H	3.77202	3.82471	-1.06046
40	H	3.11011	0.42435	2.90365
41	H	4.62903	0.94444	2.19871
42	H	3.69164	2.06742	3.20756

Conformer 3-2		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z
1	C	-0.99891	0.61341	-2.49565
2	C	-1.92167	-0.39538	-3.1356
3	C	-1.90428	-1.74665	-2.39159
4	C	-0.59673	-1.93977	-1.60066
5	C	-0.33186	-0.84251	-0.4883
6	C	0.1491	0.03545	-1.71864
7	C	-1.18188	1.93955	-2.52968
8	C	0.62892	-1.32493	-2.34048
9	C	0.74019	-1.12848	0.56095
10	C	0.47343	-0.05538	1.6161
11	O	-0.87604	0.40283	1.44111
12	C	-1.48038	-0.34995	0.38596
13	O	-2.15206	-1.49126	0.92643
14	C	-3.32317	-1.12005	1.6405
15	C	1.36574	1.14352	1.47281
16	C	2.45323	1.4437	2.21152

17	C	3.14673	2.71277	1.87557
18	O	4.10562	3.0195	2.76463
19	C	3.02741	0.60315	3.31078
20	O	2.92268	3.43761	0.92266
21	H	-1.58022	-0.55947	-4.16578
22	H	-2.94987	-0.02157	-3.19951
23	H	-2.02175	-2.55705	-3.12082
24	H	-2.76367	-1.81365	-1.71509
25	H	-0.46897	-2.97387	-1.26436
26	H	0.95856	0.74669	-1.52744
27	H	-0.50361	2.62558	-2.02978
28	H	-2.01888	2.37817	-3.06476
29	H	1.60473	-1.67688	-1.98591
30	H	0.63728	-1.40147	-3.43249
31	H	1.76852	-1.11556	0.18666
32	H	0.56802	-2.11824	1.00272
33	H	0.54366	-0.48163	2.62109
34	H	-2.19777	0.28146	-0.14612
35	H	-3.79685	-2.03085	2.01674
36	H	-3.07448	-0.48248	2.49401
37	H	-4.03091	-0.60955	0.98017
38	H	1.0576	1.83897	0.69129
39	H	4.46364	3.86724	2.42865
40	H	2.56602	-0.38558	3.37609
41	H	4.09758	0.43483	3.14763
42	H	2.89534	1.09778	4.27859

Conformer 3-3		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z
1	C	-0.47418	0.24115	-2.2207
2	C	-1.52927	-0.65133	-2.82838
3	C	-1.7429	-1.93849	-2.00555
4	C	-0.50444	-2.279	-1.15557
5	C	-0.10169	-1.16537	-0.10316
6	C	0.5456	-0.45507	-1.36562
7	C	-0.43974	1.57343	-2.3516
8	C	0.82237	-1.91133	-1.88524
9	C	0.877	-1.54208	1.00588
10	C	0.79492	-0.32781	1.93515
11	O	-0.50016	0.24905	1.7495

12	C	-1.1795	-0.44199	0.69688
13	O	-2.05681	-1.42441	1.25407
14	C	-3.17239	-0.82613	1.89935
15	C	1.89237	0.67403	1.66323
16	C	1.82956	2.01605	1.52019
17	C	3.05496	2.7923	1.18895
18	O	4.18037	2.05725	1.16606
19	C	0.59264	2.84968	1.6901
20	O	3.09548	3.98627	0.94821
21	H	-1.19426	-0.93254	-3.83512
22	H	-2.48389	-0.12661	-2.94846
23	H	-1.96423	-2.76651	-2.68947
24	H	-2.62143	-1.82923	-1.35996
25	H	-0.5495	-3.29592	-0.75232
26	H	1.45123	0.13309	-1.18852
27	H	0.32717	2.17765	-1.8754
28	H	-1.18061	2.09894	-2.94689
29	H	1.72103	-2.38598	-1.47443
30	H	0.84812	-2.05988	-2.96956
31	H	1.89348	-1.76551	0.6687
32	H	0.50672	-2.4291	1.53576
33	H	0.88895	-0.65076	2.97813
34	H	-1.75745	0.27492	0.10654
35	H	-2.84996	-0.20022	2.73667
36	H	-3.75677	-0.23464	1.18789
37	H	-3.80921	-1.62422	2.29049
38	H	2.86798	0.19626	1.57032
39	H	4.87194	2.71311	0.94036
40	H	-0.02734	2.48916	2.51644
41	H	0.83055	3.88939	1.93901
42	H	0.0033	2.8524	0.7681

Conformer 3-4		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z
1	C	-0.86732	-0.34118	-2.06056
2	C	-1.91478	-1.41346	-2.23928
3	C	-1.83728	-2.48722	-1.13436
4	C	-0.4346	-2.54706	-0.50066
5	C	0.03618	-1.19889	0.18573
6	C	0.36087	-0.75952	-1.30391

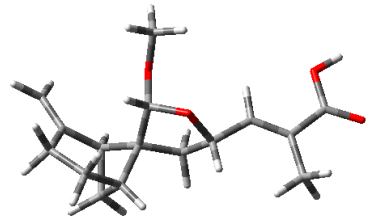
7	C	-1.00059	0.92703	-2.46953
8	C	0.68861	-2.27644	-1.5461
9	C	1.23689	-1.24794	1.12685
10	C	1.20066	0.14216	1.76828
11	O	-0.16113	0.57761	1.73383
12	C	-0.9459	-0.3784	1.01479
13	O	-1.59631	-1.25802	1.93598
14	C	-2.62885	-0.59662	2.65364
15	C	2.10861	1.11975	1.06186
16	C	1.87967	2.38887	0.66194
17	C	2.98988	3.04483	-0.07304
18	O	2.57851	4.11769	-0.7684
19	C	0.64528	3.1965	0.9233
20	O	4.15361	2.68588	-0.10695
21	H	-1.74048	-1.89726	-3.209
22	H	-2.92548	-0.99122	-2.2743
23	H	-2.09277	-3.46231	-1.56597
24	H	-2.58836	-2.28576	-0.36246
25	H	-0.29745	-3.4449	0.11075
26	H	1.21671	-0.09249	-1.44532
27	H	-0.22814	1.67044	-2.29432
28	H	-1.89065	1.25656	-2.99725
29	H	1.69248	-2.58803	-1.23492
30	H	0.52956	-2.66834	-2.55584
31	H	2.19138	-1.48198	0.6462
32	H	1.06582	-2.00807	1.89991
33	H	1.52416	0.07895	2.81333
34	H	-1.69578	0.1458	0.41536
35	H	-3.09482	-1.32102	3.32714
36	H	-2.22374	0.22265	3.25491
37	H	-3.39393	-0.22012	1.96775
38	H	3.09276	0.69612	0.85052
39	H	3.39651	4.43466	-1.20397
40	H	0.16609	2.9242	1.86757
41	H	0.87751	4.26289	1.01903
42	H	-0.07341	3.07369	0.10745

Conformer 3-5		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z
1	C	-0.83666	0.19791	-2.15083

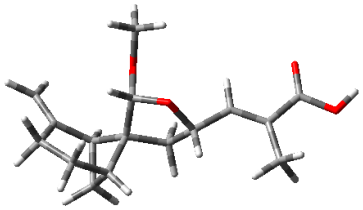
2	C	-1.78428	-0.86529	-2.65268
3	C	-1.63863	-2.1903	-1.87793
4	C	-0.25705	-2.30547	-1.20949
5	C	0.06048	-1.1636	-0.1597
6	C	0.39428	-0.30763	-1.45243
7	C	-1.05447	1.51463	-2.25962
8	C	0.87142	-1.66851	-2.07618
9	C	1.23042	-1.38717	0.79507
10	C	1.02429	-0.28564	1.83659
11	O	-0.34325	0.11893	1.77929
12	C	-1.01794	-0.68002	0.80284
13	O	-1.60452	-1.82312	1.43042
14	C	-2.71236	-1.46393	2.24439
15	C	1.97677	0.86752	1.64835
16	C	1.76767	2.17705	1.39494
17	C	2.99335	3.01628	1.32737
18	O	2.72318	4.32861	1.42071
19	C	0.45801	2.8653	1.16307
20	O	4.14087	2.62206	1.21523
21	H	-1.55085	-1.05285	-3.70876
22	H	-2.82639	-0.52805	-2.61495
23	H	-1.78826	-3.02711	-2.57056
24	H	-2.42796	-2.27166	-1.12228
25	H	-0.05601	-3.32222	-0.85633
26	H	1.18605	0.44092	-1.34803
27	H	-0.35057	2.24669	-1.87595
28	H	-1.94544	1.89759	-2.74855
29	H	1.88898	-1.97142	-1.80335
30	H	0.78309	-1.78037	-3.16166
31	H	2.21866	-1.36095	0.32574
32	H	1.12777	-2.36623	1.28046
33	H	1.20689	-0.69288	2.83831
34	H	-1.79844	-0.08325	0.32176
35	H	-3.12433	-2.3769	2.68286
36	H	-2.40116	-0.80078	3.05692
37	H	-3.49236	-0.98614	1.64369
38	H	3.01227	0.5457	1.78598
39	H	3.60747	4.74748	1.37864
40	H	-0.31761	2.19891	0.786
41	H	0.1021	3.32812	2.08877
42	H	0.55451	3.64777	0.40186

Figure S49 DFT-optimized structures for low-energy conformers of **4** (1*S*,5*S*,6*S*,9*S*,14*R*-**4**) at B3LYP/6-31+G(d) level in MeOH (PCM).

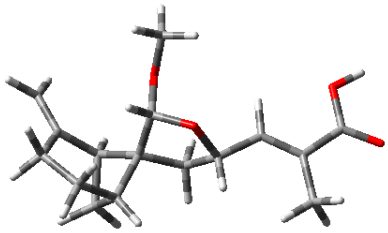
Conformer populations were calculated using the Gibbs free energy and Boltzmann population at 298 K estimated thereof.



Conf. 4-1 39.9%



Conf. 4-2 19.6%



Conf. 4-3 40.5%

Table S19 Harmonic frequencies (cm**$^{-1}$) of compound **4**.

Conformations	**Frequencies**		
	1	2	3
4-1	26.3742	31.1182	47.1196
4-2	27.7961	31.5383	48.0854
4-3	26.2287	31.0826	47.1166

Table S20 Important thermodynamic parameters (a.u.) and Boltzmann distributions of the optimized compound **4** at B3LYP/6-31G+(d) level of theory with PCM solvent model for MeOH.

Conformations	E+ZPE	G	%
4-1	-923.466817	-923.515931	39.9%
4-2	-923.466347	-923.515262	19.6%
4-3	-923.466820	-923.515944	40.5%

E+ZPE, G: total energy with zero point energy (ZPE) and Gibbs free energy at B3LYP/6-31G+(d) level of theory with PCM solvent model for MeOH. %: Boltzmann distributions, using the relative Gibbs free energies as weighting factors.

Table S21 Cartesian coordinates of the low-energy re-optimized conformers of compound **4** (1*S*,5*S*,6*S*,9*S*,14*R*-**4**) calculated at B3LYP/6-31+G(d) level of theory with PCM solvent model for MeOH.

Conformer 4-1		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z
1	C	2.53717	0.35688	-2.22331
2	C	1.89106	-0.22625	-3.45632
3	C	0.60704	-1.01158	-3.11919
4	C	0.60209	-1.4794	-1.6533
5	C	0.7168	-0.3279	-0.56274
6	C	2.25092	-0.36595	-0.93497
7	C	3.26283	1.48219	-2.20989
8	C	2.03089	-1.89927	-1.1798
9	C	0.28385	-0.74555	0.84009
10	C	-1.19509	-0.36134	0.82553
11	O	-1.35101	0.71008	-0.12339
12	C	-0.08088	0.96048	-0.73539
13	O	0.59489	2.00871	-0.03683
14	C	-0.01255	3.27131	-0.26949
15	C	-1.68764	0.1211	2.15465
16	C	-2.51295	-0.52082	3.00649
17	C	-2.93125	0.11683	4.28298
18	O	-2.3608	1.31012	4.51517
19	C	-3.08347	-1.89357	2.80185
20	O	-3.71232	-0.36604	5.08484
21	H	2.60943	-0.91382	-3.92106
22	H	1.6669	0.54584	-4.2011
23	H	0.53455	-1.87864	-3.78675
24	H	-0.27864	-0.39822	-3.31866
25	H	-0.18457	-2.21828	-1.46731
26	H	2.9463	-0.13014	-0.12295
27	H	3.67431	1.88391	-1.28823
28	H	3.45891	2.03777	-3.12163
29	H	2.06124	-2.51522	-0.27349
30	H	2.67425	-2.38604	-1.91986
31	H	0.41625	-1.80735	1.0686
32	H	0.84269	-0.17413	1.59224
33	H	-1.79479	-1.18873	0.43523
34	H	-0.22999	1.24623	-1.78049
35	H	0.55359	4.02913	0.27884

36	H	0.01567	3.52175	-1.33438
37	H	-1.04431	3.28106	0.09419
38	H	-1.32363	1.1157	2.41268
39	H	-2.73873	1.58308	5.37585
40	H	-2.90067	-2.51998	3.68208
41	H	-4.16455	-1.83444	2.63816
42	H	-2.64381	-2.41951	1.95105

Conformer 4-2		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z
1	C	1.86241	0.4078	-2.84984
2	C	1.10237	-0.50427	-3.78158
3	C	0.12986	-1.4278	-3.0197
4	C	0.55431	-1.60299	-1.55107
5	C	0.65345	-0.26425	-0.69889
6	C	2.03611	-0.09729	-1.44308
7	C	2.30685	1.62692	-3.18042
8	C	2.10908	-1.66343	-1.40597
9	C	0.64635	-0.47908	0.81244
10	C	-0.84592	-0.37371	1.12481
11	O	-1.44177	0.44792	0.10408
12	C	-0.42554	0.80437	-0.83961
13	O	0.1416	2.06852	-0.48883
14	C	-0.76855	3.13488	-0.71647
15	C	-1.12357	0.26185	2.45132
16	C	-1.59744	-0.33172	3.56535
17	C	-1.80474	0.54889	4.74333
18	O	-2.40822	-0.09252	5.75802
19	C	-1.91261	-1.78818	3.72093
20	O	-1.49138	1.72113	4.84683
21	H	1.83225	-1.12797	-4.31363
22	H	0.55442	0.05993	-4.54479
23	H	0.10222	-2.40428	-3.5181
24	H	-0.8903	-1.0312	-3.06902
25	H	0.01059	-2.42168	-1.06788
26	H	2.8257	0.40841	-0.87798
27	H	2.814	2.26307	-2.46045
28	H	2.16772	2.02619	-4.18021
29	H	2.47486	-2.08108	-0.46072
30	H	2.66223	-2.15861	-2.21055

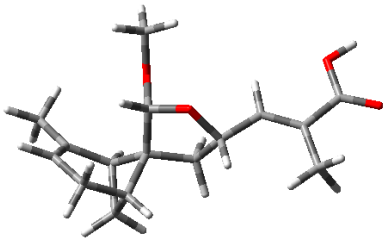
31	H	1.05516	-1.43776	1.14559
32	H	1.22038	0.31416	1.30821
33	H	-1.31959	-1.35475	1.0266
34	H	-0.86108	0.85807	-1.84137
35	H	-0.2729	4.07095	-0.44526
36	H	-1.04691	3.18447	-1.77362
37	H	-1.66202	3.02494	-0.09481
38	H	-0.92021	1.33421	2.47104
39	H	-2.48468	0.60012	6.44666
40	H	-1.59114	-2.38932	2.86697
41	H	-1.40253	-2.20035	4.59854
42	H	-2.99082	-1.93458	3.84314

Conformer 4-3		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z
1	C	2.30179	-0.62475	-2.31303
2	C	1.42311	-1.0398	-3.46773
3	C	0.03288	-1.512	-2.99521
4	C	0.06374	-1.97197	-1.52717
5	C	0.54303	-0.88125	-0.47401
6	C	1.98463	-1.2676	-0.98993
7	C	3.26315	0.30419	-2.38997
8	C	1.39827	-2.70907	-1.18419
9	C	0.16357	-1.19075	0.97066
10	C	-1.19388	-0.49015	1.08372
11	O	-1.17446	0.6021	0.15271
12	C	0.04778	0.55525	-0.59097
13	O	1.01512	1.41792	0.0109
14	C	0.70717	2.78681	-0.20664
15	C	-1.49437	-0.03187	2.48421
16	C	-2.20167	1.04393	2.89112
17	C	-2.33466	1.35621	4.33884
18	O	-1.78333	0.43844	5.15188
19	C	-2.93626	1.99379	1.99066
20	O	-2.88926	2.33736	4.80321
21	H	1.91717	-1.8716	-3.98621
22	H	1.30962	-0.23398	-4.20179
23	H	-0.2998	-2.33692	-3.6367
24	H	-0.70475	-0.71162	-3.12062
25	H	-0.84857	-2.51249	-1.25364

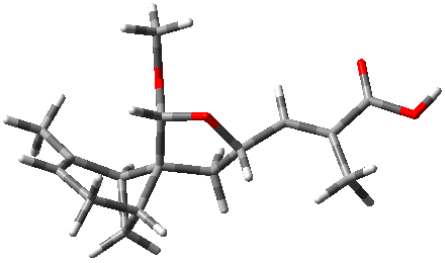
26	H	2.79081	-1.20001	-0.25234
27	H	3.8429	0.5976	-1.51935
28	H	3.49155	0.80341	-3.32645
29	H	1.37513	-3.31906	-0.27366
30	H	1.8389	-3.32725	-1.97302
31	H	0.08439	-2.25545	1.21014
32	H	0.90053	-0.75034	1.65461
33	H	-1.98426	-1.17806	0.75994
34	H	-0.14107	0.86964	-1.62134
35	H	1.47992	3.39202	0.27501
36	H	0.70631	3.01506	-1.27688
37	H	-0.25934	3.04534	0.23503
38	H	-1.05865	-0.67878	3.24514
39	H	-1.95636	0.79909	6.04566
40	H	-2.32666	2.88092	1.79379
41	H	-3.21589	1.53524	1.03828
42	H	-3.87825	2.32047	2.44533

Figure S50 DFT-optimized structures for low-energy conformers of **5** (1*S*,5*S*,6*S*,9*S*,14*R*-**5**) at B3LYP/tzvp level in MeOH (PCM).

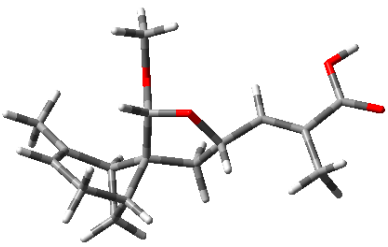
Conformer populations were calculated using the Gibbs free energy and Boltzmann population at 298 K estimated thereof.



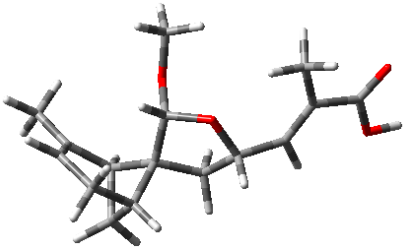
Conf. 5-1 41.3%



Conf. 5-2 17.1%



Conf. 5-3 41.4%



Conf. 5-4 0.1%

Table S22 Harmonic frequencies (cm**$^{-1}$) of compound **5**.

Conformations	**Frequencies**		
	1	2	3
5-1	20.8988	30.2225	44.1280
5-2	22.9947	30.4718	45.9334
5-3	20.8697	30.2121	44.1263
5-4	25.1160	31.5041	47.8987

Table S23 Important thermodynamic parameters (a.u.) and Boltzmann distributions of the optimized compound **5** at B3LYP/tzvp level of theory with PCM solvent model for MeOH.

Conformations	E+ZPE	G	%
5-1	-923.764225	-923.813918	41.3%
5-2	-923.763721	-923.813088	17.1%
5-3	-923.764226	-923.813921	41.4%
5-4	-923.759765	-923.808588	0.1%

E+ZPE, G: total energy with zero point energy (ZPE) and Gibbs free energy at B3LYP/tzvp level of theory with PCM solvent model for MeOH. %: Boltzmann distributions, using the relative Gibbs free energies as weighting factors.

Table S24 Cartesian coordinates of the low-energy re-optimized conformers of compound **5** (1*S*,5*S*,6*S*,9*S*,14*R*-**5**) calculated at B3LYP/tzvp level of theory with PCM solvent model for MeOH.

Conformer 5-1		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z
1	C	1.24502	-2.14306	-2.29182
2	C	0.05138	-2.71538	-2.54501
3	C	-0.97912	-2.87955	-1.44985
4	C	-0.42364	-2.28365	-0.1413
5	C	0.26714	-0.8573	-0.28129
6	C	1.47201	-1.7019	-0.86831
7	C	2.32346	-1.91537	-3.29718

8	C	1.02184	-2.81695	0.1396
9	C	0.47028	-0.10711	1.03129
10	C	-0.81299	0.71572	1.11038
11	O	-1.2607	0.94048	-0.23792
12	C	-0.40318	0.21799	-1.13013
13	O	0.61191	1.0859	-1.63932
14	C	0.08141	2.03386	-2.55435
15	C	-0.6136	2.04938	1.76078
16	C	-1.03469	2.43818	2.98159
17	C	-0.77732	3.81928	3.46876
18	O	-0.04456	4.57082	2.63121
19	C	-1.77053	1.57773	3.96645
20	O	-1.16725	4.2718	4.53148
21	H	-0.2029	-3.06698	-3.5409
22	H	-1.20334	-3.94318	-1.31437
23	H	-1.90804	-2.37417	-1.73343
24	H	-1.1252	-2.39212	0.69216
25	H	2.4712	-1.29201	-0.6929
26	H	2.03395	-2.27187	-4.29095
27	H	2.55002	-0.8473	-3.37514
28	H	3.23572	-2.44312	-3.00186
29	H	1.38257	-2.68286	1.16565
30	H	1.22616	-3.85518	-0.14301
31	H	0.58982	-0.74213	1.91413
32	H	1.3577	0.53507	0.96291
33	H	-1.60474	0.1329	1.59016
34	H	-1.00169	-0.17999	-1.95427
35	H	0.90396	2.65654	-2.91651
36	H	-0.37322	1.52847	-3.41191
37	H	-0.65173	2.68146	-2.06446
38	H	-0.076	2.75865	1.1313
39	H	0.02749	5.42988	3.09482
40	H	-1.27989	1.61012	4.94566
41	H	-2.80021	1.93126	4.08388
42	H	-1.8085	0.52568	3.67397

Conformer 5-2		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z
1	C	-1.31836	-2.36064	-2.08033
2	C	-2.5616	-2.23619	-1.57508

3	C	-2.77703	-1.91803	-0.11202
4	C	-1.40716	-1.75907	0.57657
5	C	-0.34731	-0.87206	-0.21146
6	C	-0.18973	-2.1752	-1.09832
7	C	-0.99155	-2.65255	-3.50639
8	C	-0.46977	-2.96445	0.22855
9	C	0.84439	-0.40225	0.61712
10	C	0.34822	0.95114	1.11986
11	O	-0.60067	1.44372	0.15799
12	C	-0.79527	0.44033	-0.84625
13	O	0.04609	0.70463	-1.9708
14	C	-0.38435	1.85001	-2.69204
15	C	1.44226	1.9641	1.25104
16	C	1.96773	2.46532	2.38708
17	C	3.03518	3.48526	2.22493
18	O	3.39694	4.03366	3.39692
19	C	1.58497	2.07395	3.78176
20	O	3.56474	3.83353	1.18507
21	H	-3.43834	-2.35432	-2.2055
22	H	-3.34414	-2.72808	0.35932
23	H	-3.36133	-0.99742	-0.01298
24	H	-1.50494	-1.54464	1.64571
25	H	0.8	-2.33692	-1.53586
26	H	-1.89443	-2.75726	-4.1166
27	H	-0.38985	-1.84277	-3.9311
28	H	-0.42272	-3.58451	-3.58269
29	H	0.40064	-3.08875	0.88264
30	H	-0.94632	-3.94589	0.1327
31	H	1.11793	-1.05857	1.4486
32	H	1.72852	-0.29508	-0.02428
33	H	-0.21369	0.82275	2.04958
34	H	-1.84395	0.4458	-1.15612
35	H	0.28568	1.98845	-3.5449
36	H	-1.4011	1.70706	-3.07058
37	H	-0.33601	2.74623	-2.06649
38	H	1.81907	2.32447	0.29195
39	H	4.08687	4.6794	3.13837
40	H	0.91068	1.21477	3.81534
41	H	2.47239	1.79312	4.35958
42	H	1.08733	2.90692	4.28912

Conformer 5-3		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z
1	C	0.85446	-2.63931	-1.8013
2	C	-0.42389	-2.98431	-2.05271
3	C	-1.47755	-2.90251	-0.9705
4	C	-0.83175	-2.36707	0.32263
5	C	0.11984	-1.10536	0.1375
6	C	1.14731	-2.18837	-0.39288
7	C	1.96653	-2.66428	-2.79545
8	C	0.48257	-3.15277	0.65103
9	C	0.44804	-0.34896	1.41962
10	C	-0.66852	0.69658	1.44858
11	O	-1.01967	0.96053	0.08395
12	C	-0.32265	0.04052	-0.76475
13	O	0.84458	0.66404	-1.30366
14	C	0.51651	1.62923	-2.292
15	C	-0.26925	1.94549	2.1852
16	C	-0.61351	3.22776	1.93904
17	C	-0.05307	4.33047	2.76473
18	O	0.71454	3.91568	3.78756
19	C	-1.5788	3.68331	0.88391
20	O	-0.24428	5.52025	2.58114
21	H	-0.73054	-3.32363	-3.03805
22	H	-1.90155	-3.89739	-0.79617
23	H	-2.29042	-2.24273	-1.29088
24	H	-1.54942	-2.30449	1.147
25	H	2.20453	-1.9688	-0.21618
26	H	1.62421	-3.00143	-3.77915
27	H	2.39359	-1.6632	-2.91219
28	H	2.75827	-3.34285	-2.46283
29	H	0.85182	-3.0455	1.67719
30	H	0.48796	-4.22213	0.41447
31	H	0.44869	-0.9577	2.32869
32	H	1.43535	0.12293	1.33333
33	H	-1.55369	0.26815	1.93417
34	H	-0.98878	-0.26961	-1.57471
35	H	1.44632	2.06967	-2.662
36	H	-0.00093	1.1572	-3.13282
37	H	-0.10005	2.42777	-1.86982
38	H	0.39752	1.74469	3.02349

39	H	0.99525	4.75342	4.20981
40	H	-1.04139	3.97864	-0.02233
41	H	-2.31256	2.91366	0.62953
42	H	-2.16564	4.54242	1.22781

Conformer 5-4		Standard Orientation (Ångstroms)		
I	Atom	X	Y	Z
1	C	-2.33994	-2.19477	-0.19407
2	C	-3.26322	-1.48761	0.48682
3	C	-2.88164	-0.69368	1.71579
4	C	-1.36541	-0.83404	1.95546
5	C	-0.44662	-0.66354	0.66457
6	C	-0.93571	-2.13982	0.35299
7	C	-2.6028	-2.99862	-1.42315
8	C	-0.93648	-2.33938	1.90868
9	C	1.0312	-0.42576	0.95838
10	C	1.06458	1.09544	1.00369
11	O	0.13964	1.55434	0.01324
12	C	-0.74364	0.46879	-0.32029
13	O	-0.44941	0.00786	-1.63935
14	C	-1.0095	0.85969	-2.62827
15	C	2.4458	1.66318	0.84713
16	C	3.03857	2.21575	-0.23247
17	C	4.41271	2.77497	-0.13249
18	O	5.00079	2.57306	1.05998
19	C	2.42467	2.29839	-1.59784
20	O	5.00629	3.36722	-1.01691
21	H	-4.30184	-1.46805	0.16912
22	H	-3.43655	-1.07035	2.58195
23	H	-3.14973	0.35885	1.57851
24	H	-1.03843	-0.29066	2.84787
25	H	-0.22899	-2.76907	-0.19637
26	H	-3.6546	-2.94975	-1.72289
27	H	-1.99761	-2.62774	-2.25636
28	H	-2.34945	-4.0494	-1.25103
29	H	0.04324	-2.56476	2.34469
30	H	-1.64736	-3.06581	2.31677
31	H	1.3955	-0.86715	1.89045
32	H	1.6437	-0.8125	0.1341

33	H	0.66661	1.44533	1.96513
34	H	-1.77536	0.82785	-0.26333
35	H	-0.64024	1.88371	-2.51933
36	H	-0.71173	0.48527	-3.61134
37	H	-2.10216	0.84519	-2.5692
38	H	3.00694	1.62341	1.78064
39	H	5.87756	2.99495	0.9488
40	H	1.87474	1.3856	-1.84016
41	H	1.7519	3.15881	-1.6651
42	H	3.18055	2.40097	-2.38356