Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information for

Bipolarithizole A, an Antifungal Phenylthiazole-Sativene Merosesquiterpenoid from Potato Endophytic Fungus *Bipolaris eleusines*

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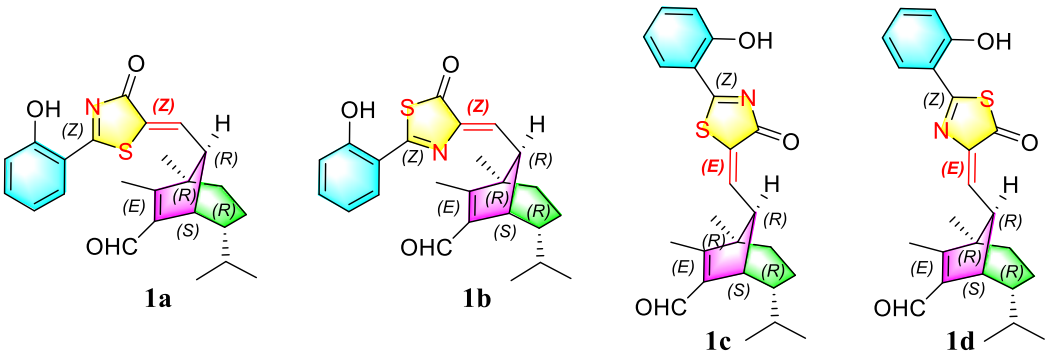
Quantum chemical calculation

The initial conformational analysis of the compound **1** was executed by employing Monte Carlo searching algorithm via the MMFF94 molecular mechanics force field[1], with the aid of the SPARTAN'16 program package, leading to afford a panel of relatively favored conformations in an energy range of 3 kcal/mol above the global minimum. The force field minimum energy conformers thus obtained were subsequently optimized by applying the density functional theory (DFT) with the M06-2X/Def2SVP level in vacuum, implemented in the Gaussian 09 software package[2]. Harmonic vibrational frequencies were also performed to confirm no imaginary frequencies of the finally optimized conformers. These predominant conformers were subjected to theoretical calculation of ECD by utilizing Time-dependent density functional theory (TDDFT) calculations at the M06-2X/Def2SVP level in MeOH using the Polarizable Continuum Model (PCM) solvent model. The energies, oscillator strengths, and rotational strengths of each conformers were carried out with Gaussian 09 software package. The oretical calculations of ECD spectra for each conformer were then approximated by the Gaussian distribution. The final ECD spectrum of the individual conformers was summed up on the basis of Boltzmann-weighed population contribution by the SpecDisv1.71[3]. Gauge Independent Atomic Orbital (GIAO) calculations of their ^{1}H and ^{13}C NMR chemical shifts using density functional theory (DFT) at the mPW1PW91/6-311+G(d,p) level with the PCM model in methanol. The calculated NMR data of these conformers were averaged according to the Boltzmann distribution theory and their relative Gibbs free energy. The ^{1}H and ^{13}C NMR chemical shifts for TMS were also calculated by the same procedures and used as the reference. After calculation, the experimental and calculated data were evaluated by the improved probability DP4+ method.

1 NMR computational details for compound 1



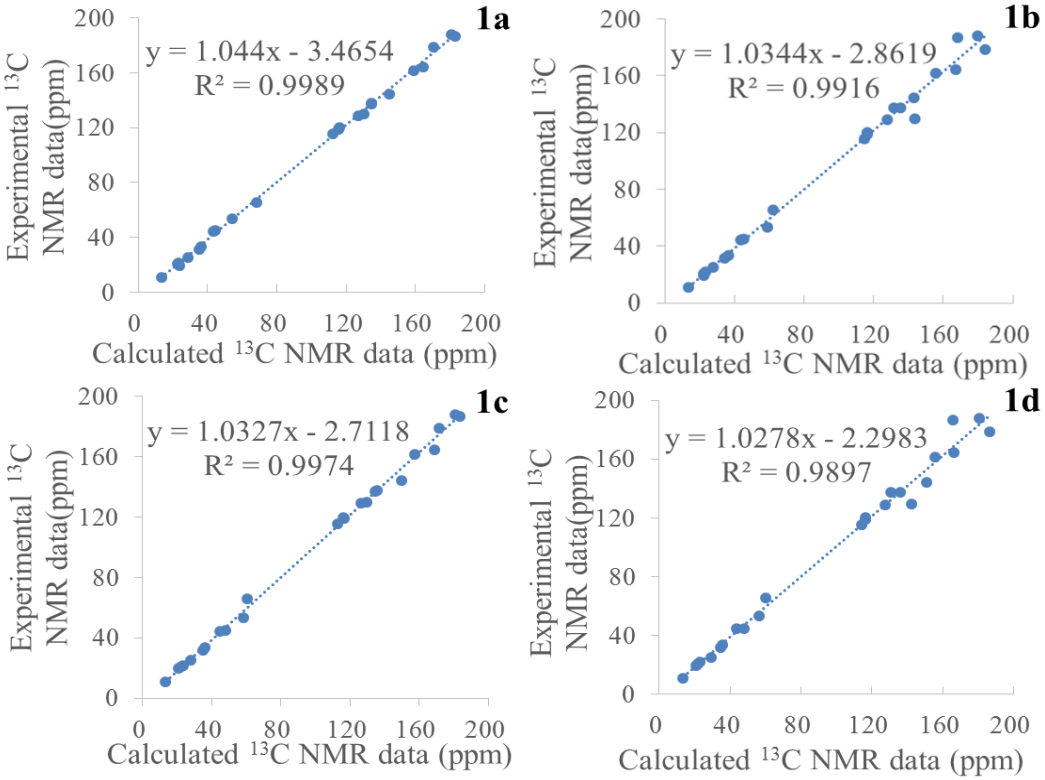


Figure S1. Correlations between calculated and experimental ^{13}C NMR chemical shifts of **1a-1d**

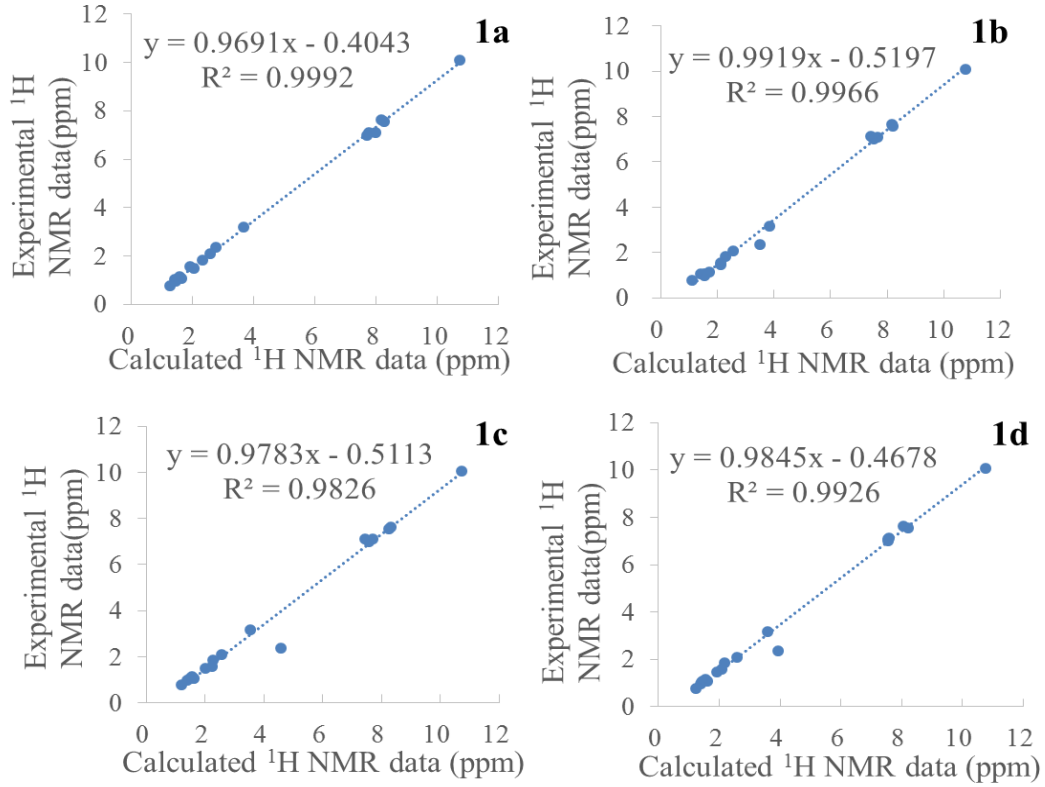


Figure S2. Correlations between calculated and experimental 1H NMR chemical shifts of 1a-1d.

Table S1. DP4+ analysis results of **1a** (Isomer 1), **1b** (Isomer 2), **1c** (Isomer 3) and **1d** (Isomer 4)

Functional	Solvent?	Basis Set	Type of Data
mPW1PW91	PCM	6-311+G(d,p)	Unscaled Shifts

		DP4+	100.00%	0.00%	0.00%	0.00%
Nuclei	sp2?	xperimenta	Isomer 1	Isomer 2	Isomer 3	Isomer 4
C	x	129.7	132.6	145.7	131.4	143.8
C	x	178.7	174.7	187.5	174.3	189.3
C	x	186.9	187.5	170.9	186.7	168.2
C	x	115.4	113.6	115.6	114.1	114.9
C	x	129	129.3	129.4	128.0	128.6
C	x	120	117.7	117.5	117.3	117.4
C	x	137.3	137.0	133.5	136.3	132.2
C	x	119	117.1	117.2	117.7	117.2
C		53.5	53.3	57.9	57.3	55.8
C	x	161.5	162.6	157.9	160.2	157.4
C		11	10.5	11.3	11.1	11.6
C		31.6	33.3	32.8	33.3	33.5
C		21.7	20.9	21.2	21.4	21.4
C		20.8	20.0	20.4	20.4	20.2
C		19.7	21.4	20.3	18.5	19.2
C	x	187.8	185.6	183.3	183.9	183.0
C		33.5	34.4	34.8	34.3	34.2
C	x	164.5	168.4	170.3	171.7	168.8
C	x	137.7	136.9	137.4	137.5	137.4
C		45	42.8	44.0	46.8	46.7
C		65.8	68.0	61.3	59.6	59.4
C		25.1	26.7	26.0	26.3	27.8
C		44.4	41.8	42.1	43.5	42.8
C	x	144.2	147.7	145.4	152.1	152.9
H		2.36	2.28	2.95	3.96	3.40
H		1.48	1.57	1.57	1.45	1.43
H		1.57	1.44	1.57	1.66	1.58
H		3.18	3.14	3.29	2.95	3.06
H		0.97	1.01	1.02	0.85	0.90
H		1.85	1.84	1.75	1.70	1.67
H		1.14	1.13	1.17	1.00	1.05
H	x	7.12	7.33	6.84	6.76	6.99
H	x	7.65	7.51	7.58	7.64	7.48
H	x	7	7.04	6.95	6.88	6.97
H	x	7.56	7.60	7.61	7.55	7.61
H	x	7.1	7.11	7.07	7.02	6.98
H		2.09	2.08	2.02	1.98	2.08
H		1.07	1.11	0.88	0.93	0.97
H		1.07	1.18	1.01	1.07	1.13
H		0.77	0.80	0.59	0.68	0.76
H		1.05	0.96	1.05	1.03	0.94
H	x	10.08	10.00	10.17	9.99	10.12

Functional	Solvent?	Basis Set	Type of Data
mPW1PW91	PCM	6-311+G(d,p)	Unscaled Shifts

	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5	Isomer 6
sDP4+ (H data)	99.60%	0.32%	0.00%	0.08%	–	–
sDP4+ (C data)	99.99%	0.00%	0.01%	0.00%	–	–
sDP4+ (all data)	100.00%	0.00%	0.00%	0.00%	–	–
uDP4+ (H data)	99.96%	0.03%	0.00%	0.01%	–	–
uDP4+ (C data)	98.75%	0.00%	1.25%	0.00%	–	–
uDP4+ (all data)	100.00%	0.00%	0.00%	0.00%	–	–
DP4+ (H data)	100.00%	0.00%	0.00%	0.00%	–	–
DP4+ (C data)	100.00%	0.00%	0.00%	0.00%	–	–
DP4+ (all data)	100.00%	0.00%	0.00%	0.00%	–	–

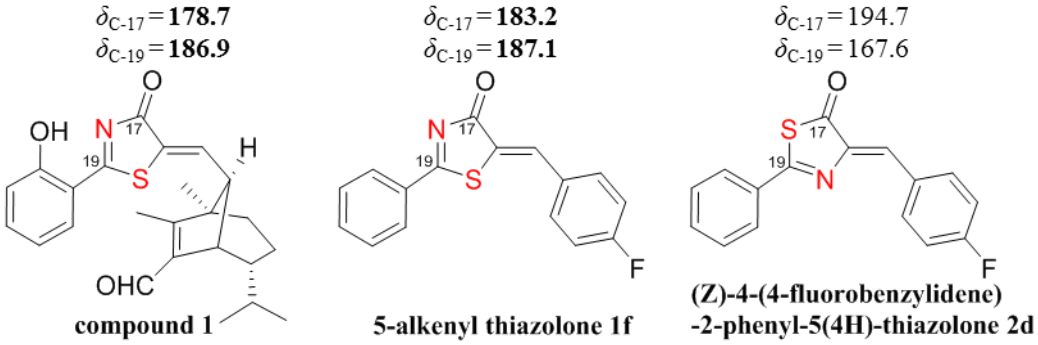


Figure S3 Comparison of chemical shift values of key carbons between compound **1** and two known compounds (**5-alkenyl thiazolone 1f** and **(Z)-4-(4-fluorobenzylidene)-2-phenyl-5(4H)-thiazolone 2d**)

Table S2. Experimental and calculated ^{13}C NMR chemical shifts of **1a**–**1d**.

Num.	Exp.	**1a**	**1b**	**1c**	**1d**
1	129.7	132.6	145.7	131.4	143.8
2	**178.7**	**174.7**	**187.5**	**174.3**	**189.3**
3	**186.9**	**187.5**	**170.9**	**186.7**	**168.2**
4	115.4	113.6	115.6	114.1	114.9
5	129.0	129.3	129.4	128.0	128.6
6	120.0	117.7	117.5	117.3	117.4
7	137.3	137.0	133.5	136.3	132.2
8	119.0	117.1	117.2	117.7	117.2
9	53.5	53.3	57.9	57.3	55.8
10	161.5	162.6	157.9	160.2	157.4
11	11.0	10.5	11.3	11.1	11.6
12	31.6	33.3	32.8	33.3	33.5
13	21.7	20.9	21.2	21.4	21.4
14	20.8	20.0	20.4	20.4	20.2
15	19.7	21.4	20.3	18.5	19.2
16	187.8	185.6	183.3	183.9	183.0
17	33.5	34.4	34.8	34.3	34.2
18	164.5	168.4	170.3	171.7	168.8
19	137.7	136.9	137.4	137.5	137.4
20	45.0	42.8	44.0	46.8	46.7
21	65.8	68.0	61.3	59.6	59.4
22	25.1	26.7	26.0	26.3	27.8
23	44.4	41.8	42.1	43.5	42.8
24	144.2	147.7	145.4	152.1	152.9
R^2		**0.9989**	0.9916	0.9974	0.9897
MAE		4.0436	30.3619	9.5626	37.2912
RMSD		2.0109	5.5102	3.0923	6.1067

Table S3. Experimental and calculated ^{1}H NMR chemical shifts of **1a**–**1d**.

Num.	Exp.	**1a**	**1b**	**1c**	**1d**
1	2.36	2.28	2.95	3.96	3.40
2	1.48	1.57	1.57	1.45	1.43
3	1.57	1.44	1.57	1.66	1.58
4	3.18	3.14	3.29	2.95	3.06
5	0.97	1.01	1.02	0.85	0.90
6	1.85	1.84	1.75	1.70	1.67
7	1.14	1.13	1.17	1.00	1.05
8	7.12	7.33	6.84	6.76	6.99
9	7.65	7.51	7.58	7.64	7.48
10	7	7.04	6.95	6.88	6.97
11	7.56	7.60	7.61	7.55	7.61
12	7.1	7.11	7.07	7.02	6.98
13	2.09	2.08	2.02	1.98	2.08
14	1.07	1.11	0.88	0.93	0.97
15	1.07	1.18	1.01	1.07	1.13
16	0.77	0.80	0.59	0.68	0.76
17	1.05	0.96	1.05	1.03	0.94
18	10.08	10.00	10.17	9.99	10.12
R^2		**0.9992**	0.9966	0.9826	0.9926
MAE		0.0072	0.0310	0.1603	0.0682
RMSD		0.0846	0.1762	0.4004	0.2612

2 ECD Computational details of compound 1

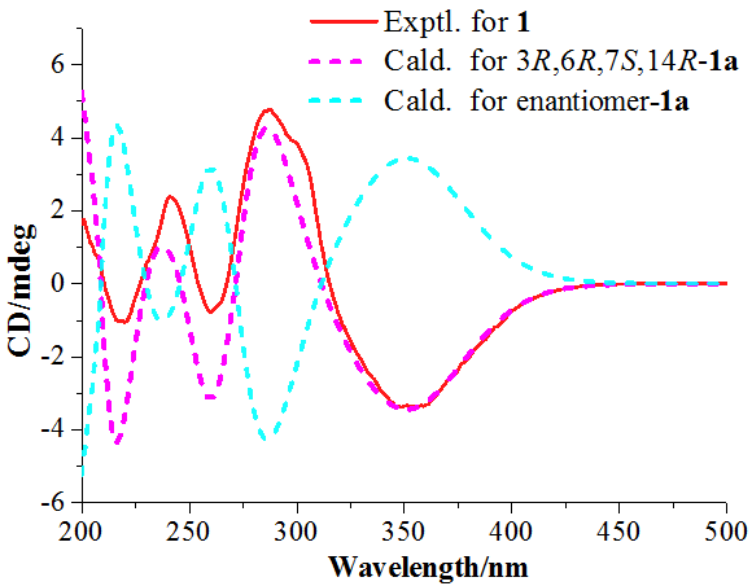


Figure S4. Experimental ECD spectra of **1** and calculated ECD spectra of **1a** and enantiomer-**1a** in methanol.

Table S4. Important thermodynamic parameters of the M06-2X/Def2SVP optimized conformers of **1a** in the gas phase

Conformers	E[a](Hartree)	C[b](Hartree)	G[c](kcal/mol)
1a_1	-1607.896393	0.407933	-1008703.831115
1a_2	-1607.891655	0.408577	-1008700.453894
1a_3	-1607.892688	0.409454	-1008700.551785
1a_4	-1607.897315	0.410427	-1008702.844681
1a_5	-1607.893027	0.407191	-1008702.184547

[a]Electronic energy; [b]Thermal correction to Gibbs free energy ; [c]Gibbs free energy (E + C).

Table S5. Conformational analysis of the M06-2X/Def2SVP optimized conformers of **1a** in the gas phase (T=298.15 K)

Conformers	ΔG (kcal/mol)[a]	Population[b]
1a_1	0.000000	79.48%
1a_2	3.377205	0.26%
1a_3	3.279315	0.31%
1a_4	0.986430	15.02%
1a_5	1.646560	4.93%

[a]The relative Gibbs free energy; [b]The Boltzmann distribution of each conformer.

Table S6. Cartesian coordinates for the low-energy optimized conformers of **1a** at M06-2X/Def2SVP level

Conformer **1a**_1							
C	-2.020398	-0.457313	1.637912	C	-4.401922	-1.744101	-1.003571
C	-2.746794	0.761149	2.255267	O	-4.700639	-1.352315	-2.106528
C	-3.07122	-1.433796	1.110801	H	-3.203859	0.47269	3.215905
C	-3.419024	-1.075487	-0.144256	H	-1.97484	1.512099	2.492038
C	-2.66391	0.174168	-0.567209	H	-2.438157	0.187739	-1.641445
C	-1.39526	0.048287	0.30449	H	-4.735411	0.755879	1.407263
C	-3.819658	1.366286	1.338567	H	-4.088266	2.361703	1.718007
C	-3.424703	1.458199	-0.148789	H	-2.71058	2.294893	-0.272285
C	-0.408397	-0.91123	-0.273359	H	-0.775073	-1.850362	-0.705375
C	0.917927	-0.745035	-0.307771	H	3.832555	2.224954	0.905007
C	1.85334	-1.769151	-0.900241	H	6.045914	3.279138	1.234085
N	3.187983	-1.336204	-0.809863	H	8.102531	2.086344	0.462431
C	3.323489	-0.181334	-0.241462	H	7.923614	-0.145738	-0.629882
S	1.837001	0.623955	0.305564	H	-4.022887	-2.085045	2.905387
C	4.616902	0.447052	-0.04436	H	-4.418373	-3.091522	1.489755
C	4.736414	1.709957	0.571614	H	-2.82079	-3.214191	2.272925
C	5.968889	2.302718	0.757276	H	-5.354594	0.938004	-0.943508
C	7.122433	1.627486	0.321118	H	-3.95617	0.913802	-2.929465
C	7.038383	0.389002	-0.286208	H	-3.430399	2.605879	-2.652576
C	5.788607	-0.230074	-0.484254	H	-5.109277	2.241589	-3.109595
C	-3.620318	-2.518765	1.97542	H	-6.169469	3.303765	-1.264115
C	-4.640399	1.774987	-1.041743	H	-5.761593	2.968447	0.427219
C	-4.254238	1.885522	-2.51717	H	-4.638893	3.904957	-0.589867
C	-5.342172	3.055641	-0.584221	H	-0.227992	-0.324857	2.843894
C	-1.021178	-1.054775	2.61905	H	-1.511531	-1.322089	3.567095
O	1.503452	-2.810731	-1.378636	H	-0.539981	-1.95581	2.21128
O	5.763465	-1.413046	-1.070312	H	4.818274	-1.713659	-1.140781
H	-0.90802	1.024575	0.460436	H	-4.865603	-2.670668	-0.591411

Conformer **1a**_2							
C	-1.95112	-0.21967	1.580445	C	-4.306071	-1.922733	-0.846721
C	-2.678569	1.06446	2.052592	O	-4.623377	-1.671707	-1.984565
C	-2.990524	-1.280094	1.210398	H	-3.092049	0.903738	3.061559
C	-3.36692	-1.101116	-0.074586	H	-1.914744	1.853827	2.150096
C	-2.660408	0.104978	-0.667796	H	-2.480176	-0.004446	-1.746858
C	-1.364575	0.106645	0.173041	H	-4.666718	0.85202	1.272544
C	-3.799495	1.505771	1.101927	H	-4.127745	2.524608	1.359369
C	-3.413508	1.431323	-0.38506	H	-2.669096	2.223792	-0.579304
C	-0.378383	-0.910972	-0.297691	H	-0.743891	-1.884771	-0.645176
C	0.949515	-0.755075	-0.323328	H	3.85686	2.298337	0.680937
C	1.890489	-1.833354	-0.798927	H	6.069498	3.367338	0.964209
N	3.225987	-1.400105	-0.719159	H	8.134626	2.100035	0.350209
C	3.357058	-0.198677	-0.256262	H	7.964883	-0.220461	-0.540752
S	1.864135	0.660881	0.180299	H	-3.907699	-1.717646	3.085479
C	4.65004	0.438638	-0.086991	H	-4.277088	-2.915069	1.819917
C	4.76438	1.751266	0.415499	H	-2.6714	-2.881299	2.597282
C	5.996453	2.352347	0.575433	H	-4.35385	1.197928	-2.2969
C	7.154819	1.635057	0.22825	H	-5.555208	3.414169	-2.307632
C	7.075852	0.347312	-0.266977	H	-3.79918	3.602228	-2.090369
C	5.826618	-0.281106	-0.436932	H	-4.894417	3.763111	-0.69651
C	-3.495195	-2.258072	2.217679	H	-6.684101	1.240539	-1.6884
C	-4.59562	1.705146	-1.348549	H	-5.899435	0.109299	-0.578495
C	-4.71514	3.204539	-1.629517	H	-6.330743	1.745887	-0.024005
C	-5.94681	1.164311	-0.876513	H	-0.134068	0.095695	2.714447
C	-0.91972	-0.668389	2.607053	H	-1.384439	-0.814492	3.593664
O	1.544301	-2.91282	-1.187464	H	-0.432463	-1.608711	2.310445
O	5.806432	-1.512121	-0.914221	H	4.861156	-1.813707	-0.978092
H	-0.884137	1.098723	0.18487	H	-4.71029	-2.826046	-0.331999

Conformer **1a**_3							
C	-1.965162	-0.036895	1.665823	C	-4.342589	-1.825758	-0.666601
C	-2.655788	1.280337	2.098527	O	-4.6225	-1.683082	-1.833616
C	-3.03313	-1.08442	1.347887	H	-3.065374	1.164888	3.115255
C	-3.419744	-0.948053	0.059805	H	-1.871835	2.053211	2.162591
C	-2.69349	0.2184	-0.590404	H	-2.51469	0.054859	-1.661327
C	-1.387936	0.218307	0.240096	H	-4.650924	1.086483	1.330067
C	-3.76926	1.714886	1.137877	H	-4.075244	2.75001	1.356378
C	-3.390291	1.586769	-0.345029	H	-2.605552	2.335368	-0.556735
C	-0.434503	-0.84316	-0.200708	H	-0.82897	-1.820375	-0.504217
C	0.896408	-0.72242	-0.24969	H	3.891348	2.295217	0.588763
C	1.803688	-1.84267	-0.692926	H	6.133285	3.318789	0.800905
N	3.150497	-1.440312	-0.648866	H	8.158165	1.975606	0.214814
C	3.317752	-0.224777	-0.237377	H	7.919506	-0.374292	-0.577521
S	1.852869	0.689132	0.183537	H	-3.917906	-1.436212	3.254721
C	4.62821	0.386183	-0.111181	H	-4.347068	-2.665587	2.040301
C	4.781528	1.71503	0.335246	H	-2.723161	-2.64728	2.779713
C	6.030029	2.290895	0.455266	H	-4.670574	3.053016	-1.173689
C	7.165621	1.530957	0.124016	H	-6.66398	1.677308	-1.677567
C	7.048415	0.226456	-0.31678	H	-6.27005	1.631666	0.047248
C	5.781903	-0.376722	-0.445535	H	-5.880729	0.242929	-1.009141
C	-3.539634	-2.016315	2.397055	H	-4.931576	2.166911	-3.422044
C	-4.55636	1.960302	-1.290705	H	-3.204443	2.064322	-3.008887
C	-5.912138	1.338816	-0.949383	H	-4.231668	0.601765	-2.954172
C	-4.205491	1.683312	-2.752947	H	-0.126212	0.273846	2.76459
C	-0.93251	-0.473067	2.696715	H	-1.387704	-0.568381	3.693885
O	1.425441	-2.928099	-1.031662	H	-0.473357	-1.436505	2.431174
O	5.724825	-1.625347	-0.871293	H	4.771627	-1.905264	-0.911274
H	-0.880382	1.196134	0.207132	H	-4.767218	-2.678486	-0.087219

Conformer **1a**_4							
C	2.864362	-1.75297	0.429045	C	1.259202	1.426925	1.703805
C	4.341091	-1.36046	0.183322	O	0.867353	2.43539	1.164014
C	2.305381	-0.853287	1.531074	H	4.962581	-1.710194	1.023744
C	1.849831	0.294459	0.982853	H	4.680476	-1.916674	-0.706053
C	2.074712	0.280461	-0.522563	H	1.306982	0.828459	-1.08325
C	2.064178	-1.230518	-0.803913	H	4.562764	0.640578	0.970563
C	4.550717	0.147408	-0.015584	H	5.546023	0.312354	-0.450547
C	3.477063	0.840985	-0.876663	H	3.653893	0.580792	-1.937869
C	0.725174	-1.891334	-0.934534	H	0.74076	-2.941992	-1.249675
C	-0.517793	-1.434506	-0.73613	H	-2.606698	2.138518	0.496261
C	-1.709024	-2.349758	-0.945491	H	-4.503095	3.626658	1.044116
N	-2.91306	-1.679064	-0.682187	H	-6.84087	2.759065	0.868901
C	-2.746342	-0.446001	-0.320876	H	-7.258481	0.410157	0.150851
S	-1.083215	0.153006	-0.234405	H	3.439777	-1.484562	3.224657
C	-3.85193	0.434287	0.008046	H	2.038289	-0.469551	3.65002
C	-3.631525	1.766049	0.418817	H	1.811164	-2.164524	3.146725
C	-4.686775	2.600612	0.7277	H	3.38182	2.650087	0.282083
C	-5.99937	2.10699	0.628202	H	2.67783	4.158337	-1.637044
C	-6.246324	0.806186	0.230928	H	1.496518	2.907213	-1.229664
C	-5.182275	-0.060117	-0.086149	H	2.548874	2.716499	-2.668878
C	2.394469	-1.248577	2.966778	H	4.997329	3.973505	-1.129389
C	3.566843	2.376012	-0.77207	H	5.742665	2.504226	-0.477086
C	2.506205	3.072411	-1.626069	H	5.218939	2.556126	-2.178458
C	4.961844	2.875167	-1.154778	H	3.058373	-3.824227	-0.178832
C	2.737809	-3.246084	0.701324	H	3.378327	-3.544027	1.544697
O	-1.626301	-3.49674	-1.285288	H	1.702925	-3.532858	0.938637
O	-5.469265	-1.295261	-0.457991	H	-4.620136	-1.77832	-0.641142
H	2.623956	-1.471024	-1.723819	H	1.162425	1.307587	2.807942

Conformer **1a**_5							
C	-2.01422	-0.380588	1.55565	C	-4.4456	-1.59627	-1.09441
C	-2.719775	0.850939	2.170835	O	-5.154423	-2.525986	-0.796028
C	-3.084371	-1.335247	1.026266	H	-3.185299	0.570705	3.129451
C	-3.42124	-0.974606	-0.232283	H	-1.936812	1.589952	2.409162
C	-2.635444	0.261197	-0.648152	H	-2.387614	0.280456	-1.718983
C	-1.373636	0.116339	0.227683	H	-4.705124	0.872154	1.320369
C	-3.782019	1.470907	1.251441	H	-4.037658	2.471067	1.627718
C	-3.383448	1.555163	-0.235903	H	-2.669612	2.390821	-0.365914
C	-0.397965	-0.854876	-0.350376	H	-0.77644	-1.781262	-0.799359
C	0.93141	-0.71141	-0.364227	H	3.879689	2.176354	0.960582
C	1.857527	-1.738608	-0.966397	H	6.106099	3.182513	1.346963
N	3.198274	-1.332602	-0.845142	H	8.152761	1.971024	0.57785
C	3.34564	-0.19274	-0.2503	H	7.951011	-0.231593	-0.568795
S	1.864994	0.628591	0.289842	H	-4.047722	-1.965294	2.818632
C	4.64672	0.407316	-0.019096	H	-4.475722	-2.933866	1.369463
C	4.779216	1.653266	0.628077	H	-2.8847	-3.125914	2.17287
C	6.018996	2.219185	0.845876	H	-5.298182	1.002305	-1.043118
C	7.166912	1.5335	0.411111	H	-3.469124	2.822406	-2.715806
C	7.07024	0.311123	-0.226172	H	-5.096349	2.297479	-3.200256
C	5.812869	-0.280684	-0.456967	H	-3.799282	1.105082	-3.037601
C	-3.666544	-2.406631	1.882527	H	-6.173059	3.348764	-1.340756
C	-4.602791	1.858877	-1.128743	H	-5.778513	2.983272	0.347813
C	-4.217585	2.021774	-2.600133	H	-4.668946	3.97565	-0.629863
C	-5.34873	3.108067	-0.654625	H	-0.225984	-0.283636	2.77304
C	-1.031108	-0.998032	2.540272	H	-1.53337	-1.26089	3.483047
O	1.496136	-2.760159	-1.477885	H	-0.565519	-1.906903	2.132112
O	5.775824	-1.449251	-1.070556	H	4.827036	-1.732406	-1.160441
H	-0.872958	1.085645	0.386299	H	-4.52705	-1.137726	-2.111923

Spectroscopic data

Figure S5. ^{1}H NMR spectrum of **1** in $CDCl_3$

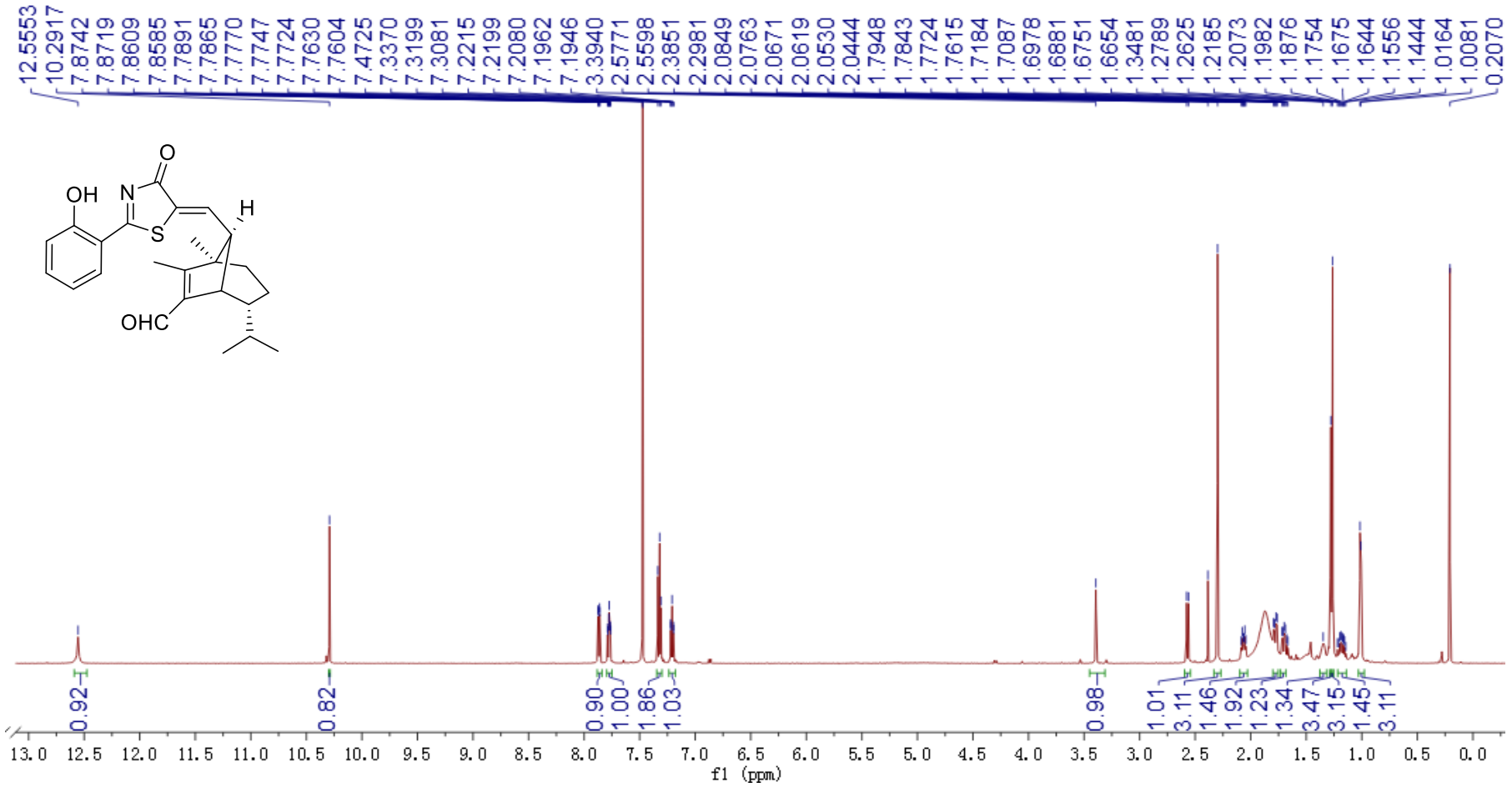


Figure S6 ^{13}C NMR spectrum of **1** in $CDCl_3$

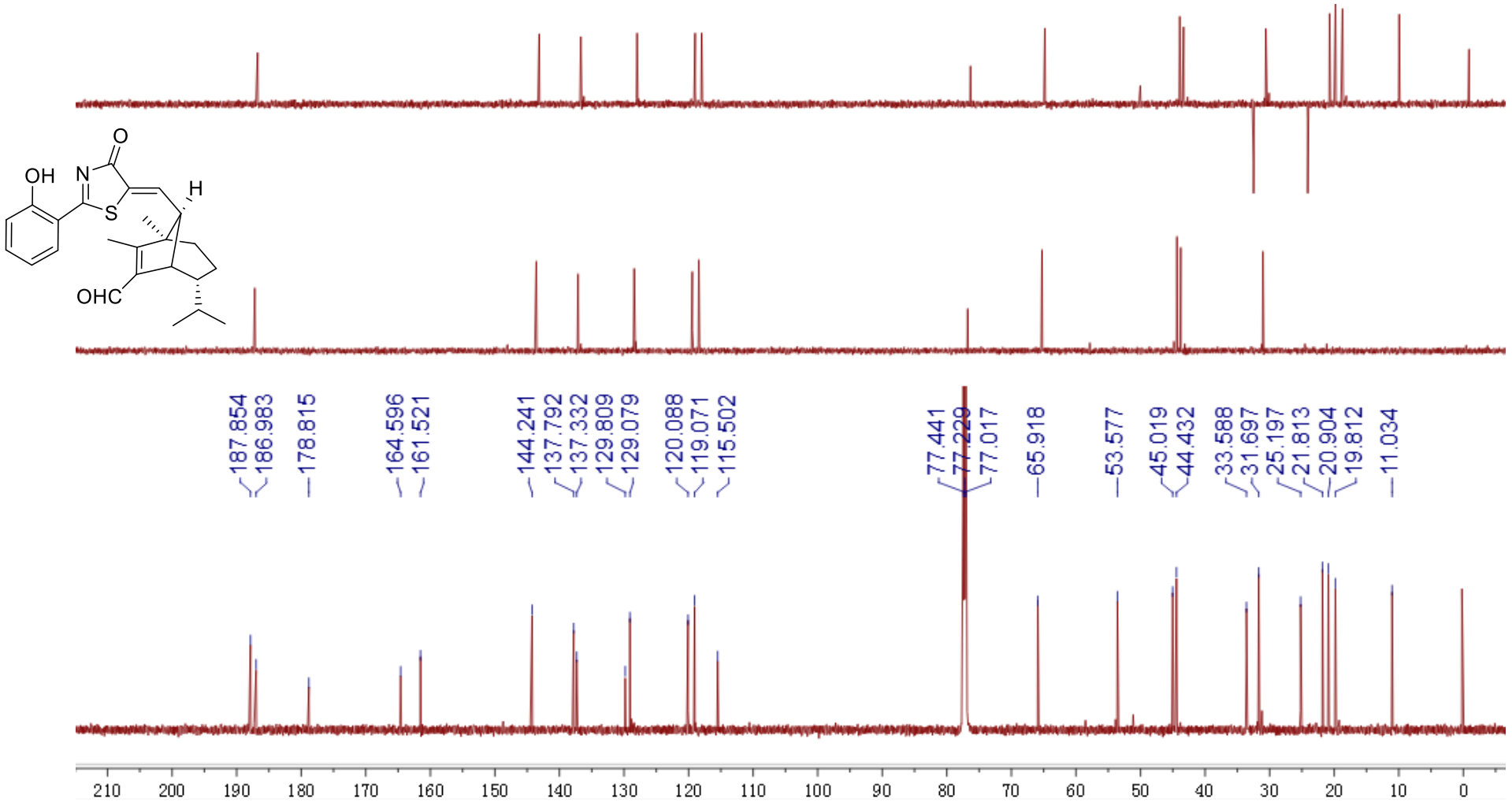


Figure S7 HSQC spectrum of **1** in $CDCl_3$

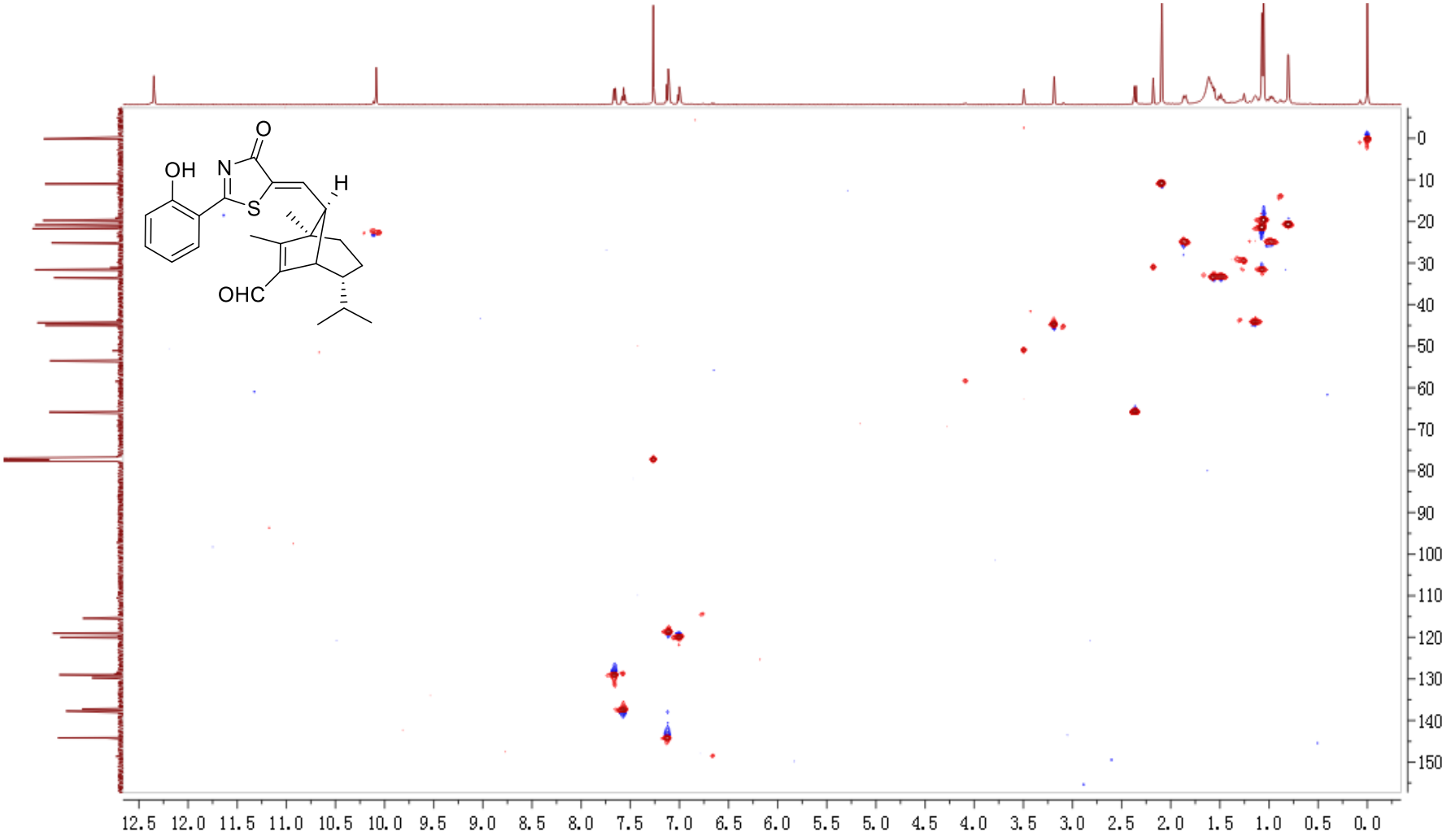


Figure S8 HMBC spectrum of **1** in $CDCl_3$

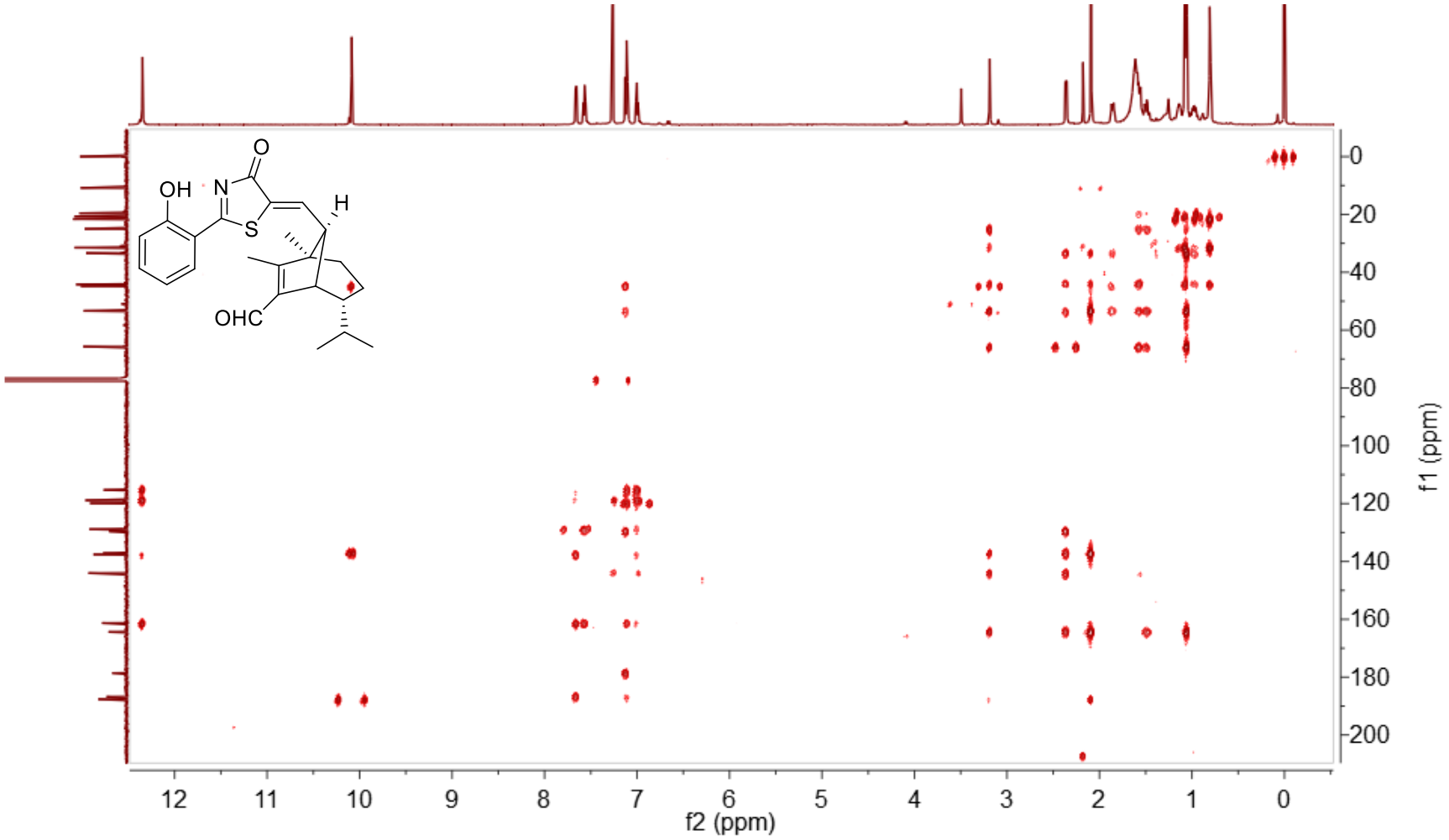


Figure S9 COSY spectrum of **1** in $CDCl_3$

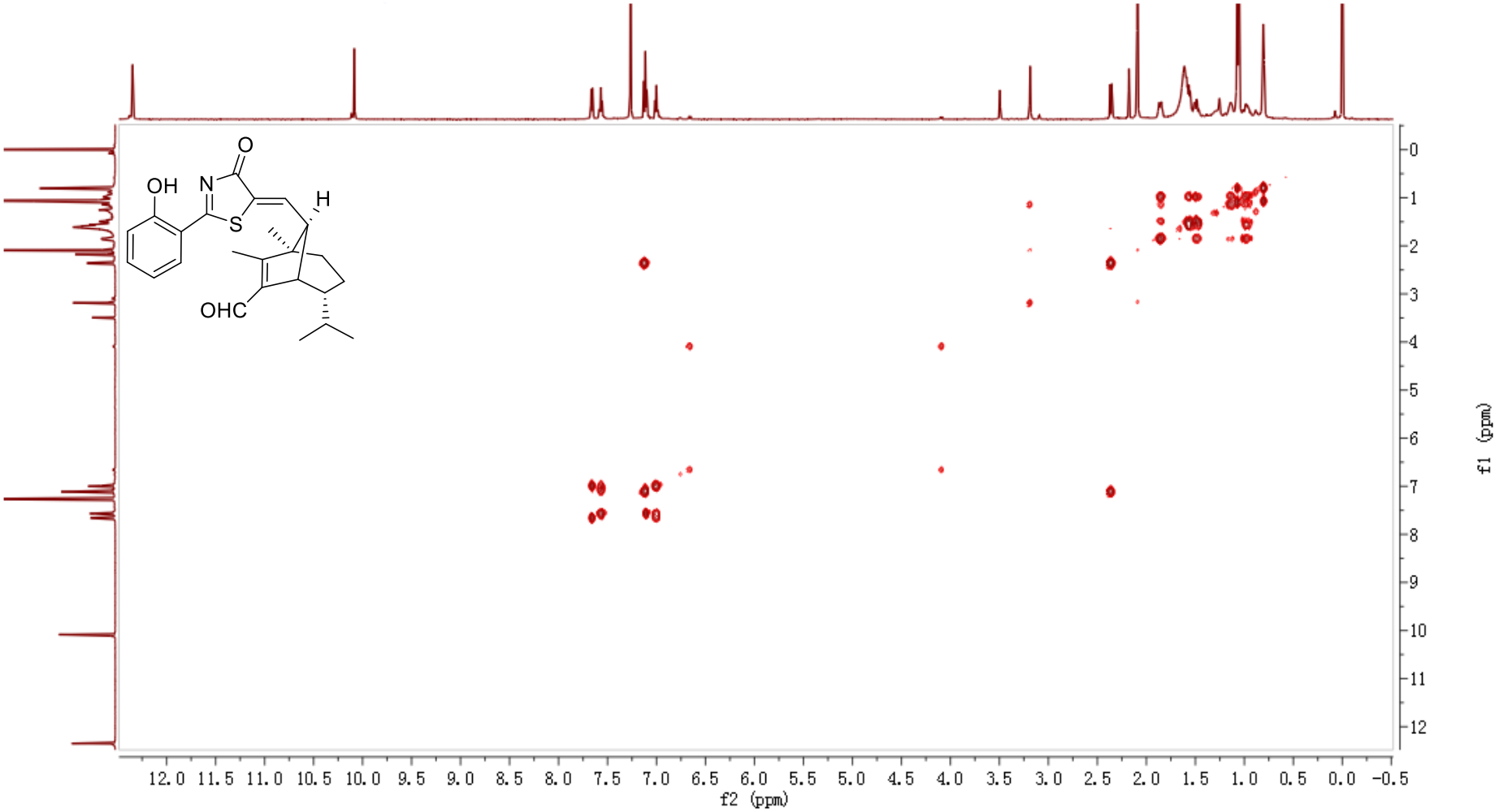


Figure S10 ROESY spectrum of **1** in $CDCl_3$

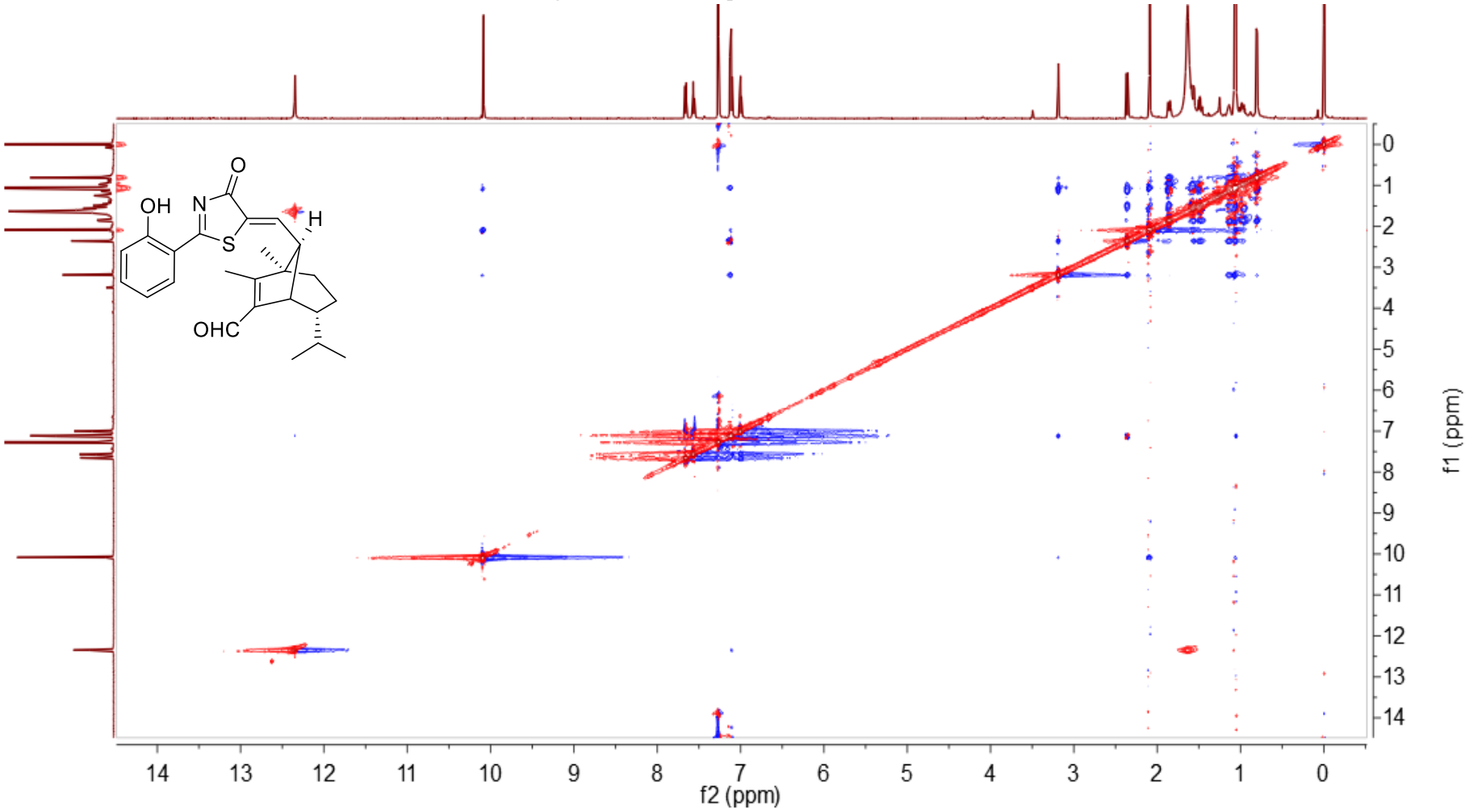


Figure S11 HRMS spectrum of **1**

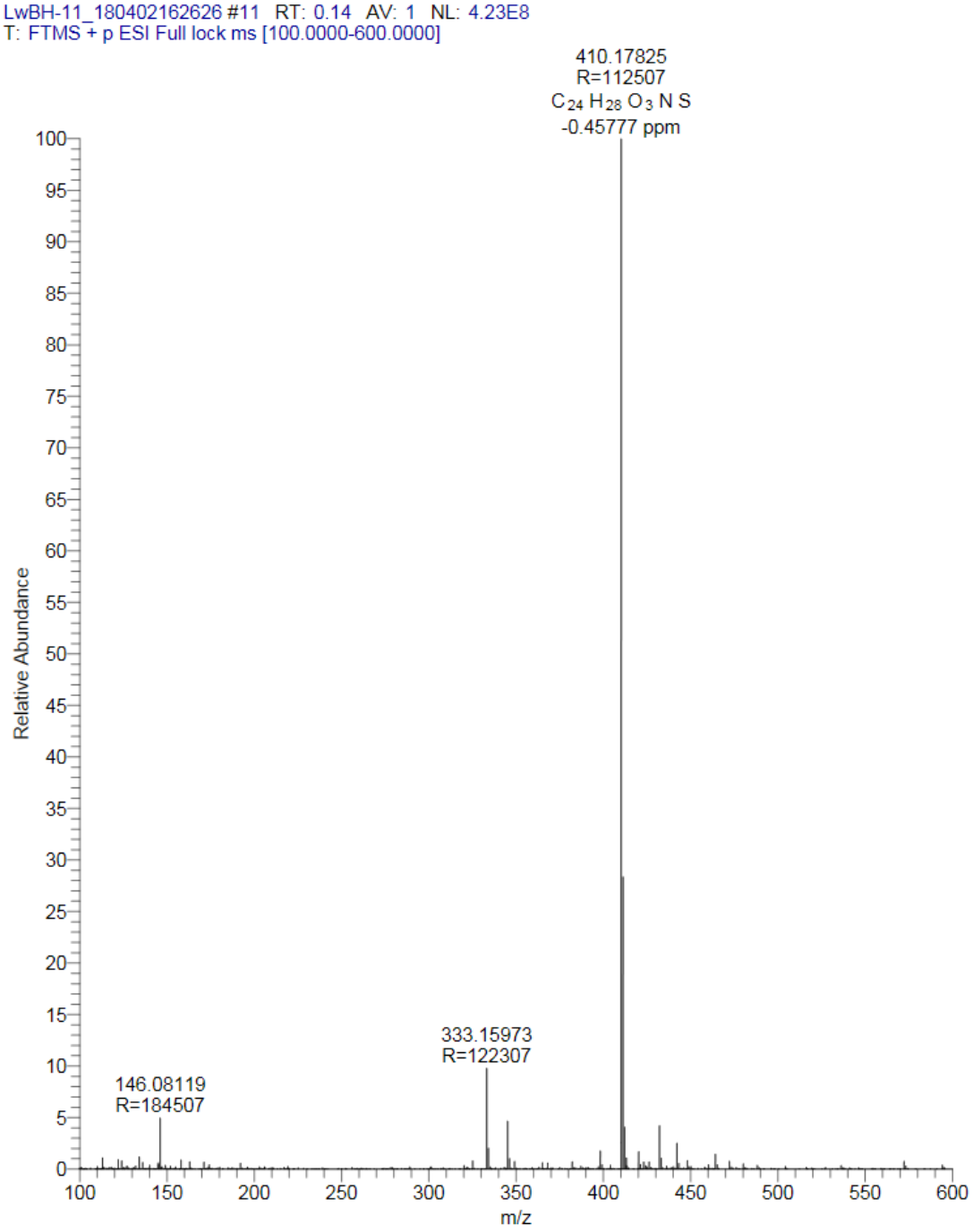


Figure S12 UV spectrum of **1** in MeOH

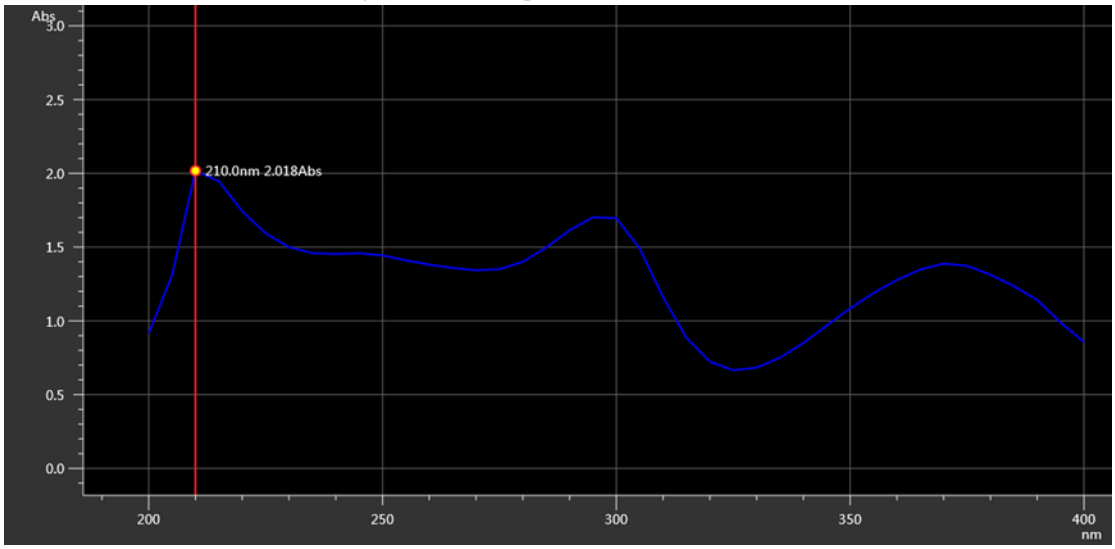


Figure S13 CD spectrum of **1** in MeOH

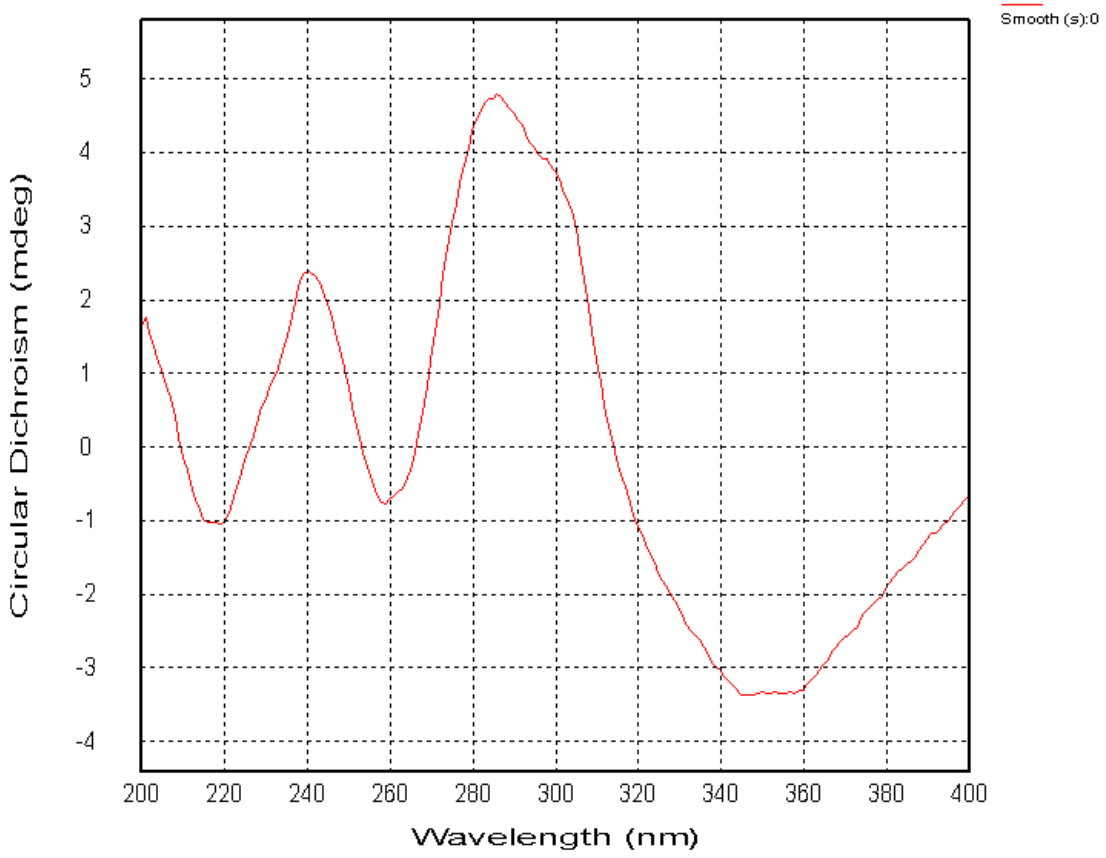


Figure S14 IR spectrum of **1**

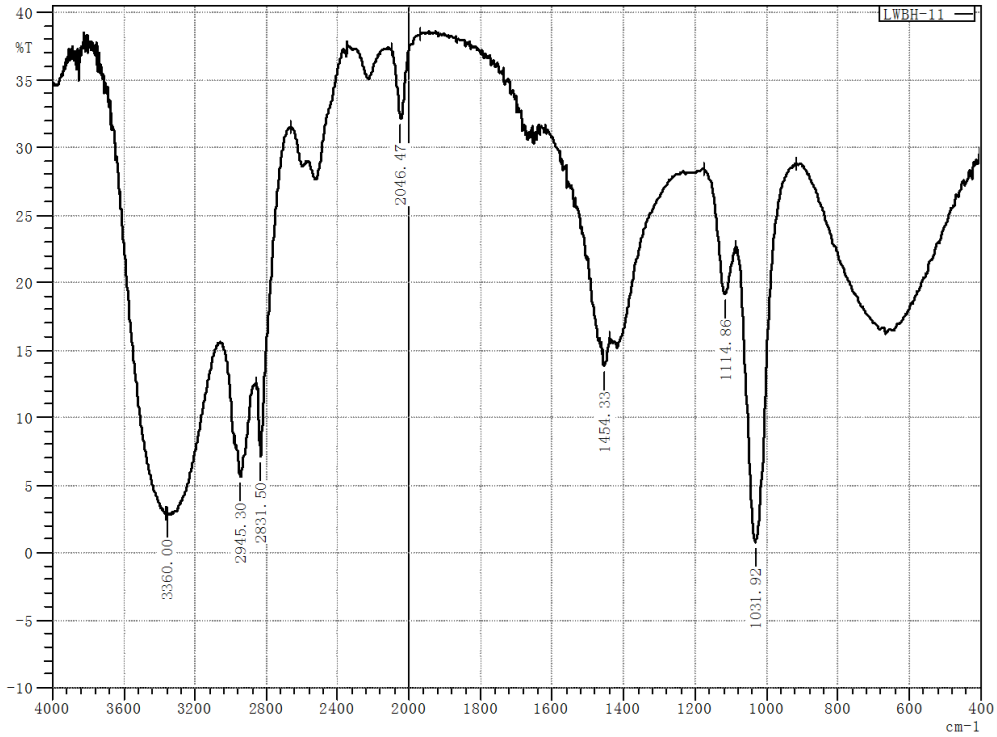


Figure S15 X-ray crystallographic data for **2**

A specimen of $C_{10}H_7NO_2S$, M = 205.23, approximate dimensions 0.032 mm x 0.067 mm x 0.432 mm, was used for the X-ray crystallographic analysis on the BRUKER D8 QUEST. The integration of the data using a monoclinic unit cell yielded a total of 12752 reflections to a maximum θ angle of 72.30° (0.81 Å resolution), of which 1836 were independent (average redundancy 6.946, completeness = 98.3%, Rint = 3.88%, Rsig = 3.09%) and 1745 (95.04%) were greater than 2σ(F2). The final cell constants of a = 12.488(13) Å, b = 4.816(6) Å, c = 16.50(2) Å, β = 107.81(4)°, volume = 944.8(19) Å3, T = 293(2) K. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, Z = 4, μ(CuKα) = 1.54178. The final anisotropic full-matrix least-squares refinement on F^2 with 135 variables converged at R1 = 3.33%, for the observed data and wR2 = 9.23% for all data. The goodness-of-fit was 1.062. All these data are available via https://www.ccdc.cam.ac.uk (CCDC number: 2127795).

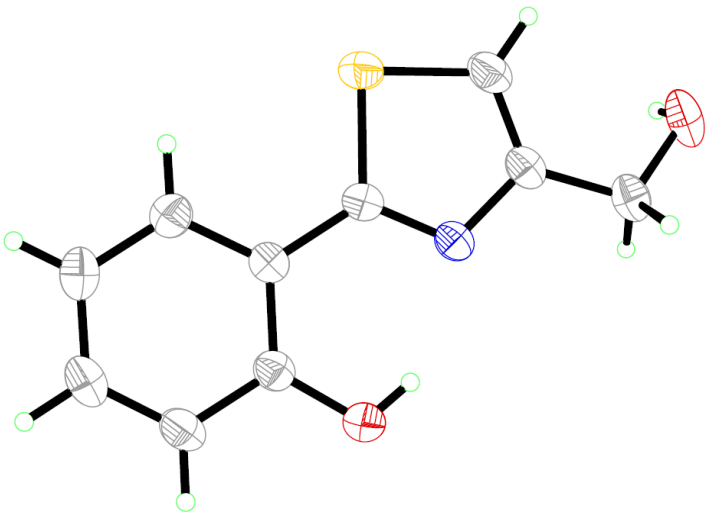
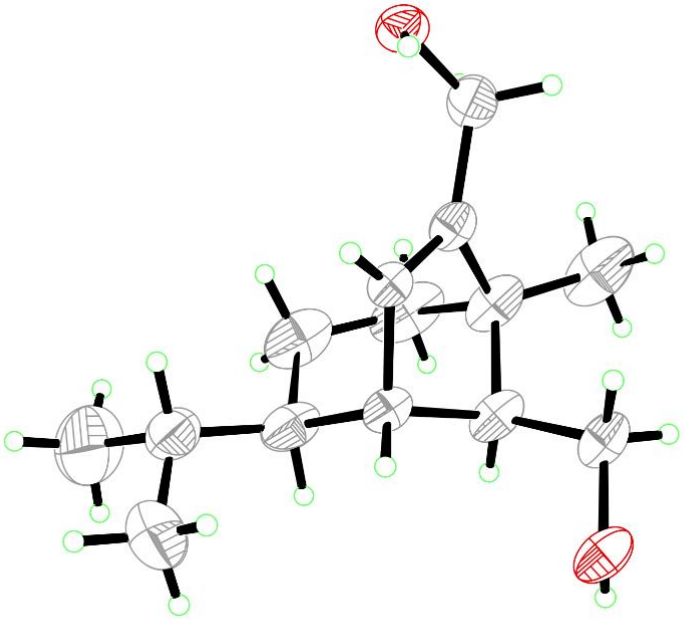


Figure S16 X-ray crystallographic data for **3**

A clear light colourless NEEDLE-like of $C_{14}H_{24}O_2$, M = 224.33, approximate dimensions 0.131 mm x 0.173 mm x 0.198 mm, was used for the X-ray crystallographic analysis on the BRUKER D8 QUEST. The integration of the data using a trigonal unit cell yielded a total of 39026 reflections to a maximum θ angle of 79.22° (0.78 Å resolution), of which 3033 were independent (average redundancy 12.867, completeness = 99.9%, R_{int} = 4.59%, R_{sig} = 1.95%) and 2920 (96.27%) were greater than $2\sigma(F^2)$. The final cell constants of a = 13.6388(2) Å, b = 13.6388(2) Å, c = 13.0174(2) Å, α = 90.00°, β = 90.00°, γ = 90.00°, volume = 2097.04(7) $Å^3$, T = 296(2) K. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 31 2 1, with Z = 6, μ(CuKα) = 1.54178. The final anisotropic full-matrix least-squares refinement on F^2 with 155 variables converged at R1 = 3.53%, for the observed data and wR2 = 10.03% for all data. The goodness-of-fit was 1.047. The absolute configuration was determined by the Flack parameter = 0.01(5), which was determined using 1236 quotients [(I+)-(I-)]/[(I+)+(I-)](Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259). All these data are available via https://www.ccdc.cam.ac.uk (CCDC number: 2126101).



Duel culture of *Bipolaris eleusines* with pathogenic fungi

Both *B. eleusines* and four plant pathogenic fungi were cultured in PDA plates simultaneously at room temperature, respectively. After twenty days, a clear antagonistic zone appeared between the *B. eleusines* and *R. solani* as shown in the picture below, which indicated that there may be antifungal metabolites produced by the fungus *B. eleusines*.

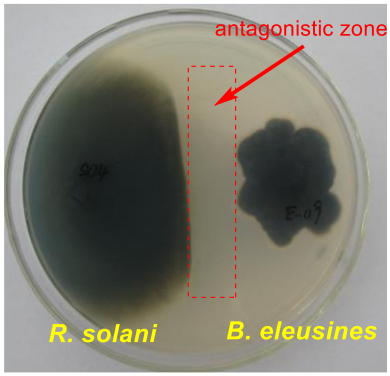


Figure S17. The inhibition assay of *B. eleusines* against phytopathogenic fungi.