Supporting Information

Frutescone A–G, Tasmanone-Based Meroterpenoids from the aerial parts of *Baeckea frutescens*

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List of Supporting Information

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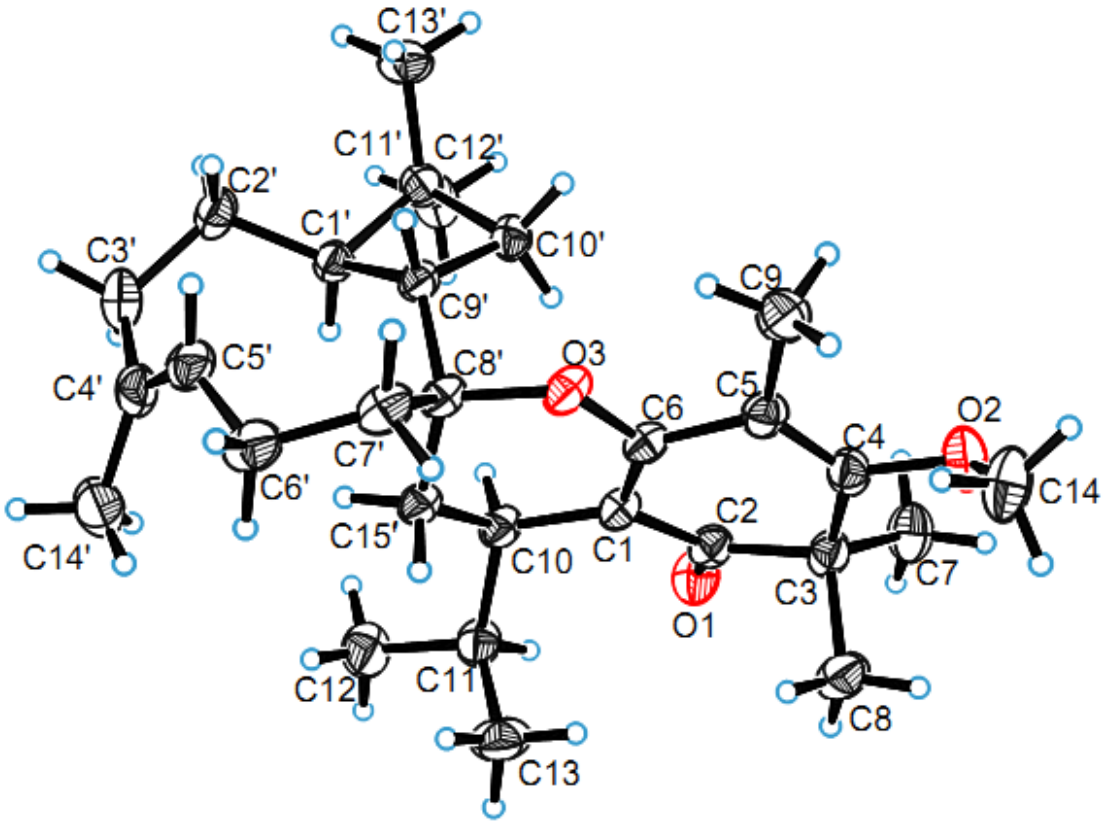

Figure S1. X-ray crystallographic structure of **1** (30% probability level)

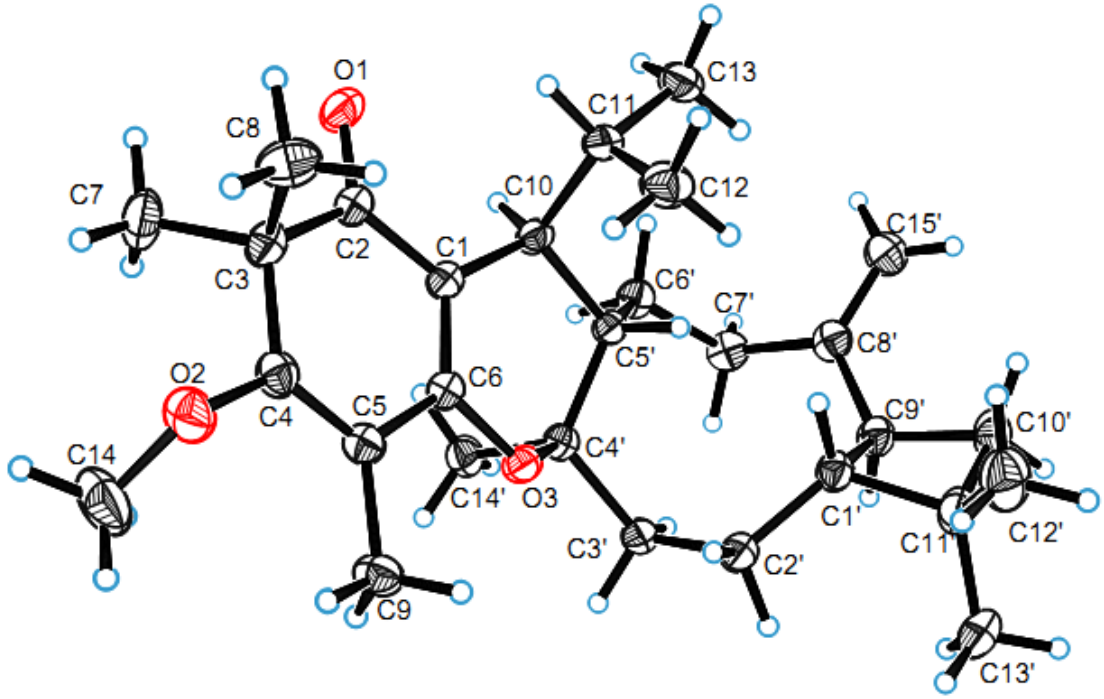

Figure S2. X-ray crystallographic structure of **2** (30% probability level)

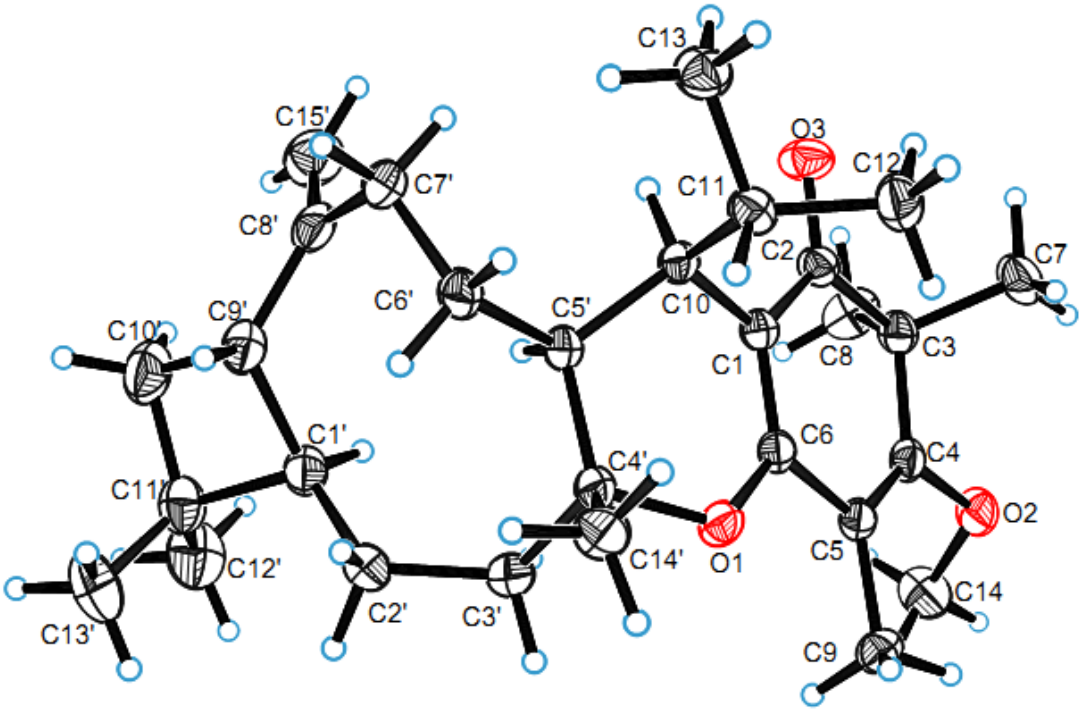

Figure S3. X-ray crystallographic structure of **3** (30% probability level)

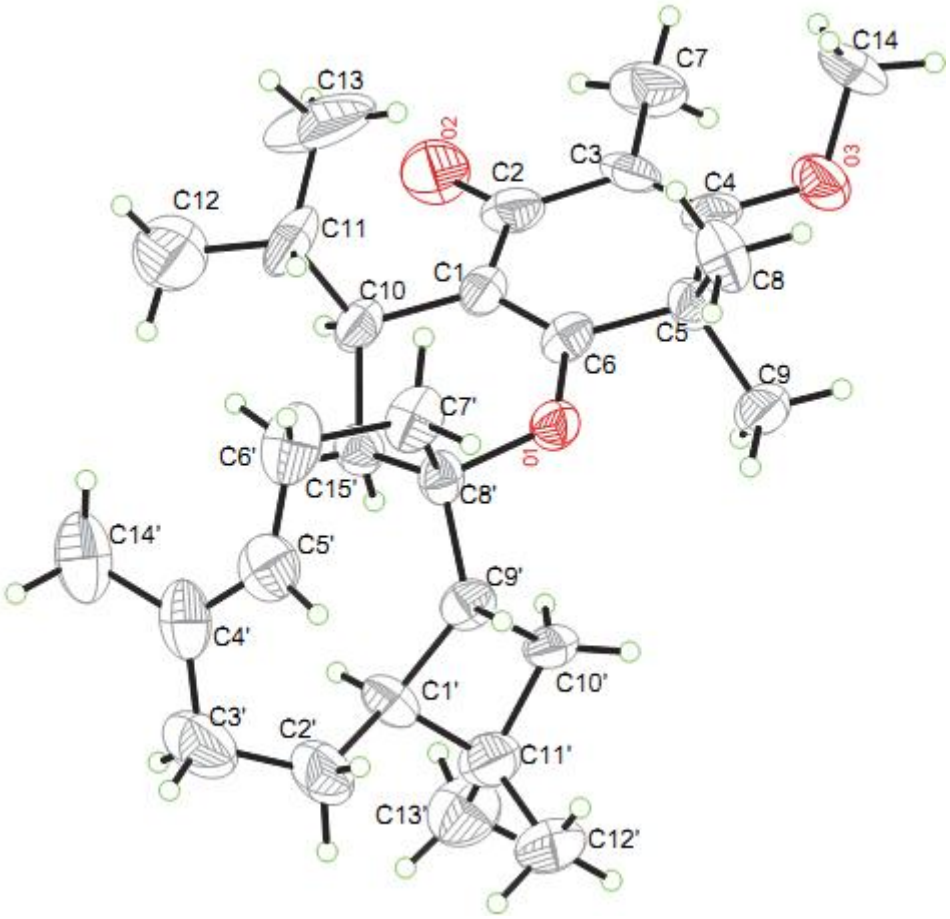

Figure S4. X-ray crystallographic structure of **4** (30% probability level)

Quantum chemical ECD calculation for 5 and (–)-7

Computational data of 5

The systematic random conformational analysis of compound **5** were performed in the SYBYL 8.1 program by using MMFF94s molecular force field, which afforded 12 conformers for **5** with an energy cutoff of 10 kcal mol^{-1} to the global minima. All of the obtained conformers were further optimized using DFT at the B3LYP/6-31+G(d) level in gas phase by using Gaussian09 software,[1] and 4 conformers of **5** were selected. All of the optimized stable conformers were used for TDDFT computation of the excited stats at the same levels, with the consideration of the first 50 excitations. The overall ECD curves of **5** were weighted by Boltzmann distribution of each conformer (with a half-bandwidth of 0.3eV). The calculated ECD spectra of **5** was subsequently compared with the experimental ones. The ECD spectra were produced by SpecDis 1.6 software.[2]

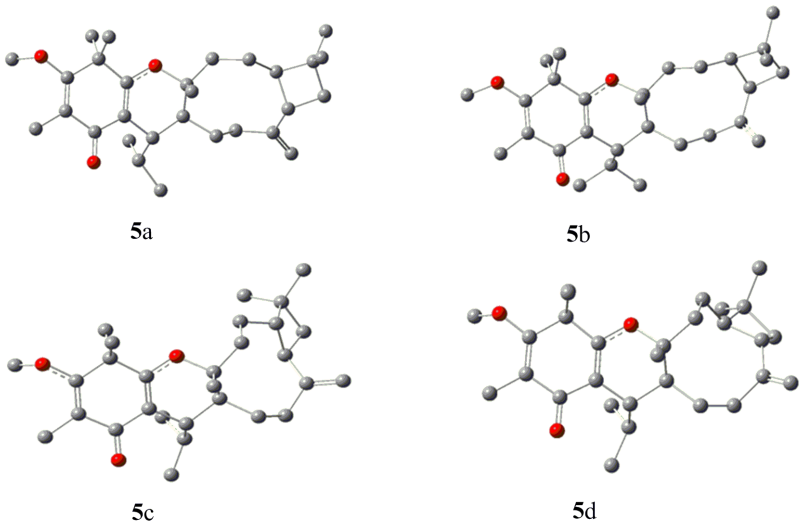

Figure S5-1. Optimized geometries of predominant conformers of **5** in the gas phase at the B3LYP/6-31+G(d) level

For **5a**

absolute energies = -1357.2675802

atom coordinates:

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%chk=C:\Users\Administrator\Desktop\BF-22\randomsearchBF22d000011.chk
%mem=200MW
# td=(nstates=50,root=1) b3lyp/6-31g(d,p) scrf=(cpcm,solvent=methanol)
guess=read geom=(connectivity,allcheck) test

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C	1.81766100	0.81099200	0.19789600
C	1.61979500	-0.49065600	0.52383500
C	2.66149300	-1.58714700	0.43757400
C	0.66593400	1.80334400	0.13968000
O	0.43862800	-0.96348600	0.97432600
O	3.48788400	2.48064800	0.08599100
C	2.83342100	-2.25975100	1.82813800
C	2.16818900	-2.64602300	-0.58610400
O	4.95401200	-2.03048100	-0.13152400
C	5.67762600	0.81275600	-0.33604000
C	0.46389300	2.46457600	-1.27806100
C	1.29080000	3.73331300	-1.53756900
C	0.62734600	1.46556400	-2.43390100
C	0.08536400	0.45686900	2.91512700
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C	-1.69827600	2.24328700	1.06912600
C	-4.07203700	1.54175800	0.22755900
C	-3.89485200	0.26590900	-0.56731400
C	-3.73197700	-1.10136800	0.17490200
C	-2.35184300	-1.59753300	0.59409700
C	-1.76117000	-0.84936500	1.81817600
C	-0.49925500	-0.00086800	1.57018600
C	-0.69566800	1.15751400	0.56410200
C	-5.07902300	-0.37560700	-1.34670900
C	-4.53635600	-1.79243800	-0.98194700
C	-5.17971800	1.78980800	0.93970600
C	5.53743100	-2.20686500	-1.43282300
C	-3.65172500	-2.36800900	-2.09529900
C	-5.57482600	-2.82413800	-0.54234500
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H	0.89482700	2.61611500	0.84134100
H	3.58261000	-3.05158200	1.76404100

H	1.88460500	-2.69105500	2.15260300
H	3.15961600	-1.53062800	2.57565300
H	2.88917600	-3.46355500	-0.65159200
H	2.04500300	-2.20403500	-1.57932800
H	1.20600600	-3.05160500	-0.26653400
H	5.86037500	1.05075900	-1.39123200
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H	5.79341000	1.74526100	0.22043700
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H	0.31272000	1.92319000	-3.37803800
H	1.00754000	1.02724400	2.78599800
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H	-0.62958800	1.08698000	3.44994800
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H	-2.43135800	-2.66313300	0.84294900
H	-1.65687500	-1.54593400	-0.25032100
H	-2.52159600	-0.20434300	2.27076200
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H	-6.04103500	-0.17803800	-0.86406300
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H	-6.00994100	1.09027200	0.98519900
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H	6.10450700	-1.32934200	-1.75205700
H	4.76530700	-2.42947200	-2.17610100
H	-3.11617900	-3.26224100	-1.75730900
H	-2.90761700	-1.64766500	-2.45077000
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H	-6.22950700	-2.42085300	0.23803800
H	-5.09401800	-3.72651900	-0.14487600
H	-6.20671800	-3.13172400	-1.38458300

For **5b**

absolute energies = -1357.2667287

atom coordinates:

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C	-1.78745000	0.82875600	-0.15828500
C	-1.61106200	-0.46780100	-0.51691900
C	-2.68384600	-1.53704000	-0.50080800
C	-0.61195200	1.78422800	-0.02320600
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O	-3.41192900	2.54070700	-0.02036800
C	-2.81762200	-2.16982900	-1.91414000
C	-2.26142200	-2.63566500	0.51289300
O	-5.00896000	-1.93201600	-0.04099200
C	-5.66385100	0.92369500	0.22338900
C	-0.43544800	2.37658800	1.43029900
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C	0.00086000	0.53873400	-2.81023400
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C	1.79986800	2.19216300	-0.78588900
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C	3.28752100	-0.95831200	0.32356200
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H	-3.59003300	-2.94157200	-1.89990600
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H	-3.09336800	-1.41391100	-2.65536900
H	-3.00891000	-3.43149800	0.52894300
H	-2.16330700	-2.22303500	1.52135000
H	-1.30056600	-3.06346500	0.21915500
H	-5.88341400	1.13922500	1.27636900
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H	-5.73181800	1.87348800	-0.31140500
H	0.63155500	2.62177000	1.51105400

H	-0.86478500	4.11433200	2.65332300
H	-2.26166500	3.55412800	1.70823400
H	-0.95479400	4.43500800	0.91528800
H	-1.80138100	1.12092700	2.59273600
H	-0.42956900	1.75366500	3.51167400
H	-0.19672600	0.41140100	2.38531100
H	0.75552600	1.14434700	-3.31789100
H	-0.88967000	1.15452800	-2.67096600
H	-0.25659300	-0.29652100	-3.46713300
H	3.55662000	3.19926000	-0.08207500
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H	2.55670500	-0.23945300	-2.21647900
H	5.05014600	0.36071600	1.82576600
H	6.30587600	-0.58861100	0.99205100
H	4.91114000	2.82367700	-2.05286500
H	5.75385800	1.18617800	-2.22540100
H	-6.33852000	-2.96605200	1.08902800
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H	-4.91830600	-2.38540600	1.99894700
H	3.03321500	-2.65275100	2.76451000
H	3.37276400	-0.95577800	3.14618200
H	4.62110000	-2.18859900	3.39093100
H	4.19425000	-3.76176100	0.74325500
H	5.76437200	-3.25669700	1.38268000
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For **5c**

absolute energies = -1357.2667286

atom coordinates:

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C	1.78747100	0.82879800	-0.15832600
C	1.61107400	-0.46775300	-0.51698600
C	2.68387300	-1.53698900	-0.50090200

C	0.61197600	1.78426600	-0.02316500
O	0.42635500	-0.95800100	-0.93967000
O	3.41196600	2.54075800	-0.02037400
C	2.81765100	-2.16968100	-1.91427400
C	2.26144700	-2.63567500	0.51273200
O	5.00897000	-1.93199400	-0.04099400
C	5.66387400	0.92371200	0.22353100
C	0.43547400	2.37640700	1.43040700
C	1.18090600	3.69391700	1.69132300
C	0.73250900	1.35363900	2.53785600
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C	-3.18812800	2.16781700	-0.07763700
C	-1.79988000	2.19218400	-0.78588400
C	-4.25288800	1.29790400	-0.72760600
C	-4.45861900	-0.12051800	-0.25323600
C	-3.28755000	-0.95825300	0.32353300
C	-2.38923700	-1.72874500	-0.63936700
C	-1.78313300	-0.87841200	-1.77751700
C	-0.55090300	0.00059800	-1.47832200
C	-0.74386400	1.10698000	-0.41380700
C	-5.22785300	-0.41506600	1.07264700
C	-4.30307200	-1.65365200	1.30254000
C	-5.00936000	1.79417400	-1.71726000
C	5.65257400	-2.12917800	1.22870300
C	-3.80417000	-1.87310200	2.73055400
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H	-2.67941000	-0.30374800	0.95433900
H	-4.94373000	-0.68443900	-1.05859300
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H	1.86855000	-2.61936800	-2.21168500
H	3.09352400	-1.41373700	-2.65543100
H	3.58995900	-2.94152700	-1.90004800
H	3.00883600	-3.43160700	0.52858700
H	2.16353900	-2.22314800	1.52125100
H	1.30049500	-3.06332500	0.21908500
H	6.43026400	0.24343000	-0.15359300
H	5.73195100	1.87347500	-0.31130500
H	5.88331900	1.13924900	1.27653500
H	-0.63145300	2.62195900	1.51102500
H	0.86535400	4.11368600	2.65389700
H	2.26208900	3.55316400	1.70880300
H	0.95561300	4.43477300	0.91594900
H	1.80080800	1.12018000	2.59291000
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H	0.19607400	0.41099300	2.38478200
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H	0.25671500	-0.29637900	-3.46711900

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H	-3.05627500	1.89924100	0.97762300
H	-1.35826800	3.16704500	-0.55567400
H	-1.97155800	2.20664800	-1.86710900
H	-2.98115800	-2.51874300	-1.11732600
H	-1.58490300	-2.23574800	-0.09355100
H	-1.47201300	-1.56271100	-2.57562400
H	-2.55674000	-0.23931700	-2.21645800
H	-5.05031100	0.36066800	1.82574200
H	-6.30593200	-0.58871800	0.99192400
H	-4.91118600	2.82384900	-2.05269200
H	-5.75395600	1.18638300	-2.22528400
H	6.33867700	-2.96585100	1.08902700
H	6.21634700	-1.24865500	1.54534700
H	4.91825900	-2.38559700	1.99889600
H	-3.03327900	-2.65272400	2.76449900
H	-3.37282200	-0.95574000	3.14613000
H	-4.62117500	-2.18854500	3.39086400
H	-5.76431800	-3.25676600	1.38258200
H	-5.30285500	-2.82435900	-0.26695600
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For **5d**

absolute energies = -1357.2681166

atom coordinates:

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randomsearchBF22d000014

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C	-4.08768700	-0.98469500	-0.02896800
C	-4.34867100	0.33390300	-0.15752800
C	-3.24318500	1.31613600	-0.02356300
C	-1.86879800	0.83246900	0.16699700
C	-1.69371000	-0.47124300	0.49431400
C	-2.75043700	-1.55122000	0.39809800
C	-0.71256000	1.82358400	0.13247600
O	-0.52449200	-0.95537900	0.95798500
O	-3.49845300	2.53222900	-0.05952600
C	-2.93291800	-2.22974900	1.78444100
C	-2.27193800	-2.61016200	-0.63262500
O	-5.05154000	-1.95680100	-0.15915700
C	-5.72517400	0.89710700	-0.39370100
C	-0.69736800	2.54617200	-1.26674900
C	-0.14608400	1.68175000	-2.41081800

C	-0.04339300	3.93715700	-1.24911300
C	-0.15939500	0.47869100	2.88326900
C	2.94737000	2.46507000	0.17755100
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C	4.05951900	1.43258400	0.24422600
C	3.87568000	0.15211300	-0.54092200
C	3.65682400	-1.20197900	0.20875300
C	2.25039500	-1.64423500	0.59805800
C	1.66995600	-0.86528400	1.80753500
C	0.42394400	0.00177000	1.54365800
C	0.64663800	1.15651300	0.52930300
C	5.06175800	-0.52844700	-1.28313500
C	4.46844900	-1.92618300	-0.92208100
C	5.15774600	1.67105100	0.97386300
C	-5.64250500	-2.13431700	-1.45706600
C	3.59474700	-2.48447300	-2.05275300
C	5.46407100	-2.98481900	-0.44881300
H	1.04535300	0.67289900	-0.36657200
H	4.28725800	-1.18890500	1.10842000
H	3.05883200	0.29088800	-1.25748300
H	-0.93792600	2.60526500	0.87119900
H	-3.69494400	-3.00860200	1.71529100
H	-1.99125000	-2.67832600	2.10609800
H	-3.24704300	-1.50012300	2.53663600
H	-3.00272100	-3.41869200	-0.70150000
H	-2.14526100	-2.16366300	-1.62346900
H	-1.31411300	-3.02914600	-0.31693000
H	-5.82629300	1.83670800	0.15371800
H	-5.90267200	1.12873700	-1.45113400
H	-6.49933400	0.20288800	-0.06046900
H	-1.75086200	2.72910000	-1.48767700
H	-0.38444400	2.14075500	-3.37649900
H	0.94315600	1.57235300	-2.36952200
H	-0.58481400	0.67804500	-2.40359200
H	-0.22863400	4.44644800	-2.20183100
H	-0.46455100	4.56227400	-0.45394400
H	1.03951300	3.90110500	-1.11075500
H	-0.38378500	-0.38387200	3.51658900
H	0.55954000	1.10812800	3.41336000
H	-1.07720000	1.05452800	2.74834200
H	3.35640700	3.42919800	0.49959700
H	2.64874500	2.59120000	-0.87053500
H	1.17842300	3.15623900	1.18182100
H	2.04180400	1.92103200	2.04470400
H	2.27912000	-2.71135800	0.85104100
H	1.57706100	-1.56529500	-0.26174100
H	2.44121100	-0.22882000	2.25281200
H	1.38597200	-1.57619600	2.59053100
H	5.18084800	-0.28888600	-2.34515600

H	6.01570900	−0.35465100	−0.77587600
H	5.27524600	2.59364100	1.53617700
H	5.97572600	0.95907600	1.04173600
H	−6.32653600	−2.97873900	−1.36051500
H	−6.20076000	−1.25236200	−1.77937700
H	−4.87615600	−2.37055800	−2.20204000
H	2.88340900	−1.74453300	−2.43387200
H	4.22260800	−2.80034900	−2.89404300
H	3.02240500	−3.35776500	−1.72030800
H	6.10889300	−2.59620700	0.34704000
H	4.94620700	−3.87023400	−0.05977300
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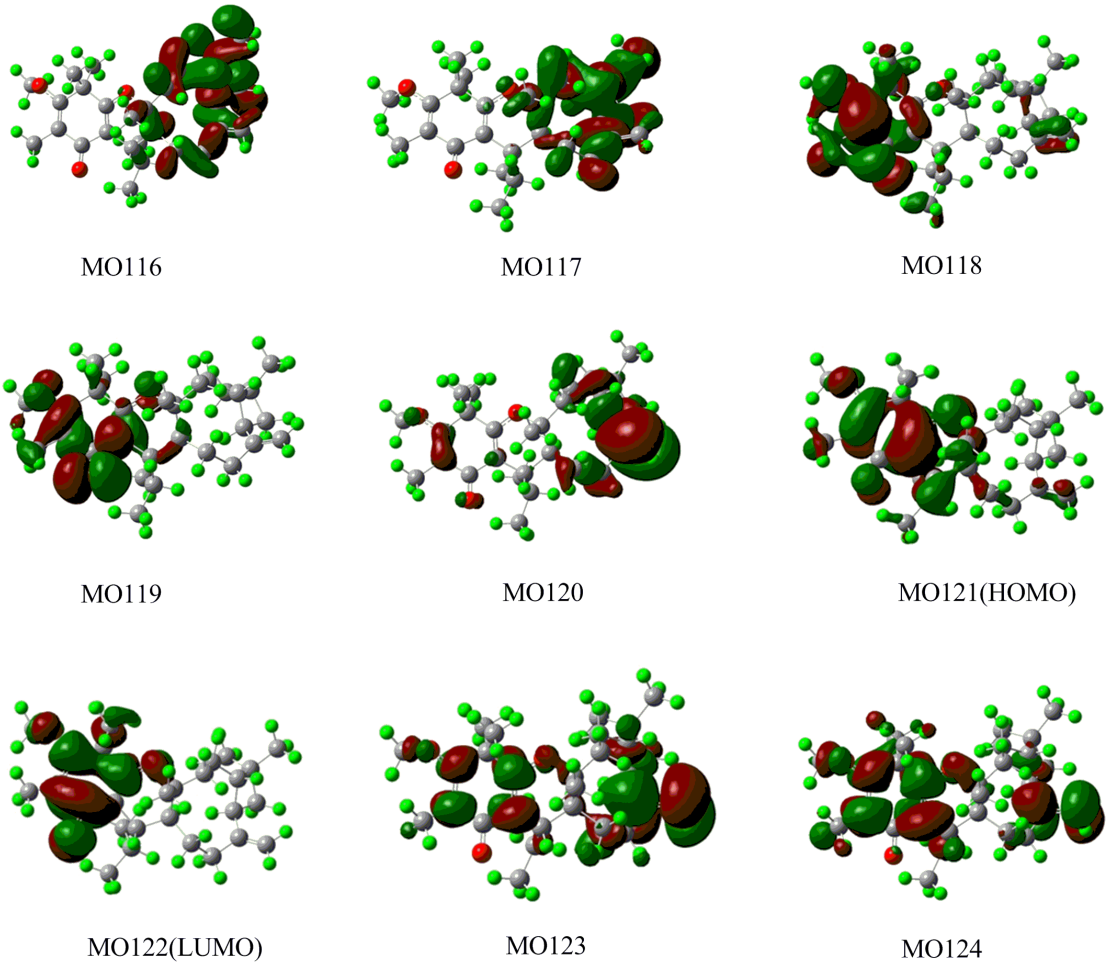

Figure S5-2. Key molecular orbitals involved in important transitions regarding the ECD spectra of conformer **5**c in the gas phase at the B3LYP/6-31+G(d) level

Table S1-1. Selected key transitions and their related rotatory and oscillator strengths of conformer **5**c of **5** at the B3LYP/6-31+G(d) level in the gas phase

HOMO is 121

NO	Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	R (length)	Major contribtions
1	31156.8913	320.95	0.0042	-7.9869	H-2->LUMO (72%)
2	33826.5602	295.62	0.1196	48.8292	HOMO->LUMO(82%)
3	39287.6865	254.53	0.0172	8.9492	H-1->LUMO (94%)
4	40066.0039	249.59	0.1448	47.5732	H-3->LUMO(69%)
5	45076.2707	221.84	0.0008	5.1191	H-6->LUMO (61%)
6	46483.6944	215.13	0.0055	4.0404	H-4->LUMO(29%), H-6->LUMO (21%)
7	47126.5120	212.19	0.0633	4.1758	HOMO->L+1(43%)
8	47520.1066	210.44	0.0033	-3.209	HOMO->L+1(38%)
9	47704.8058	209.62	0.0022	2.7044	H-4->LUMO (63%)
10	48342.7841	206.85	0.0002	0.2577	H-5->LUMO (85%)
11	48723.4740	205.24	0.095	28.5924	HOMO->L+1(32%)
12	49288.0566	202.89	0.0295	-28.0208	H-8->LUMO (76%)
13	50837.4324	196.7	0.2659	-33.3617	H-3->L+1(28%) H-3->L+2(35%)
14	51800.4489	193.05	0.035	-45.8772	H-1->L+1 (53%) H-1->L+2(43%)
15	52216.6269	191.51	0.0213	-17.5747	H-9->LUMO (50%)
16	52258.5673	191.35	0.0037	1.6795	H-2->L+1(56%) H-2->L+2 (28%)
17	52903.8045	189.02	0.0257	18.9683	H-3->L+1(47%) H-3->L+2 (30%)
18	53292.5599	187.64	0.2461	-49.5004	H-1->L+2 (39%)
19	54379.7846	183.89	0.0006	0.2376	H-9->LUMO (36%)
20	55095.1914	181.5	0.0451	38.9386	H-4->L+1(61%)

Computational data of (–)-7

The systematic random conformational analysis of compound (–)-**7** were performed in the SYBYL 8.1 program by using MMFF94s molecular force field, which afforded 8 conformers for (–)-**7** with an energy cutoff of 10 kcal mol^{-1} to the global minima. All of the obtained conformers were further optimized using DFT at the B3LYP/6-31+G(d) level in gas phase by using Gaussian09 software,[1] and 4 conformers of (–)-**7** were selected. All of the optimized stable conformers were used for TDDFT computation of the excited stats at the same levels, with the consideration of the first 50 excitations. The overall ECD curves of (–)-**7** were weighted by Boltzmann distribution of each conformer (with a half-bandwidth of 0.3eV). The calculated ECD spectra of (–)-**7** was subsequently compared with the experimental ones. The ECD spectra were produced by SpecDis 1.6 software.[2]

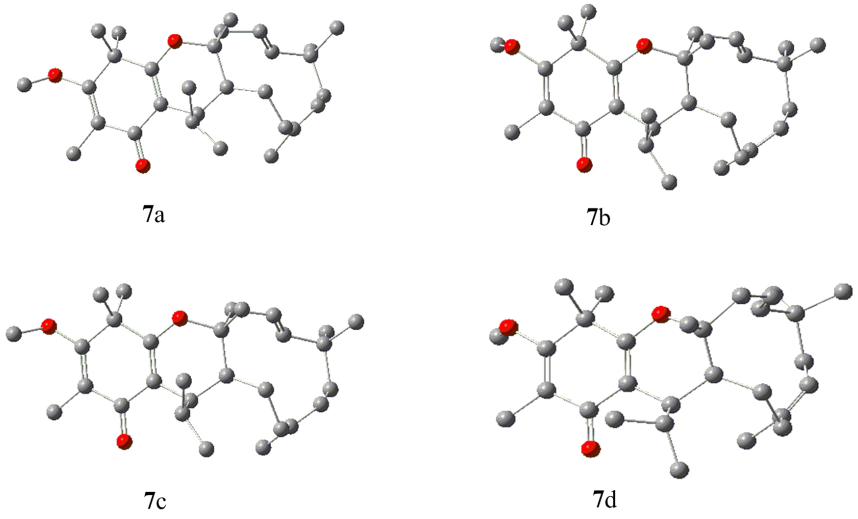

Figure S5-3. Optimized geometries of predominant conformers of (–)-**7** in the gas phase at the B3LYP/6-31+G(d) level

For (–)-7a

absolute energies = -1357.2716973

atom coordinates:

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guess=read geom=(connectivity,allcheck) test

BF25randomsearch200010

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 C                  3.74383700   -1.21017900   -0.66096900
 C                  3.63365500   -0.14722200   -1.48872400
 C                  2.57248300    0.86229800   -1.24672200
 C                  1.63775800    0.65044300   -0.14226100
 C                  1.70781300   -0.47951900    0.59804400
 C                  2.76816400   -1.54859100    0.45043300
 C                  0.57230700    1.66814200    0.18394400
 C                 -0.74153700    0.88961800    0.51867000
 C                 -0.55246600   -0.23610200    1.58087700
 O                  0.84697000   -0.73476000    1.60760100
 O                  2.49407000    1.86522300   -1.97704500
 C                  3.53299800   -1.69031400    1.79447100
 C                  2.08885100   -2.90363700    0.10607900
 O                  4.71838800   -2.17058000   -0.80420500
 C                  1.04723900    2.76155400    1.21884000
 C                  2.18206300    2.32754100    2.16126700
 C                  1.45080900    4.05098900    0.48271100
 C                  6.08286000   -1.77156400   -0.59286600
 C                  4.52444300    0.08406600   -2.68083500
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 C                 -2.83553600   -1.41463000    1.03265500
 C                 -1.34470200   -1.53070000    1.21198000
 C                 -2.54542700    2.52345300   -0.42939200
 C                 -3.45620200   -1.64191200   -0.13019700
 C                 -4.92978000   -1.48500900   -0.45811100
 C                 -5.07326900   -0.26541000   -1.45007000
 C                 -4.38592000    0.96050700   -0.92219700
 C                 -3.25378700    1.53819700   -1.35418200
 C                 -5.79802300   -1.26161900    0.79191100
 C                 -5.42359600   -2.75420900   -1.18597500
 C                 -2.57147800    1.23482300   -2.66491800
 C                 -0.81917400    0.18734800    3.02578000
 H                 -0.97885300    0.35800700   -0.40947300
 H                  0.36470800    2.20586500   -0.74617800
 H                  4.28381500   -2.47912300    1.71393600
 H                  2.83389700   -1.95140300    2.59144700
 H                  4.03148900   -0.75477400    2.06462300
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H	2.84881100	-3.67980900	-0.00377400
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H	1.77522000	4.82226000	1.19033900
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H	6.43296600	-1.07708800	-1.36009600
H	6.20377000	-1.31296200	0.39346800
H	4.94574000	-0.85431100	-3.04748500
H	3.94359500	0.55194000	-3.47890300
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H	-2.74984900	1.23888000	1.26948800
H	-1.66371300	2.57667300	1.55402500
H	-3.41474300	-1.13478900	1.91093500
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H	-1.11828500	-2.26154100	2.00025000
H	-3.25909000	3.27431700	-0.06859600
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H	-5.38361500	-3.62666100	-0.52495800
H	-6.45977800	-2.63024200	-1.52037400
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H	-2.47101200	2.15404900	-3.25714400
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H	-0.51037200	-0.61413100	3.70280400
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For (–)-**7b**

absolute energies = -1357.2676662

atom coordinates:

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guess=read geom=(connectivity,allcheck) test

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C	1.64524800	0.68481500	-0.21167800
C	1.81059100	-0.26790700	0.73213000
C	2.97715100	-1.23012600	0.79798400
C	0.51168900	1.67840300	-0.10249100
C	-0.75073700	0.93630700	0.44962800
C	-0.48225400	-0.09515300	1.60908600
O	0.95435100	-0.41169200	1.76732700
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C	3.75727000	-0.97894000	2.12074900
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C	-1.97052000	1.84735400	0.72281300
C	-2.59813100	-1.52726800	1.06496800
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C	-2.65257500	2.42807700	-0.54428700
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H	1.79923100	2.08893400	2.38357400
H	0.34170100	3.07228500	2.60257400

H	1.89743200	3.85382500	2.34775300
H	4.27850900	-3.49499800	-1.41915800
H	5.33807500	-2.38297400	-2.32686000
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H	5.80620300	-0.17300000	-2.09790200
H	4.55414200	-0.34497800	-3.34159700
H	-2.73559800	1.26568200	1.24258100
H	-1.69465500	2.66098900	1.40055300
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H	-2.57708100	1.95623200	-3.34709200
H	-0.55895300	-0.41858500	3.73278600
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H	-1.98196300	0.41822800	3.10451200

For **(–)-7c**

absolute energies = -1357.2680772

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BF25randomsearch200035

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C	1.78310200	-0.42055100	0.61745900
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C	0.50890300	1.62334500	0.00999100
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C	-0.48465800	-0.29369000	1.56148300
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O	2.38472300	1.74590700	-2.15153100
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C	2.37651600	-2.84238800	0.38423800
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C	-2.64094500	-1.62353600	0.92669800
C	-1.14430700	-1.63019700	1.08942200
C	-2.65313600	2.48988400	-0.24858400
C	-3.26516000	-1.78128000	-0.24543500
C	-4.75340200	-1.69923800	-0.53176600
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C	-3.31889200	1.51120600	-1.21120100
C	-5.60367800	-1.64759900	0.74936200
C	-5.17789300	-2.92926600	-1.36299100
C	-2.66234200	1.35460500	-2.56085800
C	-0.85925400	-0.00170200	3.01594600
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H	1.72234000	-3.09384300	1.22132800
H	3.20285000	-3.55504600	0.35077000
H	2.08951500	2.99369900	0.28559100
H	0.95689400	5.03467600	0.85722100
H	0.21180400	4.34636600	-0.58946900
H	-0.61122400	4.24107400	0.97484000
H	1.86878500	1.75588800	2.48814200
H	0.43698300	2.73936200	2.83906700
H	2.00316900	3.51333700	2.62740800
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H	6.53322100	-0.86732600	-1.38936600
H	6.34744900	-0.89002400	0.38498700
H	4.99706800	-0.88959700	-3.03903900
H	5.31090900	0.79678200	-2.58960700
H	3.90229700	0.41174400	-3.56351400
H	-2.71032300	1.14580900	1.40401300
H	-1.63220500	2.49440500	1.67706800

H	-3.22504700	-1.47246500	1.83276700
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H	-4.77442400	1.07112000	0.19750800
H	-5.37700700	-0.77339500	1.36592500
H	-6.66789200	-1.60824400	0.49391600
H	-5.43855700	-2.53934100	1.36304400
H	-5.06597400	-3.85189700	-0.78339300
H	-6.22690600	-2.84688300	-1.66901600
H	-4.56929300	-3.02426900	-2.26895500
H	-2.65688900	2.31677300	-3.08984900
H	-3.16232100	0.62594400	-3.20192300
H	-1.61109600	1.05418900	-2.46603100
H	-1.93961700	0.09131600	3.13843800
H	-0.52052500	-0.83124400	3.64321100
H	-0.39159000	0.91296300	3.38030400

For **(–)-7d**

absolute energies = -1357.2562663

atom coordinates:

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guess=read geom=(connectivity,allcheck) test

BF25randomsearch200001

0 1
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C	-3.84146100	0.34863800	-1.34195100
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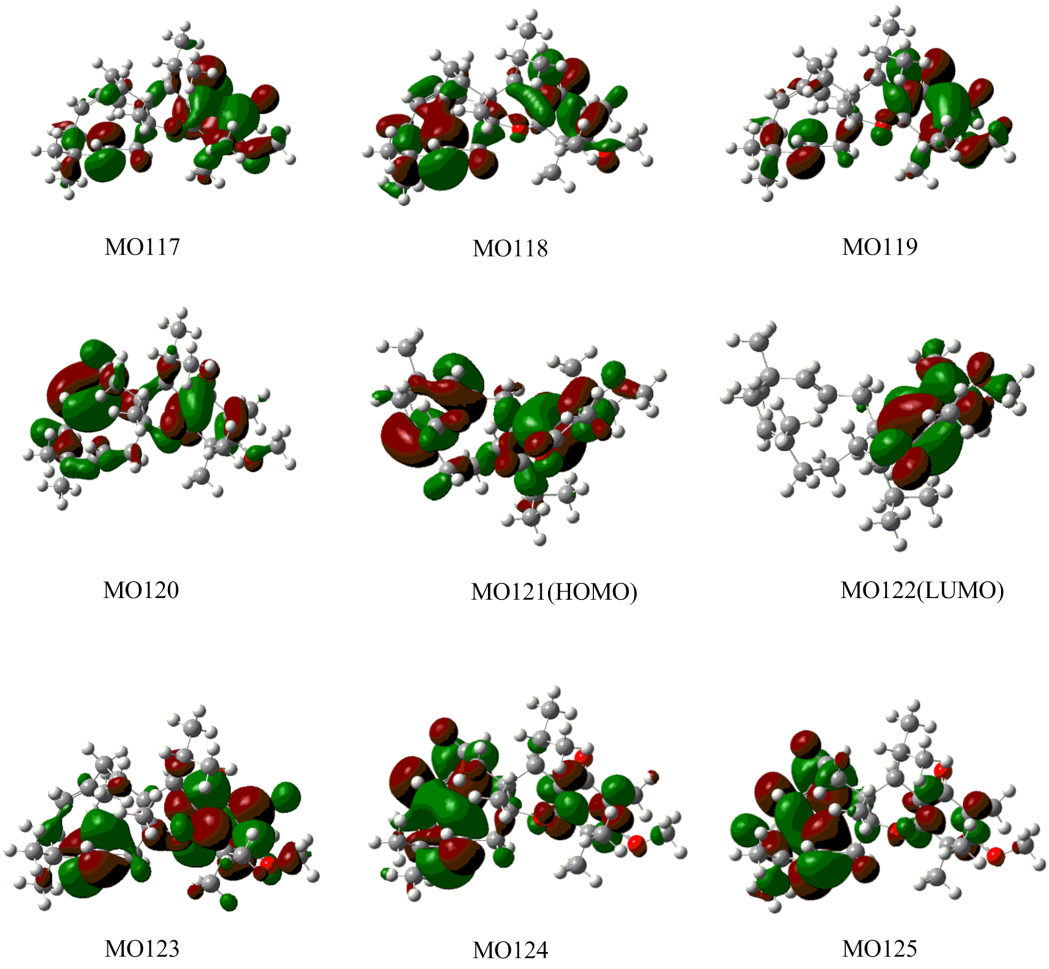


Figure S5-4. Key molecular orbitals involved in important transitions regarding the ECD spectra of conformer **7**a in the gas phase at the B3LYP/6-31+G(d) level

Table S1-2. Selected key transitions and their related rotatory and oscillator strengths of conformer **7**a of (–)-**7** at the B3LYP/6-31+G(d) level in the gas phase

HOMO is 121

NO	Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	R (length)	Major contribtions
1	31055.7647	321.55	0.0043	-0.7762	H-3->LUMO (32%) H-2->LUMO (48%)
2	33112.0271	301.58	0.1292	-80.2237	H-1->LUMO (13%) H->LUMO (78%)
3	34983.8462	285.45	0.0048	-0.3988	H-1->LUMO (84%) H->LUMO (15%)
4	38887.7647	256.79	0.0235	29.8081	H-3->LUMO (59%) H-2-> LUMO (36%)
5	39789.8462	250.97	0.1328	-58.6780	H-4->LUMO (71%)
6	44700.552	223.40	0.0009	3.7490	H-5->LUMO (80%)
7	45945.7466	217.34	0.0202	1.6724	HUMO->L+136%)
8	46484.5792	214.83	0.0335	46.9385	H-6->LUMO(31%) H-1->L+1(18%) HUMO->L+1(15%)
9	47271.4842	211.25	0.0510	106.9159	H-6->LUMO (28%)
10	47812.733	208.86	0.0053	-2.4385	H-2->L+1(38%) H-3->L+1(25%)
11	48014.0905	207.98	0.0041	-2.3365	H-7->LUMO (53%) H-6->LUMO (26%)
12	48327.4027	206.63	0.0193	-11.6174	HUMO->L+2(70%)
13	48822.7421	204.54	0.0094	6.6368	HUMO->L+3(40%) H-1->L+2(28%)
14	49417.1493	202.08	0.0452	-26.2473	HUMO->L+3(35%)
15	50780.7421	196.65	0.0130	-14.8683	H-8->LUMO (66%)
16	51012.7059	195.76	0.0692	40.8003	H-1->L+3(21%)
17	51205.2036	195.02	0.1173	33.1329	H-4->L+1(49%)
18	52178.1629	191.38	0.2615	80.2018	H-3->L+1(37%)
19	52532.552	190.09	0.1526	75.6914	H-3 ->L+2(18%)
20	53063.3303	188.19	0.0524	-37.7322	H-9-> LUMO (57%)

m/z	Ion	Formula	Abundance
441.3365	(M+H)+	C29 H45 O3	408459.7

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross Score	Mass	Calc Mass	Diff (ppm)
☑	C29 H44 O3	C29 H45 O3	441.3363	96.7		440.3293	440.329	-0.51

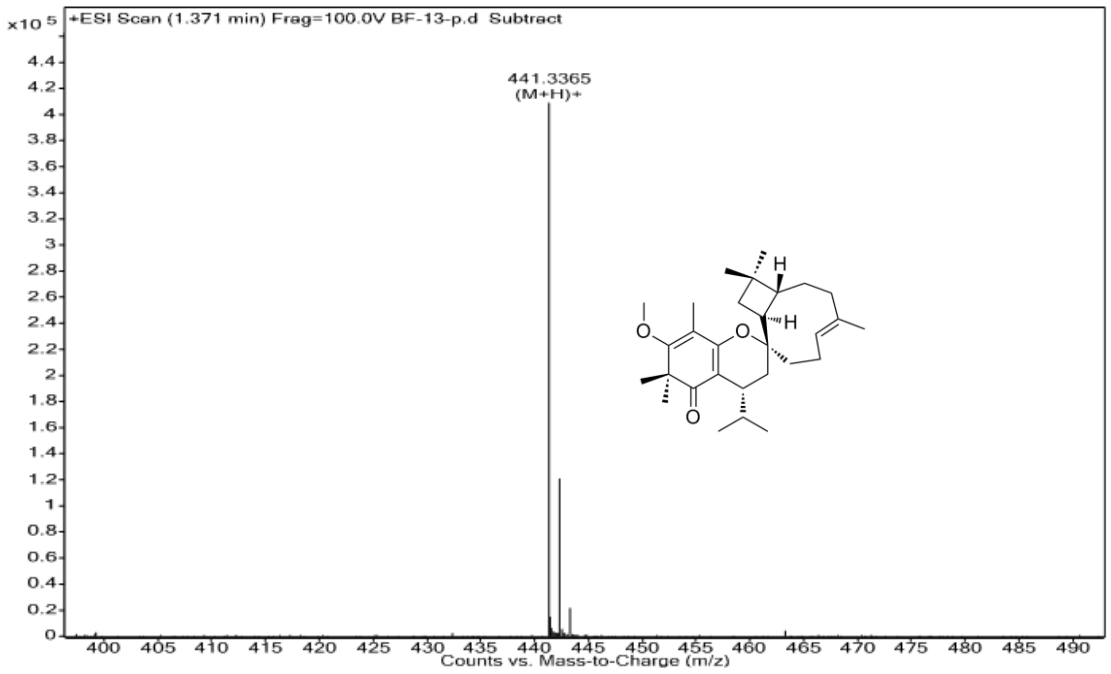
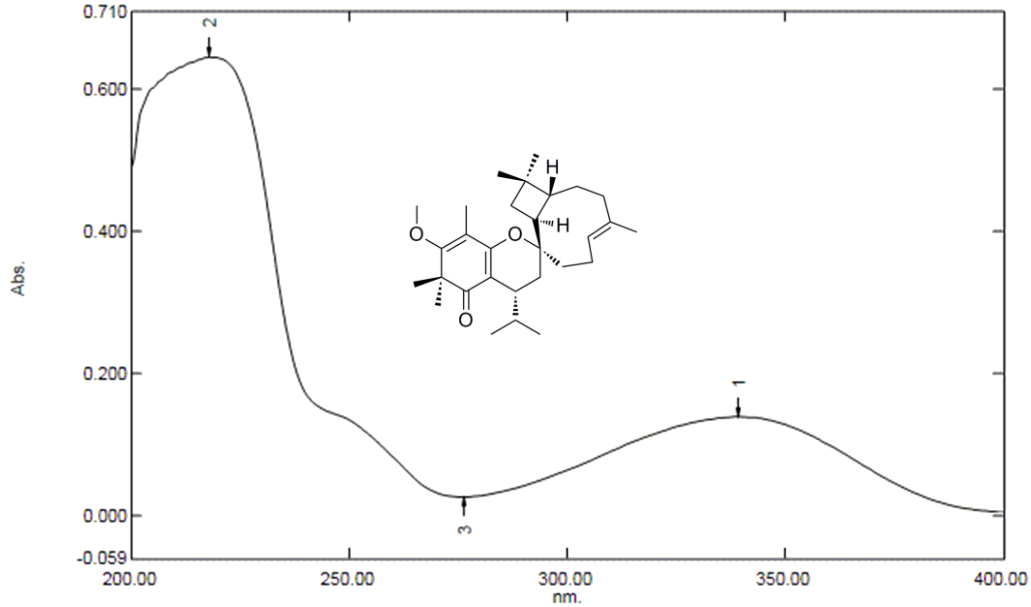


Figure S6. HR-ESI-MS spectrum of **1**



Measurement Properties	
Wavelength Range (nm.):	200.00 to 400.00
Scan Speed:	Medium
Sampling Interval:	0.2
Auto Sampling Interval:	Enabled

No.	P/V	Wavelength	Abs.	Description
1	↑	339.40	0.140	
2	↑	217.80	0.646	
3	↓	276.40	0.026	

Figure S7. UV spectrum of **1** in MeOH

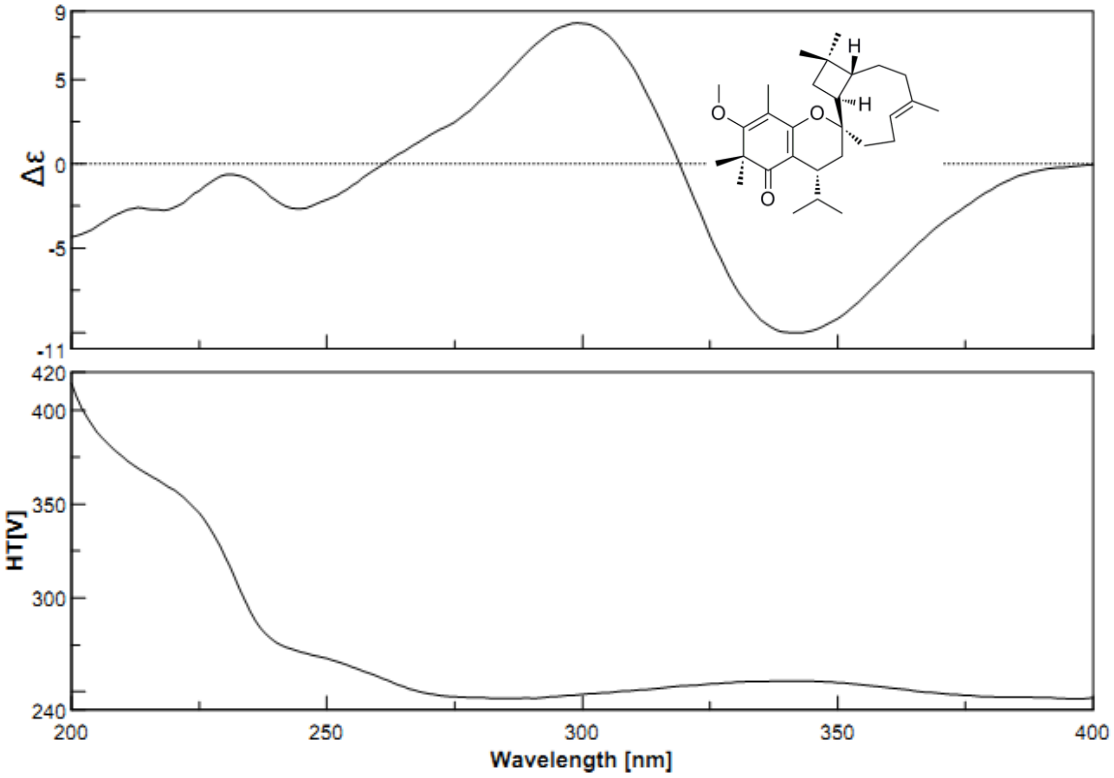


Figure S8. CD spectrum of **1** in MeOH

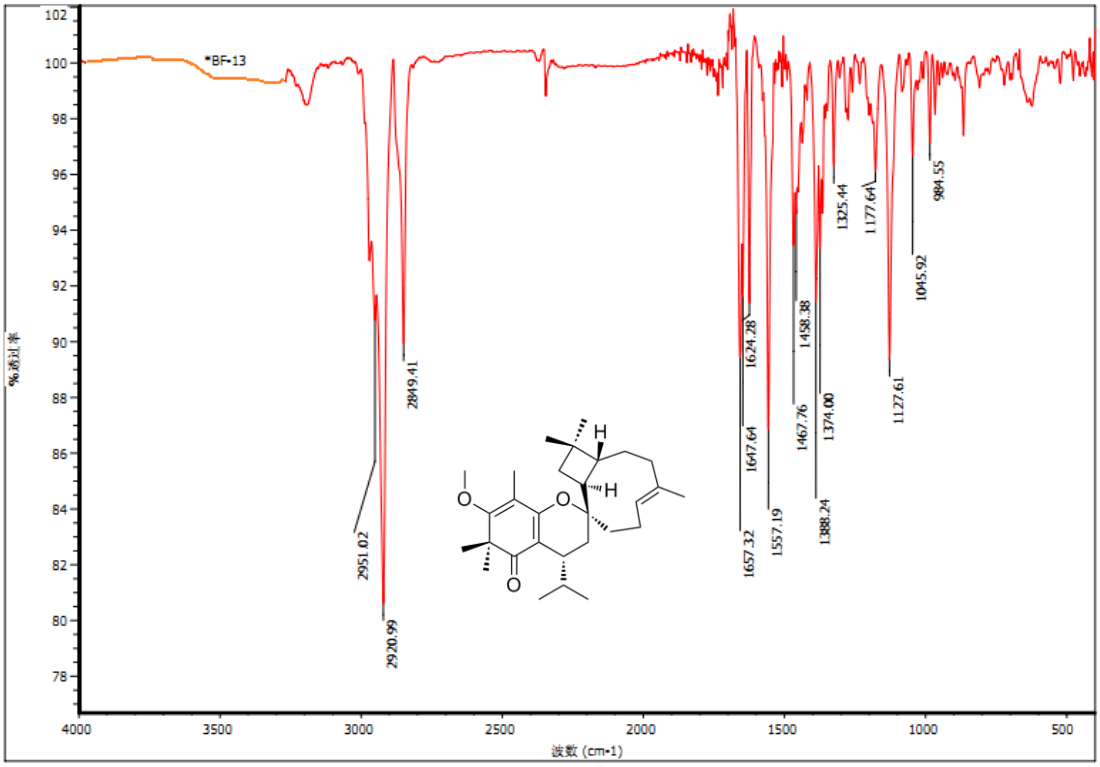


Figure S9. IR spectrum of **1**

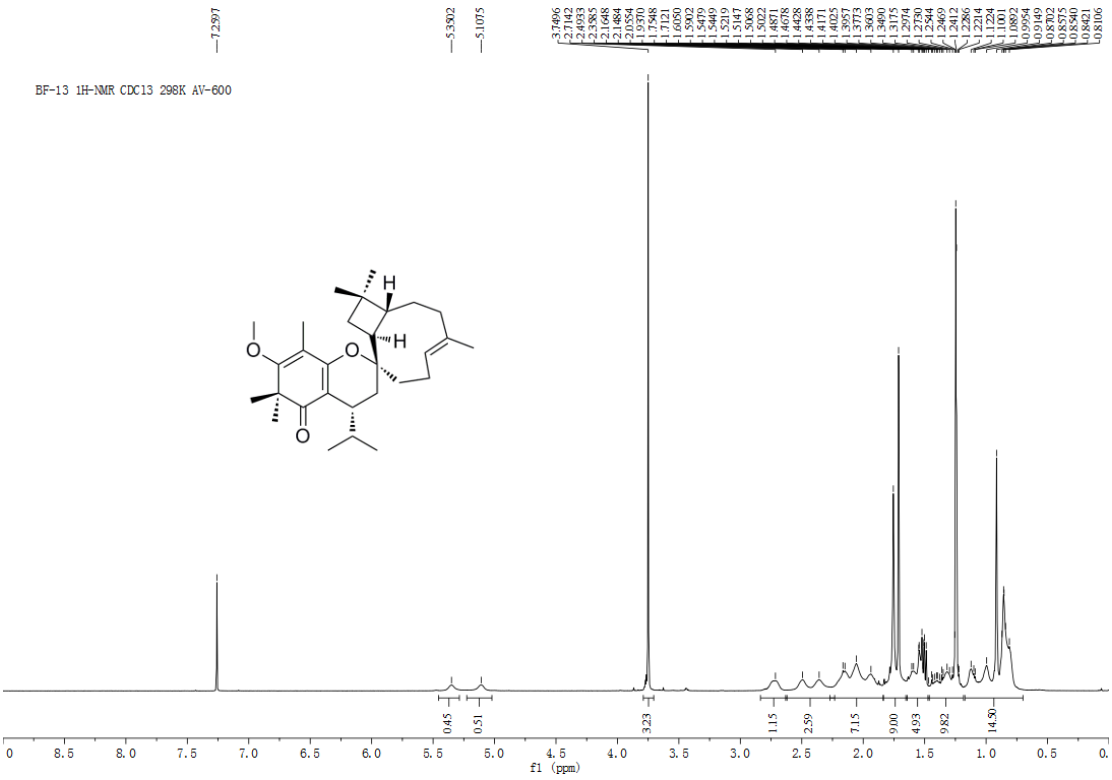


Figure S10-1. ^{1}H NMR spectrum of **1** in $CDCl_3$ (600 MHz, 298K)

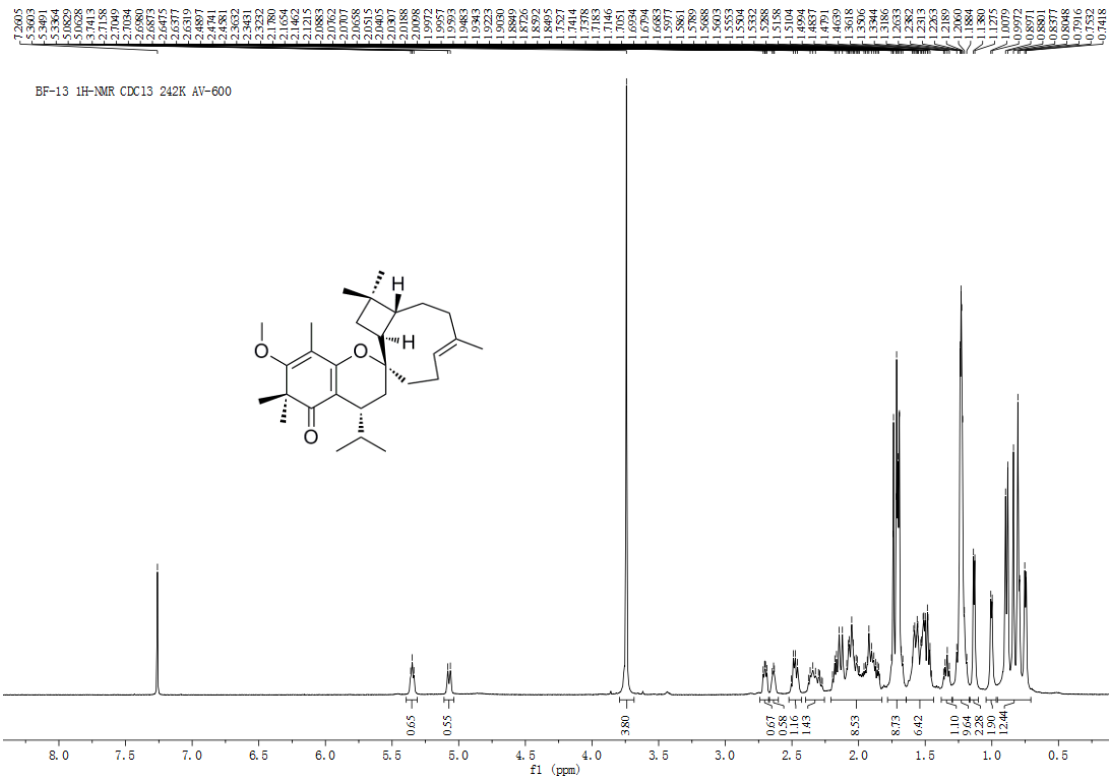


Figure S10-2. ^{1}H NMR spectrum of **1** in $CDCl_3$ (600 MHz, 242K)

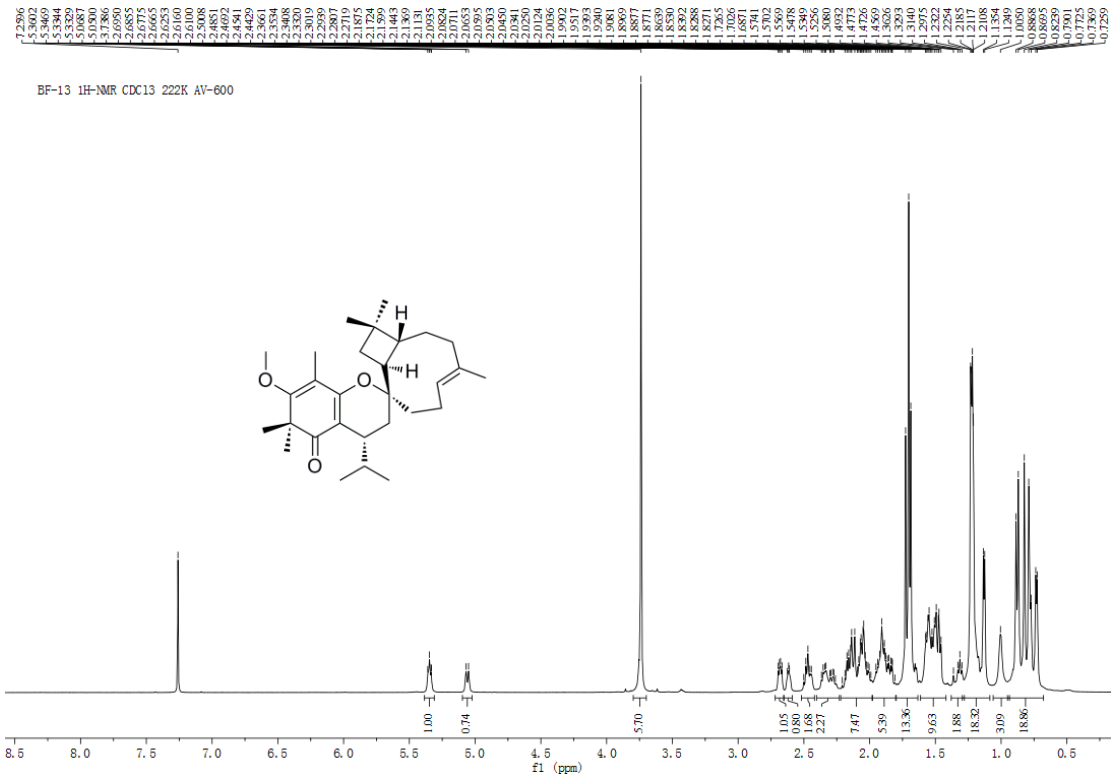


Figure S10-3. ^{1}H NMR spectrum of **1** in $CDCl_3$ (600 MHz, 222K)

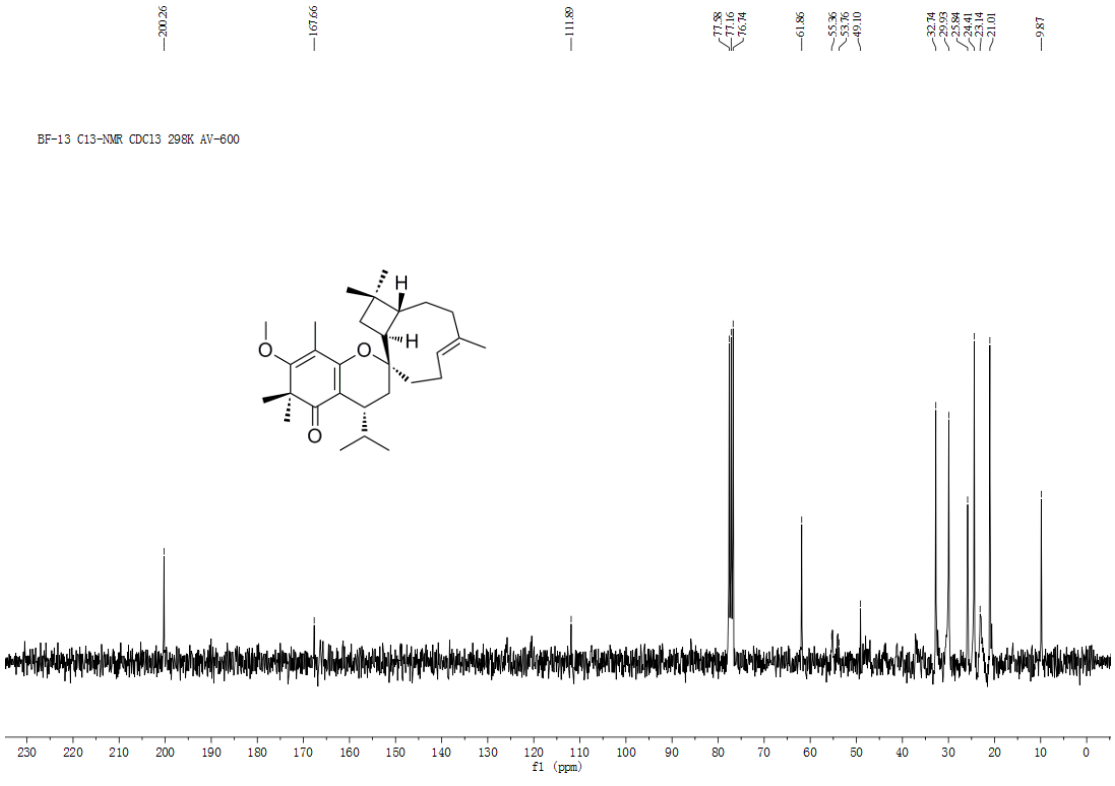


Figure S11-1. ^{13}C NMR spectrum of **1** in $CDCl_3$ (150 MHz, 298K)

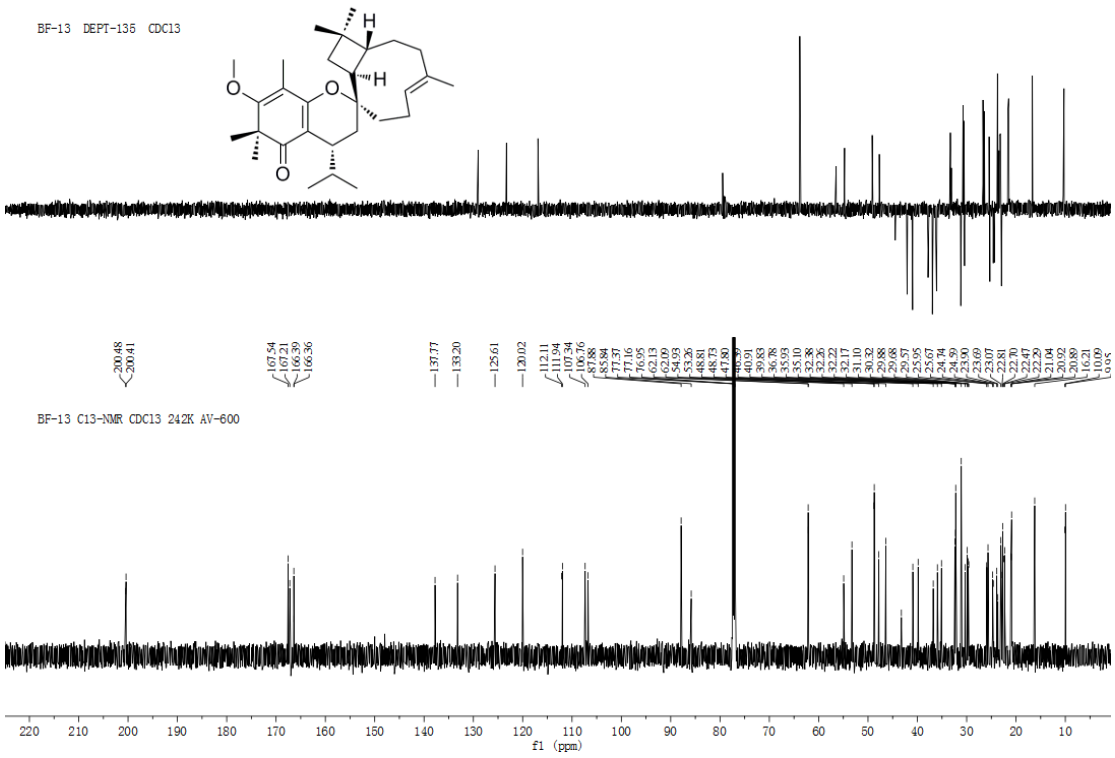


Figure S11-2. ^{13}C NMR spectrum of **1** in $CDCl_3$ (150 MHz, 242K)

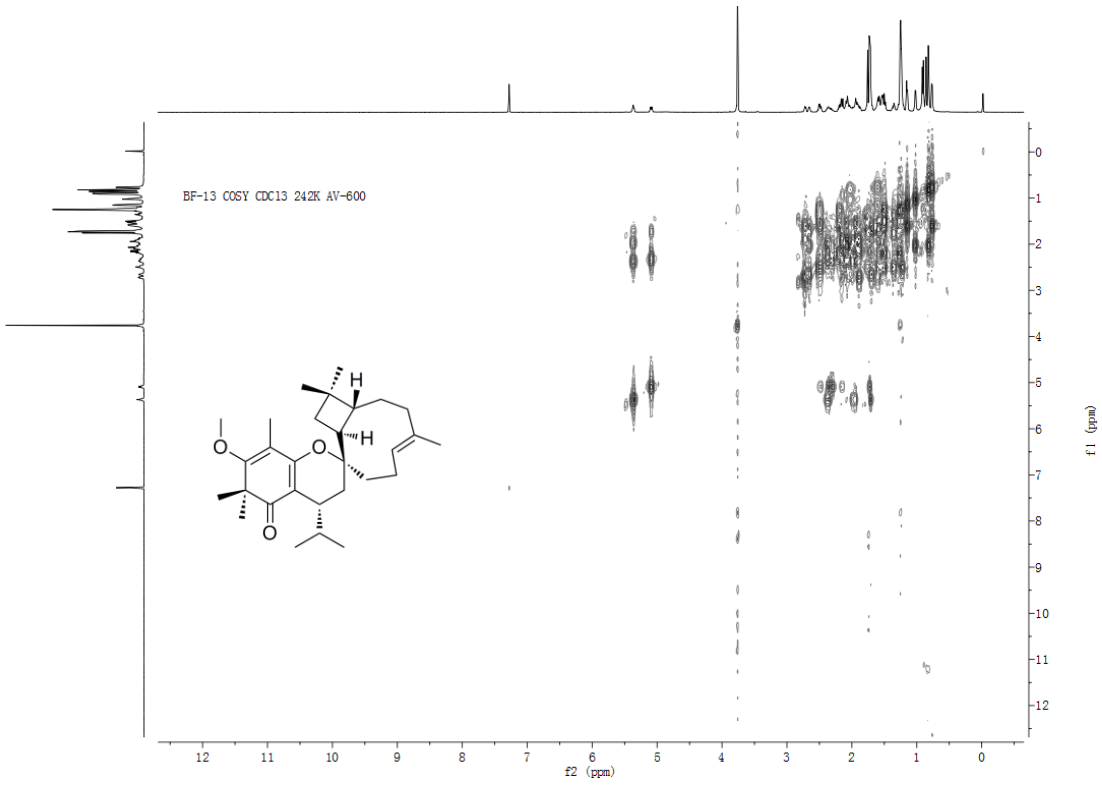


Figure S12. ^{1}H-^{1}H COSY spectrum of **1** in $CDCl_3$ (600 MHz, 242K)

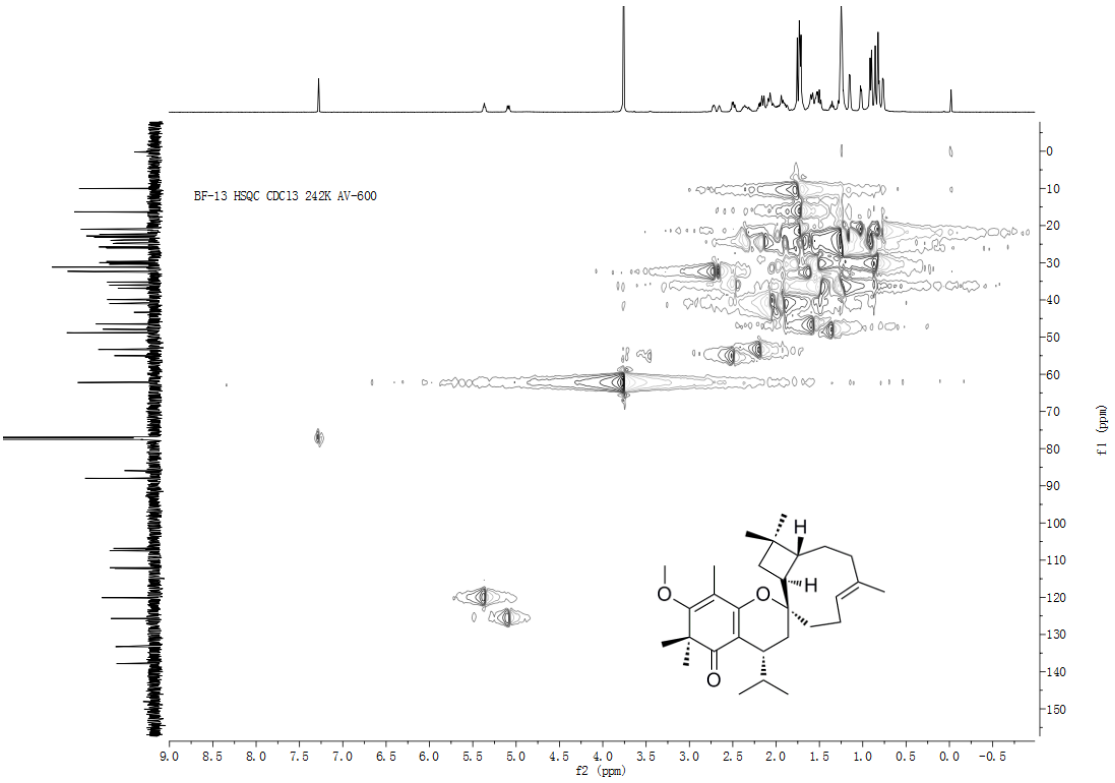


Figure S13. HSQC spectrum of **1** in $CDCl_3$ (600 MHz, 242K)

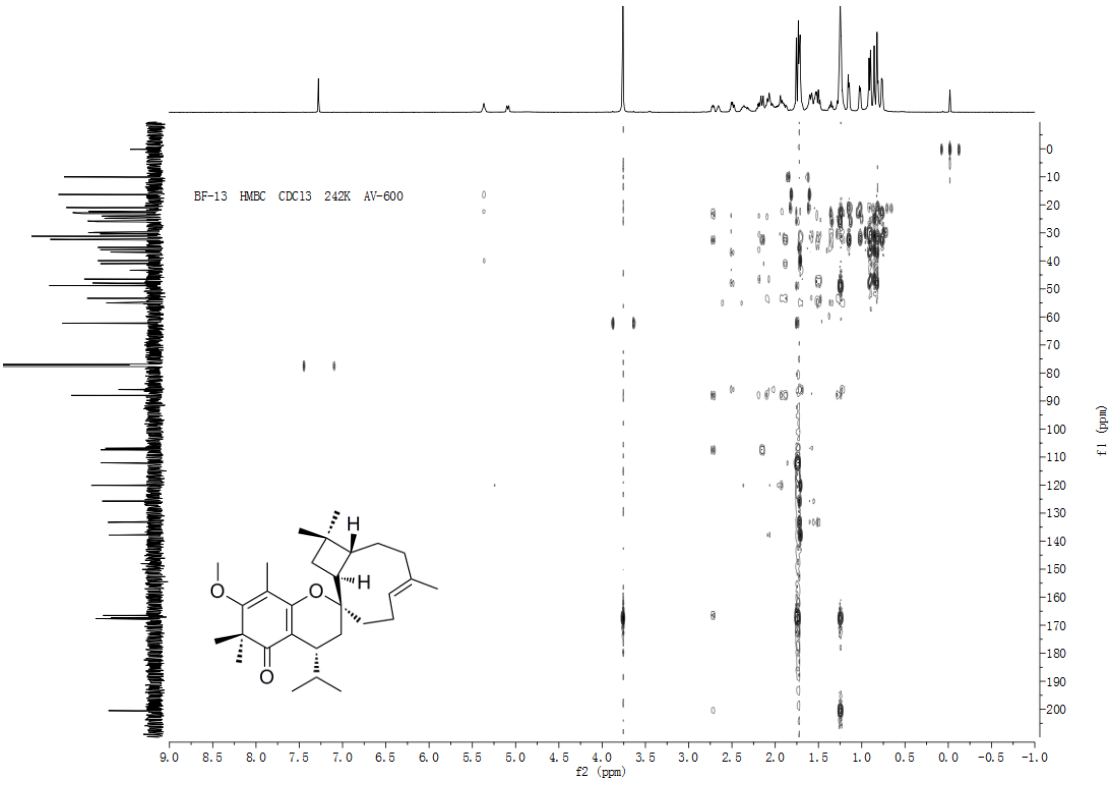


Figure S14. HMBC spectrum of **1** in $CDCl_3$ (600 MHz, 242K)

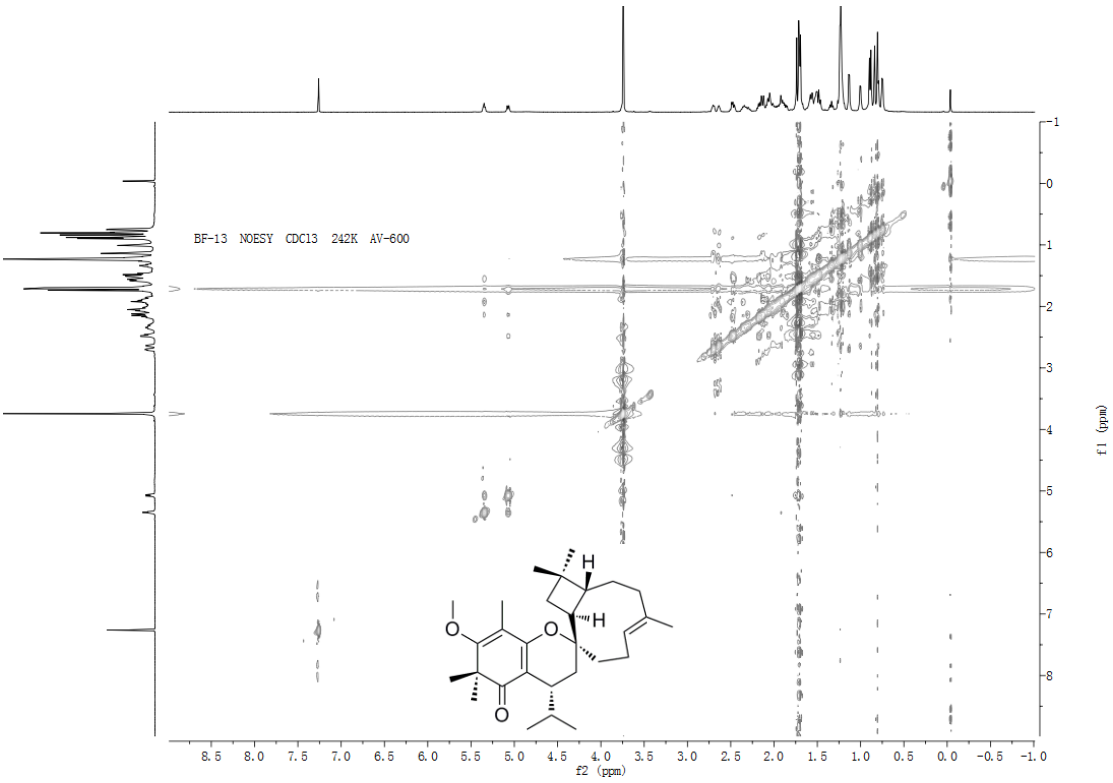


Figure S15. NOESY spectrum of **1** in $CDCl_3$ (600 MHz, 242K)

m/z	Ion	Formula	Abundance
441.3367	(M+H)+	C29 H45 O3	549500.9

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross Score	Mass	Calc Mass	Diff (ppm)
☑	C29 H44 O3	C29 H45 O3	441.3363	98.21		440.3294	440.329	-0.82

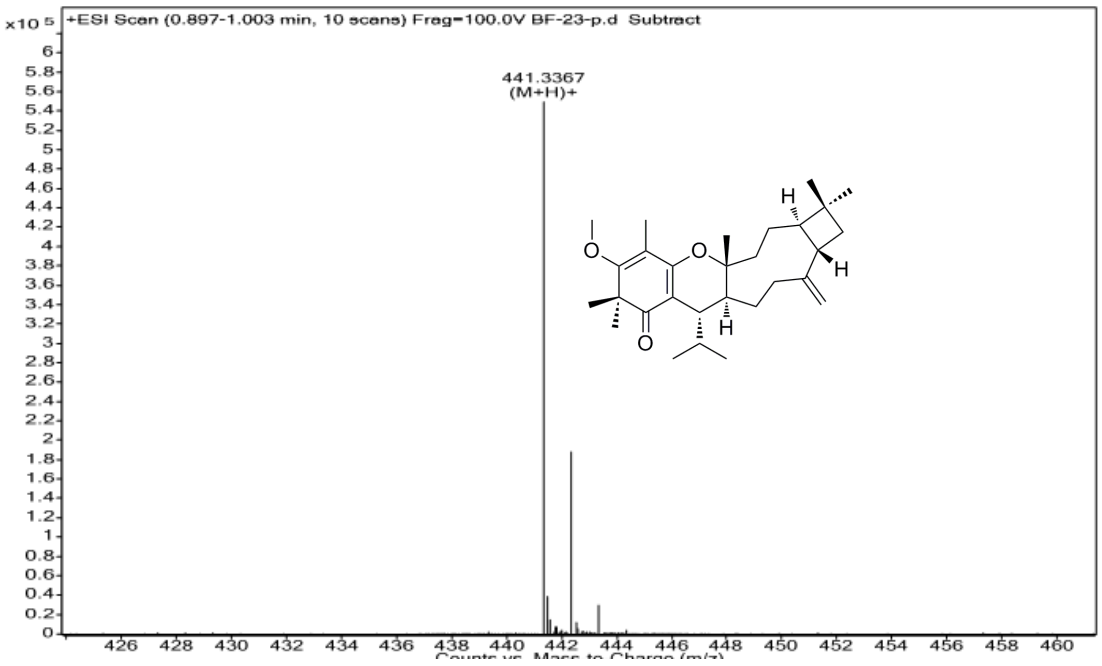
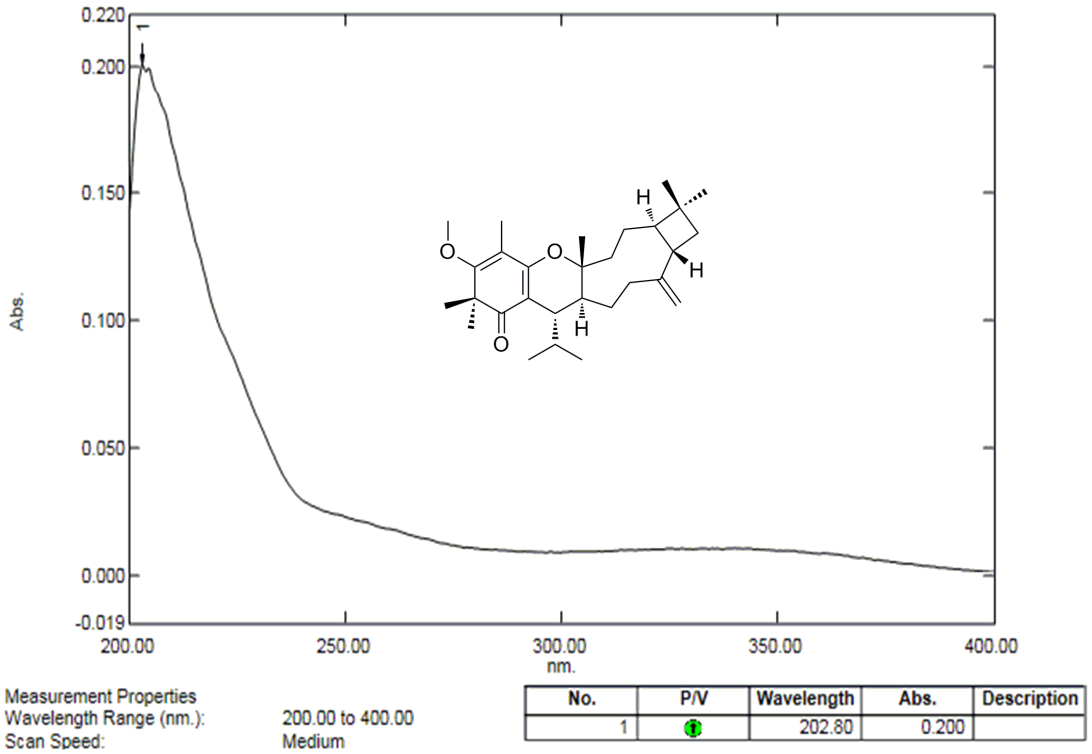


Figure S16. HR-ESI-MS spectrum of **2**



Measurement Properties
Wavelength Range (nm.): 200.00 to 400.00
Scan Speed: Medium

No.	P/V	Wavelength	Abs.	Description
1		202.80	0.200	

Figure S17. UV spectrum of **2** in MeOH

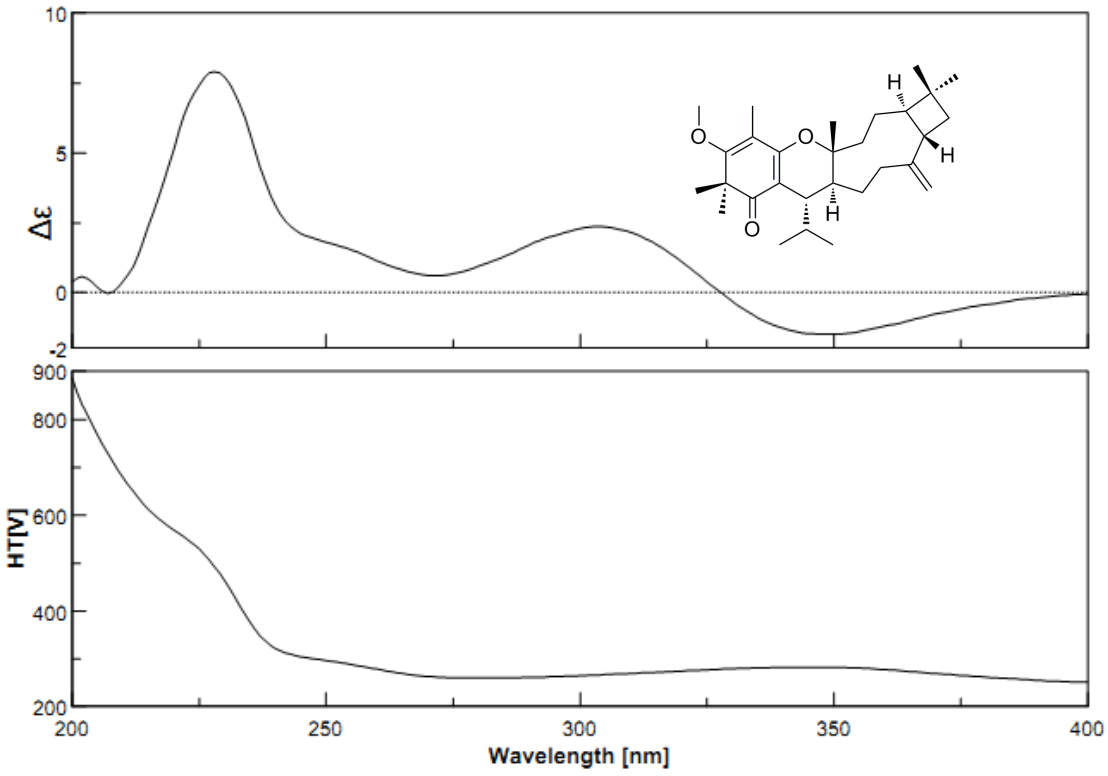


Figure S18. CD spectrum of **2** in MeOH

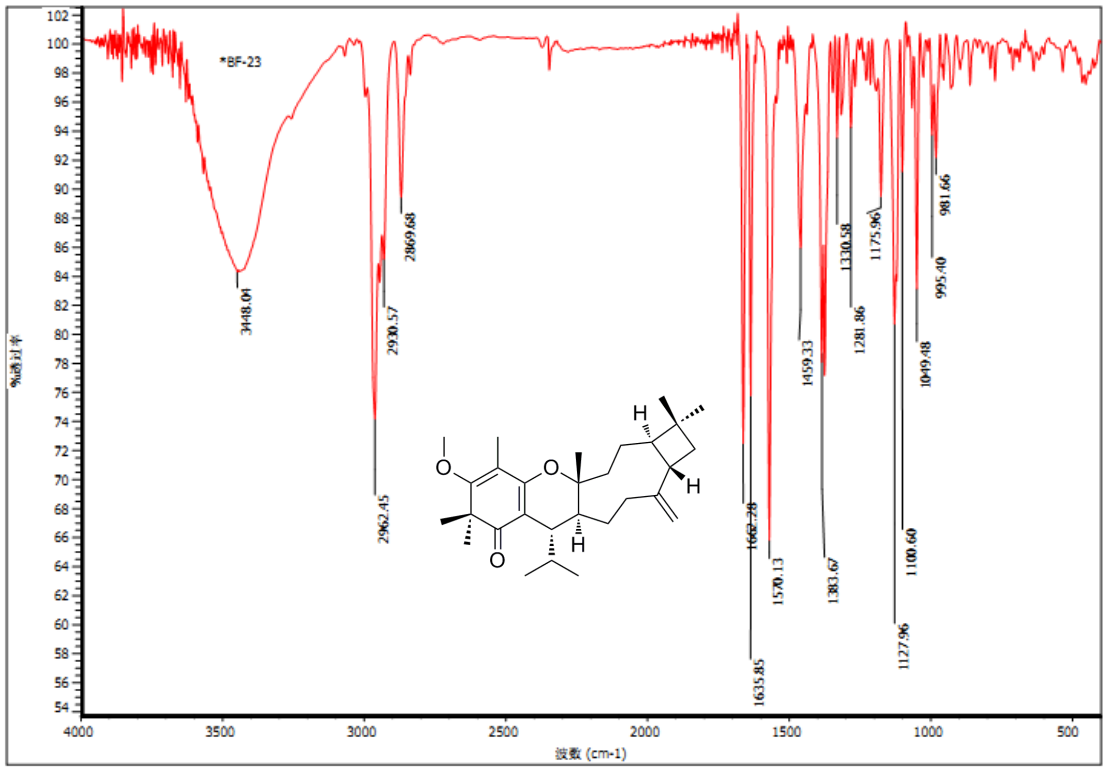


Figure S19. IR spectrum of **2**

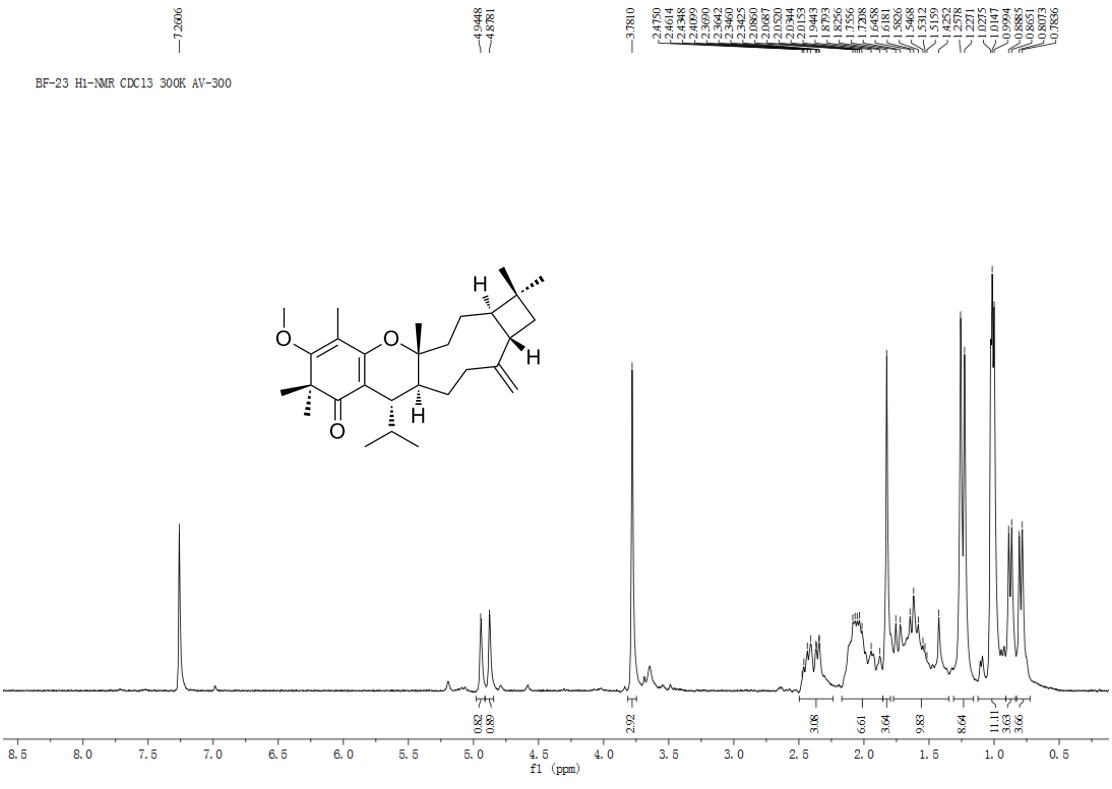


Figure S20. ^{1}H NMR spectrum of **2** in $CDCl_3$ (300 MHz)

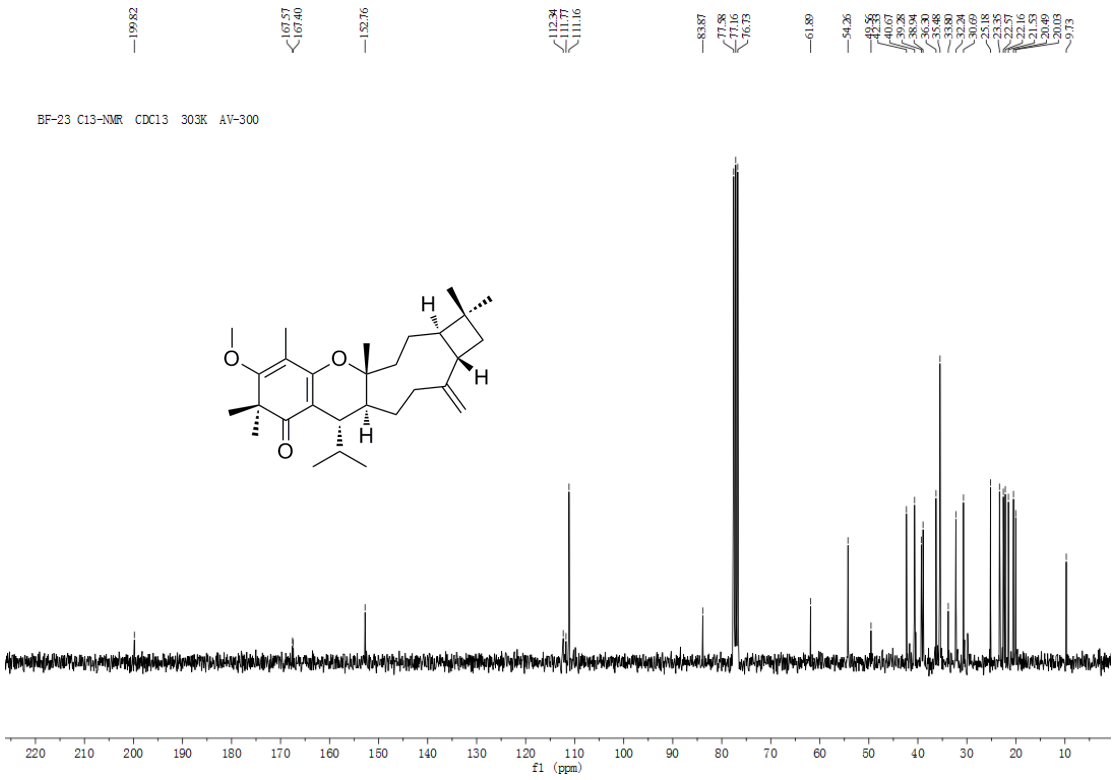


Figure S21. ^{13}C NMR spectrum of **2** in $CDCl_3$ (75 MHz)

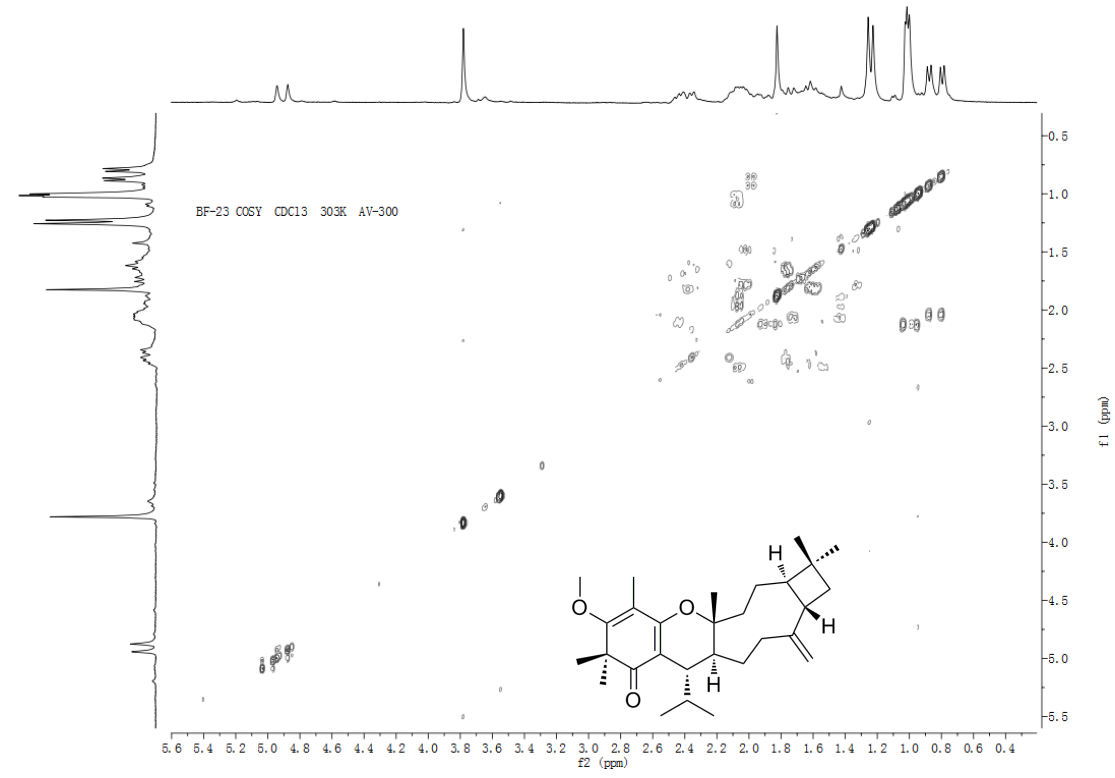


Figure S22. ^{1}H-^{1}H COSY spectrum of **2** in $CDCl_3$ (300 MHz)

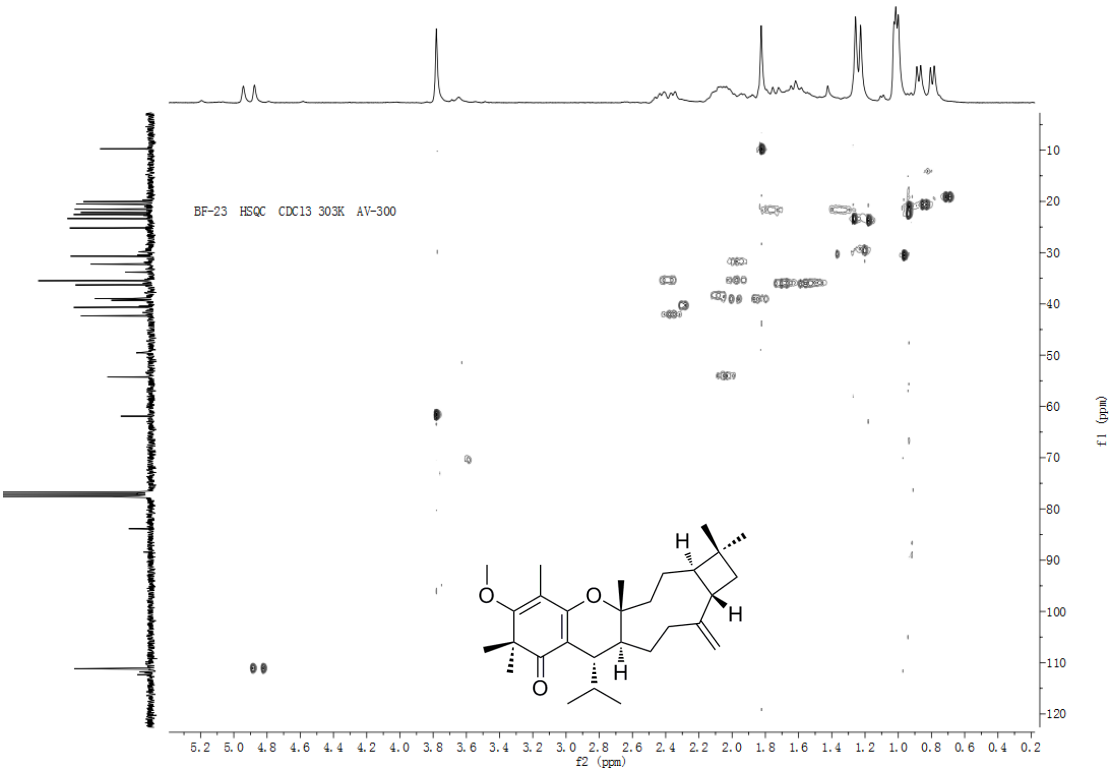


Figure S23. HSQC spectrum of **2** in $CDCl_3$ (300 MHz)

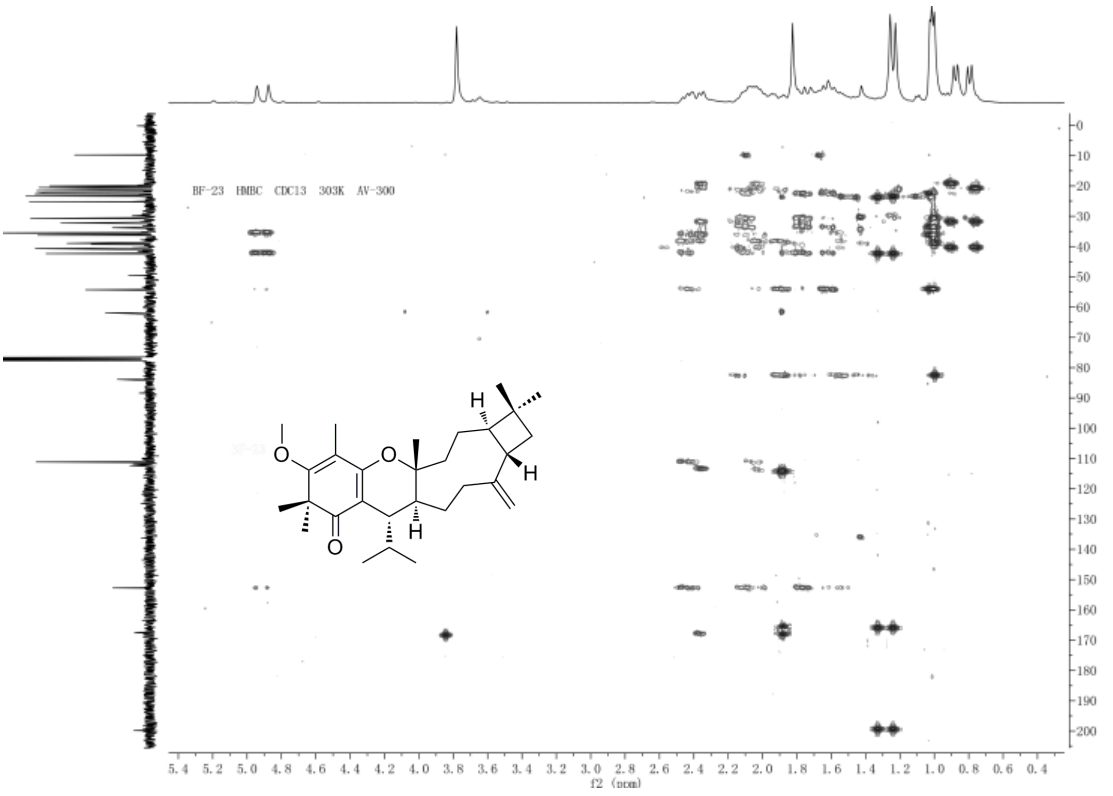


Figure S24. HMBC spectrum of **2** in $CDCl_3$ (300 MHz)

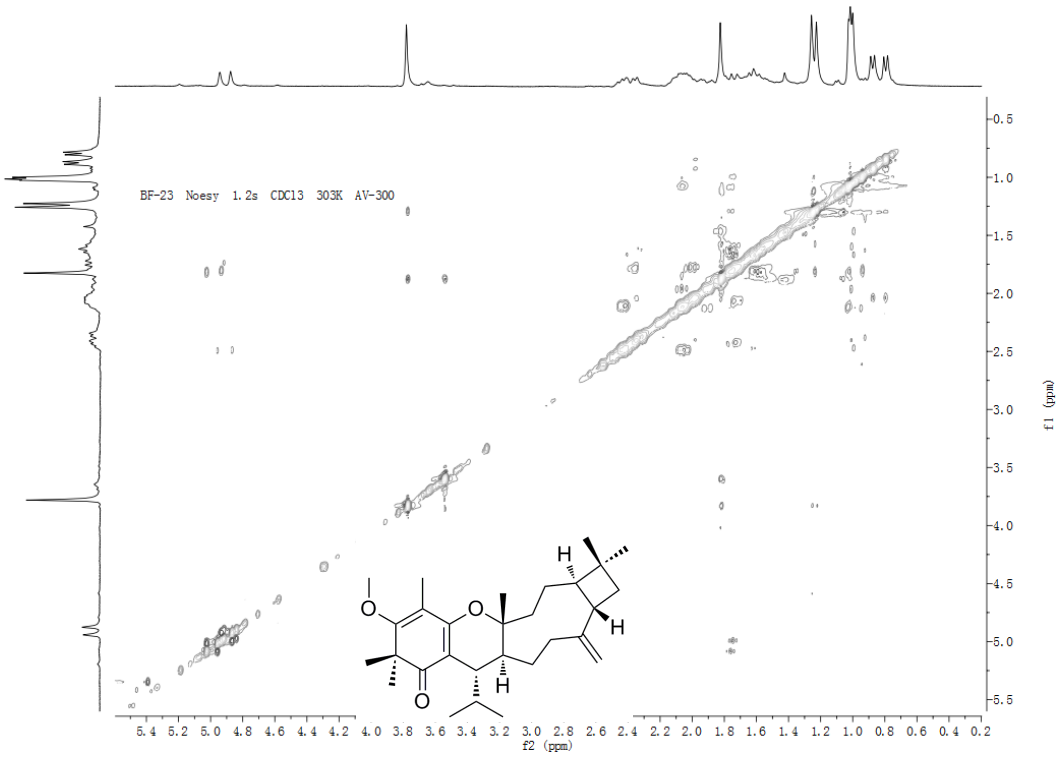


Figure S25. NOESY spectrum of **2** in $CDCl_3$ (300 MHz)

m/z	Ion	Formula	Abundance
441.3359	(M+H)+	C29 H45 O3	814759

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross Score	Mass	Calc Mass	Diff (ppm)
✓	C29 H44 O3	C29 H45 O3	441.3363	97.64		440.3287	440.329	0.79

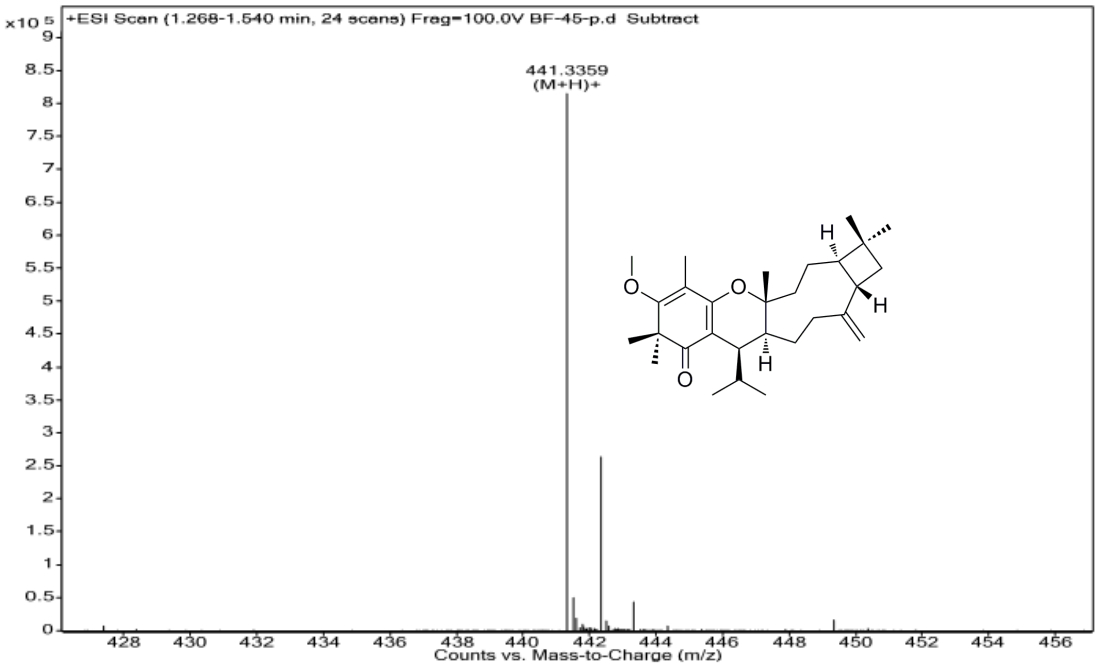
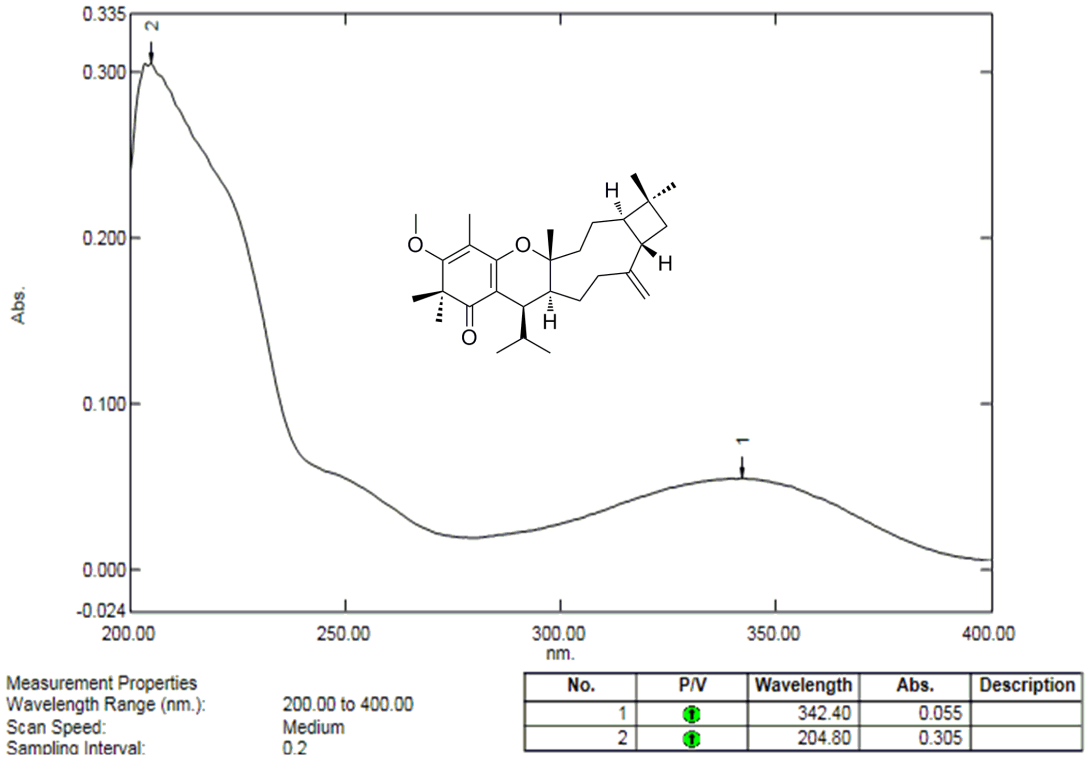


Figure S26. HR-ESI-MS spectrum of **3**



Measurement Properties
Wavelength Range (nm.): 200.00 to 400.00
Scan Speed: Medium
Sampling Interval: 0.2

No.	P/V	Wavelength	Abs.	Description
1		342.40	0.055	
2		204.80	0.305	

Figure S27. UV spectrum of **3** in MeOH

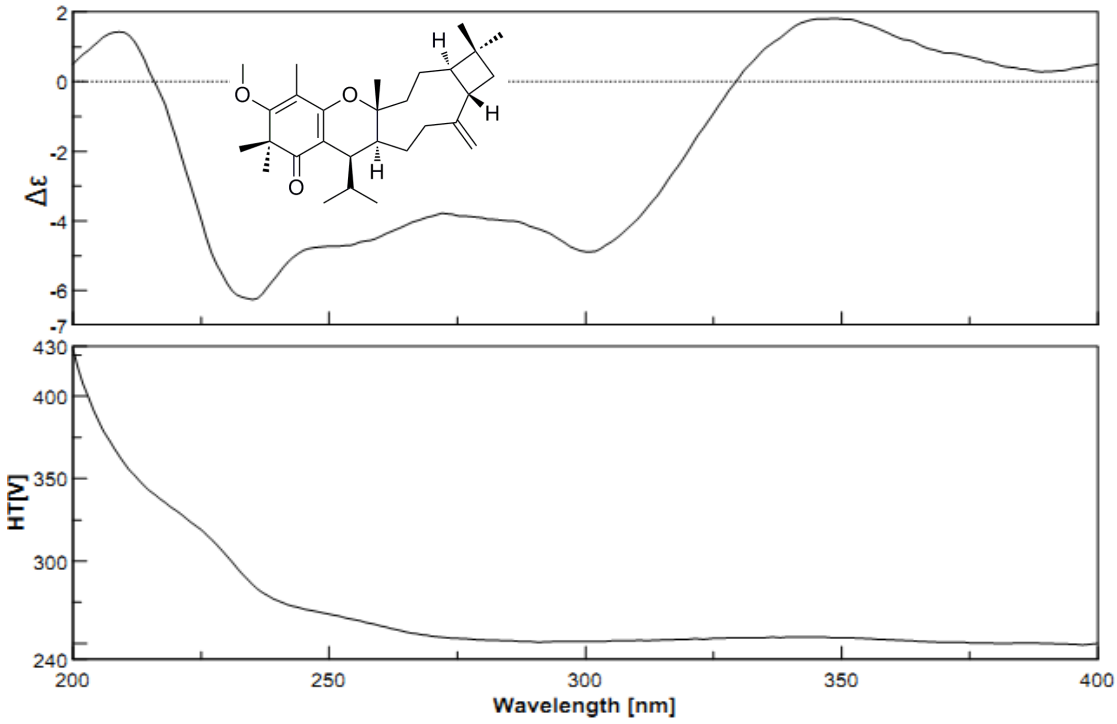


Figure S28. CD spectrum of **3** in MeOH

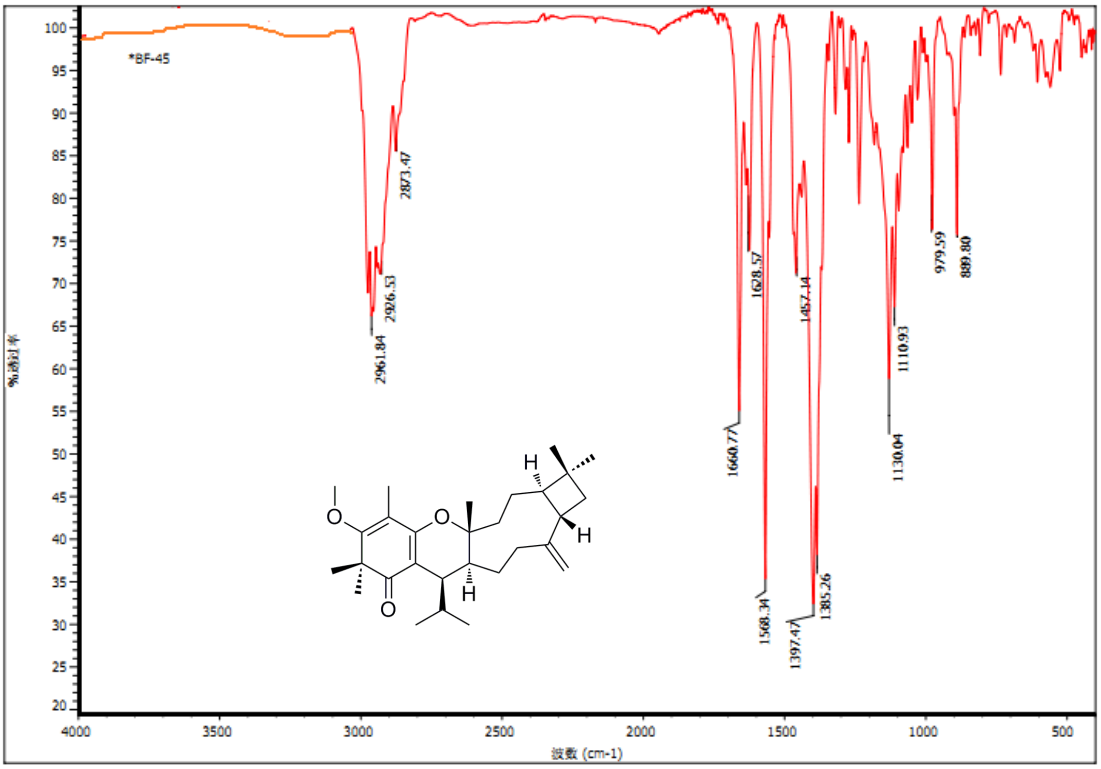


Figure S29. IR spectrum of **3**

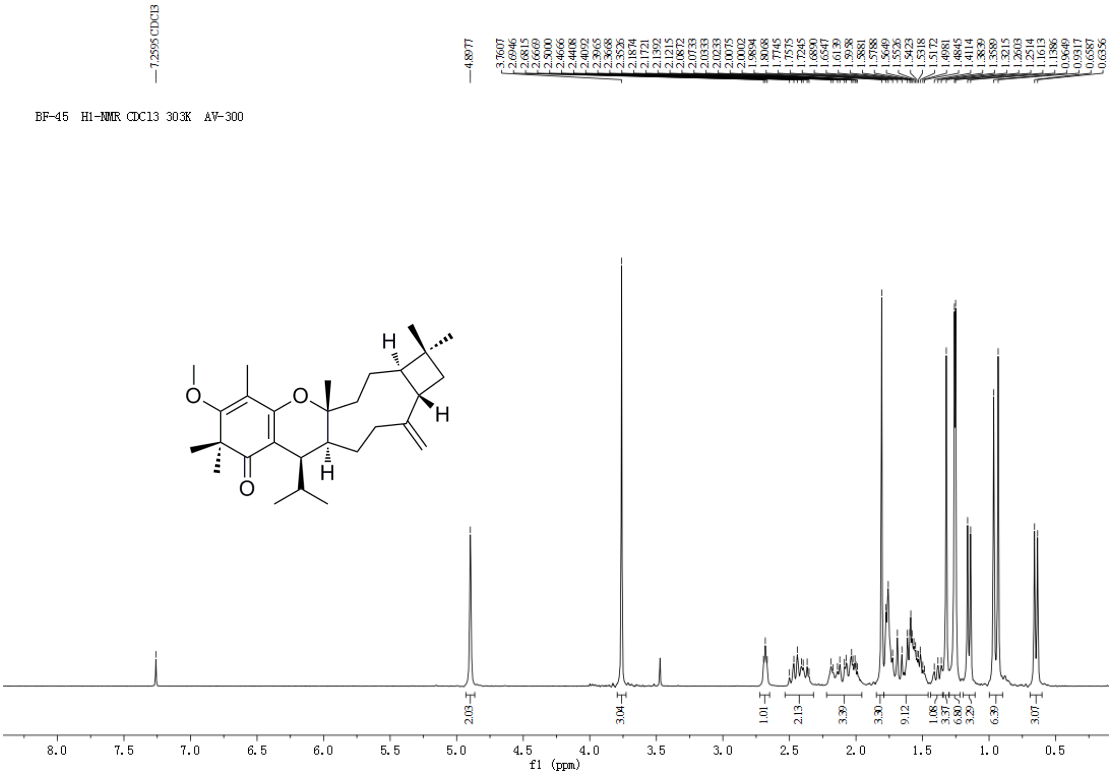


Figure S30. ^{1}H NMR spectrum of **3** in $CDCl_3$ (300 MHz)

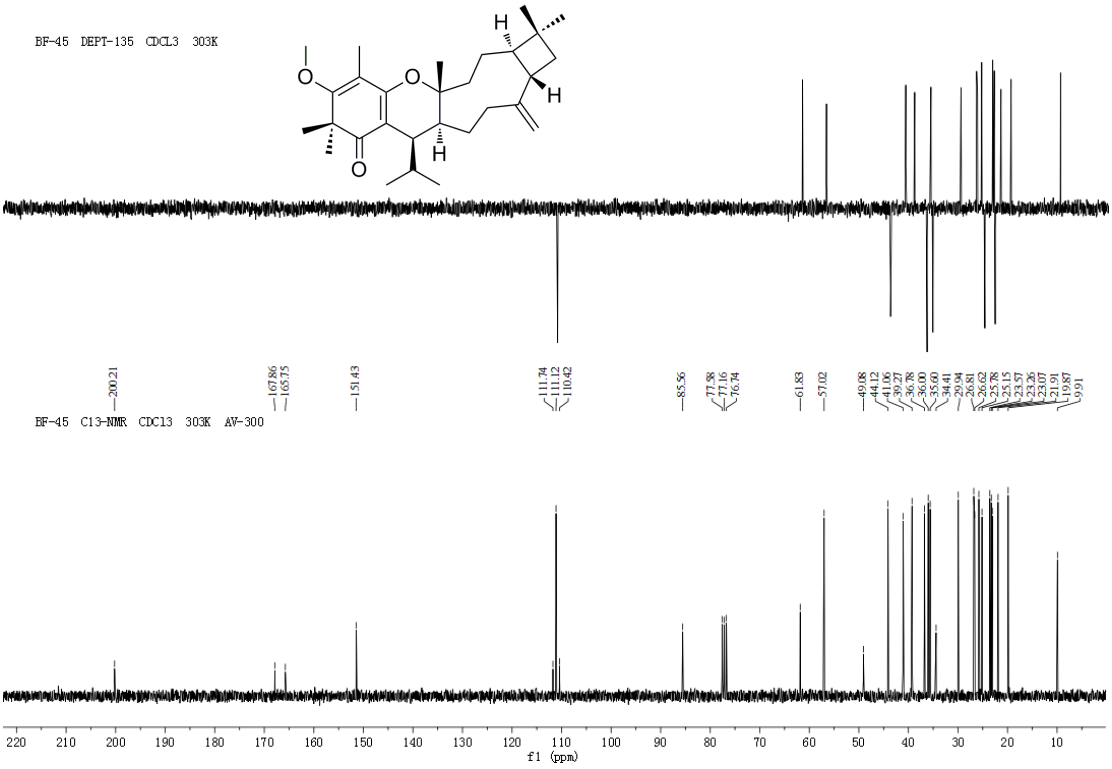


Figure S31. ^{13}C NMR spectrum of **3** in $CDCl_3$ (75 MHz)

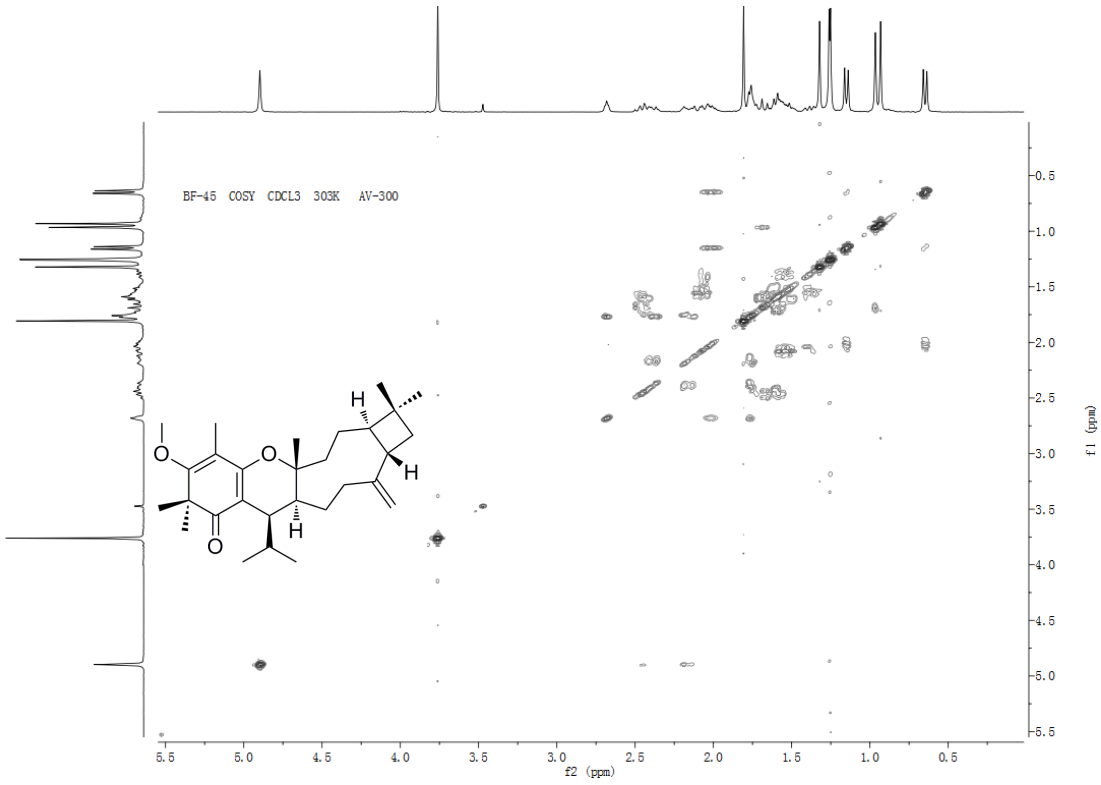


Figure S32. ^{1}H-^{1}H COSY spectrum of **3** in $CDCl_3$ (300 MHz)

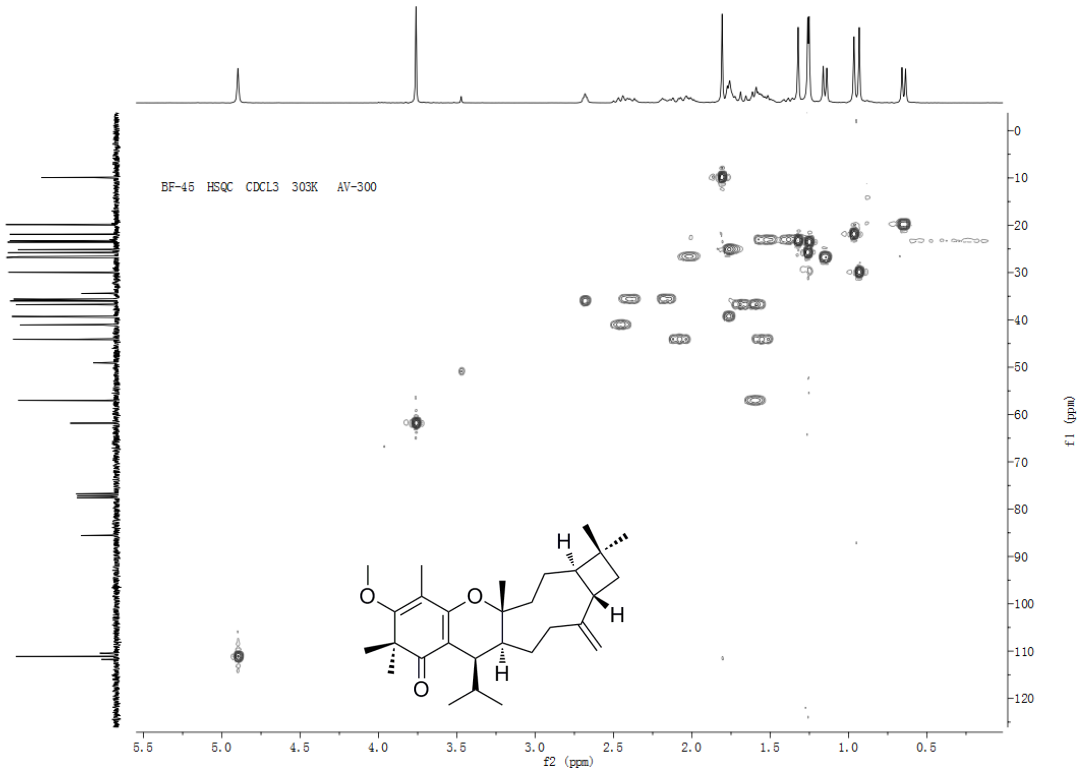


Figure S33. HSQC spectrum of **3** in $CDCl_3$ (300 MHz)

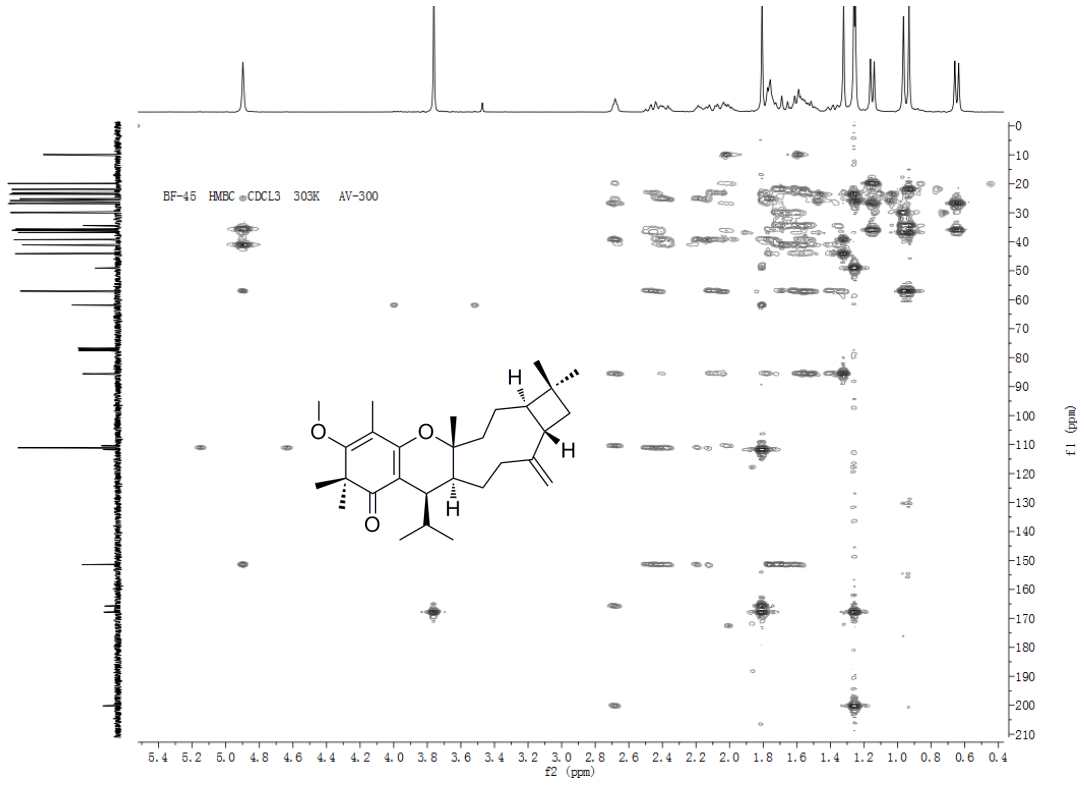


Figure S34. HMBC spectrum of **3** in $CDCl_3$ (300 MHz)

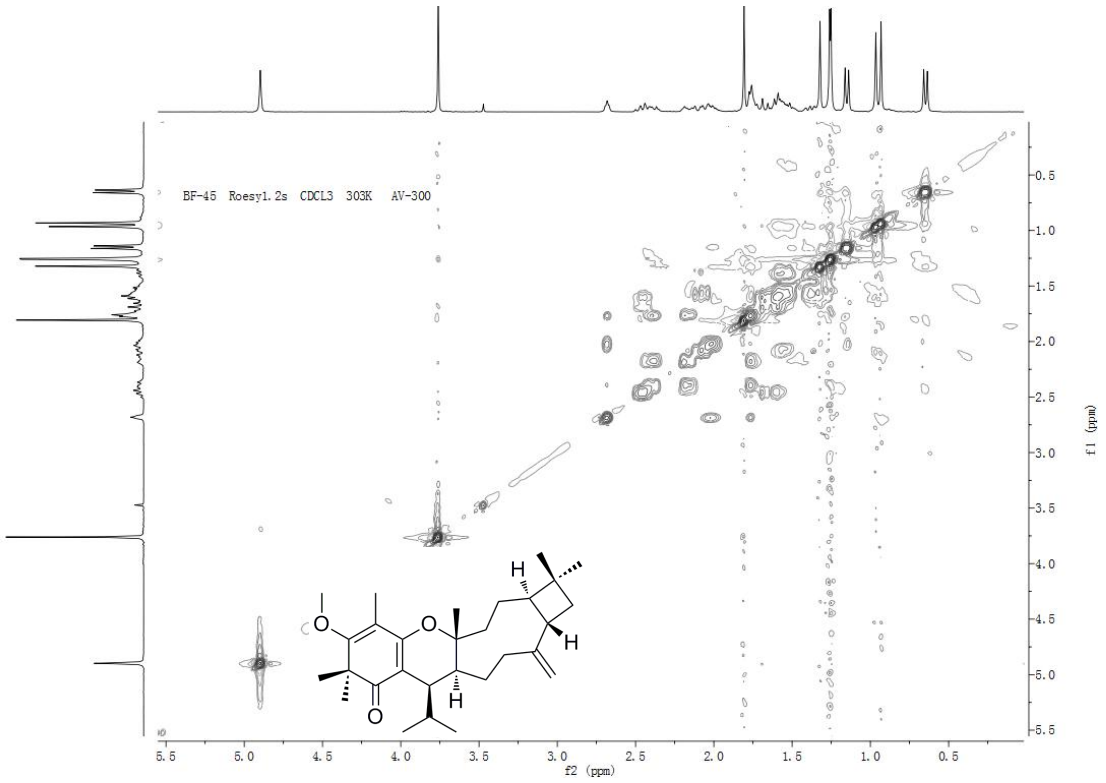


Figure S35. ROESY spectrum of **3** in $CDCl_3$ (300 MHz)

m/z	Ion	Formula	Abundance
441.3357	(M+H)+	C29 H45 O3	780117.9

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross Score	Mass	Calc Mass	Diff (ppm)
☑	C29 H44 O3	C29 H45 O3	441.3363	96.55		440.3285	440.329	1.24

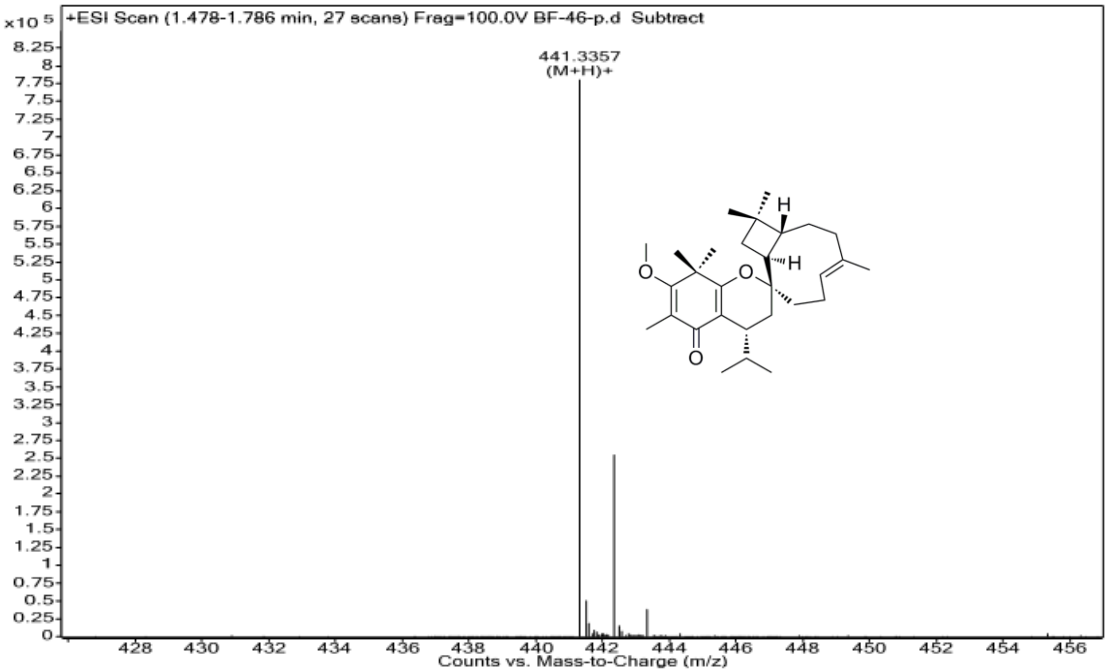
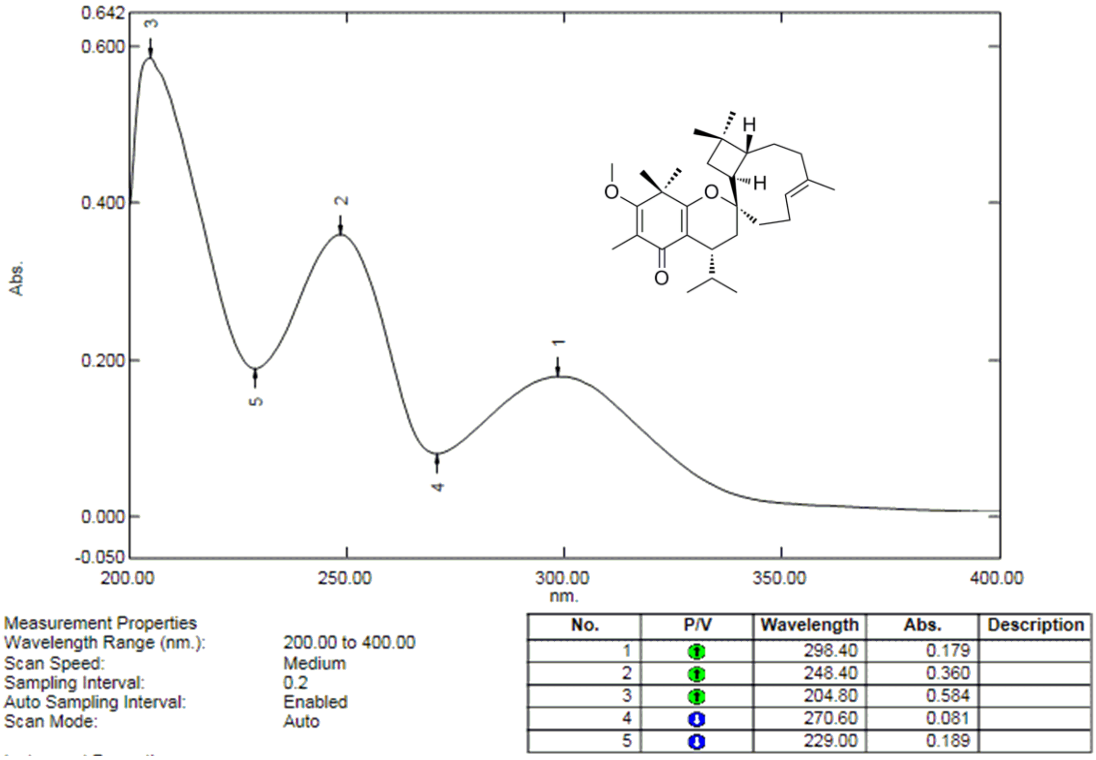


Figure S36. HR-ESI-MS spectrum of **4**



Measurement Properties

Wavelength Range (nm.):	200.00 to 400.00
Scan Speed:	Medium
Sampling Interval:	0.2
Auto Sampling Interval:	Enabled
Scan Mode:	Auto

No.	P/V	Wavelength	Abs.	Description
1	↑	298.40	0.179	
2	↑	248.40	0.360	
3	↑	204.80	0.584	
4	↓	270.60	0.081	
5	↓	229.00	0.189	

Figure S37. UV spectrum of **4** in MeOH

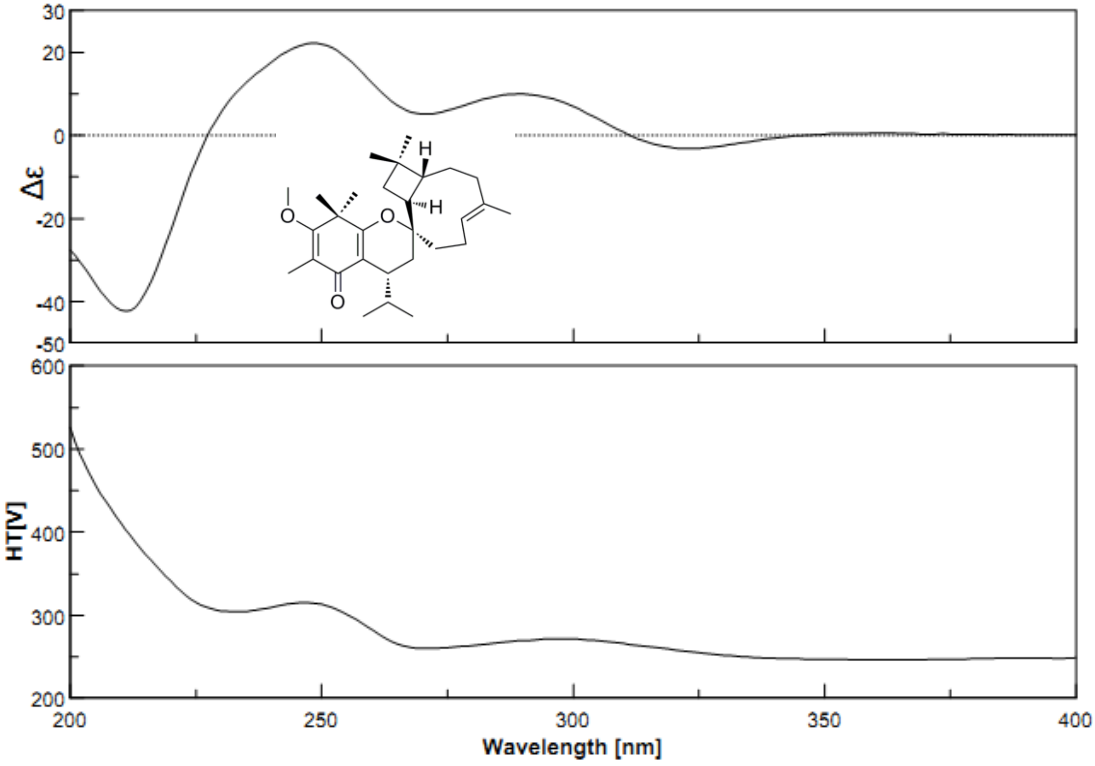


Figure S38. CD spectrum of **4** in MeOH

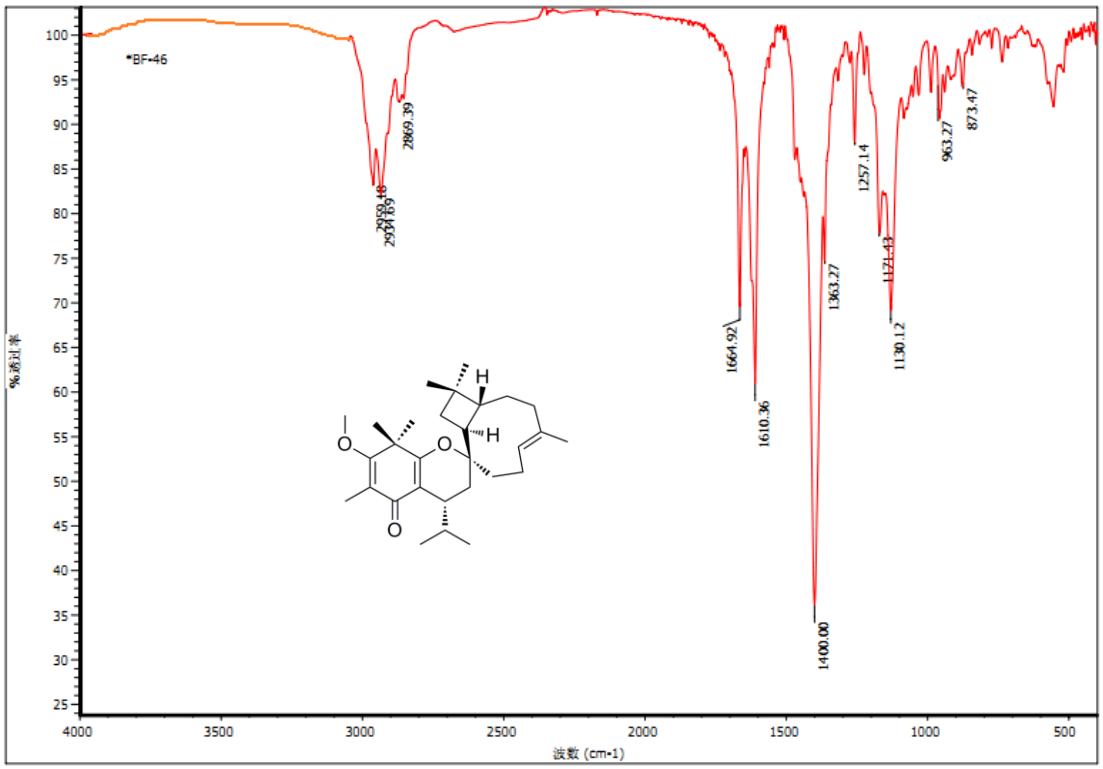


Figure S39. IR spectrum of **4**

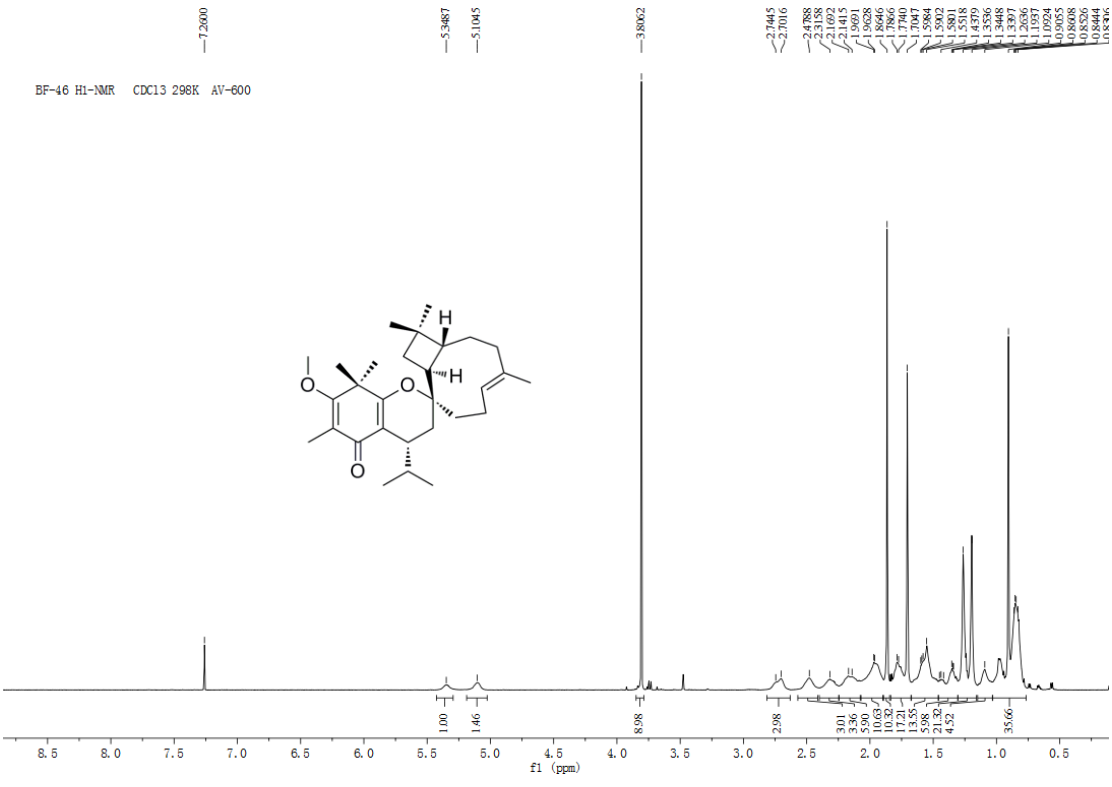


Figure S40-1. ^{1}H NMR spectrum of **4** in $CDCl_3$ (600 MHz, 298K)

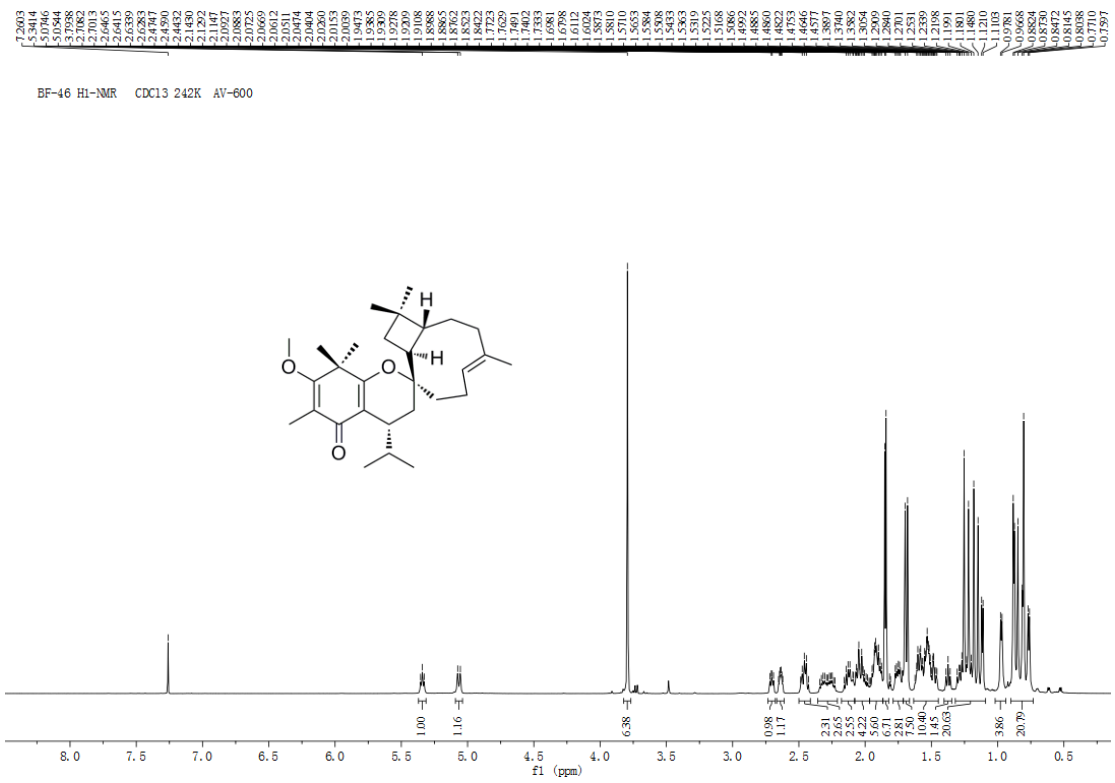


Figure S40-2. ^{1}H NMR spectrum of **4** in $CDCl_3$ (600 MHz, 242K)

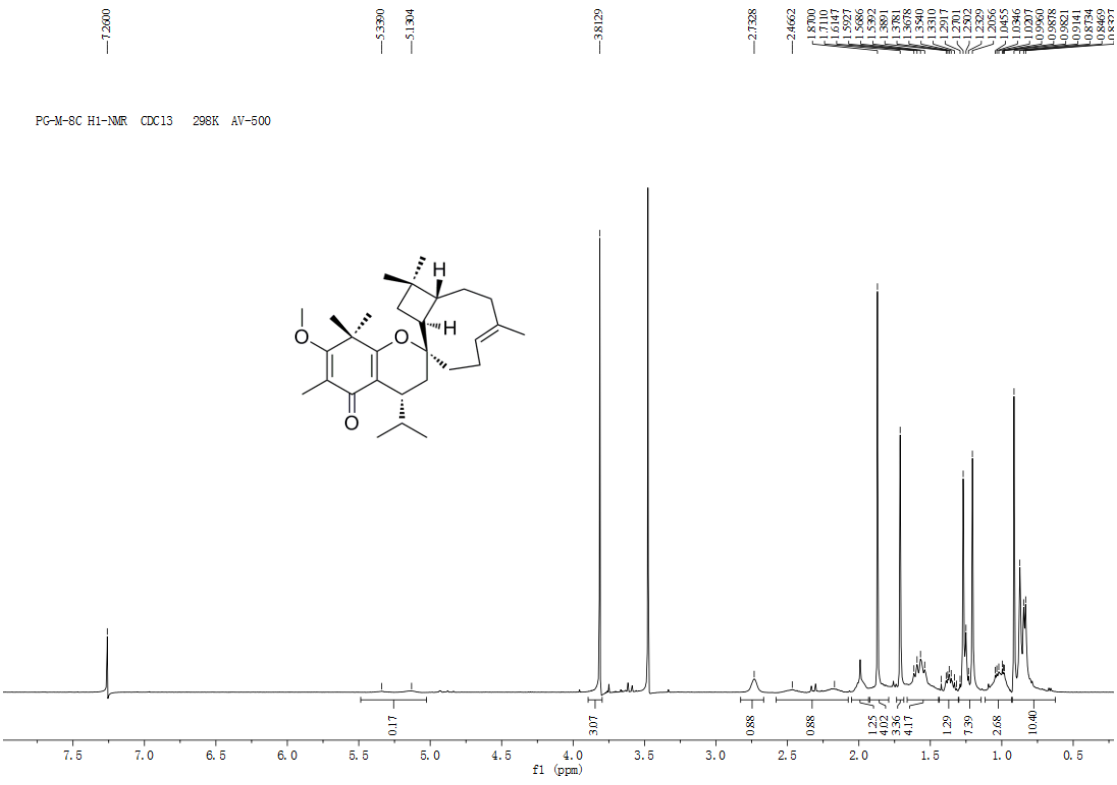


Figure S41. ^{1}H NMR spectrum of **4** (synthetic) in $CDCl_3$ (500 MHz, 298K)

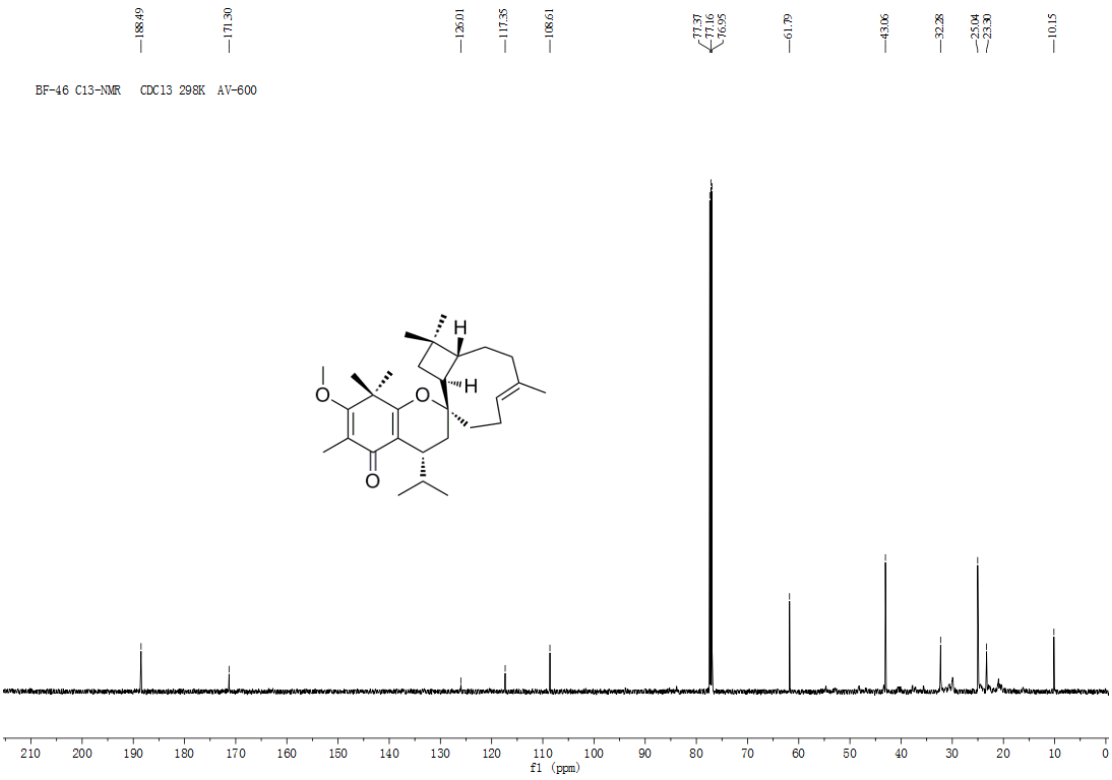


Figure S42-1. ^{13}C NMR spectrum of **4** in $CDCl_3$ (150 MHz, 298K)

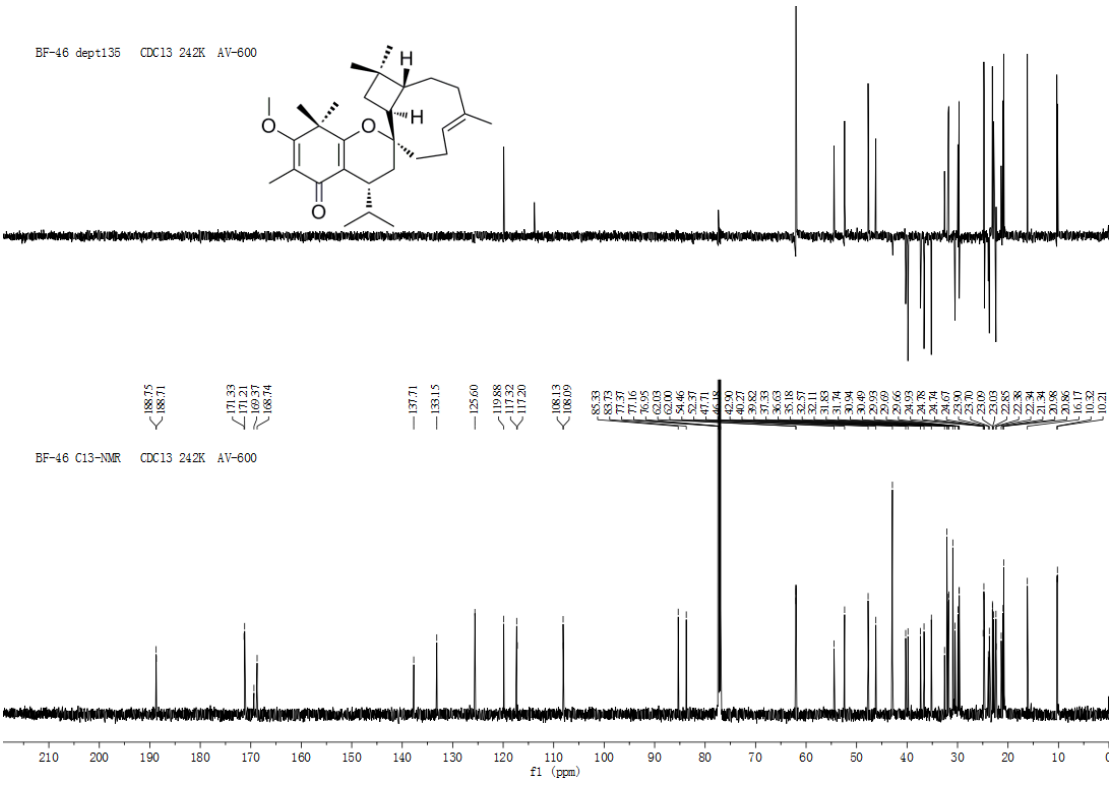


Figure S42-2. ^{13}C NMR spectrum of **4** in $CDCl_3$ (150 MHz, 242K)

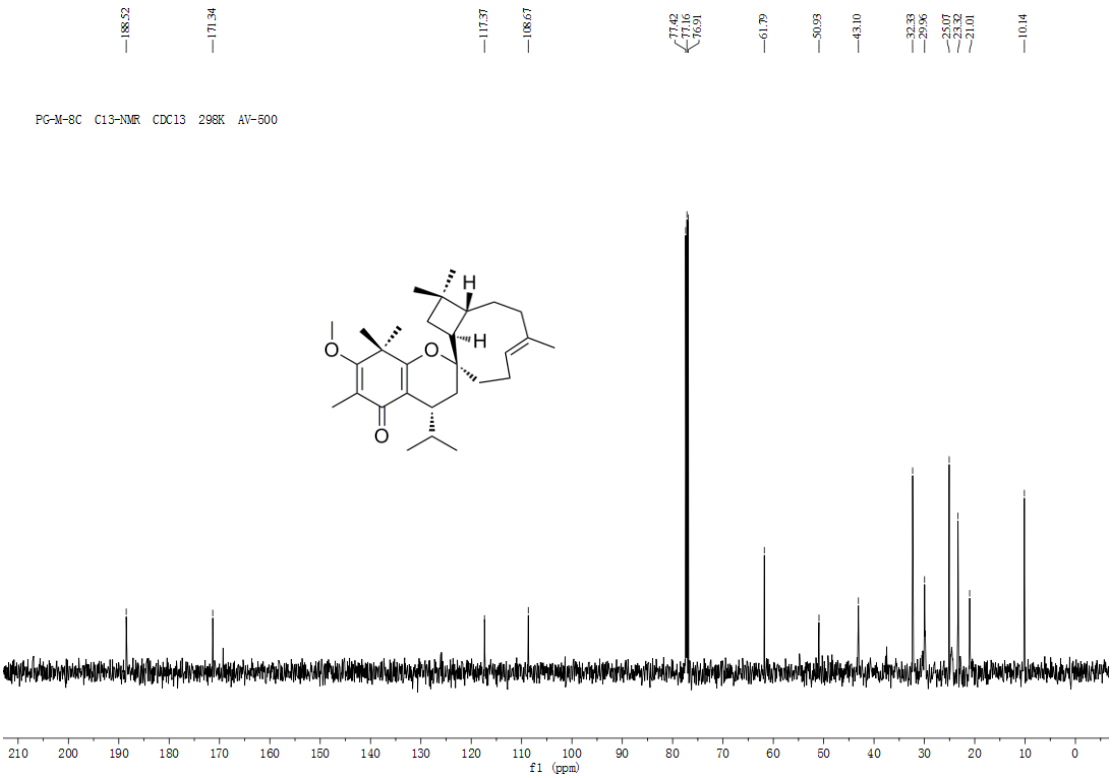


Figure S43. ^{13}C NMR spectrum of **4** (synthetic) in $CDCl_3$ (125 MHz, 298K)

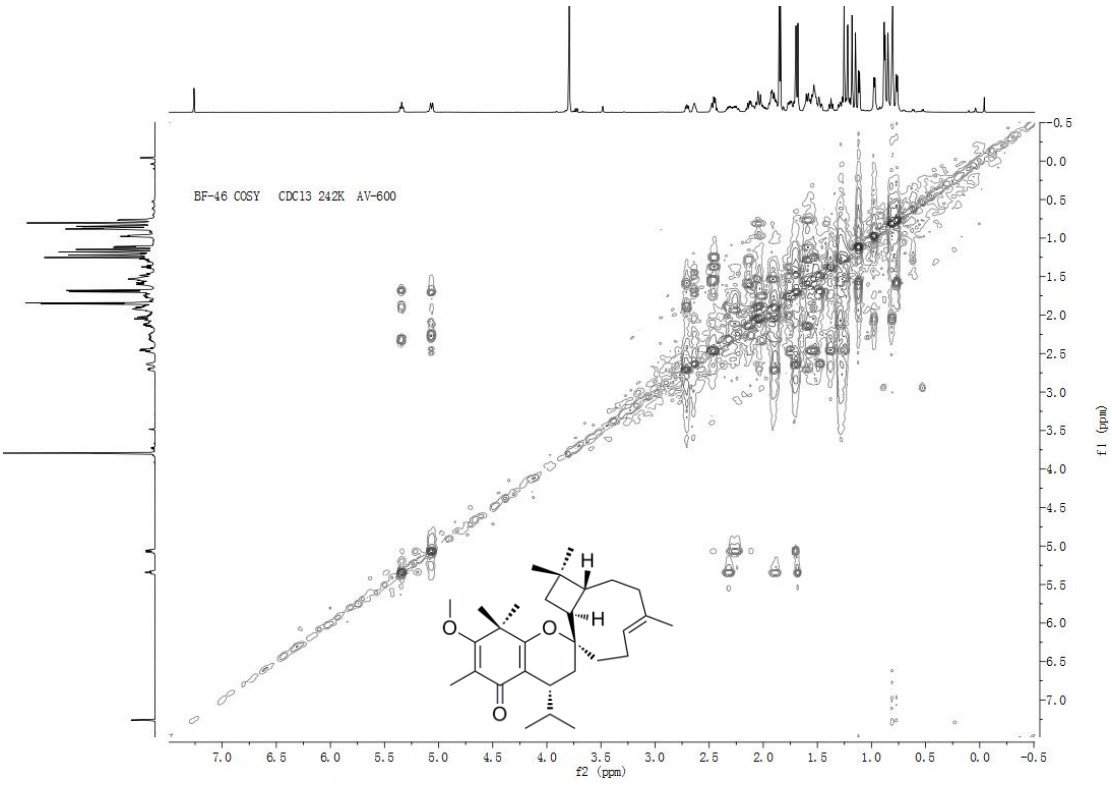


Figure S44. ^{1}H-^{1}H COSY spectrum of **4** in $CDCl_3$ (600 MHz, 242K)

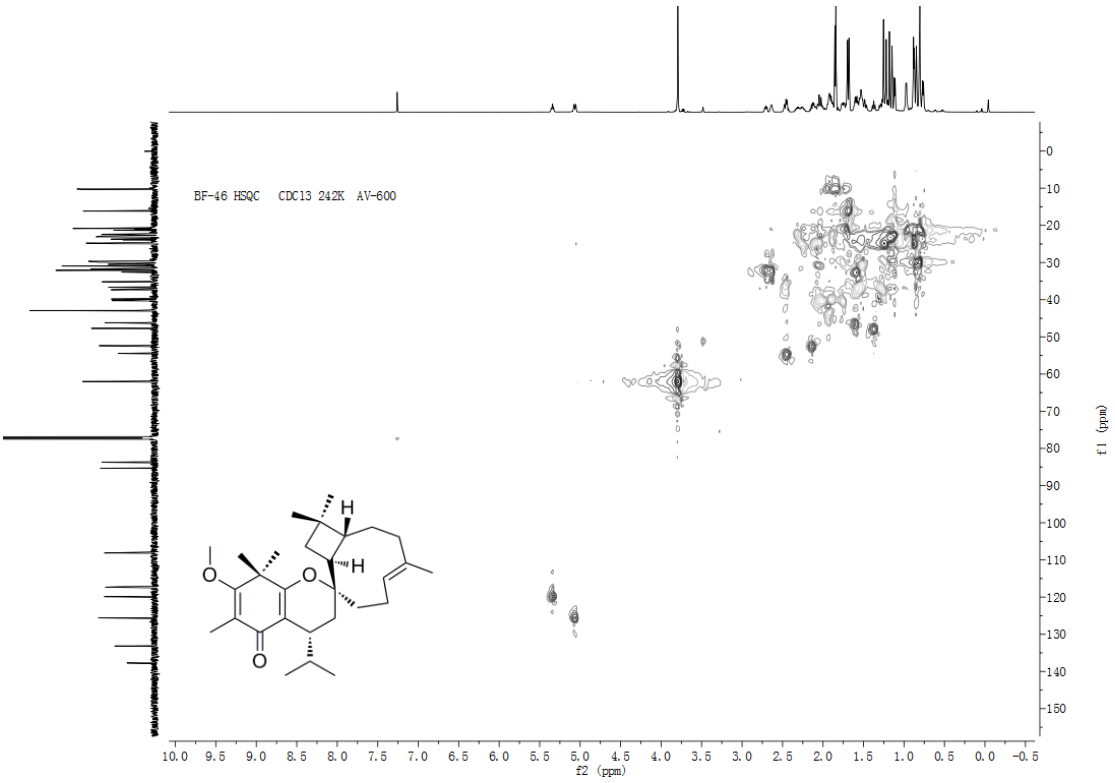


Figure S45. HSQC spectrum of **4** in $CDCl_3$ (600 MHz, 242K)

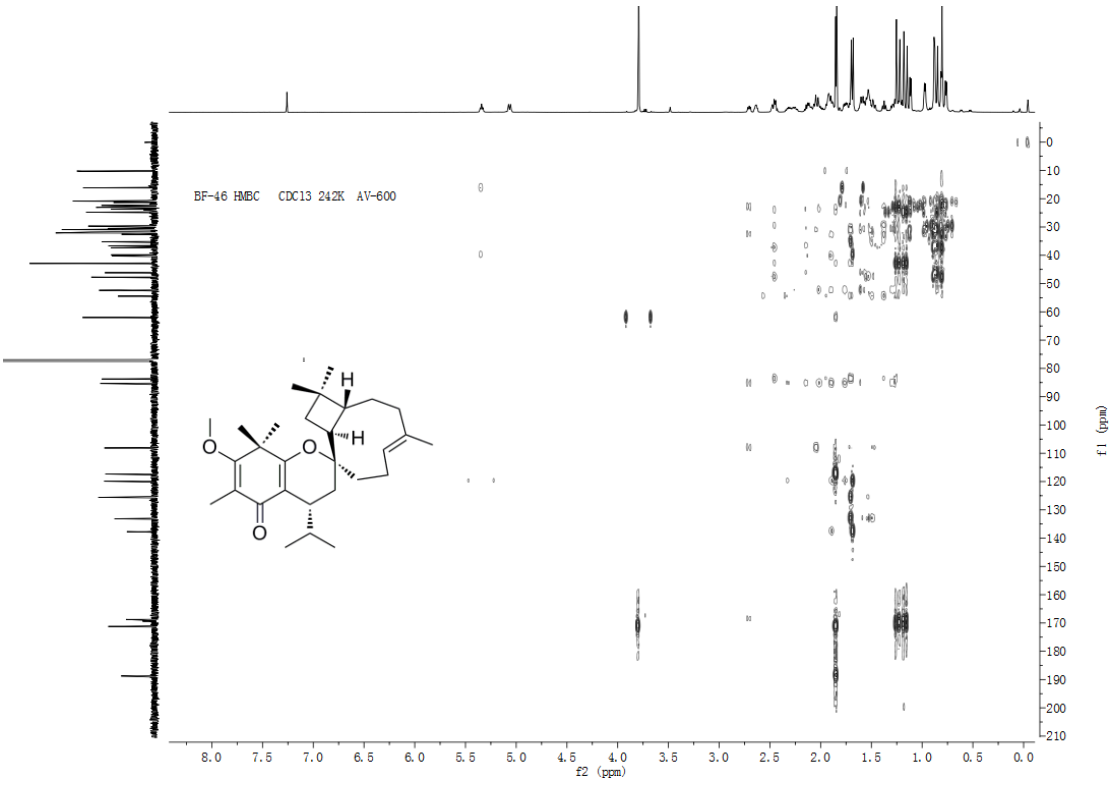


Figure S46. HMBC spectrum of **4** in $CDCl_3$ (600 MHz, 242K)

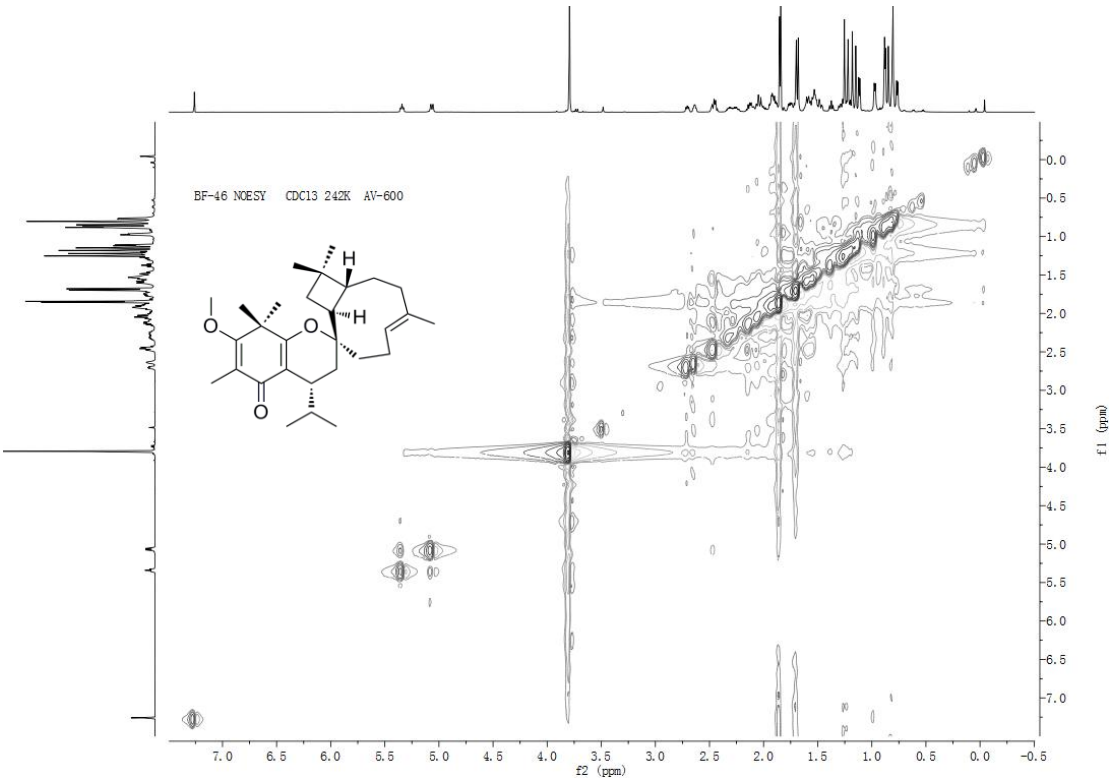


Figure S47. NOESY spectrum of **4** in $CDCl_3$ (600 MHz, 242K)

m/z	Ion	Formula	Abundance
441.3363	(M+H)+	C29 H45 O3	1285718

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross Score	Mass	Calc Mass	Diff (ppm)
☑	C29 H44 O3	C29 H45 O3	441.3363	98.94		440.329	440.329	0.05

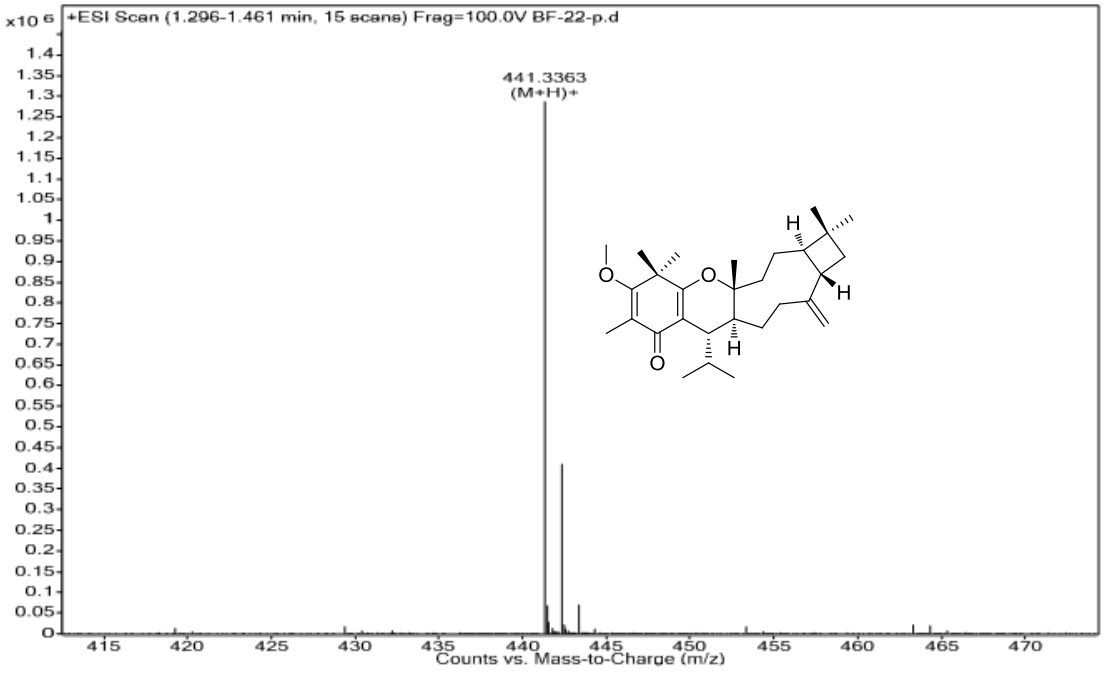
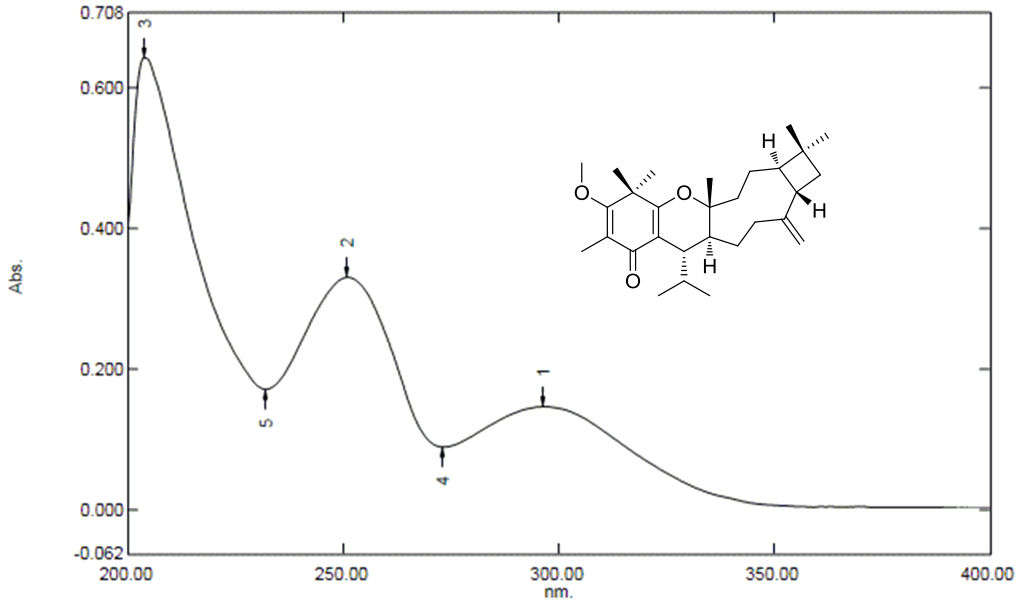


Figure S48. HR-ESI-MS spectrum of **5**



Measurement Properties

Wavelength Range (nm.):	200.00 to 400.00
Scan Speed:	Medium
Sampling Interval:	0.2
Auto Sampling Interval:	Enabled
Scan Mode:	Auto

No.	P/V	Wavelength	Abs.	Description
1	P	296.20	0.147	
2	P	250.80	0.331	
3	P	203.60	0.644	
4	V	273.00	0.090	
5	V	232.00	0.172	

Figure S49. UV spectrum of **5** in MeOH

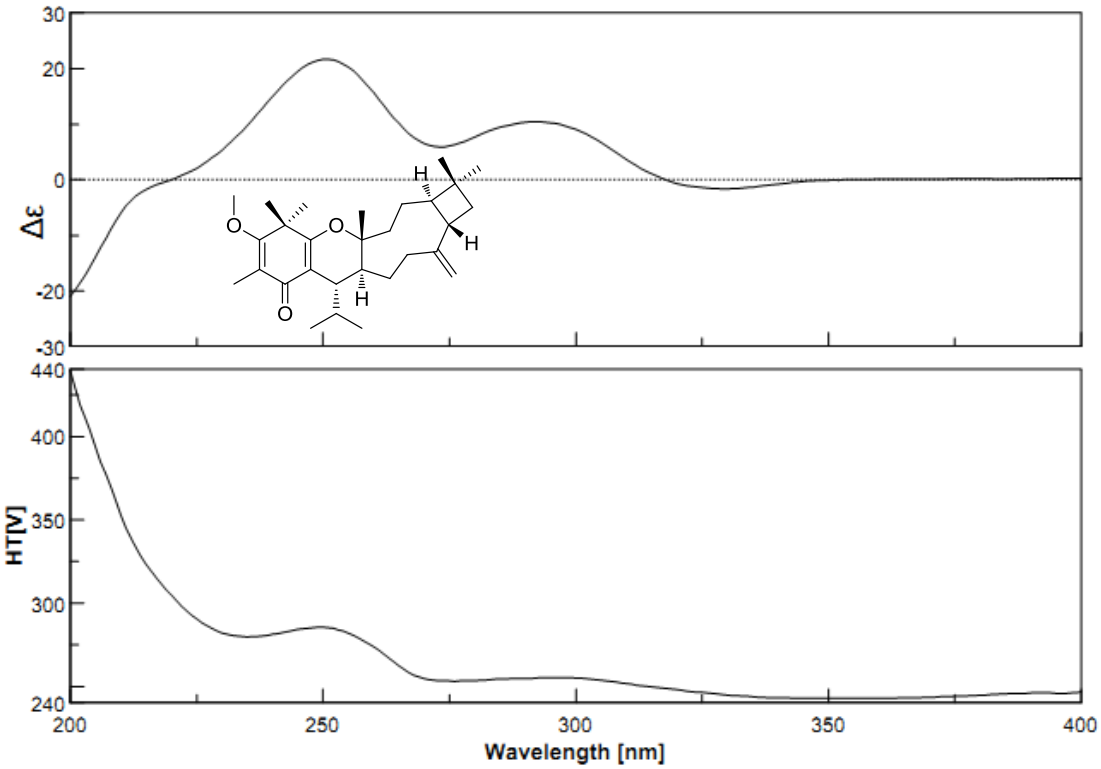


Figure S50. CD spectrum of **5** in MeOH

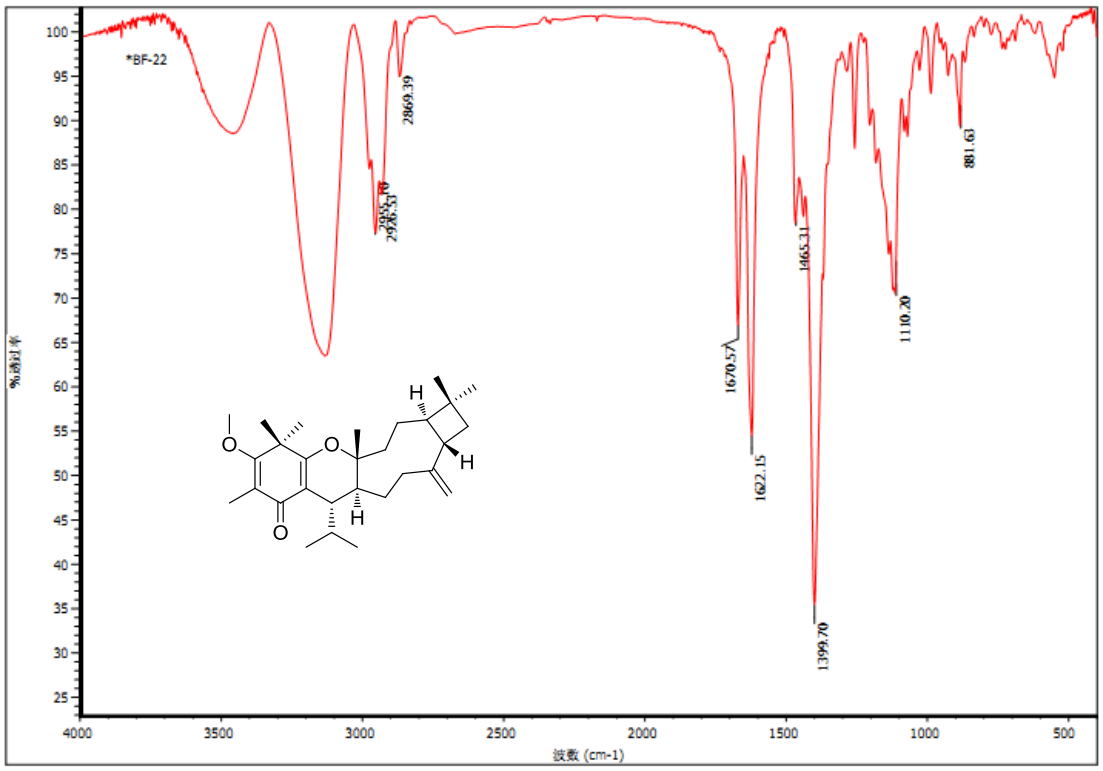


Figure S51. IR spectrum of **5**

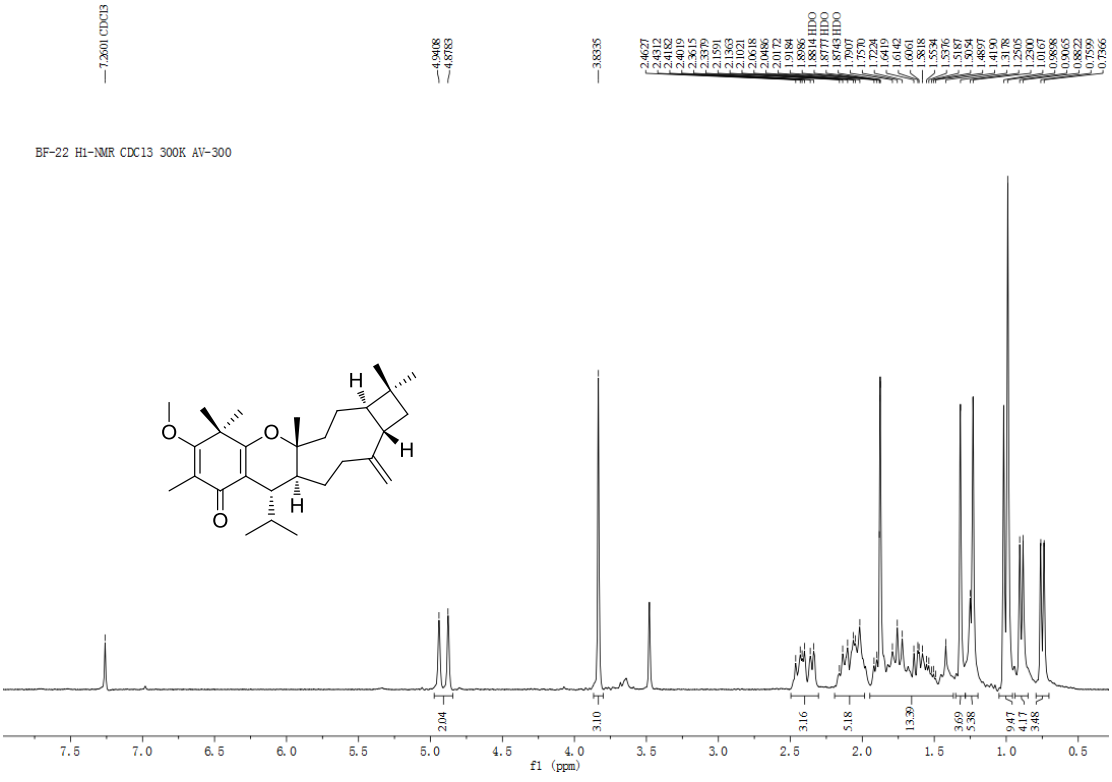


Figure S52. ^{1}H NMR spectrum of **5** in $CDCl_3$ (300 MHz)

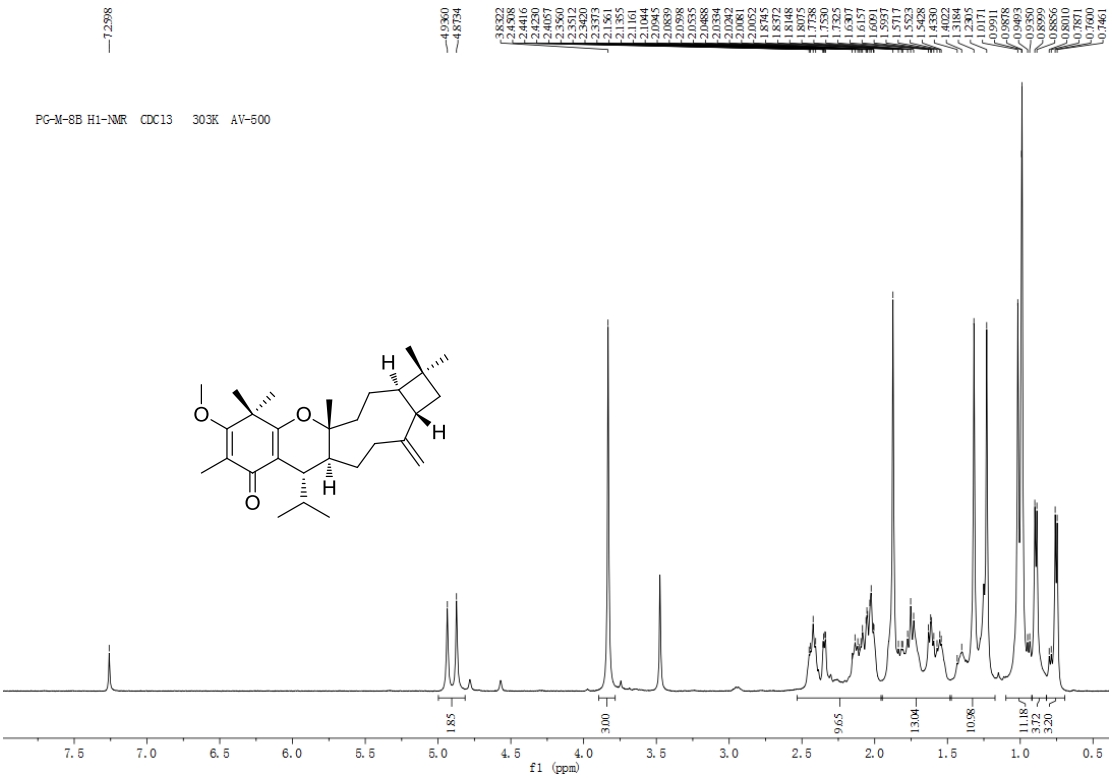


Figure S53. ^{1}H NMR spectrum of **5** (synthetic) in $CDCl_3$ (500 MHz)

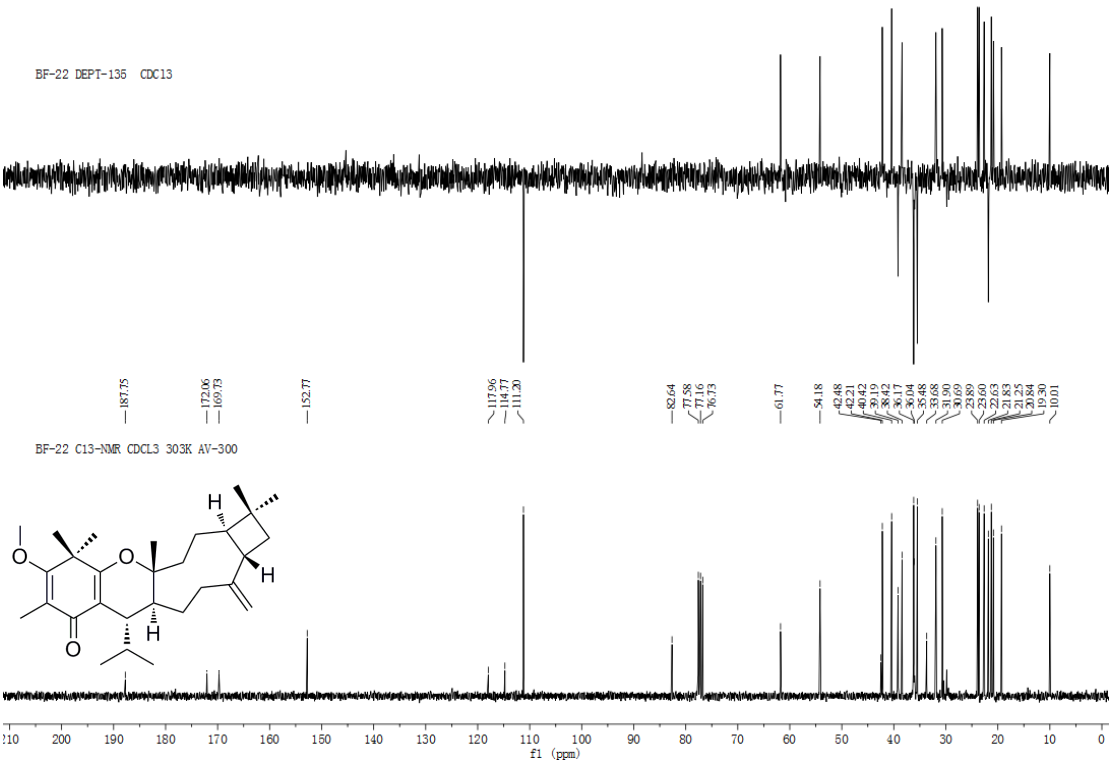


Figure S54. ^{13}C NMR spectrum of **5** in $CDCl_3$ (75 MHz)

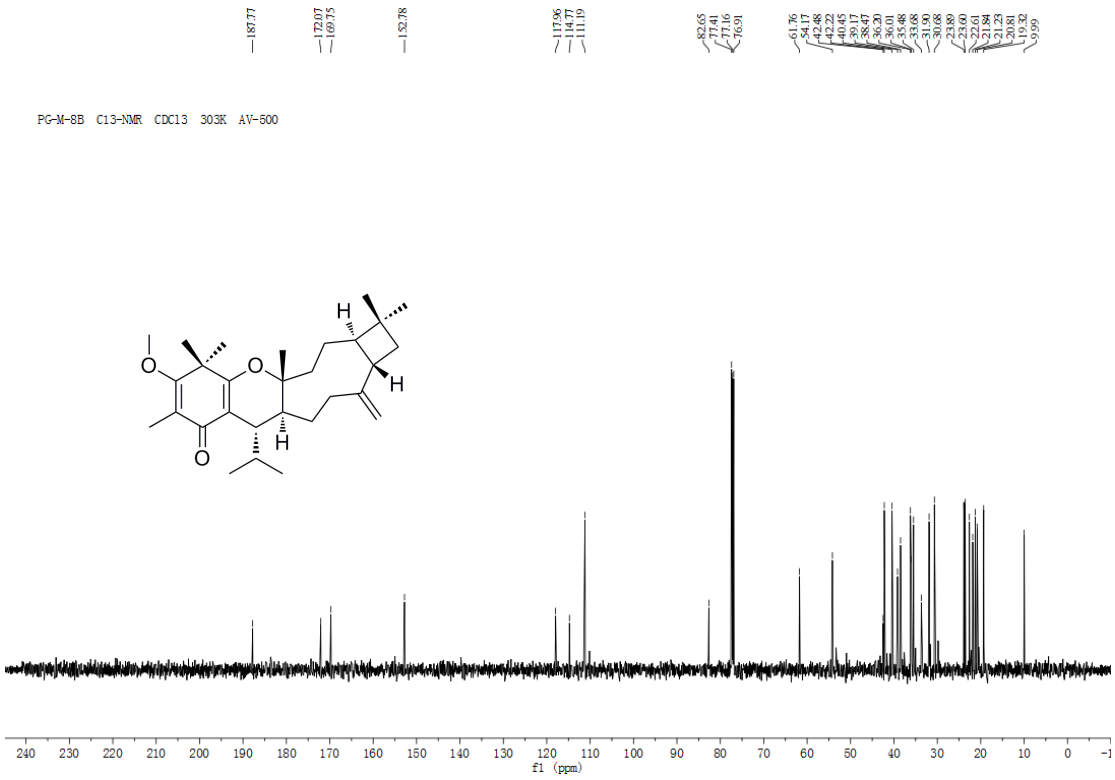


Figure S55. ^{13}C NMR spectrum of **5** (synthetic) in $CDCl_3$ (125 MHz)

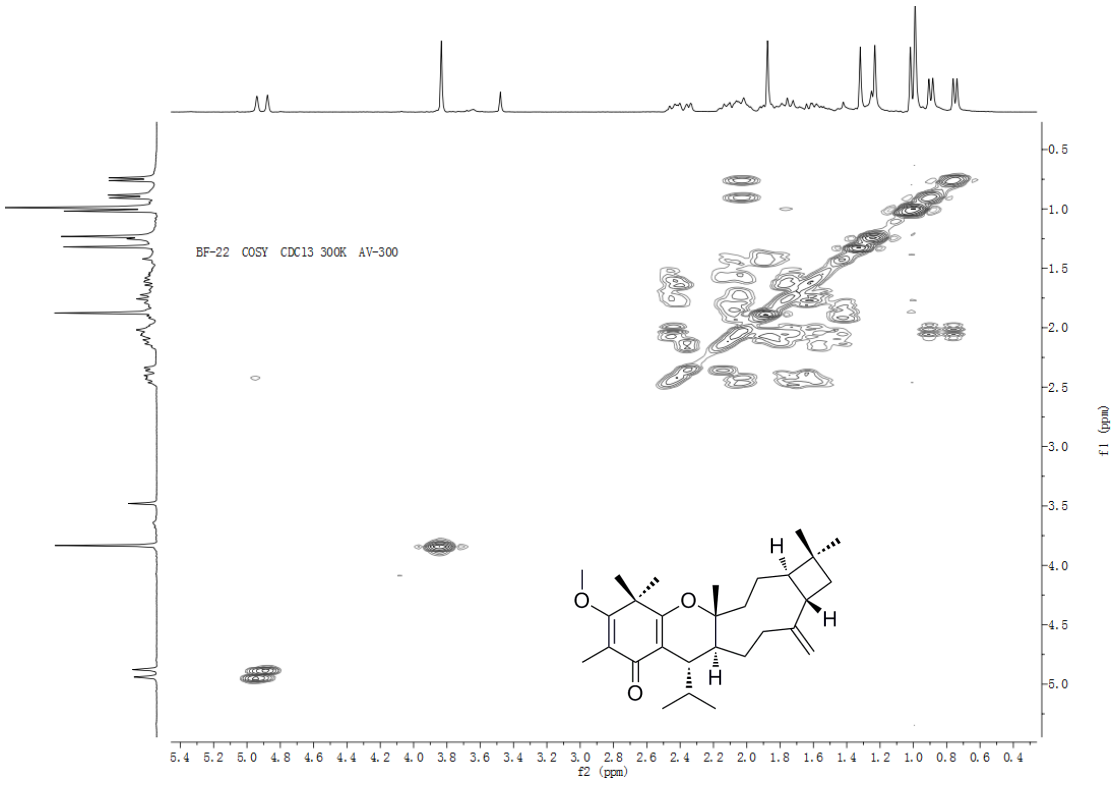


Figure S56. ^{1}H-^{1}H COSY spectrum of **5** in $CDCl_3$ (300 MHz)

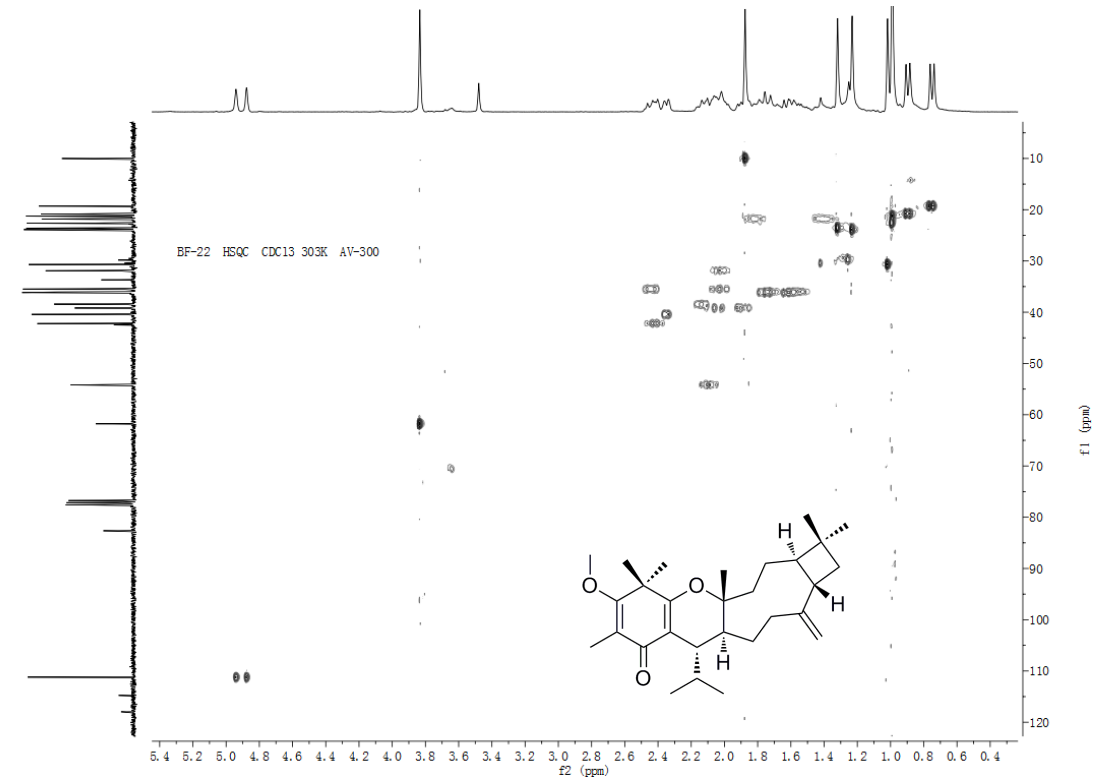


Figure S57. HSQC spectrum of **5** in $CDCl_3$ (300 MHz)

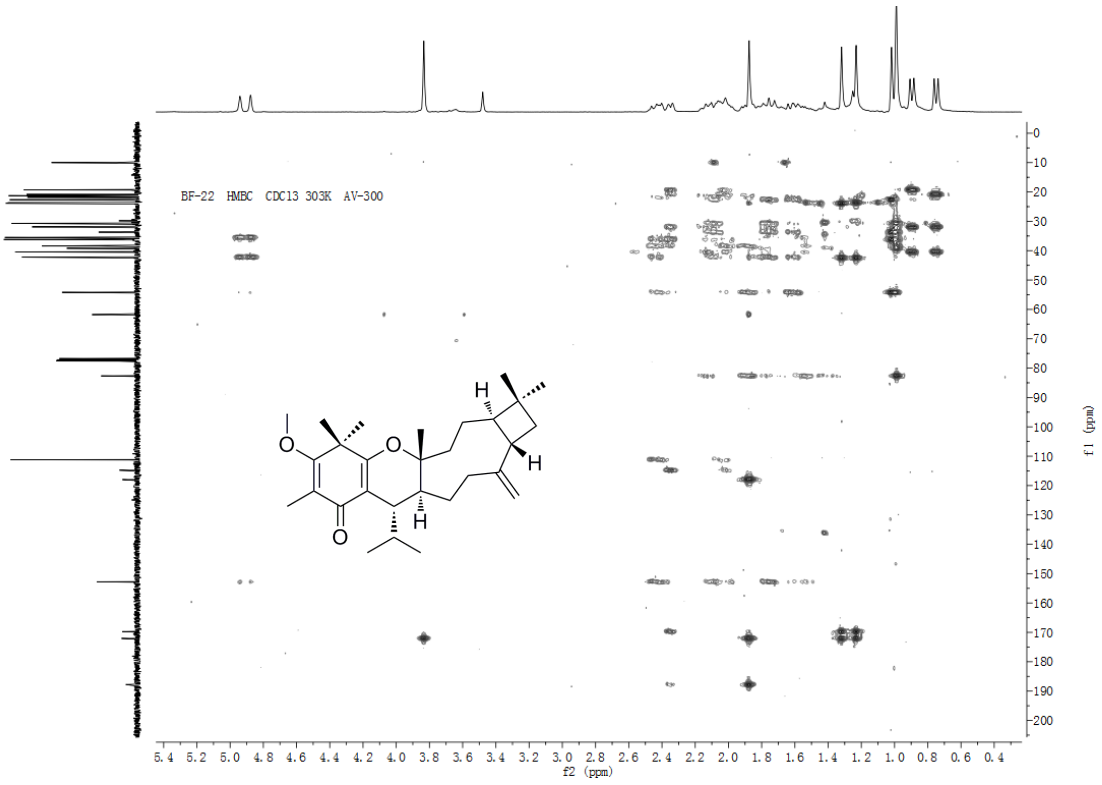


Figure S58. HMBC spectrum of **5** in $CDCl_3$ (300 MHz)

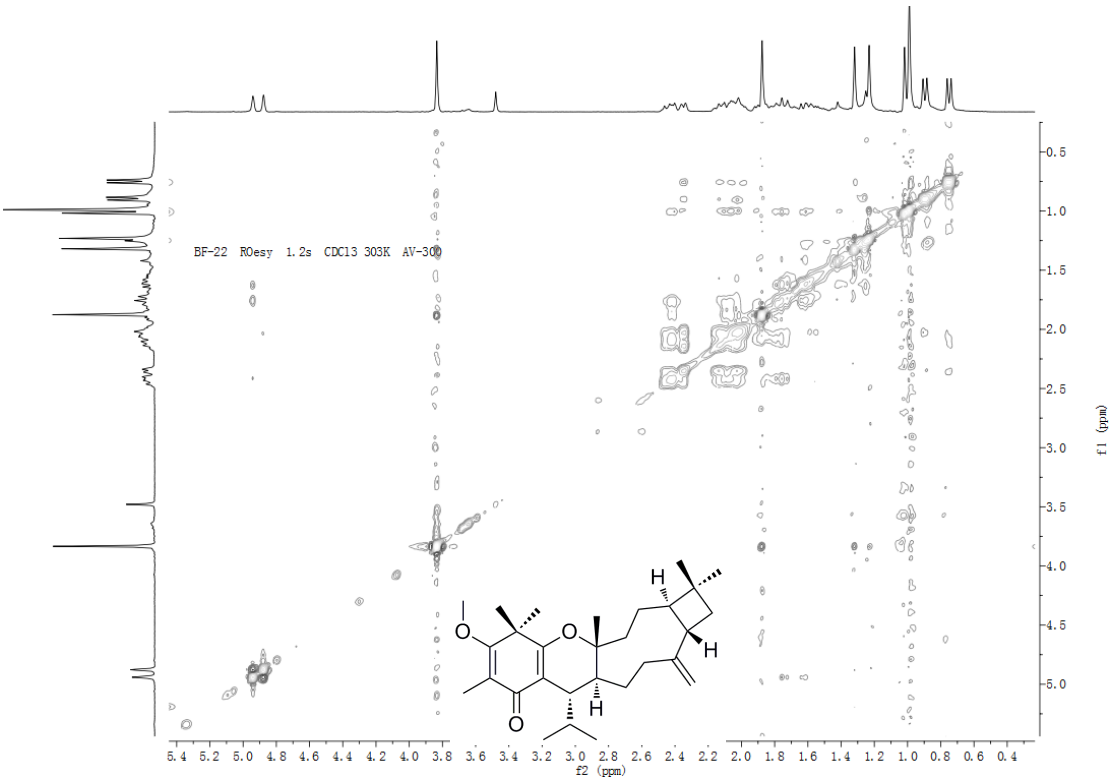


Figure S59. ROESY spectrum of **5** in $CDCl_3$ (300 MHz)

m/z	Ion	Formula	Abundance
441.3363	(M+H)+	C29 H45 O3	1249737.6

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross Score	Mass	Calc Mass	Diff (ppm)
☑	C29 H44 O3	C29 H45 O3	441.3363	98.06		440.329	440.329	0

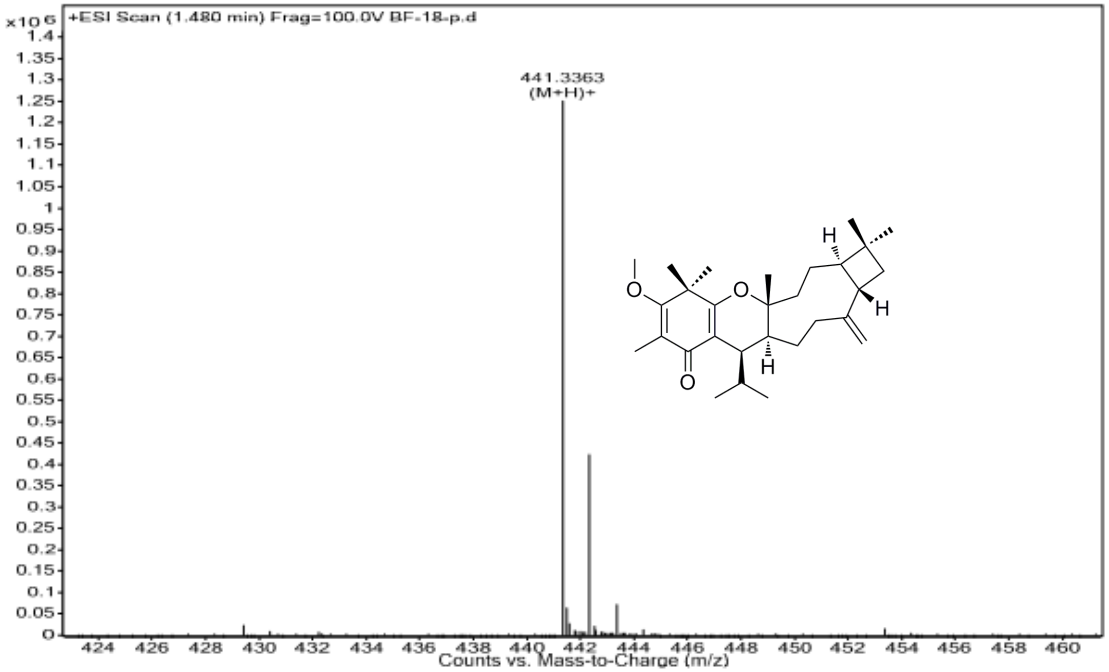
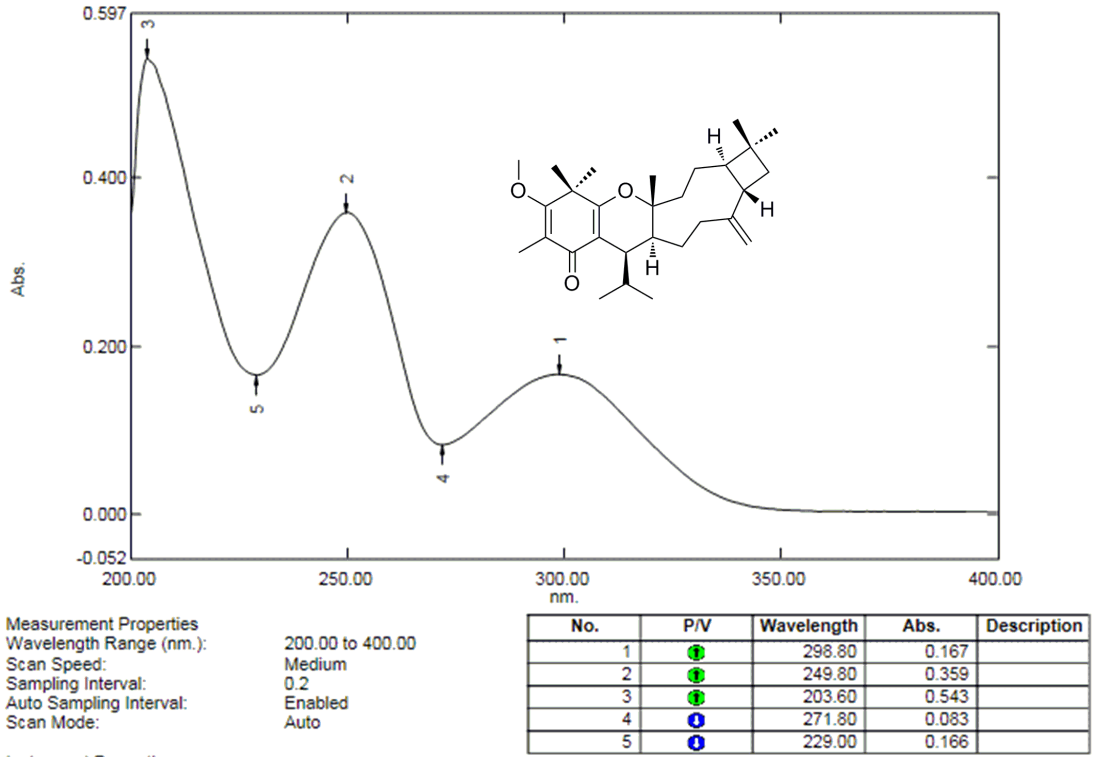


Figure S60. HR-ESI-MS spectrum of **6**



Measurement Properties

Wavelength Range (nm.):	200.00 to 400.00
Scan Speed:	Medium
Sampling Interval:	0.2
Auto Sampling Interval:	Enabled
Scan Mode:	Auto

No.	P/V	Wavelength	Abs.	Description
1	P	298.80	0.167	
2	P	249.80	0.359	
3	P	203.60	0.543	
4	V	271.80	0.083	
5	V	229.00	0.166	

Figure S61. UV spectrum of **6** in MeOH

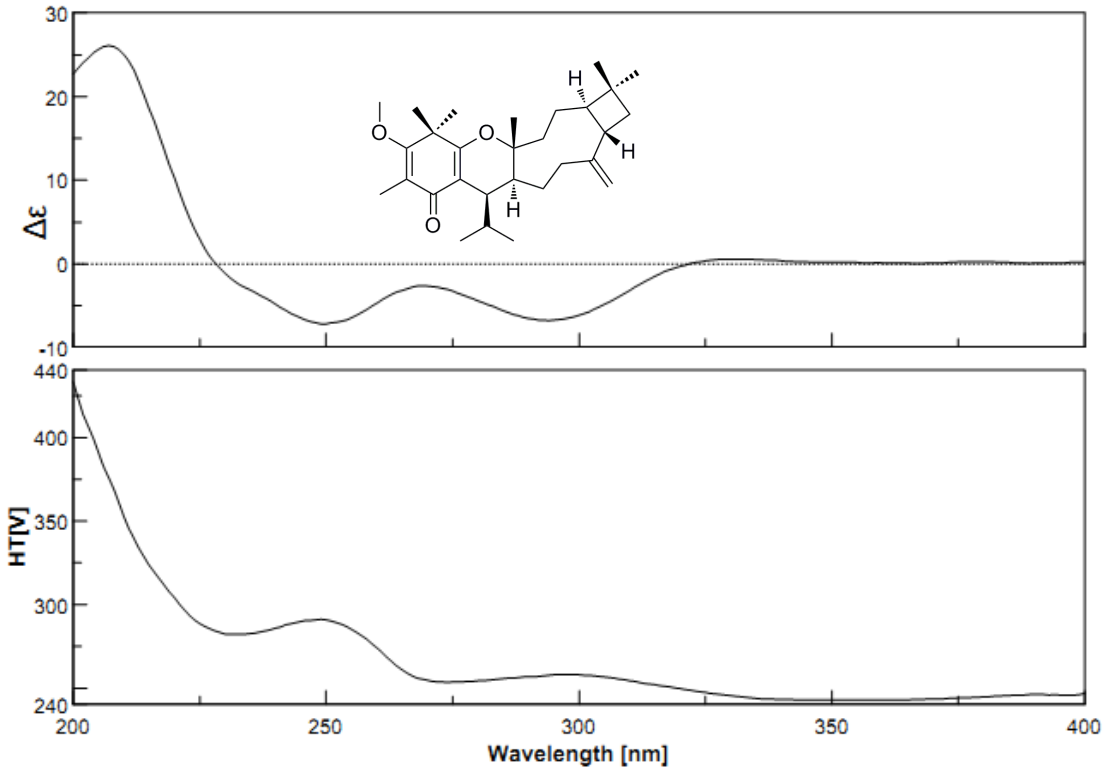


Figure S62. CD spectrum of **6** in MeOH

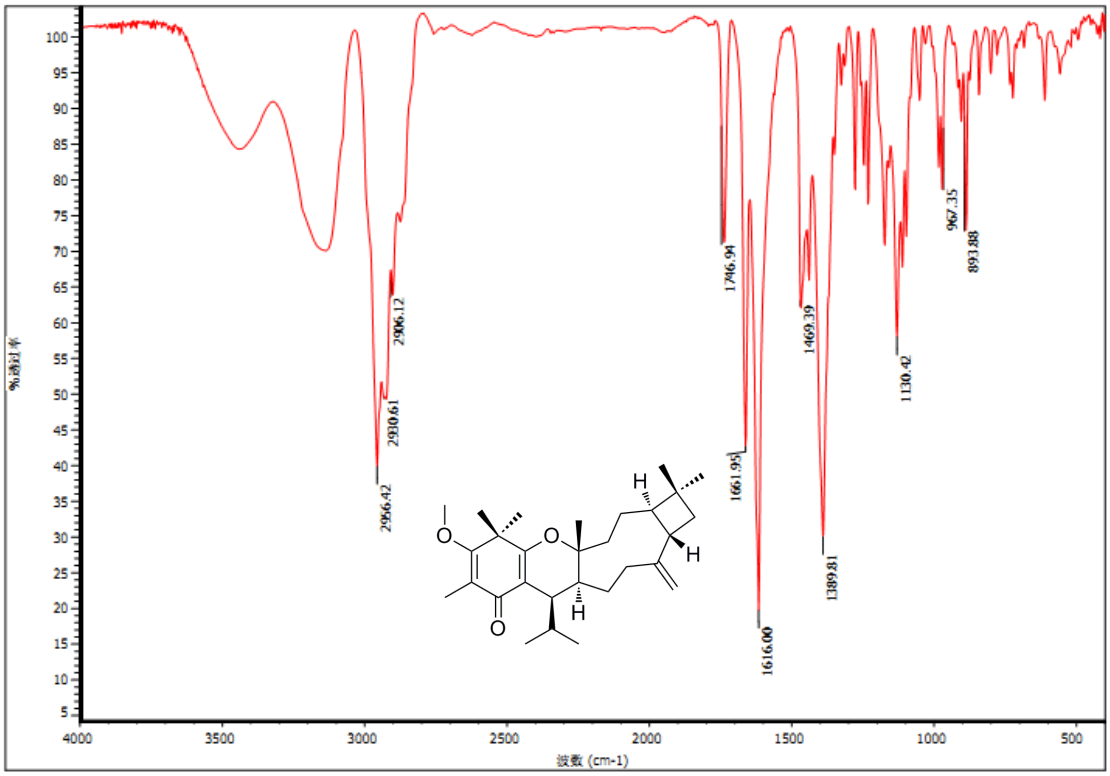


Figure S63. IR spectrum of **6**

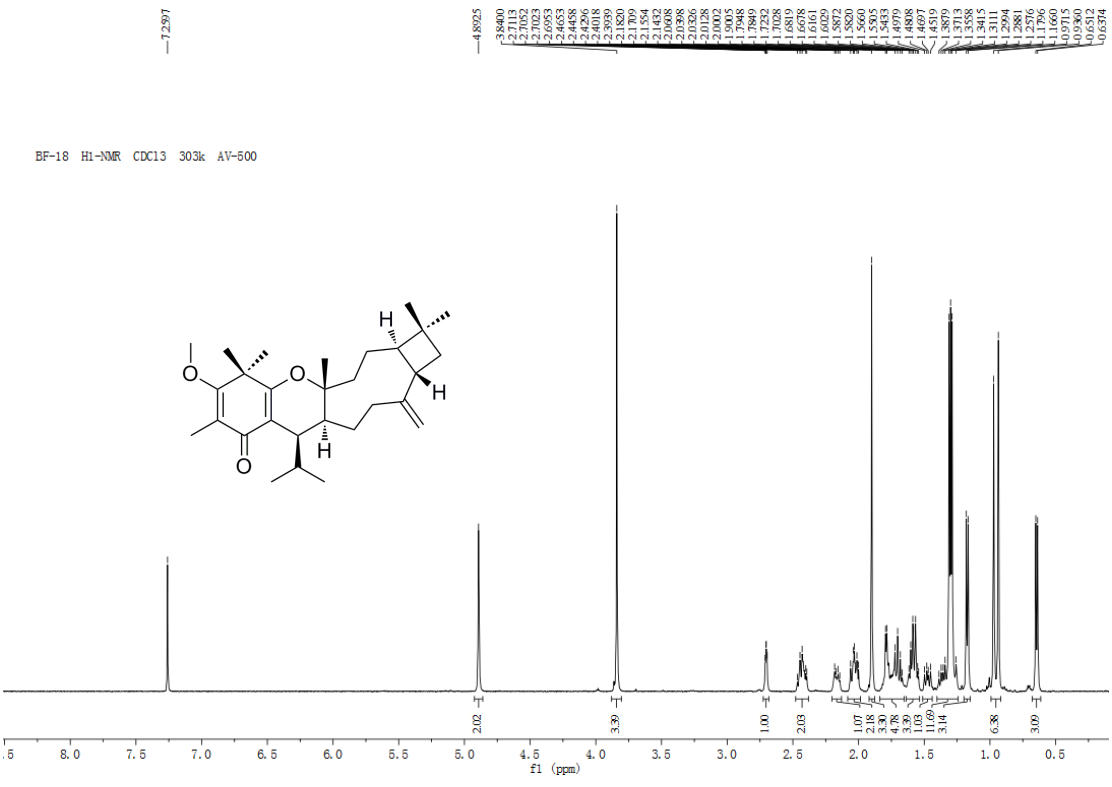


Figure S64. ^{1}H NMR spectrum of **6** in $CDCl_3$ (500 MHz)

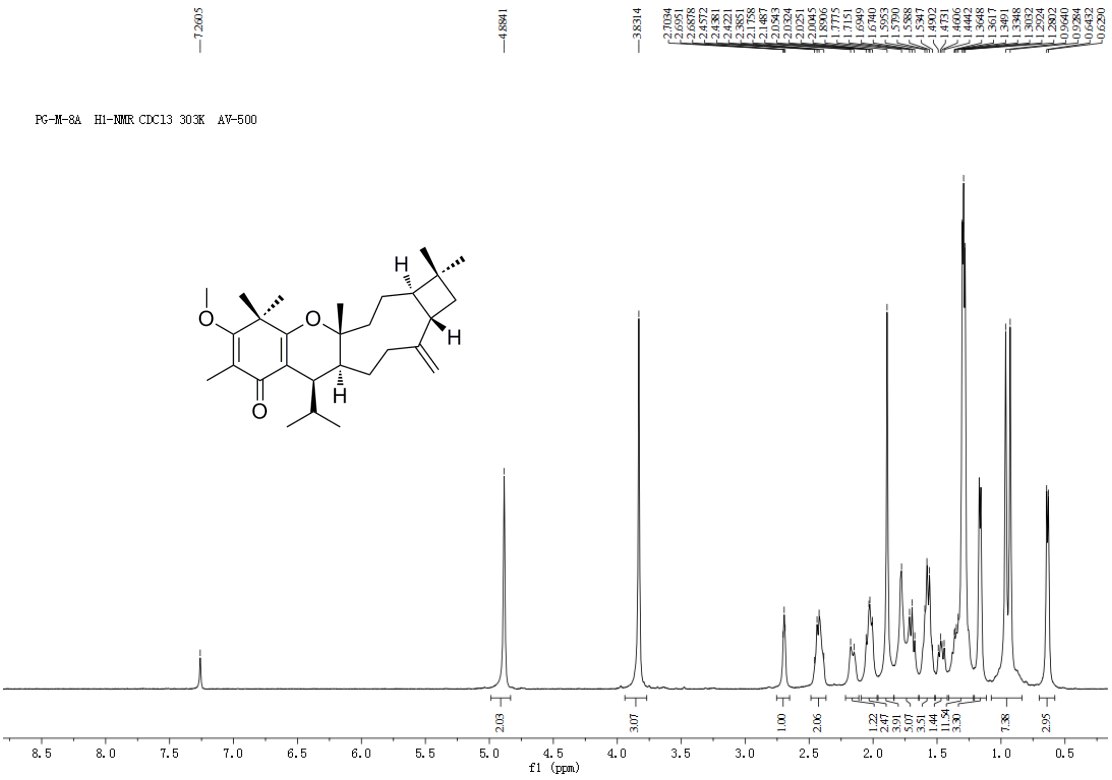


Figure S65. ^{1}H NMR spectrum of **6** (synthetic) in $CDCl_3$ (500 MHz)

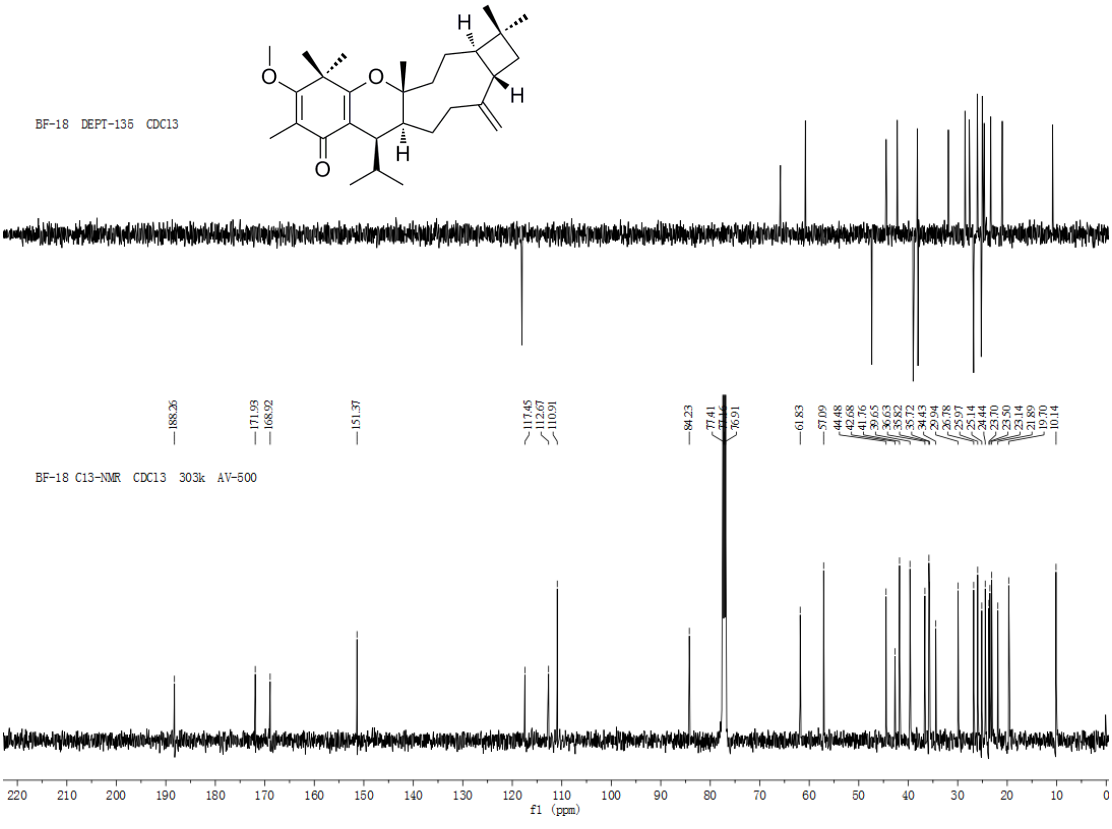


Figure S66. ^{13}C NMR spectrum of **6** in $CDCl_3$ (125 MHz)

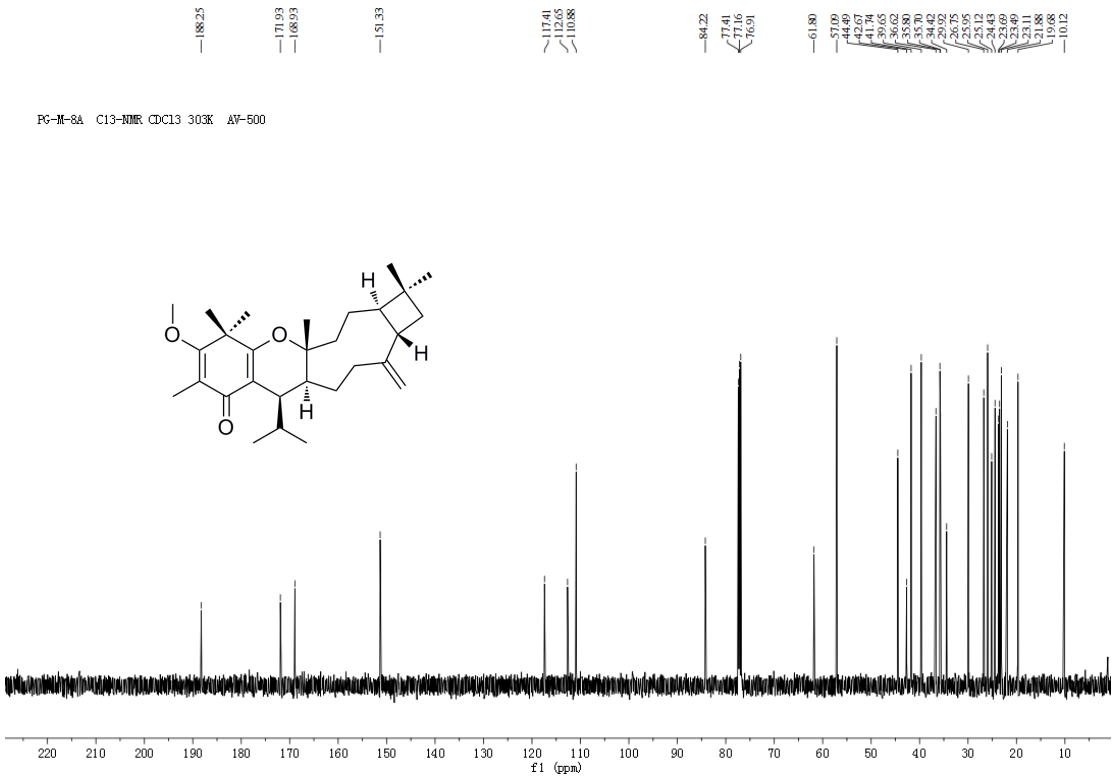


Figure S67. ^{13}C NMR spectrum of **6** (synthetic) in $CDCl_3$ (125 MHz)

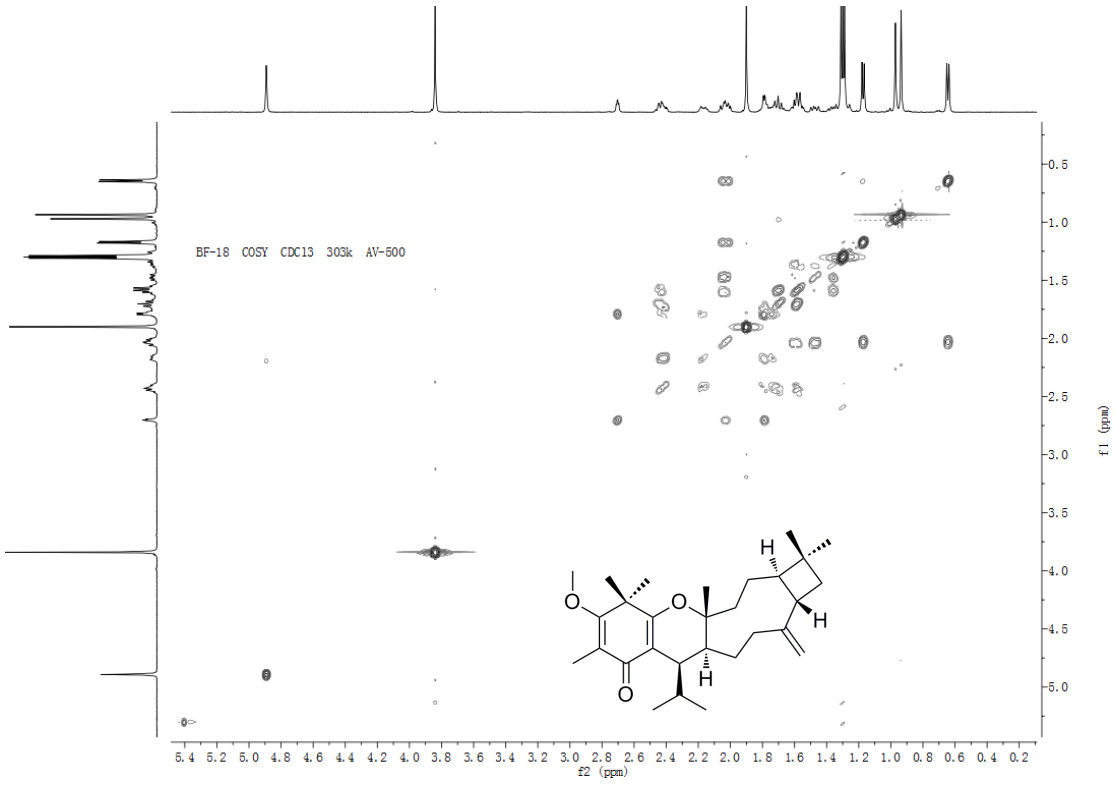


Figure S68. ^{1}H-^{1}H COSY spectrum of **6** in $CDCl_3$ (500 MHz)

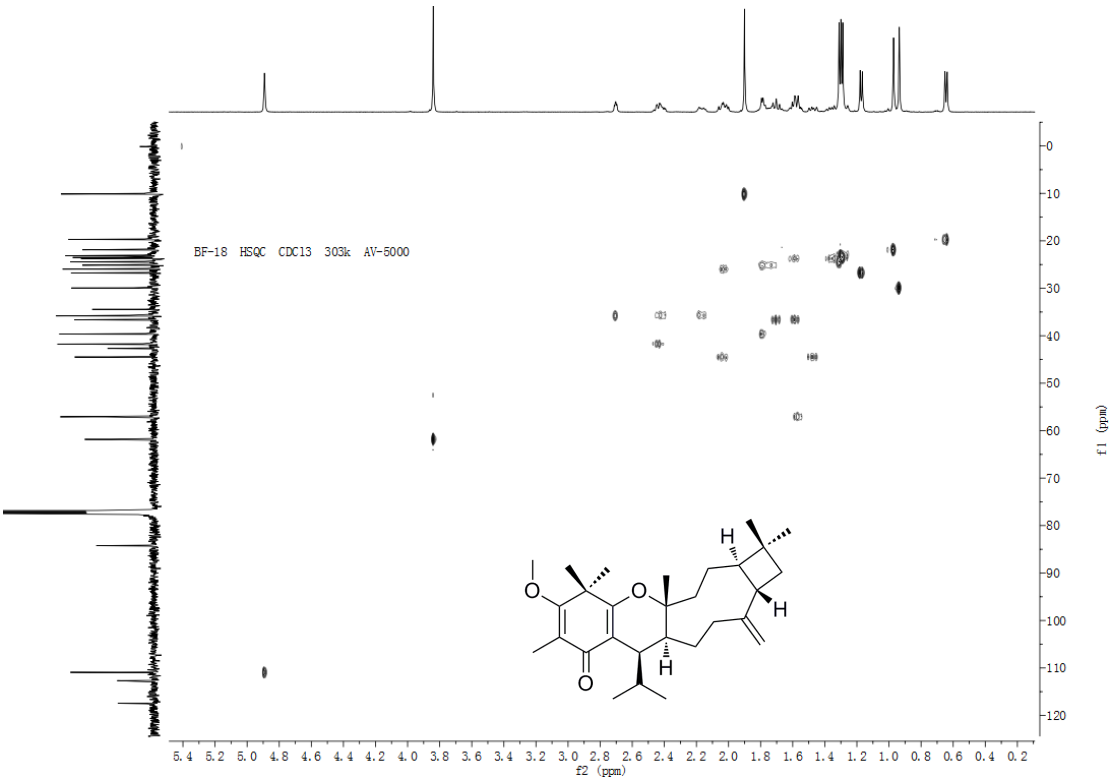


Figure S69. HSQC spectrum of **6** in $CDCl_3$ (500 MHz)

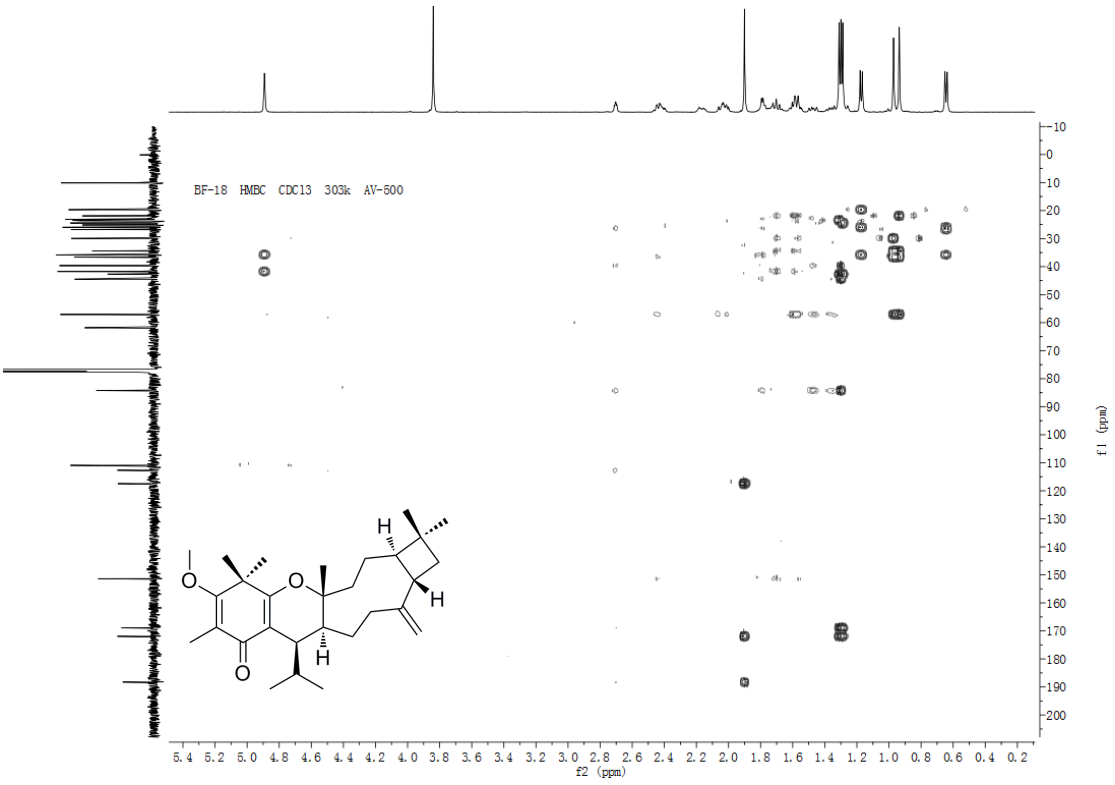


Figure S70. HMBC spectrum of **6** in $CDCl_3$ (500 MHz)

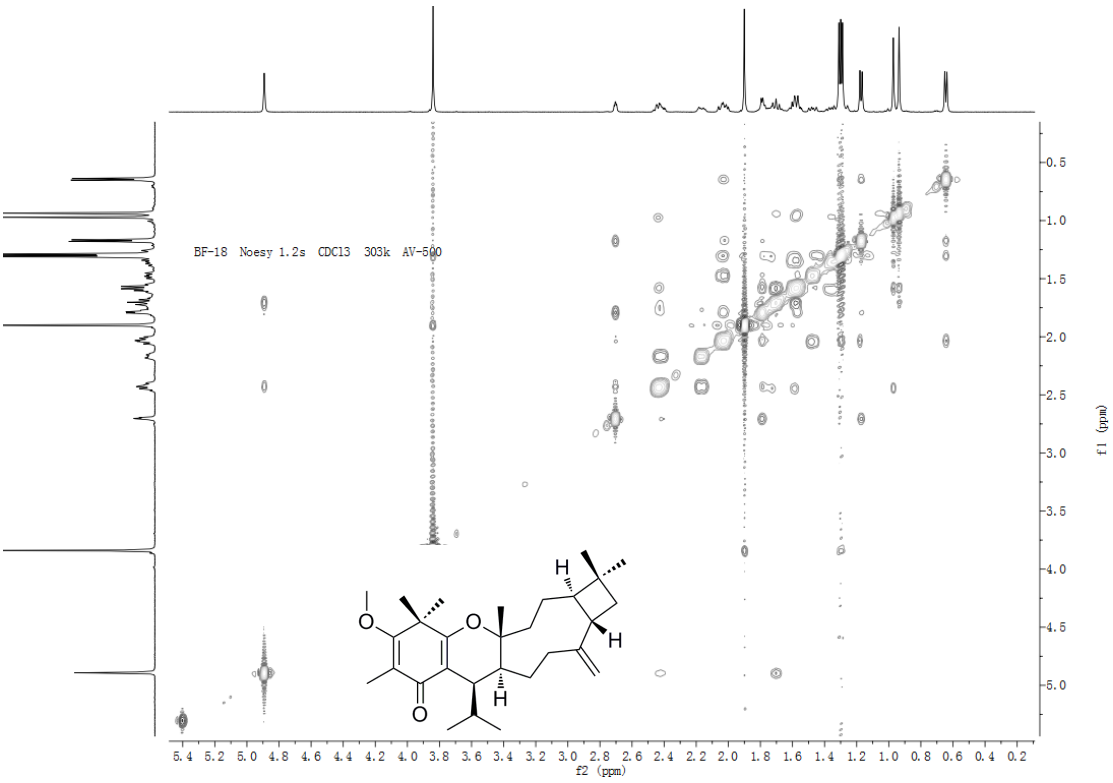


Figure S71. NOESY spectrum of **6** in $CDCl_3$ (500 MHz)

m/z	Ion	Formula	Abundance
441.3366	(M+H)+	C29 H45 O3	1192332.3

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross Score	Mass	Calc Mass	Diff (ppm)
☑	C29 H44 O3	C29 H45 O3	441.3363	99.71		440.3293	440.329	-0.53

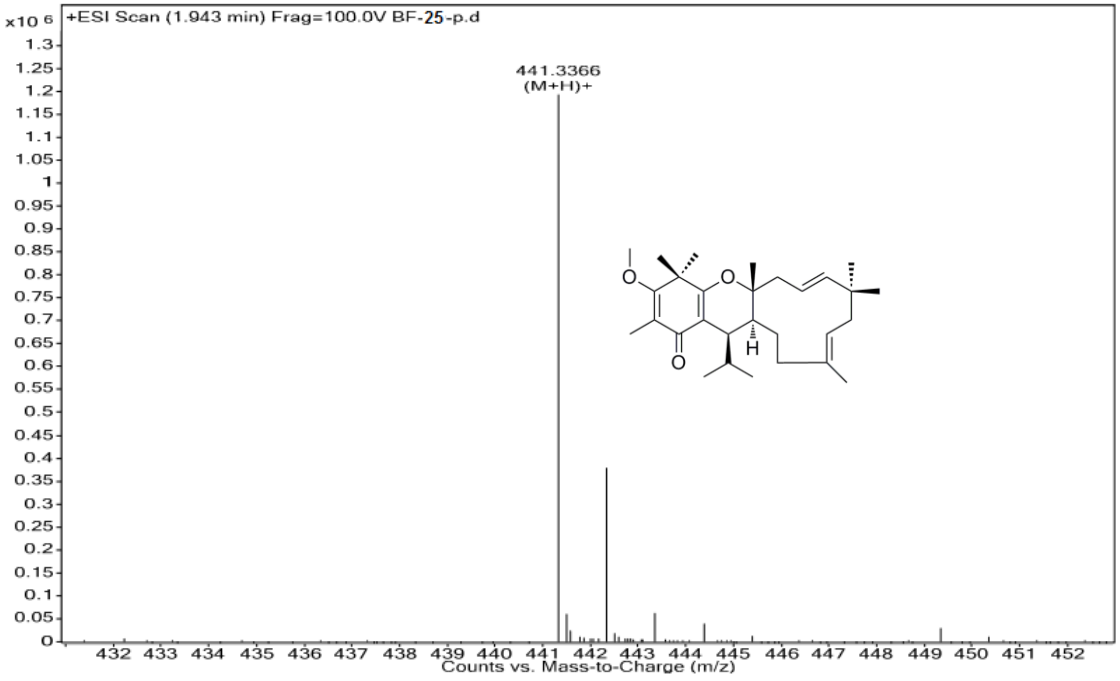
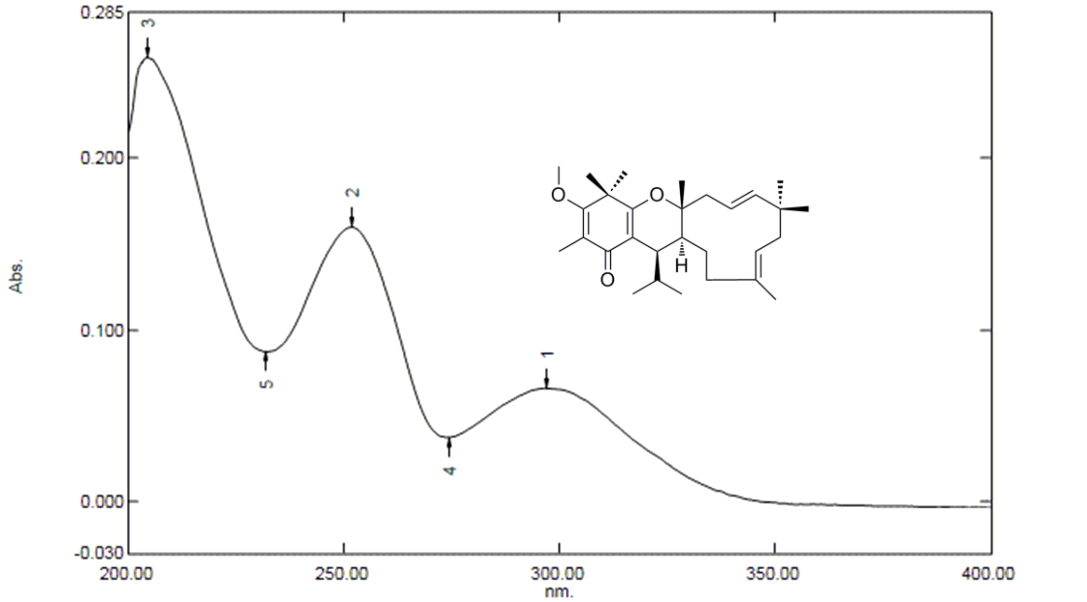


Figure S72. HR-ESI-MS spectrum of (±)-**7**



Measurement Properties

Wavelength Range (nm.):	200.00 to 400.00
Scan Speed:	Medium
Sampling Interval:	0.2
Auto Sampling Interval:	Disabled
Scan Mode:	Auto

No.	P/V	Wavelength	Abs.	Description
1	↑	297.00	0.066	
2	↑	252.00	0.160	
3	↑	204.40	0.259	
4	↓	274.40	0.037	
5	↓	231.80	0.087	

Figure S73. UV spectrum of (±)-**7** in MeOH

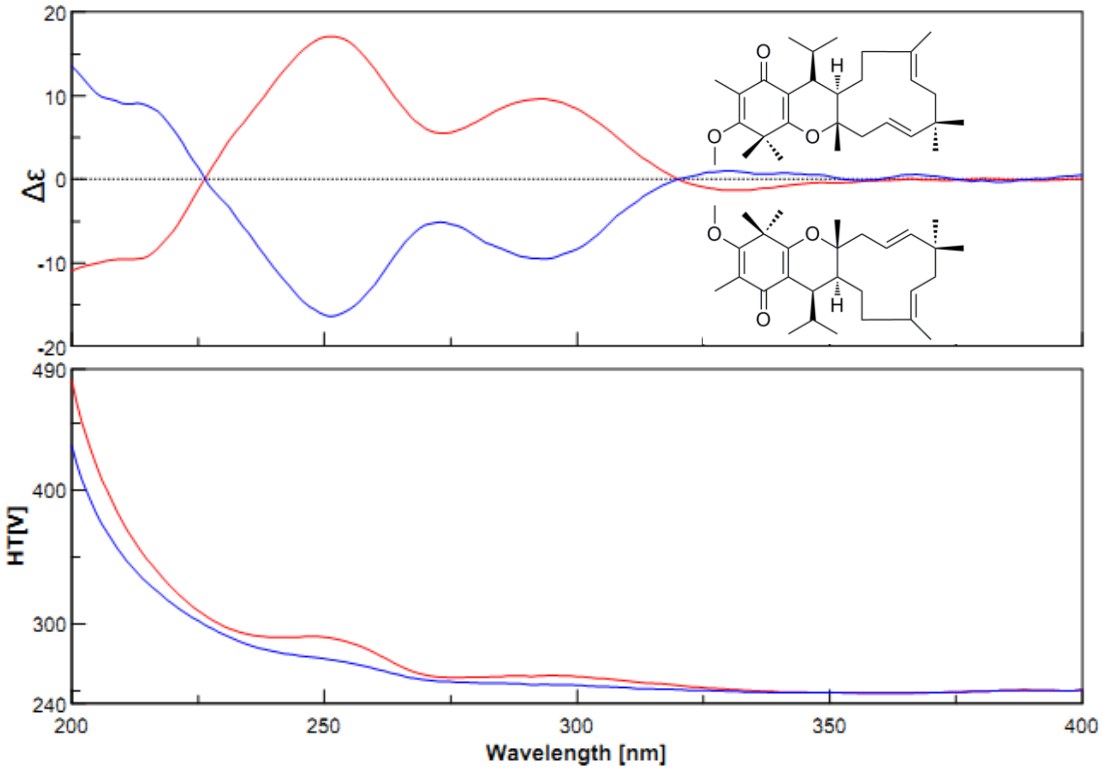


Figure S74. CD spectrum of (+)-**7** and (–)-**7** in MeOH

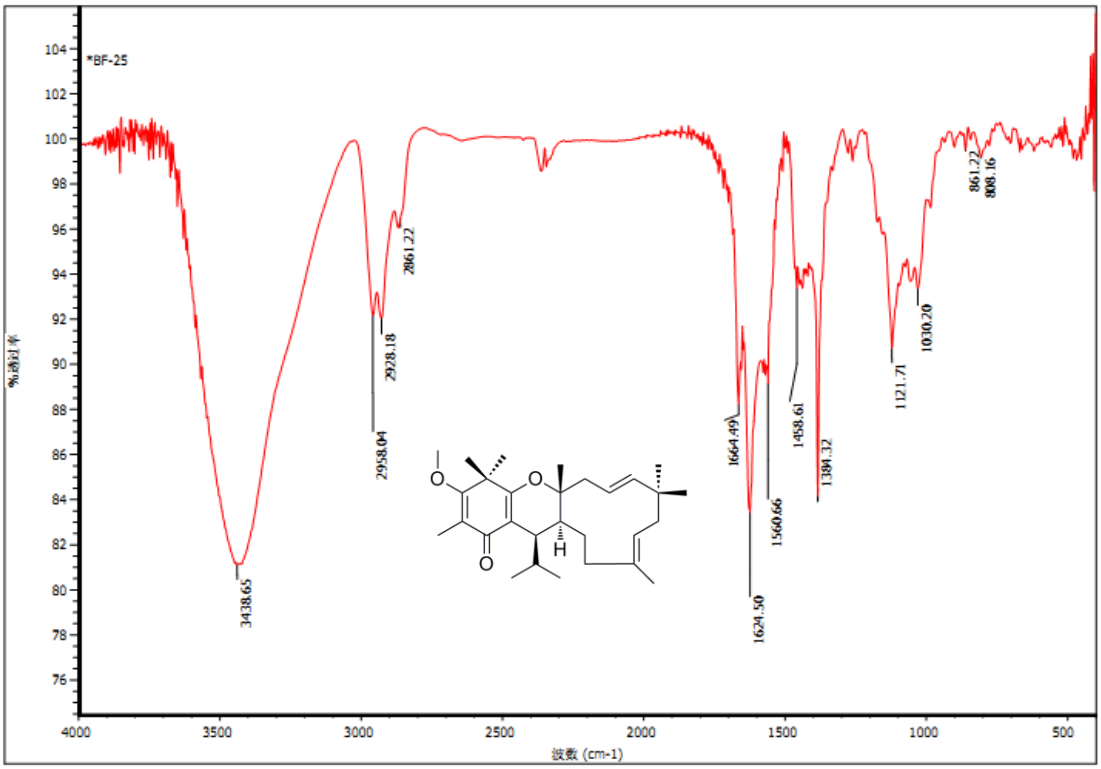


Figure S75. IR spectrum of (±)-**7**

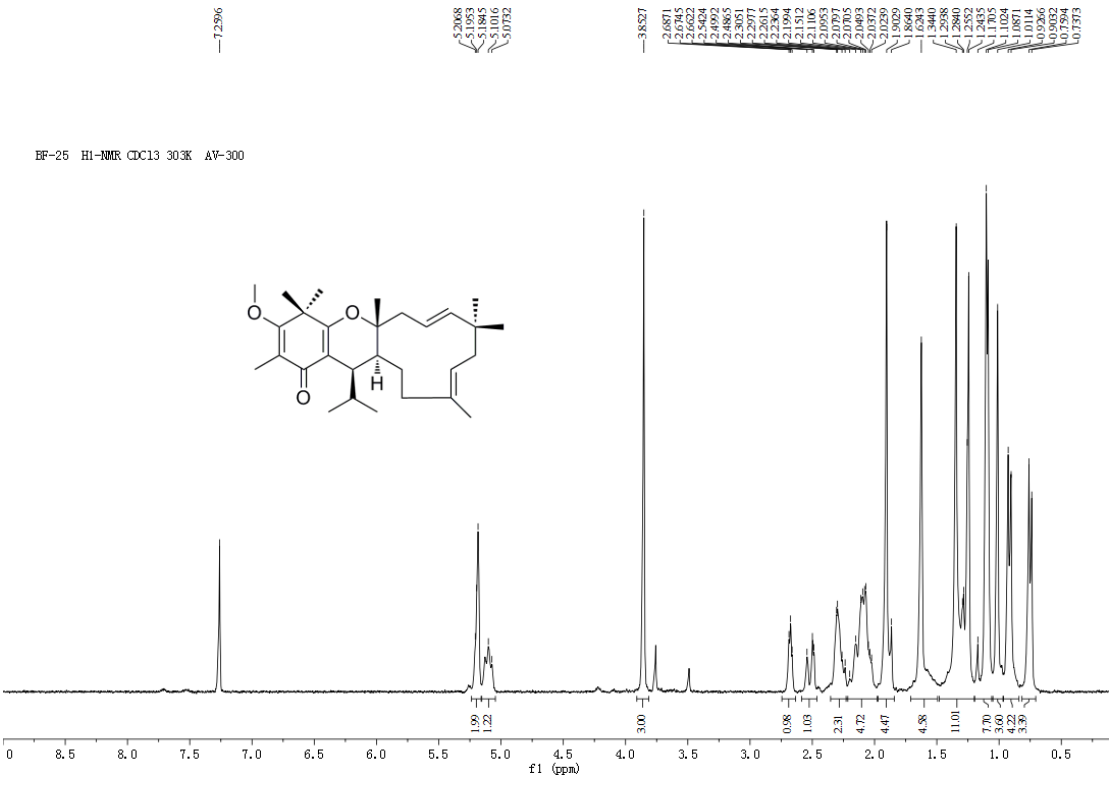


Figure S76. ^{1}H NMR spectrum of (±)-**7** in $CDCl_3$ (300 MHz)

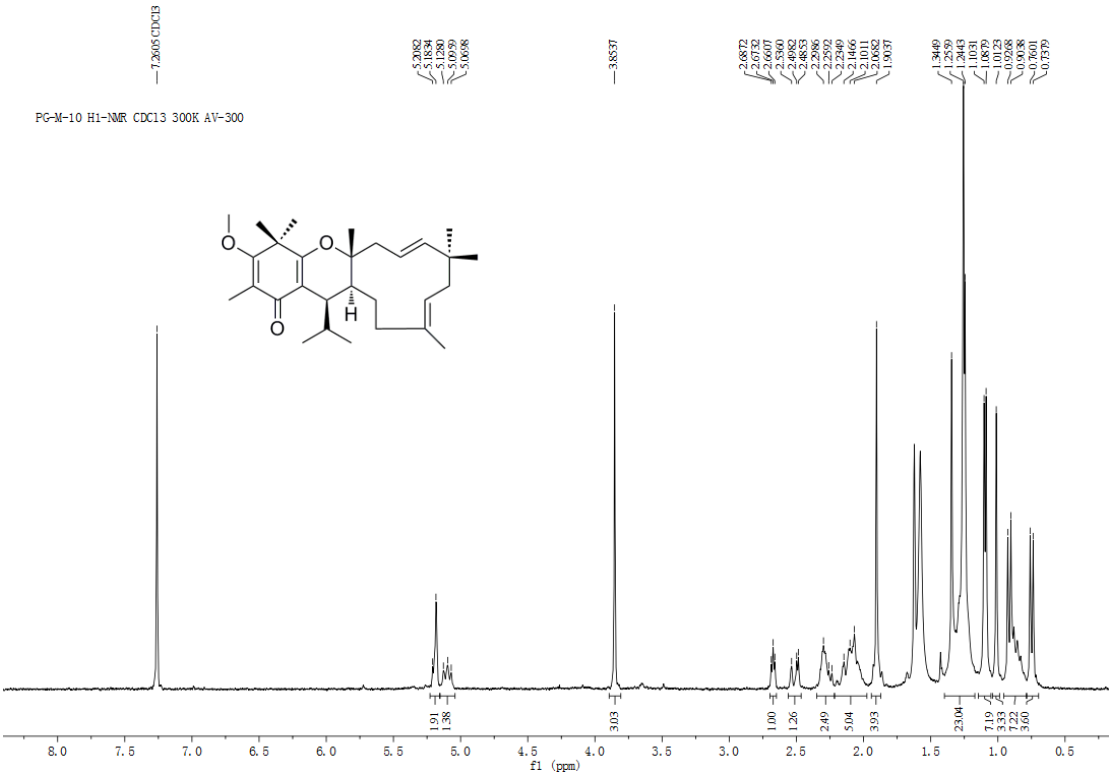


Figure S77. ^{1}H NMR spectrum of (±)-**7** (synthetic) in $CDCl_3$ (300 MHz)

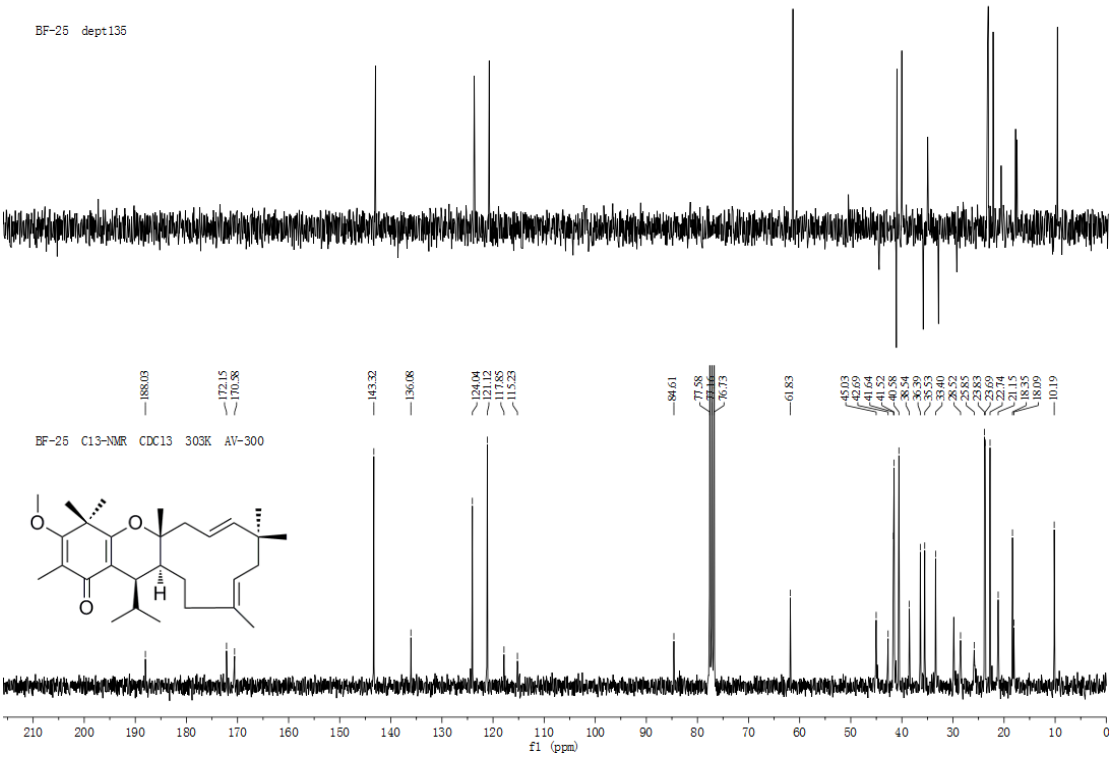


Figure S78. ^{13}C NMR spectrum of (±)-**7** in $CDCl_3$ (75 MHz)

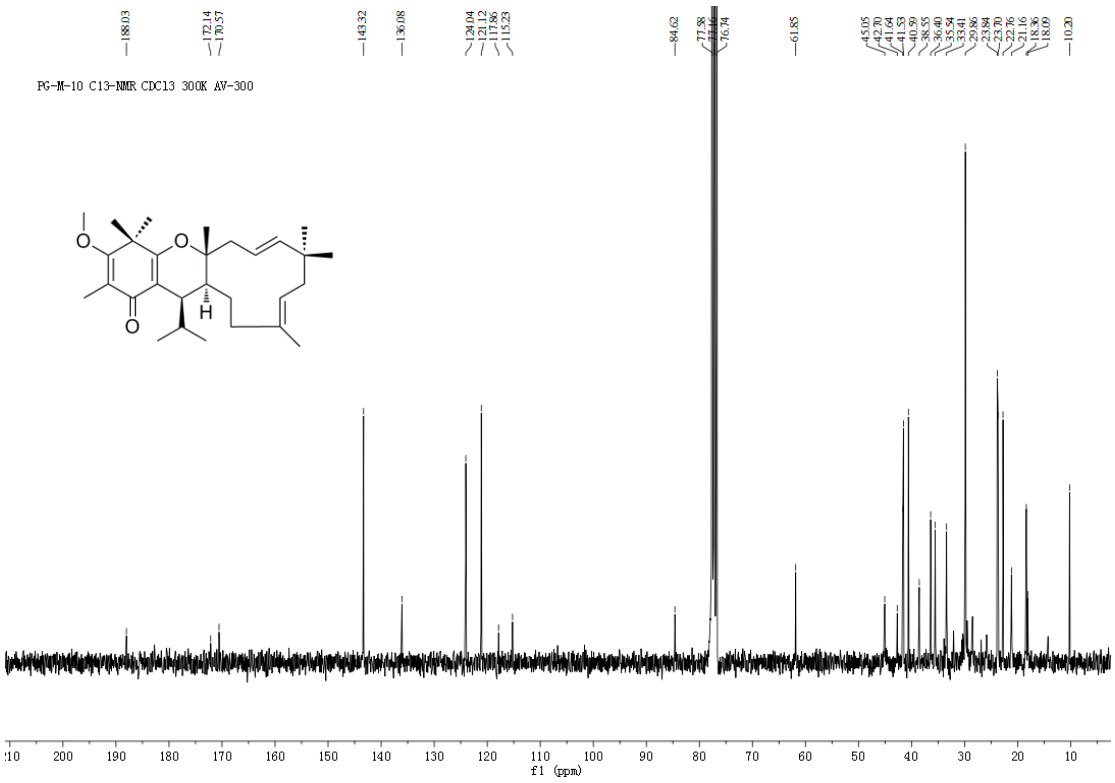


Figure S79. ^{13}C NMR spectrum of (±)-**7** (synthetic) in $CDCl_3$ (75 MHz)

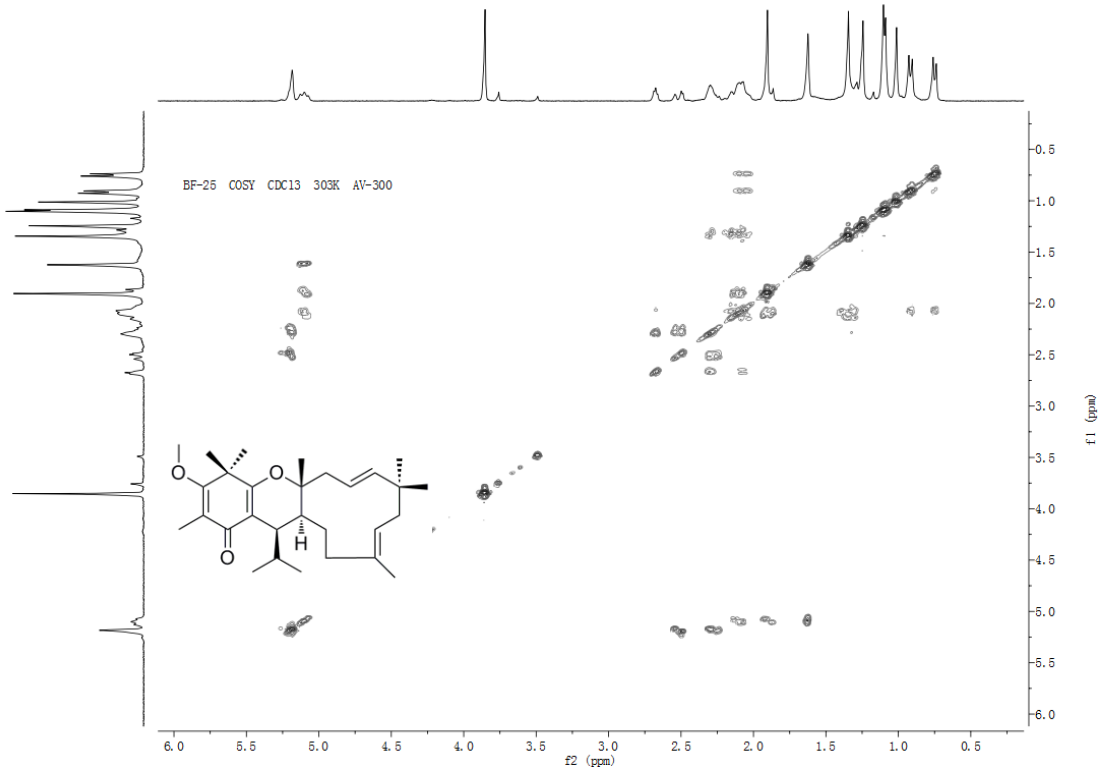


Figure S80. ^{1}H-^{1}H COSY spectrum of (±)-**7** in $CDCl_3$ (300 MHz)

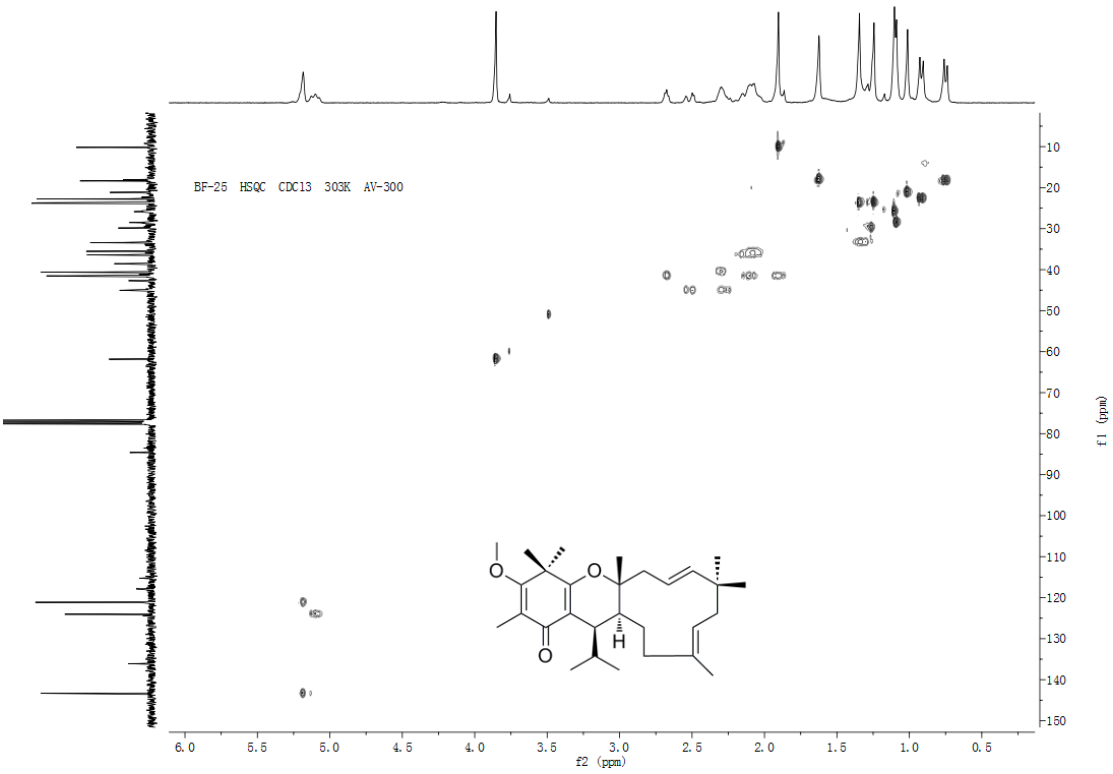


Figure S81. HSQC spectrum of (±)-**7** in $CDCl_3$ (300 MHz)

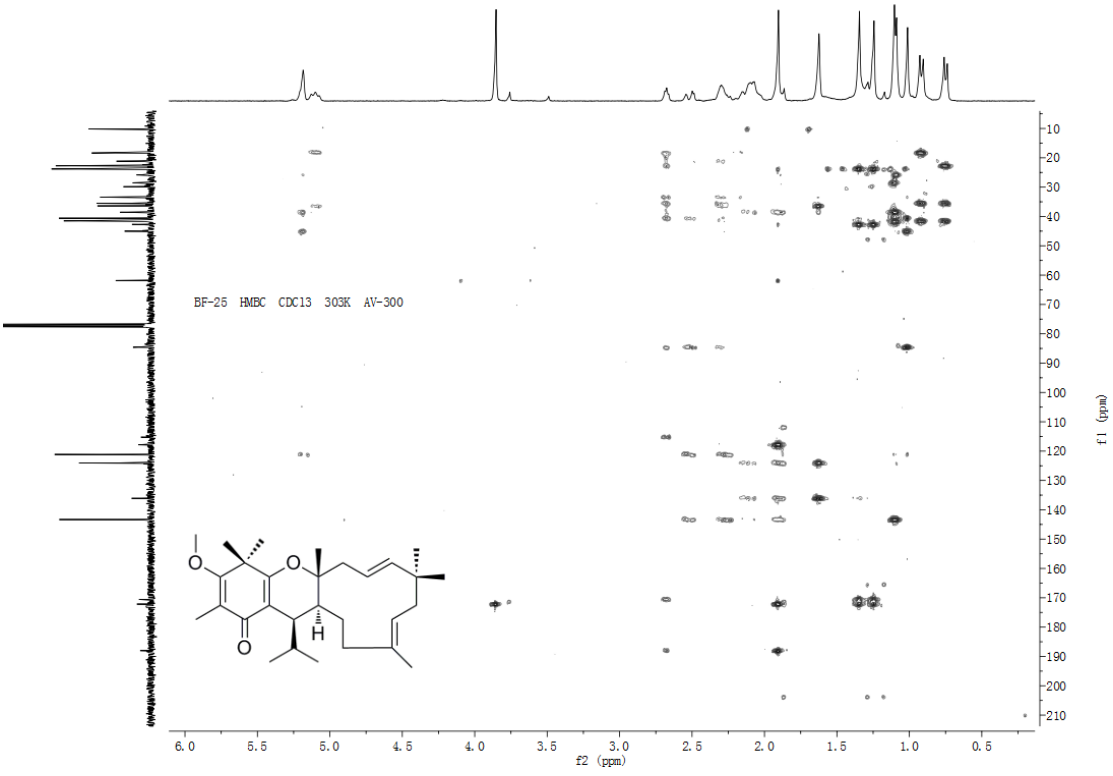


Figure S82. HMBC spectrum of (±)-**7** in $CDCl_3$ (300 MHz)

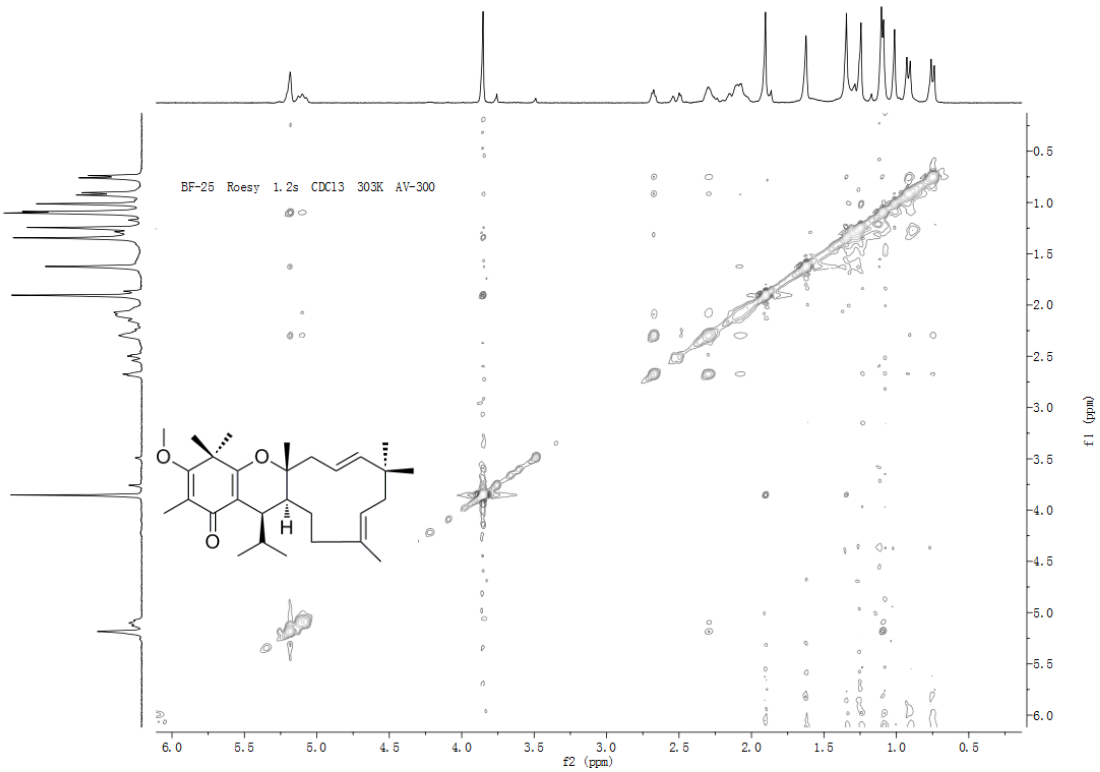


Figure S83. ROESY spectrum of (±)-**7** in $CDCl_3$ (300 MHz)

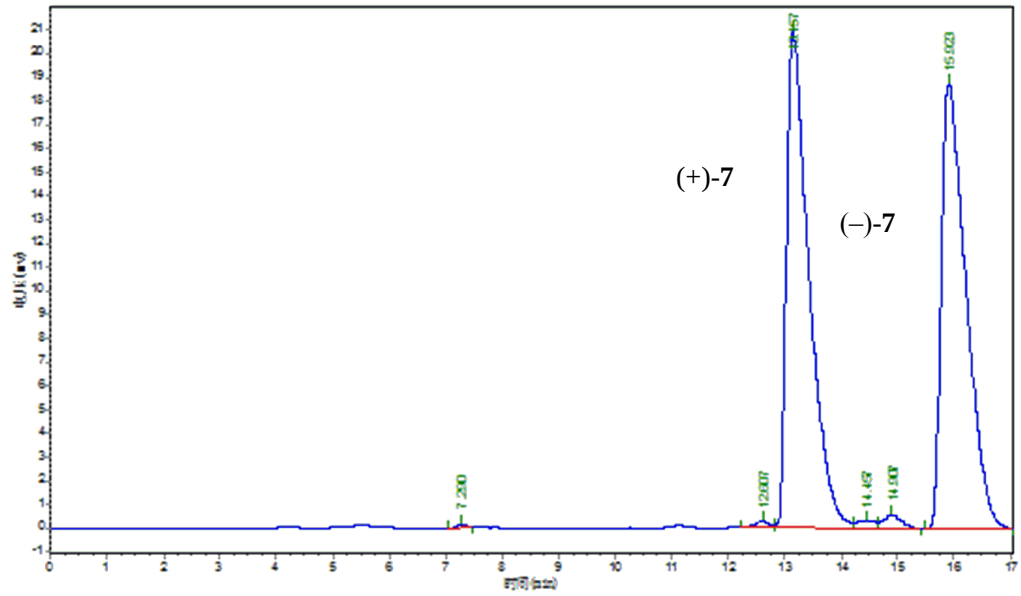


Figure 84. Chiral HPLC chromatogram of (±)-**7**

[Chiral HPLC separation of (±)-**7** was carried out on a Daicel Chiralcel OD-RH (250 × 10 mm, 5 μm), using MeCN-H_2O (85:15, v/v) as mobile phase at a flow rate of 4 mL/min at room temperature with UV detection at 254 nm.]

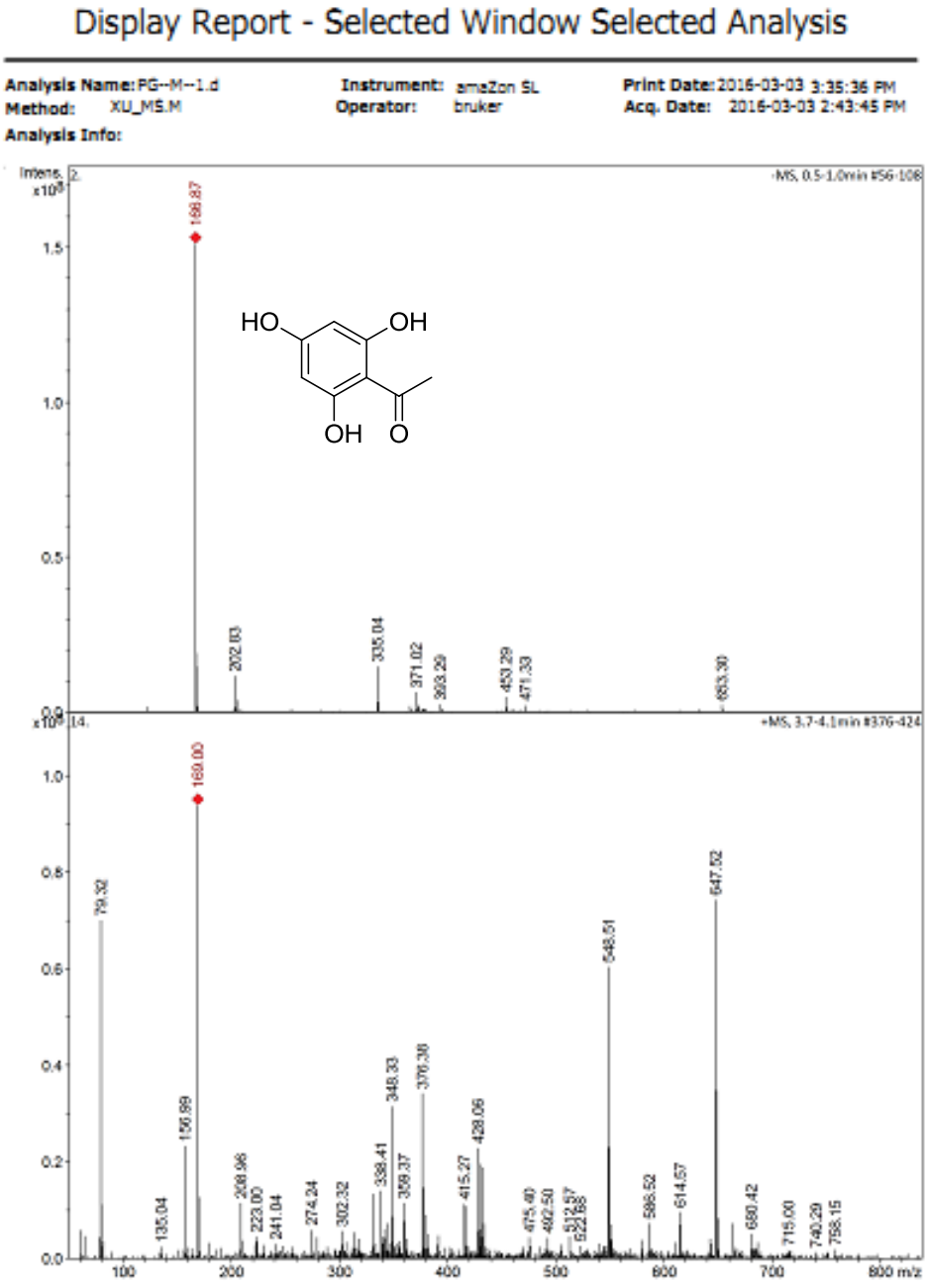


Figure S85. ESI-MS spectrum of **12**

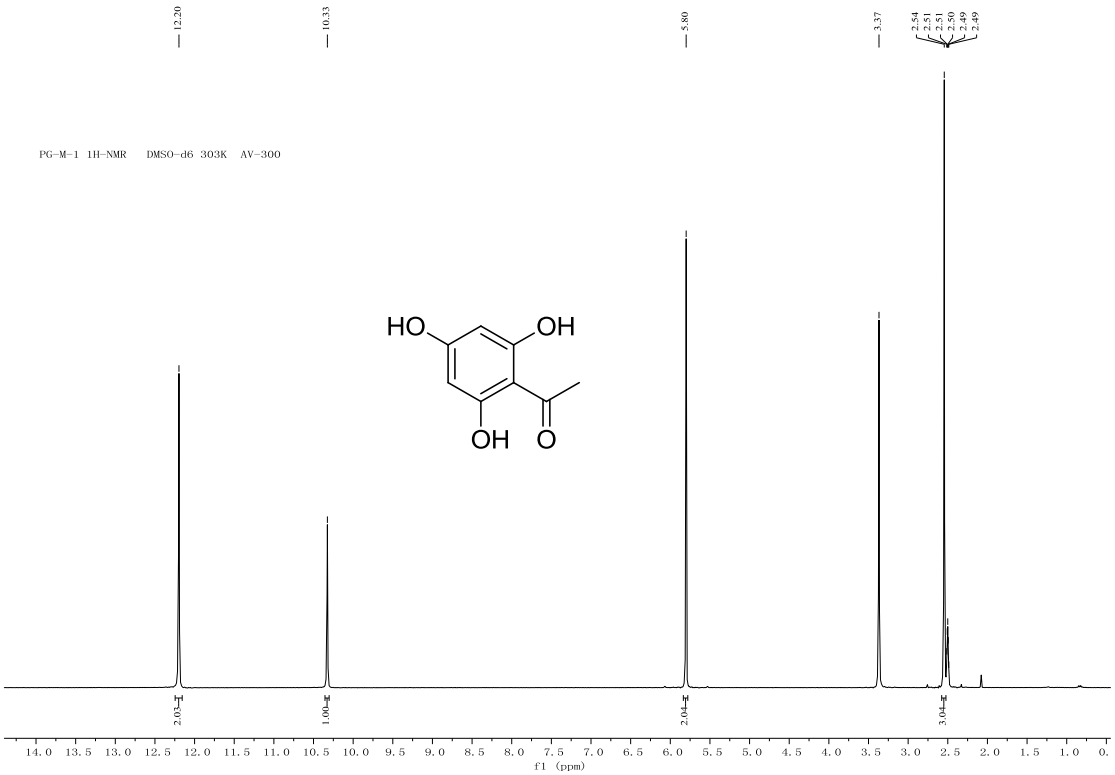


Figure S86. ^{1}H NMR spectrum of **12** in $CDCl_3$ (300 MHz)

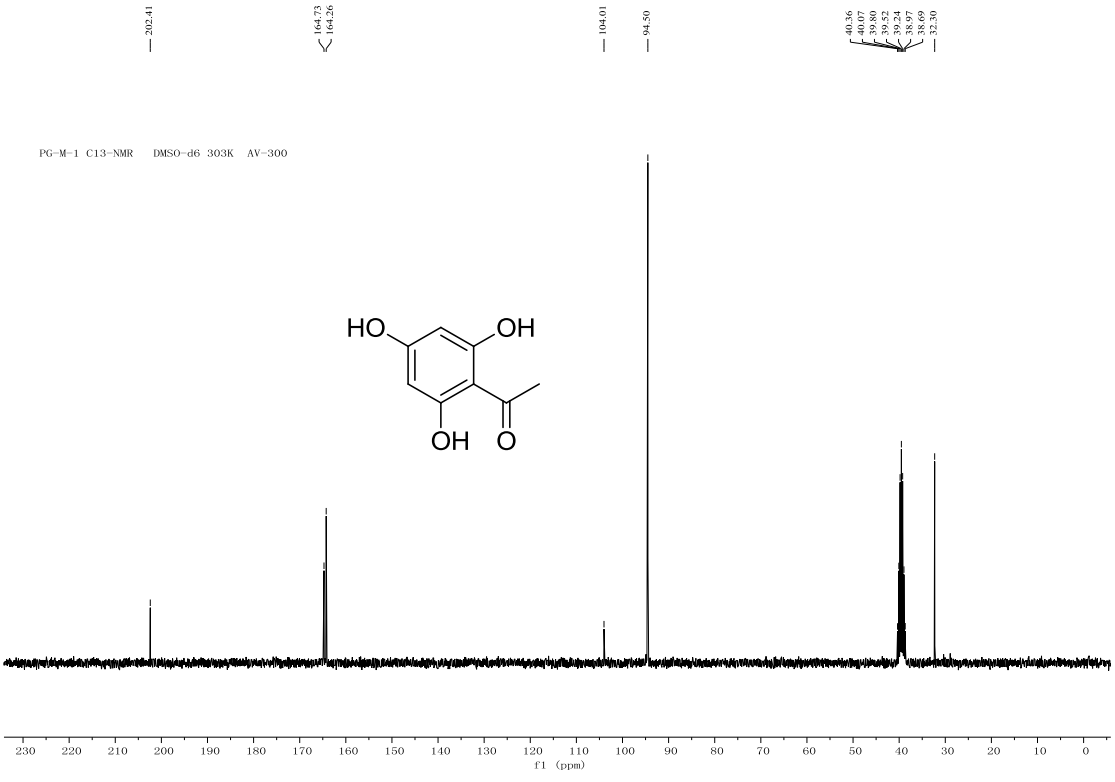


Figure S87. ^{13}C NMR spectrum of **12** in $CDCl_3$ (75 MHz)

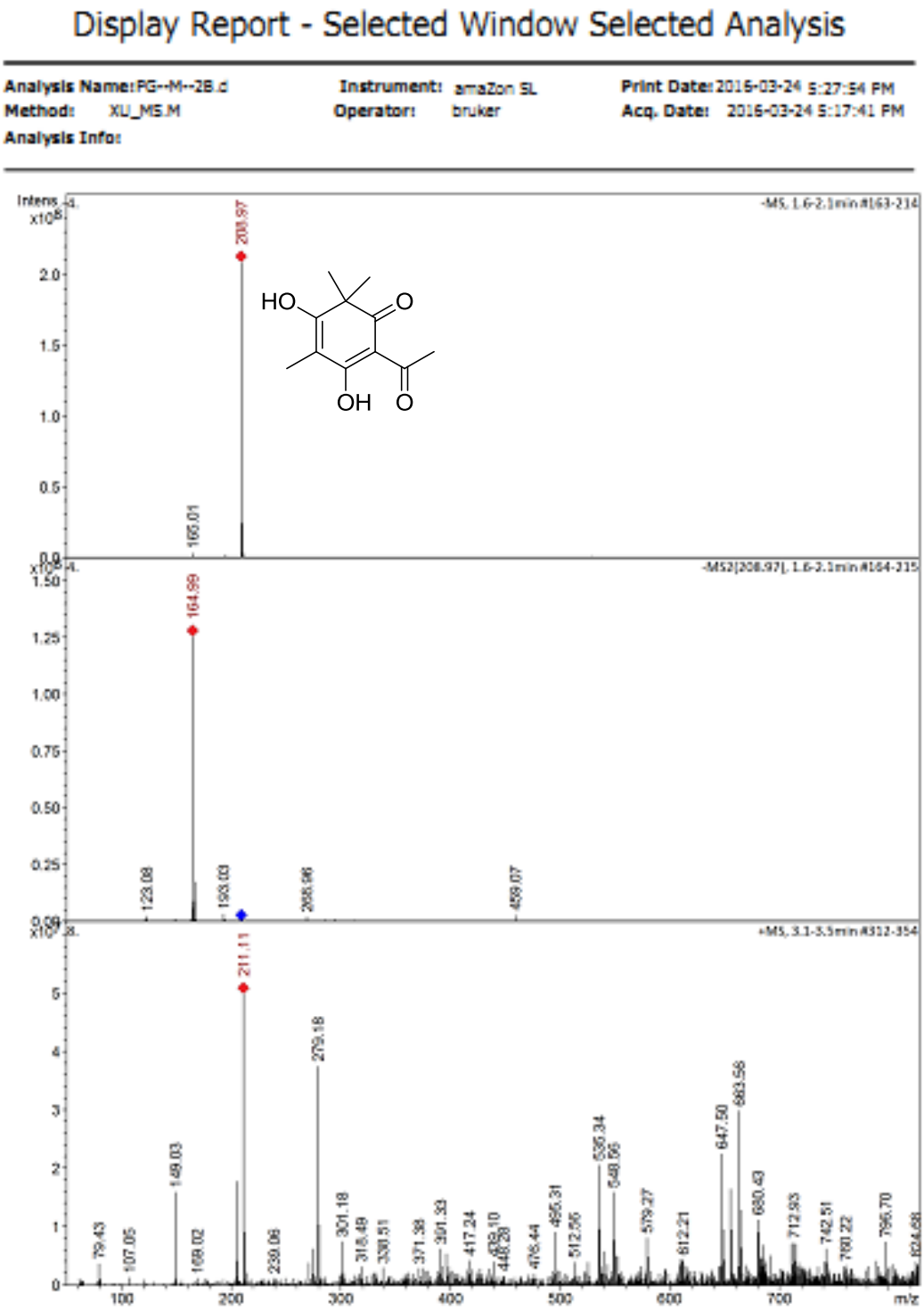


Figure S88. ESI-MS spectrum of **13**

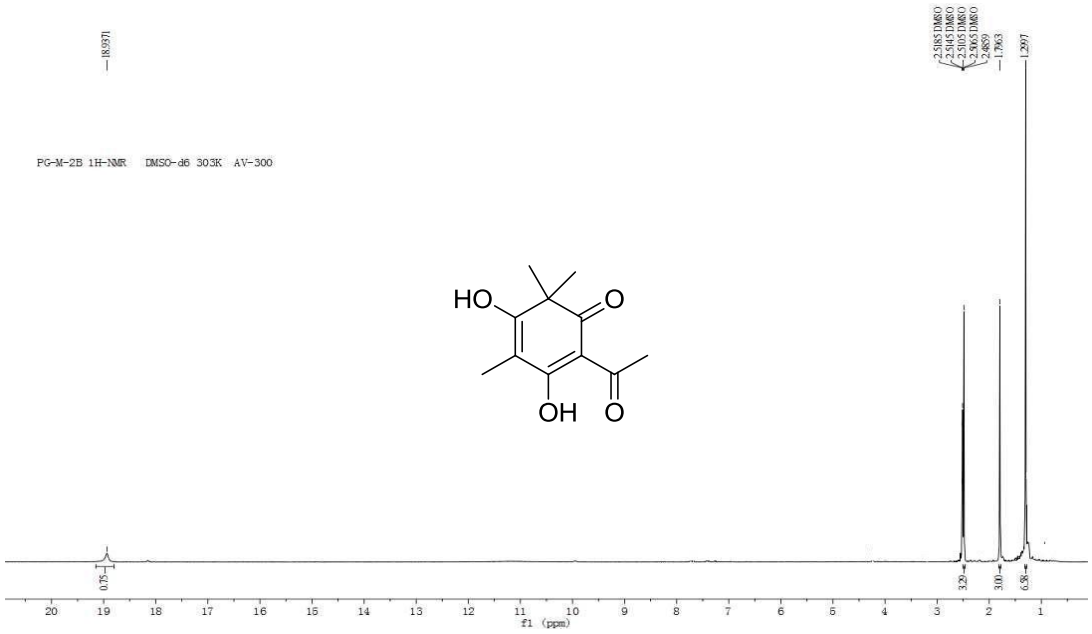


Figure S89. ^{1}H NMR spectrum of **13** in $CDCl_3$ (300 MHz)

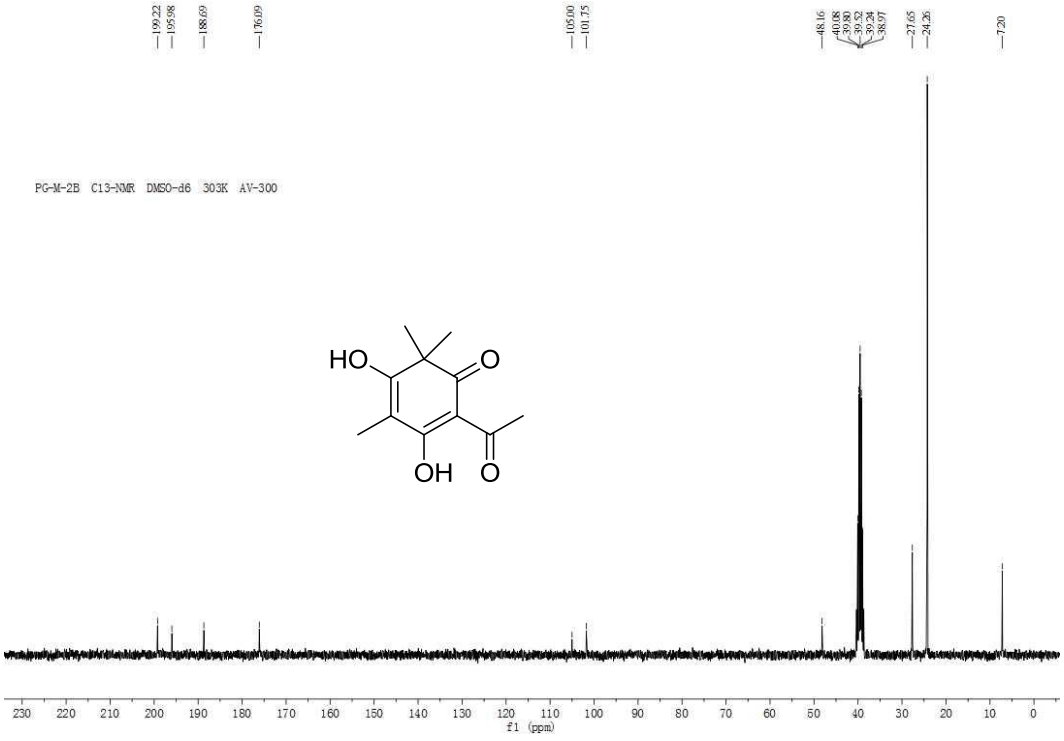


Figure S90. ^{13}C NMR spectrum of **13** in $CDCl_3$ (75 MHz)

References

[1] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J . Fox , Gaussian, Inc ., Wallingford C T, **2009**.

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

HPLC-Q/TOF-MS analysis of the petroleum ether portion of the aerial parts of *B. frutescens*

Preparation of sample solution

The fresh aerial parts of *B. frutescens* L. were ground into powders. Sample powders (5 g) were percolated with 100 mL methanol at room temperature for 48 h. The crude methanol extract was concentrated *in vacuo*, suspended in H_2O and partitioned with petroleum ether (PE, 60–90 ℃). The petroleum ether extract of *B. frutescens* was subjected on a silica flash column (25-40 μm, 25 g) with PE-EtOAc (100:0, 95:5, each 100 mL) as eluent. Then, the PE: EtOAc (95:5) fraction was concentrated and analyzed on LC-MS.

Preparation of mixed standards

Mixed standards (0.02~0.1 mg/mL for **1**–**7**) were prepared in methanol. 2 μL was injected into LC-MS for analysis.

Instrument and chromatographic conditions

The HPLC analysis was performed on an Agilent series 1200 HPLC system equipped with a quaternary pump, a degasser, an autosampler, a thermostated column compartment and a diode array detector. Chromatographic separation was carried out at 25 ℃ on an Agilent Poroshell 120 EC-C18 column (4.6 × 50 mm, 2.7 μm) with the gradient program of mobile phase MeCN/H_2O (85:15→95:5). The flow rate was 1 mL/min.

All MS experiments were conducted on an Agilent 6210 Q/TOF mass spectrometer equipped with an ESI source. The MS conditions were as follows: The mass range was set at *m/z* 100–1200; drying gas temperature, 350 °C; drying gas flow, 8 L/min; nebulizer pressure, 35 psi; capillary voltage, 4000 V. Both MS and MS/MS data were performed in positive mode. Collision energy was set at 25 V. Data acquisition was performed with MassHunter Workstation.

Result and Conclusion

To confirm that compounds **1**–**7** are naturally occurring in the plant, the petroleum ether portion extract of the aerial parts of *B. frutescens* was analyzed by LC-Q/TOF-MS (**Figure S91**). Compounds **1**–**7** were detected in the crude petroleum ether portion extract by comparsion of the HPLC retention times, HRMS spectra, MS^2 spectra, and UV absorptions with those of isolates (**Figure S92–S98**). The above results indicated that compounds **1**–**7** are naturally occurring products.

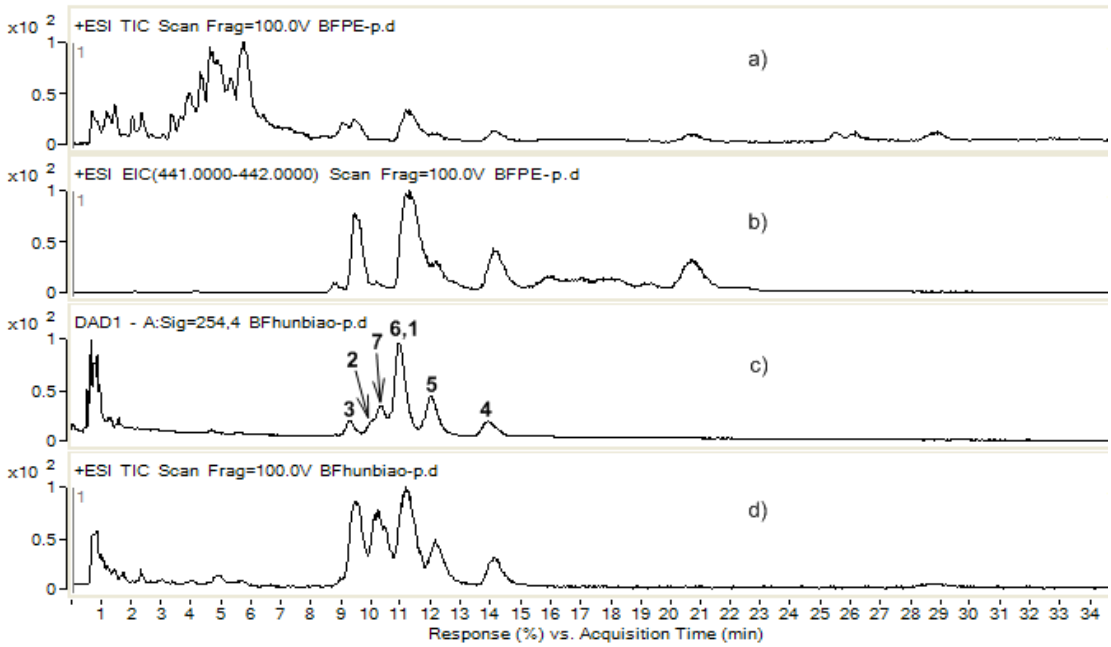


Figure S91. The HPLC-Q/TOF-MS analysis of the petroleum ether portion from *B. frutescens* and the mixed standards. a) The total ion chromatogram (TIC) for the petroleum ether portion extract of *B. frutescens.* b) The extracted ion chromatogram (EIC) for *m/z* 441.0000 to 442.0000 from the petroleum ether portion extract. c) The HPLC-UV chromatogram for the mixed standards. d) The total ion chromatogram (TIC) for the mixed standards.

Figure S92-1. The extracted ion chromatogram (EIC) for *m/z* 441.0000 to 442.0000, retention time: 9.44 min; *m/z* 441.3384 $[M+H]^+$ (calcd for $C_{29}H_{45}O_3$, *m/z* 441.3333)

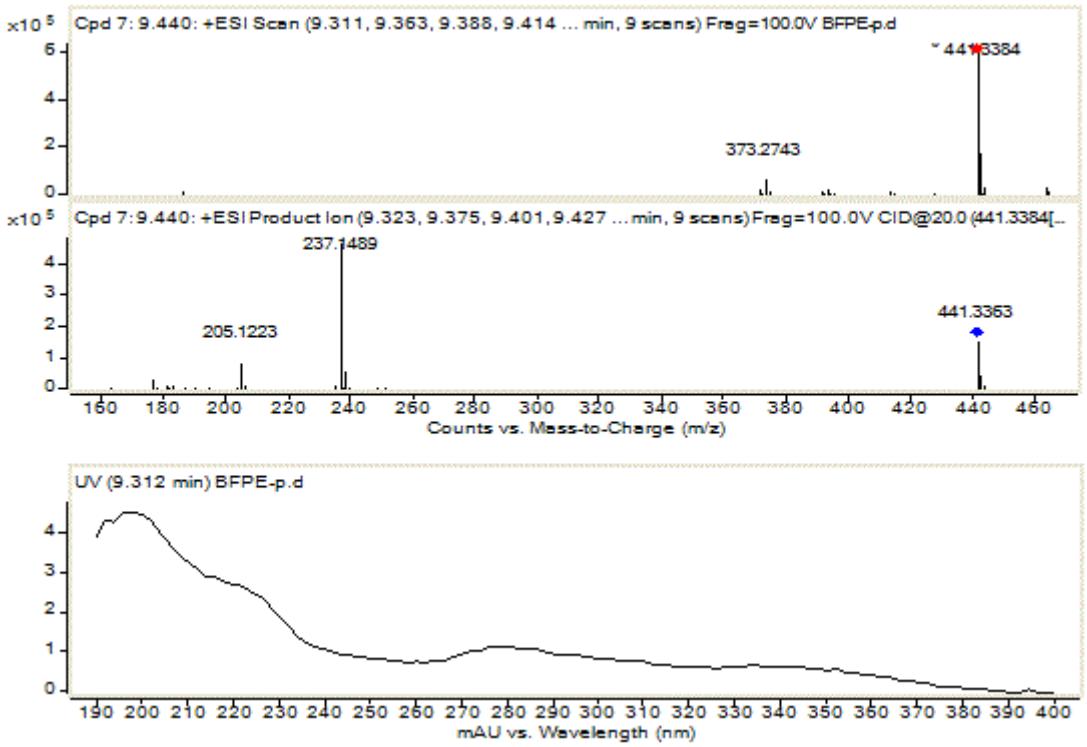


Figure S92-2. The total ion chromatogram (TIC) for compound **3**, retention time: 9.20 min; *m/z* 441.3420 $[M+H]^+$

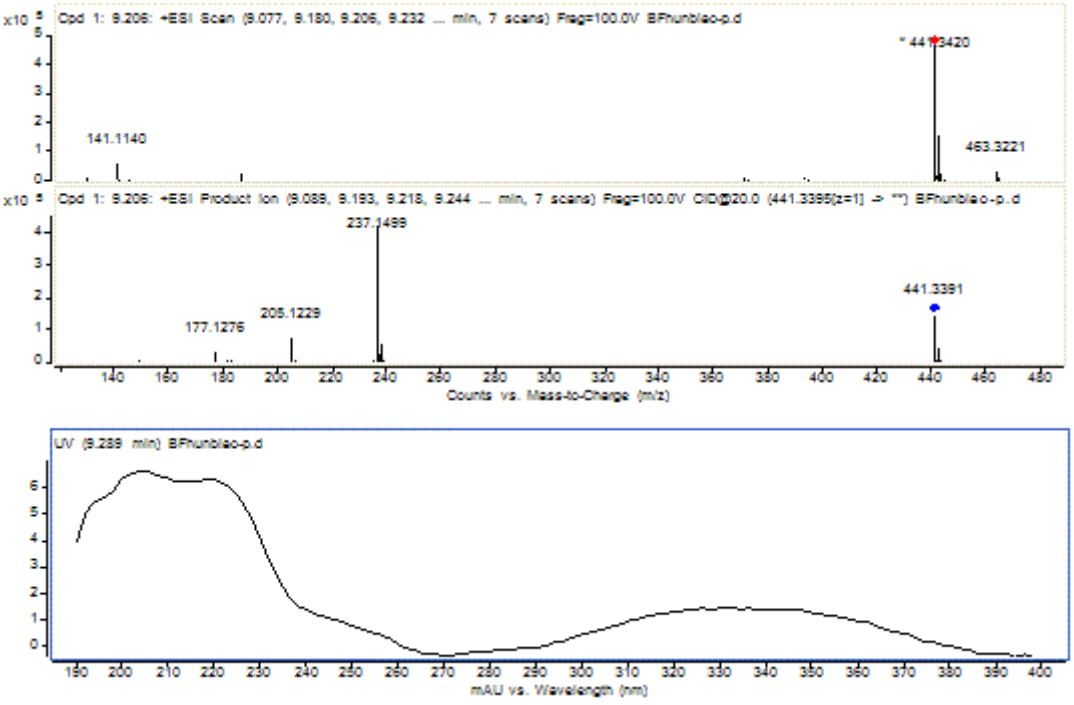


Figure S93-1. The extracted ion chromatogram (EIC) for *m/z* 441.0000 to 442.0000, retention time: 9.97 min; *m/z* 441.3390 $[M+H]^+$ (calcd for $C_{29}H_{45}O_3$, *m/z* 441.3316)

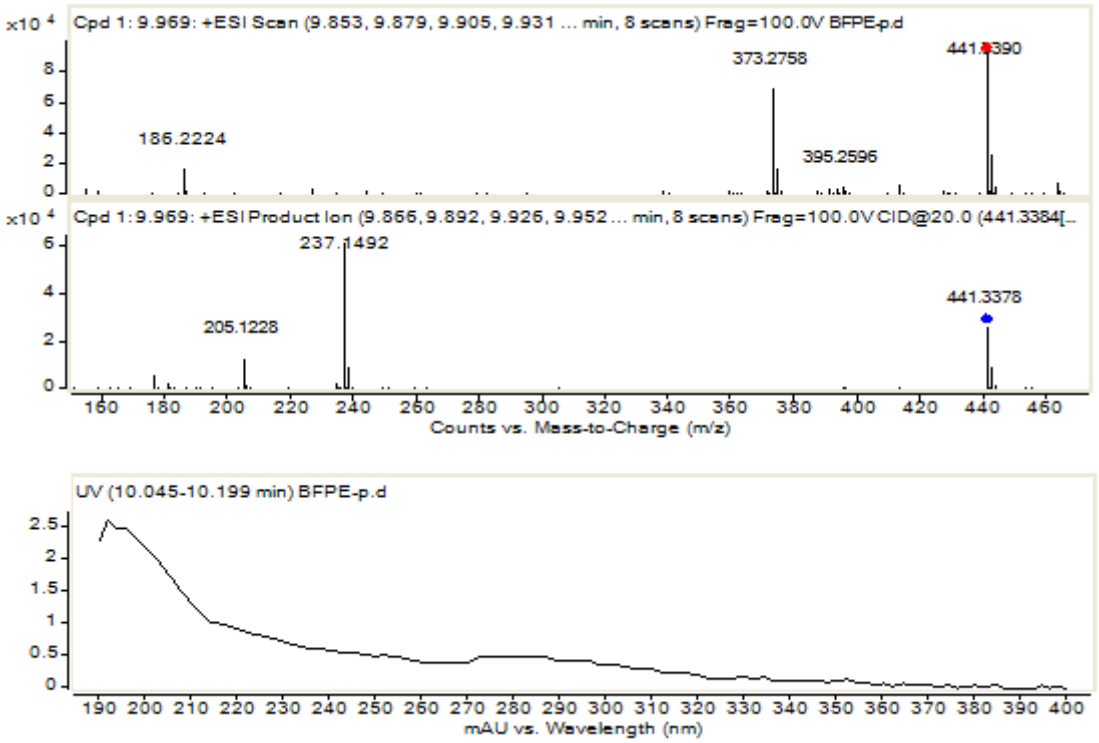


Figure S93-2. The total ion chromatogram (TIC) for compound **2**, retention time: 9.75 min; *m/z* 441. 3416 $[M+H]^+$

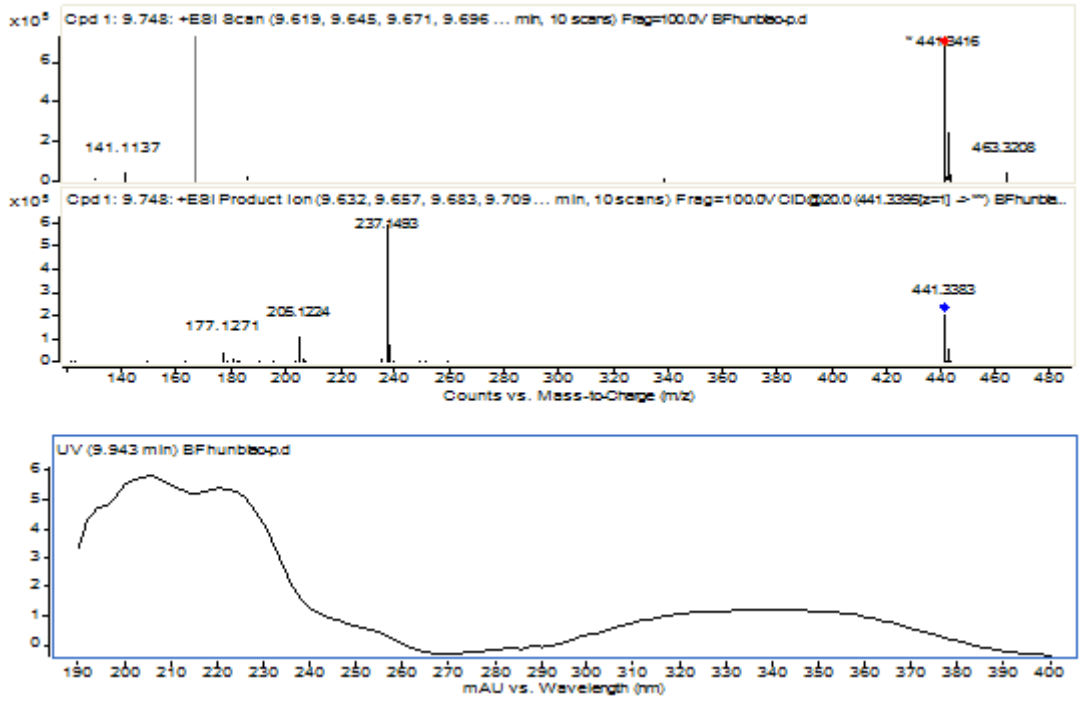


Figure S94-1. The extracted ion chromatogram (EIC) for *m/z* 441.0000 to 442.0000, retention time: 10.25 min; *m/z* 441.3417 $[M+H]^+$ (calcd for $C_{29}H_{45}O_3$, *m/z* 441.3428)

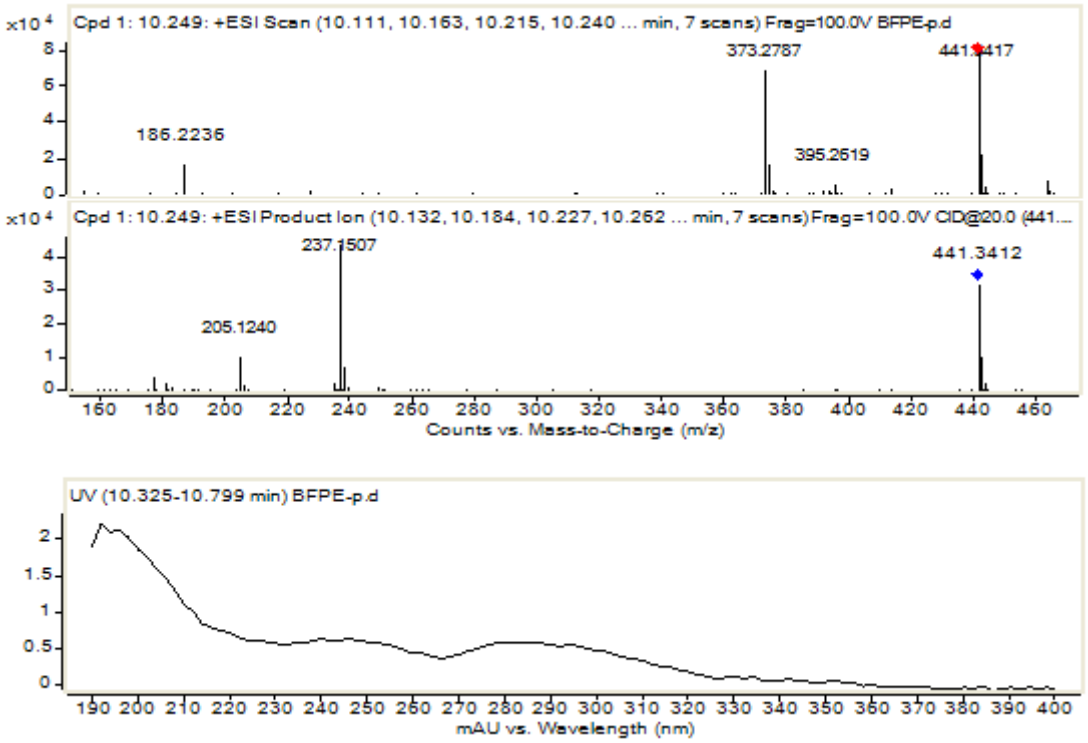


Figure S94-2. The total ion chromatogram (TIC) for compound **7**, retention time: 10.26 min; *m/z* 441.3501 $[M+H]^+$

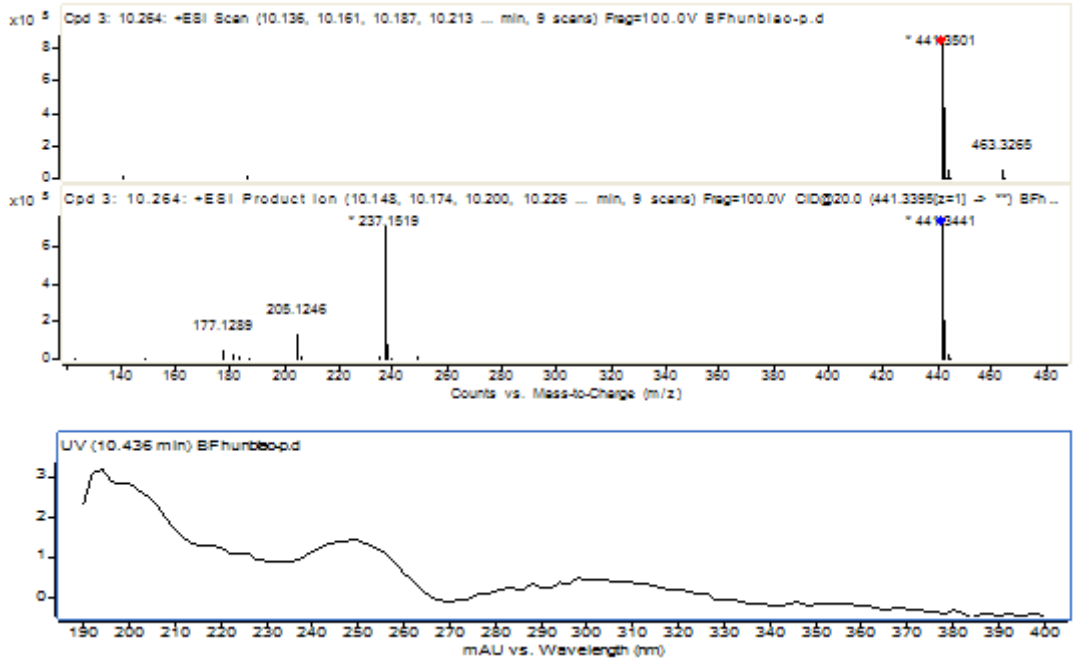


Figure S95-1. The extracted ion chromatogram (EIC) for *m/z* 441.0000 to 442.0000, retention time: 10.82 min; *m/z* 441. 3390 $[M+H]^+$ (calcd for $C_{29}H_{45}O_3$, *m/z* 441.3354)

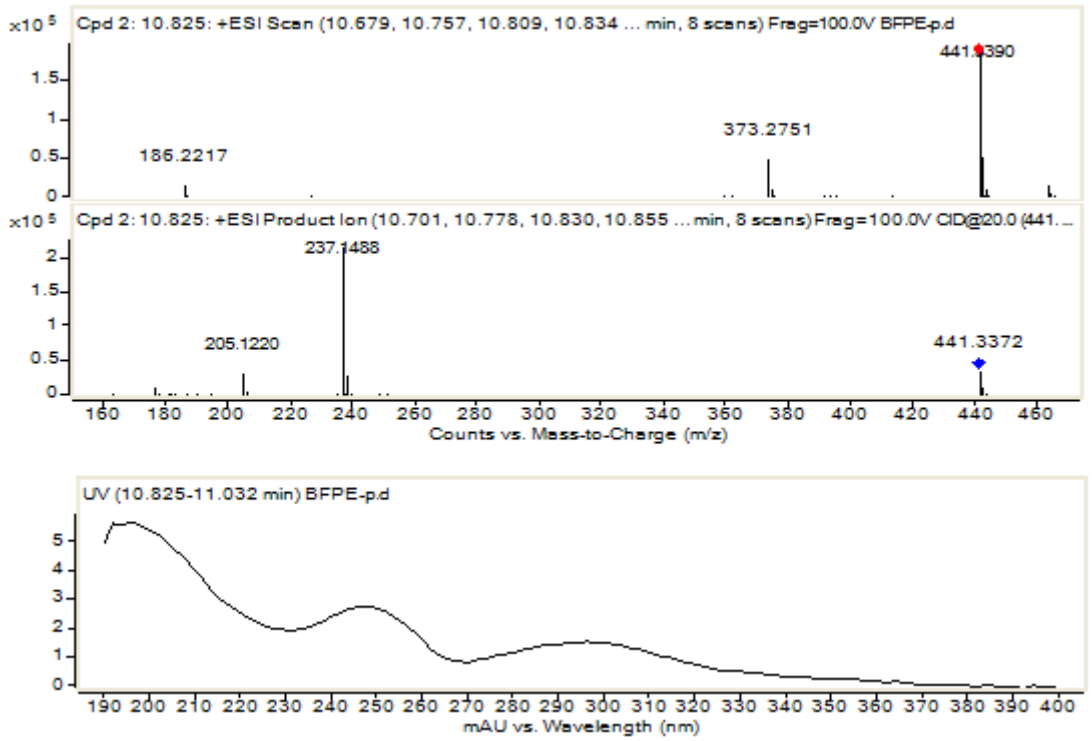


Figure S95-2. The total ion chromatogram (TIC) for compound **6**, retention time: 10.78 min; *m/z* 441. 3373 $[M+H]^+$

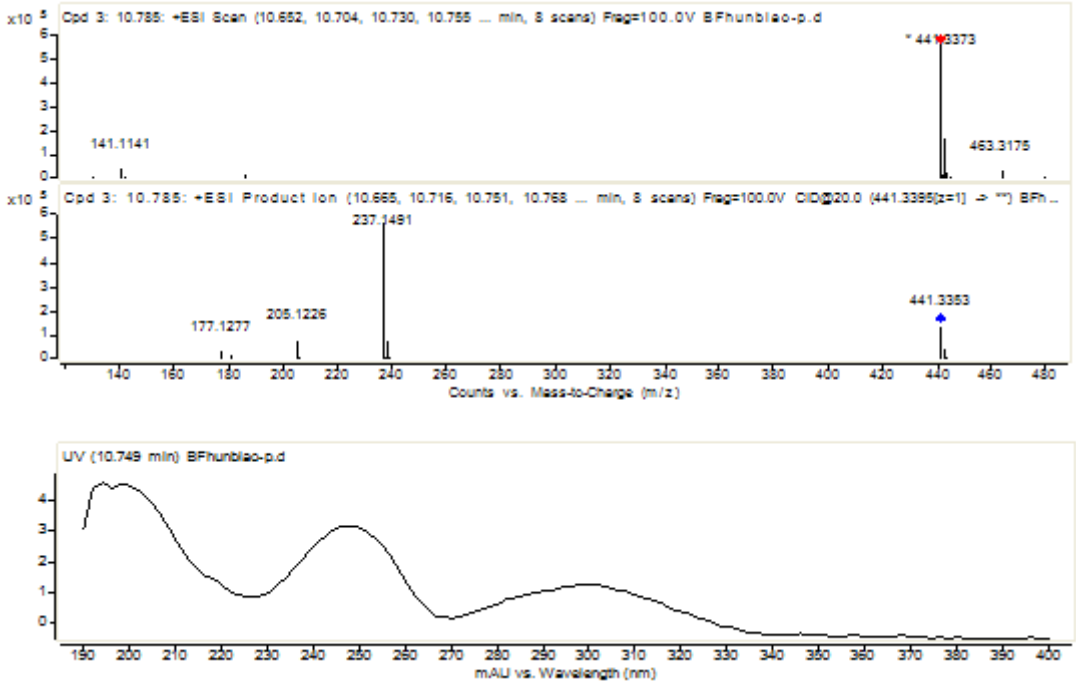


Figure S96-1. The extracted ion chromatogram (EIC) for *m/z* 441.0000 to 442.0000, retention time: 11.61 min; *m/z* 441. 3394 $[M+H]^+$ (calcd for $C_{29}H_{45}O_3$, *m/z* 441.3317)

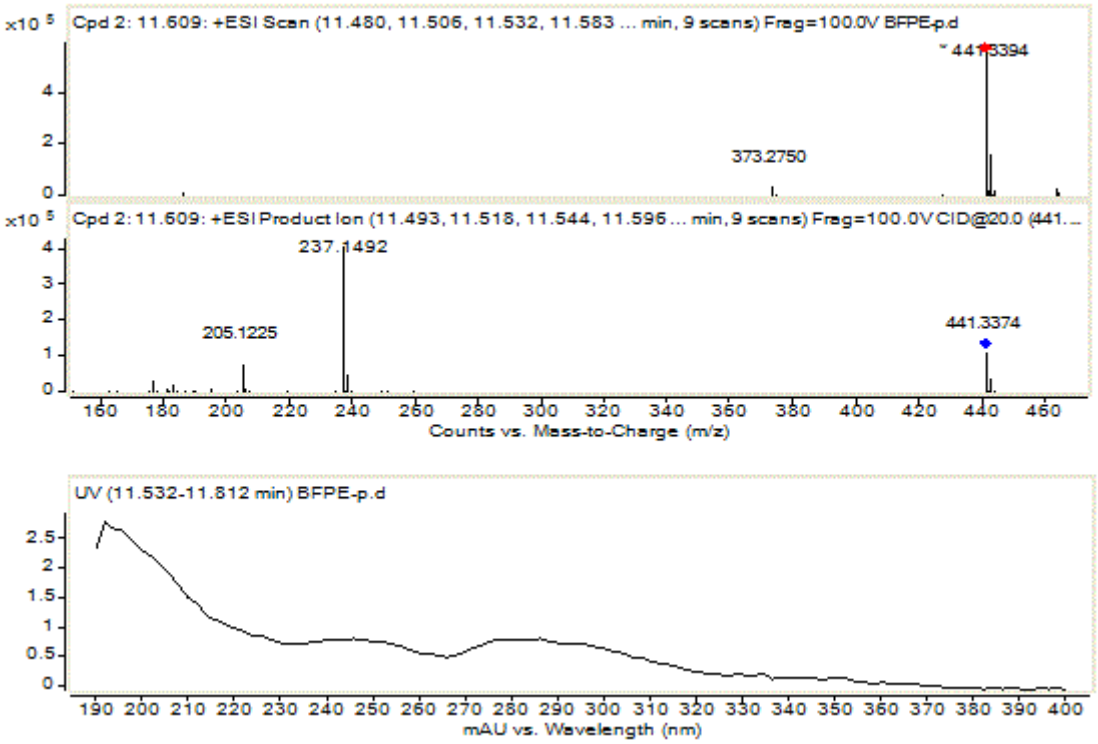


Figure S96-2. The total ion chromatogram (TIC) for compound **1**, retention time: 11.50 min; *m/z* 441. 3482 $[M+H]^+$

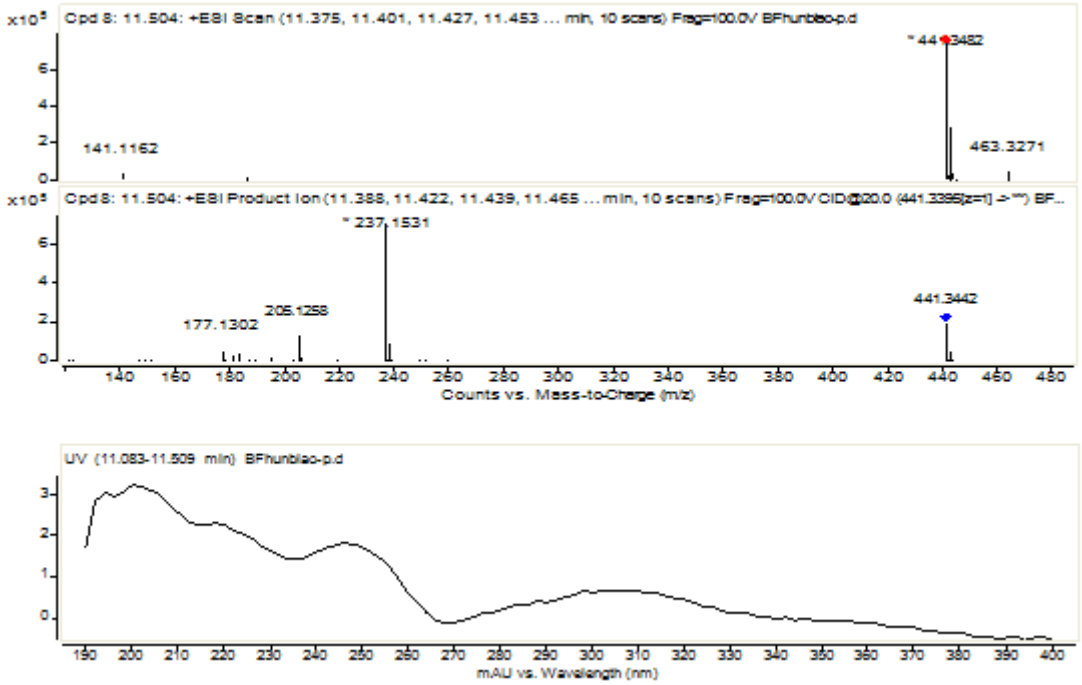


Figure S97-1. The extracted ion chromatogram (EIC) for *m/z* 441.0000 to 442.0000, retention time: 12.14 min; *m/z* 441. 3392 $[M+H]^+$ (calcd for $C_{29}H_{45}O_3$, *m/z* 441.3306)

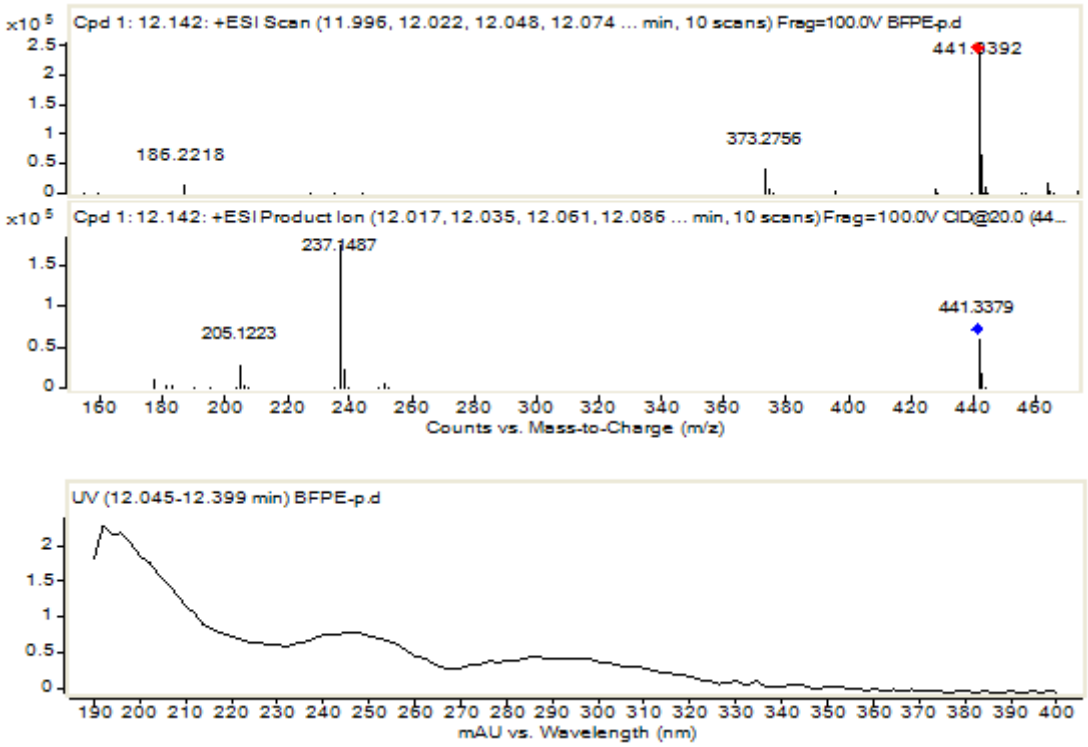


Figure S97-2. The total ion chromatogram (TIC) for compound **5**, retention time: 11.76 min; *m/z* 441. 3375 $[M+H]^+$

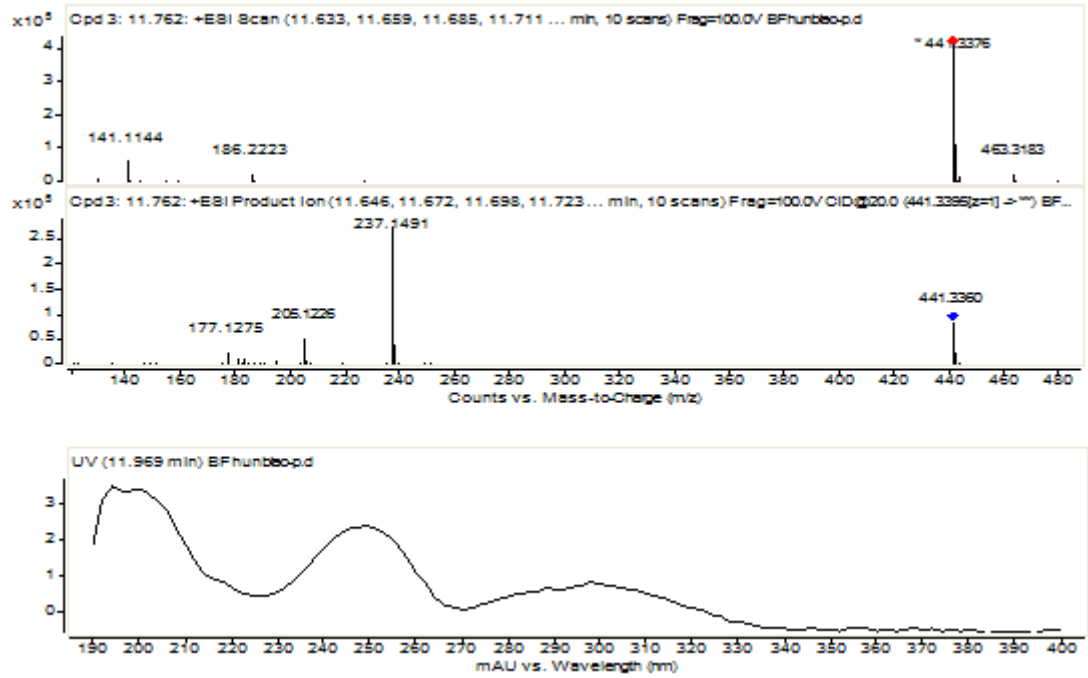


Figure S98-1. The extracted ion chromatogram (EIC) for *m/z* 441.0000 to 442.0000, retention time: 13.97 min; *m/z* 441. 3439 $[M+H]^+$ (calcd for $C_{29}H_{45}O_3$, *m/z* 441.3397)

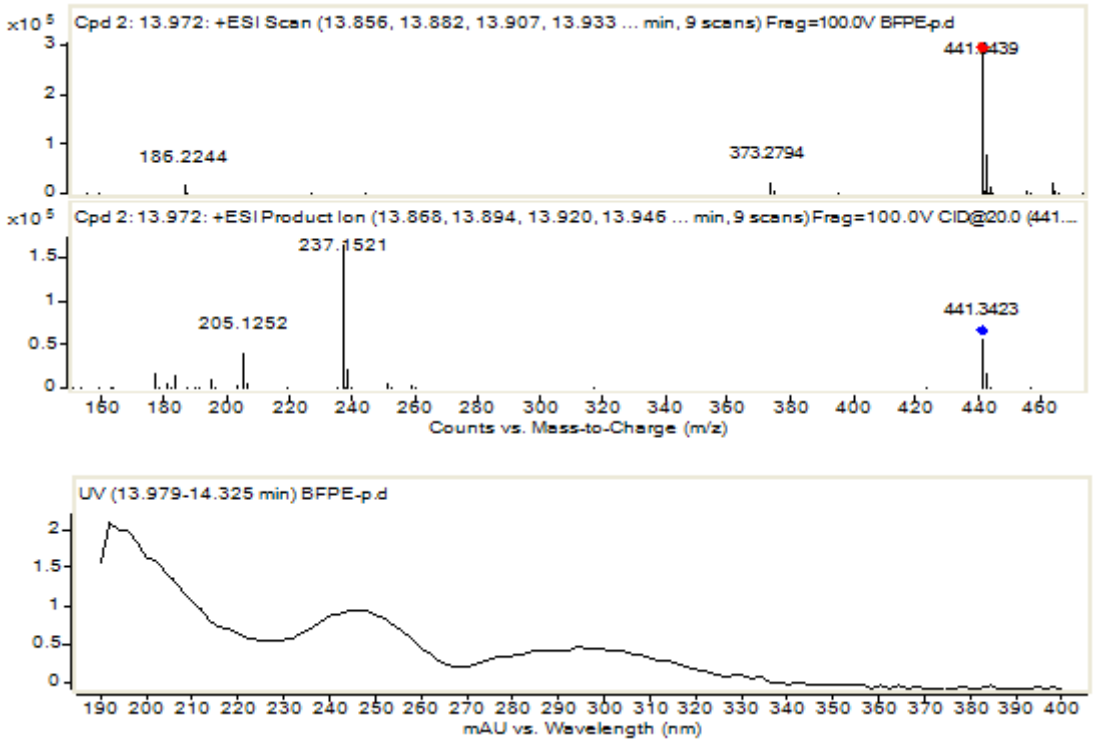
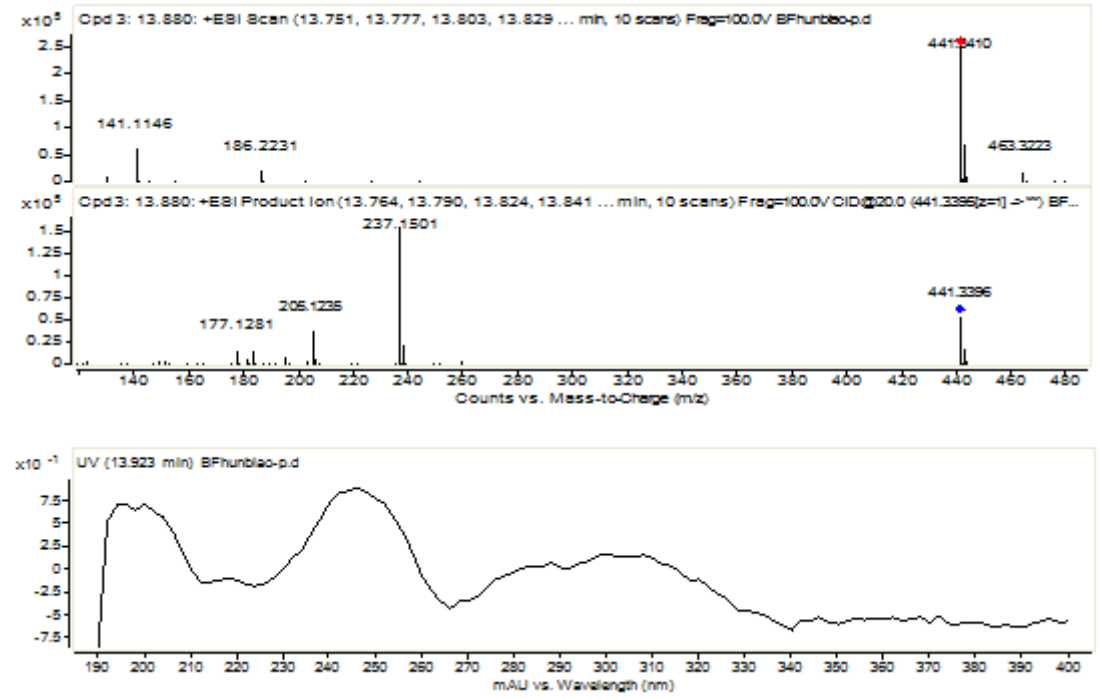
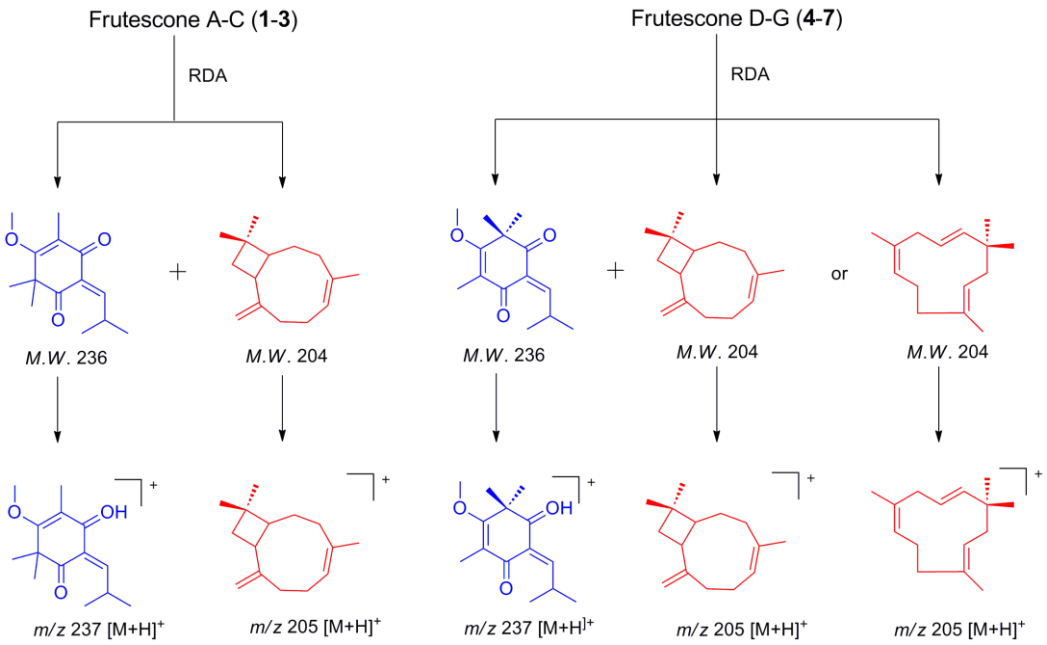


Figure S98-2. The total ion chromatogram (TIC) for compound **4**, retention time: 13.88 min; *m/z* 441. 3410 $[M+H]^+$



Scheme S1. Possible Formation for Major Fragments of Frutescone A–G (**1**–**7**) in (+) ESI-MS^2 Spectrum



HPLC-MSD Trap analysis of the CH_2Cl_2 extract of the aerial parts of *B. frutescens*

Preparation of sample solution

The fresh aerial parts of *B. frutescens* were ground into powders and passed through a 60-mesh (0.3 mm) sieve. Sample powders (5 g) were extracted by ultrasonator with 100 mL CH_2Cl_2 at room temperature with for 40 min. The crude CH_2Cl_2 extract was concentrated *in vacuo*, and was subjected to a silica flash column (25-40 μm, 25 g) with PE-EtOAc (100:0, 95:5, each 100 mL) as eluent. Then, the PE: EtOAc (95:5) fraction was concentrated and analyzed on LC-MS.

Preparation of mixed standards

Mixed standards (0.02~0.1 mg/mL for **1**–**7**) were prepared in methanol. 2 μL was injected into LC-MS for analysis.

Instrument and chromatographic conditions

The HPLC analysis was performed on an Agilent series 1100 HPLC system

equipped with a quaternary pump, a degasser, an autosampler, a thermostated column compartment and a diode array detector. Chromatographic separation was carried out at 25 ℃ on an Agilent Poroshell 120 EC-C18 column (4.6 × 50 mm, 2.7 μm) with the gradient program of mobile phase MeCN/H_2O (85:15→95:5). The flow rate was 1 mL/min.

All MS experiments were conducted on an Agilent 1100 series LC-MSD Trap mass spectra with an electrospray interface (ESI). The MS conditions were as follows: The mass range was set at *m/z* 50–1200; drying gas temperature, 190 ℃; drying gas flow, 9 L/min; nebulizer pressure, 16 psi; capillary voltage, 140 V.; Trap drive, 63.4; rolling averages, 1 cts. Both MS and MS/MS data were performed in positive mode. Data acquisition was performed with Bruker Compass DataAnalysis 4.1.

Result and Conclusion

The fresh aerial parts of *B. frutescens* L. was extracted by ultrasonator at room temperature with CH_2Cl_2, more efficient than petroleum ether. Then the CH_2Cl_2 extract was analyzed by HPLC-MSD Trap (**Figure S99**). Compounds **1**−**7** were also detected in the CH_2Cl_2 extract by comparison of the HPLC retention time and MS^n spectra, with those of isolates (see the Supporting Information, **Figure S99**-**S106**). Thus, compounds **1**−**7** are proved to be natural occurring products in *B. frutescens*, not artifacts produced during the extraction and isolation procedure.

Figure S99. The LC-MSD Trap analysis of the CH_2Cl_2 extract of *B. frutescens* and the mixed standards. a) The HPLC-UV chromatogram (254 nm) for the CH_2Cl_2 extract of *B. frutescens.* b) The base peak chromatogram (BPC) for the CH_2Cl_2 extract. c) The extracted ion chromatogram (EIC) for *m/z* 441 from CH_2Cl_2 extract. d) The HPLC-UV chromatogram (254 nm) for the mixed standards. e) The base peak chromatogram (BPC) for the mixed standards. f) The extracted ion chromatogram (EIC) for *m/z* 441 from the mixed standards.

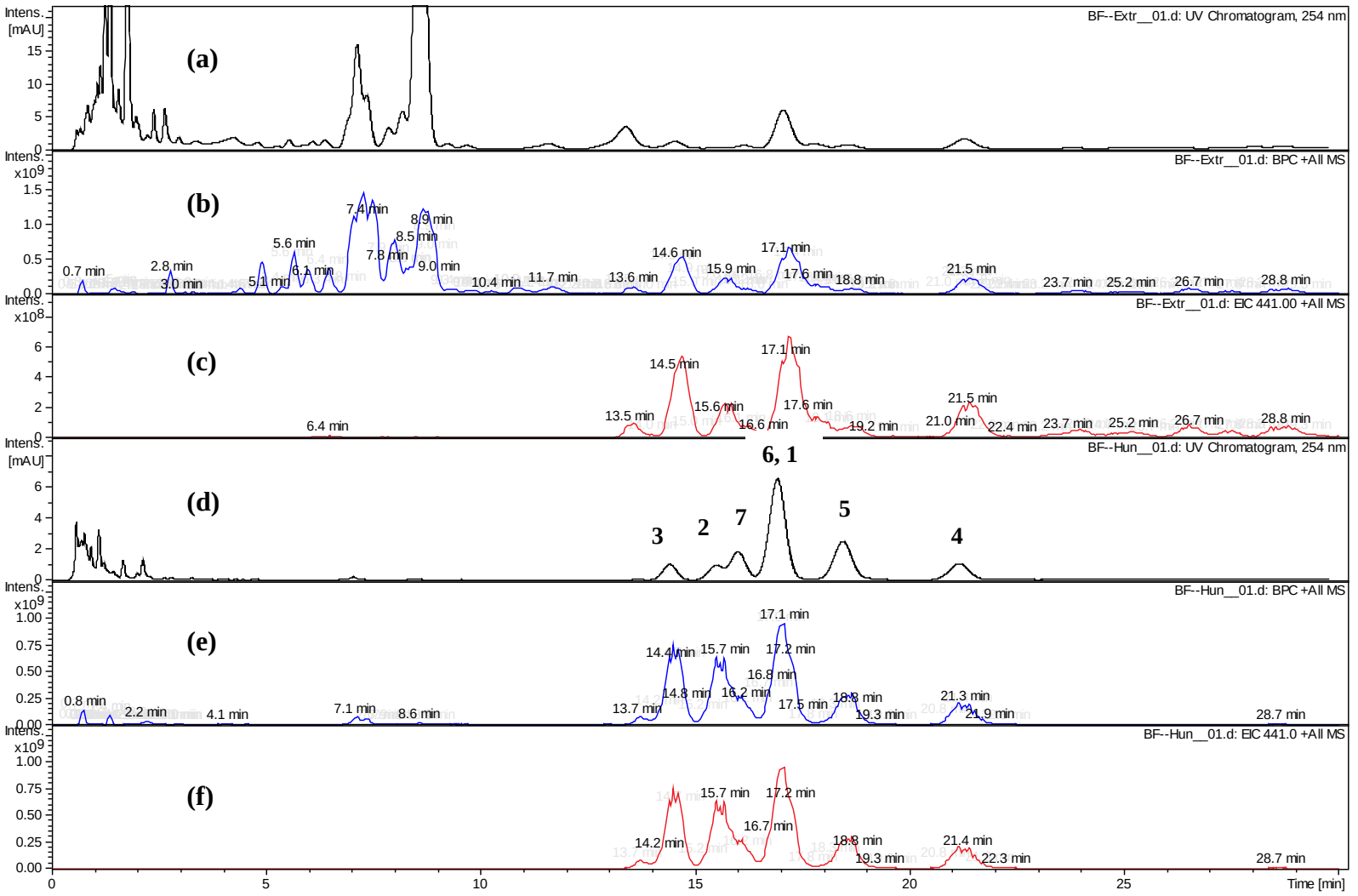

Intens. [mAU]
BF--Extr__01.d: UV Chromatogram, 254 nm
(a)
Intens. x10^9
BF--Extr__01.d: BPC +All MS
(b)
0.7 min
2.8 min
3.0 min
5.1 min
5.6 min
6.1 min
7.4 min
7.8 min
8.5 min
8.9 min
9.0 min
10.4 min
11.7 min
13.6 min
14.6 min
15.9 min
17.1 min
17.6 min
18.8 min
21.5 min
23.7 min
25.2 min
26.7 min
28.8 min
Intens. x10^8
BF--Extr__01.d: EIC 441.00 +All MS
(c)
6.4 min
13.5 min
14.5 min
15.6 min
16.6 min
17.1 min
17.6 min
19.2 min
21.0 min
21.5 min
22.4 min
23.7 min
25.2 min
26.7 min
28.8 min
Intens. [mAU]
BF--Hun__01.d: UV Chromatogram, 254 nm
(d)
6, 1
3
2
7
5
4
Intens. x10^9
BF--Hun__01.d: BPC +All MS
(e)
0.8 min
2.2 min
4.1 min
7.1 min
8.6 min
13.7 min
14.4 min
14.8 min
15.7 min
16.2 min
16.8 min
17.1 min
17.2 min
17.5 min
18.8 min
19.3 min
21.3 min
21.9 min
28.7 min
Intens. x10^9
BF--Hun__01.d: EIC 441.0 +All MS
(f)
14.2 min
15.7 min
16.7 min
17.2 min
18.8 min
19.3 min
21.4 min
22.3 min
28.7 min
0
5
10
15
20
25
Time [min]

Figure S100-1. The extracted ion chromatogram (EIC) for *m/z* 441, retention time: 14.5 min; *m/z* 441.29 $[M+H]^+$

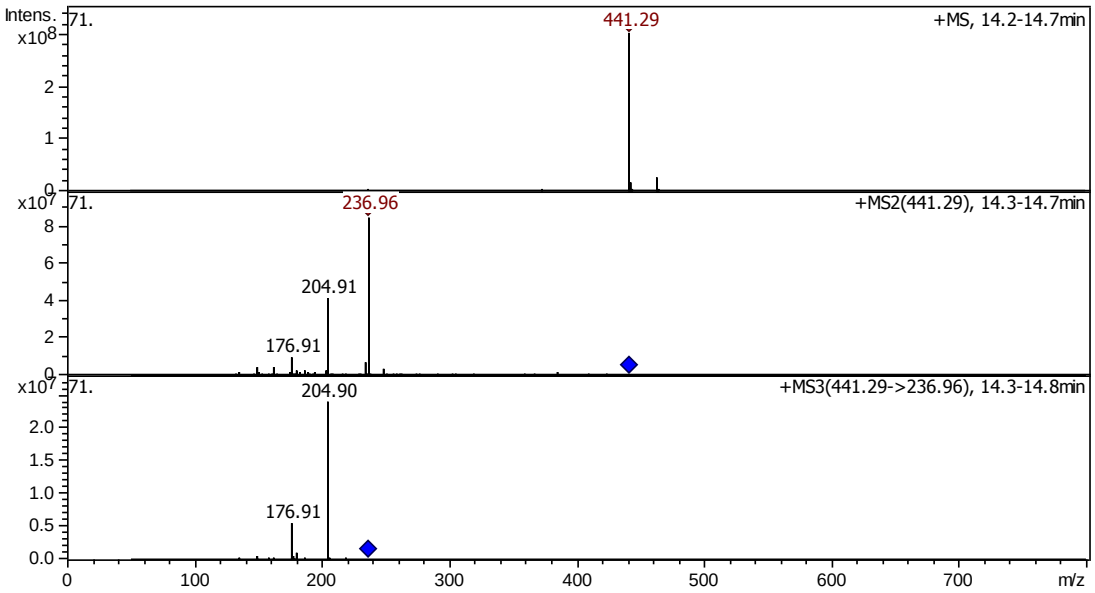


Figure S100-2. The base peak chromatogram (BPC) for compound **3**, retention time: 14.5 min; *m/z* 441.29 $[M+H]^+$

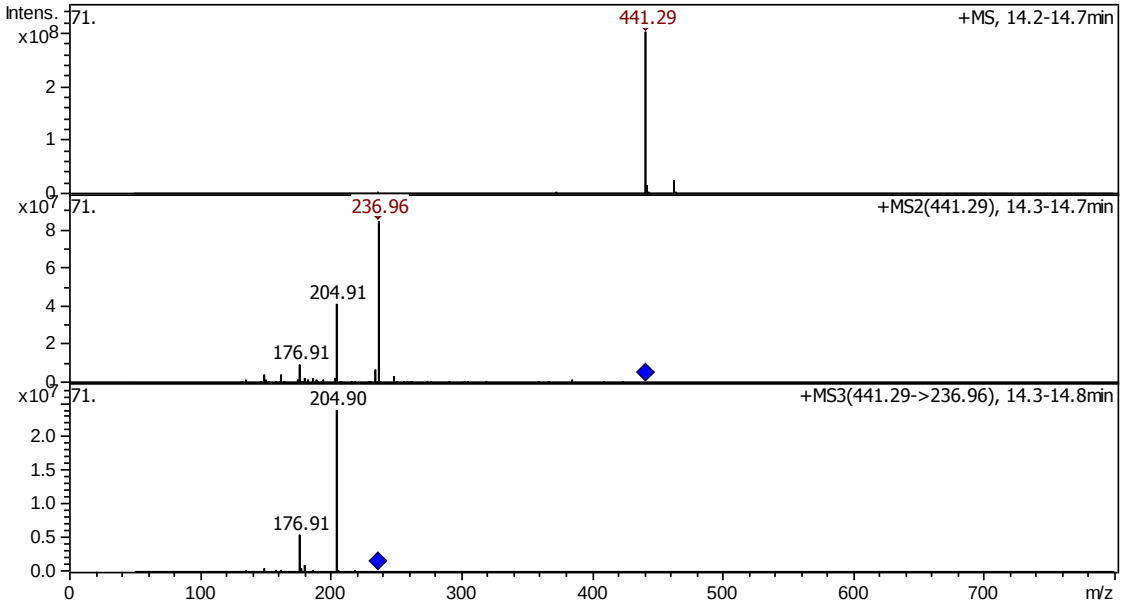


Figure S101-1. The extracted ion chromatogram (EIC) for *m/z* 441, retention time: 15.6 min; *m/z* 441.29 $[M+H]^+$

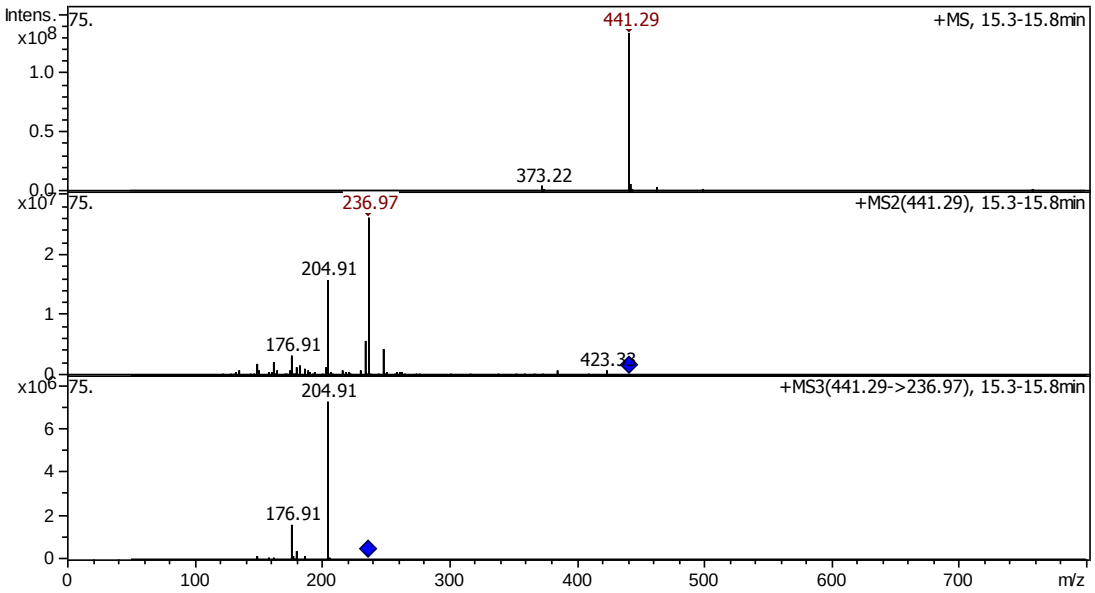


Figure S101-2. The base peak chromatogram (BPC) for compound **2**, retention time: 15.6 min; *m/z* 441. 29 $[M+H]^+$

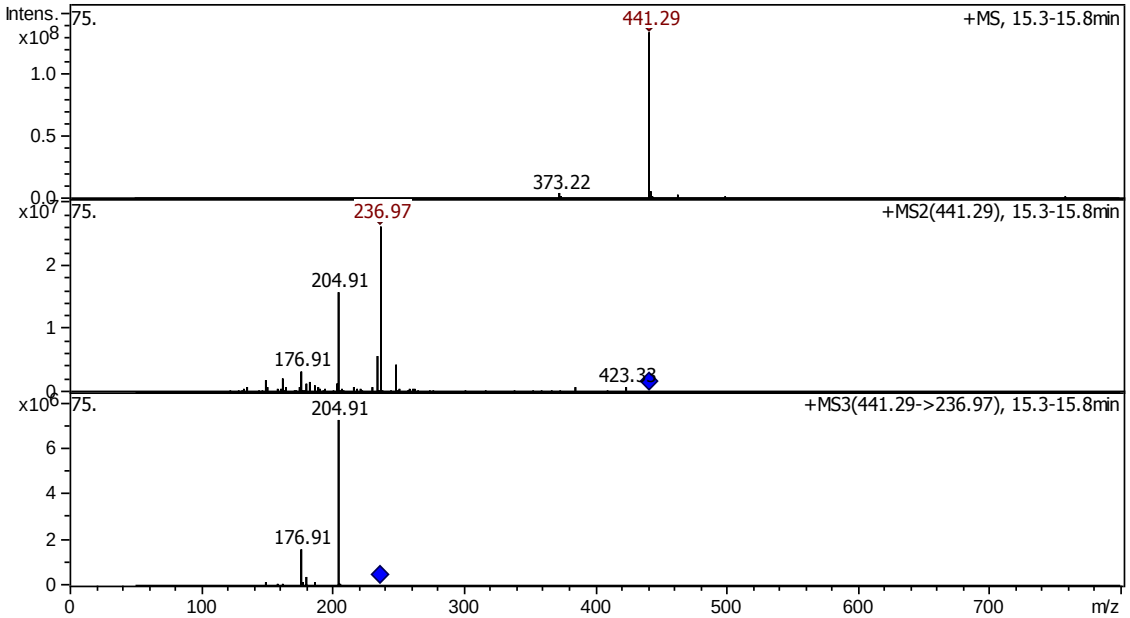


Figure S102-1. The extracted ion chromatogram (EIC) for *m/z* 441, retention time: 16.1 min; *m/z* 441.29 $[M+H]^+$

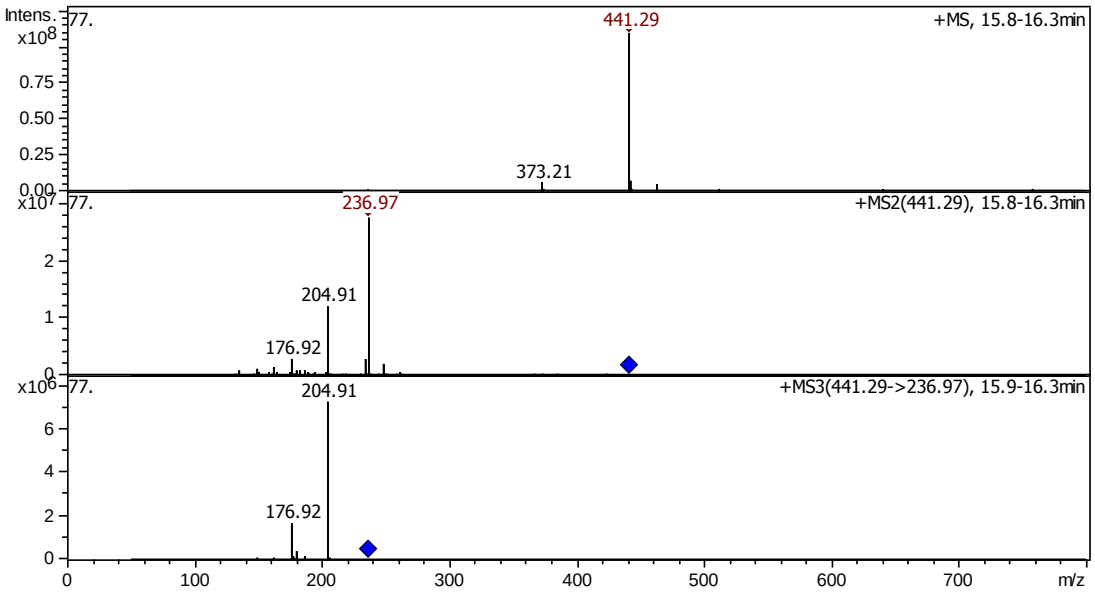


Figure S102-2. The base peak chromatogram (BPC) for compound **7**, retention time: 16.2 min; *m/z* 441.29 $[M+H]^+$

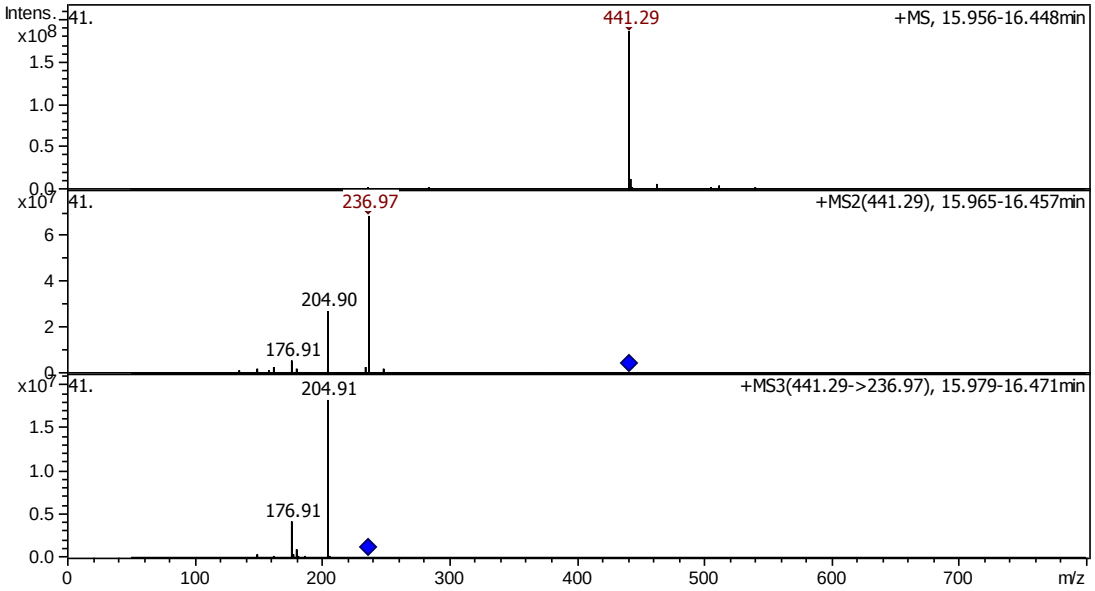


Figure S103-1. The extracted ion chromatogram (EIC) for *m/z* 441, retention time: 17.1 min; *m/z* 441. 29 $[M+H]^+$

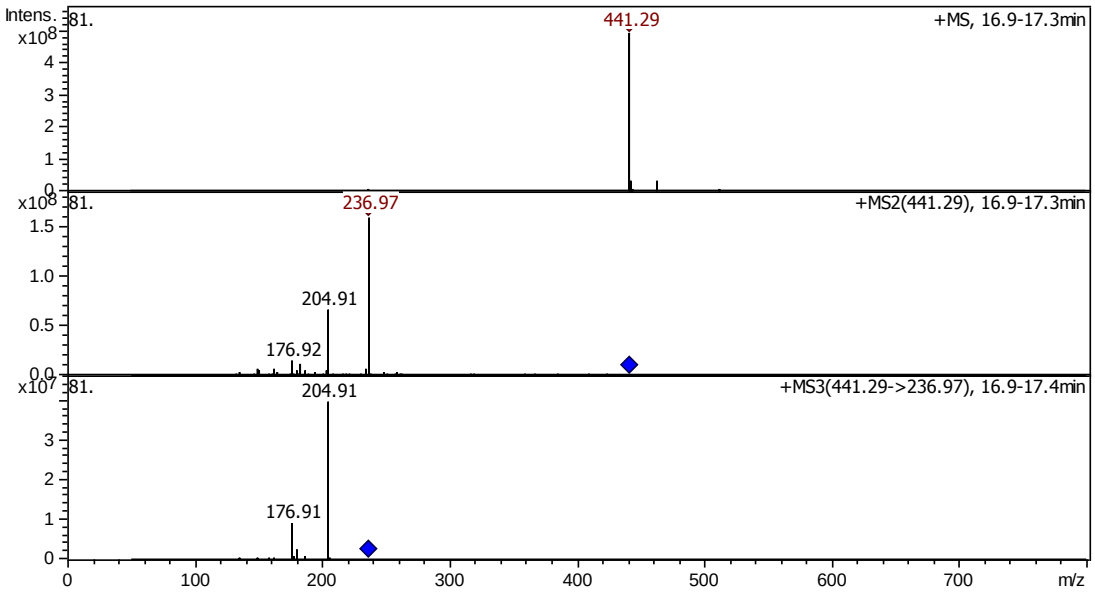


Figure S103-2. The base peak chromatogram (BPC) for compound **6**, retention time: 17.2 min; *m/z* 441. 29 $[M+H]^+$

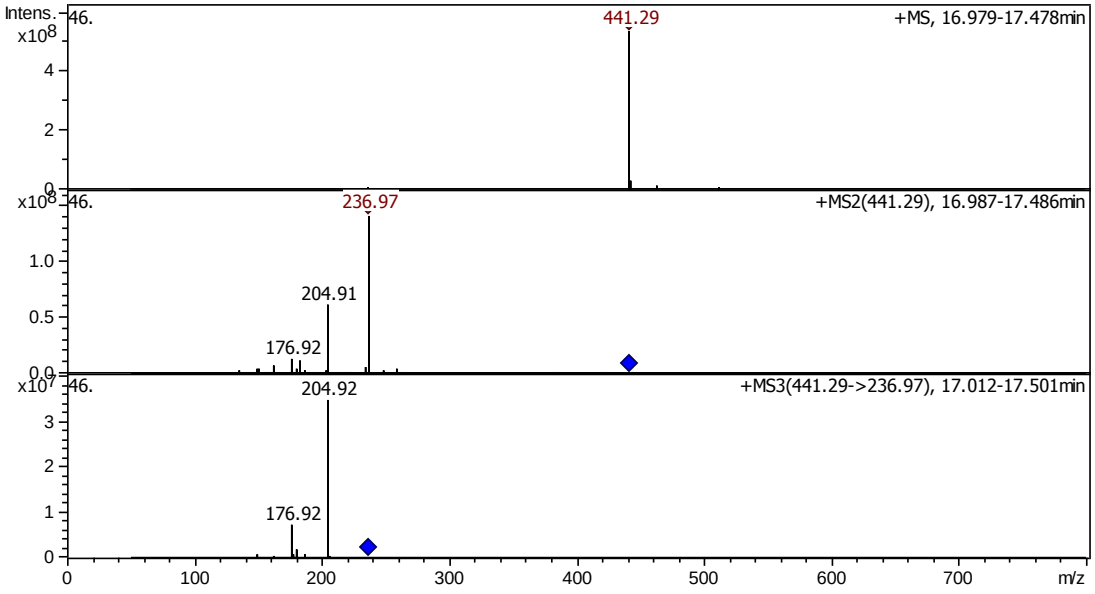


Figure S104-1. The extracted ion chromatogram (EIC) for *m/z* 441, retention time: 17.6 min; *m/z* 441. 28 $[M+H]^+$

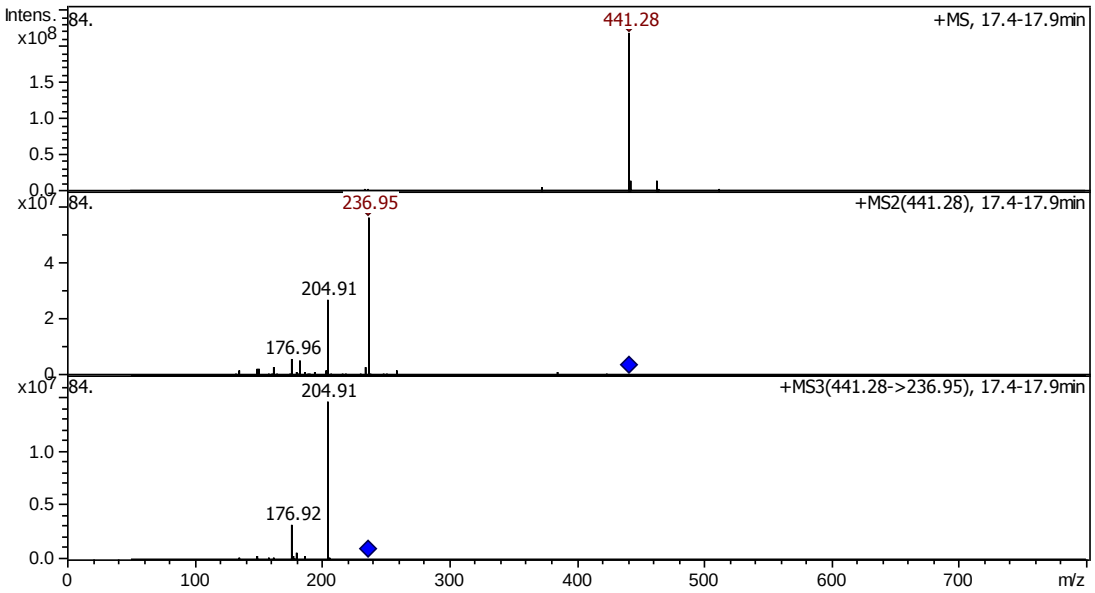


Figure S104-2. The base peak chromatogram (BPC) for compound **1**, retention time: 17.6 min; *m/z* 441. 28 $[M+H]^+$

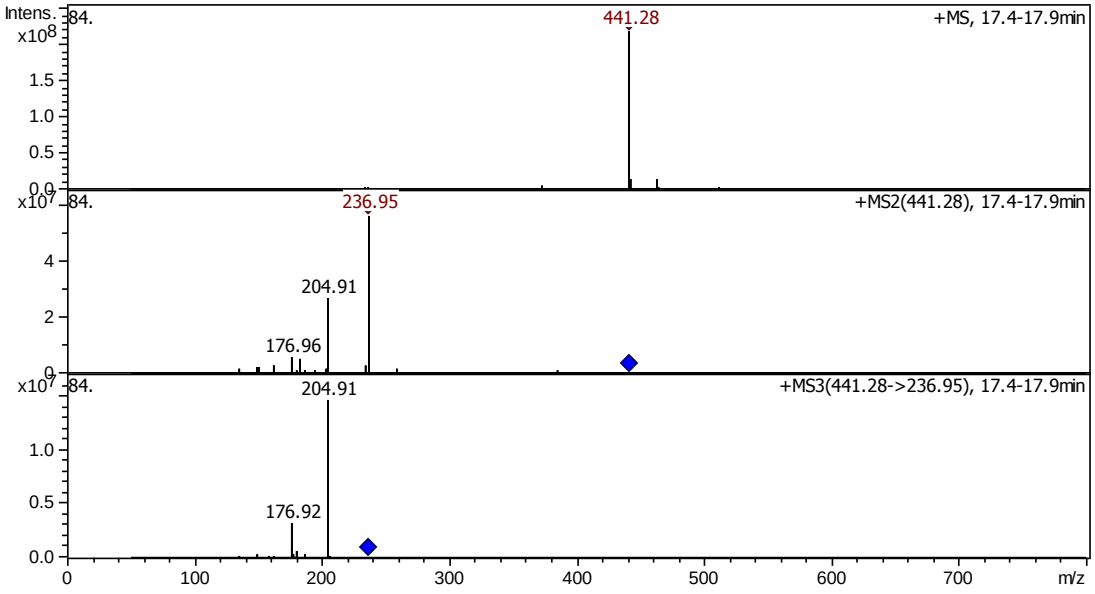


Figure S105-1. The extracted ion chromatogram (EIC) for *m/z* 441, retention time: 18.6 min; *m/z* 441. 28 $[M+H]^+$

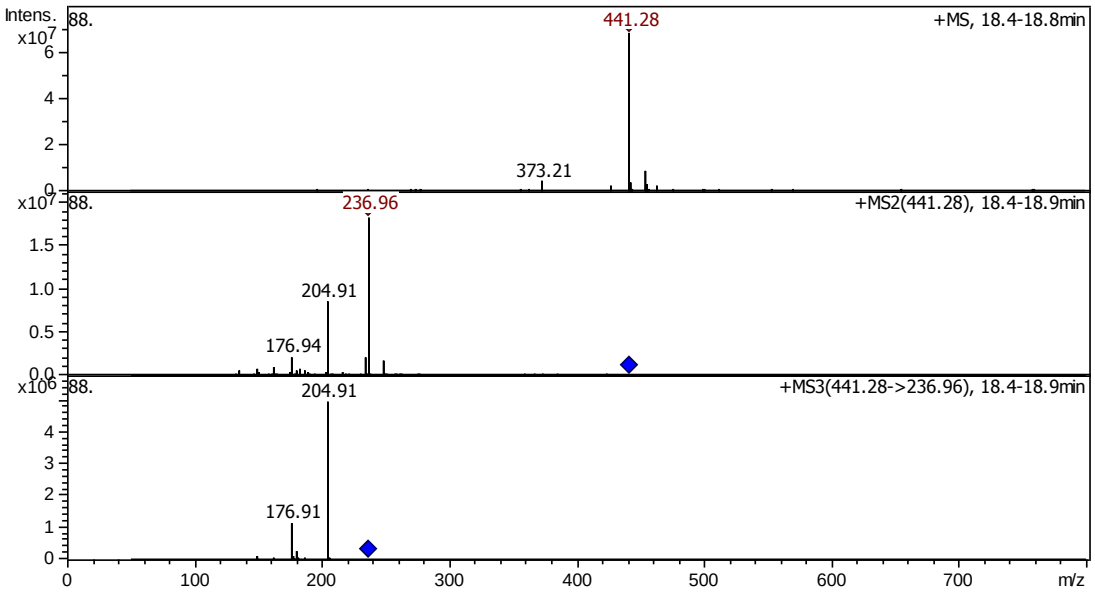


Figure S105-2. The base peak chromatogram (BPC) for compound **5**, retention time: 18.7 min; *m/z* 441. 28 $[M+H]^+$

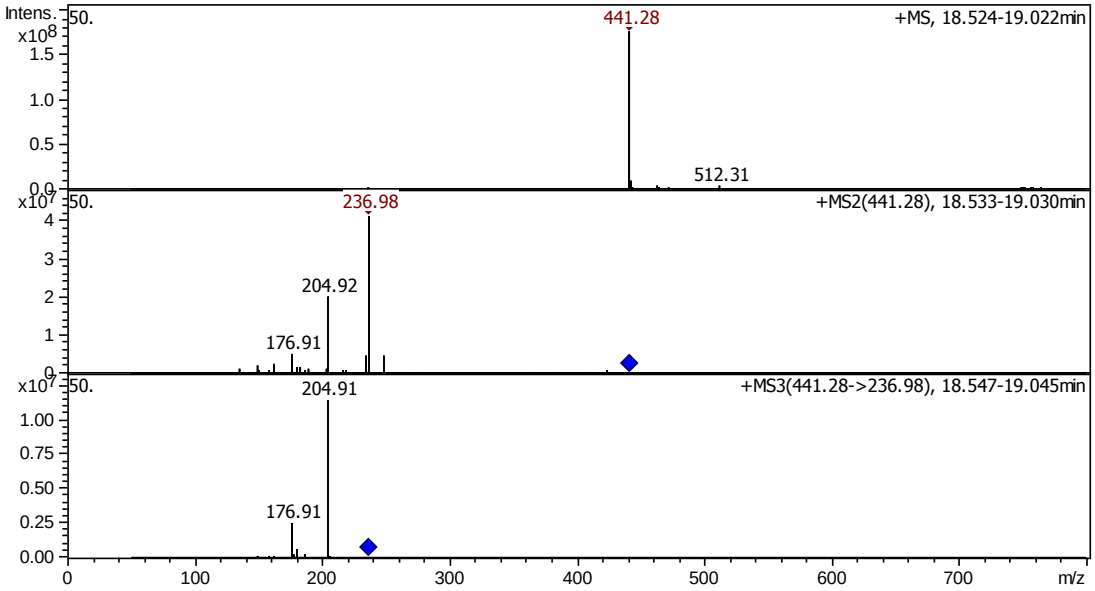


Figure S106-1. The extracted ion chromatogram (EIC) for *m/z* 441, retention time: 21.5 min; *m/z* 441. 30 $[M+H]^+$

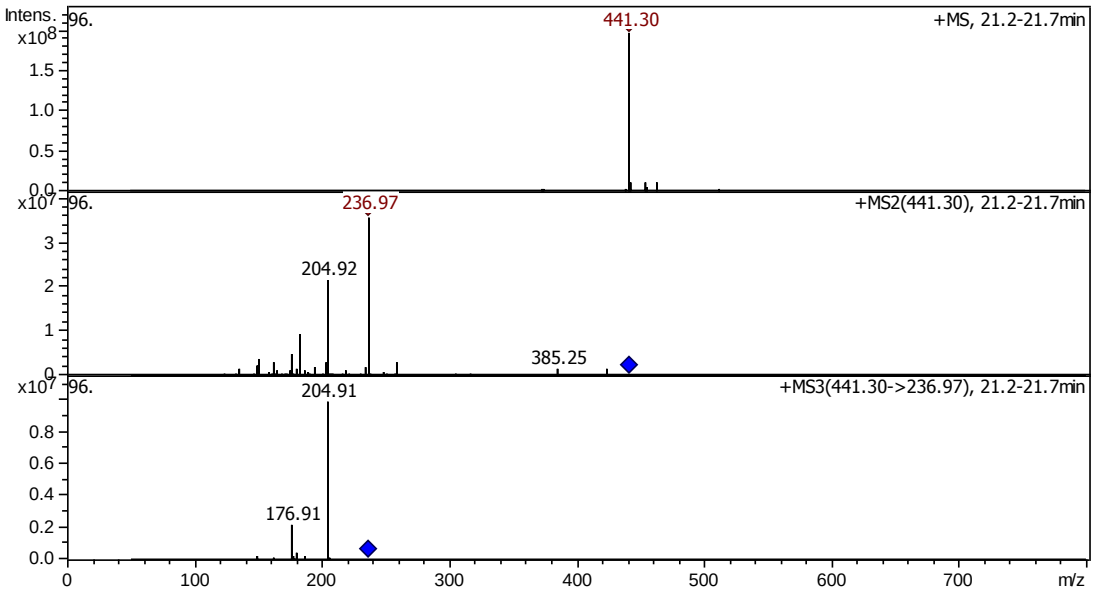


Figure S106-2. The base peak chromatogram (BPC) for compound **4**, retention time: 21.3 min; *m/z* 441. 29 $[M+H]^+$