Monoterpenoid coumarins and monoterpenoid phenylpropanoids from the root barks of *Ailanthus altissima*

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[1] These authors contributed equally to this work.

List of supplementary content

relevant conformers of **4a**

Table S9 DFT B3LYP/6-311+G(d, p) relative free energies and population for the most relevant conformers of **4b**

Table S10 DFT B3LYP/6-311+G(d, p) relative free energies and population for the most relevant conformers of **5a**

Table S11 DFT B3LYP/6-311+G(d, p) relative free energies and population for the most relevant conformers of **5b**

Table S12 Calculated ^{13}C chemical shift values (cal.) of structure **3a-5a**, **3b-5b**

Spectrum Peak Pick Report

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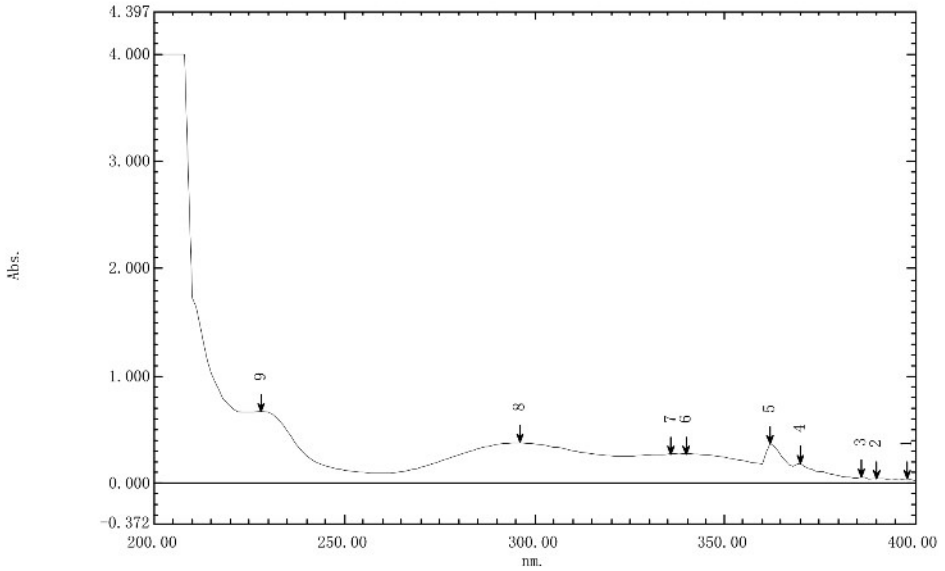

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采样间隔: 1.0
自动采样间隔: 停用
扫描模式: 单一的

试样准备属性
重量:
体积 :
稀释:
光程长:
附加信息:

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测定方式: 吸收值
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光源改变波长: 360.0 nm
S/R 转换: 标准

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17	↓	259.00	.092	
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FIELD TEXT

Figure S1.1 UV spectrum of compound **1**

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
17 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 21-21 H: 0-50 O: 0-8 S: 0-1
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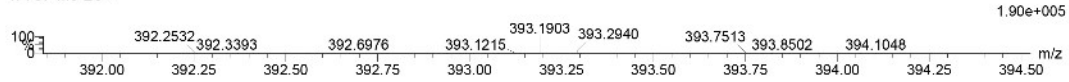

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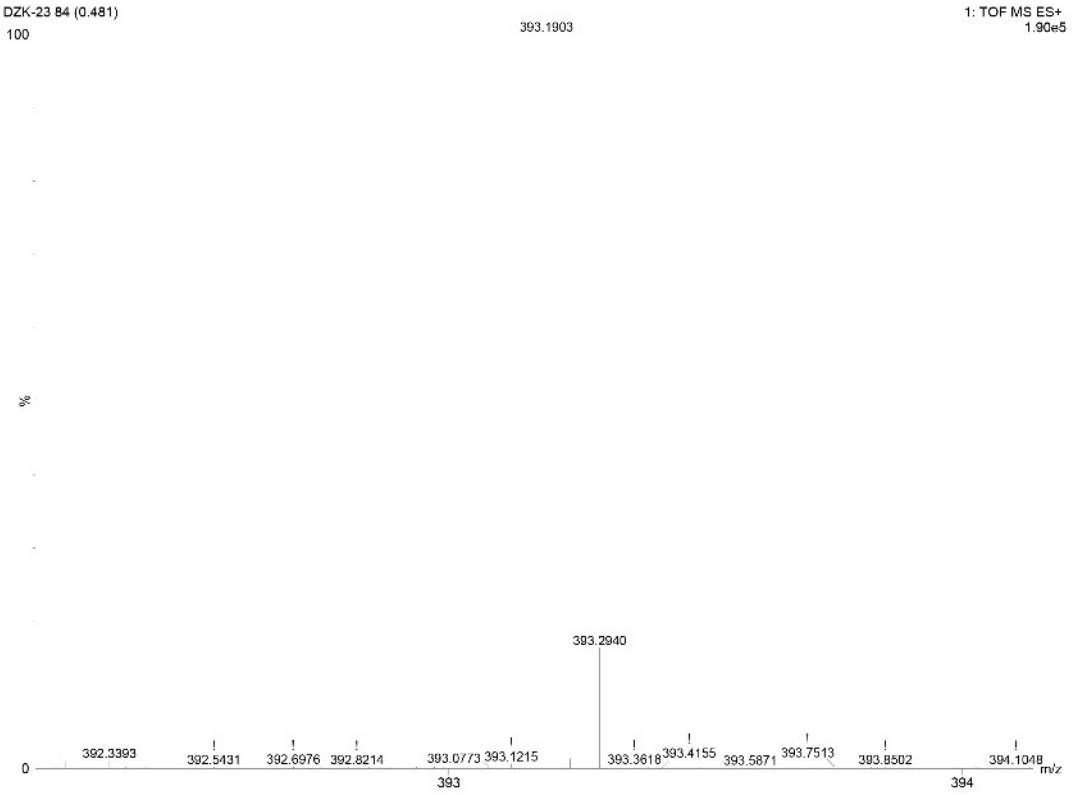

Figure S1.2 HRESIMS spectrum of compound **1**

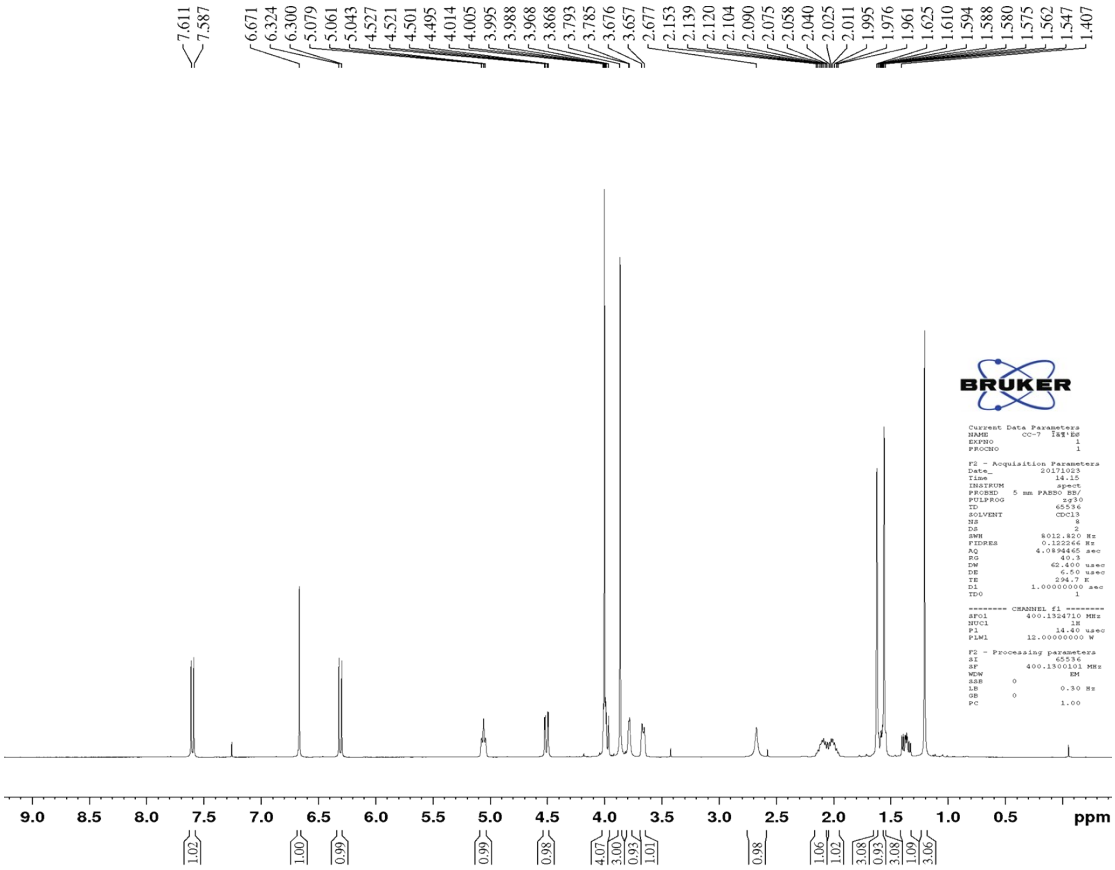

Figure S1.3 ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **1**

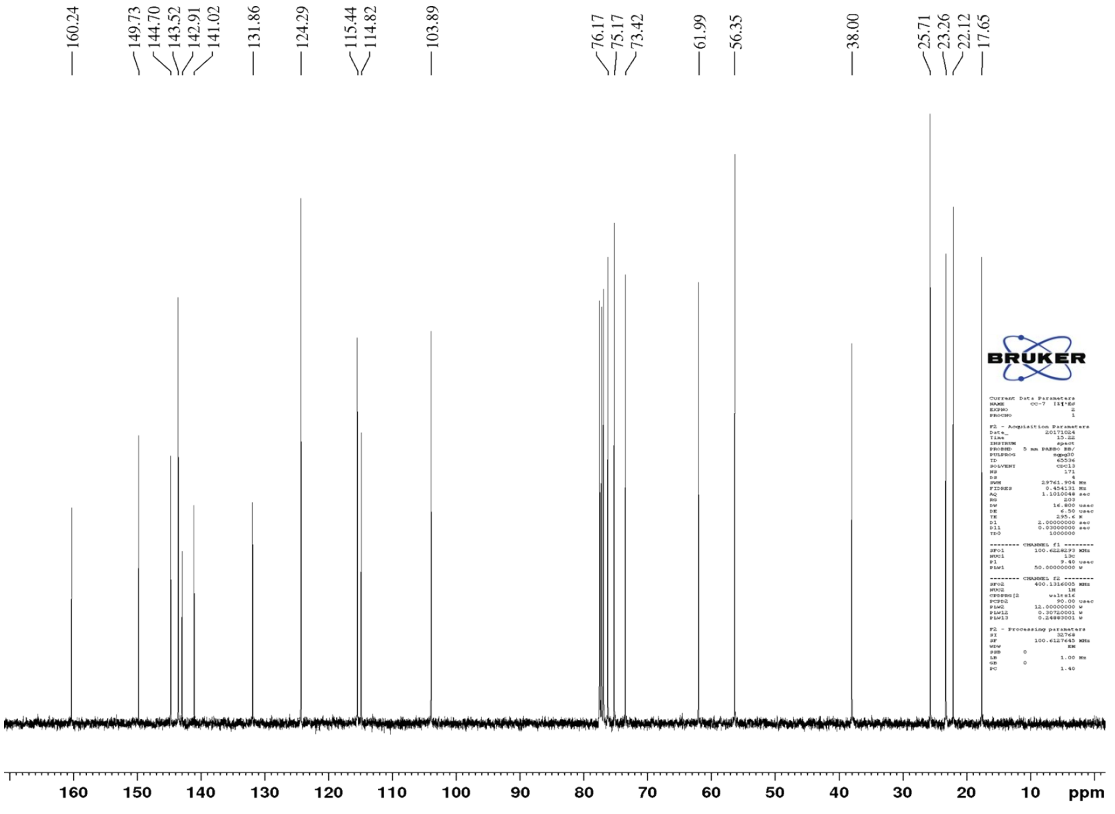

Figure S1.4 ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of compound **1**

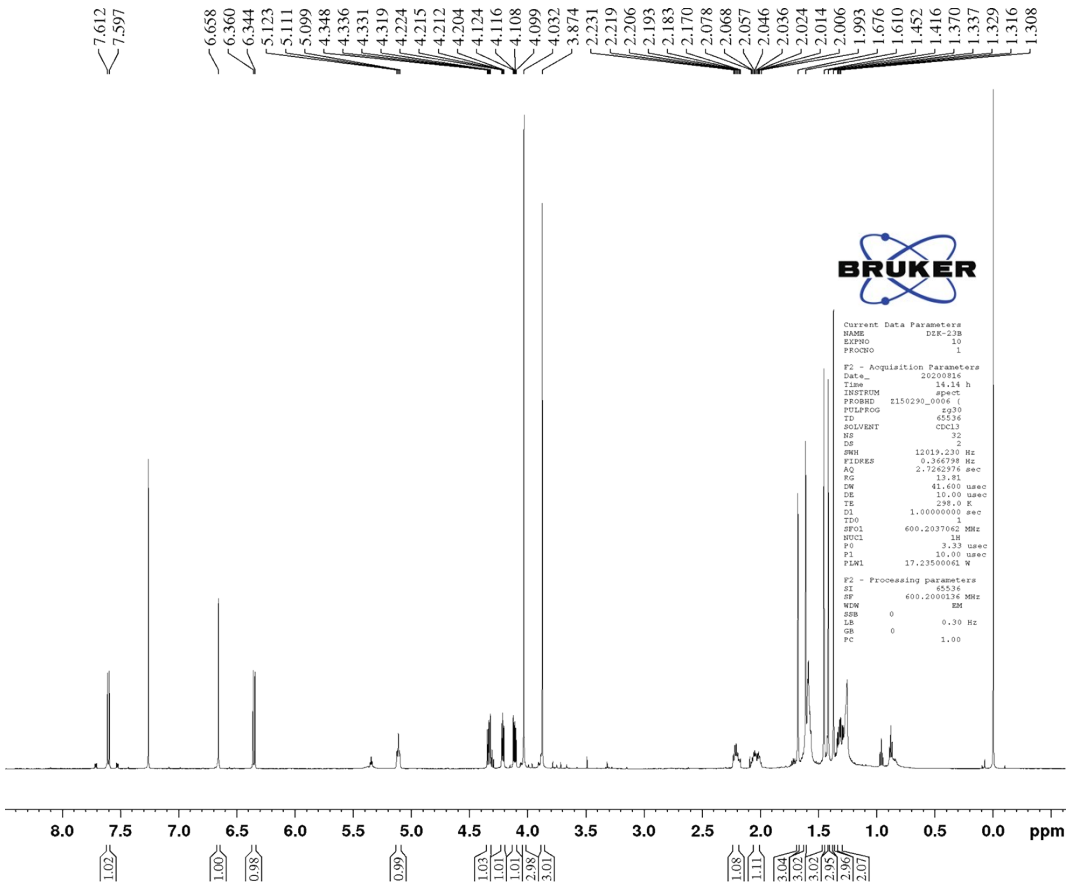

Figure S1.5 ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **1a**

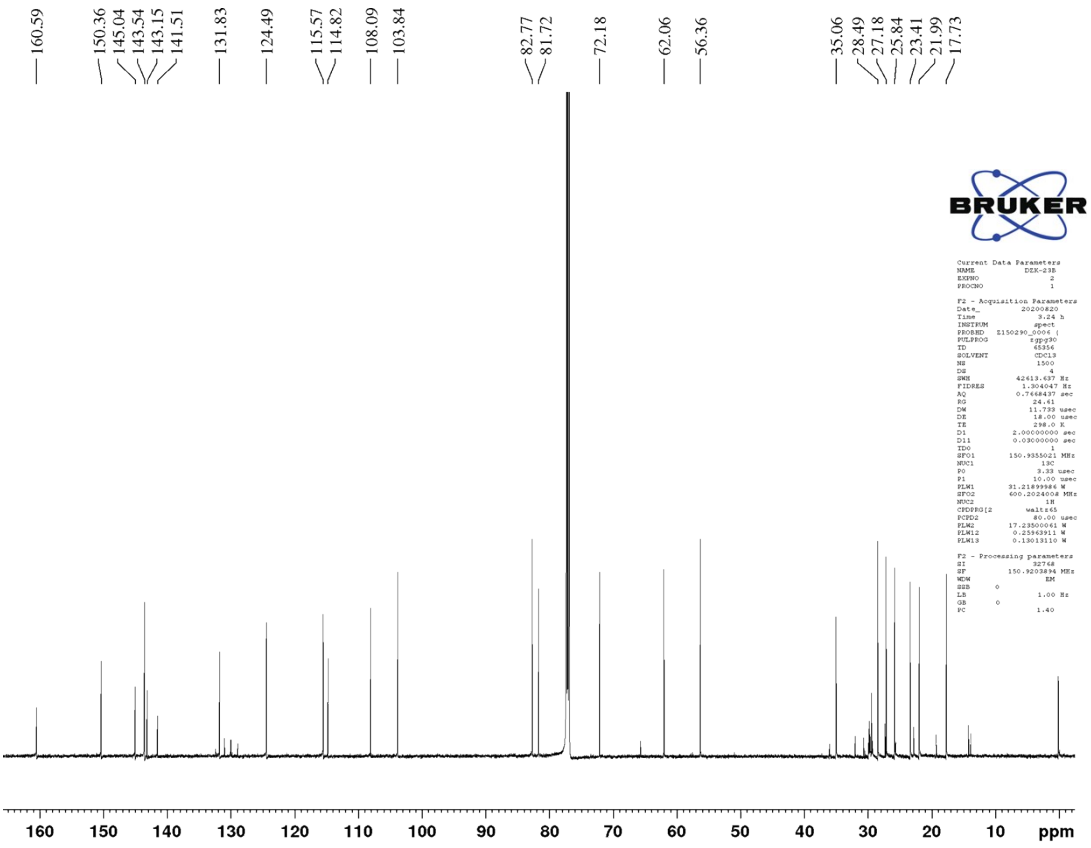

Figure S1.6 ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of compound **1a**

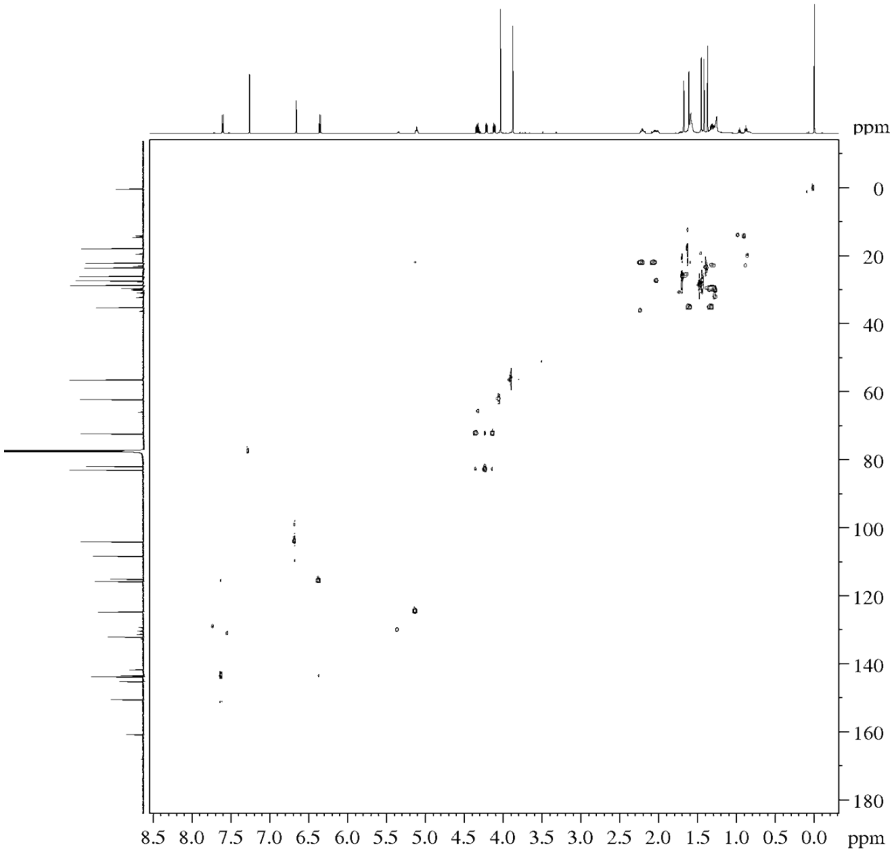

Figure S1.7 HSQC spectrum (600 MHz, $CDCl_3$) of compound **1a**

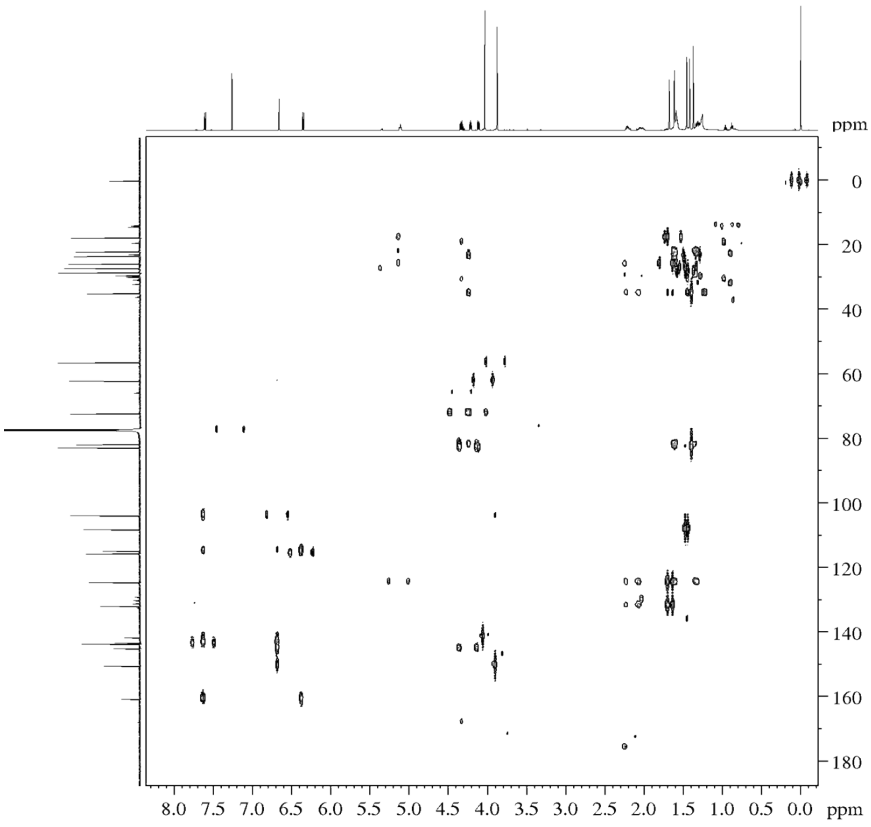

Figure S1.8 HMBC spectrum (600 MHz, $CDCl_3$) of compound **1a**

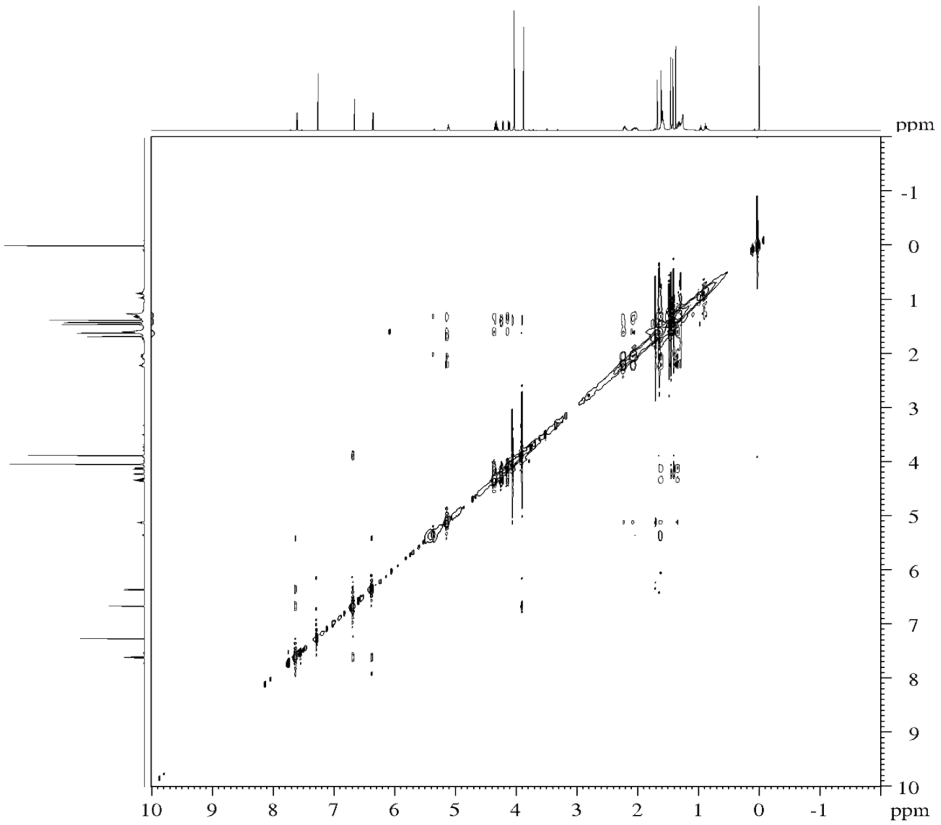

Figure S1.9 NOESY spectrum of compound **1a**

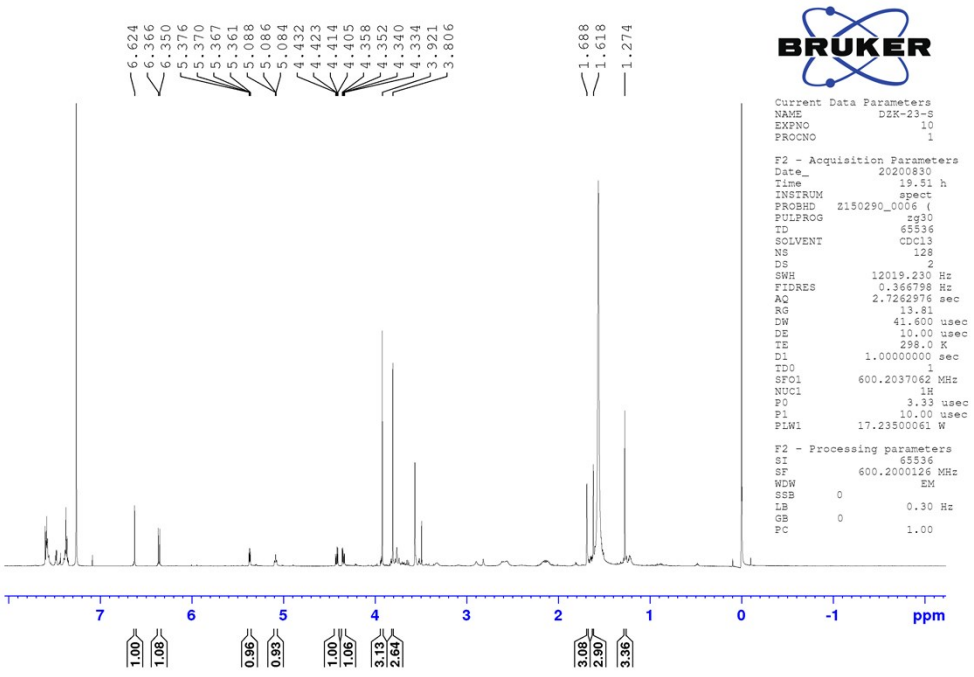

Figure S1.10 ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of (*S*)-MTPA ester derivative of **1**

Figure S1.11 ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of (*R*)-MTPA ester derivative of **1**

Spectrum Peak Pick Report

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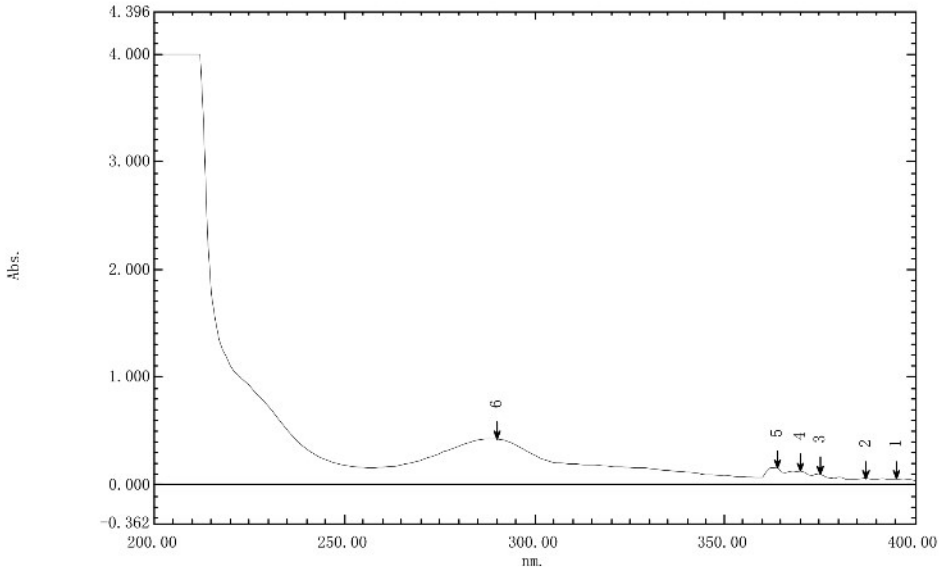

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采样间隔: 1.0
自动采样间隔: 停用
扫描模式: 单一的

试样准备属性
重量:
体积 :
稀释:
光程长:
附加信息:

仪器属性
仪器类型: UV-1700
测定方式: 吸收值
狭缝宽: 1.0 nm
光源改变波长: 360.0 nm
S/R 转换: 标准

附件属性
附件: 无

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10	↓	366.00	.104	
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FIELD TEXT

Figure S2.1 UV spectrum of compound **2**

Mass Spectrum SmartFormula Report

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Sample Name	DZK-25	Instrument / Ser#	micrOTOF-Q 125
Comment			

Acquisition Parameter

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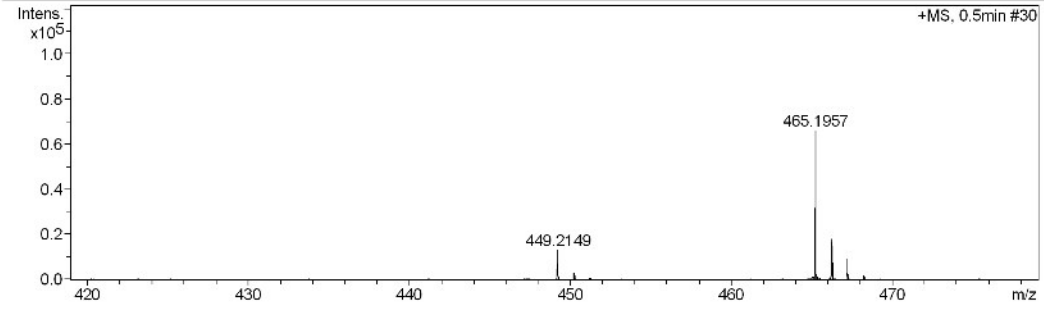

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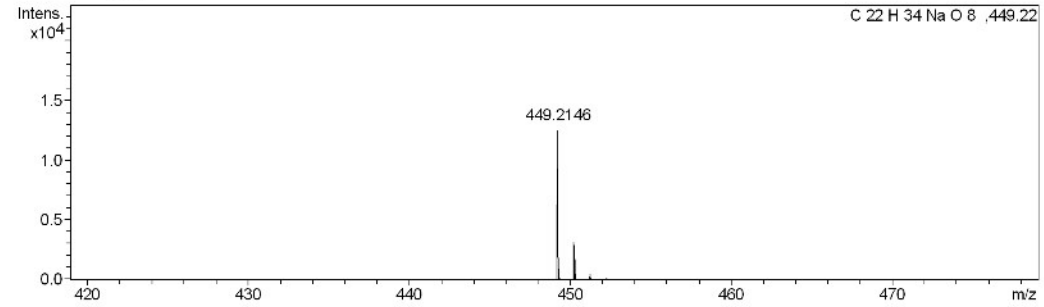

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Figure S2.2 HRESIMS spectrum of compound **2**

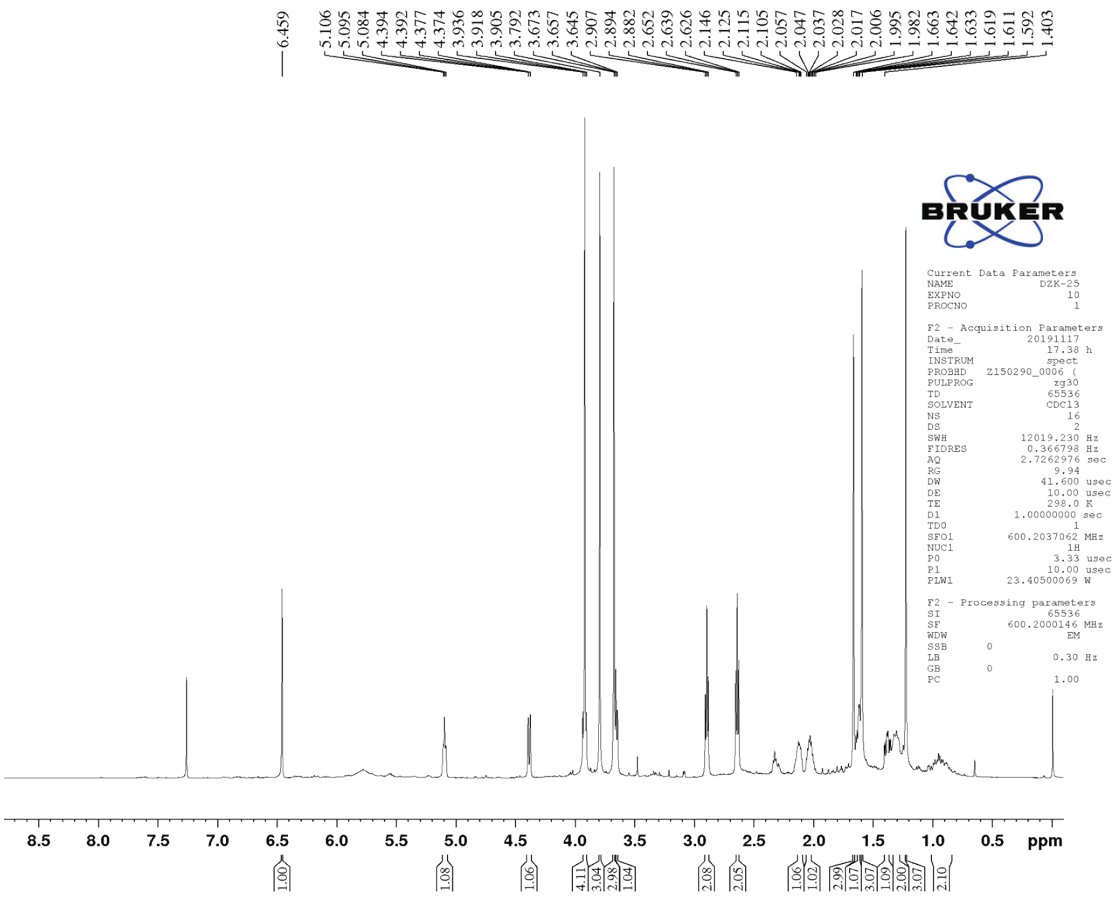

Figure S2.3 ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **2**

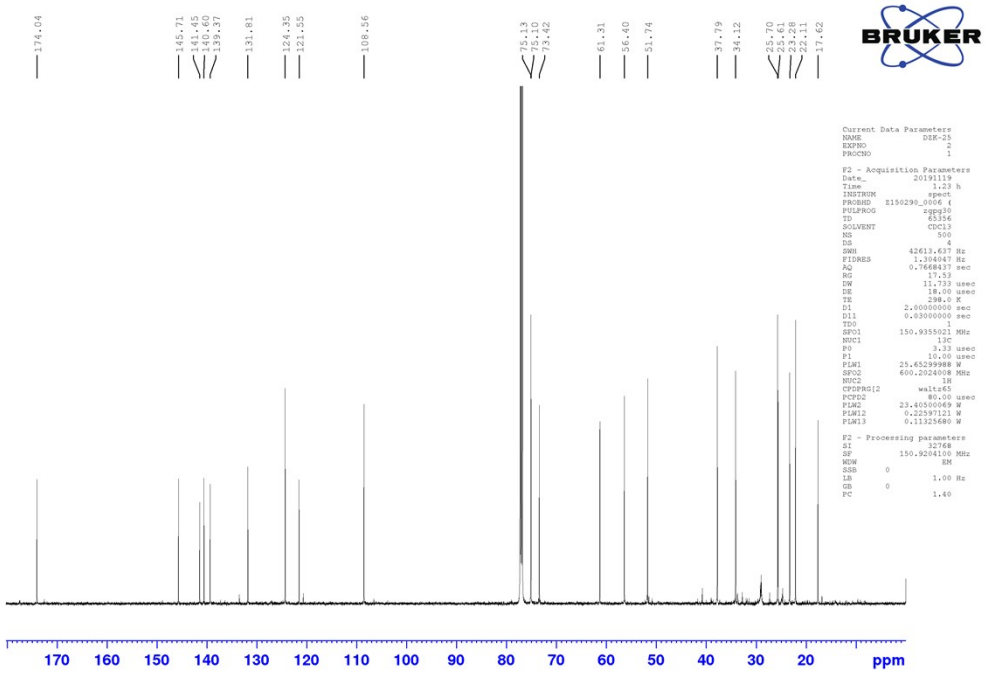

Figure S2.4 ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **2**

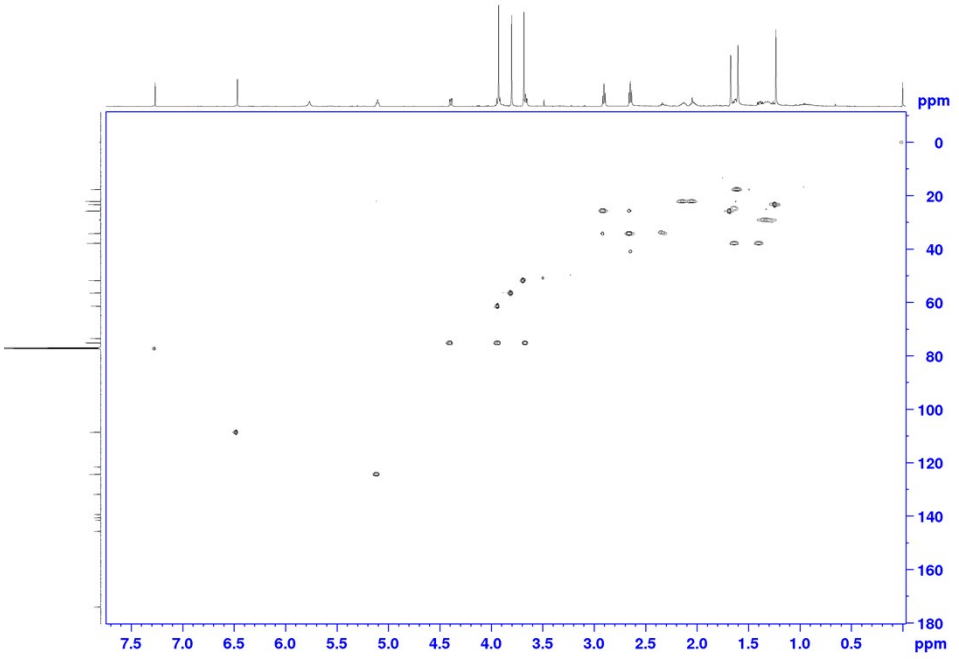

Figure S2.5 HSQC spectrum (600 MHz, $CDCl_3$) of compound **2**

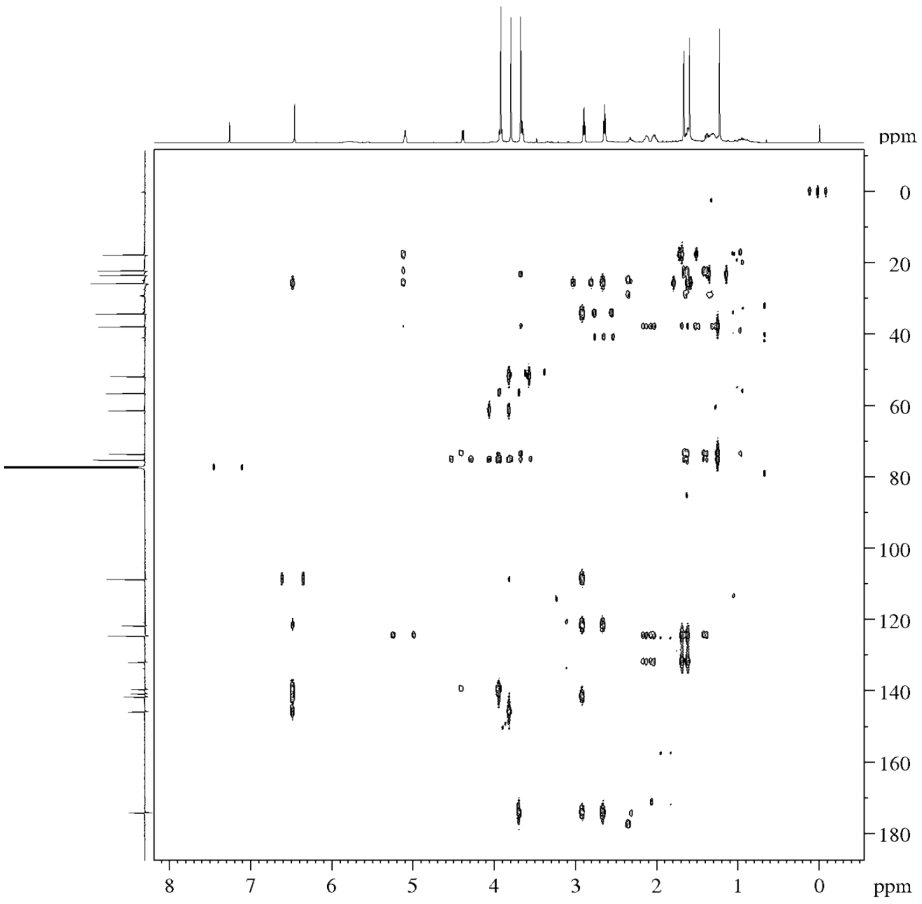

Figure S2.6 HMBC spectrum (600 MHz, $CDCl_3$) of compound **2**

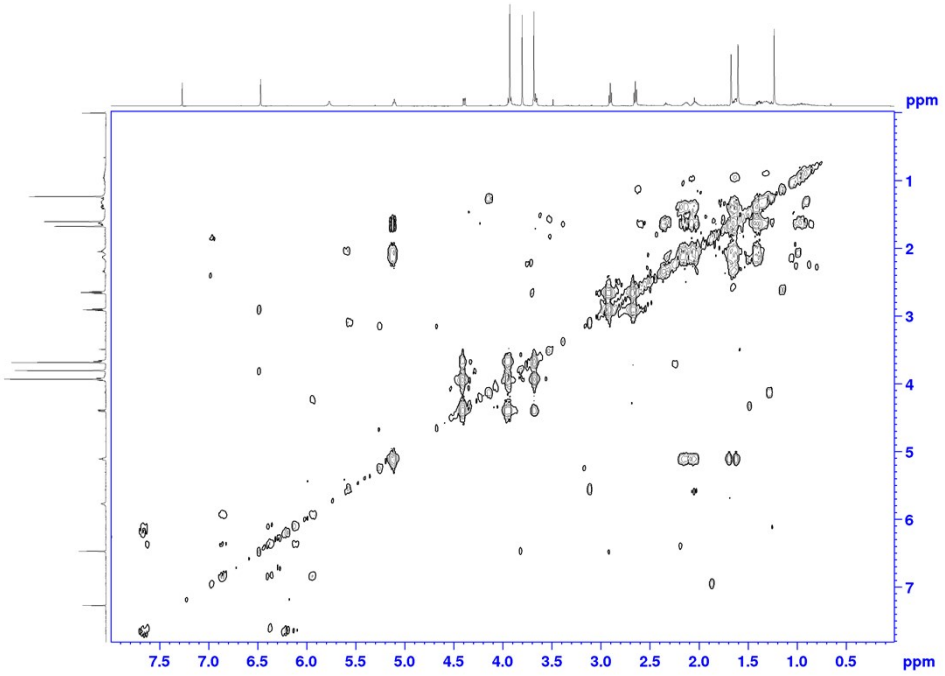

Figure S2.7 ^{1}H-^{1}H COSY spectrum of compound **2**

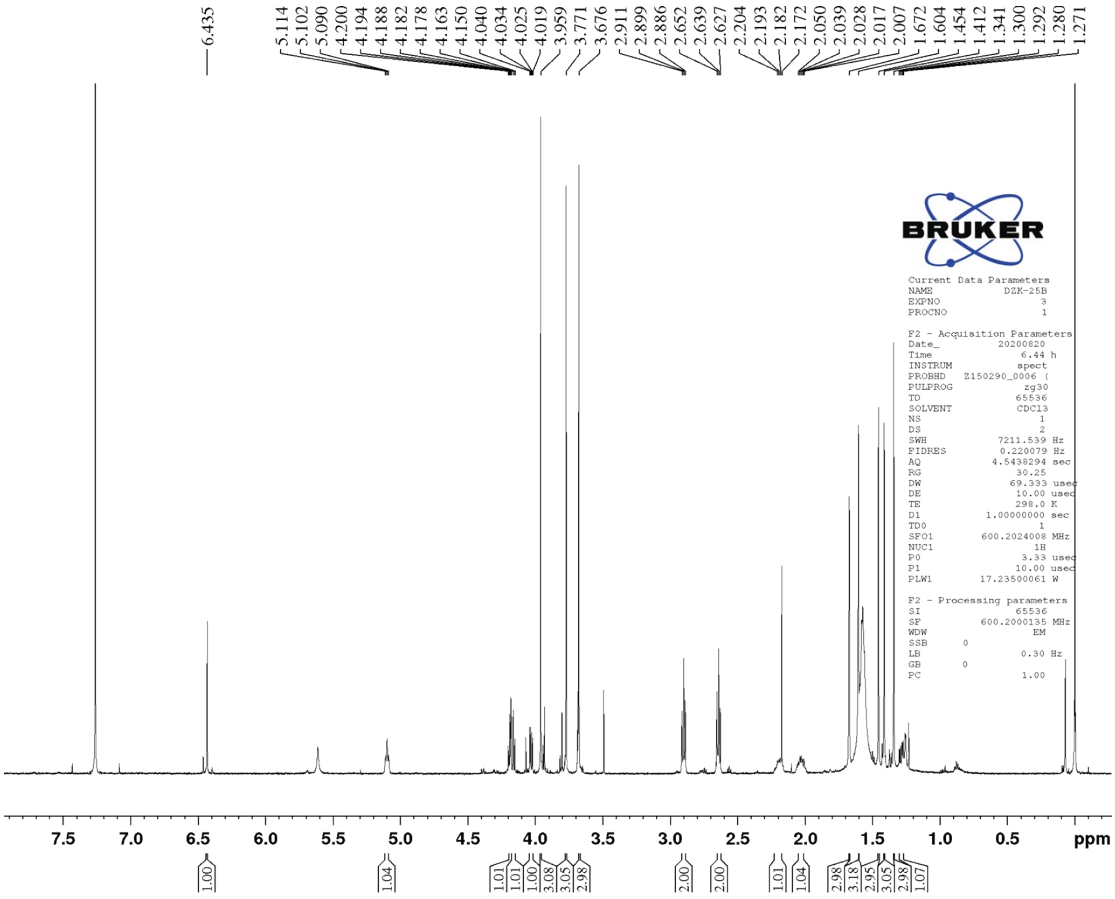

Figure S2.8 ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **2a**

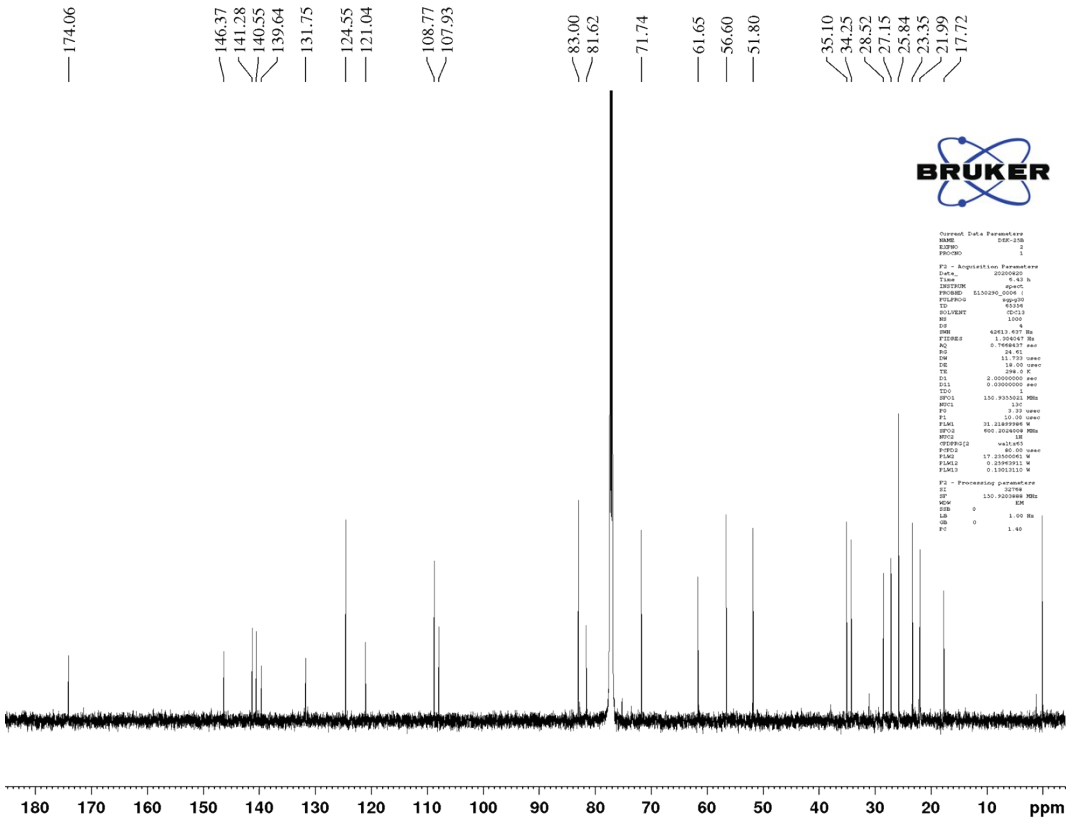

Figure S2.9 ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of compound **2a**

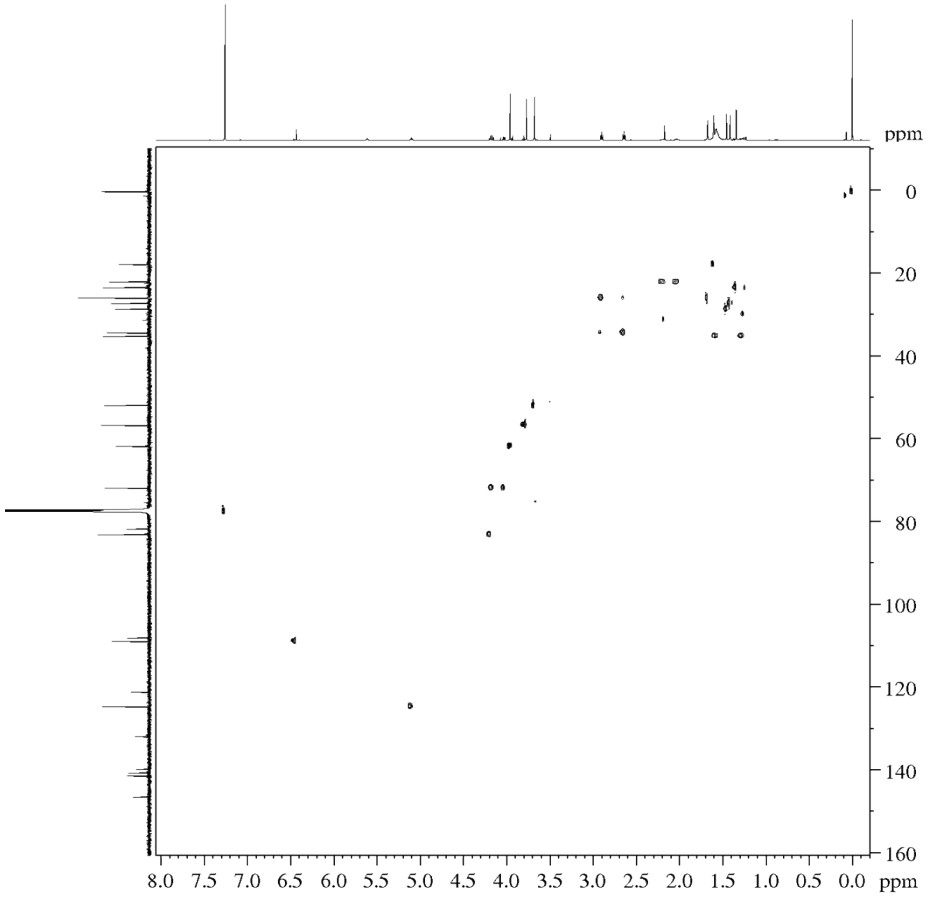

Figure S2.10 HSQC spectrum (600 MHz, $CDCl_3$) of compound **2a**

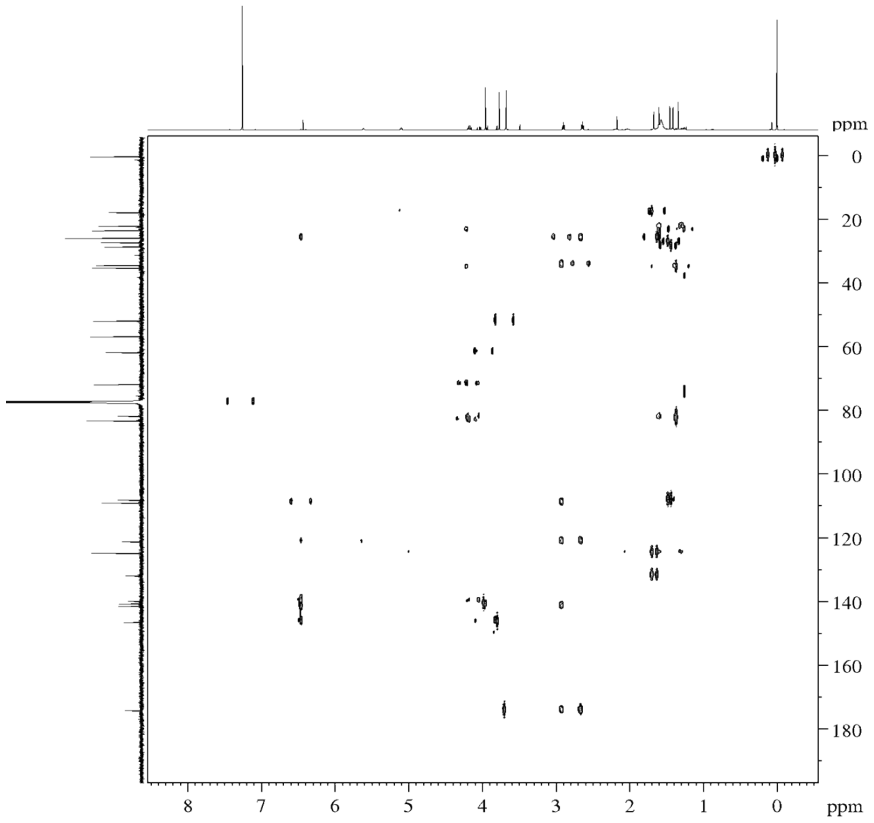

Figure S2.11 HMBC spectrum (600 MHz, $CDCl_3$) of compound **2a**

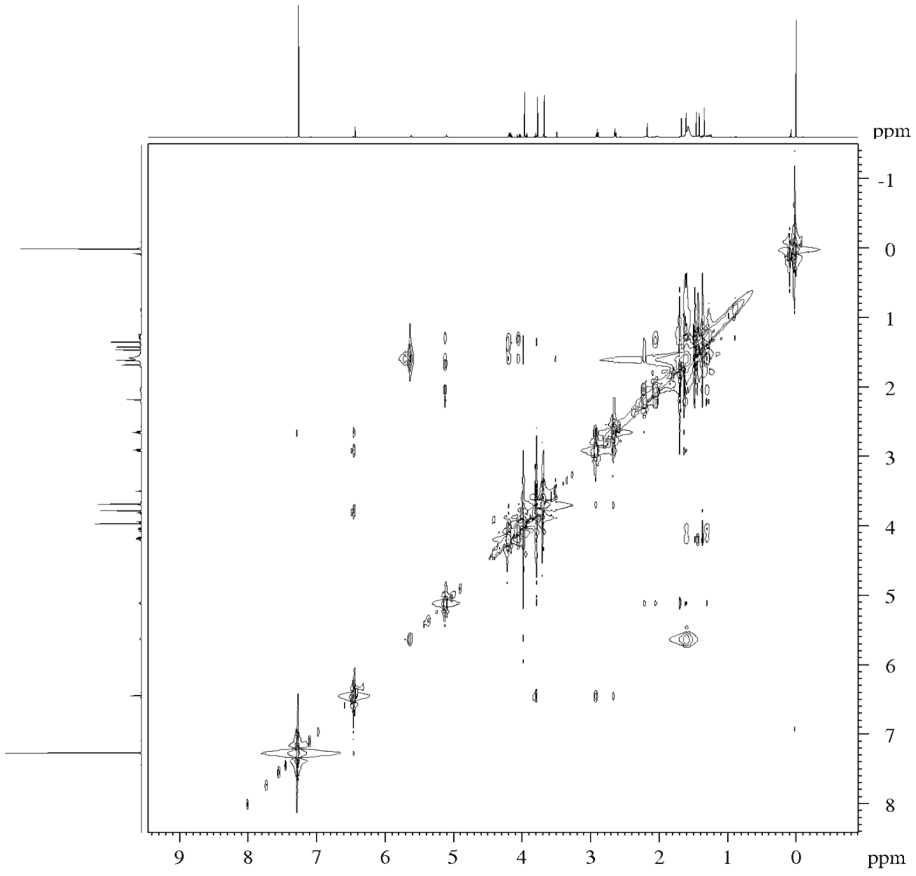

Figure S2.12 NOESY spectrum of compound **2a**

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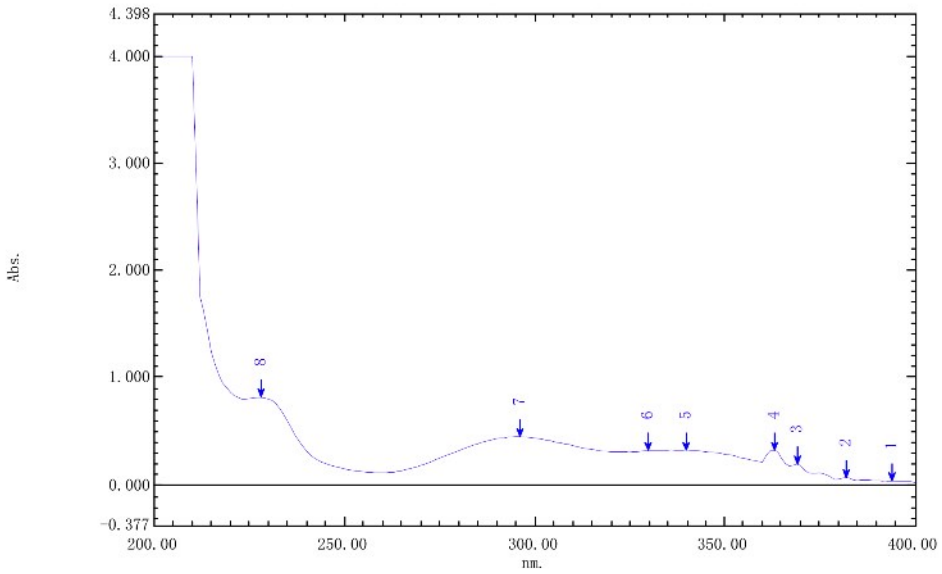

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扫描速度: 中速
采样间隔: 1.0
自动采样间隔: 停用
扫描模式: 单一的

试样准备属性
重量:
体积 :
稀释:
光程长:
附加信息:

仪器属性
仪器类型: UV-1700
测定方式: 吸收值
狭缝宽: 1.0 nm
光源改变波长: 360.0 nm
S/R 转换: 标准

附件属性
附件: 无

No.	P/V	Wavelength	Abs.	描述
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2	↑	382.00	.064	
3	↑	369.00	.193	
4	↑	363.00	.316	
5	↑	340.00	.324	
6	↑	330.00	.317	
7	↑	296.00	.448	
8	↑	228.00	.816	
9	↓	392.00	.026	
10	↓	379.00	.046	
11	↓	367.00	.177	
12	↓	360.00	.210	
13	↓	332.00	.317	
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15	↓	260.00	.112	
16	↓	224.00	.799	

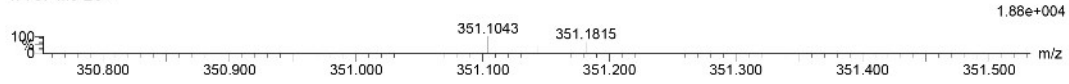
FIELD TEXT

Fig. S3.1 UV spectrum of compound **3**

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
32 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 18-21 H: 0-50 O: 0-8 S: 0-1
DZK-27 68 (0.398) Cm (68)
1: TOF MS ES+



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Maximum:		20.0	10.0	50.0				
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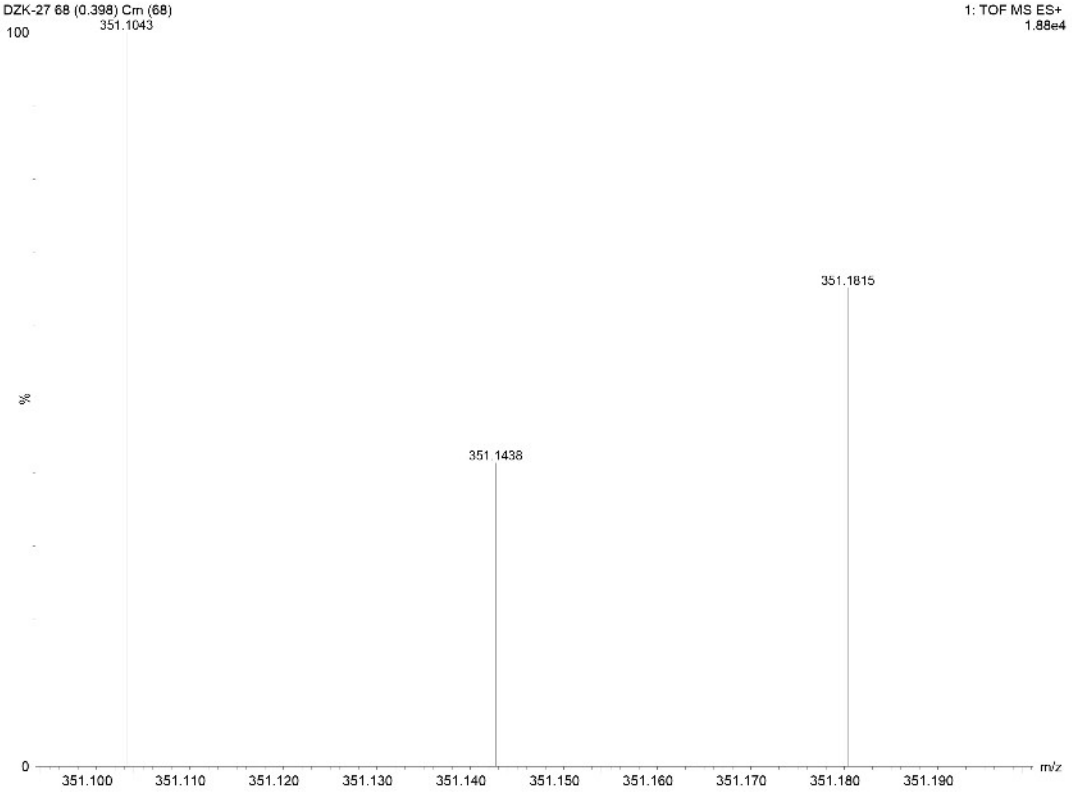

Fig. S3.2 HRESIMS spectrum of compound **3**

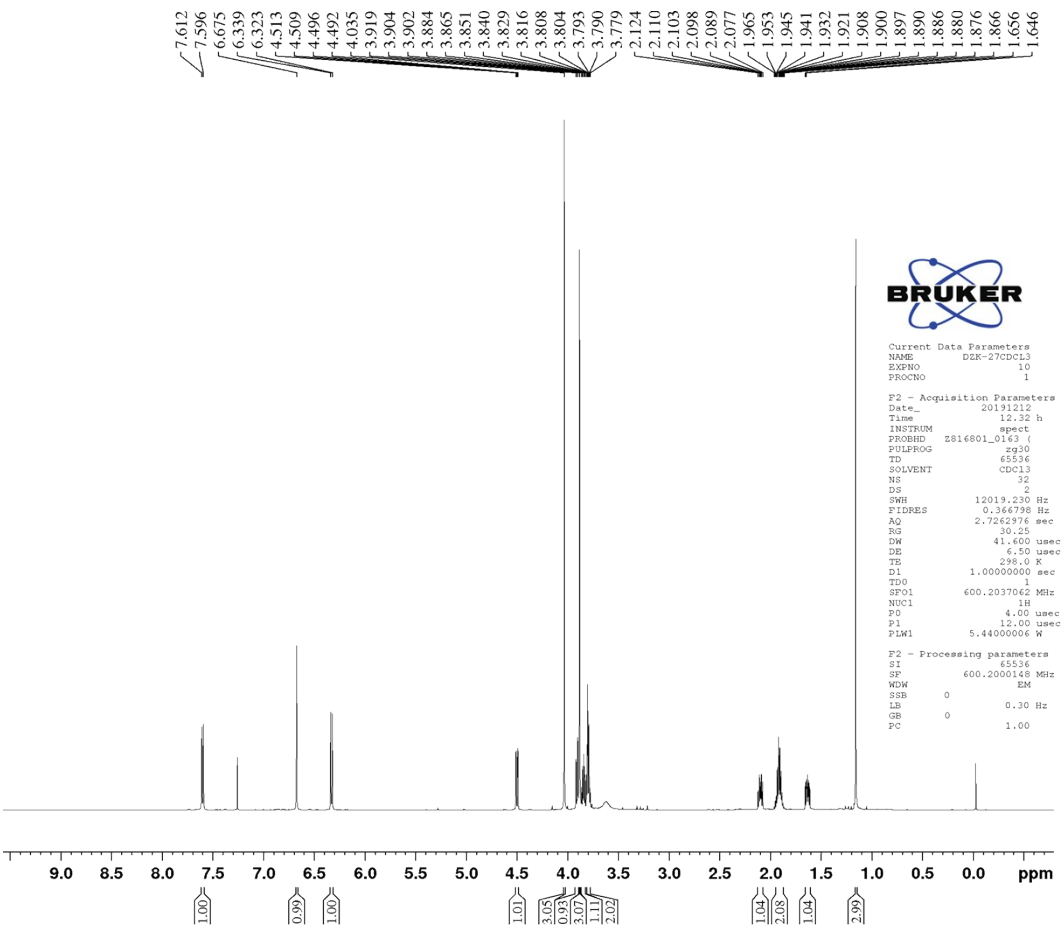

Fig. S3.3 ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **3**

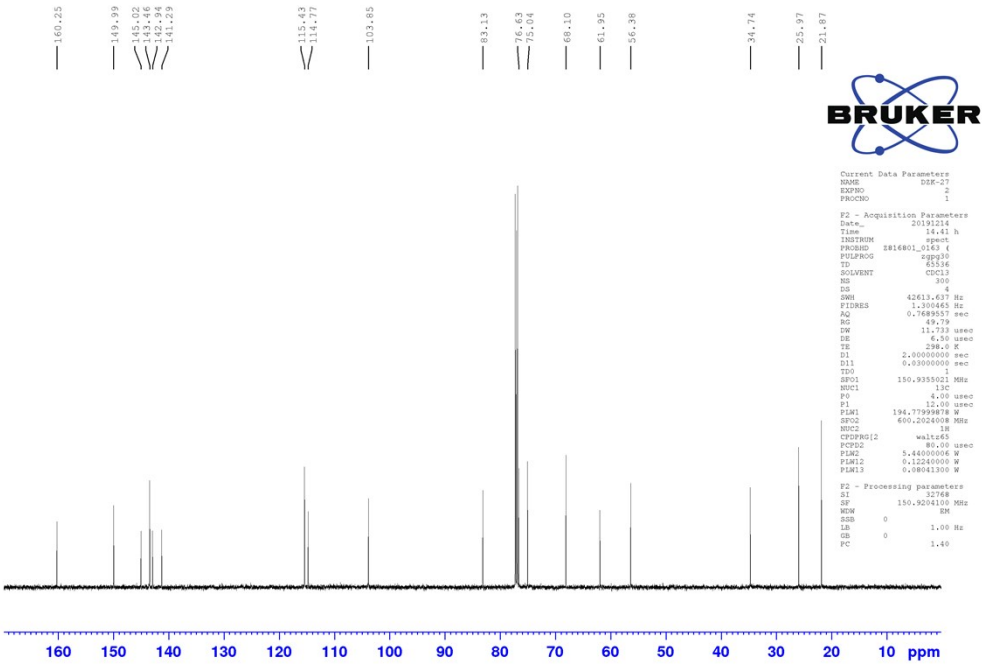

Figure S3.4 ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of compound **3**

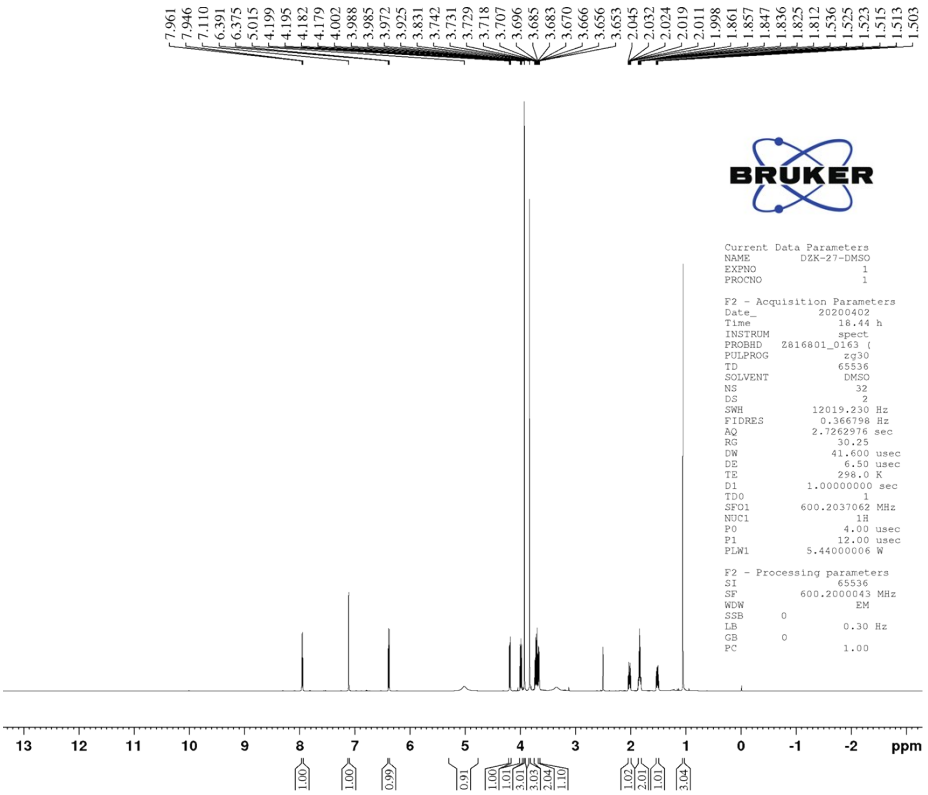

Fig. S3.5 ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of compound **3**

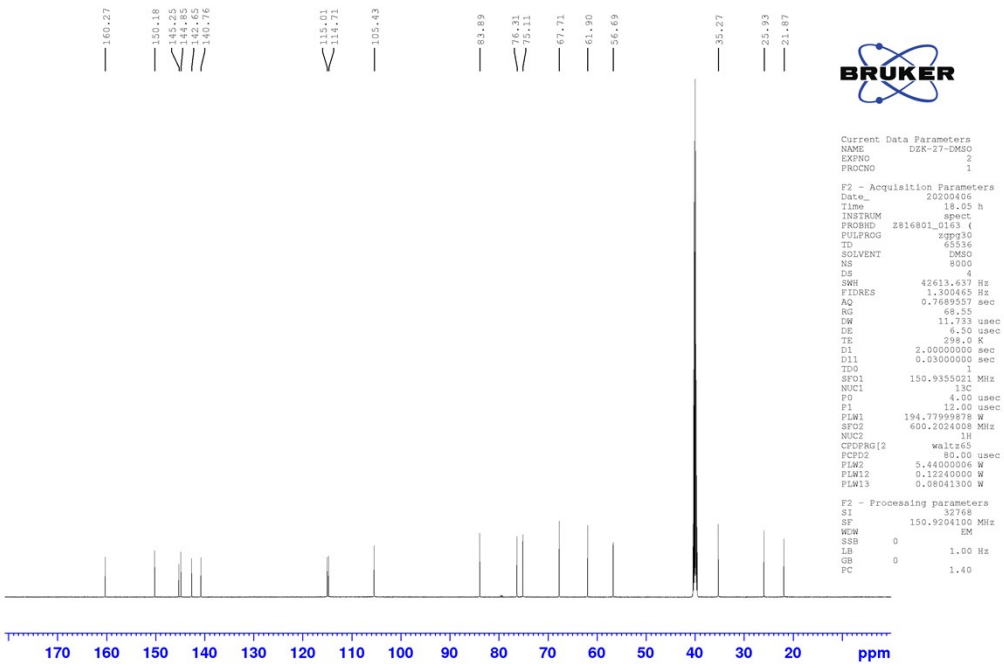

Figure S3.6 ^{13}C NMR spectrum (150 MHz, DMSO-d_6) of compound **3**

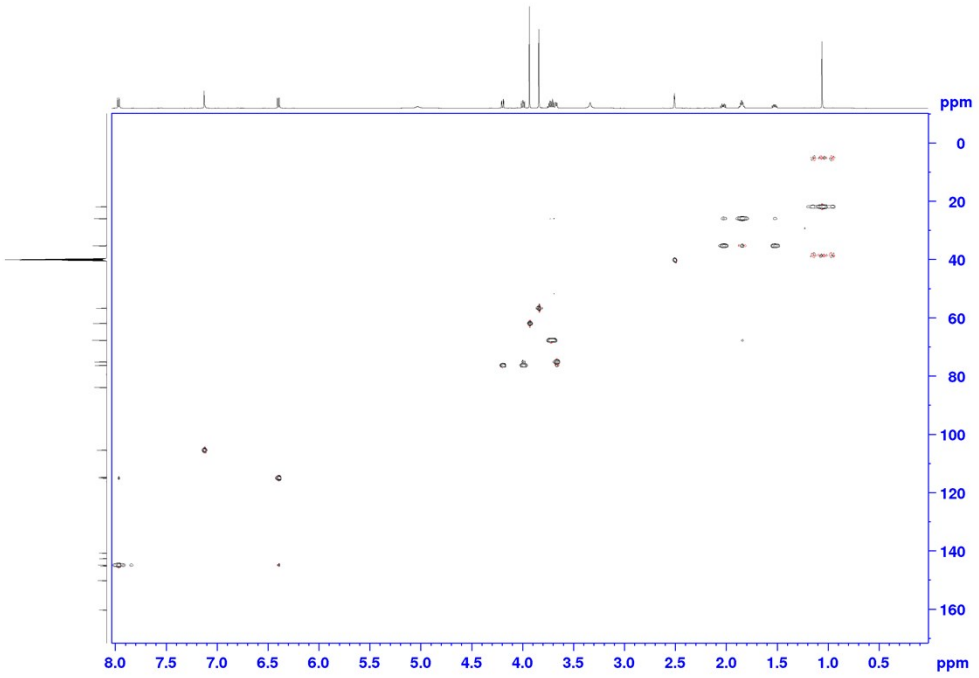

Figure S3.7 HSQC spectrum (150 MHz, DMSO-d_6) of compound **3**

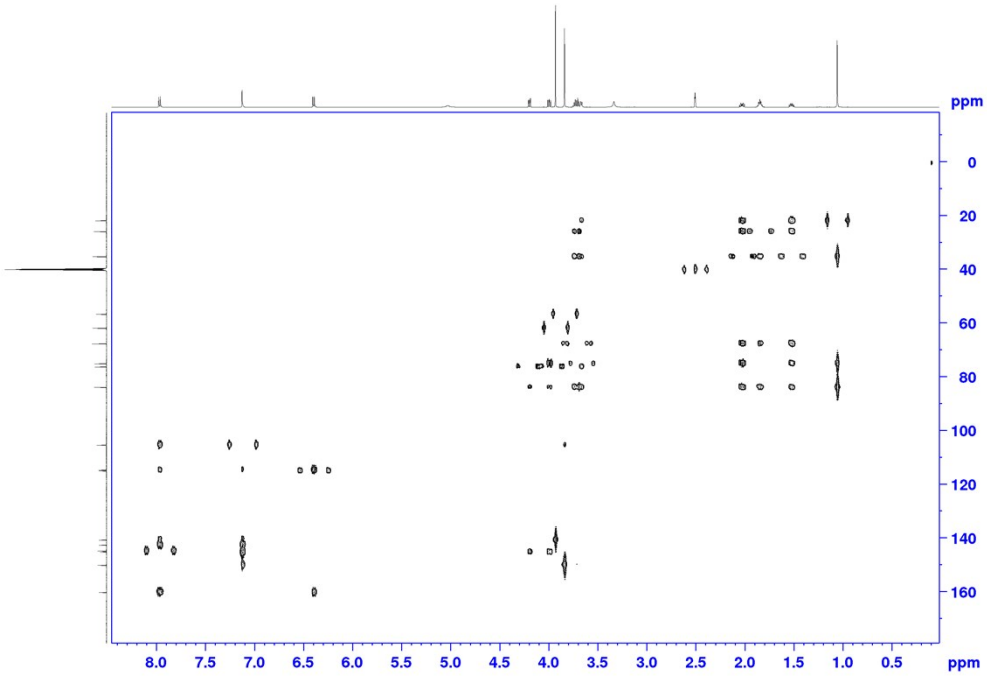

Figure S3.8 HMBC spectrum (150 MHz, DMSO-d_6) of compound **3**

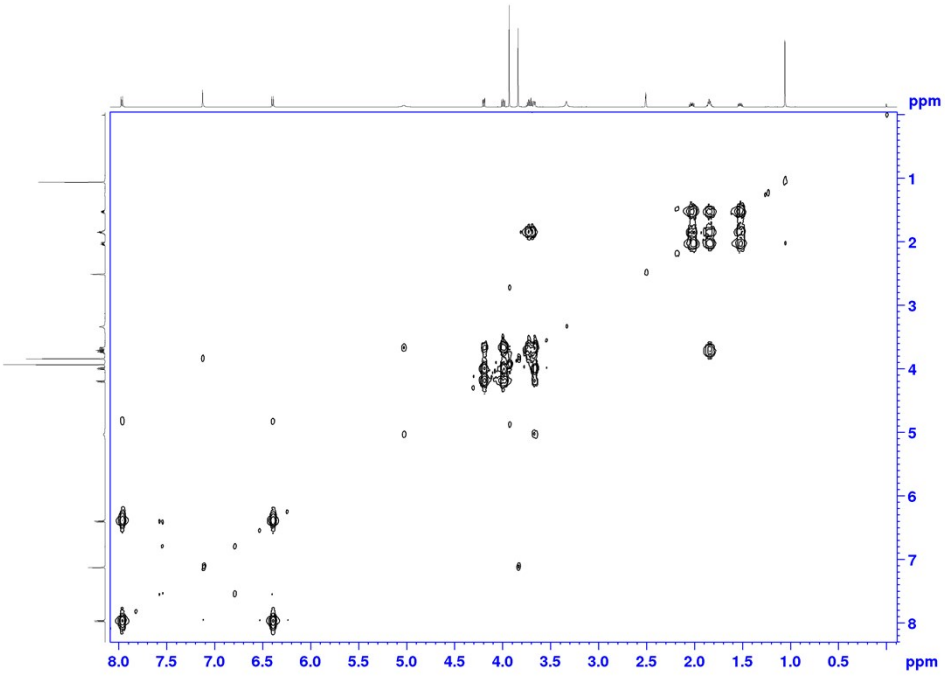

Figure S3.9 ^{1}H-^{1}H COSY spectrum (150 MHz, DMSO-d_6) of compound **3**

Functional	Solvent?	Basis Set	Type of Data
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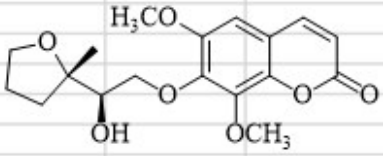
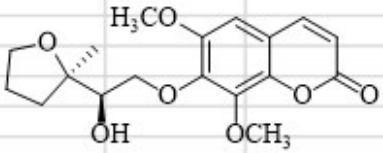
		DP4+	0.00%	100.00%	-	-	-
Nuclei	sp2?	xperiment	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5
C	x	159.8	174.9	175.0			
C	x	149.7	166.9339	166.8152			
C	x	144.8	165.0869	165.538			
C	x	144.4	161.9222	162.3606			
C	x	142.2	160.6986	160.8472			
C	x	140.3	157.1928	157.062			
C	x	114.5	129.9657	130.2141			
C	x	114.2	128.0281	127.9499			
C	x	105	117.0567	117.2583			
C		83.4	99.09457	99.06178			
C		75.8	94.1119	93.78059			
C		74.6	90.2547	90.61629			
C		67.2	82.1649	82.16784			
C		61.5	71.7203	71.58025			
C		56.2	65.71487	65.73771			
C		34.8	50.07366	45.83079			
C		25.5	39.66333	40.18812			
C		21.4	31.46886	36.3597			
H	x	7.6	7.71836	7.73361			
H	x	6.67	6.69335	6.65221			
H	x	6.33	6.104	6.14962			
H		4.5	4.91778	4.91059			
H		4.03	4.47103	4.40674			
H		4.03	4.26026	4.18832			
H		4.03	4.07224	4.06286			
H		3.91	4.06789	3.97103			
H		3.88	3.85228	3.92898			
H		3.88	3.7734	3.89182			
H		3.88	3.7704	3.81882			
H		3.84	3.7623	3.76351			
H		3.8	3.73329	3.66965			
H		3.8	3.63924	3.63044			
H		2.1	3.41419	3.41201			
H		1.91	2.08571	2.11019			
H		1.63	1.78198	1.72141			
H		1.16	1.77546	1.71433			
H		1.16	1.57957	1.41128			
H		1.16	1.25057	1.35528			
H		1.05	0.77683	1.06572			
H		1.05	0.75846	1.05783			



3A (Isomer 1)



3B (Isomer 2)

Figure S3.10 Results of DP4+ analysis of compound **3**

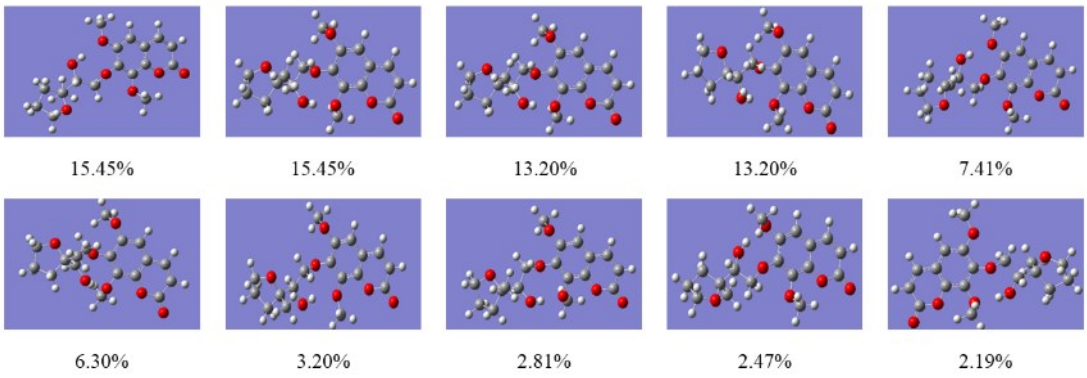


Figure S3.11 The low-energy conformers of the **3a**

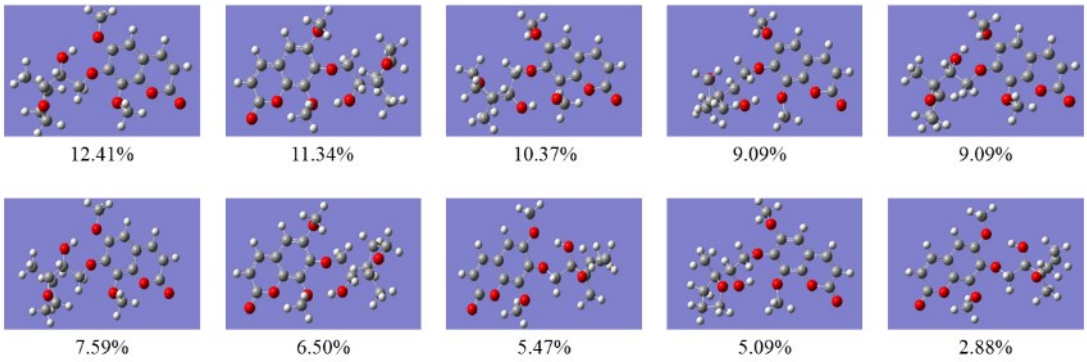


Figure S3.12 The low-energy conformers of the **3b**

Spectrum Peak Pick Report

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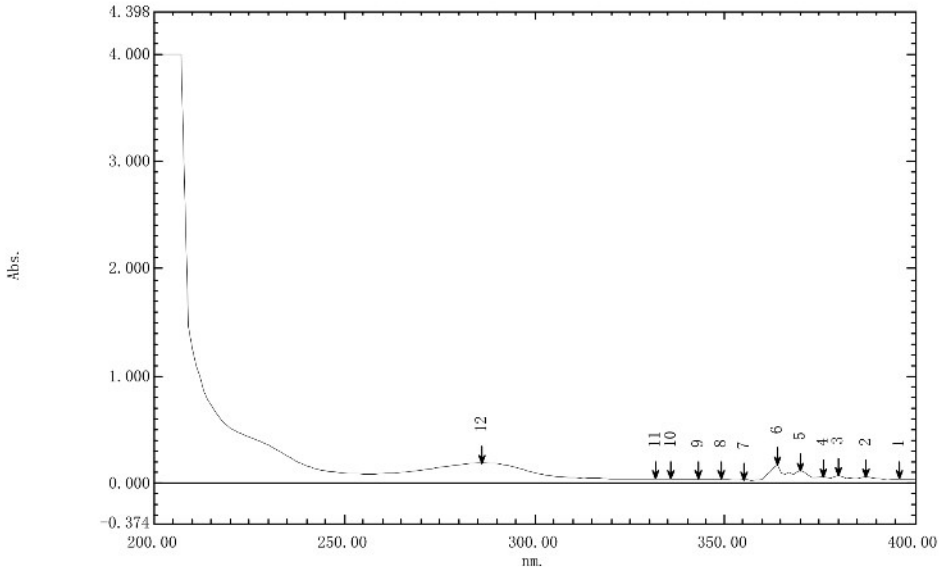

测定属性
波长范围 (nm.): 200.00到400.00
扫描速度: 中速
采样间隔: 1.0
自动采样间隔: 停用
扫描模式: 单一的

试样准备属性
重量:
体积 :
稀释:
光程长:
附加信息:

仪器属性
仪器类型: UV-1700
测定方式: 吸收值
狭缝宽: 1.0 nm
光源改变波长: 360.0 nm
S/R 转换: 标准

附件属性
附件: 无

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3	↑	380.00	.066	
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5	↑	370.00	.116	
6	↑	364.00	.167	
7	↑	355.00	.030	
8	↑	349.00	.033	
9	↑	343.00	.034	
10	↑	336.00	.036	
11	↑	332.00	.037	
12	↑	286.00	.187	
13	↓	393.00	.025	
14	↓	385.00	.039	
15	↓	378.00	.046	
16	↓	374.00	.047	
17	↓	368.00	.078	
18	↓	357.00	.023	
19	↓	353.00	.027	
20	↓	346.00	.030	
21	↓	338.00	.030	
22	↓	334.00	.035	
23	↓	327.00	.035	
24	↓	256.00	.083	

FIELD TEXT

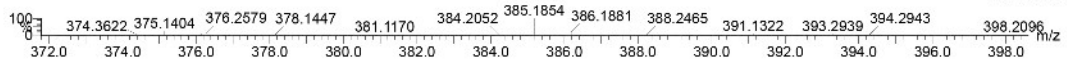
Fig. S4.1 UV spectrum of compound **4**

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
9 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 19-19 H: 0-50 O: 0-8

DZK-36 75 (0.434)
1: TOF MS ES+
8.74e+005



Minimum:				-1.5				
Maximum:		20.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
385.1854	385.1862	-0.8	-2.1	5.5	890.9	n/a	n/a	C19 H29 O8

DZK-36 75 (0.434)
100
385.1854
1: TOF MS ES+
8.74e5

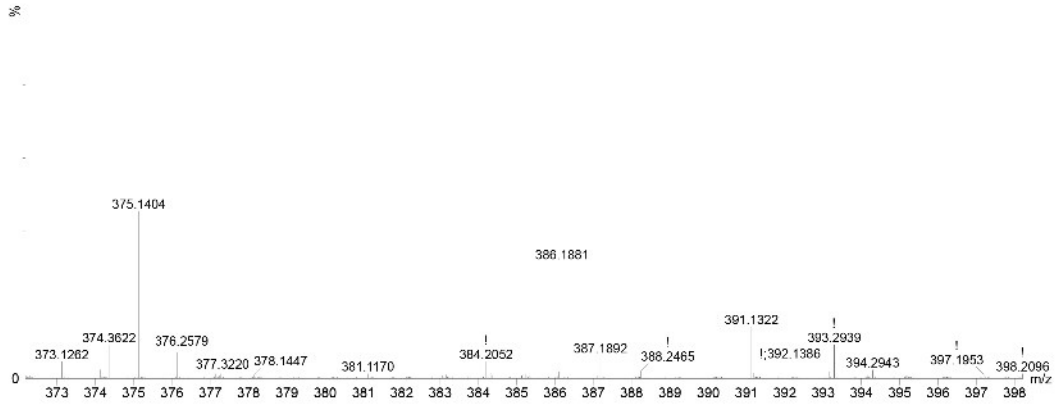


Fig. S4.2 HRESIMS spectrum of compound **4**

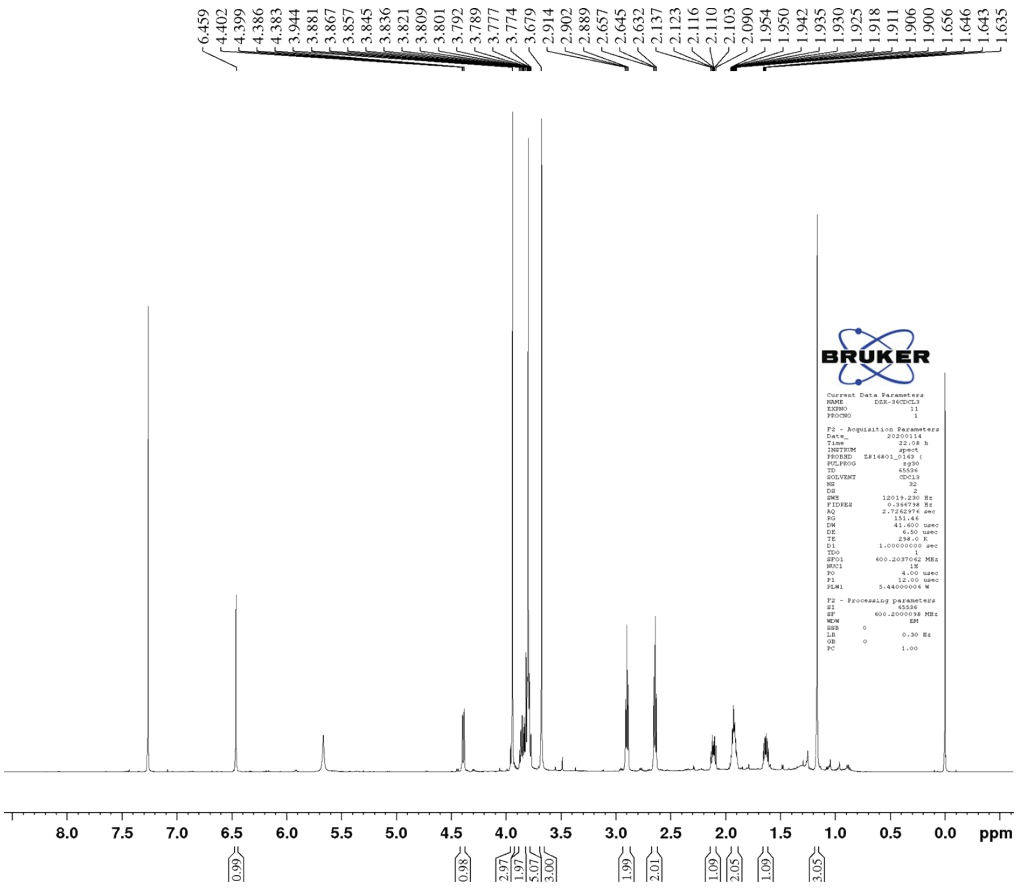


Fig. S4.3 ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **4**

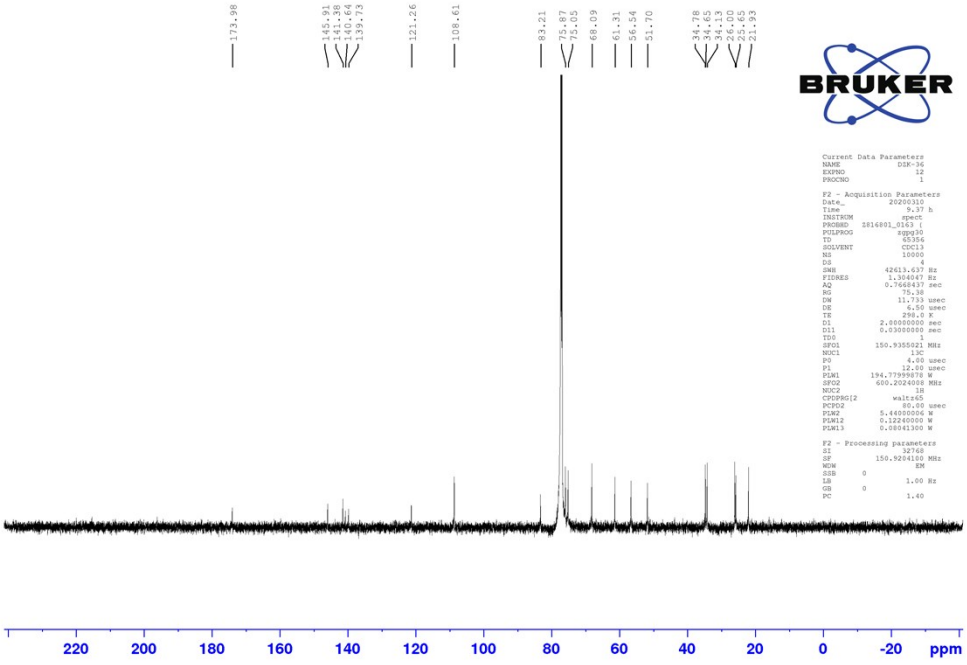


Figure S4.4 ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **4**

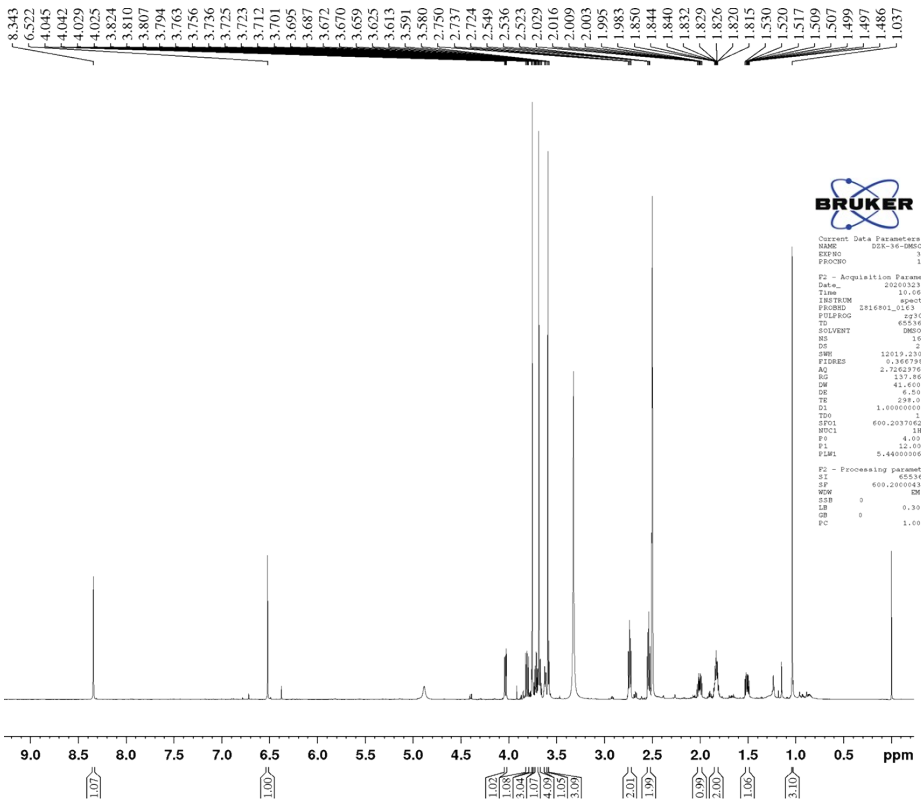


Figure S4.5 ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of compound **4**

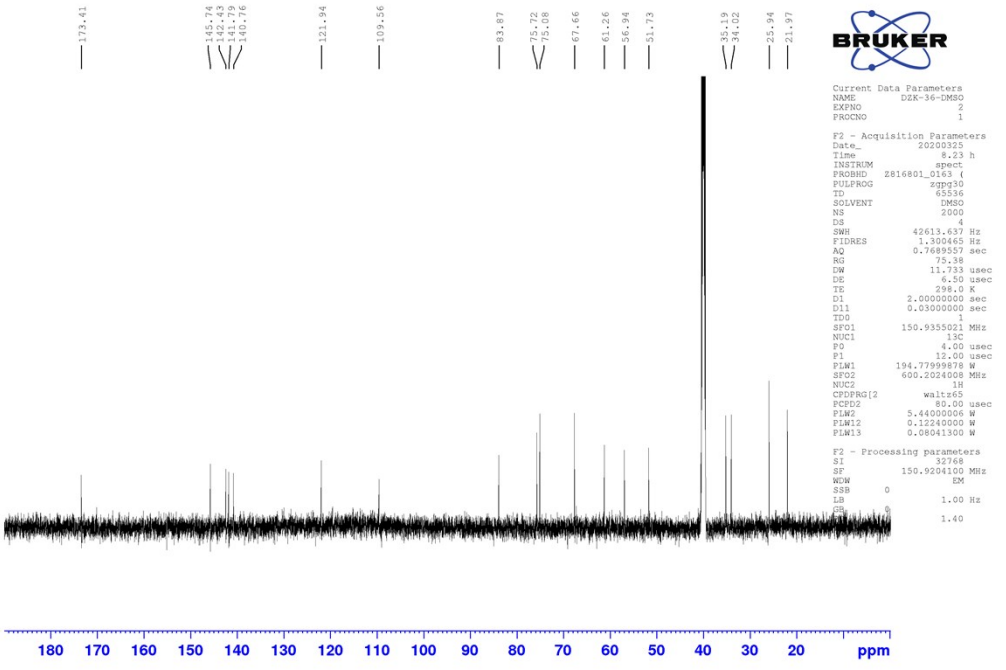


Figure S4.6 ^{13}C NMR spectrum (150 MHz, DMSO-d_6) of compound **4**

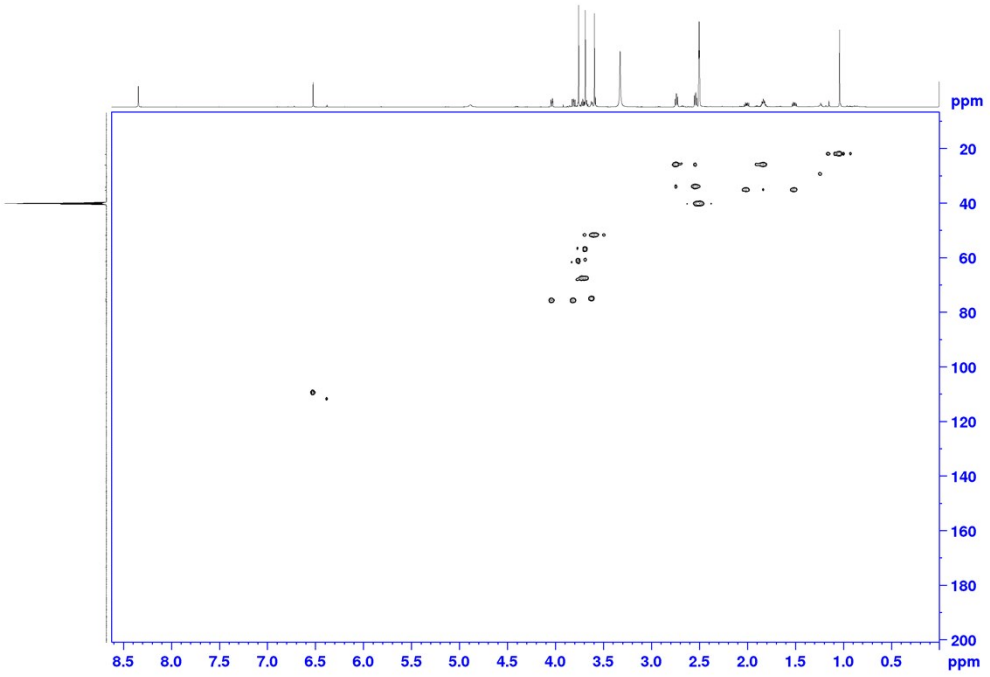


Figure S4.7 HSQC spectrum (600 MHz, DMSO-d_6) of compound **4**

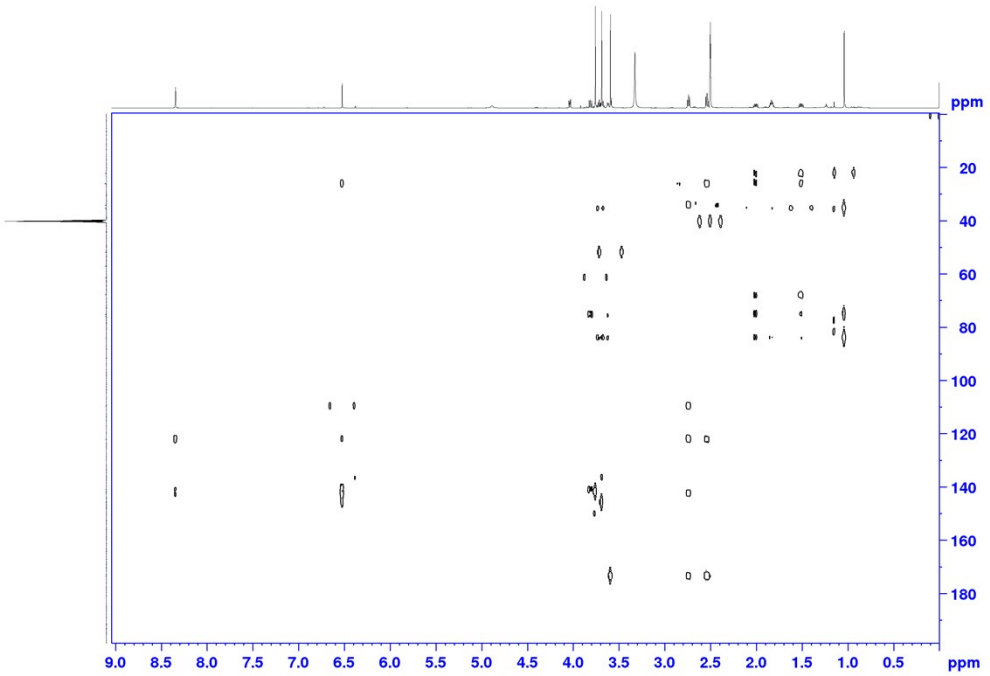


Figure S4.8 HMBC spectrum (600 MHz, DMSO-d_6) of compound **4**

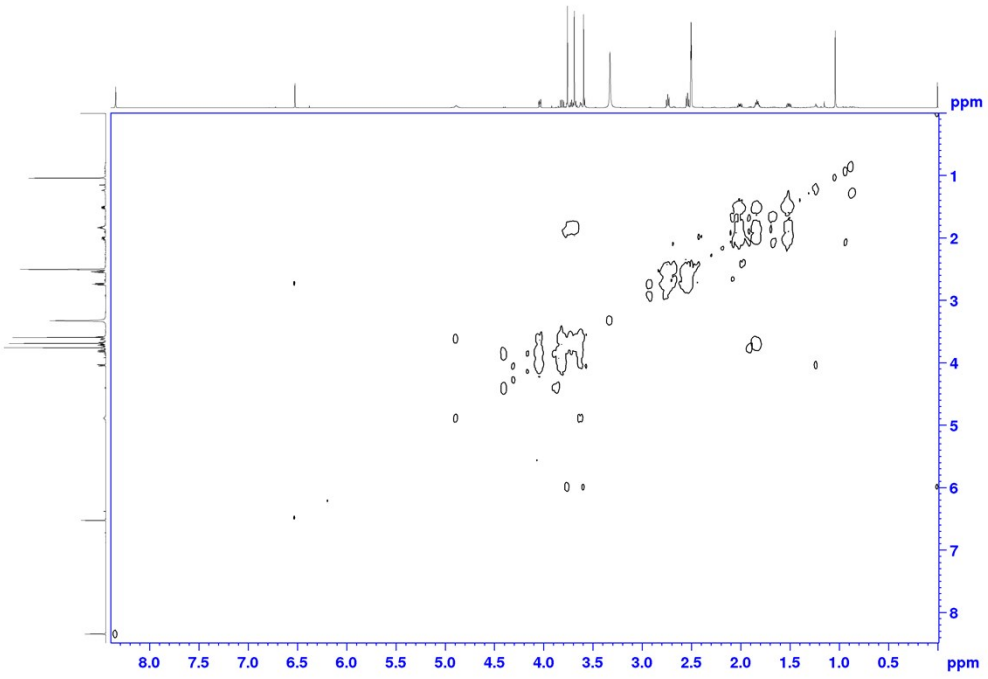
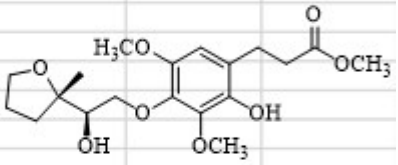
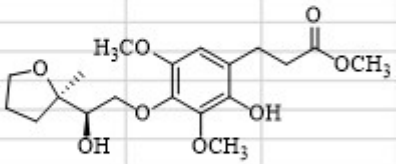


Figure S4.9 ^{1}H-^{1}H COSY spectrum (600 MHz, DMSO-d_6) of compound **4**

Functional	Solvent?	Basis Set	Type of Data		
B3LYP	PCM	6-311+G(d,p)	Unscaled Shifts		
	DP4+	0.00%	100.00%	-	-	-
Nuclei	sp2?	Experimental	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5
C	x	174.11	192.8	192.8			
C	x	146.03	170.3584	170.327			
C	x	141.51	169.7085	169.955			
C	x	140.77	154.619	154.6937			
C	x	139.87	153.0821	152.4927			
C	x	121.86	117.4827	118.114			
C	x	108.74	117.4639	117.2879			
C		83.35	98.76766	96.6766			
C		76	92.9867	89.6866			
C		75.18	90.19046	90.36065			
C		68.22	82.02282	81.98159			
C		61.45	65.53452	65.4296			
C		56.67	65.37688	65.2725			
C		51.84	63.01482	62.95871			
C		34.78	50.67735	50.53293			
C		34.26	50.28783	46.36262			
C		26.13	44.61705	44.52254			
C		25.78	39.707	40.63714			
C		22.07	31.35834	36.37506			
H	x	6.46	6.49893	6.54602			
H		4.39	4.8662	4.88804			
H		3.94	4.41917	4.37661			
H		3.94	4.05364	4.04149			
H		3.94	3.9679	3.93475			
H		3.85	3.8398	3.84429			
H		3.8	3.74739	3.73117			
H		3.8	3.71874	3.70427			
H		3.8	3.71593	3.67153			
H		3.8	3.67508	3.64635			
H		3.78	3.61909	3.63119			
H		3.68	3.61204	3.61104			
H		3.68	3.6088	3.60252			
H		3.68	3.59345	3.5944			
H		2.9	3.45283	3.44383			
H		2.9	2.95583	3.03333			
H		2.64	2.65457	2.68096			
H		2.64	2.61478	2.5945			
H		2.11	2.45723	2.46365			
H		1.93	2.44626	2.43119			
H		1.93	2.02228	2.03543			
H		1.64	1.78861	1.75635			
H		1.16	1.77864	1.64419			
H		1.16	1.61697	1.48514			
H		1.16	1.31765	1.35825			



4A (Isomer 1)



4B (Isomer 2)

Figure S4.10 Results of DP4+ analysis of compound **4**

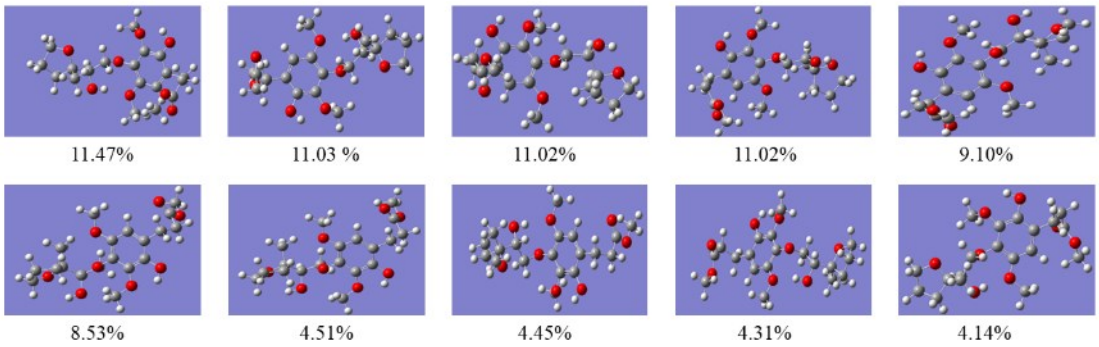


Figure S4.11 The low-energy conformers of the **4a**

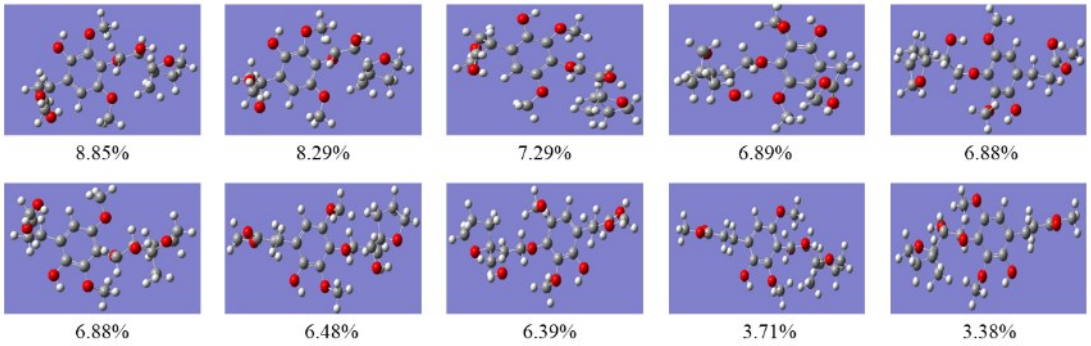


Figure S4.12 The low-energy conformers of the **4b**

Spectrum Peak Pick Report

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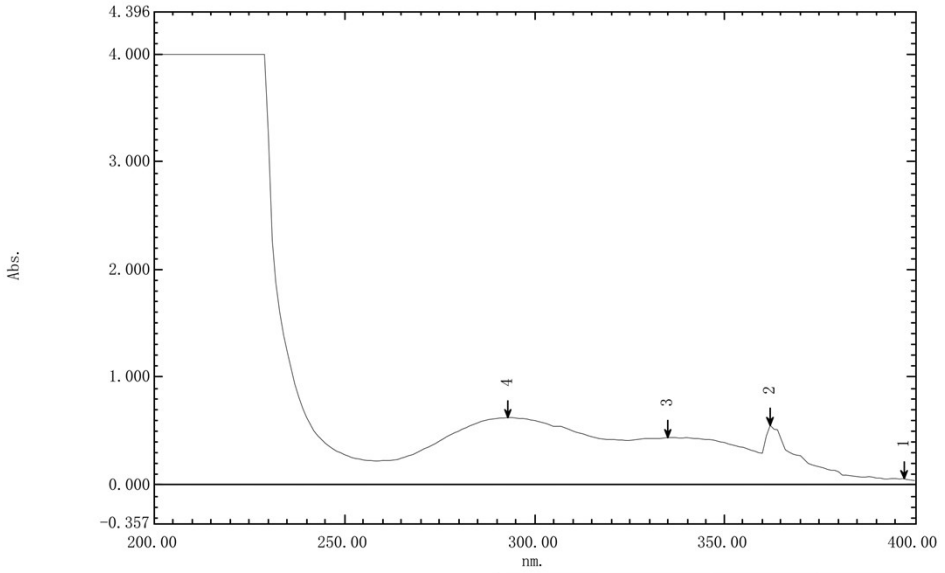

测定属性
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扫描速度: 中速
采样间隔: 1.0
自动采样间隔: 停用
扫描模式: 单一的

试样准备属性
重量:
体积 :
稀释:
光程长:
附加信息:

仪器属性
仪器类型: UV-1700
测定方式: 吸收值
狭缝宽: 1.0 nm
光源改变波长: 360.0 nm
S/R 转换: 标准

附件属性
附件: 无

No.	P/V	Wavelength	Abs.	描述
1	↑	397.00	.057	
2	↑	362.00	.552	
3	↑	335.00	.437	
4	↑	293.00	.622	
5	↓	392.00	.050	
6	↓	360.00	.291	
7	↓	325.00	.411	
8	↓	259.00	.220	

FIELD TEXT

Figure S5.1 UV spectrum of compound **5**

Mass Spectrum Molecular Formula Report

Analysis Info

Analysis Name	D:\Data\20190430CEYANG\AAS-65_1-D,3_01_13688.d	Acquisition Date	4/30/2019 12:44:58 PM
Method	20190425yezhi.m	Instrument / Ser#	Bruker Customer
Sample Name	AAS-65	Operator	micrOTOF-Q 125
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	1500 m/z	Set Collision Cell RF	400.0 Vpp	Set Divert Valve	Source

Generate Molecular Formula Parameter

Formula, min.		
Formula, max.		
Measured m/z	Tolerance	Charge
Check Valence	Minimum	Maximum
Nirogen Rule	Electron Configuration	
Filter H/C Ratio	Minimum	Maximum
Estimate Carbon		

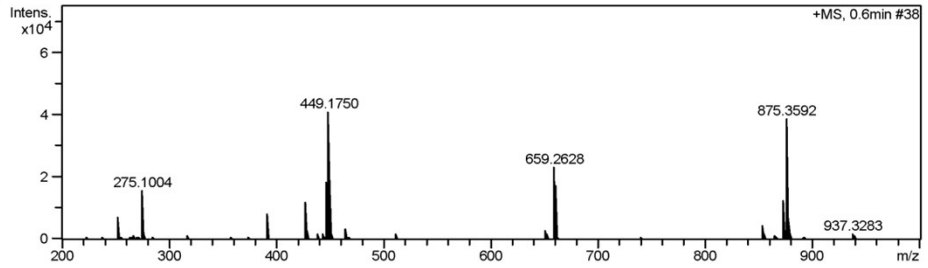


Figure S5.2 HRESIMS spectrum of compound **5**

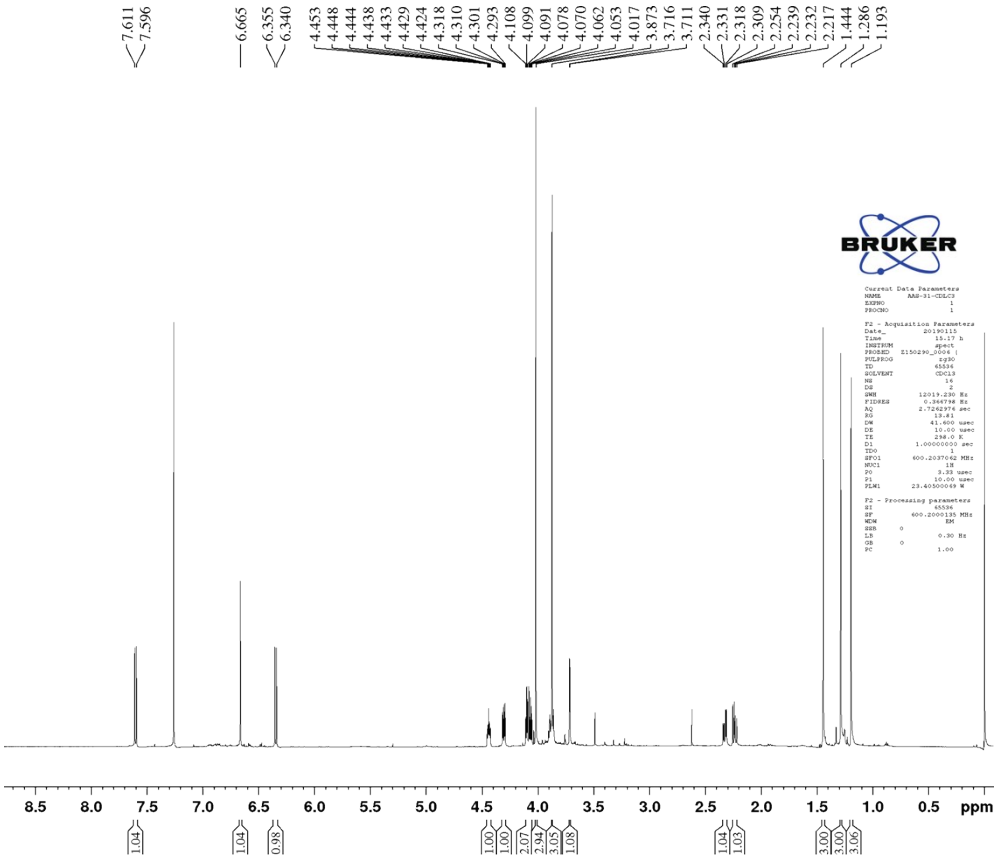


Figure S5.3 ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **5**

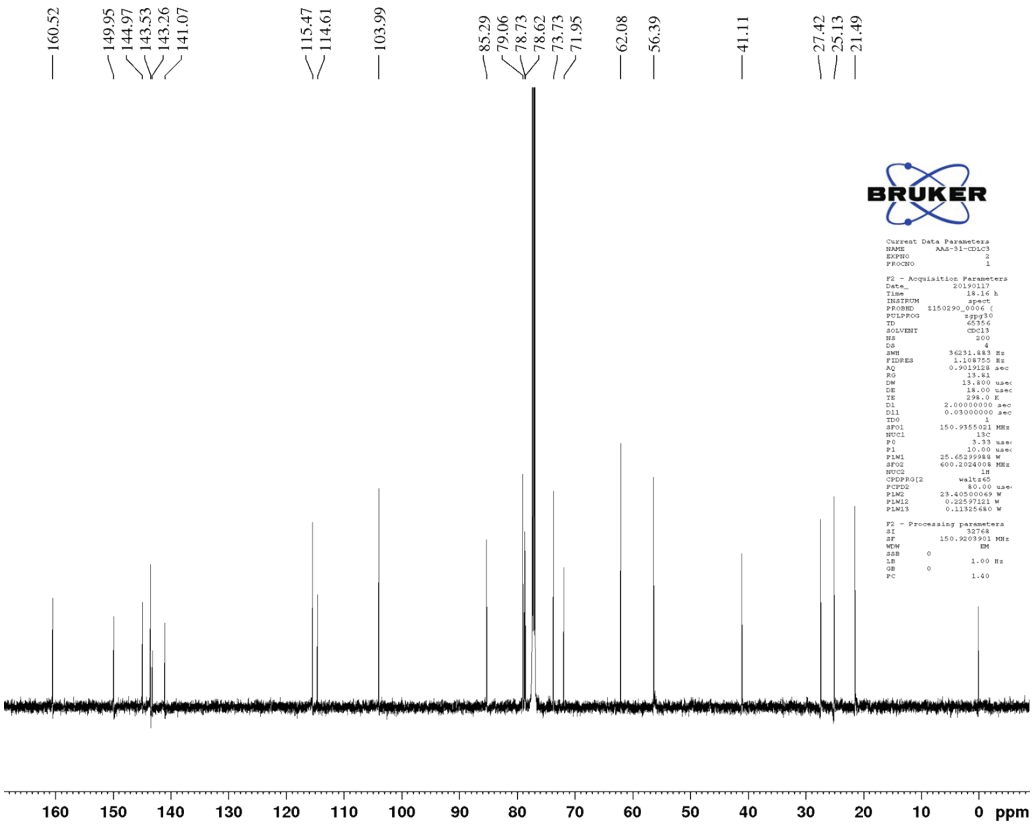


Figure S5.4 ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of compound **5**

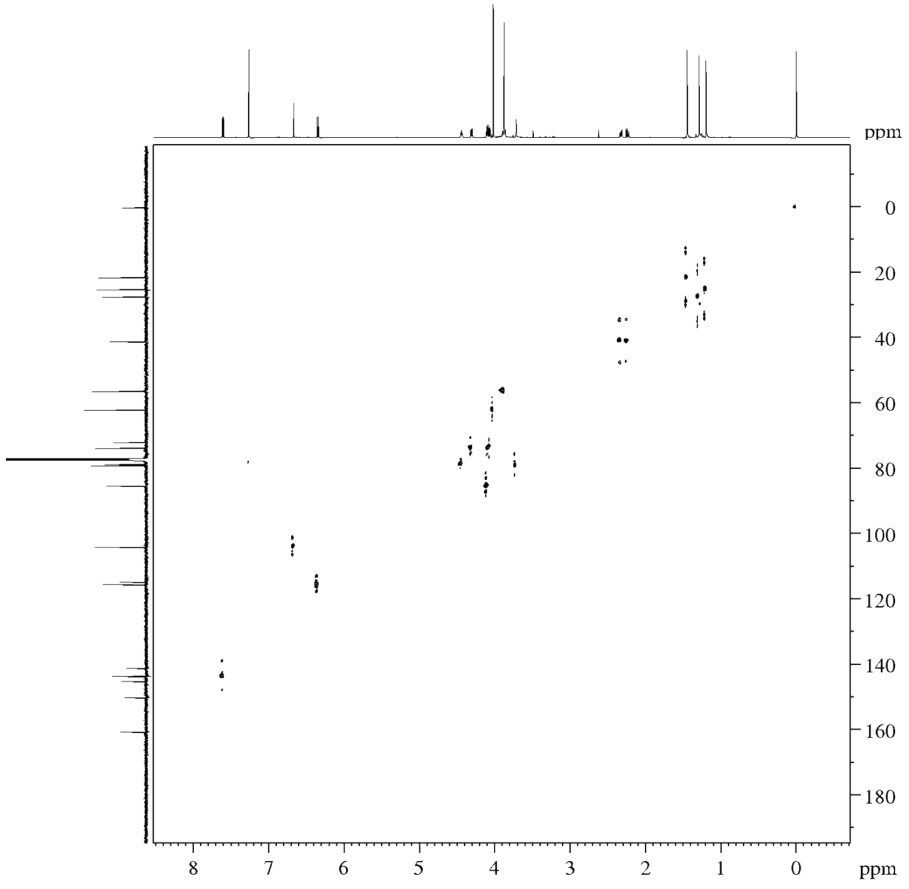


Figure S5.5 HSQC spectrum (600 MHz, $CDCl_3$) of compound **5**

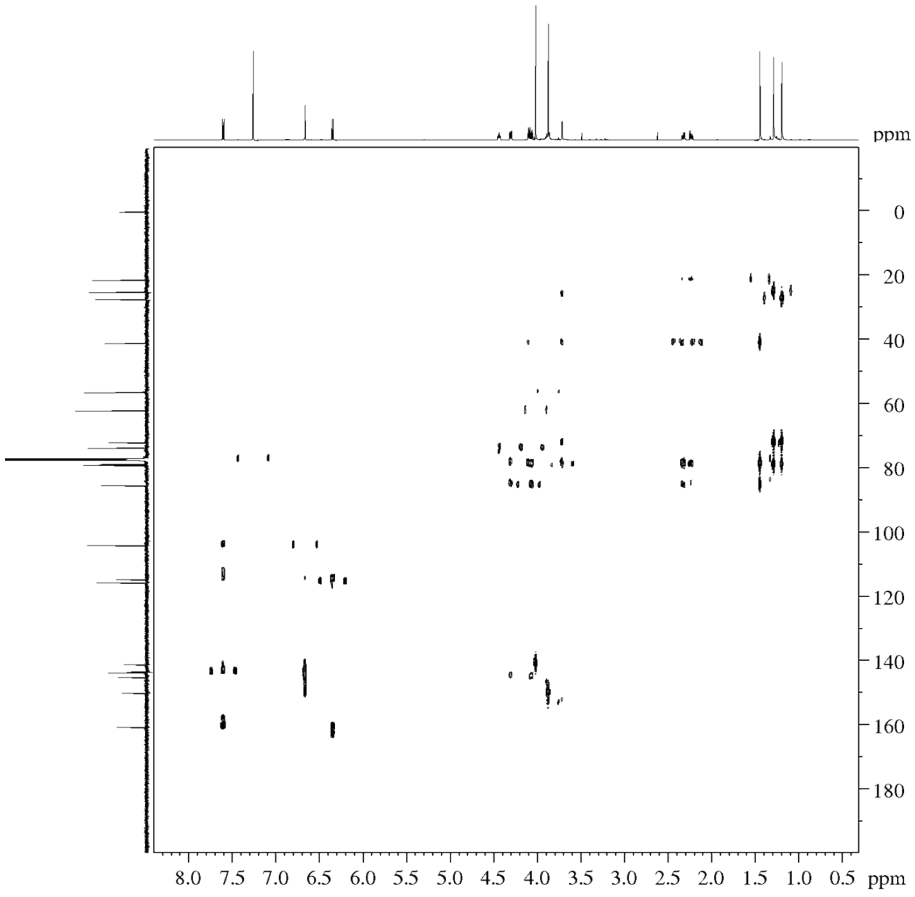


Figure S5.6 HMBC spectrum (600 MHz, $CDCl_3$) of compound **5**

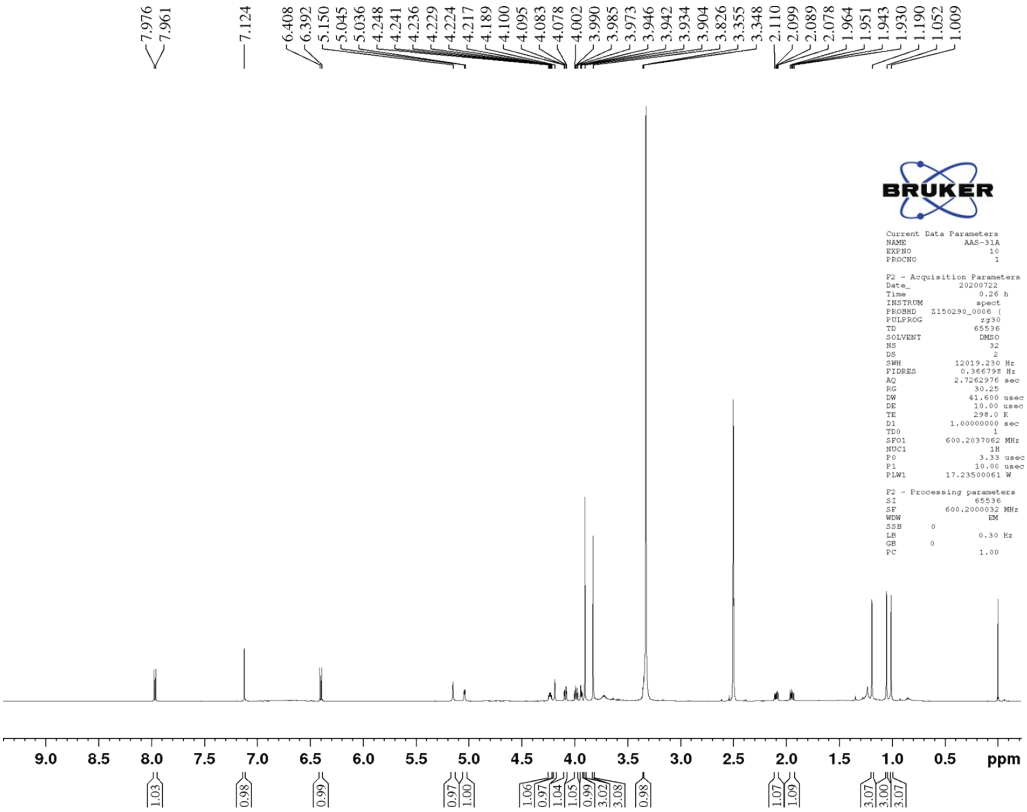


Figure S5.7 ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of compound **5**

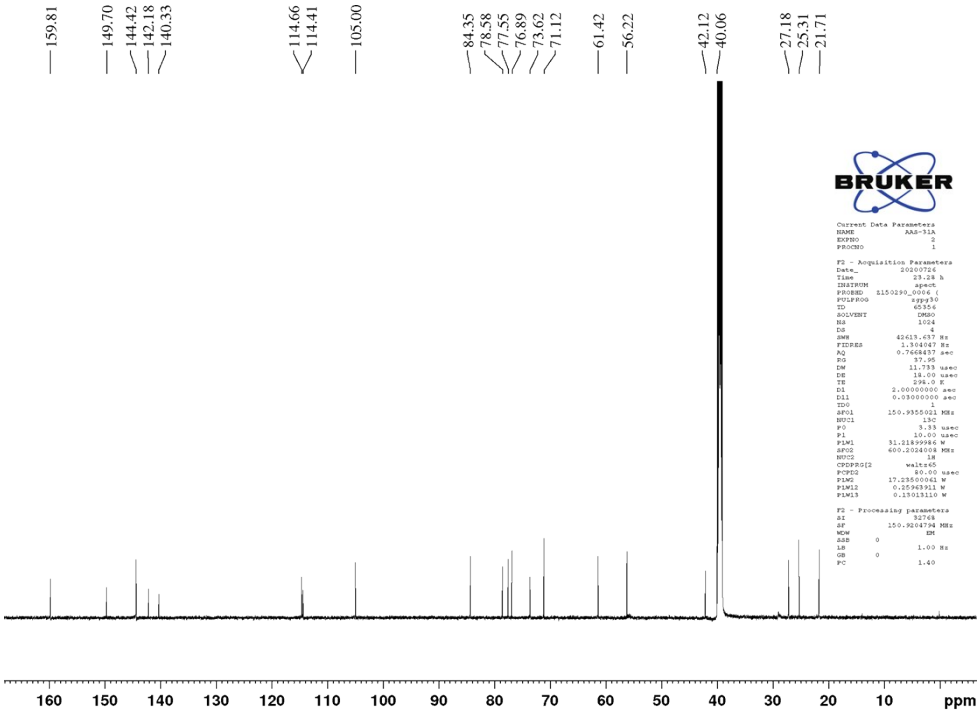


Figure S5.8 ^{13}C NMR spectrum (150 MHz, DMSO-d_6) of compound **5**

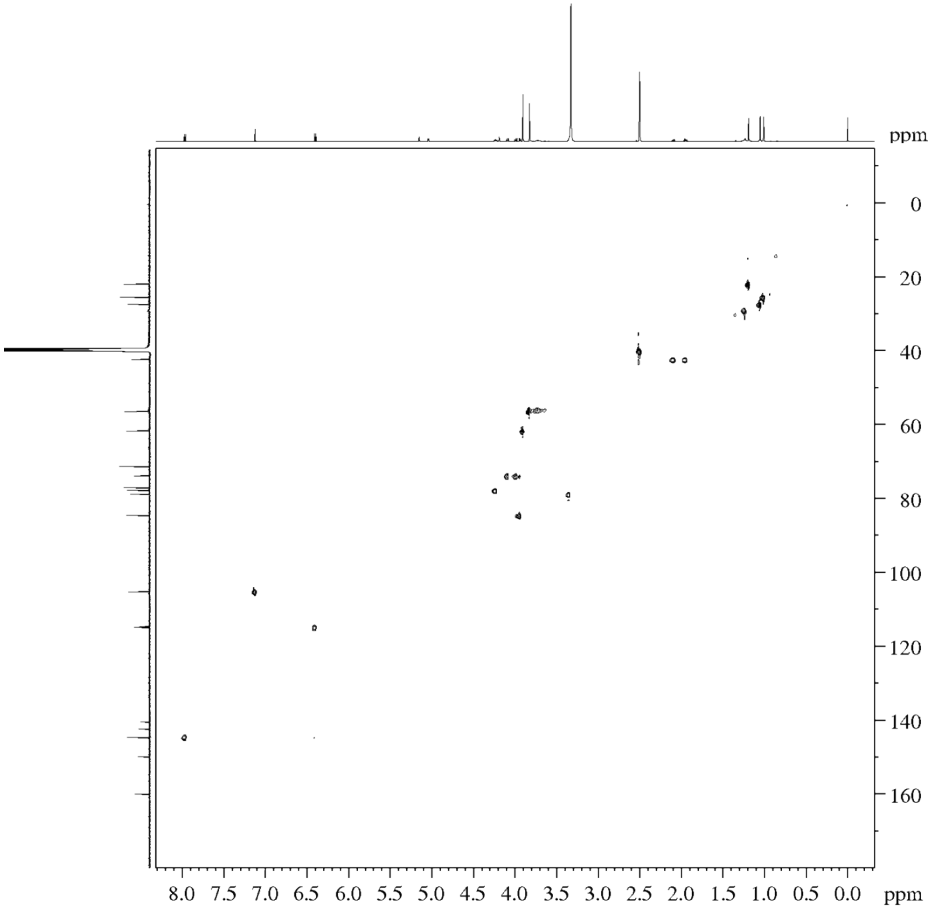


Figure S5.9 HSQC spectrum (600 MHz, DMSO-d_6) of compound **5**

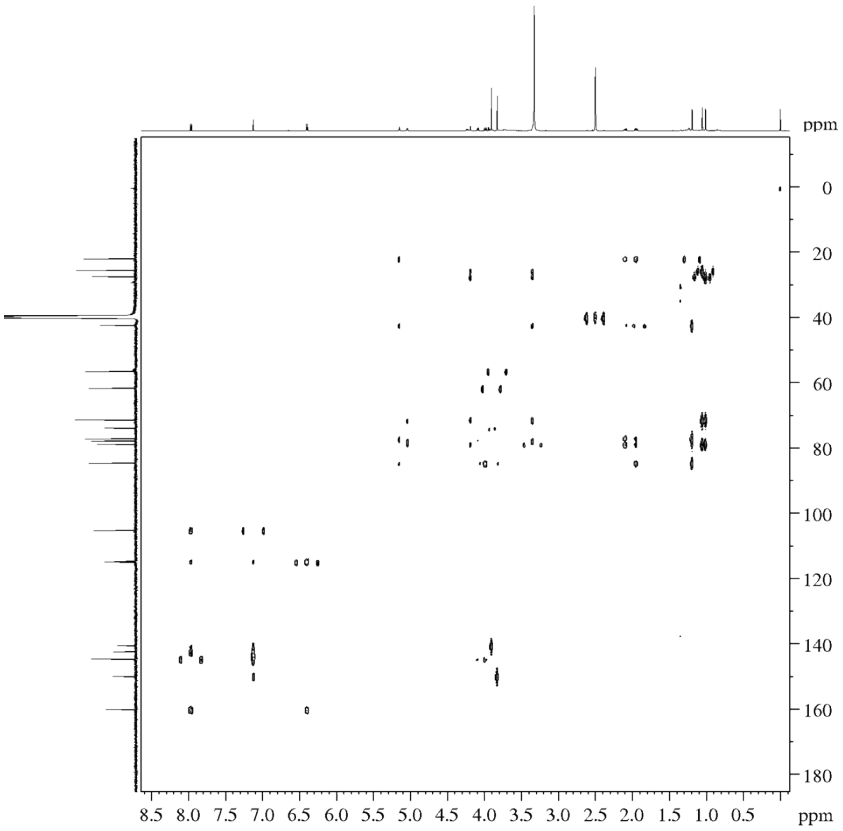


Figure S5.10 HMBC spectrum (600 MHz, DMSO-d_6) of compound **5**

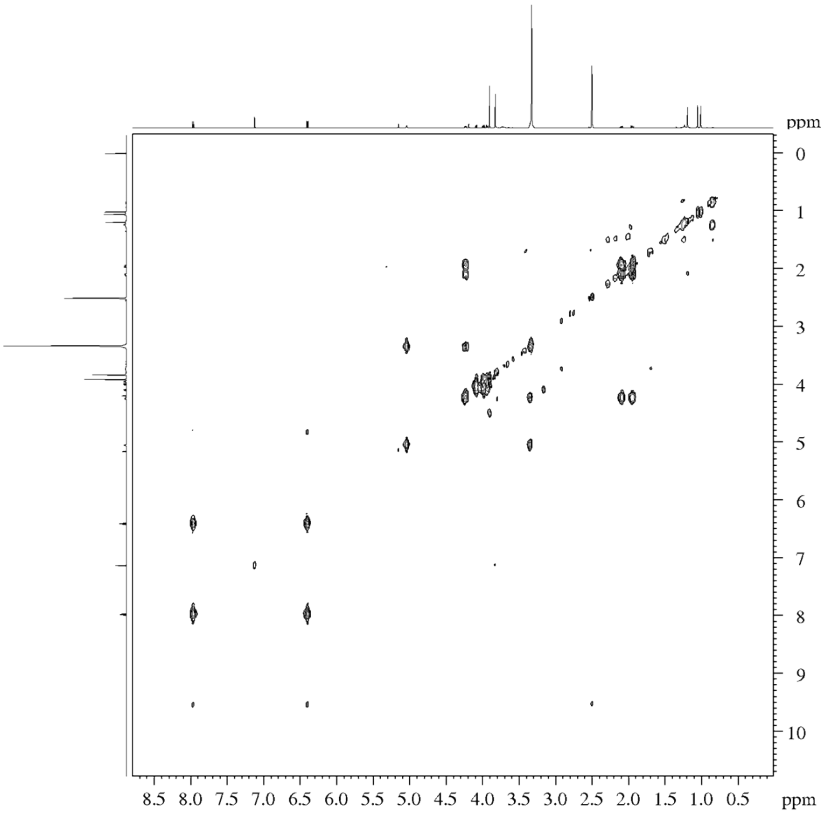


Figure S5.11 ^{1}H-^{1}H COSY spectrum (600 MHz, DMSO-d_6) of compound **5**

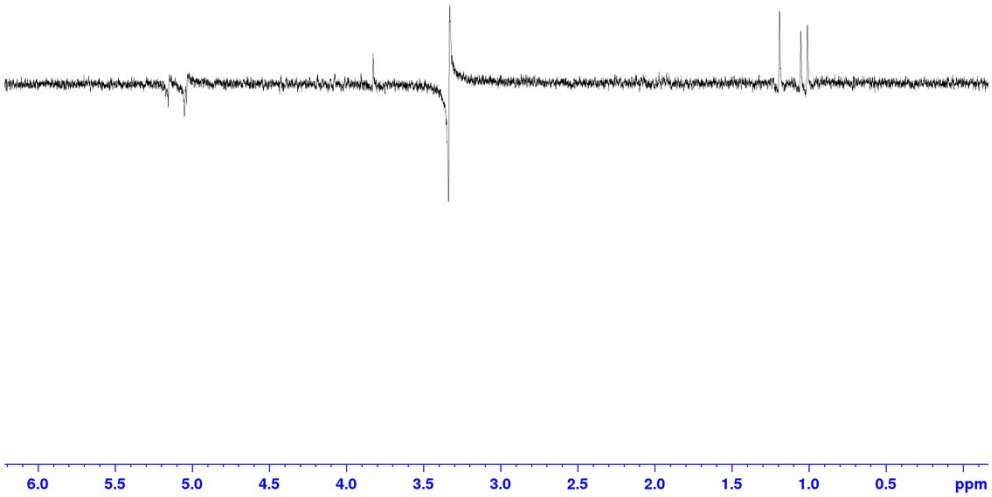
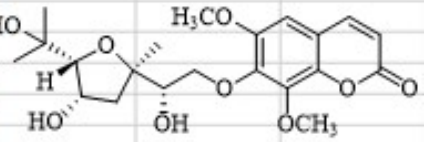


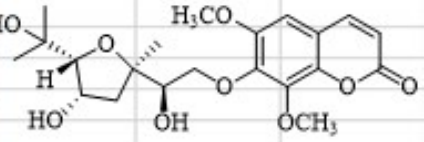
Figure S5.12 1D NOESY spectrum (600 MHz, DMSO-d_6) of compound **5**: selective excitation at δ_H 5.12 (5′-OH), full spectrum

Functional	Solvent?	Basis Set	Type of Data
B3LYP	PCM	6-311+G(d,p)	Unscaled Shifts

		DP4+	0.00%	100.00%	-	-	-
Nuclei	sp2?	xperiment	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5
C	x	160.52	168.2	168.3			
C	x	149.95	158.0048	158.0329			
C	x	144.97	156.6379	156.1129			
C	x	143.54	154.8346	153.9685			
C	x	143.26	153.4626	153.3754			
C	x	141.07	150.228	150.2183			
C	x	115.47	150.0541	122.9936			
C	x	114.61	119.8703	120.3344			
C	x	103.99	111.1762	109.1907			
C		85.29	94.40885309	94.40885309			
C		79.06	90.85250608	90.85250608			
C		78.73	84.63819817	84.63819817			
C		78.62	81.95009739	81.95009739			
C		73.73	80.06880265	80.06880265			
C		71.95	78.83146441	78.83146441			
C		62.08	63.45079407	63.45079407			
C		56.4	58.10961073	58.10961073			
C		41.11	47.36325484	47.36325484			
C		27.43	27.3492086	27.3492086			
C		25.13	26.43771076	26.43771076			
C		21.5	26.08646431	26.08646431			
H	x	7.97	8.97	8.7839			
H	x	7.12	7.9166	8.2284			
H	x	6.4	7.366	7.1956			
H		4.23	7.02672223	6.89883263			
H		4.09	6.65895849	6.83086538			
H		3.99	6.31574757	6.30806312			
H		3.94	5.62334185	6.28820193			
H		3.9	5.52972158	6.22670327			
H		3.9	5.49796781	6.1365072			
H		3.9	5.43914671	6.08912693			
H		3.84	5.32355889	5.88091041			
H		3.84	5.22840201	5.83347355			
H		3.84	5.07513711	5.73683761			
H		3.35	4.97952293	5.72433249			
H		2.09	4.93334971	5.71066903			
H		1.95	4.92939646	5.37067494			
H		1.18	4.73180577	4.51012289			
H		1.18	3.71106121	4.28657508			
H		1.18	3.24037063	3.99850835			
H		1.05	2.66553159	3.93028256			
H		1.05	2.62056587	3.91434128			
H		1.05	2.55237927	3.49100913			
H		1.01	2.44925192	3.490956			
H		1.01	2.44545436	3.44238113			
H		1.01	2.39277685	3.43790513			



5A (Isomer 1)



5B (Isomer 2)

Figure S5.13 Results of DP4+ analysis of compound **5**

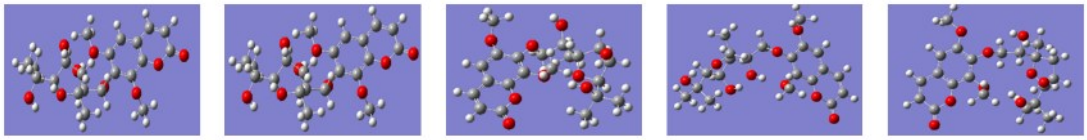


Figure S5.14 The low-energy conformers of the **5a**

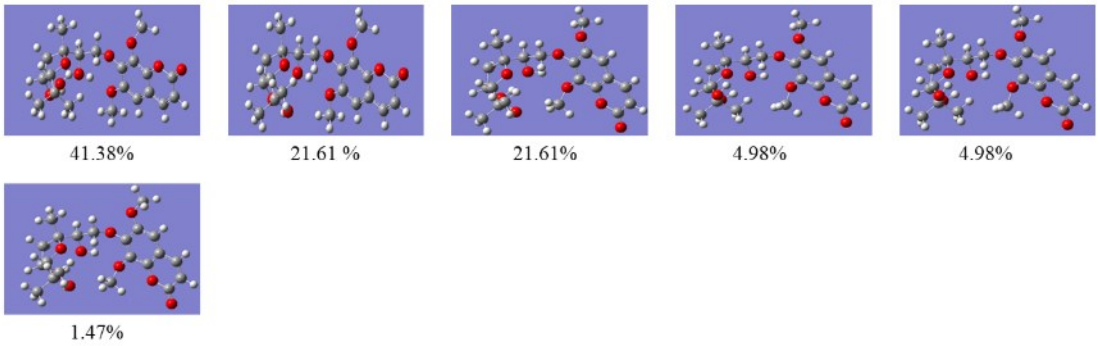
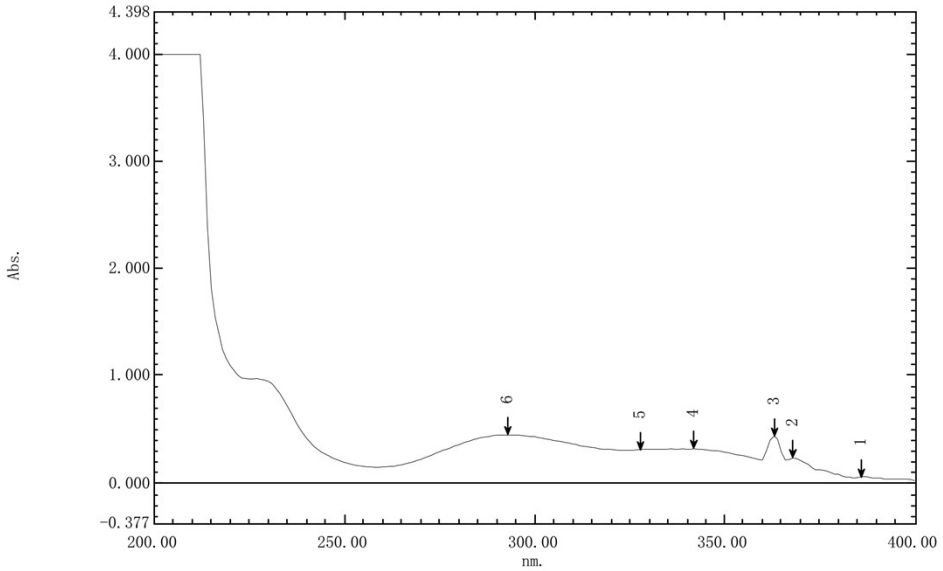


Figure S5.15 The low-energy conformers of the **5b**

Spectrum Peak Pick Report

FIELD FIELD TEXT

Data Set: 没有



测定属性
波长范围 (nm.): 200.00到400.00
扫描速度: 中速
采样间隔: 1.0
自动采样间隔: 停用
扫描模式: 单一的

试样准备属性
重量:
体积 :
稀释:
光程长:
附加信息:

仪器属性
仪器类型: UV-1700
测定方式: 吸收值
狭缝宽: 1.0 nm
光源改变波长: 360.0 nm
S/R 转换: 标准

附件属性
附件: 无

No.	P/V	Wavelength	Abs.	描述
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2	↑	368.00	.231	
3	↑	363.00	.433	
4	↑	342.00	.315	
5	↑	328.00	.313	
6	↑	293.00	.445	
7	↓	384.00	.043	
8	↓	366.00	.210	
9	↓	360.00	.212	
10	↓	330.00	.309	
11	↓	322.00	.301	
12	↓	259.00	.145	

FIELD TEXT

Figure S6.1 UV spectrum of compound **6**

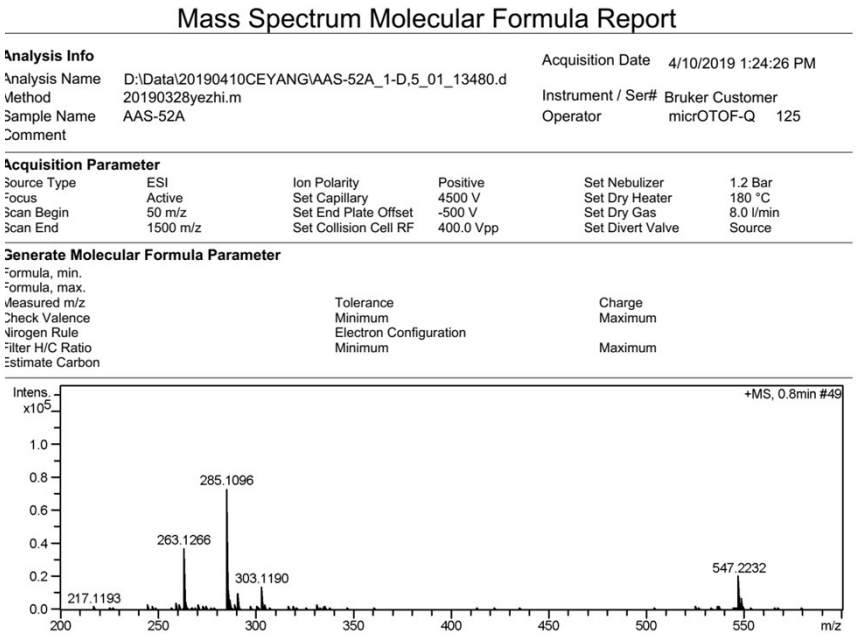

Figure S6.2 HRESIMS spectrum of compound **6**

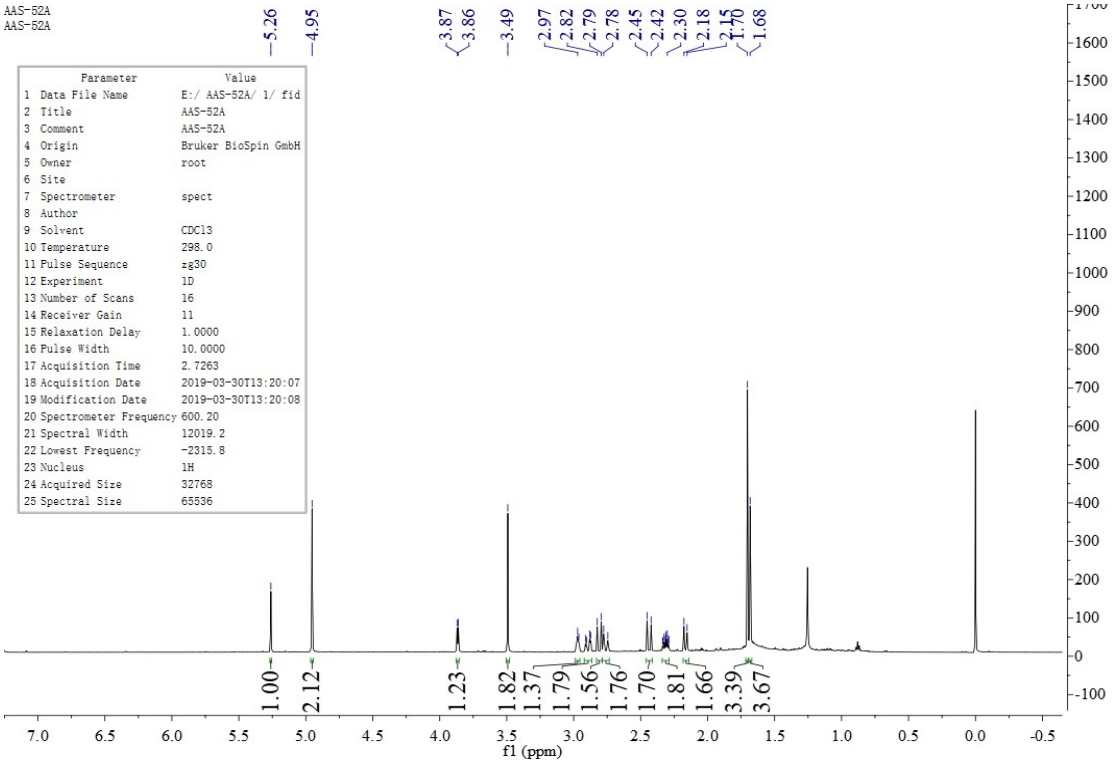

Figure S6.3 ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of compound **6**

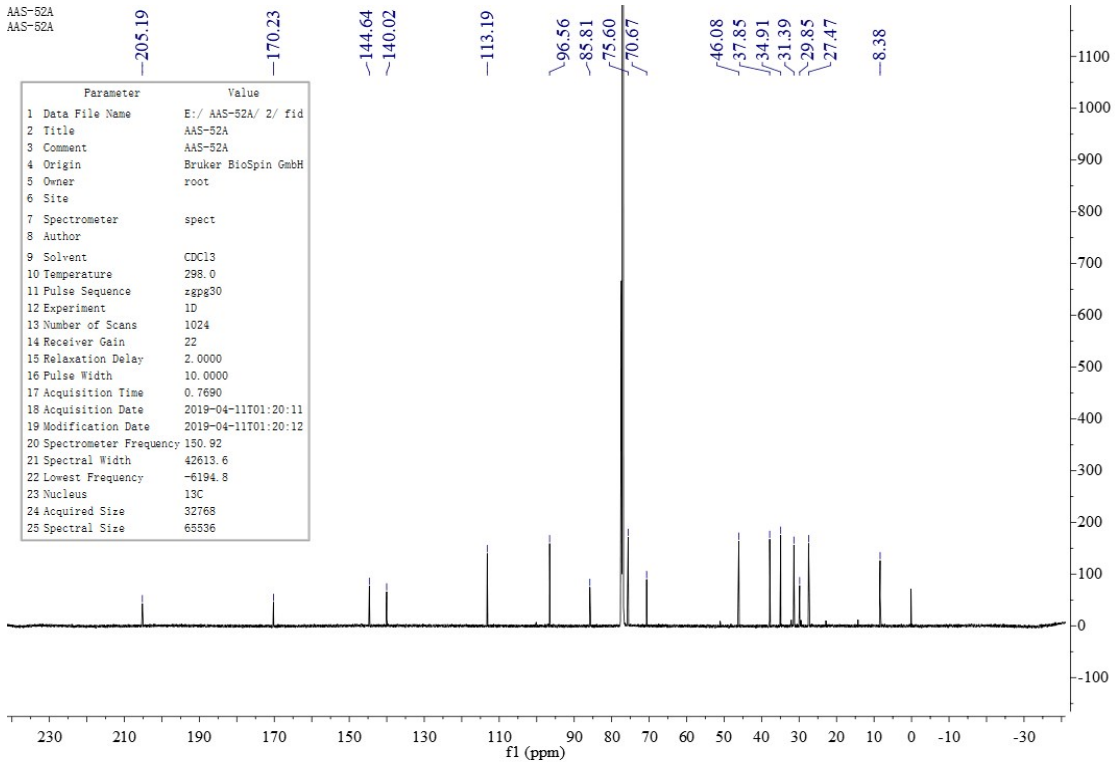

Figure S6.4 ^{13}C NMR spectrum (150 MHz, DMSO-d_6) of compound **6**

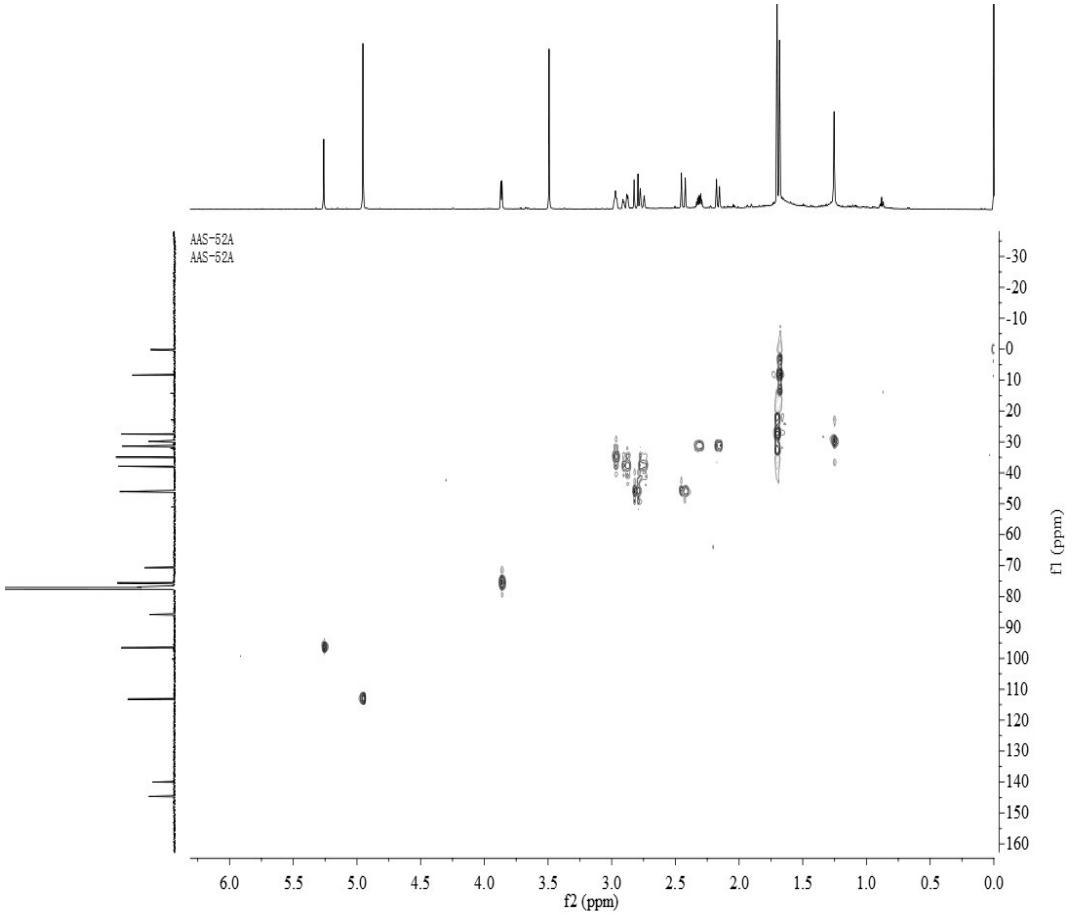

Figure S6.5 HSQC spectrum (600 MHz, DMSO-d_6) of compound **6**

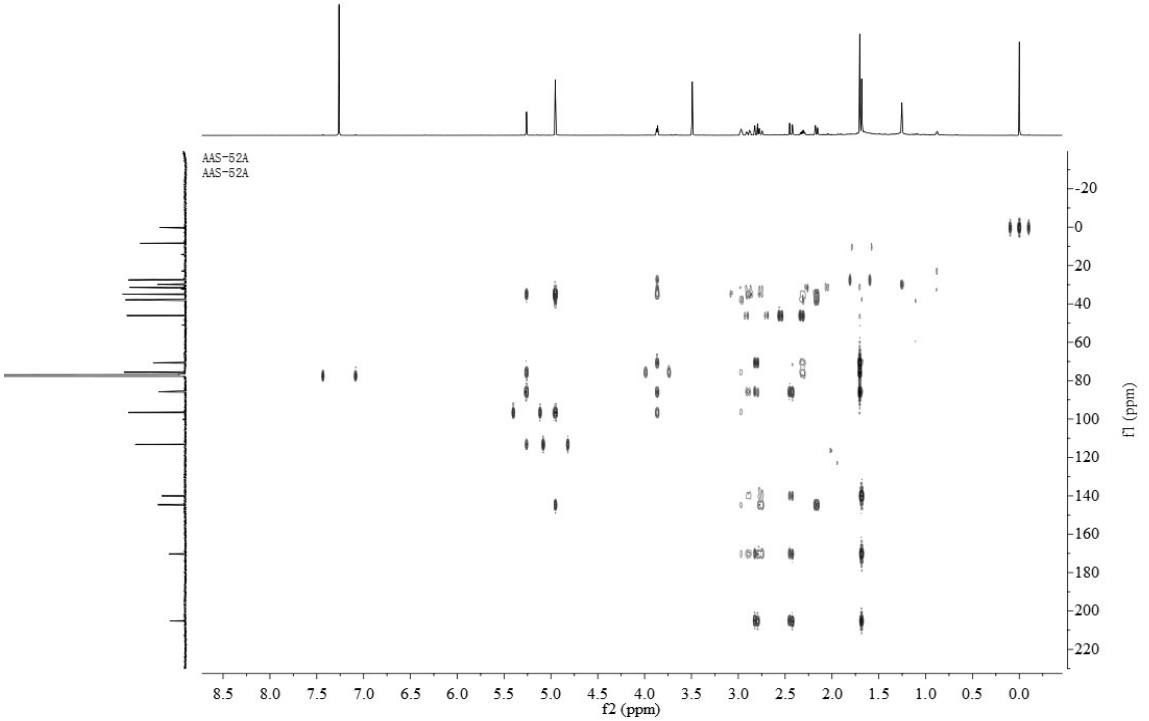

Figure S6.6HMBC spectrum (600 MHz, DMSO-d_6) of compound **6**

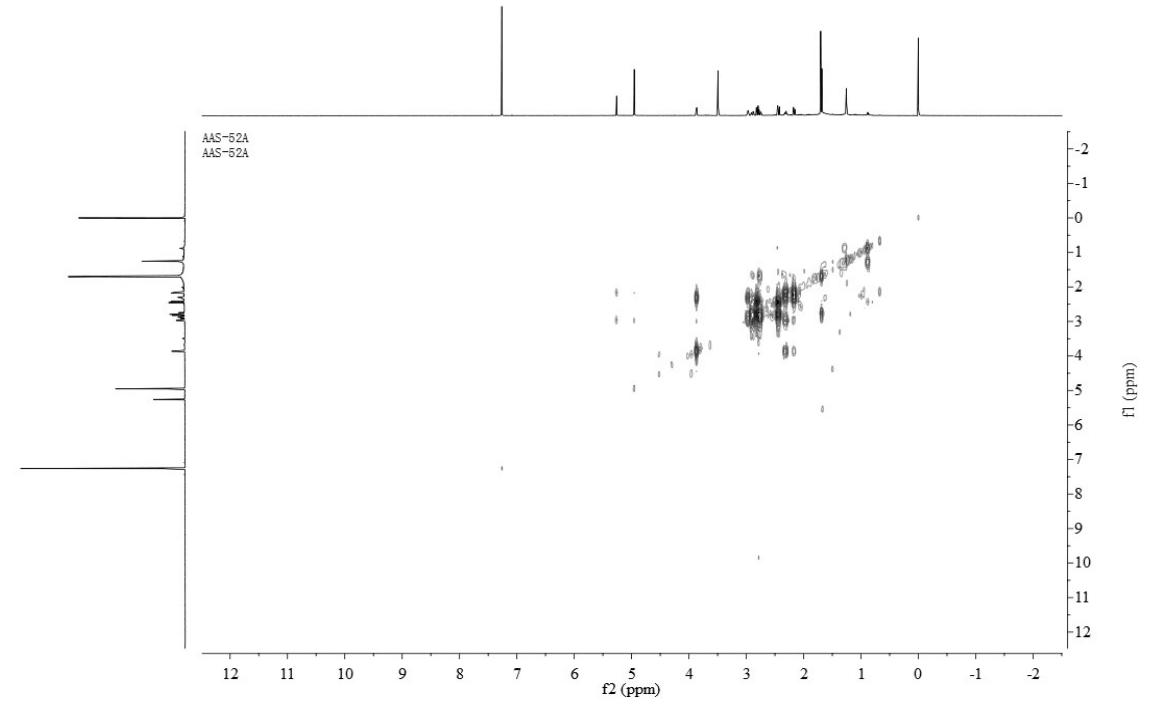

Figure S6.7 ^{1}H-^{1}H COSY spectrum of compound **6**

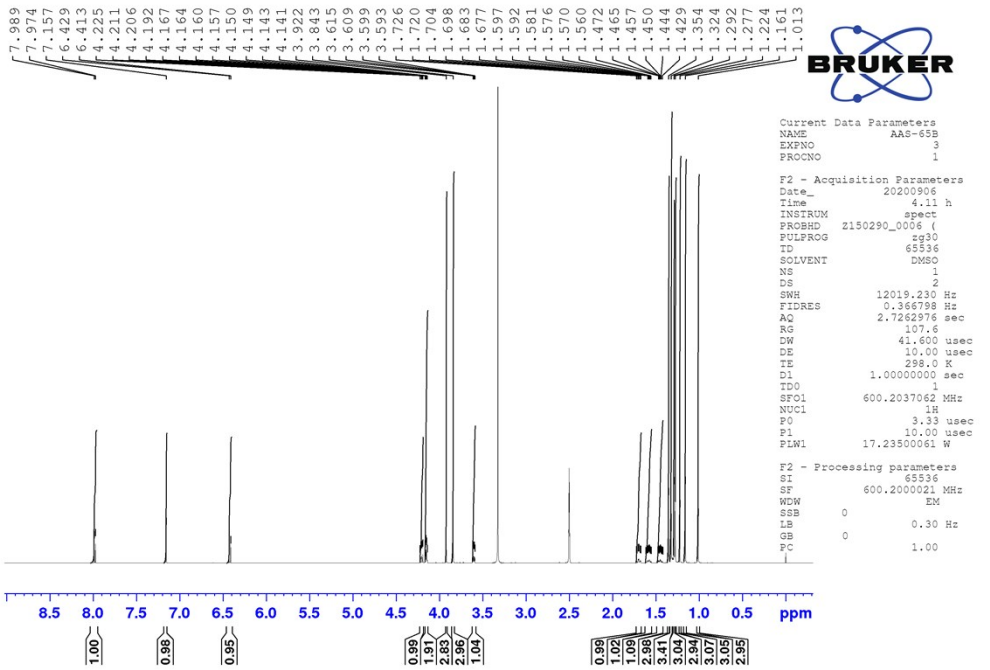

Figure S6.8 ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of compound **6a**

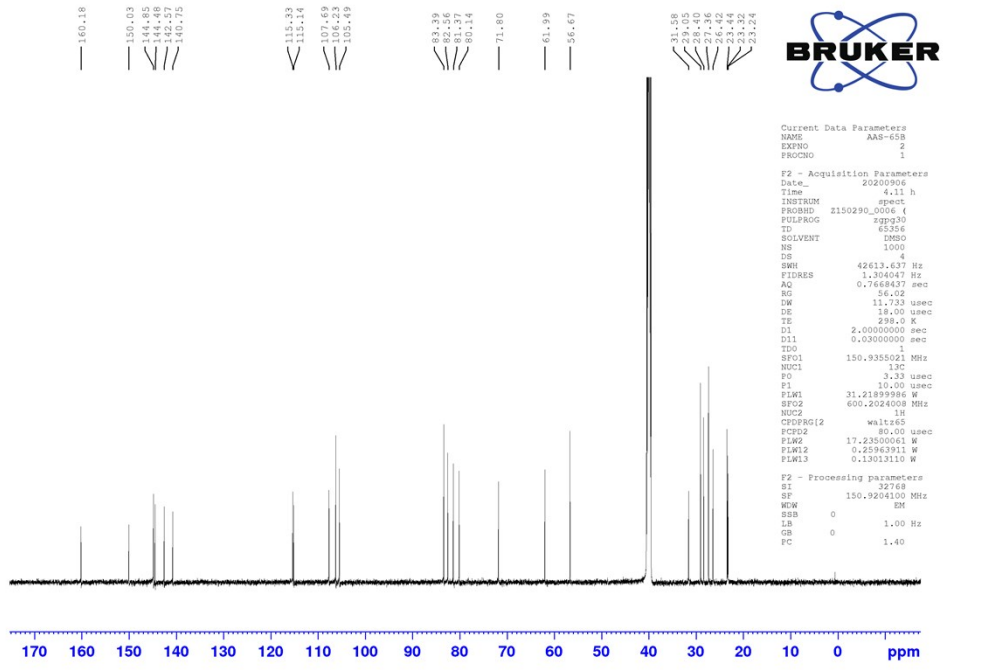

Figure S6.9 ^{13}C NMR spectrum (150 MHz, DMSO-d_6) of compound **6a**

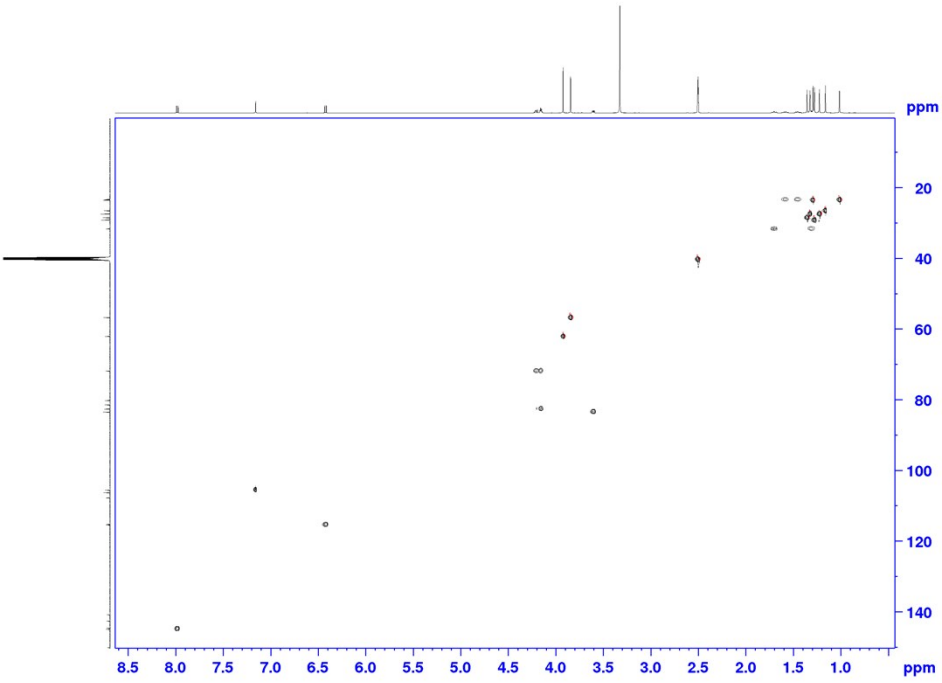

Figure S6.10 HSQC spectrum (600 MHz, DMSO-d_6) of compound **6a**

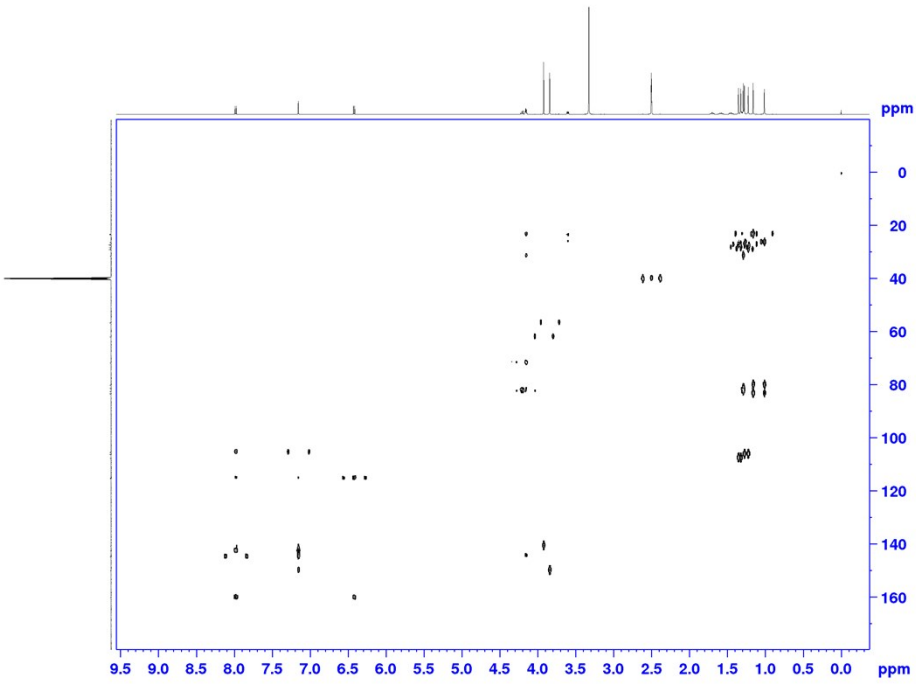

Figure S6.11 HMBC spectrum (600 MHz, DMSO-d_6) of compound **6a**

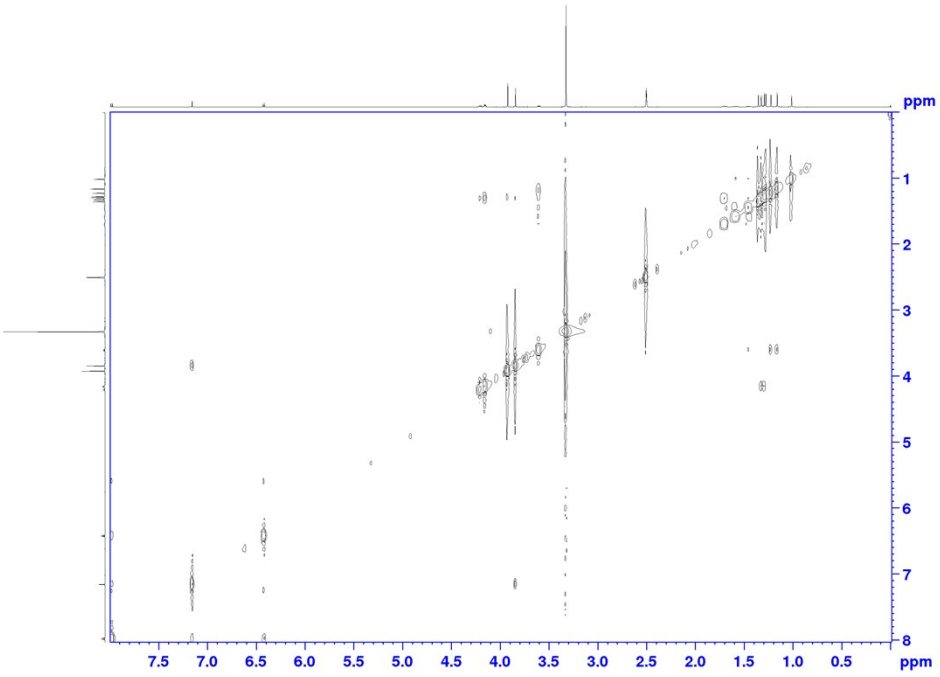

Figure S6.12 NOESY spectrum of compound **6a**

Table S1 ^{1}H NMR spectroscopic data for compounds **1, 5**, **7**, **8**.

NO.	**1**[a]	**5**[b]	**7**[a]	**8**[a]
3	6.36 (d, 9.5)	6.40 (d, 9.5)	6.33 (d, 9.5)	6.34 (d, 9.5)
4	7.63 (d, 9.5)	7.97 (d, 9.5)	7.60 (d, 9.5)	7.61 (d, 9.5)
5	6.70 (s)	7.12 (s)	6.55 (s)	6.65 (s)
1'	4.56 (dd, 10.6, 2.5) 4.06 (dd, 10.6, 7.9)	4.09 (dd, 10.6, 2.7) 3.99 (dd, 10.6, 7.0)	4.67 (d, 6.9)	4.67 (d, 6.9)
2'	3.71 (dd, 7.9, 2.5)	3.94 (dd, 7.0, 2.7)	5.55 (dq, 6.9, 1.5)	5.55 (1H, m)
4'	1.61 (m), 1.41 (m)	2.09 (dd, 12.5, 6.7) 1.95 (dd, 12.5, 8.0)	2.03 (m)	1.77 (d, 1.5)
5'	2.15 (m), 2.06 (m)	4.23 (m)	2.05 (m)	1.71 (d, 1.5)
6'	5.11 (t, 7.0)	3.35 (m)	5.06 (m)	-
7'	-	-	-	-
8'	1.67 (s)	1.05 (s)	1.66 (d, 1.5)	-
9'	1.25 (s)	1.18 (s)	1.69 (d, 1.5)	-
10'	1.61 (s)	1.01 (s)	1.58 (d, 1.5)	-
6-OCH_3	3.87 (s)	3.84 (s)	3.88 (s)	3.89 (s)
8-OCH_3	4.01 (s)	3.90 (s)	4.03 (s)	4.03 (s)
2'-OH	-	5.15 (s)	-	-
6'-OH	-	5.04 (d, 5.2)	-	-
7'-OH	-	4.19 (s)	-	-

[a] Recorded in $CDCl_3$ and 600 MHz. o: The abbreviation for overlapped.

[b] Recorded in DMSO-d_6 and 600 MHz.

Table S2 ^{13}C NMR spectroscopic data for compounds **1, 5**, **7**, **8**.

NO.	**1**[a]	**5**[b]	**7**[a]	**8**[a]
2	160.2	159.8	160.7	160.7
3	115.4	114.6	115.3	115.2
4	143.5	144.4	143.6	143.6
5	103.9	105.0	103.6	103.7
6	149.7	149.7	150.8	150.8
7	144.7	144.4	145.0	145.0
8	141.0	140.3	141.9	141.1
9	142.9	142.2	142.7	143.1
10	114.8	114.4	114.6	114.3
1'	76.1	73.6	70.4	70.4
2'	75.1	84.4	119.7	120.1
3'	73.4	78.6	143.1	139.4
4'	38.0	42.1	39.7	26.0
5'	22.1	77.6	26.5	18.1
6'	124.3	76.9	23.9	
7'	131.8	71.1	131.9	
8'	25.7	25.3	25.8	
9'	23.3	21.7	16.4	
10'	17.7	27.2	17.6	
6-OCH_3	56.4	56.2	56.4	56.4
8-OCH_3	62.0	61.4	61.8	61.8

[a] Recorded in $CDCl_3$ and 150 MHz.

[b] Recorded in DMSO-d_6 and 150 MHz.

Table S3 ^{1}H NMR (600MHz) and ^{13}C NMR (150MHz) spectroscopic data for compounds **1a, 2a** (in $CDCl_3$).

NO.	**2a**		**1a**	
	δ_H	δ_C	δ_H	δ_C
2	-	174.1	-	160.6
3	2.64 (t, 7.6)	34.3	6.35 (d, 9.5)	115.6
4	2.90 (t, 7.6)	25.8	7.60 (d, 9.5)	143.5
5	6.44 (s)	108.8	6.60 (s)	103.8
6	-	146.4	-	150.3
7	-	139.6	-	145.0
8	-	140.5	-	141.5
9	-	141.3	-	143.1
10	-	121.0	-	114.8

1'	4.16 (m) 4.03 (dd, 9.2, 36)	71.7	4.33 (dd, 10.1, 7.0) 4.11 (dd, 10.1, 4.9)	72.2
2'	4.19 (m)	83.0	4.21 (dd, 7.0, 4.9)	82.7
3'	-	81.6	-	81.7
4'	1.59 (dd, 12.7, 7.5) 1.29 (dd, 12.7, 6.0)	35.1	1.58 (m), 1.31 (m)	35.1
5'	2.17 (m), 2.03 (m)	22.0	2.20 (m), 2.03 (m)	22.0
6'	5.10 (t, 7.4)	125.6	5.11 (t, 7.2)	124.5
7'	-	131.7	-	131.8
8'	1.67 (s)	25.8	1.67 (s)	25.8
9'	1.34 (s)	23.4	1.34 (s)	23.5
10'	1.60 (s)	17.7	1.61 (s)	17.7
1''	-	107.9	-	108.1
2''	1.41 (s)	27.2	1.42 (s)	27.2
3''	1.45 (s)	28.5	1.45 (s)	28.5
2-OCH_3	3.68 (s)	51.8	-	-
6-OCH_3	3.77 (s)	56.6	3.87 (s)	56.4
8-OCH_3	3.95 (s)	61.8	4.03 (s)	62.1

Table S4 ^{1}H NMR (600MHz) and ^{13}C NMR (150MHz) spectroscopic data for compounds **6a** (in DMSO-d_6).

NO.	**6a**	
	δ_H	δ_C
2	-	159.7
3	6.42 (d, 9.5)	114.6
4	7.98 (d, 9.5)	144.0
5	7.16 (s)	105.0
6	-	149.7
7	-	144.4
8	-	140.3
9	-	142.1
10	-	114.9
1'	4.21 (dd, 10.5, 8.2) 4.15 (o)	71.3
2'	3.60 (8.2, 3.8)	82.9
3'	-	79.7
4'	1.70 (dt, 12.9, 3.8) 1.31 (o)	31.1
5'	1.58 (m), 1.45 (m)	22.8
6'	4.15 (o)	82.1
7'	-	80.9
8'	1.01 (s)	22.9
9'	1.16 (s)	26.0

10'	1.29 (s)	23.0
1"	-	105.8
2"	1.23 (s)	26.9
3"	1.27 (s)	27.9
1"	-	107.2
2"	1.32 (s)	26.9
3"	1.35 (s)	28.6
6-OCH_3	3.92 (s)	61.5
8-OCH_3	3.84 (s)	56.2

Table S5 Cytotoxicity of compounds **1**-**8** against two human cancer cell lines.

	IC_{50} (μM) ± SD[a]	
Compounds	hep 3B	hepG2
1	27.86 ± 1.11	38.55 ± 1.37
2	>50	>50
3	>50	>50
4	>50	>50
5	>50	>50
6	>50	>50
7	>50	>50
8	>50	>50
sorafenib[b]	6.436 ± 0.70	9.014 ± 0.62

a Cytotoxicity was expressed as the mean value of three experiments ± SD

b Sorafenib was used as positive control

Table S6 DFT B3LYP/6-311+G(d, p) relative free energies and population for the most relevant conformers of **3a**

Conformer	ΔG^a	Population[b]
3a-1	0.0000	0.1545
3a-2	0.0001	0.1545
3a-3	0.0001	0.1320
3a-4	0.0002	0.1320
3a-5	0.0007	0.0747

3a-6	0.0008	0.0630
3a-7	0.0009	0.0320
3a-8	0.0012	0.0281
3a-9	0.0015	0.0247
3a-10	0.0018	0.0219

Table S7 DFT B3LYP/6-311+G(d, p) relative free energies and population for the most relevant conformers of **3b**

Conformer	ΔG^a	Population[b]
3b-1	0.0000	0.1241
3b-2	0.0001	0.1134
3b-3	0.0002	0.1037
3b-4	0.0003	0.0909
3b-5	0.0003	0.0909
3b-6	0.0005	0.0759
3b-7	0.0006	0.0650
3b-8	0.0008	0.0547
3b-9	0.0008	0.0509
3b-10	0.0013	0.0288

Table S8 DFT B3LYP/6-311+G(d, p) relative free energies and population for the most relevant conformers of **4a**

Conformer	ΔG^a	Population[b]
4a-1	0.0000	0.1147
4a-2	0.0000	0.1103
4a-3	0.0000	0.1102
4a-4	0.0000	0.1102
4a-5	0.0002	0.0910
4a-6	0.0003	0.0853
4a-7	0.0009	0.0451

4a-8	0.0009	0.0445
4a-9	0.0009	0.0431
4a-10	0.0010	0.0414

Table S9 DFT B3LYP/6-311+G(d, p) relative free energies and population for the most relevant conformers of **4b**

Conformer	ΔG^a	Population[b]
4b-1	0.0000	0.0885
4b-2	0.0001	0.0829
4b-3	0.0002	0.0729
4b-4	0.0002	0.0689
4b-5	0.0002	0.0688
4b-6	0.0002	0.0688
4b-7	0.0003	0.0648
4b-8	0.0003	0.0639
4b-9	0.0008	0.0371
4b-10	0.0009	0.0338

Table S10 DFT B3LYP/6-311+G(d, p) relative free energies and population for the most relevant conformers of **5a**

Conformer	ΔG^a	Population[b]
5a-1	0.0000	0.4053
5a-2	0.0000	0.4053
5a-3	0.0020	0.0452
5a-4	0.0026	0.0261
5a-5	0.0032	0.0137

Table S11 DFT B3LYP/6-311+G(d, p) relative free energies and population for the most relevant conformers of **5b**

Conformer	ΔG^a	Population[b]

5b-1	0.0000	0.4138
5b-2	0.0006	0.2161
5b-3	0.0006	0.2161
5b-4	0.0020	0.0498
5b-5	0.0020	0.0498
5b-6	0.0032	0.0147

Table S12 Calculated ^{13}C chemical shift values (cal.) of structure **3a-5a**, **3b-5b**

NO.	**3a**	**3b**	**4a**	**4b**	**5a**	**5b**
1	-	-	117.5	117.3	-	-
2	147.9	175.0	117.5	118.1	168.2	168.3
3	128.0	127.9	169.7	169.9	120.5	123.0
4	161.9	162.4	154.6	154.7	154.8	154.0
5	117.1	117.3	153.1	152.5	111.2	109.2
6	166.9	166.8	170.4	170.3	158.0	158.0
7	165.1	166.5	-	-	156.6	156.1
8	157.2	157.1	-	-	150.2	150.2
9	160.7	160.8	-	-	153.5	153.4
10	130.0	130.2	-	-	119.9	120.3
1'	94.1	93.8	93.0	89.7	80.1	81.8
2'	90.3	90.6	90.2	90.3	94.4	91.4
3'	99.1	99.0	98.7	96.7	84.6	83.8
4'	50.1	45.8	50.7	50.5	47.4	48.7
5'	39.6	40.0	39.7	40.6	81.9	82.7
6'	82.2	82.2	82.0	82.0	90.8	90.9
7'	31.5	36.4	31.4	36.4	78.8	78.8
8'	-	-	-	-	27.3	30.3
9'	-	-	-	-	26.1	26.9
10'	-	-	-	-	26.4	28.3
1"	-	-	44.6	44.5	-	-
2"	-	-	50.3	46.3	-	-
3"	-	-	192.8	192.8	-	-
6-OCH_3	65.7	65.7	65.4	65.3	58.1	58.1
8-OCH_3	71.7	71.6	65.5	65.4	63.5	63.8
3"-OCH_3	-	-	63.0	63.0	-	-