Supporting information

Highly modified steroids from *Inonotus obliquus*

Chun-Xin Zou[a], Zi-Lin Hou[a], Ming Bai[a], Rui Guo[a], Bin Lin[b], Xiao-Bo Wang[c], Xiao-Xiao Huang*[a], Shao-Jiang Song*[a]

[a] Key Laboratory of Computational Chemistry-Based Natural Antitumor Drug Research & Development, Liaoning province, School of Traditional Chinese Materia Medica, Shenyang Pharmaceutical University, Shenyang 110016, China

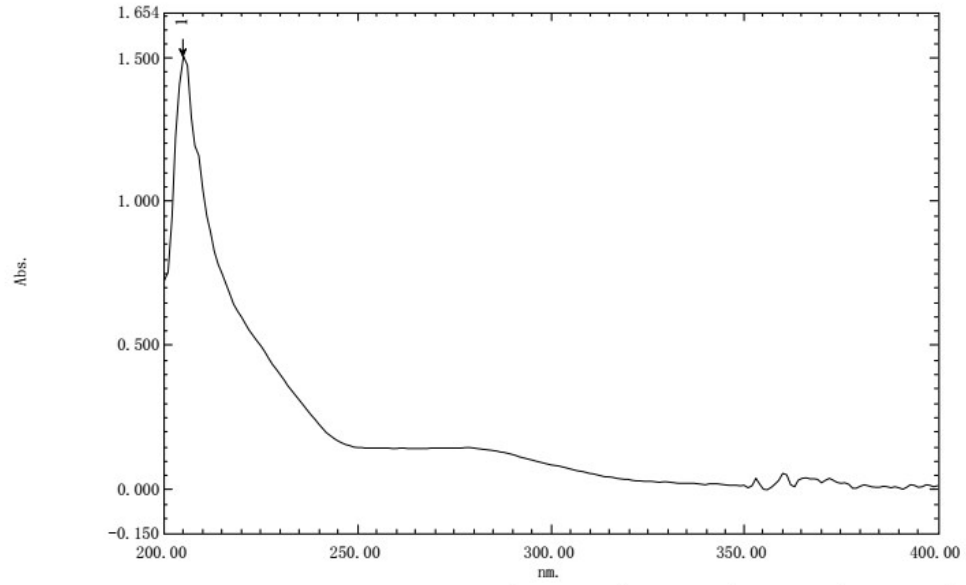
[b] School of Pharmaceutical Engineering, Shenyang Pharmaceutical University, Shenyang 110016, China

[c] Chinese People′s Liberation Army Logistics support force No.967 Hospital, Dalian 116021, China

***Corresponding author:**

E-mail addresses: xiaoxiao270@163.com (X.-X. Huang), songsj99@163.com (S.-J. Song).

List of supplementary content



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采样间隔： 1.0
自动采样间隔: 停用
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No.	P/V	Wavelength	Abs.	描述
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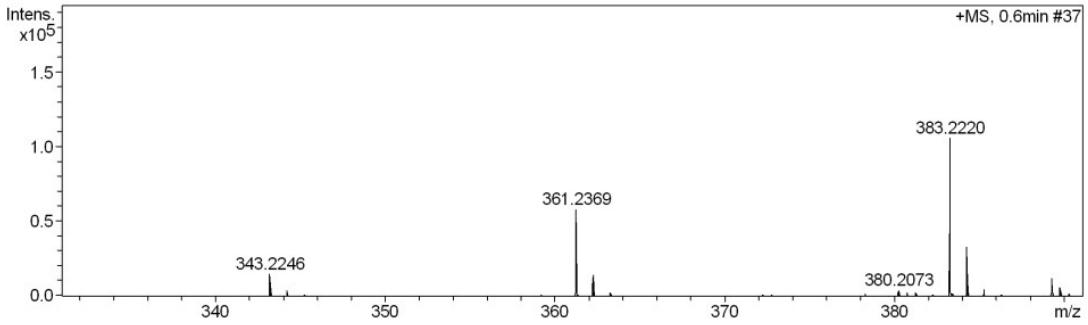
Fig. S1 UV spectrum of compound **1**



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361.2369														
	1	C 22 H 33 O 4	361.2373	1.3	3.0	6.5	ok	even	3.07	0.0056	0.0017	0.0033	0.0023	0.8427

Fig. S2 HRESIMS spectrum of compound **1**

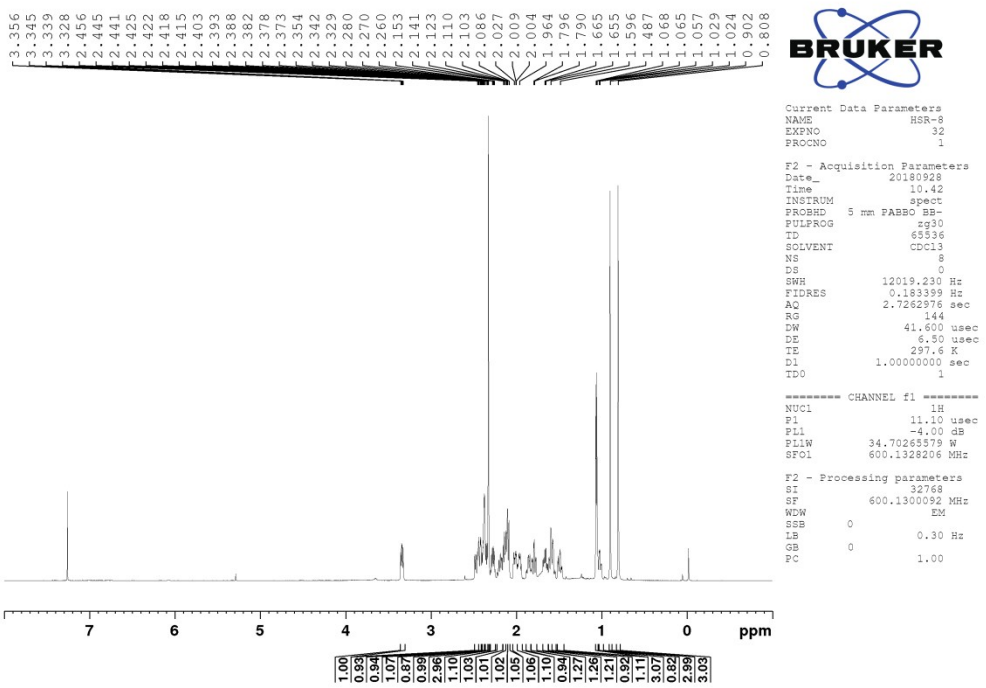
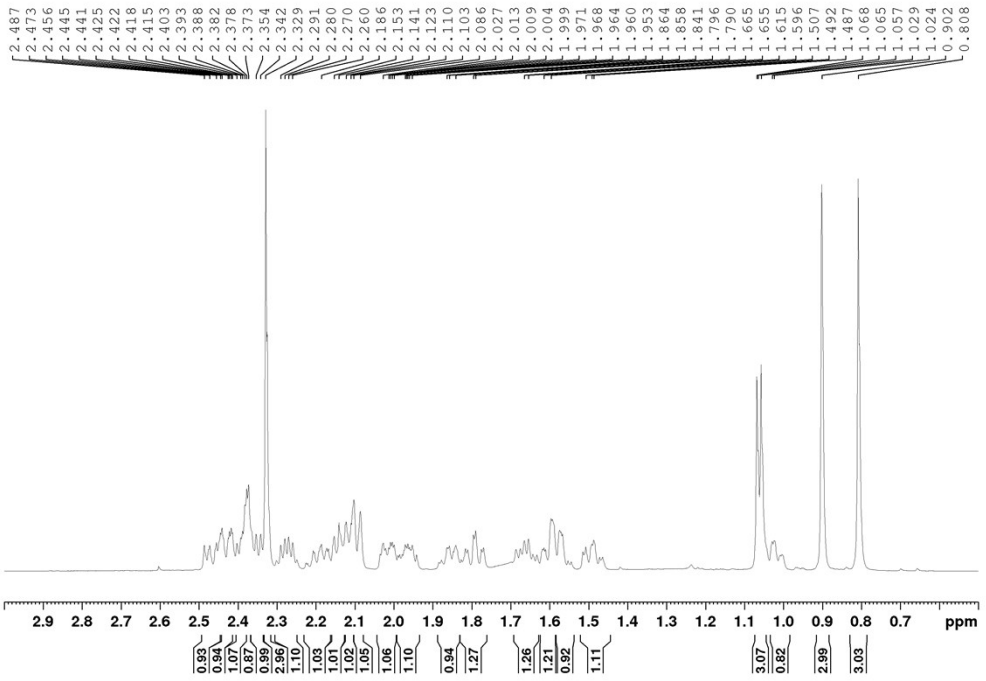


Fig. S3 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1**



Locally amplified ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1**

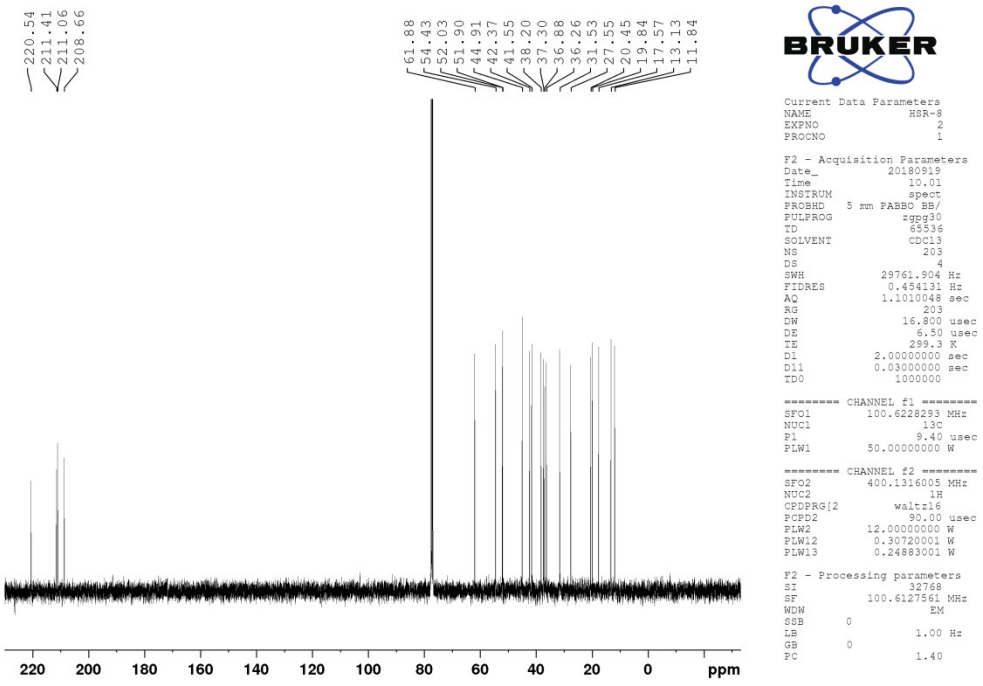
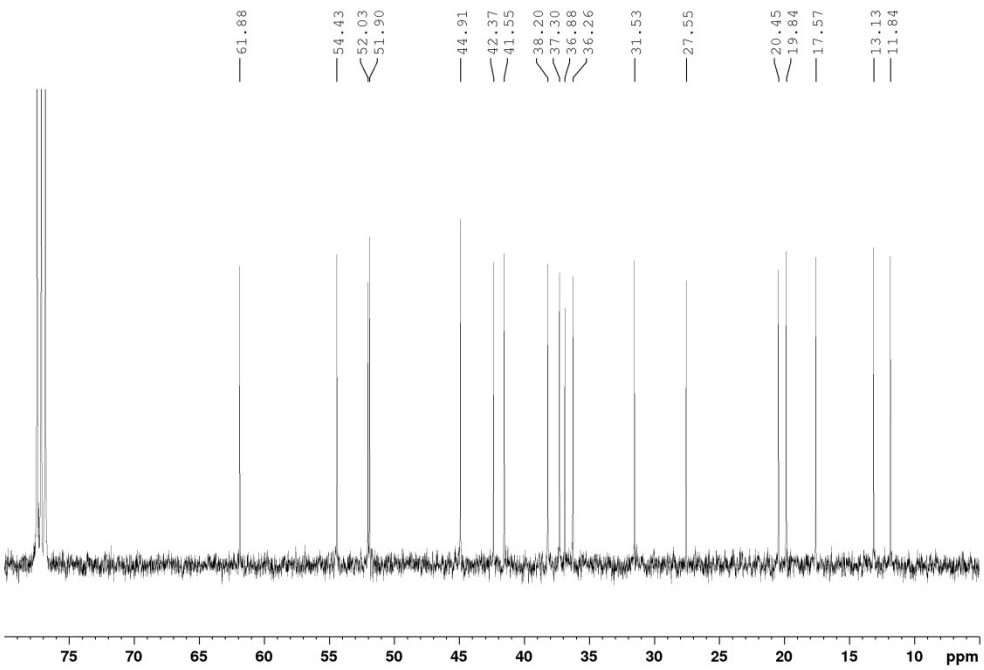


Fig. S4 ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **1**



Locally Amplified ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **1**

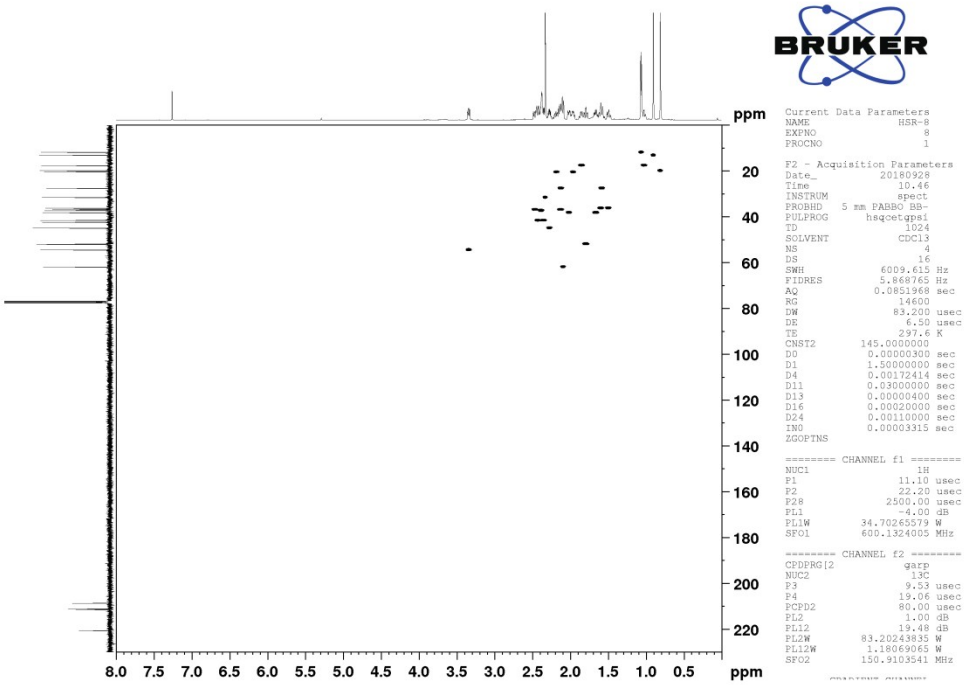


Fig. S5 HSQC spectrum (600 MHz, $CDCl_3$) of compound **1**

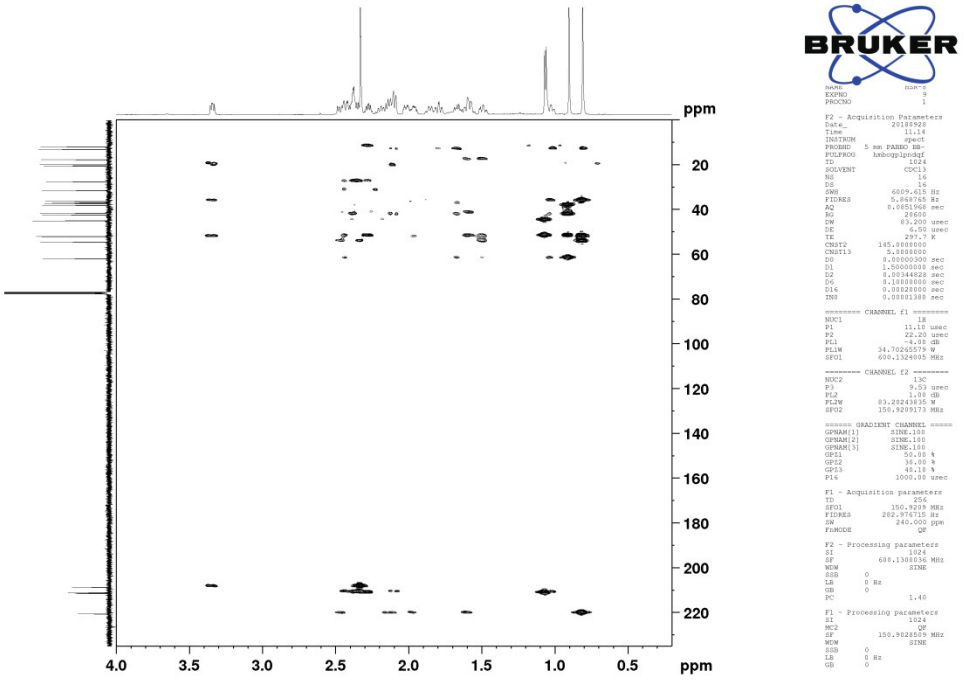


Fig. S6 HMBC spectrum (600 MHz, $CDCl_3$) of compound **1**

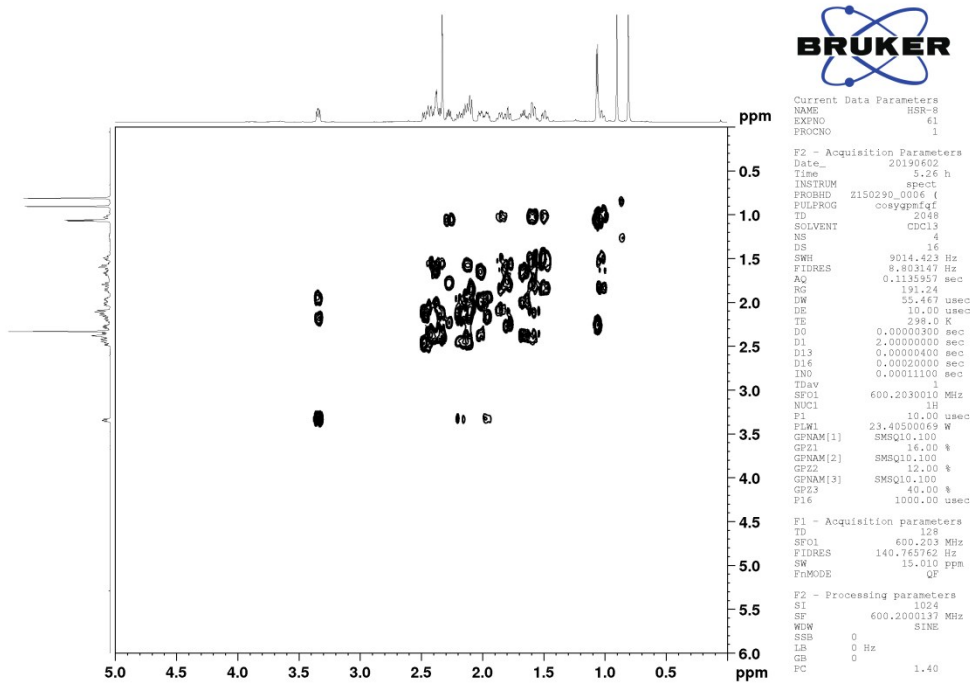


Fig. S7 ^{1}H-^{1}H COSY spectrum (600 MHz, $CDCl_3$) of compound **1**

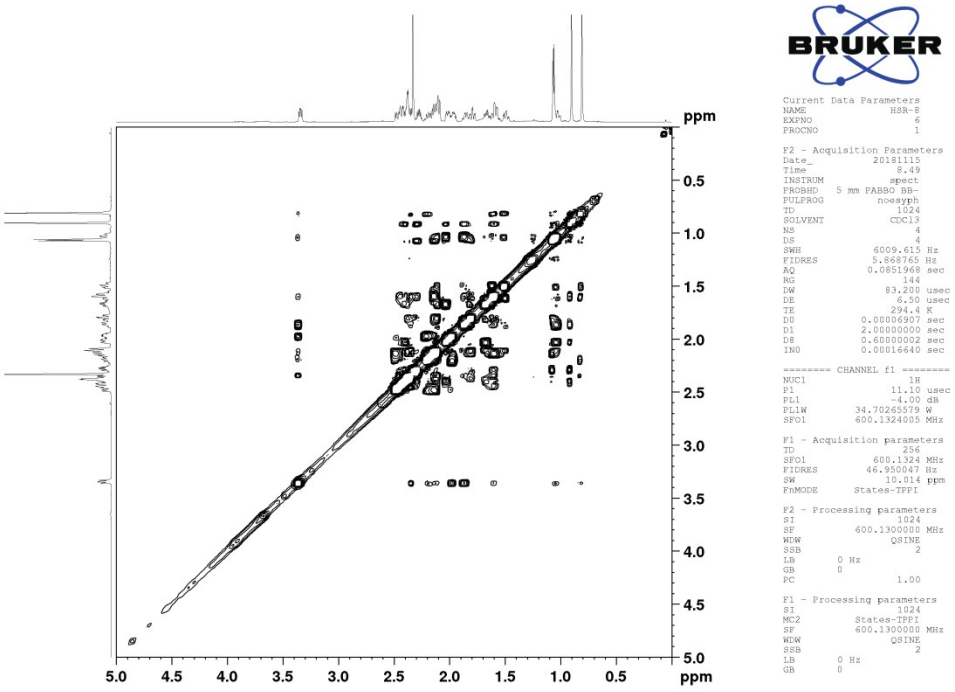
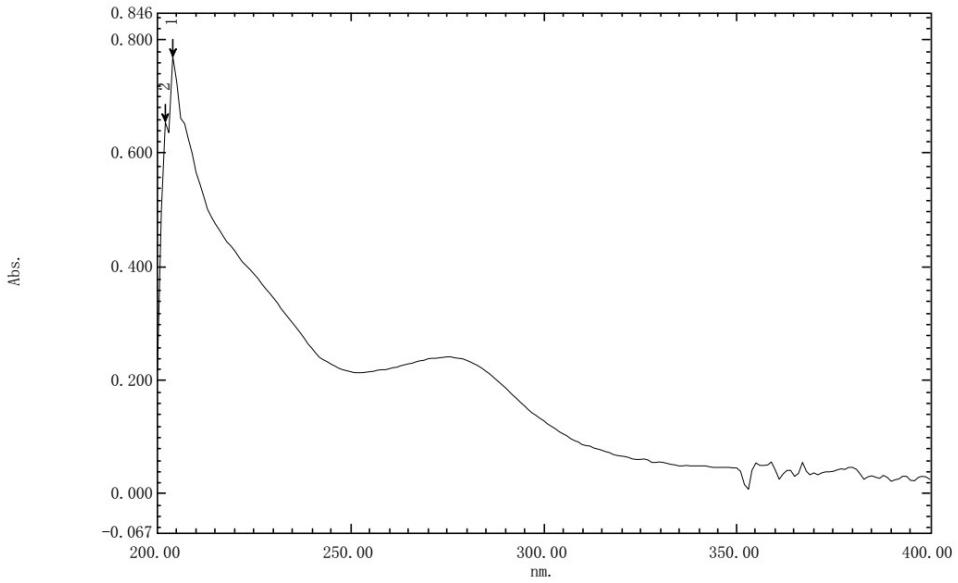


Fig. S8 NOESY spectrum (600 MHz, $CDCl_3$) of compound **1**



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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

No.	P/V	Wavelength	Abs.	描述
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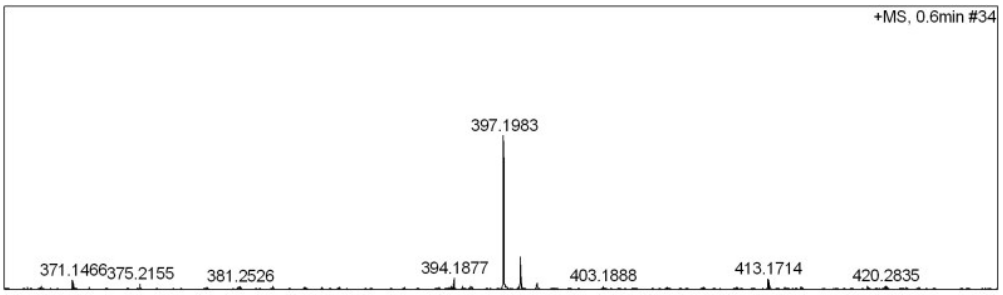
2	↑	202.00	.654	
3	↓	252.00	.214	

Fig. S9 UV spectrum of compound **2**



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
397.1983	1	C 22 H 30 Na O 5	397.1985	0.5	0.9	7.5	ok	even	13.22	0.0202	0.0006	0.0089	0.0011	0.8427

Fig. S10 HRESIMS spectrum of compound **2**

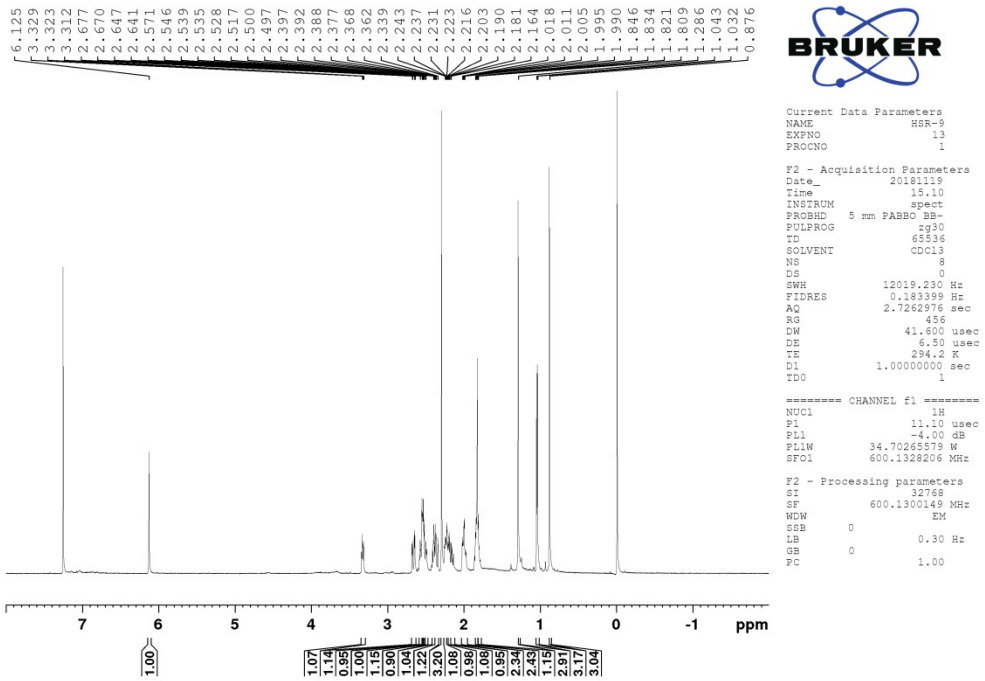
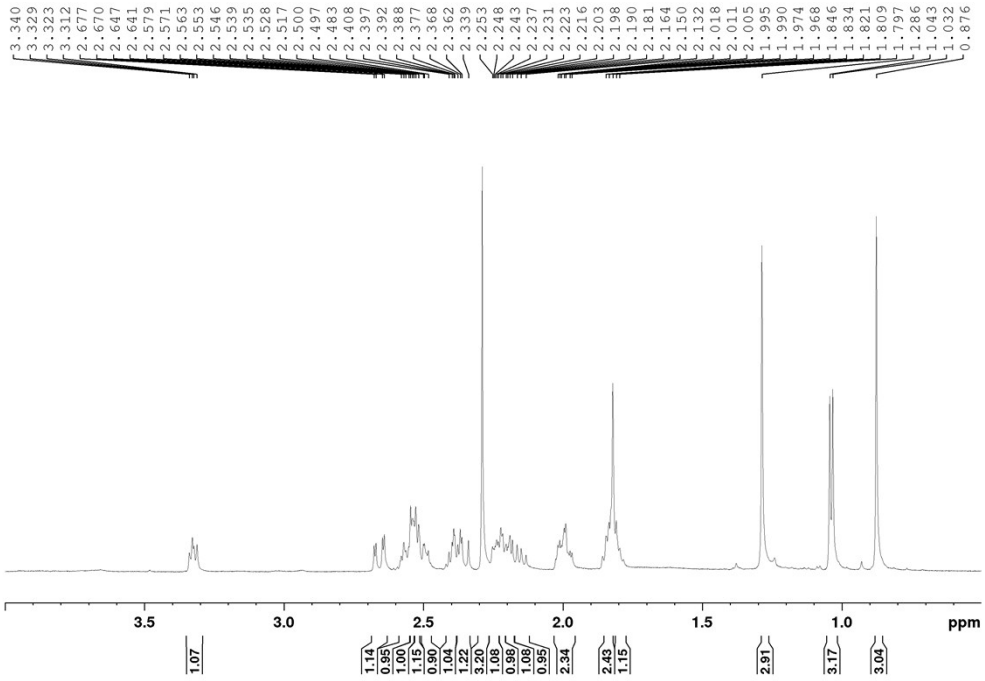


Fig. S11 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2**



Locally amplified ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2**

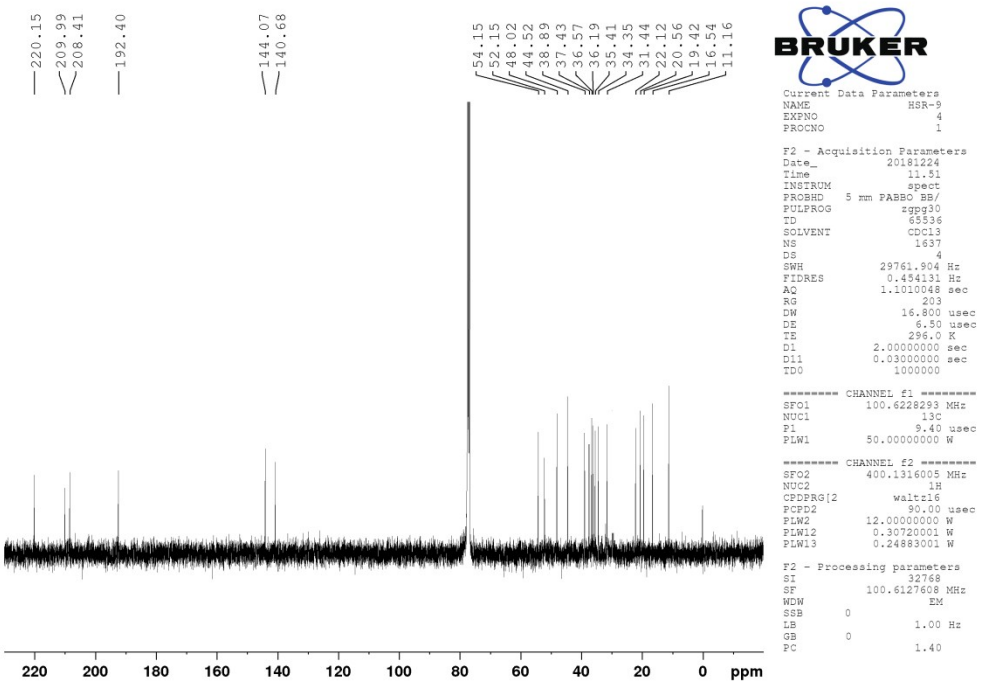
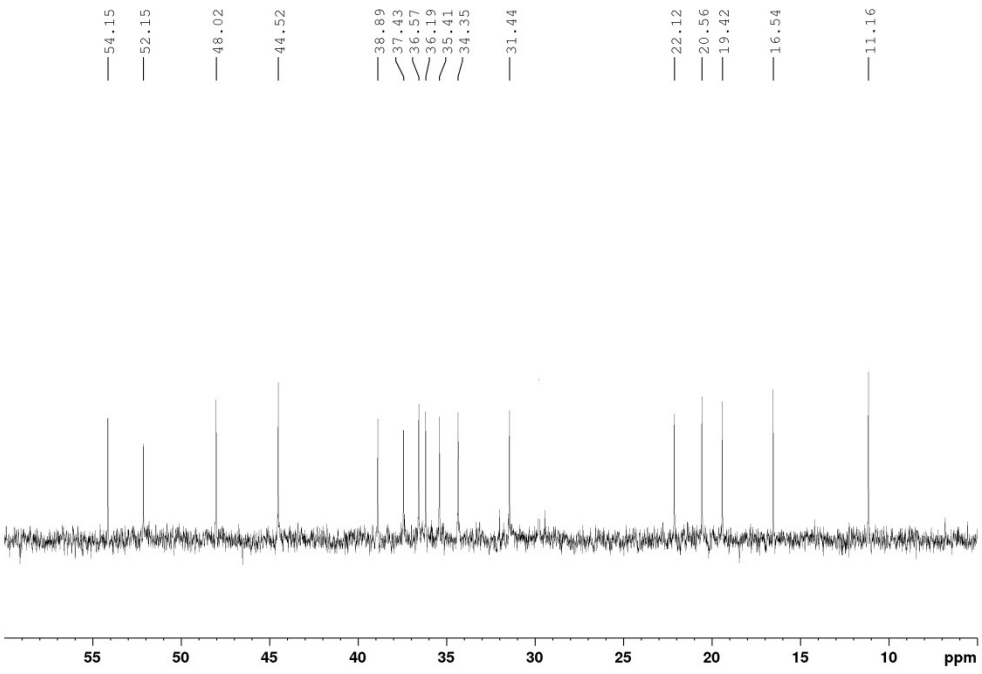


Fig. S12 ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **2**



Locally amplified ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **2**

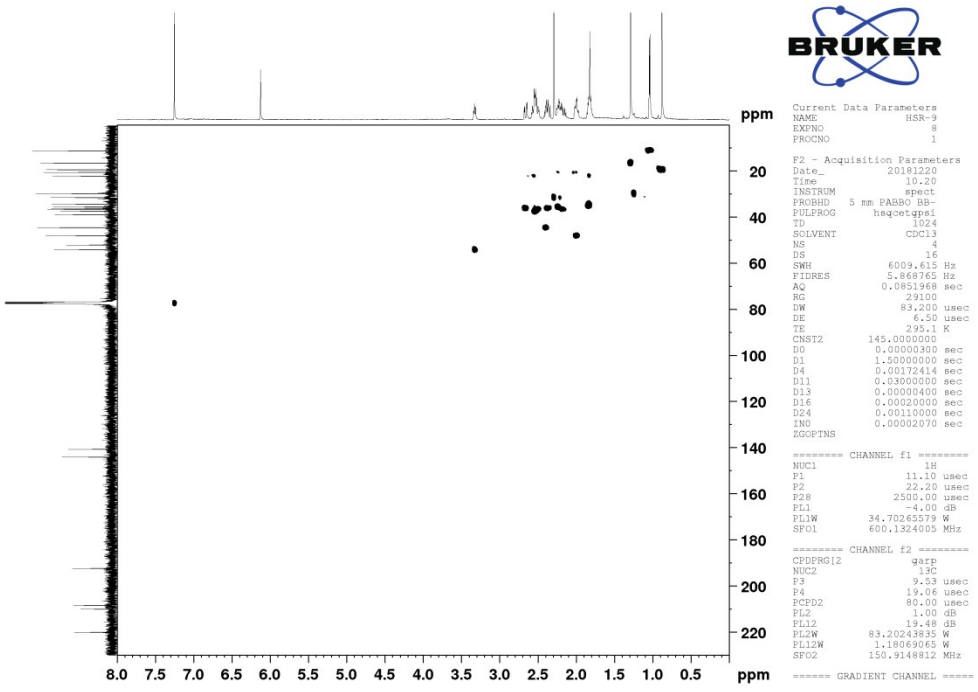


Fig. S13 HSQC spectrum (600 MHz, $CDCl_3$) of compound **2**

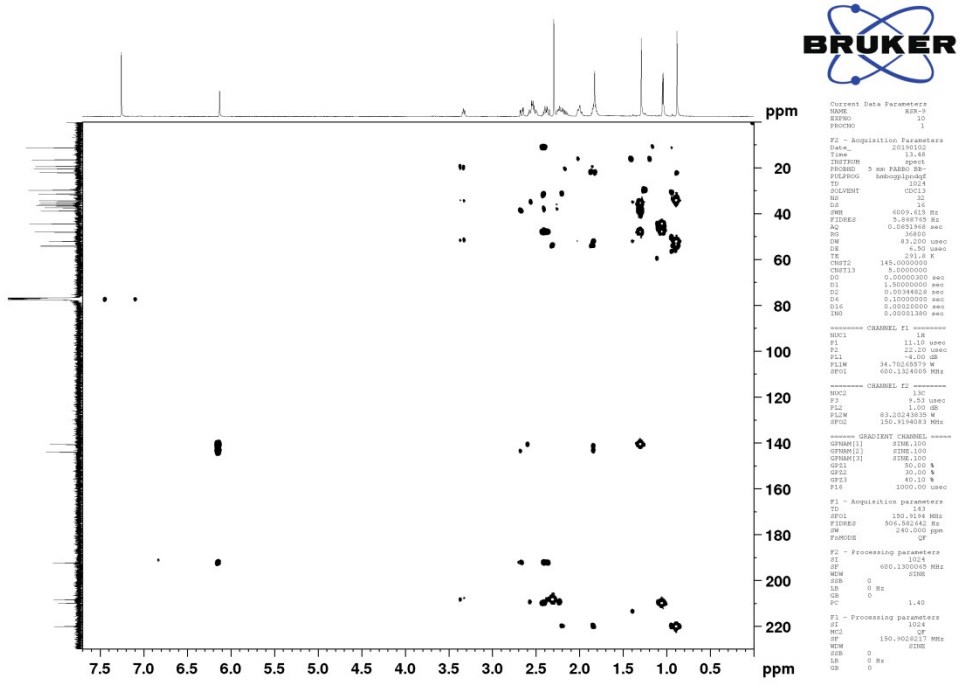


Fig. S14 HMBC spectrum (600 MHz, $CDCl_3$) of compound **2**

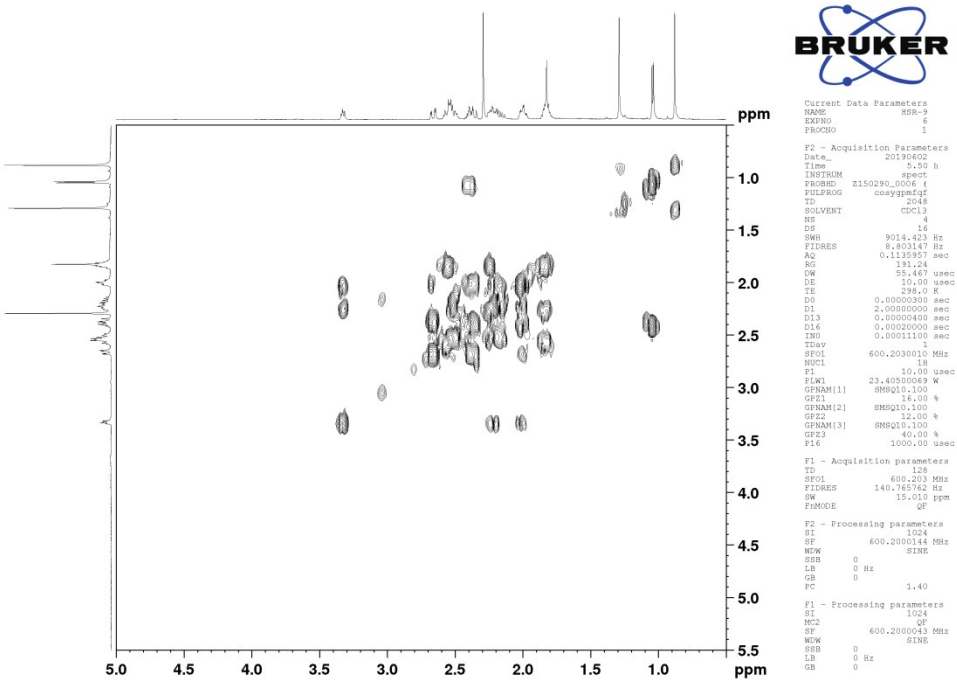


Fig. S15 ^{1}H-^{1}H COSY spectrum (600 MHz, $CDCl_3$) of compound **2**

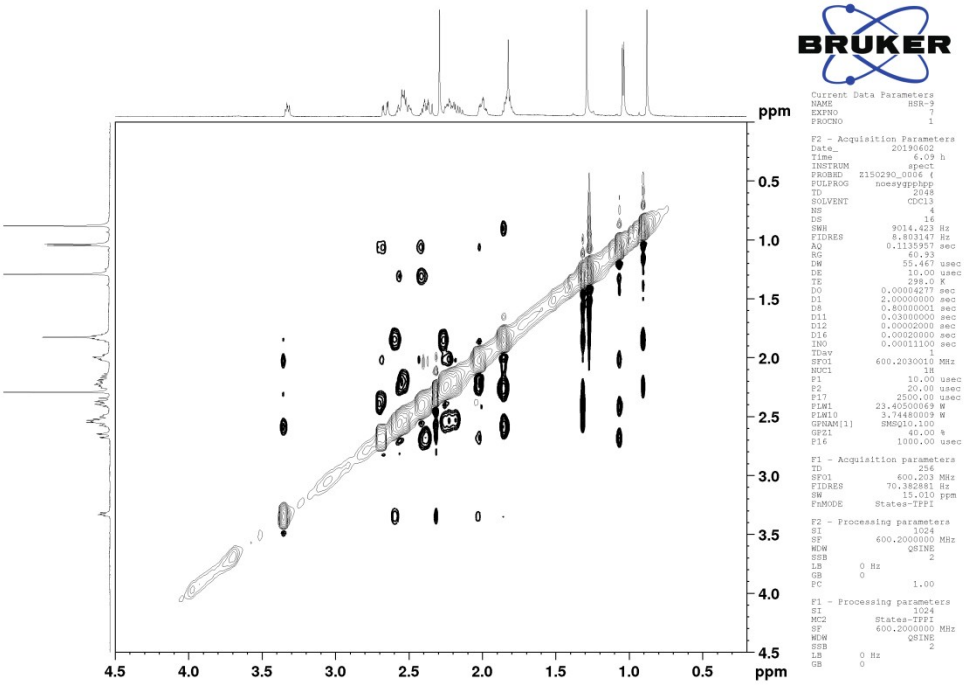
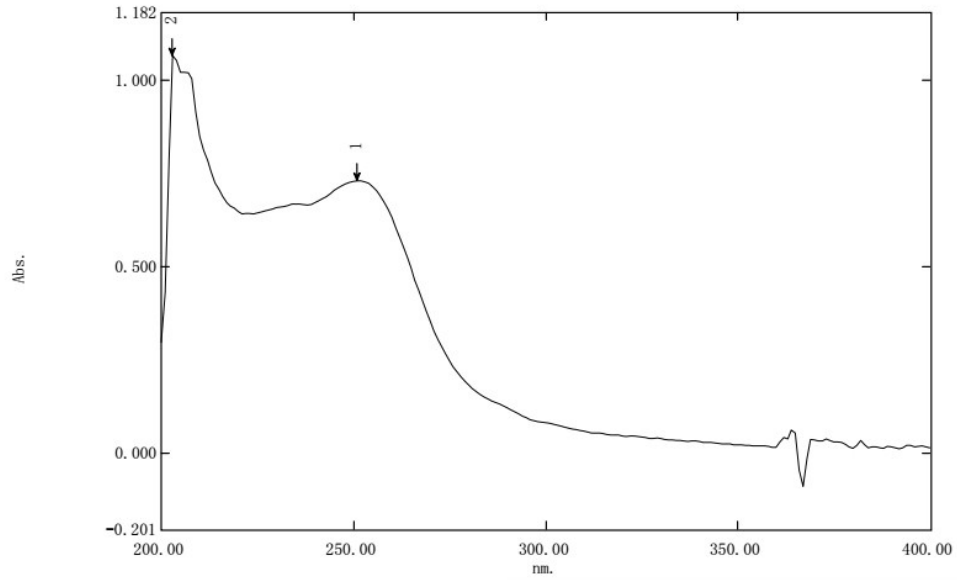


Fig. S16 NOESY spectrum (600 MHz, $CDCl_3$) of compound **2**



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扫描速度： 中速
采样间隔： 1.0
自动采样间隔: 停用
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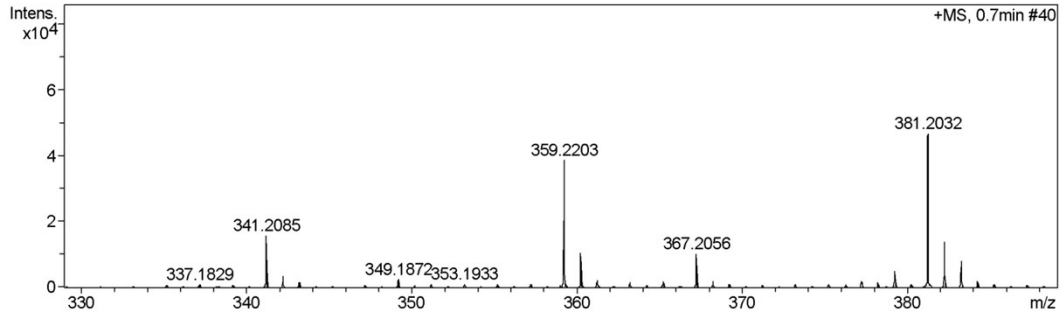
2	↑	203.00	1.067	

Fig. S17 UV spectrum of compound **3**



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
359.2203	1	C 22 H 31 O 4	359.2217	4.0	6.5	7.5	ok	even	20.64	0.0353	0.0038	0.0161	0.0015	0.8427

Fig. S18 HRESIMS spectrum of compound **3**

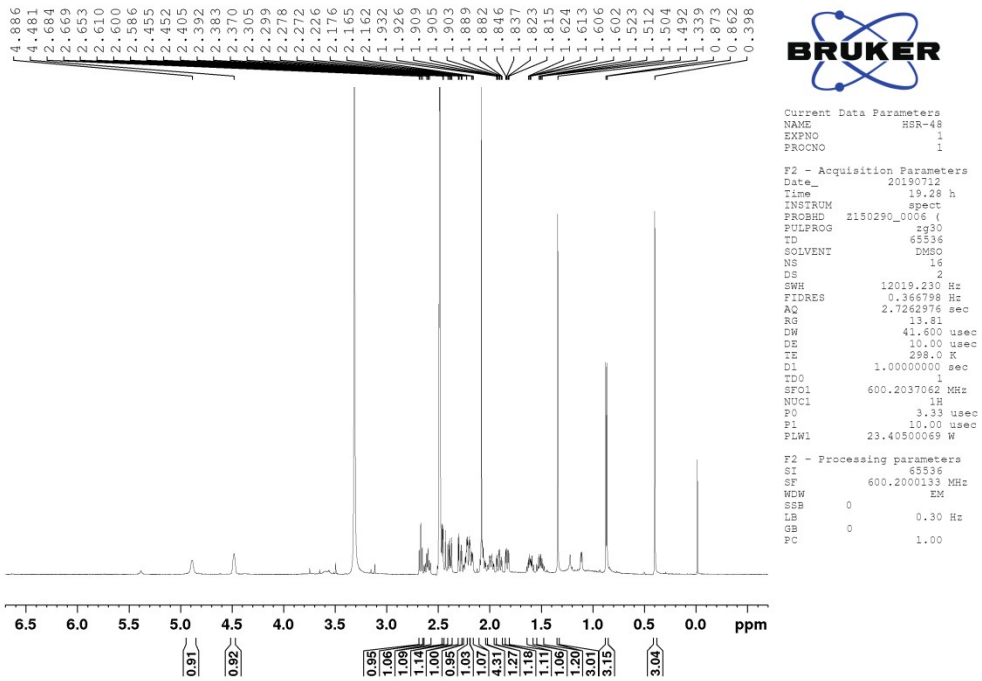


Fig. S19 ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of compound **3**

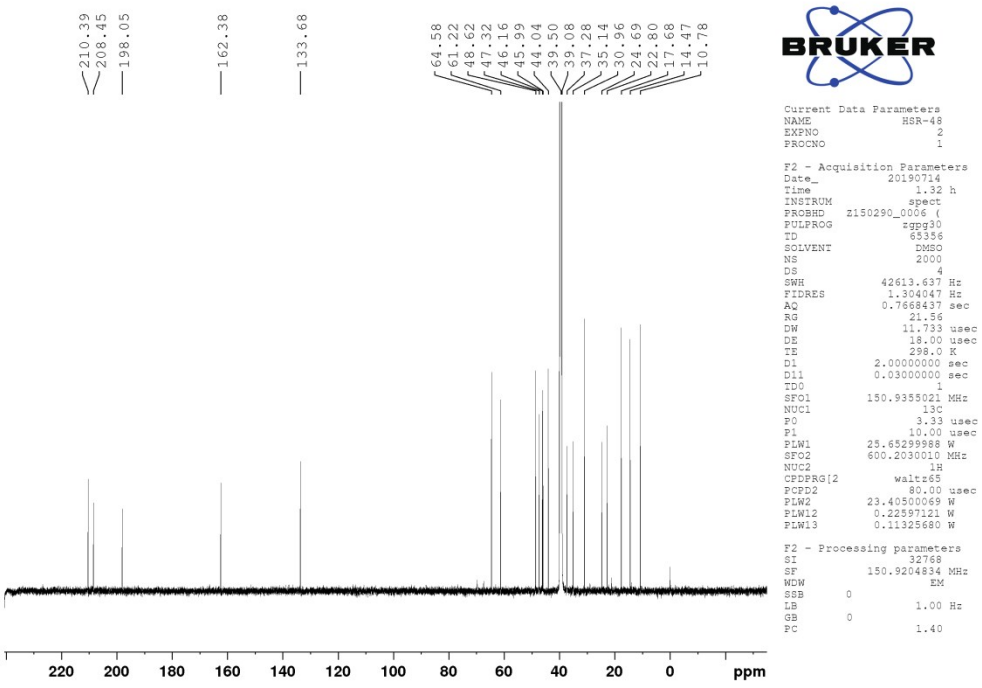
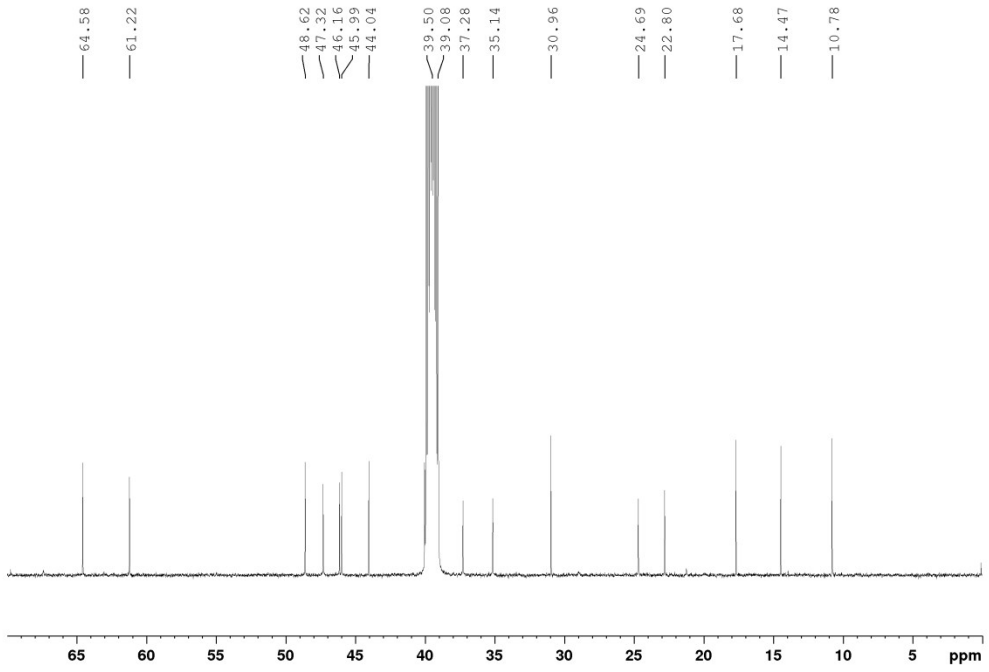


Fig. S20 ^{13}C NMR spectrum (150 MHz, DMSO-d_6) of compound **3**



Locally amplified ^{13}C NMR spectrum (150 MHz, DMSO-d_6) of compound **3**

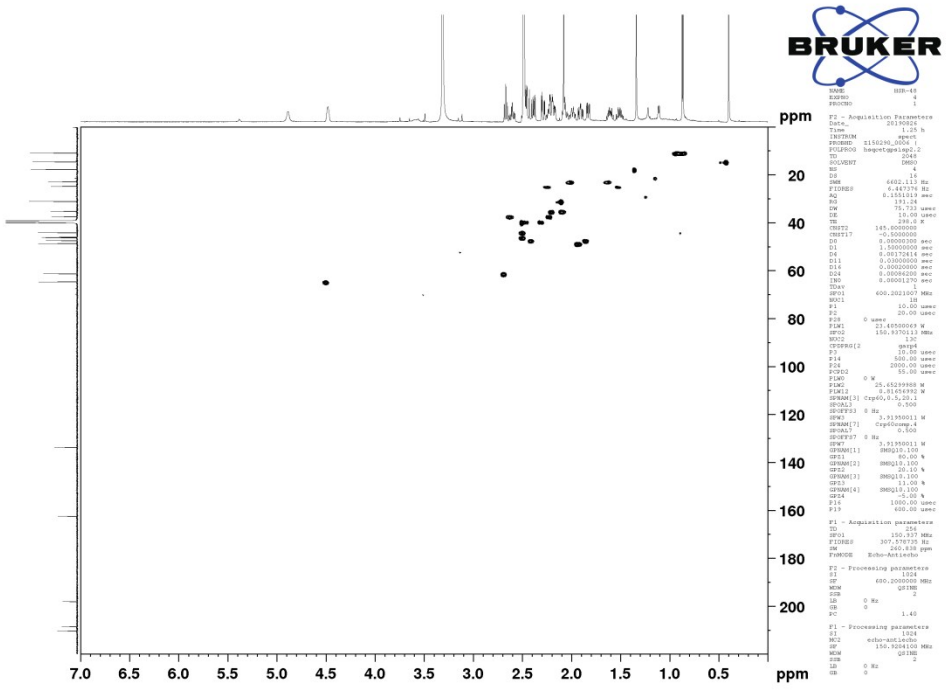


Fig. S21 HSQC spectrum (600 MHz, DMSO-d_6) of compound **3**

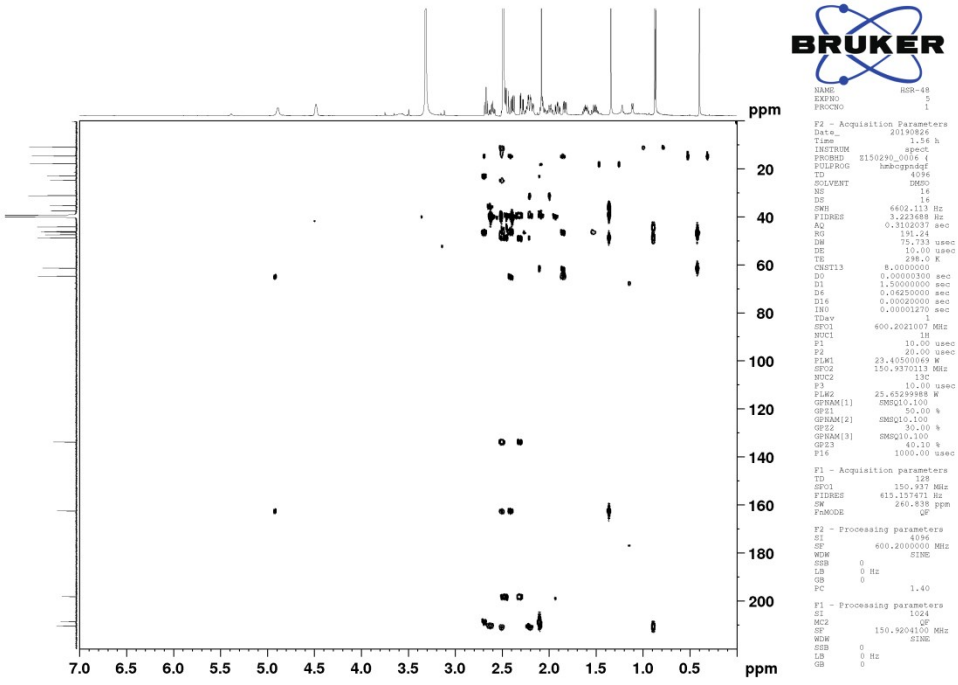


Fig. S22 HMBC spectrum (600 MHz, DMSO-d_6) of compound **3**

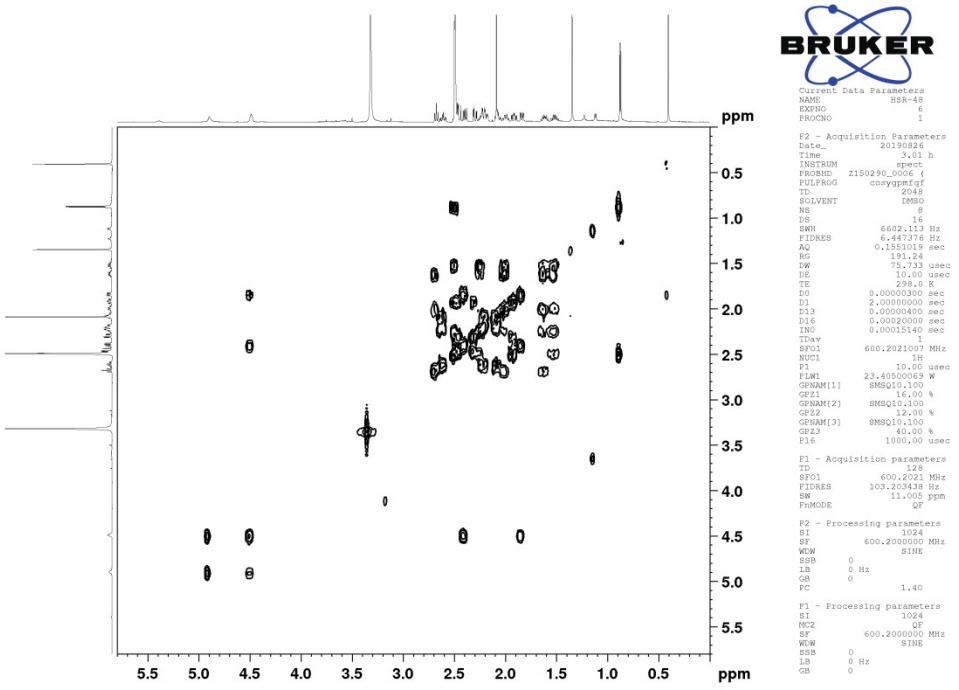


Fig. S23 ^{1}H-^{1}H COSY spectrum (600 MHz, DMSO-d_6) of compound **3**

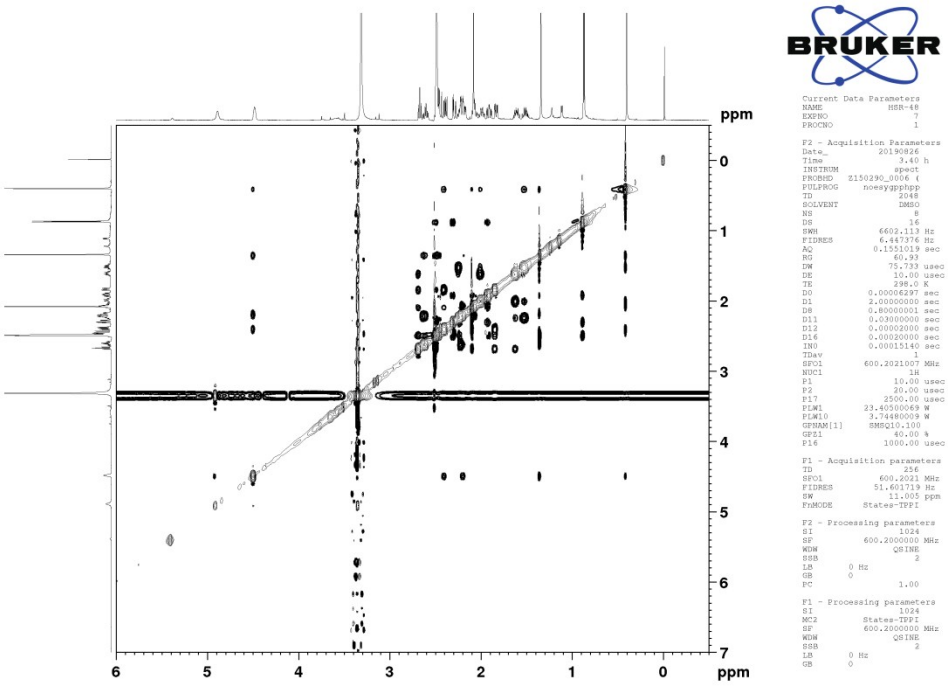


Fig. S24 NOESY spectrum (600 MHz, DMSO-d_6) of compound **3**

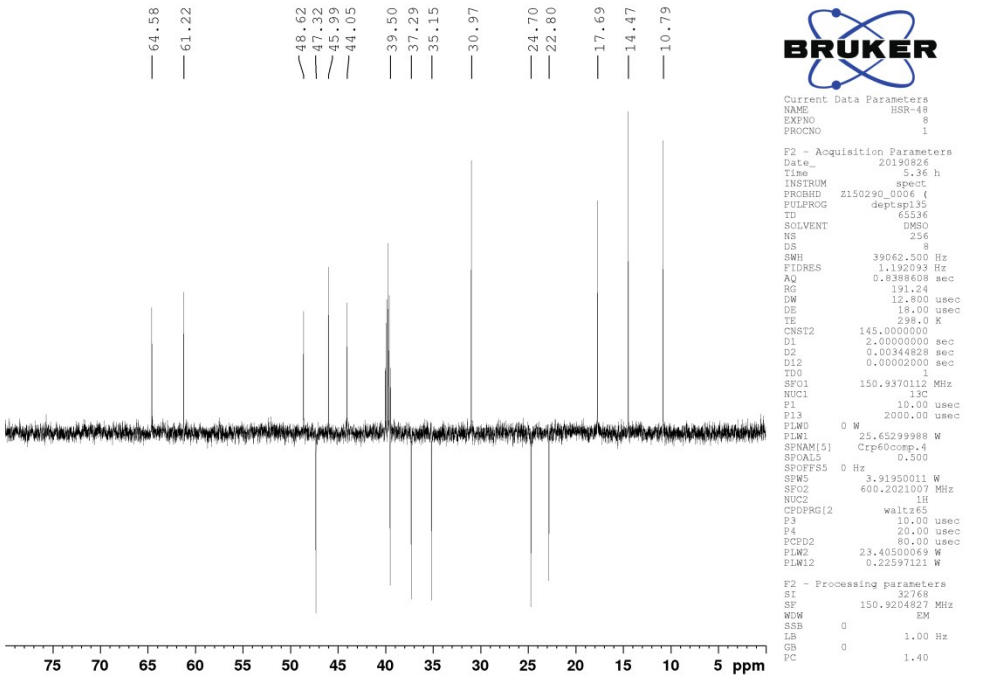
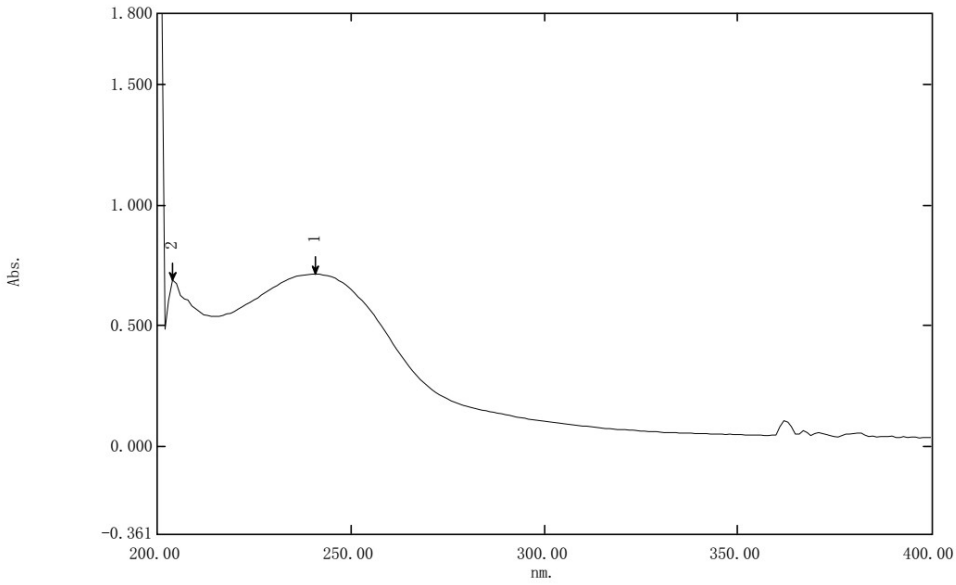


Fig. S25 DEPT spectrum (600 MHz, DMSO-d_6) of compound **3**



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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

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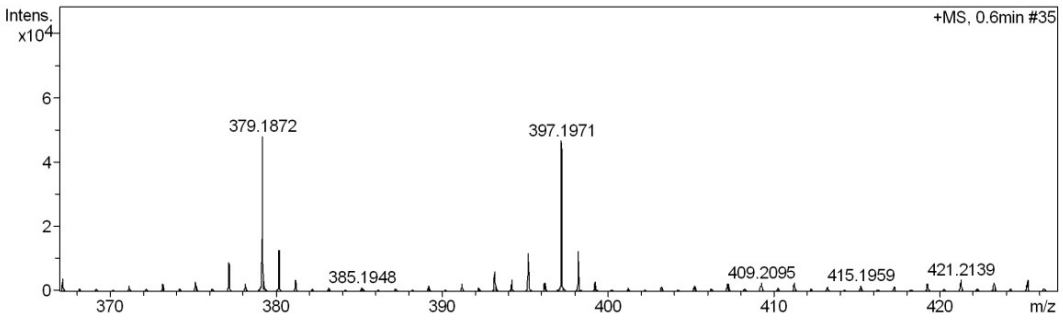
Fig. S26 UV spectrum of compound **4**



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
397.1971														
	1	C 22 H 30 Na O 5	397.1985	3.6	5.0	7.5	ok	even	22.67	0.0401	0.0022	0.0199	0.0022	0.8427

Fig. S27 HRESIMS spectrum of compound **4**

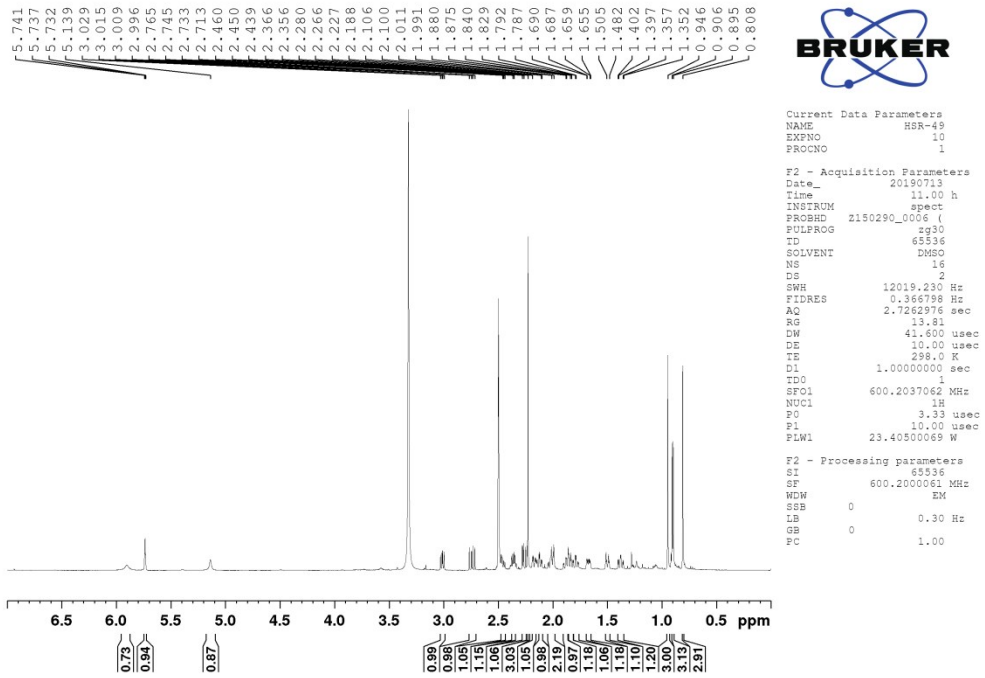


Fig. S28 ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of compound **4**

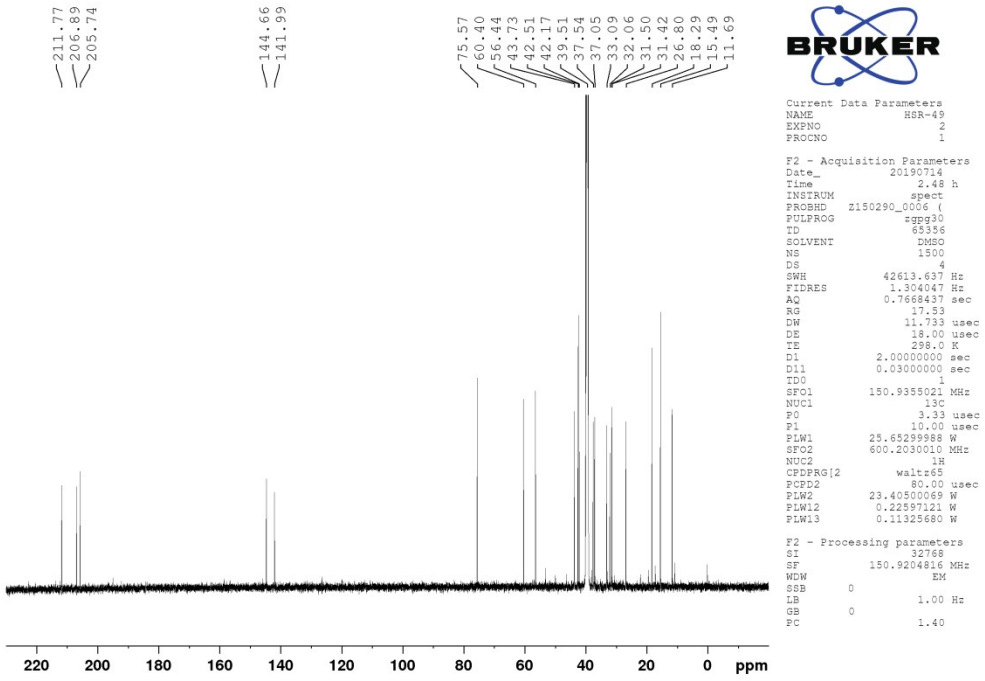


Fig. S29 ^{13}C NMR spectrum (150 MHz, DMSO-d_6) of compound **4**

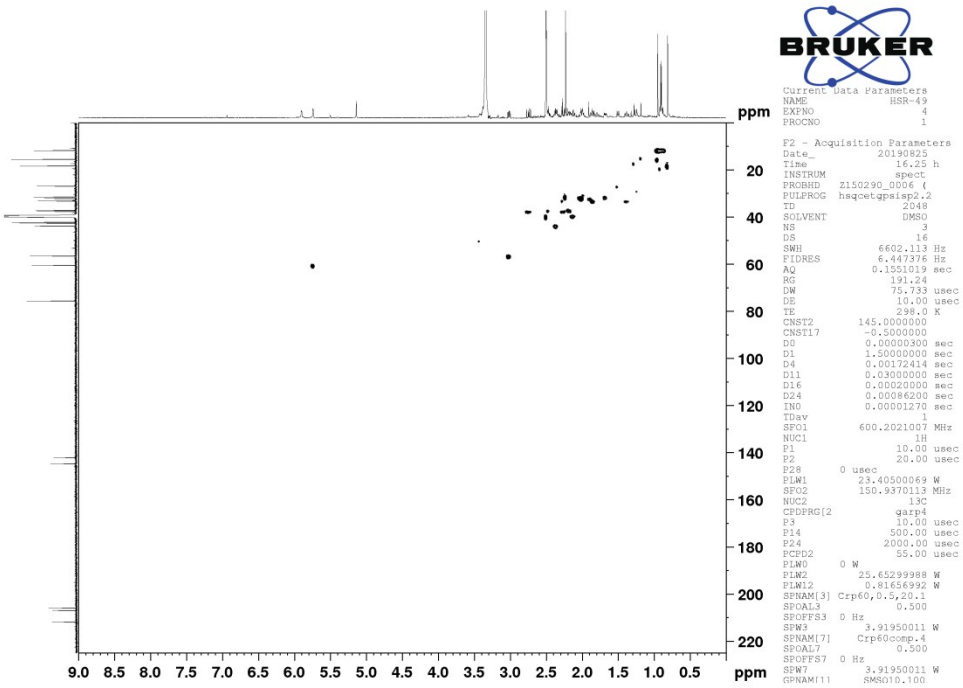


Fig. S30 HSQC spectrum (600 MHz, DMSO-d_6) of compound **4**

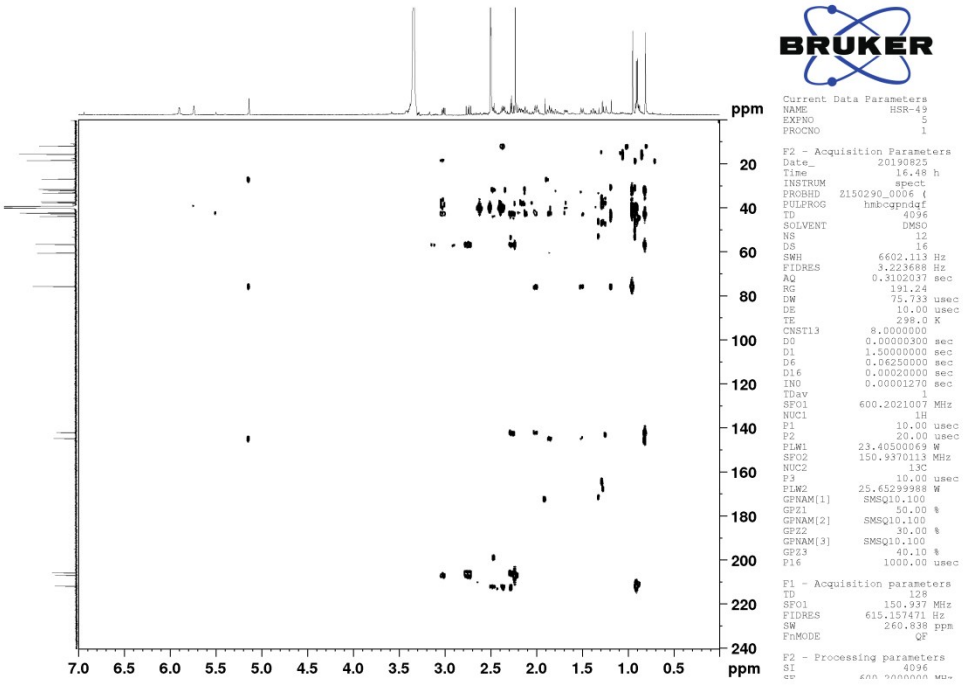


Fig. S31 HMBC spectrum (600 MHz, DMSO-d_6) of compound **4**

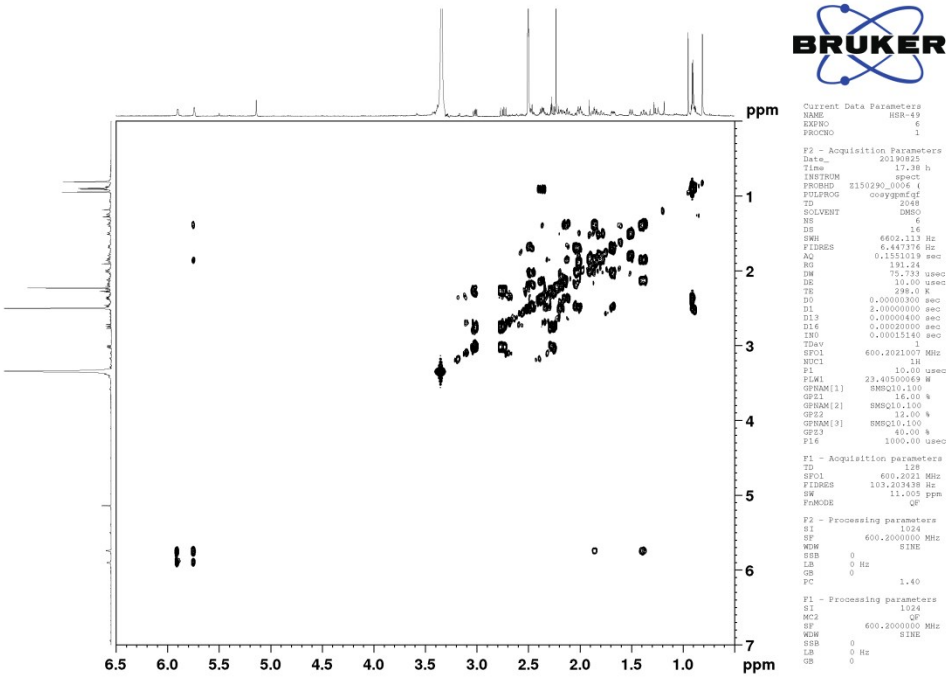


Fig. S32 ^{1}H-^{1}H COSY spectrum (600 MHz, DMSO-d_6) of compound **4**

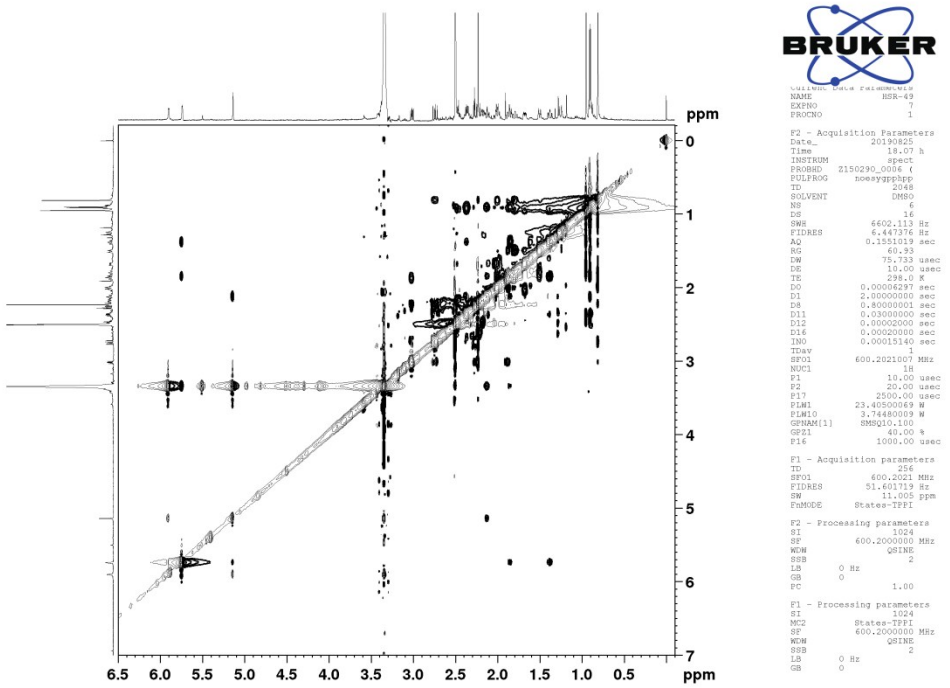


Fig. S33 NOESY spectrum (600 MHz, DMSO-d_6) of compound **4**

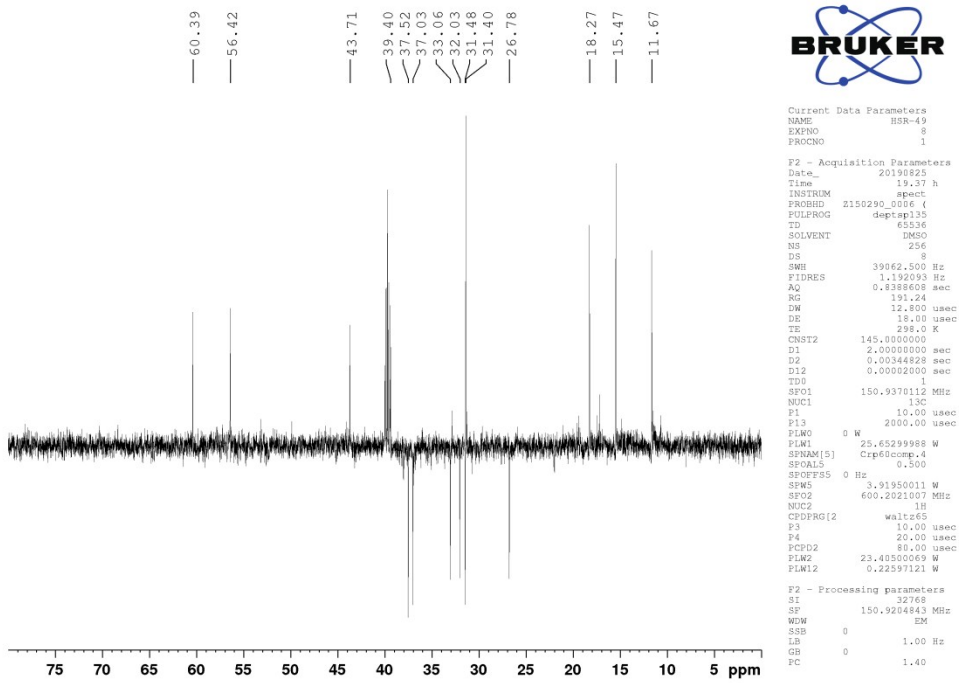
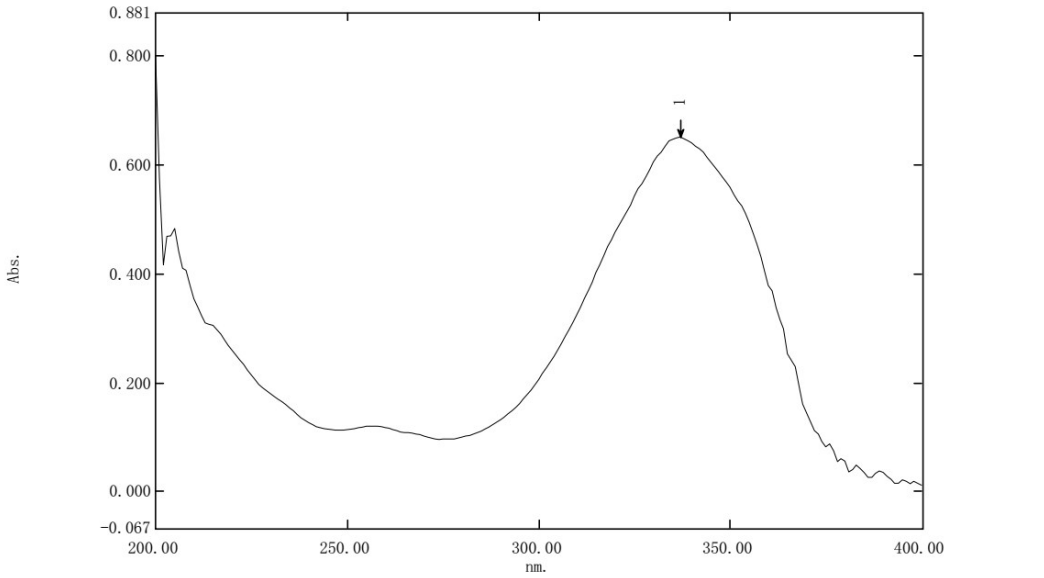


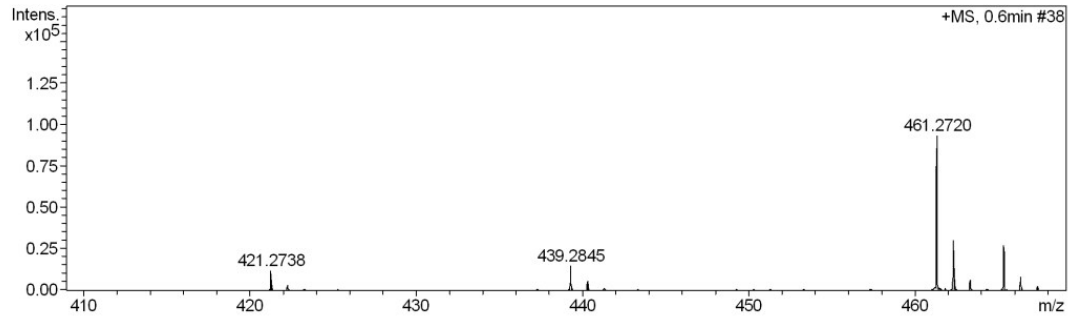
Fig. S34 DEPT spectrum (600 MHz, DMSO-d_6) of compound **4**



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

No.	P/V	Wavelength	Abs.	描述
1	↑	337.00	.652	
2	↓	202.00	.417	

Fig. S35 UV spectrum of compound **5**



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
439.2845	1	C 28 H 39 O 4	439.2843	-0.5	1.8	9.5	ok	even	34.97	0.0584	0.0027	0.0184	0.0052	0.8427

Fig. 36 HRESIMS spectrum of compound **5**

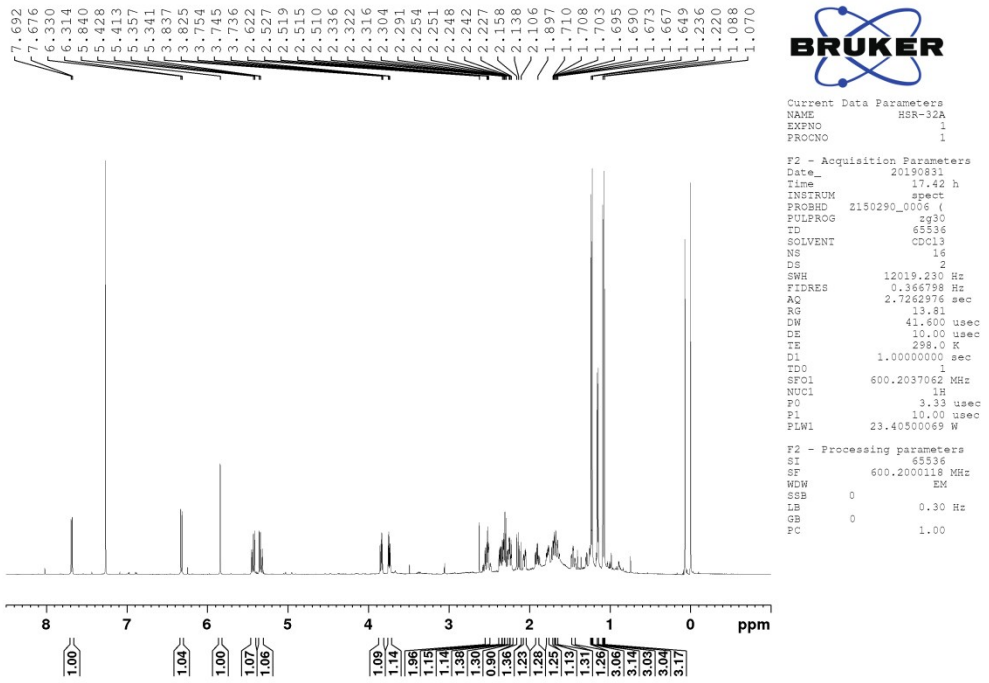


Fig. S37 ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **5**

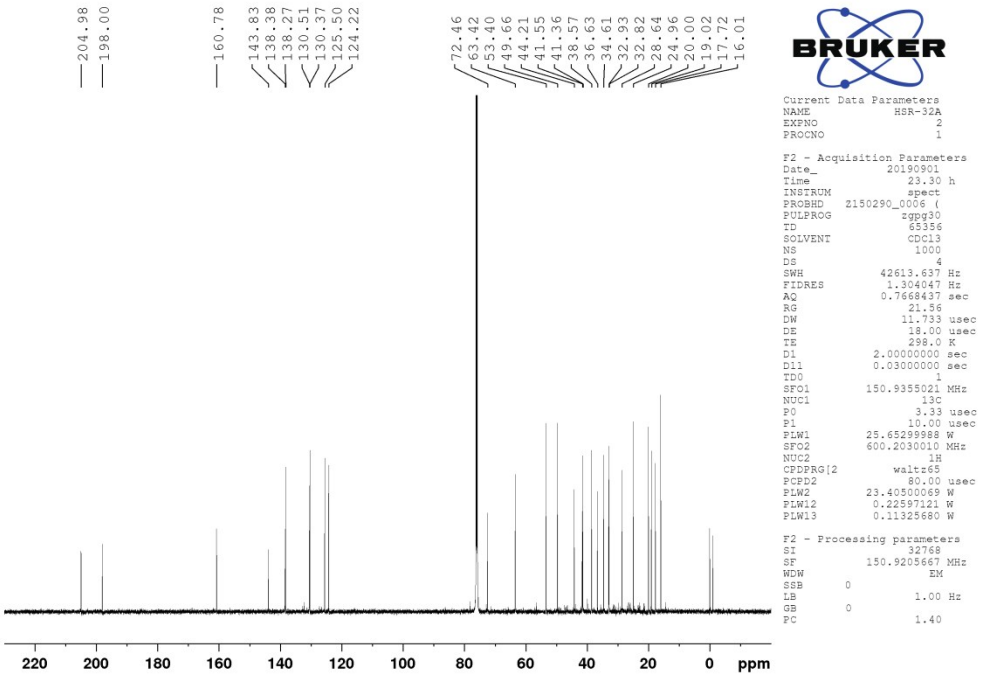
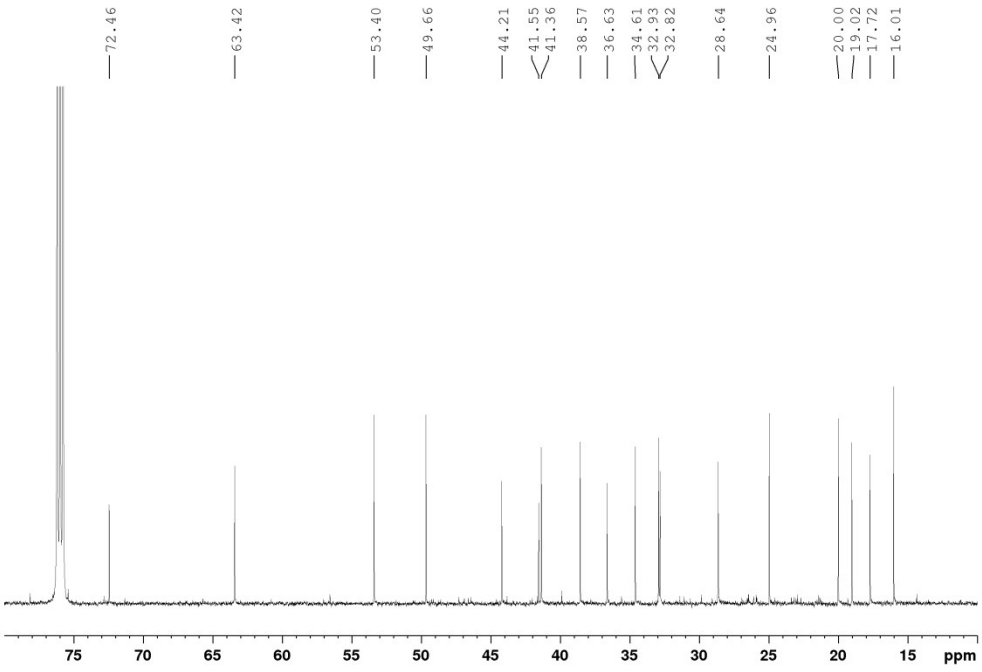


Fig. S38 ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of compound **5**



Locally amplified ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of compound **5**

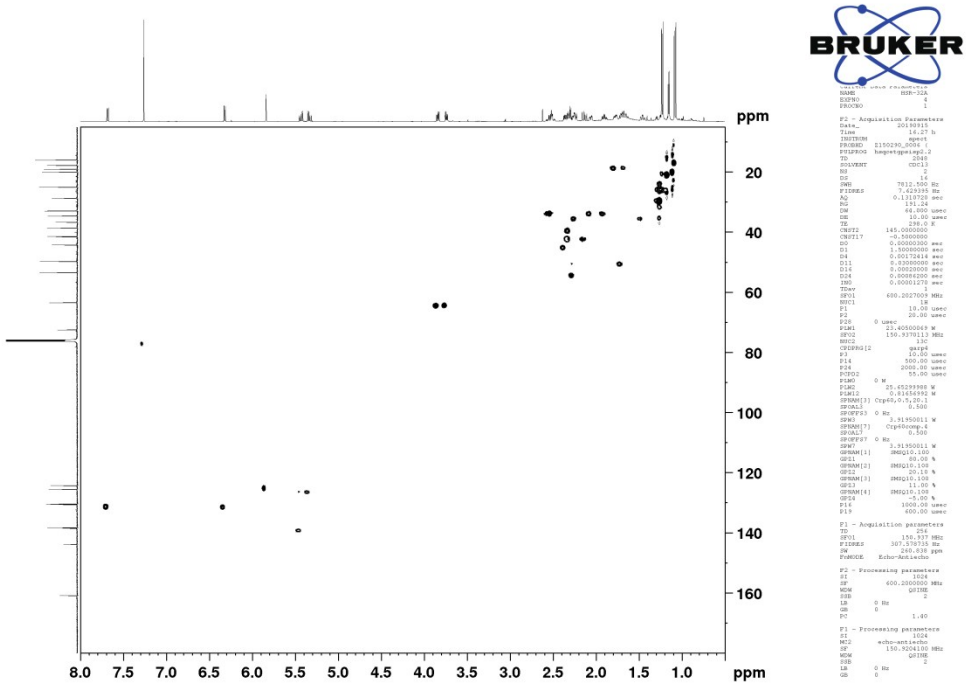


Fig. S39 HSQC spectrum (600 MHz, $CDCl_3$) of compound **5**

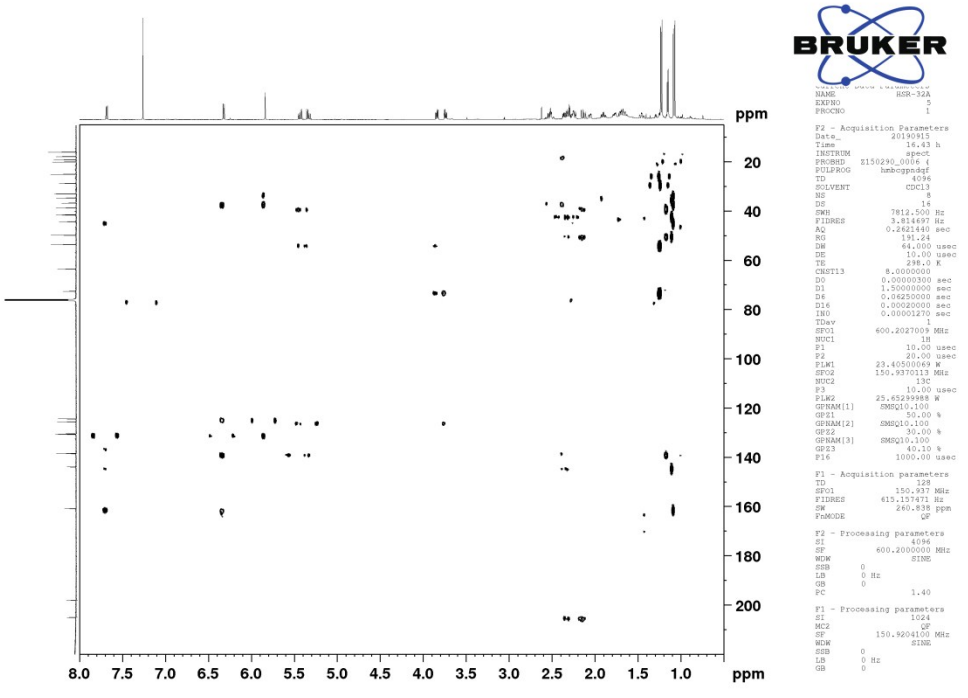


Fig. S40 HMBC spectrum (600 MHz, $CDCl_3$) of compound **5**

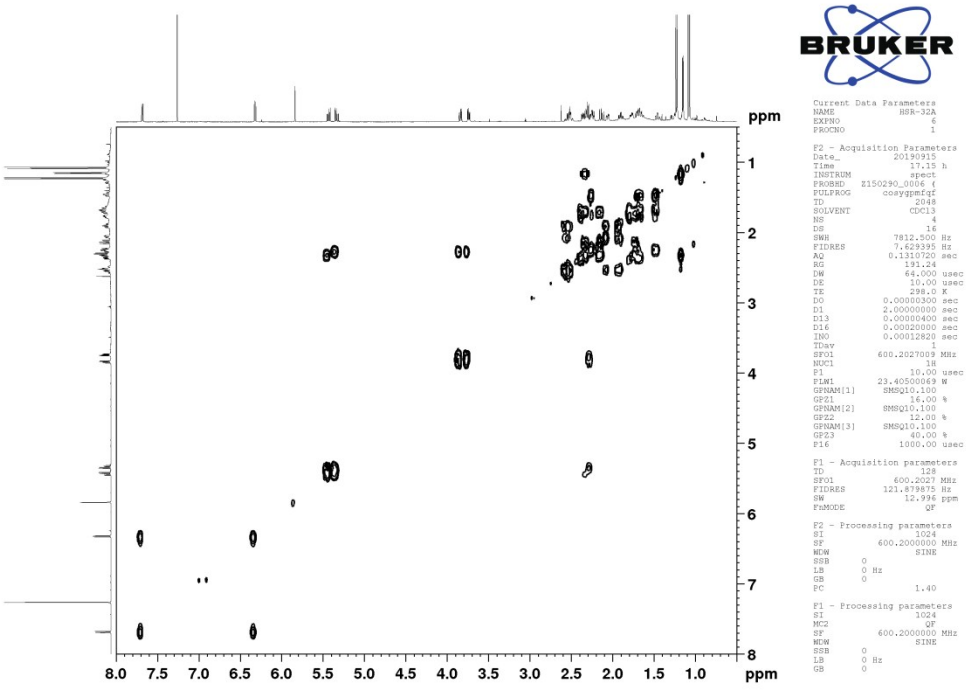


Fig. S41 ^{1}H-^{1}H COSY spectrum (600 MHz, $CDCl_3$) of compound **5**

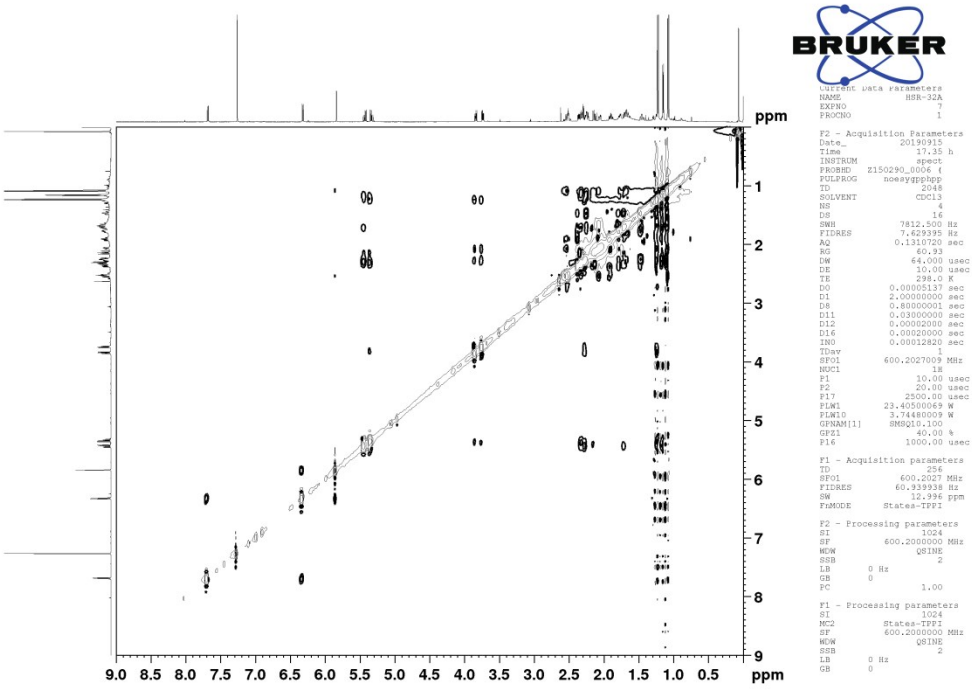


Fig. S42 NOESY spectrum (600 MHz, $CDCl_3$) of compound **5**

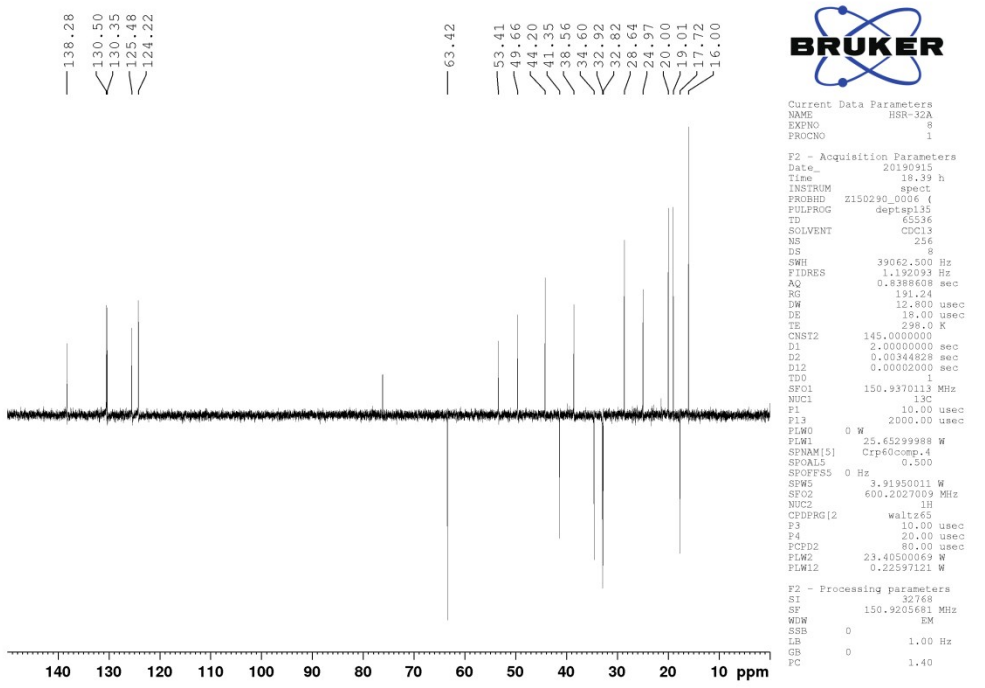
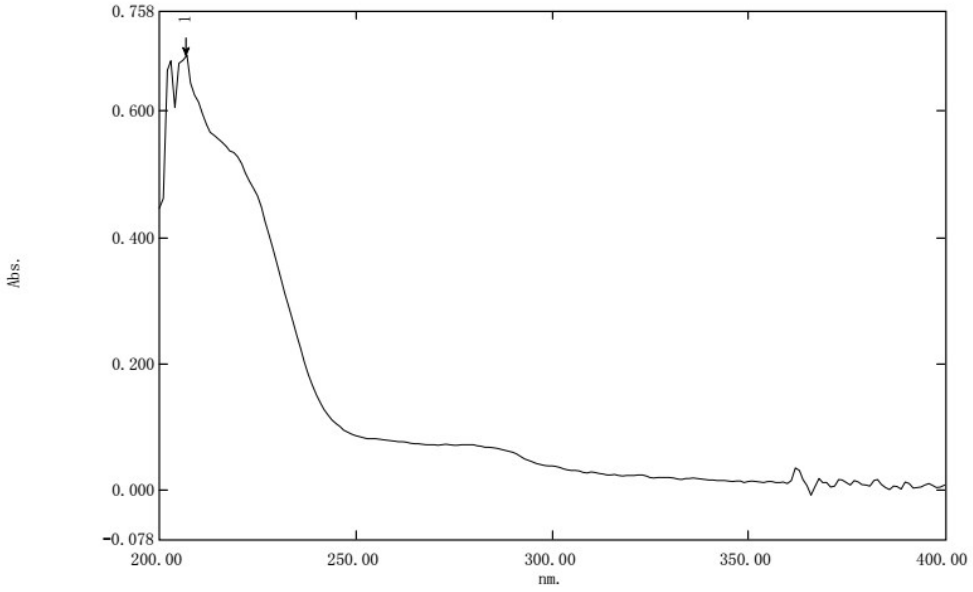


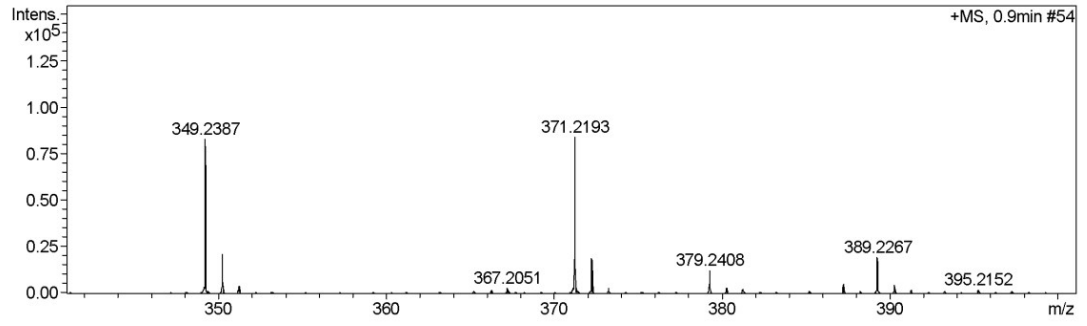
Fig. S43 DEPT spectrum (600 MHz, $CDCl_3$) of compound **5**



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

No.	P/V	Wavelength	Abs.	描述
1	↑	207.00	.688	

Fig. S44 UV spectrum of compound **6**



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
371.2193	1	C 21 H 32 Na O 4	371.2193	-0.2	1.4	5.5	ok	even	4.38	0.0062	0.0014	0.0031	0.0025	0.8427

Fig. S45 HRESIMS spectrum of compound **6**

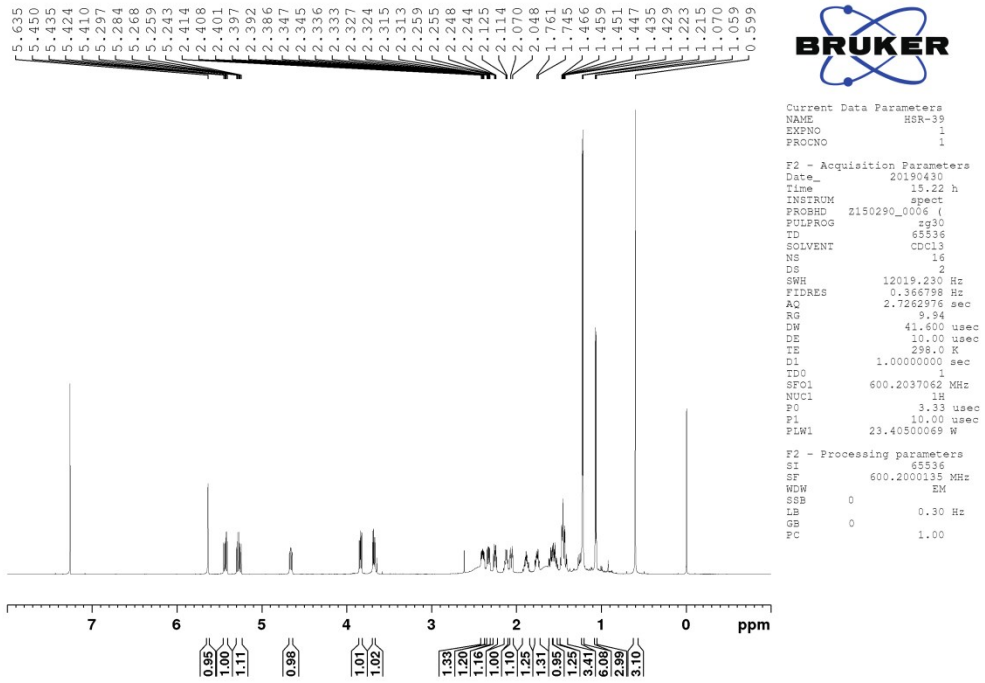


Fig. S46 ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **6**

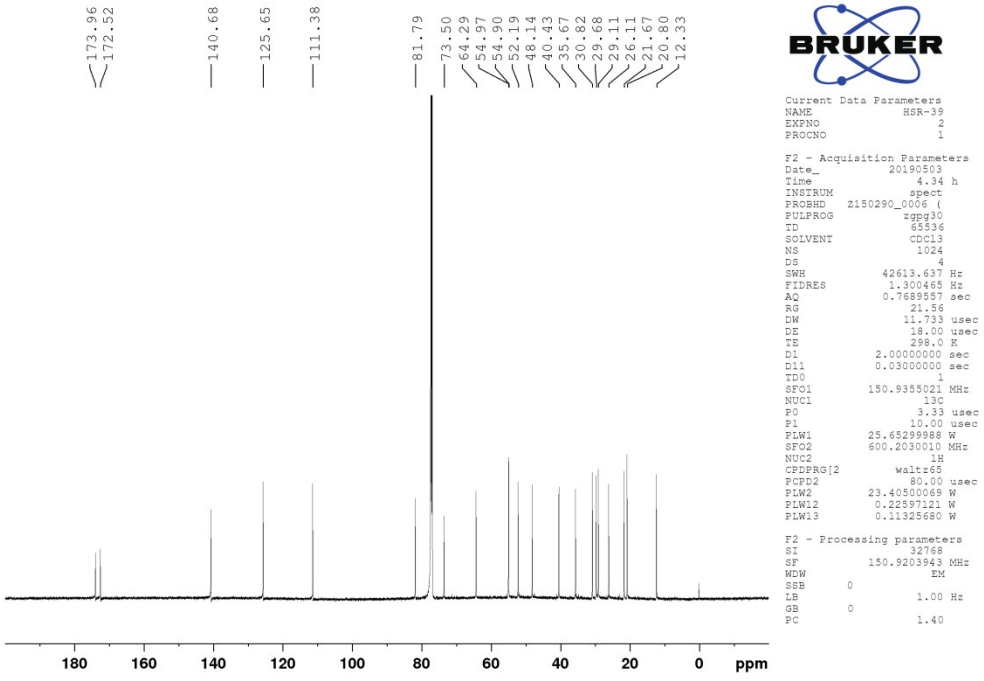


Fig. S47 ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of compound **6**

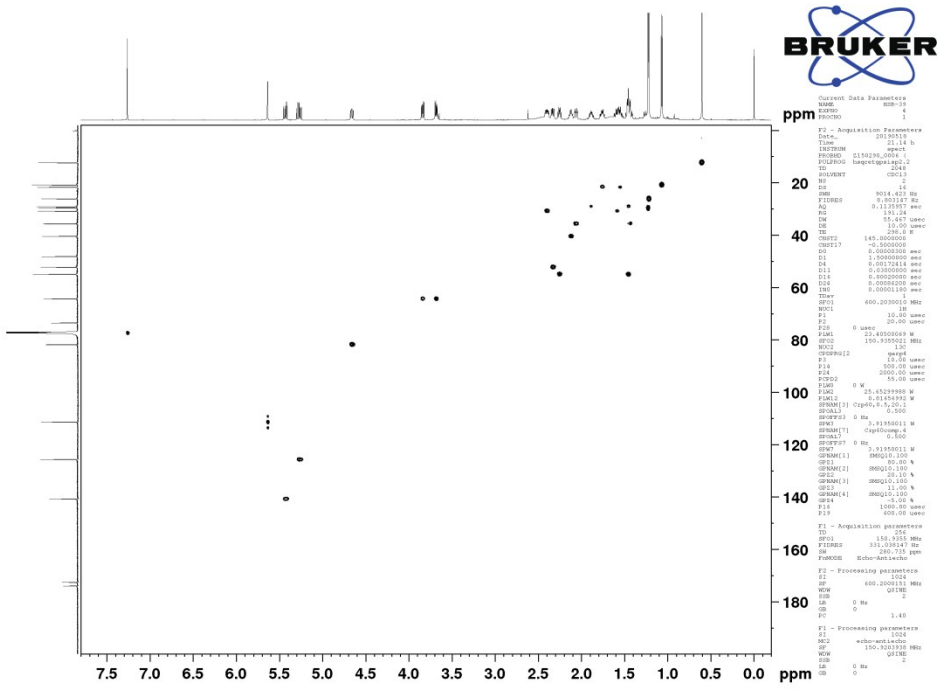


Fig. S48 HSQC spectrum (600 MHz, $CDCl_3$) of compound **6**

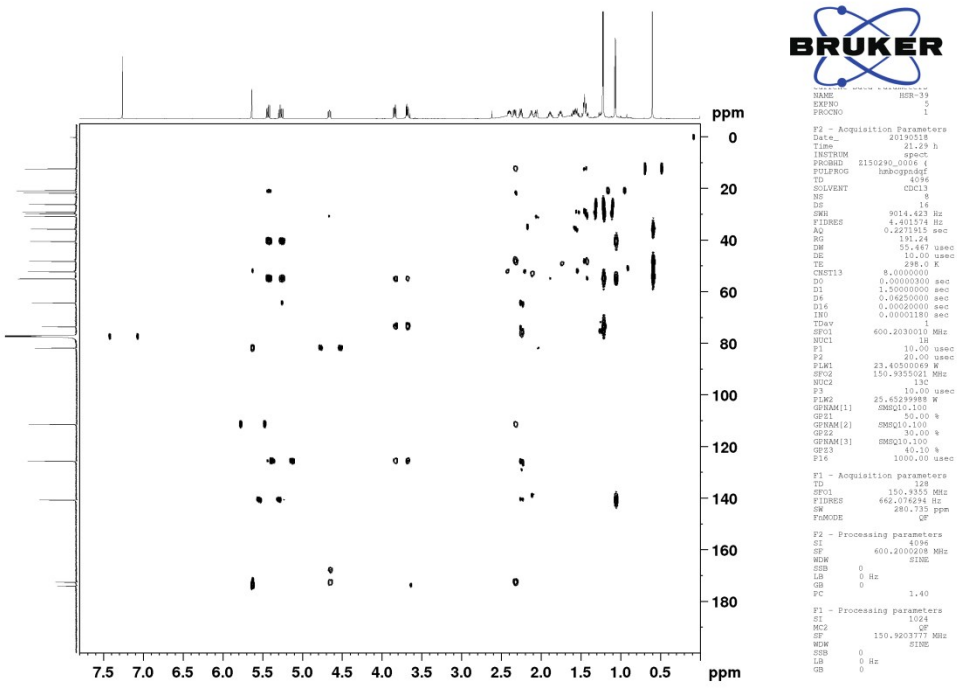


Fig. S49 HMBC spectrum (600 MHz, $CDCl_3$) of compound **6**

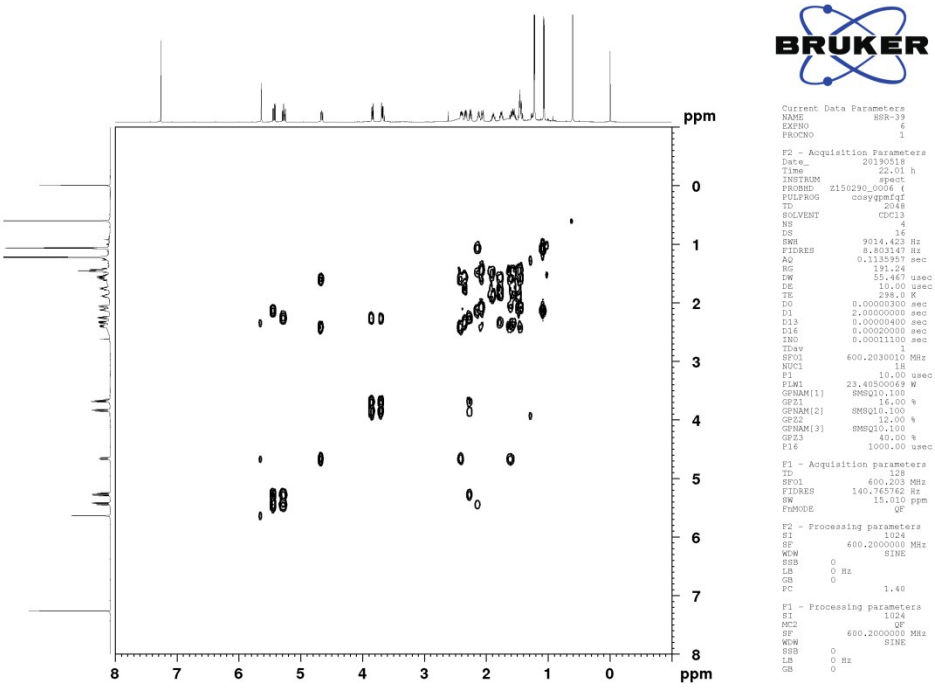


Fig. S50 ^{1}H-^{1}H COSY spectrum (600 MHz, $CDCl_3$) of compound **6**

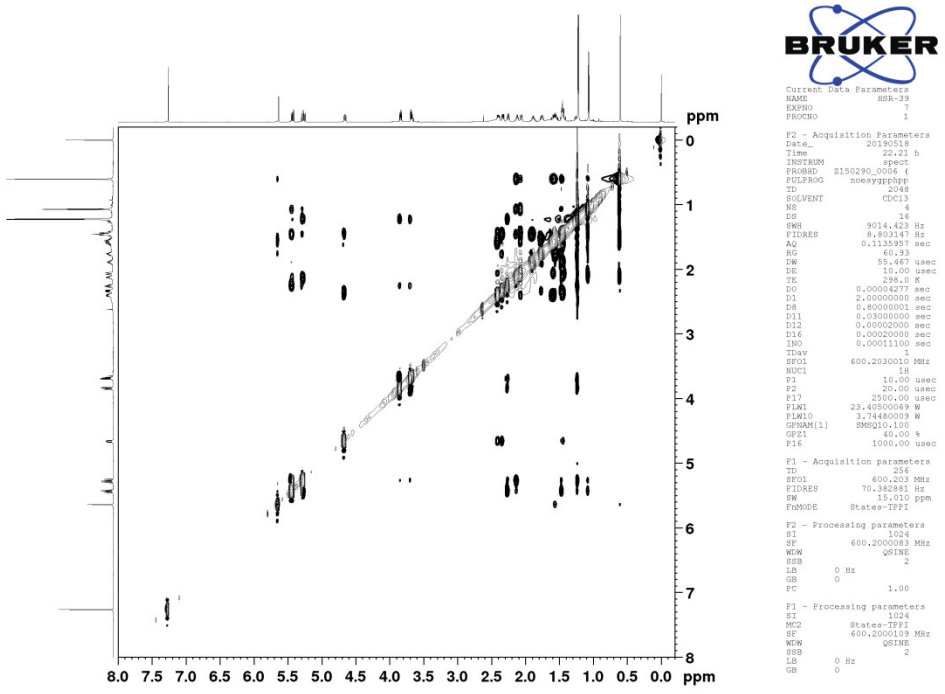


Fig. S51 NOESY spectrum (600 MHz, $CDCl_3$) of compound **6**

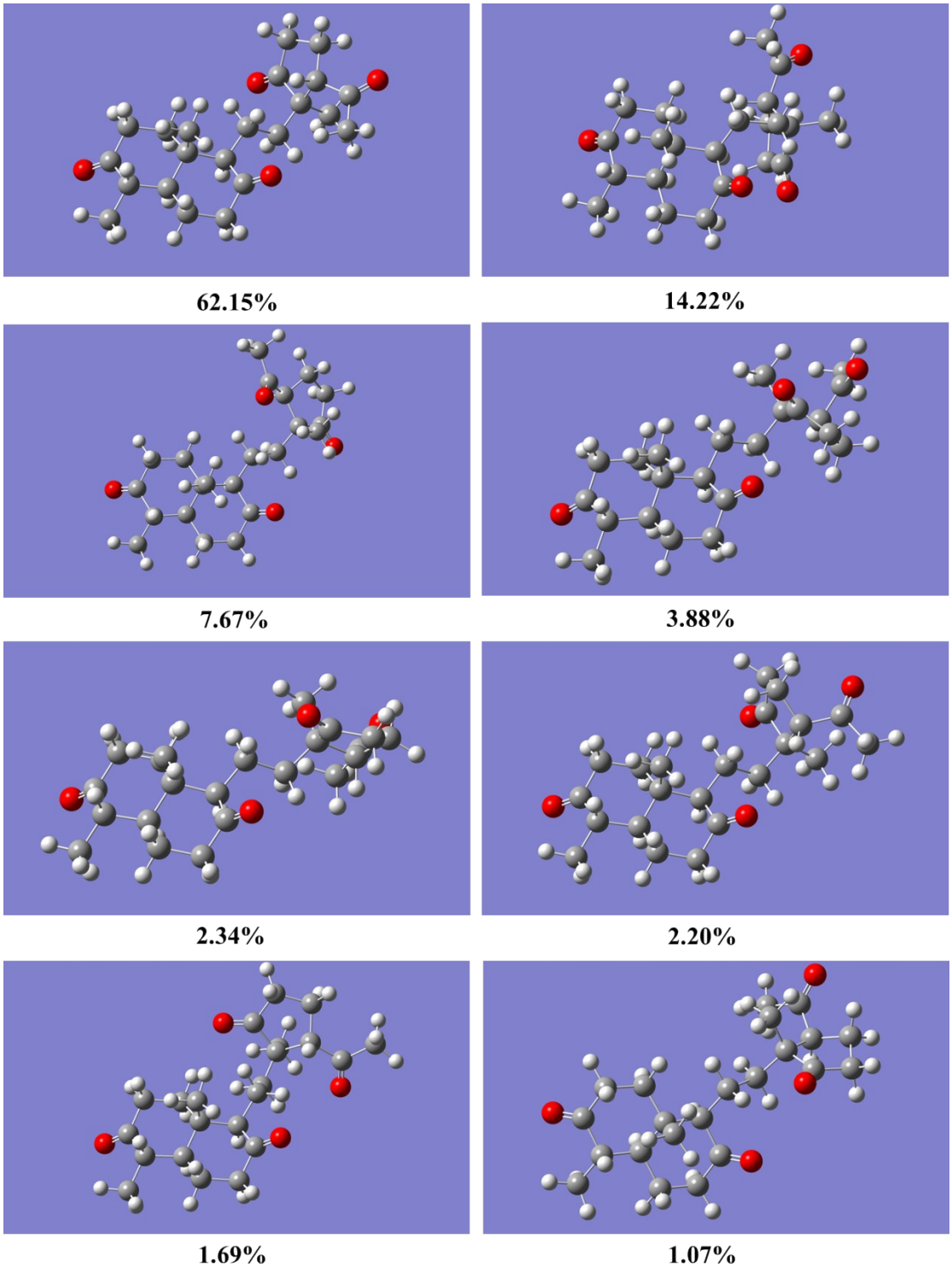


Fig. S52 The low-energy conformers of compound **1**

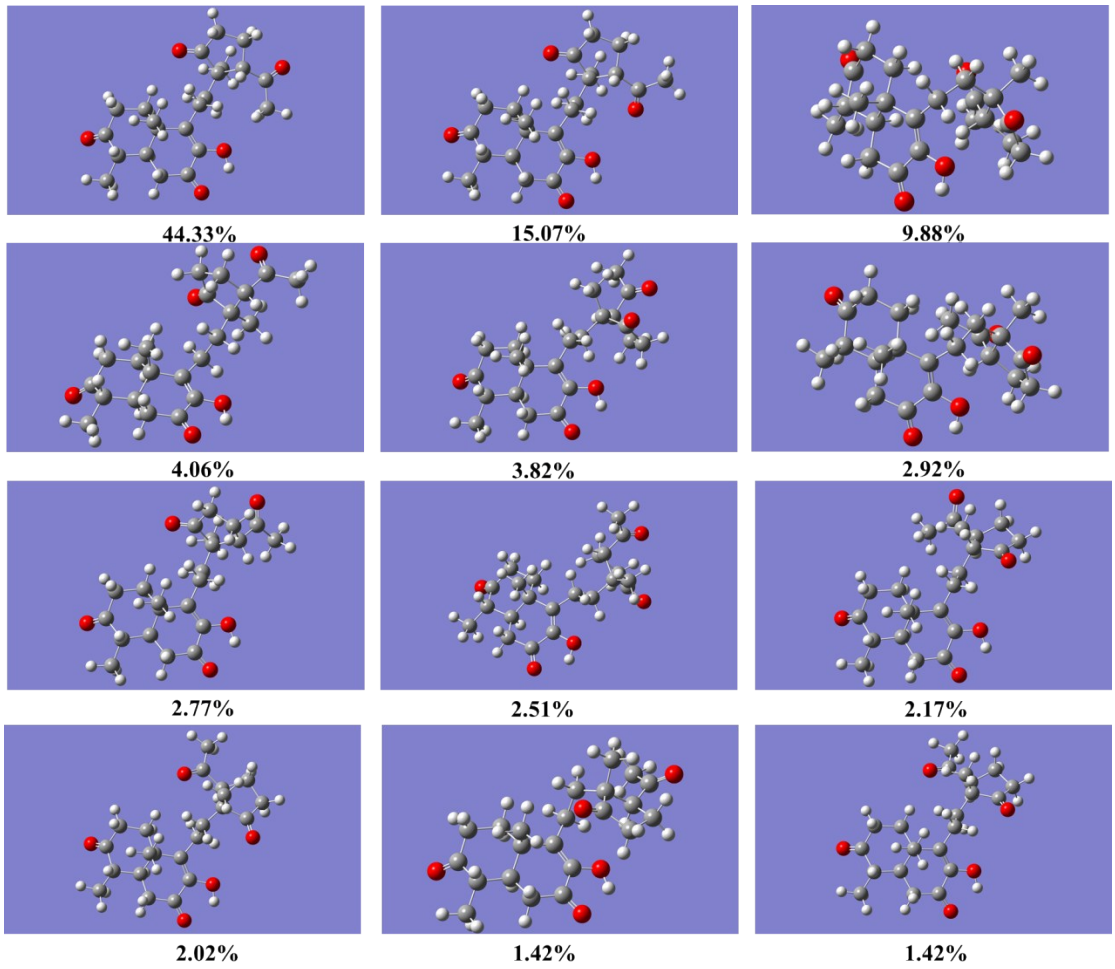


Fig. S53 The low-energy conformers of compound **2**

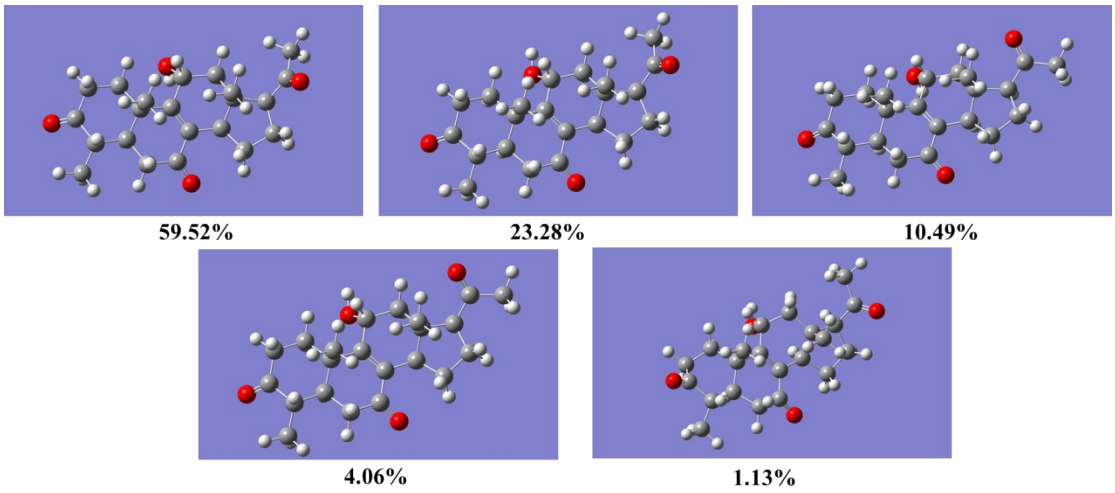


Fig. S54 The low-energy conformers of compound **3**

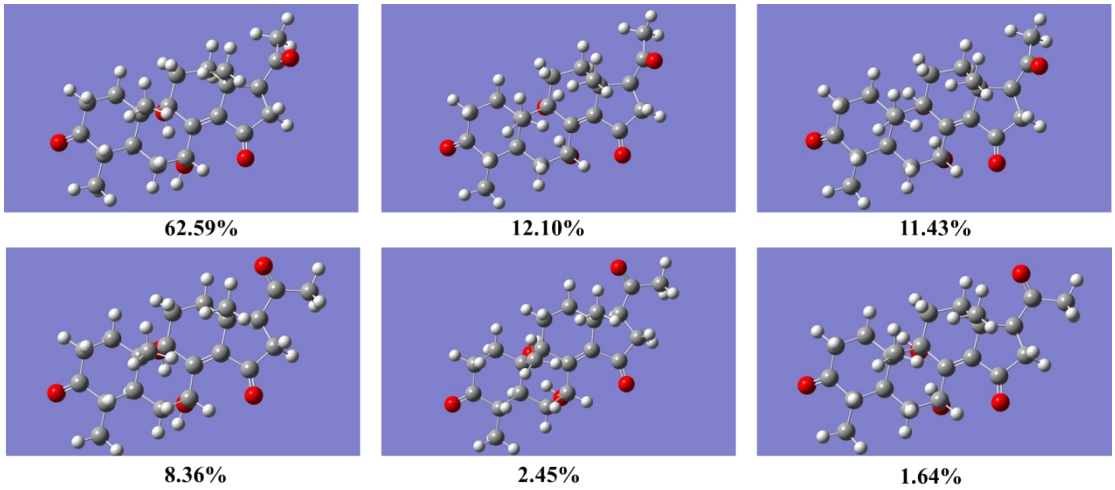


Fig. S55 The low-energy conformers of compound **4**

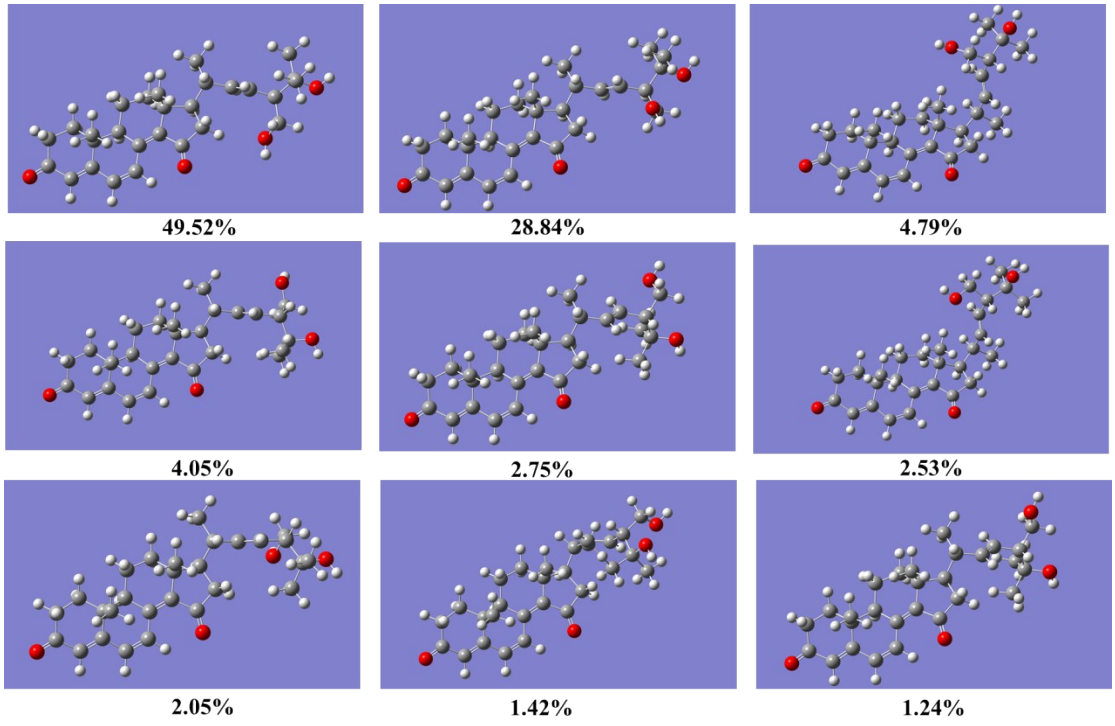


Fig. S56 The low-energy conformers of compound **5**

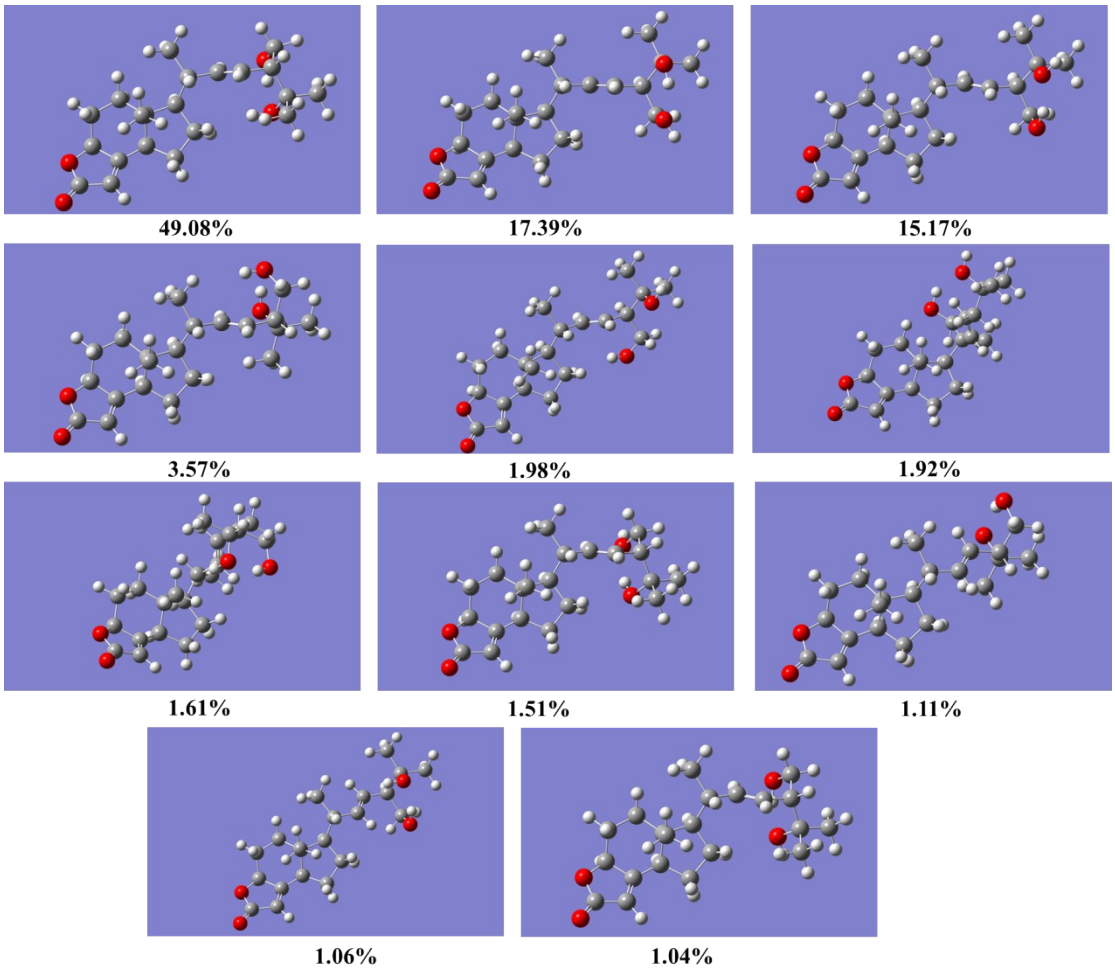


Fig. S57 The low-energy conformers of compound **6**

Table S1 Experimental (Exp.) and calculated (Cal.) ^{13}C chemical shift values of **1** and its possible isomers, respectively

Carbon	Exp.	Cal.	
	1	(4*S**, 5*S**, 9*R**, 10*S**, 13*R**, 17*S**)-**1**	(4*S**, 5*S**, 9*R**, 10*S**, 13S*, 17*R**)-**1**
14	220.5	233.6179328	233.0446077
8	211	225.1380818	224.0330025
3	211.4	222.9595938	225.0896599
20	208.9	221.4261198	222.8467758
9	61.9	65.36531339	65.65835021
13	52	58.32907007	58.99574416

17	54.4	58.14902435	60.22301323
5	51.9	55.62241446	55.43191908
10	42.4	47.7716589	48.9376168
4	44.9	48.90718728	47.68117735
7	41.6	46.36671451	46.33784762
1	38.2	41.94817042	41.87809199
2	37.3	41.94230918	40.69070029
15	36.9	41.16837937	42.0459175
12	36.2	38.69142416	39.69722379
21	31.5	35.56044745	36.55640478
6	27.6	32.09283318	32.00048687
16	20.5	24.66034568	27.46991554
19	13.1	14.65515647	20.96515978
11	17.6	19.97653435	18.63366838
18	19.8	22.45490725	14.6504127
22	11.8	13.69080548	13.65083549

Table S2 Results of DP4+ analysis of **1**

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

	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5	Isomer 6
sDP4+ (H data)	95.68%	4.32%	–	–	–	–
sDP4+ (C data)	100.00%	0.00%	–	–	–	–
sDP4+ (all data)	100.00%	0.00%	–	–	–	–
uDP4+ (H data)	25.36%	74.64%	–	–	–	–
uDP4+ (C data)	100.00%	0.00%	–	–	–	–
uDP4+ (all data)	100.00%	0.00%	–	–	–	–
DP4+ (H data)	88.27%	11.73%	–	–	–	–
DP4+ (C data)	100.00%	0.00%	–	–	–	–
DP4+ (all data)	100.00%	0.00%	–	–	–	–

Table S3 Experimental (Exp.) and calculated (Cal.) ^{13}C chemical shift values of **2** and its possible isomers, respectively

Carbon	Exp.	Cal.	
	2	(4*S**, 5*S**, 10*S**, 13*R**, 17*S**)-**2**	(4*S**, 5*S**, 10*S**, 13*S**, 17*R**)-**2**
14	220.19	233.7677515	233.3475578
3	210.04	221.3320221	221.6015892
20	208.46	220.6424817	223.7026298
7	192.45	200.568171	200.3170087
9	140.73	152.4403506	152.8957476
8	144.12	150.6195052	150.6020621
17	54.21	59.5346857	60.73731867
13	52.21	57.57651874	57.75315091
5	48.09	51.98108737	52.10379331
4	44.59	48.66862634	48.51981961
10	38.95	43.66049212	43.31372974
2	36.6	42.28124568	42.07896521
15	37.5	41.45612266	41.36955596
1	35.47	39.38830872	39.01744023
12	34.42	39.26369292	38.60087521
6	36.25	36.75857295	39.11346912

21	31.51	34.02730691	36.29976621
11	22.19	26.40881131	26.26142097
16	20.63	24.3226833	26.99226103
18	19.48	21.51439368	18.64661821
19	16.61	17.2287699	17.6379833
22	11.22	12.91166739	12.8822016

Table S4 Results of DP4+ analysis of **2**

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

	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5	Isomer 6
sDP4+ (H data)	99.90%	0.10%	-	-	-	-
sDP4+ (C data)	98.86%	1.14%	-	-	-	-
sDP4+ (all data)	100.00%	0.00%	-	-	-	-
uDP4+ (H data)	89.23%	10.77%	-	-	-	-
uDP4+ (C data)	98.56%	1.44%	-	-	-	-
uDP4+ (all data)	99.82%	0.18%	-	-	-	-
DP4+ (H data)	99.99%	0.01%	-	-	-	-
DP4+ (C data)	99.98%	0.02%	-	-	-	-
DP4+ (all data)	100.00%	0.00%	-	-	-	-

Table S5 Conformational analysis for compounds **1-6**

Gibbs free energy of compound **1** (298.15 K)

conf.	G (Hartree)	ΔG (Kcal/mol)	Boltzmann Distribution
C1	-1156.879595	0	0.621538604
C2	-1156.878203	0.87348	0.142161554
C3	-1156.877621	1.238685	0.0767201
C4	-1156.876977	1.642795	0.038770362
C5	-1156.876502	1.9408575	0.023435541
C6	-1156.876442	1.9785075	0.021991721
C7	-1156.876196	2.1328725	0.016944726
C8	-1156.875763	2.40458	0.010708798

Gibbs free energy of compound **2** (298.15 K)

conf.	G (Hartree)	ΔG (Kcal/mol)	Boltzmann Distribution

C1	-1230.818935	0	0.44326962
C2	-1230.817917	0.638795	0.150702461
C3	-1230.817519	0.88854	0.098840677
C4	-1230.816679	1.41564	0.040580266
C5	-1230.816622	1.4514075	0.038201455
C6	-1230.816367	1.61142	0.029154988
C7	-1230.816317	1.642795	0.027650292
C8	-1230.816226	1.6998975	0.025108212
C9	-1230.81609	1.7852375	0.021738023
C10	-1230.816023	1.82728	0.020248014
C11	-1230.815691	2.03561	0.014242137
C12	-1230.815689	2.036865	0.014211981

Gibbs free energy of compound **3** (298.15 K)

conf.	G (Hartree)	ΔG (Kcal/mol)	Boltzmann Distribution
C1	-1155.659596	0	0.595234227
C2	-1155.65871	0.555965	0.232752832
C3	-1155.657958	1.027845	0.104900433
C4	-1155.657063	1.5894575	0.040629548
C5	-1155.655857	2.3462225	0.011317876

Gibbs free energy of compound **4** (298.15 K)

conf.	G (Hartree)	ΔG (Kcal/mol)	Boltzmann Distribution
C1	-1230.806586	0	0.625884957
C2	-1230.805035	0.9732525	0.12095582
C3	-1230.804982	1.00651	0.114349123
C4	-1230.804687	1.1916225	0.083647946
C5	-1230.803528	1.918895	0.02449123
C6	-1230.803151	2.1554625	0.016424474

Gibbs free energy of compound **5** (298.15 K)

conf.	G (Hartree)	ΔG (Kcal/mol)	Boltzmann Distribution
C1	-1388.711407	0	0.495194073
C2	-1388.710897	0.320025	0.28843062
C3	-1388.709203	1.38301	0.047902262
C4	-1388.709044	1.4827825	0.040473823
C5	-1388.70868	1.7111925	0.027519373
C6	-1388.708601	1.760765	0.025309162
C7	-1388.708404	1.8843825	0.020540262
C8	-1388.708056	2.1027525	0.014204779
C9	-1388.707929	2.182445	0.012415983

Gibbs free energy of compound **6** (298.15 K)

conf.	G (Hartree)	ΔG (Kcal/mol)	Boltzmann Distribution
C1	-1118.762491	0	0.490845881
C2	-1118.761512	0.6143225	0.173919301
C3	-1118.761383	0.69527	0.151695909
C4	-1118.760018	1.5518075	0.035703848
C5	-1118.75946	1.9019525	0.019764614
C6	-1118.759431	1.92015	0.019166407
C7	-1118.759265	2.024315	0.016074485
C8	-1118.759206	2.0613375	0.01510016
C9	-1118.758917	2.242685	0.011116436
C10	-1118.758868	2.2734325	0.010553893
C11	-1118.758851	2.2841	0.010365452