Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Elodeoidins A-H, acylphloroglucinol meroterpenoids possessing diverse rearranged skeletons from *Hypericum elodeoides*

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Table S1. ^{1}H (600MHz) and ^{13}C (150MHz) NMR Data for 1-4 (δ in ppm, J in Hz).

No.	1				2		3				4	
	$\delta_H{}^a$	$\delta_C{}^a$	$\delta_H{}^b$	$\delta_C{}^b$	$\delta_H{}^b$	$\delta_C{}^b$	$\delta_H{}^a$	$\delta_C{}^a$	$\delta_H{}^b$	$\delta_C{}^b$	$\delta_H{}^c$	$\delta_C{}^c$
1		153.1		154.2		154.2		151.4		151.3		152.0
2		150.9		153.4		153.3		150.2		149.0		149.7
3		101.9		103.8		103.8		100.6		101.7		101.0
4		203.1		203.6		203.8		203.0		203.3		203.7
5		47.2		48.1		48.0		46.9		48.2		47.2
6		203.6		203.2		203.2		203.7		205.6		203.8
7		203.9		206.3		205.9		94.6		96.4		95.7
8	3.02, sept (7.0)	41.0	2.95, sept (7.0)	41.9	2.76, m	48.4	2.47, sept (6.8)	34.1	2.68, sept (6.8)	34.9	2.40, m	41.4
9	1.09, d (7.0)	16.6	1.20, d (7.0)	17.4	1.16, d (7.0)	13.6	0.65, d (6.8)	17.6	1.13, d (6.8)	14.1	1.13, d (6.8)	9.7
10	1.06, d (7.0)	16.9	1.18, d (7.0)	16.9	1.83, m; 1.45, m	24.3	1.02, d (6.8)	14.3	0.80, d (6.8)	18.0	1.08, m	25.3
11	1.12, s	20.4	1.24, s	20.9	0.99, t (7.4)	11.7	1.04, s	19.9	1.21, s	19.0	0.87, t (7.4)	11.1
12	1.11, s	19.1	1.20, s	19.5	1.23, s	20.9	1.06, s	19.3	1.20, s	20.7	1.16, s	18.0
13					1.20, s	19.5					1.15, s	19.2
1'	2.61, dd (13.2, 4.0); 2.20, dd (13.2, 6.0)	44.3	2.89, dd (14.6, 6.0); 2.20, dd (14.6, 4.0)	48.2	2.90, dd (14.6, 6.0); 2.19, dd (14.6, 4.0	48.1	3.96, d (6.2)	75.2	4.20, d (6.2)	75.4	4.13, d (6.2)	75.5
2'	4.13, dd (6.0 4.0)	74.6	4.15, dd (6.0 4.0)	77.0	4.16, dd, (6.0, 4.0)	77.0	2.73, t (6.2)	50.8	2.78, t (6.2)	51.9	2.81, t (6.2)	51.6
3'		86.9		89.8		89.8		95.3		97.0		96.2
4'	1.50, m; 1.45, m	40.9	1.63, m; 1.56, m	40.0	1.63, m; 1.56, m	40.0	1.63, m	40.5	1.81, m	40.6	1.79, m; 1.66, m	40.2
5'	1.97, m	22.5	2.02, q (7.8)	23.3	2.02, q (7.8)	23.3	1.71, dd (7.5, 4.8); 1.64, m	28.2	1.91, m; 1.58, m	29.5	1.87, m; 1.34, m	28.4
6'	5.09, q (6.8)	124.3	5.07, t (7.1)	123.9	5.07 t, (7.1)	123.9	2.47, td (6.4, 3.2)	45.7	2.65, m	46.2	2.69, dt (10.9, 7.0)	45.9
7'		130.8		132.1		132.1		69.2		71.9		70.6
8'	1.64, s	25.5	1.67, s	25.8	1.67, s	25.8	1.07, s	28.7	1.22, s	26.9	1.21, s	27.3
9'	1.56, s	17.4	1.60, s	17.8	1.60, s	17.8	1.07, s	28.4	1.23, s	29.2	1.23, s	26.4
10'	0.96, s	19.3	1.17, s	18.2	1.17, s	18.3	1.39, s	28.6	1.53, s	29.1	1.52, s	27.8
	3.16, s, 3-OMe	49.9	3.16, s, 3-OMe	51.2	3.14, s, 3-OMe	51.2	6.82, s, 7-OH; 6.15, s , 1'-OH					

[a] ^{1}H and ^{13}C NMR data were recorded in DMSO-d_6; [b] recorded in $CDCl_3$; [c] recorded in MeOD..

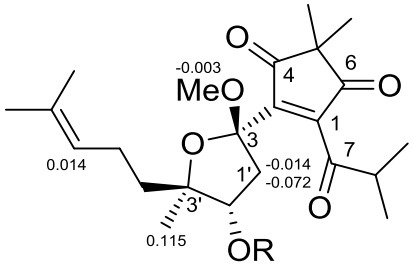
Table S2. ^{1}H (600MHz) and ^{13}C (150MHz) NMR Data for 5-8 (δ in ppm, J in Hz).

No.	5		6		7		8		
	δ_H[a]	δ_C[a]	δ_H[b]	δ_C[b]	δ_H[b]	δ_C[b]	δ_H[b]	δ_C[b]	δ_H[b]	δ_C[b]
1		143.3		145.3		145.3		162.5		162.7
2		142.1		142.8		142.8		143.6		143.8
3		146.8		148.4		148.4		159.4		158.9
4		203.9		204.7		204.8		206.5		206.6
5		47.3		48.0		47.9		47.0		46.7
6		203.3		203.6		203.7		201.8		201.6
7		204.4		205.1		204.9				
8	2.86, sept (7.0)	41.2	2.89, sept (7.0)	41.9	2.70, m	48.5	4.38, q (7.2)	61.9	4.40, q (7.2)	62.0
9	1.07, d (7.0)	16.9	1.17, d (7.0)	17.3	1.14, d (7.0)	13.8	1.40, t (7.2)	14.4	1.40, t (7.2)	14.2
10	1.09, d (7.0)	16.9	1.16, d (7.0)	17.3	1.36, m; 1.24, m	24.3				
11	1.12, s	19.9	1.21, s	19.9	0.95, t (7.4)	11.7	1.18, s	19.8	1.20, s	19.9
12	1.12, s	20.3	1.20, s	20.6	1.20, s	20.2	1.18, s	20.2	1.21, s	20.0
13					1.20, s	20.6				
1'	6.58, d (2.5)	115.7	6.55, d, (2.6)	112.6	6.55, d (2.6)	112.7	2.78, dd (12.1, 10.8); 2.68, dd (12.1, 3.7)	25.9	2.97, dd (12.0, 10.7); 2.73, dd (12.0, 3.4)	28.0
2'	1.89, dd (12.7, 2.5)	47.3	1.95, dd (7.0, 2.6)	48.2	1.95, m	48.2	3.81, dd (10.8, 3.7)	75.8	4.00, dd (10.7, 3.4)	78.0
3'		75.9		77.8		77.7		82.0		71.5
4'	1.83, dd (11.0, 3.1); 1.75, ddd (13.6, 8.9, 6.7)	40.7	1.92, m; 1.77, m	40.6	1.93, m	40.6	2.08, ddd (12.0, 9.7, 5.0); 1.39, td (7.1, 3.2)	28.9	1.85, m; 1.76, m	25.8
5'	1.62, m; 1.20, m	22.8	1.78, m; 1.24, m	23.4	1.80, m	23.4	2.00, ddd (13.5, 9.7, 4.0); 1.86, m	26.1	1.93, m	21.5
6'	2.07, td (12.4, 7.0)	46.5	2.21, td (12.4, 7.0)	47.1	2.20, td (12.4, 7.0)	47.1	3.74, d (7.0)	81.7	3.33, t (2.7)	71.4
7'		80.7		81.3		81.3		74.8		75.8
8'	1.06, s	19.9	1.12, s	20.2	1.12, s	19.9	1.17, s	22.1	1.17, s	26.9
9'	1.22, s	27.9	1.31, s	28.2	1.30, s	28.1	0.91, s	25.4	1.22, s	27.7
10'	1.33, s	26.7	1.48, s	27.2	1.47, s	27.2	1.29, s	21.2	1.11, s	23.3
	4.42, s, 3'-OH									

[a] ^{1}H and ^{13}C NMR data were recorded in DMSO-d_6; [b] recorded in $CDCl_3$.

Mosher's method

Preparation of Mosher Esters: (+)-elodeoidin A [(+)-**1**] (1.0 mg dissolved in 0.8 mL of CH_2Cl_2) were sequentially added pyridine (0.2 mL), 4-(dimethyl-amino) pyridine (0.1 mg), and 10 mg of (*R*)-(−)-α-methoxy-α-(trifluoromethyl)-phenylacetyl chloride. The mixture was stirred at rt overnight and passed through a glass pipette (0.5×5 cm) containing silica gel (200-300 mesh) and eluted with 3.0 mL of CH_2Cl_2. The CH_2Cl_2 residue, dried in vacuo, was redissolved in MeOH and was separated with Pre-HPLC (MeOH-H_2O, 80:20, v/v) to obtain the (*S*)-Mosher esters. Using (*S*)-(+)-α-methoxy-α-(trifluoromethyl)phenyl-acetyl chloride gave the (*R*)-Mosher esters by the foregoing method. Finally, the 2'S-configuration of (+)-**1** was confirmed by Mosher model and the ^{1}H NMR spectra difference value ($\Delta\delta_H$ (*S*–*R*)) between (*S*)- and (*R*)-MTPA esters.



(+)-**1** R= S-MTPA
(+)-**1** R= R-MTPA

Figure S1 Key Values of $\Delta\delta_H$ (*S* – *R*) for the MTPA Esters of (+)-1

ECD and ^{13}C NMR calculated spectra

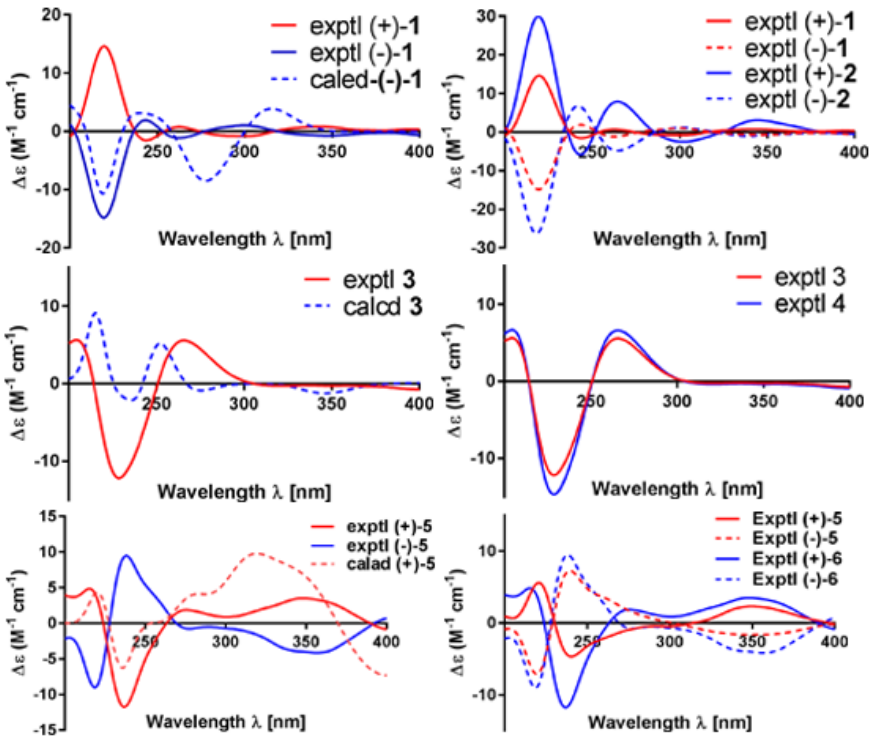


Figure S2 Experimental and computational ECD spectra of 1-6.

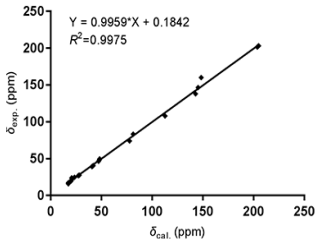


Figure S3 The experimental and calculated ^{13}C NMR linear correlation

2D NMR correlations and HPLC chiral analysis chromatogram analysis

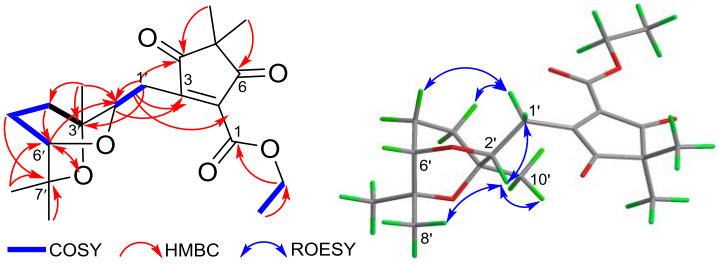


Figure S4 Key ^{1}H-^{1}H COSY, HMBC and ROESY correlations of 7.

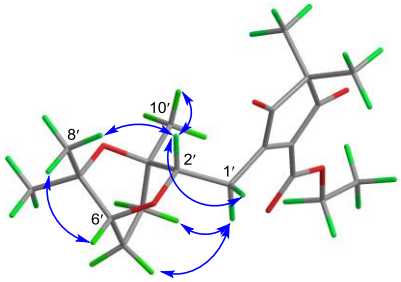


Figure S5 Key ROESY correlations of 8.

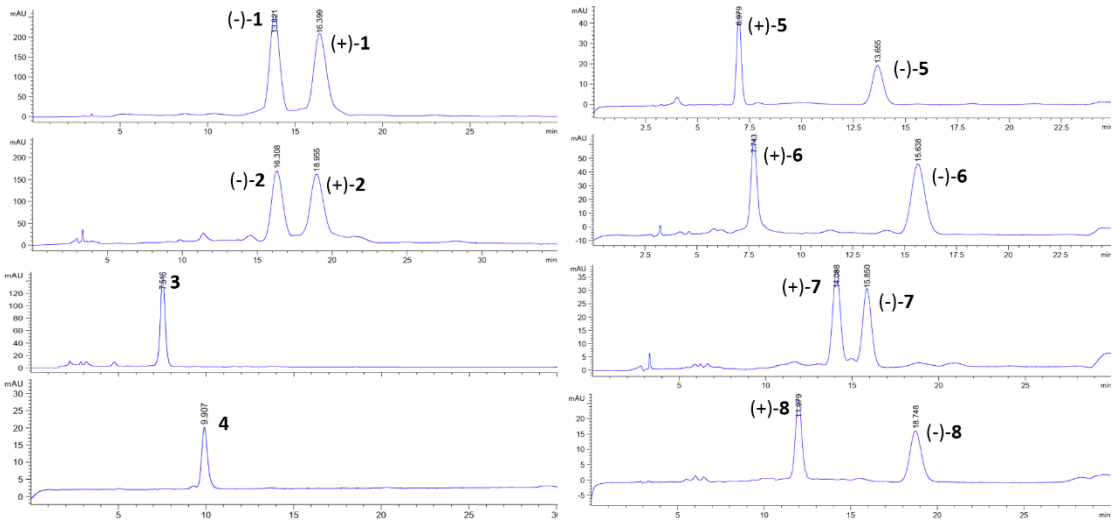


Figure S6 HPLC chiral analysis chromatogram for 1-8.

EXPERIMENTAL SECTION

Experimental Procedures

Optical rotations were measured on a JASCOP-1020 polarimeter in MeOH at room temperature. UV spectra were scanned on a UV–2450 UV/Vis spectrophotometer (Shimadzu, Tokyo, Japan). A JASCO J–810 spectropolarimeter (Jasco, Tokyo, Japan) was used to collect electronic circular dichroism (ECD) spectra. IR spectra (KBr disks, in cm^{-1}) were acquired using a Bruker Tensor 27 spectrometer (Bruker, Karlsruhe, Germany). Nuclear magnetic resonance (NMR) spectra were on a Bruker AVIII-600 NMR instrument (^{1}H: 600 MHz, ^{13}C: 150 MHz) equipped with CryoProbe (Bruker, Karlsruhe, Germany), with tetramethylsilane (TMS) as an internal standard. Chemical shift values (δ) are given in parts per million (ppm) and coupling constants in Hertz (Hz). The following abbreviations are used to designate multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. Electrospray ionization (ESI) and high-resolution electrospray ionization (HRESIMS) were carried out an Agilent 1100 series LC/MSD ion trap mass spectrometer and an Agilent 6529B Q-TOF instrument (Agilent Technologies, Santa Clara, CA, USA), respectively. Preparative high performance liquid chromatography (Pre-HPLC) was performed on a Shimadzu LC-6A system (Shimadzu, Tokyo, Japan) equipped with a Shim-pack RP-C18 column (200 mm ×20 mm i.d., 10 μm, Shimadzu, Tokyo, Japan) and chiral preparative column (200 mm ×20 mm i.d., 10 μm, Phenomenex Cellulose-2, USA) with flow rate at 10.0 ml/min and column temperature at 25℃, detected by a binary channel UV detector at 210 and 240 nm.. All solvents used were of analytical grade (Jiangsu Hanbang Science and Technology. Co., Ltd.). Silica gel (200-300 mesh, Qingdao Haiyang Chemical Co., Ltd, Qingdao China) and RP-C18 silica (40-63 μm, FuJi, Japan) were used for column chromatography. Fractions obtained from column chromatography (CC) were monitored by thin-layer chromatography (TLC) with precoated silica gel GF254 (Qingdao Haiyang Chemical Co., Ltd, China) plates.

Plant material

Air-dried the whole plants of *Hypericum elodeoides* were collected from Yunnan Province, China, in September 2017. A voucher specimen was deposited in the Department of Natural Medicinal Chemistry, China Pharmaceutical University (No. 2017-LHE) and authenticated by Professor Mian Zhang of the Research Department of Pharmacognosy, China Pharmaceutical University, China.

Extraction and isolation

The dried the whole plants of *H. elodeoides* (10.0 kg) was extracted three times (3 × 25L) with 95% aqueous EtOH under heating reflux, and the crude (583 g) was suspended in H_2O and extracted with petroleum ether (PE) (3 × 1L), methylene dichloride (MD) (3 × 1L), ethyl acetate (EA) (3 × 1L). The petroleum ether extract (206g) was subjected to a silica gel column, eluted with a gradient of PE-Me_2CO (1:0, 20:1, 10:1, 5:1, 1:1, v/v) to give ten fractions (A-J), which were combined based on HPLC and TLC. Fraction C (33.7 g) was chromatographed over a C18 silica gel column eluted with a gradient system of MeOH-H_2O (1:4, 5:5, 7:3, 8:2, 9:1, 1:0, v/v) to give twelve subfractions (Fr.C1 - Fr. C12). Fr. C1 (0.73 g) was separated with Pre-HPLC (MeOH-H_2O, 85:15, v/v) to **9** (t_R = 27.3 min, 6.8 mg). Fr. C2 (0.45 g) was separated with Pre-HPLC (MeOH-H_2O, 85:15, v/v) to obtain **7** (t_R = 25.1 min, 0.9 mg) and **8** (t_R = 26.5 min, 0.5 mg). Fr. C3 (0.68 g) was separated with Pre-HPLC (MeOH-H_2O, 85:15, v/v) to obtain **1** (t_R = 40.2 min, 2.1 mg) and **2** (t_R = 59.7 min, 2.7 mg). Fraction E (17.9 g) was chromatographed over a C18 silica gel column eluted with a gradient system of MeOH-H_2O (5:5, 7:3, 8:2, 9:1, 1:0, v/v) to give ten subfractions (Fr. E1 - Fr. E10). E3 (0.25 g) was separated with Pre-HPLC (MeOH−H2O, 70:30, v/v) to obtain compound **3** (t_R = 22.9 min, 1.5 mg). E4 (0.23 g) was separated with Pre-HPLC (MeOH−H_2O, 70:30, v/v) to obtain

compound **5** (t_R = 26.7 min, 2.4 mg) and **6** (t_R = 32.8 min, 2.3 mg). E5 (0.36 g) was separated with Pre-HPLC (MeOH−H2O, 75:25, v/v) to obtain compound **4** (t_R = 24.8 min, 1.8 mg).

Furtherly, compounds **1**-**2** and **5**-**6** were chirally separated *via* using a chiral preparative column eluting with MeOH-H_2O (v/v, 80:20).

Physical and chemical data

Elodeoidin A (**1)**, yellowish gum; (+)-**1**: $[\alpha]_D^{25}$= +39.2 (c 0.10, MeOH); ECD (MeOH) λ_{max} ($\Delta\varepsilon$) 219 (14.62), 244 (-1.55), 262 (0.74), 300 (-0.79), 342 (0.78), 379 (0.15); (-)-**1**: $[\alpha]_D^{25}$= +40.7 (c 0.10, MeOH); ECD (MeOH) λ_{max} ($\Delta\varepsilon$) 219 (-14.84), 243 (1.93), 262 (-1.13), 299 (1.01), 346 (-0.71), 382 (-0.23); UV (MeOH) λ_{max}(log ε) = 227 (3.79); IR (KBr) ν_{max} 3473, 2971, 2931, 1716, 1463, 1383, 1288, 1151, 1050, 900 cm^{-1}; ^1H and ^{13}C NMR ($CDCl_3$), see Table S1; HRESIMS *m/z* 429.2242 $[M + Na]^+$ (calcd for $C_{23}H_{34}O_6Na$, 429.2248).

Elodeoidin B (**2)**, yellowish gum; (+)-**2**: $[\alpha]_D^{25}$= +81.7 (c 0.10, MeOH); ECD (MeOH) λ_{max} ($\Delta\varepsilon$) 219 (30.02), 243(-5.82), 264 (7.92), 302 (-2.50), 345 (3.13); (-)-**2**: $[\alpha]_D^{25}$= +67.6 (c 0.10, MeOH); ECD (MeOH) λ_{max} ($\Delta\varepsilon$) 218 (-26.28), 242 (6.81), 264 (-4.79), 301 (1.16), 339 (-0.99), 378 (-0.28); UV (MeOH) λ_{max}(log ε) = 227 (4.11); IR (KBr) ν_{max} 3455, 2969, 2931, 2877, 1752, 1716, 1461, 1383, 1287, 1178, 1148, 1116, 963 cm^{-1}; ^1H and ^{13}C NMR ($CDCl_3$), see Table S1; HRESIMS *m/z* 443.2396 $[M + Na]^+$ (calcd for $C_{24}H_{36}O_6Na$, 443.2404).

Elodeoidin C (**3**), yellowish gum; $[\alpha]_D^{25}$= -18.4 (c 0.10, MeOH); ECD (MeOH) λ_{max} ($\Delta\varepsilon$) 204 (5.6), 229 (-12.19), 266 (+5.58); UV (MeOH) λ_{max}(log ε) = 225 (4.08); IR (KBr) ν_{max} 3441, 2968, 2933, 2874, 1745, 1709, 1642, 1466, 1383, 1291, 1215, 1056, 954 cm^{-1}; ^1H and ^{13}C NMR ($CDCl_3$), see Table S1; HRESIMS *m/z* 431.2034 $[M + Na]^+$ (calcd for $C_{22}H_{32}O_7Na$, 431.2040).

Elodeoidin D (**4**): yellowish gum; $[\alpha]_D^{25}$= -18.0 (c 0.10, MeOH); ECD (MeOH) λ_{max} ($\Delta\varepsilon$) 229 (-1.05), 261 (+0.77), 333 (-0.15); UV (MeOH) λ_{max}(log ε) = 236 (4.09); IR (KBr) ν_{max} 3395, 2963, 2921, 2849, 1707, 1645, 1467, 1421, 1381, 1291, 1216, 953 cm^{-1}; ^1H and ^{13}C NMR (MeOD), see Table S1; HRESIMS *m/z* 445.2193 $[M + Na]^+$ (calcd for $C_{23}H_{34}O_7Na$, 445.2197).

Elodeoidin E (**5)**, yellowish gum; (**+**)-**5**: $[\alpha]_D^{25}$= +24.3 (c 0.10, MeOH); ECD (MeOH) λ_{max} ($\Delta\varepsilon$) 215 (+4.87), 237 (-11.74), 275 (+1.88), 300 (+0.88), 348 (+3.52); **(-)-5**: $[\alpha]_D^{25}$= -48.1 (c 0.10, MeOH); ECD (MeOH) λ_{max} ($\Delta\varepsilon$) 219 (-8.99), 238 (+9.50), 277 (-0.76), 289 (-0.51), 357 (-4.14); UV (MeOH) λ_{max}(log ε) = 240 (4.15), 360 (3.92); IR (KBr) ν_{max} 3451, 2972, 2937, 2874, 1743, 1711, 1692, 1641, 1463, 1378, 1286, 1127, 1022, 979 cm^{-1}; ^1H and ^{13}C NMR ($CDCl_3$), see Table S2; HRESIMS *m/z* 391.2114 $[M + H]^+$ (calcd for $C_{22}H_{31}O_6$, 391.2115).

Elodeoidin F (**6)**, yellowish gum; (+)-**6**: $[\alpha]_D^{25}$= +13.1 (c 0.10, MeOH); ECD (MeOH) λ_{max} ($\Delta\varepsilon$) 205 (0.67), 221 (5.61), 240 (-4.66), 349 (2.34); (-)-**6**: $[\alpha]_D^{25}$= -26.7 (c 0.10, MeOH); ECD (MeOH) λ_{max} ($\Delta\varepsilon$) 219 (-7.08), 239 (7.28), 347 (-1.60); UV (MeOH) λ_{max}(log ε) = 240 (4.18), 355 (4.01); IR (KBr) ν_{max} 3429, 2967, 2932, 2875, 1745, 1710, 1643, 1615, 1462, 1382, 1286, 1126, 1091, 1061 cm^{-1}; ^1H and ^{13}C NMR ($CDCl_3$), see Table S2; HRESIMS *m/z* 405.2269 $[M + H]^+$ (calcd for $C_{23}H_{33}O_6$, 405.2272).

Elodeoidin G (**7)**, yellowish gum; (+)-**7**: $[\alpha]_D^{25}$= +15.2 (c 0.10, MeOH); (-)-**7**: $[\alpha]_D^{25}$= -13.5 (c 0.10, MeOH); UV (MeOH) λ_{max}(log ε) = 236 (3.95); IR (KBr) ν_{max} 2926, 2850, 1639, 1465, 1383, 1119, 1015, 863, 690, 627 cm^{-1}; ^1H and ^{13}C NMR ($CDCl_3$), see Table S3; HRESIMS *m/z* 387.1781 $[M + Na]^+$ (calcd for $C_{20}H_{28}O_6Na$, 387.1778).

Elodeoidin H (**8)**, yellowish gum; UV (MeOH) λ_{max}(log ε) = 234 (3.90); IR (KBr) ν_{max} 2925, 2851, 1640, 1466, 1383, 1119, 1014, 862, 689, 628 cm^{-1}; ^1H and ^{13}C NMR ($CDCl_3$), see Table S3; HRESIMS *m/z* 387.1778 $[M + Na]^+$ (calcd for $C_{20}H_{28}O_6Na$, 387.1778).

Ethyl (E)-4-hydroxy-4,8-dimethylnona-2,7-dienoate (**9**), white powder; ^1H NMR (600 MHz, $CDCl_3$) δ_H 6.96 (d, *J* = 15.6 Hz, 1H), 6.03 (d, *J* = 15.6 Hz, 1H), 5.18 – 5.05 (m, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.10 – 2.04

(m, 1H), 2.02 – 1.97 (m, 1H), 1.68 (s, 3H), 1.66 – 1.63 (m, 2H), 1.59 (s, 3H), 1.33 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ_C 166.9, 154.2, 132.8, 123.9, 118.9, 73.6, 60.6, 41.8, 28.1, 25.8, 22.9, 17.9, 14.4. HRESIMS *m/z* 227.1637 $[M + H]^+$ (calcd for $C_{13}H_{23}O_3$, 227.1643).

Anti-inflammatory activity[1]

The RAW264.7 cell line was purchased from the Chinese Academic of Sciences. The cells were cultured in DMEM containing 10% FBS with penicillin (100 U/mL) and streptomycin (100 U/mL) at 37 ºC in a humidified atmosphere with 5% CO_2. The cells were allowed to grow in 96-well plates with 1 × 105 cells/well to treat test compounds. AfterS5 being incubated for 2 h, the cells were treated with 100 ng/mL of LPS for 18 h. Nitrite in culture media was measured to assess NO production using Griess reagent. The absorbance at 540 nm was measured on a microplate reader. N-monomethyl-L-arginine was used as the positive control. Cytotoxicity was determined by the MTT method, after 48 h incubation with test compounds. All the experiments were performed in three independent replicates.

Cells were initially treated with LPS (1 μg/mL) for a certain time. The total proteins were extracted as previously described.[1] Total proteins were electrophoresed on SDS-PAGE and transferred onto a PVDF membrane (Bio-Rad Laboratories, Hercules, CA, USA). The membranes were washed with TBST buffer, treated with 5% skimmed milk for 2 h at 25 °C, and then treated with primary antibodies for 12 h at 4 °C. After being washed with TBST, the membranes were probed with secondary antibody at room temperature. Lastly, the protein blots were read on a ChemiDOC XRS + system (Bio-Rad Laboratories).

Table S4 The anti-inflammatory and antibacterial activity of the tested compounds

Compound	IC_{50} (μM)
(+)-**1**	33.36 ± 4.30
(+)-**5**	9.05 ± 0.97
(-)-**5**	6.06 ± 0.41
(+)-**6**	9.73 ± 0.47
(-)-**6**	10.46 ± 0.14
NMLA	39.38 ± 0.90

NMLA was n-monomethyl-l-arginine, each value represents as the mean ± sd from three independent experiments.

References:

(1) Wei S.S; Chi J.; Zhou M.M.; Li R.J.; Li Y.R.; Luo J.; Kong L.Y. *Ind. Crop. Prod.* 2019, 137: 367-376.

CALCULATION SECTION

Calculation quantum-chemical ^{13}C NMR for 5

In general, conformational analyses were carried out *via* random searching in the Sybyl-X 2.0 using the MMFF94 force field with an energy cutoff of 3.0 kcal/mol.[1] The results showed one lowest energy conformer for **5**. Subsequently, All conformers for **5** was re-optimized using DFT at the b3lyp/6-311+g(2d, p) level by the GAUSSIAN 09 program.[2] The 13C shielding constants were calculated using the Gauge-Independent Atomic Orbital (GIAO) method at the b3lyp/6-31g(d) level with SMD in $CDCl_3$.[3] To get the final ^{13}CNMR chemical shifts, the ^{13}C NMR chemical shifts of the conformers were averaged according to the Boltzmann distribution theory and their relative Gibbs free energy (ΔG).

Table S5 Experimental and calculated ^{13}C NMR data for **5**

No.	$\delta_{calcd.}$	$\delta_{exp.}$	$\delta_{corr.}$	Δ_δ	No.	$\delta_{calcd.}$	$\delta_{exp.}$	$\delta_{corr.}$	Δ_δ
1	141.3	145.3	146.6	-1.3	1'	107.1	112.6	108.0	4.6
2	129.8	142.8	138.0	4.8	2'	45.4	48.2	49.7	-1.4
3	156.6	148.4	160.1	-11.7	3'	69.6	77.8	74.2	3.6
4	196.9	204.7	202.8	1.9	4'	35.2	40.6	39.4	1.3
5	44.1	48.0	48.3	-0.4	5'	20.7	23.4	24.7	-1.3
6	195.6	203.6	201.5	2.1	6'	42.3	47.1	46.5	0.6
7	197.2	205.1	203.1	2.0	7'	78.6	81.3	83.2	-1.9
8	36.3	41.9	40.5	1.4	8'	16.8	20.2	20.8	-0.5
9	12.1	17.3	16.0	1.2	9'	23.6	28.2	27.6	0.6
10	13.3	17.3	17.2	0.0	10'	22.9	27.2	26.9	0.3
11	15.6	19.9	19.5	0.4					
12	19.8	20.6	23.8	-3.2					

$\Delta_\delta = \delta_{exp.} - \delta_{corr.}$

References:

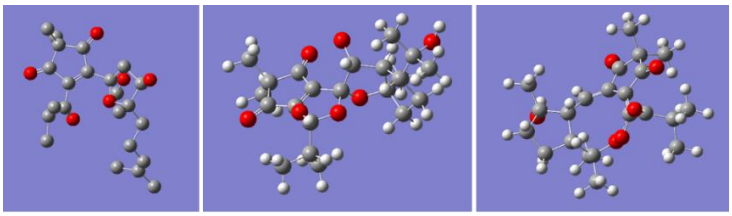
(1) Sybyl Software, version X 2.0; Tripos Associates Inc.: St. Louis, MO, 2013.

(2) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., Gaussian 09, Rev. C 01; Gaussian, Inc., Wallingford CT, 2009.

(3) K. Wolinski, J. F. Hilton, and P. Pulay, Efficient Implementation of the Gauge-Independent Atomic Orbital Method for NMR Chemical Shift Calculations, J. Am. Chem. Soc., 1990, 112, 8251-60.

Calculation ECD for 1-6

Monte Carlo conformational searches were carried out by means of the Spartan's 10 software using Merck Molecular Force Field (MMFF). The conformers with Boltzmann-population of over 5% were chosen for ECD calculations, and then the conformers were initially optimized at B3LYP/6-31g (d, p) level in MeOH using the CPCM polarizable conductor calculation model. The theoretical calculation of ECD was conducted in MeOH using Time-dependent Density functional theory (TD-DFT) at the B3LYP/6-31+g (d, p) level for all conformers of compounds **1**-**6**. Rotatory strengths for a total of 30 excited states were calculated. ECD spectra were generated using the program SpecDis 1.6 (University of Würzburg, Würzburg, Germany) and GraphPad Prism 8 (University of California San Diego, USA) from dipole-length rotational strengths by applying Gaussian band shapes with sigma = 0.3 eV. The calculated conformation as follows:



1 **3** **5**

Table S6 The coordinate for lowest-energy conformer (-)-**1** and **3** in ECD calculation

Atom	(-)-**1**			Atom	**3**		
	X	Y	Z		X	Y	Z
C	-5.228727	0.22243	0.120562	C	3.982721	-0.5364	-2.37594
C	-4.046798	-0.156185	-0.78928	C	4.464489	0.02246	-1.02673
C	-3.000598	0.961352	-0.832612	C	5.417224	1.206836	-1.25977
C	-1.680664	0.415362	-0.364656	C	3.276473	0.435596	-0.12591
C	-0.432956	1.277165	-0.37562	C	3.678455	0.979507	1.264869
C	0.4251	0.316248	-2.439197	C	2.393775	0.851621	2.093713
C	-0.588075	2.685409	0.205594	C	1.779705	-0.49682	1.649909
C	0.868805	3.030194	0.54462	C	2.083955	-1.63619	2.615538
C	1.475741	1.664321	0.982538	C	2.298021	-0.72812	0.194463
C	1.469997	1.49285	2.501865	C	1.023468	-0.81087	-0.67127
C	2.863167	1.43706	0.359017	C	-0.05622	-0.15463	0.229427
C	3.48327	0.052538	0.639847	C	-1.46909	-0.59765	0.001418
C	4.743911	-0.174016	-0.151496	C	-2.21114	-1.87278	0.093975
C	5.000787	-1.134022	-1.053958	C	-3.68153	-1.558	-0.24173
C	4.038617	-2.225214	-1.458959	C	-4.59912	-1.87712	0.952475
C	6.338967	-1.193686	-1.753348	C	-4.12412	-2.32973	-1.49934
C	-1.819925	-0.889129	-0.024996	C	-3.66468	-0.03321	-0.52102
C	-0.770015	-1.891794	0.400773	C	-2.25658	0.422859	-0.35933
C	-0.943006	-2.548192	1.764332	C	-1.434	1.689046	-0.49851
C	0.208891	-3.510558	2.064755	C	-1.87441	2.921271	0.322616
C	-1.153448	-1.514497	2.887012	C	-3.08918	3.630787	-0.29448
C	-4.535031	-0.494893	-2.212188	C	-2.11562	2.564248	1.796577
C	-3.248333	-1.319668	-0.203315	H	2.724898	1.22437	-0.65637
H	1.3819	3.372378	-0.363102	H	2.829375	-1.68016	0.121812
H	-5.741623	1.098561	-0.2875	H	1.106839	-0.25228	-1.60529
H	-5.932378	-0.613148	0.181558	H	3.419478	0.214383	-2.94259
H	-4.896373	0.464333	1.136421	H	4.842753	-0.83162	-2.99198
H	-0.391299	-0.397285	-2.603626	H	3.348108	-1.41685	-2.23971
H	0.776962	0.690547	-3.40323	H	5.843391	1.557603	-0.31575
H	1.235518	-0.200747	-1.919404	H	6.246337	0.906383	-1.91345
H	-1.065781	3.364039	-0.500812	H	4.902757	2.045585	-1.74354
H	-1.177354	2.653304	1.128314	H	5.868843	-1.34075	-0.87459
H	0.755924	4.850225	1.224169	H	4.050423	2.009048	1.229512
H	1.742079	0.466874	2.765019	H	4.476115	0.353729	1.681268

H	2.183238	2.177918	2.968248	H	1.694833	1.651619	1.831004
H	0.480425	1.706638	2.915375	H	2.56637	0.897976	3.17479
H	2.768793	1.570296	-0.725268	H	1.712462	-2.58955	2.224667
H	3.533456	2.231544	0.716897	H	3.164825	-1.72546	2.769976
H	3.720397	-0.025845	1.710914	H	1.608812	-1.45234	3.585332
H	2.734779	-0.71615	0.427338	H	0.281852	-2.60159	-0.28392
H	5.536739	0.551721	0.044158	H	-5.62609	-1.58085	0.718047
H	3.870458	-2.205376	-2.545056	H	-4.57405	-2.95062	1.163766
H	4.461976	-3.214498	-1.233832	H	-4.28611	-1.34328	1.856856
H	3.064219	-2.16155	-0.969581	H	-3.47823	-2.10938	-2.35633
H	7.007282	-0.389347	-1.429525	H	-4.08133	-3.40621	-1.3071
H	6.843452	-2.151844	-1.563233	H	-5.14965	-2.05165	-1.76118
H	6.219962	-1.118836	-2.843736	H	-0.80316	2.752898	-1.98386
H	-1.879283	-3.119822	1.662914	H	-1.00754	3.599566	0.279352
H	1.155765	-2.968782	2.166559	H	-3.95455	2.962245	-0.34269
H	0.018507	-4.045399	3.00153	H	-3.35873	4.502611	0.312423
H	0.332911	-4.243832	1.263585	H	-2.88411	3.975499	-1.31219
H	-2.004835	-0.855608	2.685482	H	-3.03263	1.973196	1.912513
H	-1.349865	-2.029257	3.833269	H	-1.28136	1.991796	2.211944
H	-0.265293	-0.888482	3.015772	H	-2.23949	3.476296	2.390273
H	-3.704499	-0.773991	-2.870078	O	5.157778	-1.01152	-0.30264
H	-5.237414	-1.333228	-2.172465	O	0.671154	-2.13392	-1.04586
H	-5.037001	0.375675	-2.645438	O	-4.64229	0.636739	-0.7869
O	-0.01097	1.47133	-1.721075	O	-1.75275	-2.96826	0.366295
O	1.021415	3.989818	1.582476	O	-1.35581	1.959914	-1.87977
O	0.554728	0.666459	0.429412	O	-0.13728	1.27403	-0.00712
O	0.098612	-2.208595	-0.391112	O	0.325806	-0.4218	1.546141
O	-3.215638	2.105858	-1.181037				
O	-3.693124	-2.417305	0.076413				

Table S7 The coordinate for lowest-energy conformer (+)-**5** in ECD calculation

Atom	X	Y	Z	Atom	X	Y	Z
C	2.292602	1.349431	-0.24391	H	3.173465	3.86267	-1.06889
C	1.089698	0.493451	-0.09384	H	-1.95437	2.015009	0.614612
C	-0.02333	1.32611	0.371883	H	-3.89712	-0.8293	-2.49362
C	0.549256	2.629183	0.83795	H	-5.33174	-0.37881	-1.56323
C	2.01278	2.727455	0.370842	H	-4.03496	-2.60067	-0.76829
C	2.960516	2.990639	1.555413	H	-4.41725	-1.39384	0.467281
C	2.147309	3.836128	-0.69235	H	-1.89067	-1.24223	3.269042
C	-1.35867	1.200704	0.208253	H	-2.52431	0.039839	2.211247
C	-2.10147	0.204523	-0.64475	H	-3.47464	-1.42534	2.505977
C	-4.24883	-0.53393	-1.49699	H	-1.32498	-3.77489	0.530579
C	1.212394	-0.85344	-0.24316	H	-1.46097	-3.56931	2.287263
C	-2.3349	-1.30525	-0.2122	H	-2.92209	-3.61522	1.283114
C	-3.84408	-1.57304	-0.44637	H	3.725618	-1.20448	0.666062
C	-3.51243	0.736382	-1.03872	H	4.709396	-2.75928	-1.79373
C	-1.80895	-1.74764	1.165586	H	5.081777	-1.07133	-1.40707
C	-2.4633	-1.03858	2.359955	H	5.698407	-2.37526	-0.36893
C	-1.8845	-3.27231	1.323852	H	3.095154	-4.09037	-0.18137
C	2.391704	-1.53438	-0.95714	H	2.36505	-3.24806	1.196723
C	3.58597	-1.96181	-0.11348	H	4.098429	-3.61514	1.199799
C	4.848627	-2.04739	-0.97576	H	-3.01567	1.521323	-3.00983
C	3.257916	-3.30986	0.568924	H	-4.49797	2.189921	-2.31628
C	-3.48054	1.85654	-2.07736	H	-2.92203	2.719003	-1.70225
H	-1.52368	0.136707	-1.57659	H	-4.97052	1.58576	-0.03572
H	-1.78651	-1.91447	-0.93636	O	-0.0441	3.510204	1.432402
H	3.995234	3.026381	1.204181	O	3.368079	1.010841	-0.7194
H	2.701755	3.943446	2.0247	O	-0.4275	-1.32454	1.319732
H	2.883247	2.205868	2.314865	O	2.26115	-1.79678	-2.13457
H	1.47691	3.665463	-1.54087	O	0.364045	-1.8165	0.179009
H	1.897017	4.803277	-0.24793	O	-4.1065	1.211233	0.182291

NMR, HRESIMS, UV, and IR spectrum of 1 (Figure S7-S15)

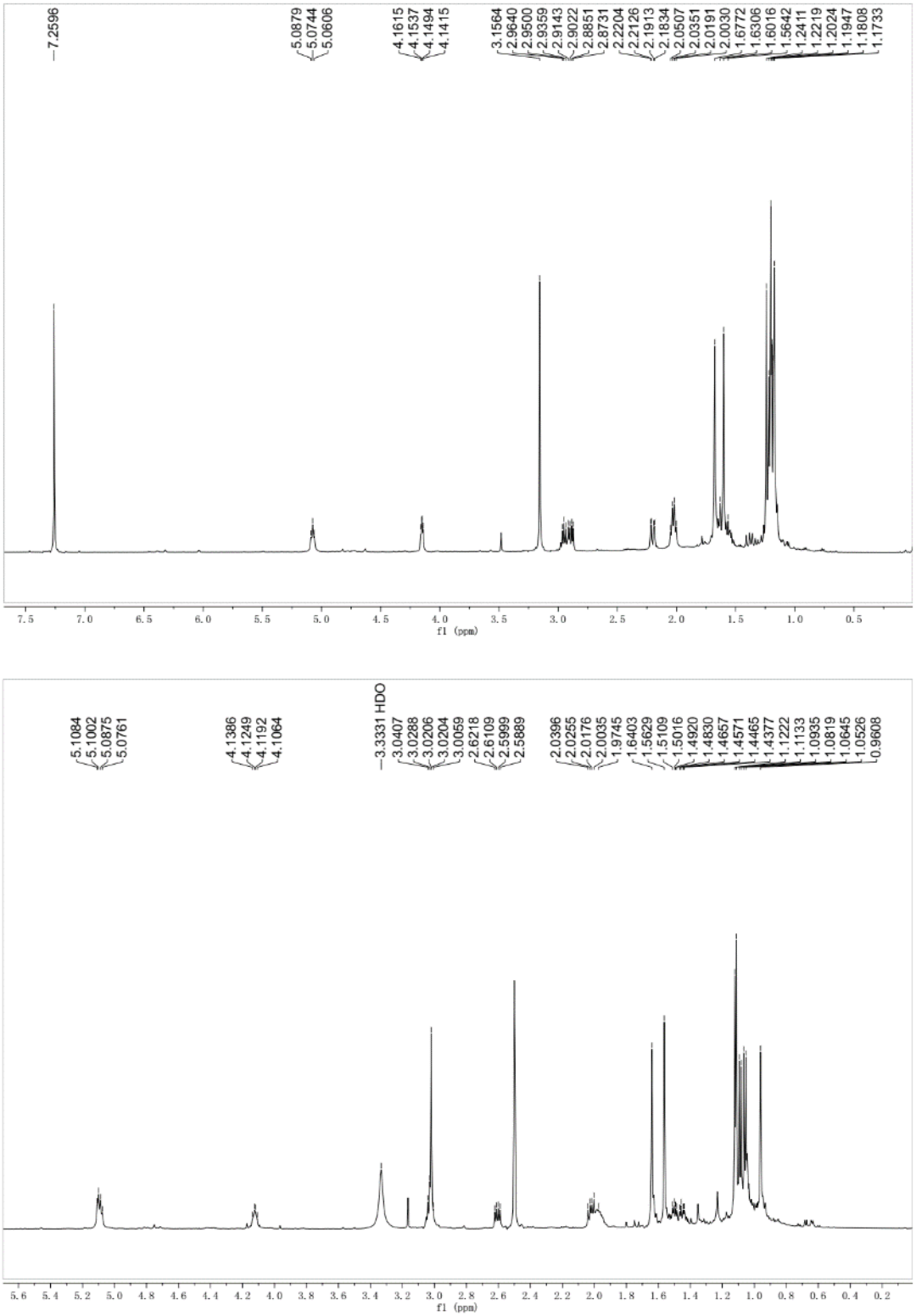


Figure S7 ^{1}H NMR (600 MHz) spectrum of 1 in $CDCl_3$ (the above) and DMSO-d_6 (the following figure).

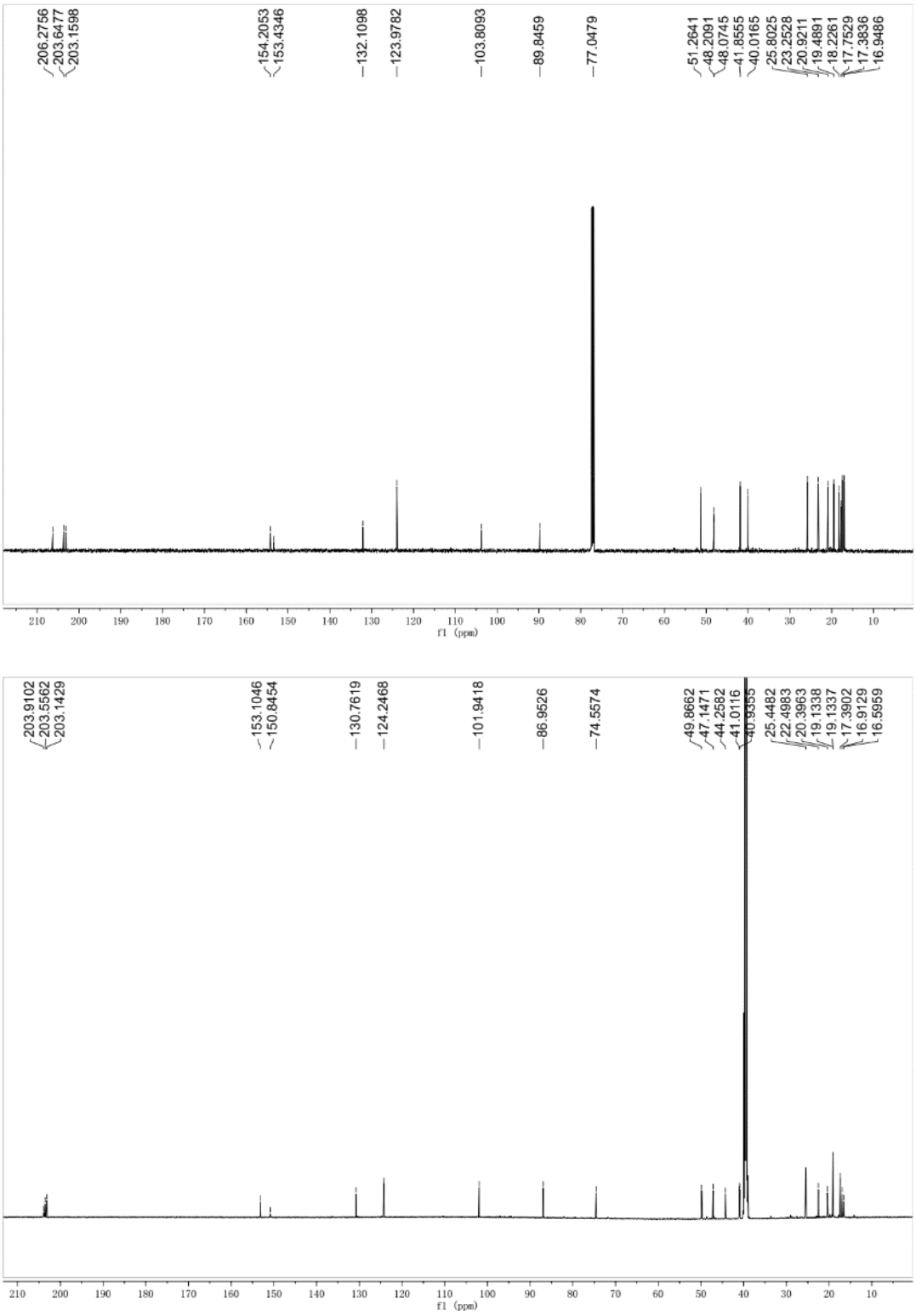


Figure S8 ^{13}C NMR (150 MHz) spectrum of 1 in $CDCl_3$ (the above figure) and DMSO-d_6 (the following figure).

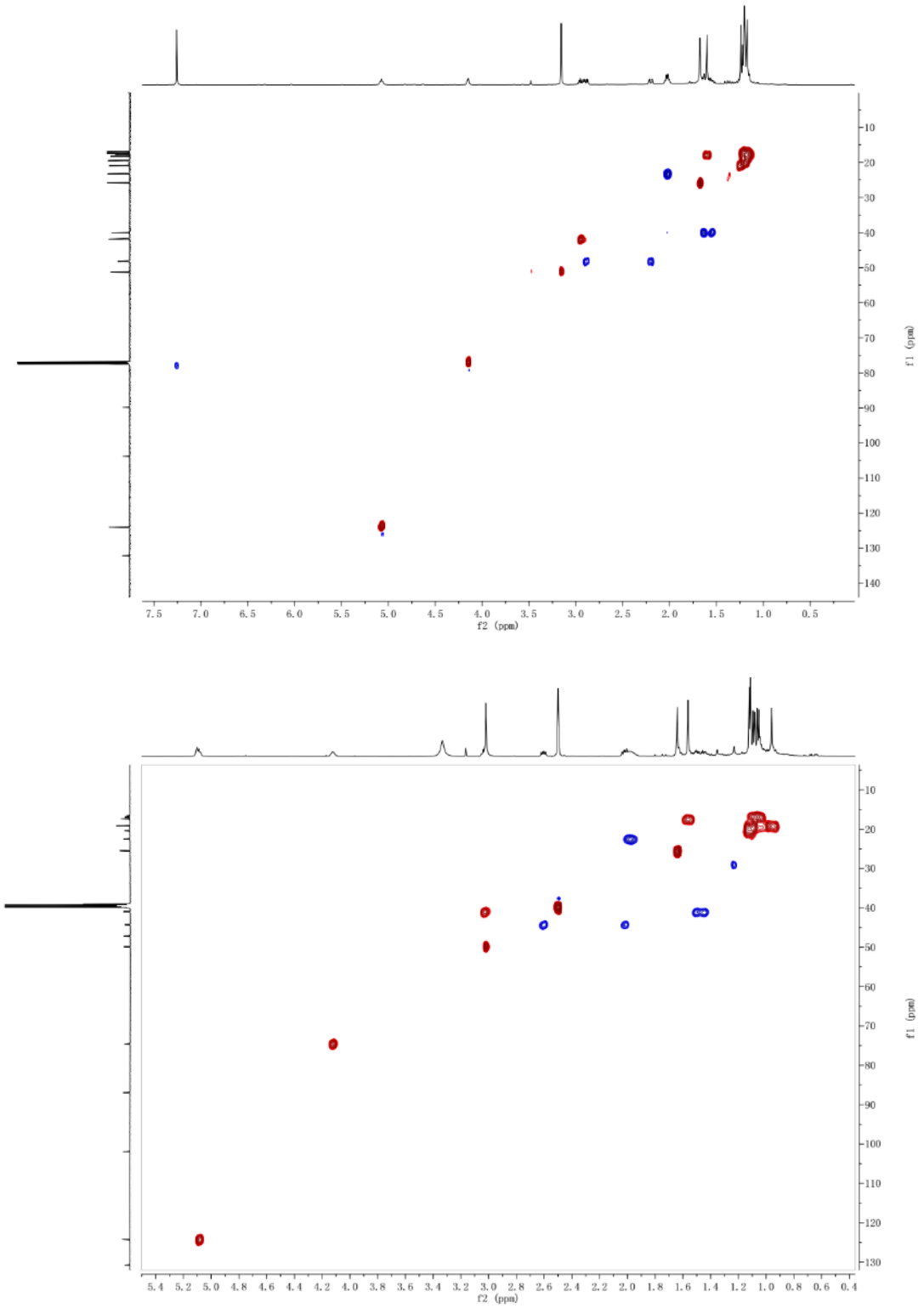


Figure S9 HSQC spectrum of 1 in $CDCl_3$ (the above figure) and DMSO-d_6 (the following figure).

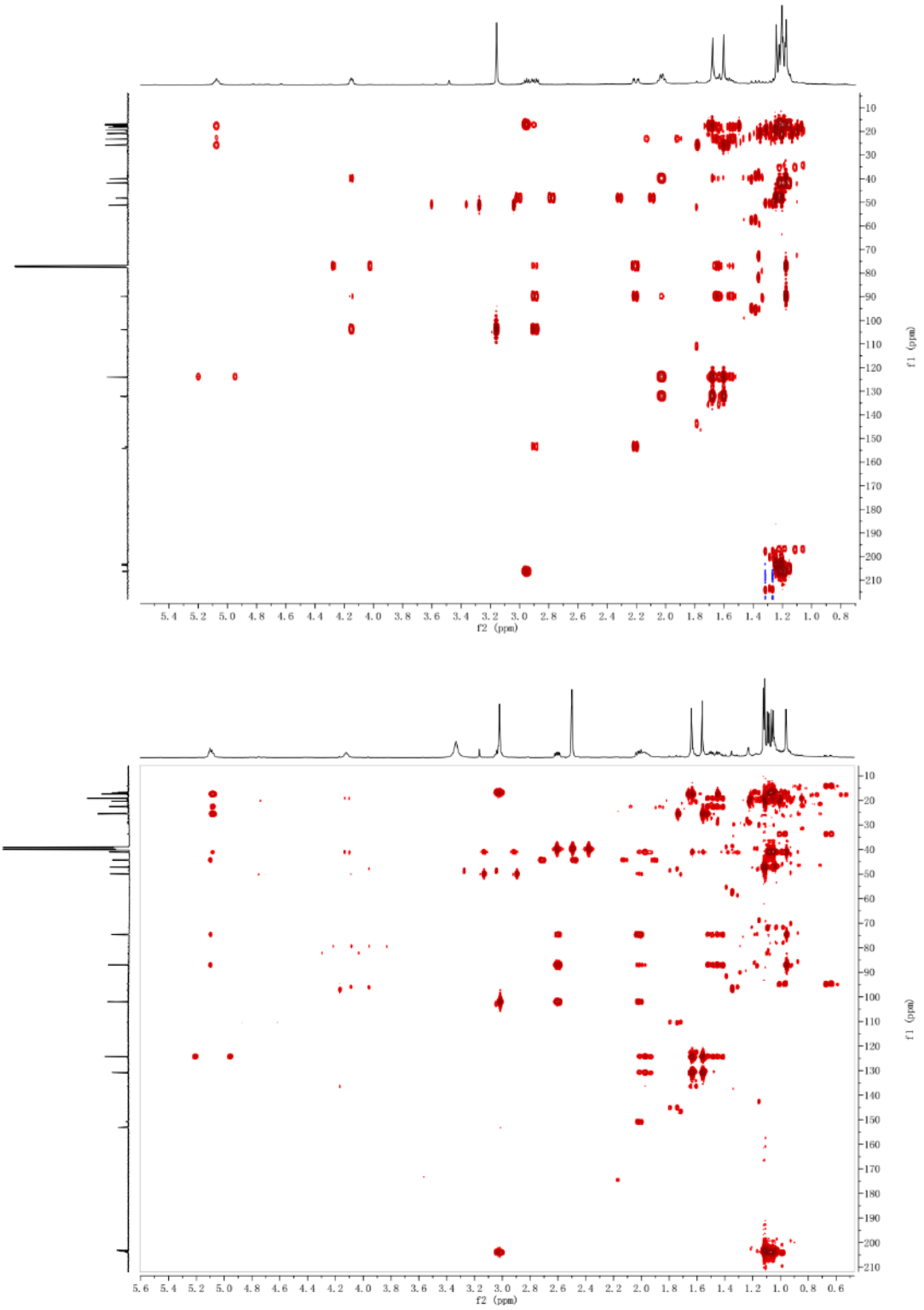
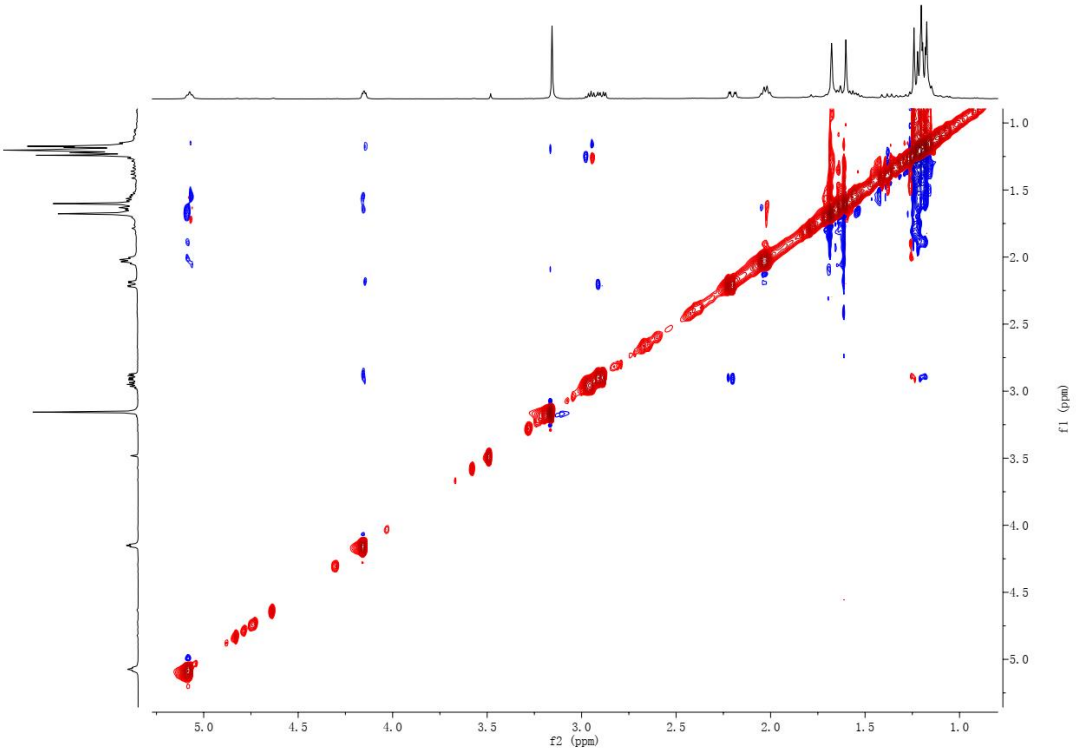


Figure S10 HMBC spectrum of 1 in $CDCl_3$ (the above figure) and DMSO-d_6 (the following figure).



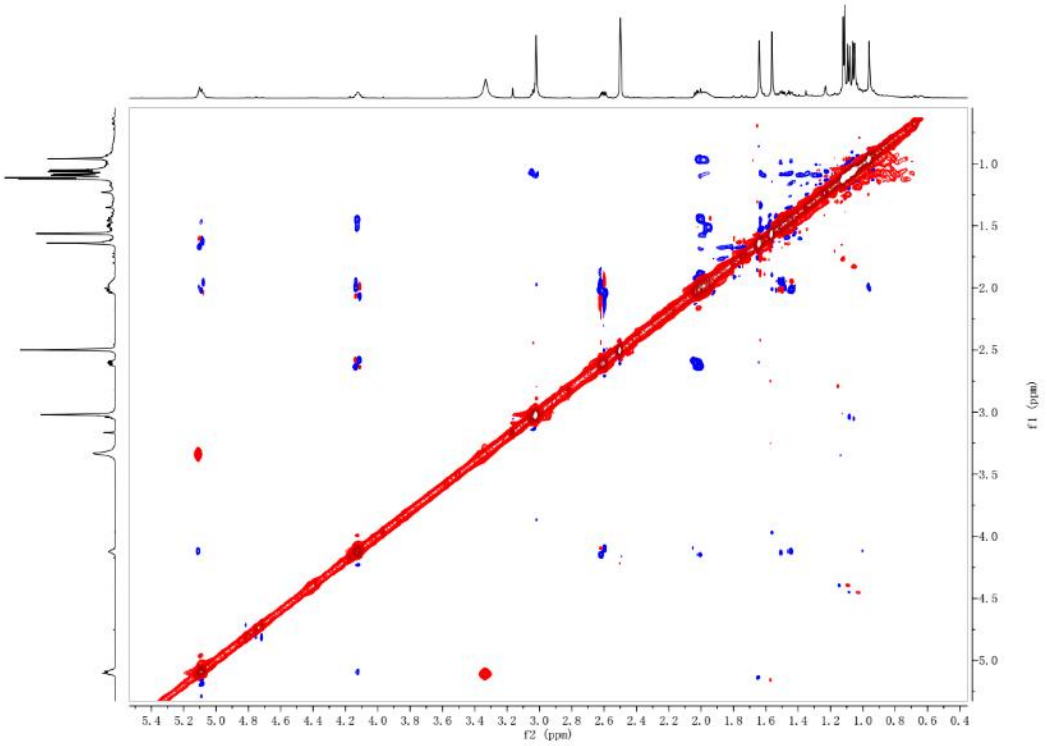


Figure S11 ROESY spectrum of 1 in $CDCl_3$ (the above figure) and DMSO-d_6 (the following figure).

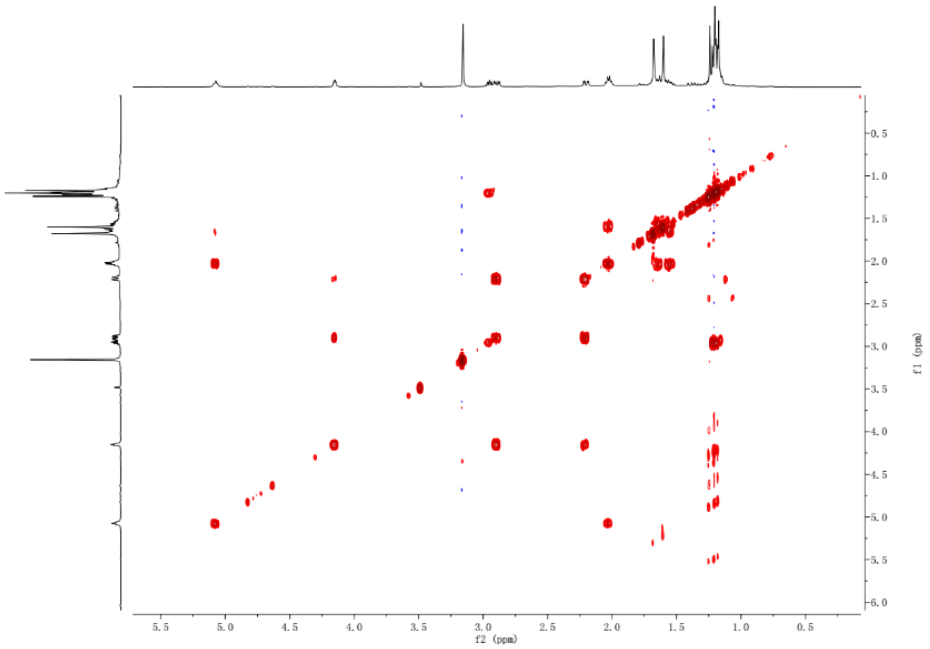
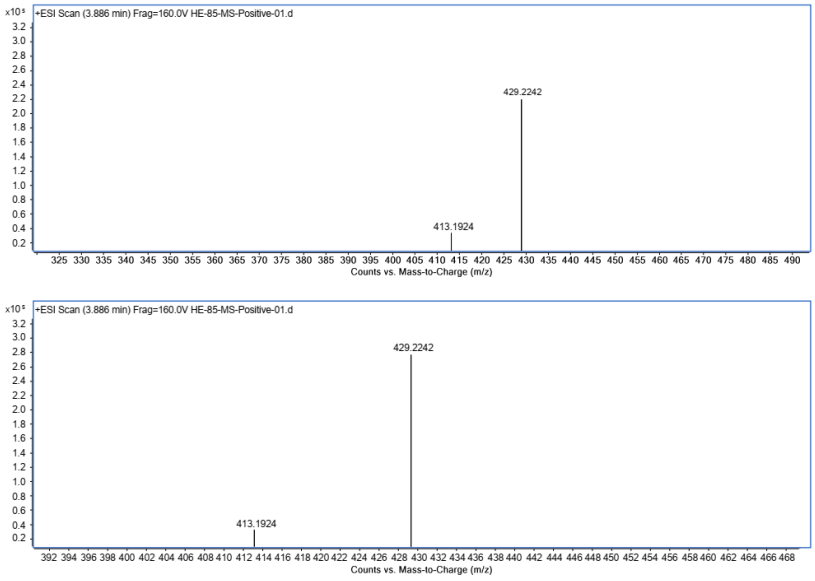


Figure S12 ^{1}H-^{1}H COSY spectrum of 1 in $CDCl_3$.



Elemental Composition Calculator

Target m/z:	429.2242	**Result type:**	Positive ions	**Species:**	$[M+Na]^+$
Elements:		C (0-80); H (0-120); O (0-30)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C23H34O6Na		429.2248		0.7	

Agilent Technologies

Figure S13 HRESIMS spectrum of 1.

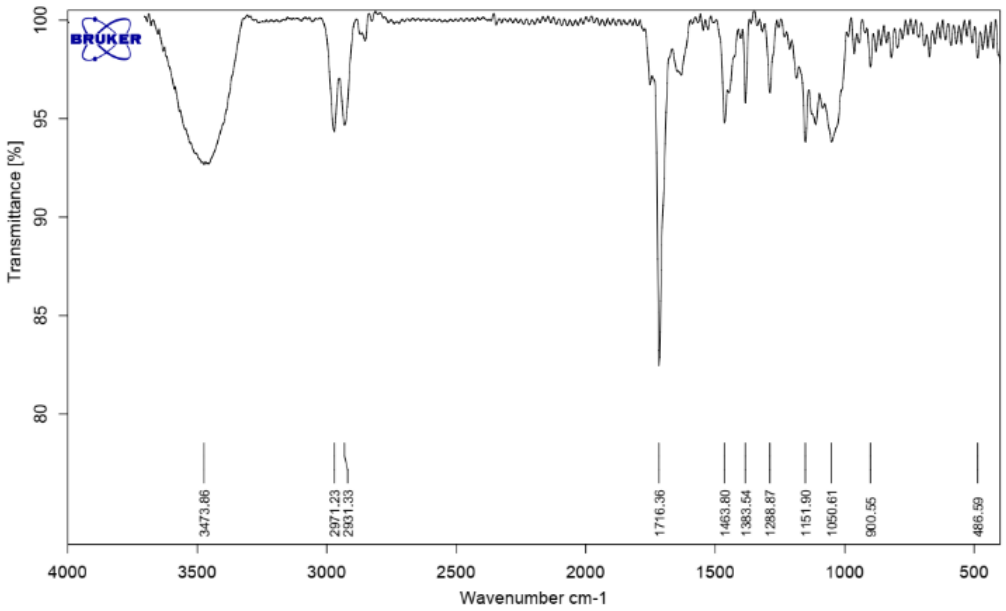


Figure S14 IR spectrum of 1.

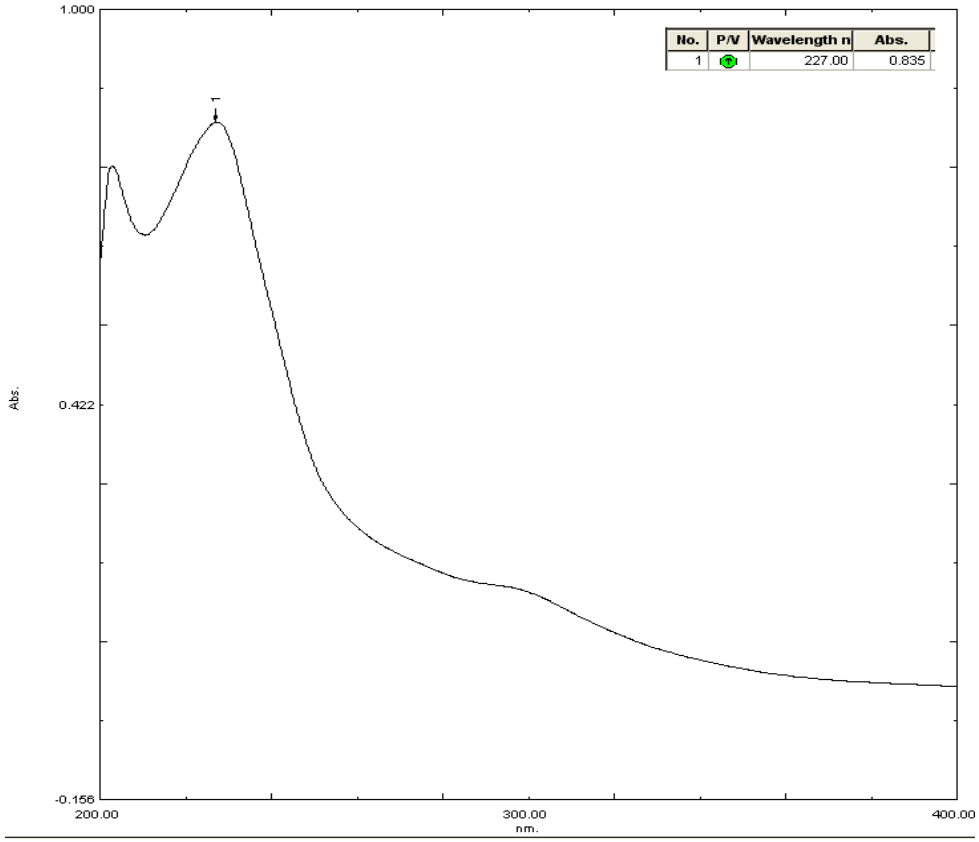


Figure S15 UV spectrum of 1.

NMR, HRESIMS, UV, and IR spectrum of 2 (Figure S16-S23)

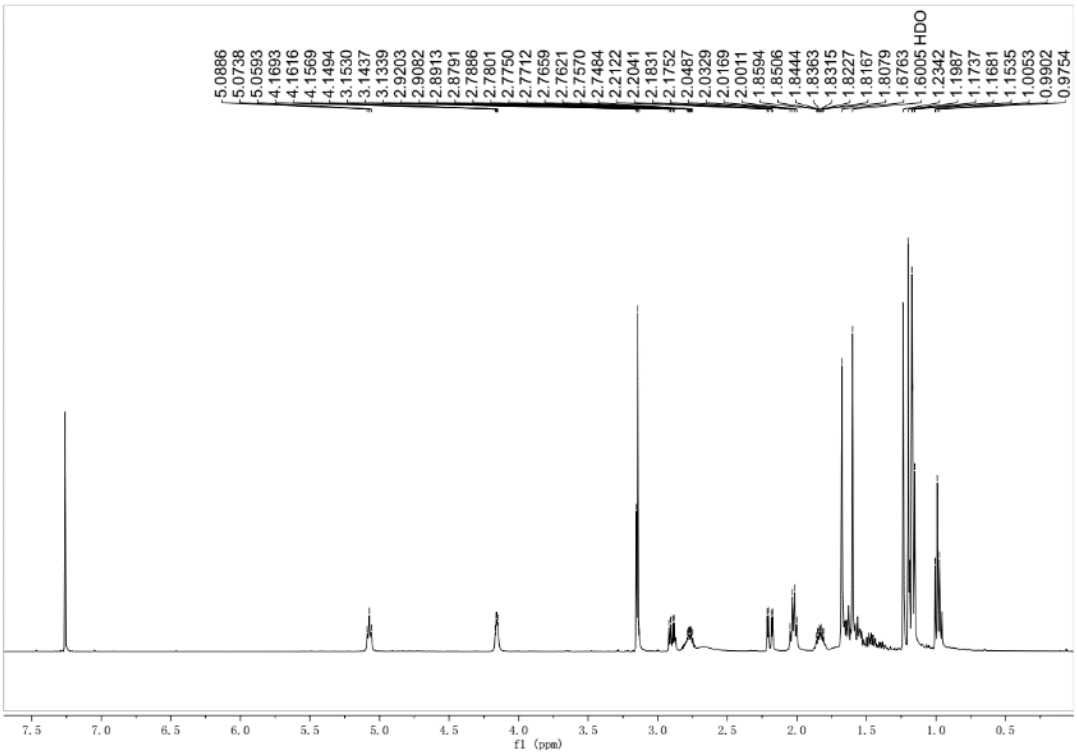


Figure S16 ^{1}H NMR (600 MHz) spectrum of 2 in $CDCl_3$.

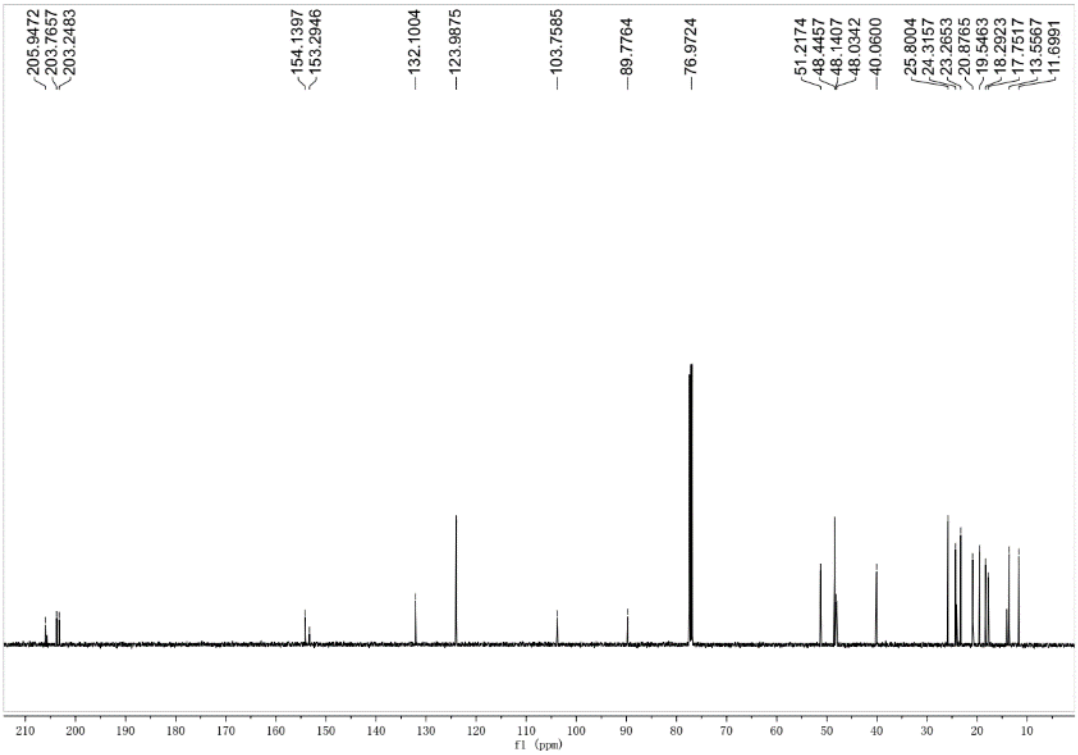


Figure S17 ^{13}C NMR (150 MHz) spectrum of 2 in $CDCl_3$.

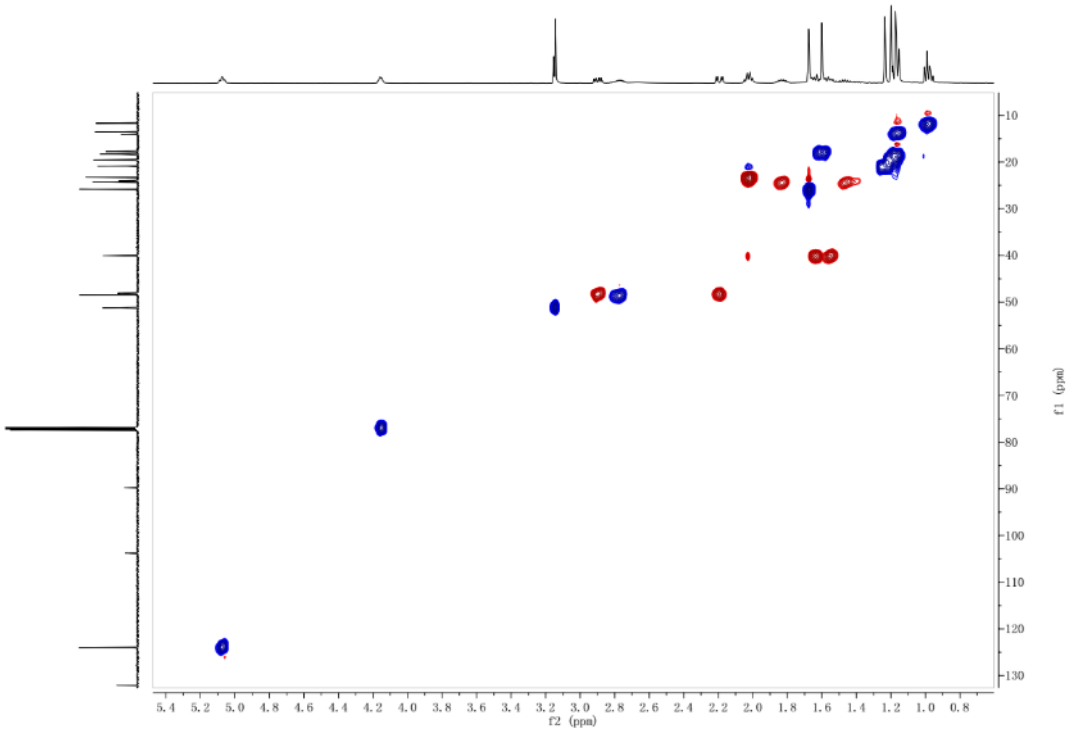


Figure S18 HSQC spectrum of 2 in $CDCl_3$.

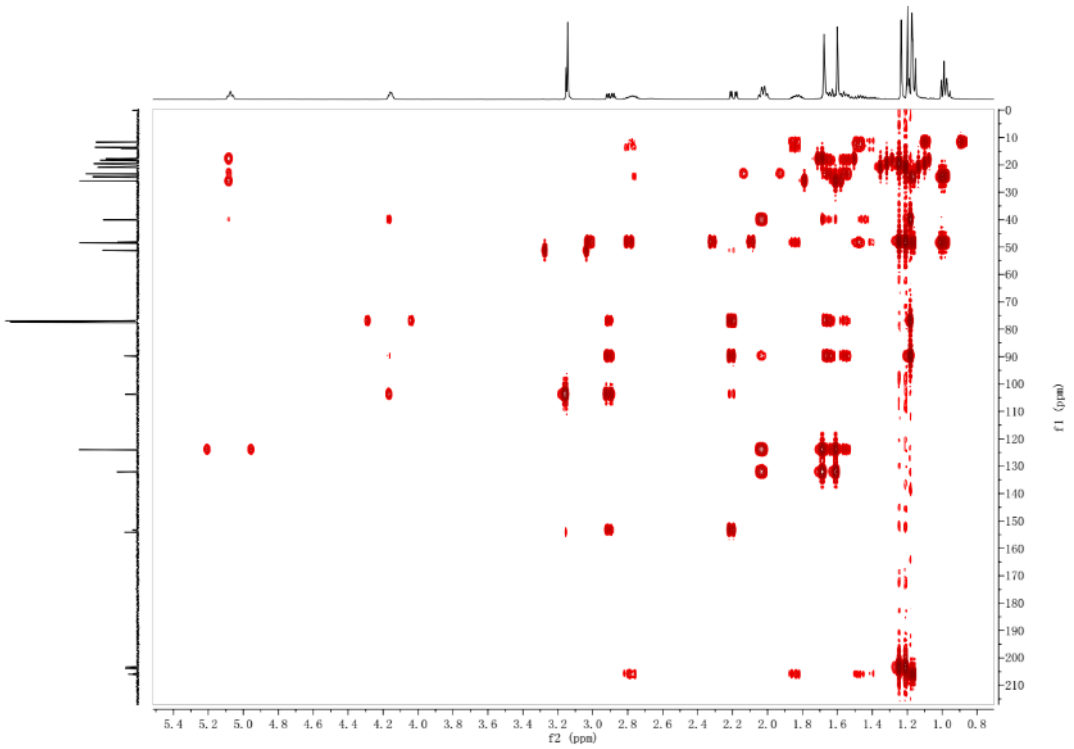


Figure S19 HMBC spectrum of 2 in $CDCl_3$.

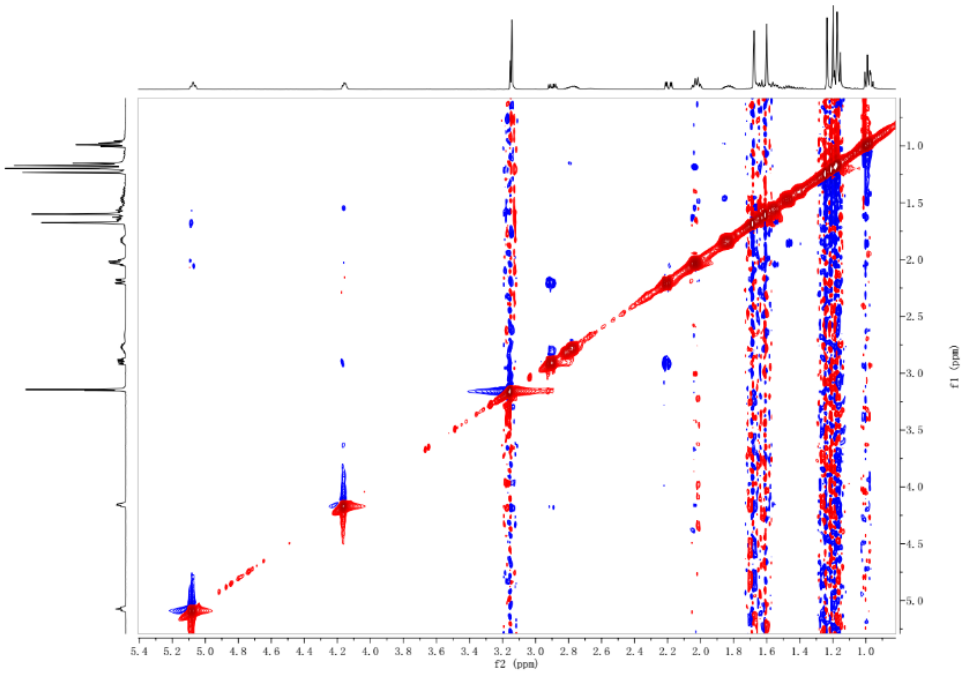
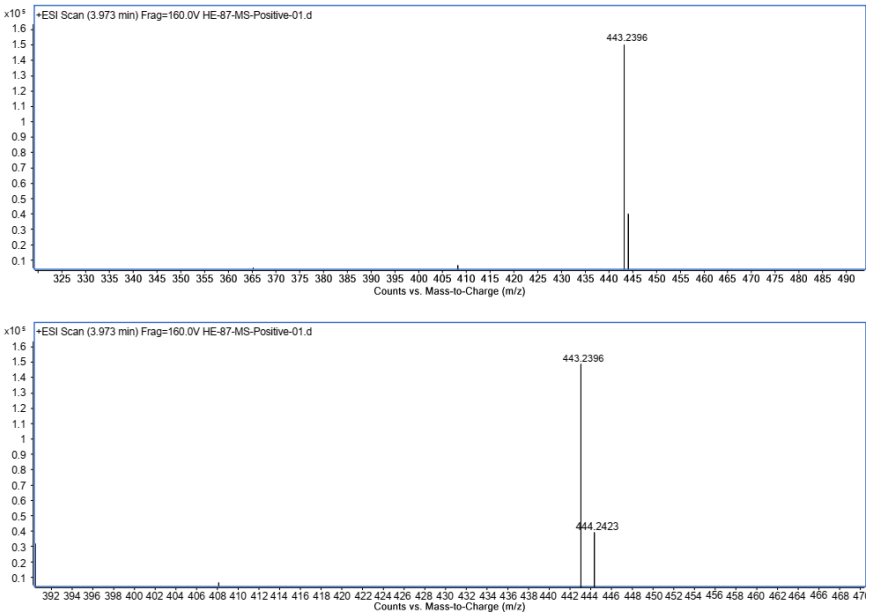


Figure S20 ROESY spectrum of 2 in $CDCl_3$.



Elemental Composition Calculator

Target m/z:	443.2396	**Result type:**	Positive ions	**Species:**	$[M+Na]^+$
Elements:		C (0-80); H (0-120); O (0-30)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C24H36O6Na		443.2404		0.8	

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Figure S21 HRESIMS spectrum of 2.

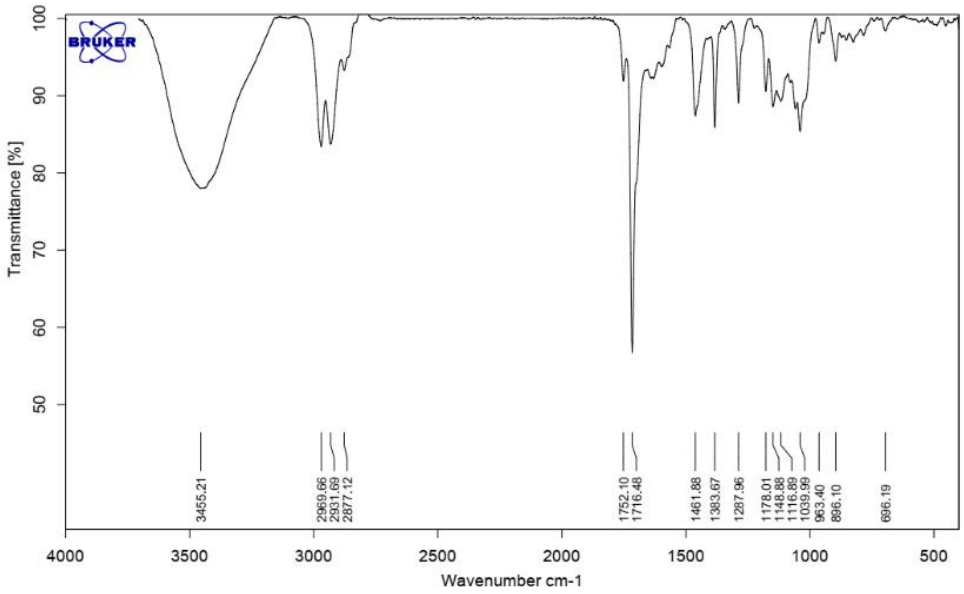


Figure S22 IR spectrum of 2.

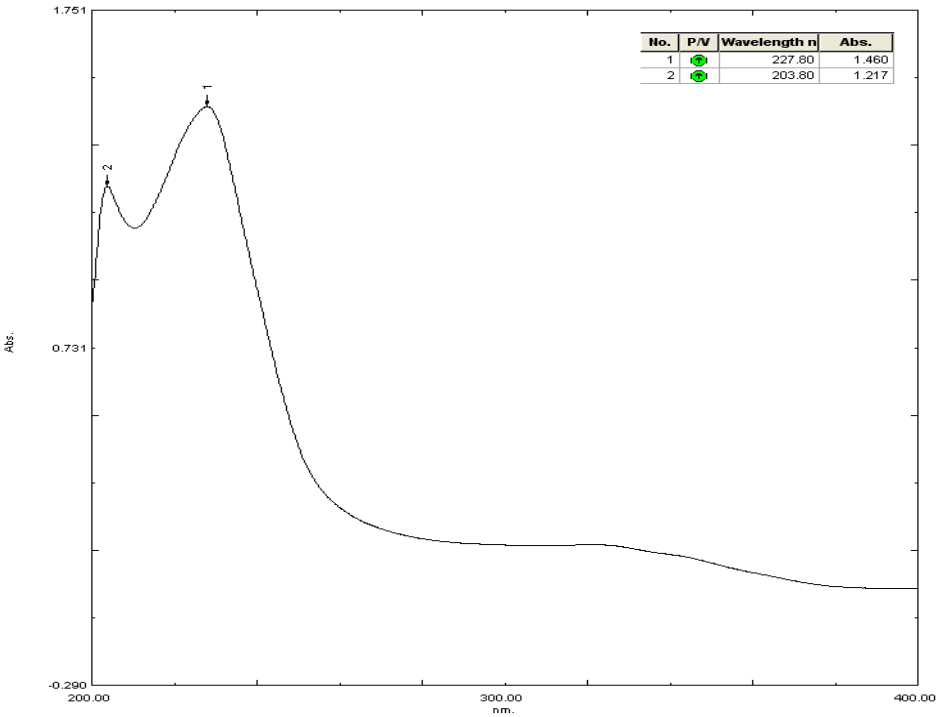


Figure S23 UV spectrum of 2.

NMR, HRESIMS, UV, and IR spectrum of 3 (Figure S24-S32)

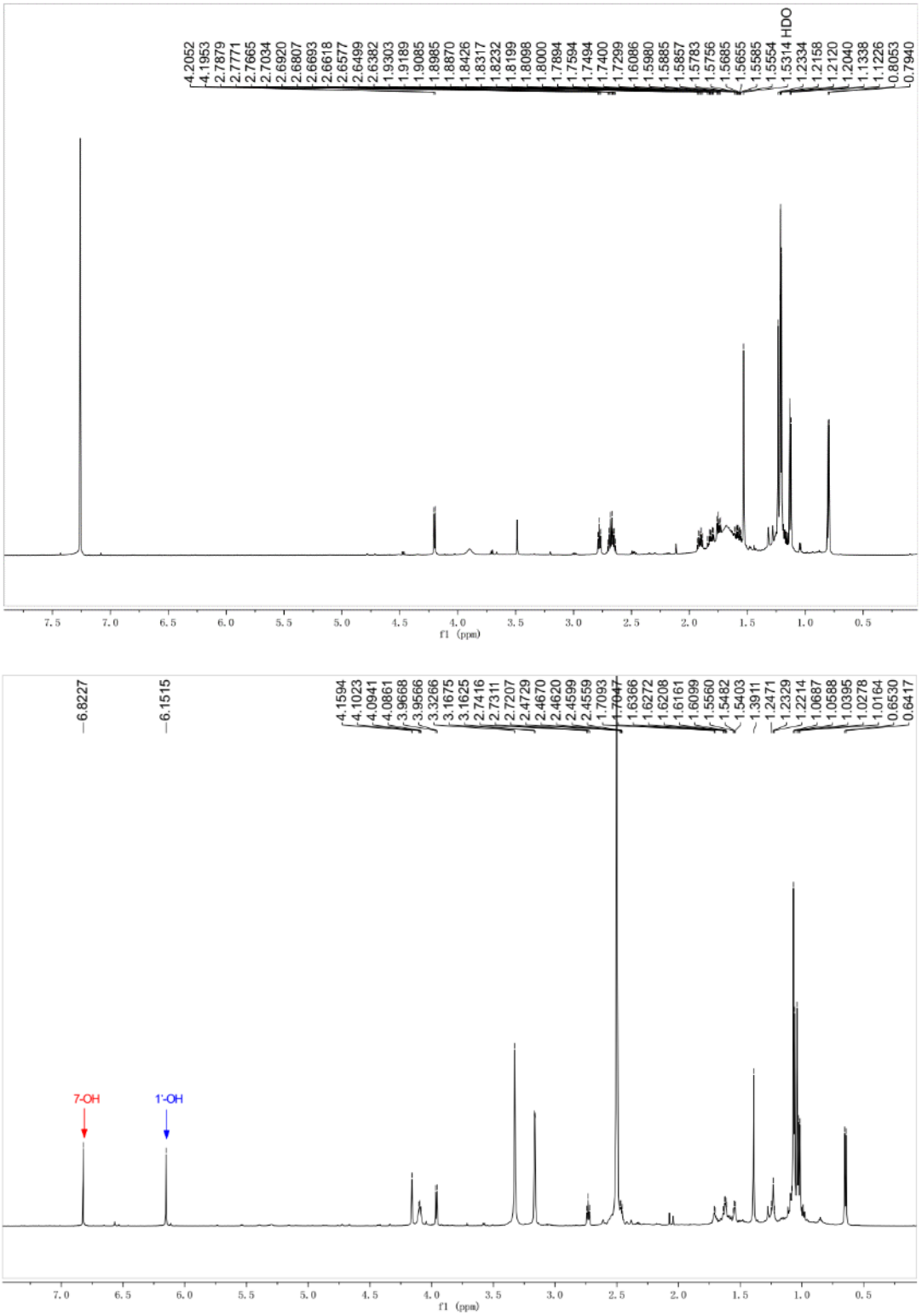


Figure S24 ^{1}H NMR (600 MHz) spectrum of 3 in $CDCl_3$ (the above figure) and DMSO-d_6 (the following figure).

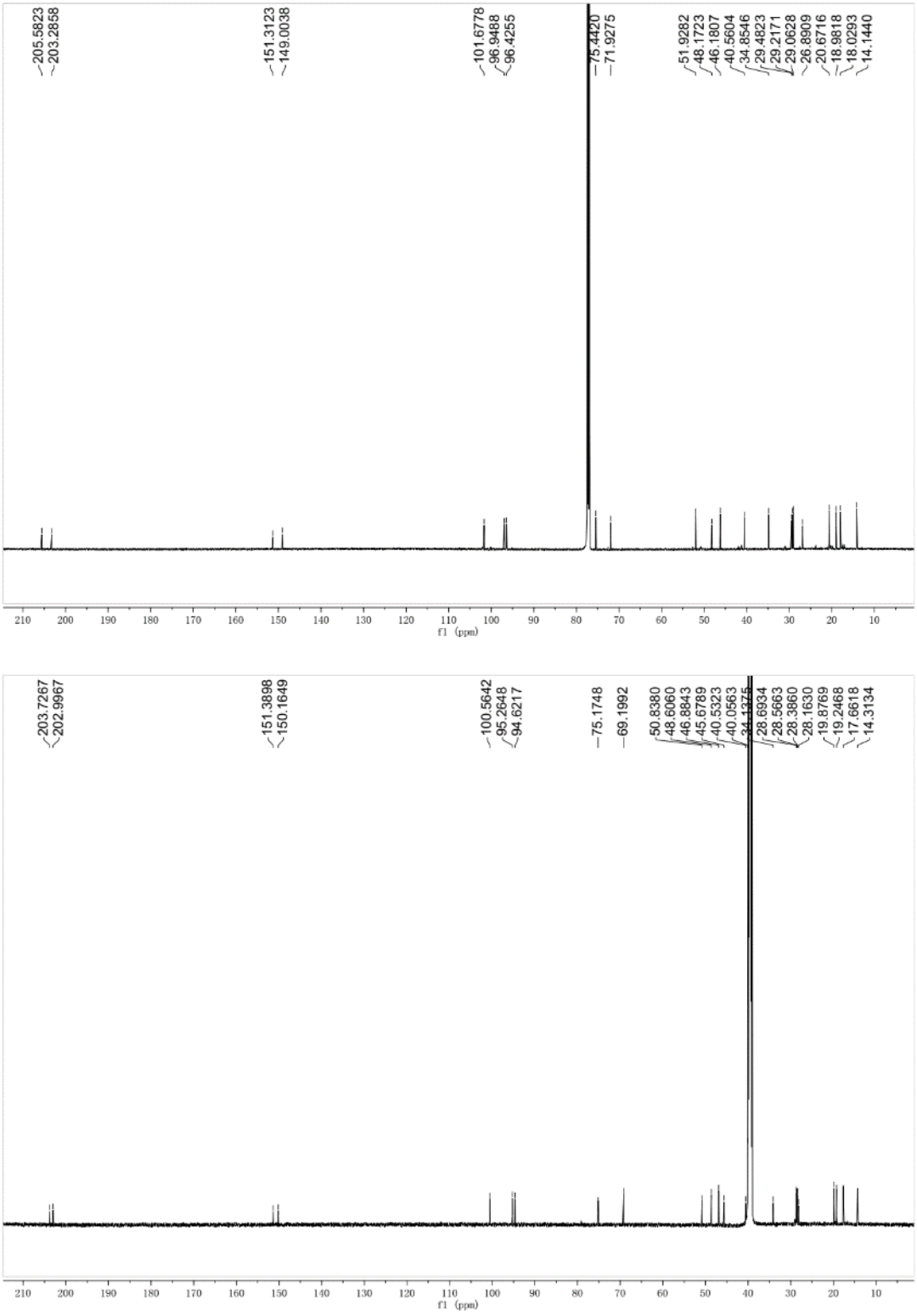


Figure S25 ^{13}C NMR (150 MHz) spectrum of 3 in $CDCl_3$ (the above figure) and DMSO-d_6 (the following figure).

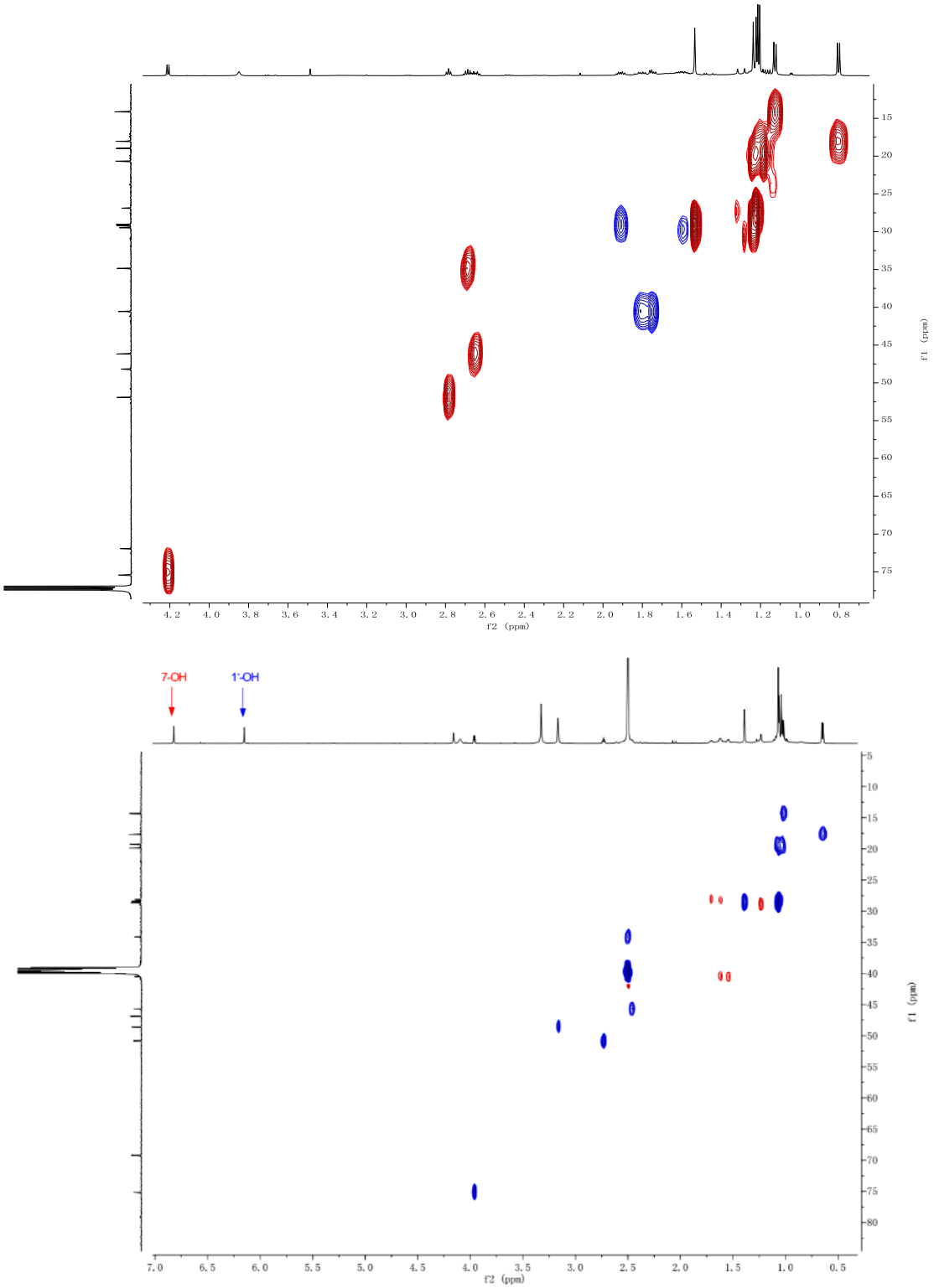


Figure S26 HSQC spectrum of 3 in $CDCl_3$ (the above figure) and DMSO-d_6 (the following figure).

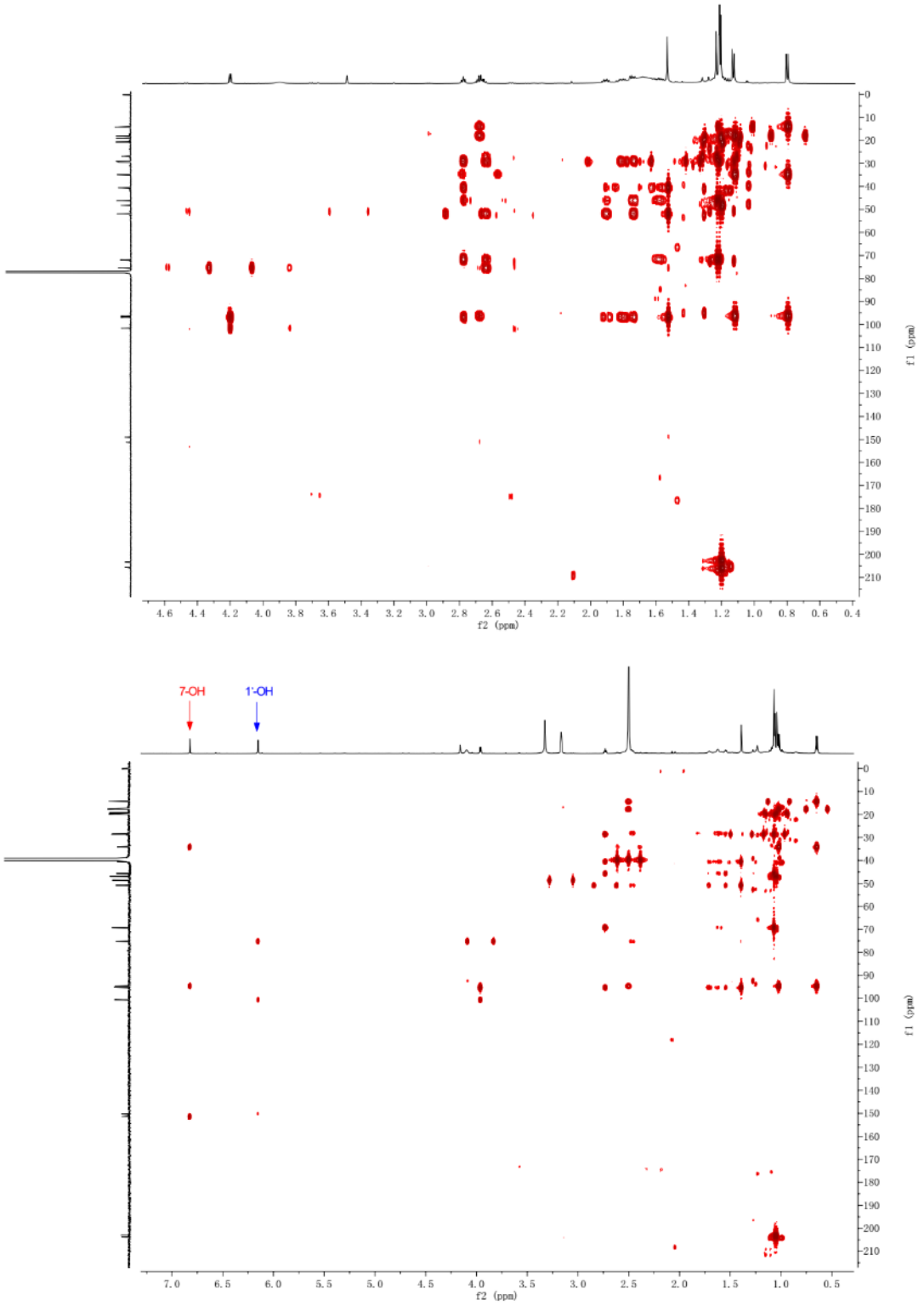


Figure S27 HMBC spectrum of 3 in $CDCl_3$ (the above figure) and DMSO-d_6 (the following figure).

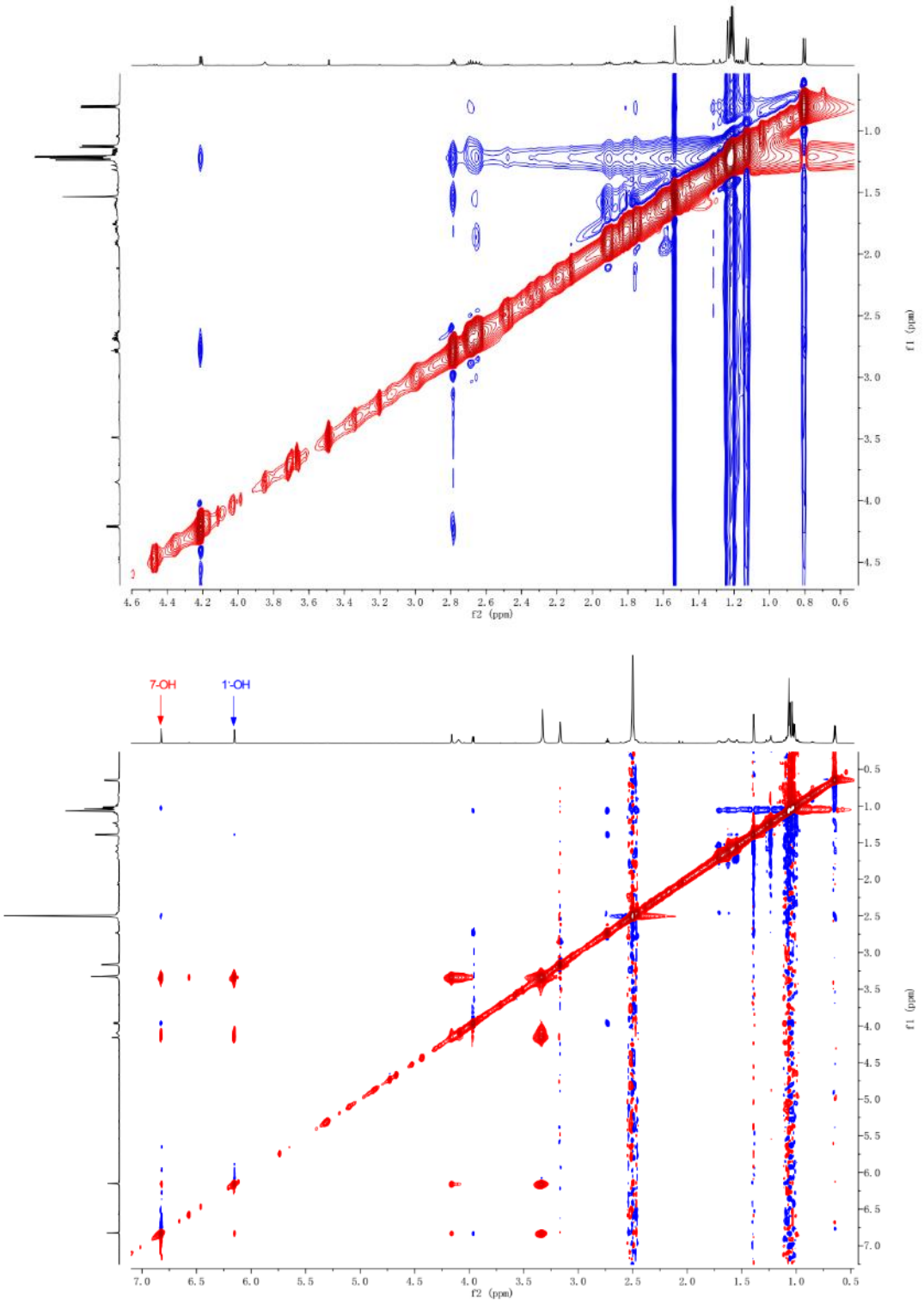


Figure S28 ROESY spectrum of 3 in $CDCl_3$ (the above figure) and DMSO-d_6 (the following figure).

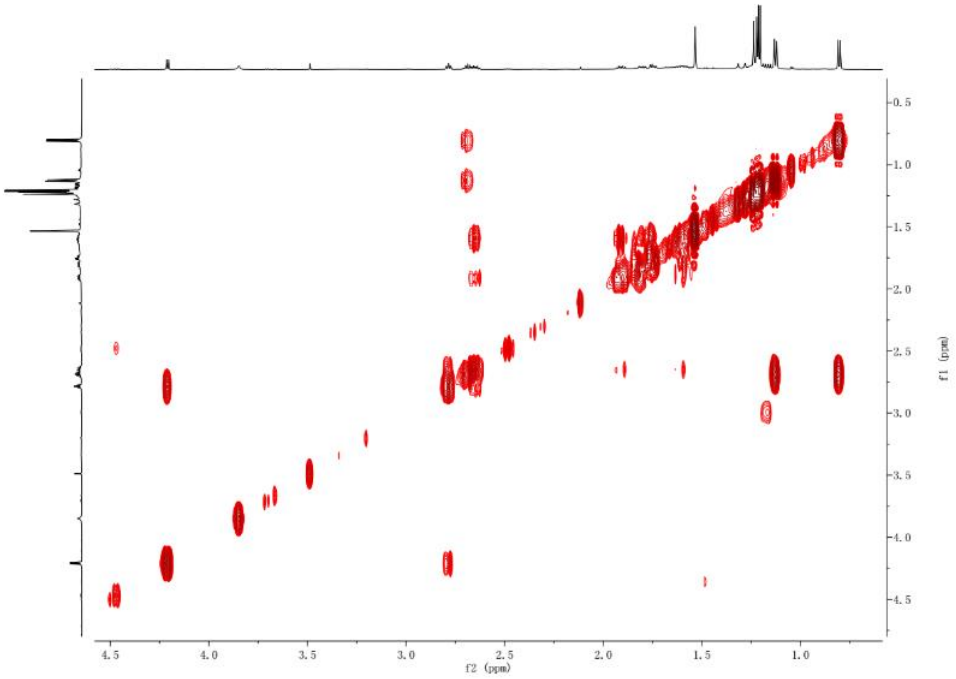
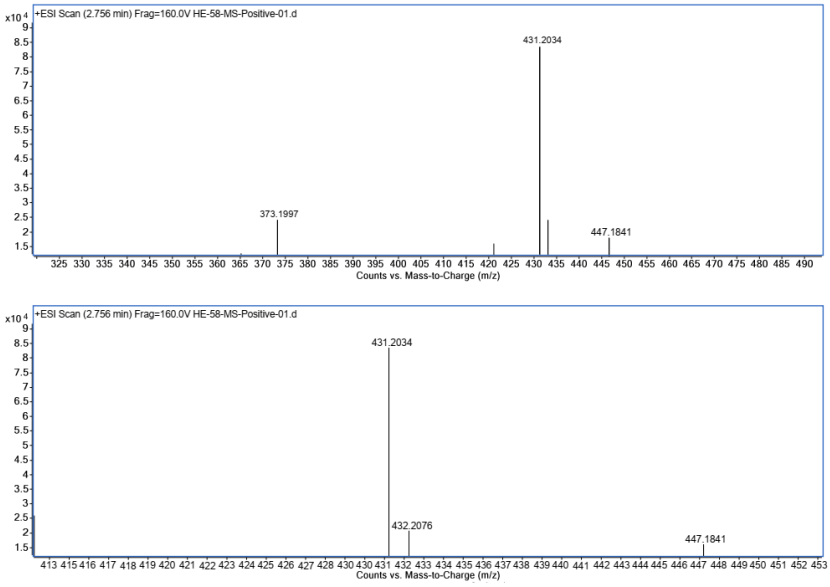


Figure S29 ^{1}H-^{1}H COSY spectrum of 3 in $CDCl_3$.



Elemental Composition Calculator

Target m/z:	431.2034	Result type:	Positive ions	Species:	$[M+Na]^+$
Elements:		C (0-80); H (0-120); O (0-30)			
Ion Formula		Calcalated m/z		PPM Error	
C22H32O7Na		431.2040		0.70	

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Figure S30 HRESIMS spectrum of 3.

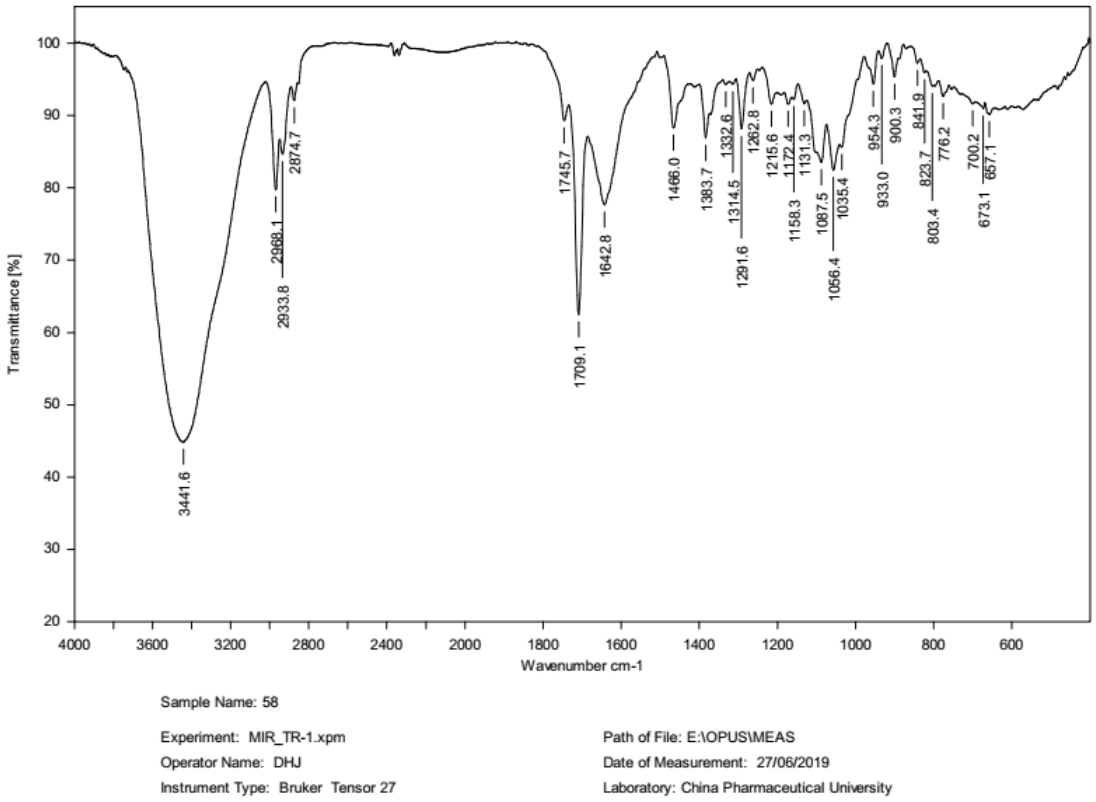


Figure S31 IR spectrum of 3.

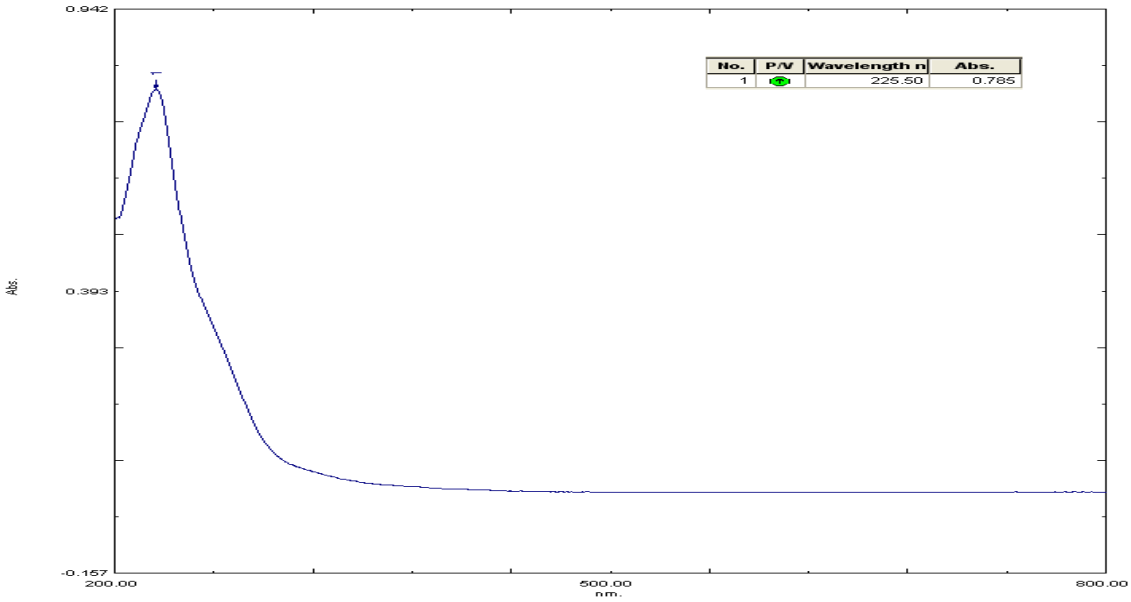


Figure S32 UV spectrum of 3.

NMR, HRESIMS, UV, and IR spectrum of 4 (Figure S33-S40)

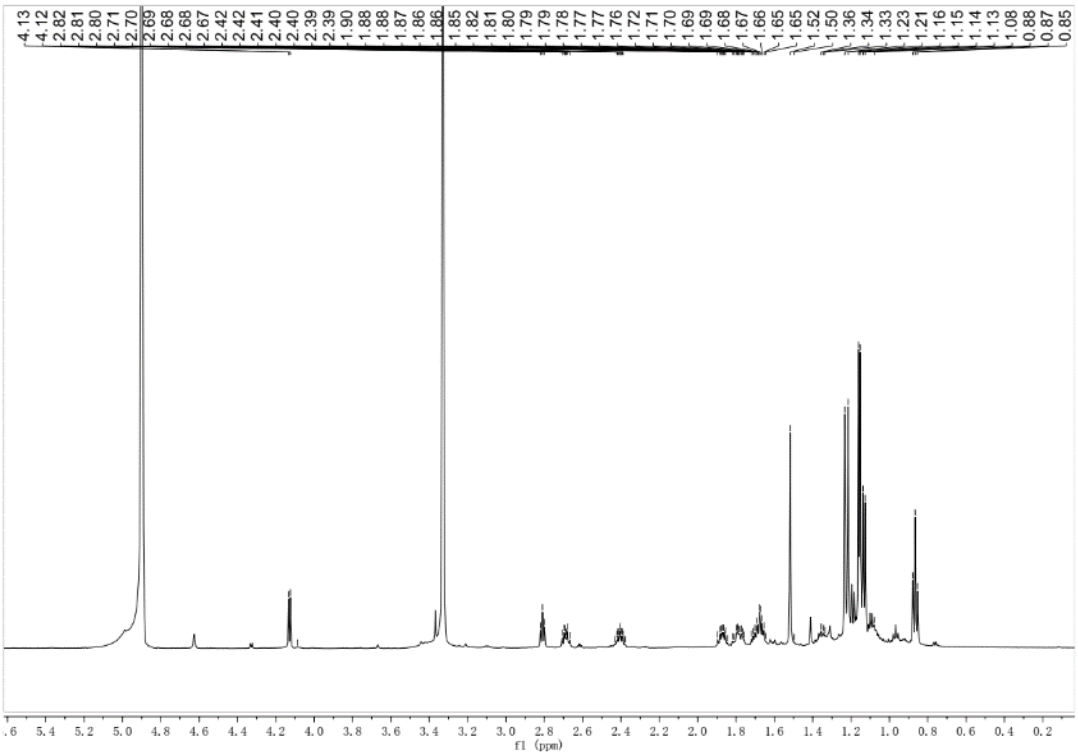


Figure S33 ^{1}H NMR (600 MHz) spectrum of 4 in MeOD.

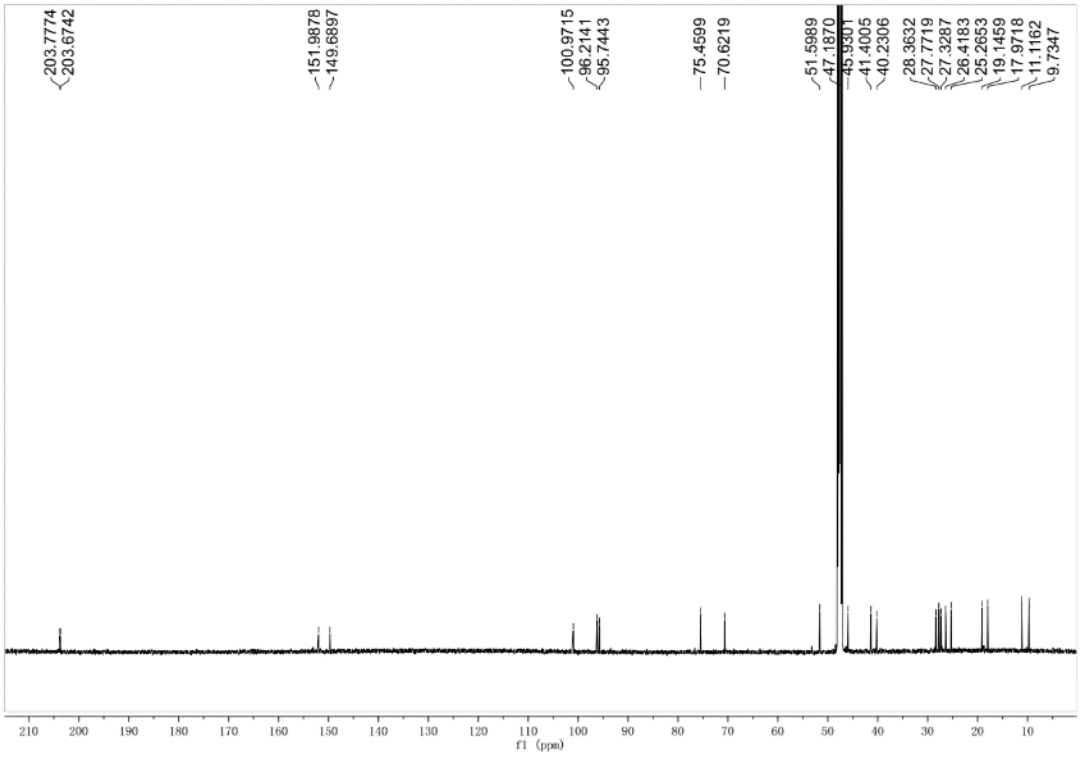


Figure S34 ^{13}C NMR (150 MHz) spectrum of 4 in MeOD.

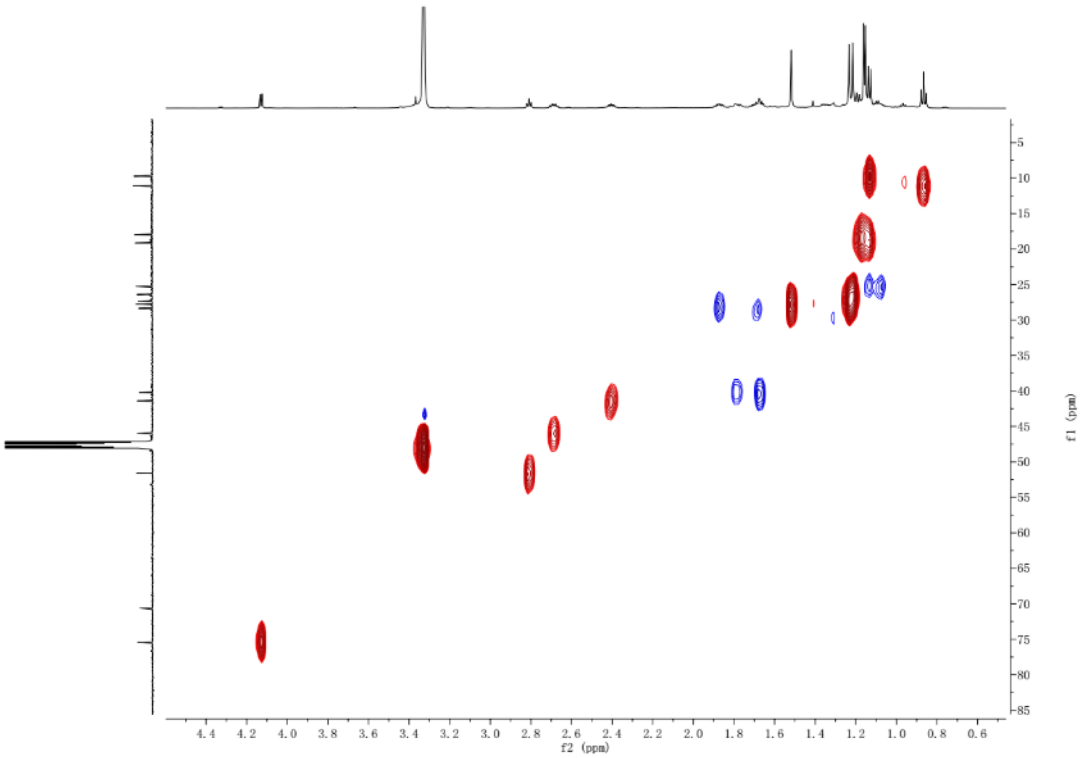


Figure S35 HSQC spectrum of 4 in MeOD.

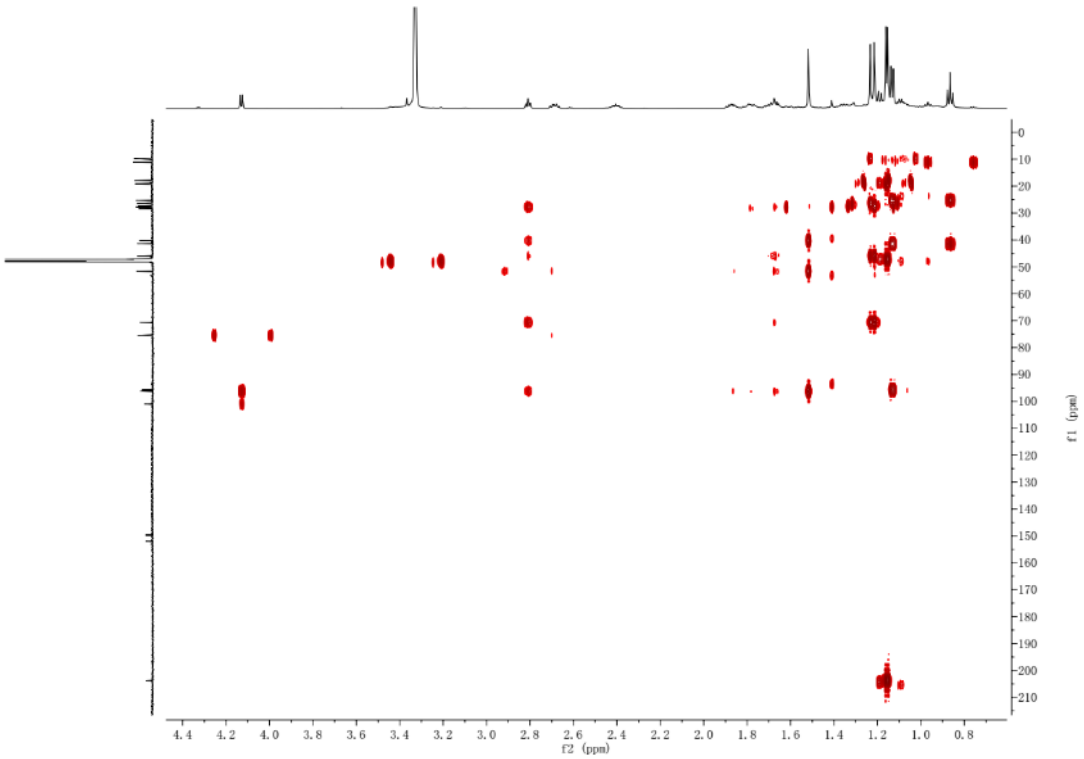


Figure S36 HMBC spectrum of 4 in MeOD.

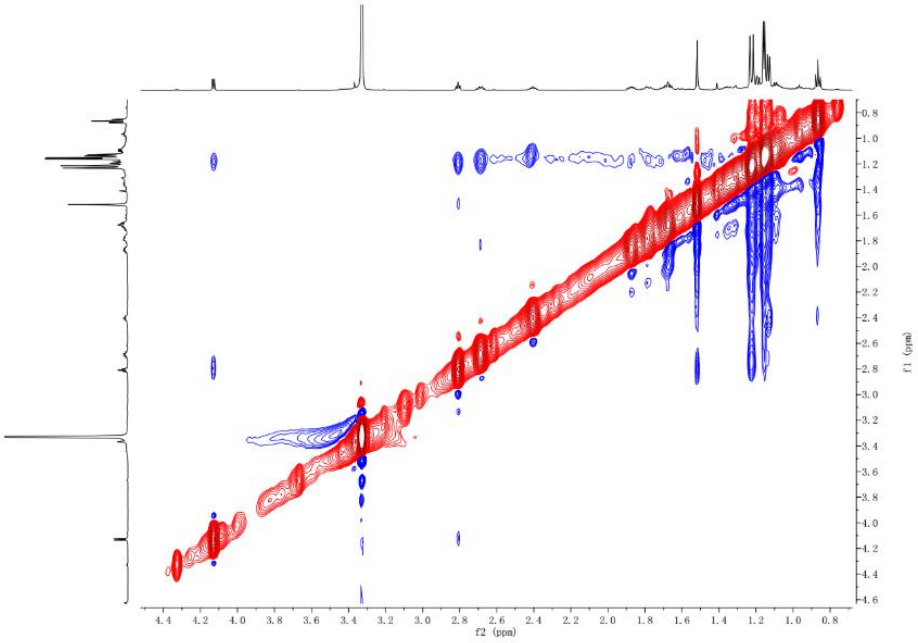
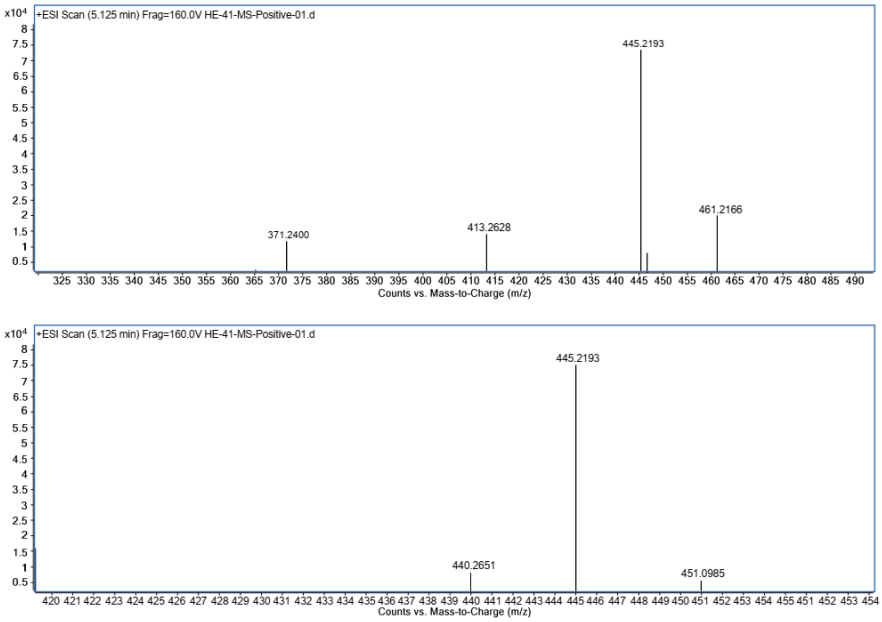


Figure S37 ROESY spectrum of 4 in MeOD.



Elemental Composition Calculator

Target m/z:	445.2193	**Result type:**	Positive ions	**Species:**	$[M+Na]^+$
Elements:		C (0-80); H (0-120); O (0-30)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C23H34O7Na		445.2197		0.76	

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Figure S38 HRESIMS spectrum of 4.

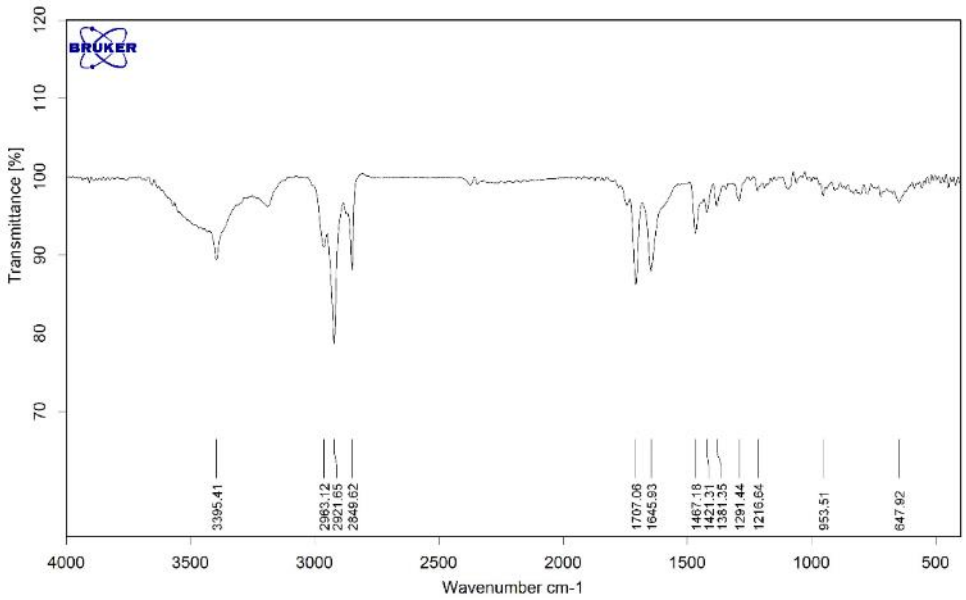


Figure S39 IR spectrum of 4.

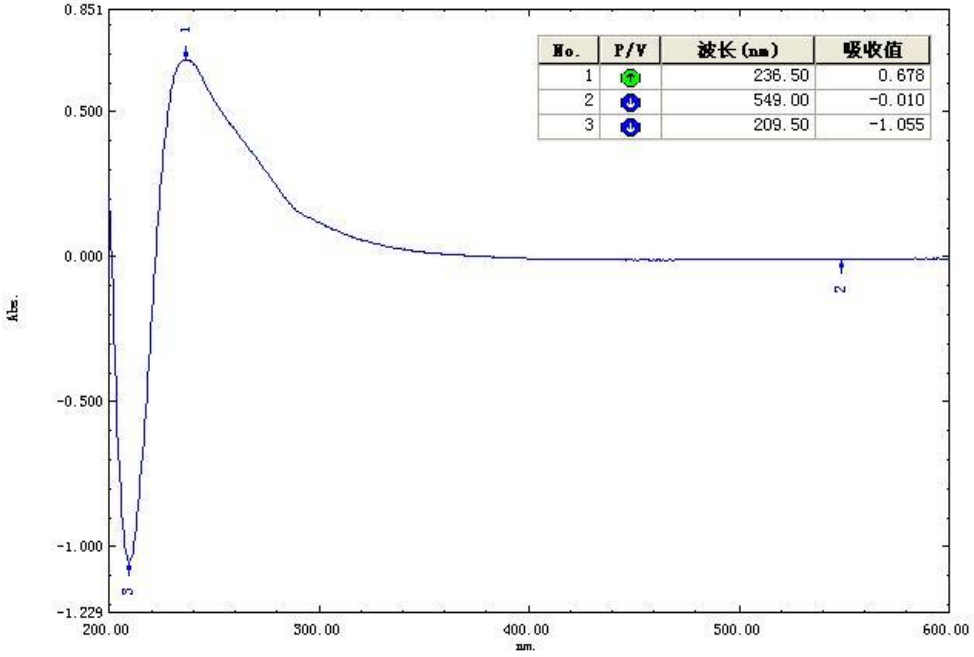


Figure S40 UV spectrum of 4.

NMR, HRESIMS, UV, and IR spectrum of 5 (Figure S41-S49)

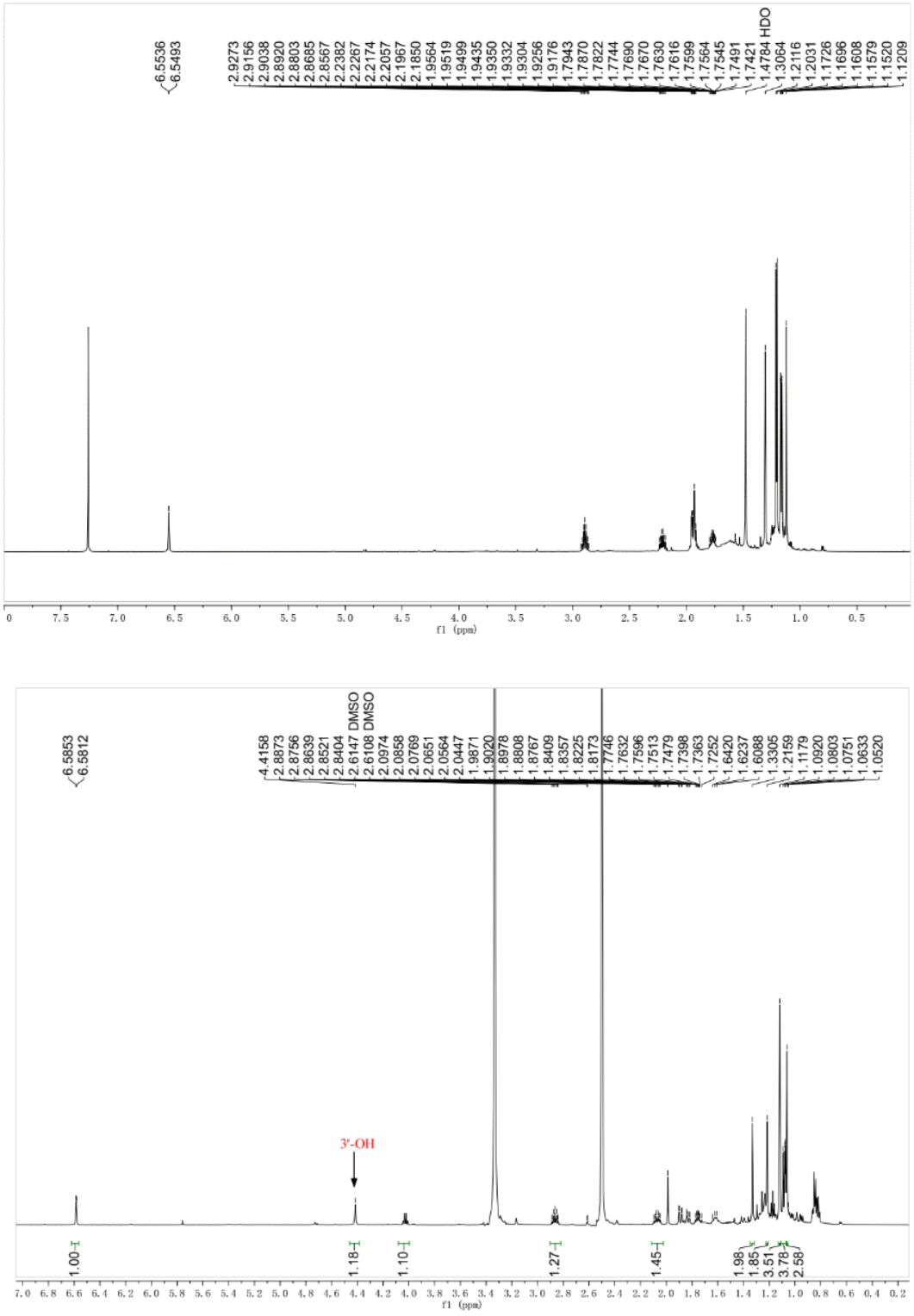


Figure S41 ^{1}H NMR (600 MHz) spectrum of 5 in $CDCl_3$ (the above figure) and DMSO-d_6 (the following figure).

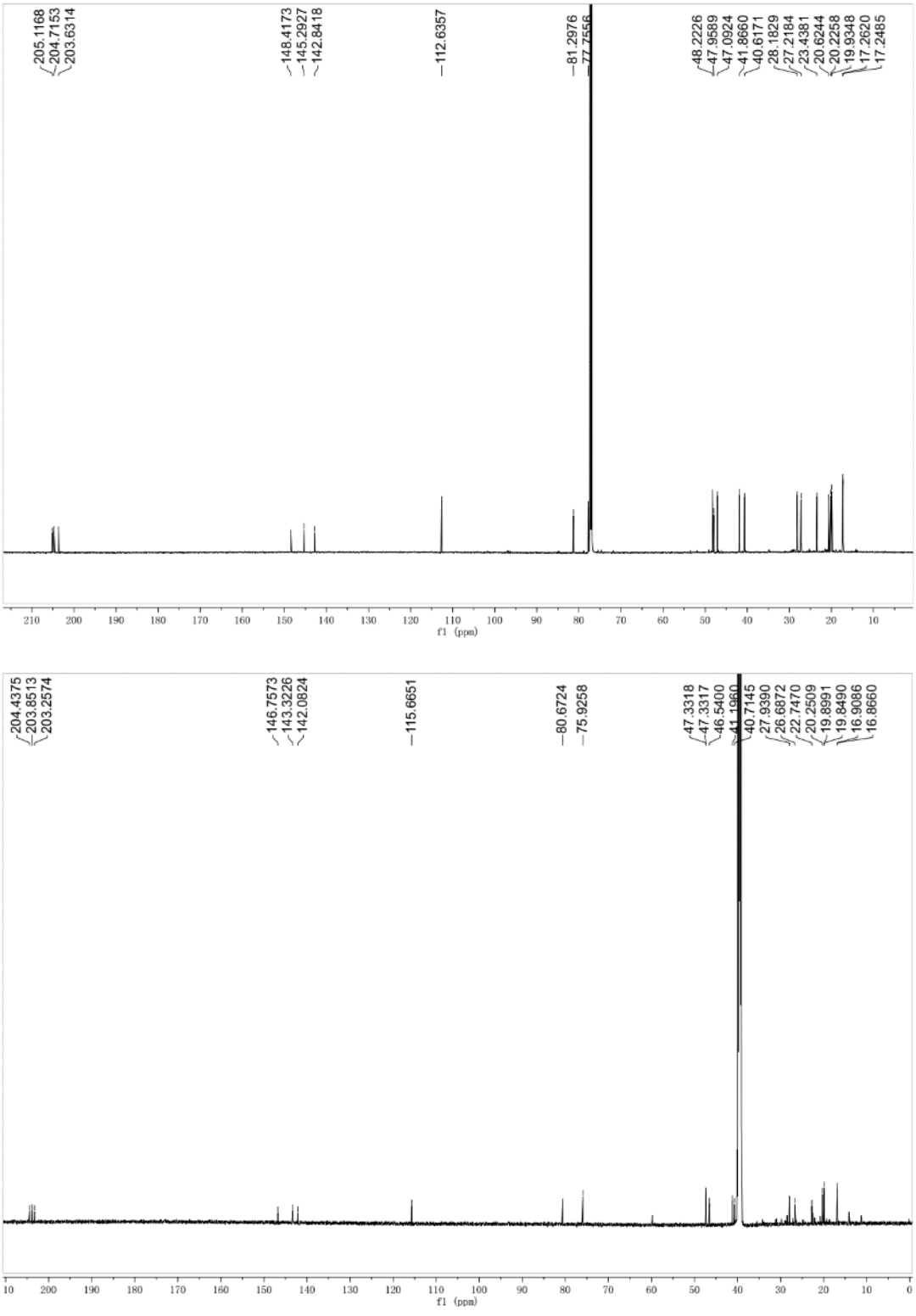


Figure S42 ^{13}C NMR (150 MHz) spectrum of 5 in $CDCl_3$ (the above figure) and DMSO-d_6 (the following figure).

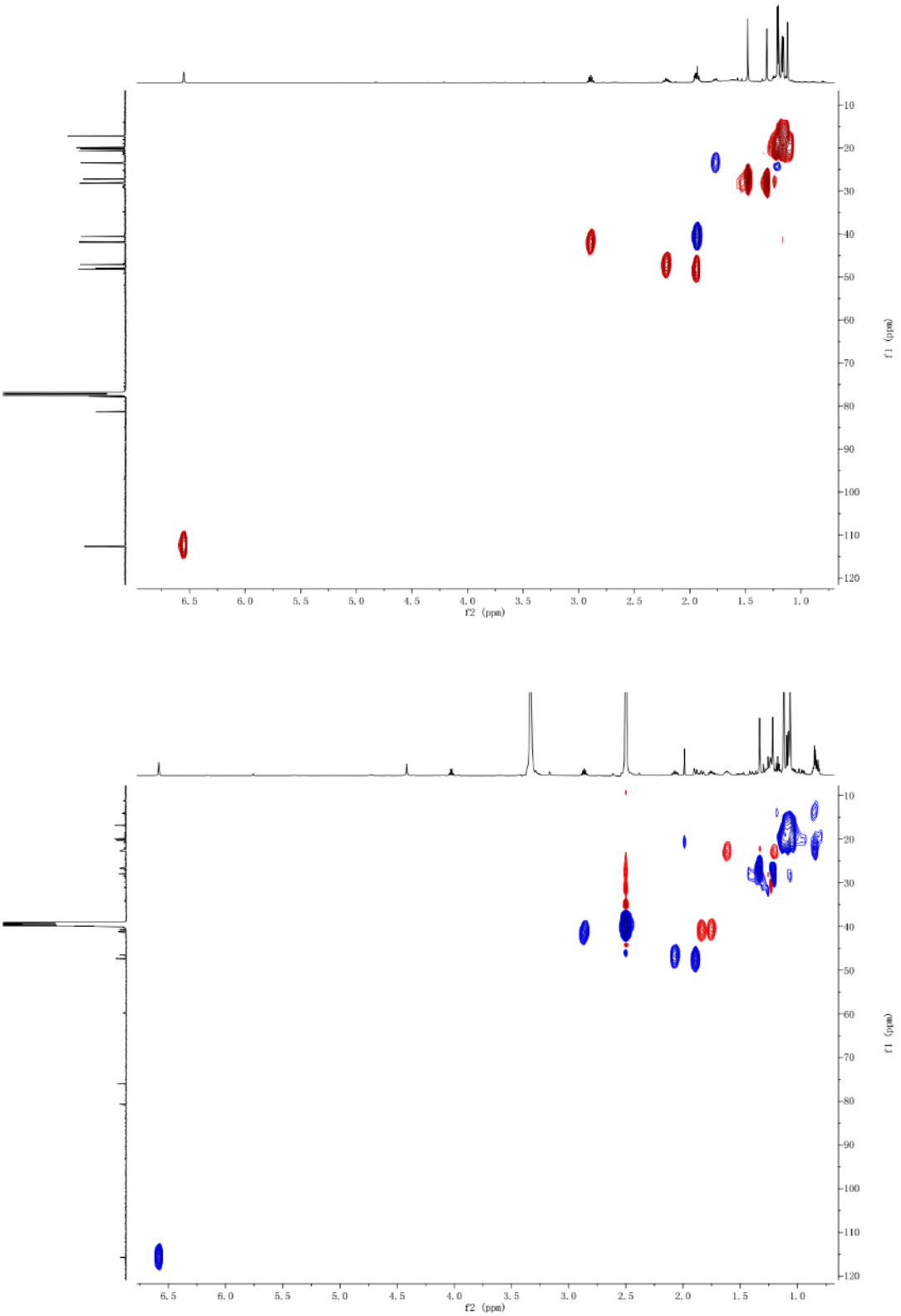


Figure S43 HSQC spectrum of 5 in $CDCl_3$ (the above figure) and DMSO-d_6 (the following figure).

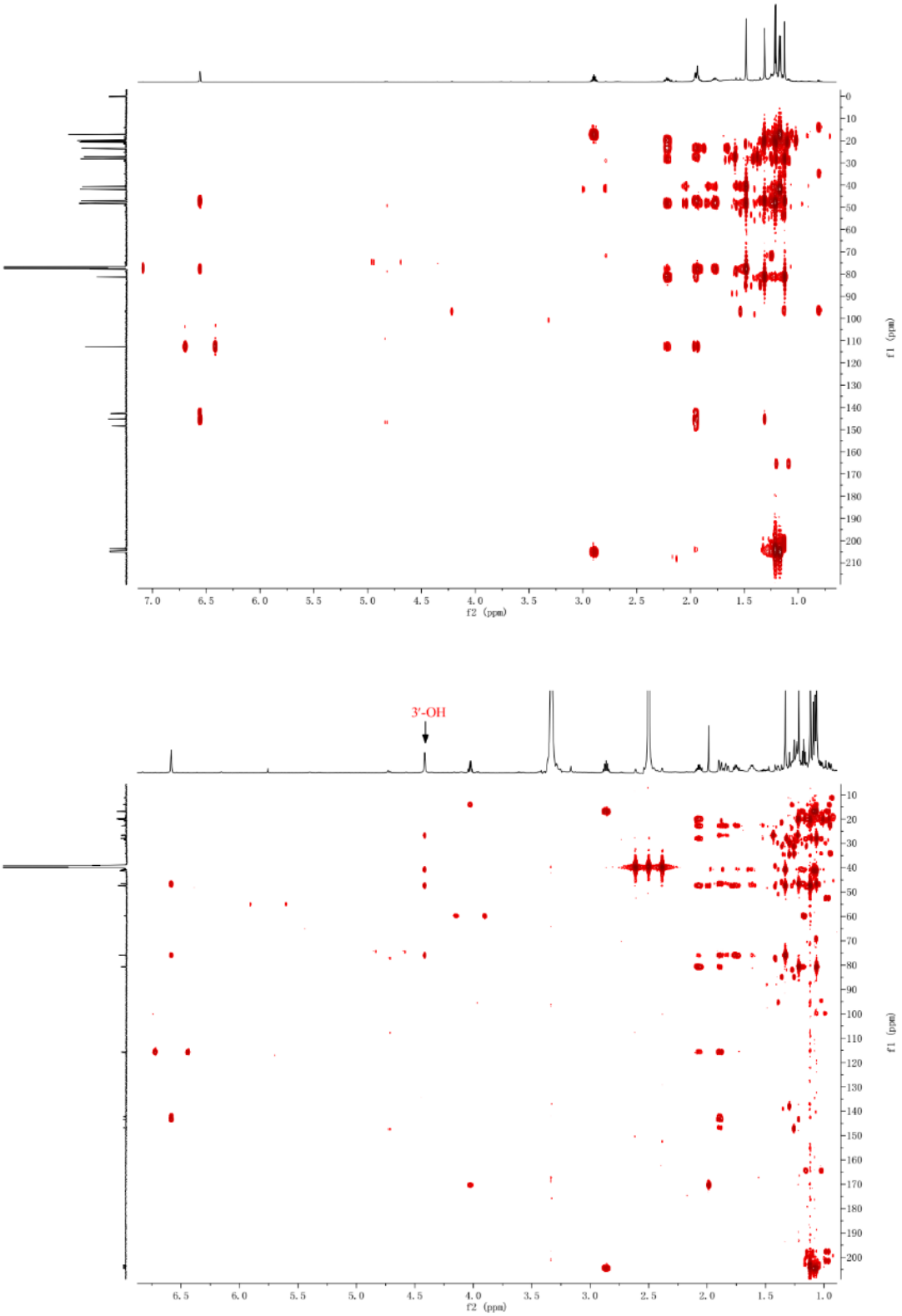


Figure S44 HMBC spectrum of 5 in $CDCl_3$ (the above figure) and DMSO-d_6 (the following figure).

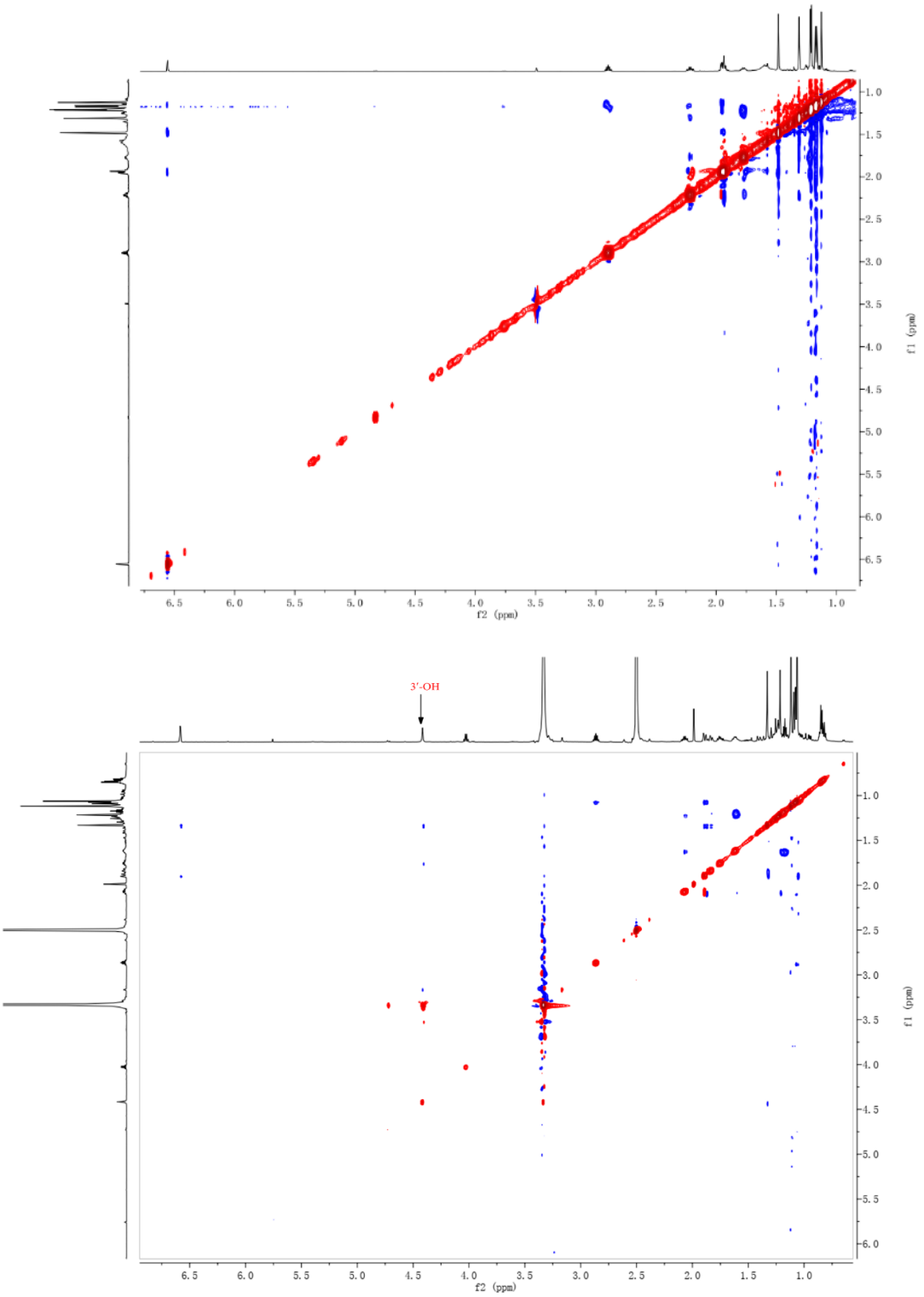


Figure S45 ROESY spectrum of 5 in $CDCl_3$ (the above figure) and DMSO-d_6 (the following figure).

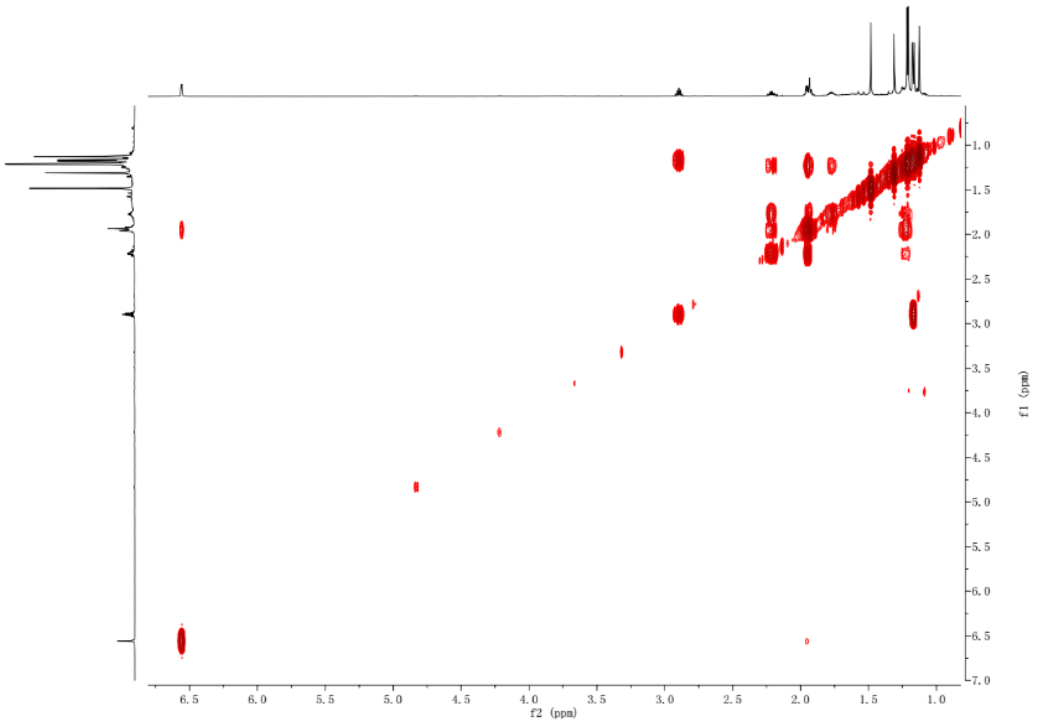
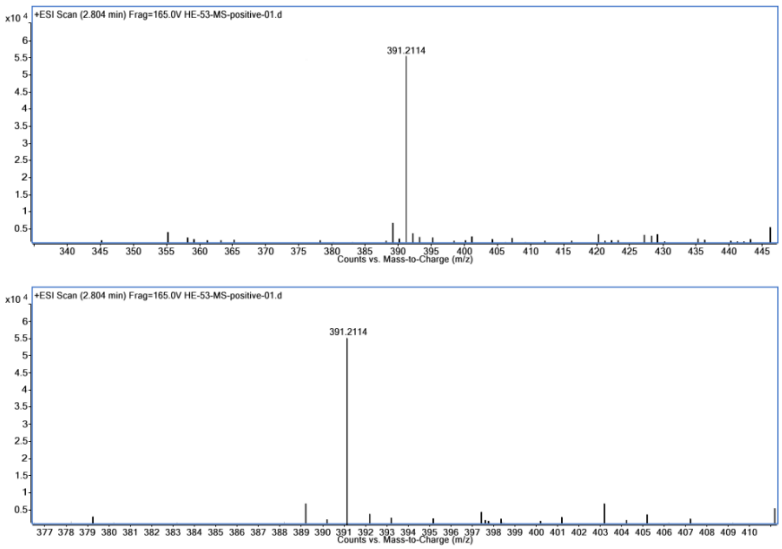


Figure S46 ^{1}H-^{1}H COSY spectrum of 5 in $CDCl_3$.



Elemental Composition Calculator

Target m/z:	391.2114	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C22H31O6		391.2115		0.17	

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Figure S47 HRESIMS spectrum of 5.

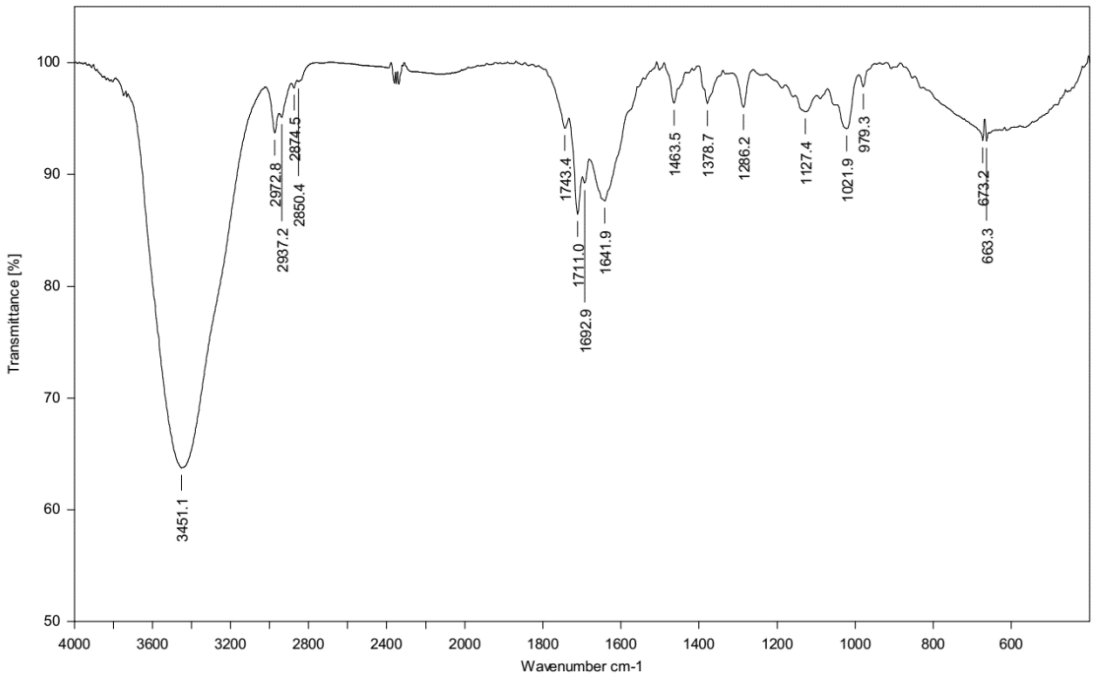


Figure S48 IR spectrum of 5.

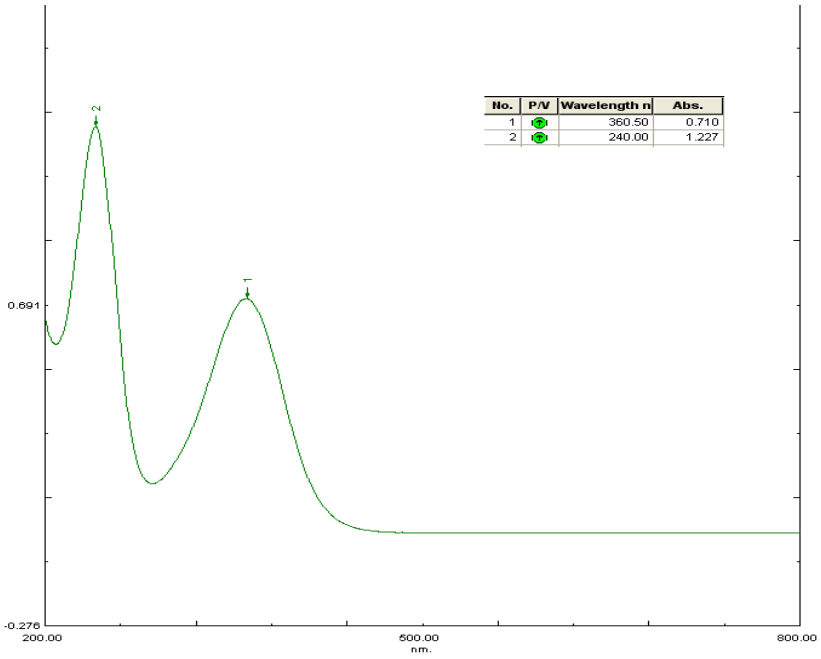


Figure S49 UV spectrum of 5.

NMR, HRESIMS, UV, and IR spectrum of 6 (Figure S50-S57)

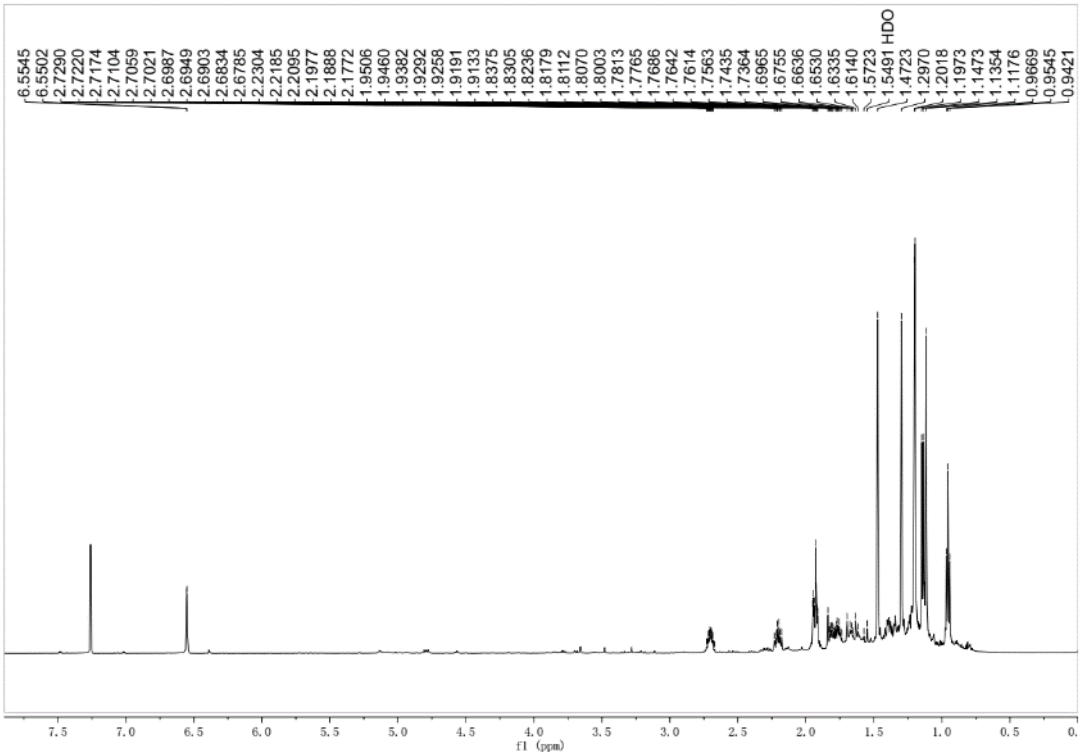


Figure S50 ^{1}H NMR (600 MHz) spectrum of 6 in $CDCl_3$.

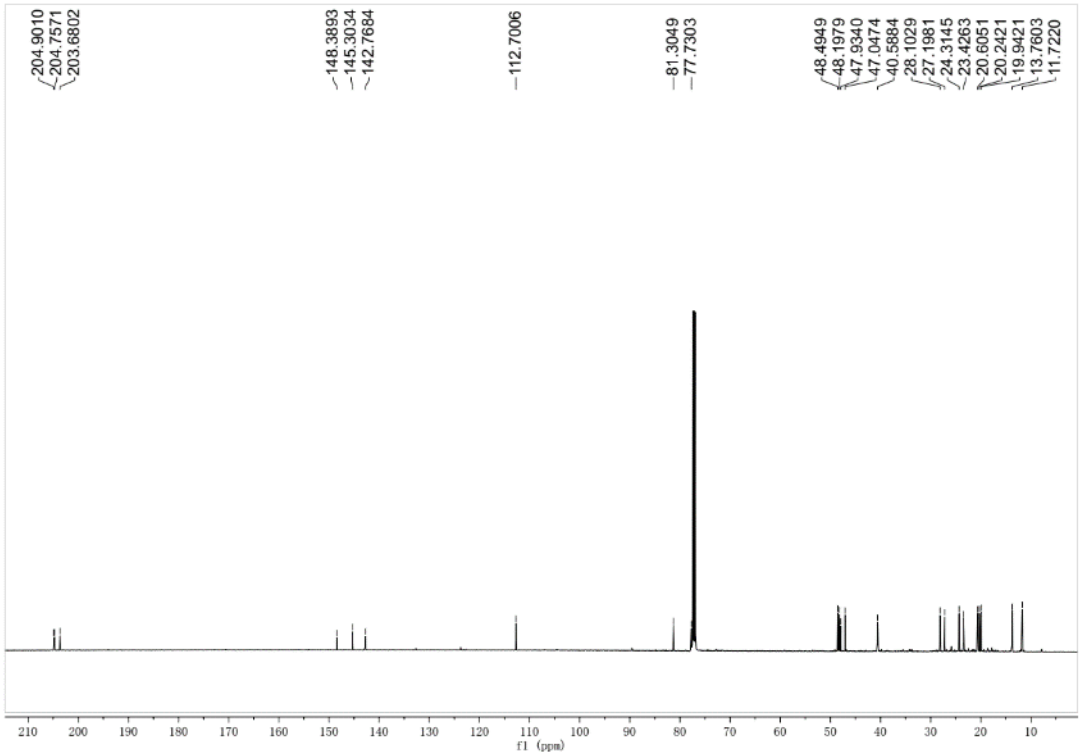


Figure S51 ^{13}C NMR (150 MHz) spectrum of 6 in $CDCl_3$.

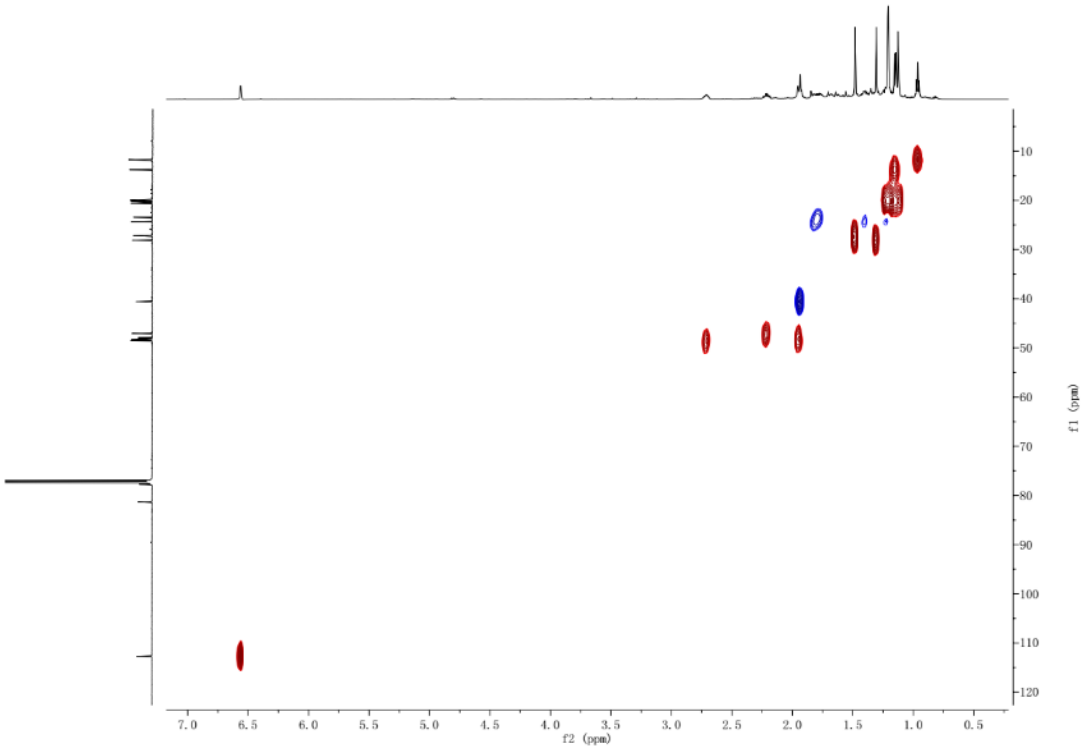


Figure S52 HSQC spectrum of 6 in $CDCl_3$.

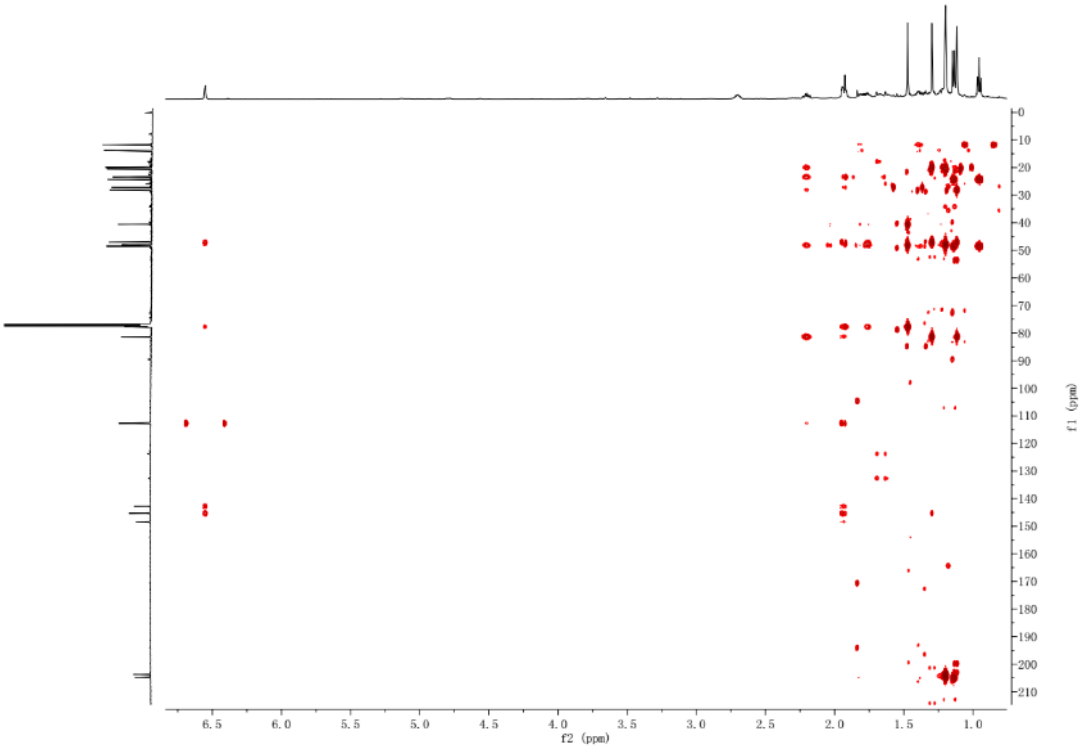


Figure S53 HMBC spectrum of 6 in $CDCl_3$.

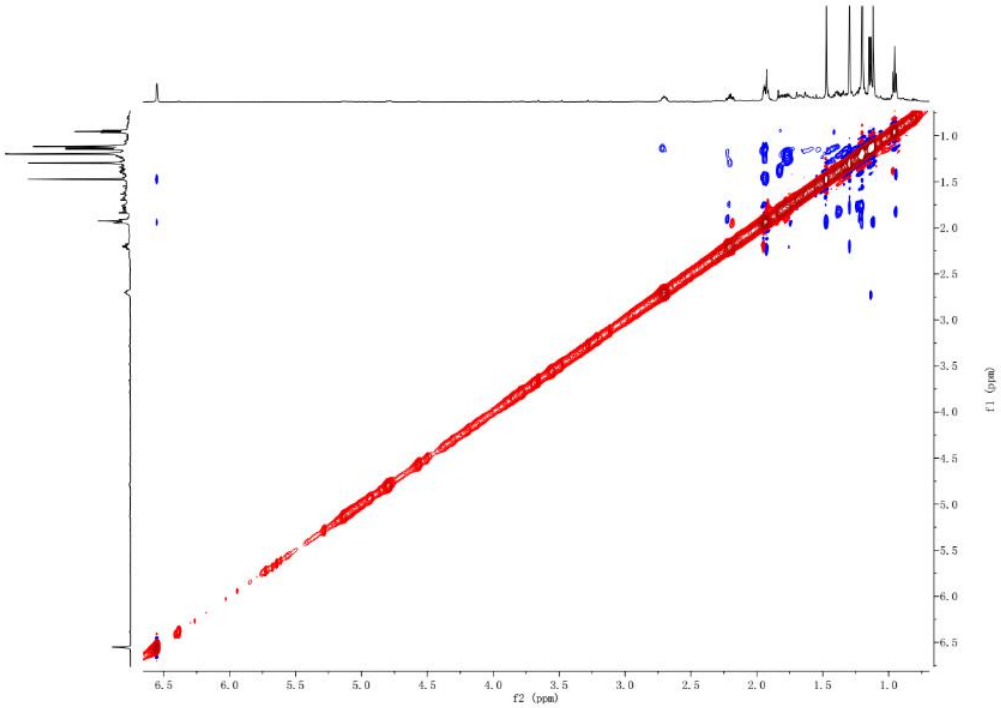
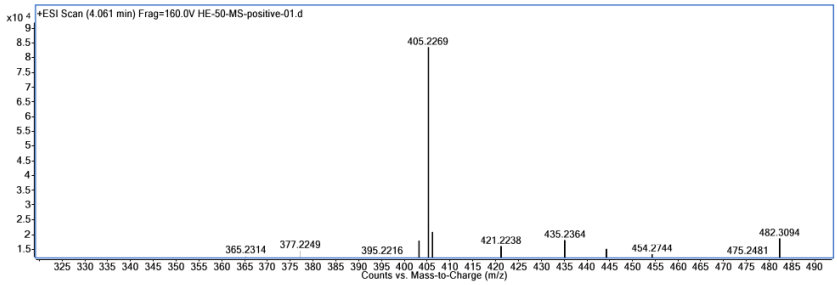
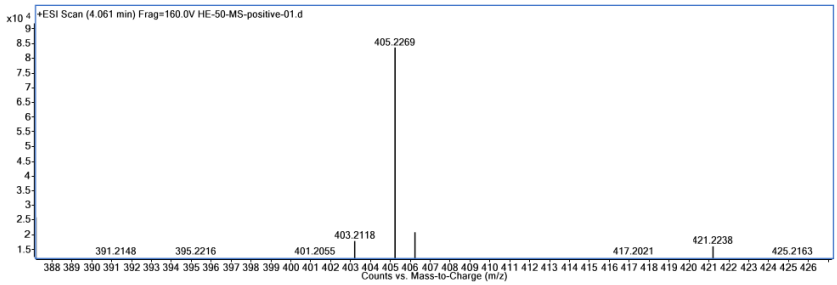


Figure S54 ROESY spectrum of 6 in $CDCl_3$.





Elemental Composition Calculator

Target m/z:	405.2269	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C23H33O6		405.2272		0.66	

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Figure S55 HRESIMS spectrum of 6.

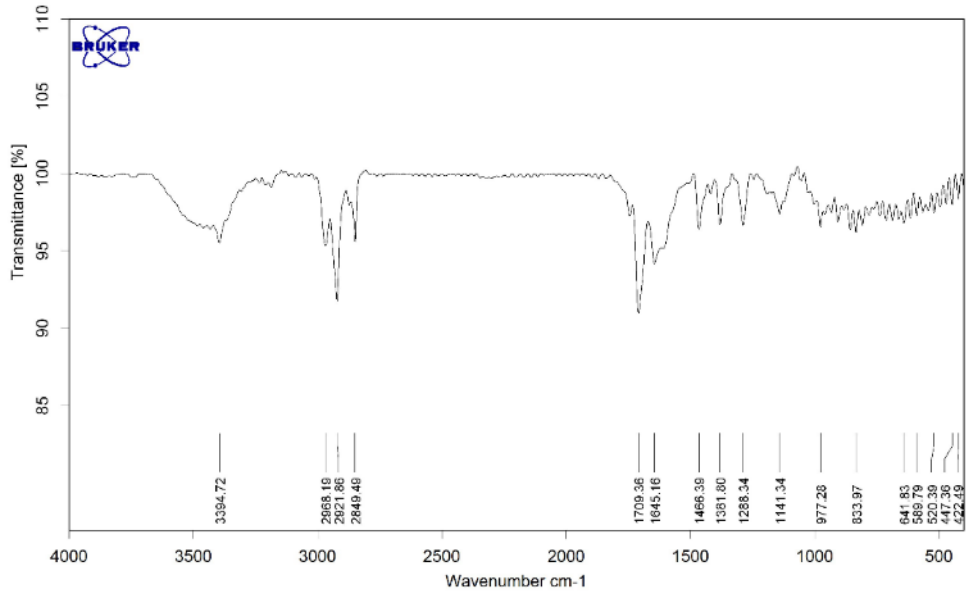


Figure S56 IR spectrum of 6.

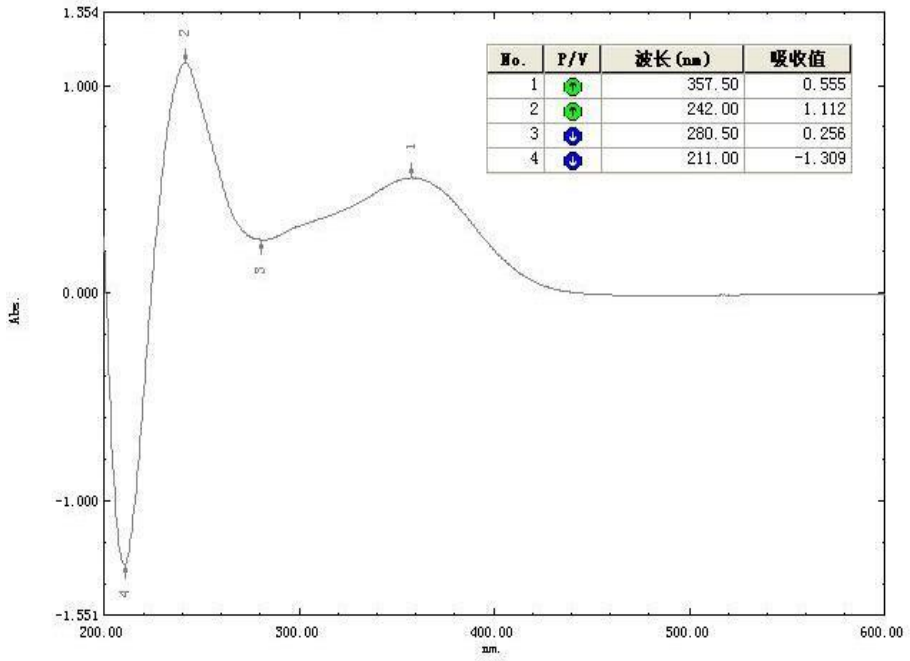


Figure S57 UV spectrum of 6.

NMR, HRESIMS, UV, and IR spectrum of 7 (Figure S58-S66)

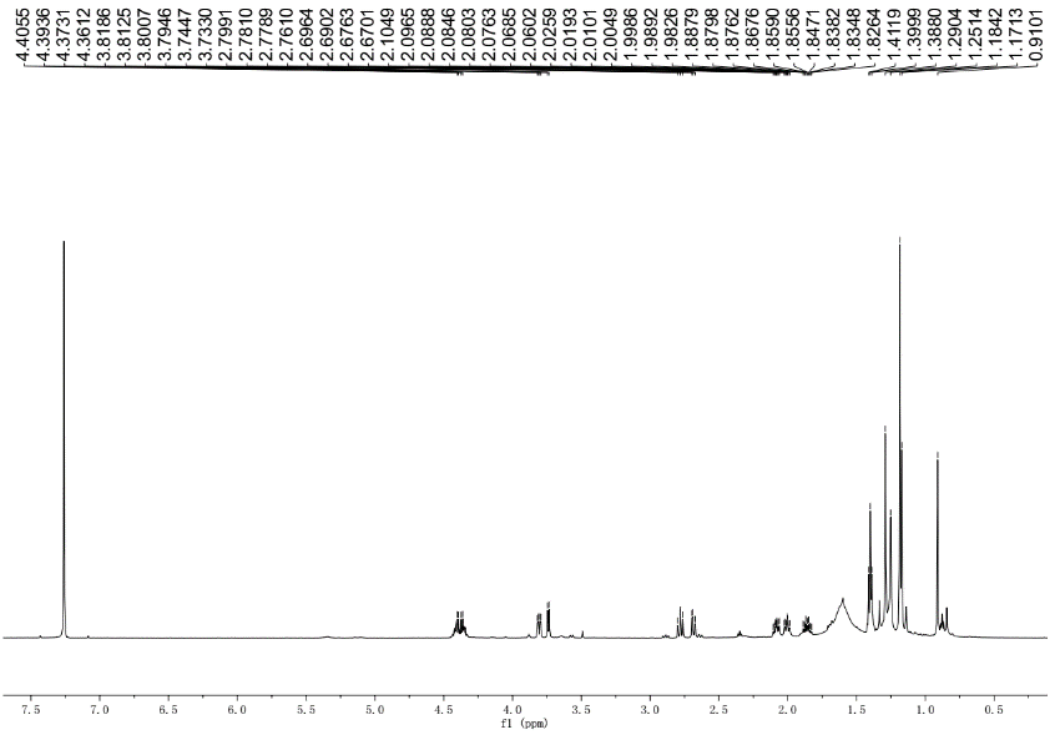


Figure S58 ^{1}H NMR (600 MHz) spectrum of 7 in $CDCl_3$.

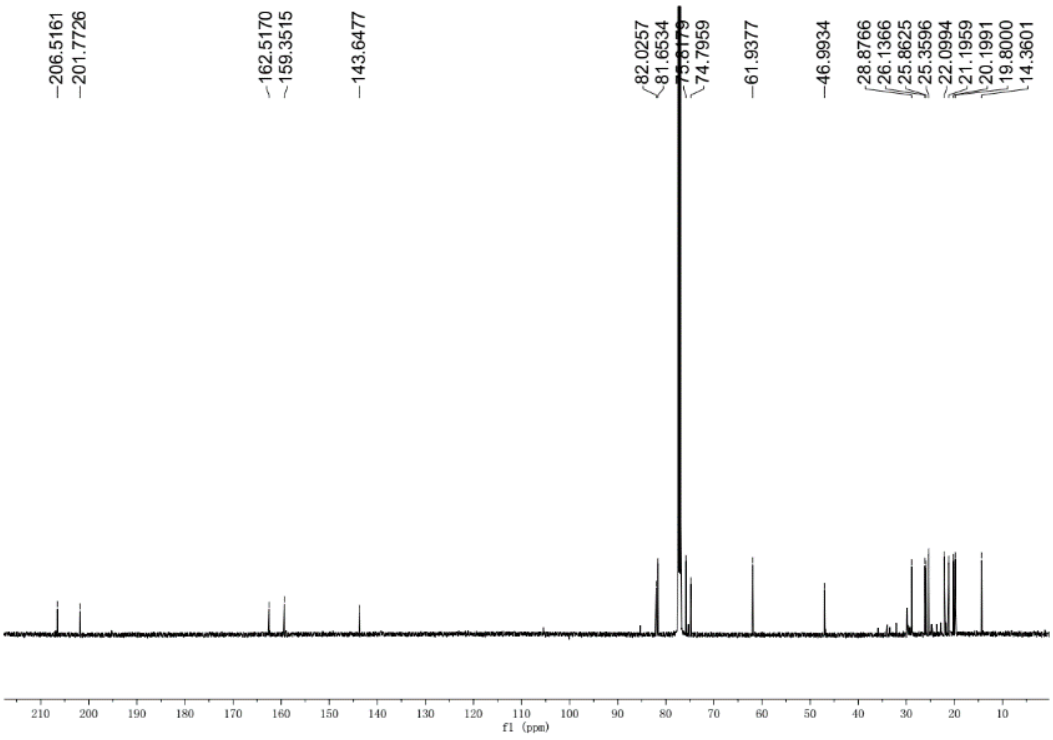


Figure S59 ^{13}C NMR (150 MHz) spectrum of 7 in $CDCl_3$.

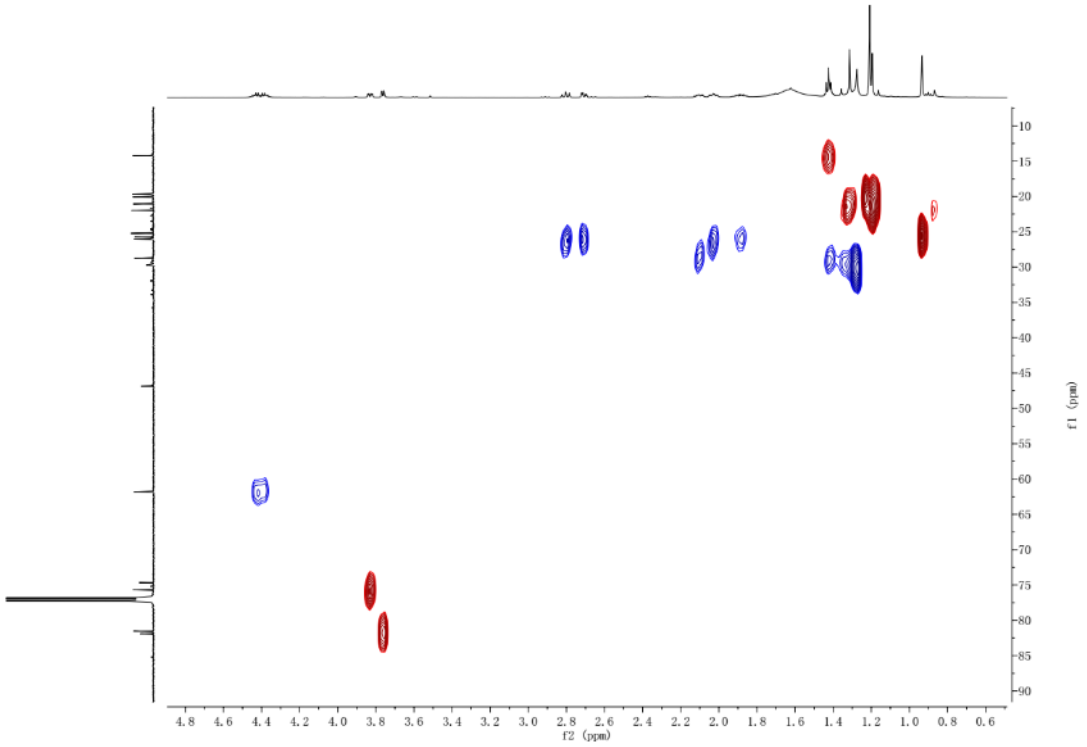


Figure S60 HSQC spectrum of 7 in $CDCl_3$.

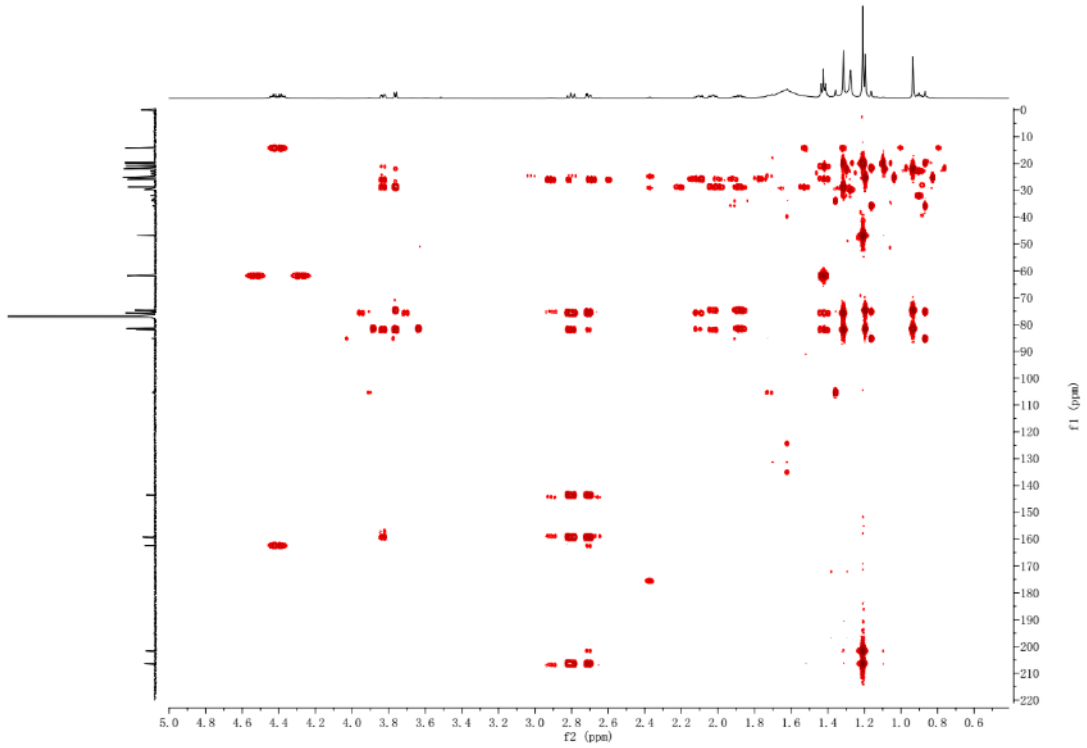


Figure S61 HMBC spectrum of 7 in $CDCl_3$.

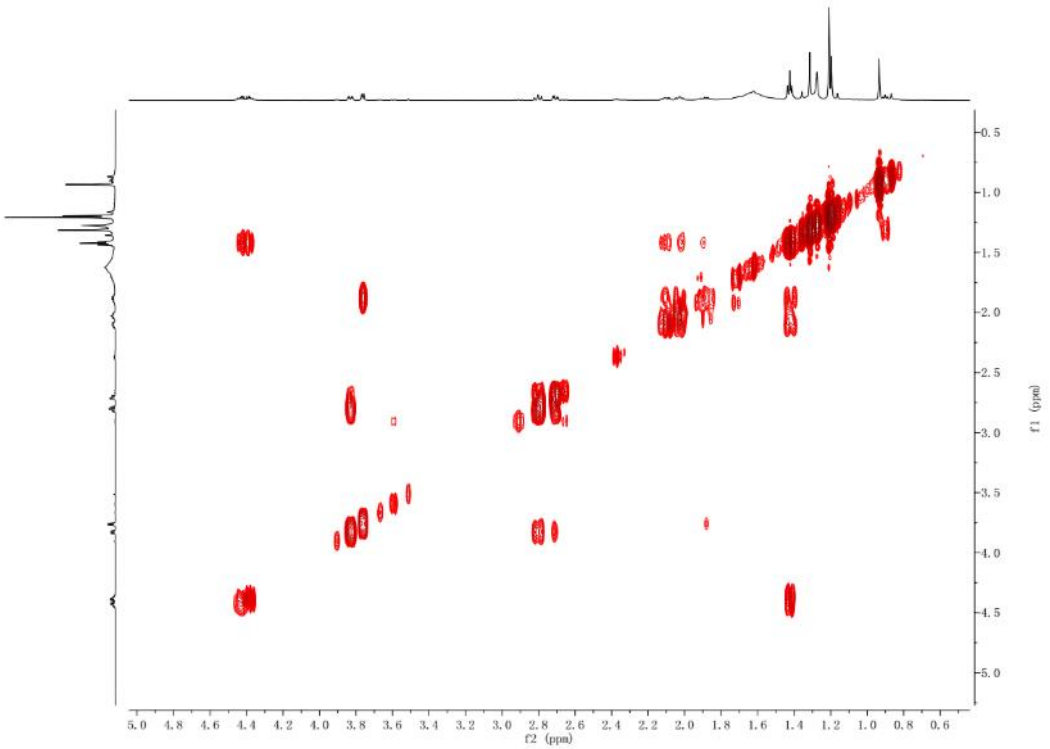


Figure S62 ^{1}H-^{1}H COSY spectrum of 7 in $CDCl_3$.

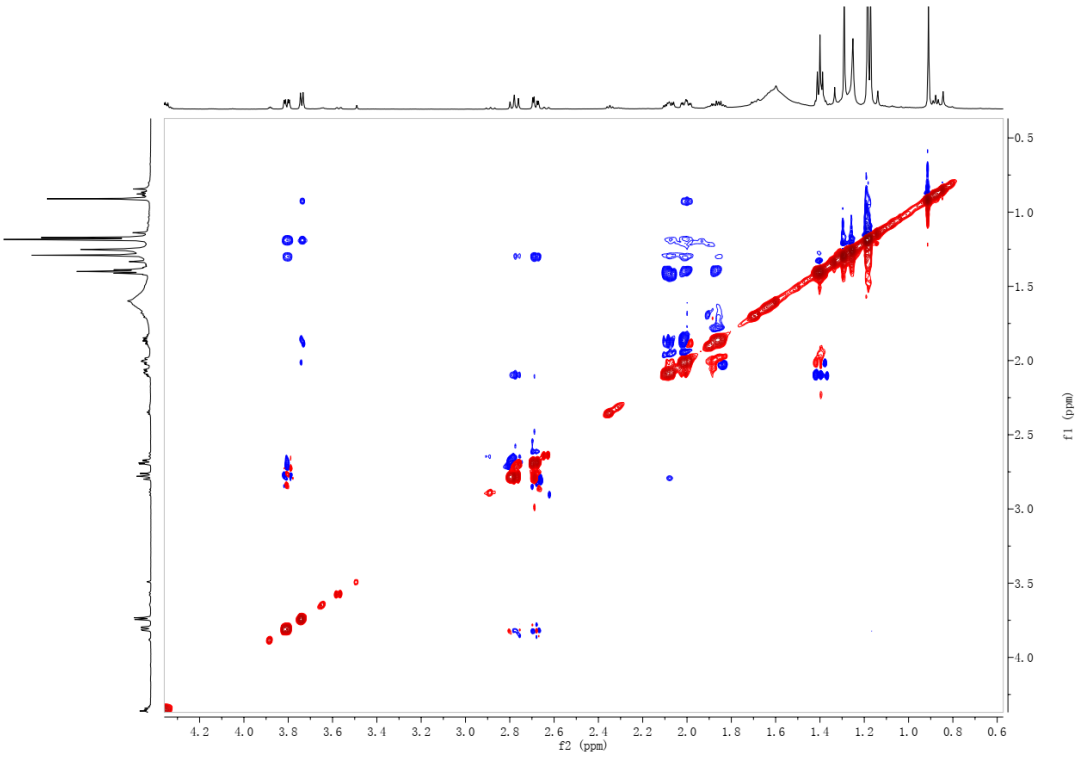
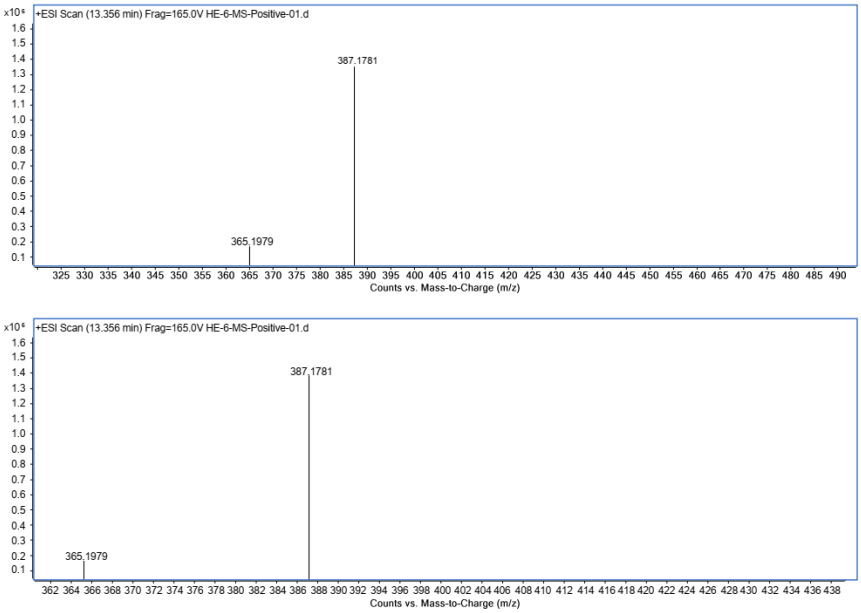


Figure S63 ROESY spectrum of 7 in $CDCl_3$.



Elemental Composition Calculator

Target m/z:	387.1781	**Result type:**	Positive ions	**Species:**	$[M+Na]^+$
Elements:		C (0-80); H (0-120); O (0-30)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C20H28O6Na		387.1778		-0.73	

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Figure S64 HRESIMS spectrum of 7.

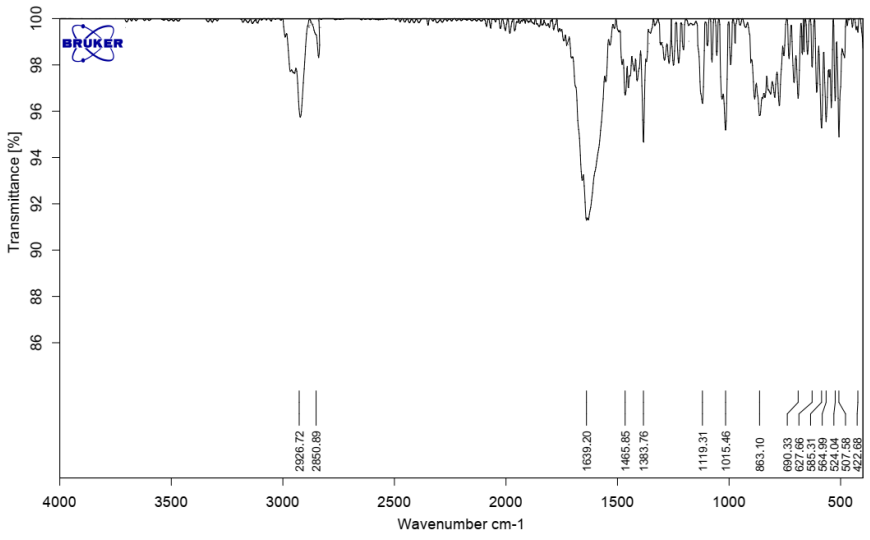


Figure S65 IR spectrum of 7.

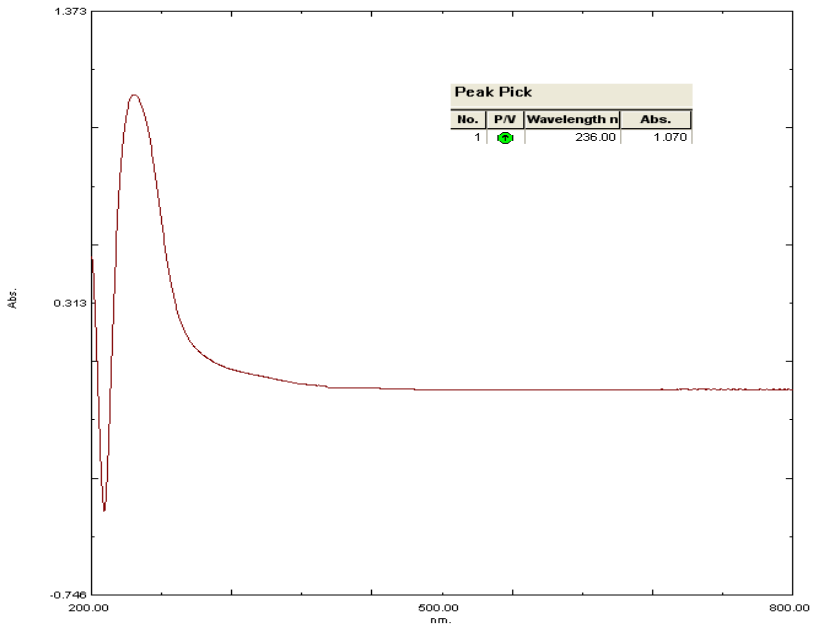


Figure S66 UV spectrum of 7.

NMR, HRESIMS, UV, and IR spectrum of 8 (Figure S67-S75)

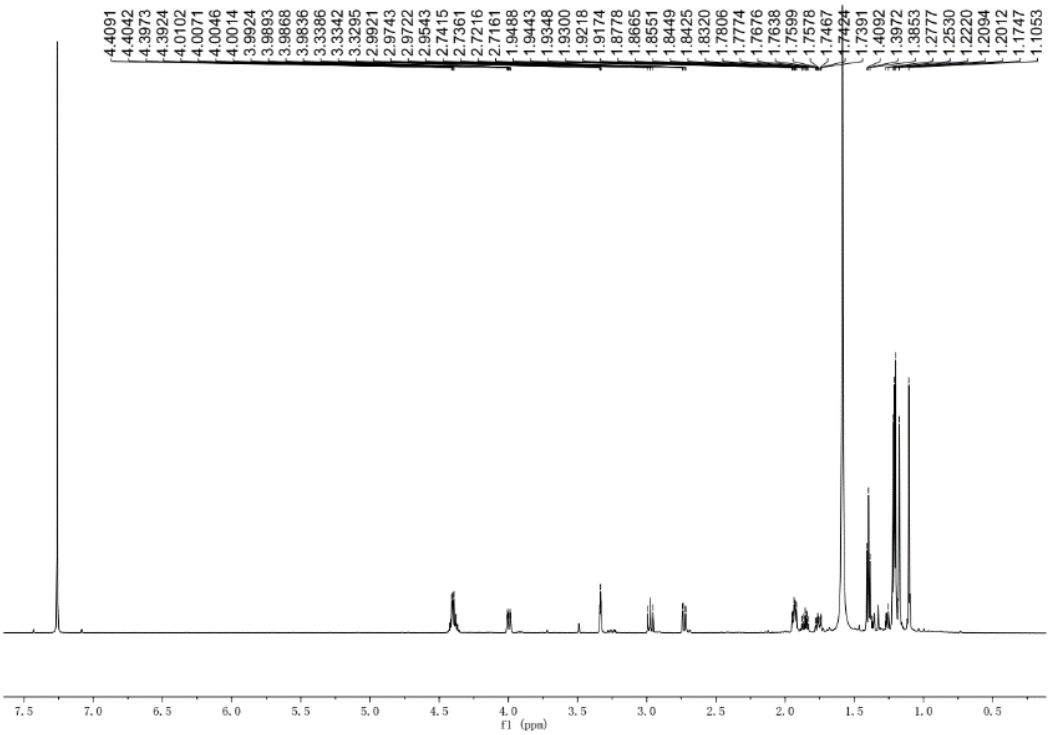


Figure S67 ^{1}H NMR (600 MHz) spectrum of 8 in $CDCl_3$.

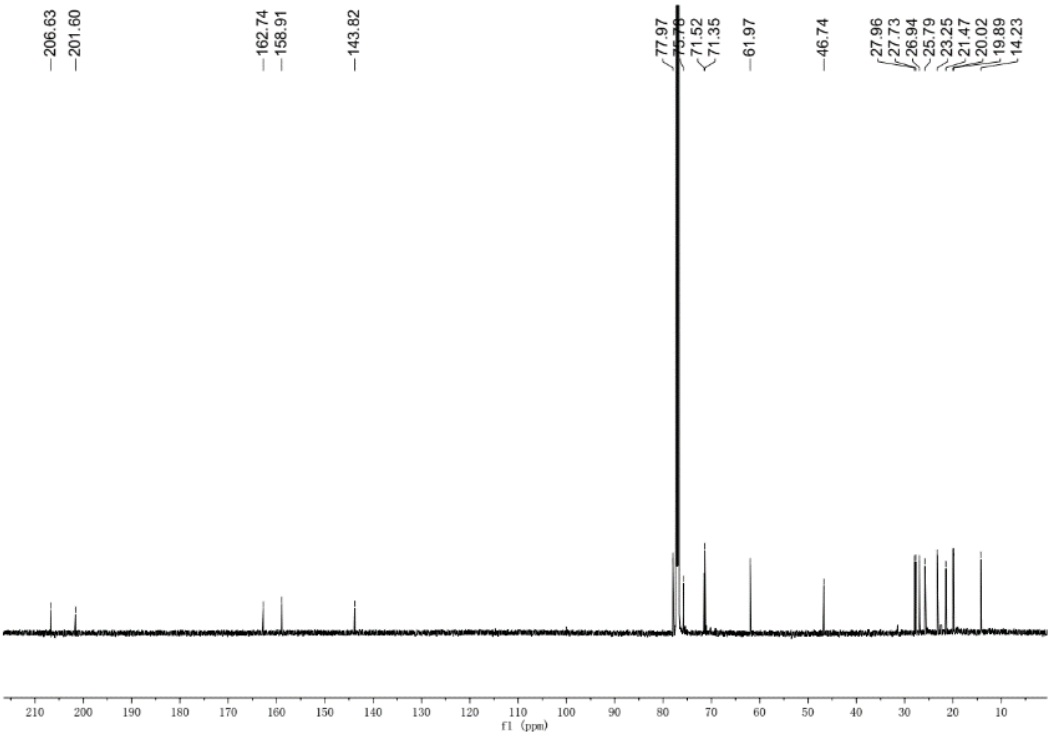


Figure S68 ^{13}C NMR (150 MHz) spectrum of 8 in $CDCl_3$.

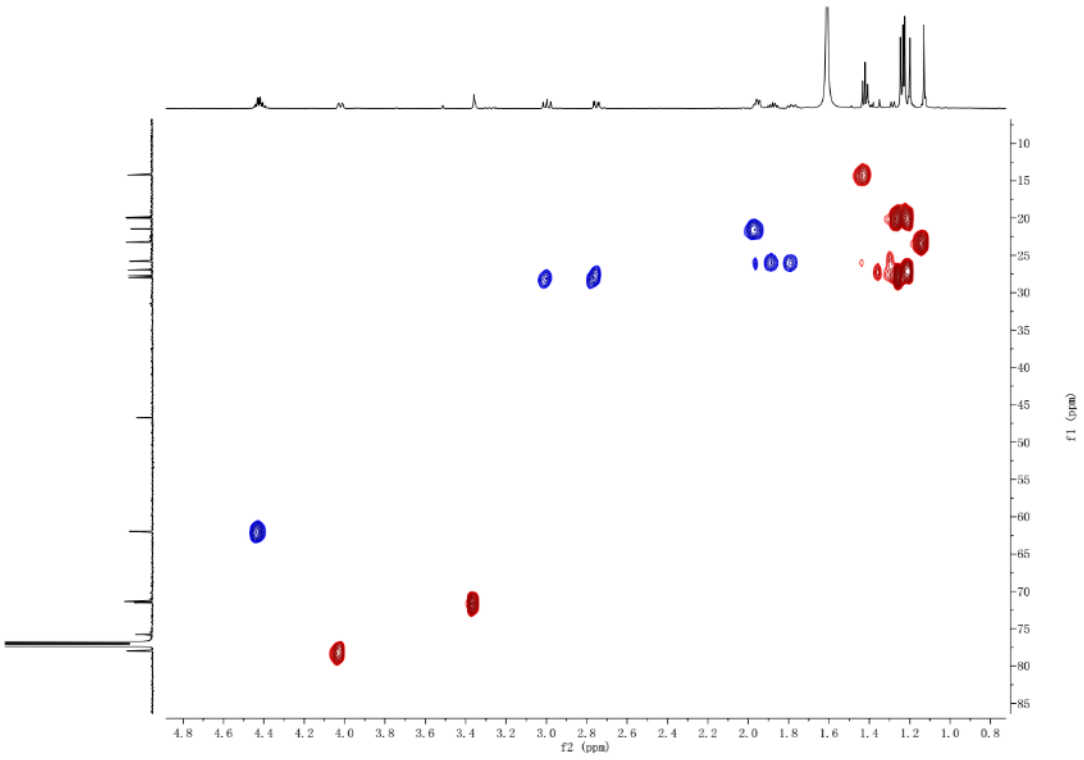


Figure S69 HSQC spectrum of 8 in $CDCl_3$.

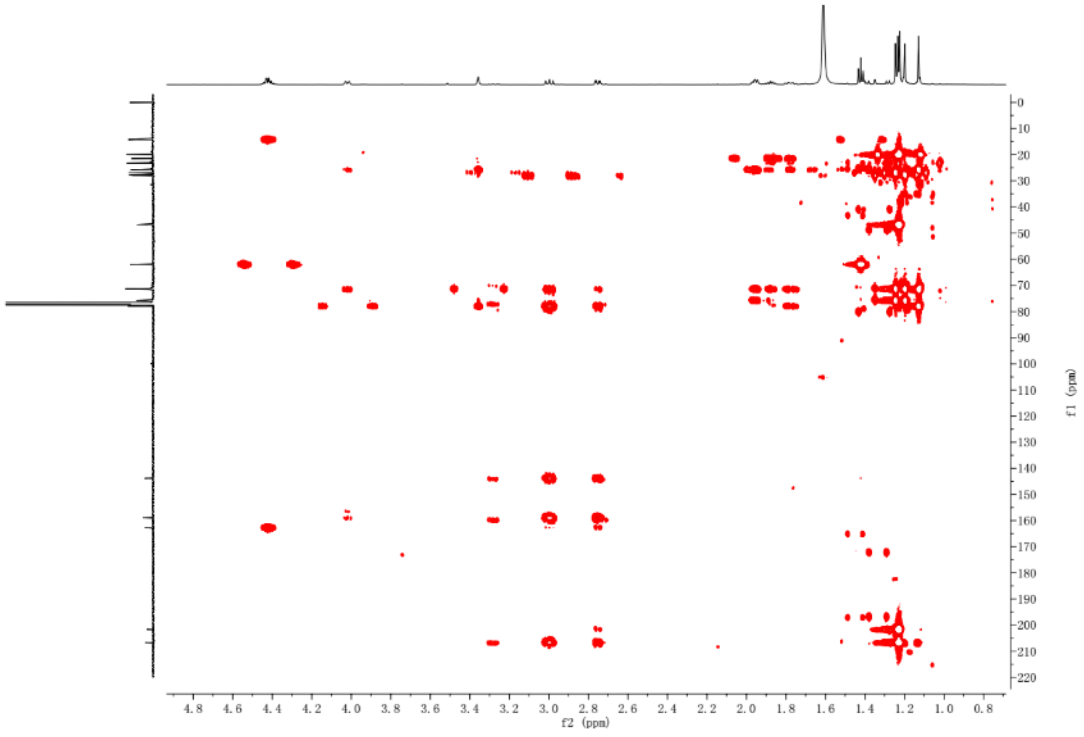


Figure S70 HMBC spectrum of 8 in $CDCl_3$.

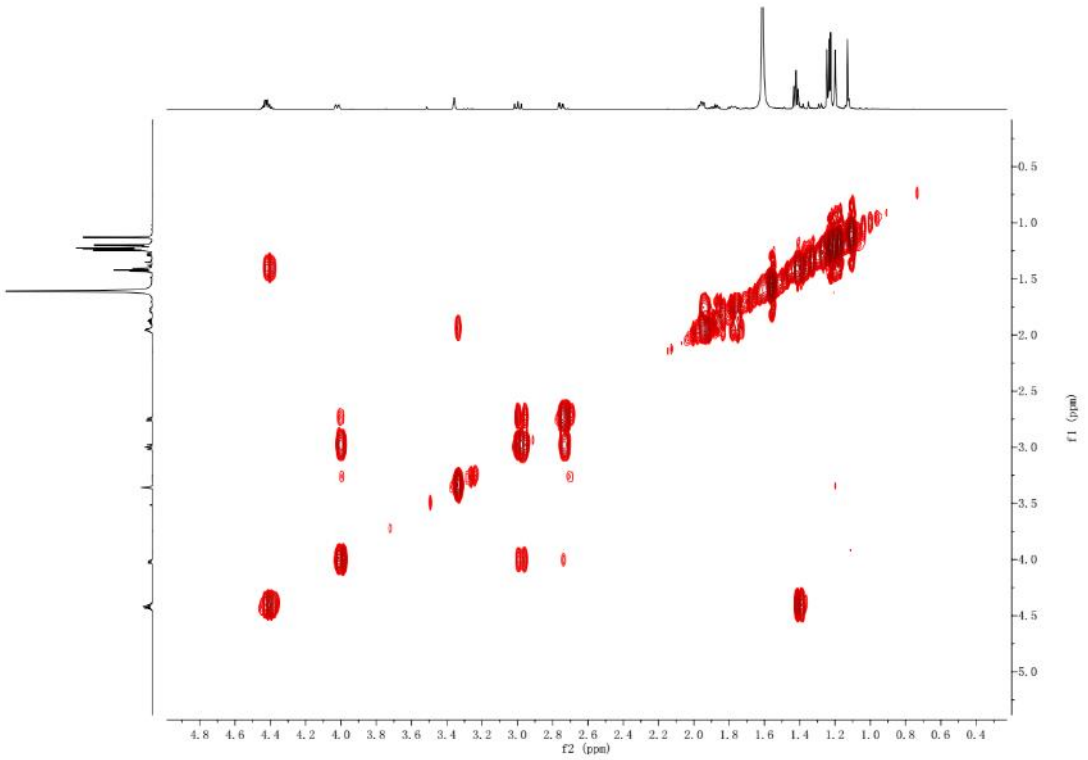


Figure S71 ^{1}H-^{1}H COSY spectrum of 8 in $CDCl_3$.

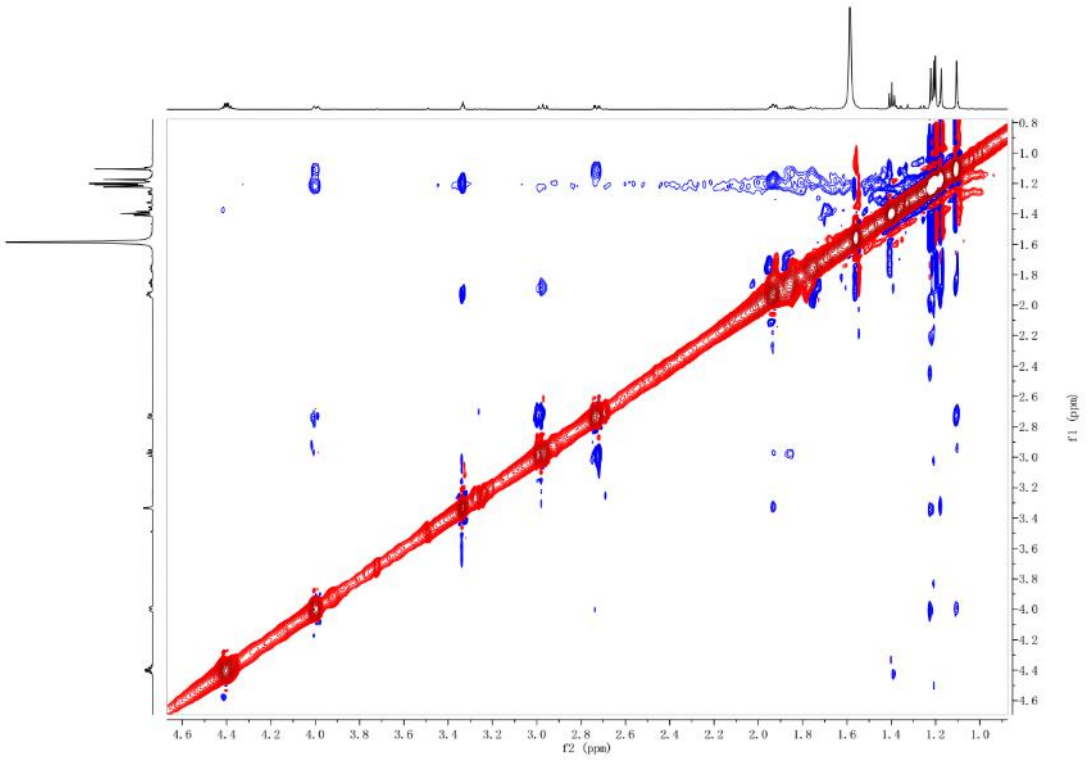
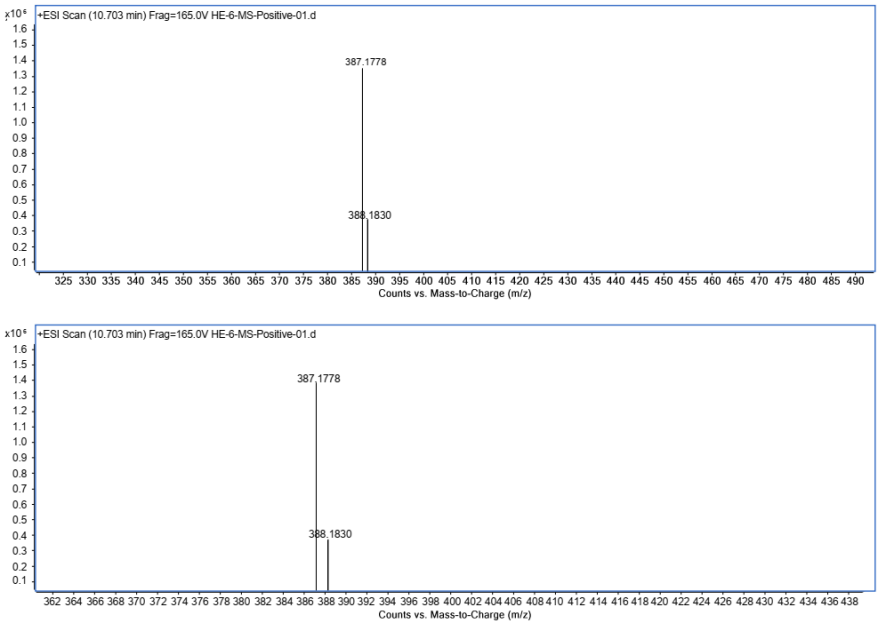


Figure S72 ROESY spectrum of 8 in $CDCl_3$.



Elemental Composition Calculator

Target m/z:	387.1778	**Result type:**	Positive ions	**Species:**	$[M+Na]^+$
Elements:		C (0-80); H (0-120); O (0-30)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C20H28O6Na		387.1778		-0.1	

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Figure S73 HRESIMS spectrum of 8.

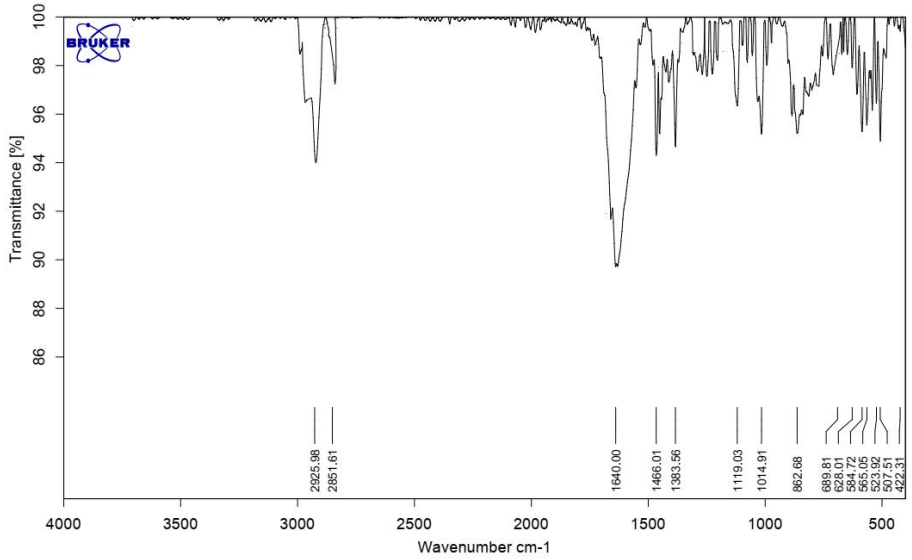


Figure S74 IR spectrum of 8.

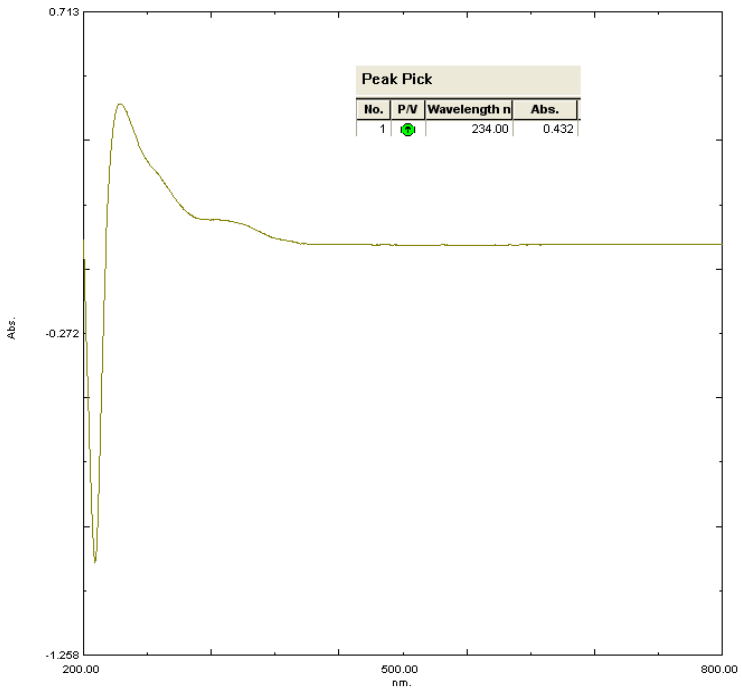


Figure S75 UV spectrum of 8.

NMR and HRESIMS spectrum of 9 (Figure S76-S78)

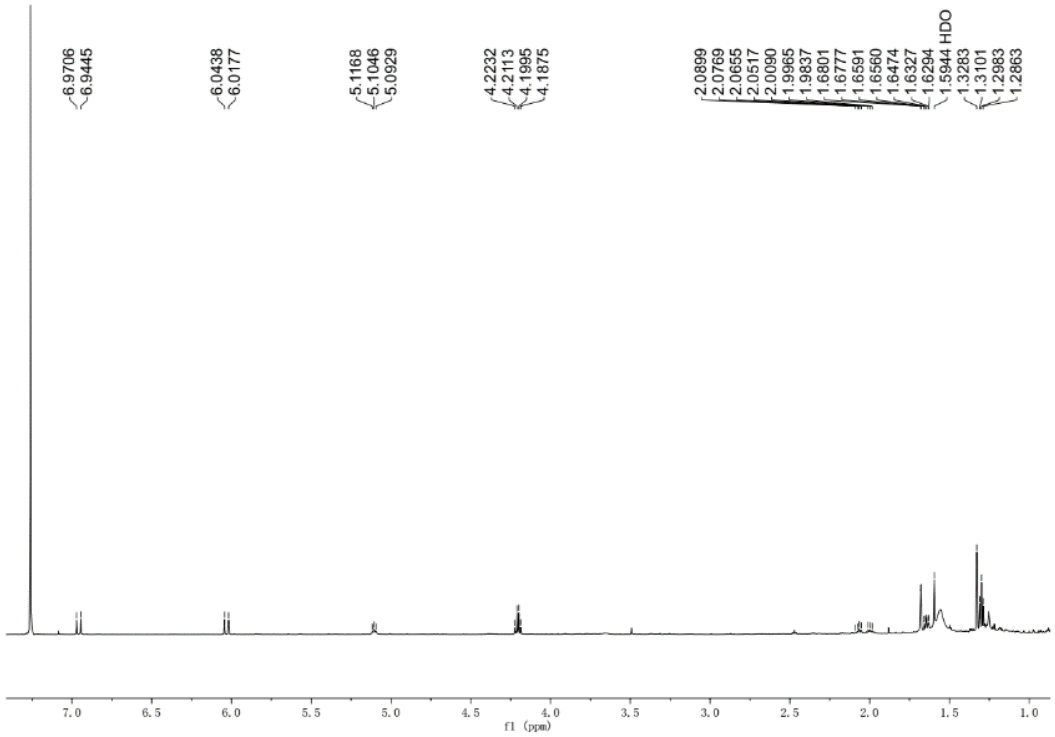


Figure S76 ^{1}H NMR (600 MHz) spectrum of 9 in $CDCl_3$.

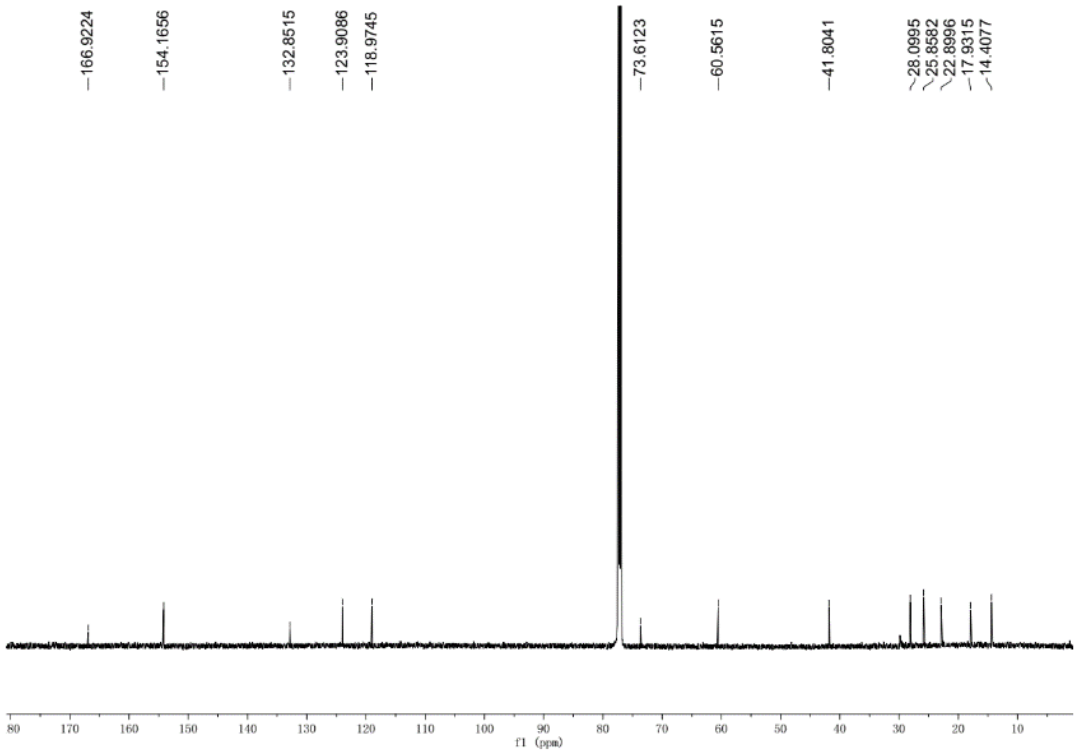
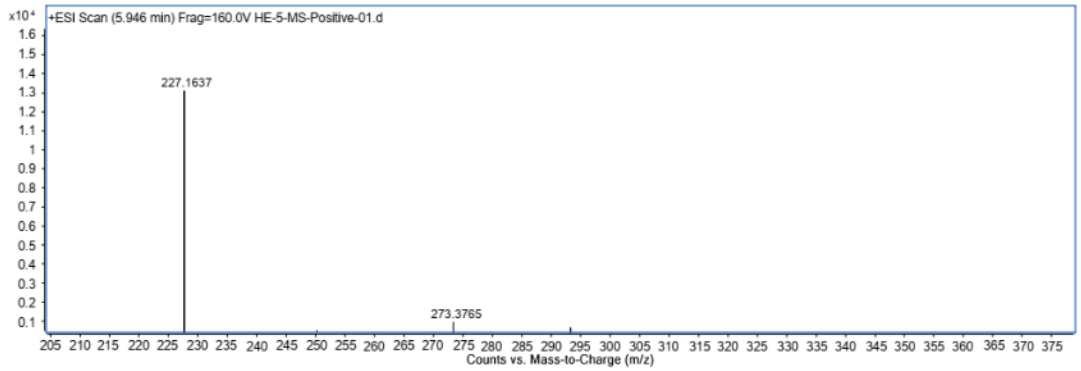
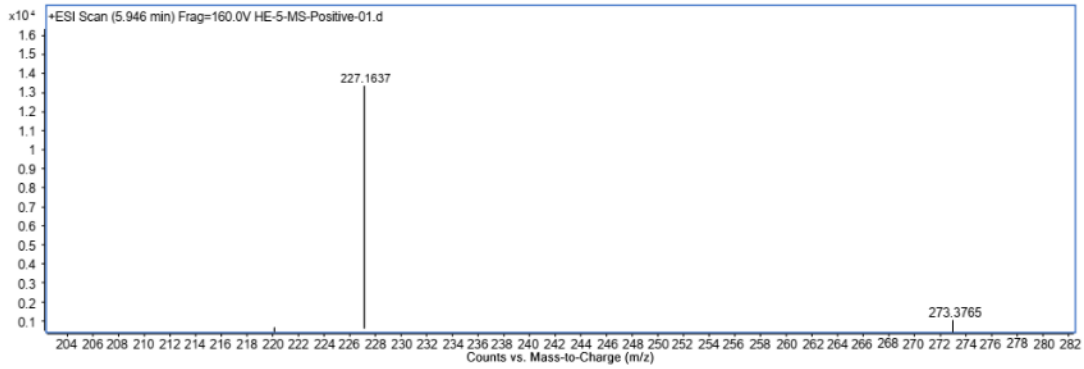


Figure S77 ^{13}C NMR (150 MHz) spectrum of 9 in $CDCl_3$.





Elemental Composition Calculator

Target m/z:	227.1637	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C13H23O3		227.1643		0.6	

Figure S78 HRESIMS spectrum of 9.

^{1}H NMR spectrum of MTPA Esters of (+)-1 (Figure S79-S80)

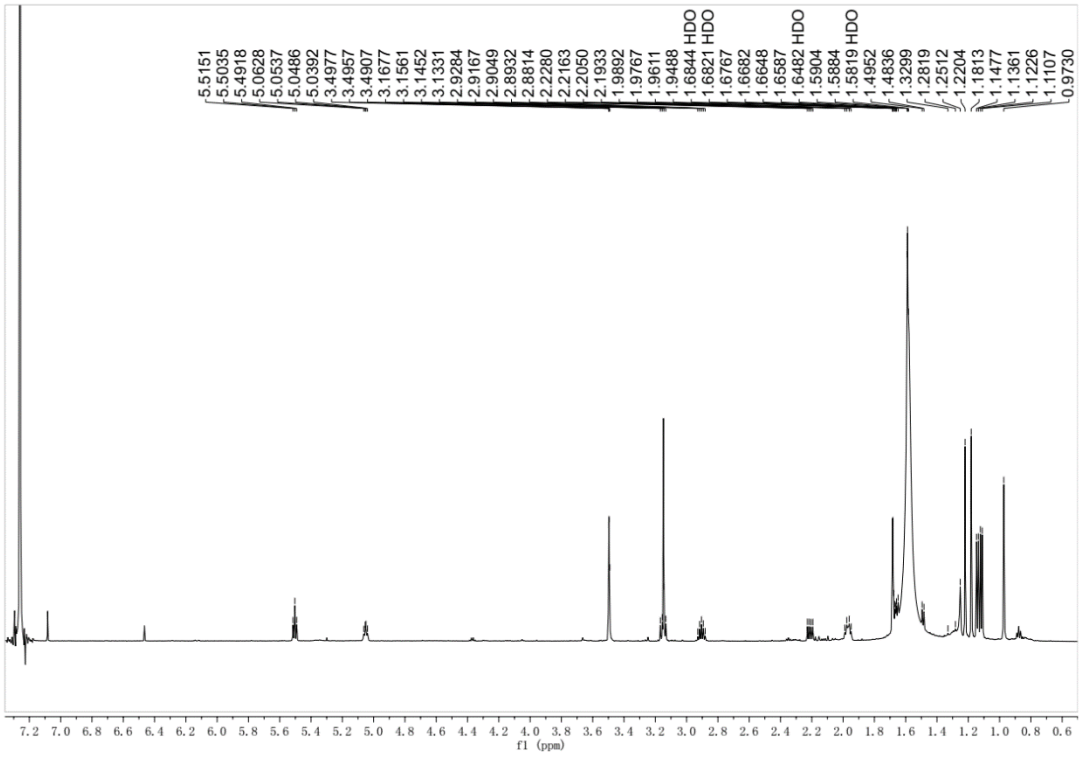


Figure S79 ^{1}H NMR (600 MHz) spectrum of *R*-MTPA Esters of (+)-1 in $CDCl_3$.

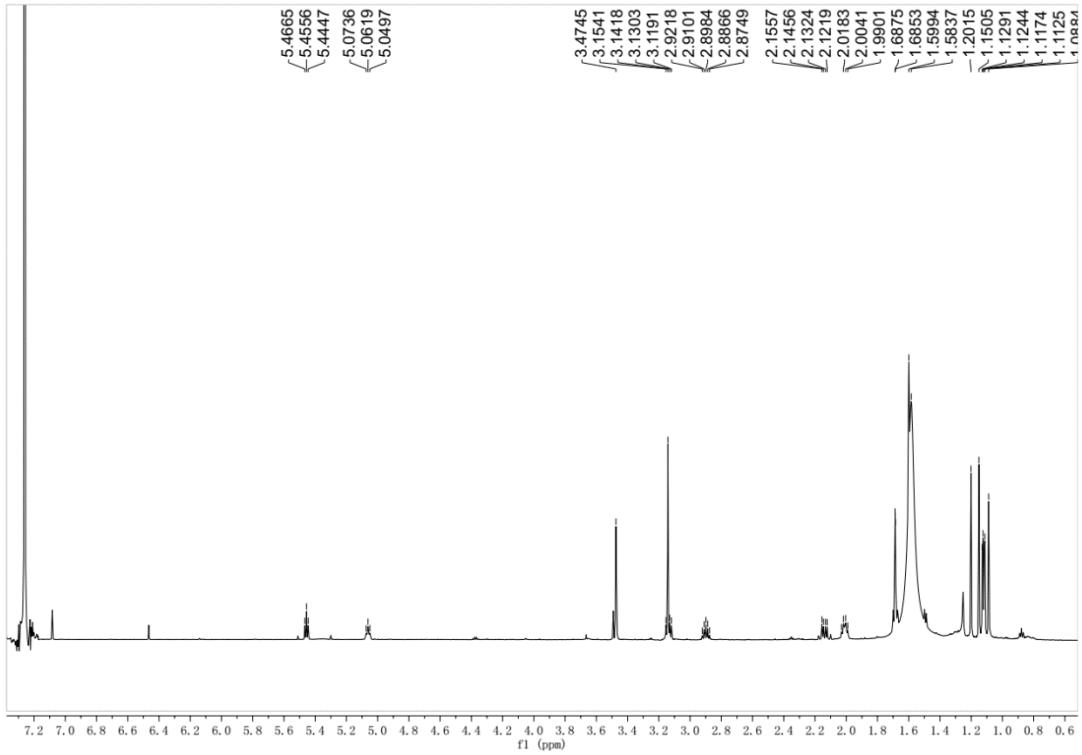


Figure S80 ^{1}H NMR (600 MHz) spectrum of *S*-MTPA Esters of (+)-1 in $CDCl_3$.