SUPPLEMENTARY MATERIAL

Eight new phenolic acids from the leaves of *Illicium dunnianum* and their osteoprotective activities

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[b] Kanion Pharmaceutical Co. Ltd., State Key Laboratory of New-tech for Chinese Medicine Pharmaceutical Process, Lianyungang 222001, China

[c] Shenzhen institute for drug control (shenzhen testing center of medical devices), Shenzhen 518057, China

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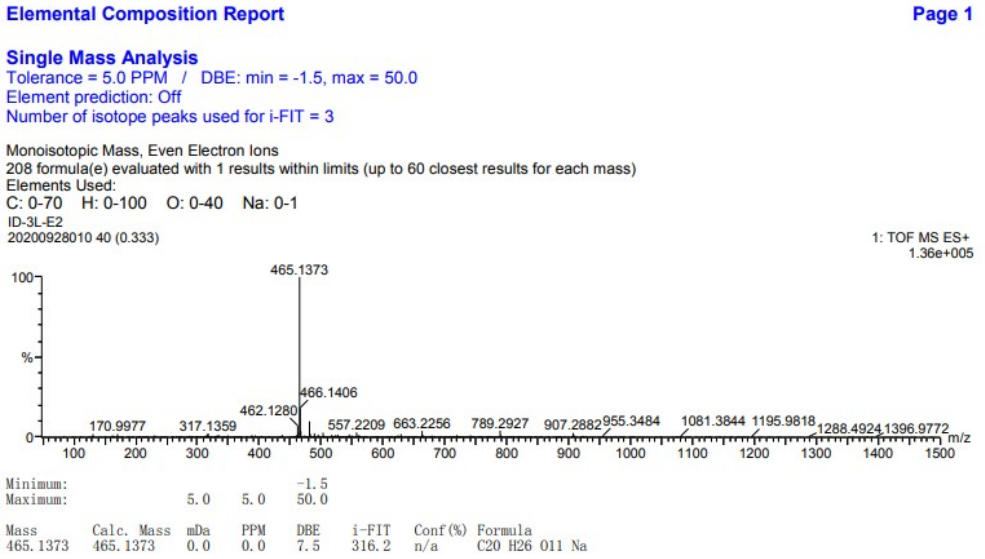
Dr. Zuo-cheng Qiu, College of Pharmacy, Jinan University, 601 Huangpu Avenue, Guangzhou 510632, PR China. Tel. +86-20-85225849. E-mail: zcqiu@jnu.edu.cn

Dr. Wei Xiao, Kanion Pharmaceutical Co. Ltd., Lianyungang 222001, PR China. Tel. +86-0518-81152371. E-mail: XWV8501@kanion.com

1. UV, IR, HRESIMS spectra and NMR spectra of compound 1



Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 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
208 formula(e) evaluated with 1 results within limits (up to 60 closest results for each mass)
Elements Used:
C: 0-70 H: 0-100 O: 0-40 Na: 0-1
ID-3L-E2
20200928010 40 (0.333)

1: TOF MS ES+
1.36e+005

Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Conf(%)	Formula
465.1373	465.1373	0.0	0.0	7.5	316.2	n/a	C20 H26 O11 Na

Fig. S1-1 HR-ESI-MS spectrum of compound 1

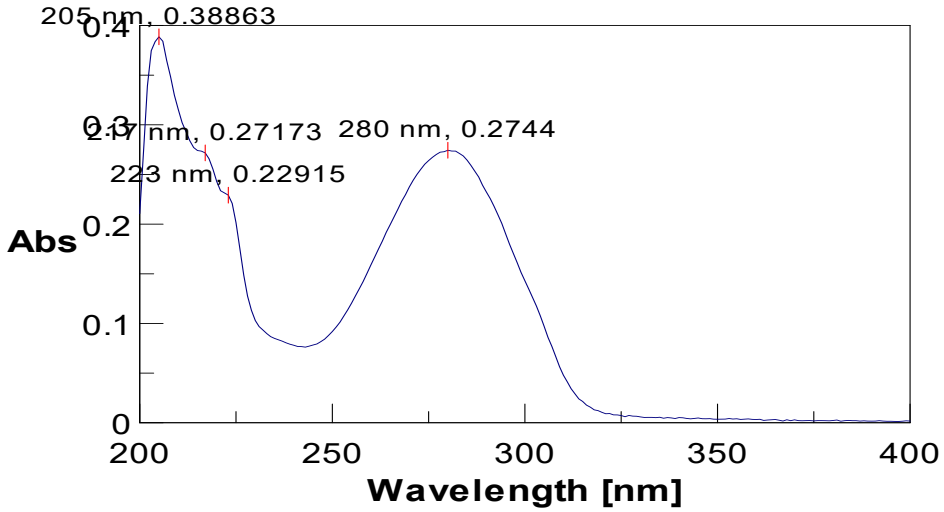


Fig. S1-2 UV spectrum of compound 1

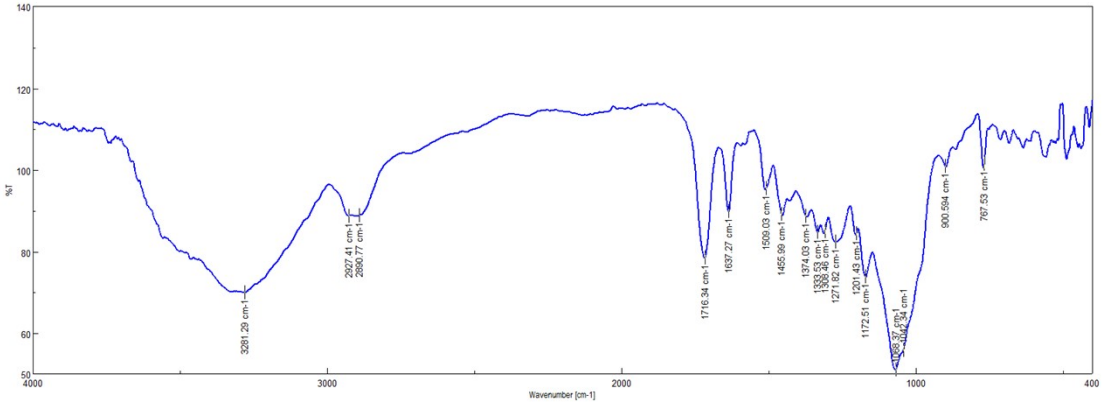


Fig. S1-3 IR spectrum of compound 1

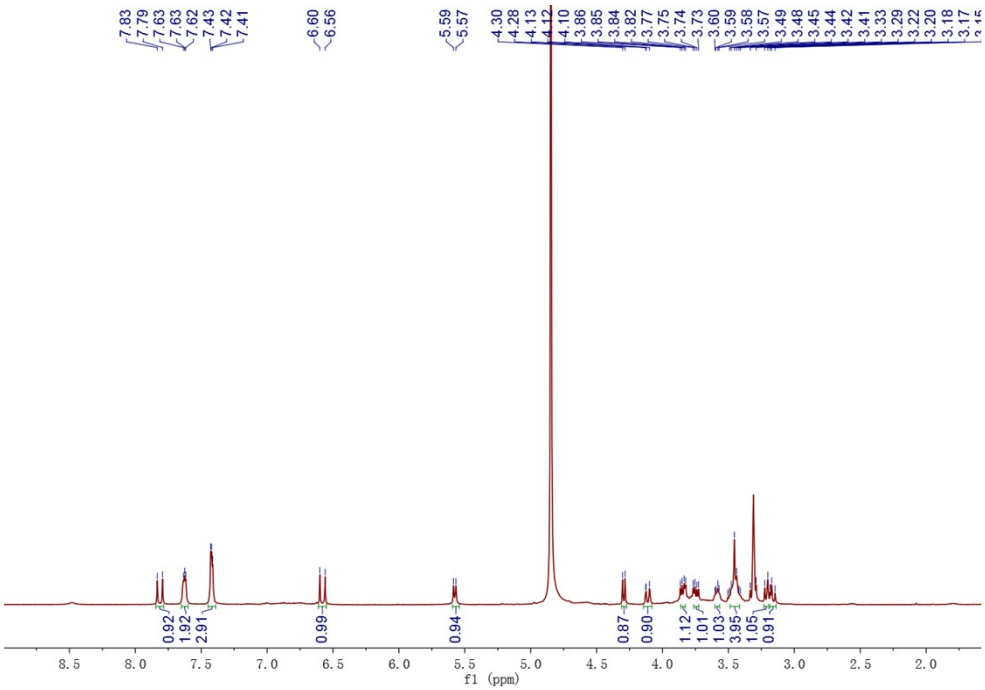


Fig. S1-4 ^{1}H NMR spectrum of compound 1

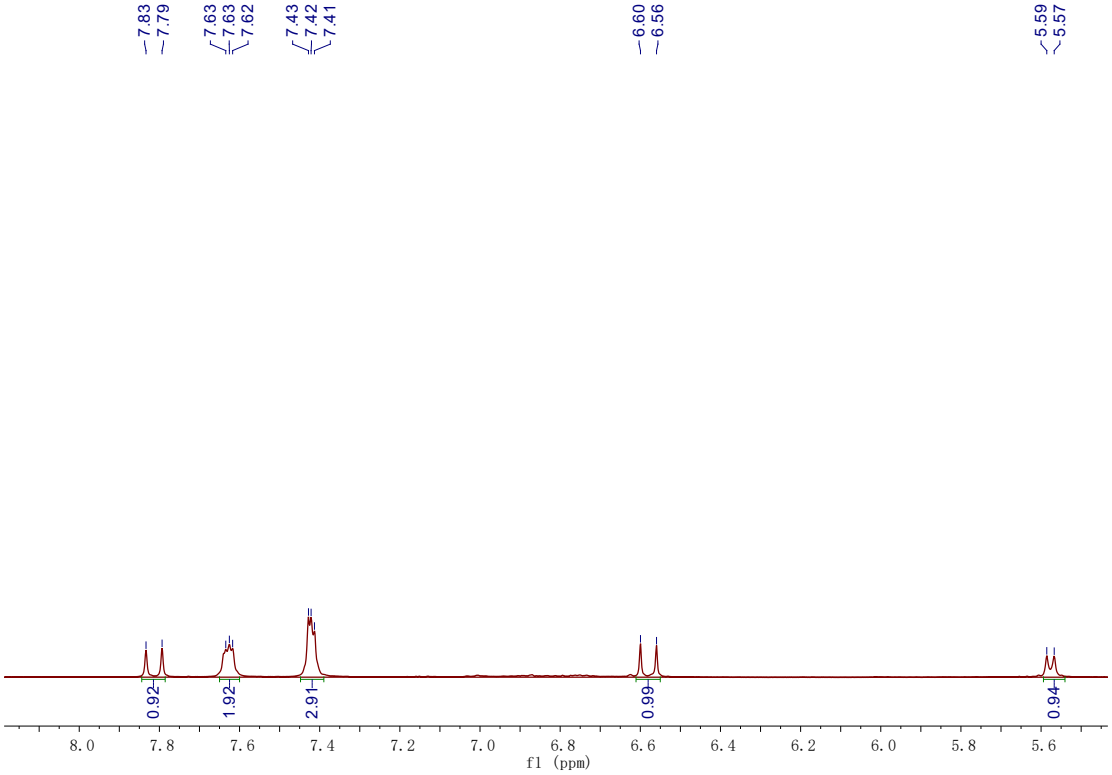


Fig. S1-5 The local enlarged ^{1}H NMR spectrum of compound 1

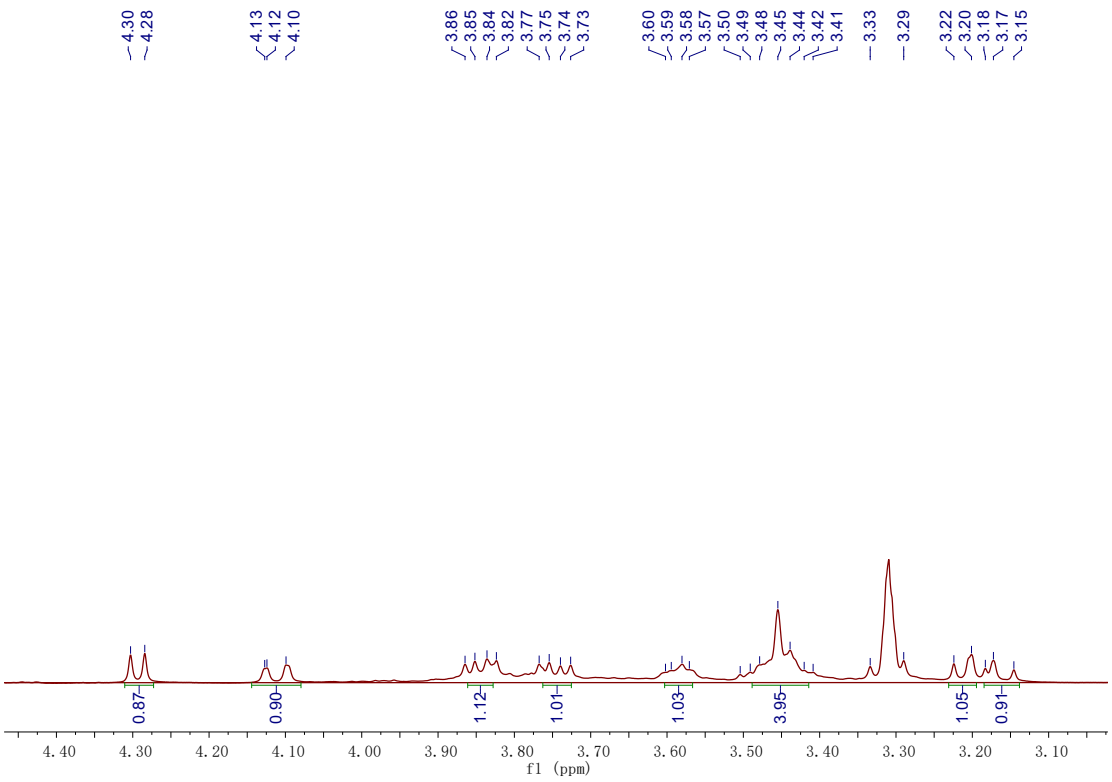


Fig. S1-6 The local enlarged ^{1}H NMR spectrum of compound 1

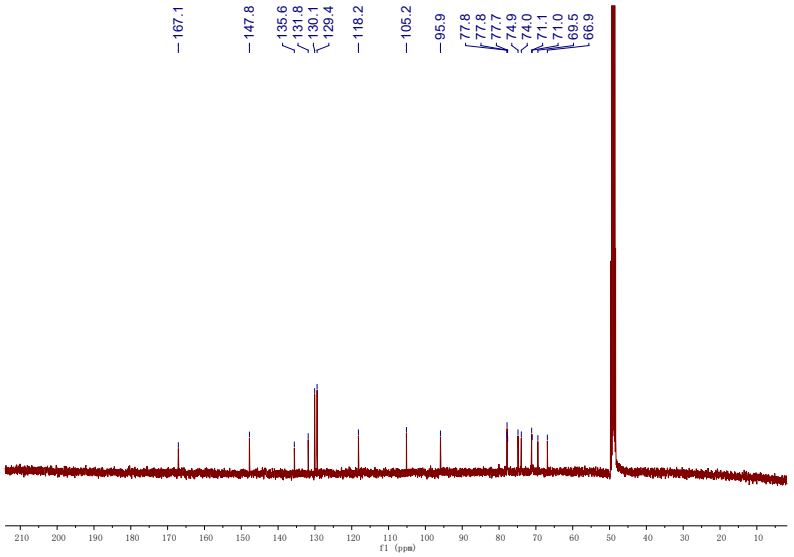


Fig. S1-7 ^{13}C NMR spectrum of compound 1

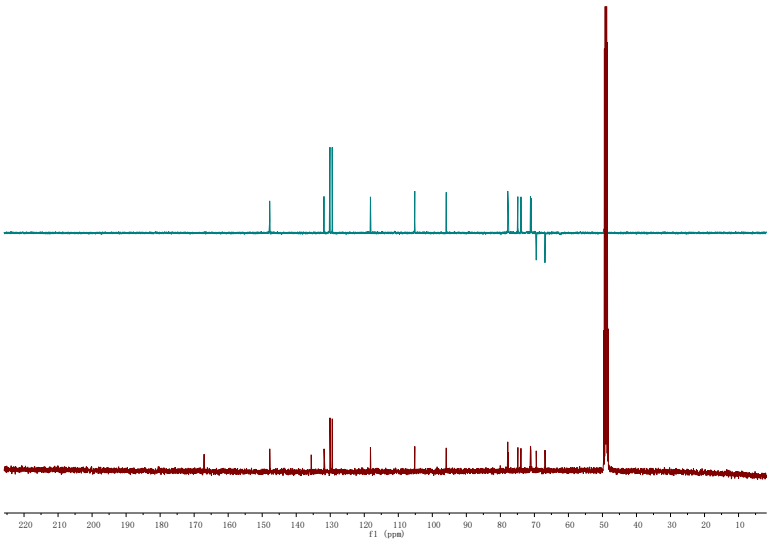


Fig. S1-8 ^{13}C-NMR and DEPT 135 spectra of compound 1

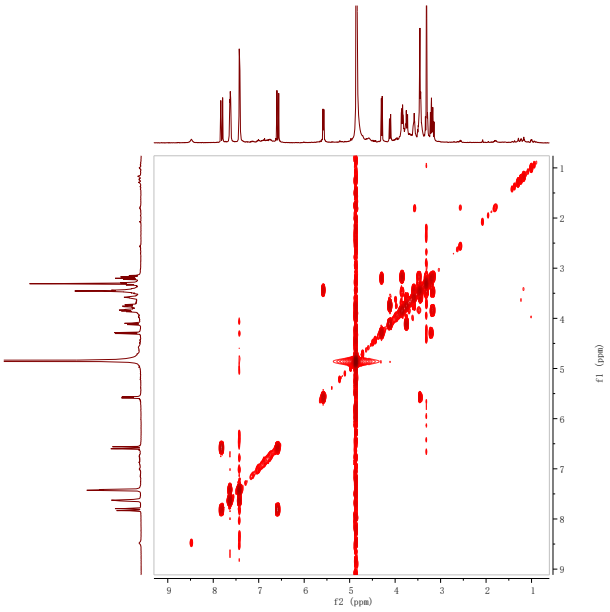


Fig. S1-9 ^{1}H-^{1}H COSY spectrum of compound 1

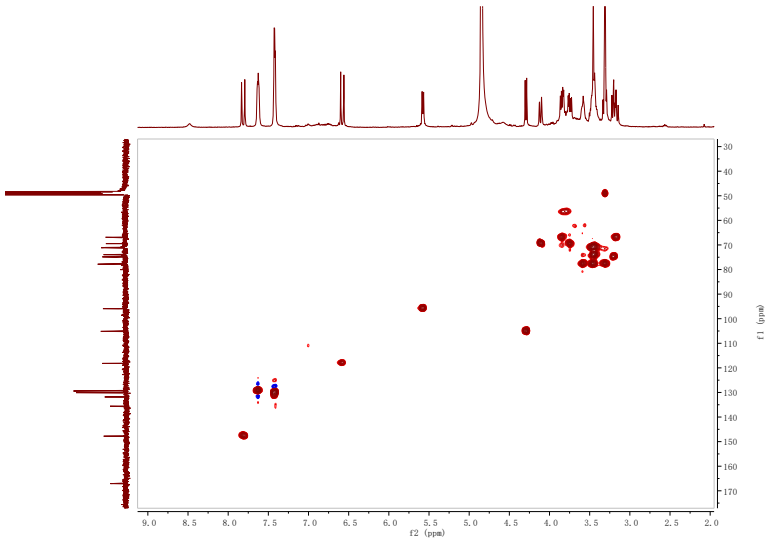


Fig. S1-10 HSQC spectrum of compound 1

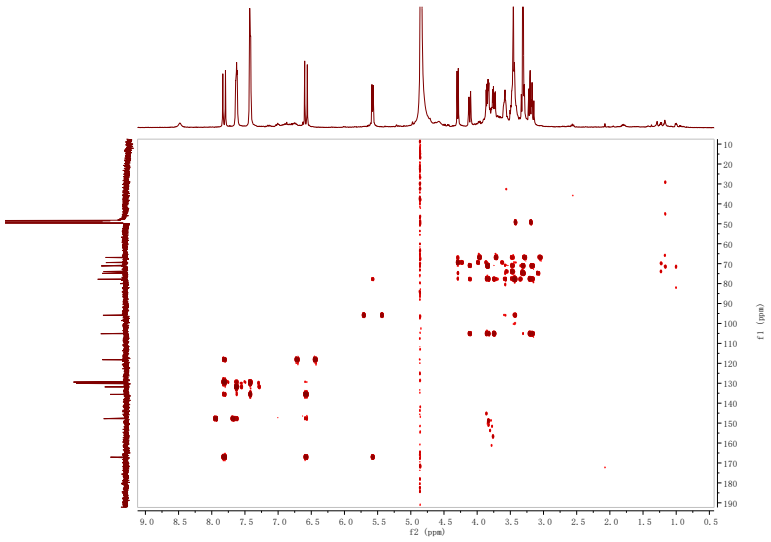


Fig. S1-11 HMBC spectrum of compound 1

2. UV, IR, HRESIMS spectra and NMR spectra of compound 2

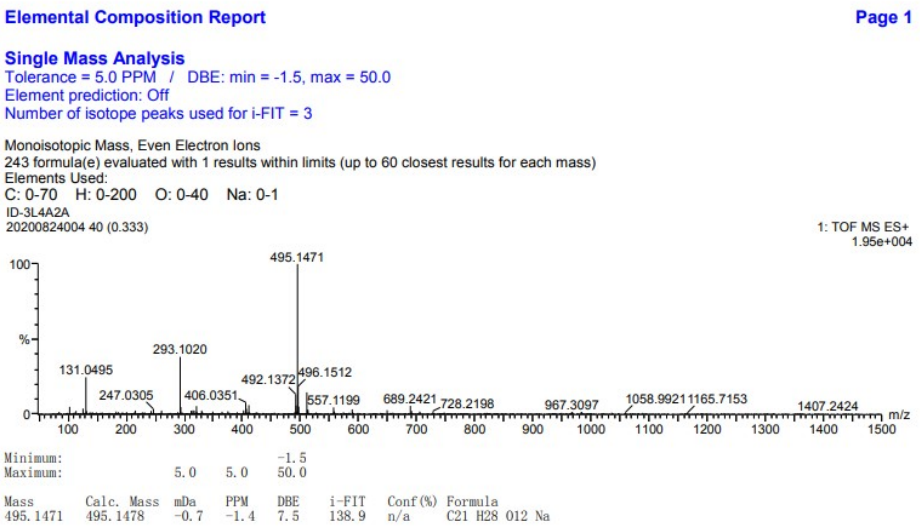


Fig. S2-1 HR-ESI-MS spectrum of compound 2

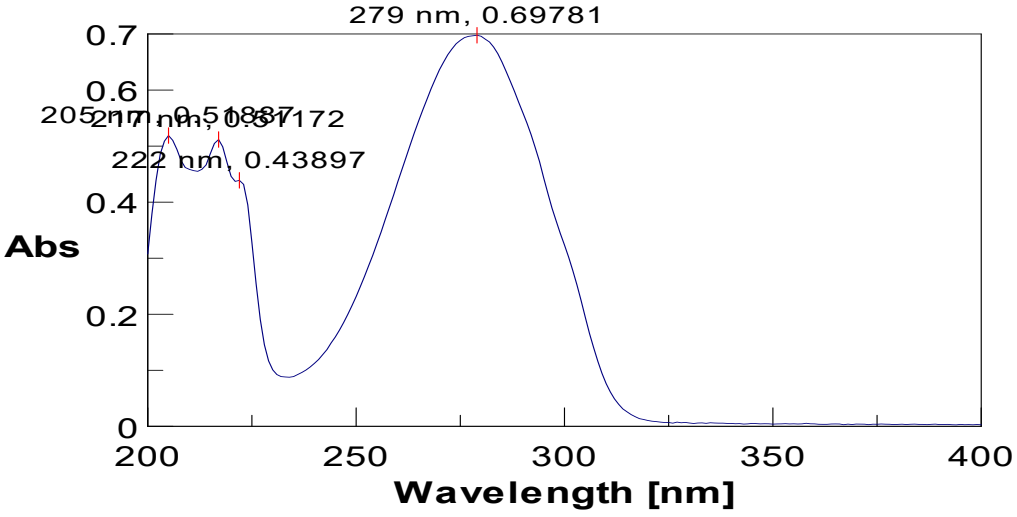


Fig. S2-2 UV spectrum of compound 2

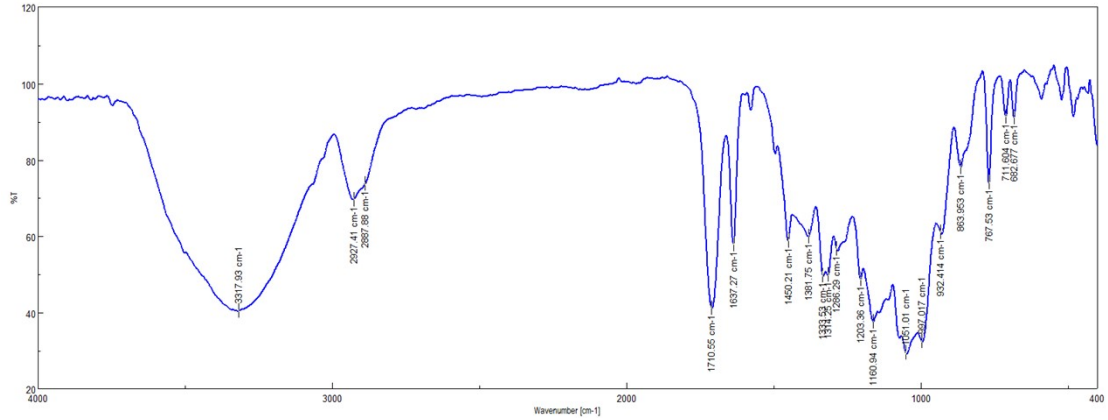


Fig. S2-3 IR spectrum of compound 2

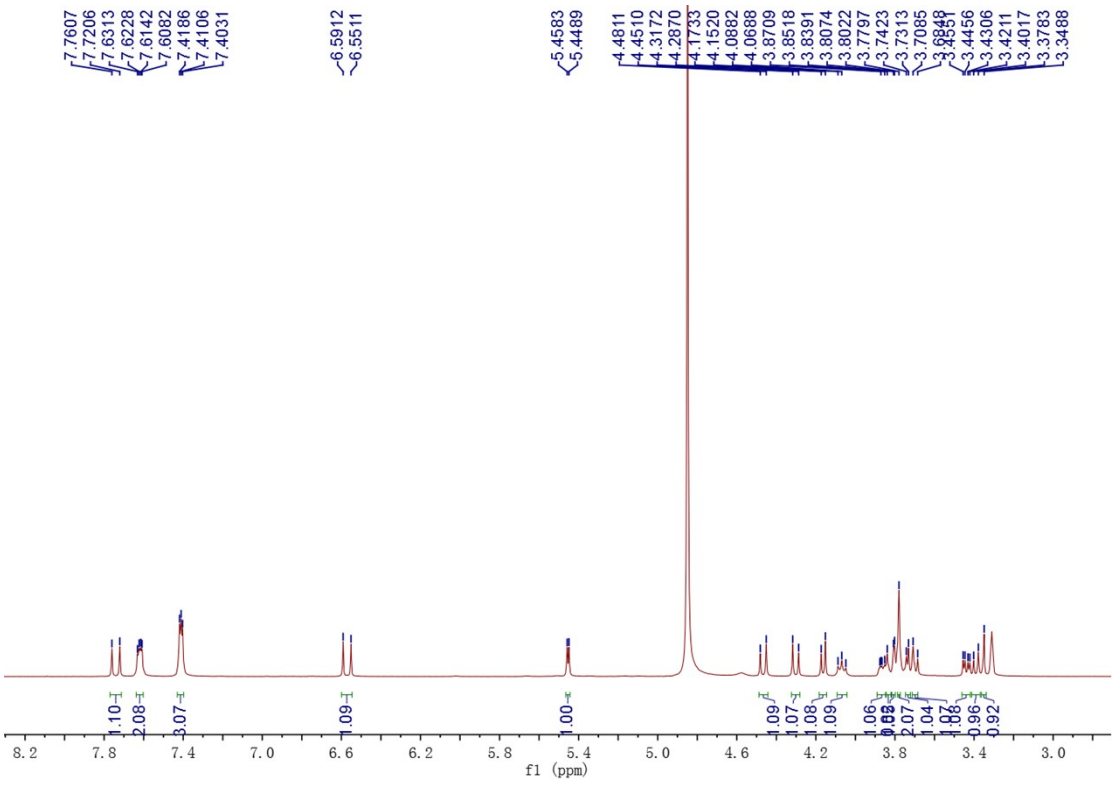


Fig. S2-4 ^{1}H NMR spectrum of compound 2

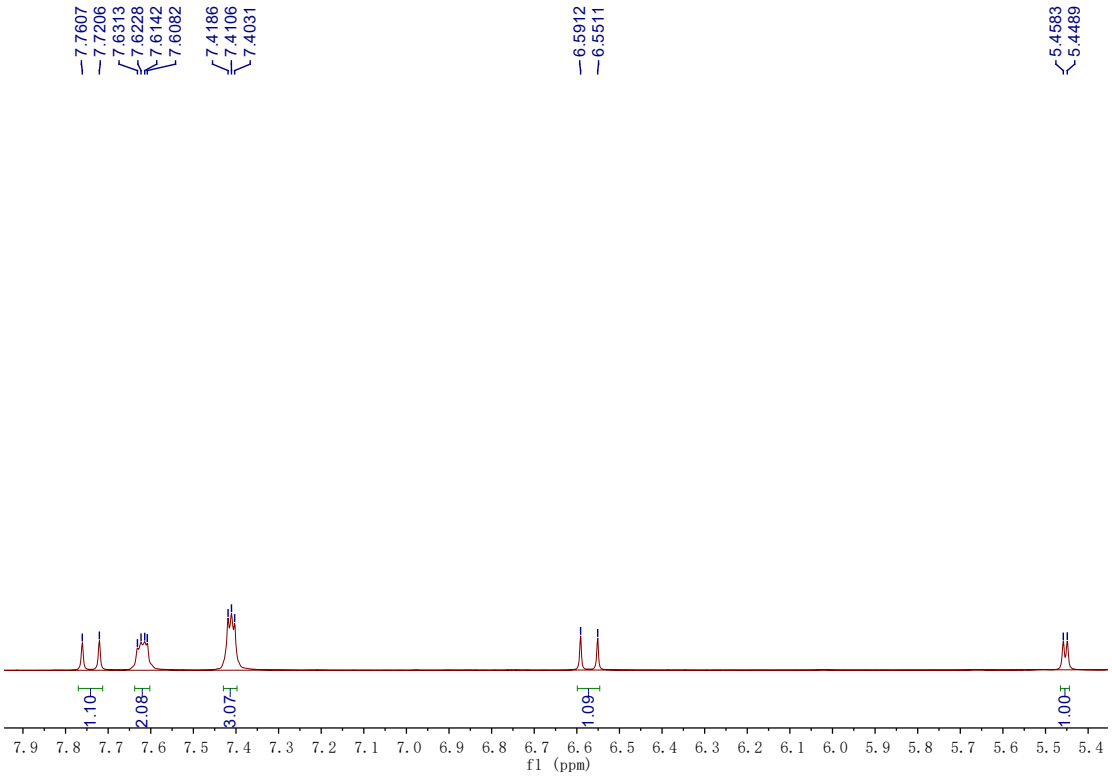


Fig. S2-5 The local enlarged ^{1}H NMR spectrum of compound 2

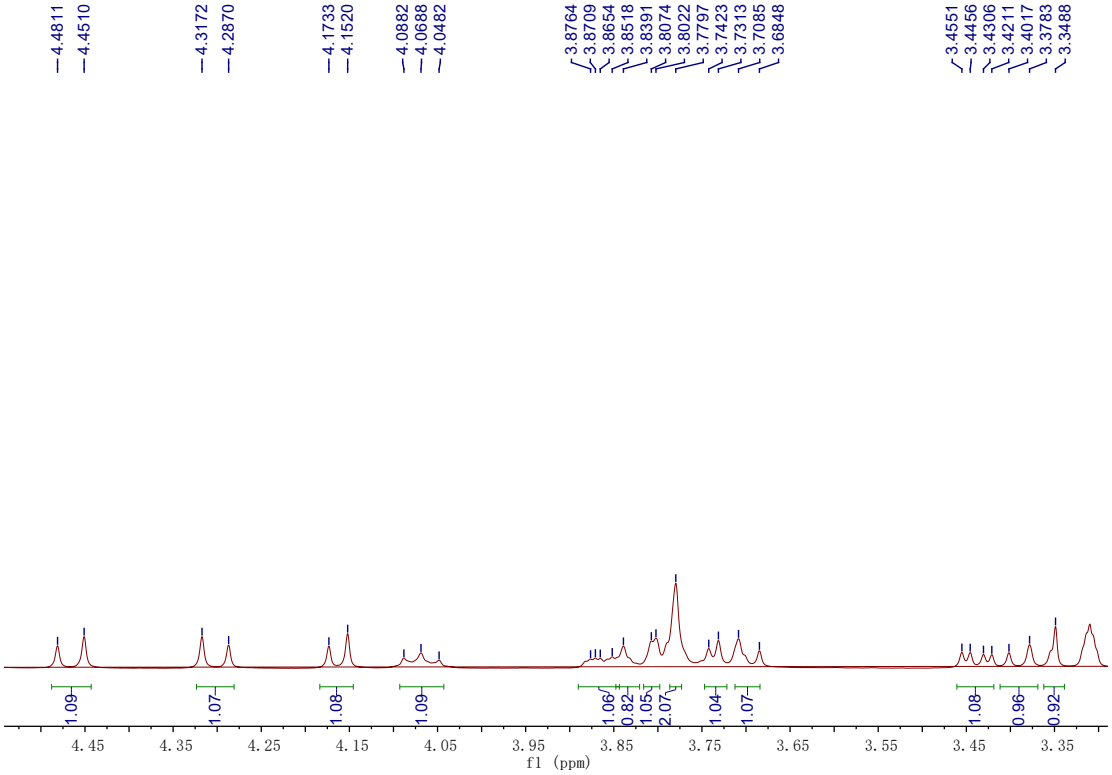


Fig. S2-6 The local enlarged ^{1}H NMR spectrum of compound 2

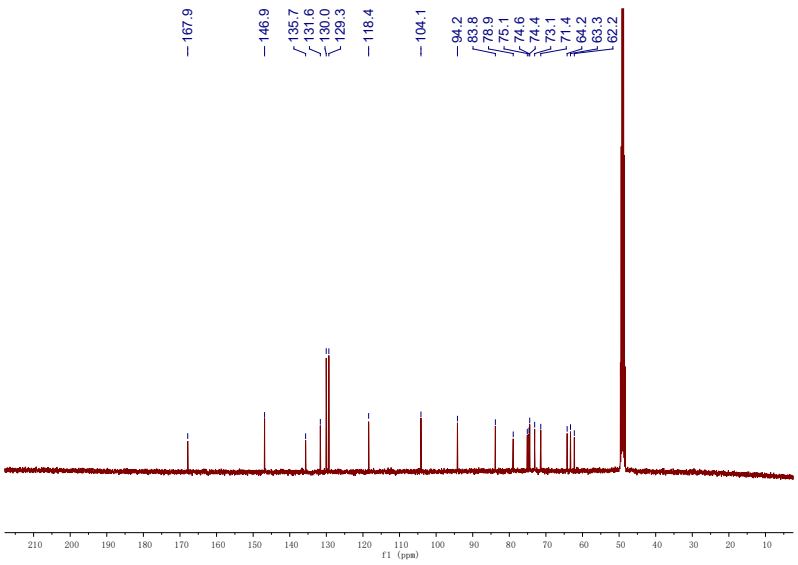


Fig. S2-7 ^{13}C NMR spectrum of compound 2

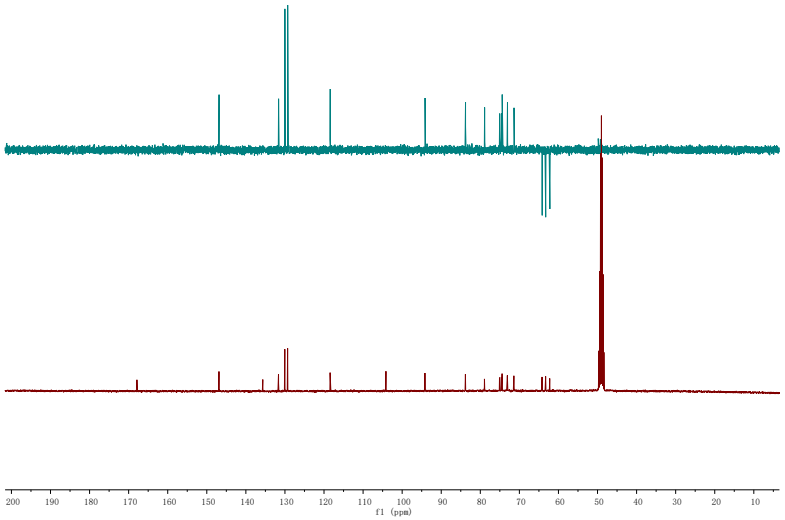


Fig. S2-8 ^{13}C-NMR and DEPT 135 spectra of compound 2

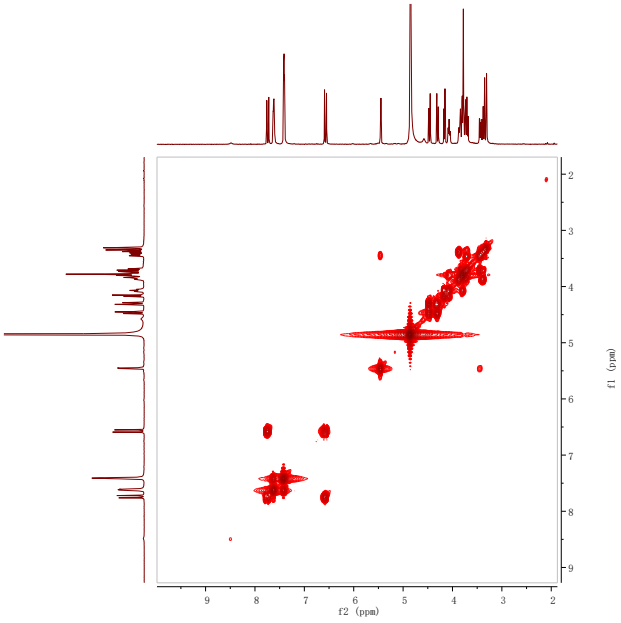


Fig. S2-9 ^{1}H-^{1}H COSY spectrum of compound 2

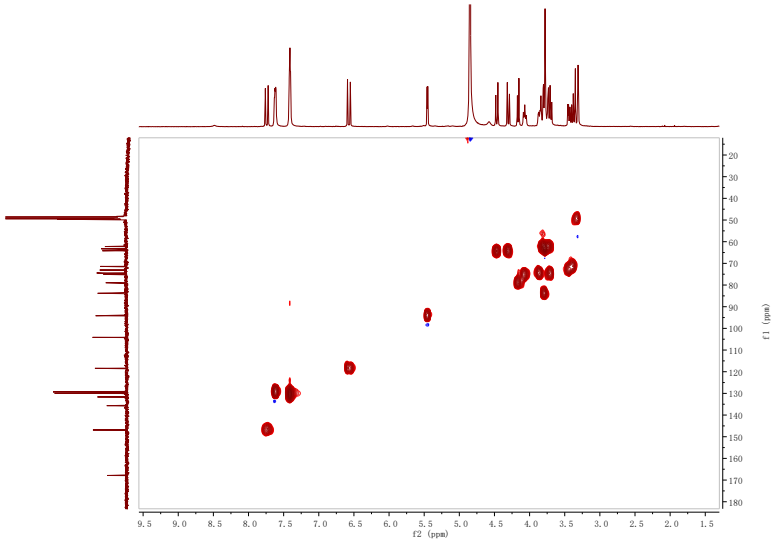


Fig. S2-10 HSQC spectrum of compound 2

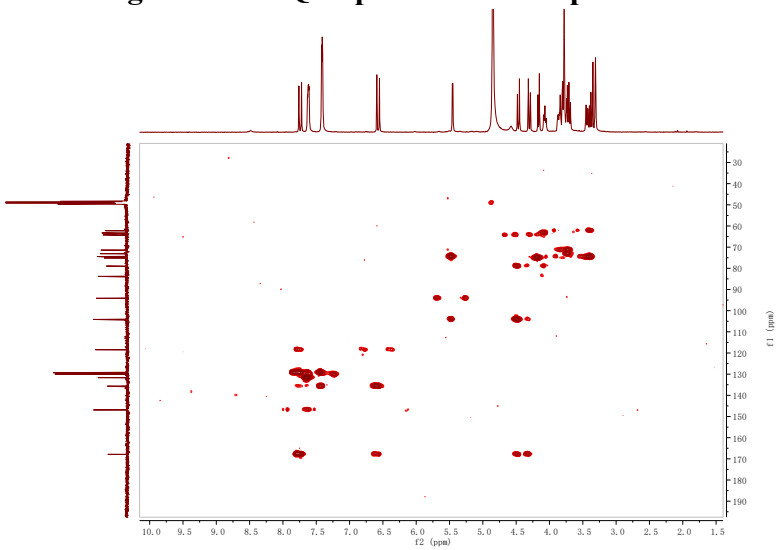
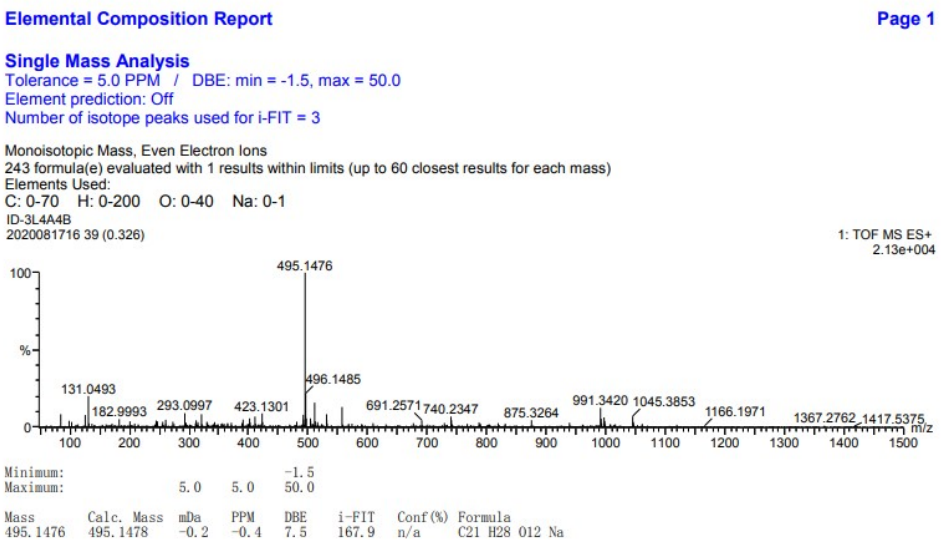


Fig. S2-11 HMBC spectrum of compound 2

3. UV, IR, HRESIMS spectra and NMR spectra of compound 3



Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 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
243 formula(e) evaluated with 1 results within limits (up to 60 closest results for each mass)
Elements Used:
C: 0-70 H: 0-200 O: 0-40 Na: 0-1
ID-3L4A4B
2020081716 39 (0.326)

1: TOF MS ES+
2.13e+004

Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Conf(%)	Formula
495.1476	495.1478	-0.2	-0.4	7.5	167.9	n/a	C21 H28 O12 Na

Fig. S3-1 HR-ESI-MS spectrum of compound 3

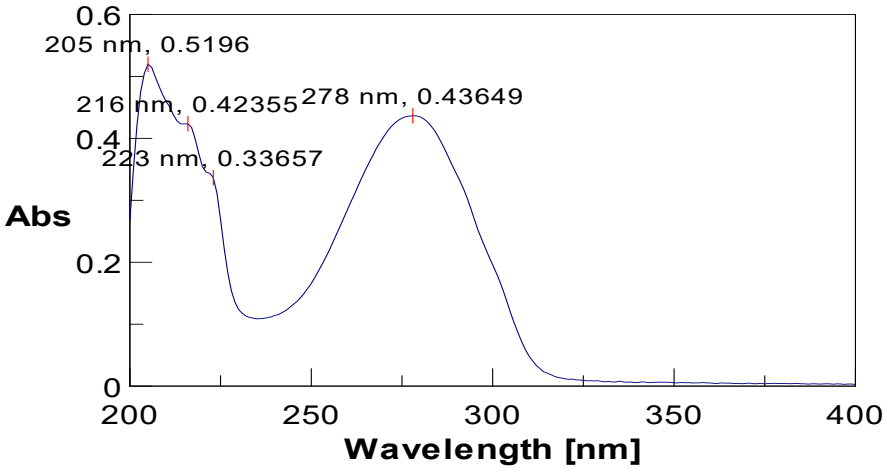


Fig. S3-2 UV spectrum of compound 3

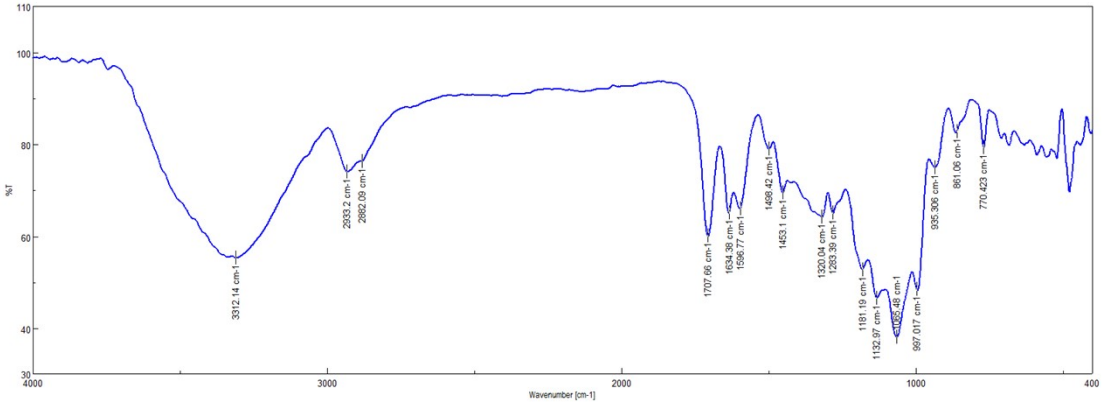


Fig. S3-3 IR spectrum of compound 3

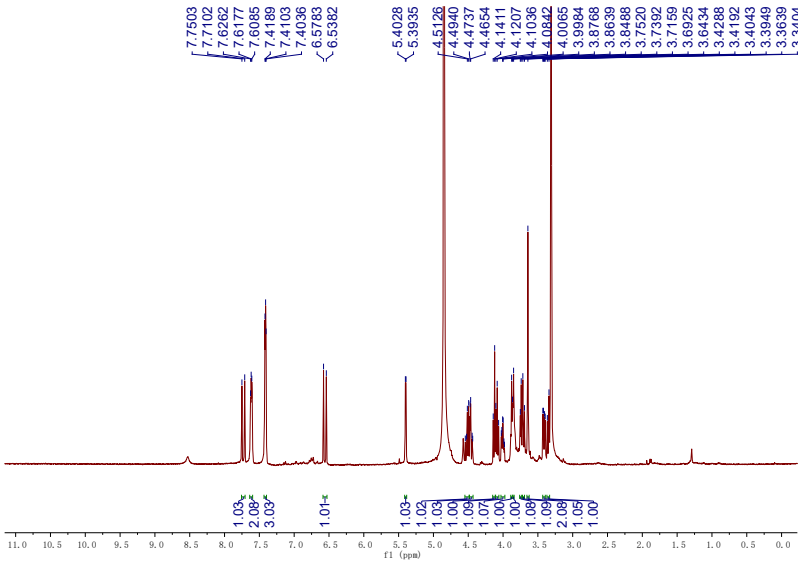


Fig. S3-4 ^{1}H NMR spectrum of compound 3

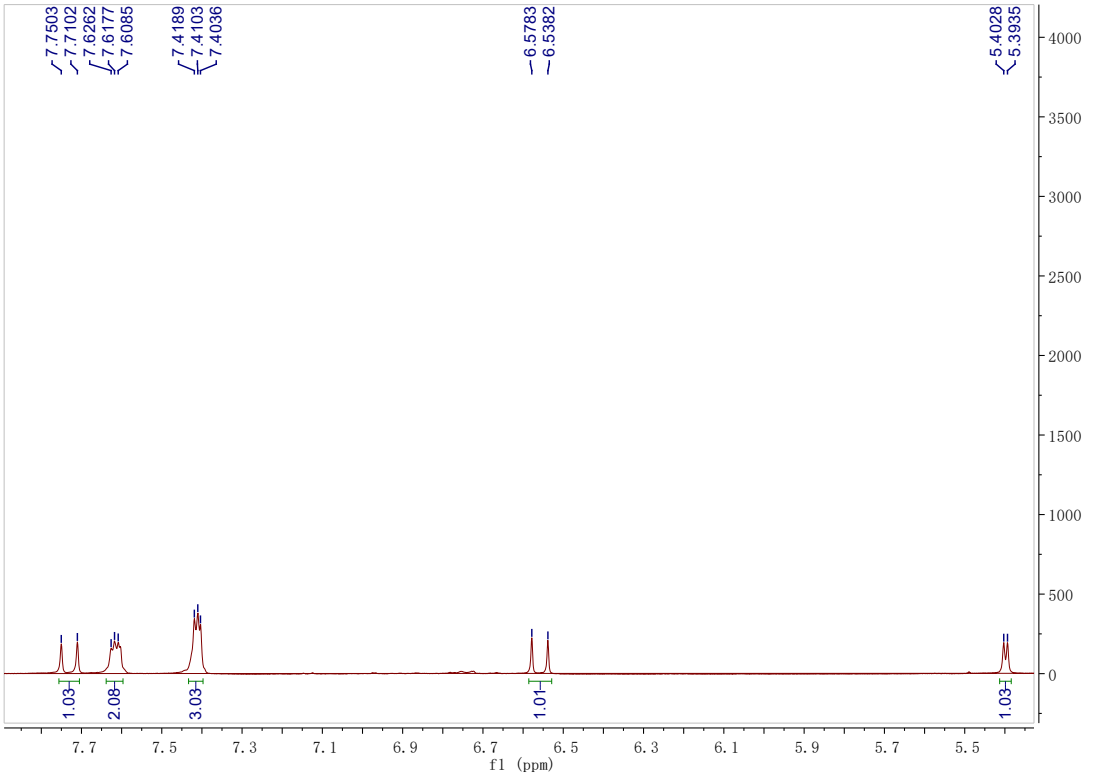


Fig. S3-5 The local enlarged ^{1}H NMR spectrum of compound 3

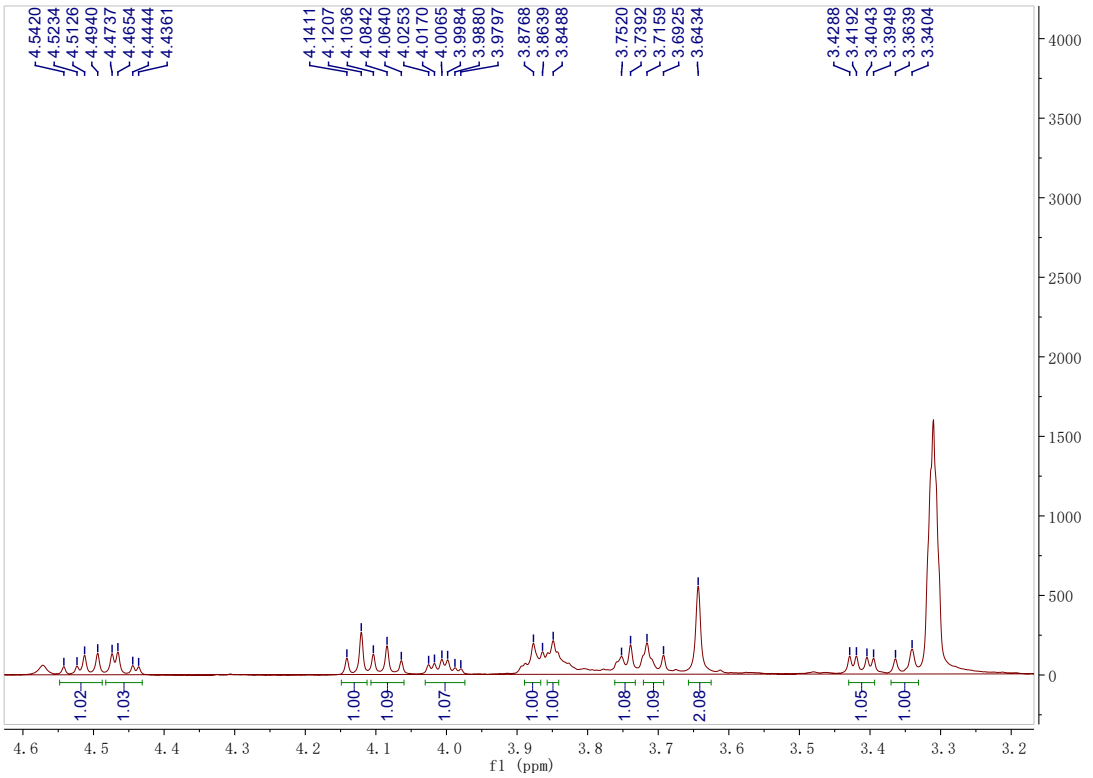


Fig. S3-6 The local enlarged ^{1}H NMR spectrum of compound 3

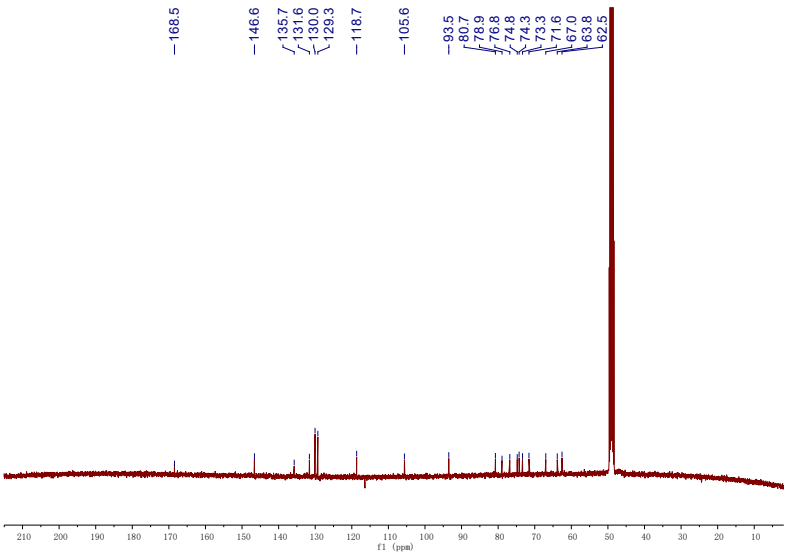


Fig. S3-5 ^{13}C NMR spectrum of compound 3

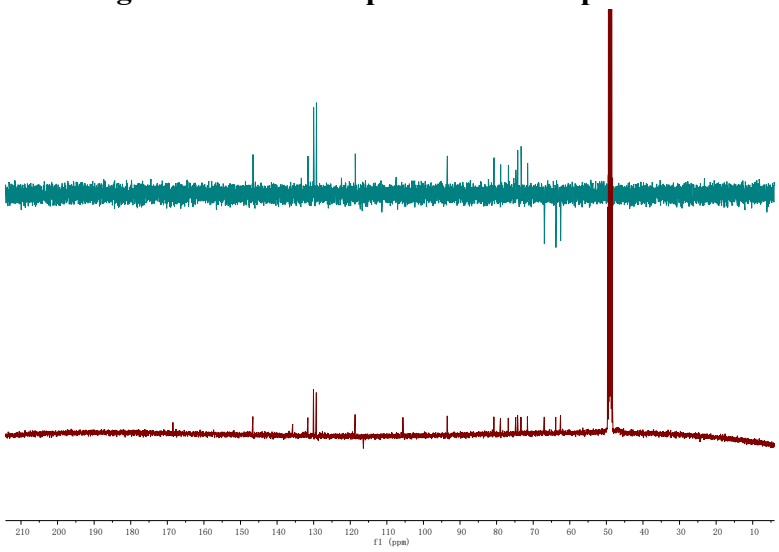


Fig. S3-6 ^{13}C-NMR and DEPT 135 spectra of compound 3

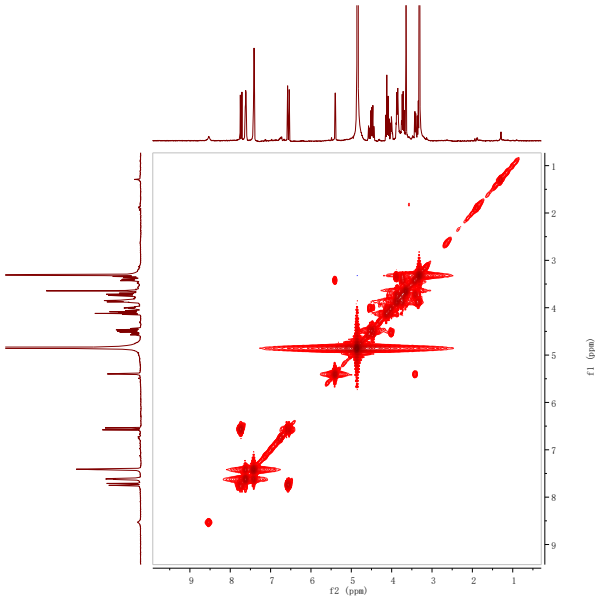


Fig. S3-7 ^{1}H-^{1}H COSY spectrum of compound 3

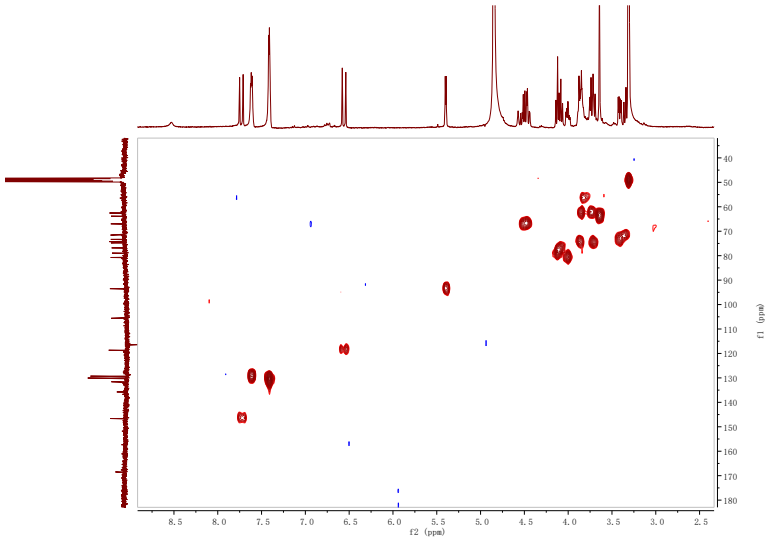


Fig. S3-8 HSQC spectrum of compound 3

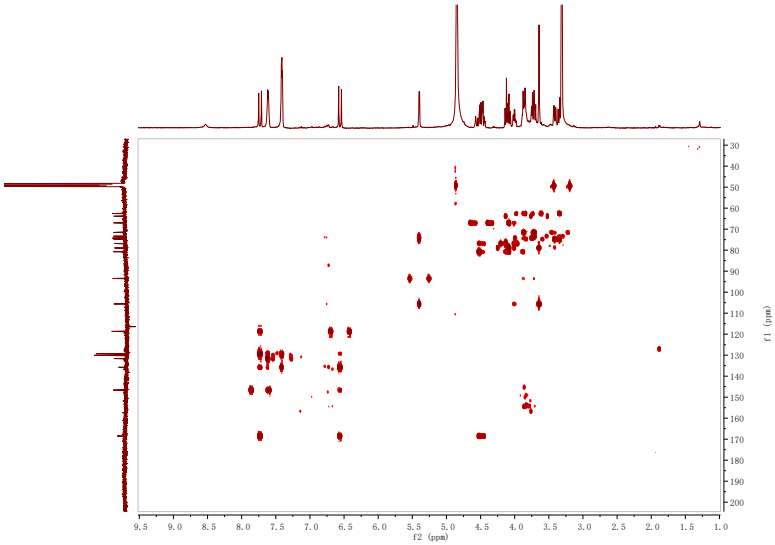
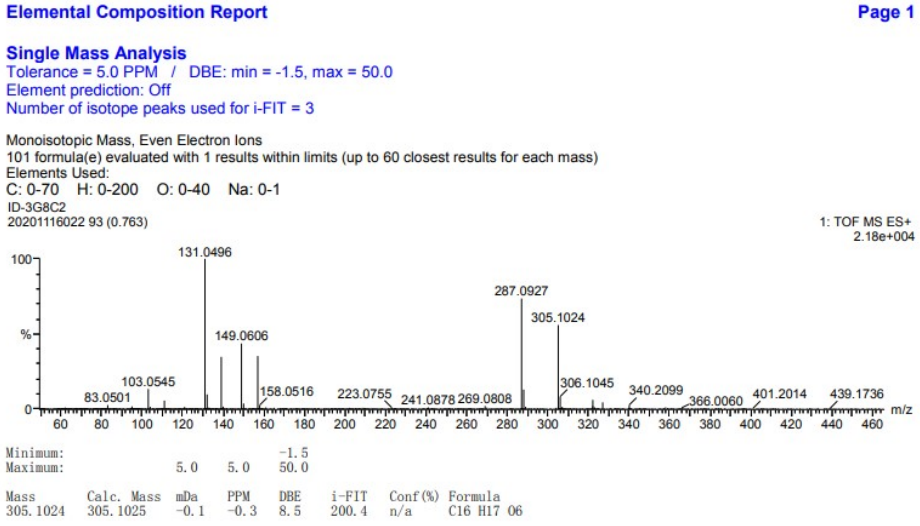


Fig. S3-9 HMBC spectrum of compound 3

4. UV, IR, HRESIMS spectra and NMR spectra of compound 4



Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 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
101 formula(e) evaluated with 1 results within limits (up to 60 closest results for each mass)
Elements Used:
C: 0-70 H: 0-200 O: 0-40 Na: 0-1

ID-3G8C2
20201116022 93 (0.763)

1: TOF MS ES+
2.18e+004

Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Conf(%)	Formula
305.1024	305.1025	-0.1	-0.3	8.5	200.4	n/a	C16 H17 O6

Fig. S4-1 HR-ESI-MS spectrum of compound 4

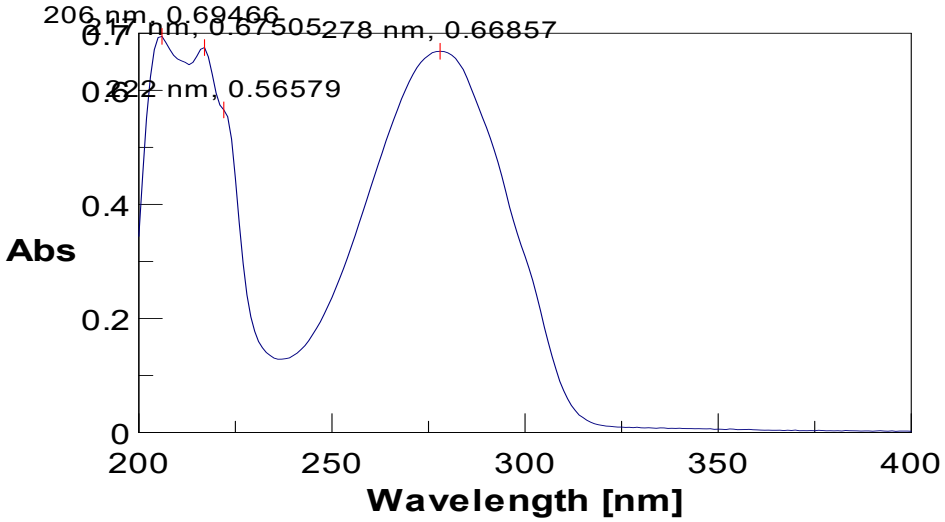


Fig. S4-2 UV spectrum of compound 4

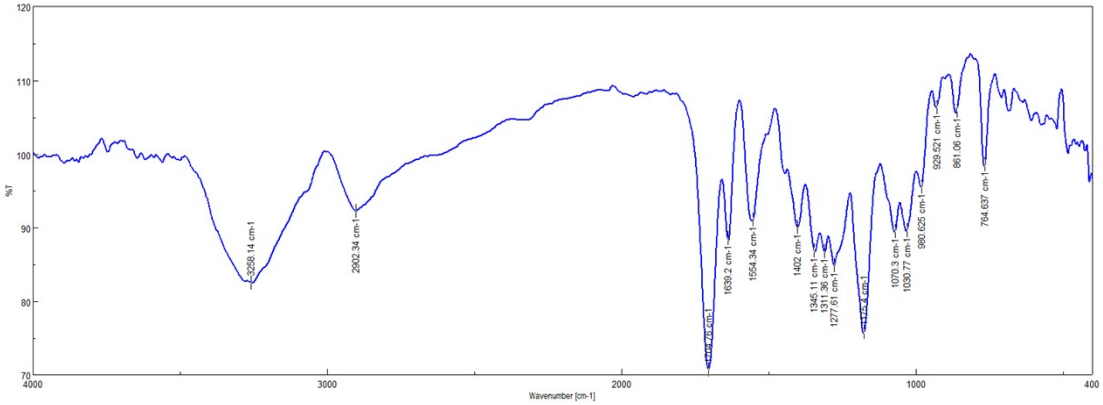


Fig. S4-3 IR spectrum of compound 4

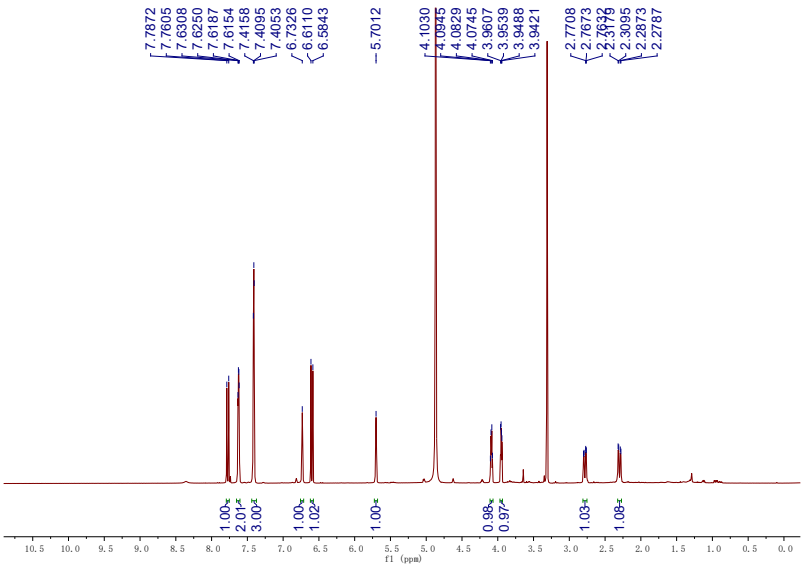


Fig. S4-4 ^{1}H NMR spectrum of compound 4

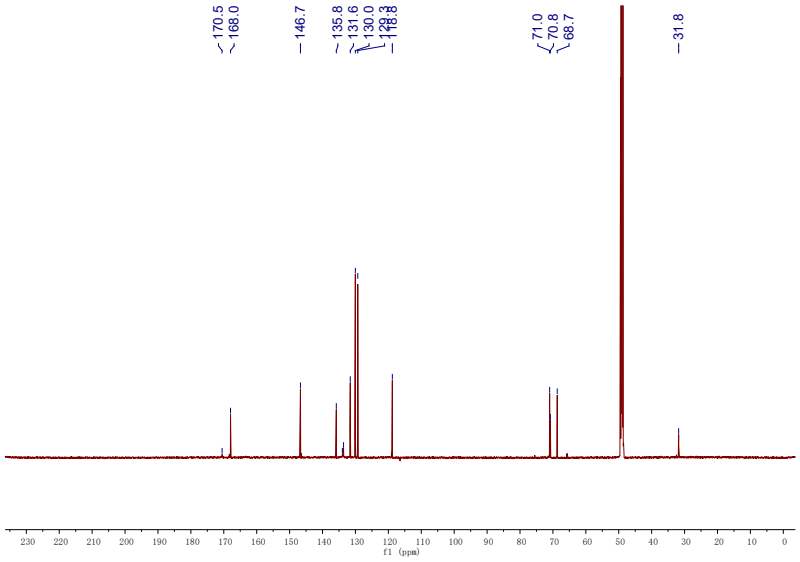


Fig. S4-5 ^{13}C NMR spectrum of compound 4

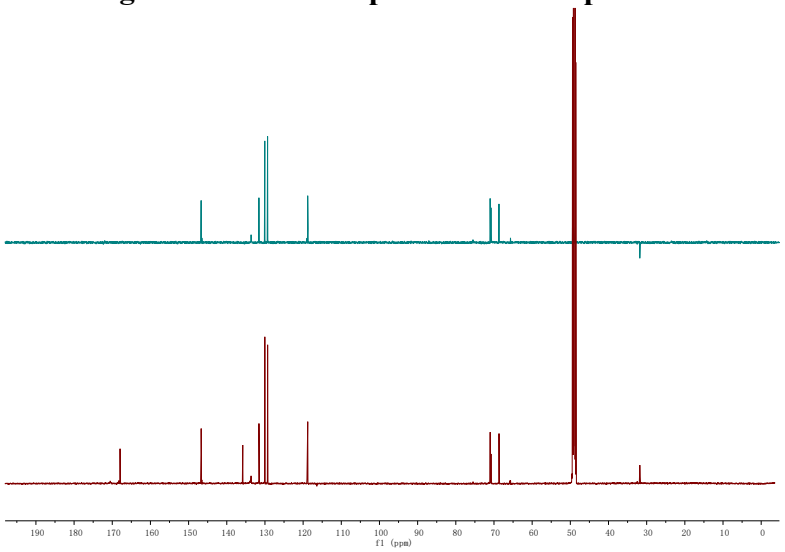


Fig. S4-6 ^{13}C-NMR and DEPT 135 spectra of compound 4

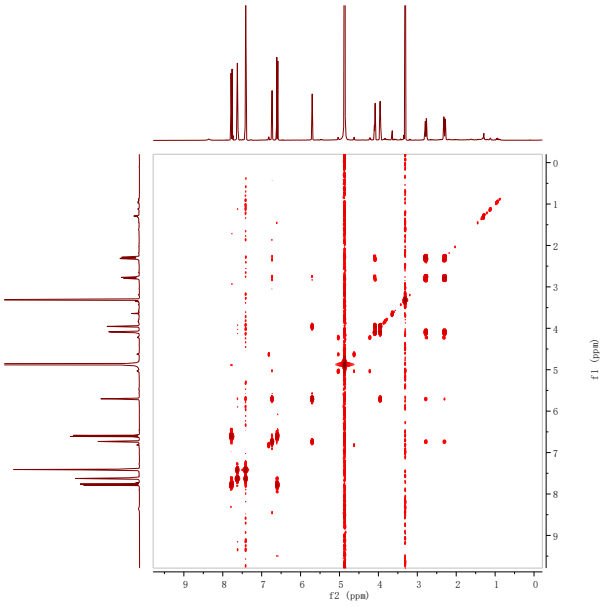


Fig. S4-7 ^{1}H-^{1}H COSY spectrum of compound 4

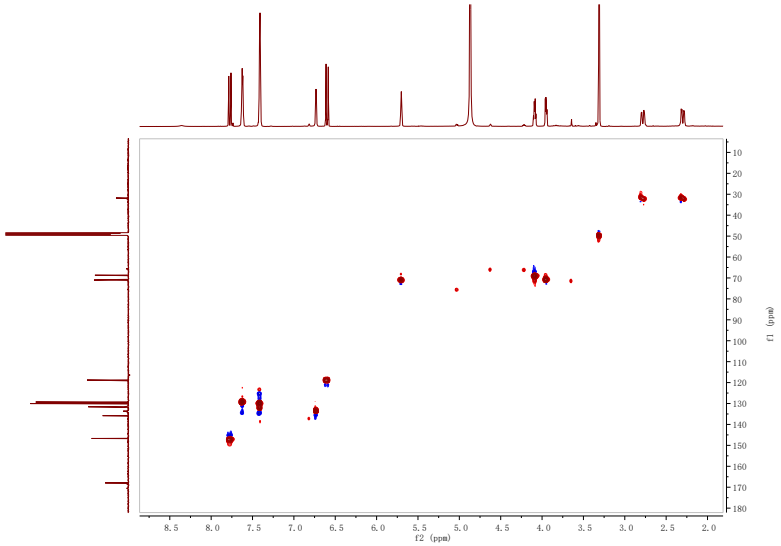


Fig. S4-8 HSQC spectrum of compound 4

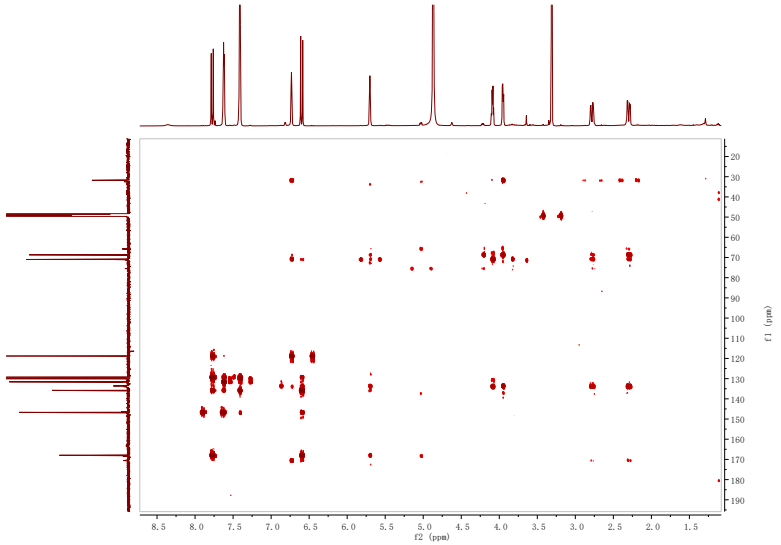


Fig. S4-9 HMBC spectrum of compound 4

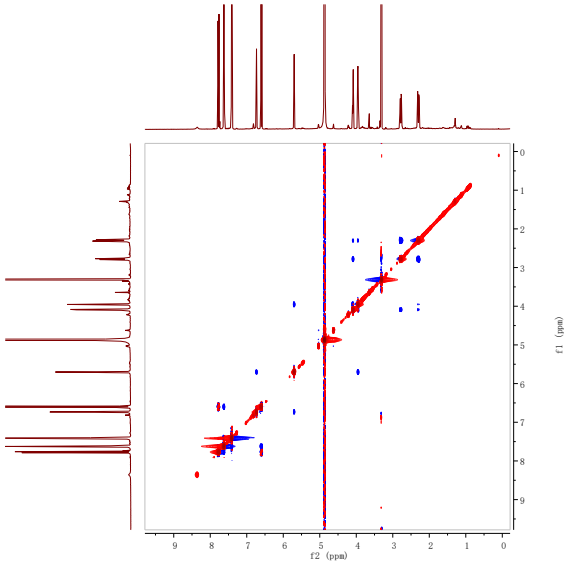


Fig. S4-10 NOESY spectrum of compound 4

5. UV, IR, HRESIMS spectra and NMR spectra of compound 5

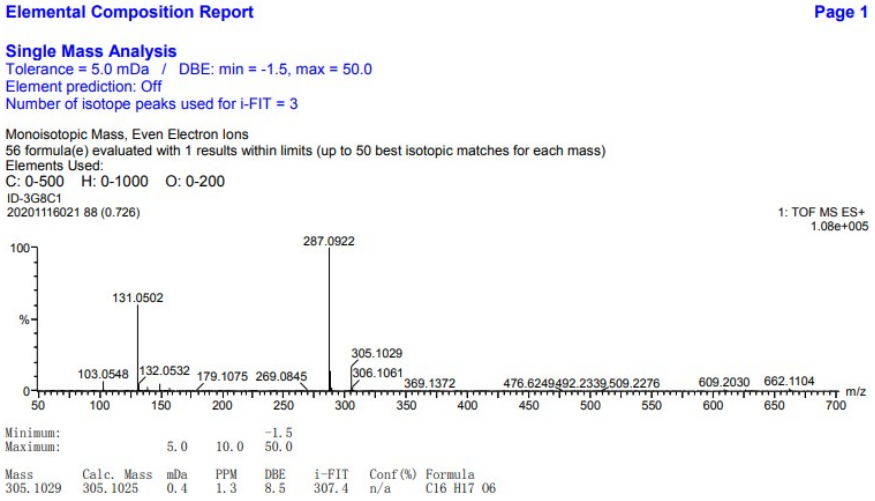


Fig. S5-1 HR-ESI-MS spectrum of compound 5

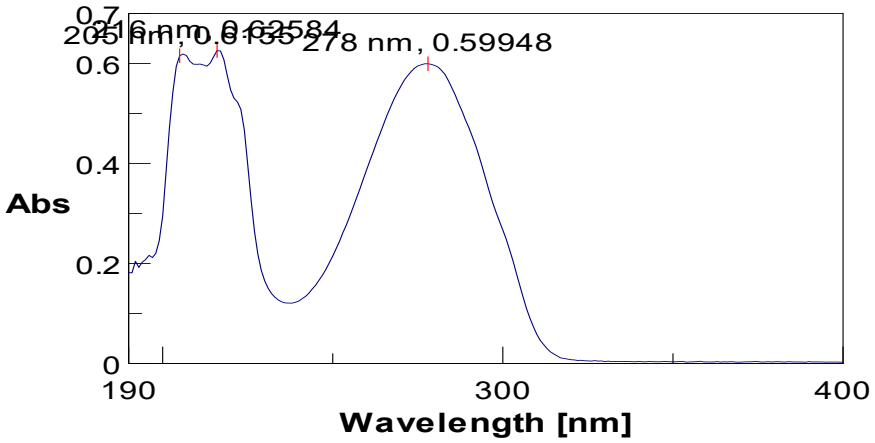


Fig. S5-2 UV spectrum of compound 5

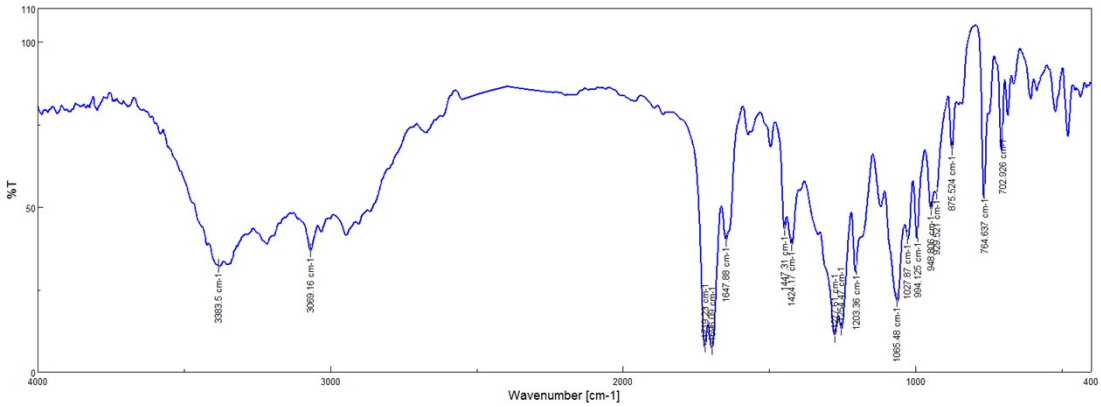


Fig. S5-3 IR spectrum of compound 5

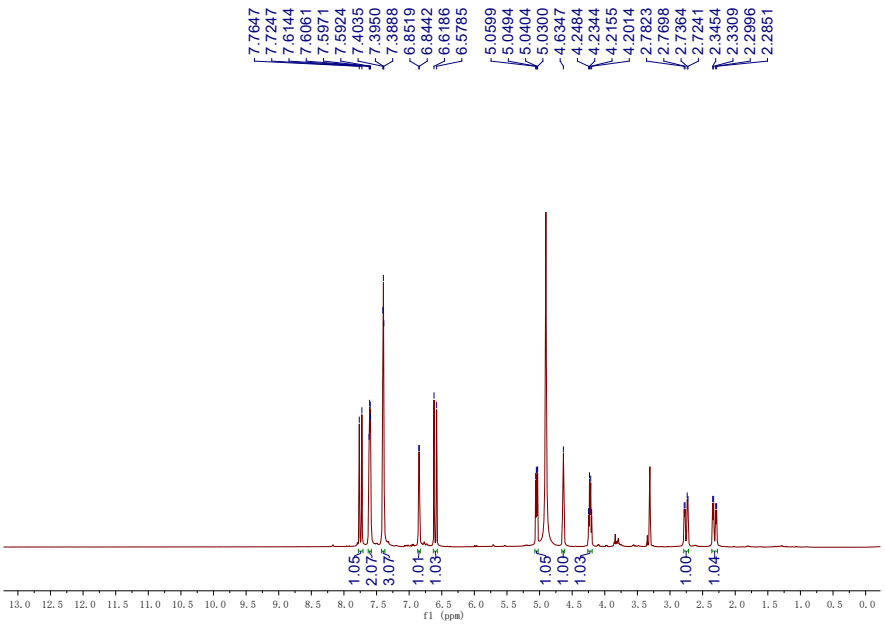


Fig. S5-4 ^{1}H NMR spectrum of compound 5

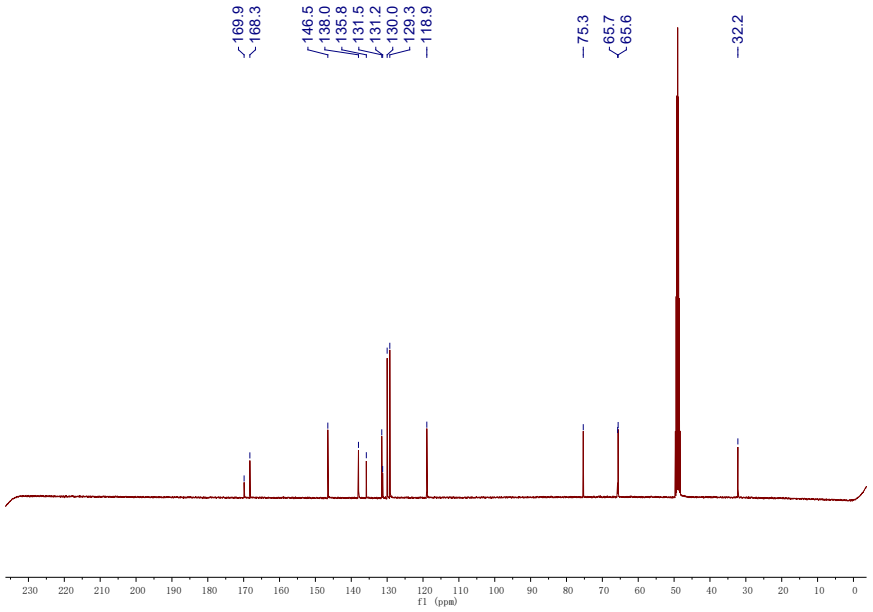


Fig. S5-5 ^{13}C NMR spectrum of compound 5

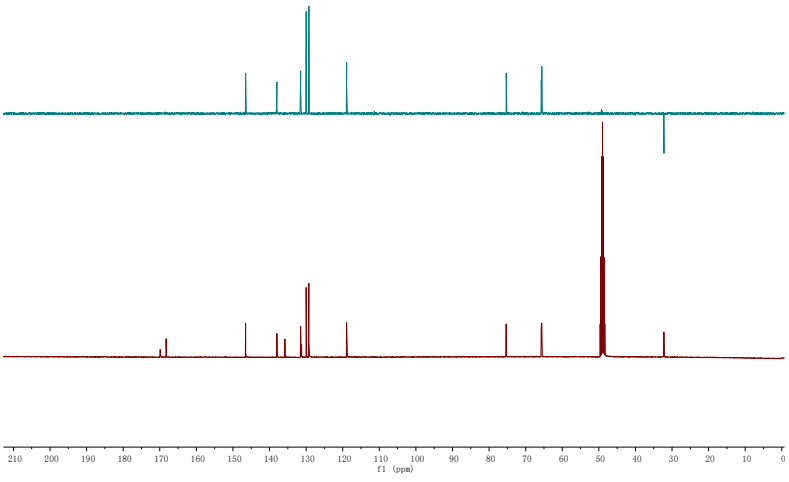


Fig. S5-6 ^{13}C-NMR and DEPT 135 spectra of compound 5

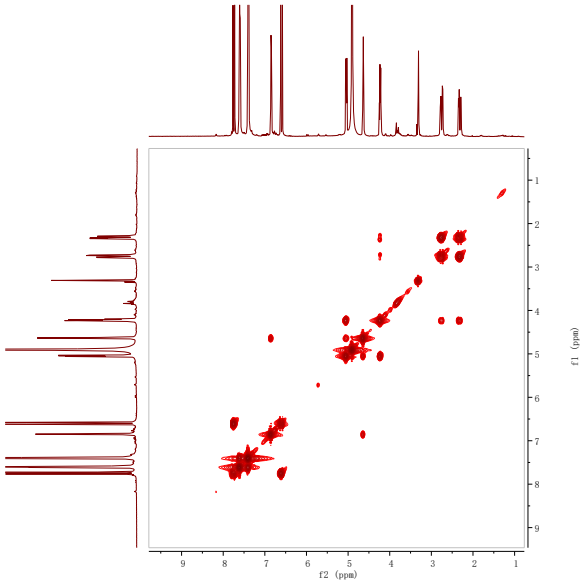


Fig. S5-7 ^{1}H-^{1}H COSY spectrum of compound 5

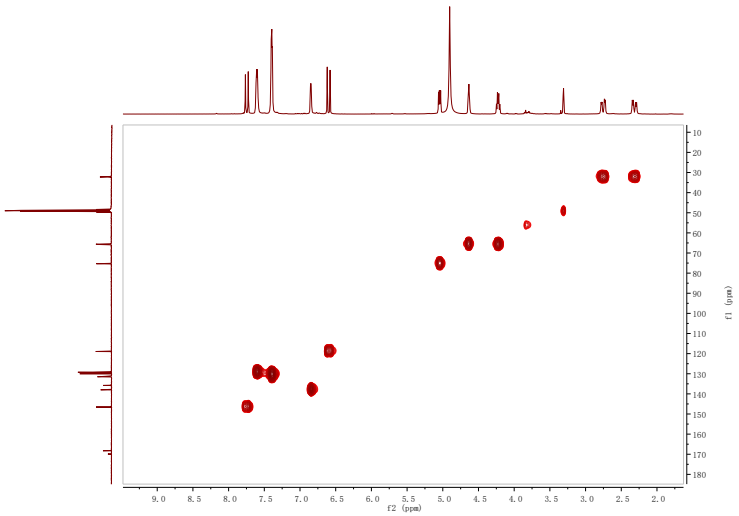


Fig. S5-8 HSQC spectrum of compound 5

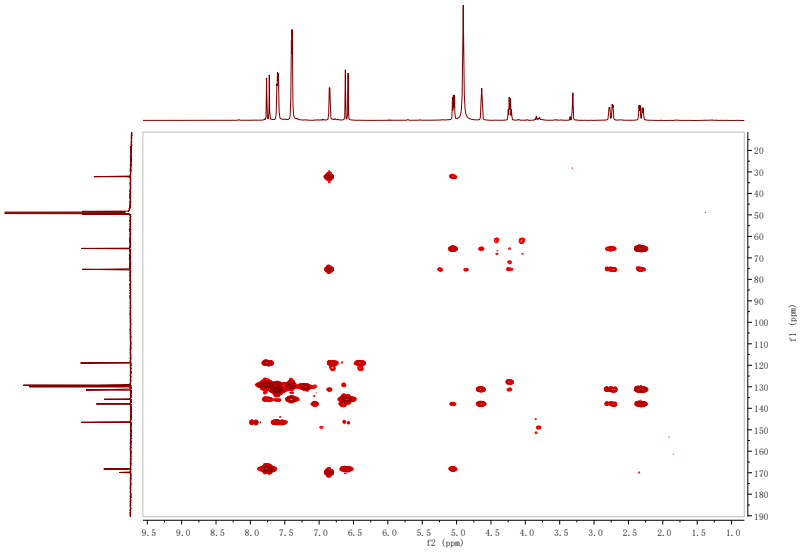


Fig. S5-9 HMBC spectrum of compound 5

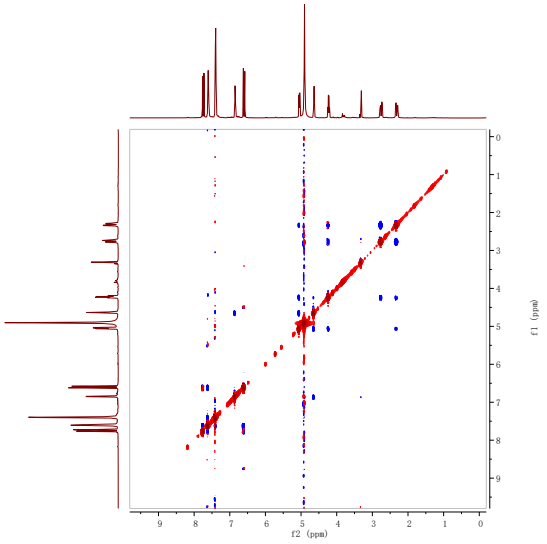


Fig. S5-10 NOESY spectrum of compound 5

6. UV, IR, HRESIMS spectra and NMR spectra of compound 6

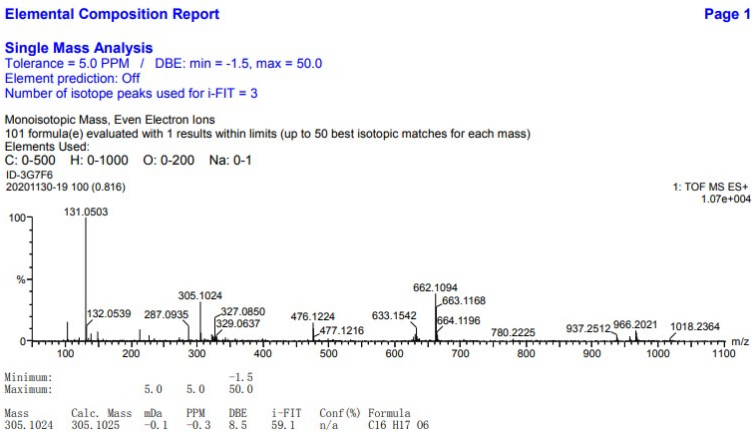


Fig. S6-1 HR-ESI-MS spectrum of compound 6

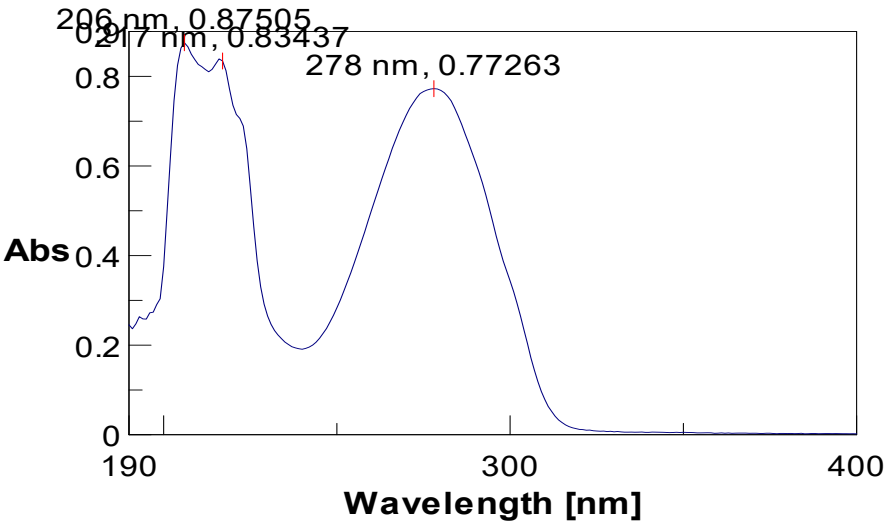


Fig. S6-2 UV spectrum of compound 6

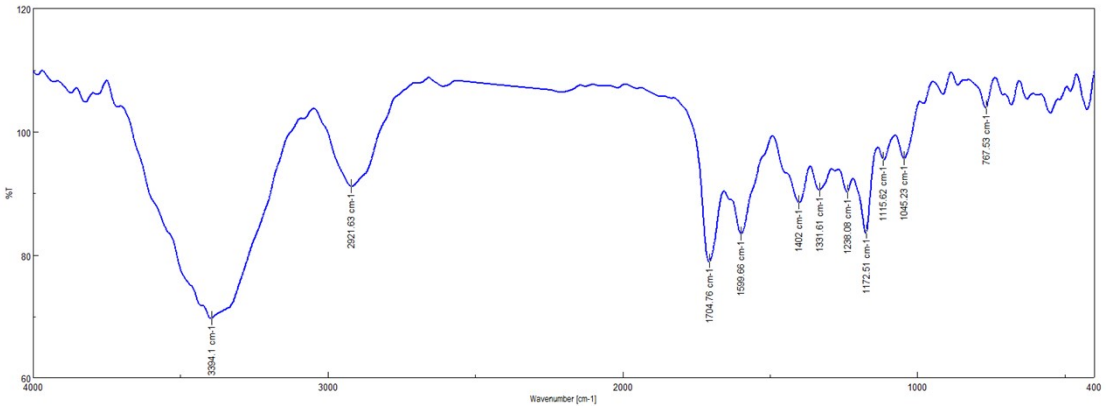


Fig. S6-3 IR spectrum of compound 6

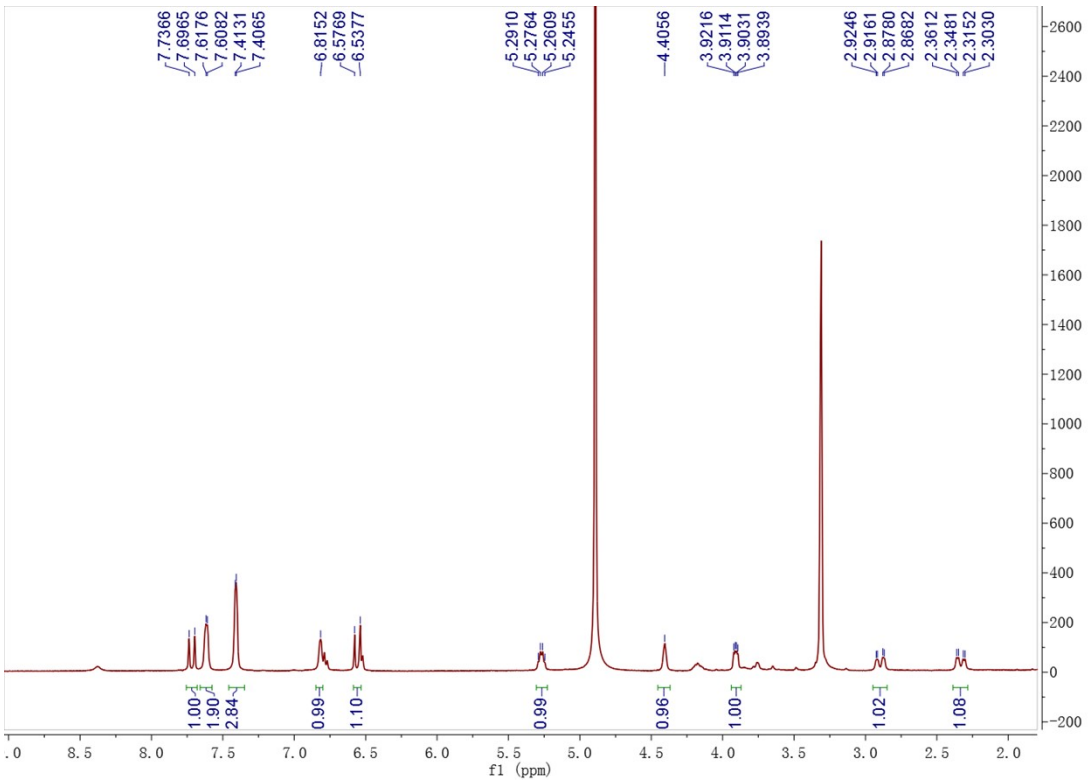


Fig. S6-4 ^{1}H NMR spectrum of compound 6

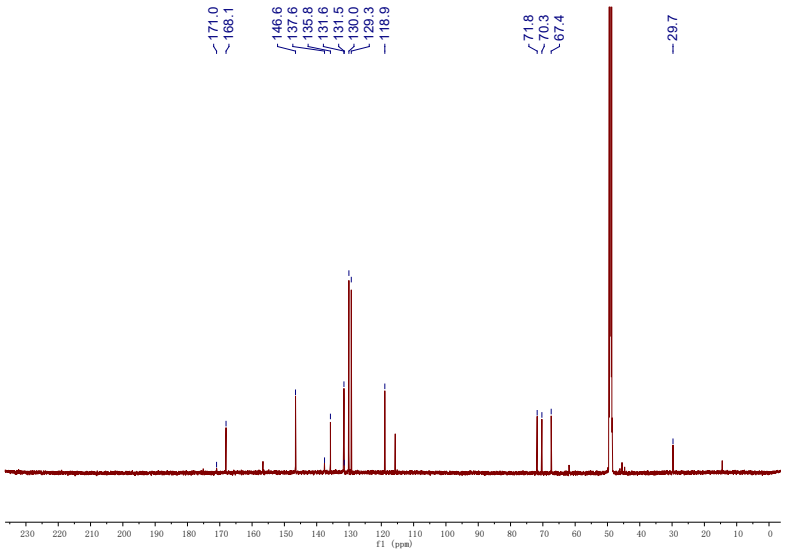


Fig. S6-5 ^{13}C NMR spectrum of compound 6

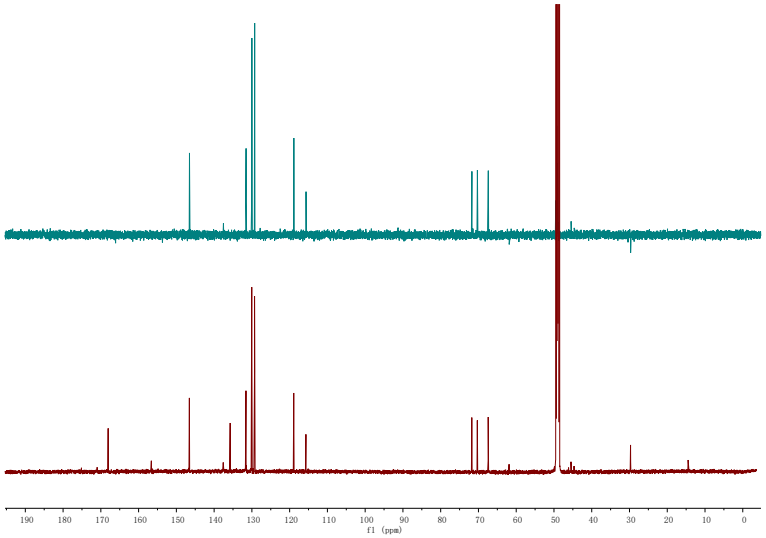


Fig. S6-6 ^{13}C-NMR and DEPT 135 spectra of compound 6

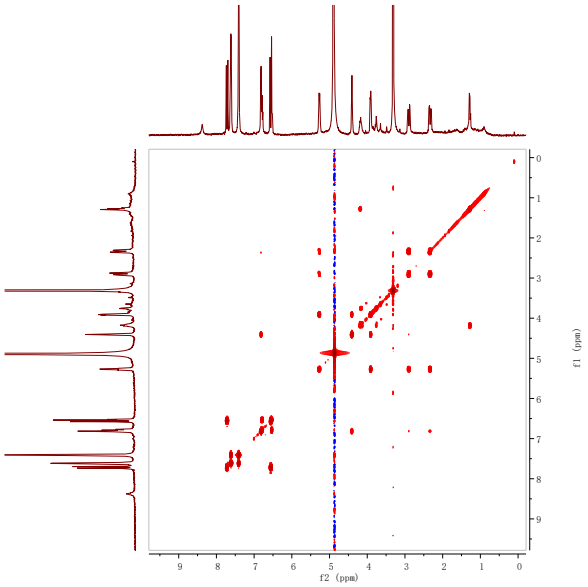


Fig. S6-7 ^{1}H-^{1}H COSY spectrum of compound 6

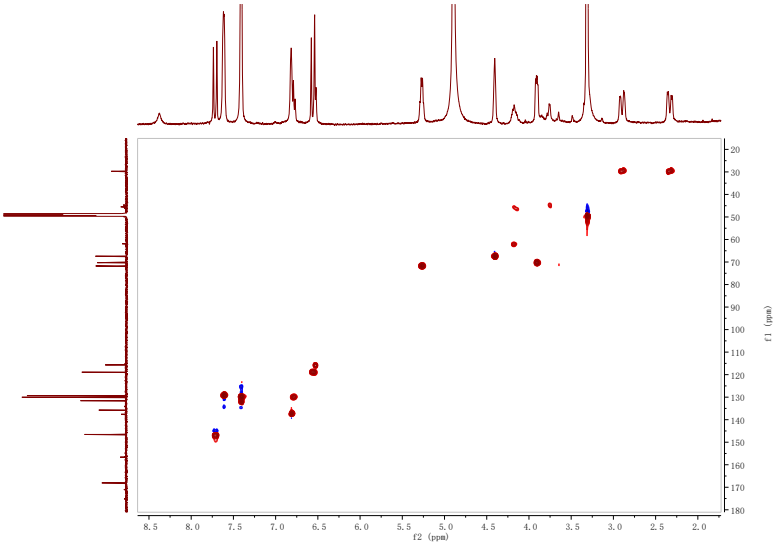


Fig. S6-8 HSQC spectrum of compound 6

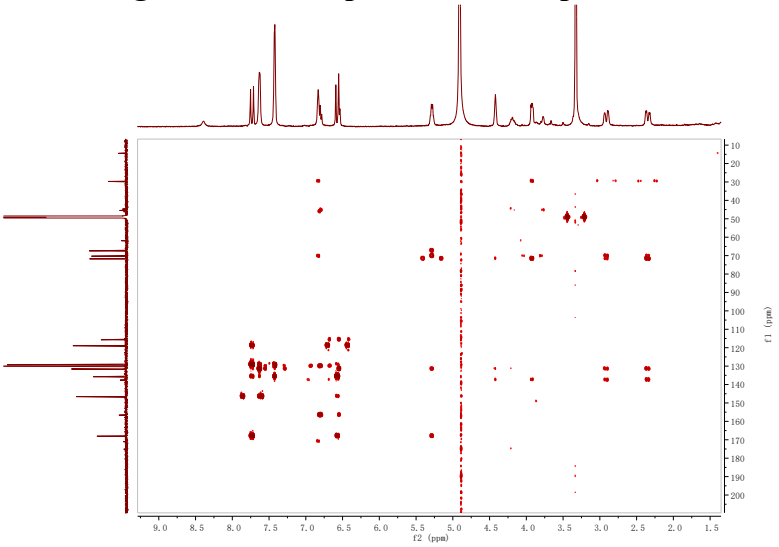


Fig. S6-9 HMBC spectrum of compound 6

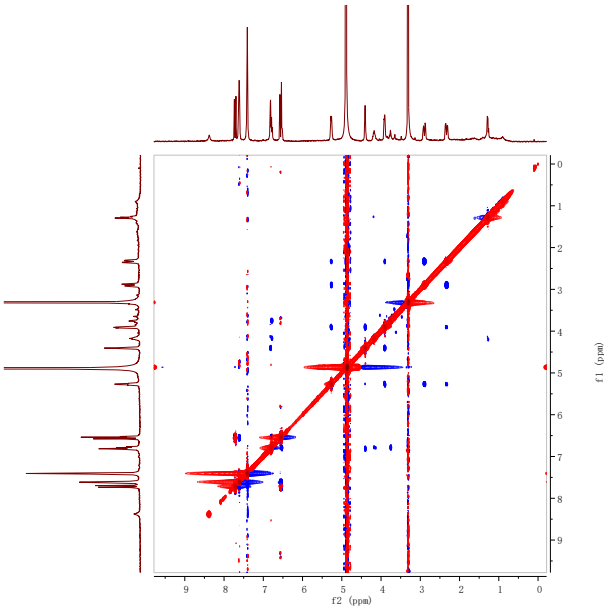


Fig. S6-10 NOESY spectrum of compound 6

7. UV, IR, HRESIMS spectra and NMR spectra of compound 7

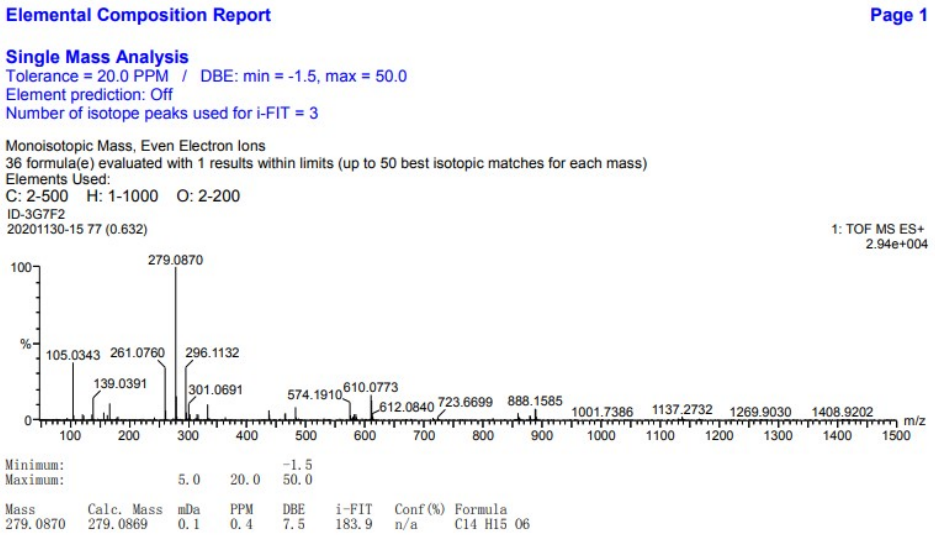


Fig. S7-1 HR-ESI-MS spectrum of compound 7

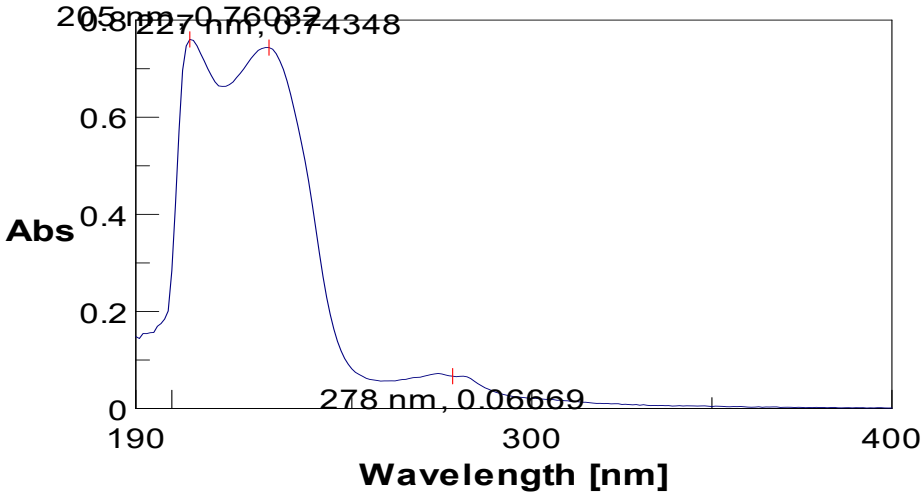


Fig. S7-2 UV spectrum of compound 7

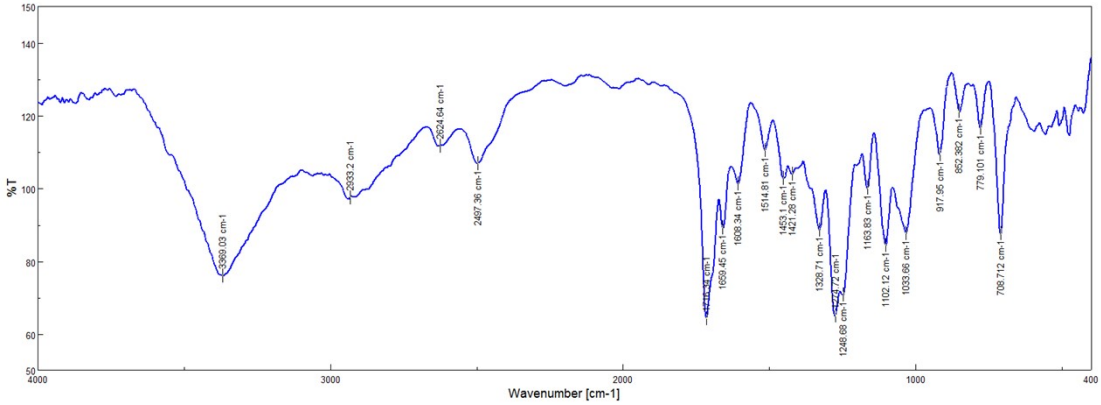


Fig. S7-3 IR spectrum of compound 7

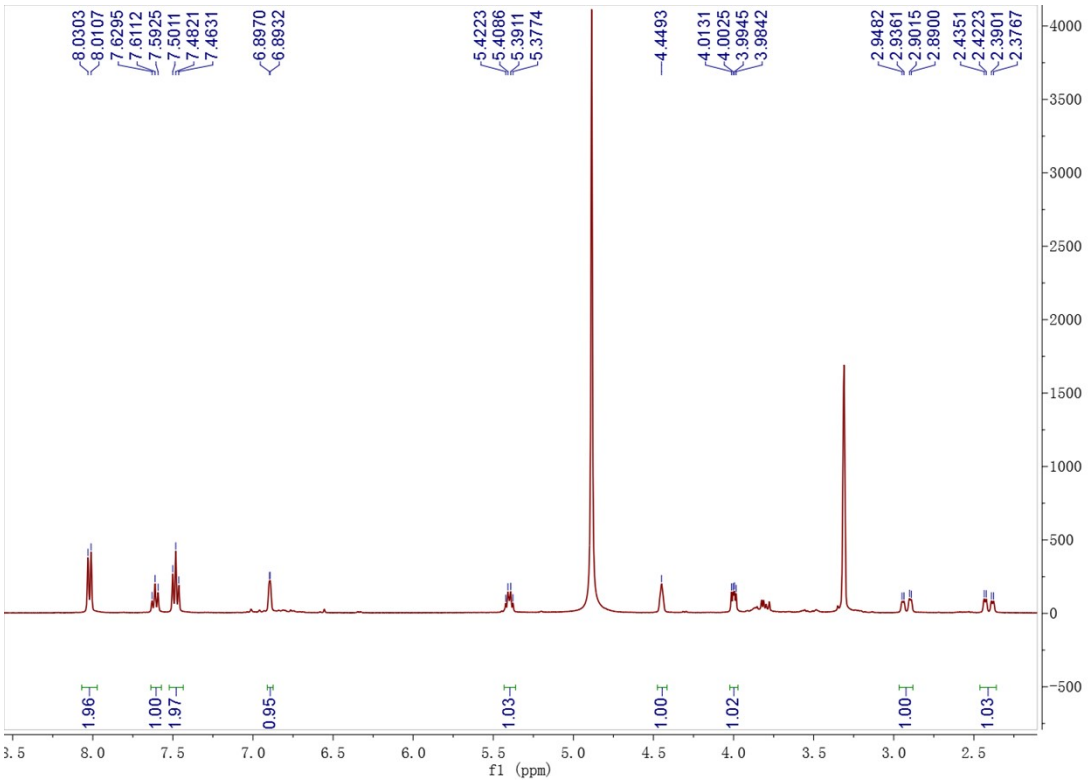


Fig. S7-4 ^{1}H NMR spectrum of compound 7

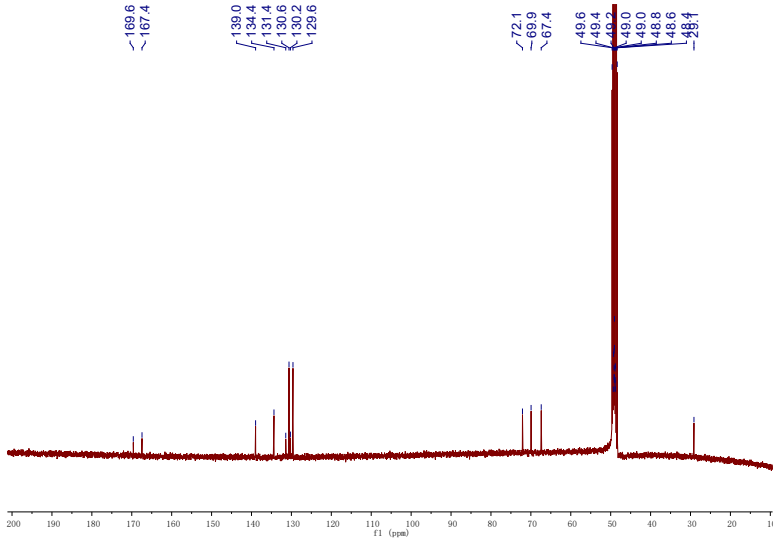


Fig. S7-5 ^{13}C NMR spectrum of compound 7

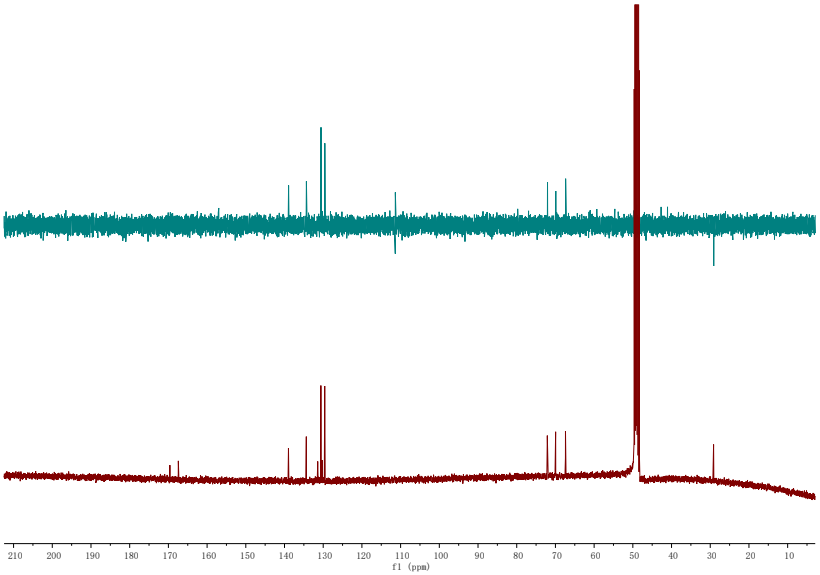


Fig. S7-6 ^{13}C-NMR and DEPT 135 spectra of compound 7

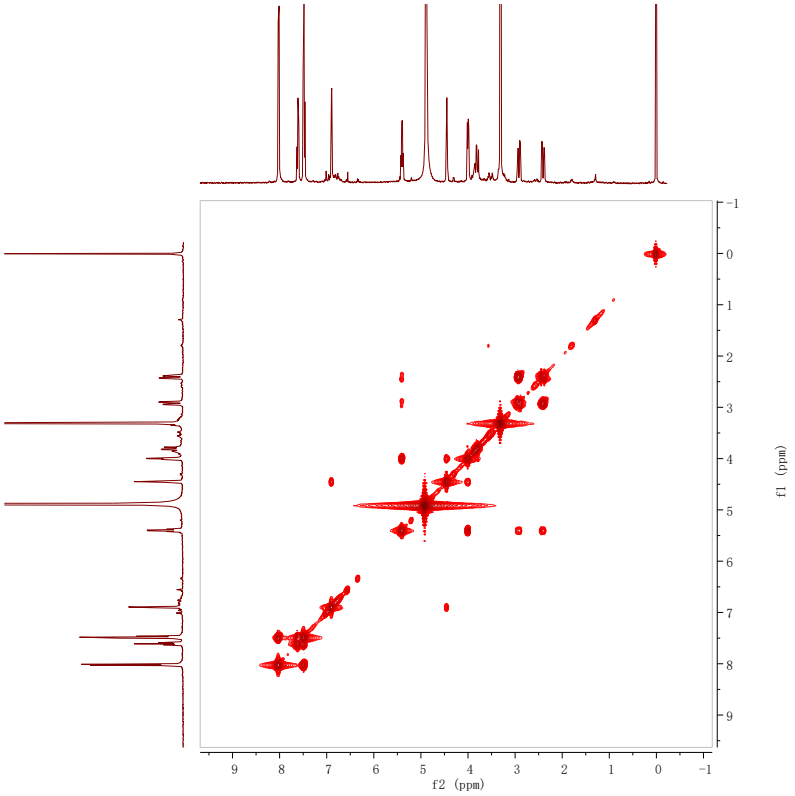


Fig. S7-7 ^{1}H-^{1}H COSY spectrum of compound 7

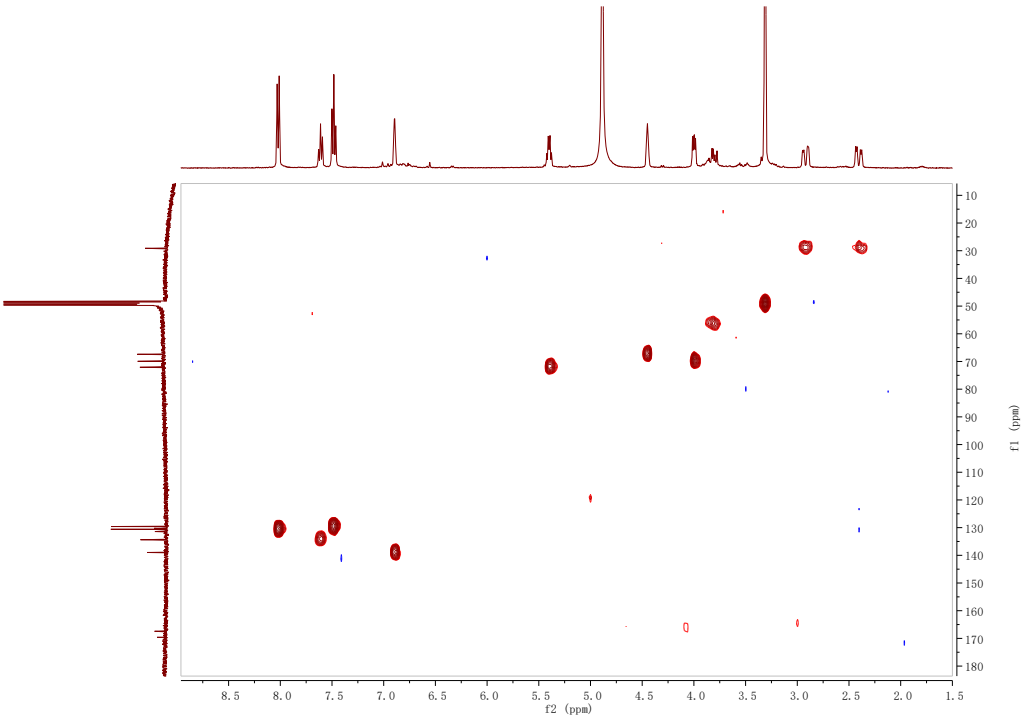


Fig. S7-8 HSQC spectrum of compound 7

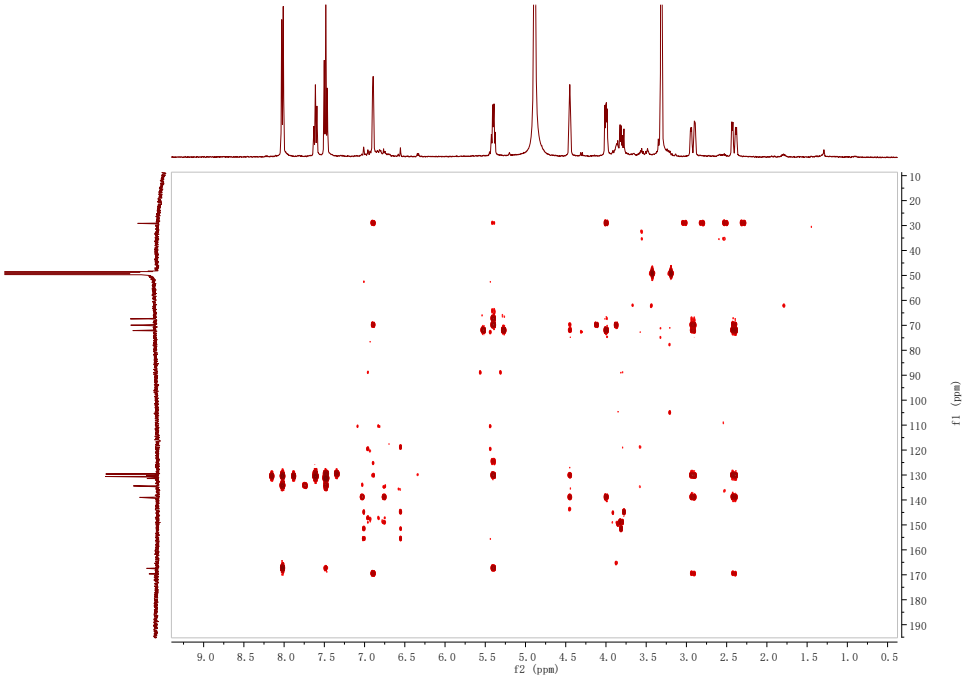


Fig. S7-9 HMBC spectrum of compound 7

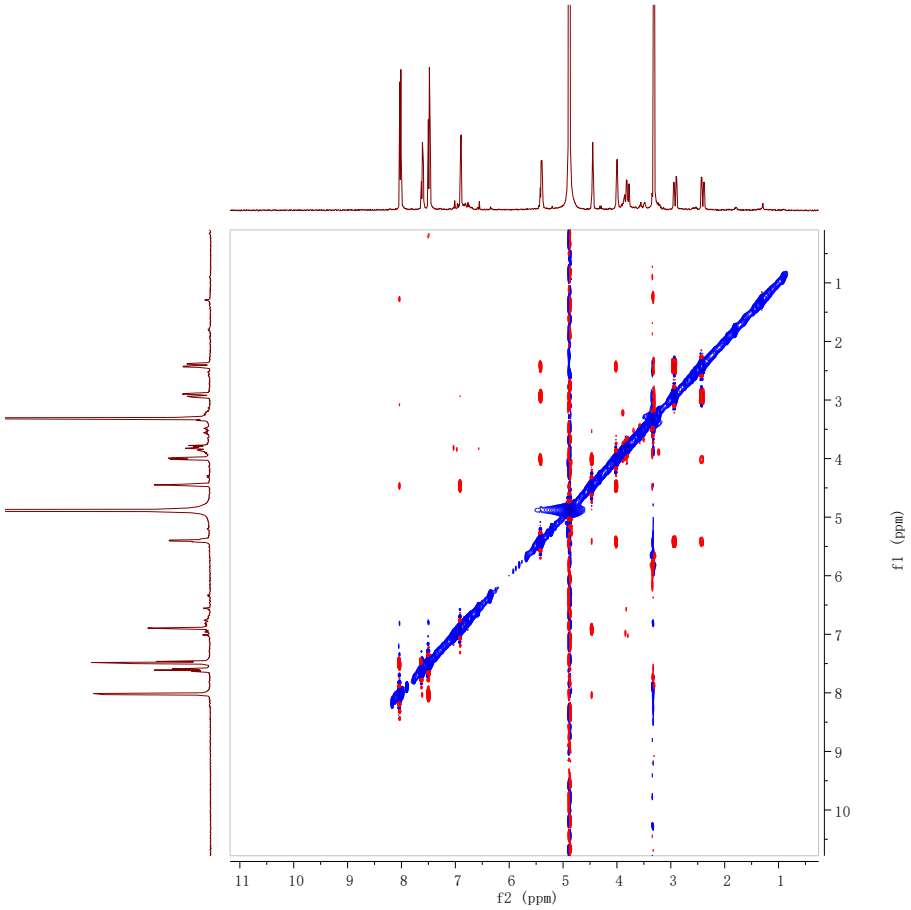


Fig. S7-10 NOESY spectrum of compound 7

8. UV, IR, HRESIMS spectra and NMR spectra of compound 8

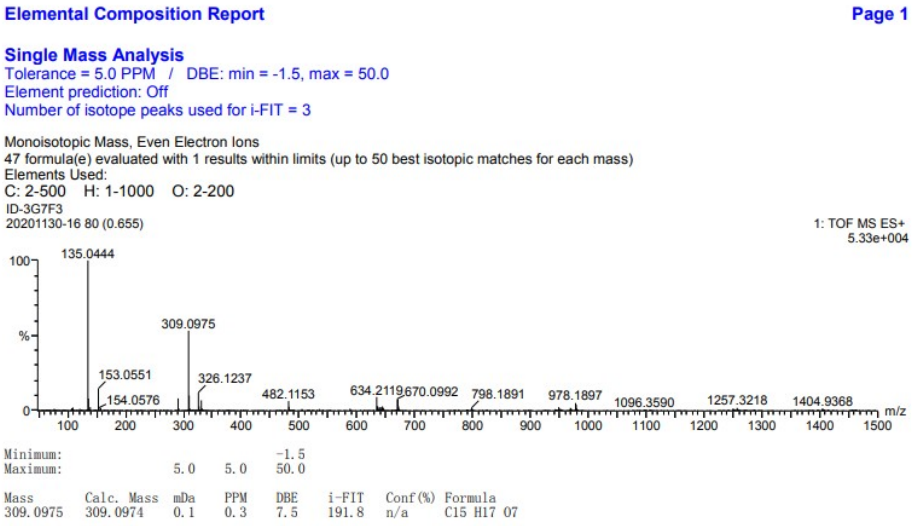


Fig. S8-1 HR-ESI-MS spectrum of compound 8

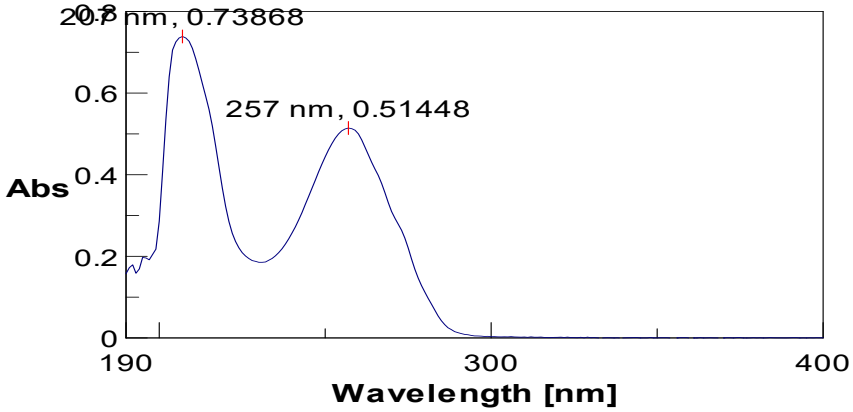


Fig. S8-2 UV spectrum of compound 8

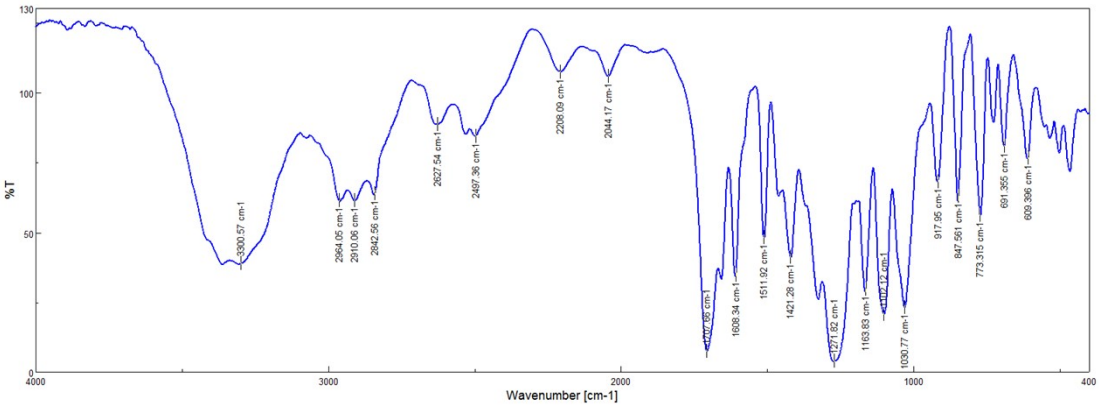


Fig. S8-3 IR spectrum of compound 8

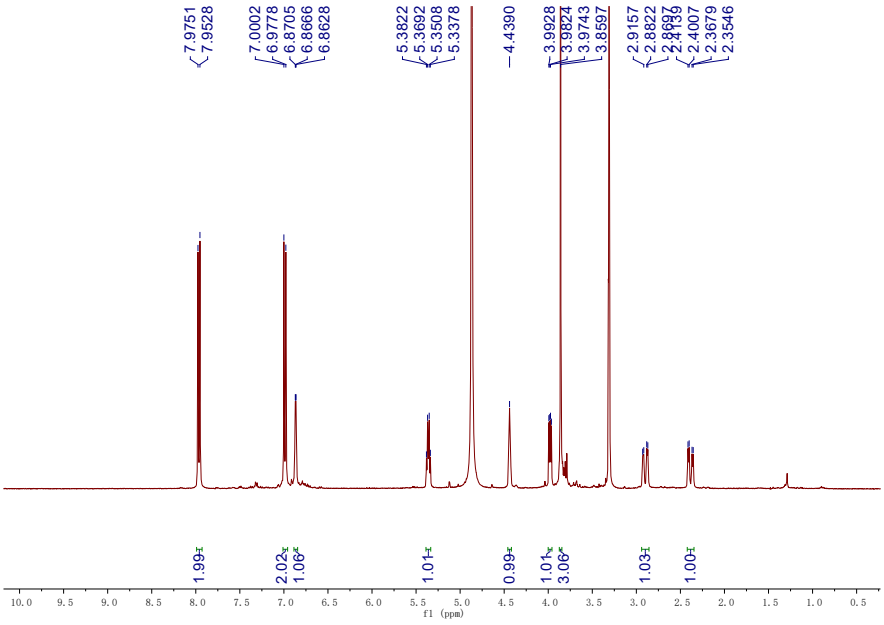


Fig. S8-4 ^{1}H NMR spectrum of compound 8

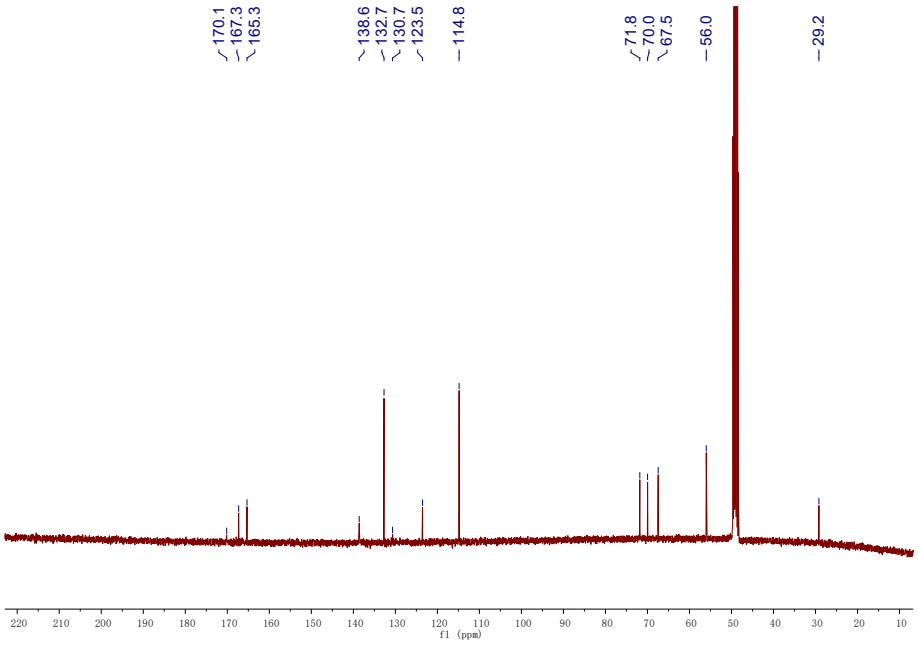


Fig. S8-5 ^{13}C NMR spectrum of compound 8

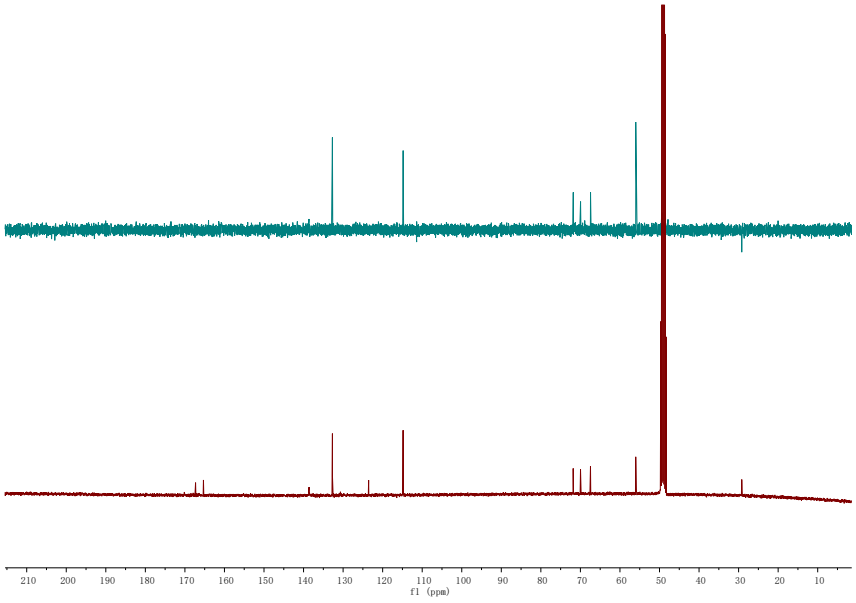


Fig. S8-6 ^{13}C-NMR and DEPT 135 spectra of compound 8

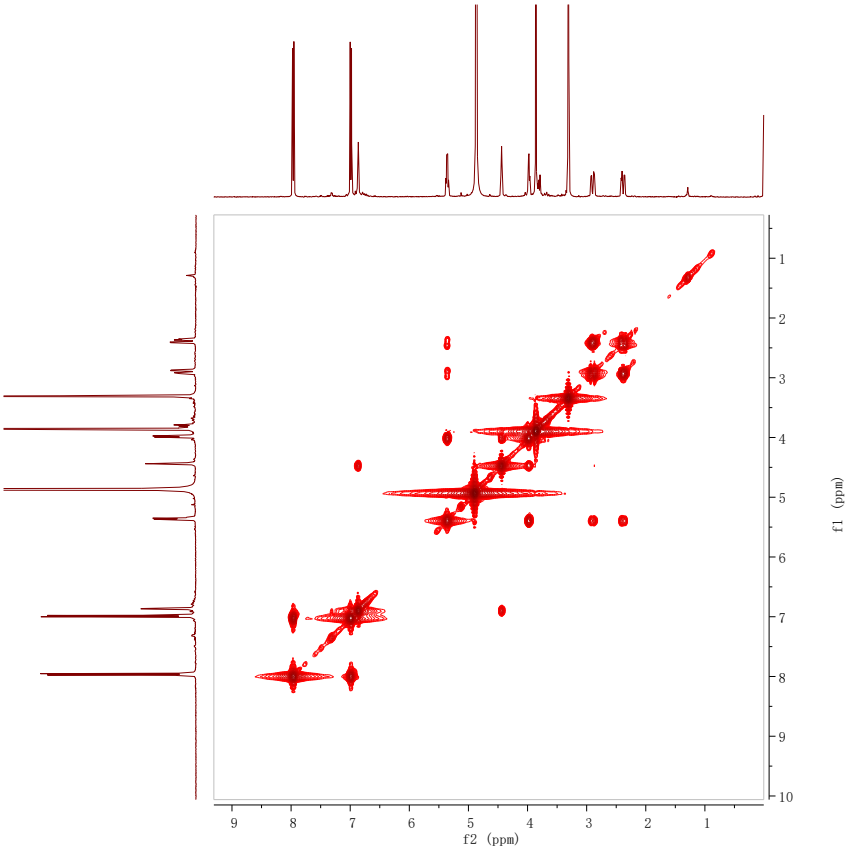


Fig. S8-7 ^{1}H-^{1}H COSY spectrum of compound 8

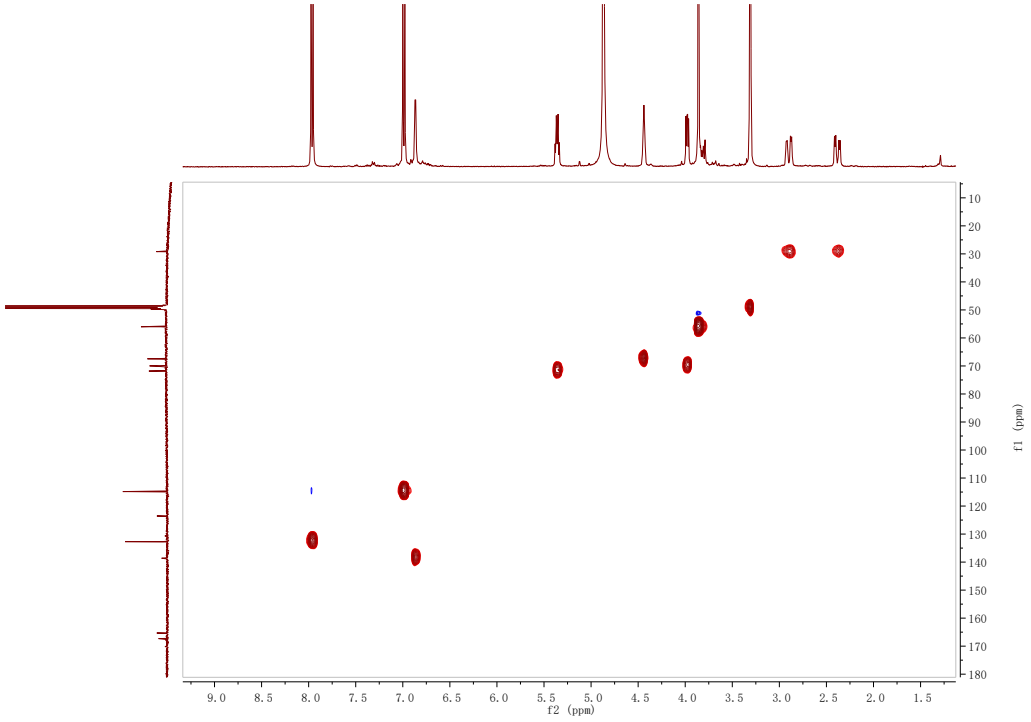


Fig. S8-8 HSQC spectrum of compound 8

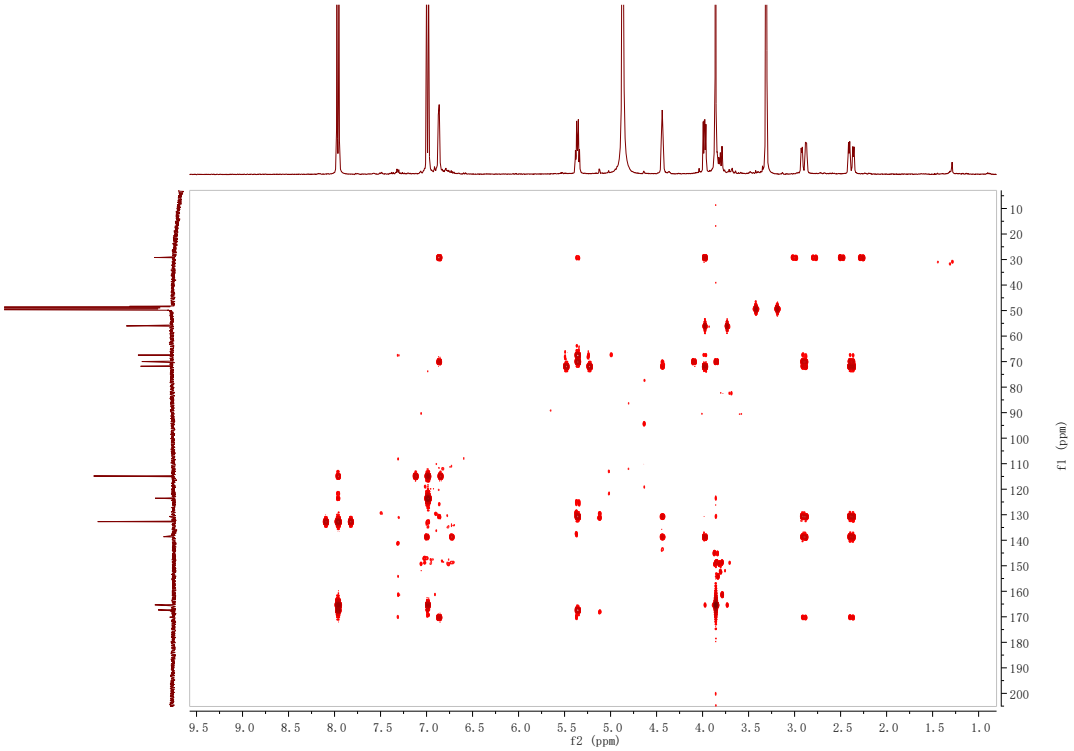


Fig. S8-9 HMBC spectrum of compound 8

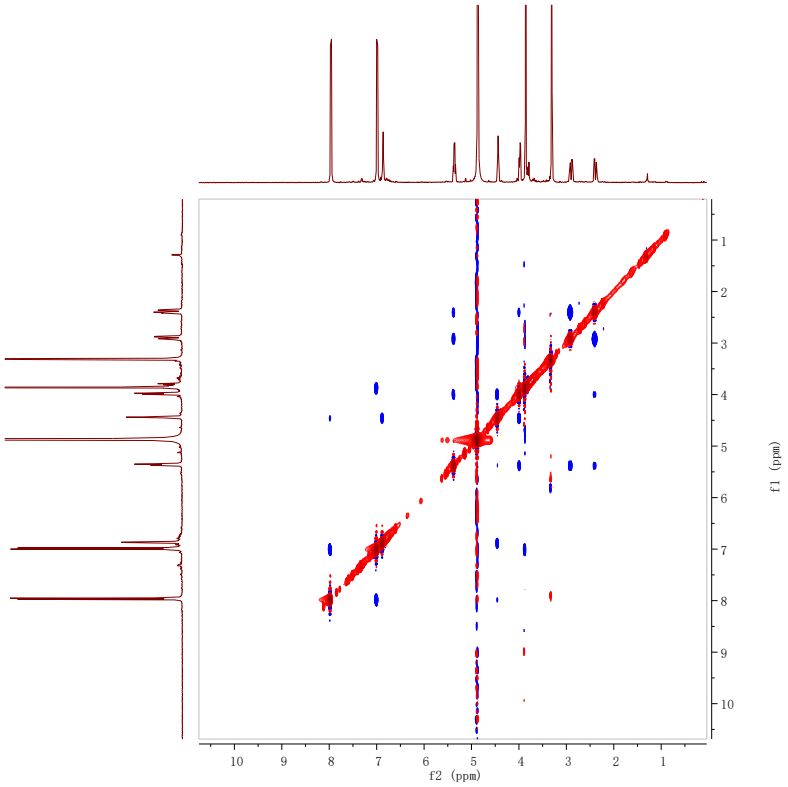


Fig. S8-10 NOESY spectrum of compound 8

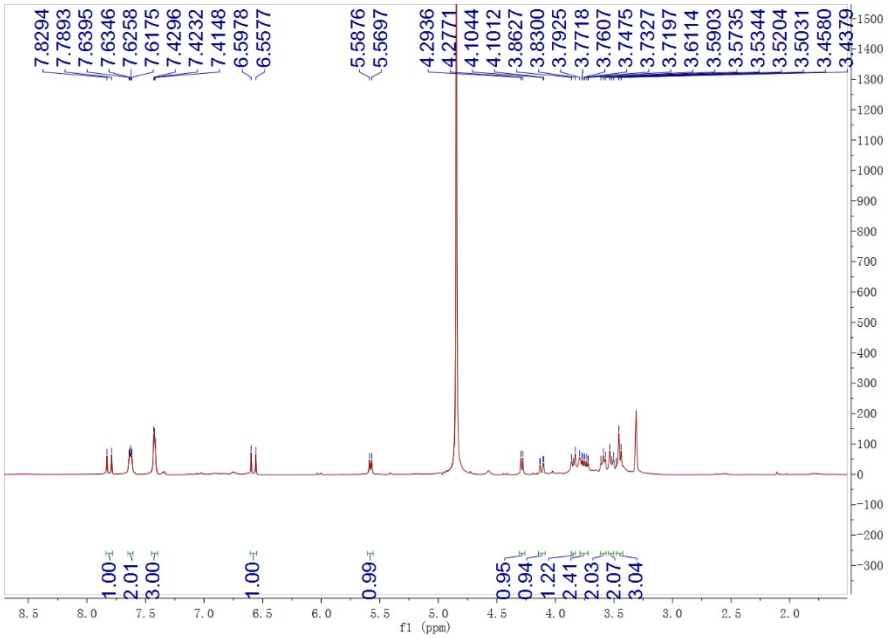


Fig. S9-1 ^{1}H NMR spectrum of compound 9

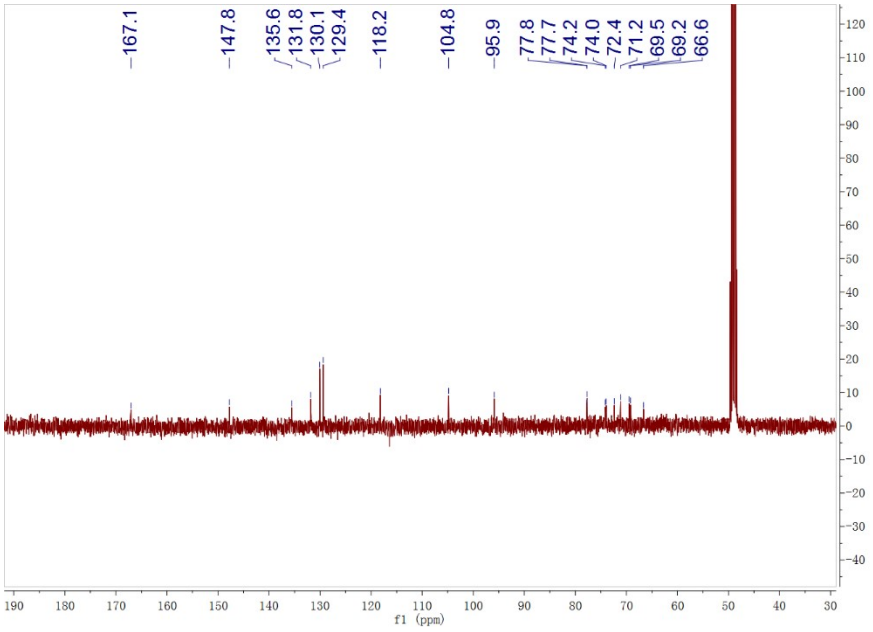


Fig. S9-2 ^{13}C NMR spectrum of compound 9

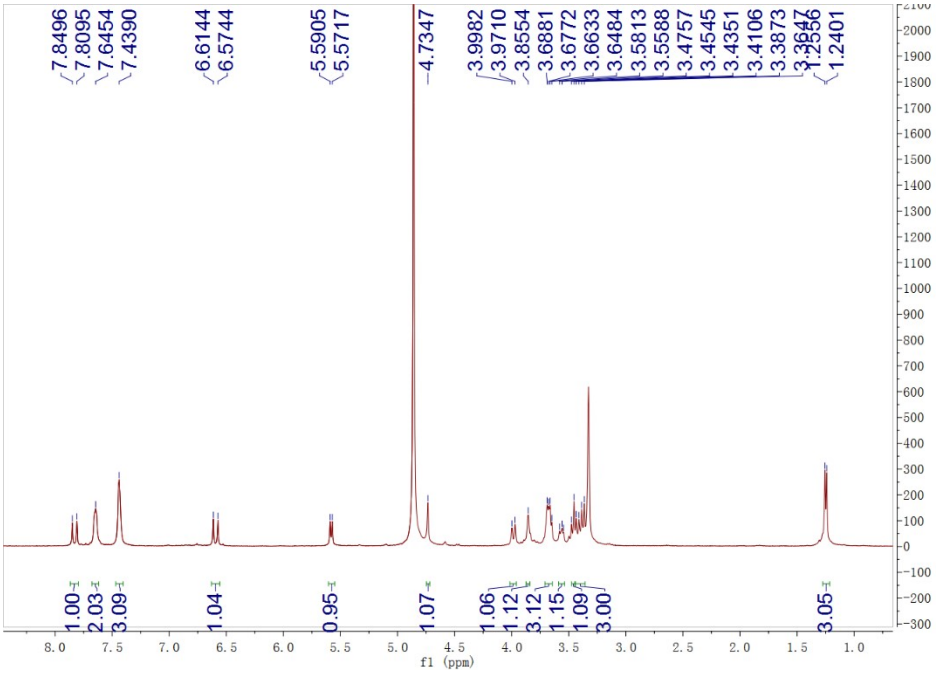


Fig. S10-1 ^{1}H NMR spectrum of compound 10

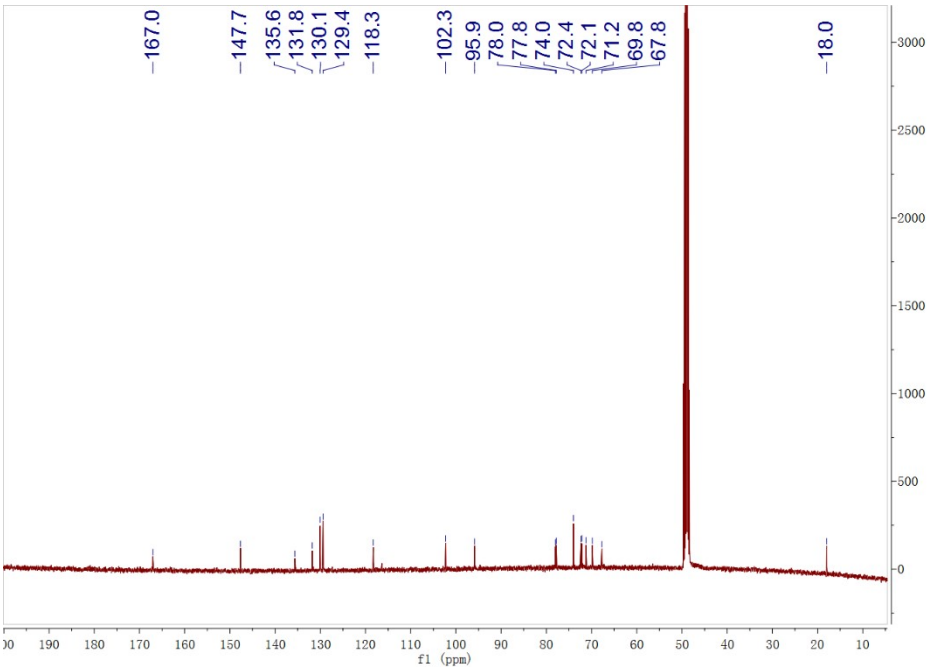


Fig. S10-2 ^{1}H NMR spectrum of compound 10

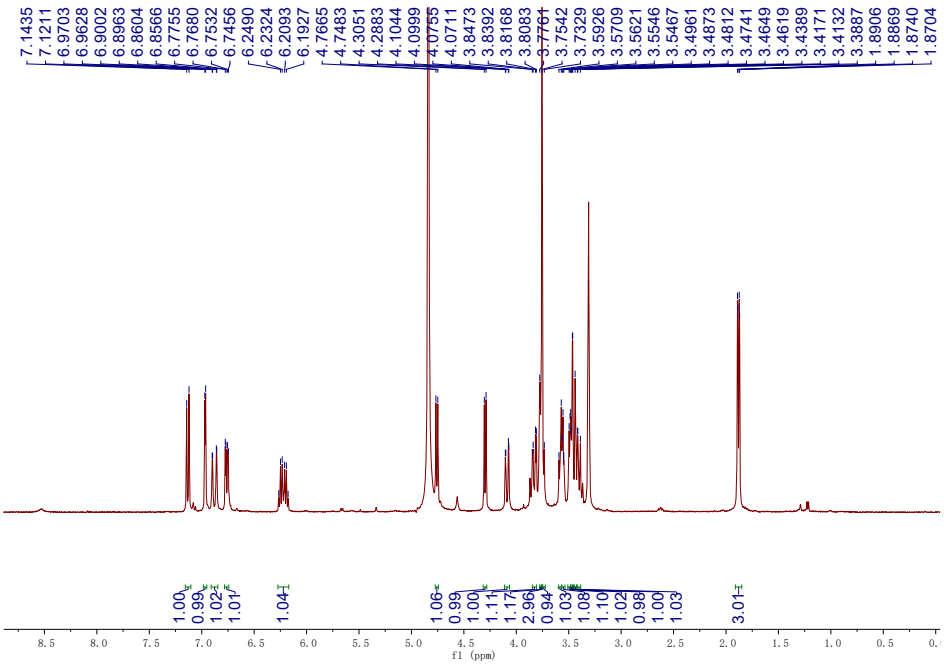


Fig. S11-1 ^{1}H NMR spectrum of compound 11

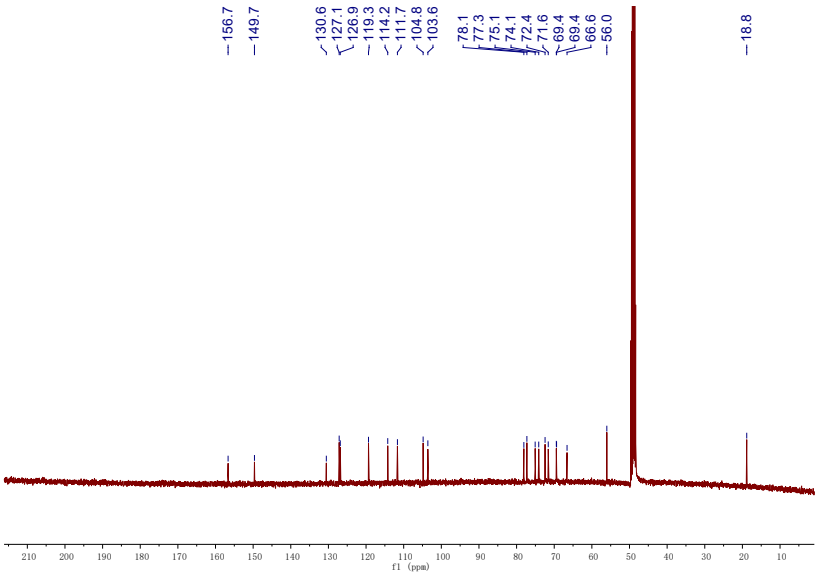


Fig. S11-2 ^{13}C NMR spectrum of compound 11

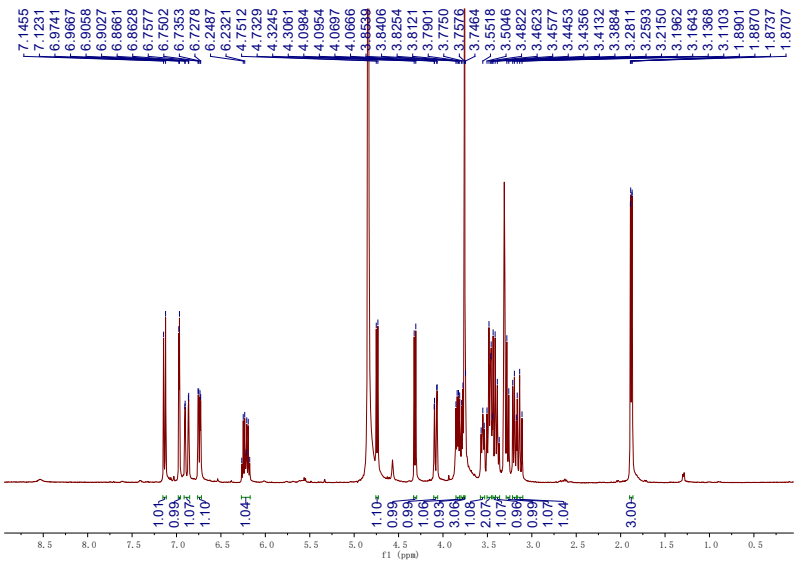


Fig. S12-1 ^{1}H NMR spectrum of compound 12

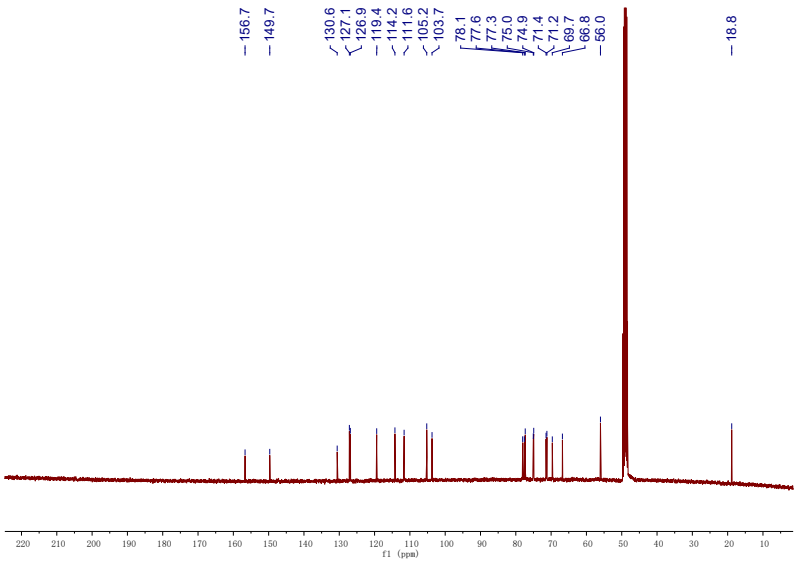


Fig. S12-2 ^{13}C NMR spectrum of compound 12

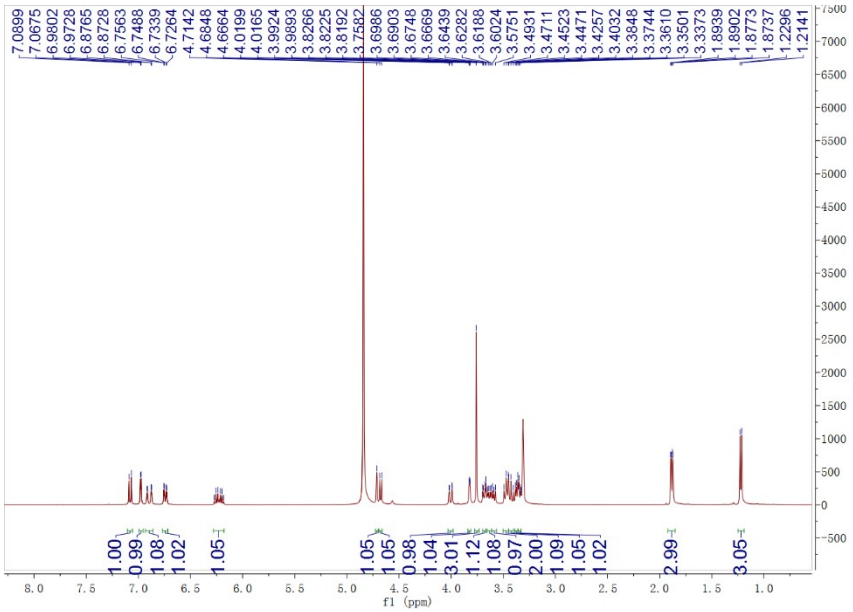


Fig. S13-1 ^{1}H NMR spectrum of compound 13

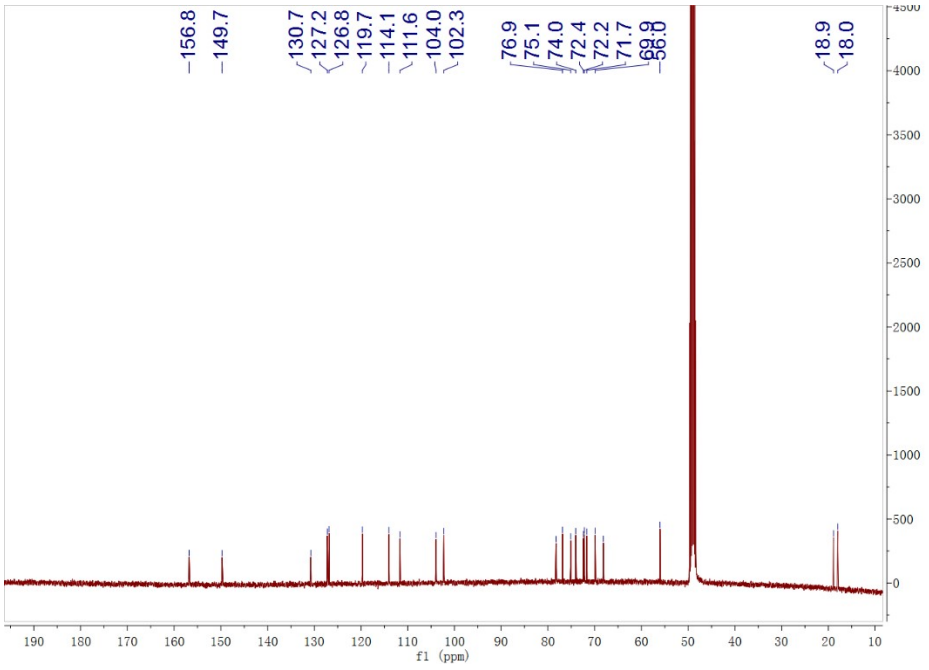


Fig. S13-2 ^{13}C NMR spectrum of compound 13

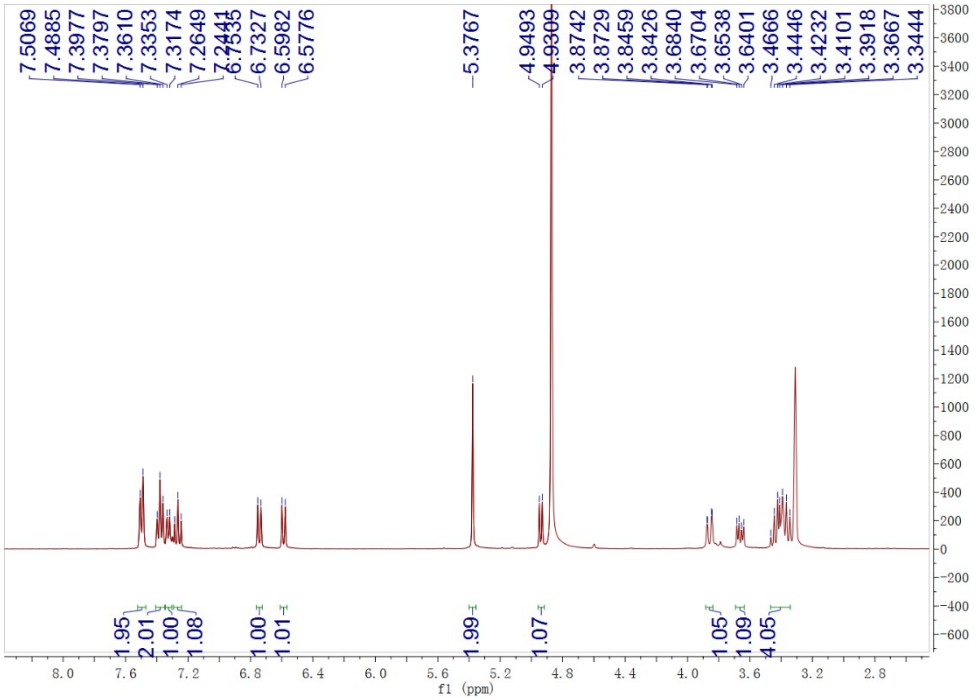


Fig. S14-1 ^{1}H NMR spectrum of compound 14

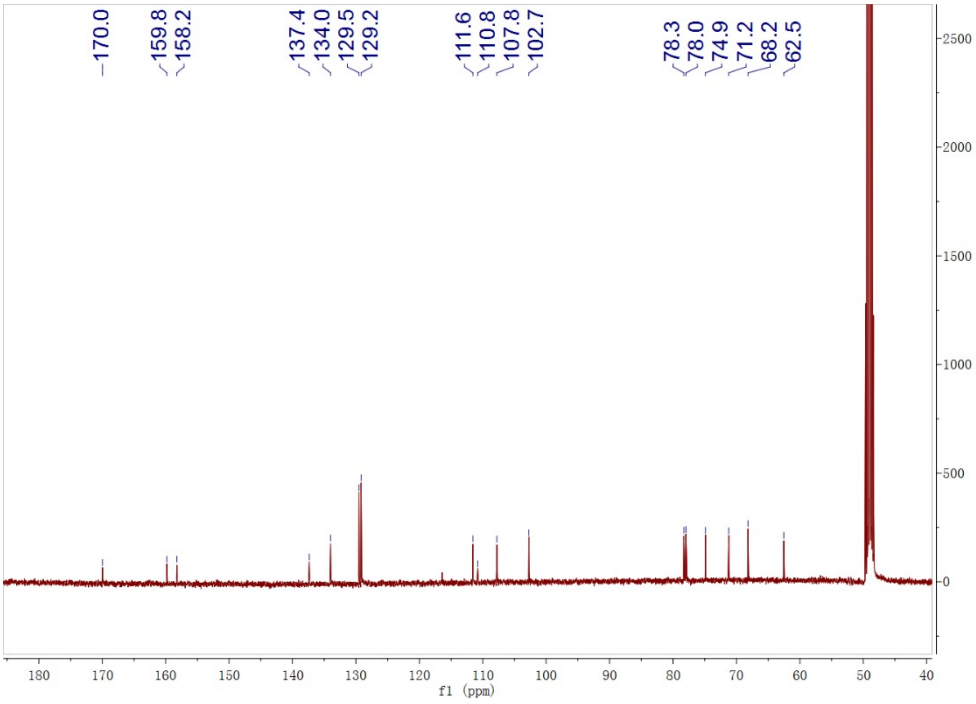


Fig. S14-2 ^{13}C NMR spectrum of compound 14

Table S1. ^{1}H and ^{13}C NMR spectral data of compounds 9, 10, and 13

Pos.	13		9		10	
	δ_C	δ_H (J in Hz)	δ_C	δ_H (J in Hz)	δ_C	δ_H (J in Hz)
1	130.7		135.6		135.6	
2	149.7		129.4	7.63	129.4	7.65
3	111.6	6.98, d (3.0)	130.1	7.42	130.1	7.44

4	156.8		131.8	7.42	131.8	7.44
5	114.1	6.74, dd (9.0, 3.0)	130.1	7.42	130.1	7.44
6	119.7	7.08, d (9.0)	129.4	7.63	129.4	7.65
7	126.8	6.89, dd (16.0, 1.5)	147.8	7.81, d (16.0)	147.7	7.83, d (16.0)
8	127.2	6.23, dq (13.3, 6.6)	118.2	6.58, d (16.0)	118.3	6.59, d (16.0)
9	18.9	1.88, dd (6.6, 1.4)	167.1		167.0	
1′	104.0	4.68, d (7.4)	95.9	5.58, d (7.2)	95.9	5.58, d (7.5)
2′	75.1	3.47	74.0	3.44	74.0	3.40
3′	78.3	3.43, t (8.8)	77.8	3.46	78.0	3.47
4′	71.7	3.34	71.2	3.44	71.2	3.40
5′	76.9	3.47	77.7	3.59	77.8	3.56
6′	68.2	4.0, dd (11.0, 1.3) 3.59	69.2	4.12, dd (11.0, 1.3) 3.75	67.8	3.98, d (10.9) 3.67
1″	102.3	4.71, brs	104.8	4.29, d (6.6)	102.3	4.73, brs
2″	72.4	3.68, dd (9.5, 3.3)	72.4	3.59	72.4	3.67
3″	72.2	3.82	74.2	3.52	72.1	3.86
4″	74.0	3.37	69.5	3.75	74.0	3.40
5″	69.9	3.64, dd (9.8, 3.5)	66.6	3.85, 3.52	69.8	3.67
6″	18.0	1.22, d (6.2)			18.0	1.25, d (6.2)
4-OCH$_3$	56.0	3.76, s				

Measured at 400 MHz for ^{1}H and 100 MHz for ^{13}C in CD_3OD

Multiplets and or overlapped signals are reported without designating multiplicity

Table S2. ^{1}H and ^{13}C NMR spectral data of compounds 11-12

Pos.	**11**		**12**	
	δ_C	**δ_H (*J* in Hz)**	**δ_C**	**δ_H (*J* in Hz)**
1	130.6		130.6	
2	149.7		149.7	
3	111.7	6.97, d (3.0)	111.6	6.97, d (3.0)
4	156.7		156.7	
5	114.2	6.76, dd (9.0, 3.0)	114.2	6.74, dd (9.0, 3.0)
6	119.3	7.13, d (9.0)	119.4	7.13, d (9.0)
7	126.9	6.88, dd (15.9, 1.5)	126.9	6.88, dd (15.9, 1.3)
8	127.1	6.22, dq (13.3, 6.6)	127.1	6.22, dq (13.3, 6.6)
9	18.8	1.88, dd (6.6, 1.5)	18.8	1.88, dd (6.6, 1.3)
1′	103.6	4.76, d (7.3)	103.7	4.74, d (7.4)
2′	75.1	3.49	74.9	3.44
3′	78.1	3.44	78.1	3.44
4′	71.6	3.41	71.4	3.44
5′	77.3	3.55	77.3	3.55
6′	69.4	4.09, dd (11.5, 1.8) 3.73	69.7	4.08, dd (11.5, 1.2) 3.78, d (6.1)
1″	104.9	4.30, d (6.7)	105.2	4.32, d (7.4)

2″	72.4	3.58	77.6	3.27, d (8.7)
3″	74.1	3.49	75.0	3.20
4″	69.4	3.78	71.2	3.44
5″	66.6	3.83, dd (12.3, 3.3) 3.46	66.8	3.83, dd (11.4, 5.3) 3.14
4-OCH$_3$	56.0	3.75, s	56.0	3.76, s

Measured at 400 MHz for ^{1}H and 100 MHz for ^{13}C in CD_3OD

Multiplets and or overlapped signals are reported without designating multiplicity

Table S3. ^{1}H and ^{13}C NMR spectral data of compound 14

Pos.	14		Pos.	14	
	δ_C	δ_H (*J* in Hz)		δ_C	δ_H (*J* in Hz)
1	170.0		**4′**	129.5	7.38, t (7.3)
2	110.8		**5′**	129.2	7.33, d (7.2)
3	158.2		**6′**	129.5	7.38, t (7.3)
4	107.8	6.74, d (8.3)	**7′**	129.2	7.50, t (7.4)
5	134.0	7.26, t (8.3)	**1″**	102.7	4.94, d (7.4)
6	111.6	6.59, t (8.3)	**2″**	74.9	3.41
7	159.8		**3″**	78.0	3.41
1′	68.2	5.38, s	**4″**	71.2	3.41
2′	137.4		**5″**	78.3	3.41
3′	129.2	7.50, t (7.4)	**6″**	62.5	3.86, dd (11.7, 0.9) 3.66, dd (12.1, 5.4)

Measured at 400 MHz for ^{1}H and 100 MHz for ^{13}C in CD_3OD

Multiplets and or overlapped signals are reported without designating multiplicity