Electronic supplementary information (ESI)

Eremophilane and cadinane sesquiterpenoids from the fruits of *Alpinia oxyphylla* and their anti-inflammatory activities

Jie Dong, ‡[a] Mi Zhou, [a, d] Da-bo Pan, [c] Qian-yu Qin, [a] Ting Li, [a] Xin-sheng Yao, [a] Hai-bo Li, *[b] and Yang Yu *[a]

[a] *Institute of Traditional Chinese Medicine & Natural Products, College of Pharmacy; International Cooperative Laboratory of Traditional Chinese Medicine Modernization and Innovative Drug Development of Ministry of Education (MOE) of China; and Guangdong Province Key Laboratory of Pharmacodynamic Constituents of TCM and New Drugs Research, Jinan University, Guangzhou 510632, China*

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

[c] *Department of Medical Technology, Qiandongnan Vocational and Technical College for Nationalities, Kaili 556000, China*

[d] *Shenzhen institute for drug control (shenzhen testing center ofmedical devices) Shenzhen 518057, China*

[*] Corresponding authors:

Dr. Yang Yu, College of Pharmacy, Jinan University, 601 Huangpu Avenue, Guangzhou 510632, PR China. Tel. +86-20-85225849. E-mail: 1018yuyang@163.com

Dr. Hai-bo Li, Kanion Pharmaceutical Co. Ltd., Lianyungang 222001, PR China. Tel. +86-0518-81152371. E-mail: lihaibo1985124@sina.com

Contents

S1. Physical constants and spectral data of 1-6, 23-24, 26-29

alpinoxyphllaone C (**1**): yellow oil; $[\alpha]_D^{27}$ +18.8 (0.5, $CHCl_3$); HR-ESI-MS (positive) *m/z* 237.1855 $[M + H]^+$ (calcd for $C_{15}H_{25}O_2^+$, 237.1855); UV (MeOH) λ_{max} (log ε): 201 (3.26) nm; IR (KBr) ν_{max} 3438, 2934, 1716, 1643, 1401, 1385, 1073, 890 cm^{-1}; ^1H and ^{13}C-NMR spectroscopic data, see **Table 1**.

(3*S*,4*S*,5*R*,7*R*)-eremophila-3,4-epoxy-1(10),11-dien-2-one (**2**): colorless crystals; $[\alpha]_D^{27}$ -124.1 (0.5, $CHCl_3$); HR-ESI-MS (positive) *m/z* 233.1540 $[M + H]^+$ (calcd for $C_{15}H_{21}O_2^+$, 233.1542); UV (MeOH) λ_{max} (log ε): 245 (3.69) nm; IR (KBr) ν_{max} 2961, 2931, 1671, 1641, 1626, 1451, 1401, 1384, 1314, 1107, 905, 875, 828, 664, 547, 481 cm^{-1}; ^1H and ^{13}C-NMR spectroscopic data, see **Table 1**.

Crystal Data for **2**. $C_{15}H_{20}O_2$ (*M* = 232.31 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), *a* = 9.12559(16) Å, *b* = 9.43073(17) Å, *c* = 14.8426(3) Å, *V* = 1277.37(4) $Å^3$, *Z* = 4, *T* = 170.0(2) K, μ(CuKα) = 0.617 mm^{-1}, *Dcalc* = 1.208 g/cm^3, 10537 reflections measured (11.116° ≤2Θ ≤ 147.726°), 2556 unique (R_{int} = 0.0442, R_{sigma} = 0.0279) which were used in all calculations. The final R_1 = 0.0323 (I > 2σ(I)), wR_2 = 0.0872 (all data), CCDC number: 2217170.

(3*R*,4*R*,5*R*,7*R*)-eremophila-3,4-epoxy-1(10),11-dien-2-one (**3**): colorless oil; $[\alpha]_D^{27}$ +105.8 (0.5, $CHCl_3$); HR-ESI-MS (positive) *m/z* 233.1540 $[M + H]^+$ (calcd for $C_{15}H_{21}O_2^+$, 233.1542); UV (MeOH) λ_{max} (log ε): 202 (3.69), 242 (3.71) nm; IR (KBr) ν_{max} 2935, 1673, 1437, 1400, 1385, 1302, 1206, 1073, 890, 538 cm^{-1}; ^1H and ^{13}C-NMR spectroscopic data, see **Table 1**.

(4*R*,5*S*,7*S*,9*R*)-eremophila-1(10),11-dien-9-ol (**4**): colorless oil; $[\alpha]_D^{27}$ +53.0 (0.5, $CHCl_3$); HR-ESI-MS (positive) *m/z* 203.1810 $[M + H - H_2O]^+$ (calcd for $C_{15}H_{23}^+$, 203.1800); UV (MeOH) λ_{max} (log ε): 203 (3.52) nm; IR (KBr) ν_{max} 3424, 2927, 2363, 1642, 1441, 1400, 1384, 1051, 887, 472 cm^{-1}; ^1H and ^{13}C-NMR spectroscopic data, see **Table 1**.

(2*R*,4*R*,5*S*,7*S*,9*R*)-eremophila-1(10),11-dien-2,9-diol (**5**): colorless crystals; $[\alpha]_D^{21}$ +115.2 (0.5, $CHCl_3$); HR-ESI-MS (positive) *m/z* 237.1859 $[M + H]^+$ (calcd for $C_{15}H_{25}O_2^+$, 237.1855); UV (MeOH)

λ_{max} nm (log ε): 204 (2.46), 234 (1.45); IR (KBr) ν_{max} 3323, 2928, 1647, 1441, 1375, 1284, 1052, 1007, 885, 682 cm^{-1}; ^{1}H and ^{13}C-NMR spectroscopic data, see **Table 1**.

Crystal Data for **5**. $C_{15}H_{24}O_2$ (*M* =236.34 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), *a* = 8.155(1) Å, *b* = 20.429(2) Å, *c* = 27.192(3) Å, *V* = 4530.3(7) $Å^3$, *Z* = 4, *T* = 149.99(10) K, μ(Cu Kα) = 1.54184 mm^{-1}, *Dcalc* = 1.087 g/cm^3, 12357 reflections measured ($5.41° \leq 2\Theta \leq 147.374°$), 7861 unique ($R_{int}$ = 0.0727, R_{sigma} = 0.1223) which were used in all calculations. The final R_1 = 0.0731 ($I > 2\sigma(I)$) and wR_2 = 0.1626 (all data), CCDC number: 2221275.

Table S1 Hydrogen Bond Interactions in Compound 5

D-H	d (D-H)	d (H..A)	<DHA	d (D..A)	A
O1C-H1C	0.99(8)	1.74(8)	174(9)	2.732(5)	O2C [x-1, y, z]
O1A-H1A	0.97(5)	1.75(5)	174(10)	2.711(5)	O2A [x-1, y, z]
O2A-H2A	0.91(10)	1.87(11)	152(10)	2.706(6)	O1B
O2C-H2C	0.91(10)	1.89(10)	174(11)	2.799(6)	O2B [-x+2, y+1/2, -z+3/2]
O1B-H1B	1.03(12)	1.71(13)	171(11)	2.727(6)	O1C
O2B-H2B	1.04(11)	1.70(11)	176(10)	2.735(7)	O1M [-x+1, y-1/2, -z+3/2]
O1M-H1M	0.96(6)	1.75(5)	161(11)	2.676(7)	O1A

(1*R*,2*R*,4*R*,5*S*,7*R*)-eremophila-9,11-dien-1,2-diol (**6**): yellow amorphous solid;$[\alpha]_D^{26}$ -46.4 (0.5, $CHCl_3$); HR-ESI-MS (positive) *m/z* 259.1677 $[M + Na]^+$ (calcd for $C_{15}H_{24}O_2Na^+$, 259.1674); UV (MeOH) λ_{max} nm (log *ε*): 204 (3.01); IR (KBr) ν_{max} 3339, 2962, 2925, 1639, 1447, 1374, 1071, 1006, 889cm^{-1}; ^{1}H and ^{13}C-NMR spectroscopic data, see **Table 1**.

oxyphyllone J (**23**): yellow oil; $[\alpha]_D^{27}$ +16.8 (0.5, $CHCl_3$)。 HR-ESI-MS (positive) *m/z* 235.1338 $[M+H]^+$ (calcd for $C_{14}H_{19}O_3$, 235.1334); UV (MeOH) λ_{max} (log *ε*): 208 (4.08), 237 (3.90), 274 (3.90) nm; IR (KBr) ν_{max} 2961, 2872, 1636, 1470, 1385, 1354, 1259, 1218, 1185, 1124, 1058, 1008, 938, 907, 872, 846, 810, 616, 549 cm^{-1}; ^{1}H and ^{13}C-NMR spectroscopic data, see **Table 2**.

oxyphyllone H (**24**): yellow oil; $[\alpha]_D^{30}$ +197.5 (0.5, $CHCl_3$); HR-ESI-MS (positive) *m/z* 237.1499 $[M+H]^+$ (calcd for $C_{14}H_{21}O_3^+$, 237.1491); UV (MeOH) λ_{max} nm (log *ε*): 202 (3.64), 265 (4.07); IR

(KBr) ν_{max} 3498, 2963, 2872, 1680, 1457, 1372, 1158, 979, 856cm^{-1}; ^{1}H and ^{13}C-NMR spectroscopic data, see **Table 2**.

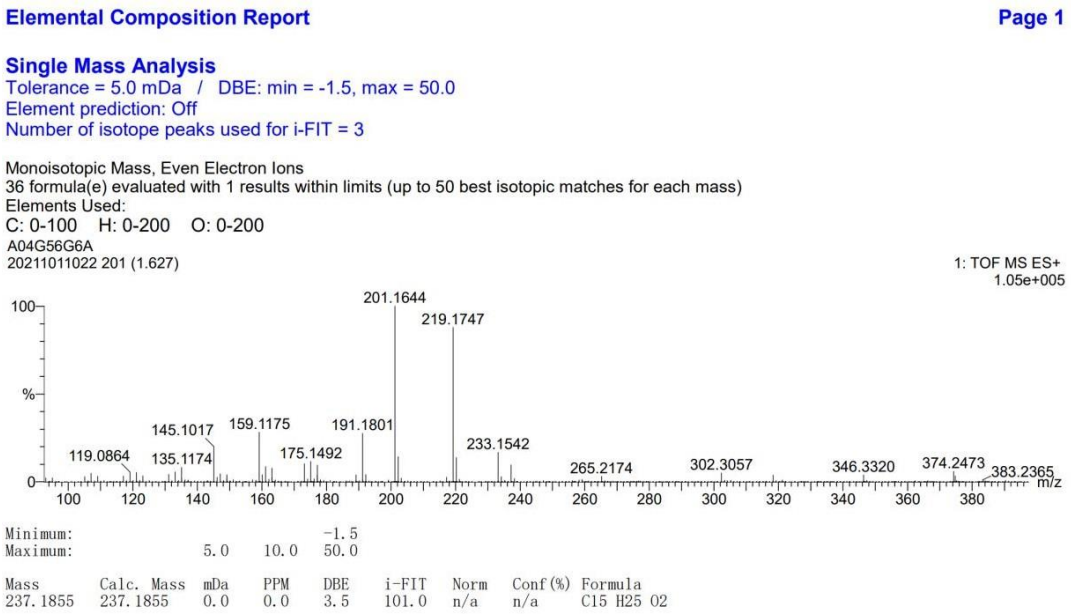
oxyphyllone K (**26**): yellow oil; HR-ESI-MS (positive) *m/z* 237.0883 $[M+Na]^+$ (calcd for $C_{14}H_{14}O_2Na$, 237.0891); UV (MeOH) λ_{max} (log ε): 207 (4.33), 230 (4.12), 256 (4.23) nm; IR (KBr) ν_{max} 3438, 2967, 2929, 1694, 1655, 1605, 1590, 1560, 1465, 1400, 1384, 1286, 1255, 1082, 880, 799, 519 cm^{-1}; ^{1}H and ^{13}C-NMR spectroscopic data, see **Table 2**.

oxyphyllone I (**27**): brown gelatinous; $[\alpha]_D^{26}$ -8.2 (0.5, $CHCl_3$); HR-ESI-MS (positive) *m/z* 233.1540 $[M+H]^+$ (calcd for $C_{15}H_{21}O_2^+$, 233.1542); UV (MeOH) λ_{max} nm (log ε): 208 (4.04), 260 (3.84); IR (KBr) ν_{max} 2930, 1676, 1606, 1450, 1386, 1283, 1053, 824cm^{-1}; ^{1}H and ^{13}C-NMR spectroscopic data, see **Table 2**.

oxyspirone A (**28**): light yellow colloid; $[\alpha]_D^{25}$ -12.0 (0.35, $CHCl_3$); HR-ESI-MS (positive) *m/z* 259.1660 $[M+Na]^+$ (calcd for $C_{15}H_{24}O_2Na^+$, 259.1674); UV (MeOH) λ_{max} nm (log ε): 203 (2.14), 237 (2.24); IR (KBr) ν_{max} 3436, 2928, 2862, 1699, 1456, 1381, 1041cm^{-1}; ^{1}H and ^{13}C-NMR spectroscopic data, see **Table 2**.

oxyspirone B (**29**): light yellow oil; $[\alpha]_D^{25}$ +6.5 (0.7, $CHCl_3$); HR-ESI-MS (positive) *m/z* 261.1790 $[M+Na]^+$ (calcd for $C_{15}H_{26}O_2Na^+$, 261.1831); UV (MeOH) λ_{max} nm (log ε): 204 (3.39); IR (KBr) ν_{max} 3470, 2943, 2873, 1641, 1455, 1377, 1055, 887, 541cm^{-1}; ^{1}H and ^{13}C-NMR spectroscopic data, see **Table 2**.

S2. Selected spectra for compounds 1-6, 23-24, 26-29



Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
36 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-200 O: 0-200
A04G56G6A
20211011022 201 (1.627)

1: TOF MS ES+
1.05e+005

Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
237.1855	237.1855	0.0	0.0	3.5	101.0	n/a	n/a	C15 H25 O2

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

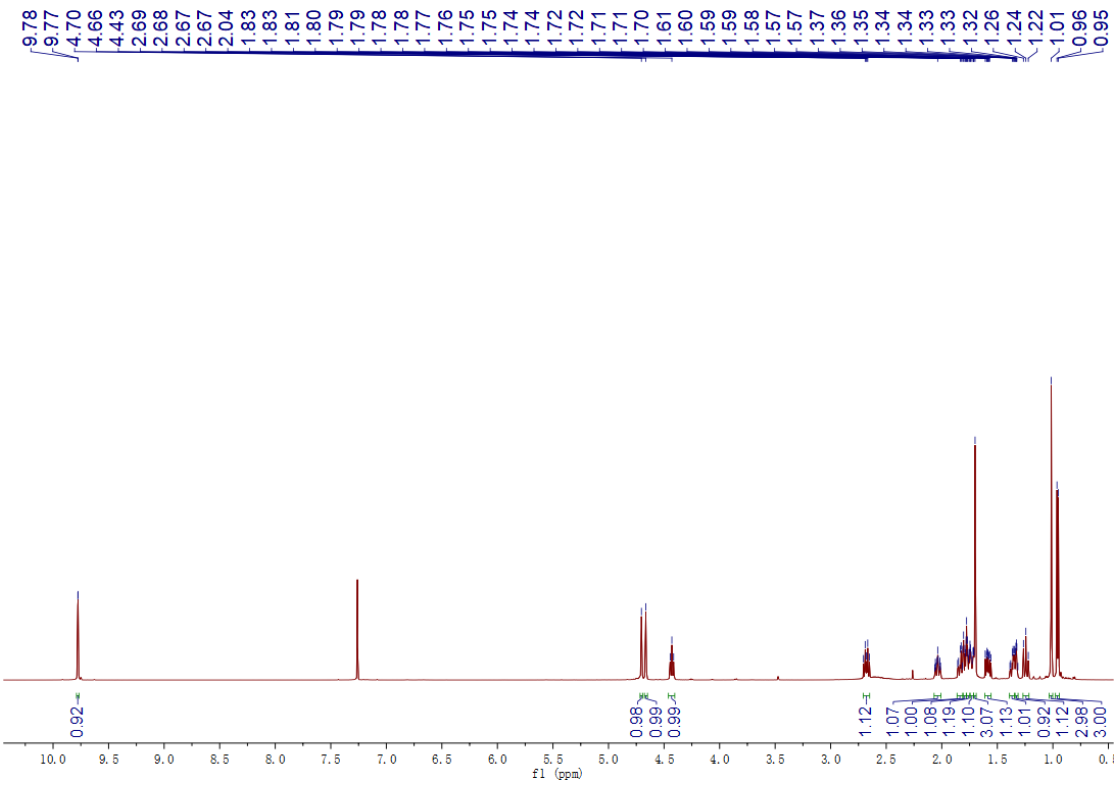


Fig. S2 ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 1

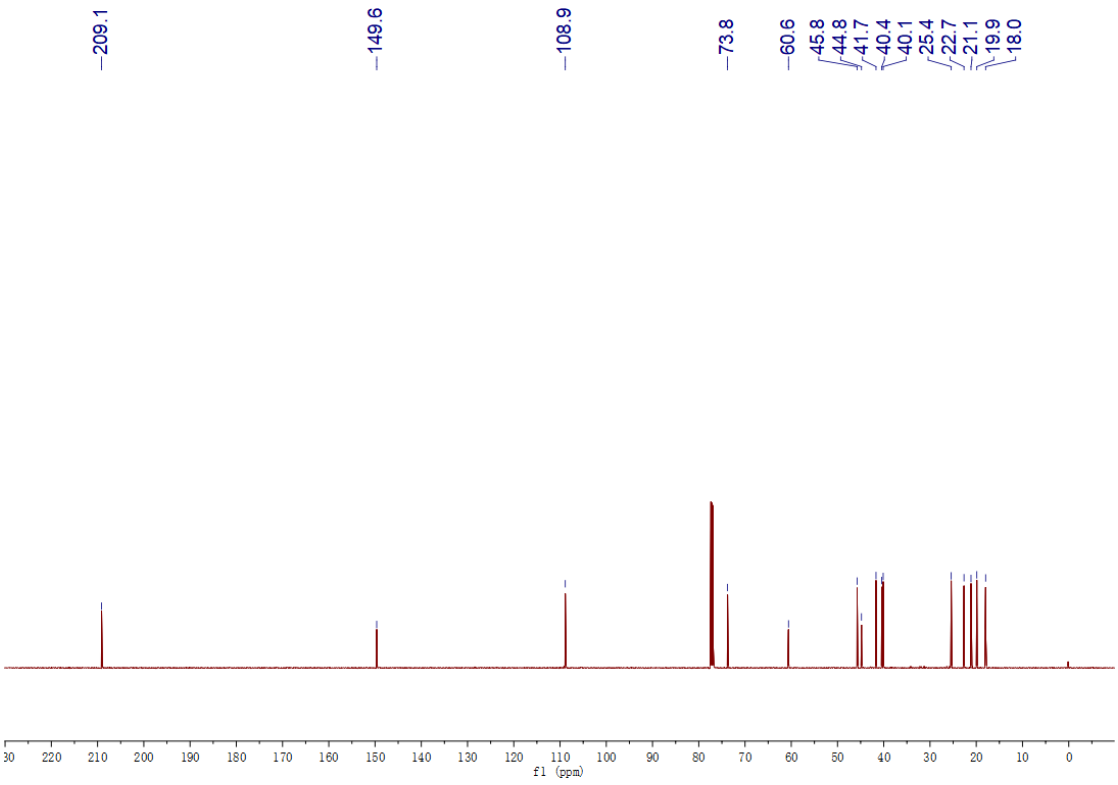


Fig. S3 ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of compound 1

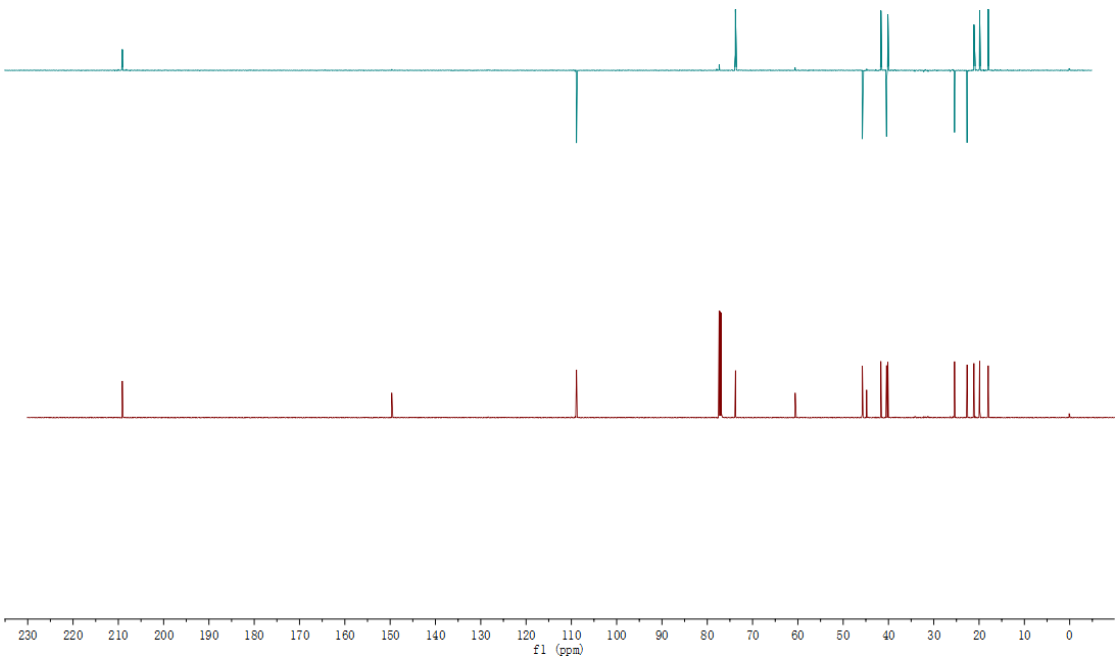


Fig. S4 DEPT (150 MHz, $CDCl_3$) and ^{13}C NMR spectra of compound 1

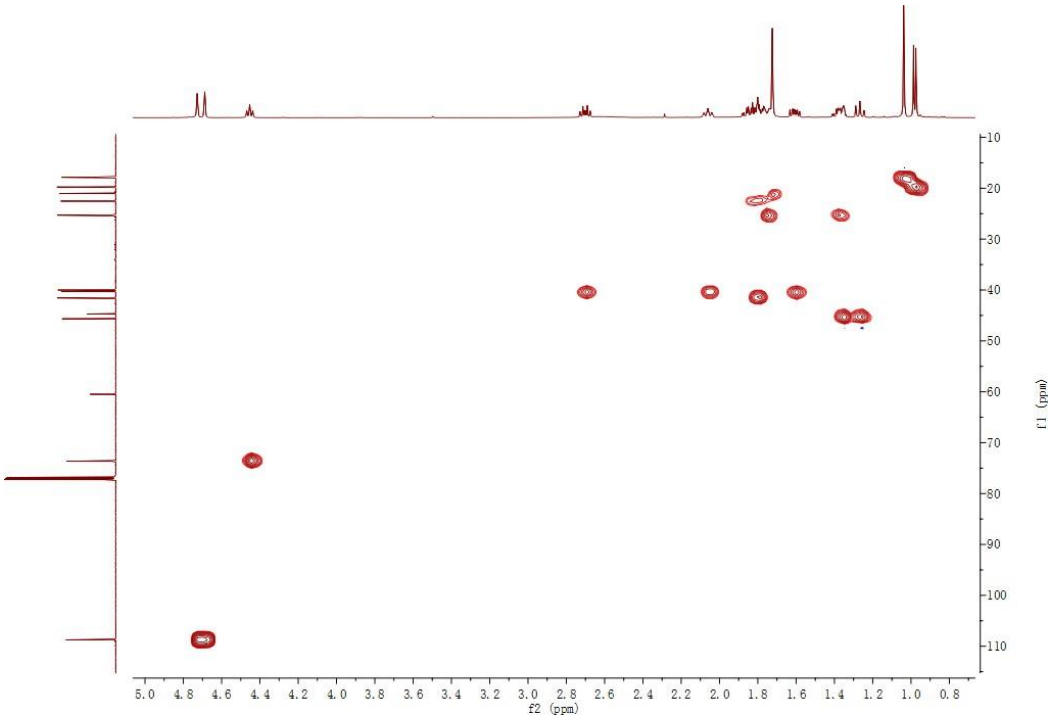


Fig. S5 HSQC spectrum of compound 1

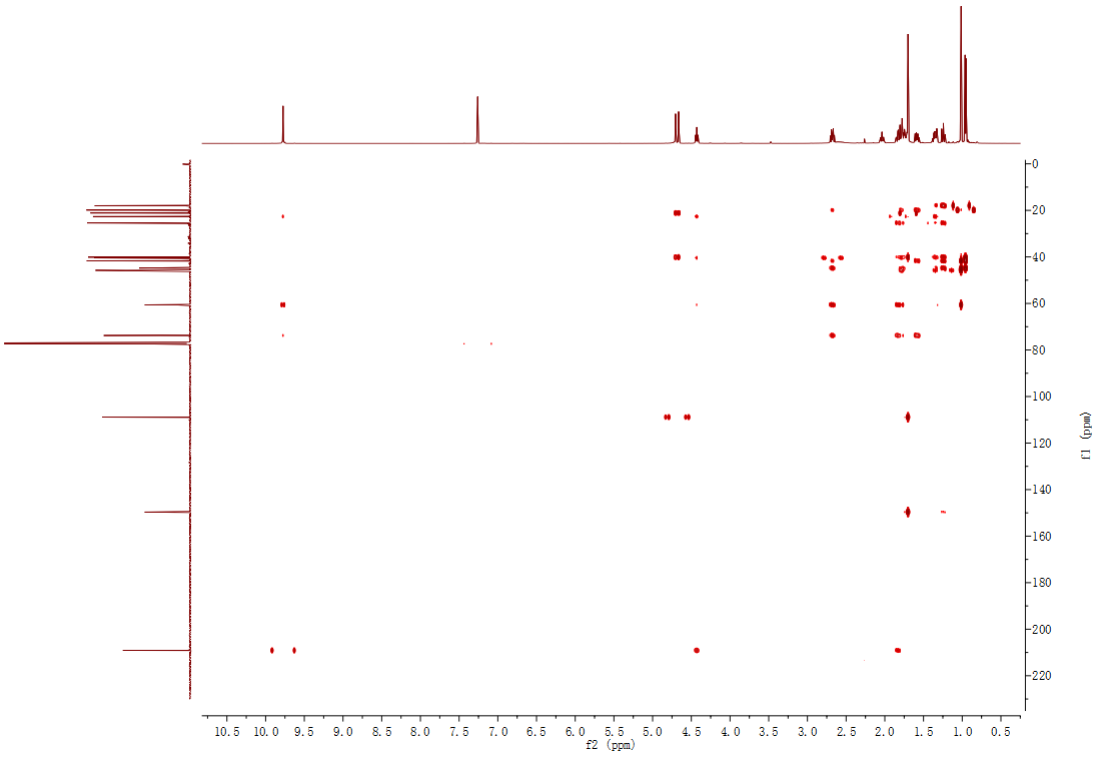


Fig. S6 HMBC spectrum of compound 1

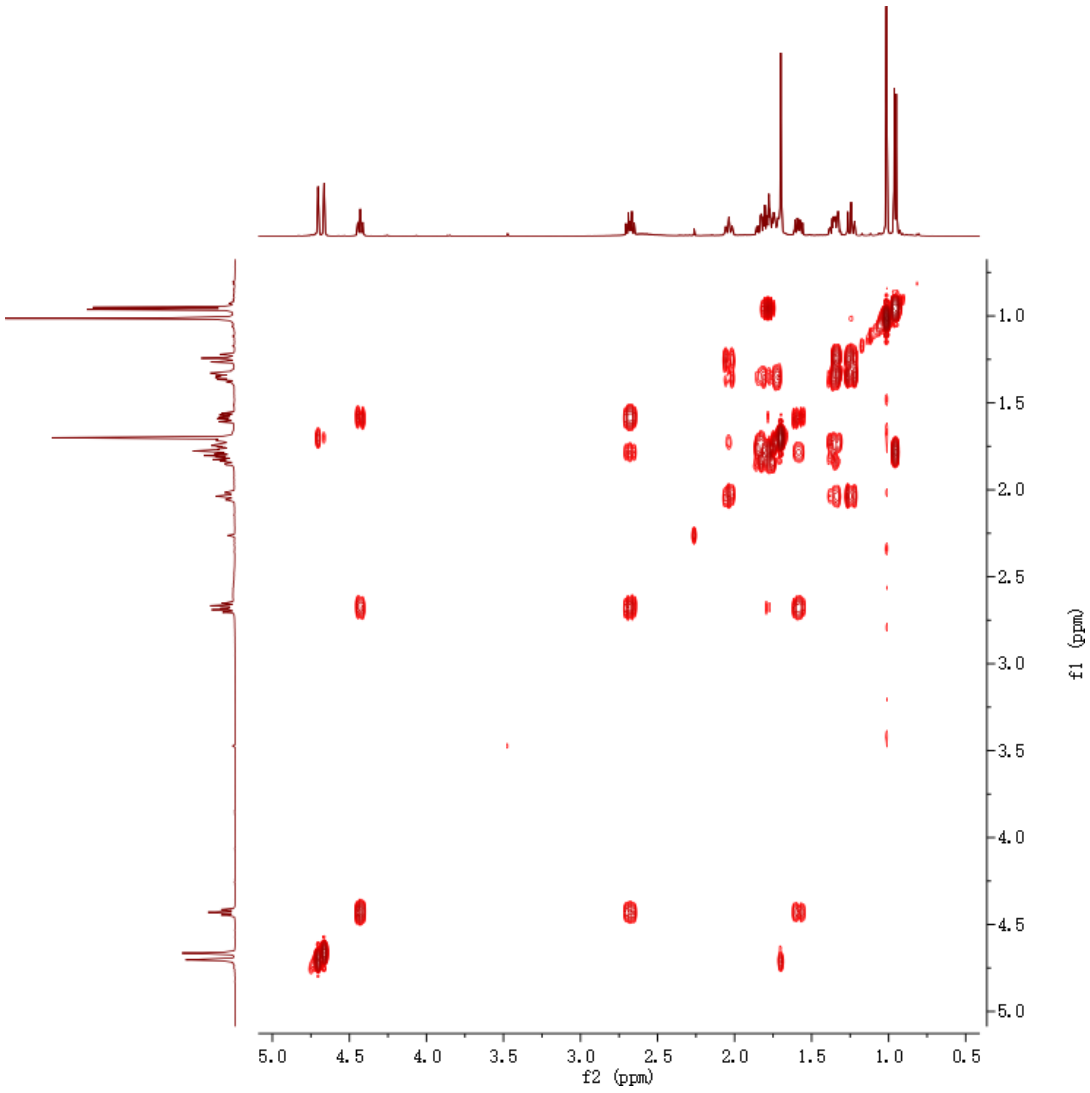


Fig. S7 ^{1}H-^{1}H COSY spectrum of compound 1

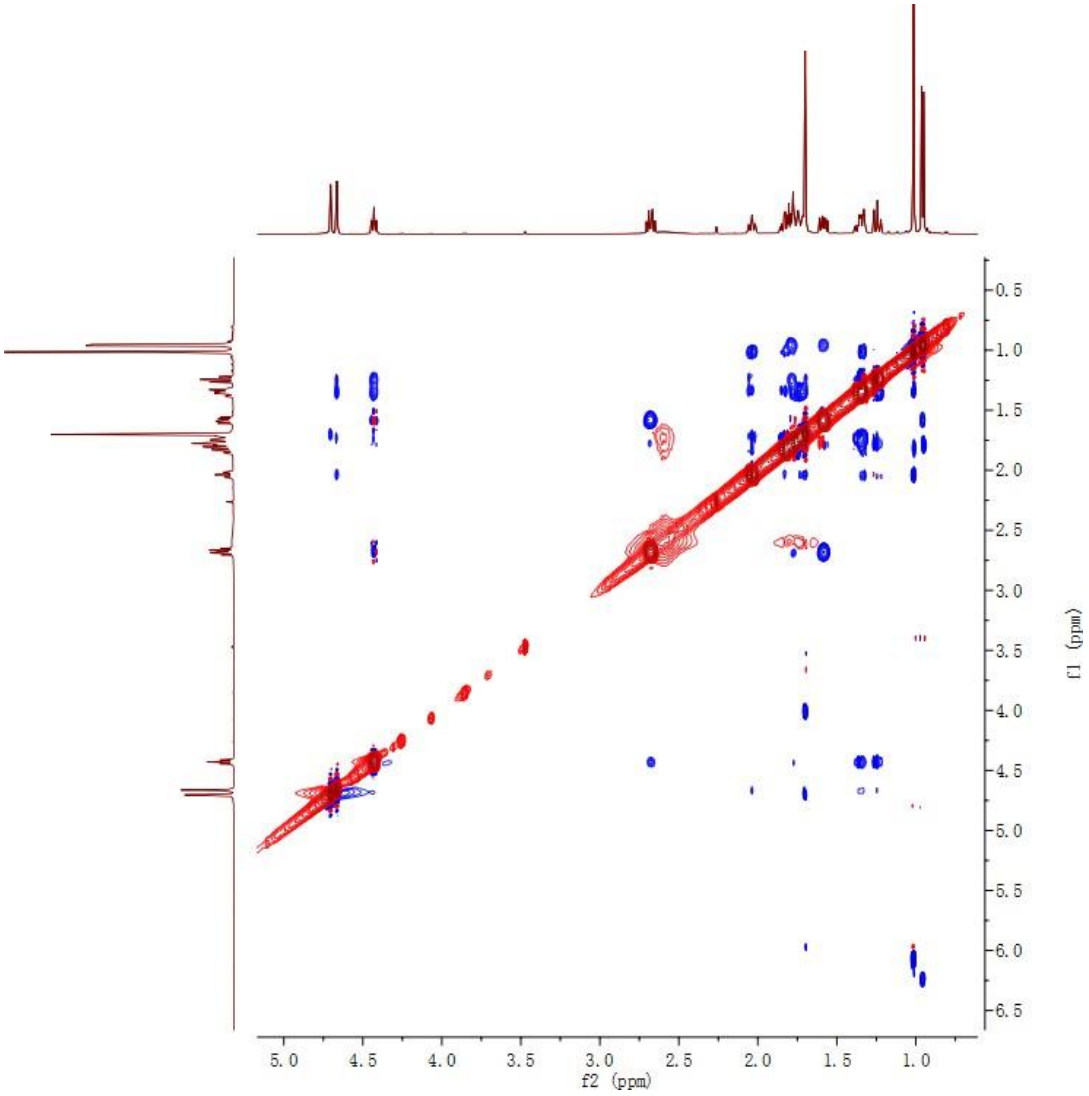


Fig. S8 NOESY spectrum of compound 1

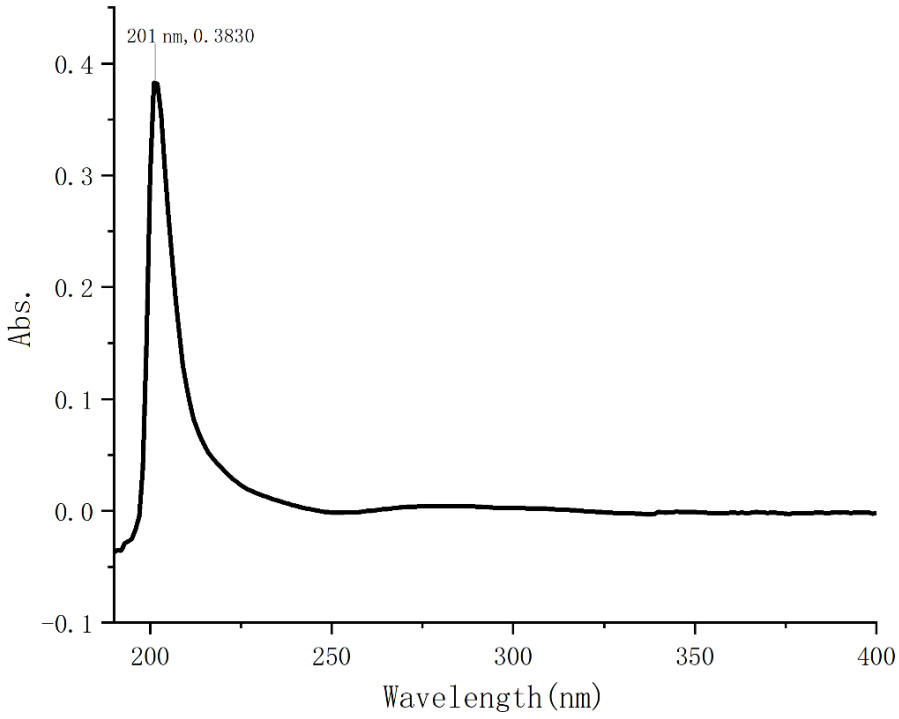


Fig. S9 UV spectrum of compound 1

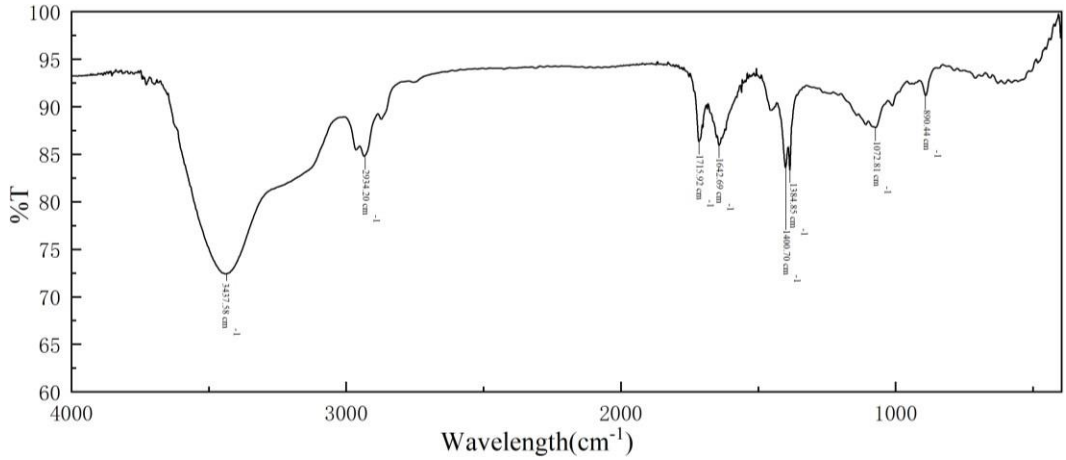


Fig. S10 IR spectrum of compound 1

Elemental Composition Report **Page 1**

Single Mass Analysis
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Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
36 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
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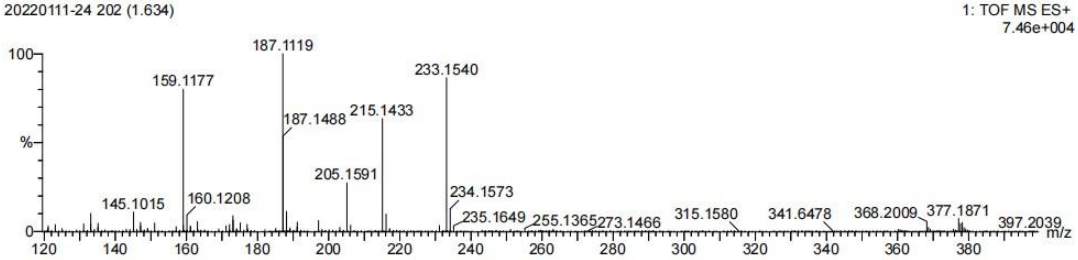
A04E4I2
20220111-24 202 (1.634)



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Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
233.1540	233.1542	-0.2	-0.9	5.5	199.3	n/a	n/a	C15 H21 O2

Fig. S11 HR-ESI-MS spectrum of compound 2

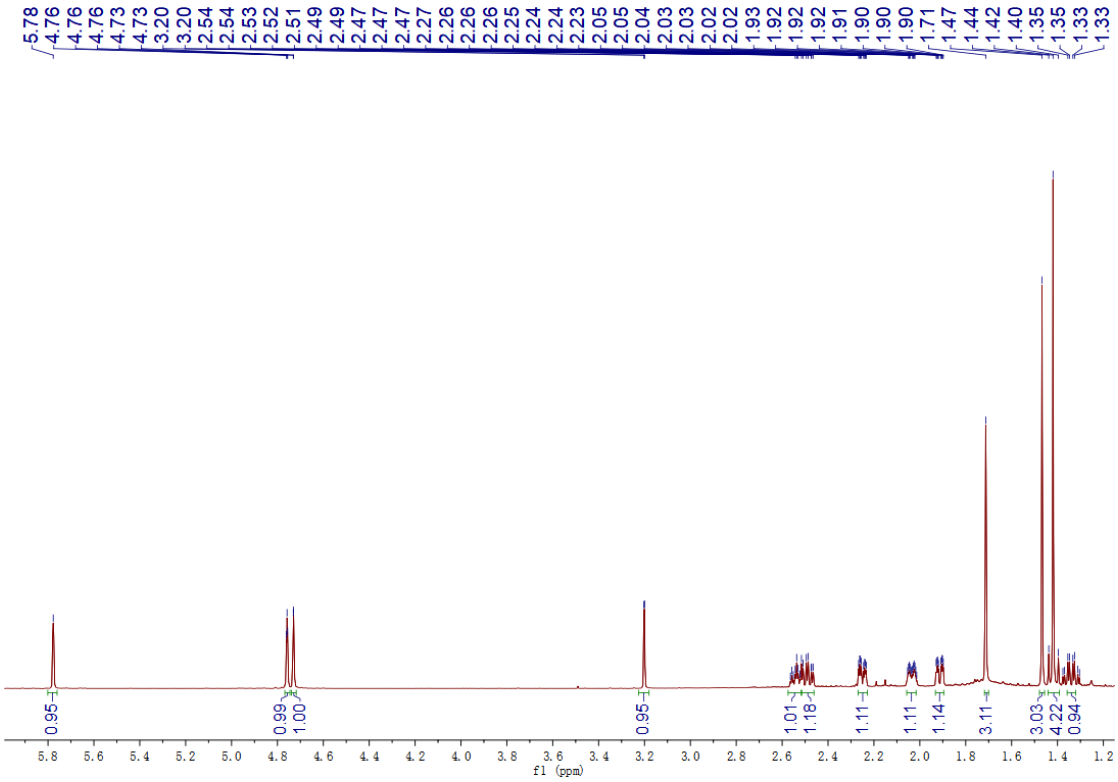

Fig. S12 ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 2

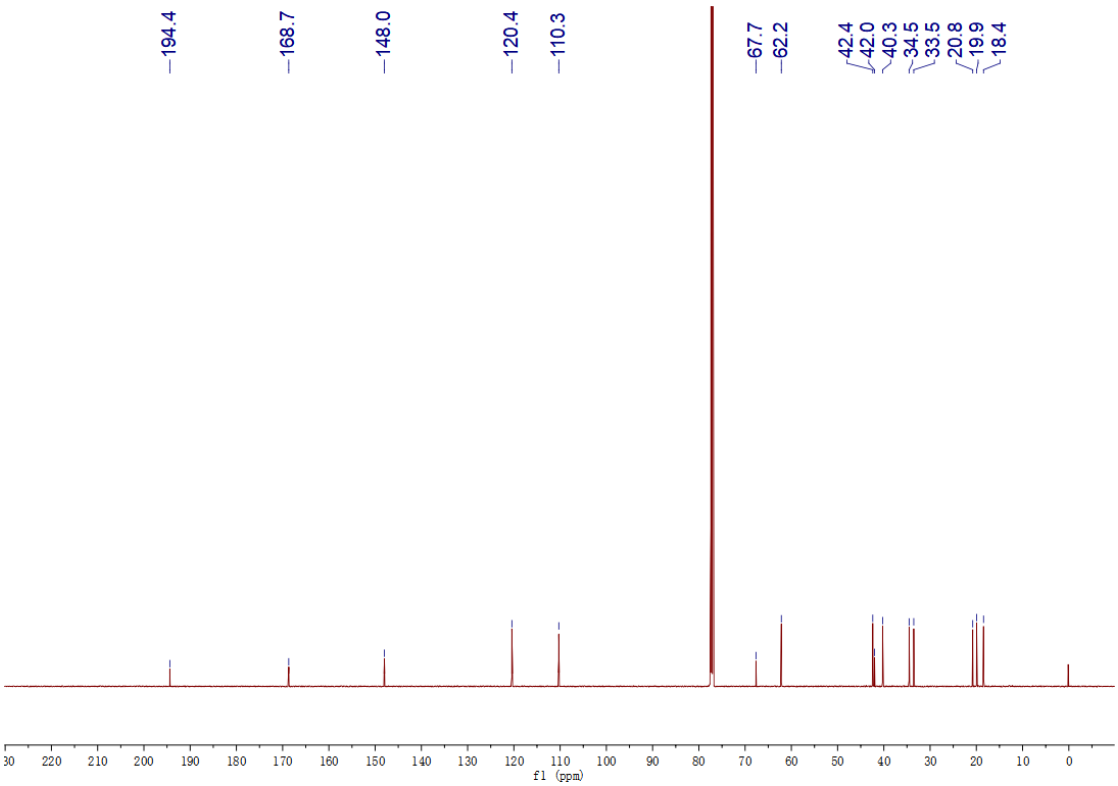

Fig. S13 ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of compound 2

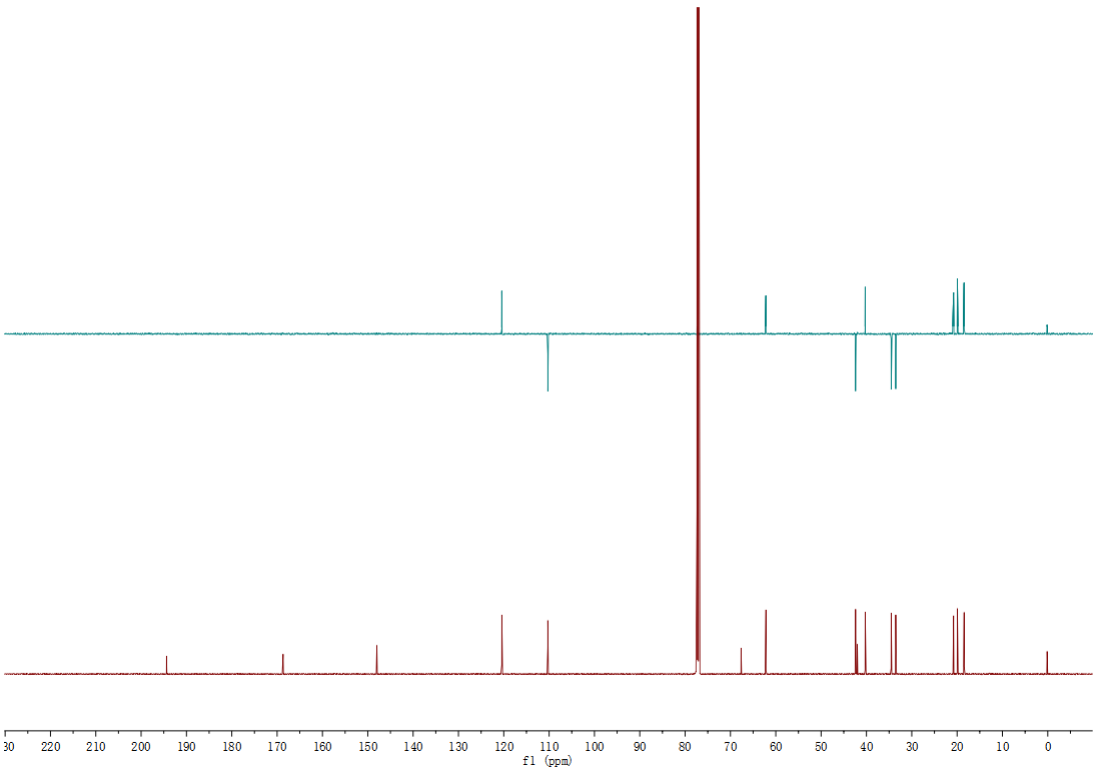

Fig. S14 DEPT (150 MHz, $CDCl_3$) and ^{13}C NMR spectra of compound 2

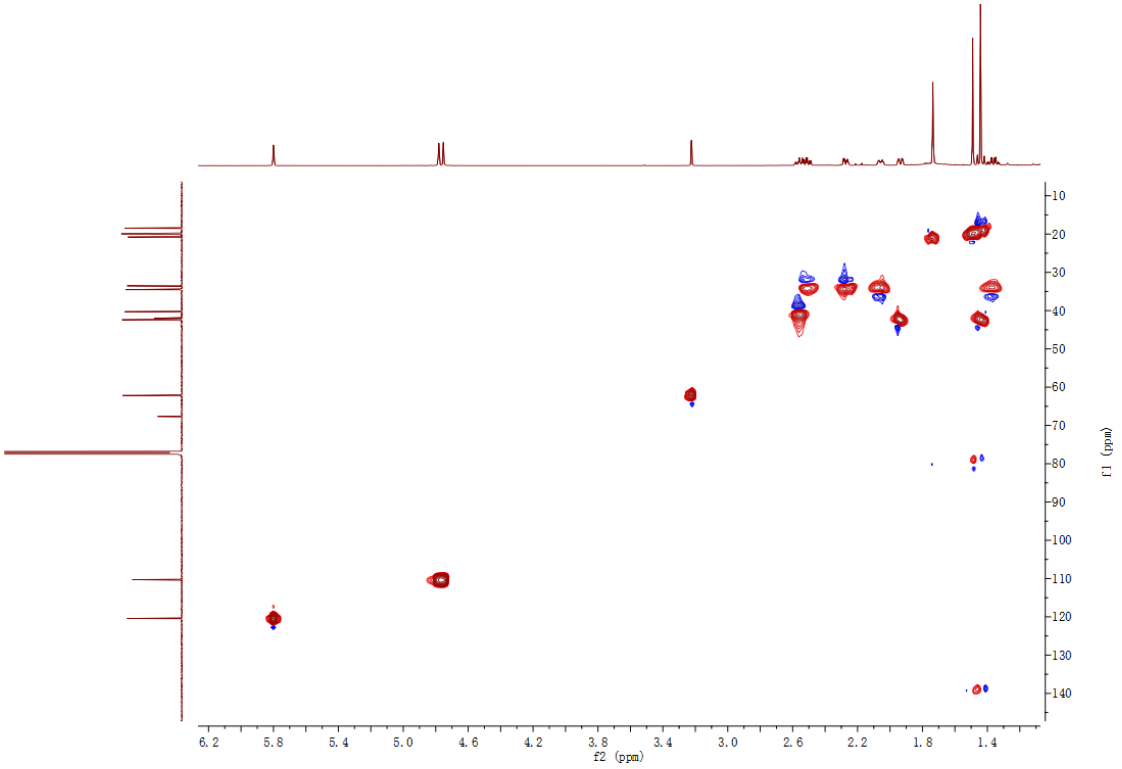

Fig. S15 HSQC spectrum of compound 2

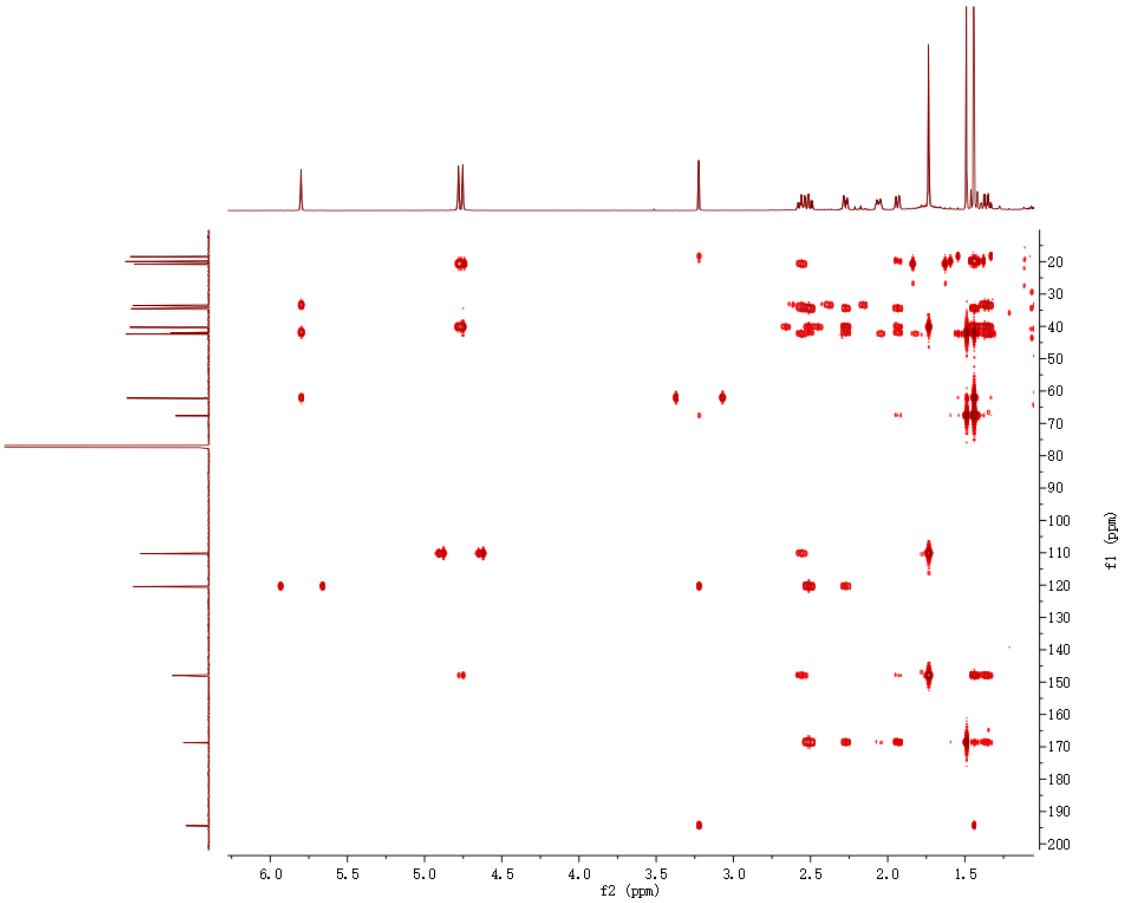

Fig. S16 HMBC spectrum of compound 2

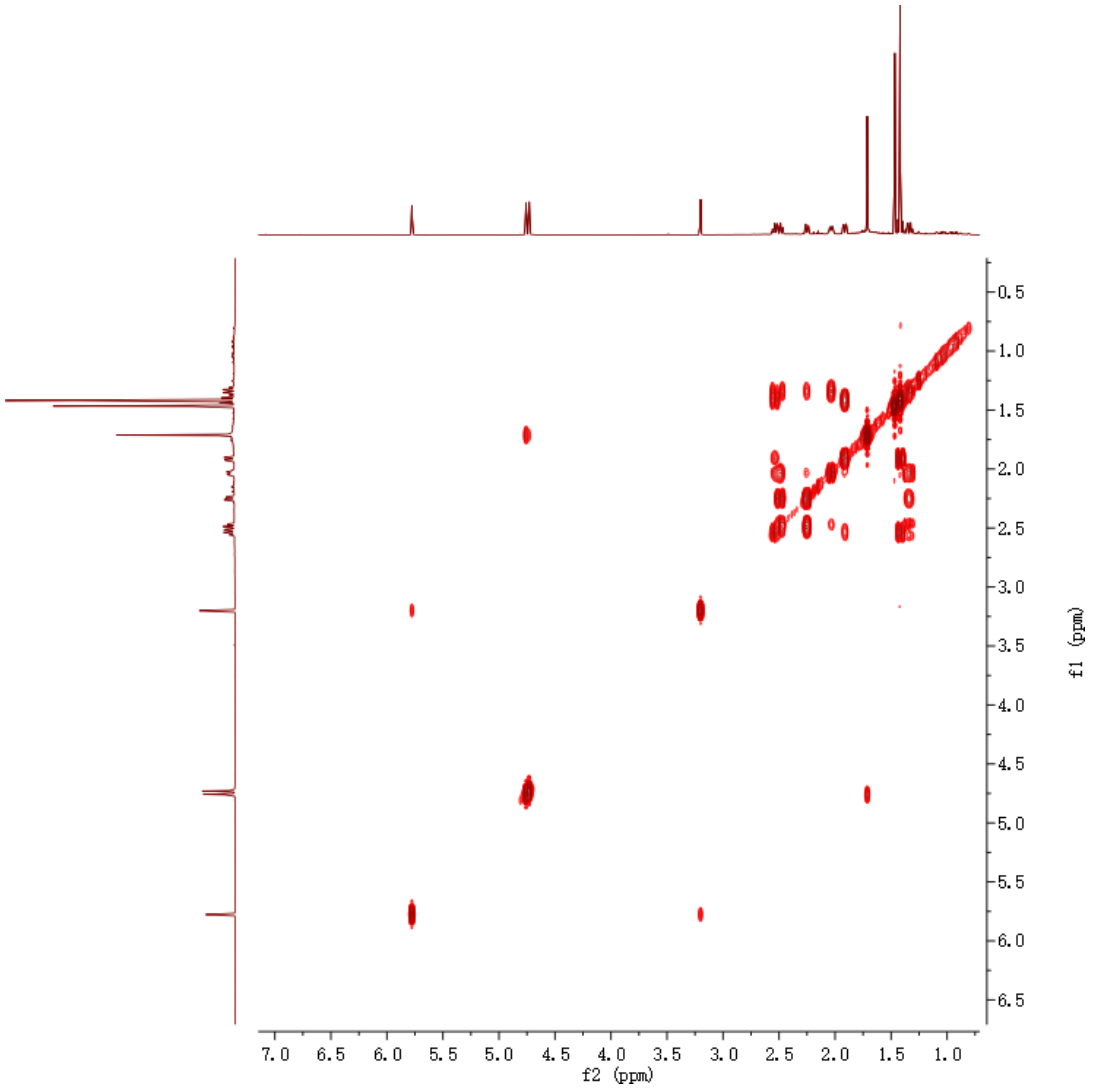

Fig. S17 ^{1}H-^{1}H COSY spectrum of compound 2

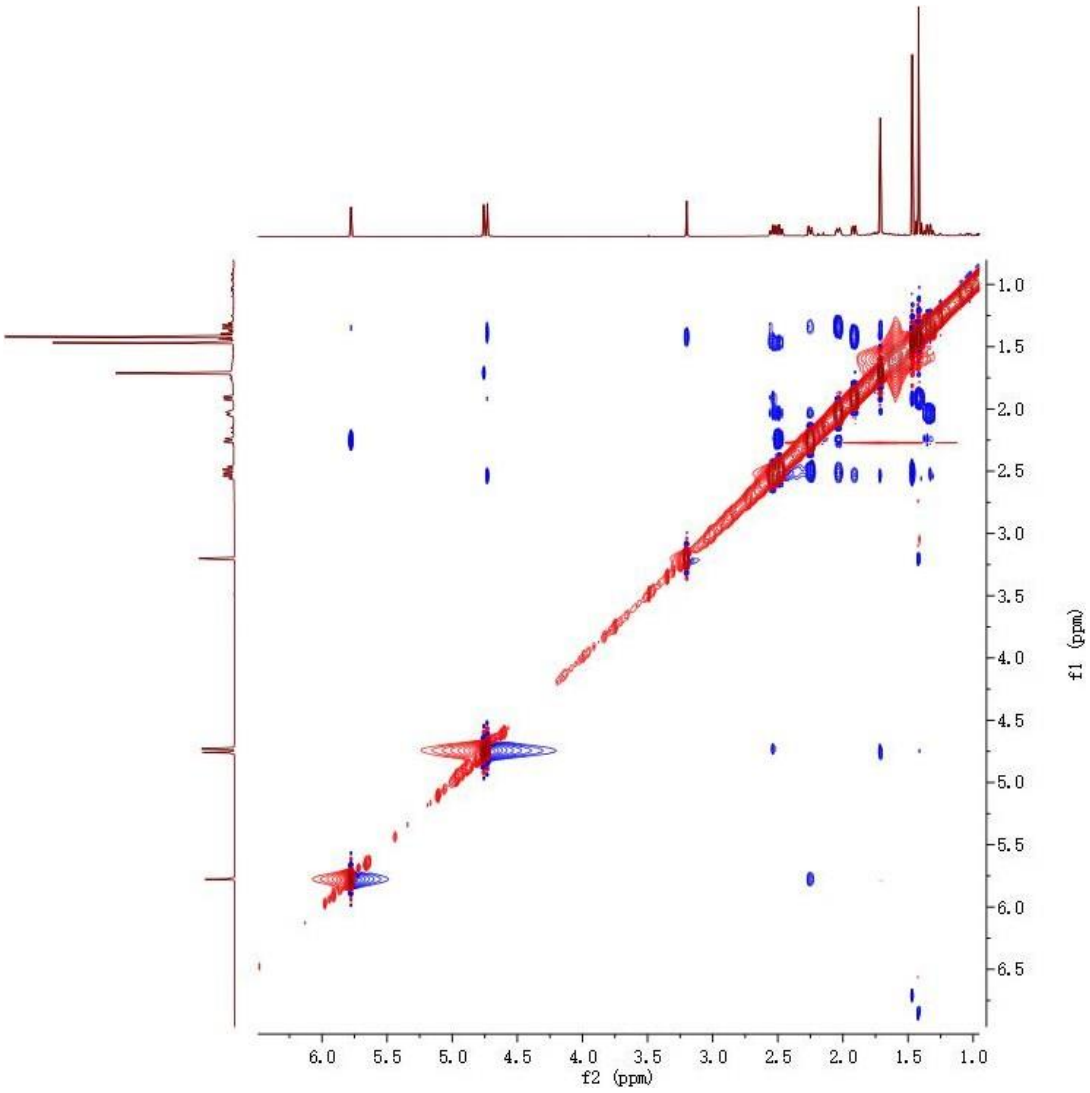

Fig. S18 NOESY spectrum of compound 2

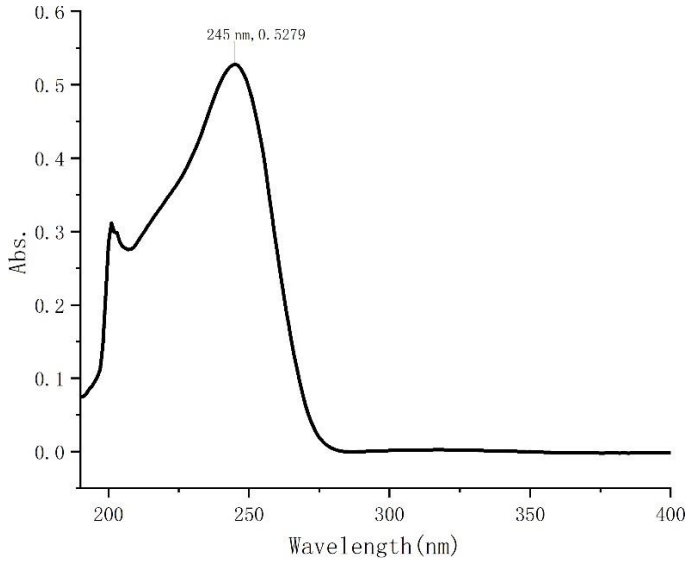

Fig. S19 UV spectrum of compound 2

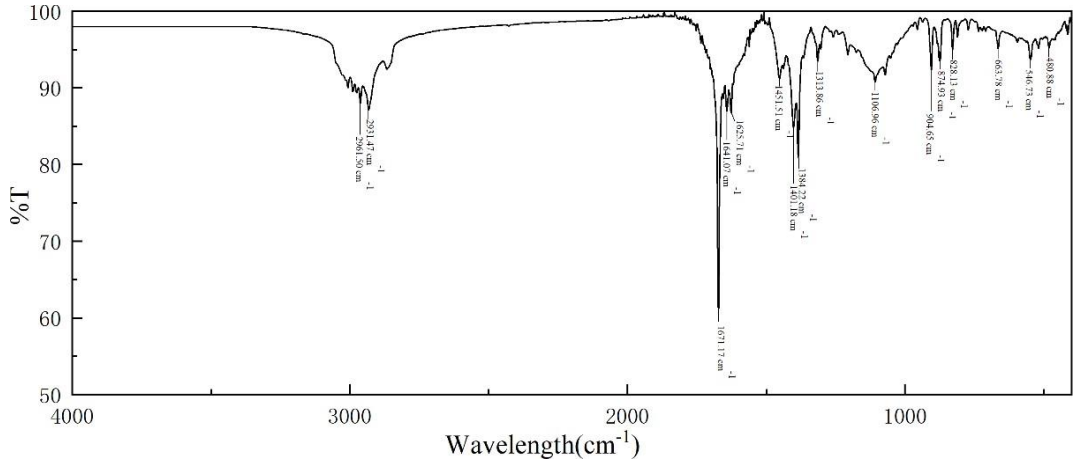

Fig. S20 IR spectrum of compound 2

Elemental Composition Report **Page 1**

Single Mass Analysis
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Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
36 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
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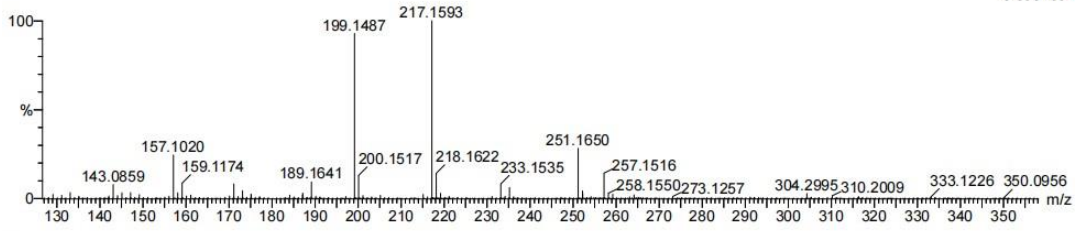
A04E4I1
20220111-22 212 (1.709)

1: TOF MS ES+
8.83e+004



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
233.1535	233.1542	-0.7	-3.0	5.5	146.8	n/a	n/a	C15 H21 O2

Fig. S21 HR-ESI-MS spectrum of compound 3

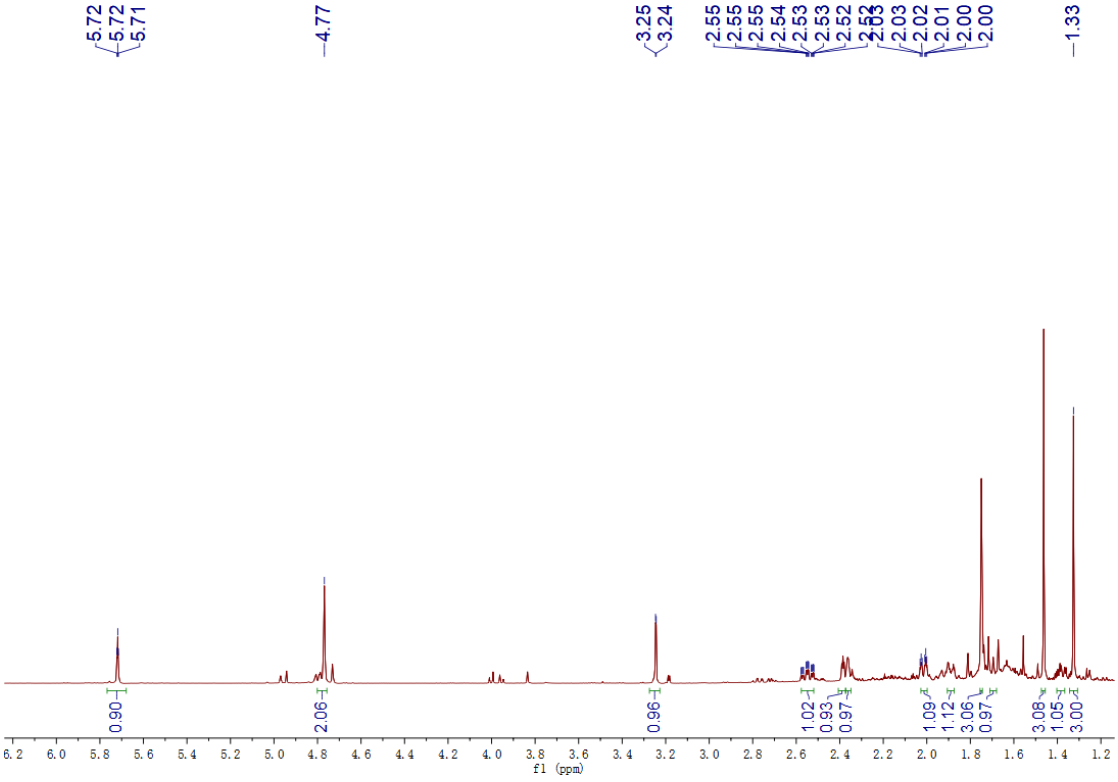


Fig. S22 ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 3

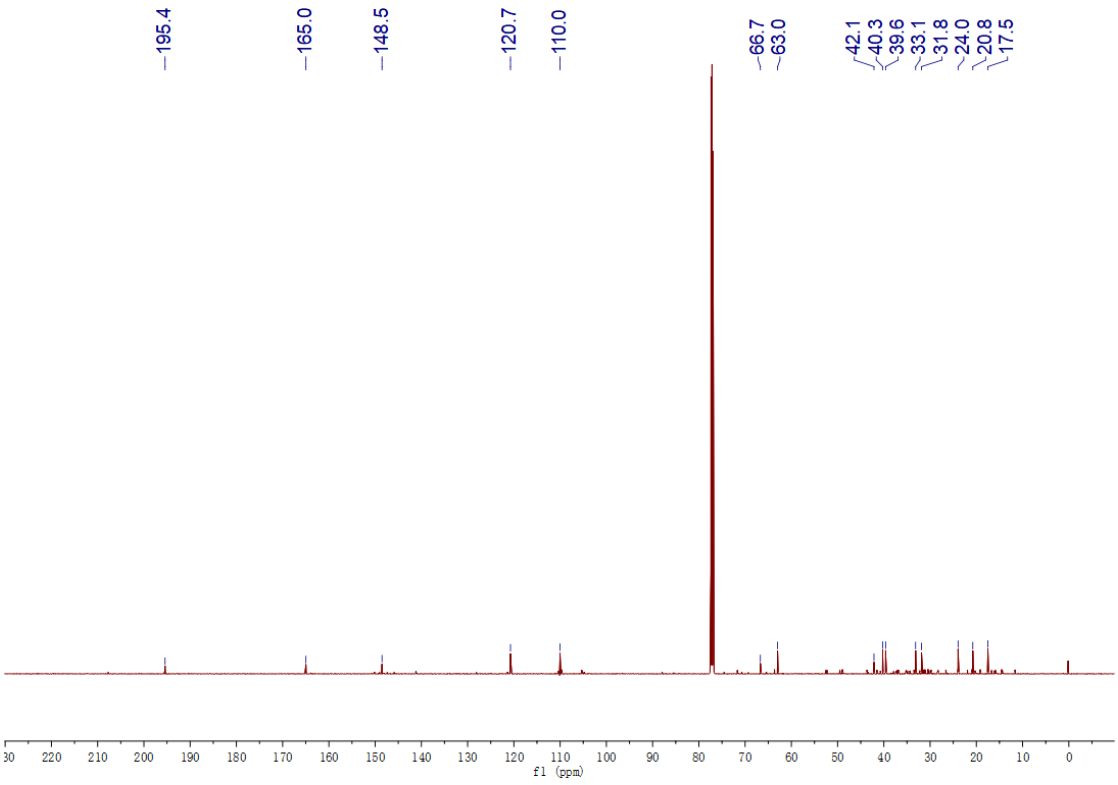


Fig. S23 ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of compound 3

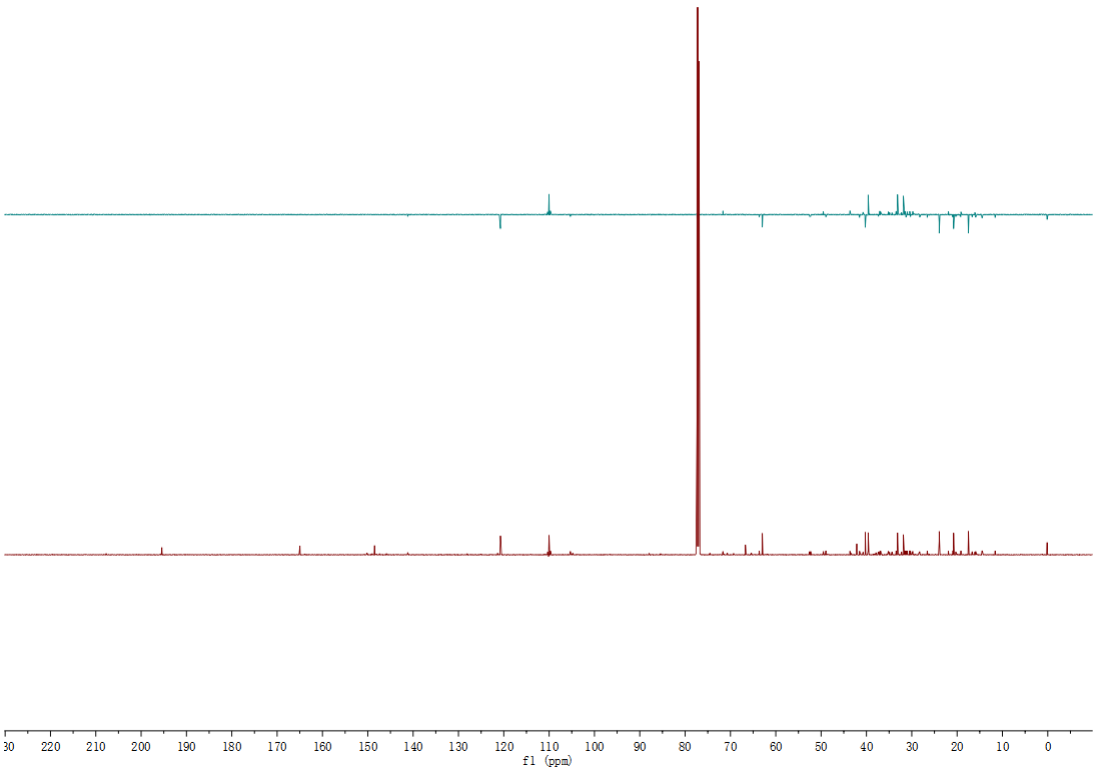


Fig. S24 DEPT (150 MHz, $CDCl_3$) and ^{13}C NMR spectra of compound 3

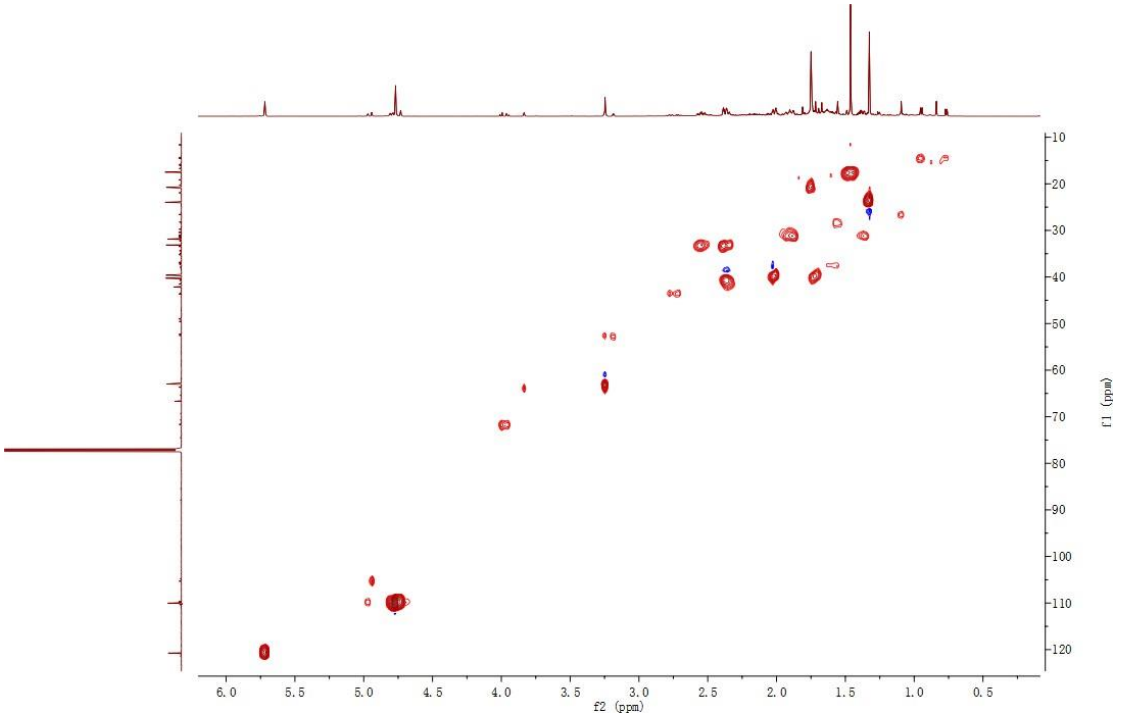


Fig. S25 HSQC spectrum of compound 3

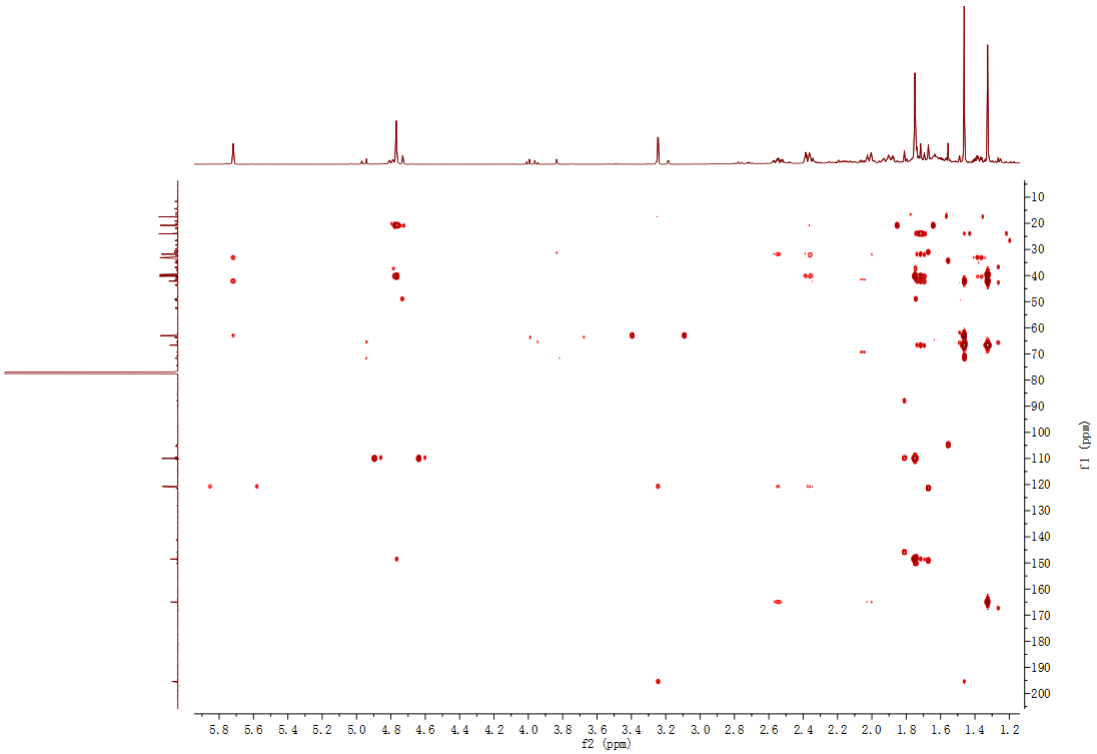


Fig. S26 HMBC spectrum of compound 3

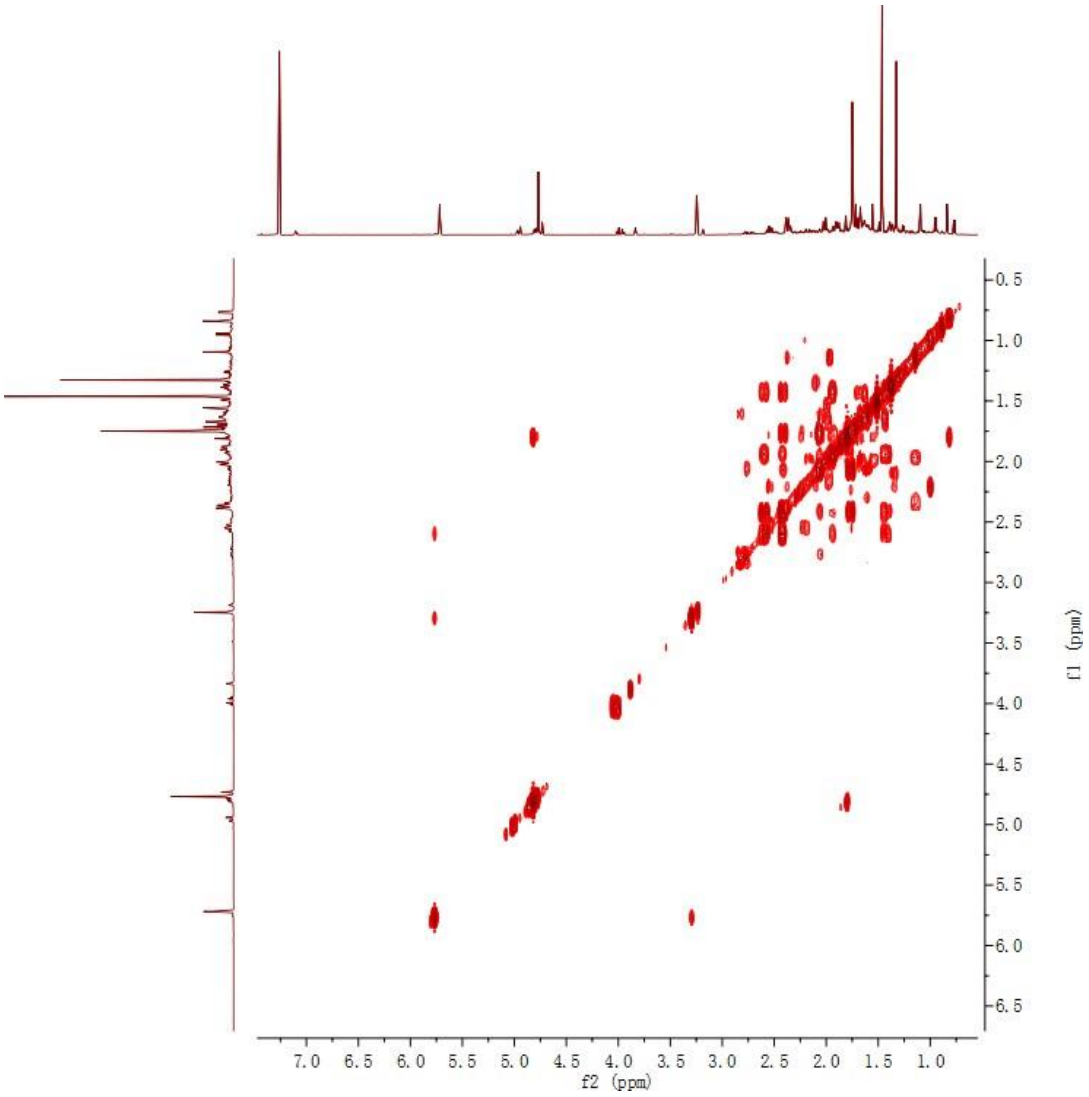


Fig. S27 ^{1}H-^{1}H COSY spectrum of compound 3

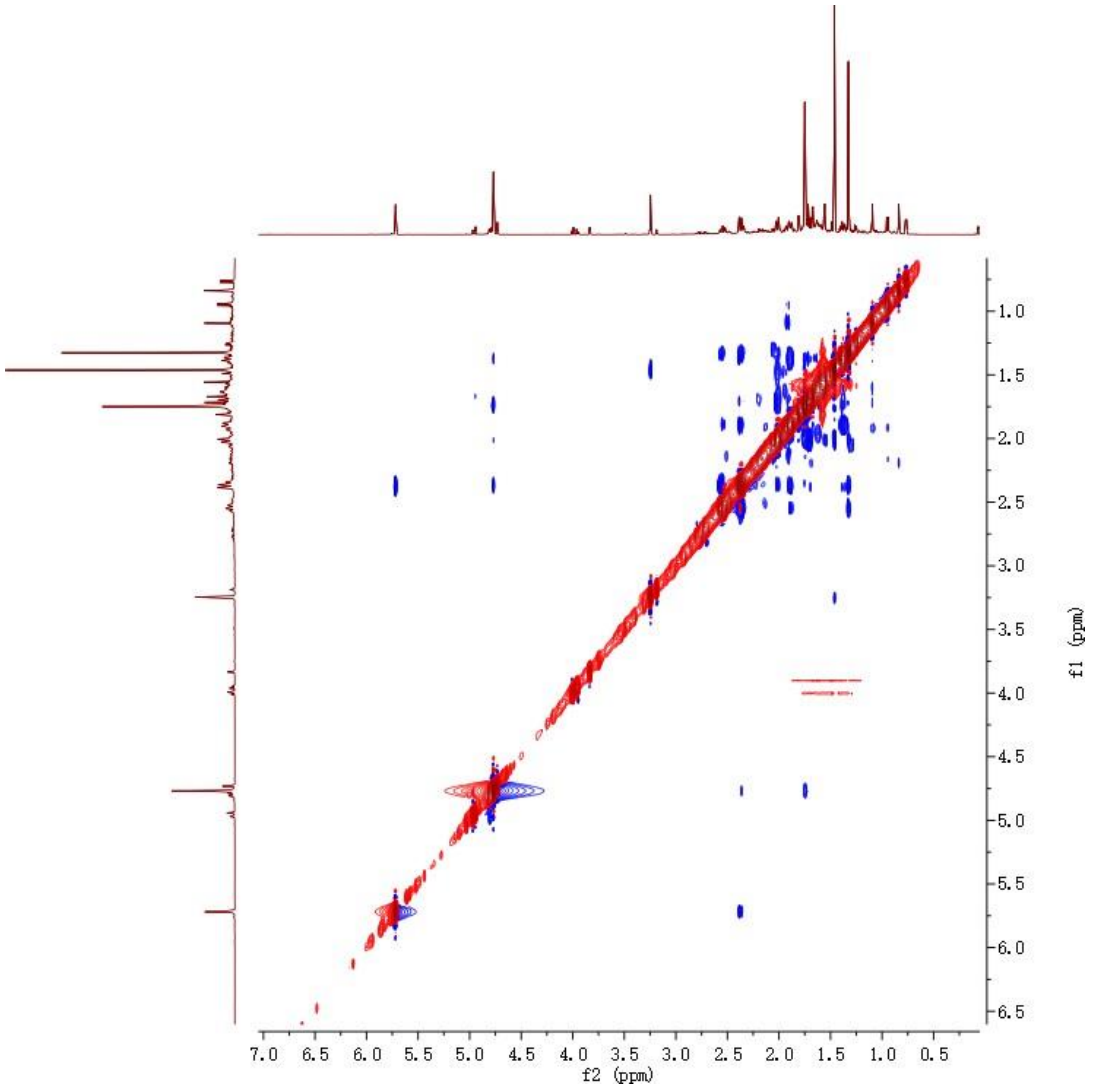


Fig. S28 NOESY spectrum of compound 3

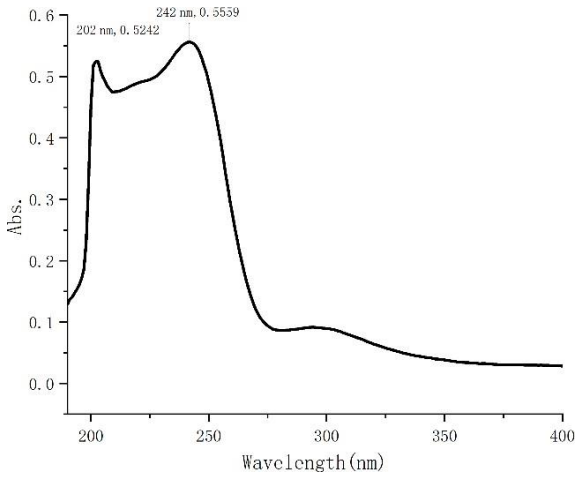


Fig. S29 UV spectrum of compound 3

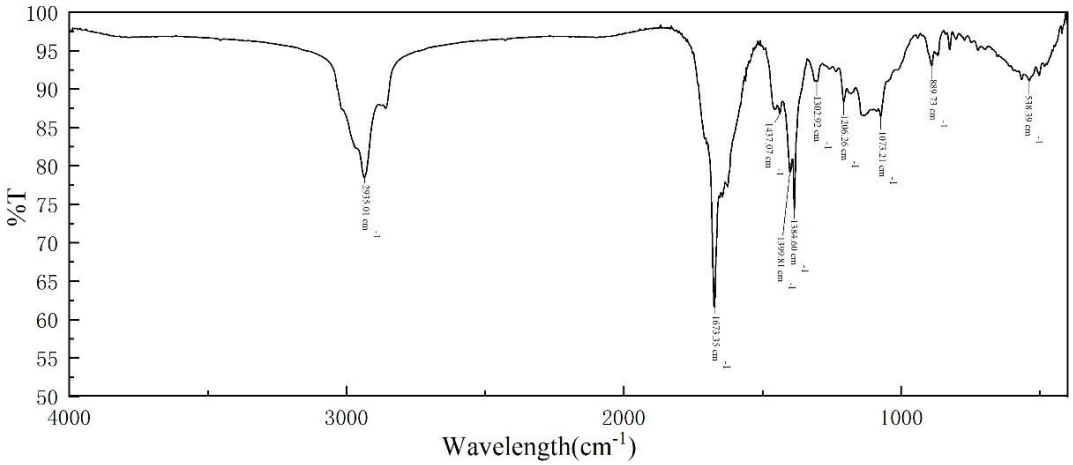
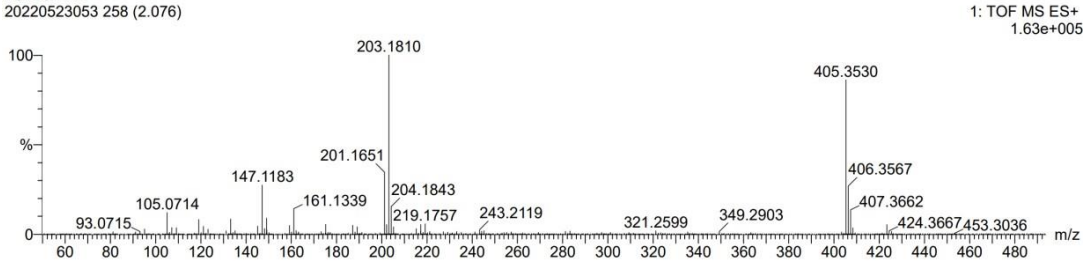


Fig. S30 IR spectrum of compound 3

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
56 formula(e) evaluated with 2 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-200 O: 0-200 Na: 0-1
A04E6D11B
20220523053 258 (2.076)



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
203.1810	203.1800	1.0	4.9	4.5	397.1	0.529	58.94	C15 H23
	203.1776	3.4	16.7	1.5	397.4	0.890	41.06	C13 H24 Na

Fig. S31 HR-ESI-MS spectrum of compound 4

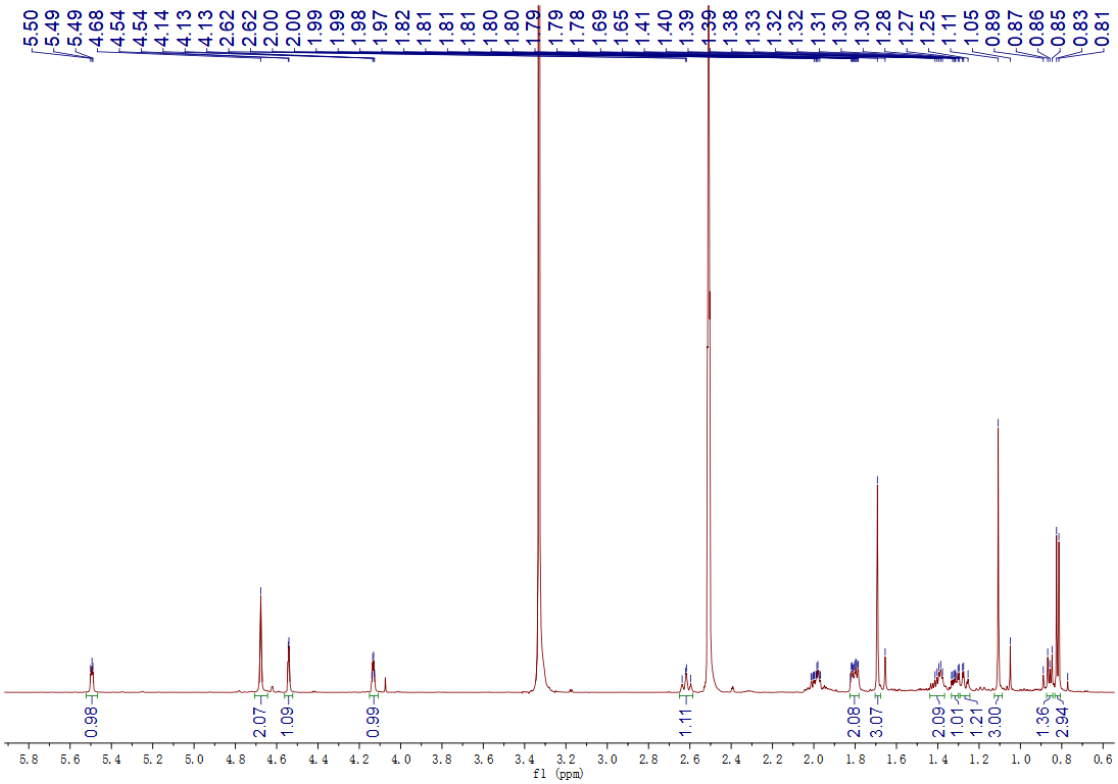


Fig. S32 ^{1}H NMR (600 MHz, DMSO-d_6) spectrum of compound 4

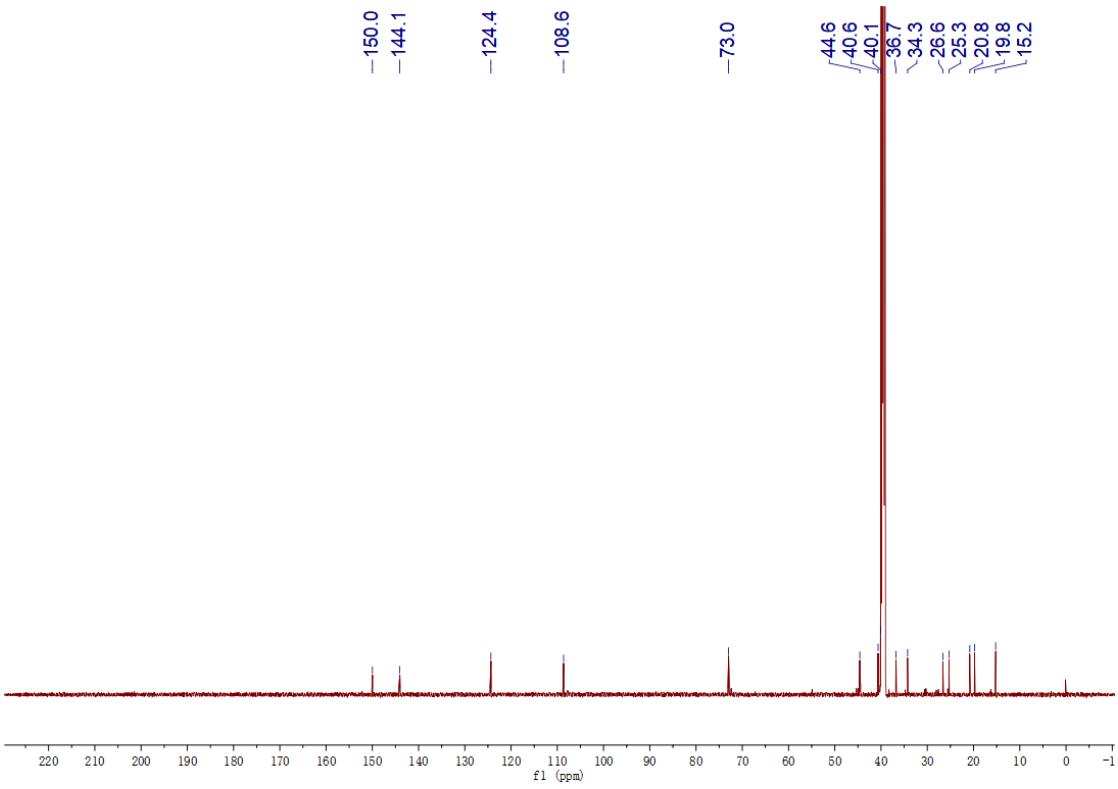


Fig. S33 ^{13}C NMR (150 MHz, DMSO-d_6) spectrum of compound 4

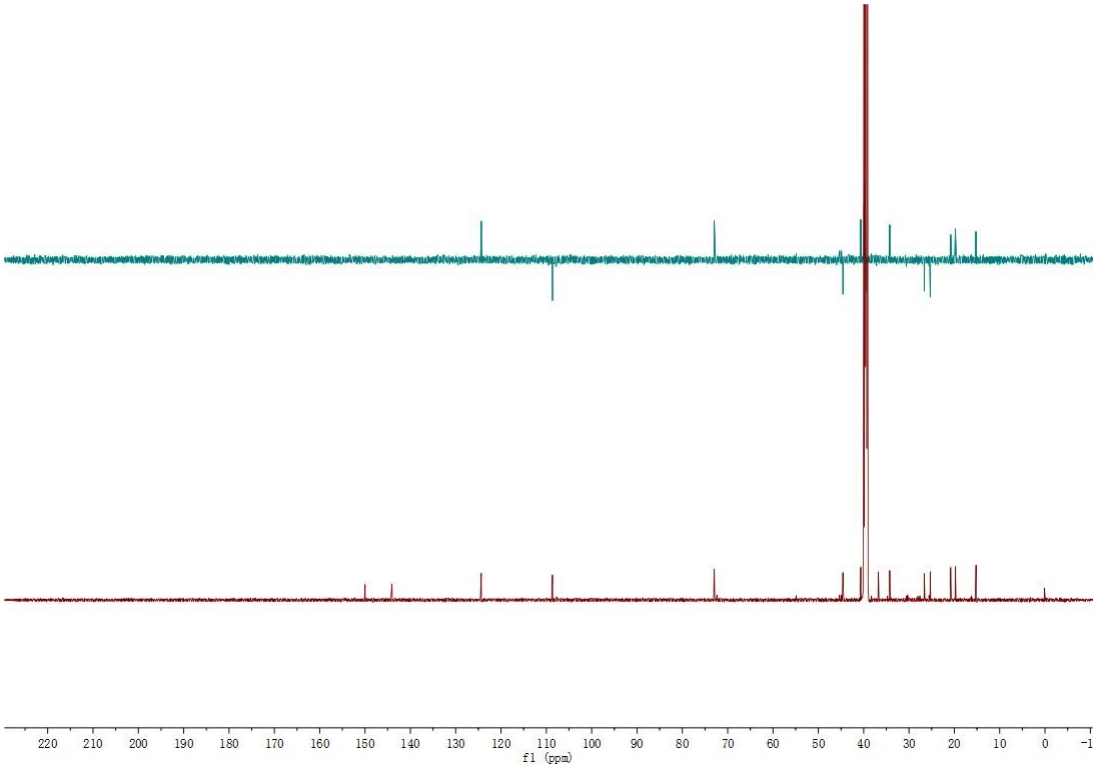


Fig. S34 DEPT (150 MHz, DMSO-d_6) and ^{13}C NMR spectra of compound 4

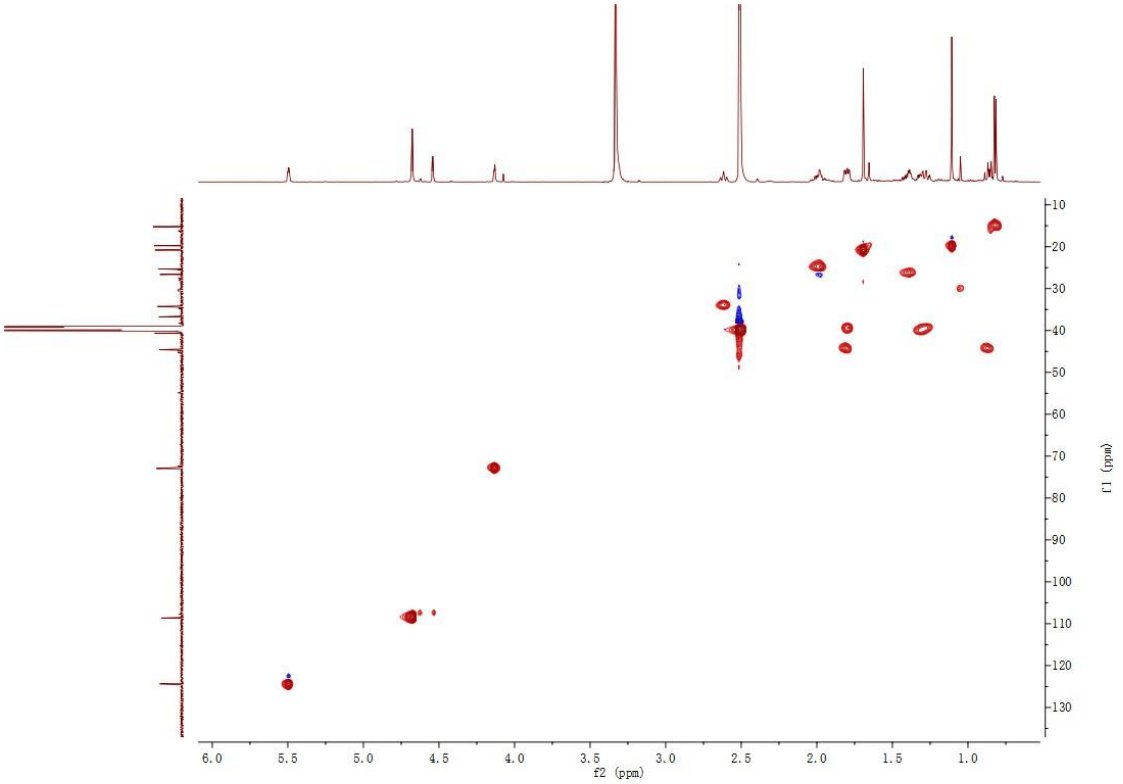


Fig. S35 HSQC spectrum of compound 4

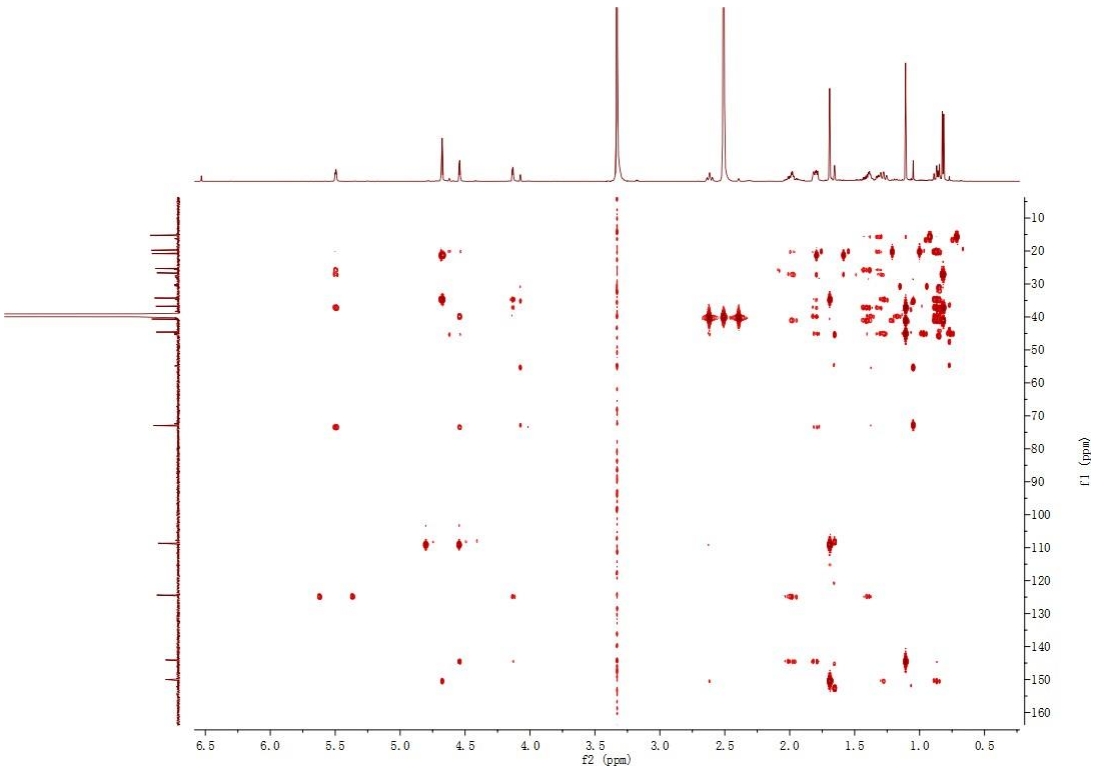


Fig. S36 HMBC spectrum of compound 4

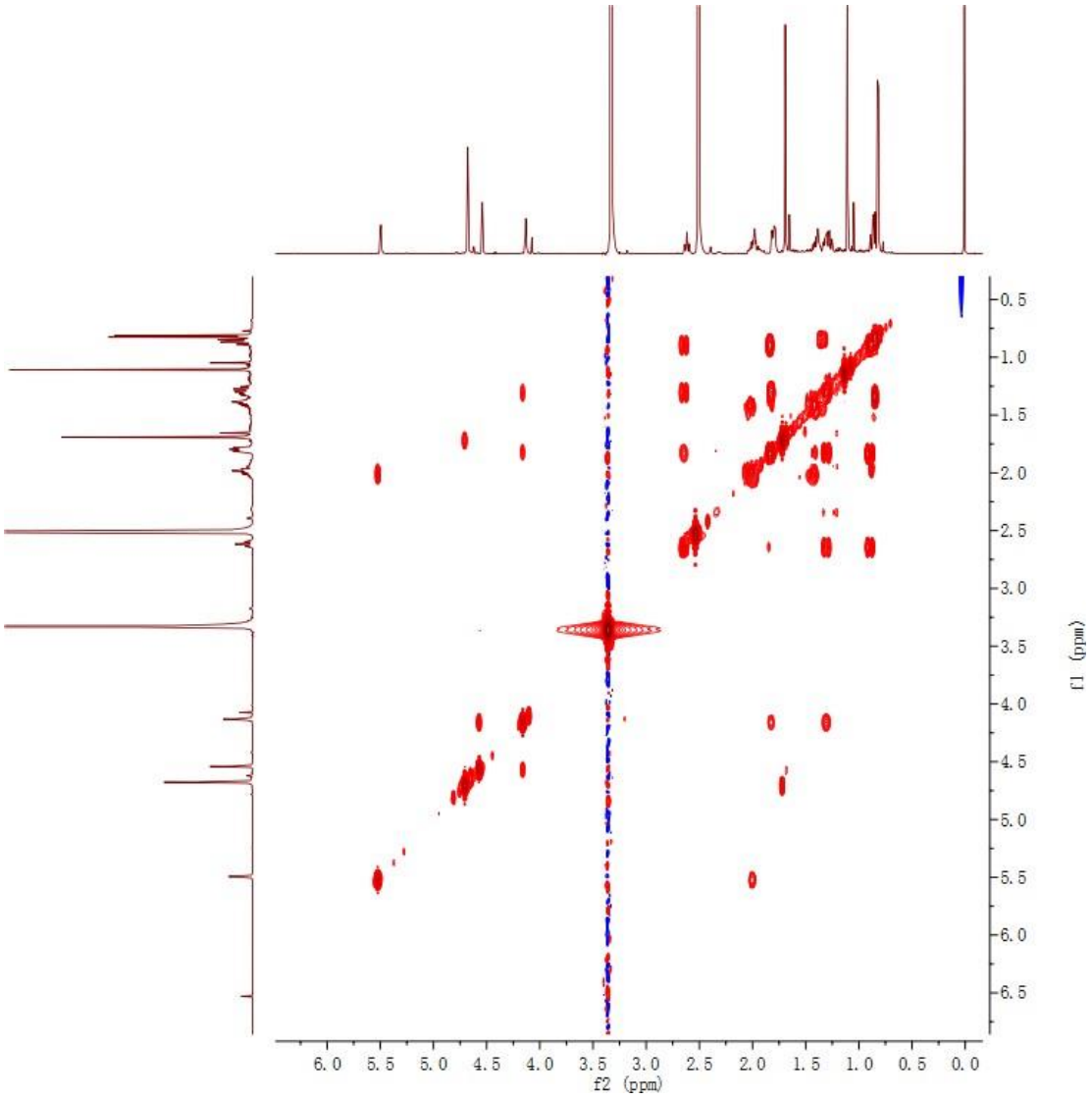


Fig. S37 ^{1}H-^{1}H COSY spectrum of compound 4

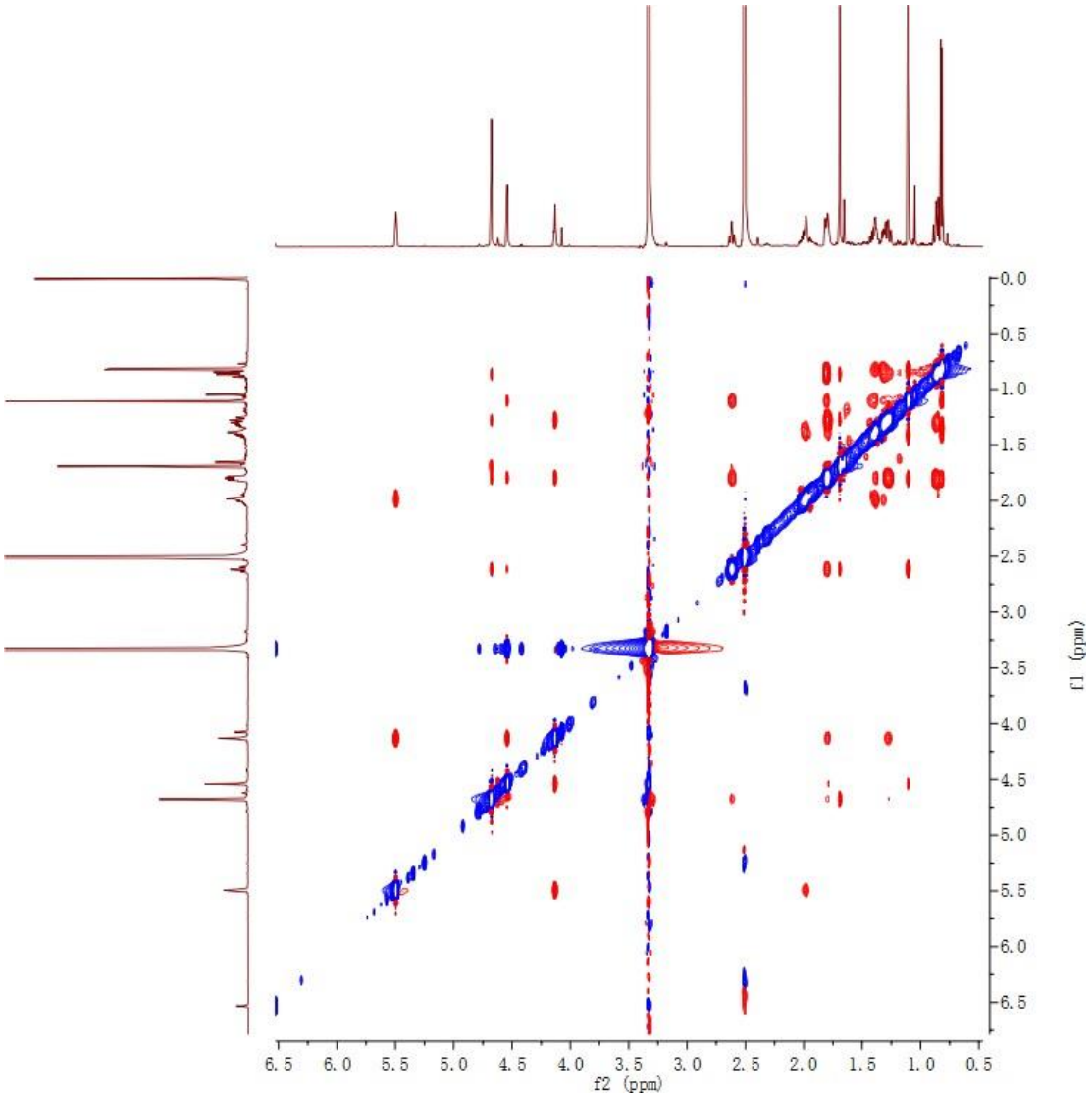


Fig. S38 NOESY spectrum of compound 4

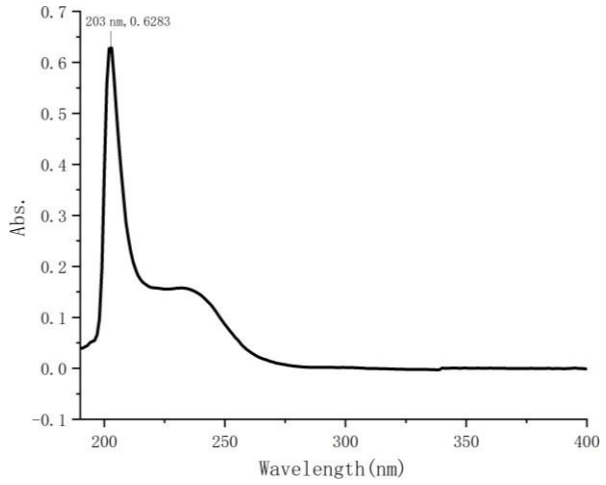


Fig. S39 UV spectrum of compound 4

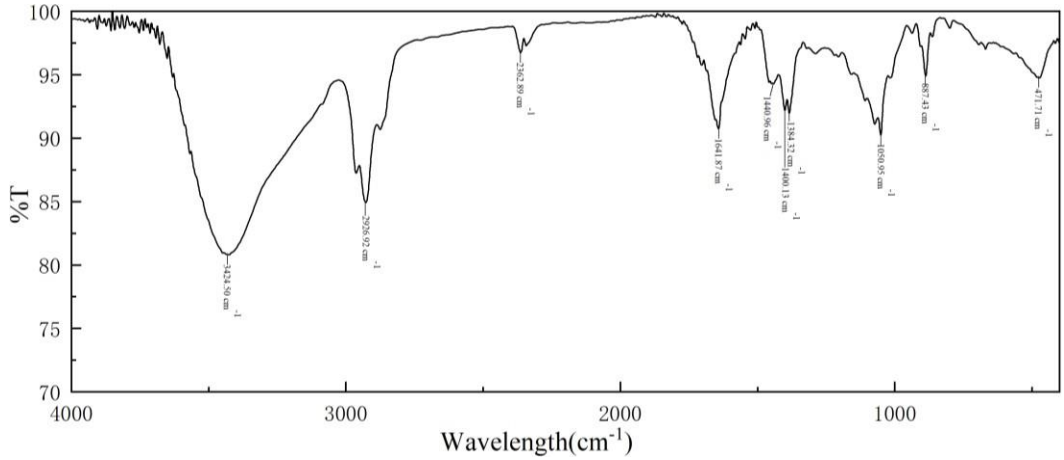
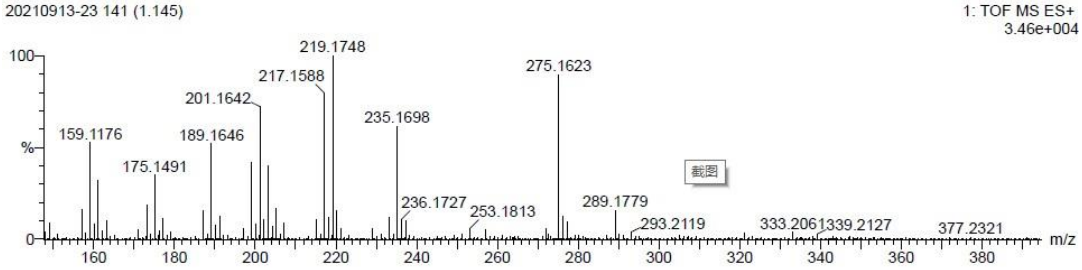


Fig. S40 IR spectrum of compound 4

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
65 formula(e) evaluated with 2 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
AO3F5E1
20210913-23 141 (1.145)



Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
237.1859	237.1855	0.4	1.7	3.5	177.1	C15 H25 O2

Fig. S41 HR-ESI-MS spectrum of compound 5

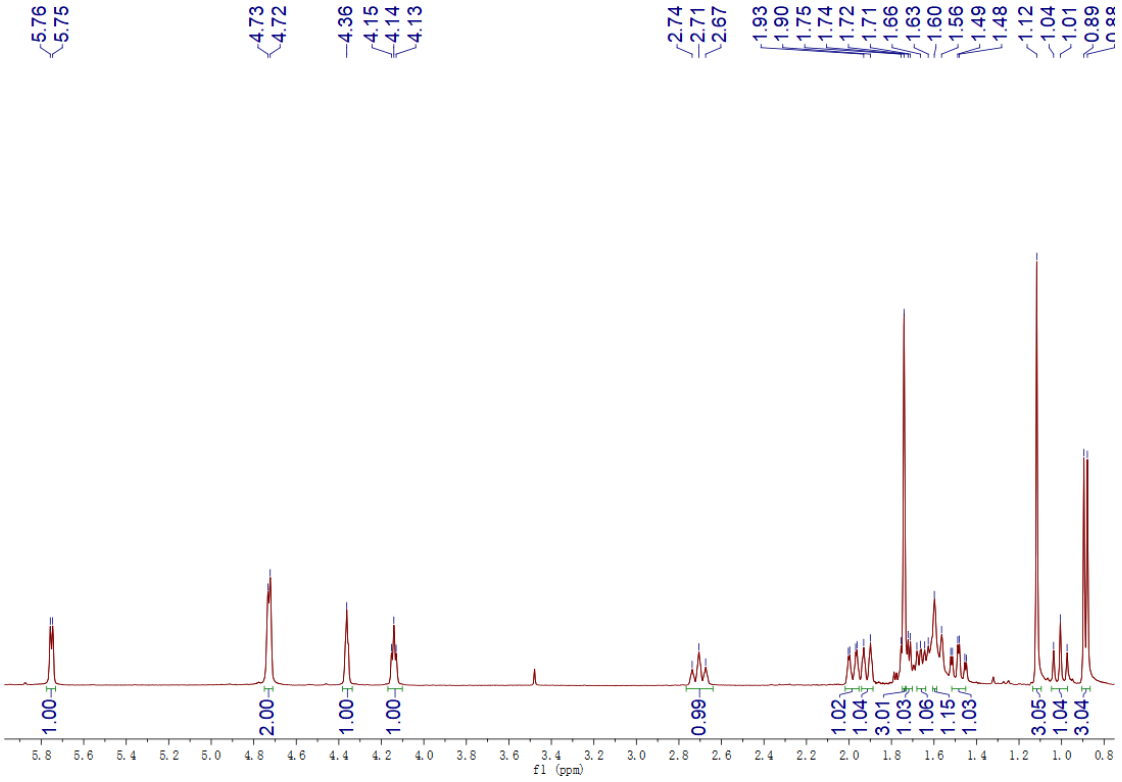


Fig. S42 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5

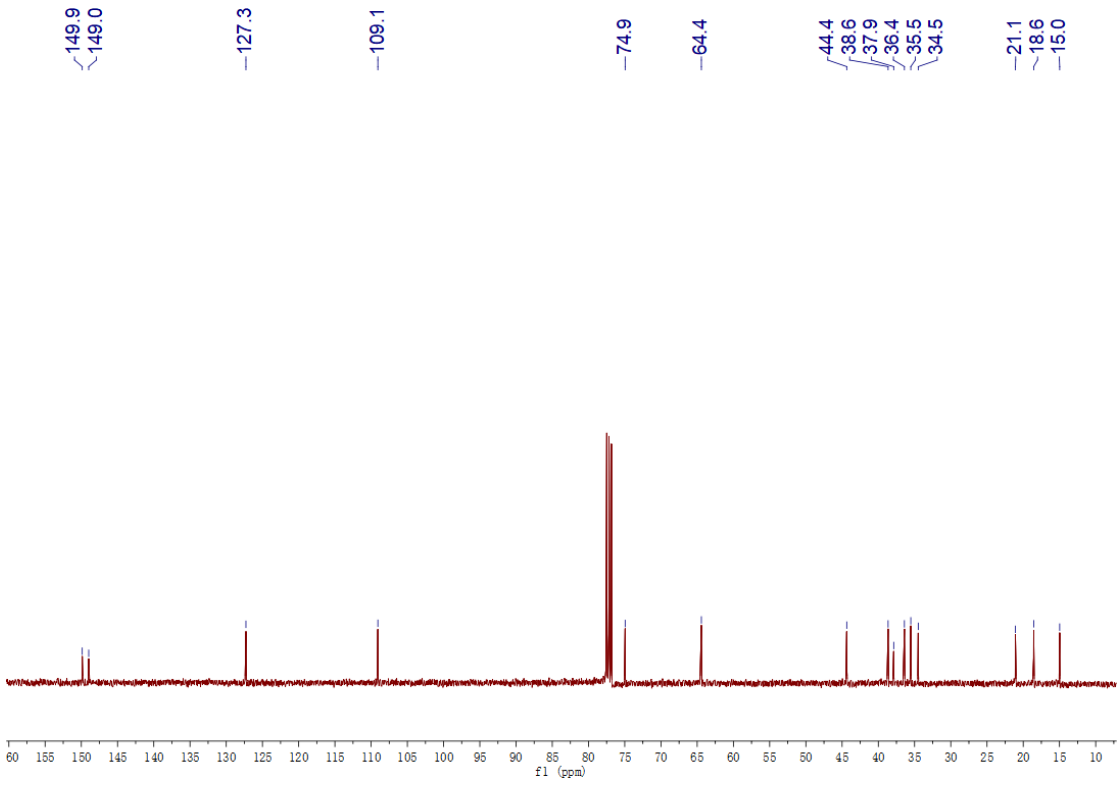


Fig. S43 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 5

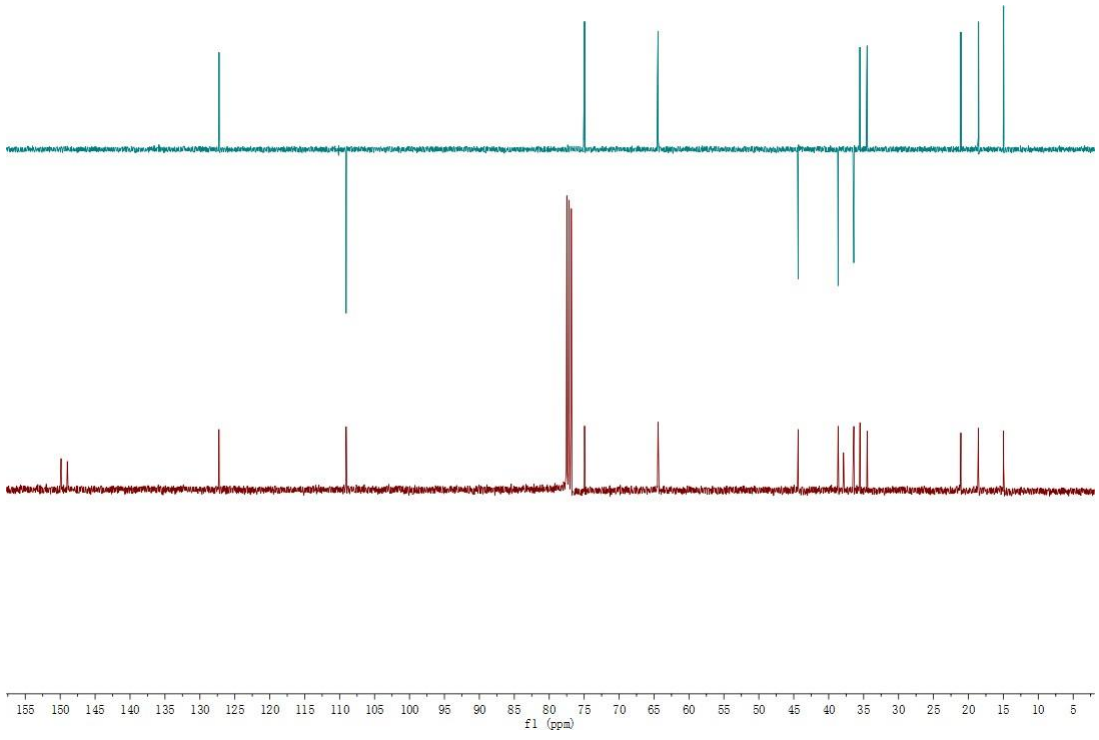


Fig. S44 DEPT (100 MHz, $CDCl_3$) and ^{13}C NMR spectra of compound 5

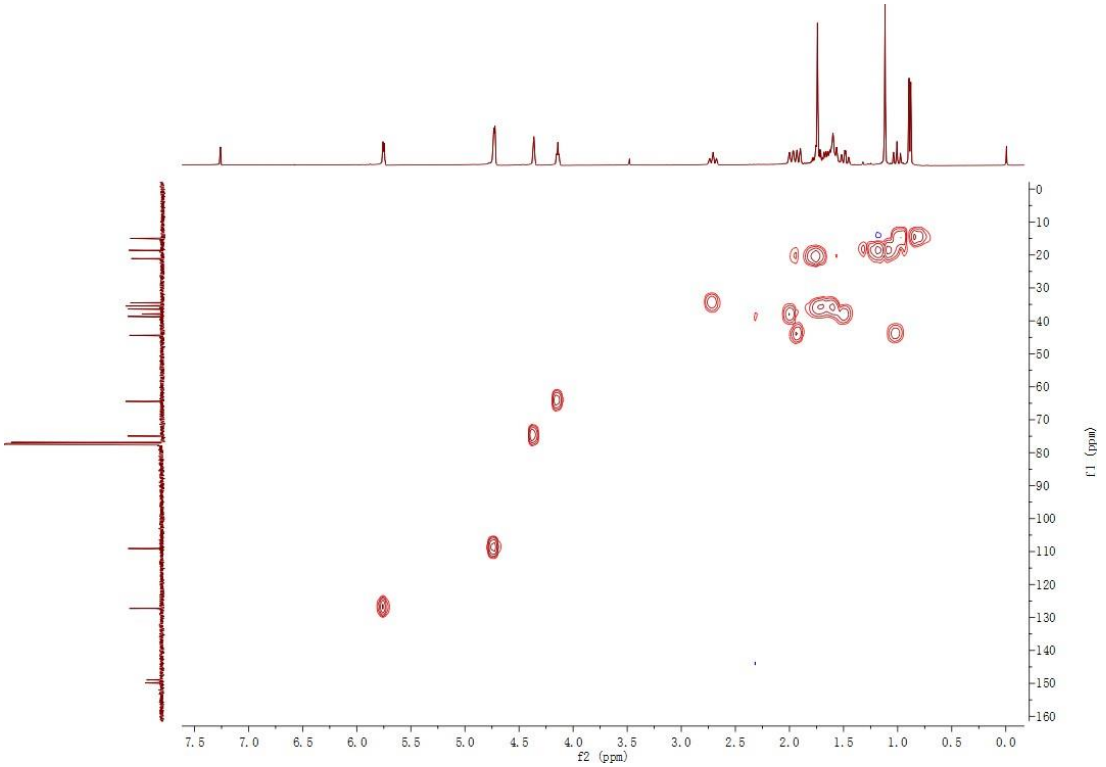


Fig. S45 HSQC spectrum of compound 5

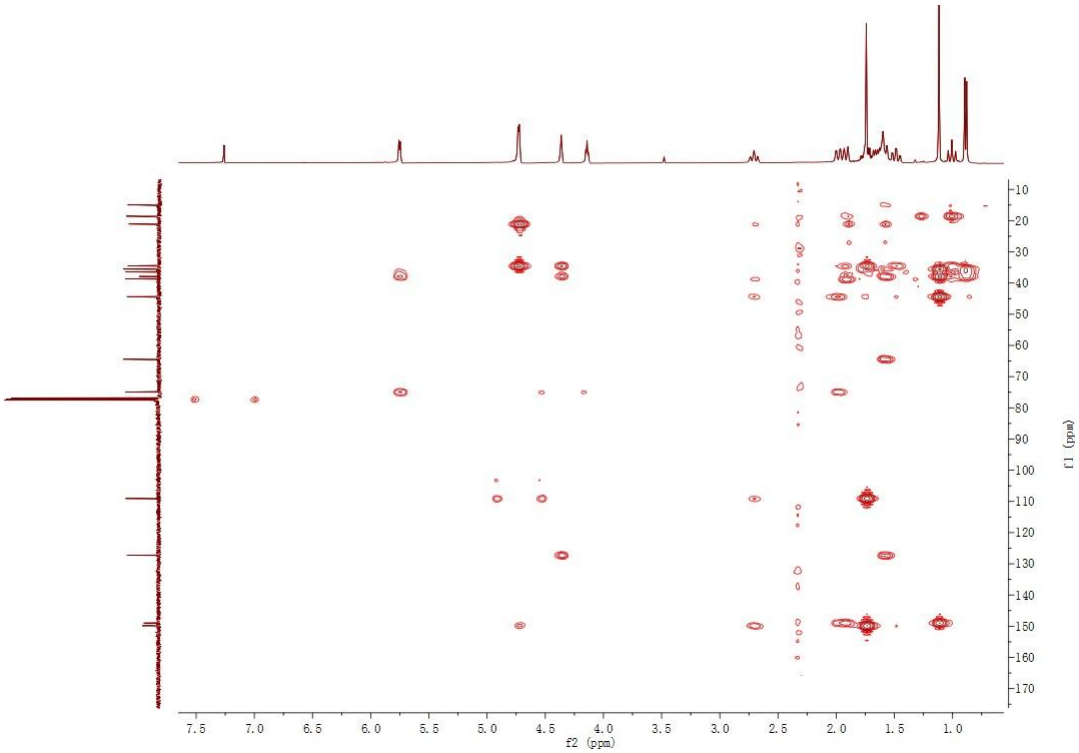


Fig. S46 HMBC spectrum of compound 5

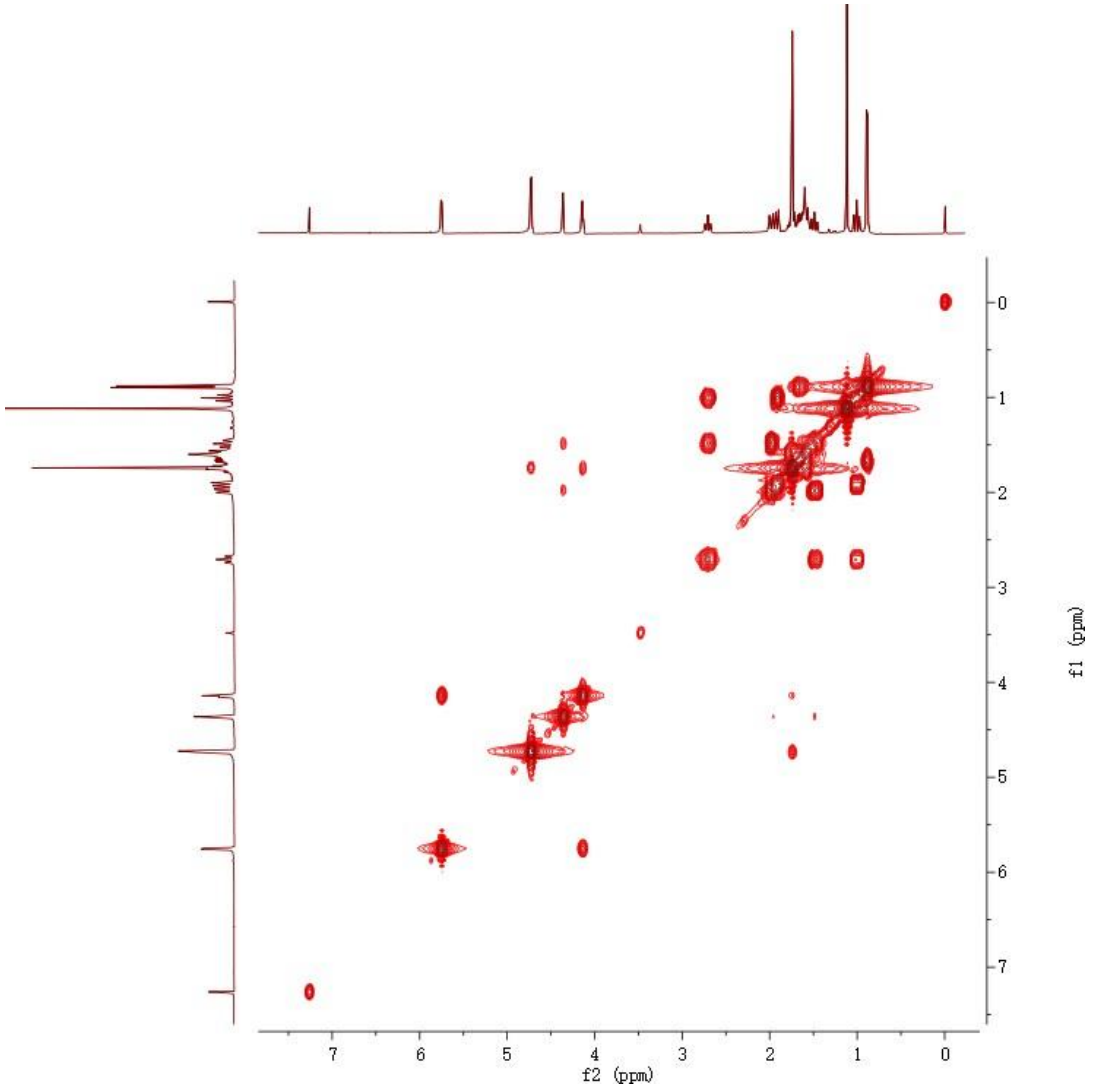


Fig. S47 ^{1}H-^{1}H COSY spectrum of compound 5

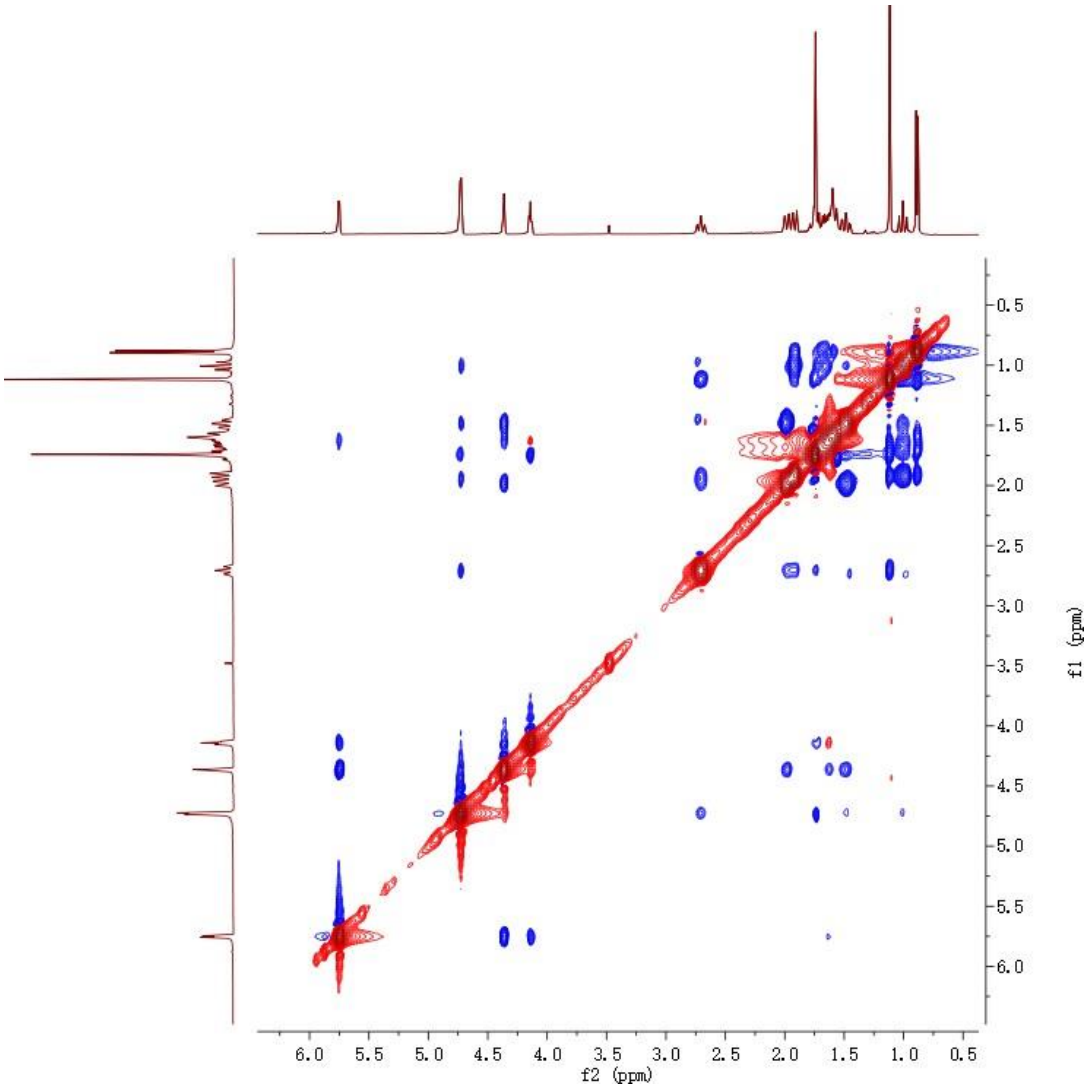


Fig. S48 NOESY spectrum of compound 5

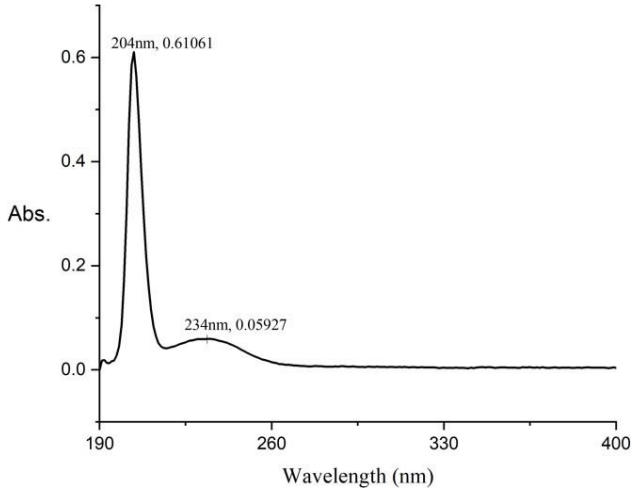


Fig. S49 UV spectrum of compound 5

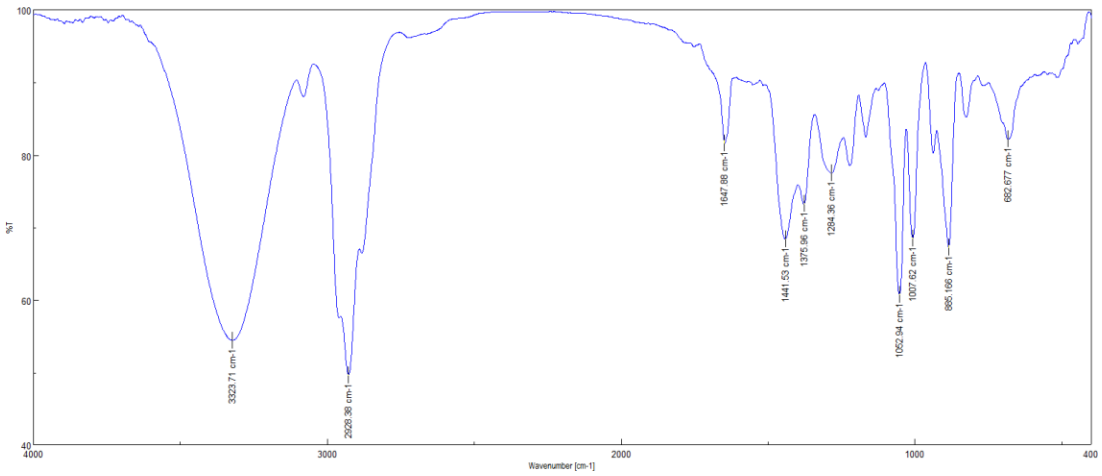
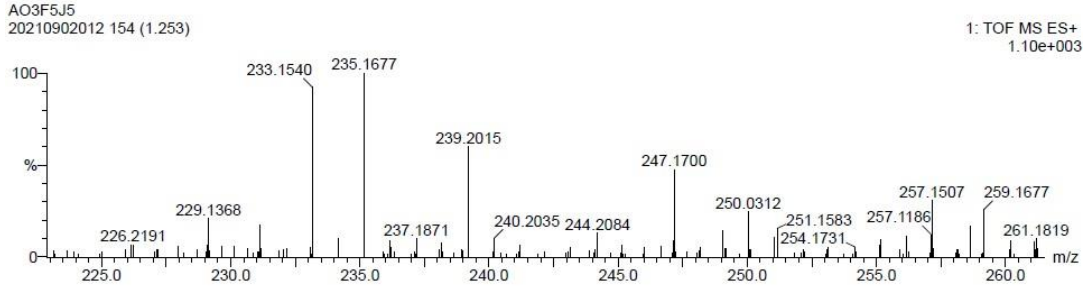


Fig. S50 IR spectrum of compound 5

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
81 formula(e) evaluated with 2 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
AO3F5J5
20210902012 154 (1.253)



Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
259.1677	259.1674	0.3	1.2	3.5	50.2	C15 H24 O2 Na

Fig. S51 HR-ESI-MS spectrum of compound 6

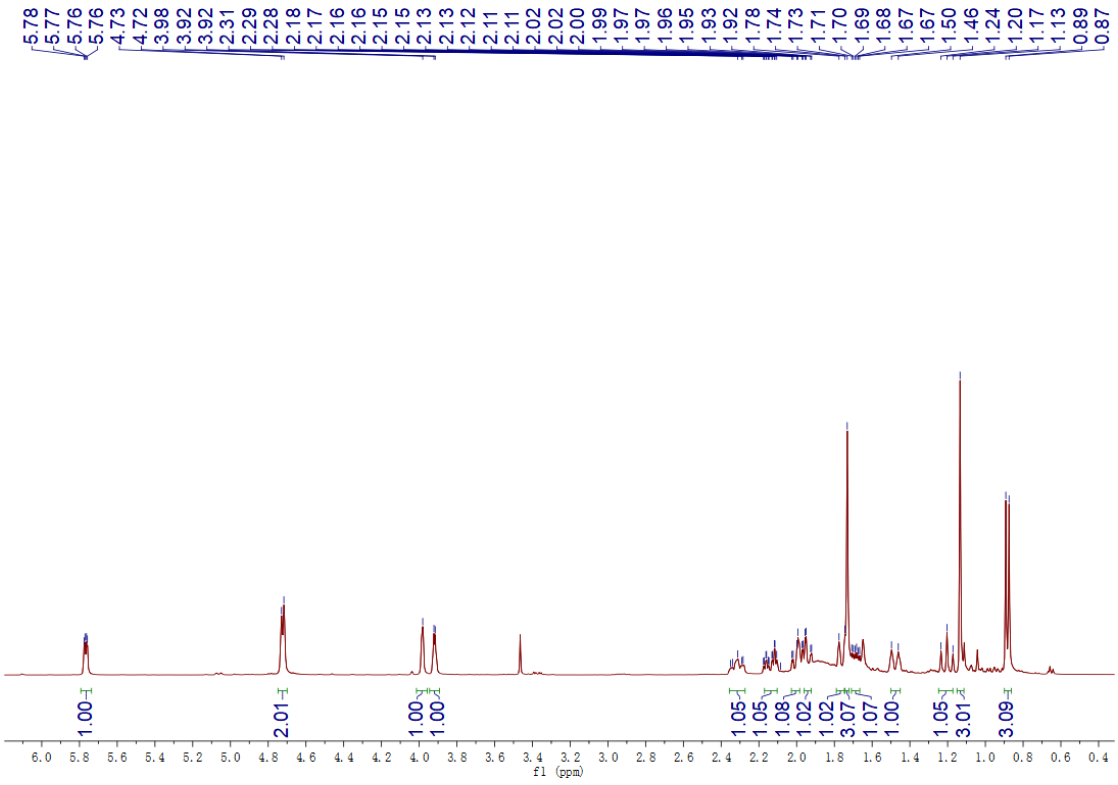


Fig. S52 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 6

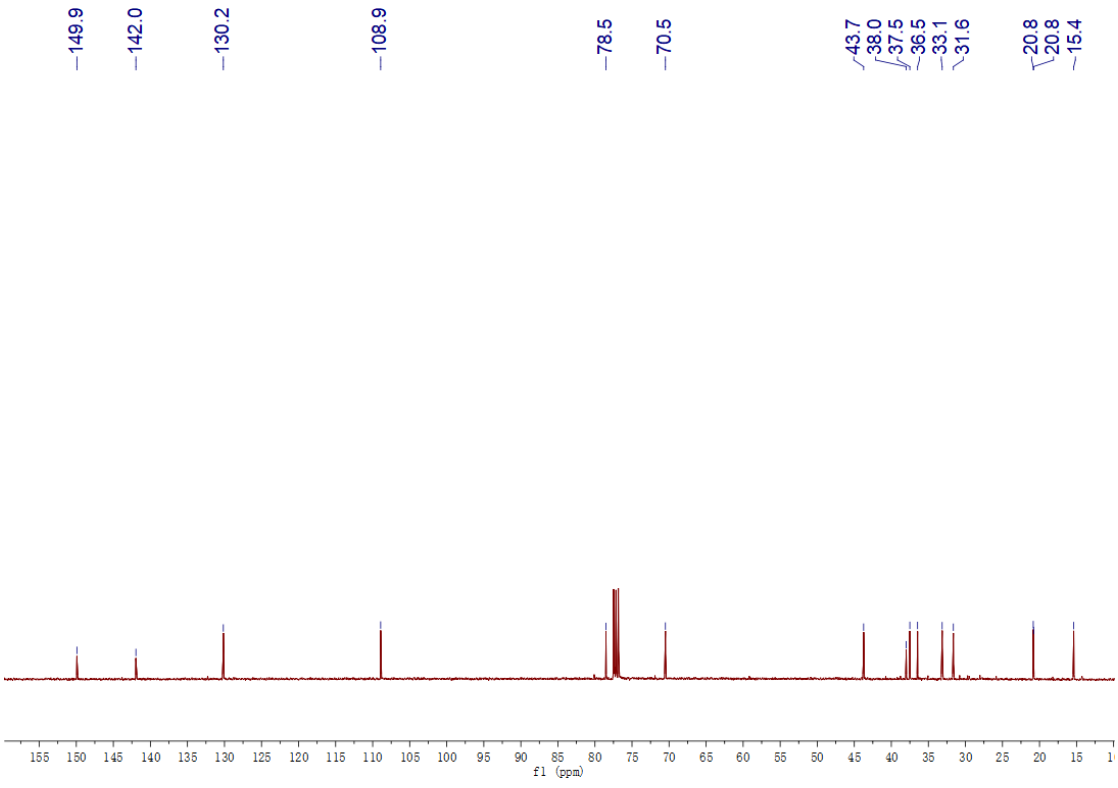


Fig. S53 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 6

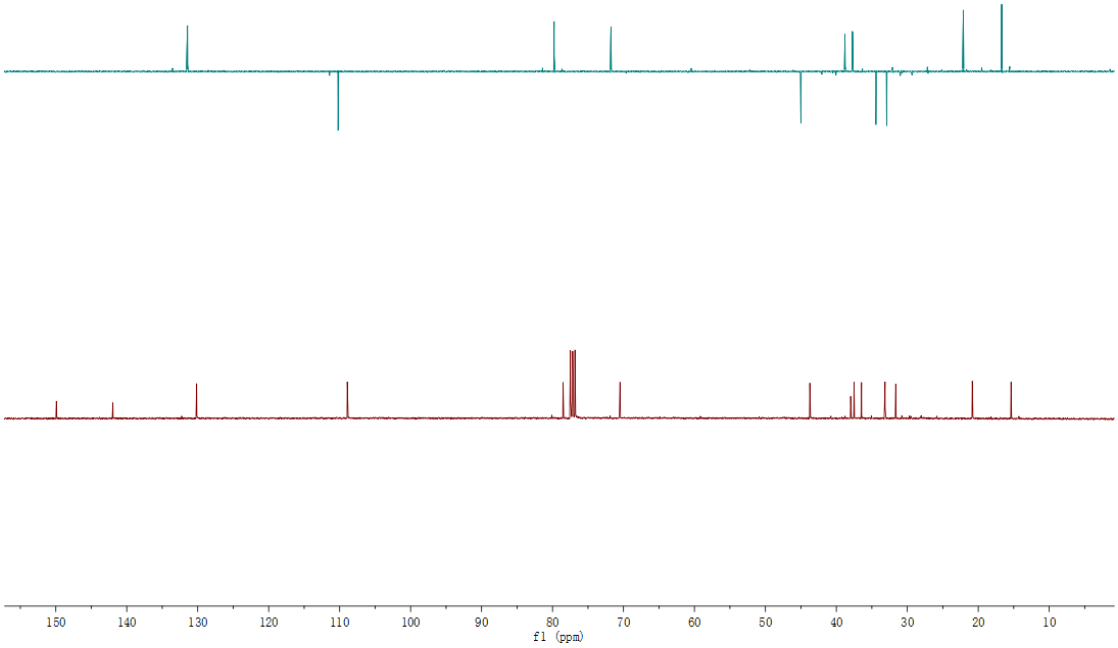


Fig. S54 DEPT (100 MHz, $CDCl_3$) and ^{13}C NMR spectra of compound 6

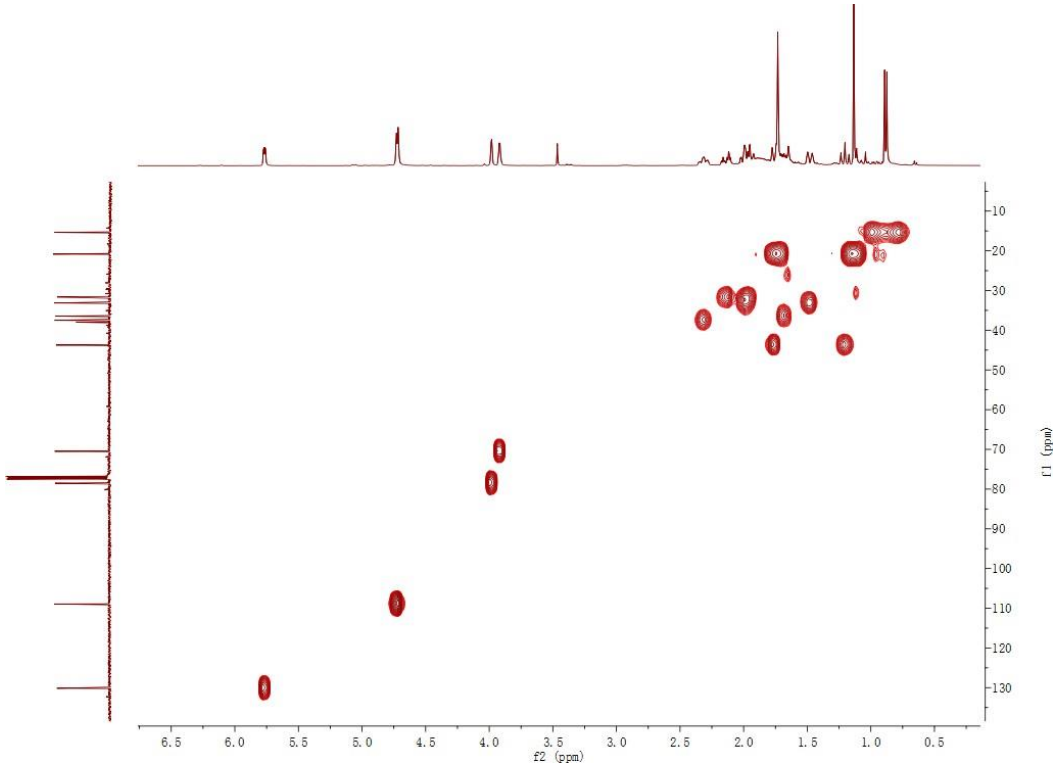


Fig. S55 HSQC spectrum of compound 6

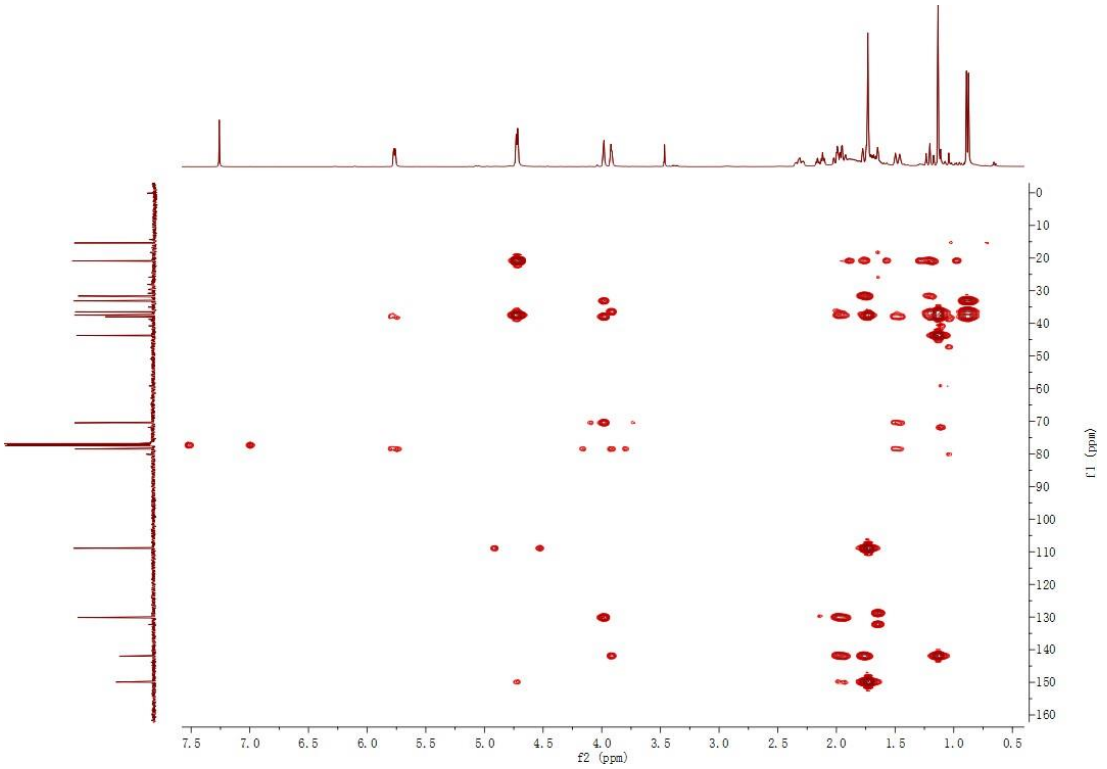


Fig. S56 HMBC spectrum of compound 6

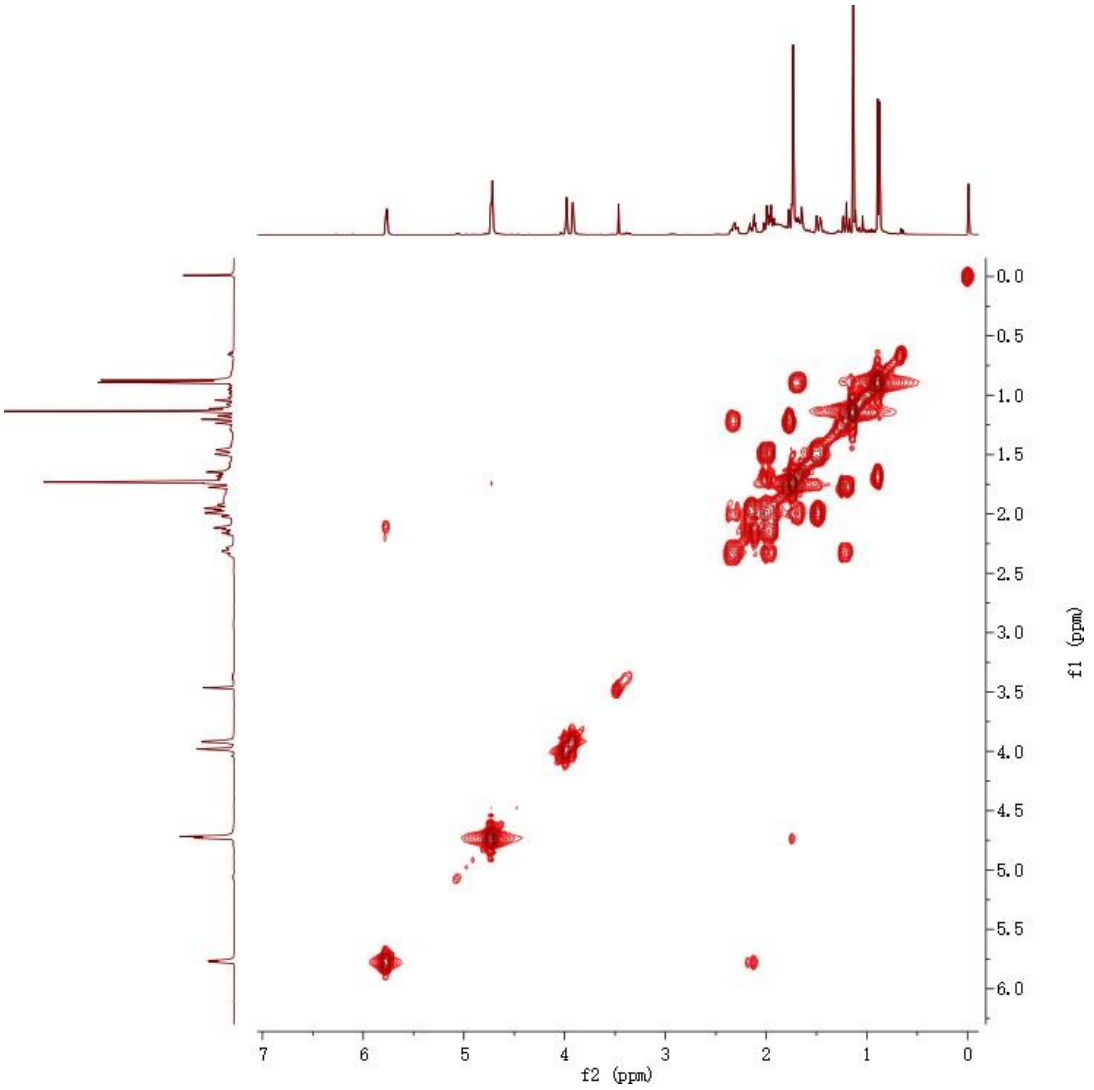


Fig. S57 ^{1}H-^{1}H COSY spectrum of compound 6

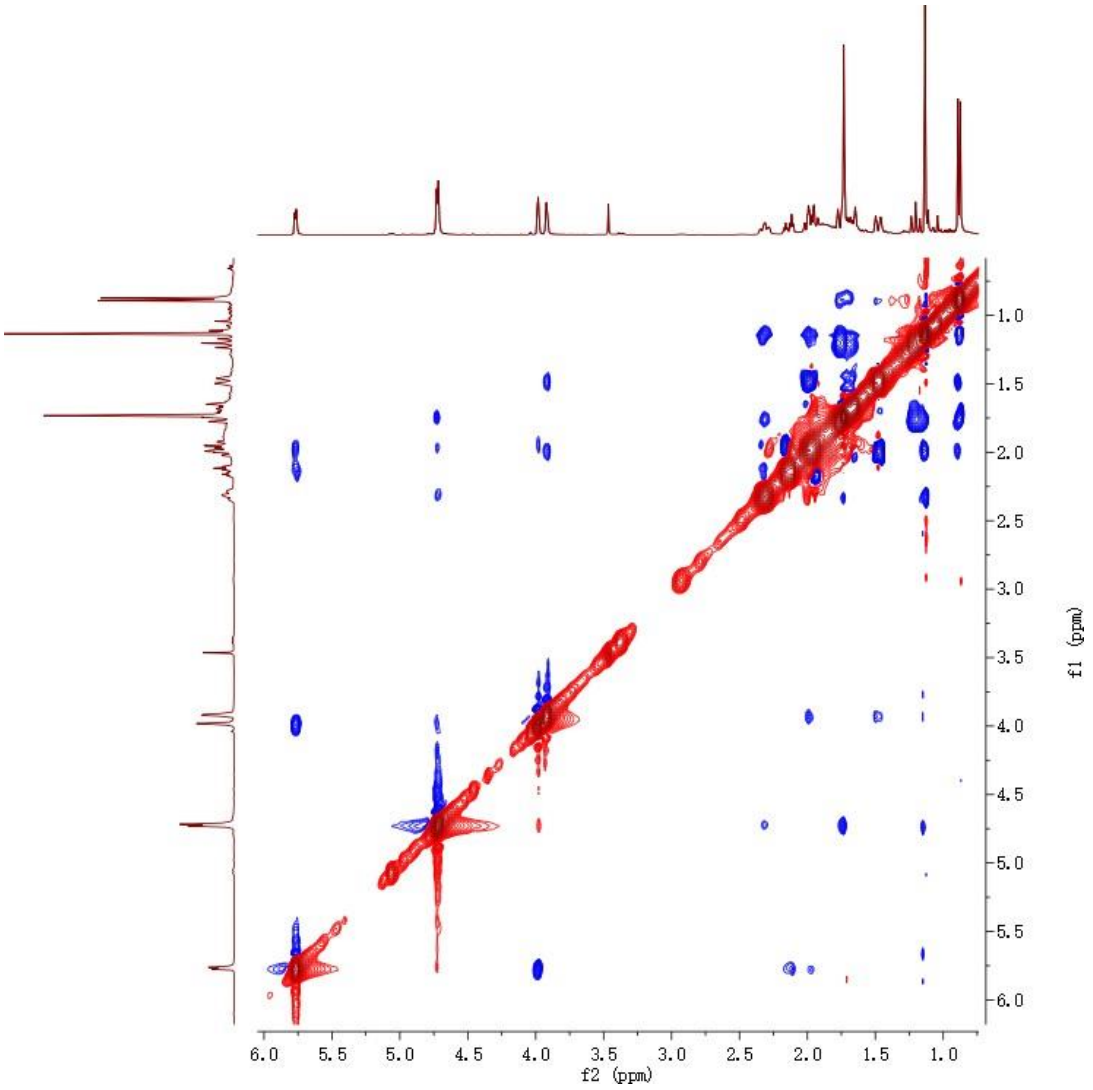


Fig. S58 NOESY spectrum of compound 6

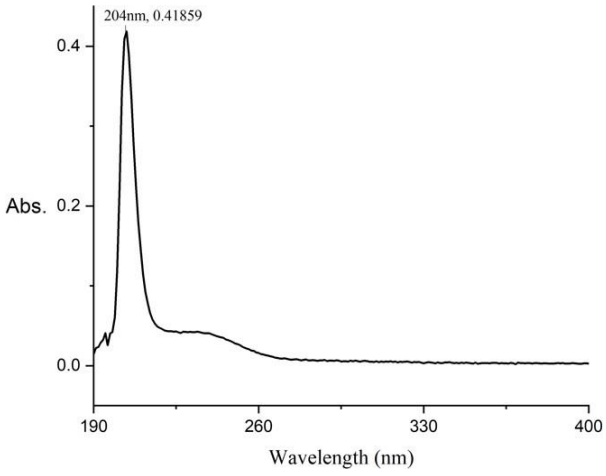


Fig. S59 UV spectrum of compound 6

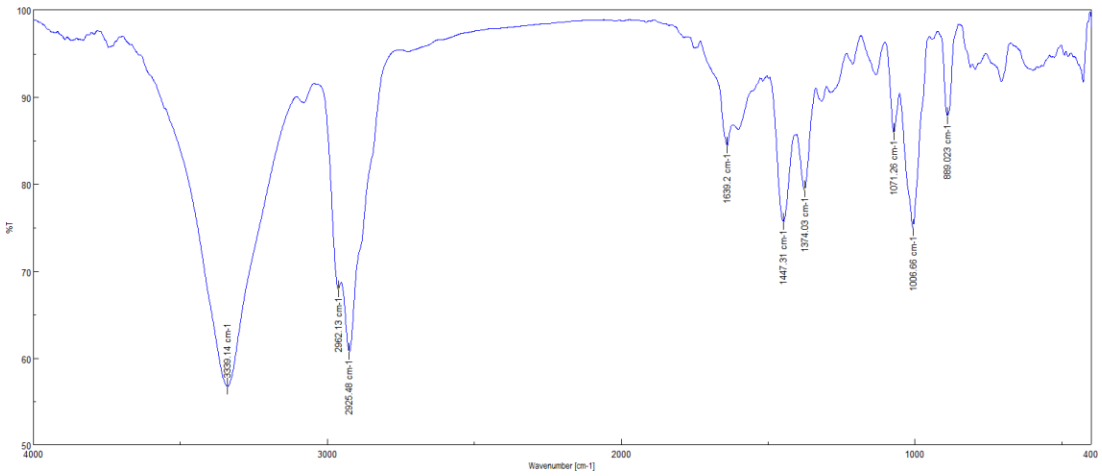


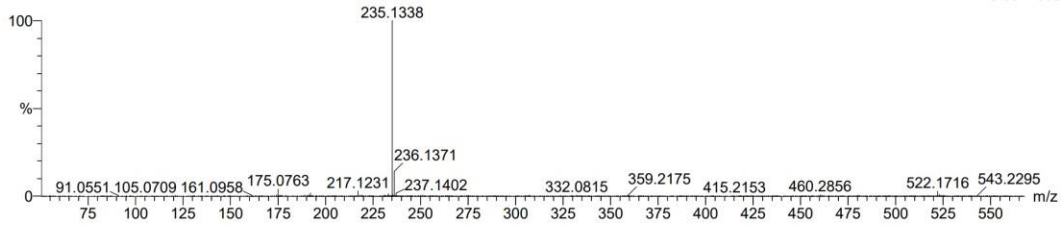
Fig. S60 IR spectrum of compound 6

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
39 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-200 O: 0-200
A04E6H1
20220523065 184 (1.489)

1: TOF MS ES+
3.69e+005



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
235.1338	235.1334	0.4	1.7	5.5	515.9	n/a	n/a	C14 H19 O3

Fig. S61 HR-ESI-MS spectrum of compound 23

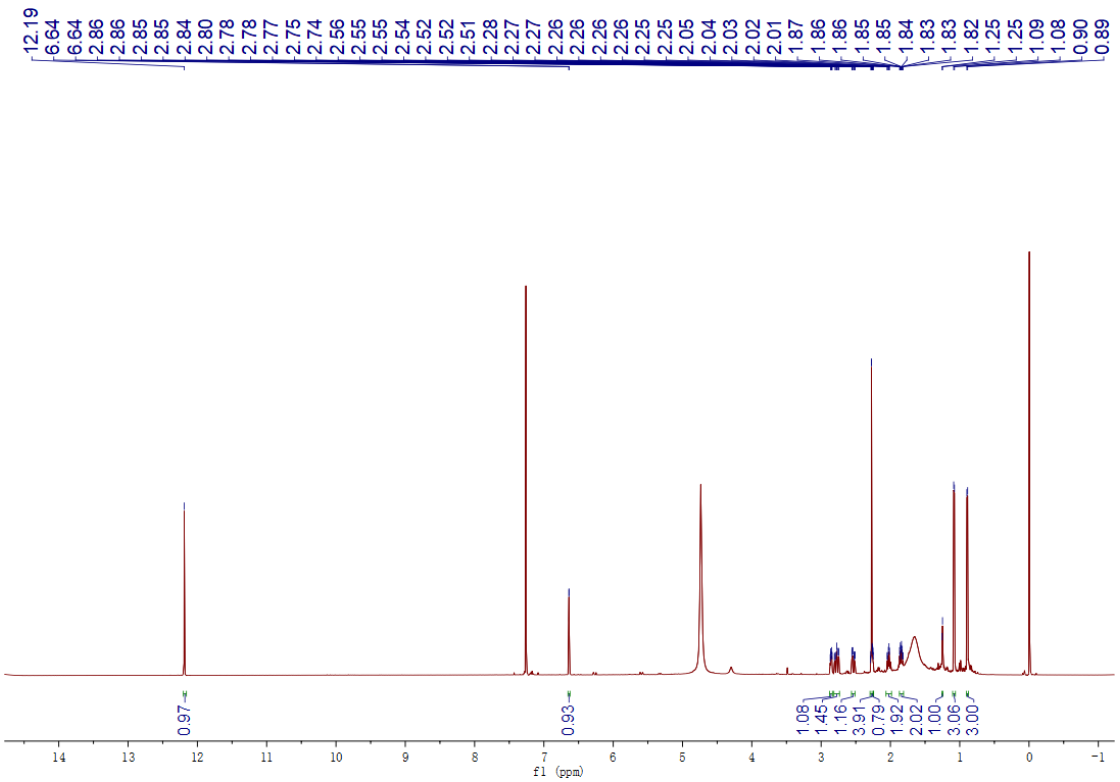


Fig. S62 ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 23

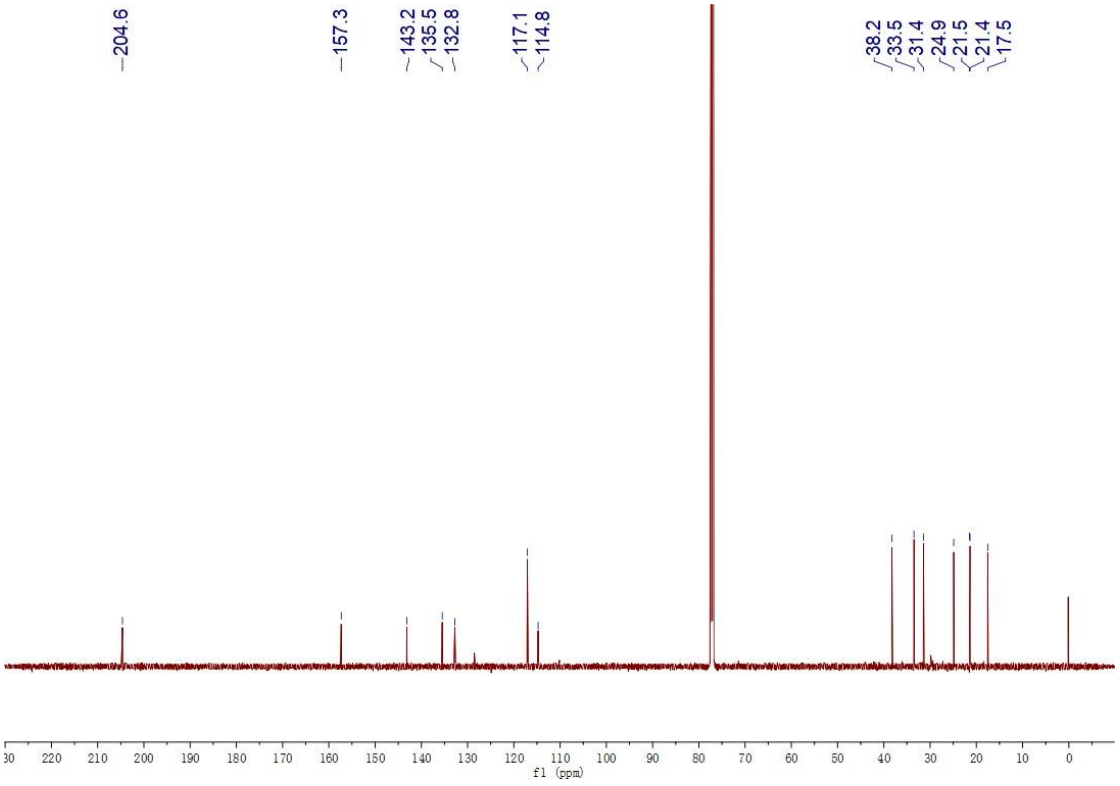


Fig. S63 ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of compound 23

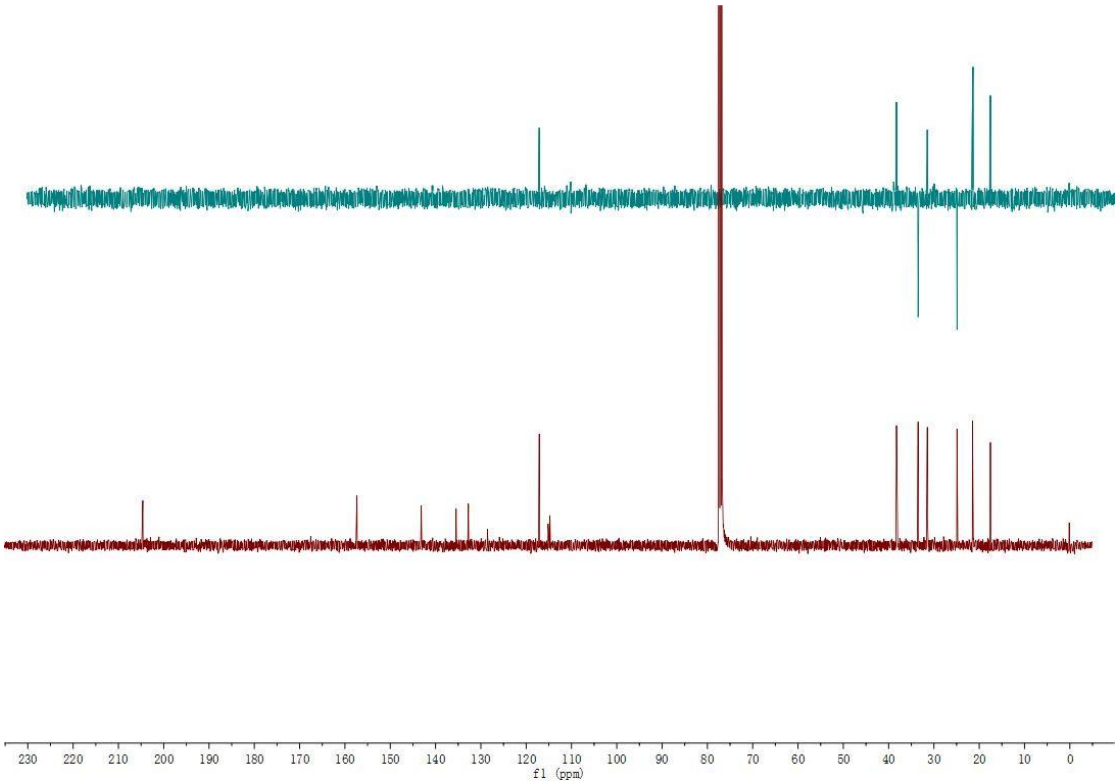


Fig. S64 DEPT (150 MHz, $CDCl_3$) and ^{13}C NMR spectra of compound 23

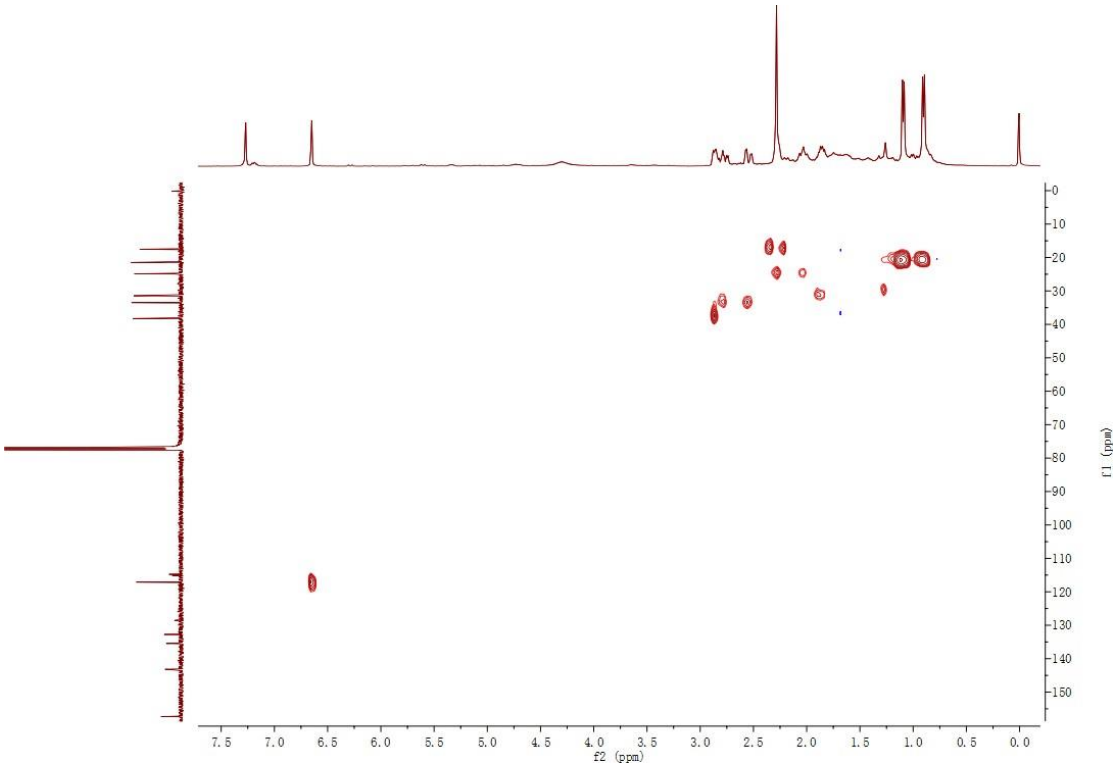


Fig. S65 HSQC spectrum of compound 23

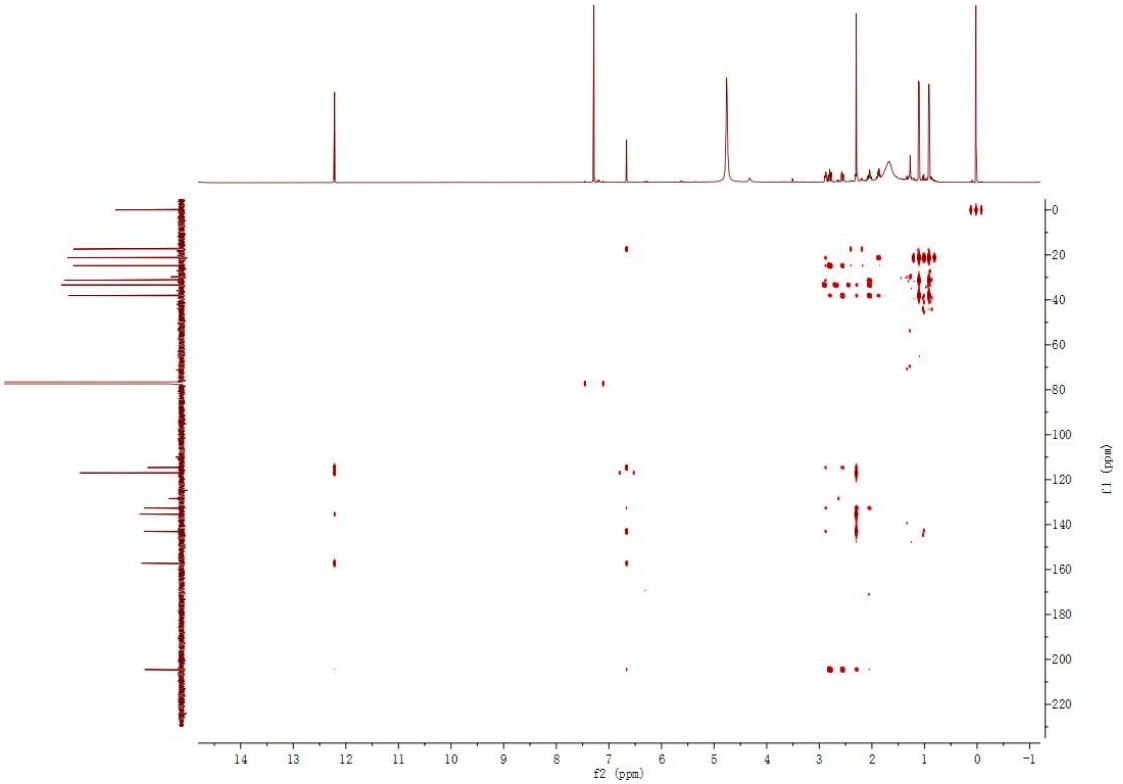


Fig. S66 HMBC spectrum of compound 23

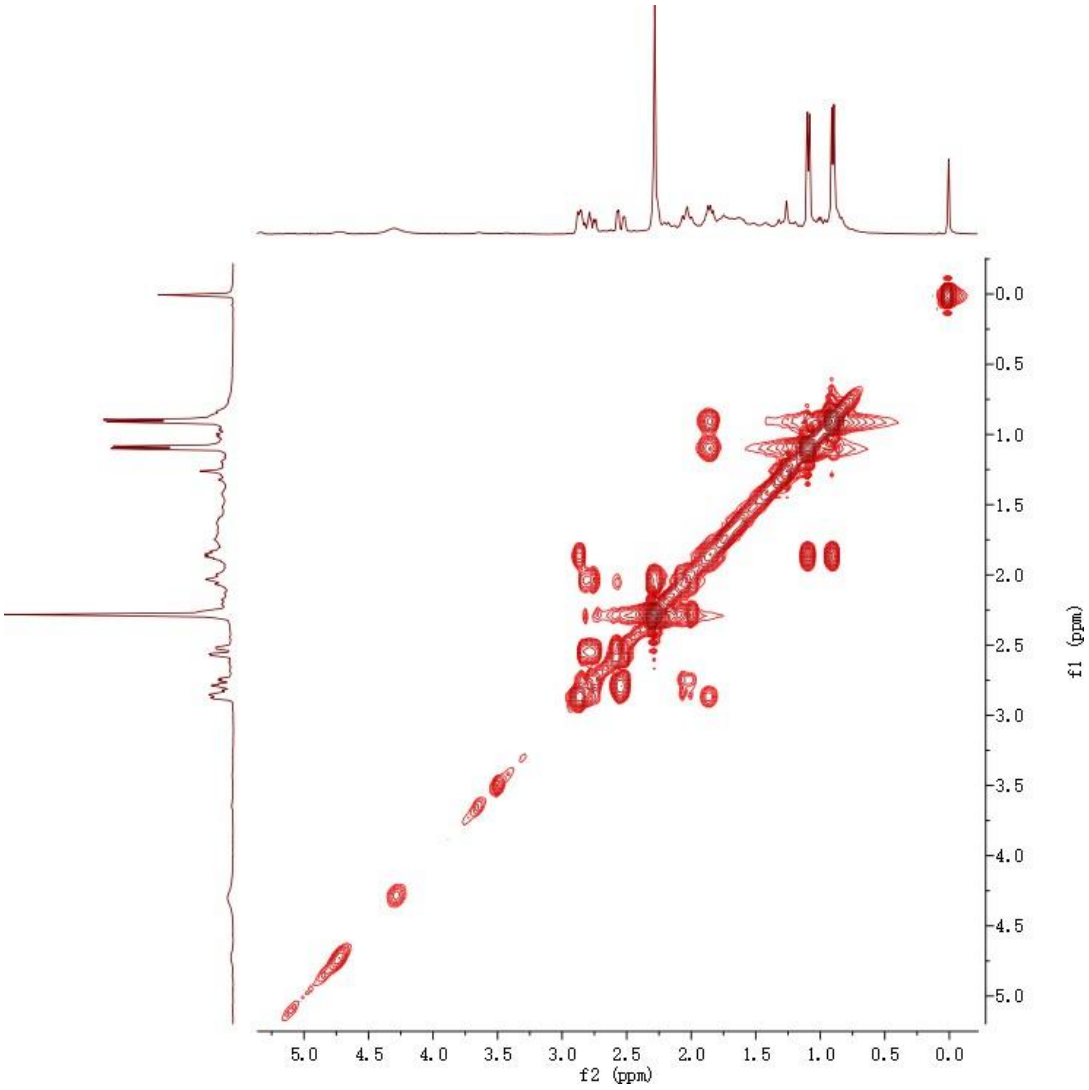


Fig. S67 ^{1}H-^{1}H COSY spectrum of compound 23

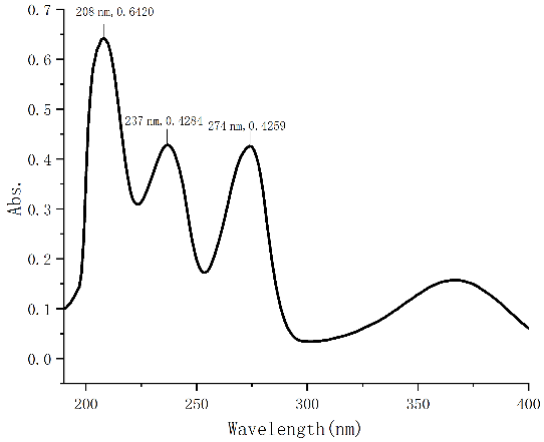


Fig. S68 UV spectrum of compound 23

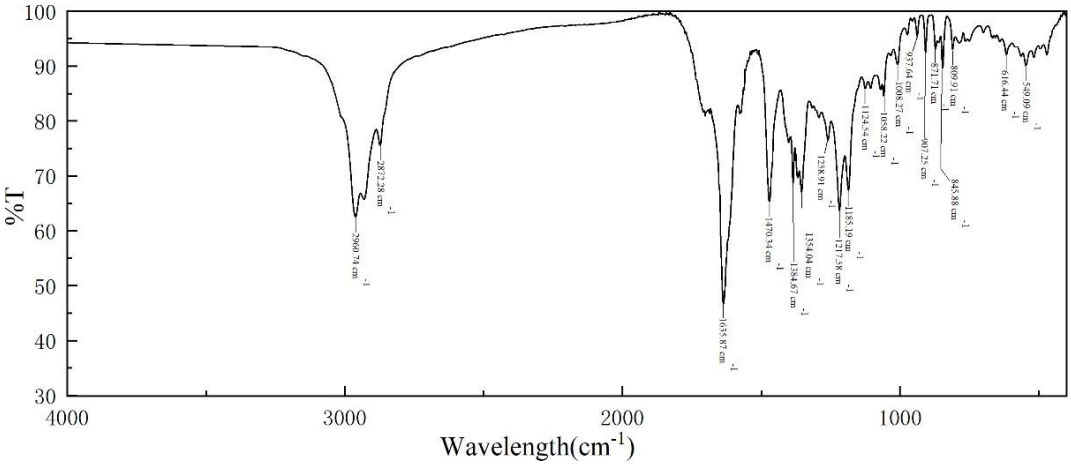


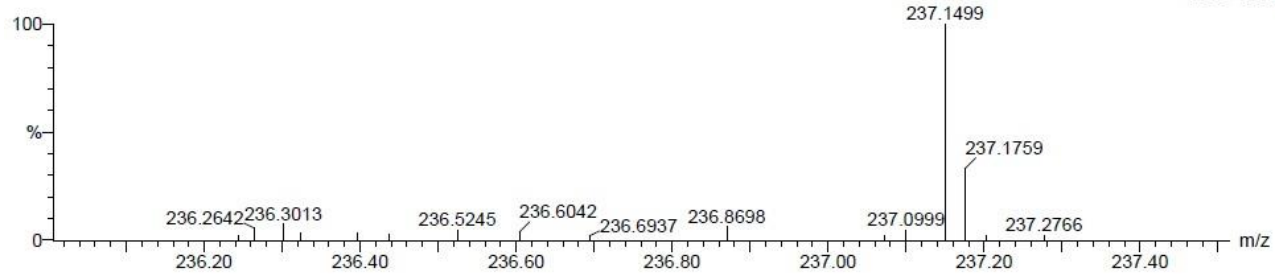
Fig. S69 IR spectrum of compound 23

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
65 formula(e) evaluated with 2 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
AO3D2A3A
20210118006 131 (1.070)

1: TOF MS ES+
8.88e+002



Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
237.1499	237.1491	0.8	3.4	4.5	n/a	C14 H21 O3

Fig. S70 HR-ESI-MS spectrum of compound 24

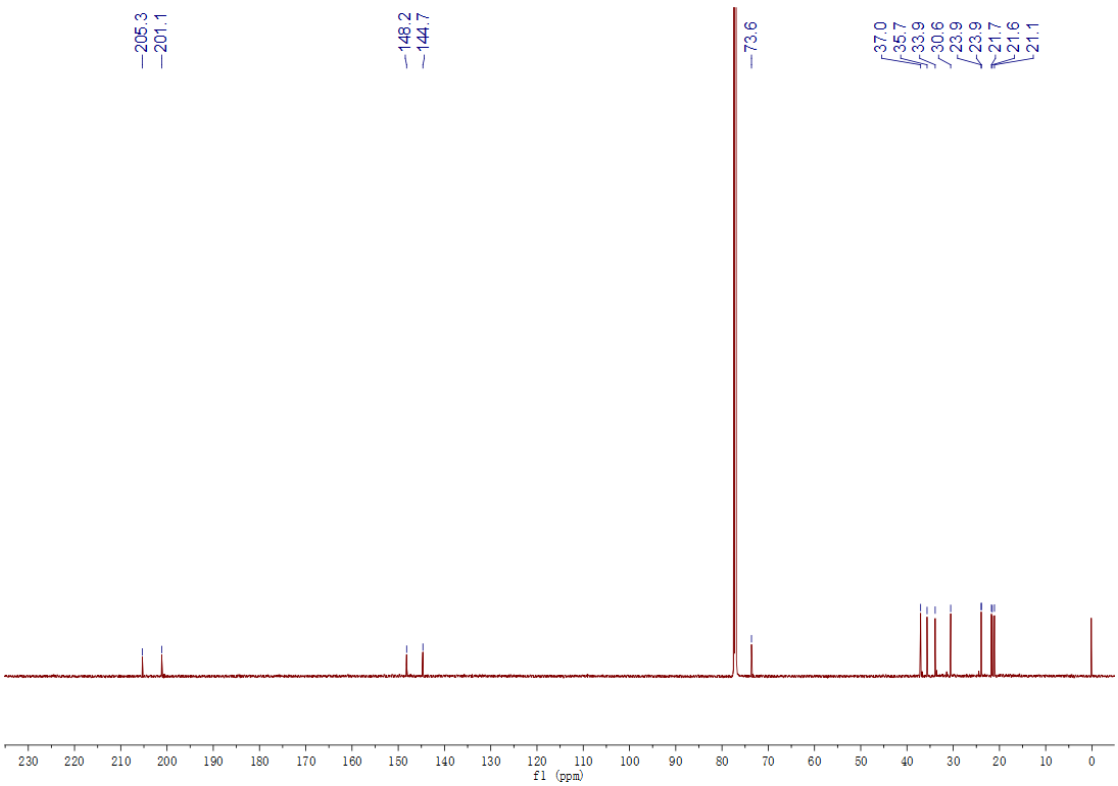


Fig. S71 ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 24

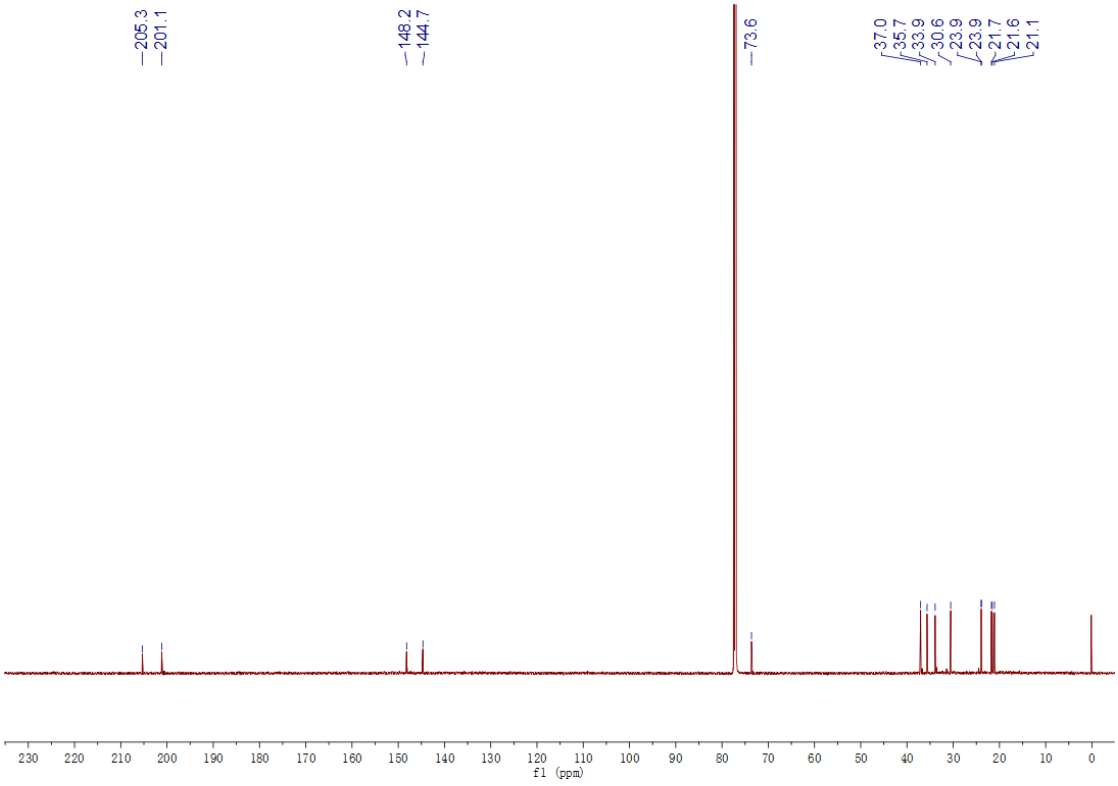


Fig. S72 ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of compound 24

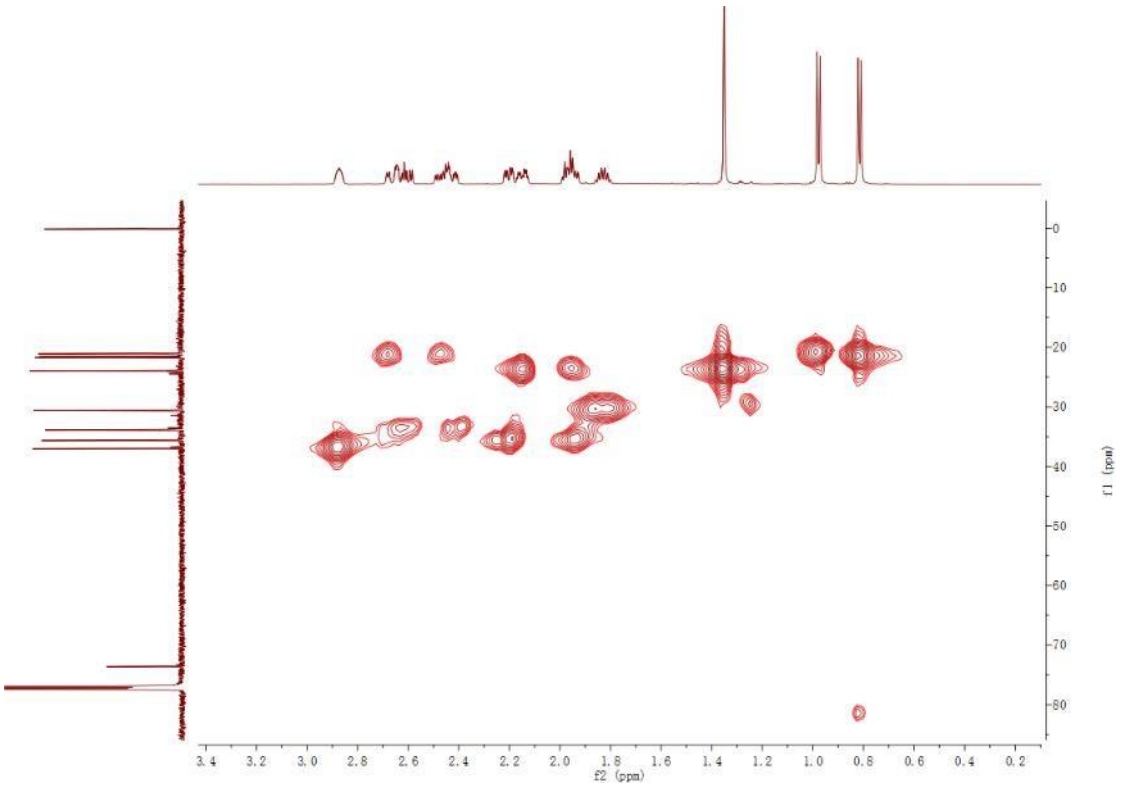


Fig. S73 HSQC spectrum of compound 24

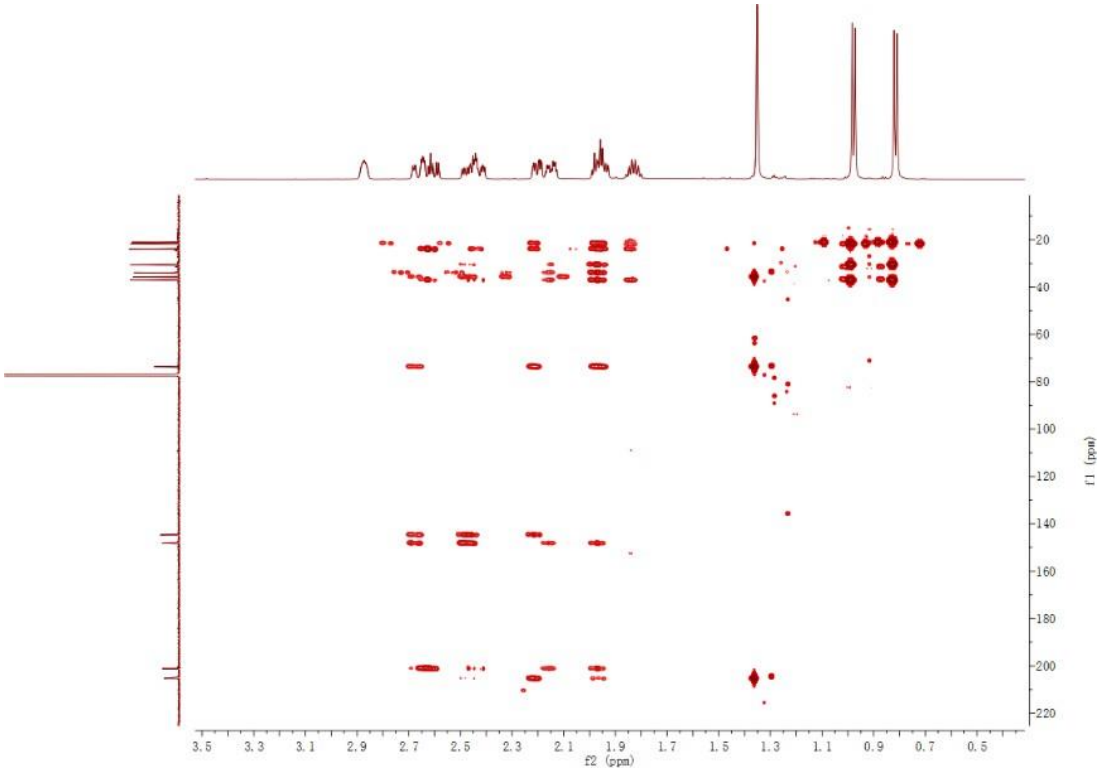


Fig. S74 HMBC spectrum of compound 24

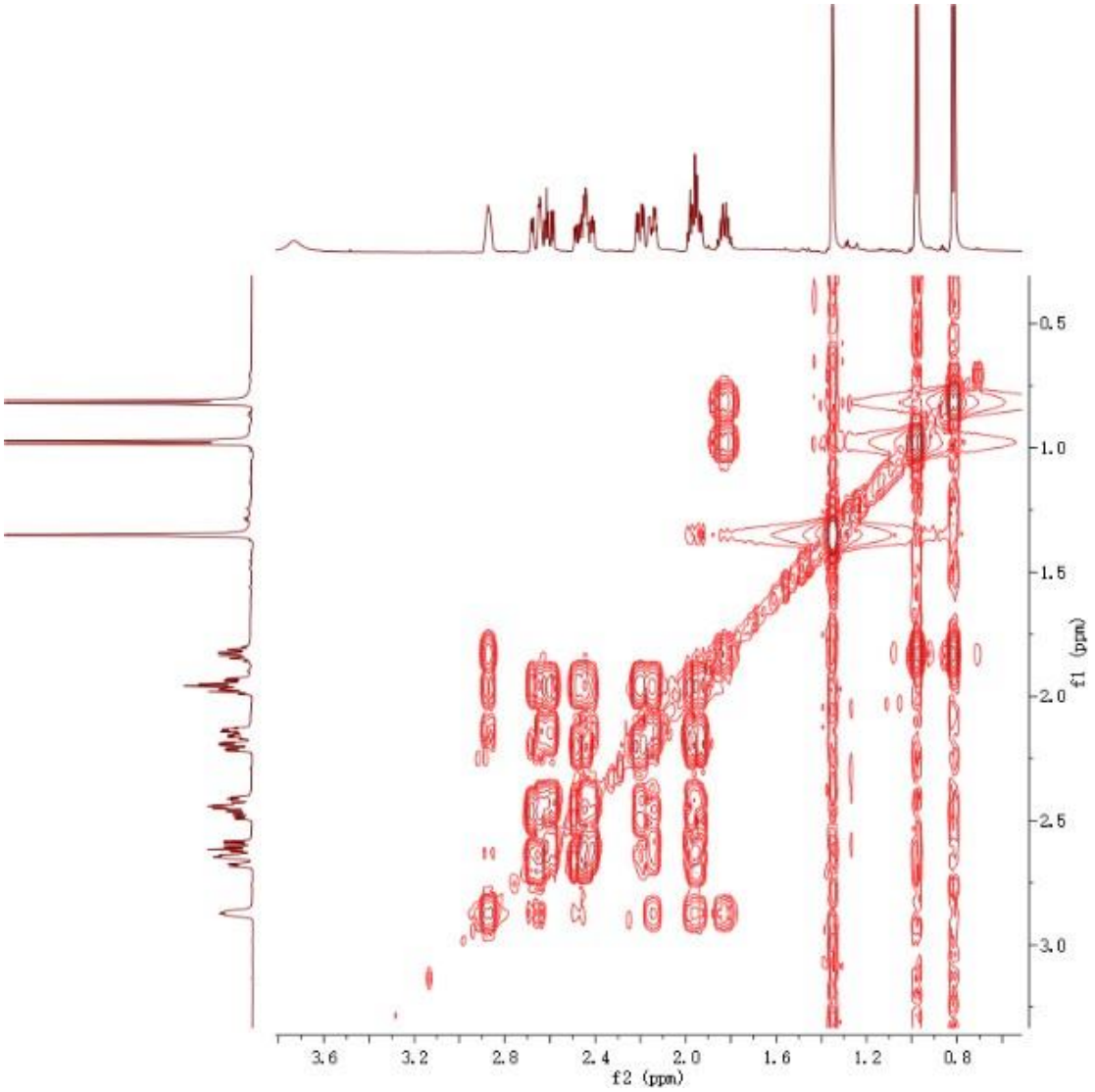


Fig. S75 ^{1}H-^{1}H COSY spectrum of compound 24

Fig. S76 NOESY spectrum of compound 24

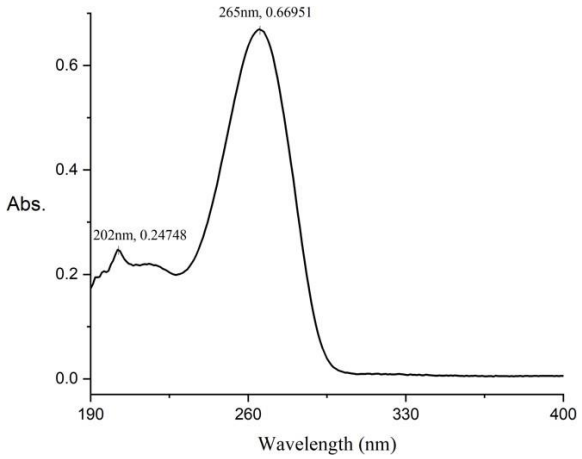


Fig. S77 UV spectrum of compound 24

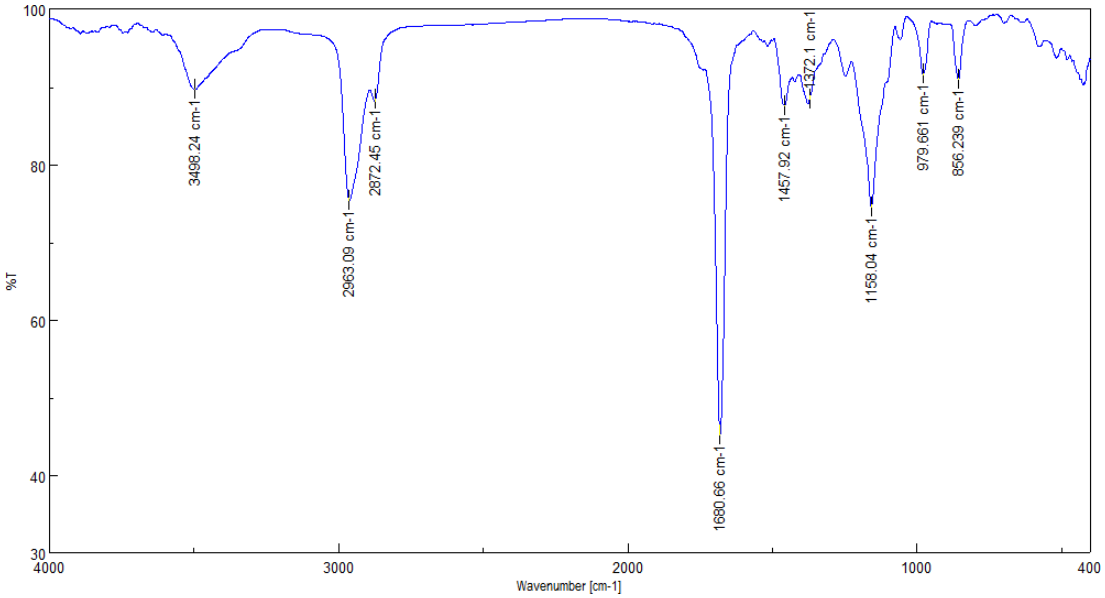


Fig. S78 IR spectrum of compound 24

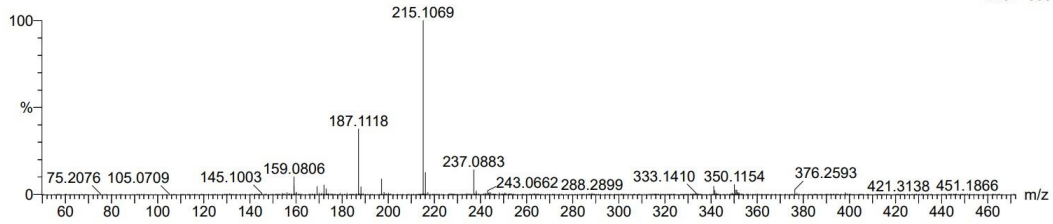
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
65 formula(e) evaluated with 2 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-200 O: 0-200 Na: 0-1

AO4E4A3
2022030732 178 (1.444)

1: TOF MS ES+
1.76e+005



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
237.0883	237.0891	-0.8	-3.4	7.5	156.7	0.028	97.27	C14 H14 O2 Na
	237.0916	-3.3	-13.9	10.5	160.2	3.602	2.73	C16 H13 O2

Fig. S79 HR-ESI-MS spectrum of compound 25

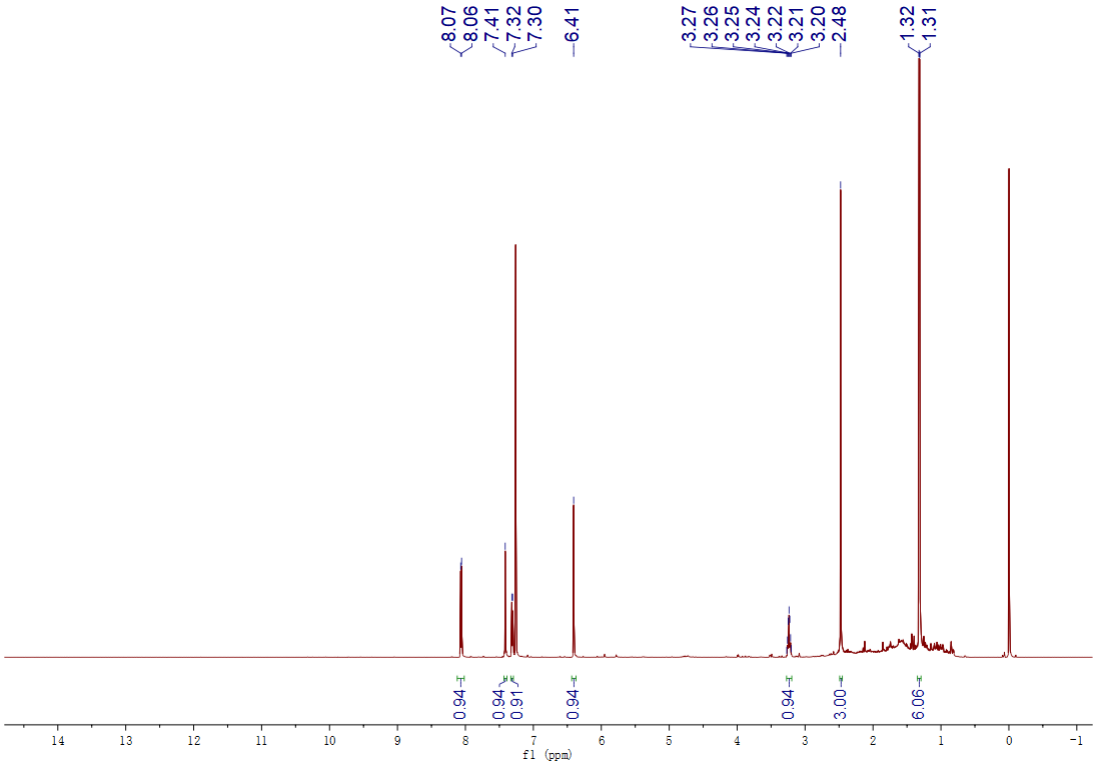


Fig. S80 ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 25

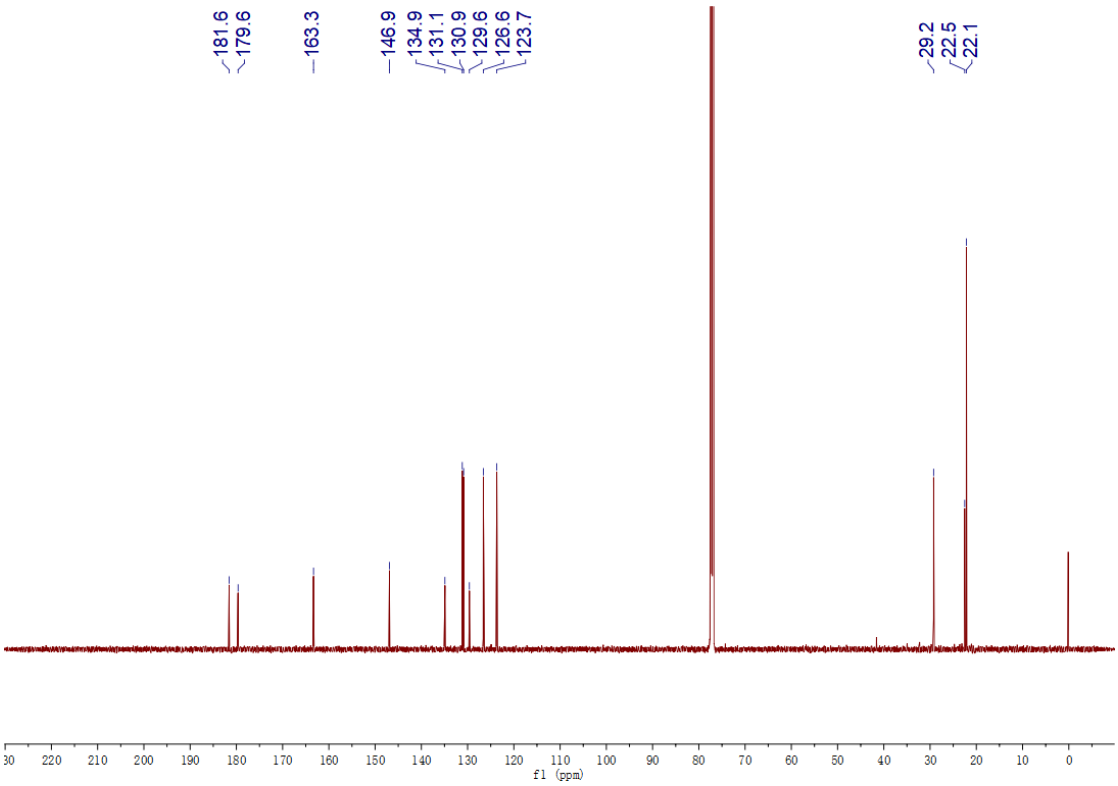


Fig. S81 ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of compound 25

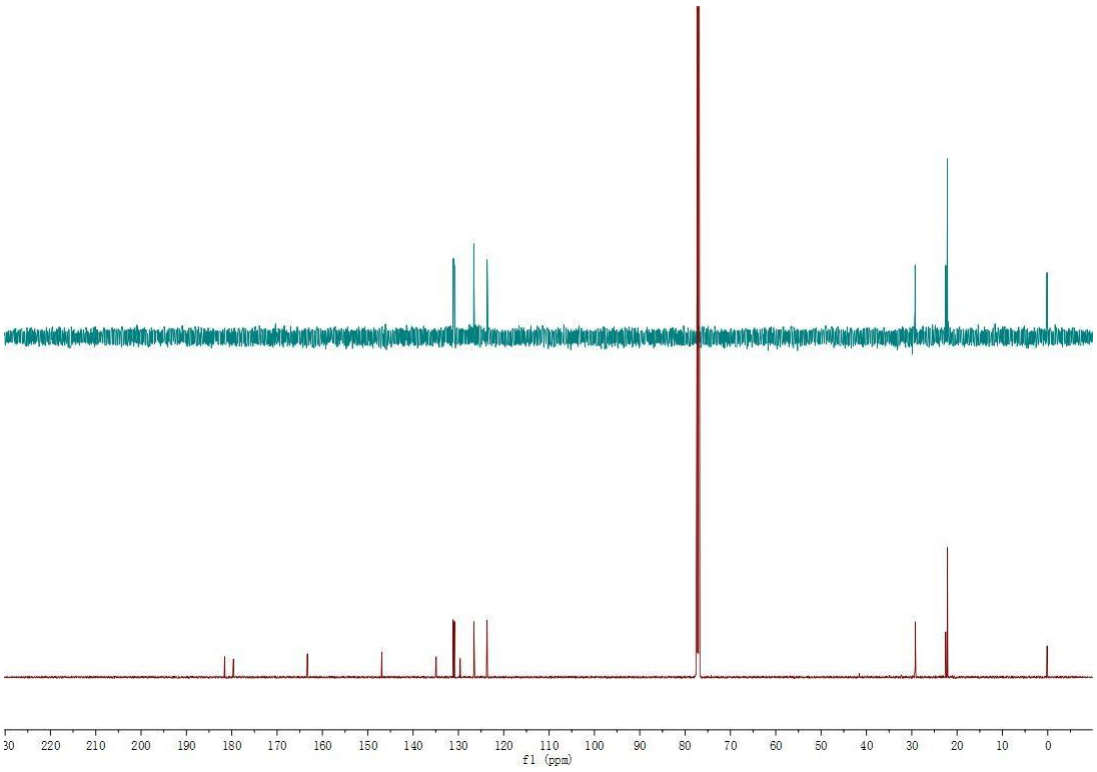


Fig. S82 DEPT (150 MHz, $CDCl_3$) and ^{13}C NMR spectra of compound 25

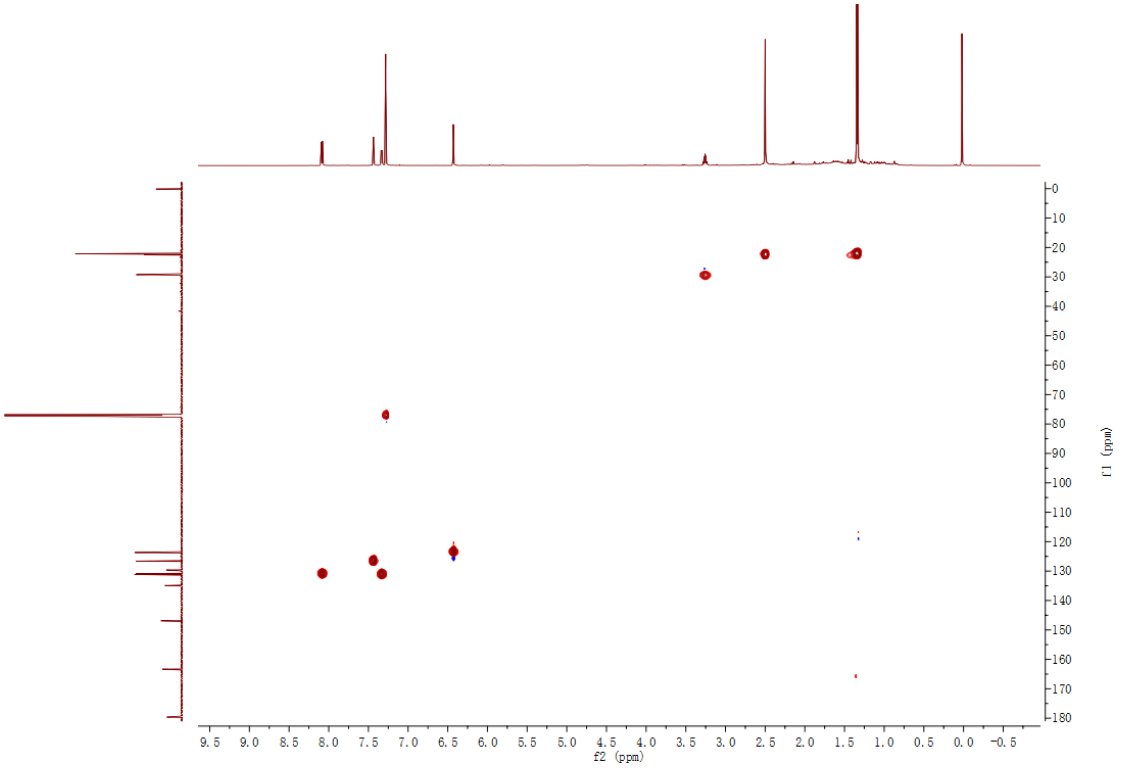


Fig. S83 HSQC spectrum of compound 25

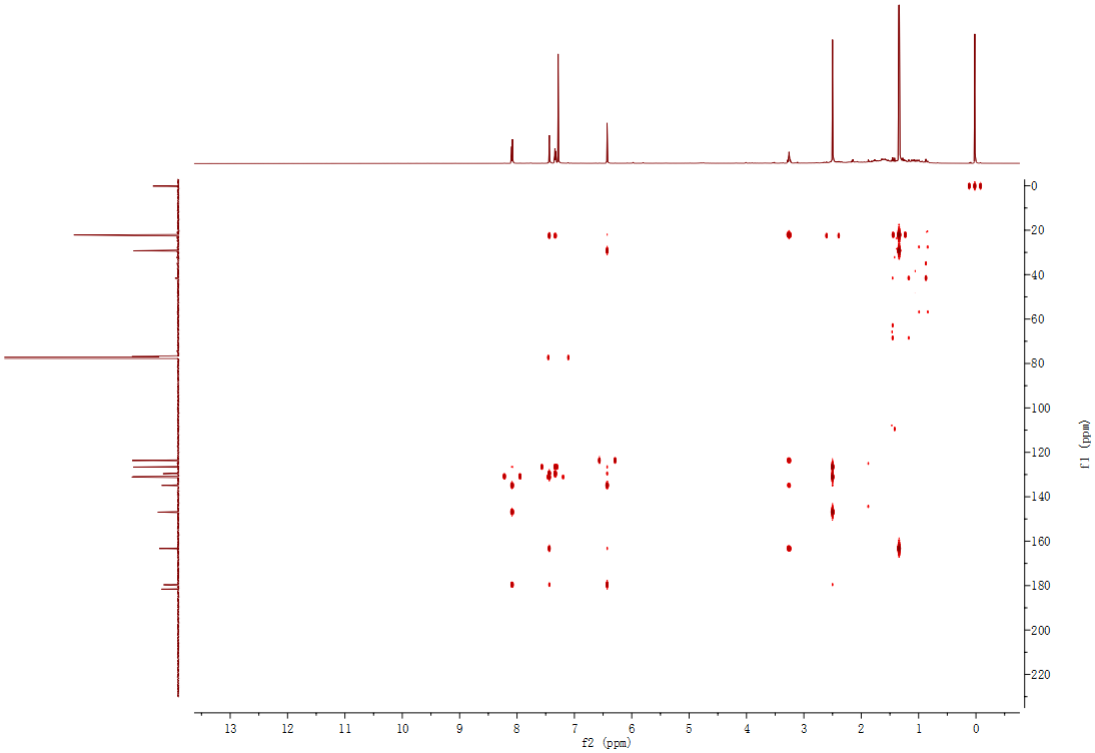


Fig. S84 HMBC spectrum of compound 25

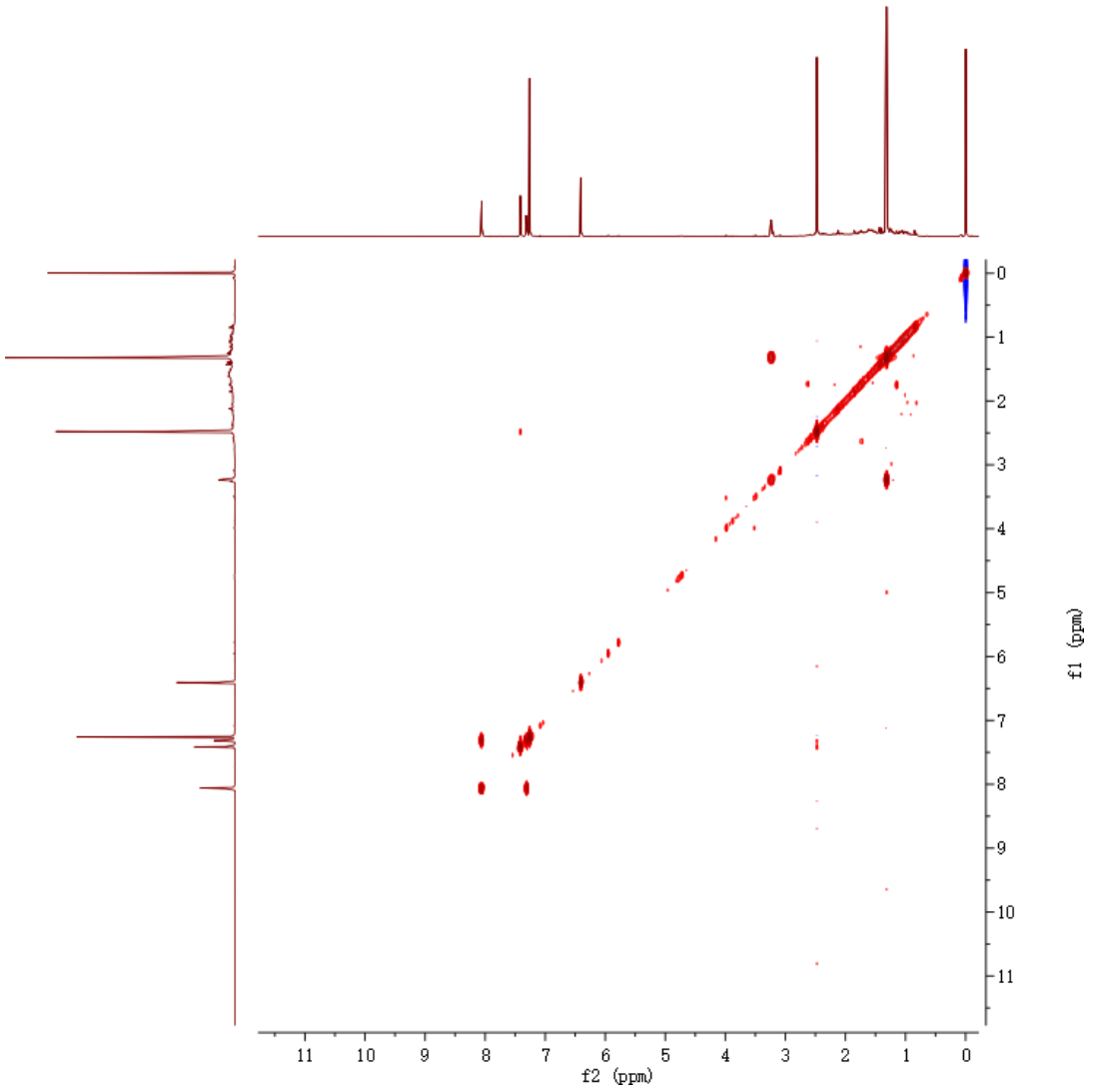


Fig. S85 ^{1}H-^{1}H COSY spectrum of compound 25

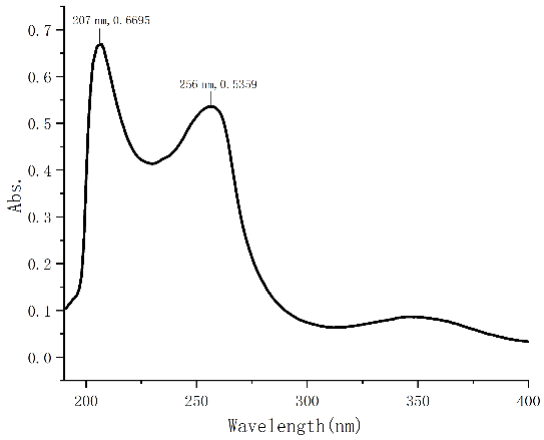


Fig. S86 UV spectrum of compound 25

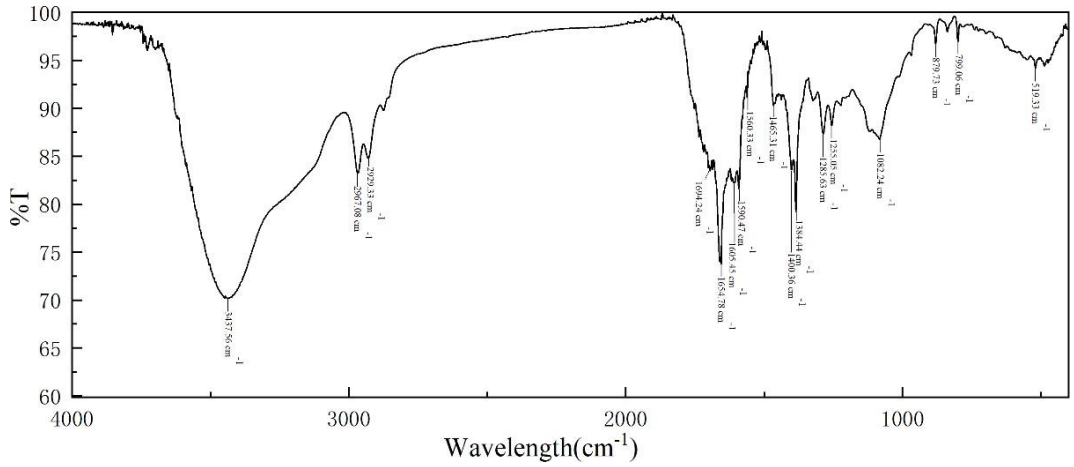
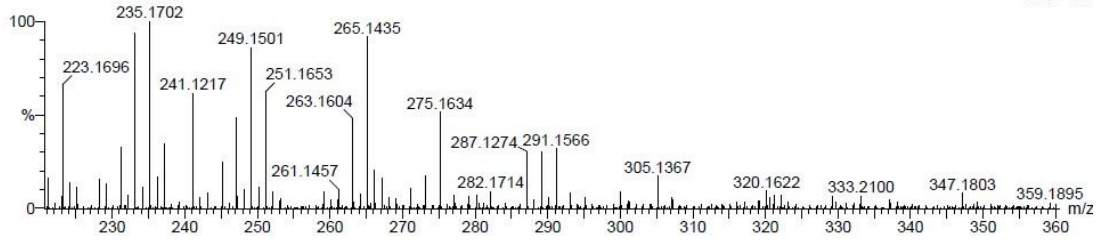


Fig. S87 IR spectrum of compound 25

Elemental Composition Report Page 1

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

Monoisotopic Mass, Even Electron Ions
1300 formula(e) evaluated with 4 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-500 H: 0-1000 N: 0-200 O: 0-200 Na: 0-1 Cl: 0-8
AO3D2C2
20210118009 146 (1.182) 1: TOF MS ES+
4.91e+00



Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
233.1541	233.1542	-0.1	-0.4	5.5	2440.8	C15 H21 O2

Fig. S88 HR-ESI-MS spectrum of compound 27

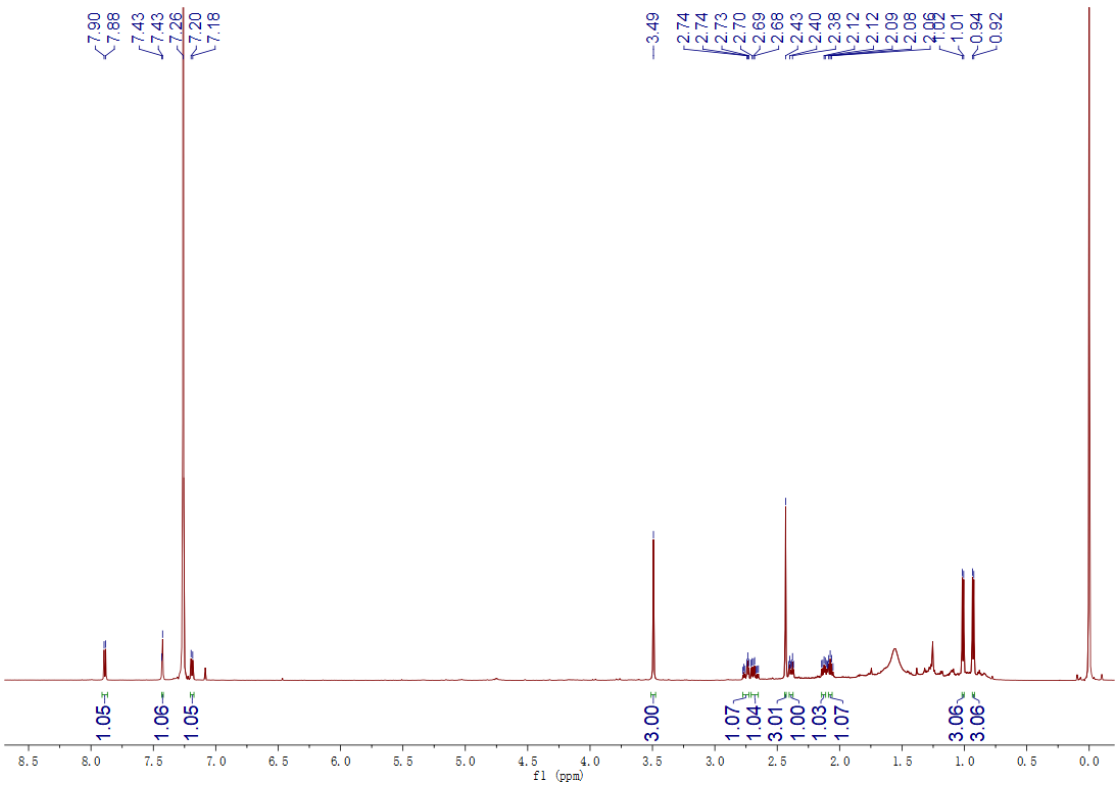


Fig. S89 ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 27

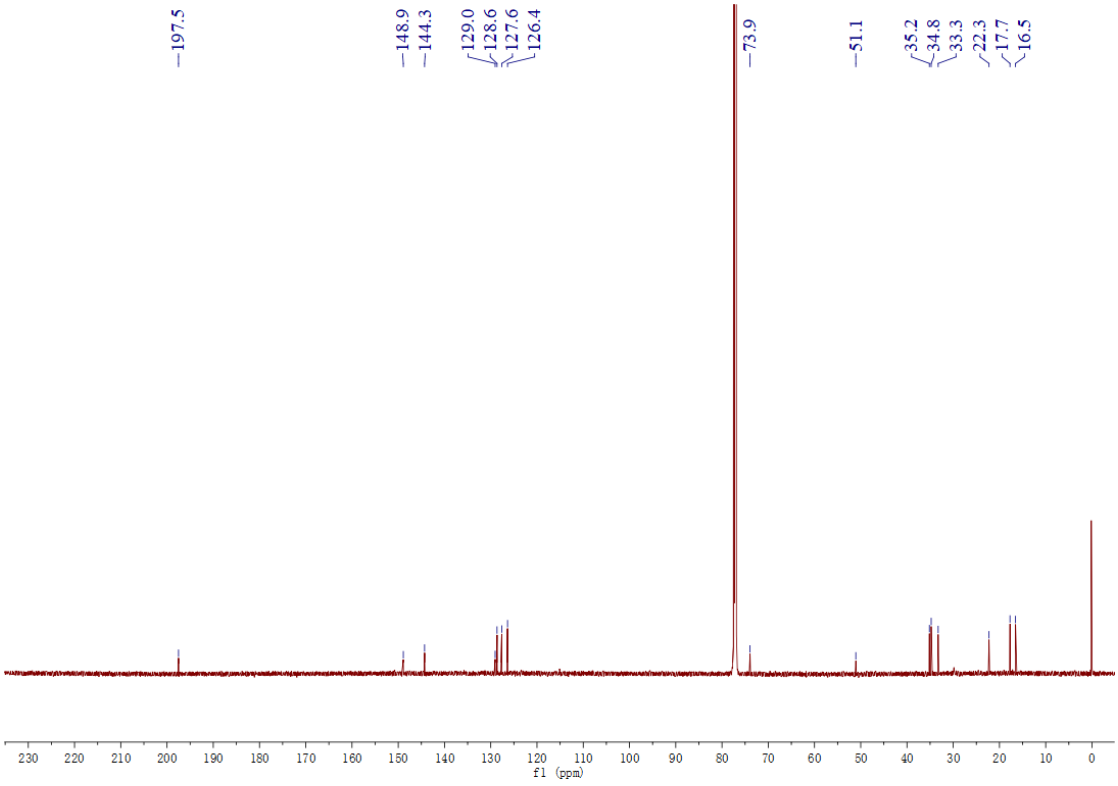


Fig. S90 ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of compound 27

Fig. S91 DEPT (150 MHz, $CDCl_3$) and ^{13}C NMR spectra of compound 27

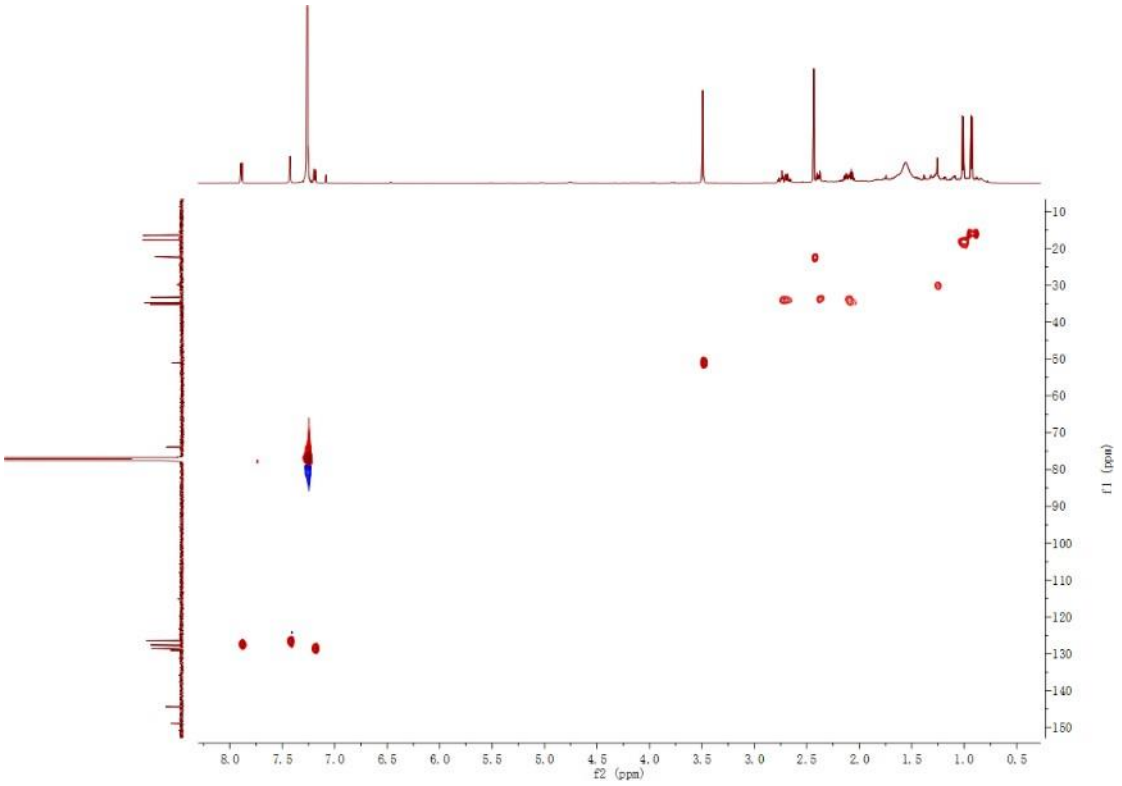


Fig. S92 HSQC spectrum of compound 27

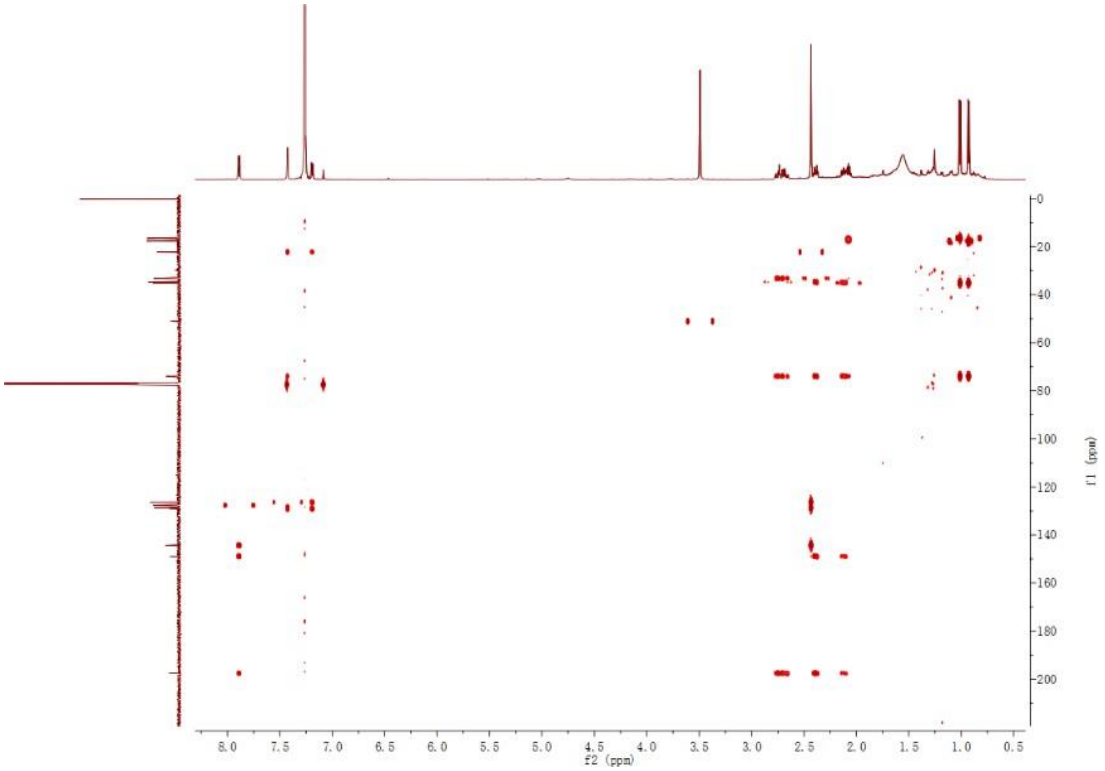


Fig. S93 HMBC spectrum of compound 27

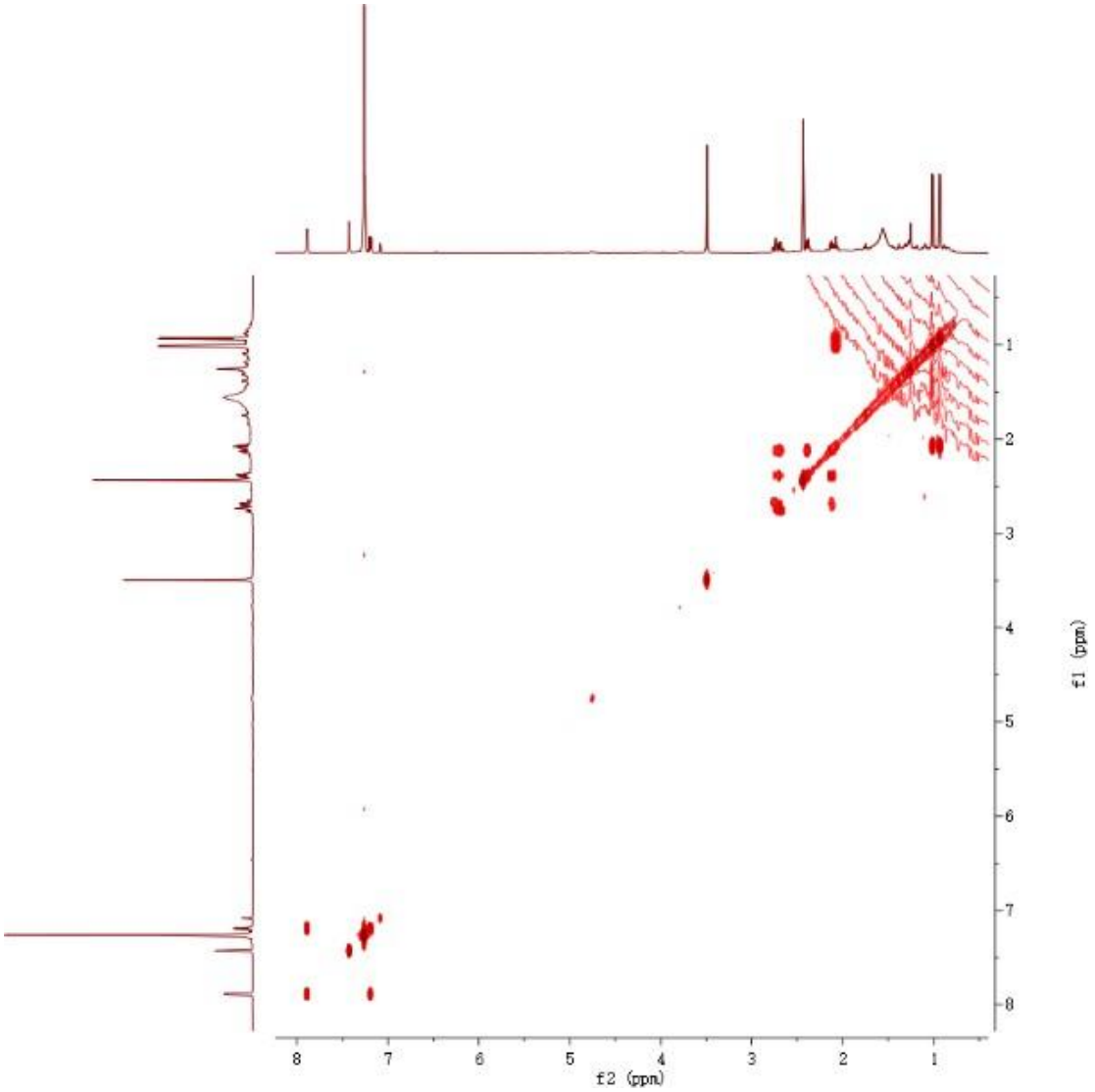


Fig. S94 ^{1}H-^{1}H COSY spectrum of compound 27

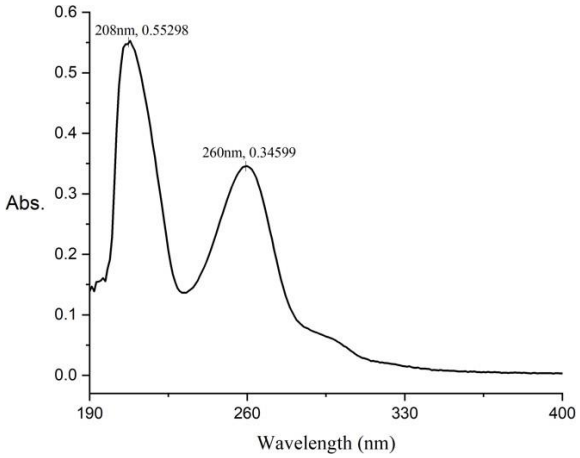


Fig. S95 UV spectrum of compound 27

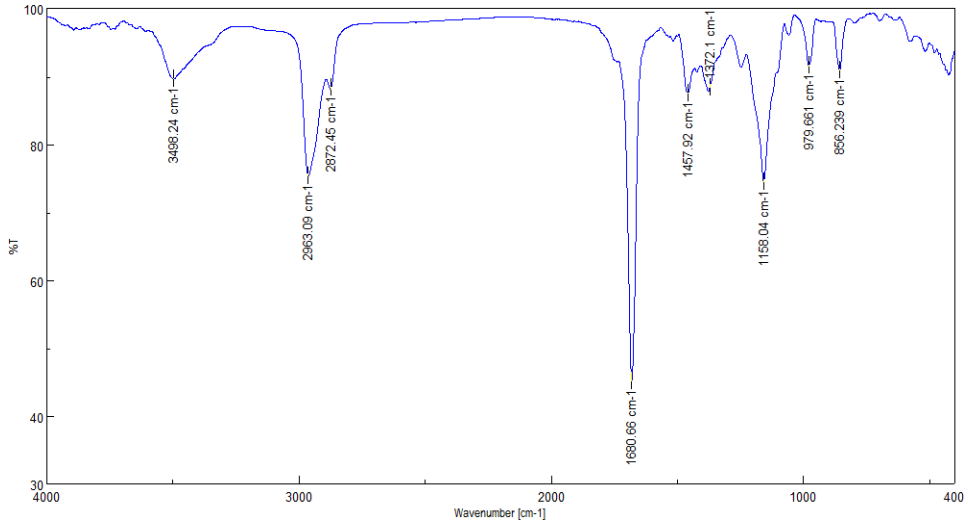
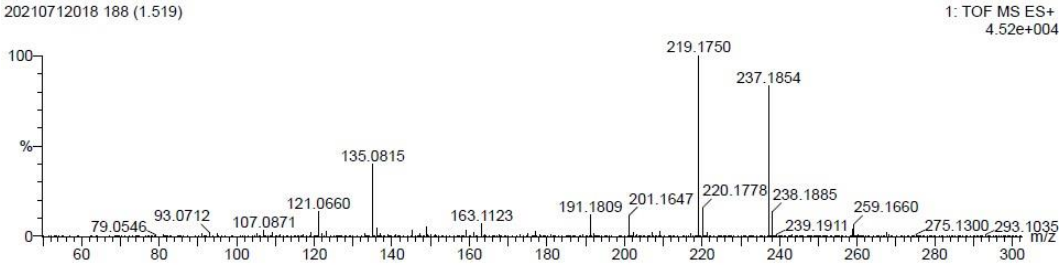


Fig. S96 IR spectrum of compound 27

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
81 formula(e) evaluated with 2 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
AO3D3G8D2
20210712018 188 (1.519)



Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
259.1660	259.1674	-1.4	-5.4	3.5	63.6	C15 H24 O2 Na

Fig. S97 HR-ESI-MS spectrum of compound 28

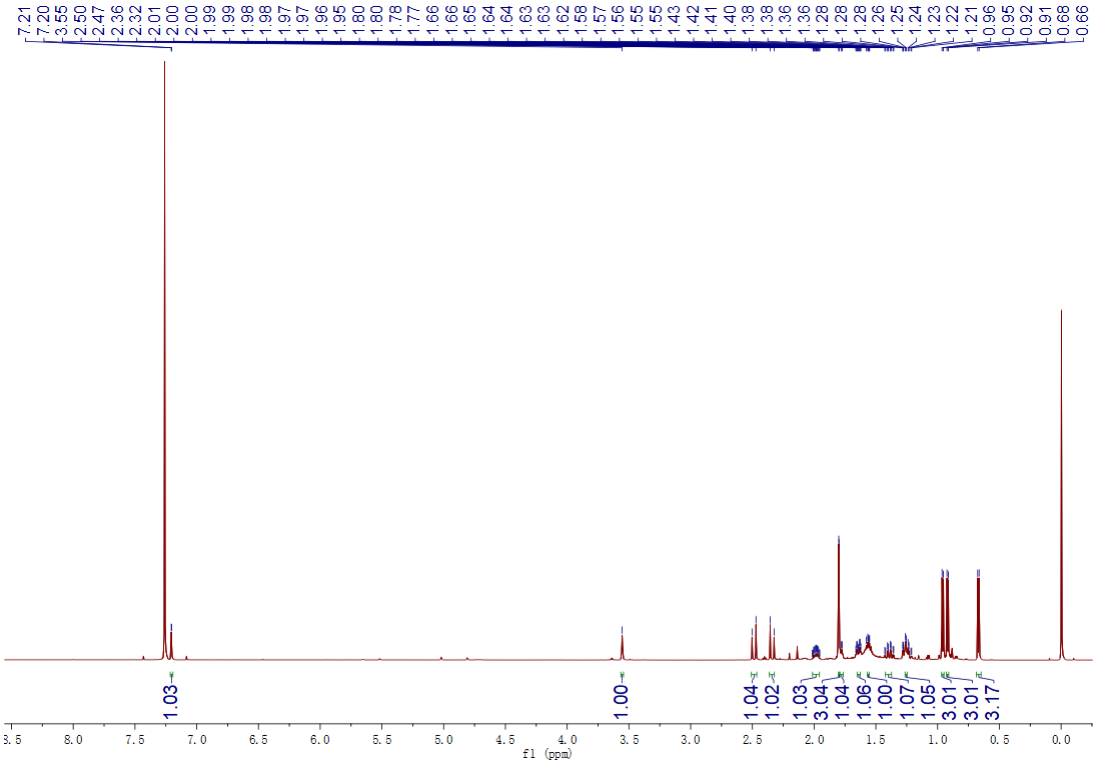


Fig. S98 ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 28

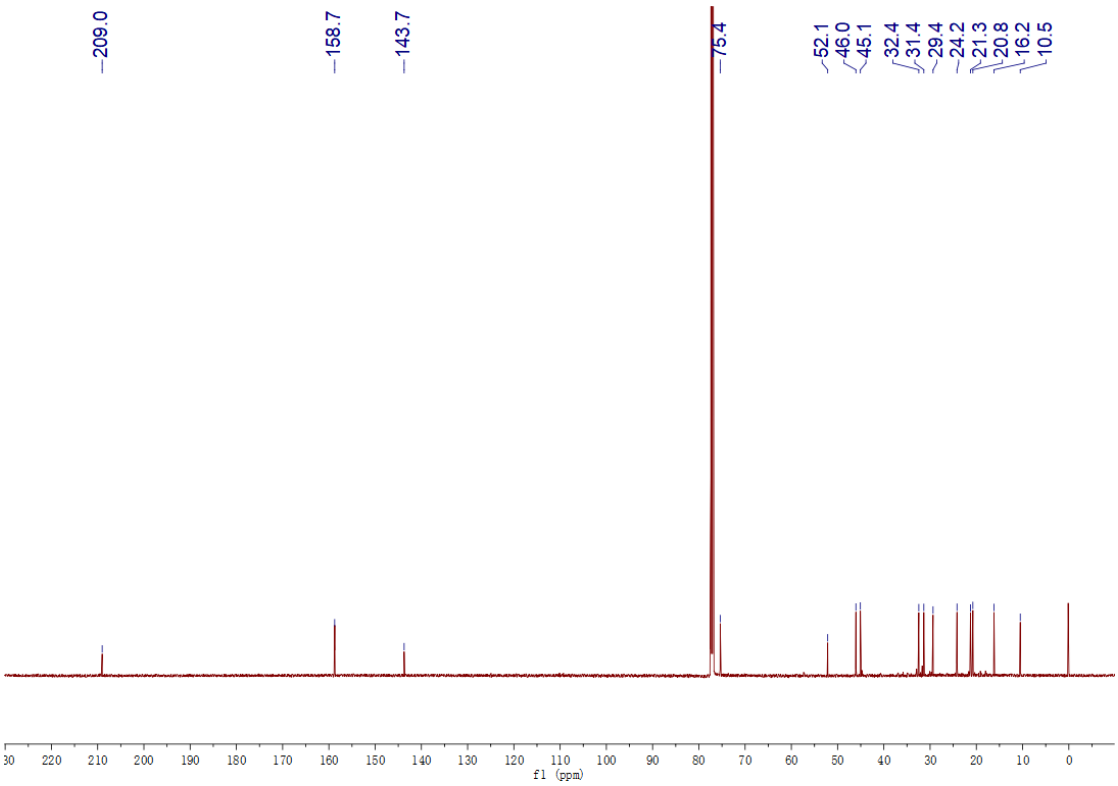


Fig. S99 ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of compound 28

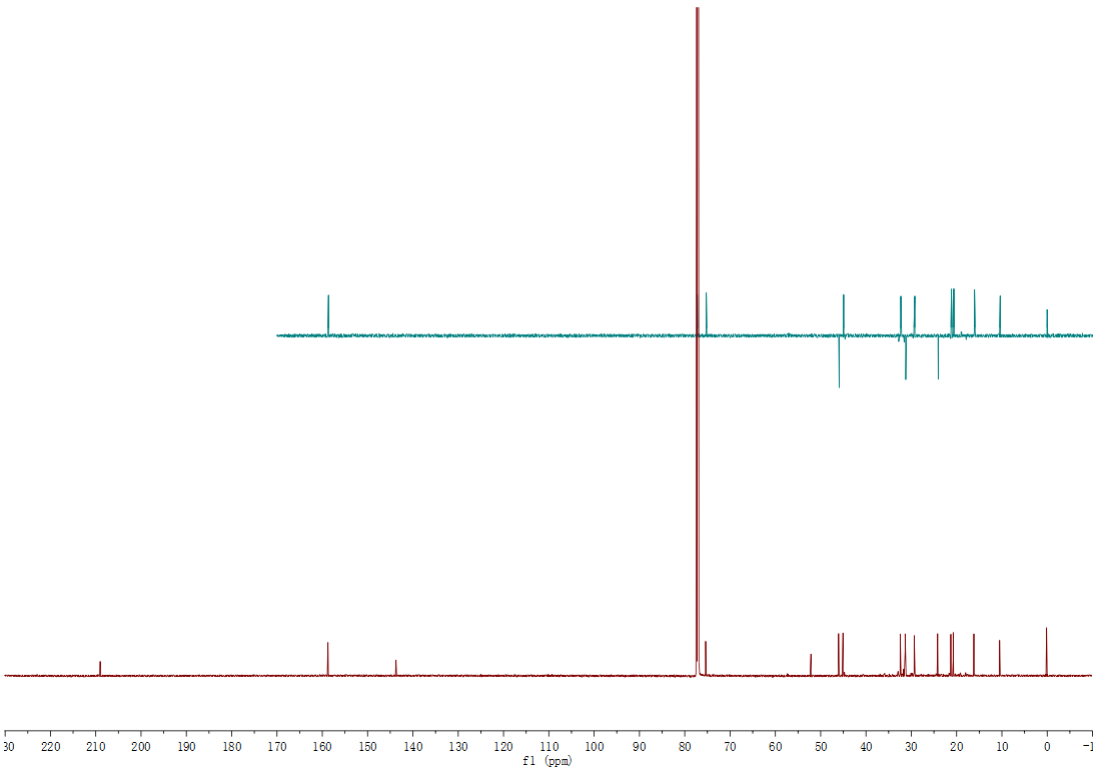


Fig. S100 DEPT (150 MHz, $CDCl_3$) and ^{13}C NMR spectra of compound 28

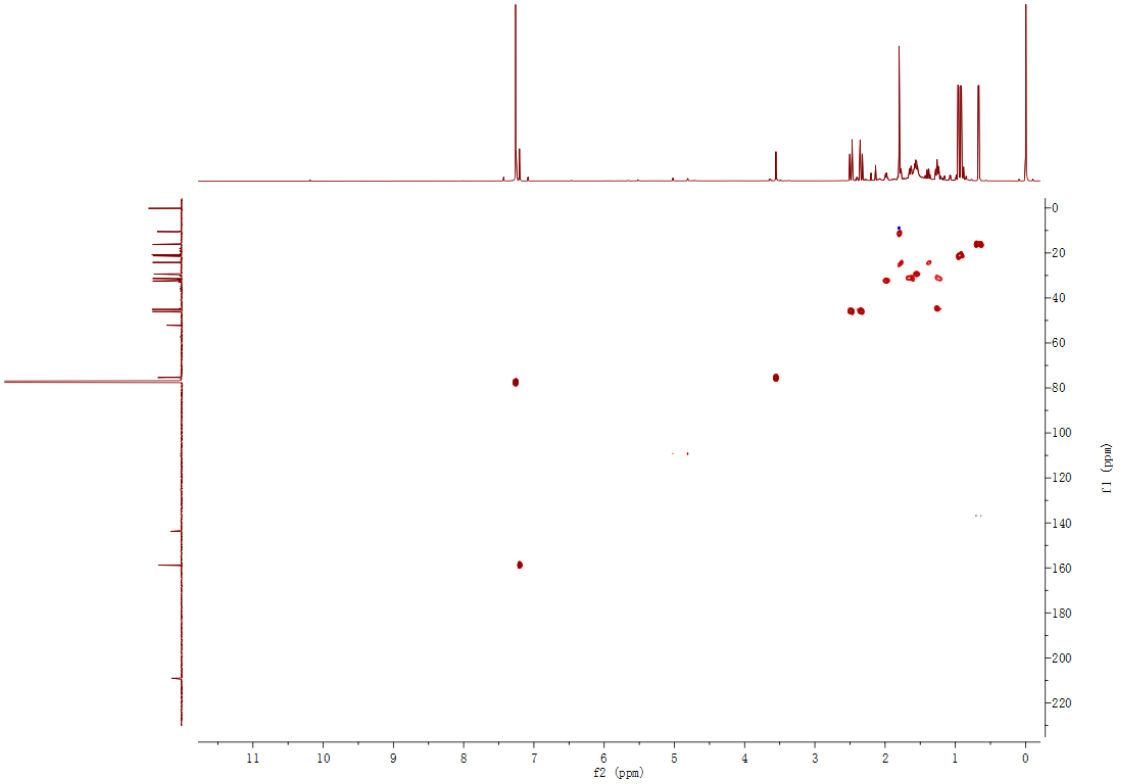


Fig. S101 HSQC spectrum of compound 28

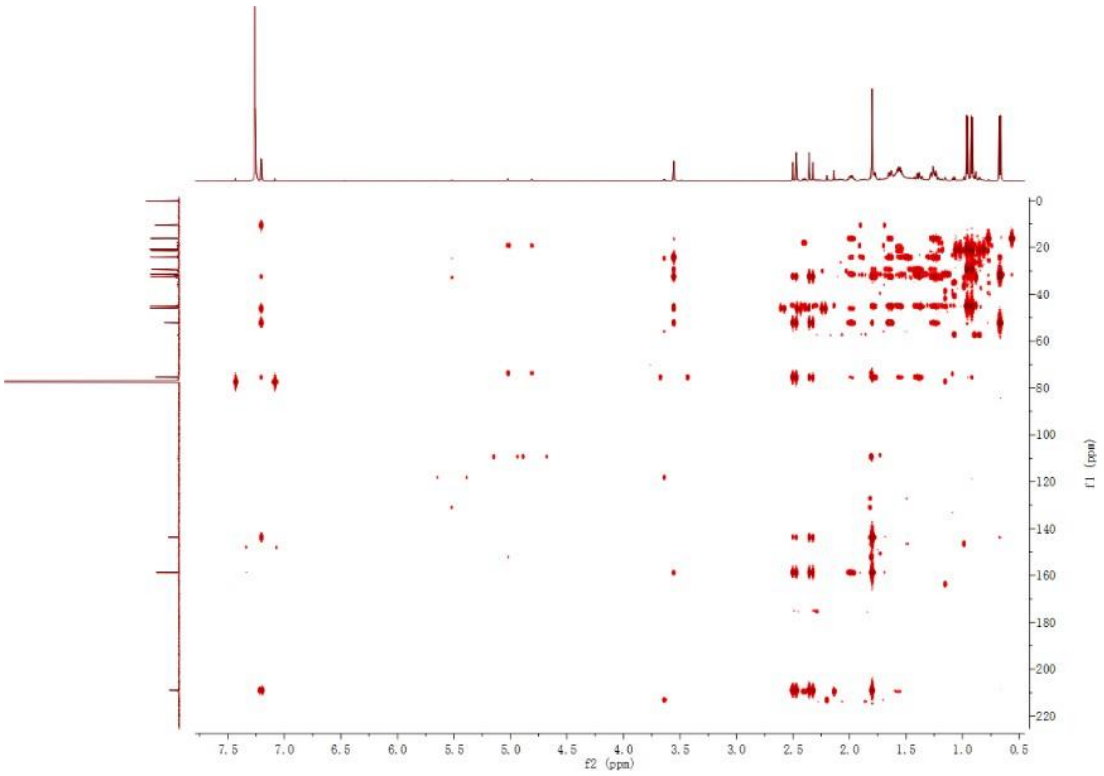


Fig. S102 HMBC spectrum of compound 28

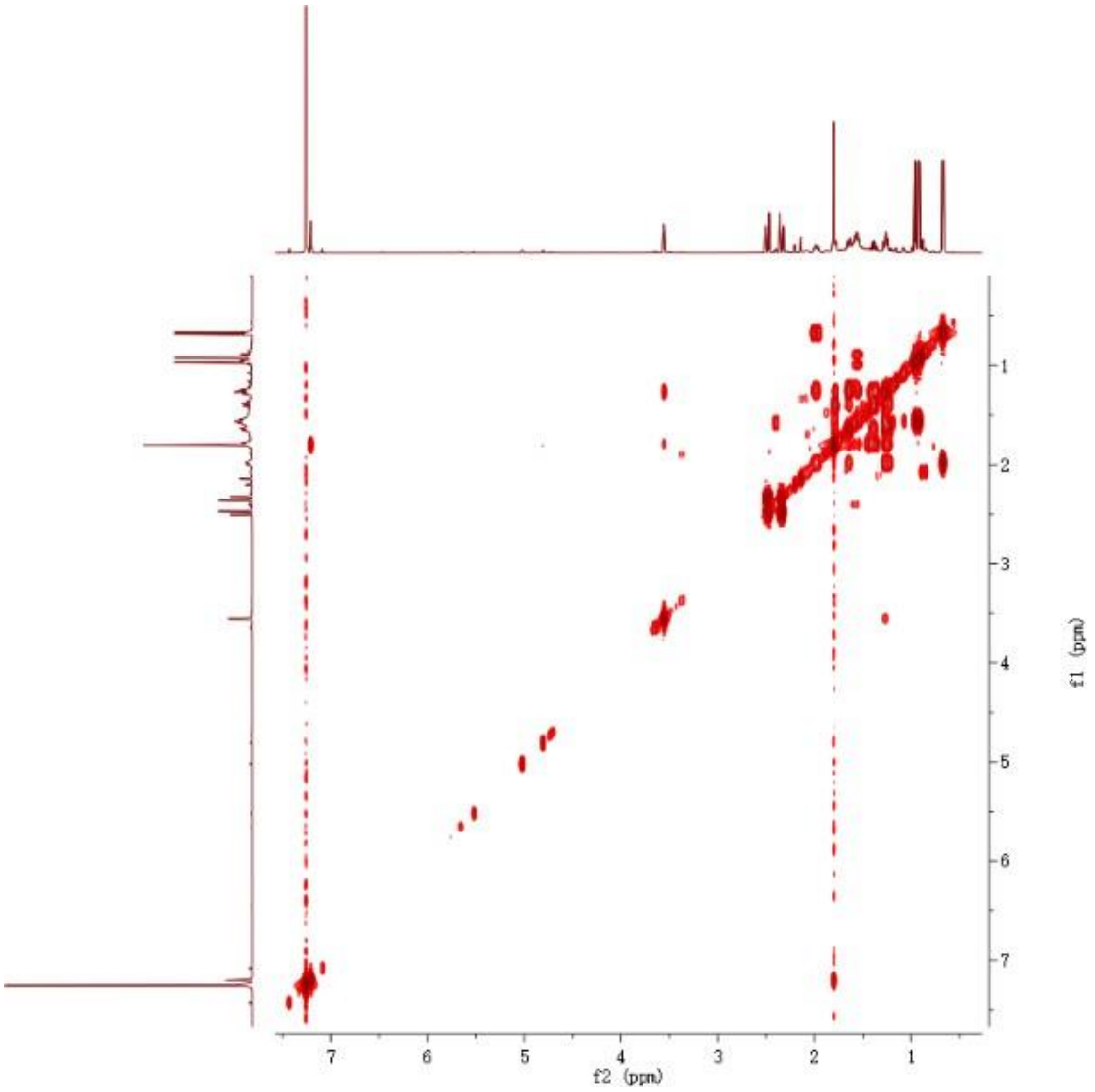


Fig. S103 ^{1}H-^{1}H COSY spectrum of compound 28

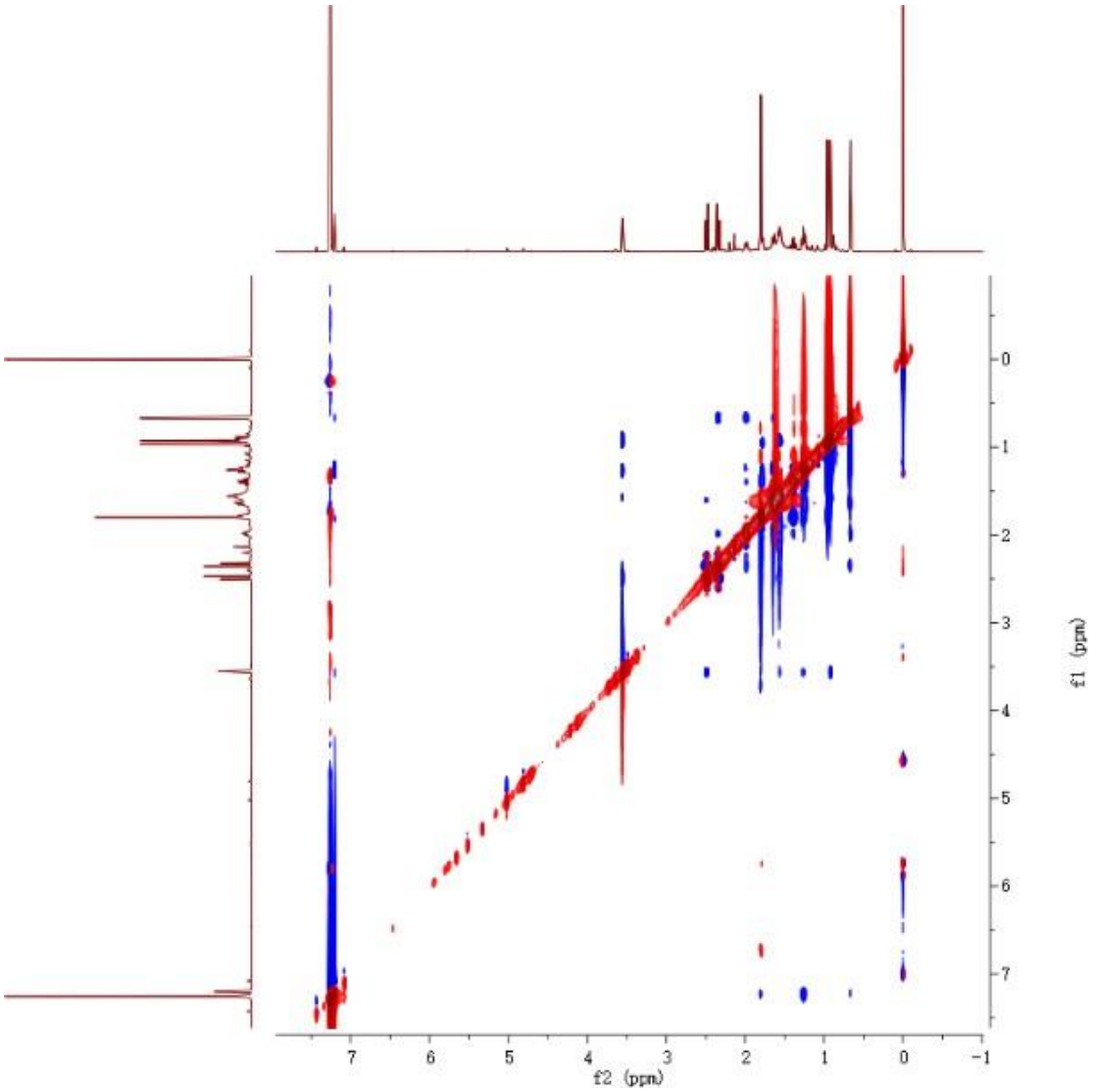


Fig. S104 NOESY spectrum of compound 28

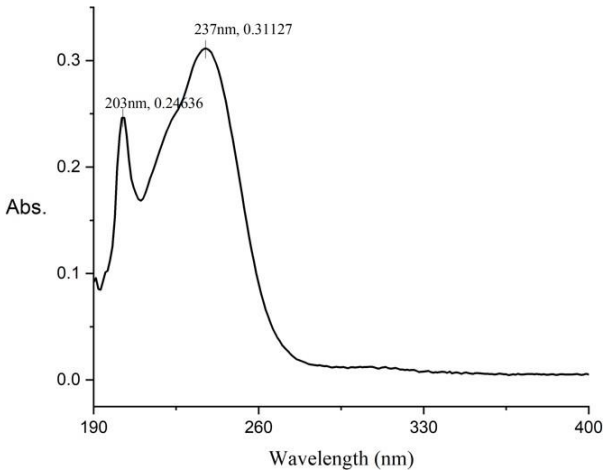


Fig. S105 UV spectrum of compound 28

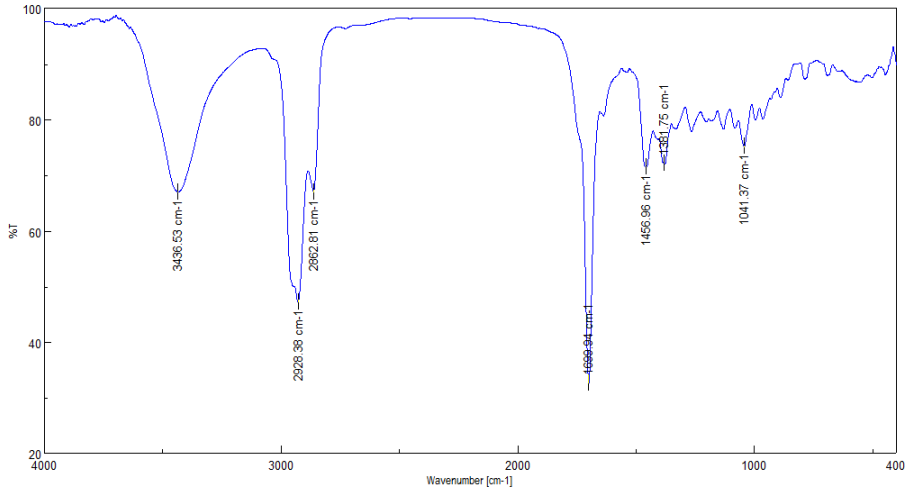


Fig. S106 IR spectrum of compound 28

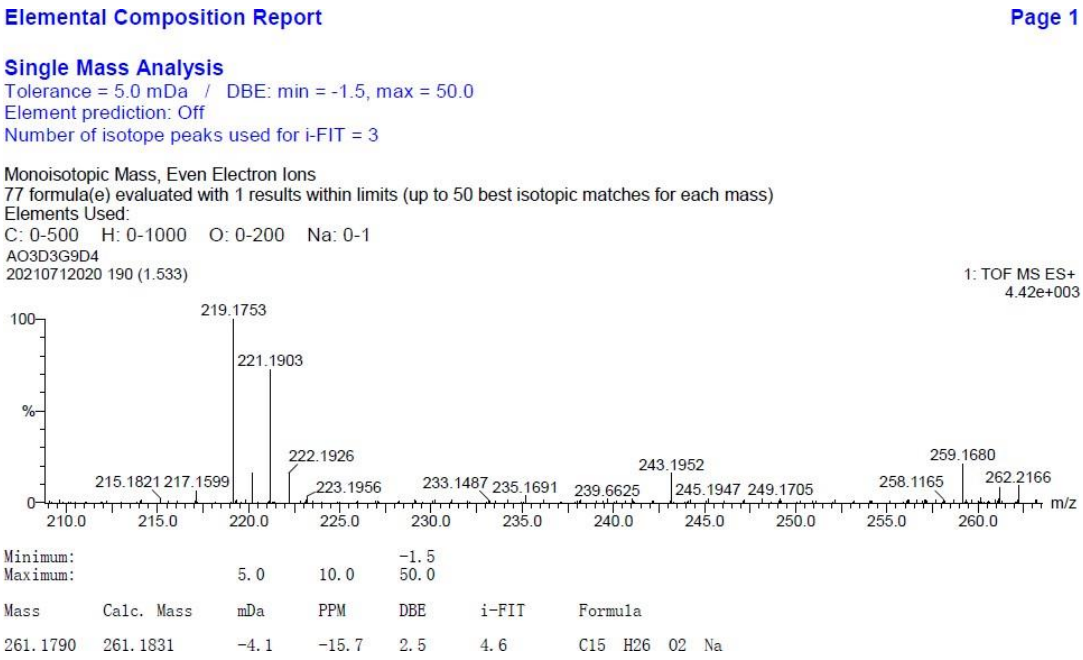


Fig. S107 HR-ESI-MS spectrum of compound 29

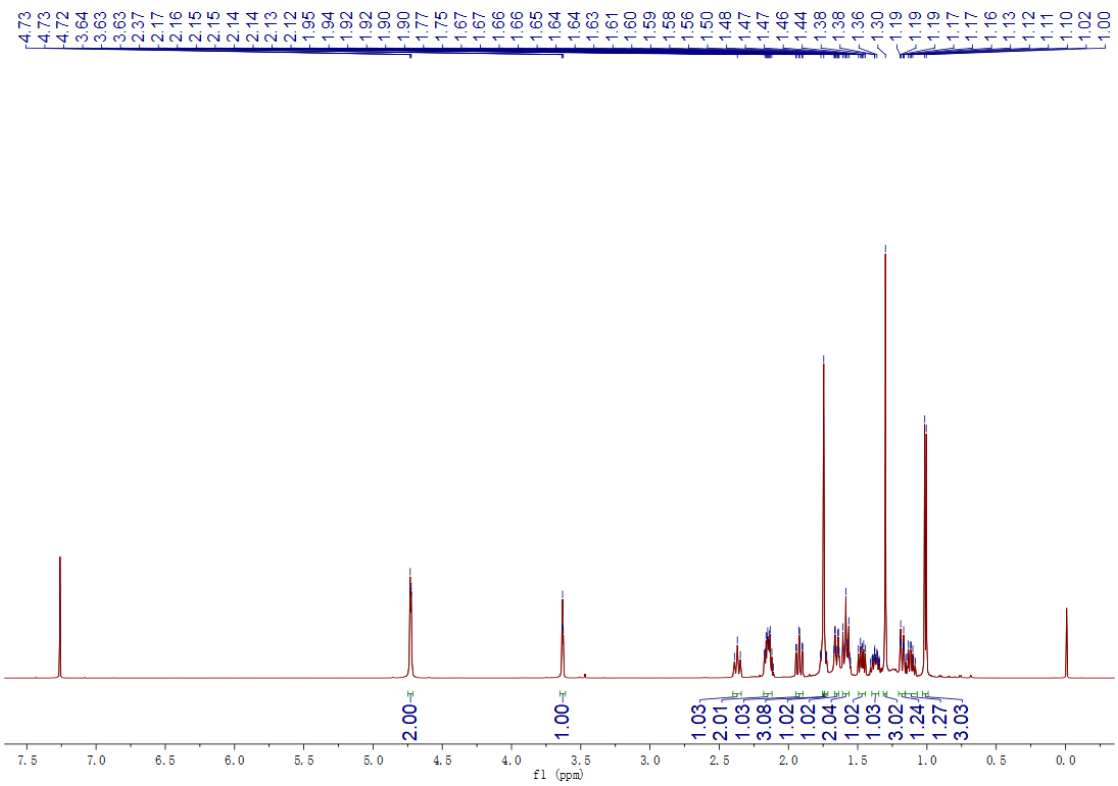


Fig. S108 ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 29

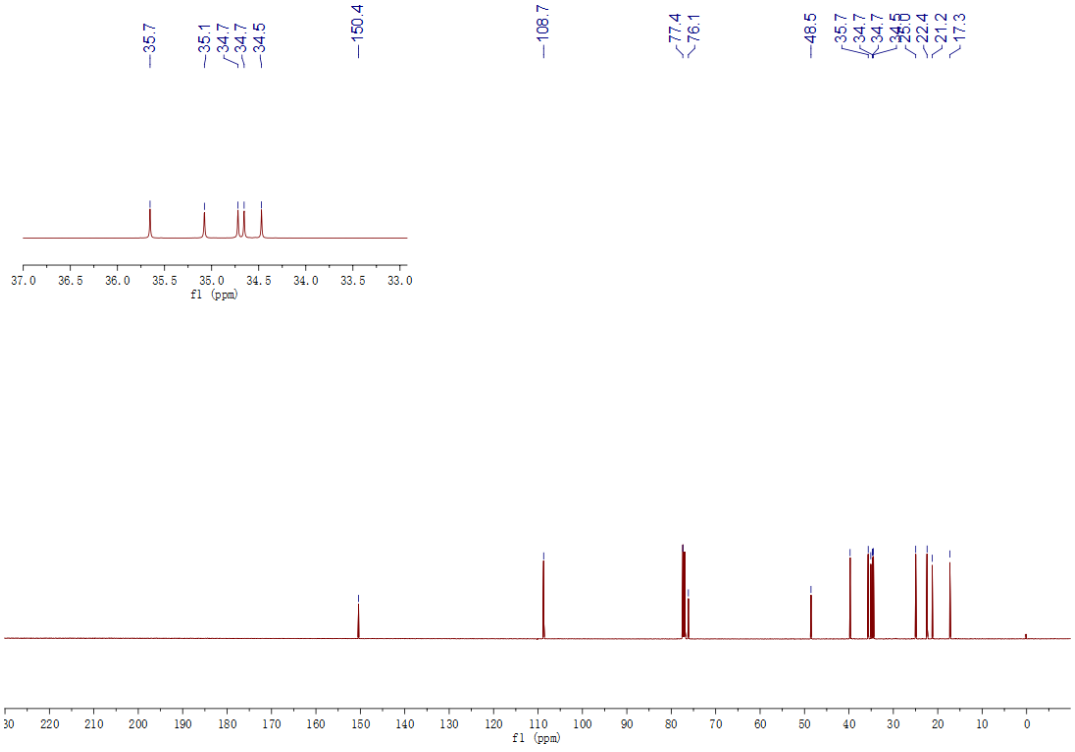


Fig. S109 ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of compound 29

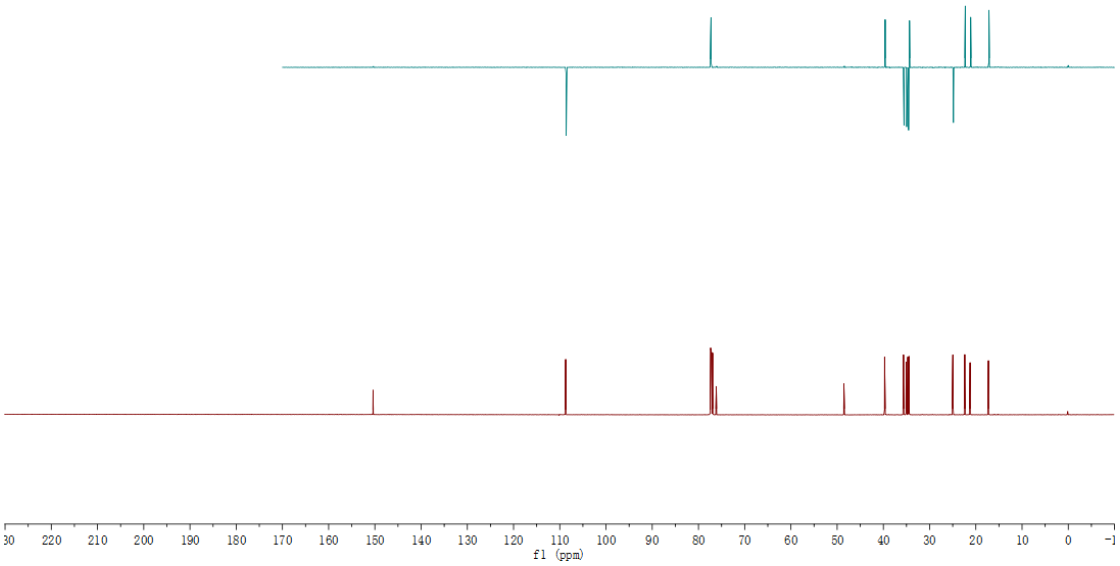


Fig. S110 DEPT (150 MHz, $CDCl_3$) and ^{13}C NMR spectra of compound 29

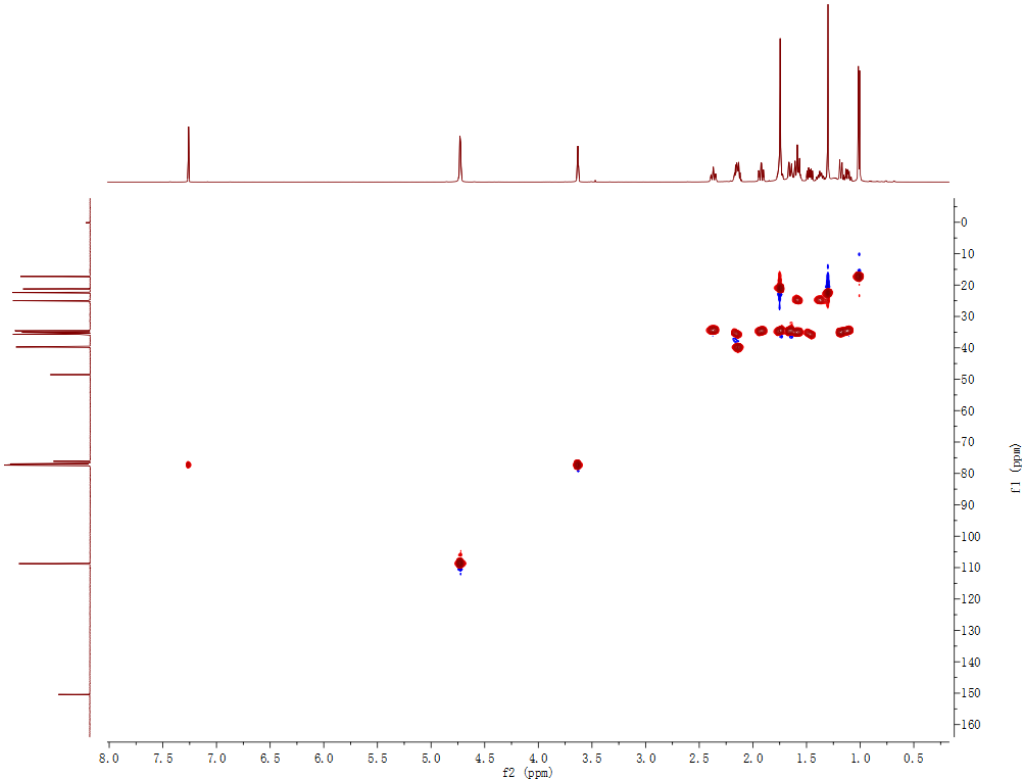


Fig. S111 HSQC spectrum of compound 29

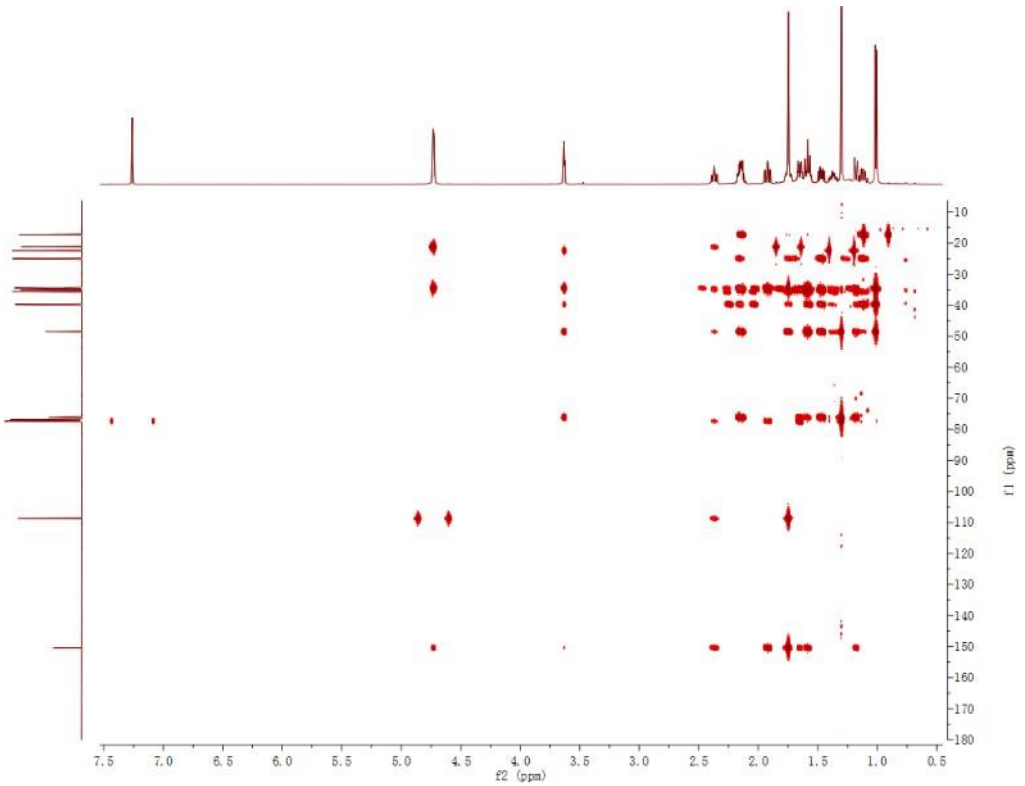


Fig. S112 HMBC spectrum of compound 29

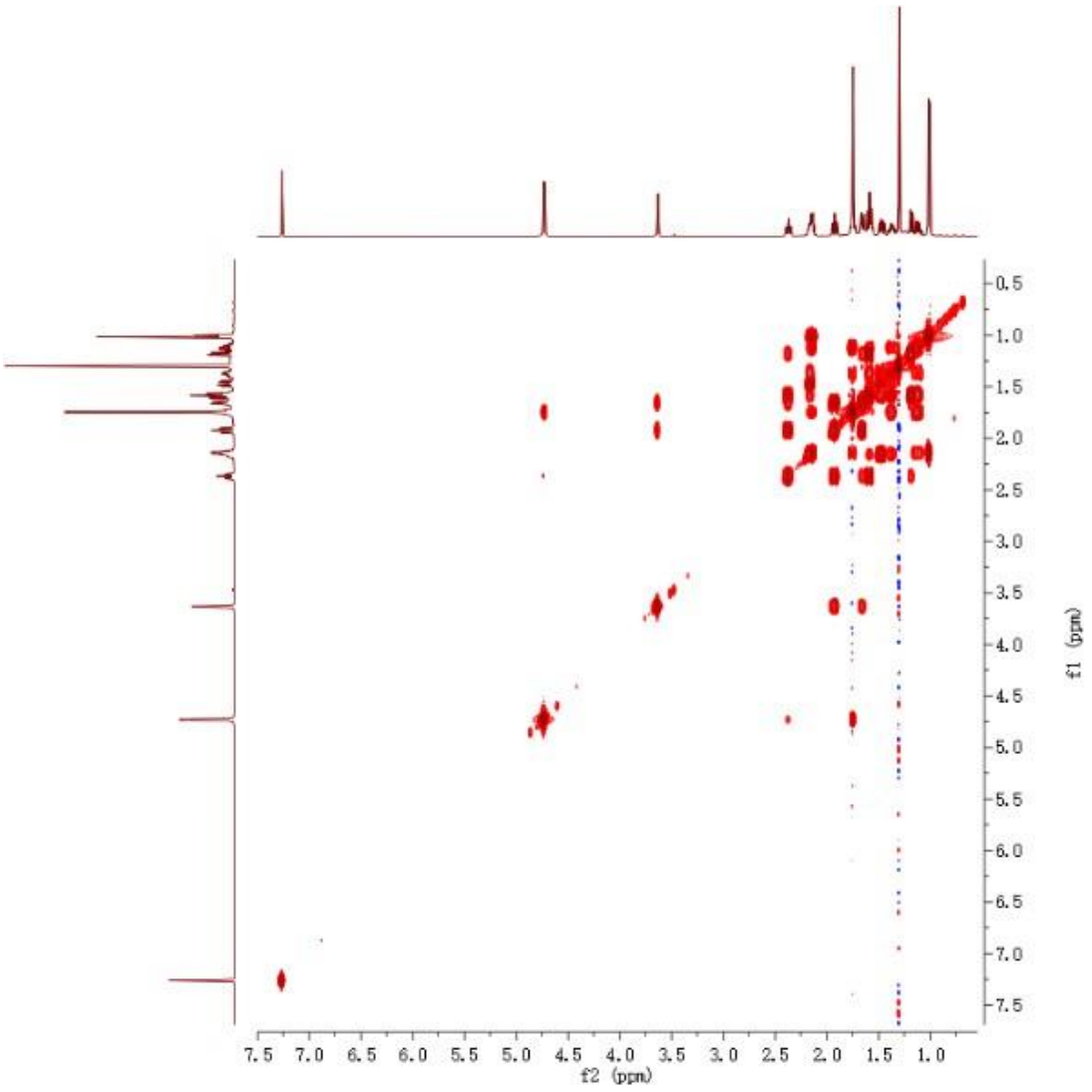


Fig. S113 ^{1}H-^{1}H COSY spectrum of compound 29

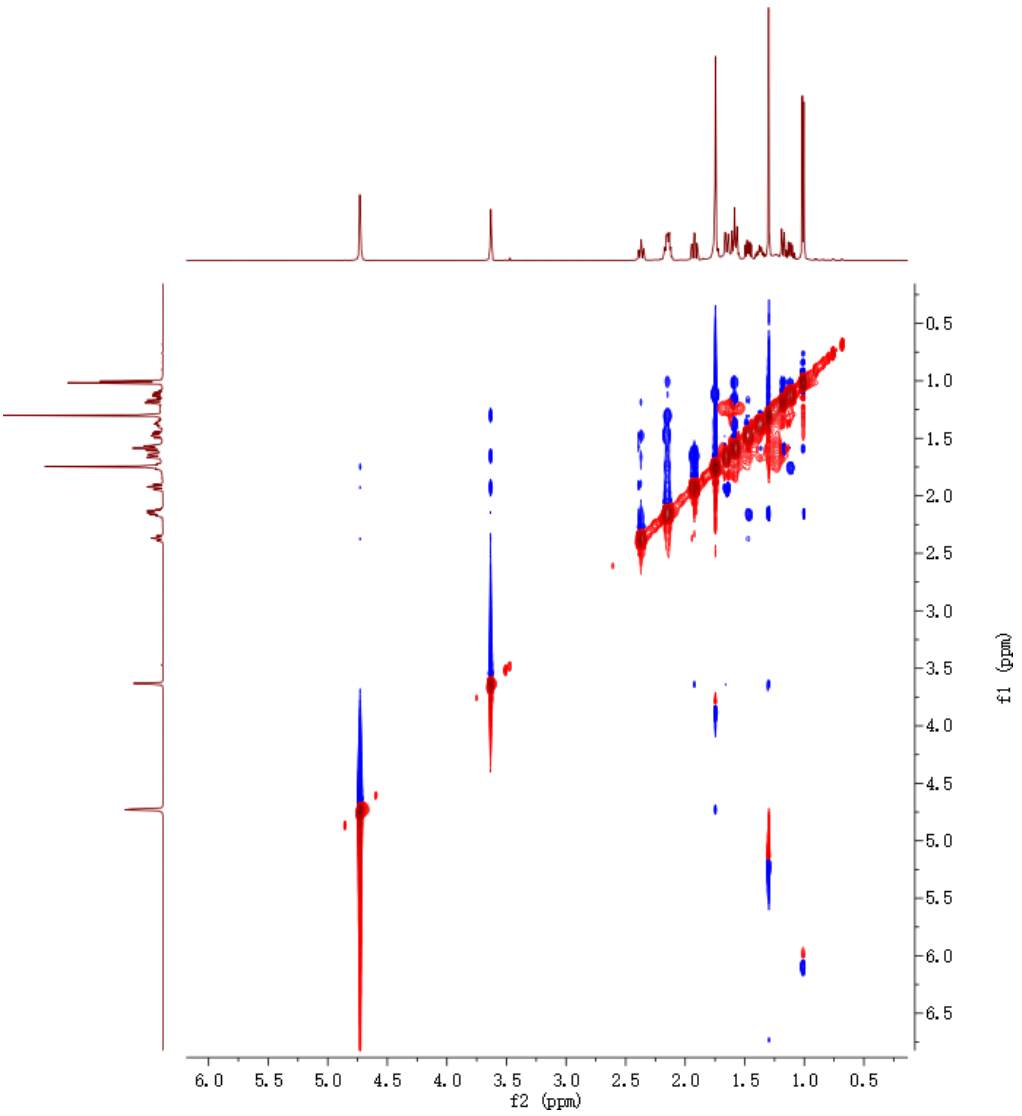


Fig. S114 NOESY spectrum of compound 29

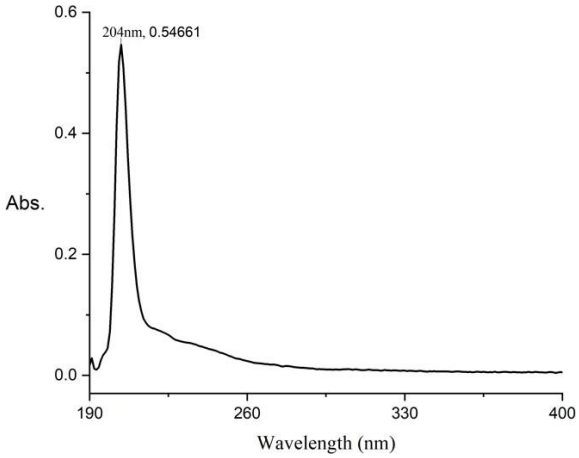


Fig. S115 UV spectrum of compound 29

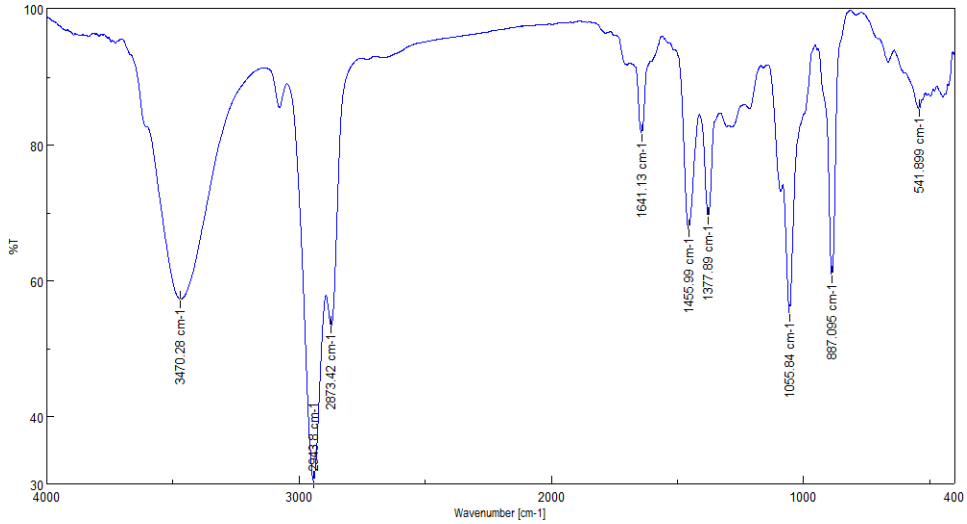


Fig. S116 IR spectrum of compound 29

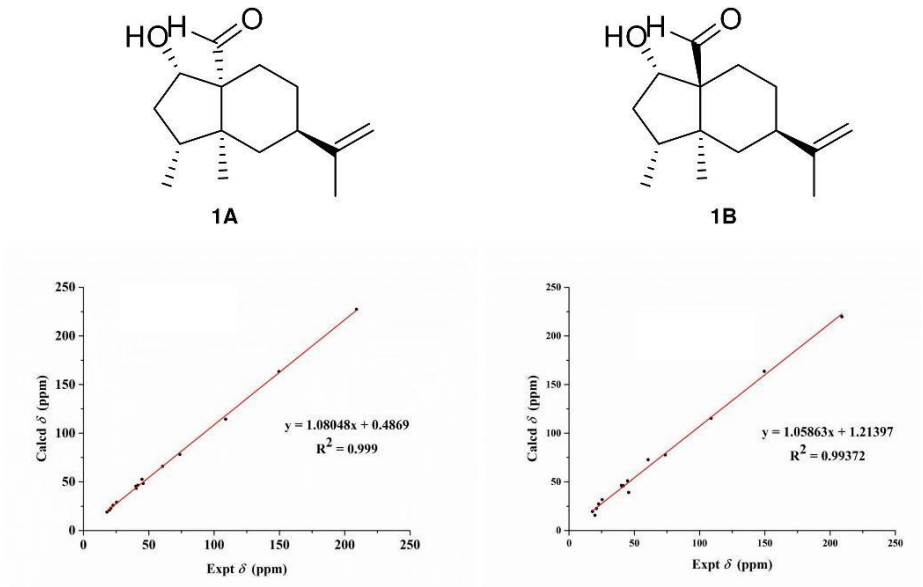


Fig. S117 Linear correlation plots of calculated and experimental 1C values of two plausible epimers 1A and 1B

Table S1. Experimental and Calculated ^{13}C NMR Chemical Shifts of 1A and 1B

NO.	exptl. δ_C	calcd. δ_C 1A	deviation	calcd. δ_C 1B	deviation
1	209.1	227.4	18.3	219.7	10.6
2	73.8	78.2	4.4	77.7	3.9
3	40.4	43.3	2.9	45.7	5.3
4	41.7	46.5	4.8	46.0	4.3
5	44.8	52.6	7.8	51.1	6.3
6	45.7	48.3	2.6	39.1	-6.6
7	40.1	45.5	5.4	46.4	6.3
8	25.4	28.9	3.5	31.7	6.3
9	22.7	25.9	3.2	27.3	4.6
10	60.6	66.0	5.4	72.8	12.2
11	149.6	163.4	13.8	163.6	14.0
12	108.9	114.4	5.5	115.32	6.4
13	21.1	23.0	1.9	22.61	1.5
14	19.9	21.0	1.1	15.61	-4.3
15	18.0	18.9	0.9	19.52	1.5
		DP4+	100%	DP4+	0%

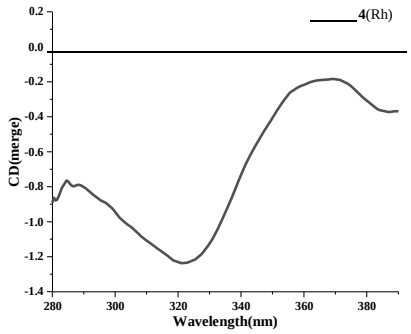


Fig. S118 $Rh_2(OCOCF_3)_4$-induced CD spectra of (4*R*,5*S*,7*S*,9*R*)-eremophila-1(10),11-dien-9-ol (4)

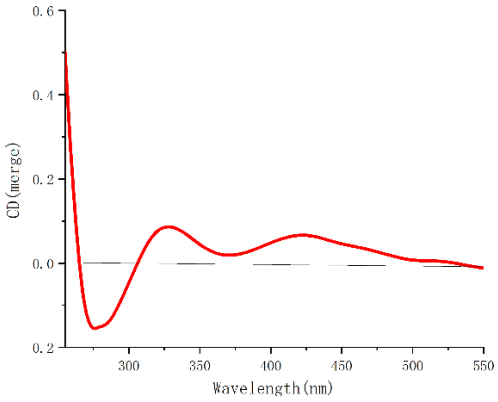


Fig. S119 CD spectra of *in situ* formed Mo-complexes of 6 recorded in DMSO after 0.5 h from dissolving in the 1:1 ligand-to-metal ratio

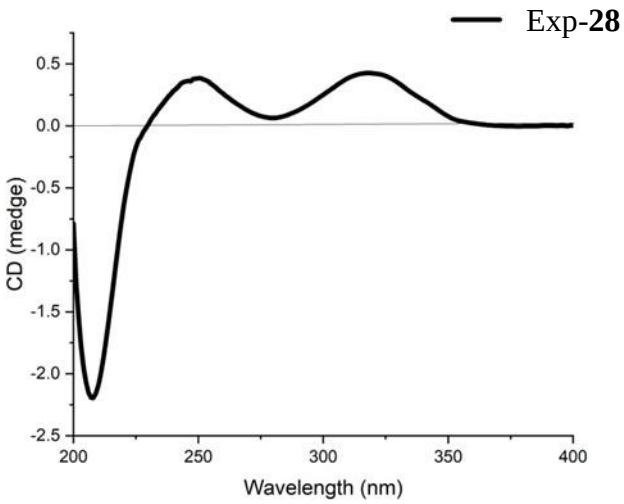


Fig. S120 CD spectra of compounds 28

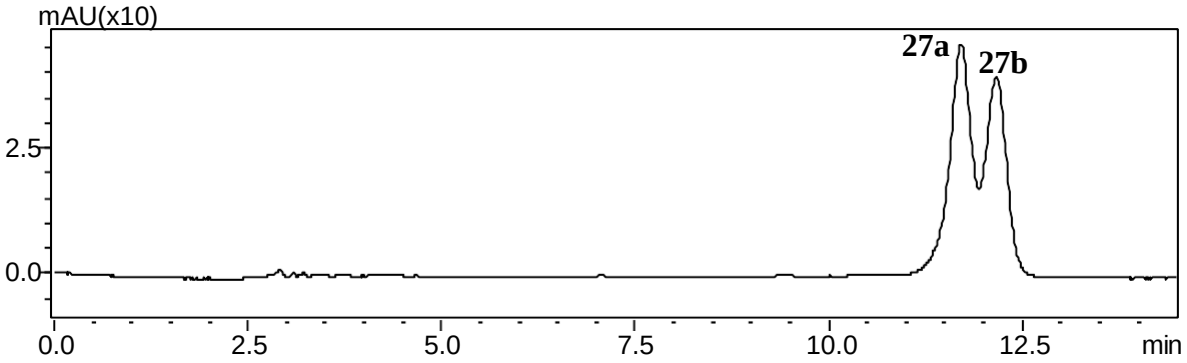


Fig. S121 Chiral HPLC chromatogram of compound 27

Table S2. Primers for qPCR

Gene	Forward	Reverse
TNF-α	CCCTCACACTCAGATCATCTTCT	GCTACGACGTGGGCTACAG
IL-6	TAGTCCTTCCTACCCCAATTTCC	TTGGTCCTTAGCCACTCCTTC
Actin	GTCGTACCACAGGCATTGTGATGG	GCAATGCCTGGGTACATGGTG
iNOS	CTGGCTGCCTTGTTCAGCTA	AGTGTAGCGTTTCGGGATCT
COX-2	TGCTGTACAAGCAGTGGCAA	AGGTGCTCGGCTTCCAGTAT

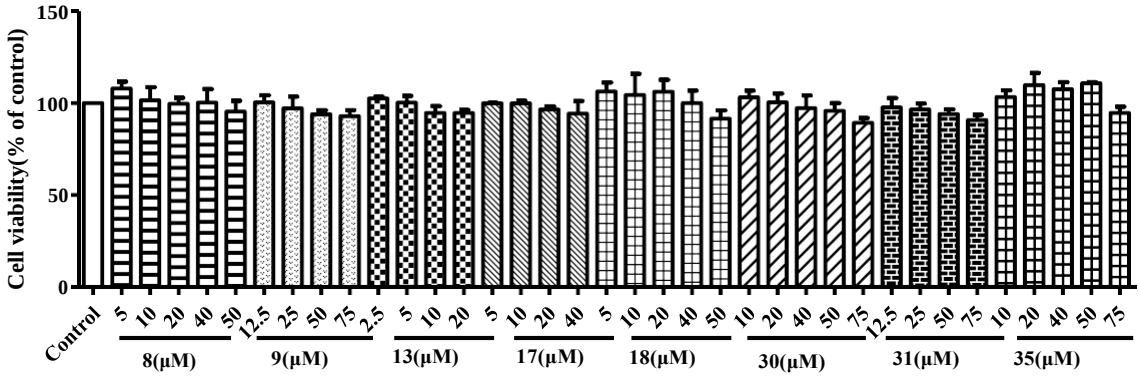


Fig. S122 Effects of different concentrations of compounds (IC_{50}) alone on cell viability

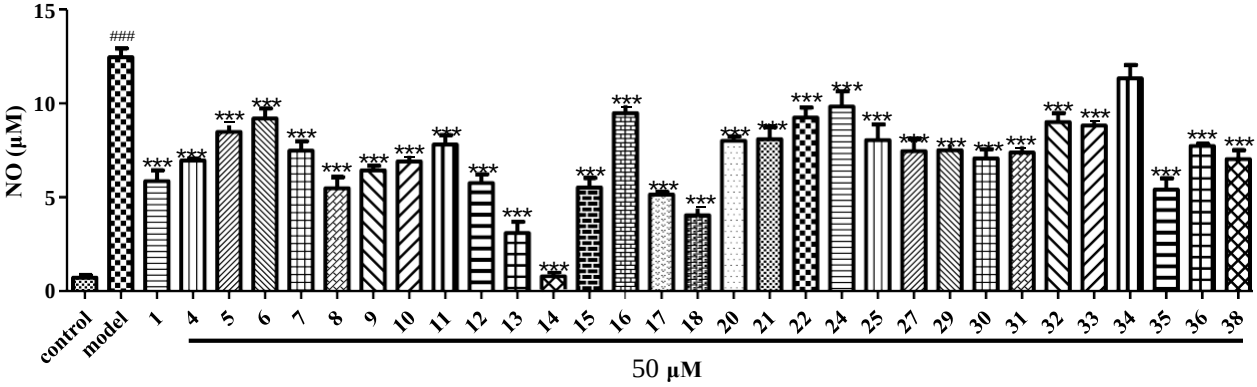


Fig. S123 NO inhibitions of all the isolated compounds at 50 *M*m

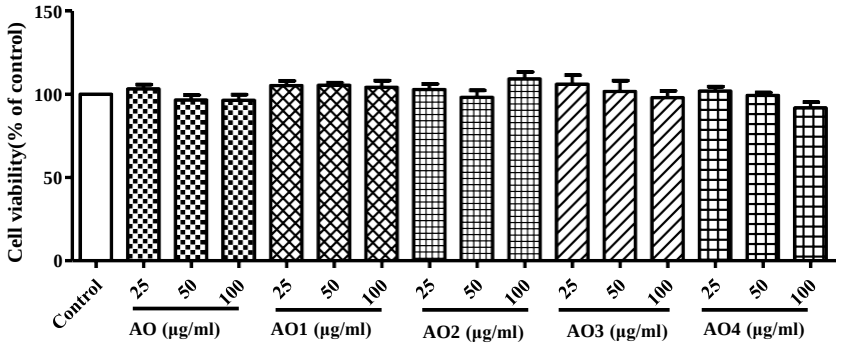


Fig. S124 Effects of different fractionations of *A. oxyphylla* on cell viability. Data represent means ± SD, n=3.

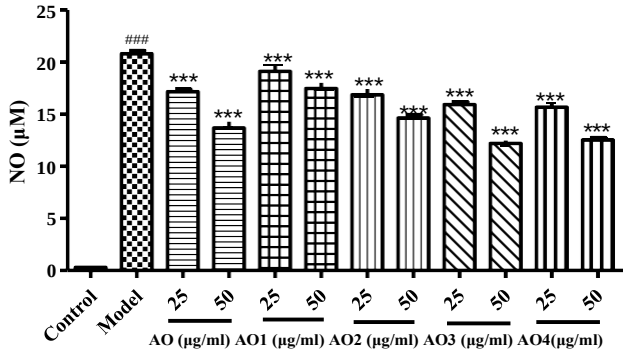


Fig. S125 NO inhibitions of different fractionations. Data represent means ± SD, n=3; ###P < 0.001, **P* < 0.05, ***P*< 0.01, *vs* LPS.