Supporting Information

Cytorhizophins A and B, benzophenone-hemiterpene adducts from the endophytic fungus *Cytospora rhizophorae*

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X-ray crytallographic data of compounds 1 and 3.

The single-crystal X-ray diffraction data were collected at 100K for **1** and **3** on Agilent Xcalibur Nova single-crystal diffractometer using CuKα radiation. The crystal structure was refined by full-matrix least-squares calculation. Hydrogen atoms bonded to carbons were located by the geometrically ideal positions by the "ride on" method. Hydrogen atoms bonded to oxygen were placed on the difference Fourier method and were included in the calculation of structure factors with isotropic temperature factors. Crystallographic data for **1** and **3** reported in this paper have been deposited in the Cambridge Crystallographic Data Centre. (Deposition number: CCDC 1879707 for **1**, CCDC 1879932 for **3**). Copies of these data can be obtained free of charge via www.ccdc.cam.au.ck/conts/retrieving.html.)

Table 1 Crystal data and structure refinement for 1.

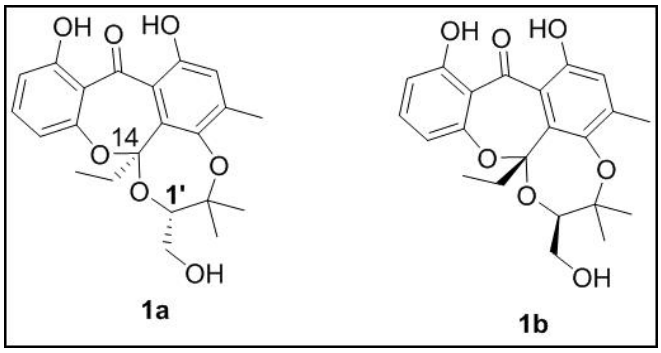
Identification code	liuhogxin_A761-12b_collect
Empirical formula	$C_{22}H_{24}O_7$
Formula weight	400.41
Temperature/K	100.00(18)
Crystal system	triclinic
Space group	P-1
a/Å	9.13750(10)
b/Å	13.1527(2)
c/Å	16.3540(3)
α/°	95.1870(10)
β/°	95.2940(10)
γ/°	103.0400(10)
Volume/Å^3	1894.04(5)
Z	4
ρ_{calc}g/cm^3	1.404
μ/mm^{-1}	0.870
F(000)	848.0
Crystal size/mm^3	0.3 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.944 to 148.284
Index ranges	-10 ≤ h ≤ 11, -16 ≤ k ≤ 11, -20 ≤ l ≤ 20
Reflections collected	19534
Independent reflections	7411 [R_{int} = 0.0230, R_{sigma} = 0.0240]
Data/restraints/parameters	7411/0/540
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0375, wR_2 = 0.0984
Final R indexes [all data]	R_1 = 0.0398, wR_2 = 0.1009
Largest diff. peak/hole / e Å^{-3}	0.33/-0.33

Table 2 Crystal data and structure refinement for lihongxin_A761-37_collect_mmmT2_twin1_hklf4.

Identification code	lihongxin_A761-37_collect_mmmT2_twin1_hklf4
Empirical formula	$C_{18}H_{17.25}Cl_3O_5$
Formula weight	419.92
Temperature/K	99.9(3)
Crystal system	monoclinic
Space group	P2
a/Å	13.8718(6)
b/Å	9.6965(5)
c/Å	13.8978(7)
α/°	90
β/°	92.204(4)
γ/°	90
Volume/Å^3	1867.98(16)
Z	4
ρ_{calc}g/cm^3	1.493
μ/mm^{-1}	4.683
F(000)	865.0
Crystal size/mm^3	0.2 × 0.15 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.838 to 134.154
Index ranges	$-16 \le h \le 16$, $-11 \le k \le 8$, $-16 \le l \le 16$
Reflections collected	8789
Independent reflections	8789 [R_{int} = ?, R_{sigma} = 0.0355]
Data/restraints/parameters	8789/1/504
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0812, wR_2 = 0.2000
Final R indexes [all data]	R_1 = 0.0917, wR_2 = 0.2129
Largest diff. peak/hole / e Å^{-3}	0.77/-0.49
Flack parameter	-0.008(19)

Computational methods

The initial coordinates of compound **1a**/**1b** for DFT calculation were from the results of single crystal X-ray diffraction experiment (CIF file). The optimization and frequency calculation of **1a**/**1b** was performed on B3PW91-D3/6-311G(d) level of theory with IEF-PCM solvent model (MeOH). Theoritical ECD of **1a**/**1b** was calculated on ωB97XD/6-311+G(d) level with the same solvent model. The calculated ECD curves were simulated by Specdis V1.71 with sigma/gamma value of 0.3 eV, and adjusted by red-shifted for 20 nm. All the DFT calculations were performed by Gaussian09 software package.[2]



References

1. Bruhn, T.; Schaumlöffel, A.; Hemberger, Y.; Bringmann, G. Chirality **2013**, *25*, 243–249.

2.Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

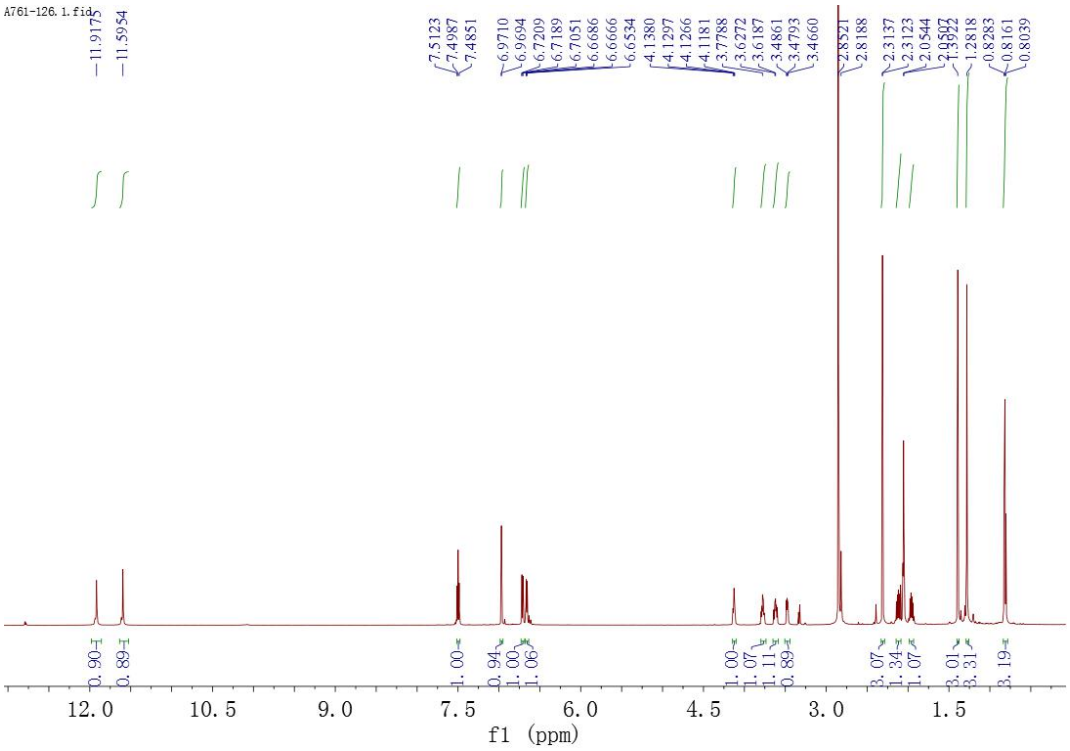


Figure S1. ^{1}H NMR spectrum (600 MHz, CD_3COCD_3) of **1**.

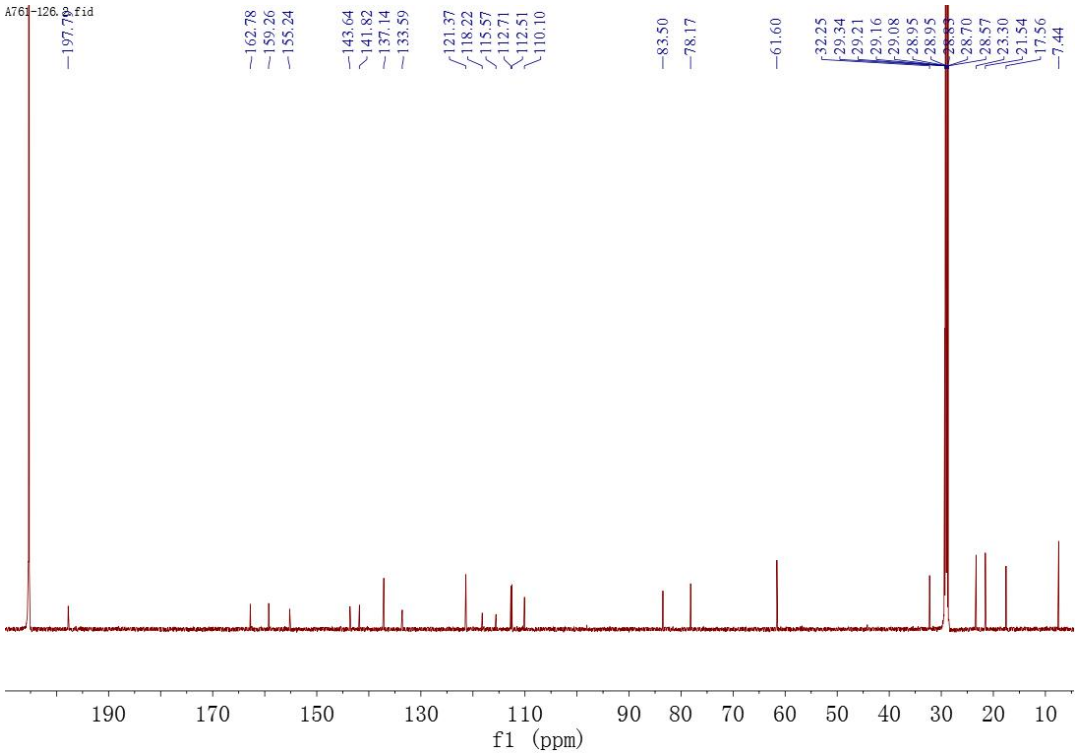


Figure S2. ^{13}C NMR spectrum (150 MHz, CD_3COCD_3) of **1**.

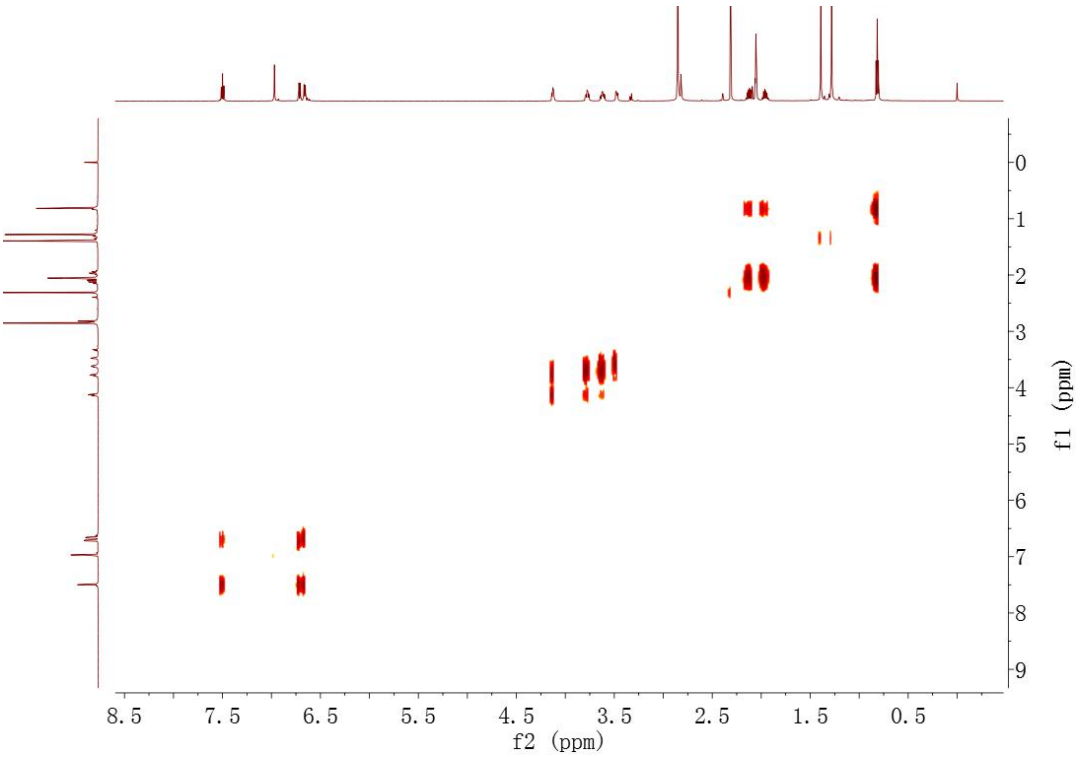


Figure S3. ^{1}H-^{1}H COSY spectrum (600 MHz, CD_3COCD_3) of **1**.

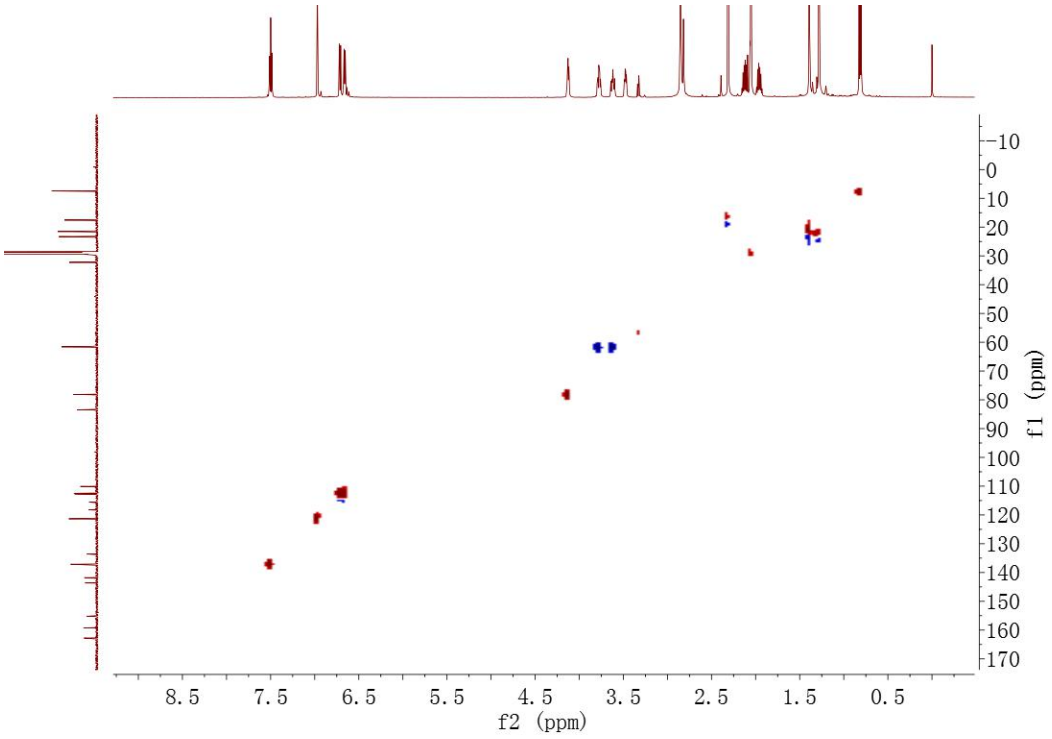


Figure S4. HSQC spectrum of **1**.

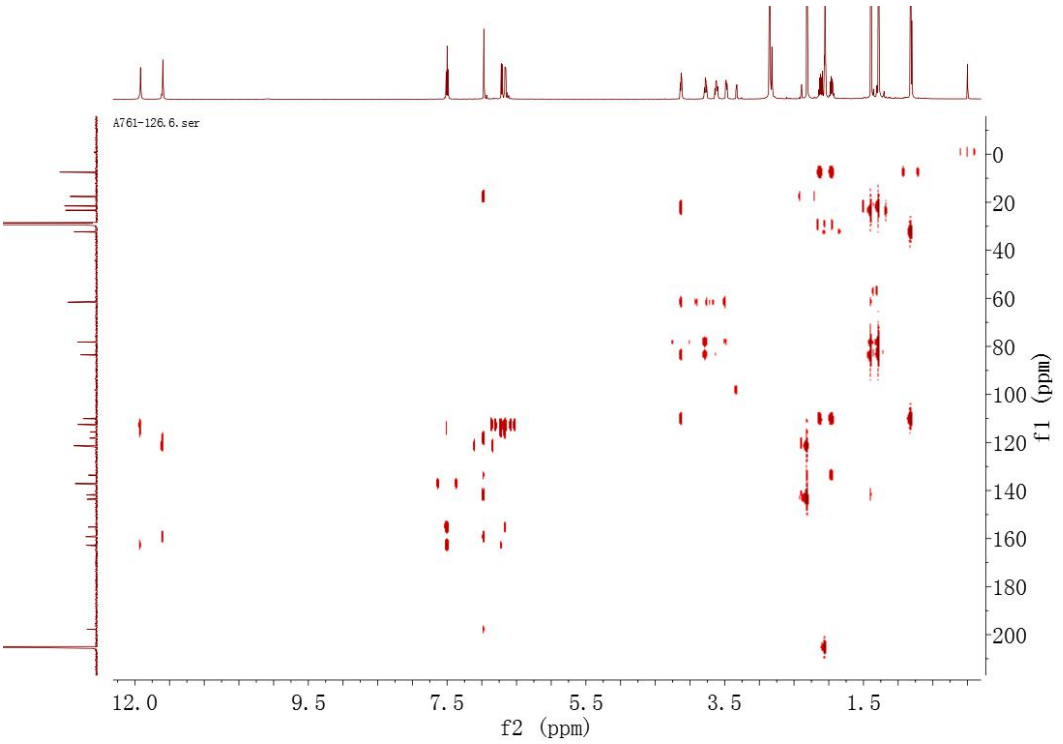


Figure S5. HMBC spectrum of **1**.

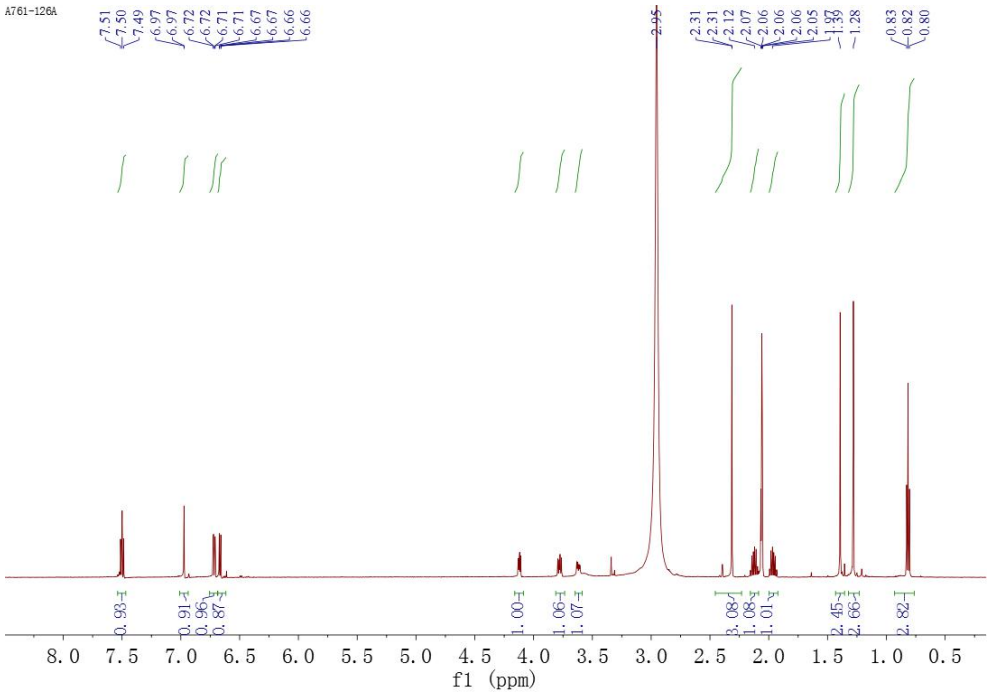


Figure S6. ^{1}H NMR spectrum (600 MHz, CD_3COCD_3) of **1a**.

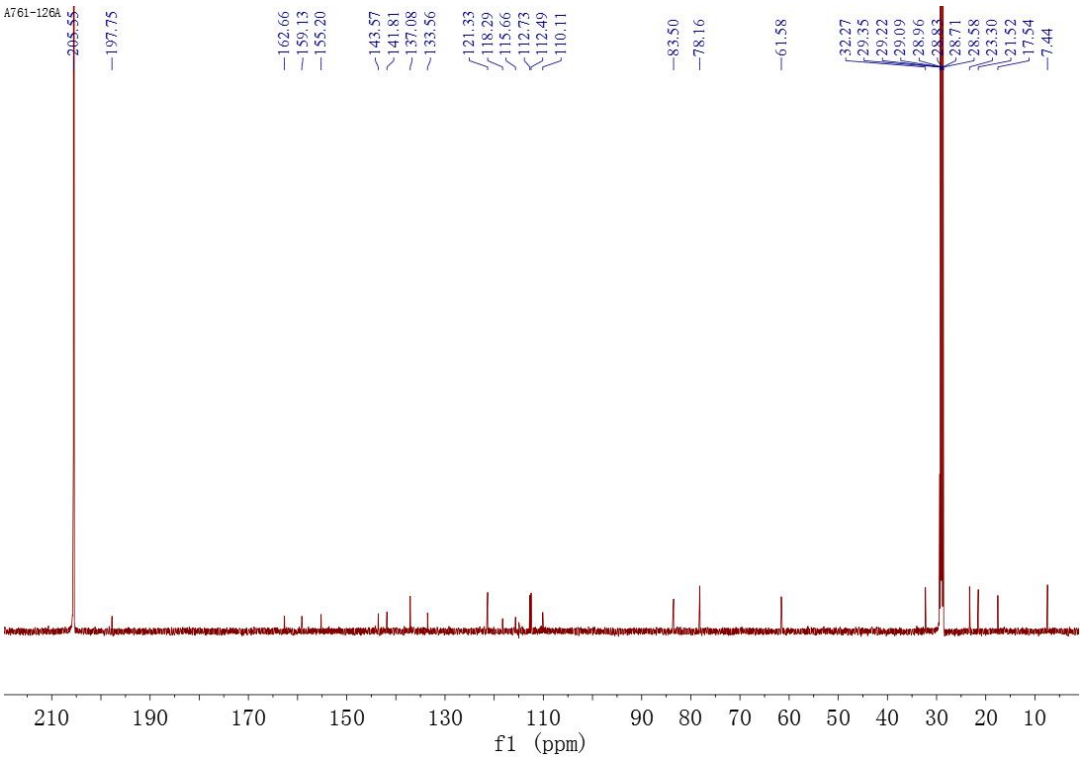


Figure S7. ^{13}C NMR spectrum (150 MHz, CD_3COCD_3) of **1a**.

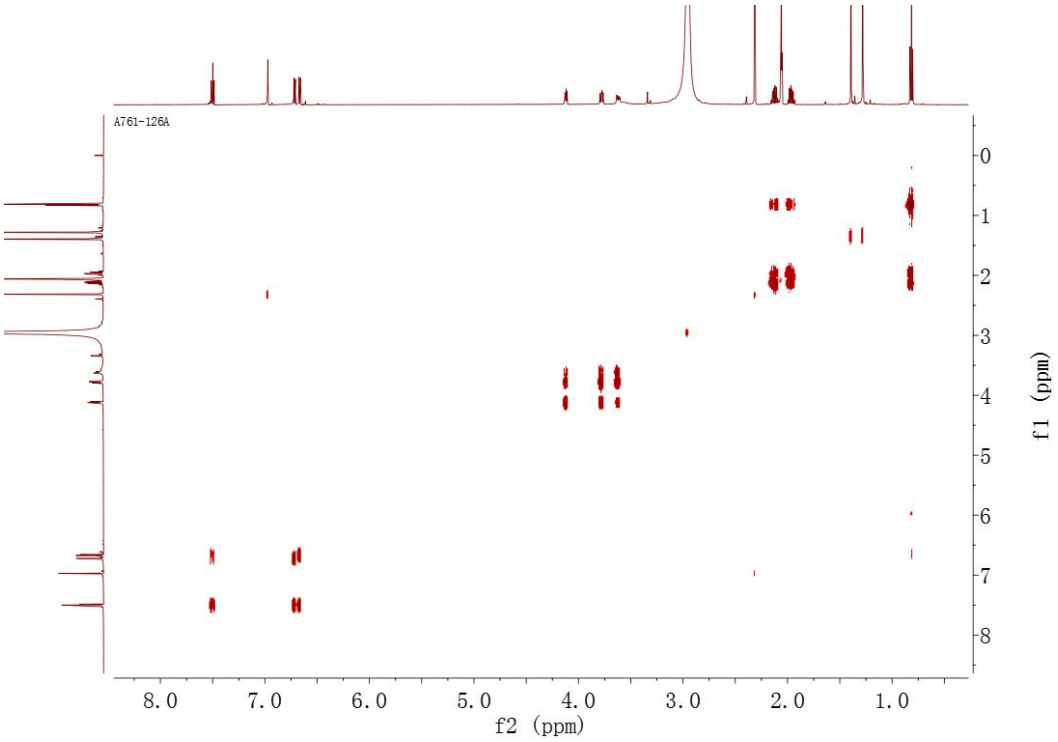


Figure S8. ^{1}H-^{1}H COSY spectrum (600 MHz, CD_3COCD_3) of **1a**.

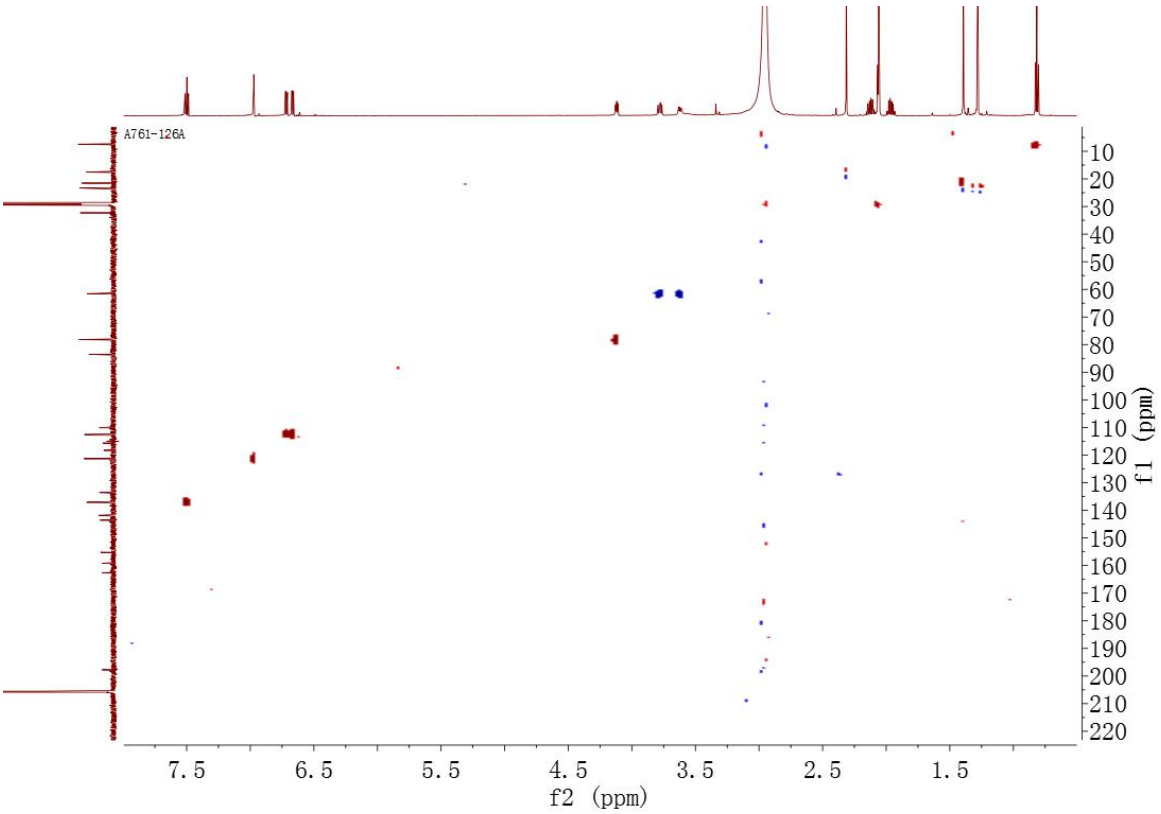


Figure S9. HSQC spectrum of **1a**.

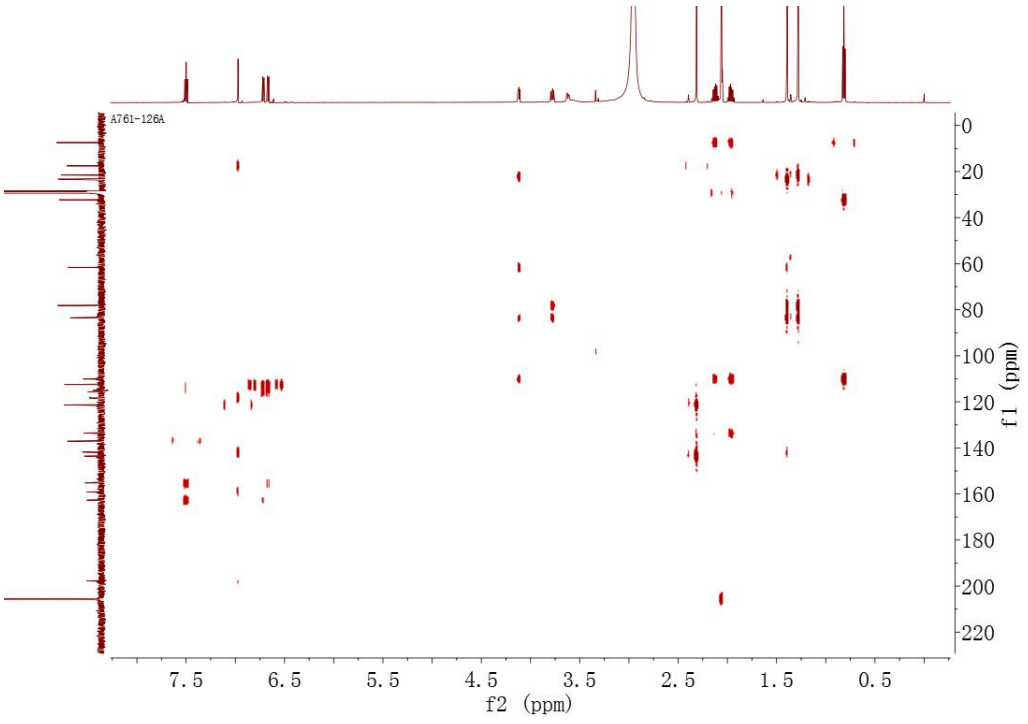


Figure S10. HMBC spectrum of **1a**.

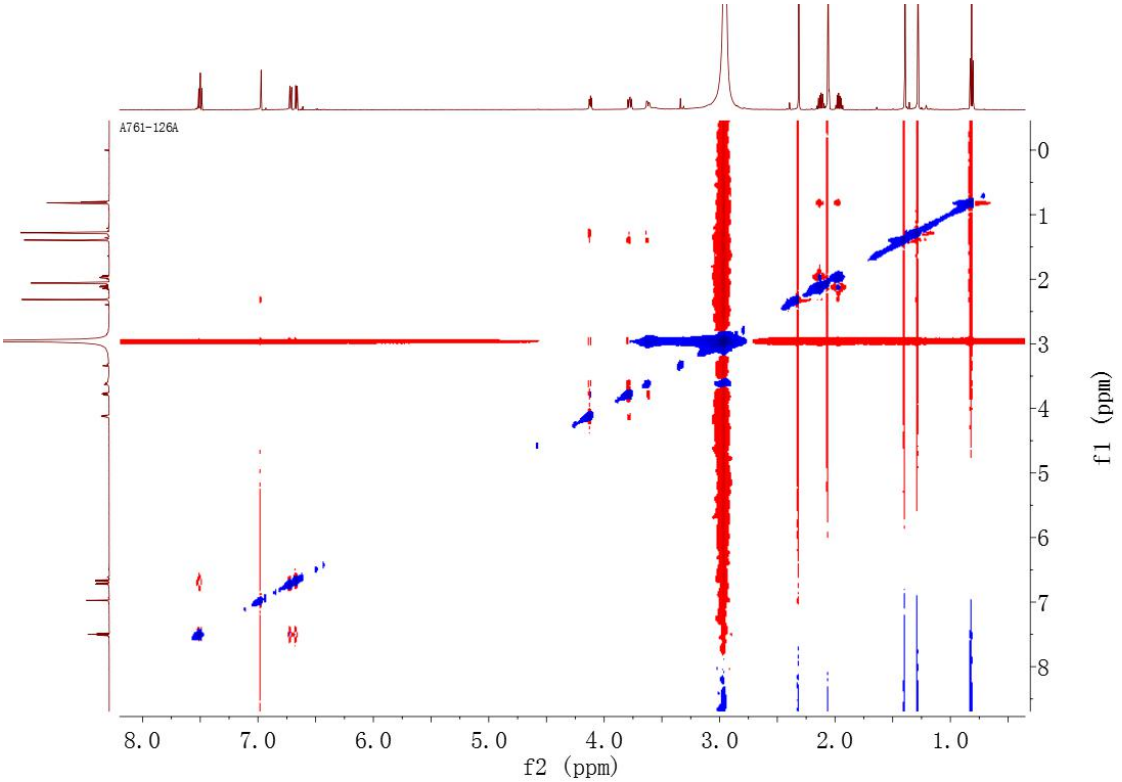


Figure S11. NOESY spectrum of **1a**.

Mass Spectrum SmartFormula Report

Analysis Info

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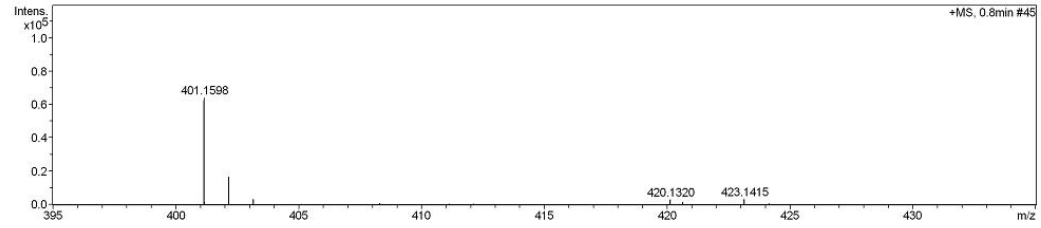
Method	LC_Direct Infusion_pos_100-1000mz.m	Operator	SCSIO
Sample Name	liuhongxin_A761-126A_pos	Instrument	maXis 255552.00029
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	err [mDa]	mSigma	rdb	e⁻ Conf	N-Rule
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423.1415	1	C22H24NaO7	100.00	423.1414	0.3	0.1	22.2	10.5	even	ok
823.2922	1	C44H48NaO14	100.00	823.2936	1.8	1.4	22.8	20.5	even	ok

liuhongxin_A761-126A_pos_31_01_5385.d
Bruker Compass DataAnalysis 4.1 printed: 9/5/2018 3:32:19 PM by: SCSIO Page 1 of 1

Figure S12. HRESIMS spectrum of **1**.

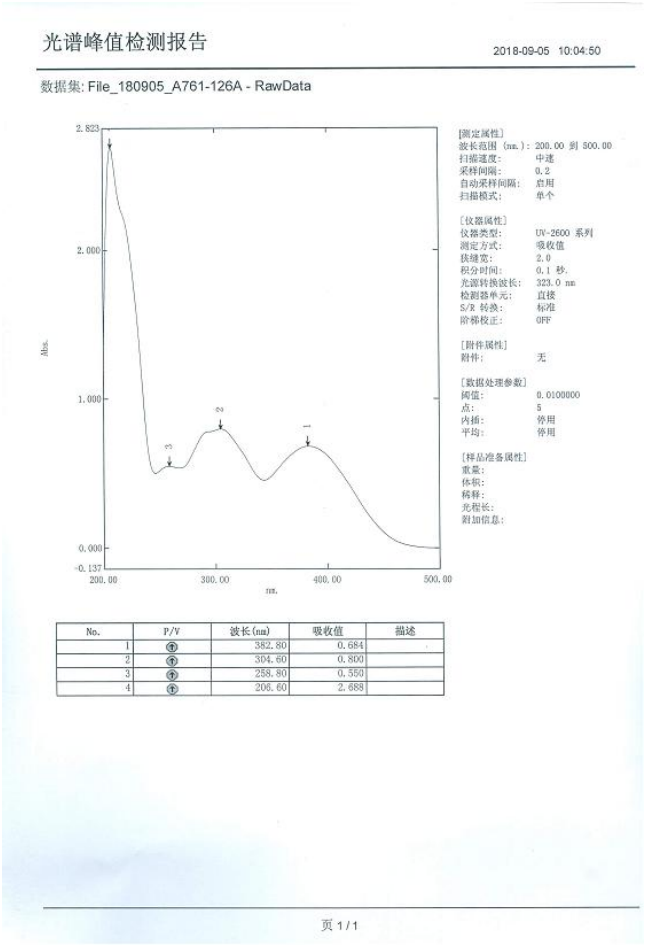

Figure S13. UV spectrum of **1a**.

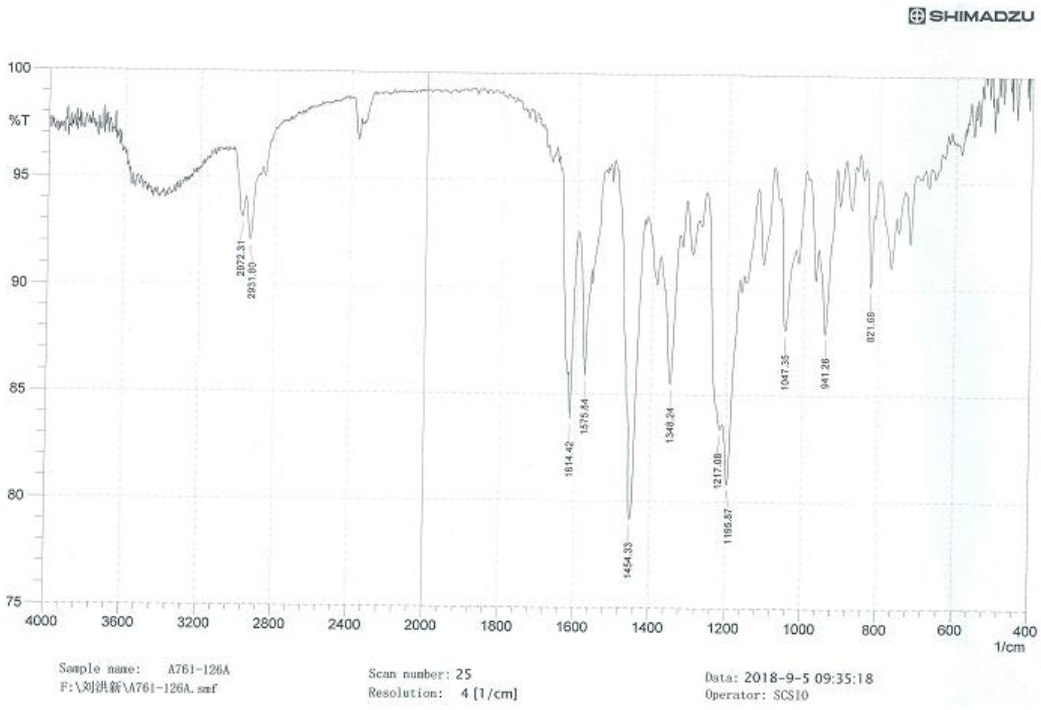

Figure S14. IR spectrum of **1a**.

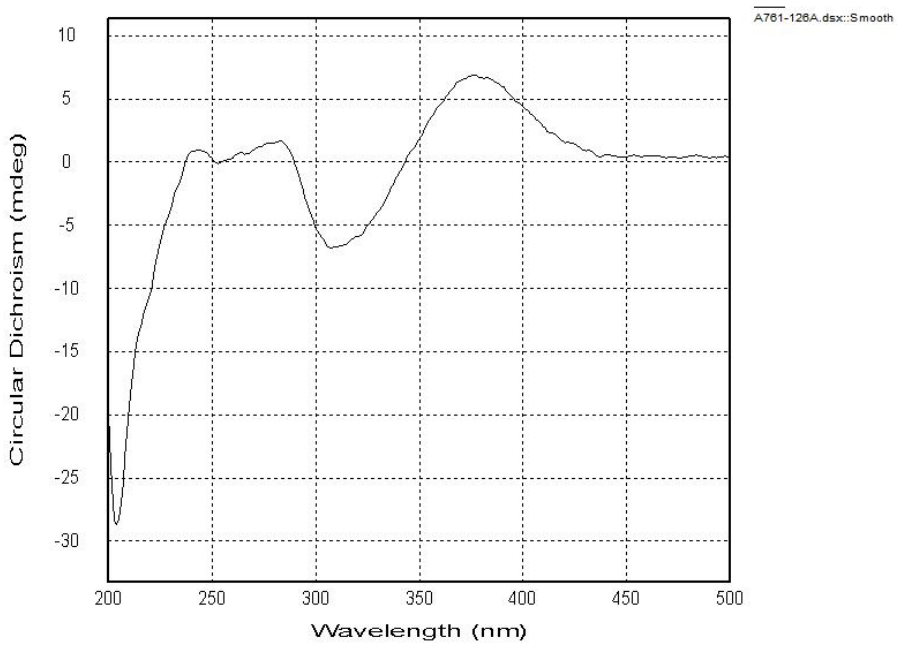

Figure S15. CD spectrum of **1b**.

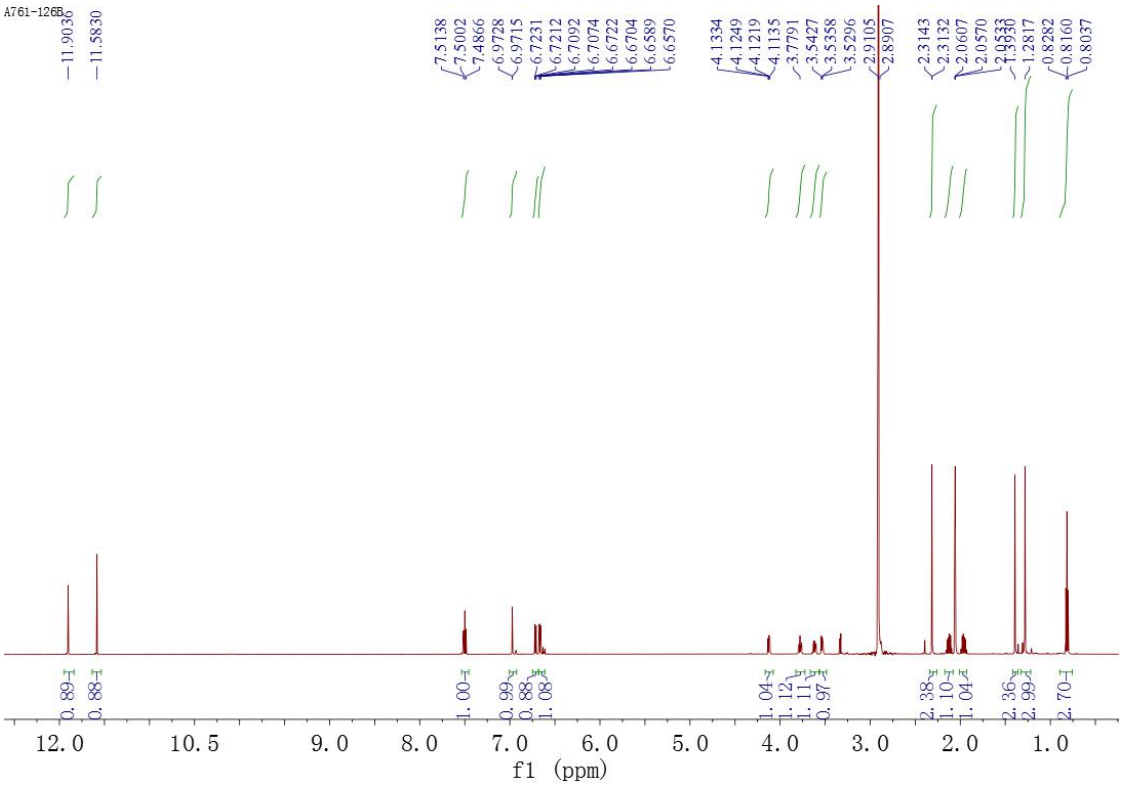

Figure S16. ^{1}H NMR spectrum (600 MHz, CD_3COCD_3) of **1b**.

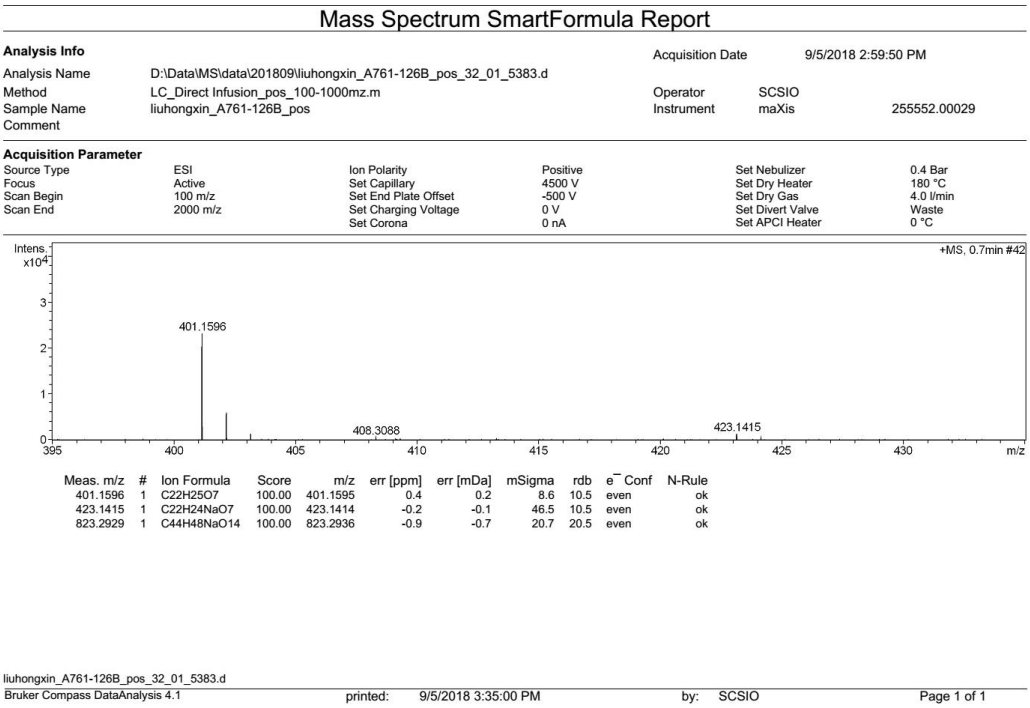

Figure S17. HRESIMS spectrum of **1b**.

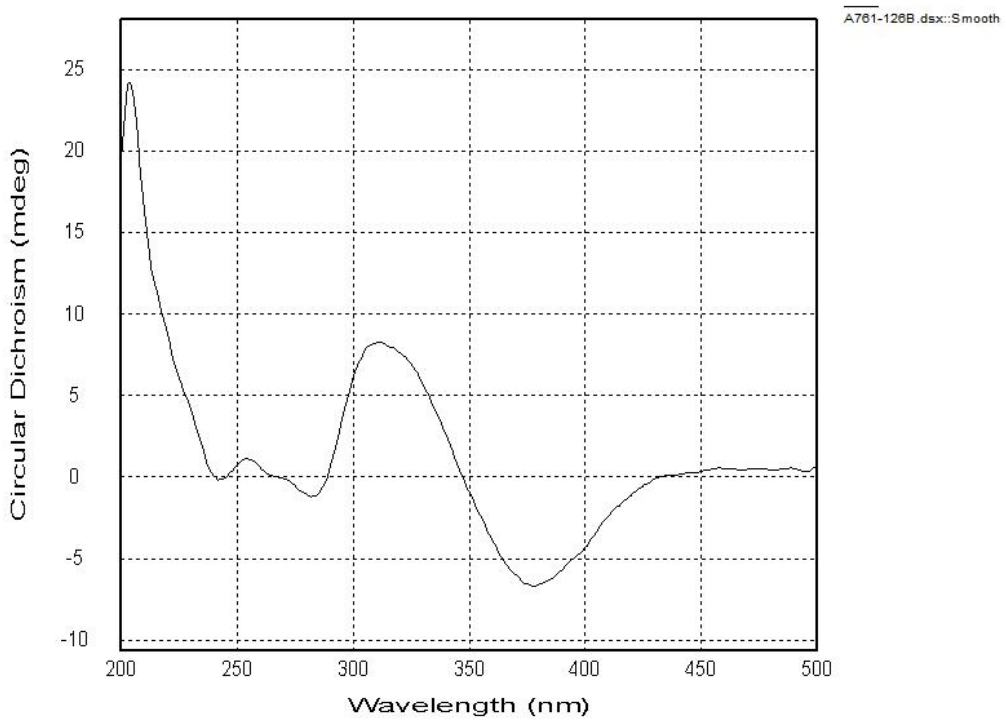

Figure S18. CD spectrum of **1b**.

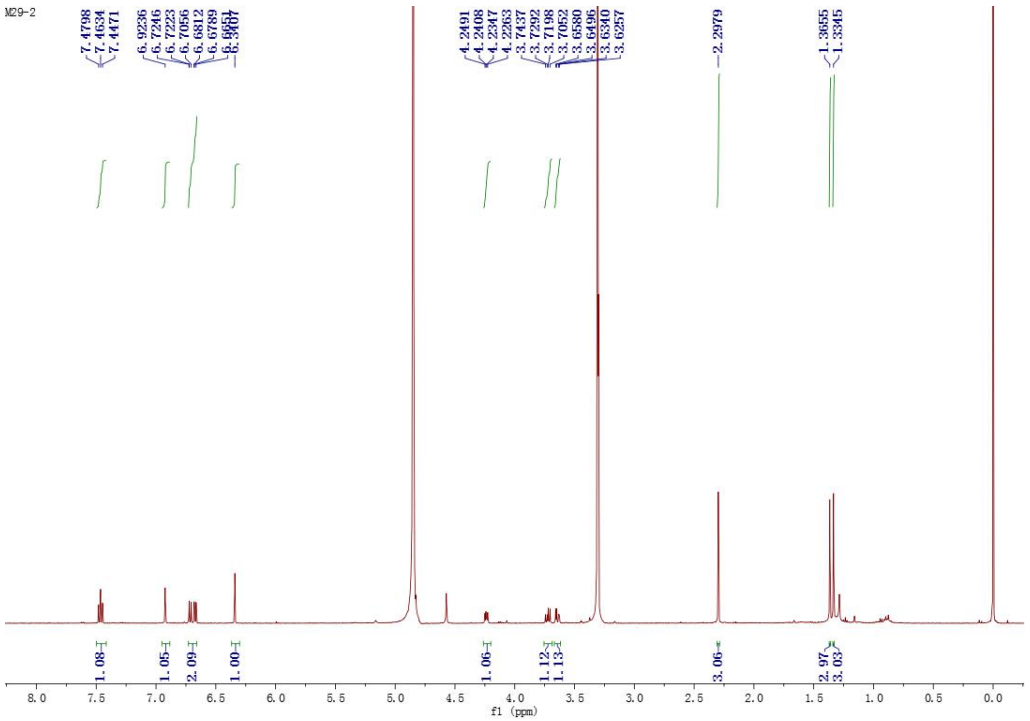

Figure S19. ^{1}H NMR spectrum (500 MHz, CD_3COCD_3) of **2**.

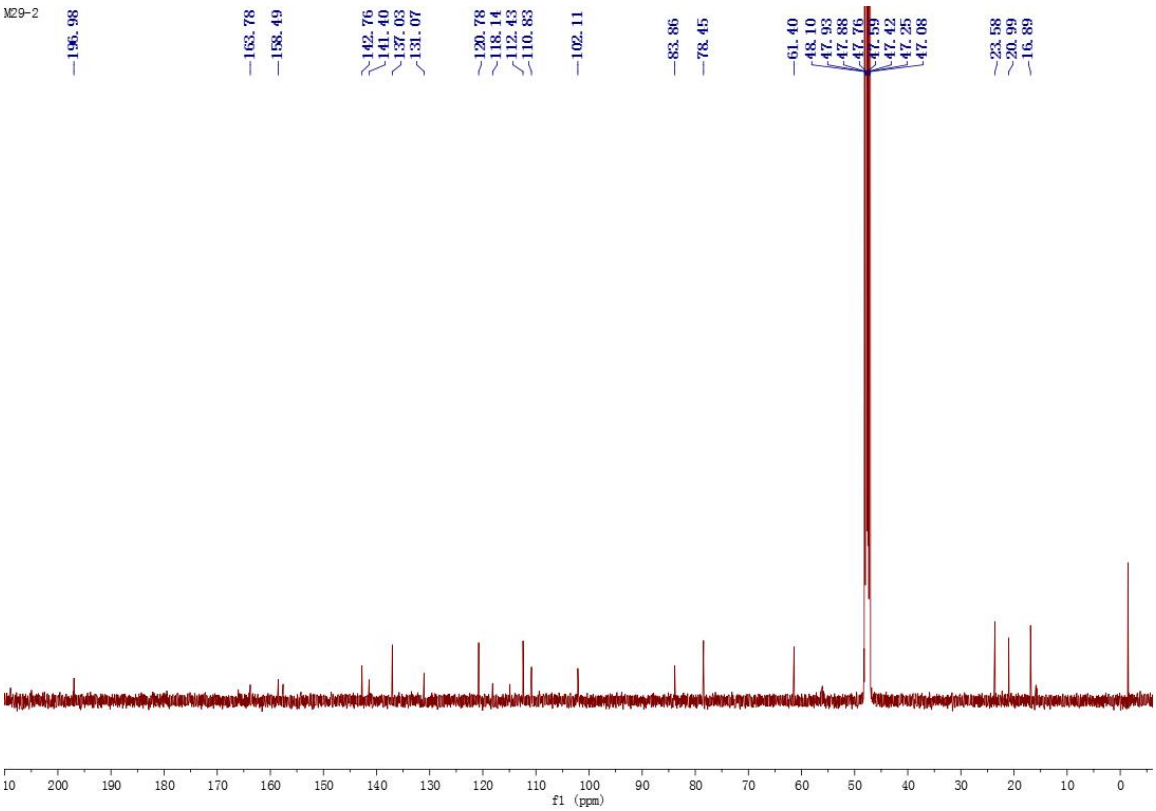

Figure S20. ^{13}C NMR spectrum (125 MHz, CD_3COCD_3) of **2**.

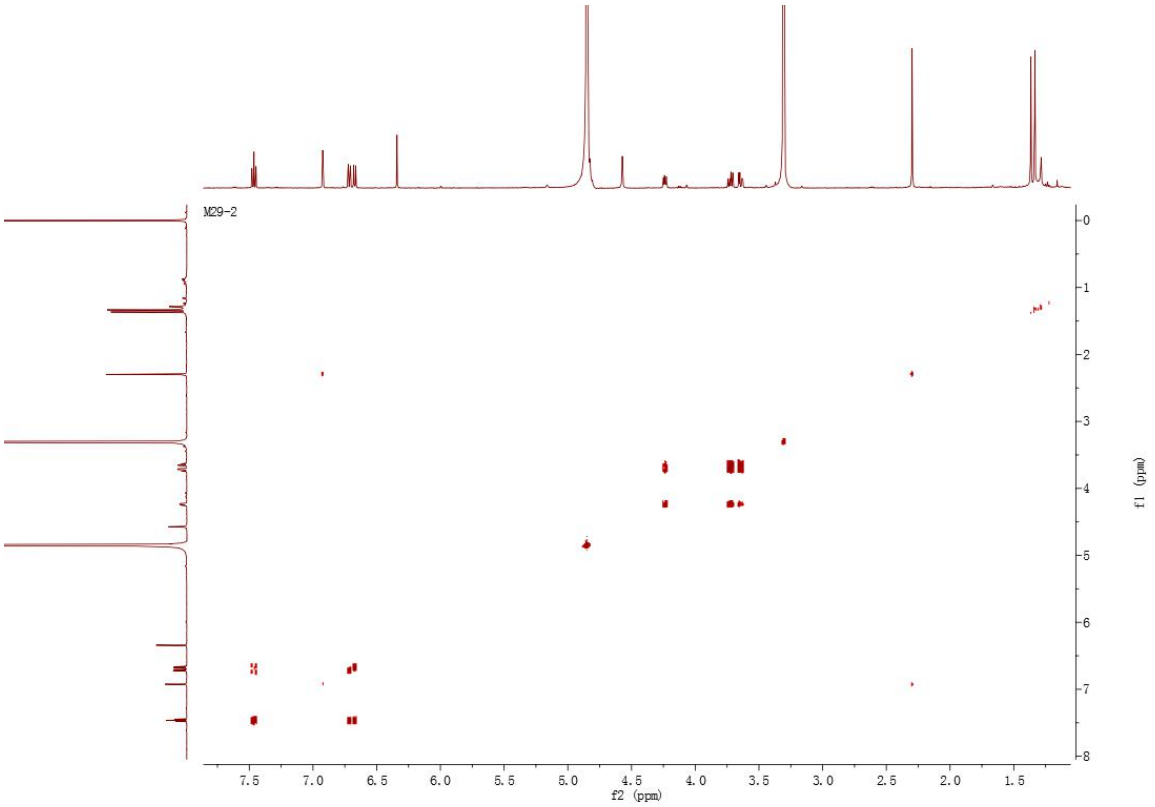

Figure S21. ^{1}H-^{1}H COSY spectrum (500 MHz, CD_3COCD_3) of **2**.

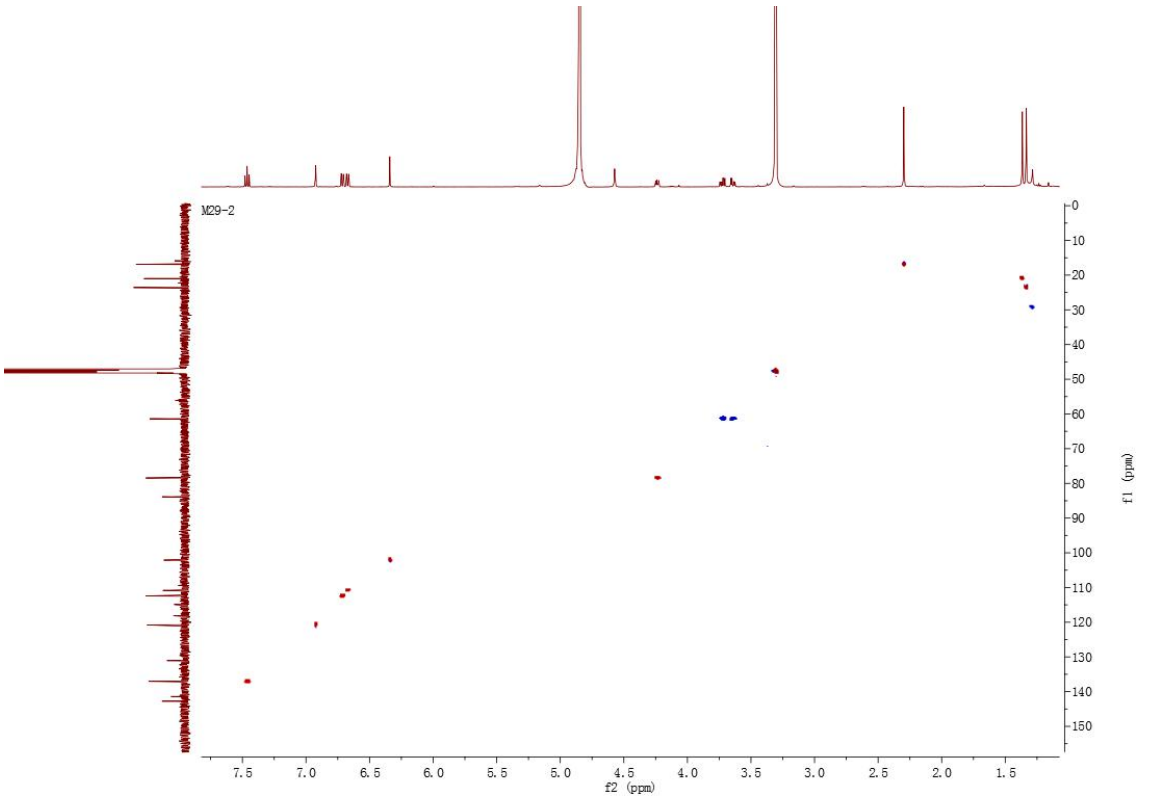

Figure S22. HSQC spectrum of **2**.

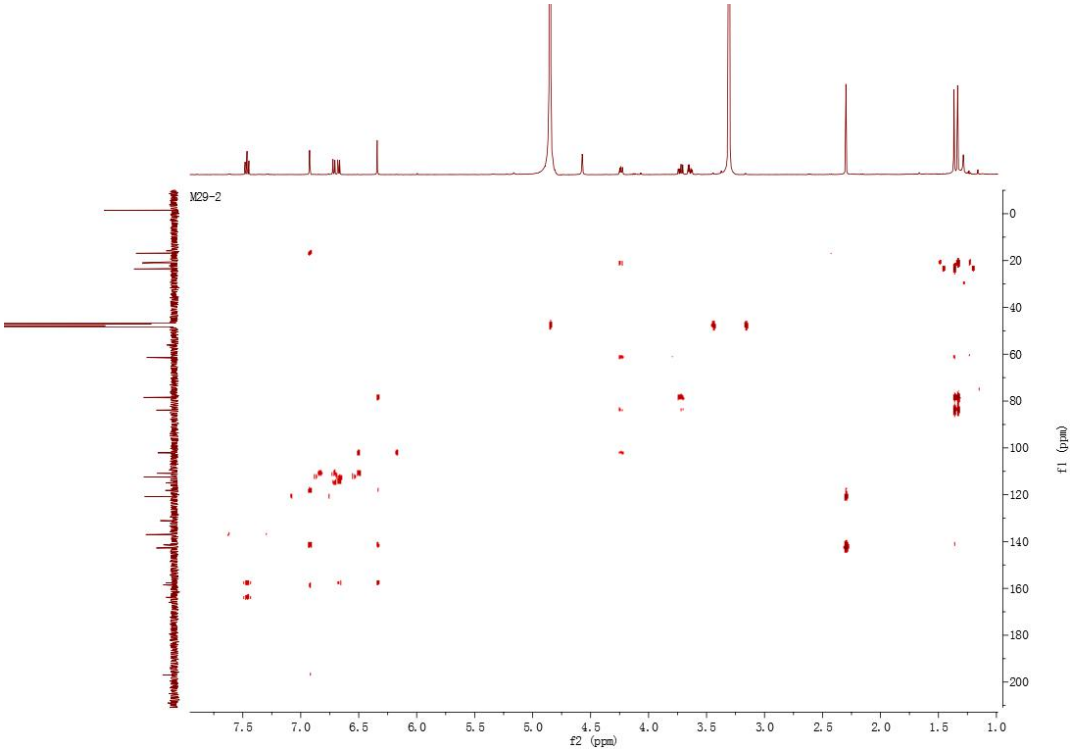

Figure S23. HMBC spectrum of **2**.

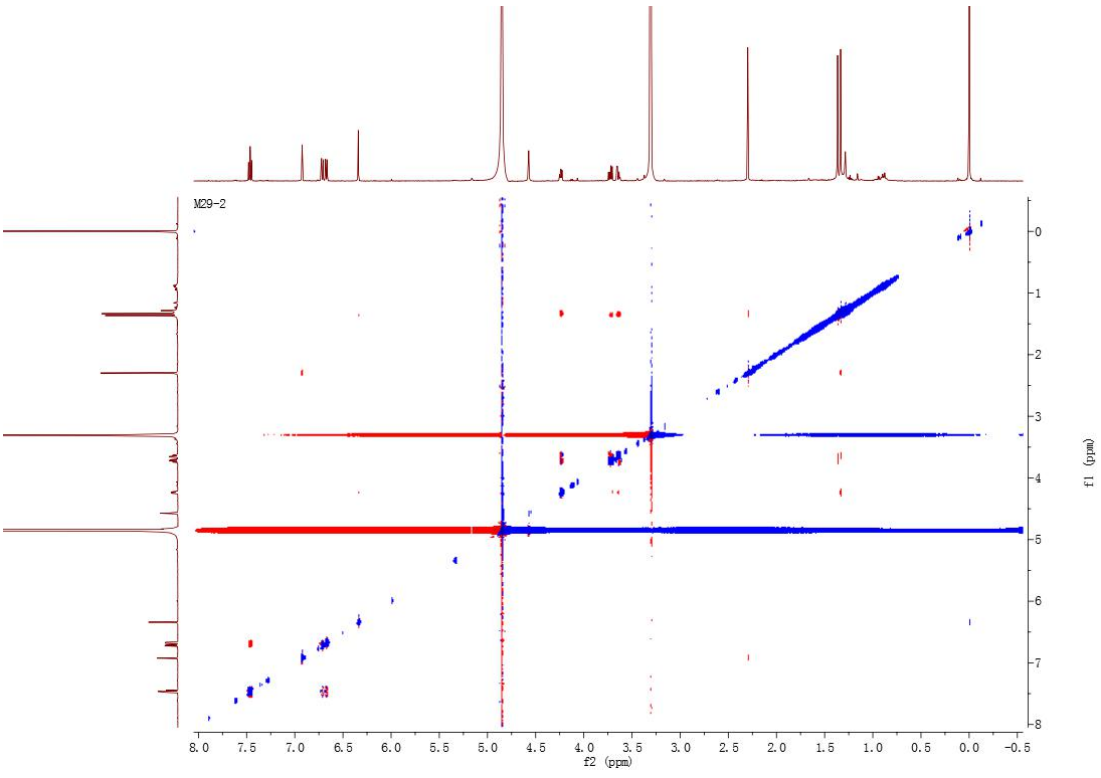

Figure S24. NOESY spectrum of **2**.

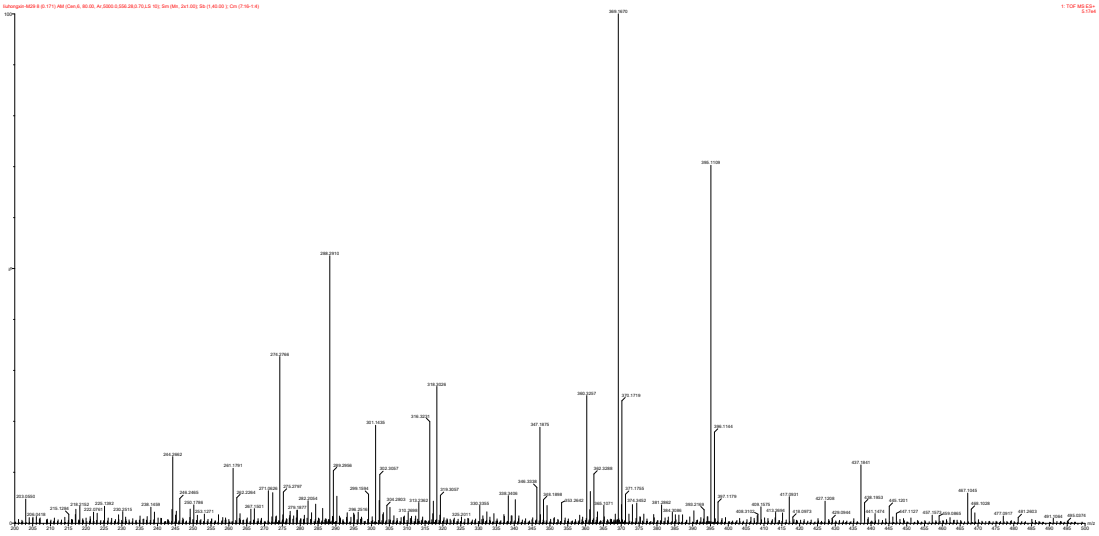

Figure S25. HRESIMS spectrum of **2**.

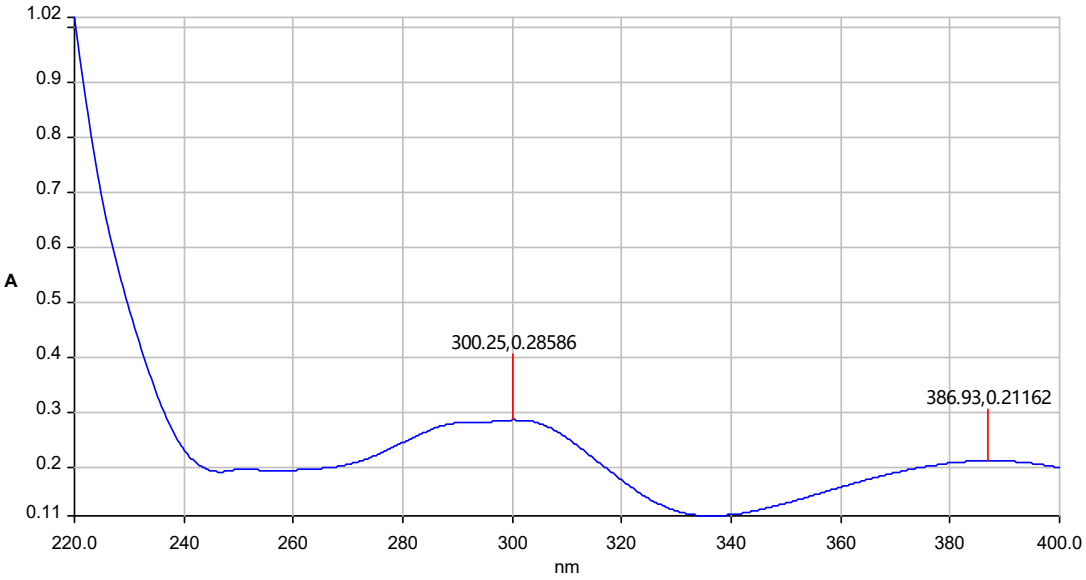

Figure S26. UV spectrum of **2**.

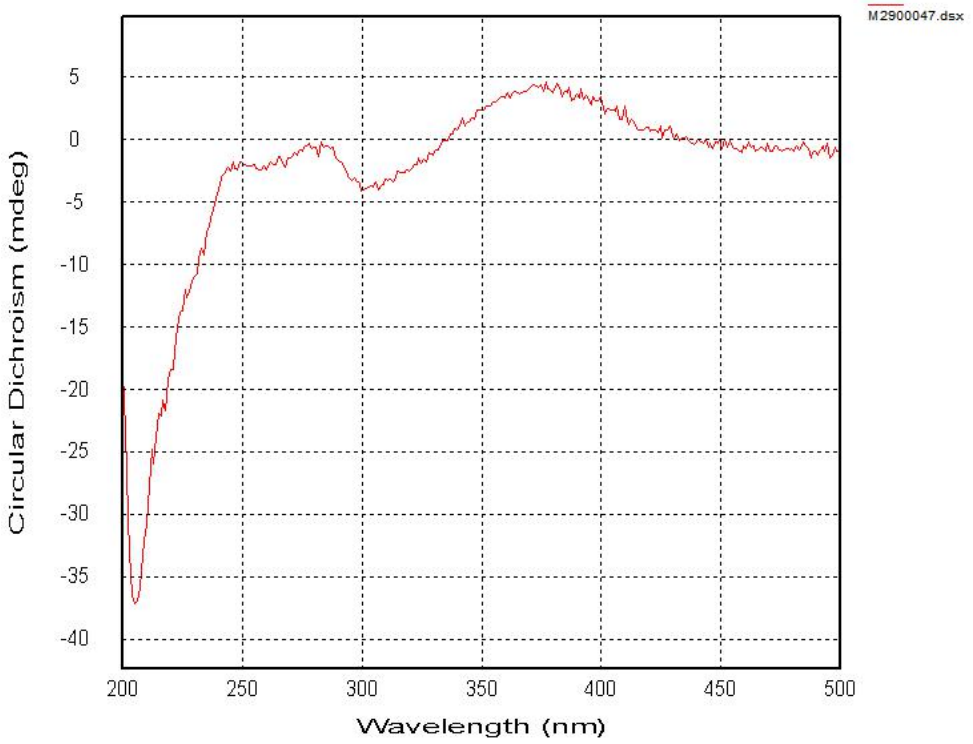

Figure S27. CD spectrum of **2**.

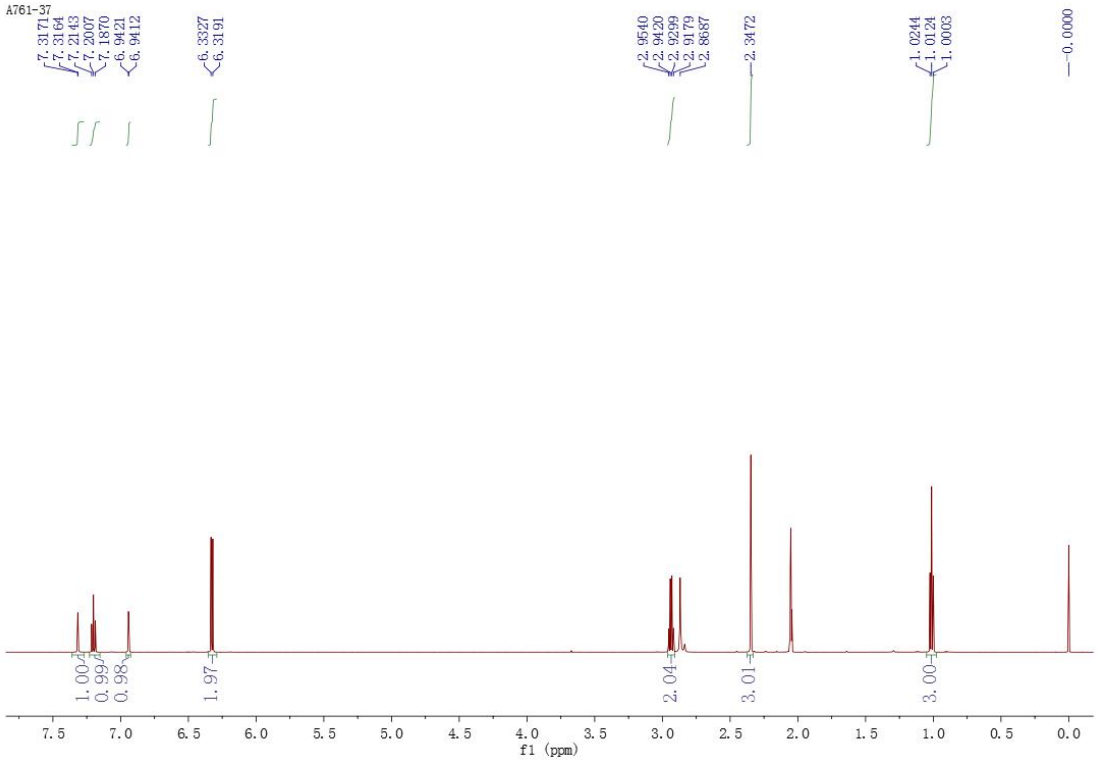

Figure S28. ^{1}H NMR spectrum (500 MHz, CD_3COCD_3) of **3**.

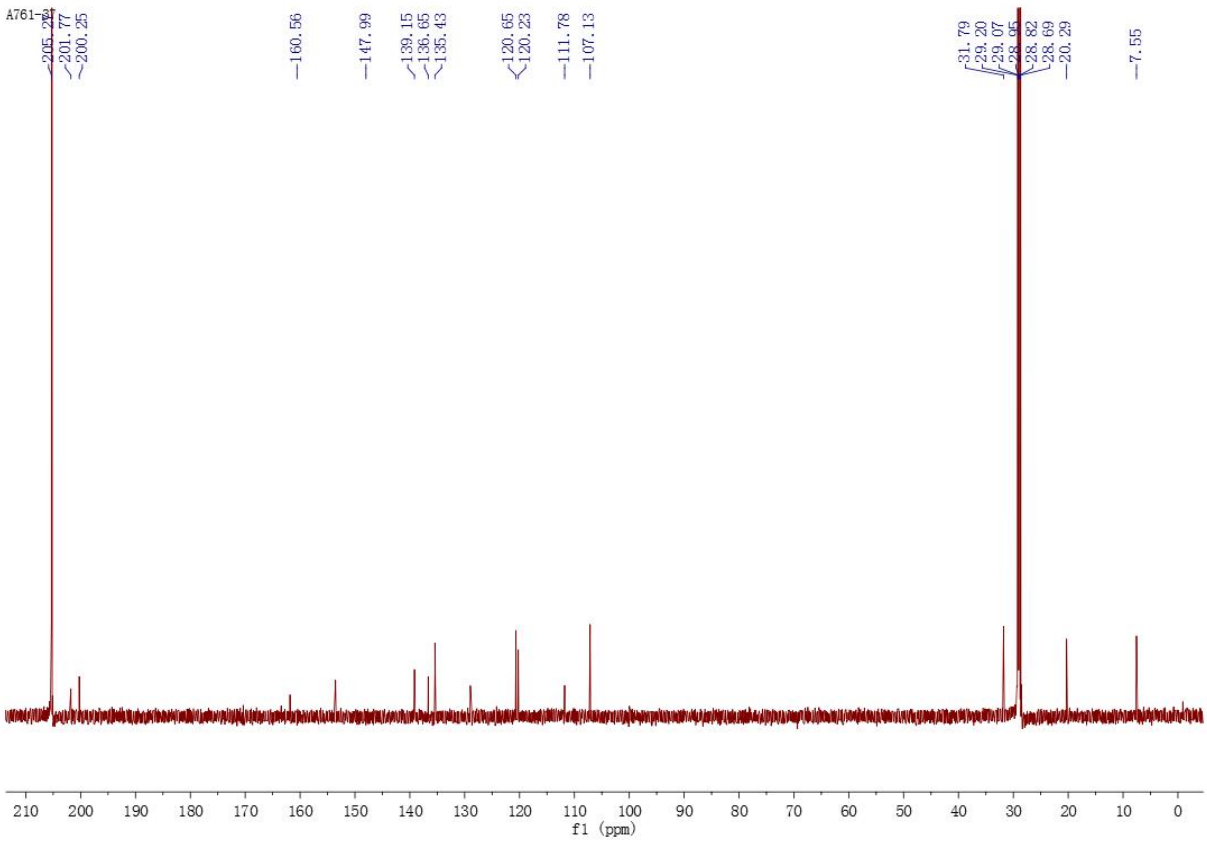

Figure S29. ^{13}C NMR spectrum (125 MHz, CD_3COCD_3) of **3**.

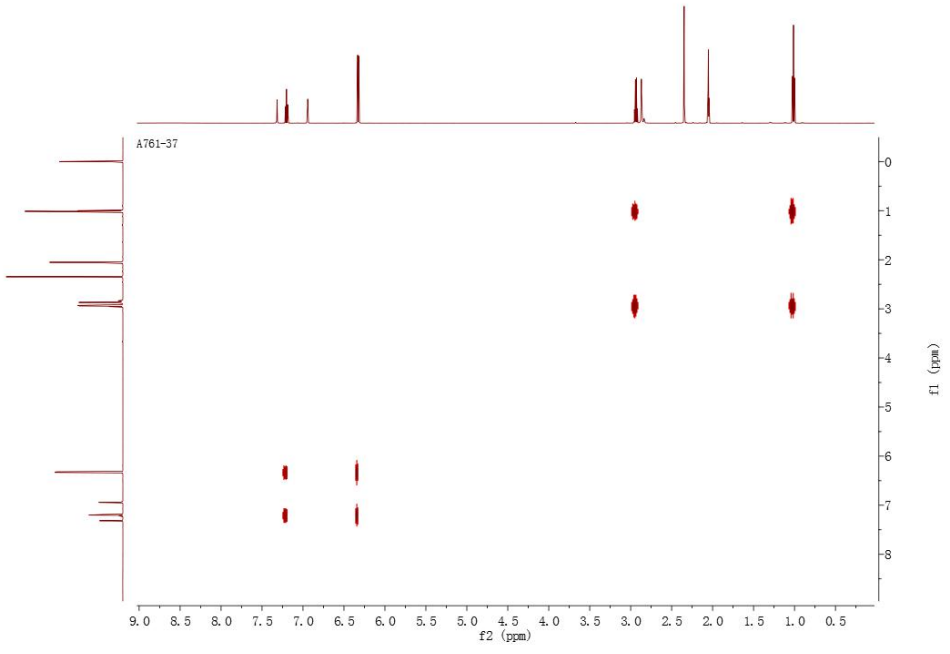

Figure S30. ^{1}H-^{1}H COSY spectrum (500 MHz, CD_3COCD_3) of **3**.

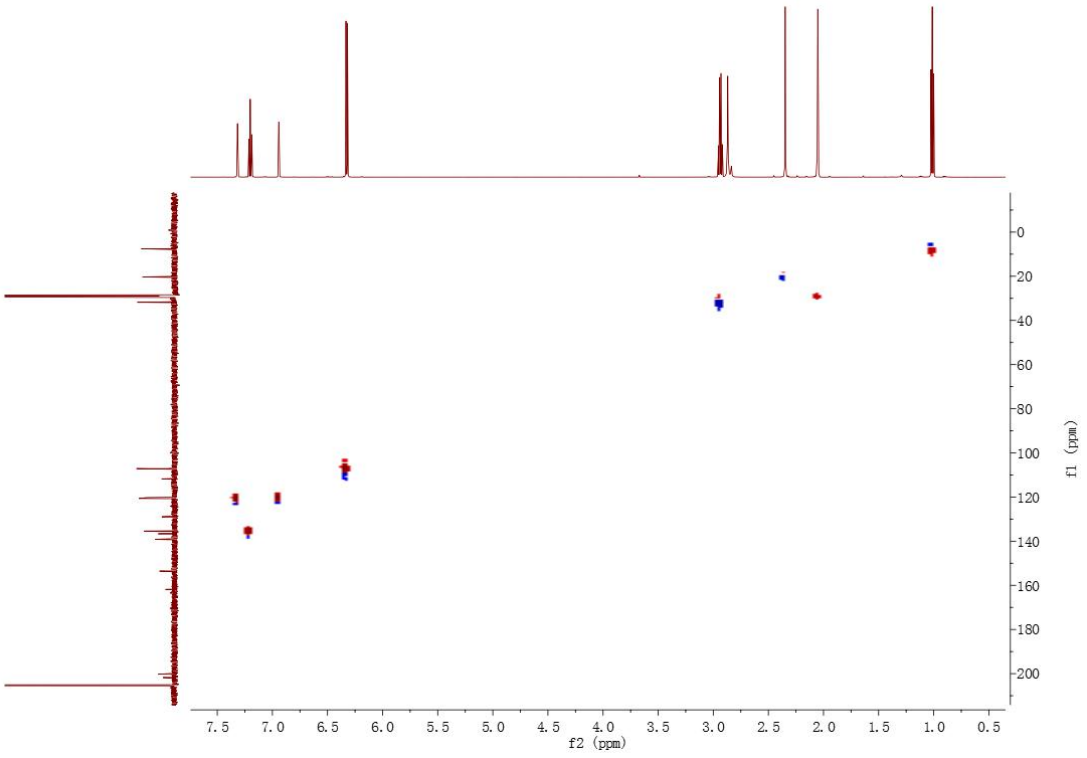

Figure S31. HSQC spectrum of **3**.

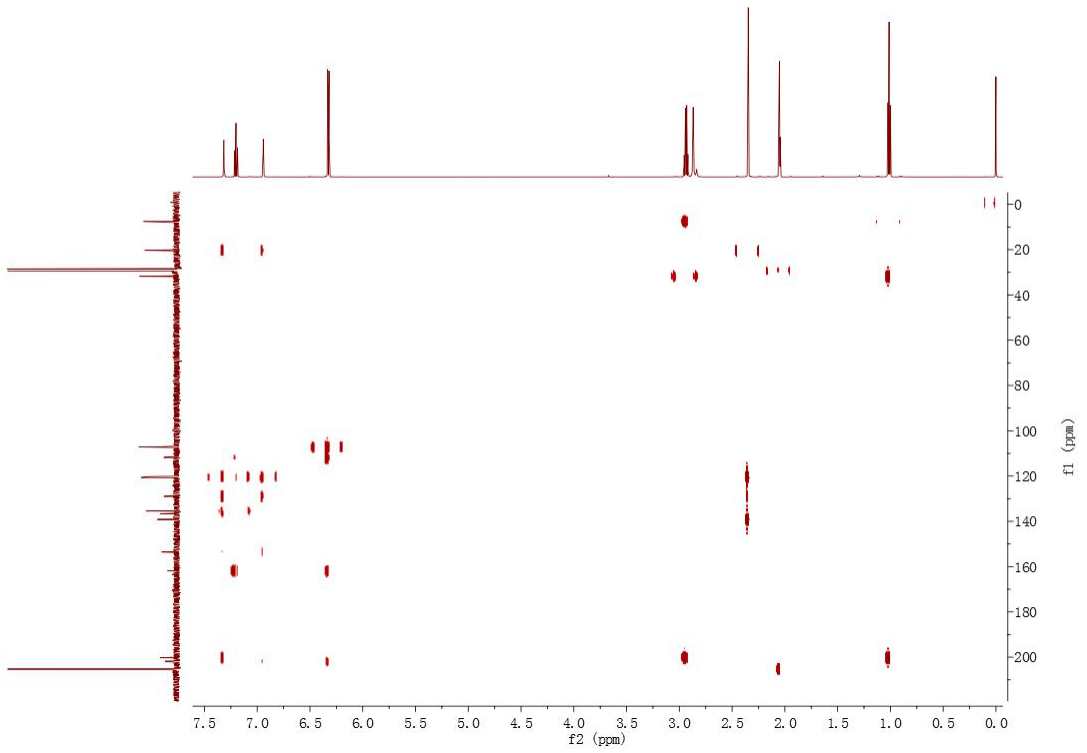

Figure S32. HMBC spectrum of **3**.

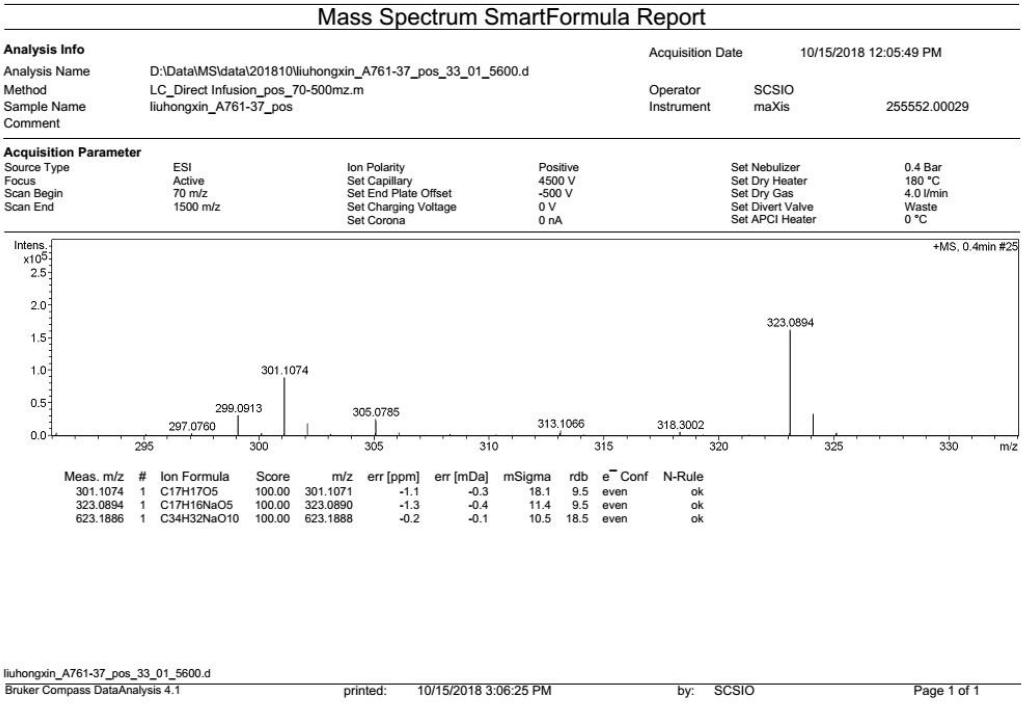

Figure S33. HRESIMS spectrum of **3**.

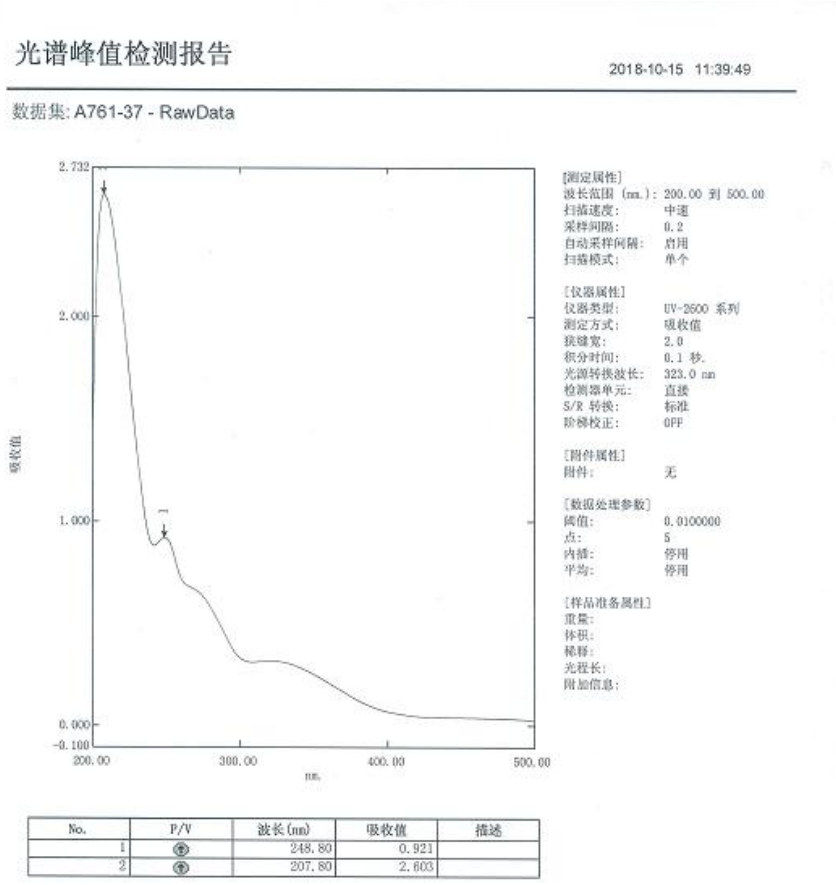

Figure S34. UV spectrum of **3**.

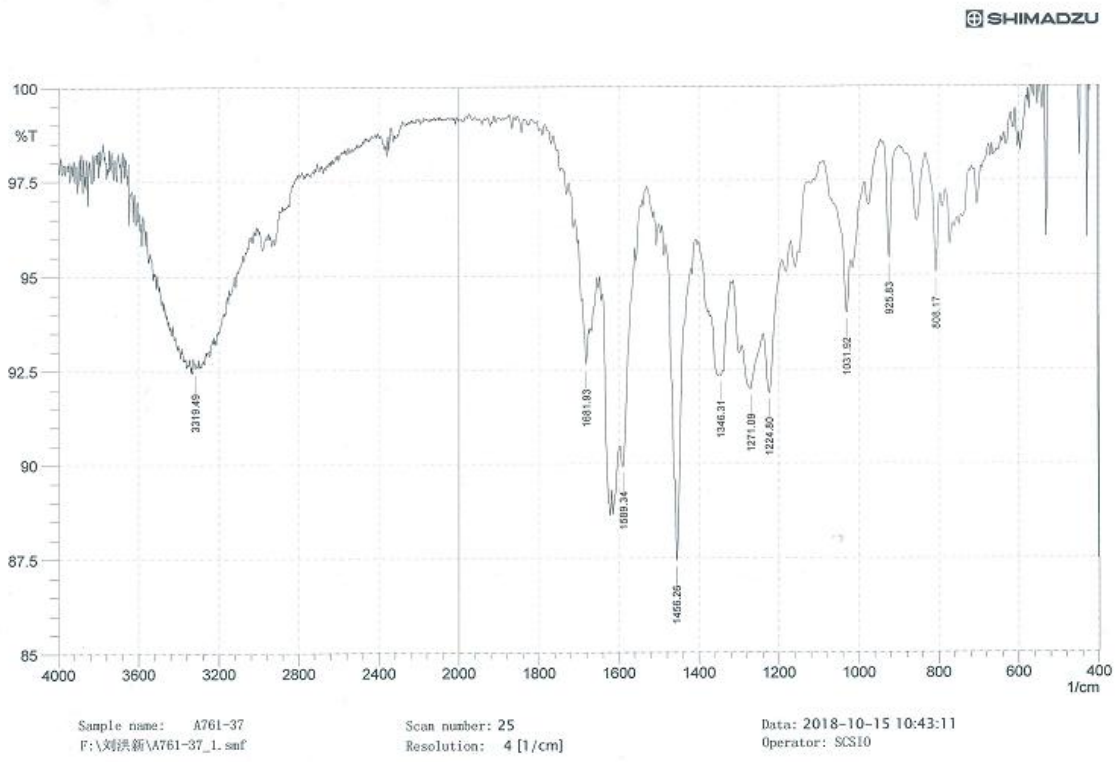

Figure S35. IR spectrum of **3**.

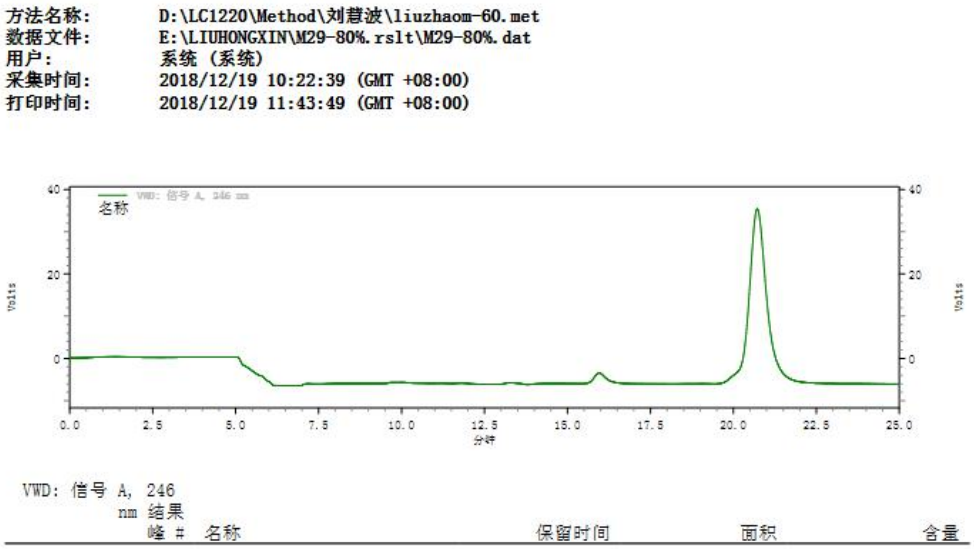

Figure S36. The spectrum of chiral analysis of **2** with Chiralpak IC column (*n*-hexane 95%/Isopropyl Alcohol, 4:1, 3 mL/min).