

Supporting Information

Jun Xie¹⁺, Yingying Wu¹⁺, Tianyuan Zhang¹, Mengyue Zhang¹, Weiwei Zhu¹,
Elizabeth A Gullen², Zhaojie Wang³, Yung-Chi Cheng², Yixuan Zhang^{1*}

¹School of Life Science and Biopharmaceutics, Shenyang Pharmaceutical University,
Shenyang, 110016, People's Republic of China

²Department of Pharmacology, Yale University School of Medicine, New Haven, CT
06520, United States of America

³Yunnan Provincial Academy of Science and Technology, Kunming, 650051, People's
Republic of China

⁺These authors contributed equally to this work

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Figure S1. ¹H NMR (600 MHz, methanol-d₄) spectrum of 1

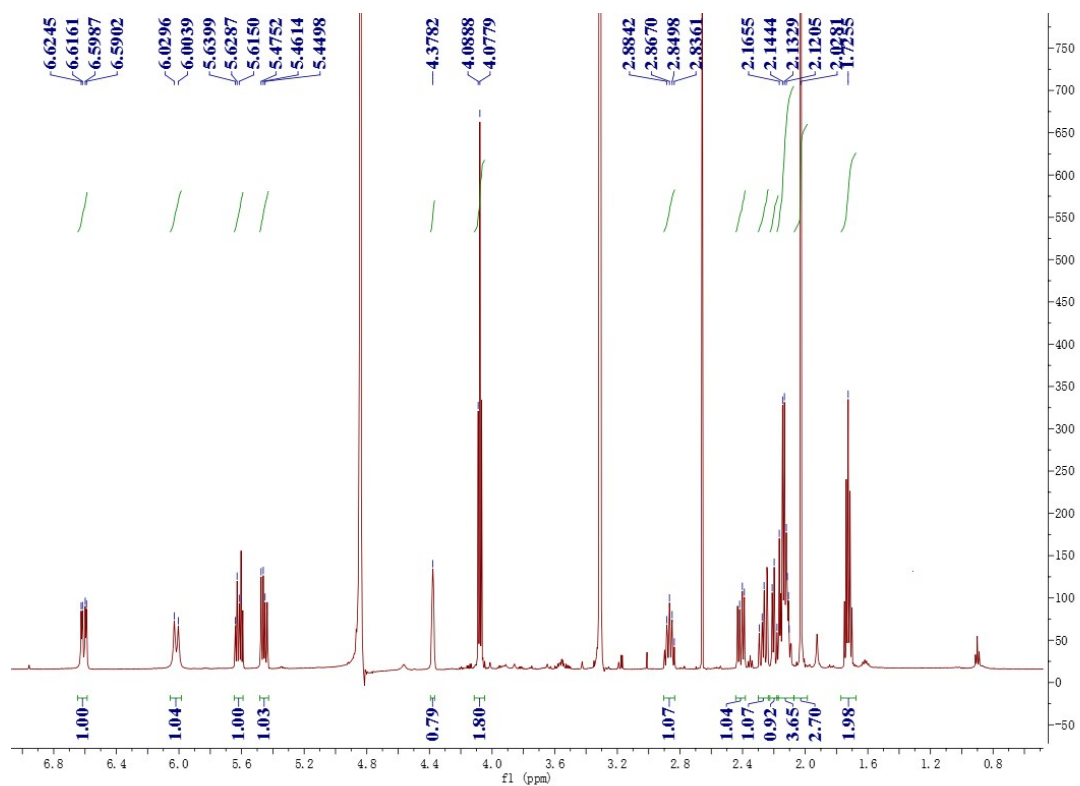


Figure S2. ^{13}C NMR (150MHz, methanol-d₄) spectrum of 1

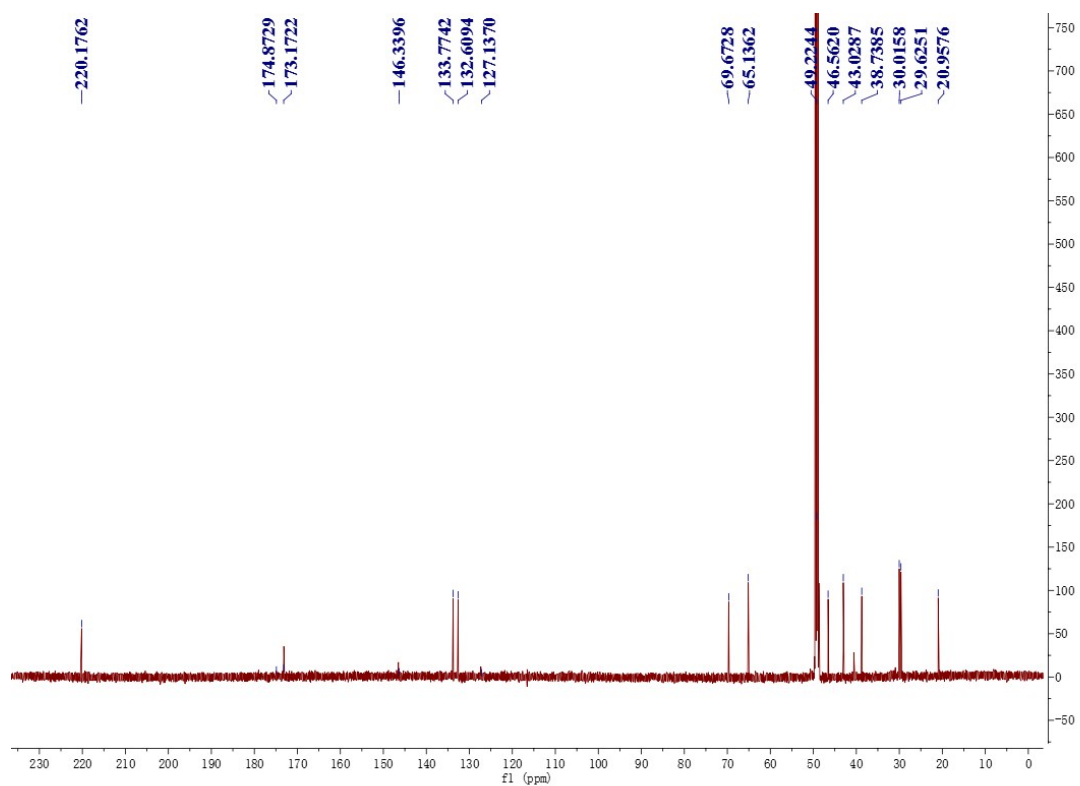


Figure S3. ^1H - ^1H COSY spectrum of 1 in methanol- d_4

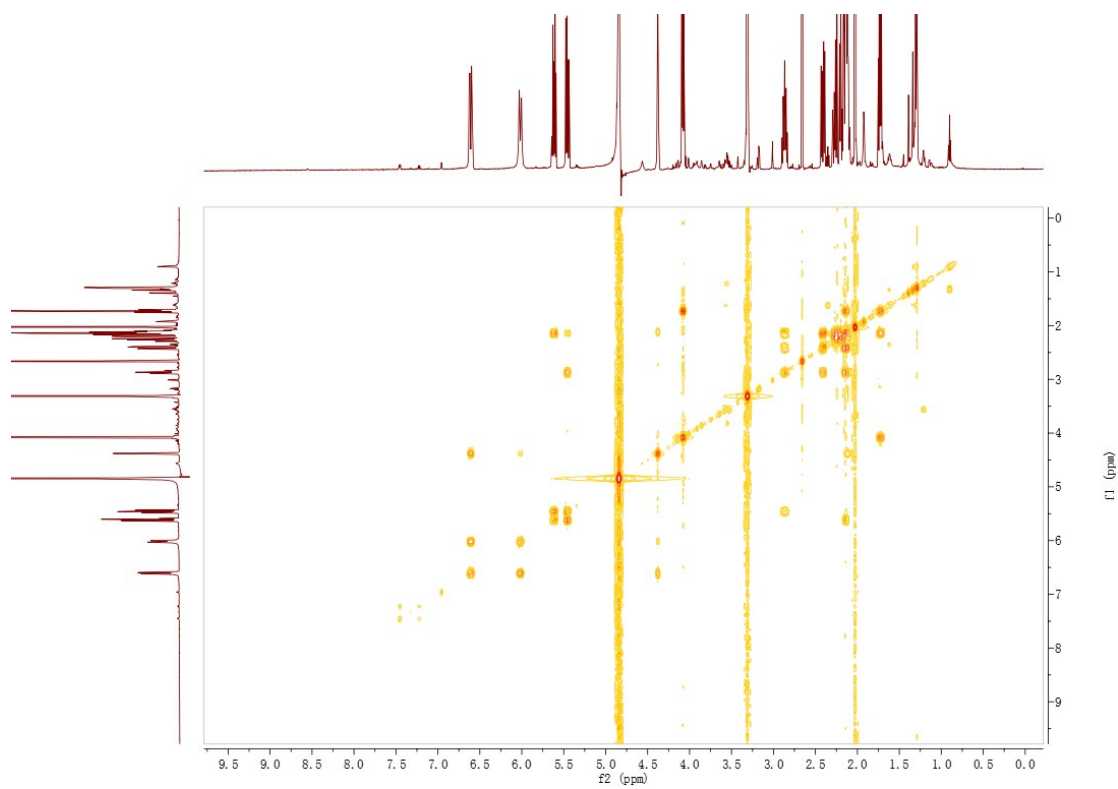


Figure S4. HSQC spectrum of 1 in methanol-d4

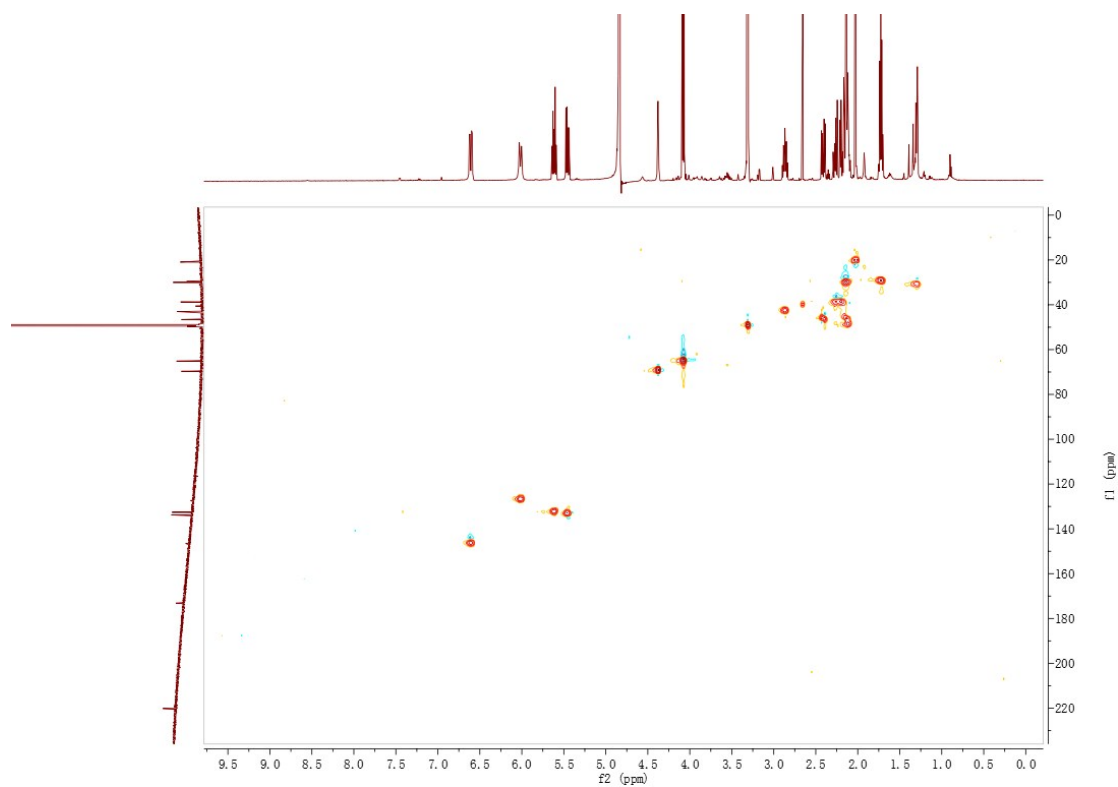


Figure S5. HMBC spectrum of 1 in methanol-d4

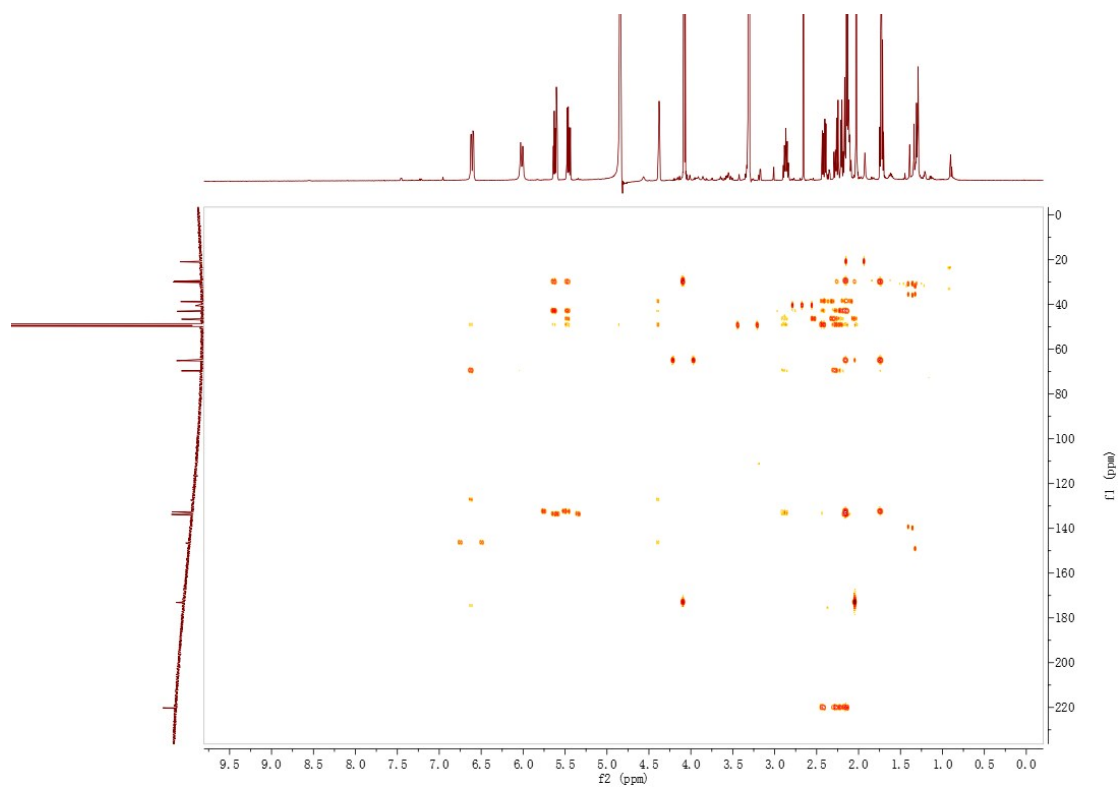


Figure S6. NOSEY spectrum of 1 in methanol-d4

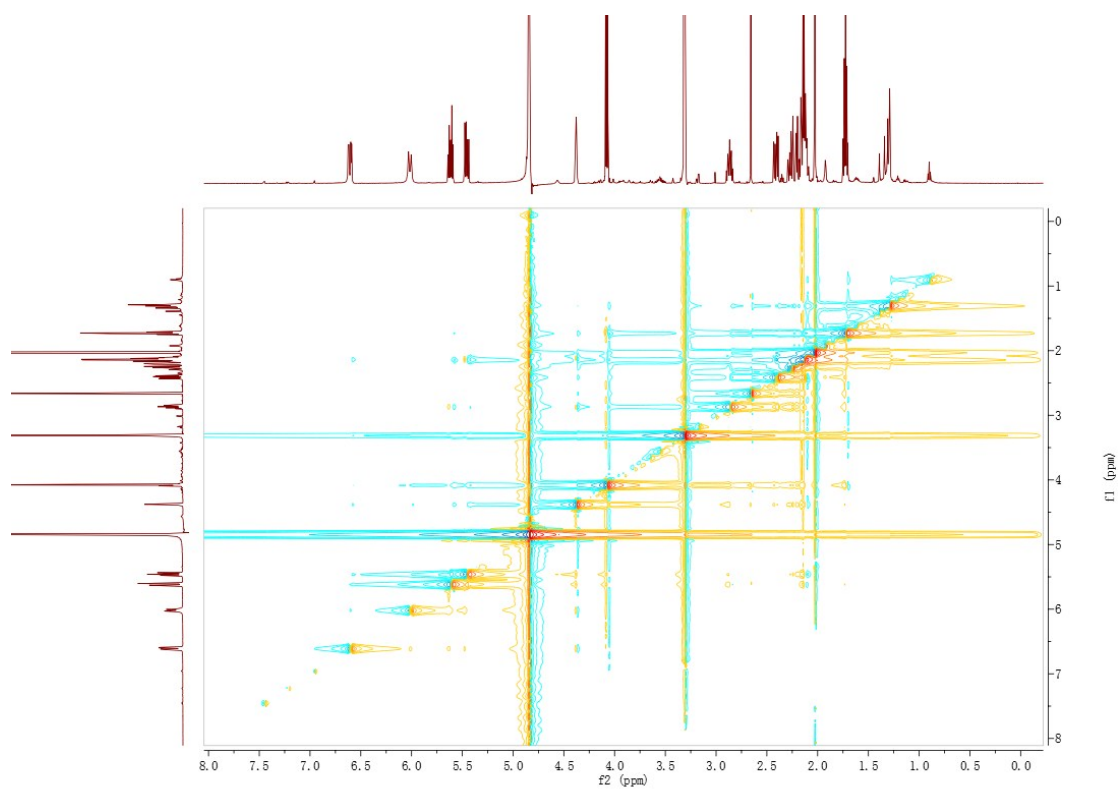


Figure S6 parts expand

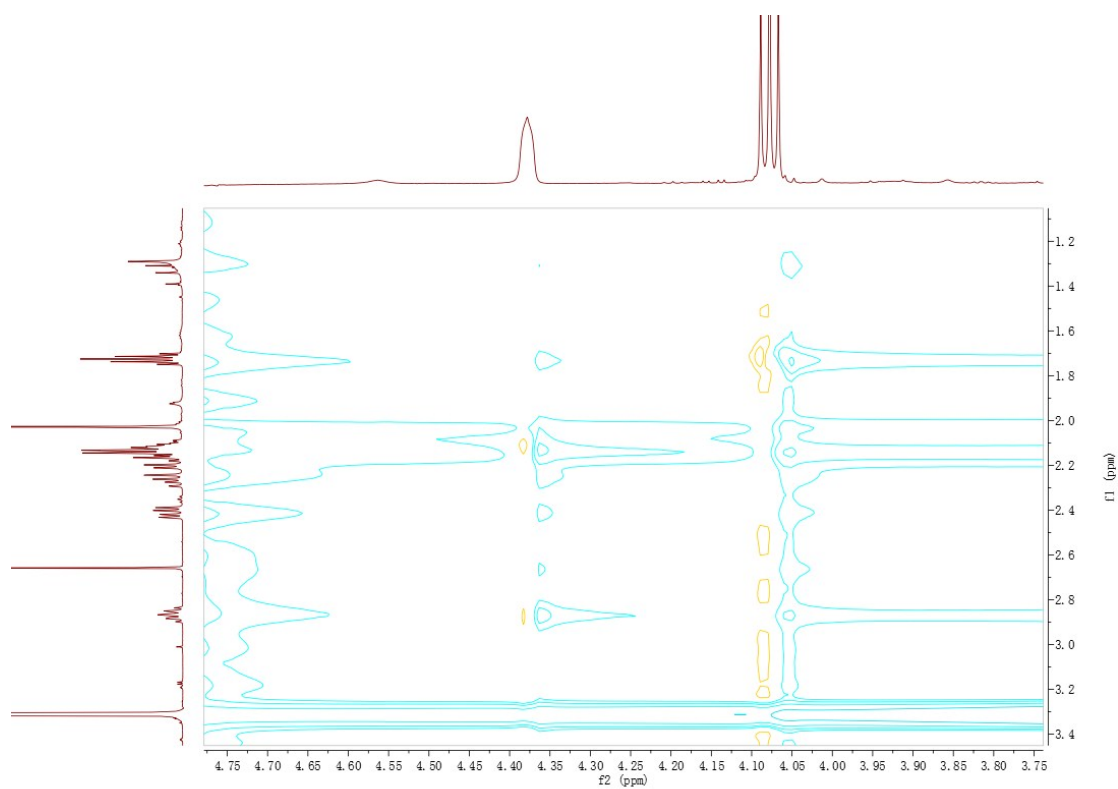


Figure S7. HRESIMS spectrum of 1

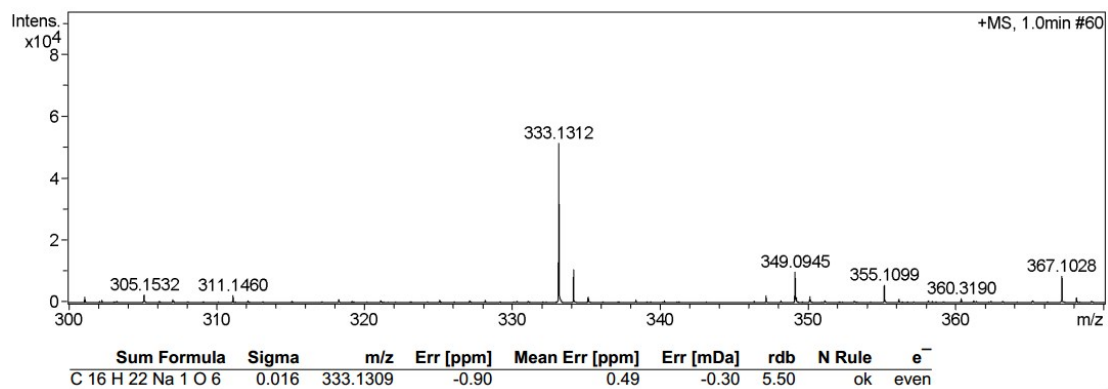


Figure S8. ¹H NMR (600 MHz, methanol-d₄) spectrum of 2

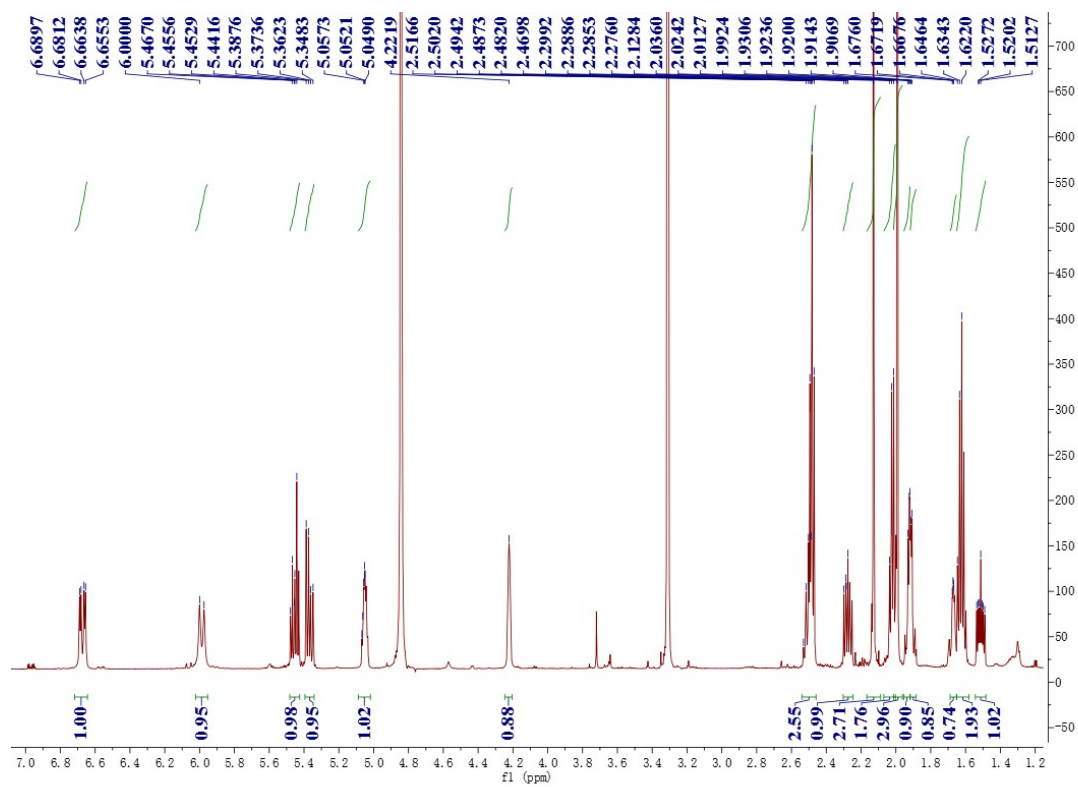


Figure S9. ^{13}C NMR (150 MHz, methanol- d_4) spectrum of 2

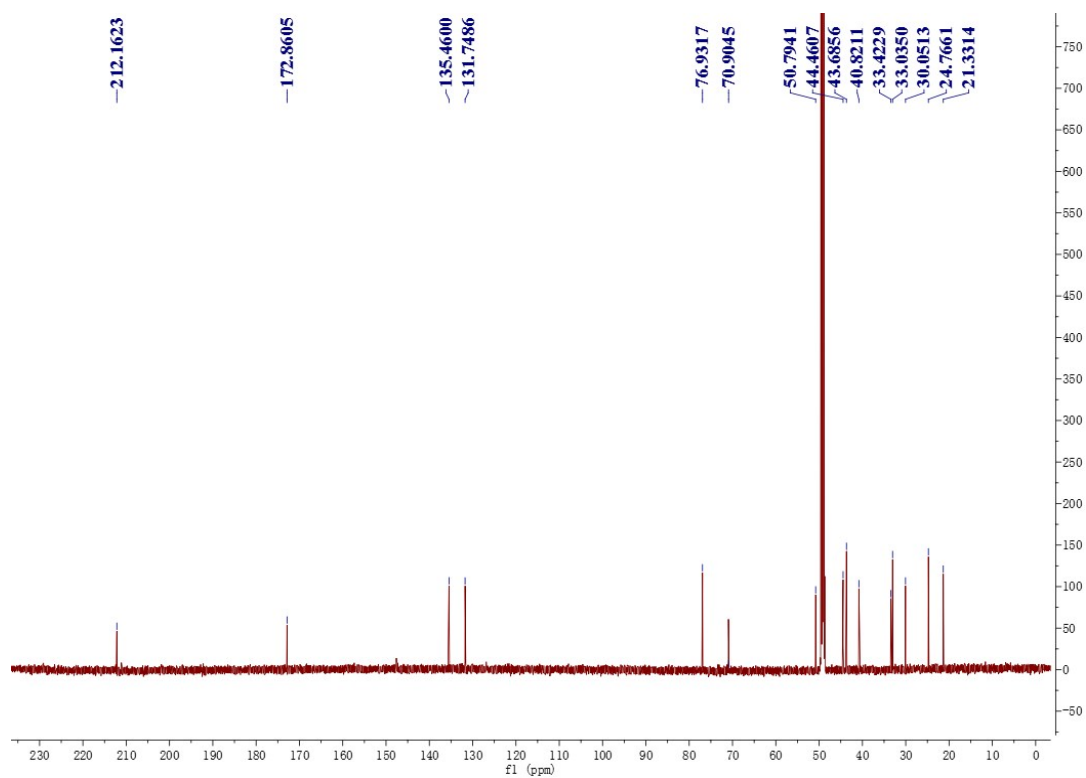


Figure S10. ^1H - ^1H COSY spectrum of 2 in methanol- d_4

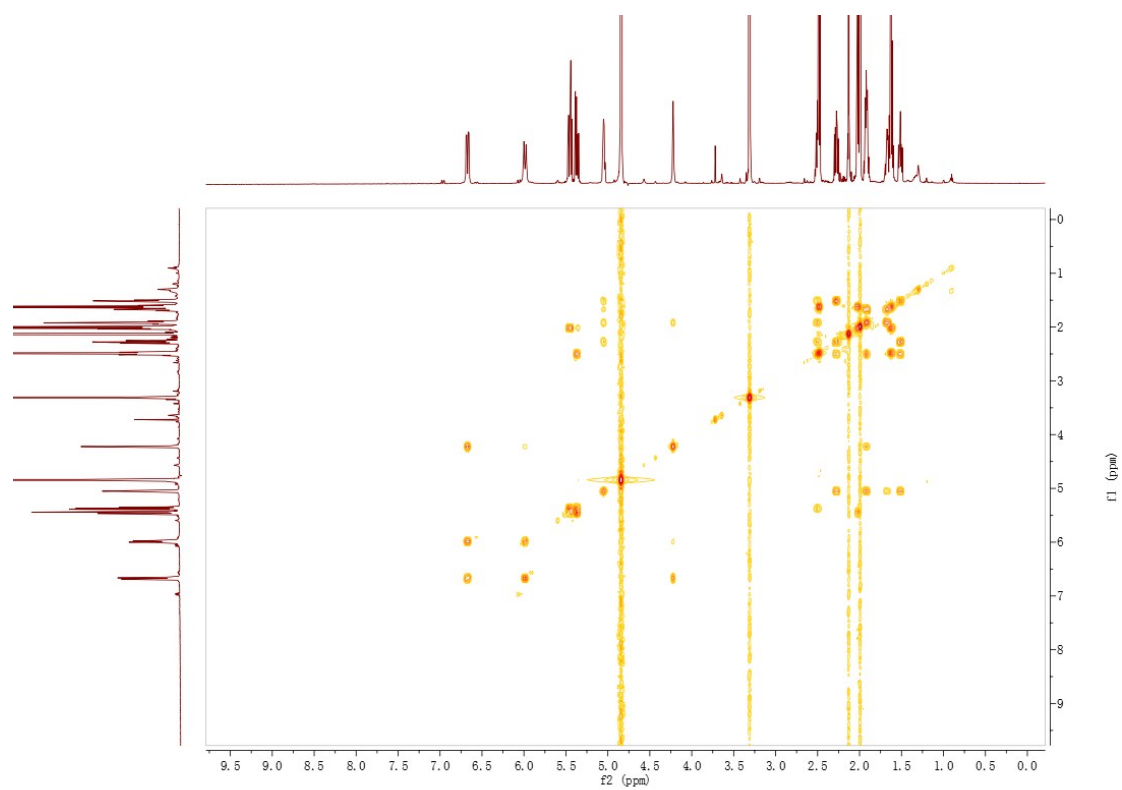


Figure S11. HSQC spectrum of 2 in methanol-d4

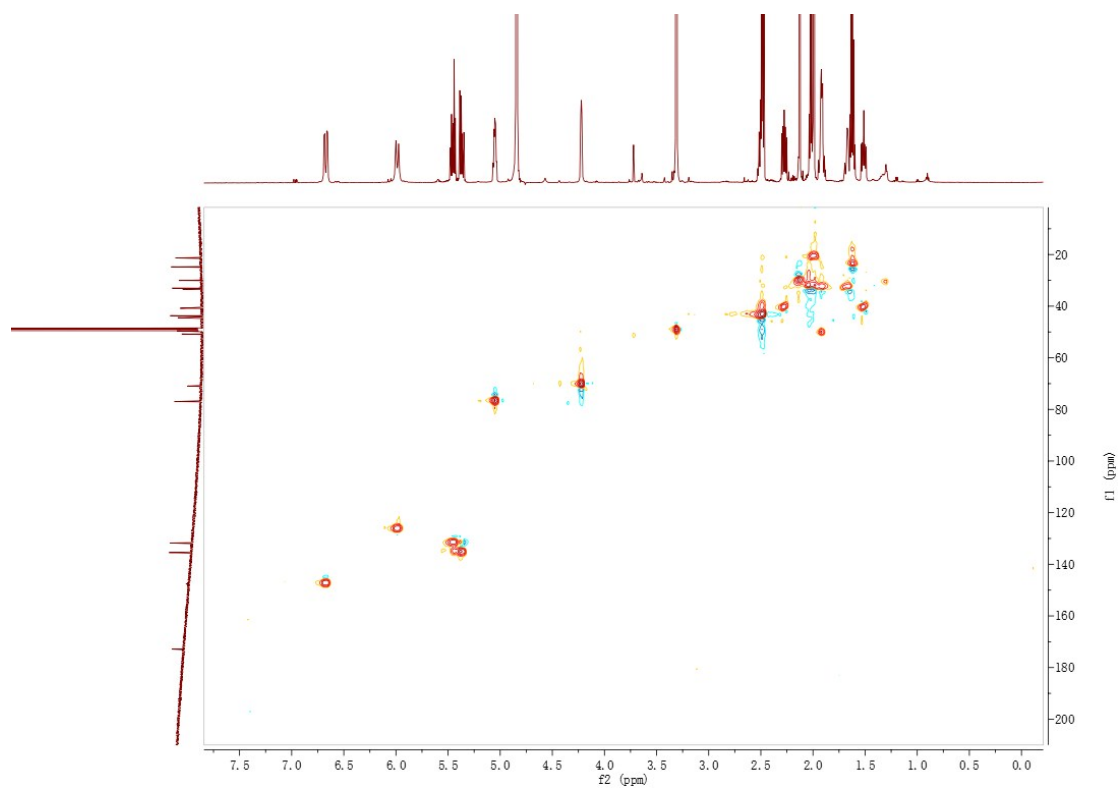


Figure S12. HMBC spectrum of 2 in methanol-d4

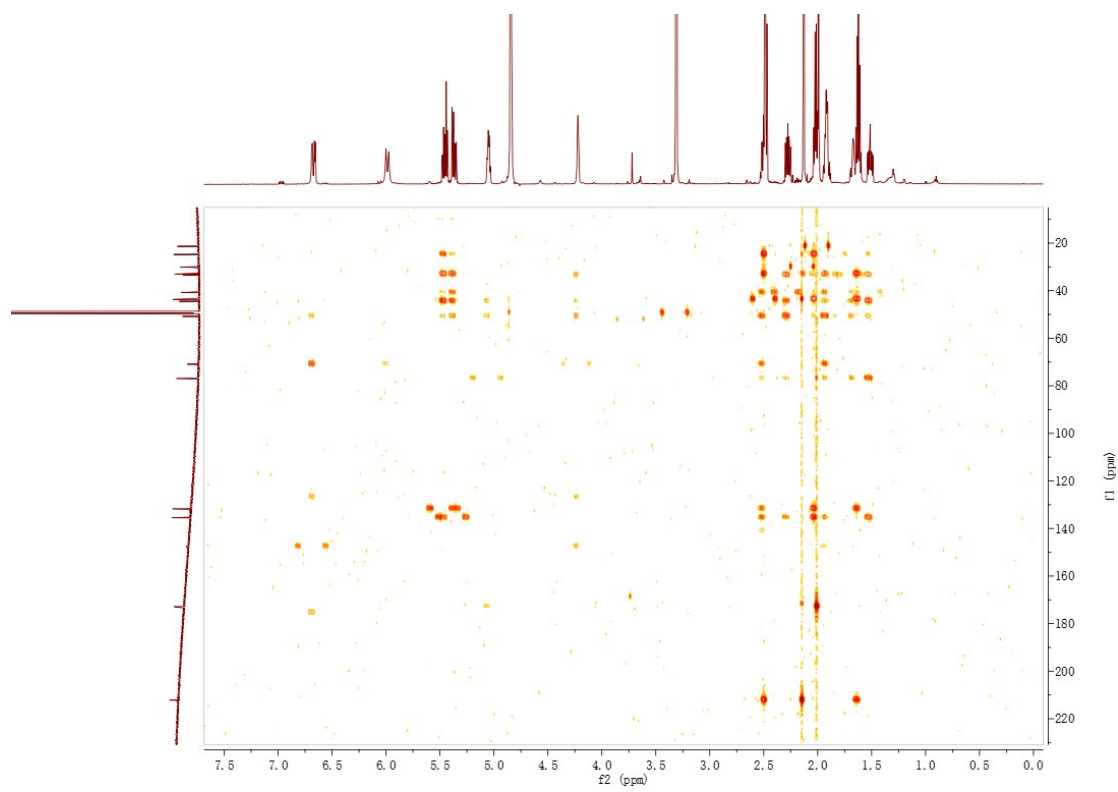


Figure S13. NOSEY spectrum of 2 in DMSO-d6

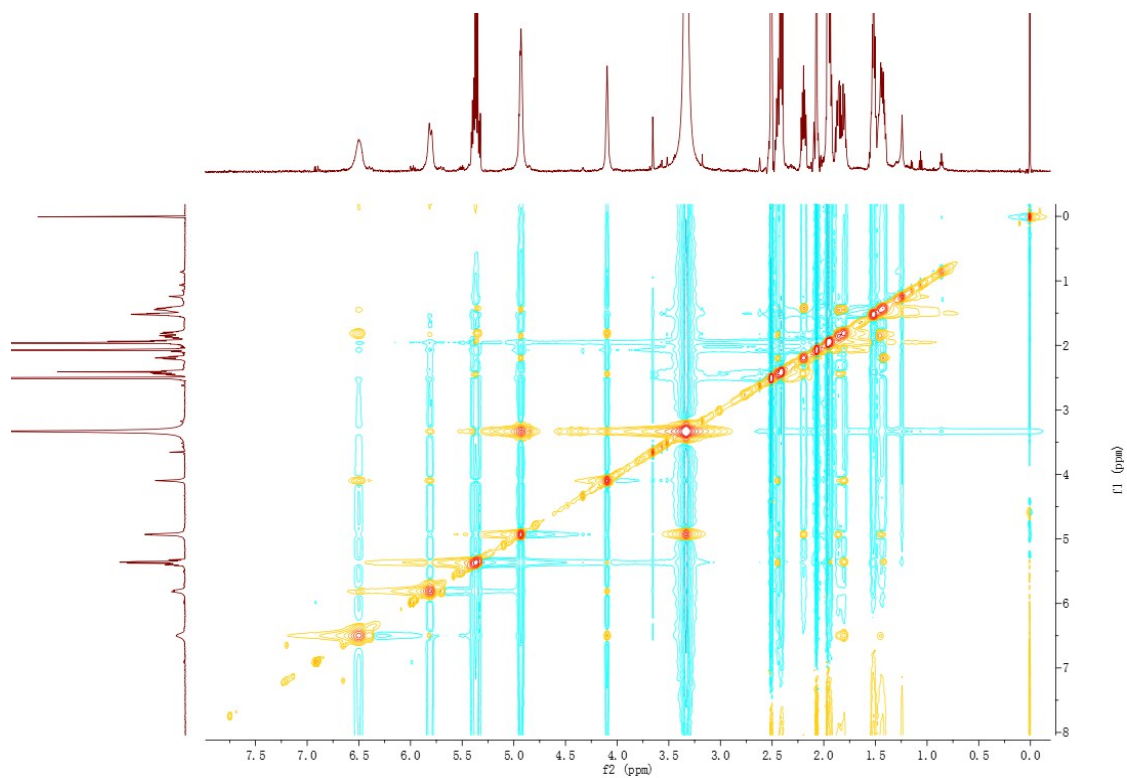


Figure S13 parts expand

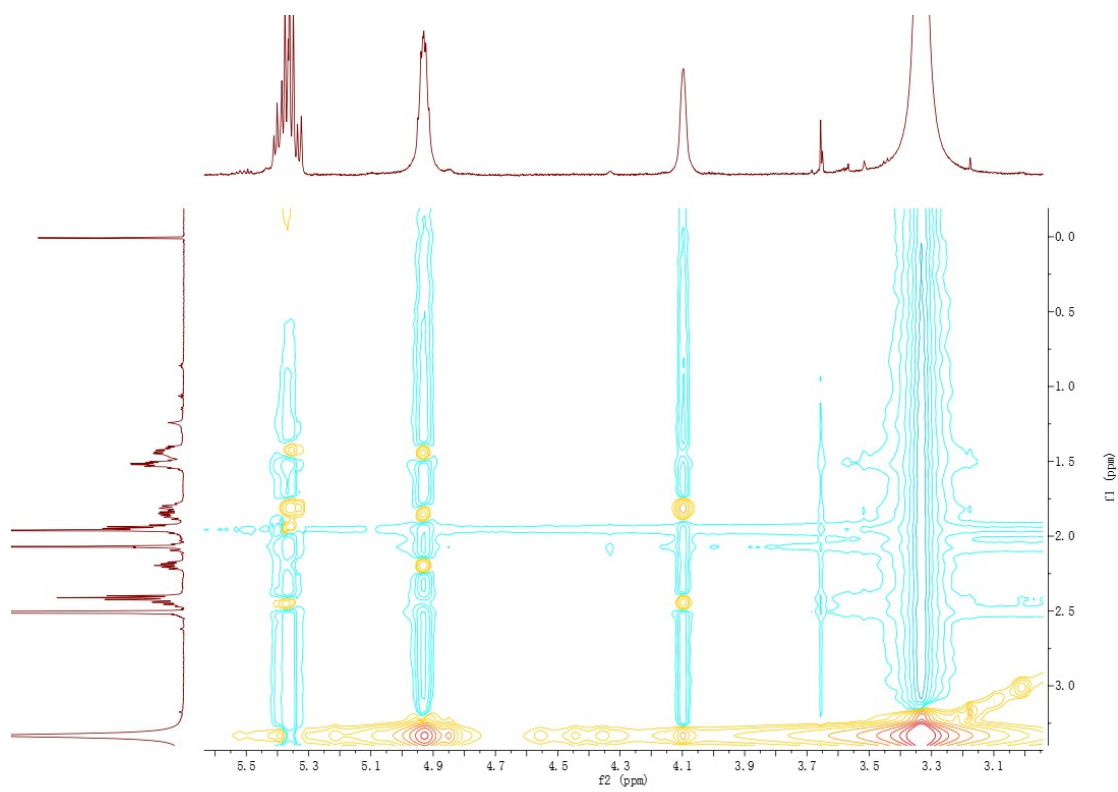


Figure S14. HRESIMS spectrum of 2

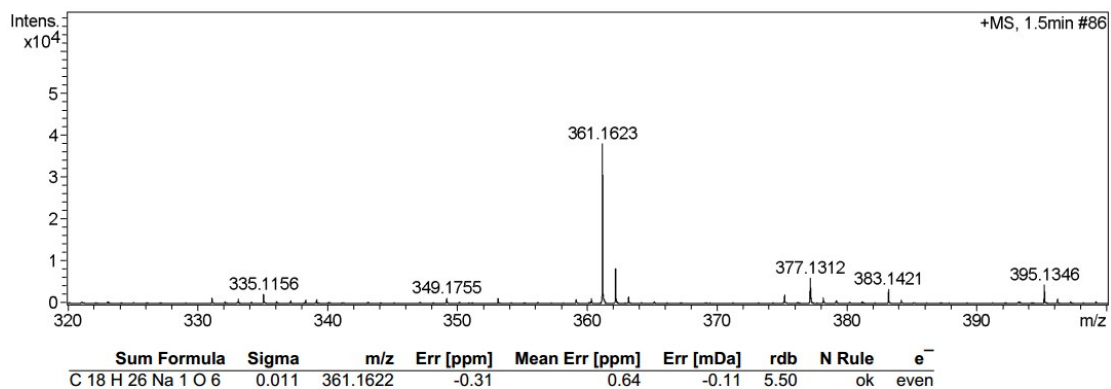


Figure S15. ¹H NMR (600 MHz, methanol-d₄) spectrum of 3

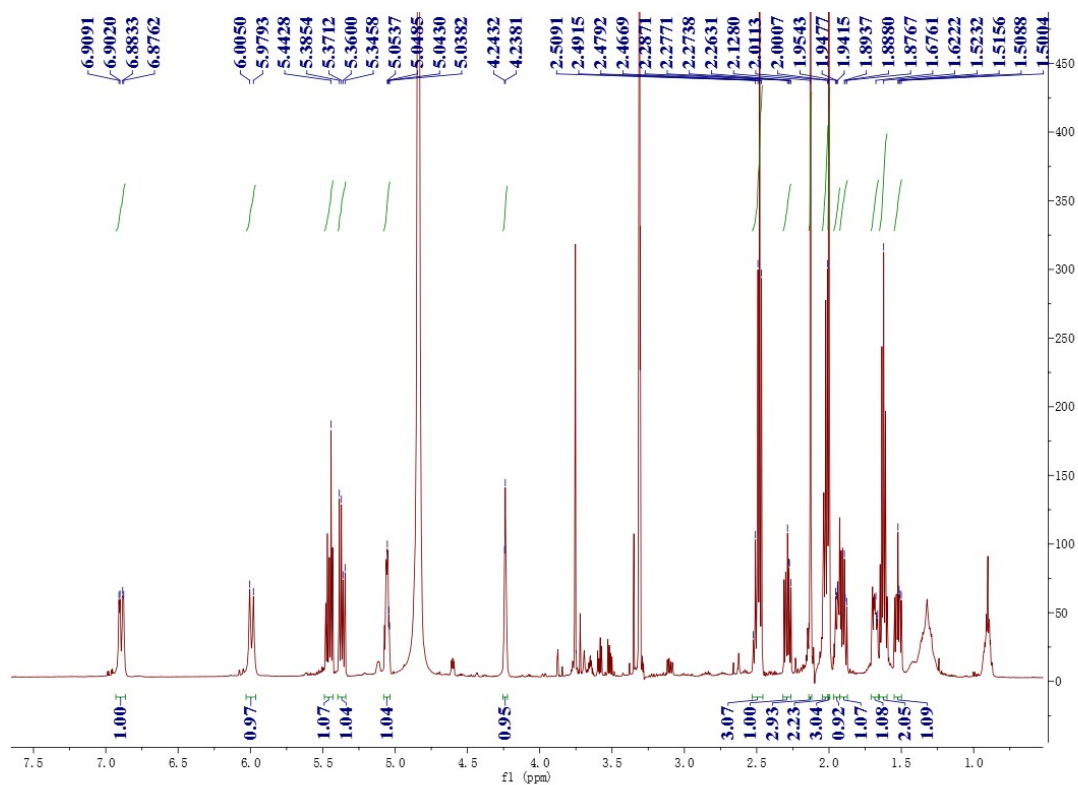


Figure S16. ^{13}C NMR (150 MHz, methanol- d_4) spectrum of 3

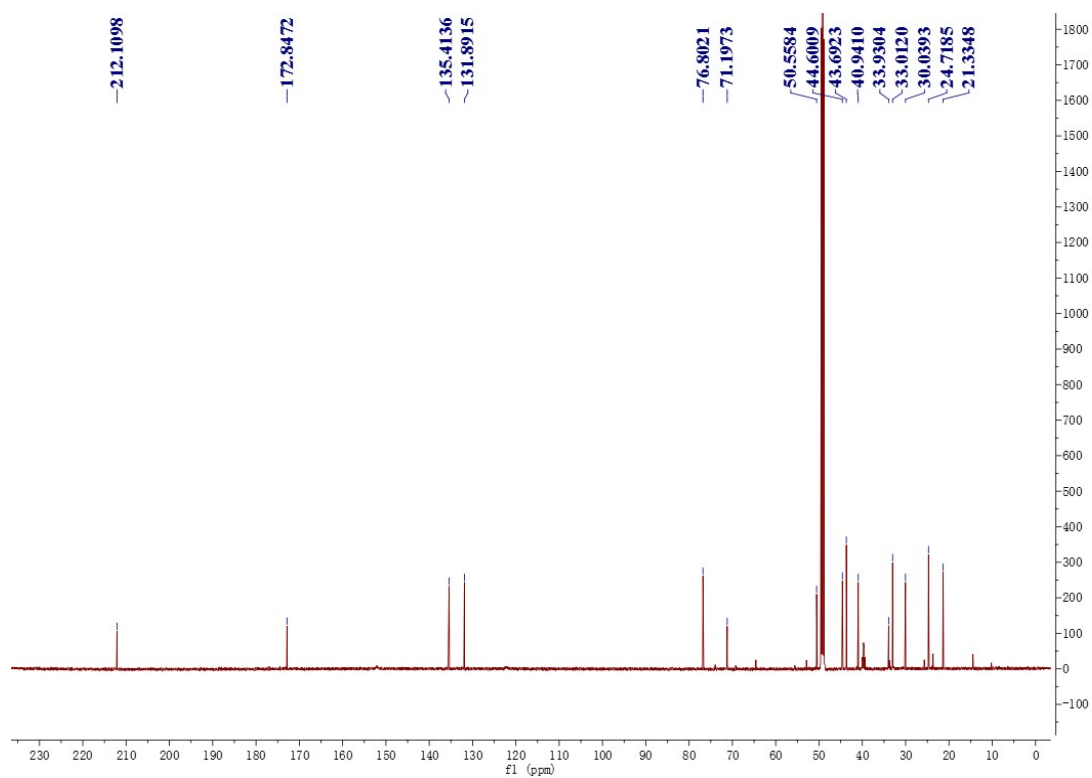


Figure S17. ^1H - ^1H COSY spectrum of 3 in methanol- d_4

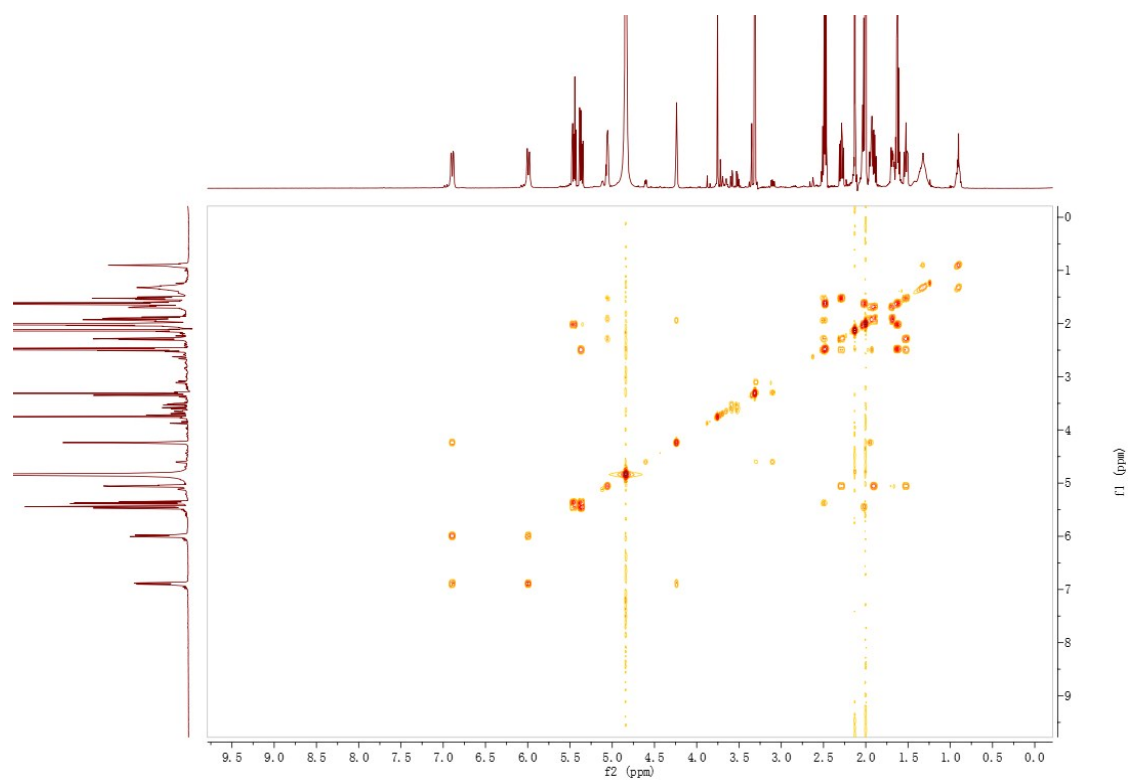


Figure S18. HSQC spectrum of 3 in methanol-d4

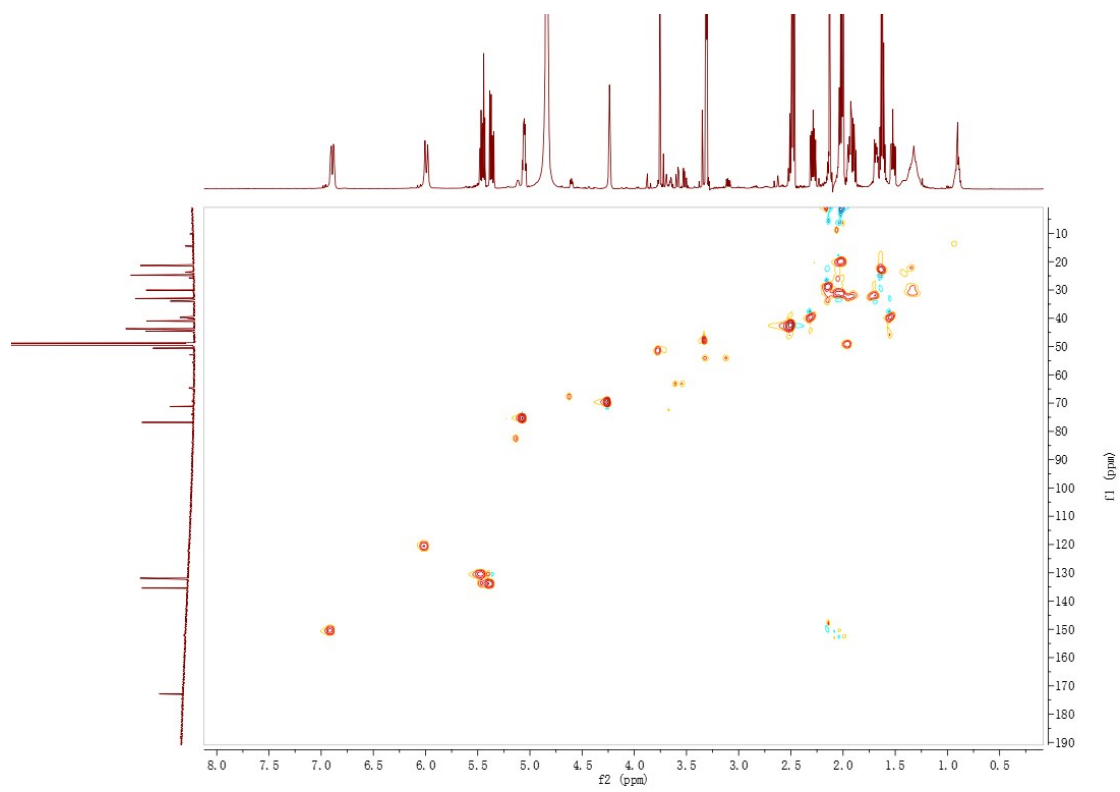


Figure S19. HMBC spectrum of 3 in methanol-d4

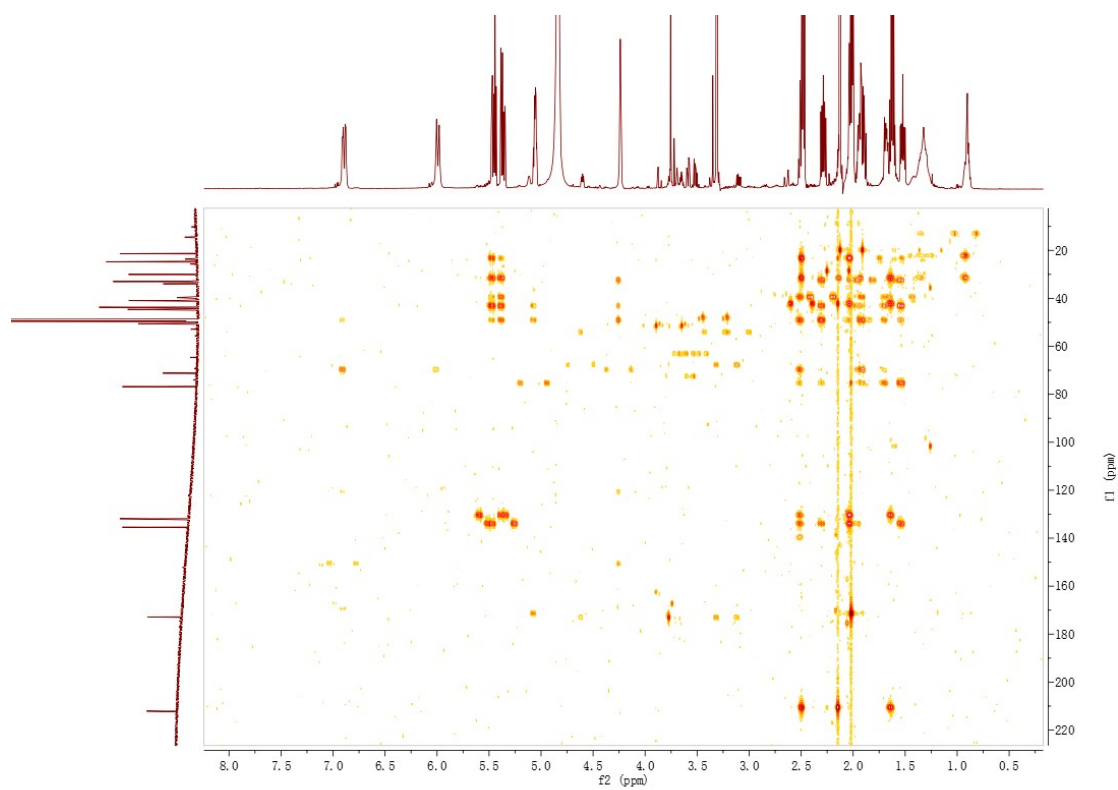


Figure S20. NOSEY spectrum of 3 in DMSO-d6

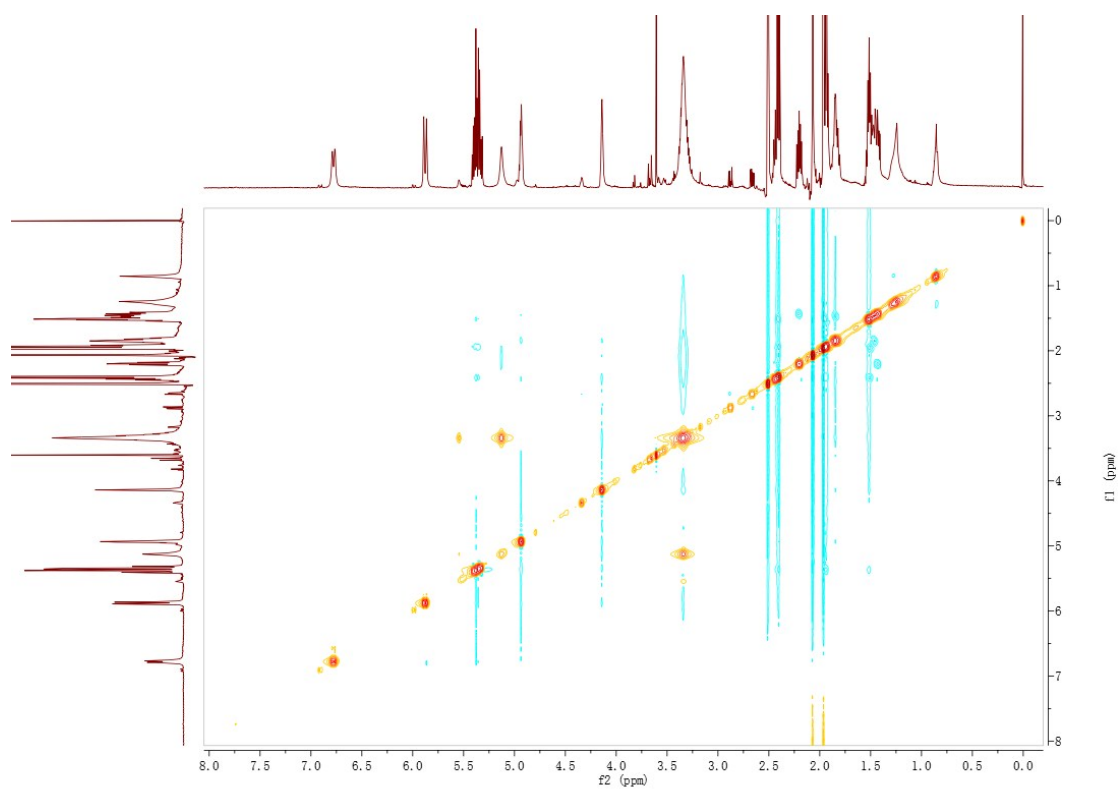


Figure S20 parts expand

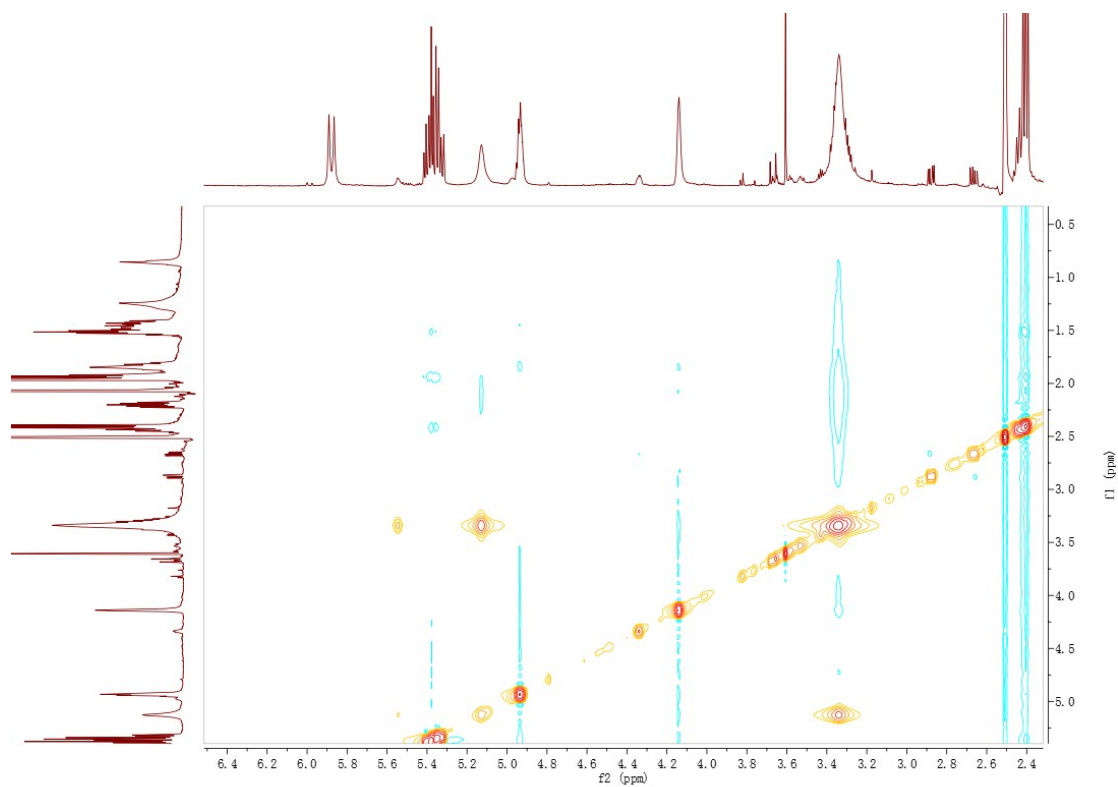


Figure S21. HRESIMS spectrum of 3

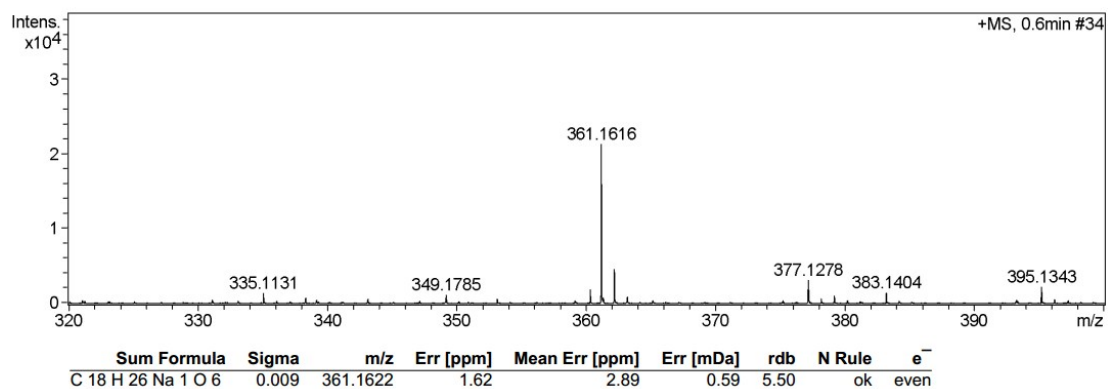


Figure S22. ¹H NMR (600 MHz, methanol-d₄) spectrum of 4

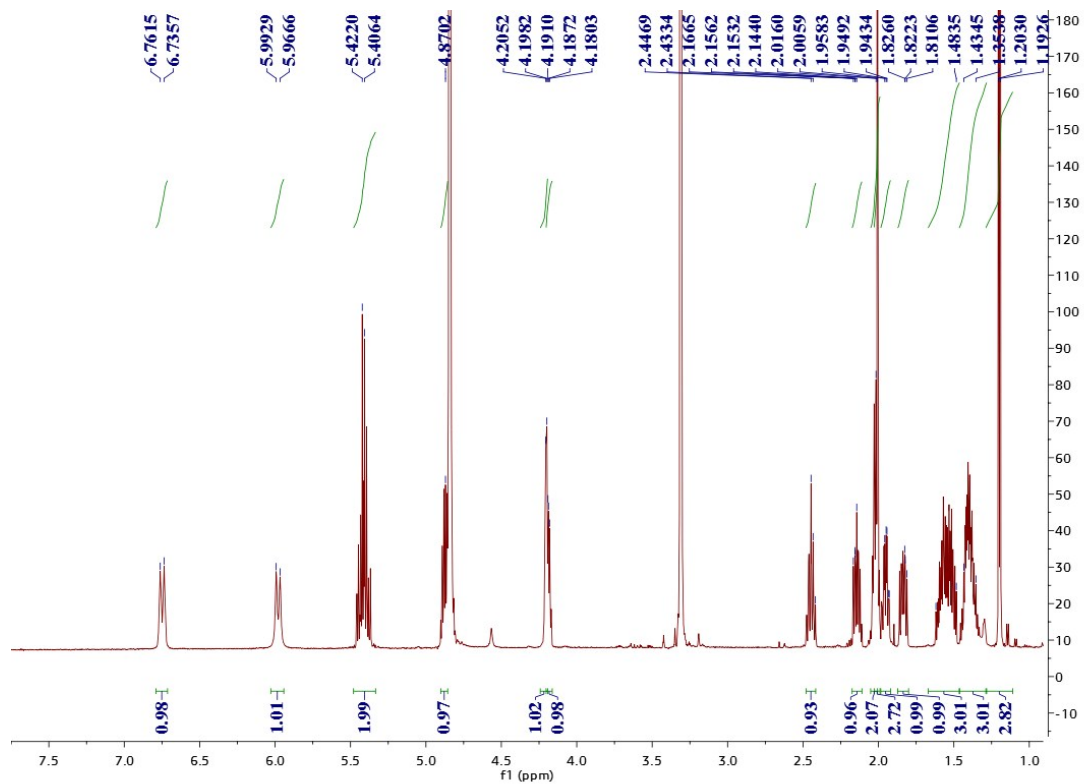


Figure S23. ^{13}C NMR (150 MHz, methanol- d_4) spectrum of 4

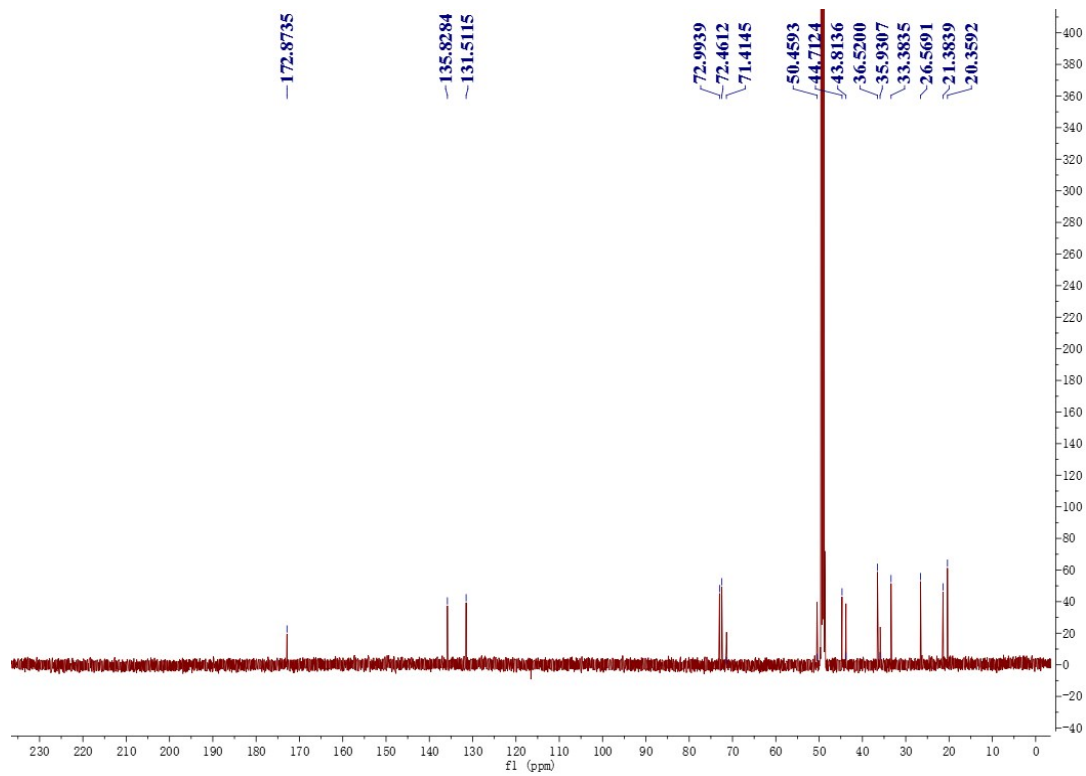


Figure S24. ^1H - ^1H COSY spectrum of 4 in methanol- d_4

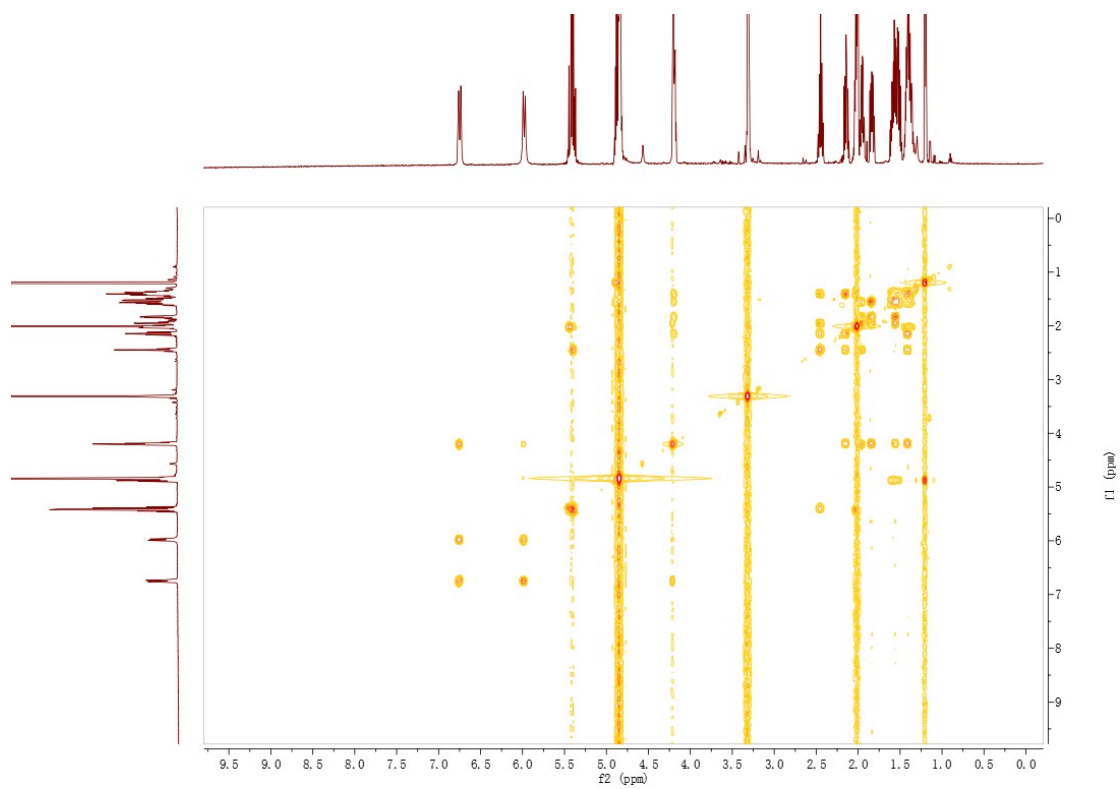


Figure S25. HSQC spectrum of 4 in methanol-d4

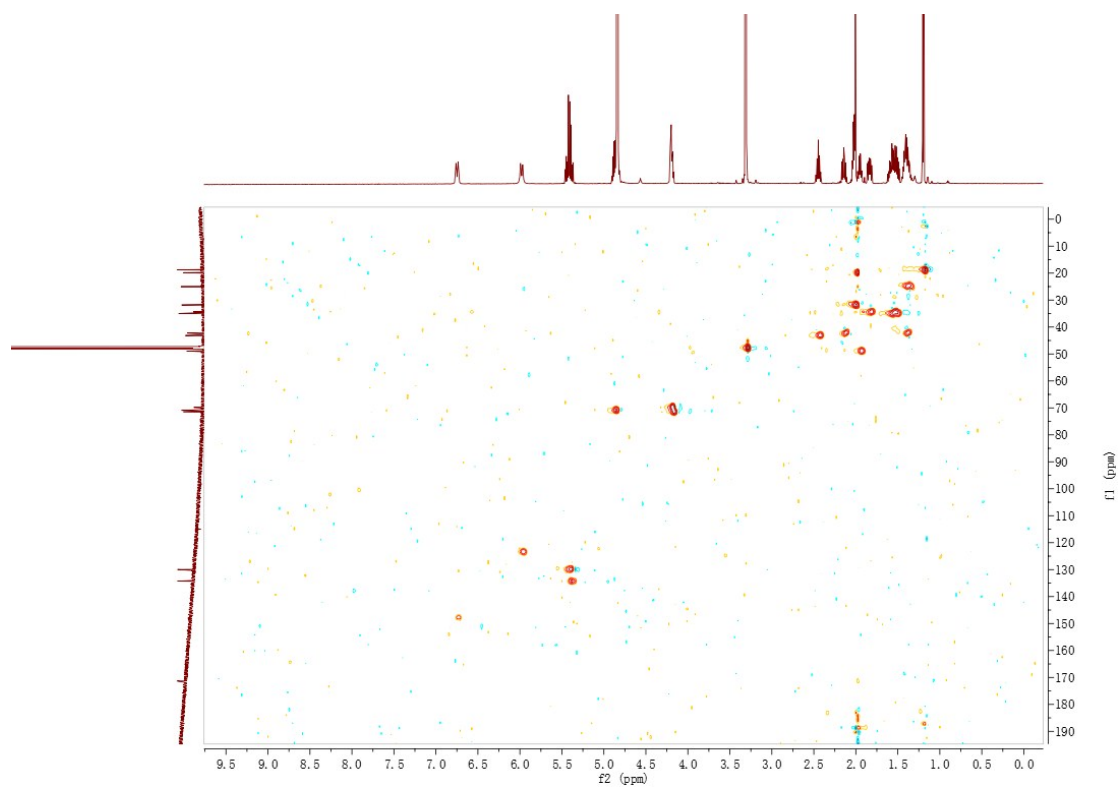


Figure S26. HMBC spectrum of 4 in methanol-d4

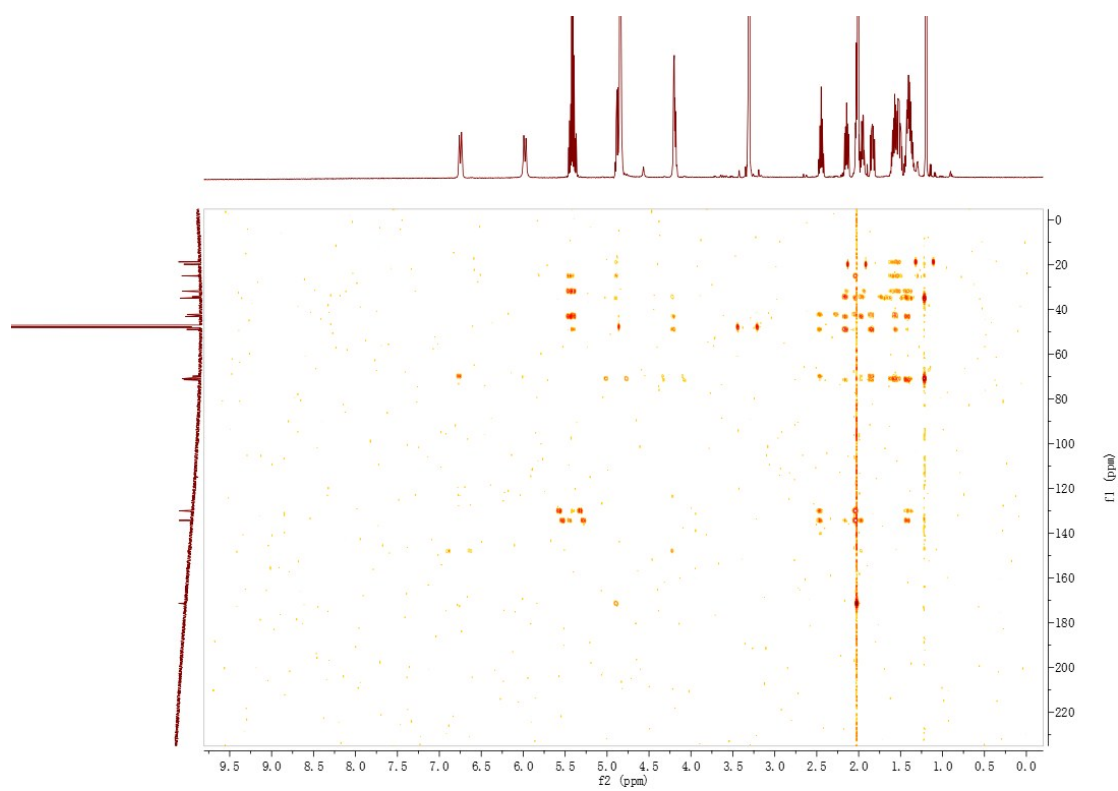


Figure S27. NOSEY spectrum of 4 in DMSO-d6

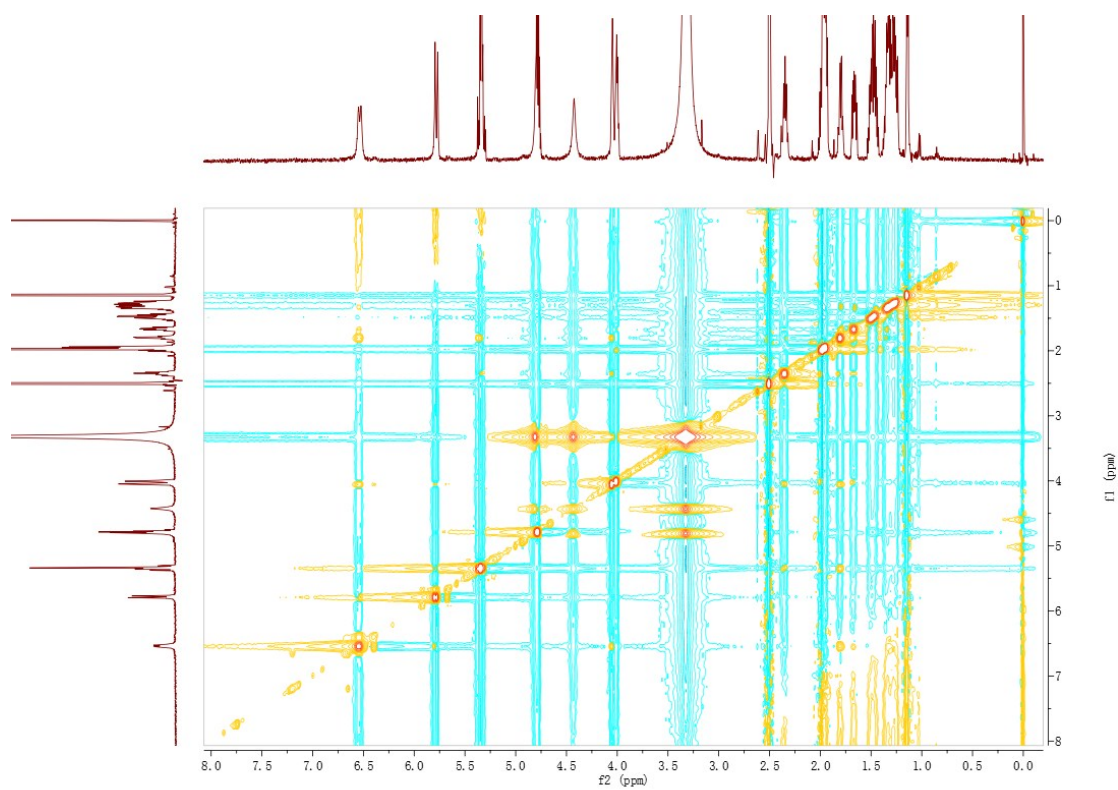


Figure S27 parts expand

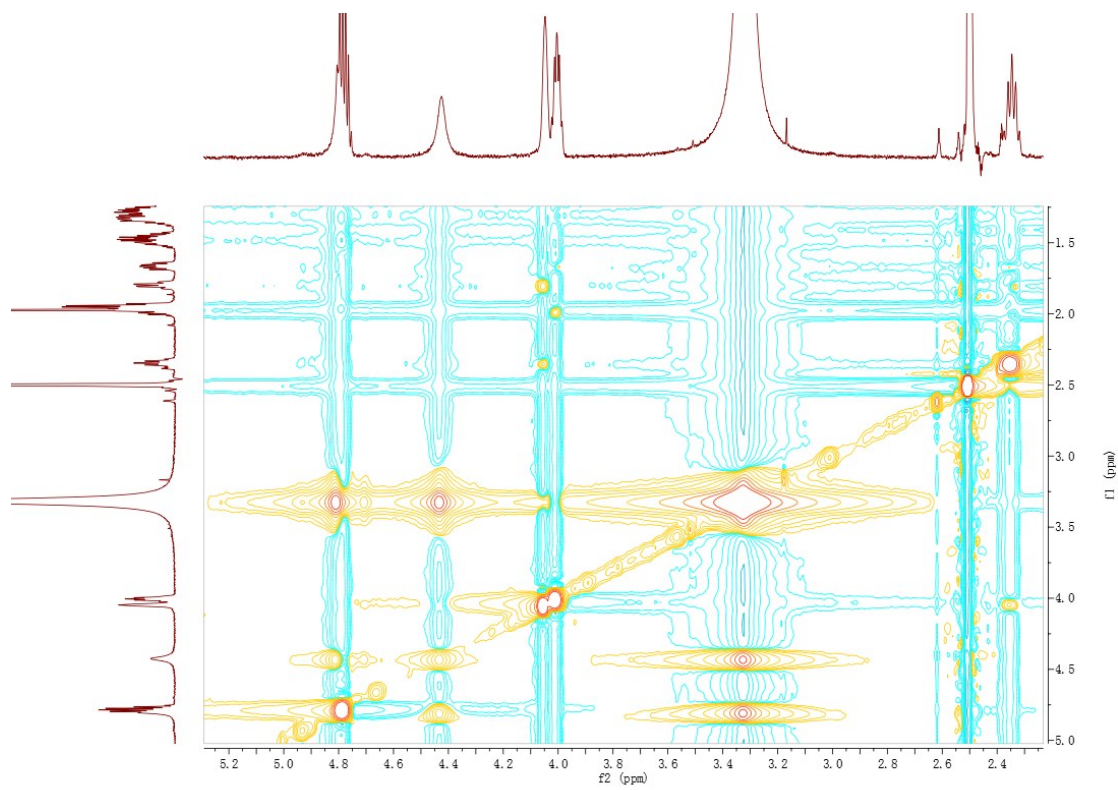


Figure S28. HRESIMS spectrum of 4

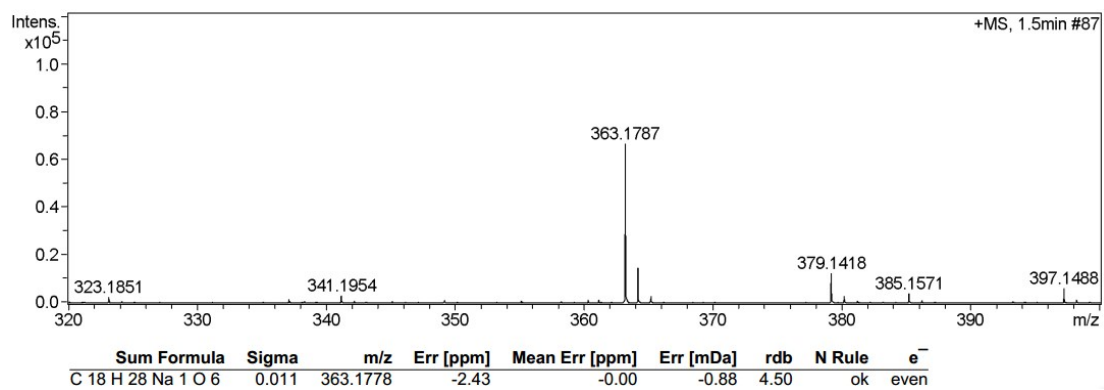


Figure S29. ¹H NMR (600 MHz, methanol-d₄) spectrum of 5

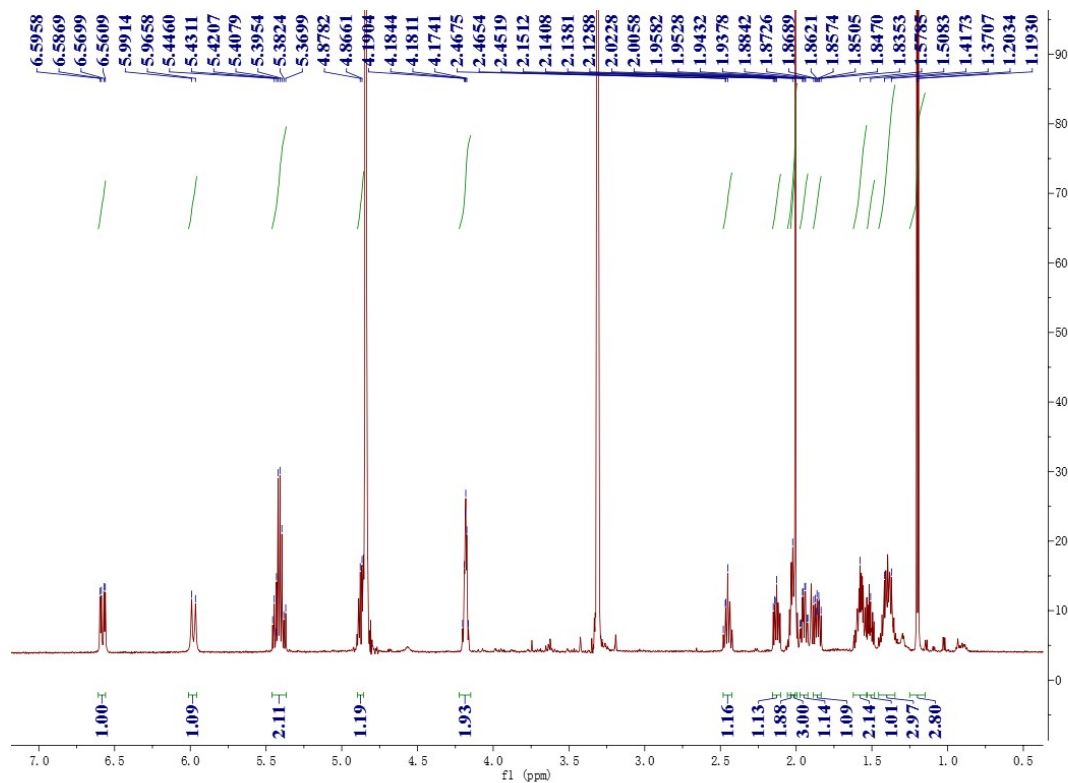


Figure S30. ^{13}C NMR (150 MHz, methanol- d_4) spectrum of 5

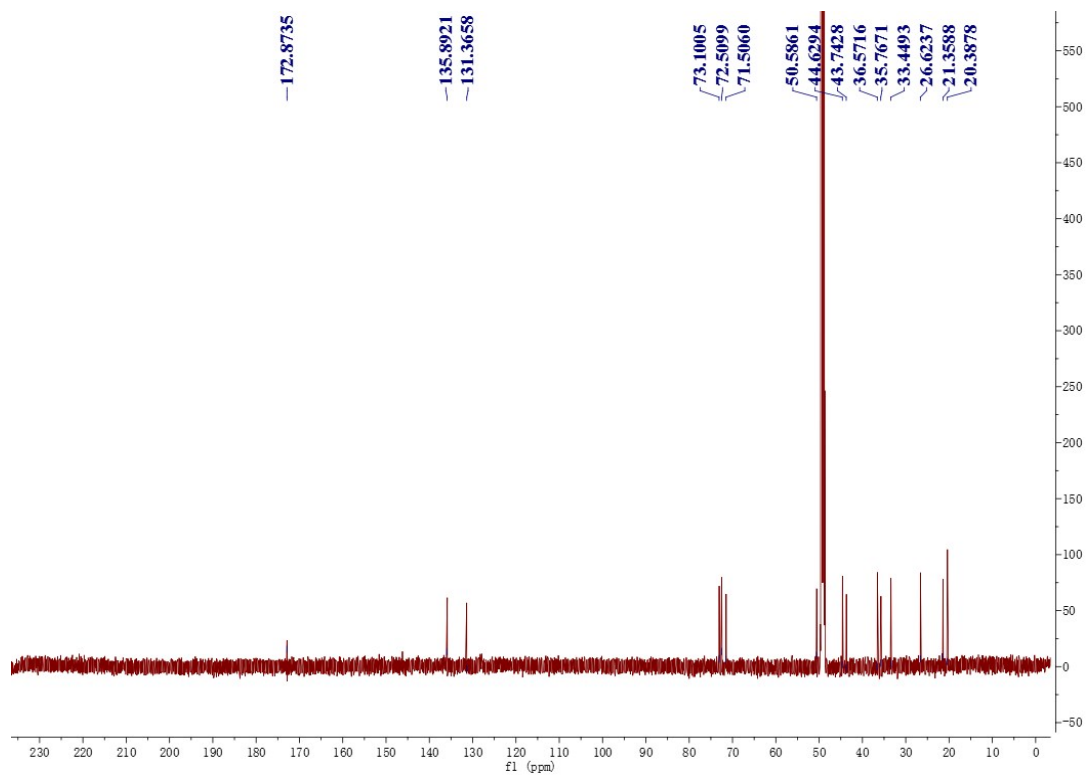


Figure S31. ^1H - ^1H COSY spectrum of 5 in methanol- d_4

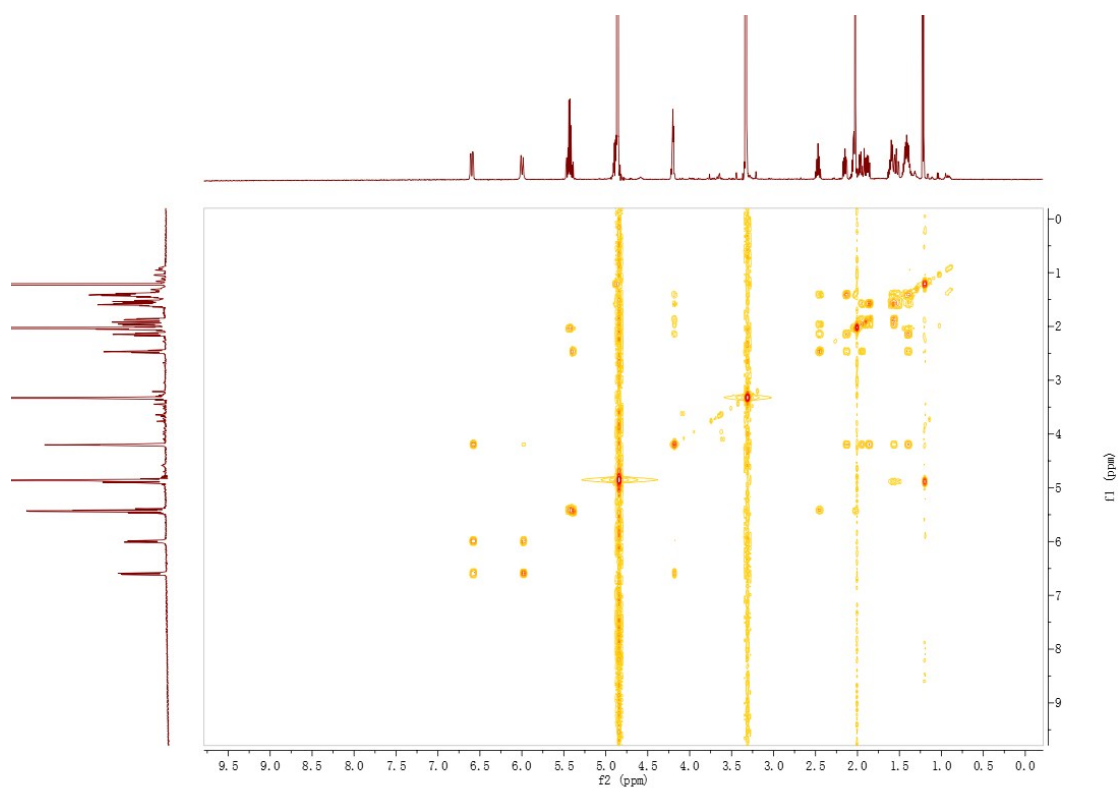


Figure S32. HSQC spectrum of 5 in methanol-d4

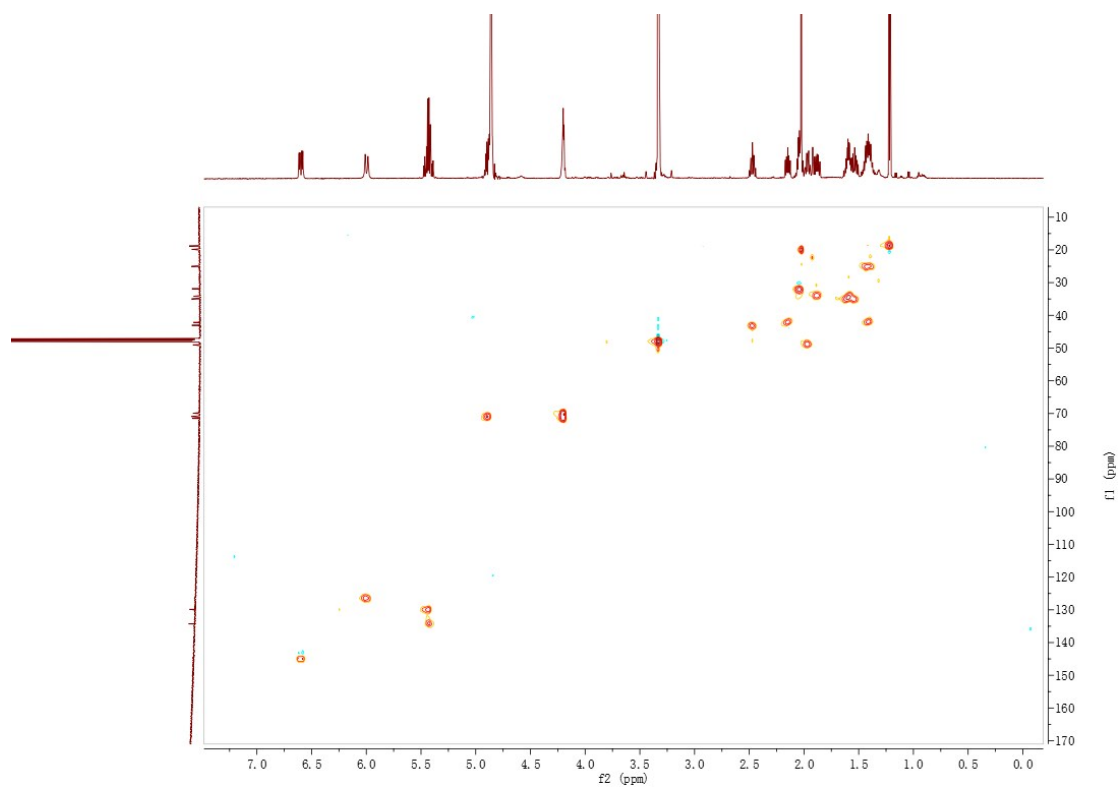


Figure S33. HMBC spectrum of 5 in methanol-d4

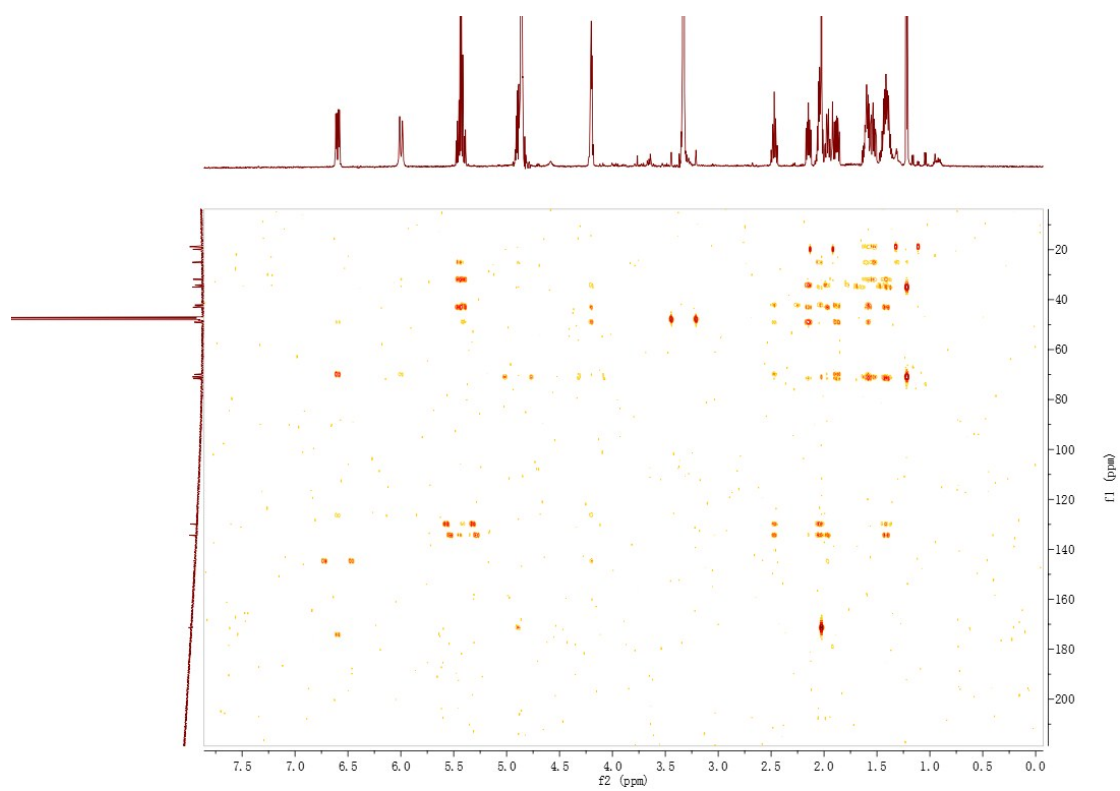


Figure S34. NOSEY spectrum of 5 in DMSO-d6

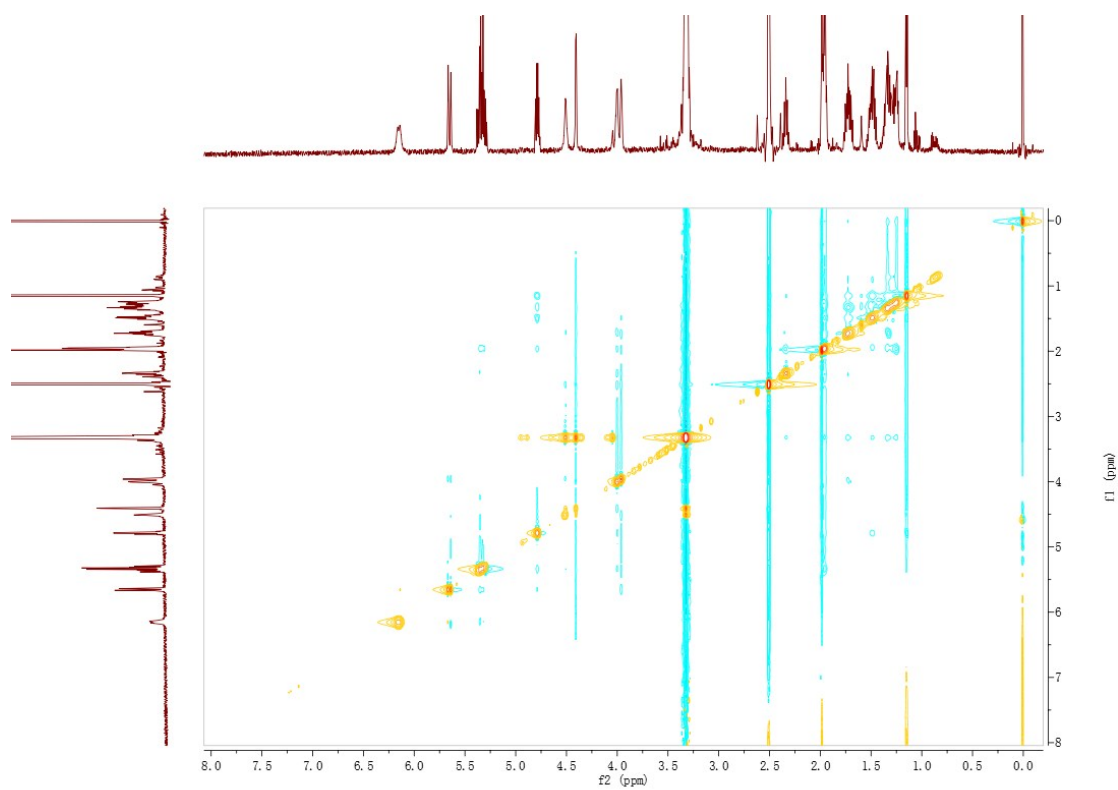


Figure S34 parts expand

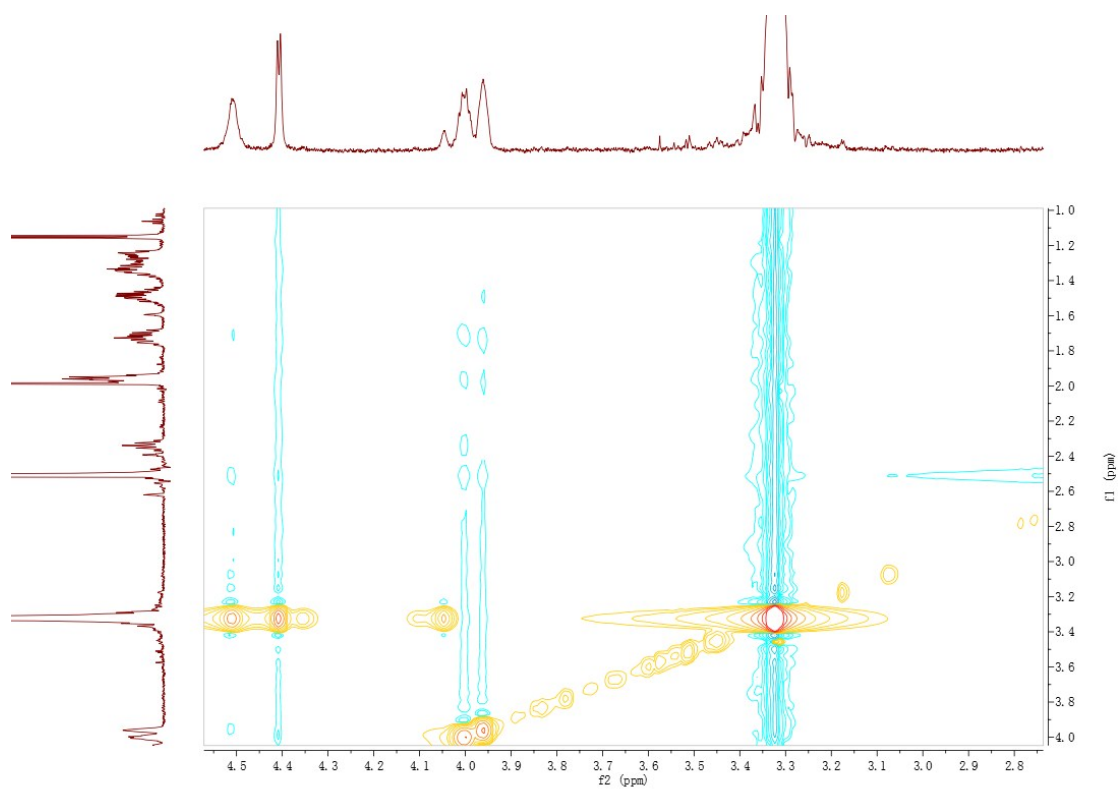


Figure S35. HRESIMS spectrum of 5

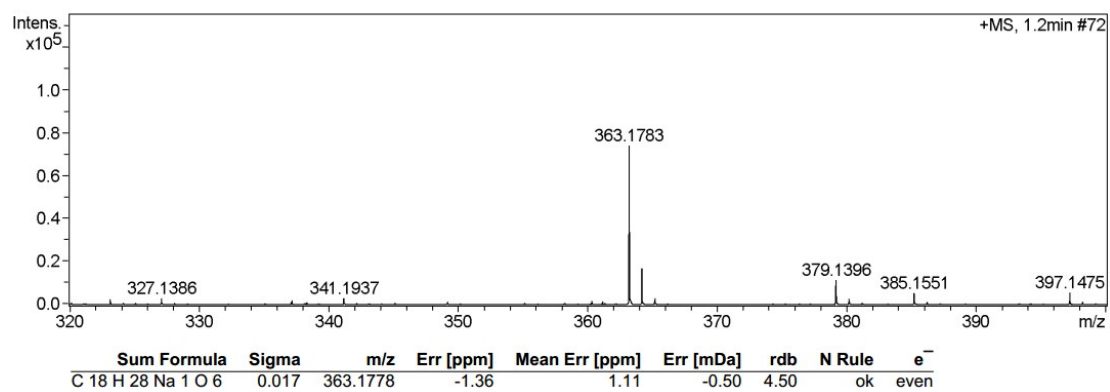


Figure S36. ¹H NMR (600 MHz, chloroform-d) spectrum of 1a-R

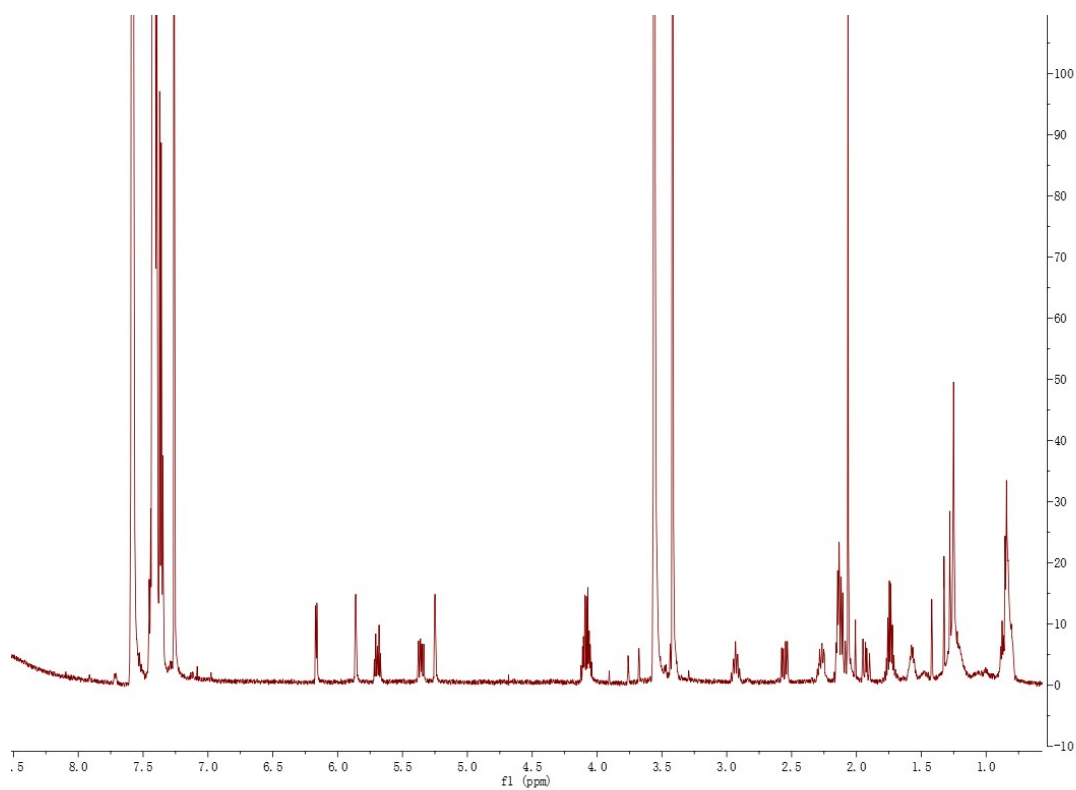


Figure S37. ^1H NMR (600 MHz, chloroform-d) spectrum of 1b-S

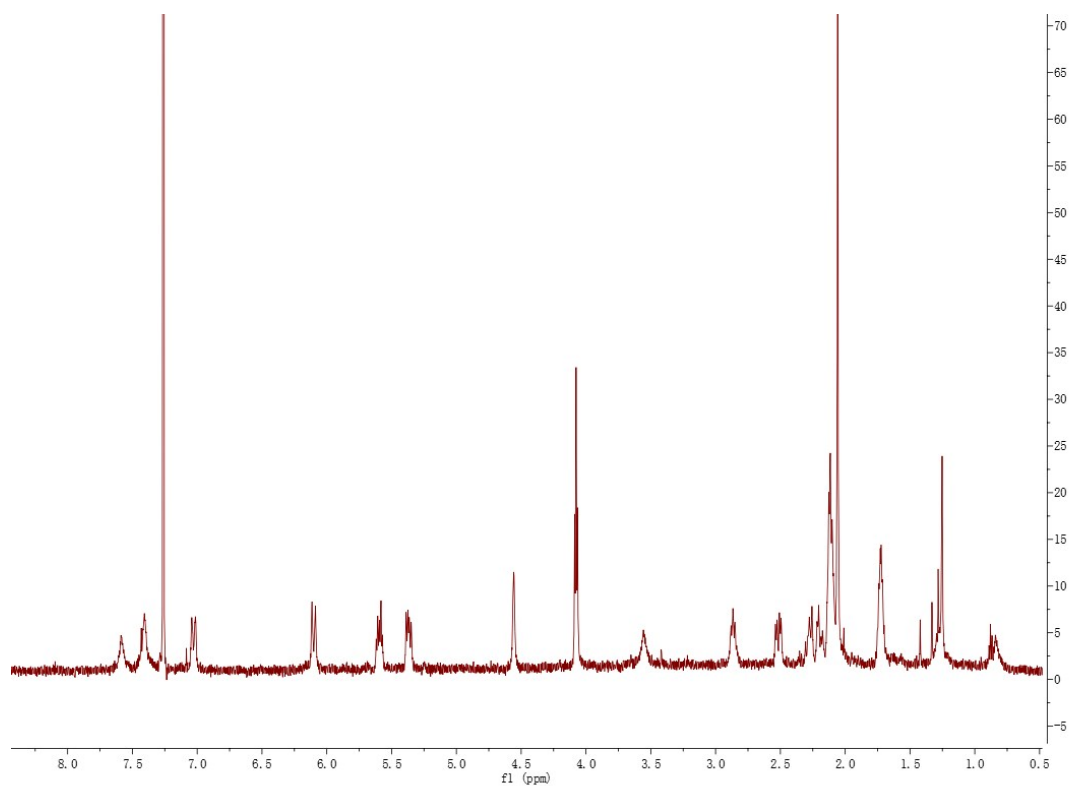


Figure S38. ^1H NMR (600 MHz, chloroform-d) spectrum of 2a-R

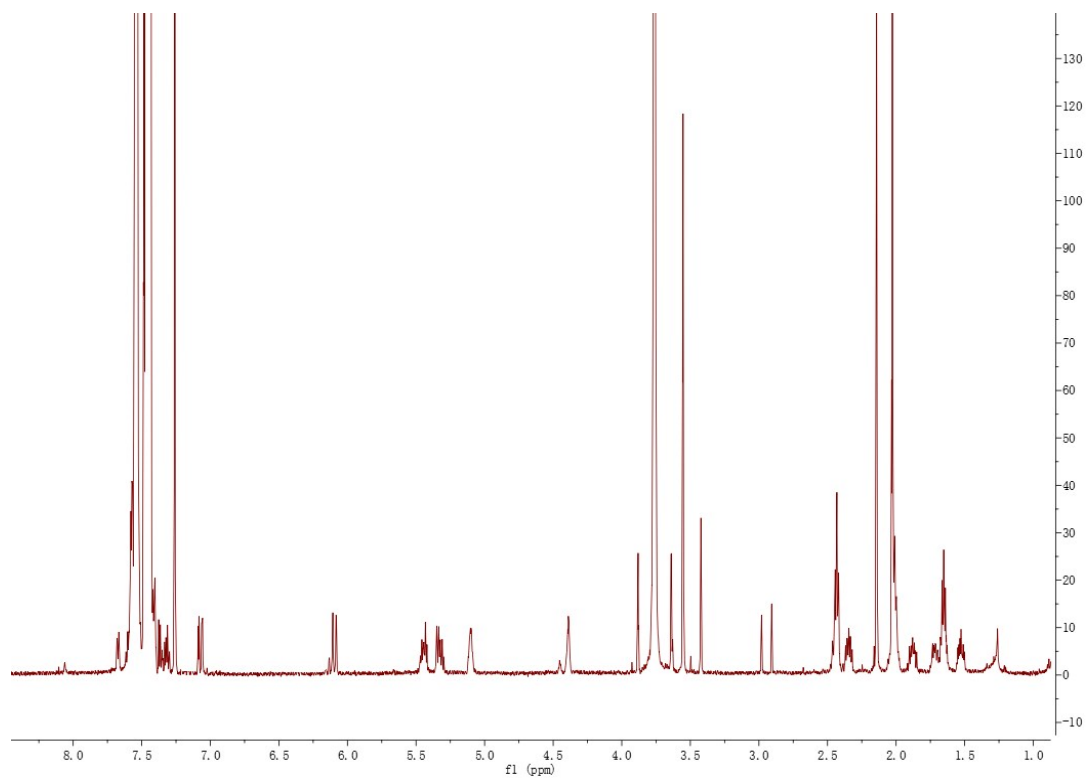


Figure S39. ^1H NMR (600 MHz, chloroform-d) spectrum of 2b-S

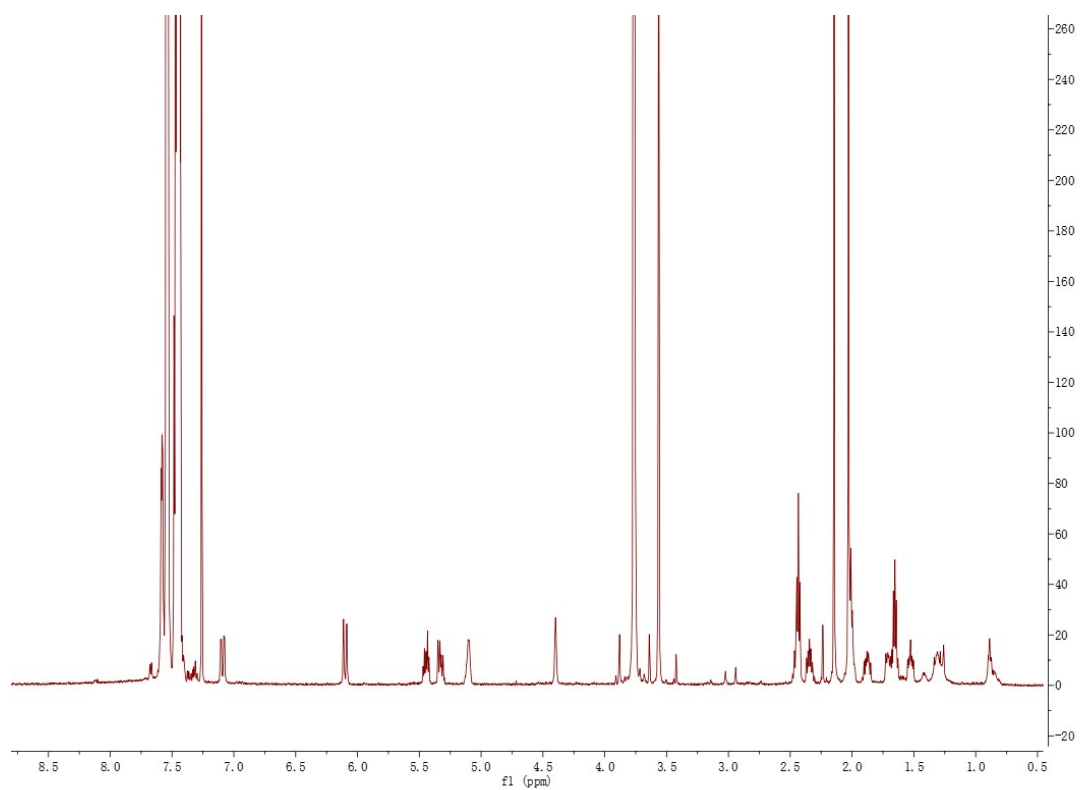


Figure S40. ^1H NMR (600 MHz, chloroform-d) spectrum of 3a-R

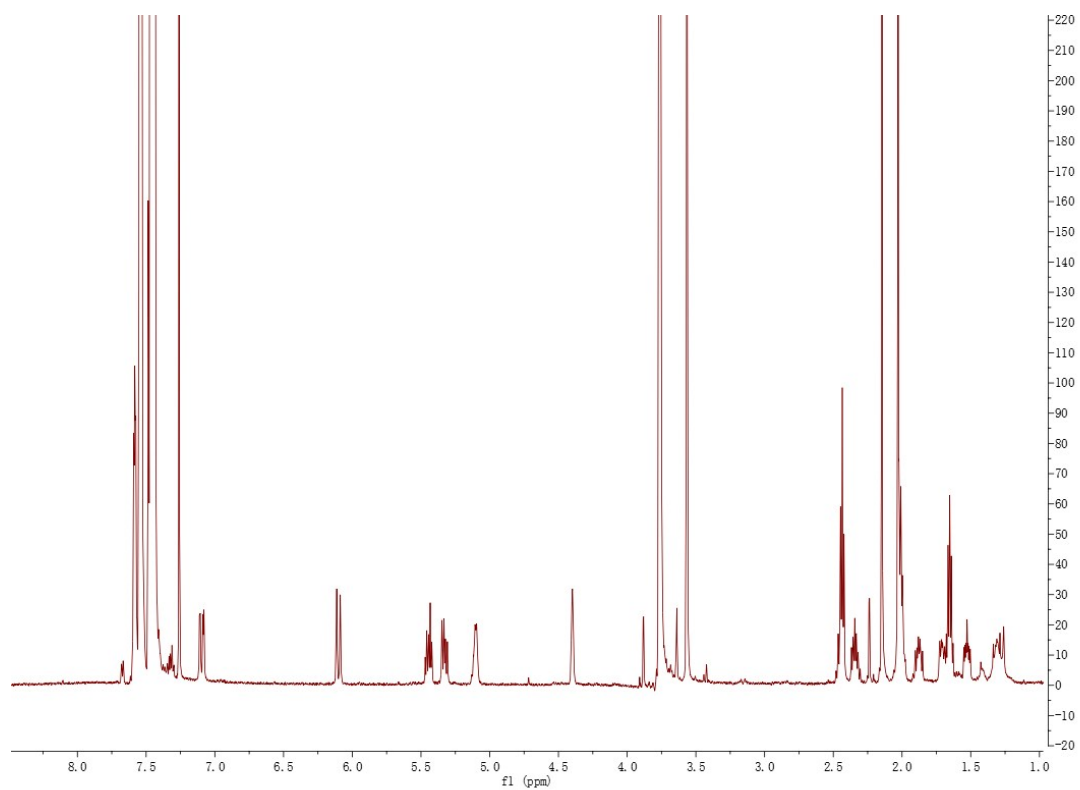


Figure S41. ^1H NMR (600 MHz, chloroform-d) spectrum of 3b-S

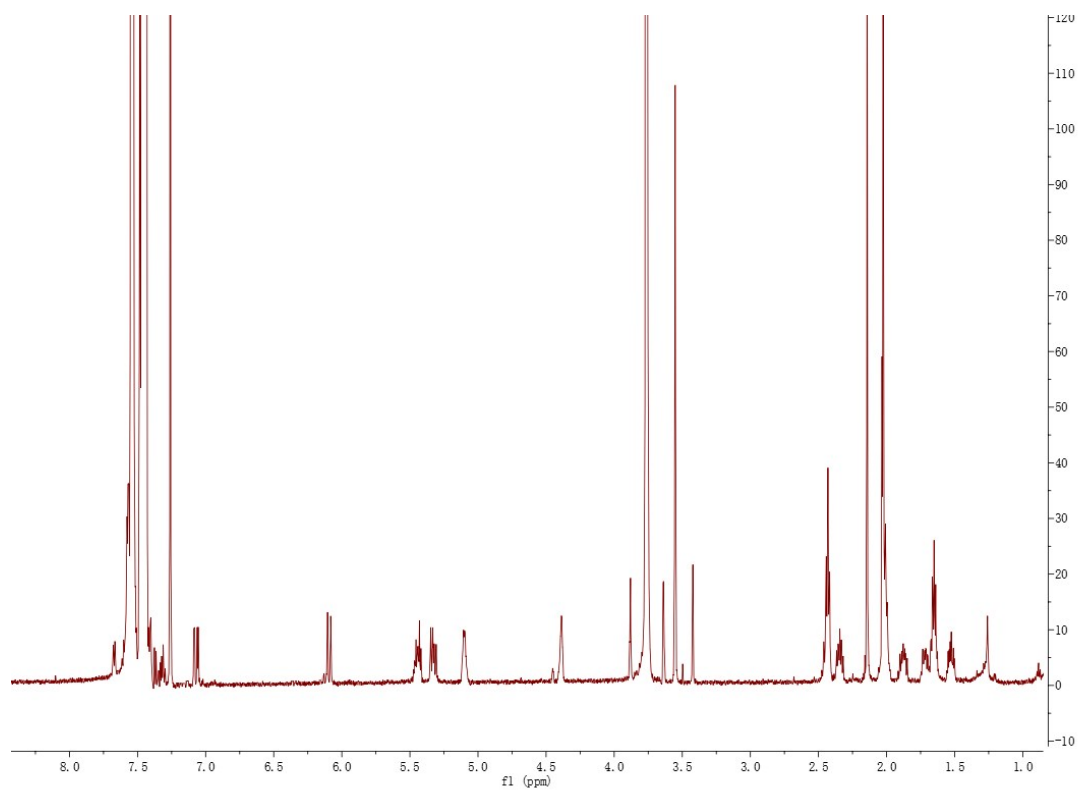


Figure S42. ^1H NMR (600 MHz, chloroform-d) spectrum of 4a-R

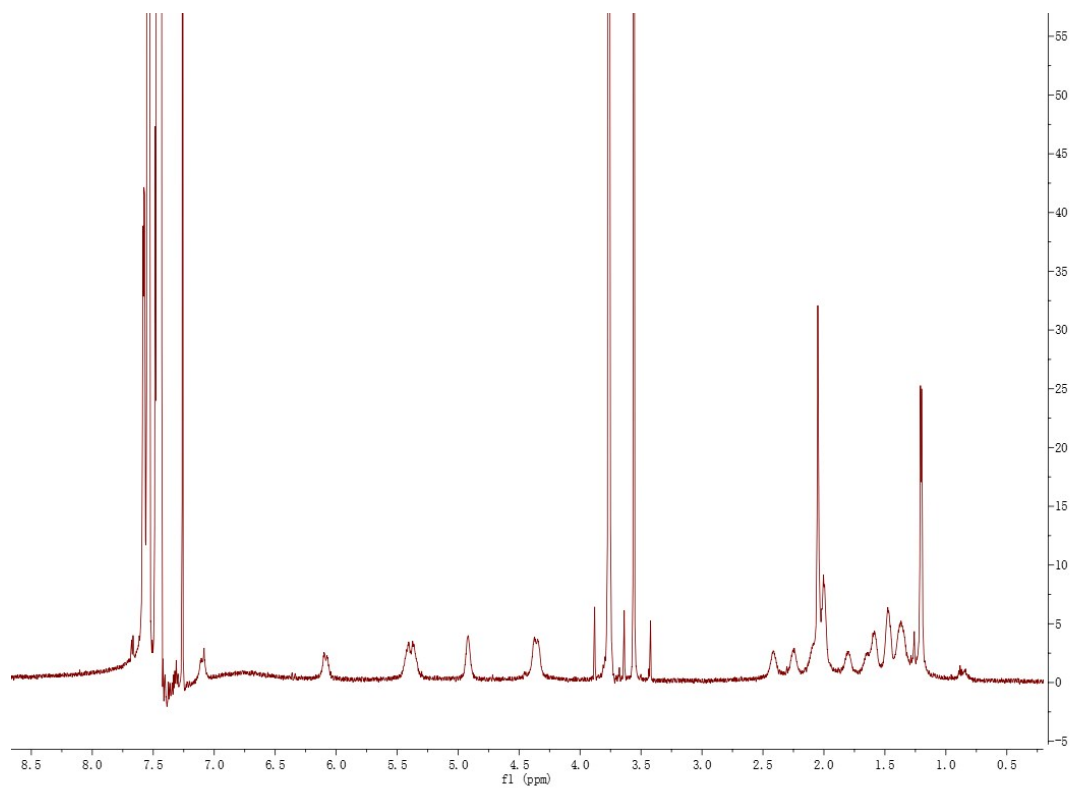


Figure S43. ^1H NMR (600 MHz, chloroform-d) spectrum of 4b-S

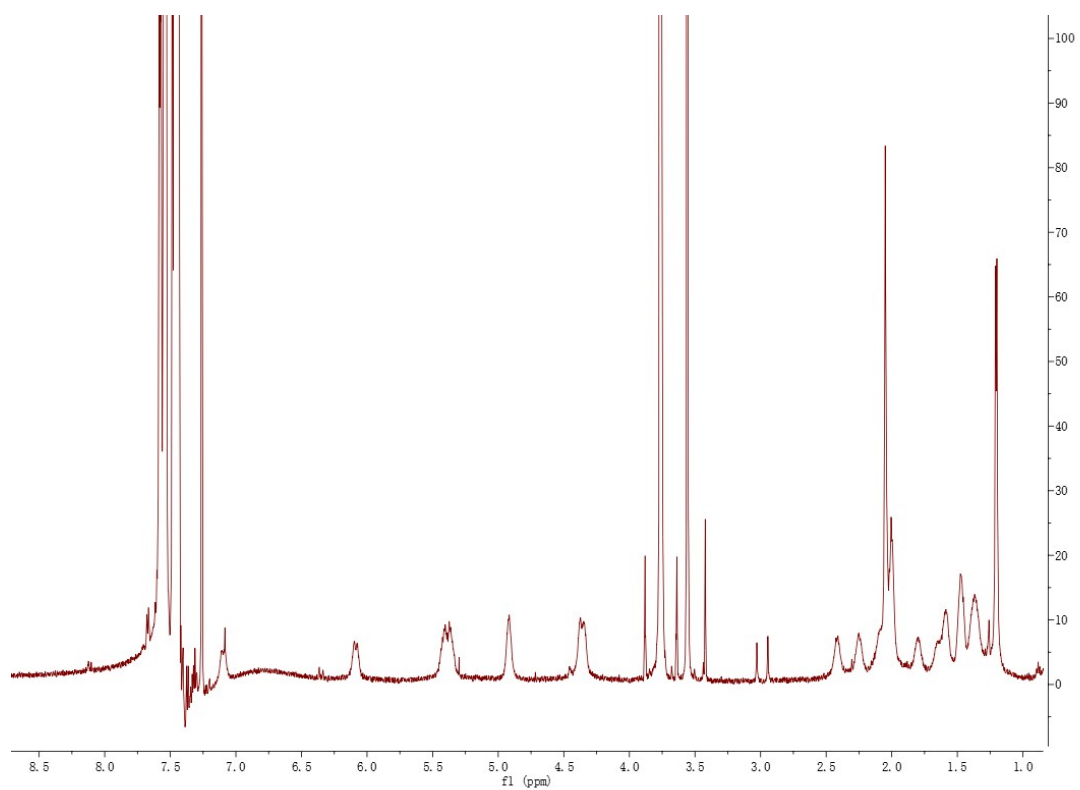


Figure S44. ^1H NMR (600 MHz, chloroform-d) spectrum of 5a-R

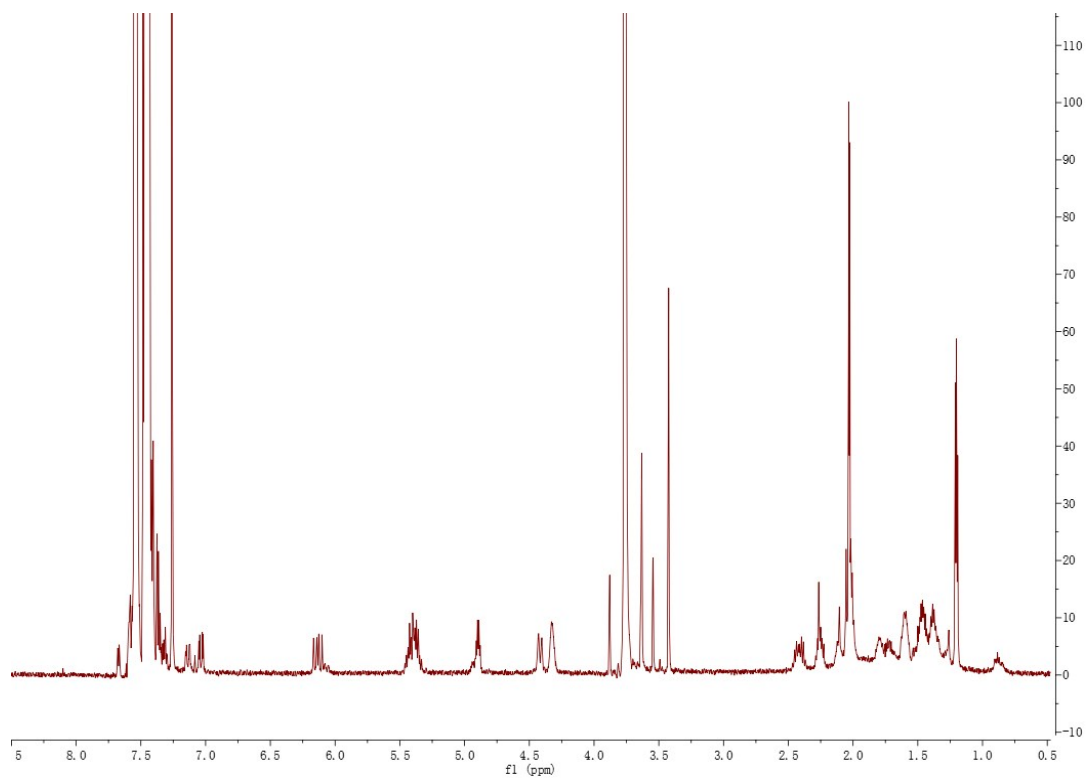


Figure S45. ^1H NMR (600 MHz, chloroform-d) spectrum of 5b-S

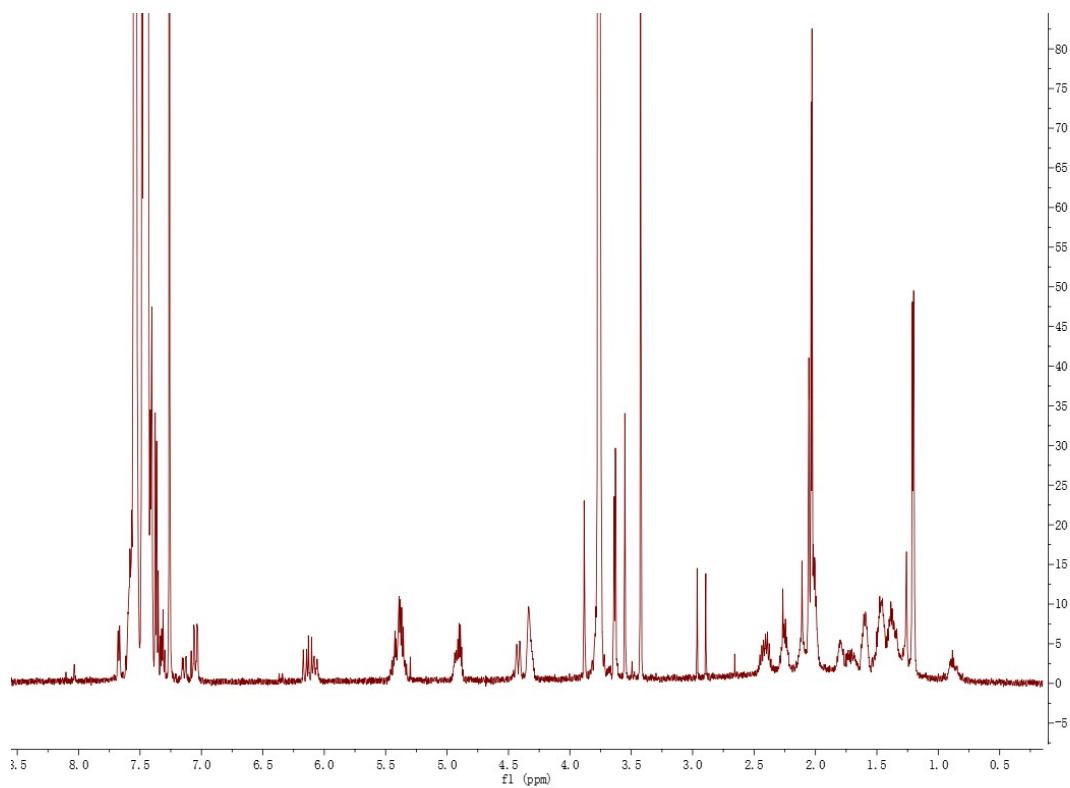
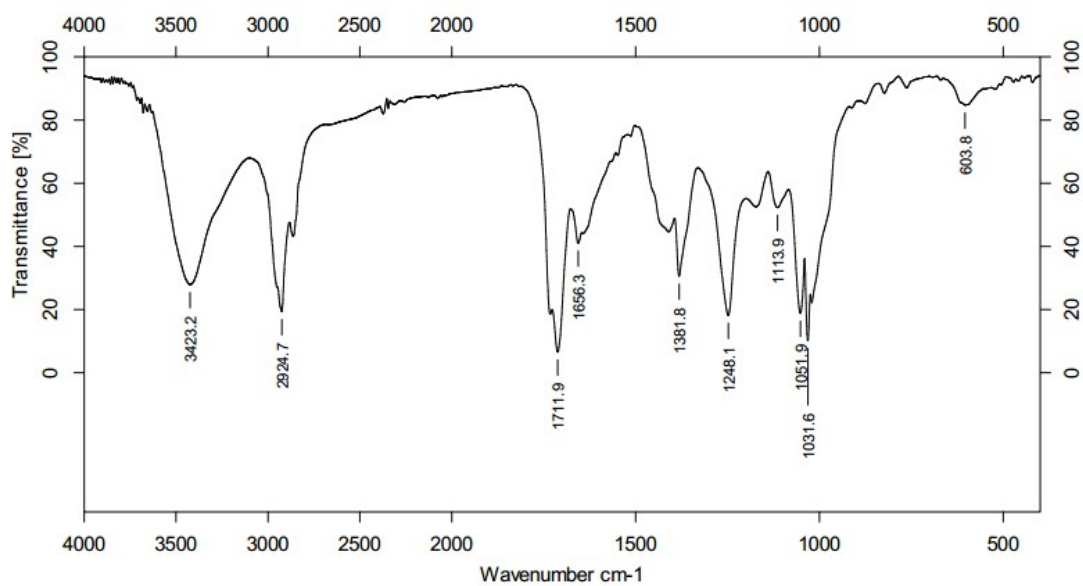
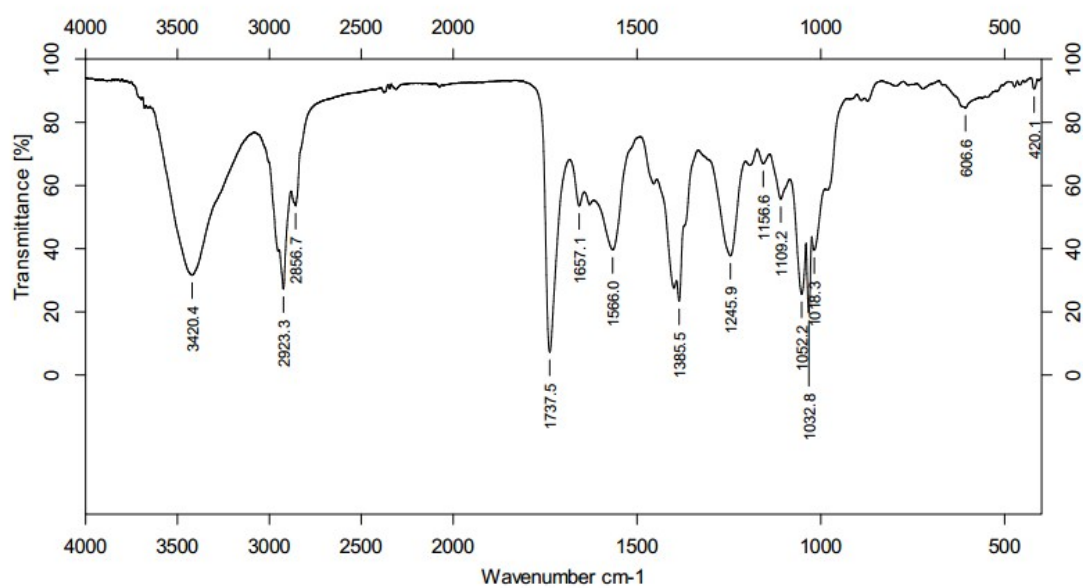
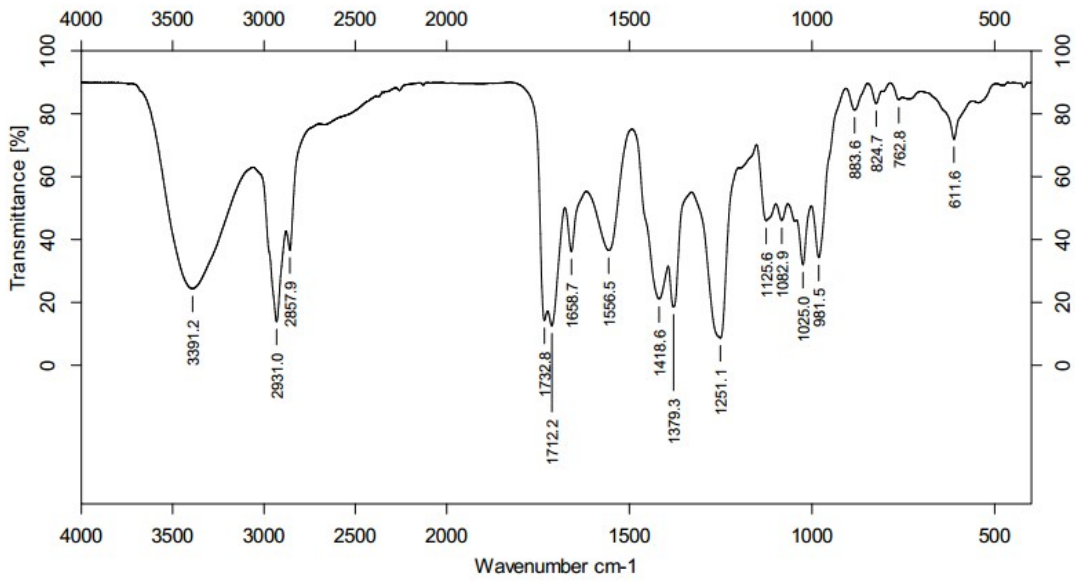
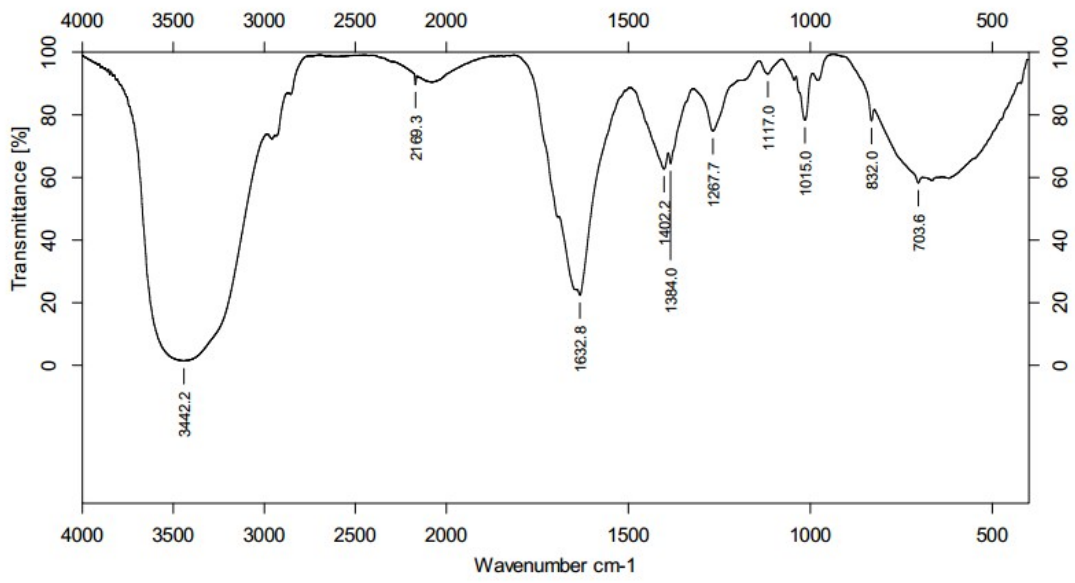


Figure S46-50. IR spectrum of 1,2,3,4,5





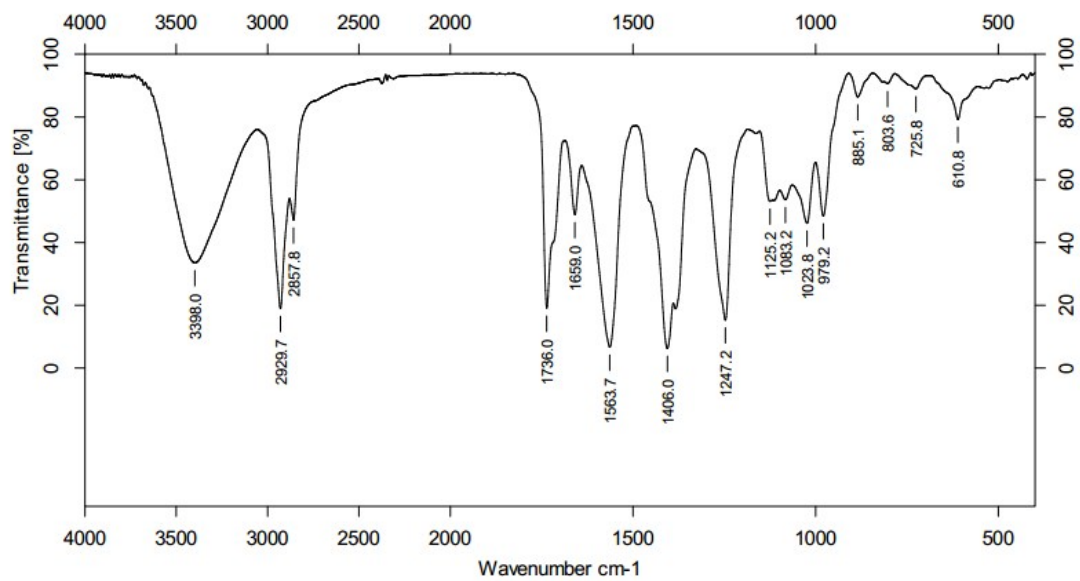
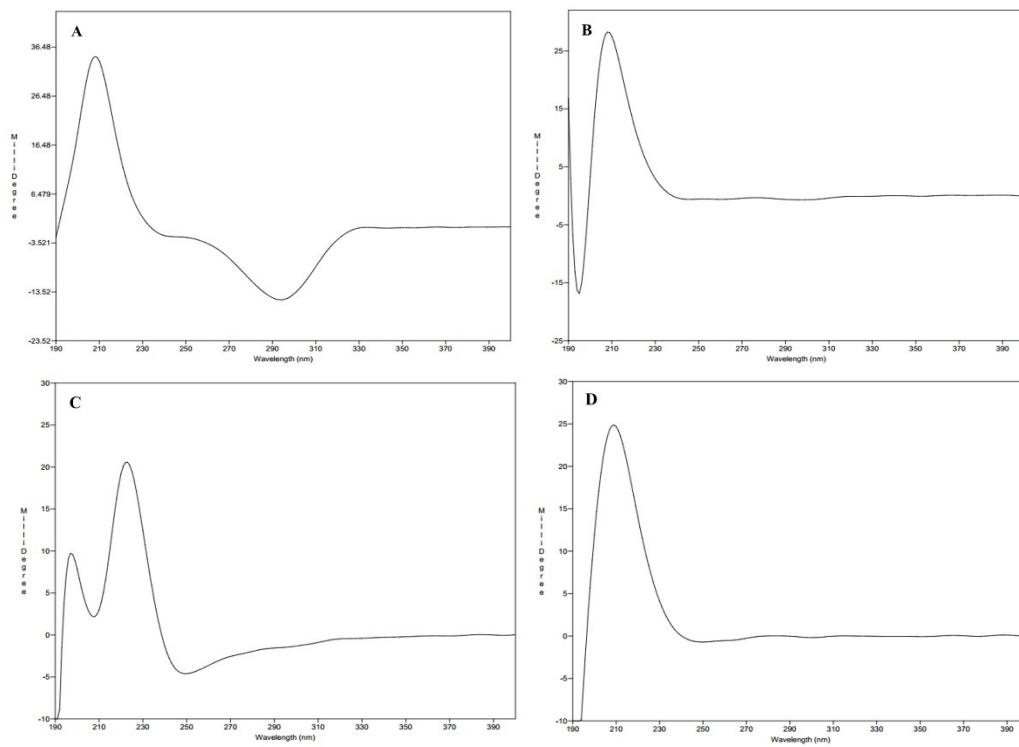


Figure S51 The CD profiles of compounds **1(A)**, **2(B)**, **3(C)**, **4(D)**, **5(E)**



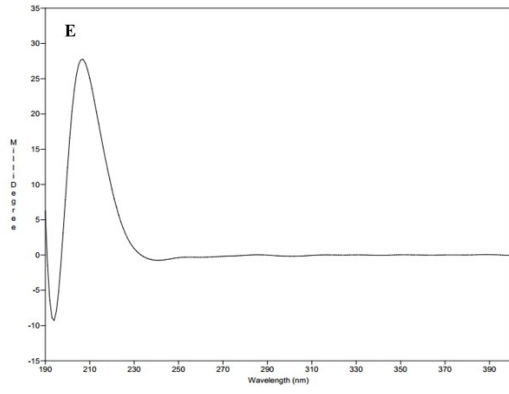
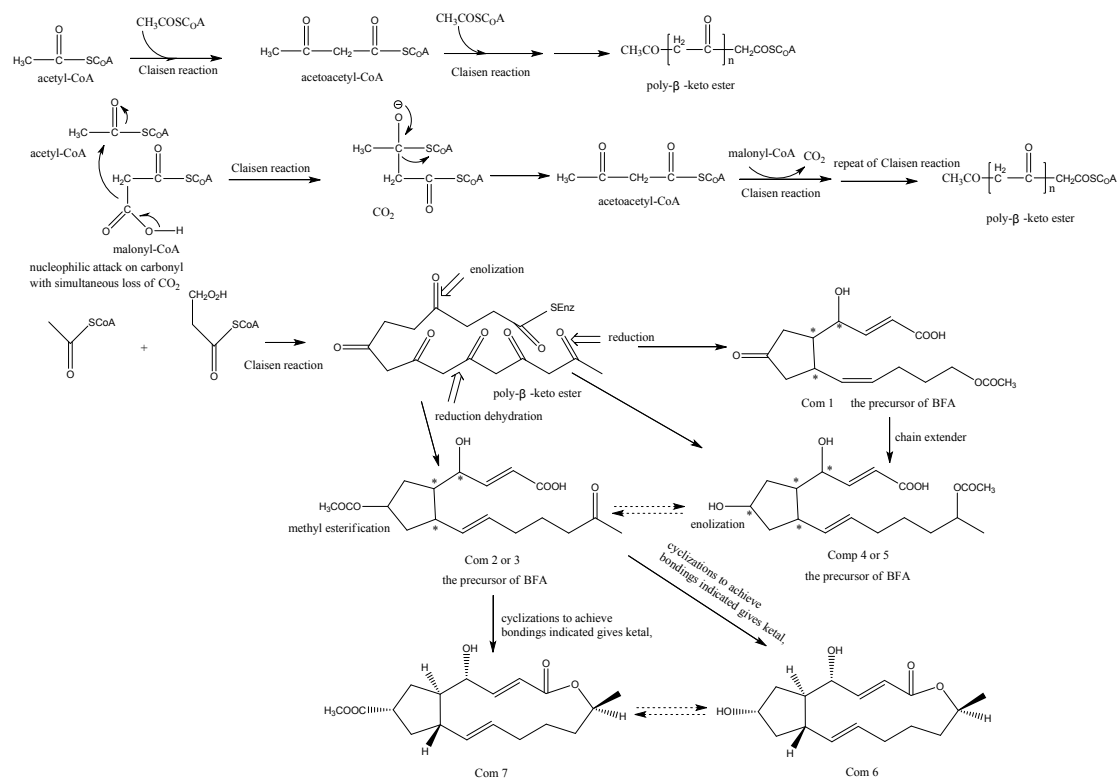


Figure S52 The plausible biosynthetic pathways of compounds 1-7



Compounds 1-7 structures could be explained as being derived from poly-β-keto chains, formed by coupling of acetic acid (C₂) units via condensation reactions. The formation of the poly-β-keto chain could be envisaged as a series of Claisen reactions. Two molecules of acetyl-CoA could participate in a Claisen condensation giving acetoacetyl-CoA, and this reaction could be repeated to generate a poly-β-keto ester of appropriate chain length. The conversion of acetyl-CoA into malonyl-CoA increased the acidity of the α-hydrogens, and thus provided a better nucleophile for the Claisen condensation. In the biosynthetic sequence, no acylated malonic acid derivatives were produced, and no label from [14C] bicarbonate was incorporated, so the carboxyl group introduced into malonyl-CoA was simultaneously lost by a decarboxylation reaction during the Claisen condensation.

Table S1 ¹H NMR Chemical Shift Data for Diagnostic Signals from the (S)- and (R)-Ester Derivatives of **1**^a,**2**^b,**3**^c,**4**^d,**5**^e (Measured at 600 MHz in CDCl₃)

		^a proton chemical shifts ($\Delta\delta_{\text{H}} = \delta_{\text{S}} - \delta_{\text{R}}$)							
MTPA-ester	H-2	H-3	H-4	H-5	H-6	H-8	H-9		
R	5.8750	6.1645	5.2496	2.1117	2.5549	2.1117	2.2745	2.2522	2.9325
S	6.1021	7.0267	4.5579	2.1095	2.5161	2.1095	2.2668	2.1963	2.8655
$\Delta\delta_{\text{H}}$	+0.2271	+0.8622		-0.0022	-0.0388	-0.0022	-0.0077	-0.0559	-0.0670

		^b proton chemical shifts ($\Delta\delta_{\text{H}} = \delta_{\text{S}} - \delta_{\text{R}}$)								
MTPA-ester	H-2	H-3	H-4	H-5	H-6	H-7	H-8	H-9		
R	6.0950	7.0727	4.3880	1.8790	1.7175	1.9981	5.1017	2.3442	1.5265	2.4436
S	6.1001	7.0909	4.3981	1.8760	1.7076	1.9982	5.1008	2.3446	1.5262	2.4463
$\Delta\delta_{\text{H}}$	+0.0051	+0.0182		-0.003	-0.0099					

		^c proton chemical shifts ($\Delta\delta_{\text{H}} = \delta_{\text{S}} - \delta_{\text{R}}$)								
MTPA-ester	H-2	H-3	H-4	H-5	H-6	H-7	H-8	H-9		
R	6.1010	7.0959	4.3979	1.8771	1.7079	1.9976	5.1009	2.3440	1.5269	2.4473
S	6.0934	7.0712	4.3865	1.8774	1.7163	1.9966	5.1001	2.3431	1.5250	2.4470
$\Delta\delta_{\text{H}}$	-0.0076	-0.0247		+0.0055	+0.0084					

		^d proton chemical shifts ($\Delta\delta_{\text{H}} = \delta_{\text{S}} - \delta_{\text{R}}$)								
MTPA-ester	H-2	H-3	H-4	H-5	H-6	H-7	H-8	H-9		
R	6.0857	7.0970	4.3755	1.8024	1.6454	1.5872	4.3456	2.2524	1.3656	2.4202
S	6.0877	7.1006	4.3744	1.7994	1.6495	1.5904	4.3483	2.2481	1.3656	2.4143
$\Delta\delta_{\text{H}}$	+0.0020	+0.0036		-0.0030	+0.0041	+0.0032		-0.0043		-0.002

		^e proton chemical shifts ($\Delta\delta_{\text{H}} = \delta_{\text{S}} - \delta_{\text{R}}$)								
MTPA-ester	H-2	H-3	H-4	H-5	H-6	H-7	H-8	H-9		
R	6.1121	7.0863	4.4173	1.7987	1.7255	1.5977	4.3249	2.2433	1.3800	2.4182
S	6.1148	7.0930	4.4199	1.7957	1.7073	1.5900	4.3360	2.2504	1.3800	2.4230
$\Delta\delta_{\text{H}}$	+0.0027	+0.0067		-0.0030	-0.0182	-0.0077		+0.0071		+0.0048