Supporting information for

New structures, chemotaxonomic significance and COX-2 inhibitory activities of cassane-type diterpenoids from the seeds of *Caesalpinia minax*

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Table S1 ^{1}H NMR (300 MHz) spectroscopic data for compounds **1-9**

Position	**1**[a]	**2**[a]	**3**[b]	**4**[a]	**5**[b]	**6**[b]	**7**[a]	**8**[b]	**9**[c]
1	4.87 t (2.4)	4.84 t (2.4)	4.97 t (2.7)	4.82 t (2.1)	4.93 t (2.7)	3.72 br s		4.85 t (2.1)	4.90 t (2.7)
2	1.70 m 2.00 m	1.68 m 1.98 m	1.74 m 1.93 m	1.68 m 1.95 m	1.77 m 1.99 m	1.68 m 2.03 m	2.08 m 2.96 m	1.76 m 1.91 m	1.70 m 2.00 m
3	1.03 m 1.91 m	1.03 m 1.90 m	1.16 m 1.80 m	1.03 m 1.84 m	1.20 m 1.74 m	1.10 m 2.07 m	1.63 m 2.06 m	1.11 m 1.74 m	1.07 m 1.86 m
6	5.42 d (9.0)	3.94 d (9.0)	2.29 d (6.6) 1.55 m	3.84 d (9.0)	2.15 m 1.67 m	2.05 m 1.67 m	1.90 m 2.04 m	5.45 d (10.2)	1.69 m 1.98 m
7	4.24 dd (9.0, 10.2)	5.48 dd (9.0, 10.2)	5.59 ddd (10.8, 6.6, 5.1)	4.04 t (9.0)	4.45 td (9.3, 6.9)	5.13 td (11.8, 5.4)	5.01 td (11.1, 5.7)	4.44 t (10.2)	4.37 td (10.8, 4.8)
8	2.63 m	2.77 m	2.63 m	2.26 m	2.63 m	2.47 m	2.37 m	2.05 m	2.16 dd (12.3, 10.2)
9	3.11 ddd (12.0, 7.2, 4.8)	3.13 ddd (12.3, 7.2, 5.1)	3.12 m	2.64 ddd (11.4, 6.9, 4.5)	2.84 m	2.92 m	2.74 td (12.0, 7.5)	2.60 td (11.4, 5.7)	2.98 td (11.4, 4.8)
11	2.51 m 2.85 m	2.50 m 2.83 m	2.51 m 2.85 m	2.27 m 2.51 m	2.39 m 2.58 m	2.54 m 2.80 m	2.37 m 3.18 dd (15.9, 4.2)	2.29 m 2.48 m	2.36 dd (16.5, 10.2) 2.52 dd (16.8, 5.7)
14						3.39 d (9.0)	3.34 d (9.5)		
15	6.62 d (2.1)	6.57 d (2.1)	6.61 d (2.1)	6.46 d (1.8)	6.44 d (2.1)	6.10 d (1.8)	6.10 d (2.1)	6.42 d (1.8)	6.03 d (1.8)
16	7.48 d (2.1)	7.46 d (2.1)	7.29 d (2.1)	7.27 d (1.8)	7.24 d (2.1)	7.22 d (1.8)	7.27 d (2.1)	7.27 d (1.8)	7.35 d (1.8)
17				5.20 br s 5.32 br s	5.23 d (2.1) 5.26 d (2.1)			1.49 s	9.47 s
18	1.12 s	1.27 s	1.05 s	1.30 s	1.09 s	0.99 s	0.99 s	1.17 s	1.01 s
19	1.16 s	1.23 s	1.10 s	1.28 s	1.14 s	1.05 s	1.30 s	1.15 s	1.11 s
20	1.33 s	1.26 s	1.27 s	1.19 s	1.21 s	1.11 s	1.49 s	1.24 s	1.22 s
1-OCOC$\underline{H_3}$	2.04 s	2.05 s	2.06 s	2.03 s	2.09 s		1.97 s	2.10 s	2.09 s
6-OCOC$\underline{H_3}$	2.11 s							2.20 s	2.09 s
7-OCOC$\underline{H_3}$		2.05 s	2.09 s			1.99 s	1.97 s		
17-OCH_3						3.72 br s	3.70 s		

[a] ^{1}H NMR data were recorded in CD_3OD; [b] ^{1}H NMR data were recorded in $CDCl_3$; [c] ^{1}H NMR data were recorded in CD_3COCD_3.

Table S2 ^{13}C NMR (75 MHz) NMR spectroscopic data for compounds **1-9**

Position	**1**[a]	**2**[a]	**3**[b]	**4**[a]	**5**[b]	**6**[b]	**7**[a]	**8**[b]	**9**[c]
1	76.2, CH	76.3, CH	75.1, CH	77.1, CH	75.6, CH	72.3, CH	216.1, C	75.8, CH	75.8, CH
2	23.4, CH_2	23.5, CH_2	22.6, CH_2	23.4, CH_2	22.5, CH_2	26.1, CH_2	36.5, CH_2	22.1, CH_2	23.3, CH_2
3	33.4, CH_2	33.5, CH_2	29.8, CH_2	33.4, CH_2	29.9, CH_2	29.7, CH_2	38.7, CH_2	32.2, CH_2	30.6, CH_2
4	39.5, C	39.7, C	38.3, C	39.7, C	38.3, C	38.6, C	39.9, C	38.6, C	39.0, C
5	79.9, C	80.2, C	77.7, C	80.0, C	77.9, C	79.8, C	83.6, C	79.4, C	78.5, C
6	77.4, CH	75.7, CH	31.7, CH_2	77.5, CH	34.9, CH_2	32.7, CH_2	33.4, CH_2	76.5, CH	35.9, CH_2
7	71.5, CH	74.8, CH	68.3,CH	75.2, CH	67.9, CH	76.9, CH	77.2, CH	72.4, CH	65.9, CH
8	51.9, CH	50.1, CH	48.9, CH	44.6, CH	44.9, CH	38.8, CH	41.2, CH	48.8, CH	47.4, CH
9	40.1, CH	40.2, CH	39.2, CH	39.4, CH	38.5, CH	36.6, CH	39.1, CH	35.0, CH	33.7, CH
10	46.3, C	45.7, C	43.1, C	45.5, C	43.3, C	43.5, C	39.9, C	45.1, C	44.1, C
11	24.4, CH_2	24.4, CH_2	23.4, CH_2	24.1, CH_2	22.9, CH_2	21.4, CH_2	24.9, CH_2	22.0, CH_2	22.5, CH_2
12	168.3, C	167.6, C	164.7, C	152.3, C	151.2, C	150.6, C	152.8, C	147.8, C	154.1, C
13	120.9, C	120.9, C	120.5, C	121.0, C	119.8, C	113.1, C	113.6, C	124.2, C	116.8, C
14	197.9, C	195.6, C	193.3, C	141.6, C	140.4, C	46.2, CH	47.8, CH	72.9, C	76.2, C
15	107.0, CH	107.0, CH	106.5, CH	107.5, CH	106.6, CH	108.3, CH	109.1, CH	107.2, CH	108.9, CH
16	145.1, CH	145.0, CH	143.1, CH	142.9, CH	141.8, CH	141.3, CH	142.5, CH	142.0, CH	142.4, CH
17				106.8, CH_2	105.9, CH_2	174.9, C	176.9, C	25.8, CH_3	201.5, CH
18	30.9, CH_3	31.7, CH_3	28.0, CH_3	31.8, CH_3	28.2, CH_3	27.7, CH_3	27.8, CH_3	30.6, CH_3	28.5, CH_3
19	24.9, CH_3	25.3, CH_3	25.2, CH_3	25.6, CH_3	25.4, CH_3	24.8, CH_3	25.9, CH_3	24.8, CH_3	25.5, CH_3
20	17.8, CH_3	17.9, CH_3	17.9, CH_3	17.6, CH_3	17.8, CH_3	17.7, CH_3	16.7, CH_3	17.2, CH_3	18.0, CH_3
1-O<u>C</u>OCH_3	171.7, C	171.9, C	170.1, C	171.7, C	169.7, C			168.8, C	170.0, C
1-OCO<u>C</u>H_3	21.1,CH_3	21.1, CH_3	21.4, CH_3	21.1, CH_3	21.5, CH_3			21.4, CH_3	21.3, CH_3
6-O<u>C</u>OCH_3	172.5, C							171.4, C	
6-OCO<u>C</u>H_3	21.9, CH_3							21.8, CH_3	
7-O<u>C</u>OCH_3		172.9, C	169.3,C			170.5, C	172.4, C		
7-OCO<u>C</u>H_3		21.6, CH_3	21.4, CH_3			21.1, CH_3	21.2, CH_3		
17-O<u>C</u>H_3						51.9, CH_3	52.6, CH_3		

[a] ^{13}C NMR data were recorded in CD_3OD; [b] ^{13}C NMR data were recorded in $CDCl_3$; [c] ^{13}C NMR data were recorded in CD_3COCD_3.

Table S3 ^{1}H (300 MHz) and ^{13}C NMR (75 MHz) NMR spectroscopic data (in $CDCl_3$) for compounds **10** and **11**

	10		**11**	
position	δ_C, type	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)
1	75.1, CH	4.98 br s	74.6, CH	4.86 br s
2	22.6, CH_2	1.73 m	22.6, CH_2	1.76 m
		1.98 m		1.94 m
3	29.9, CH_2	1.15 m	29.9, CH_2	1.15 m
		1.76 m		1.76 m
4	38.3, C		38.3, C	
5	78.5, C		78.2, C	
6	31.2, CH_2	1.51 m	32.1, CH_2	1.54 m
		2.21,m		2.17,m
7	70.6, CH	5.41 td (0.5, 4.5)	74.7, CH	5.23 td (10.8, 5.4)
8	44.0, CH	1.77 m	43.9, CH	2.21 m
9	32.7, CH	3.14 m	35.9, CH	2.80 td, (12.9, 3.0)
10	43.3, C		43.3, C	
11	37.9, CH_2	1.35 dd (13.2, 12.6)	36.2, CH_2	1.33 t (12.9)
		2.14 dd (13.2, 2.4)		2.06 m
12	104.8, C		106.5, C	
13	170.3, C		163.2, C	
14	31.8, CH	2.76 m	48.9, CH	3.16 dd (8.4, 1.8)
15	114.0,CH	5.74 s	117.5,	5.78 d (1.8)
16	171.7, C		168.6, C	
17	12.3, CH_3	1.23 d (7.2)	170.8, C	
18	28.1, CH_3	1.04 s	27.9, CH_3	1.02 s
19	25.0, CH_3	1.05 s	24.5, CH_3	1.01 s
20	17.0, CH_3	1.05 s	17.4, CH_3	1.06 s
1-O$\underline{C}$OCH_3	169.8, C		168.9, C	
1-OCO$\underline{C}H_3$	21.1, CH_3	2.15 s	21.1, CH_3	2.12 s
7-O$\underline{C}$OCH_3	170.3, C		169.8, C	
7-OCO$\underline{C}H_3$	21.1, CH_3	2.07 s	21.2, CH_3	2.00 s
12-O$\underline{C}H_2CH_3$			58.7, CH_2	3.16 m
				3.43 m
12-O$CH_2\underline{C}H_3$			15.1, CH_3	1.16 t (7.2)
17-OCH_3			52.1, CH_3	3.78 s

Figure S1. ^{1}H NMR spectrum (CD_3OD, 300 MHz) of compound **1**.

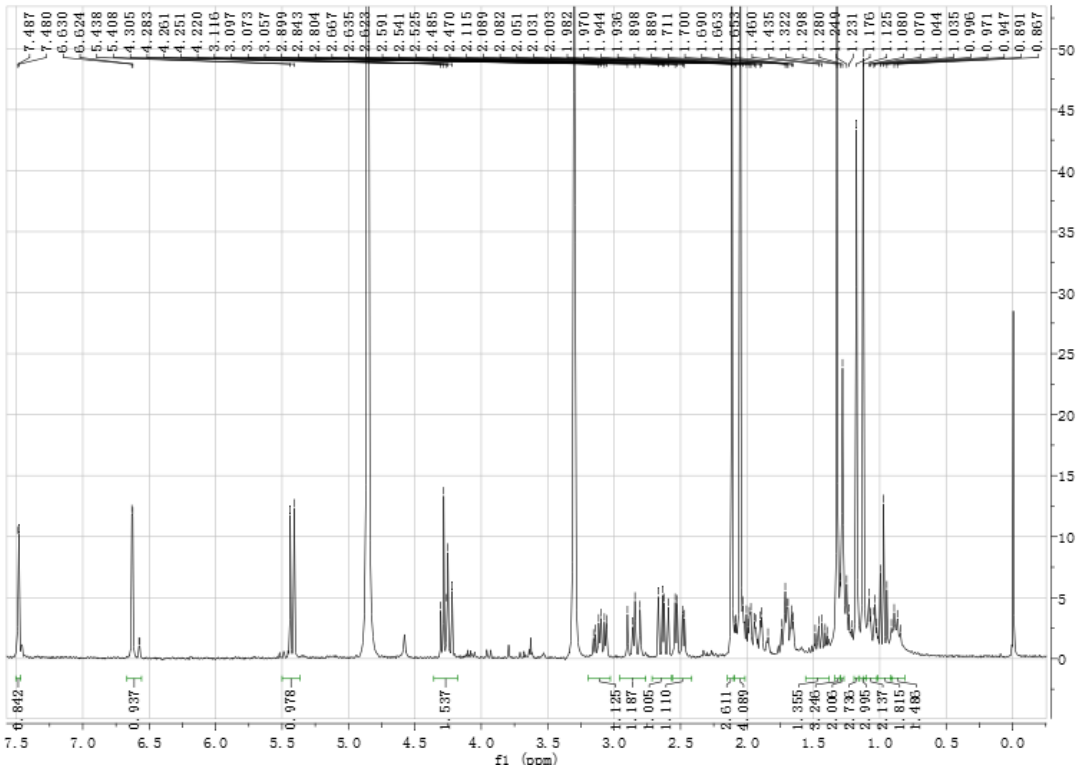


Figure S2. ^{13}C NMR spectrum (CD_3OD, 75 MHz) of compound **1**.

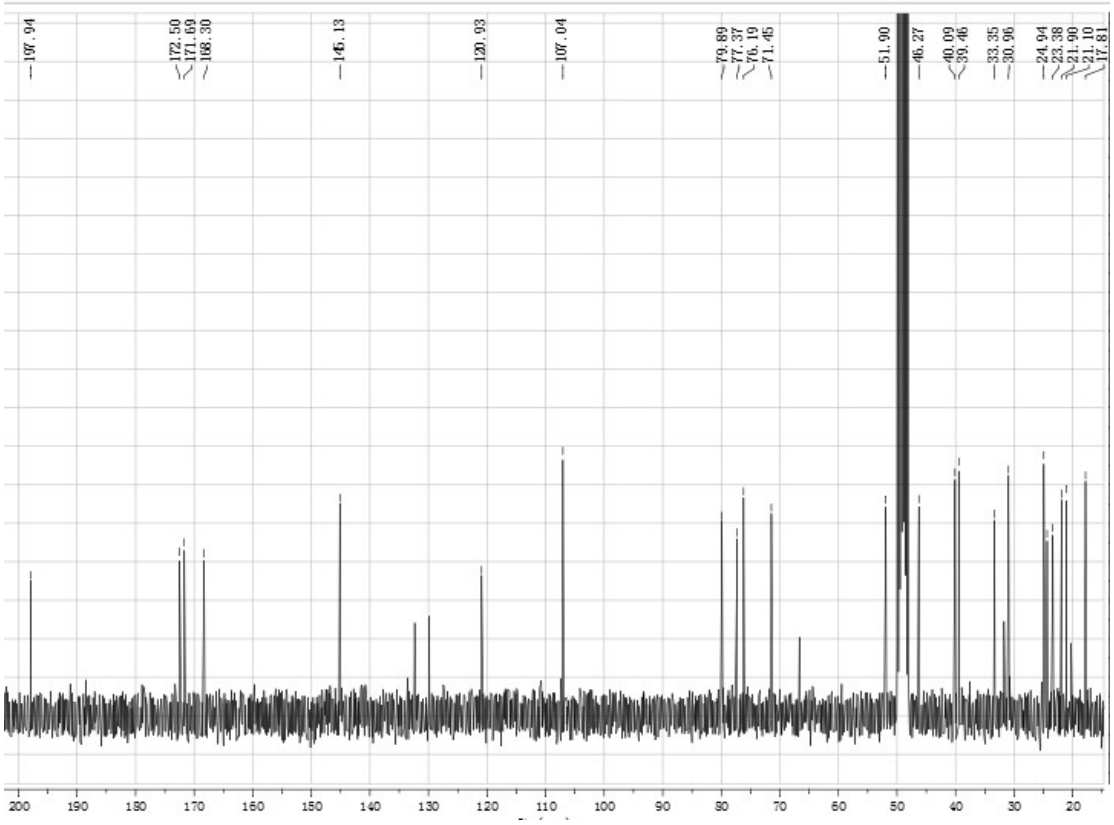


Figure S3. DEPT spectrum (CD_3OD, 75 MHz) of compound **1**.

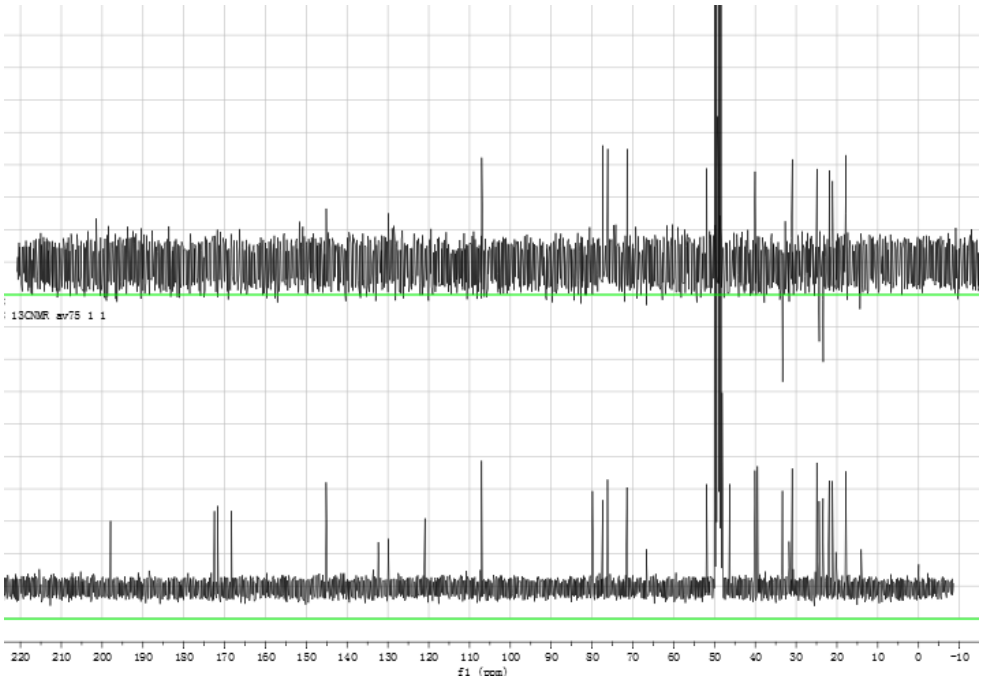


Figure S4. ^1H□^1H COSY spectrum (CD_3OD) of compound **1**.

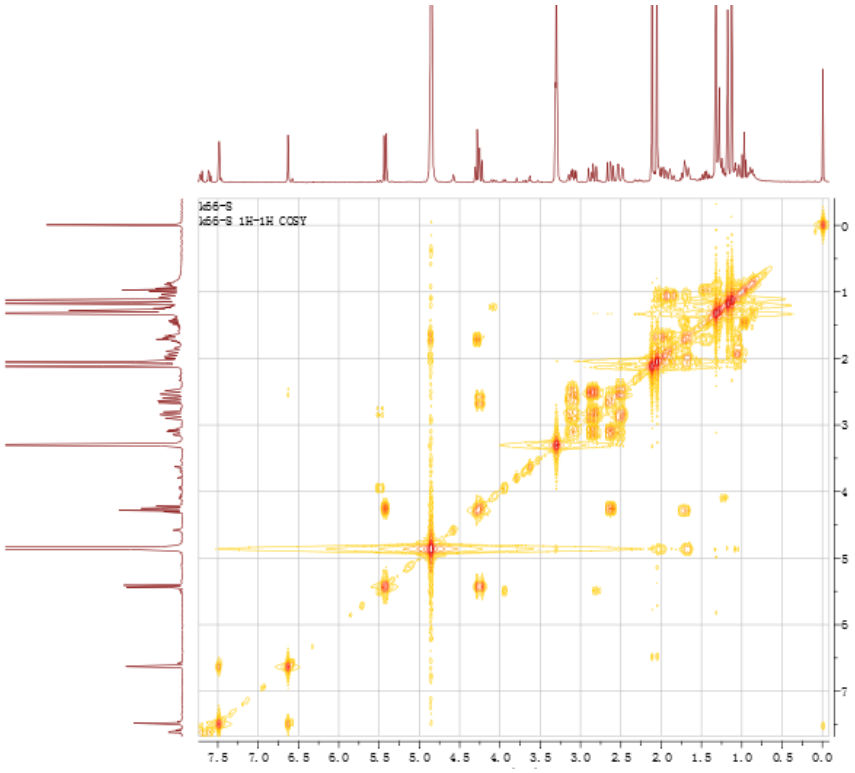


Figure S5. HSQC spectrum (CD_3OD) of compound **1**.

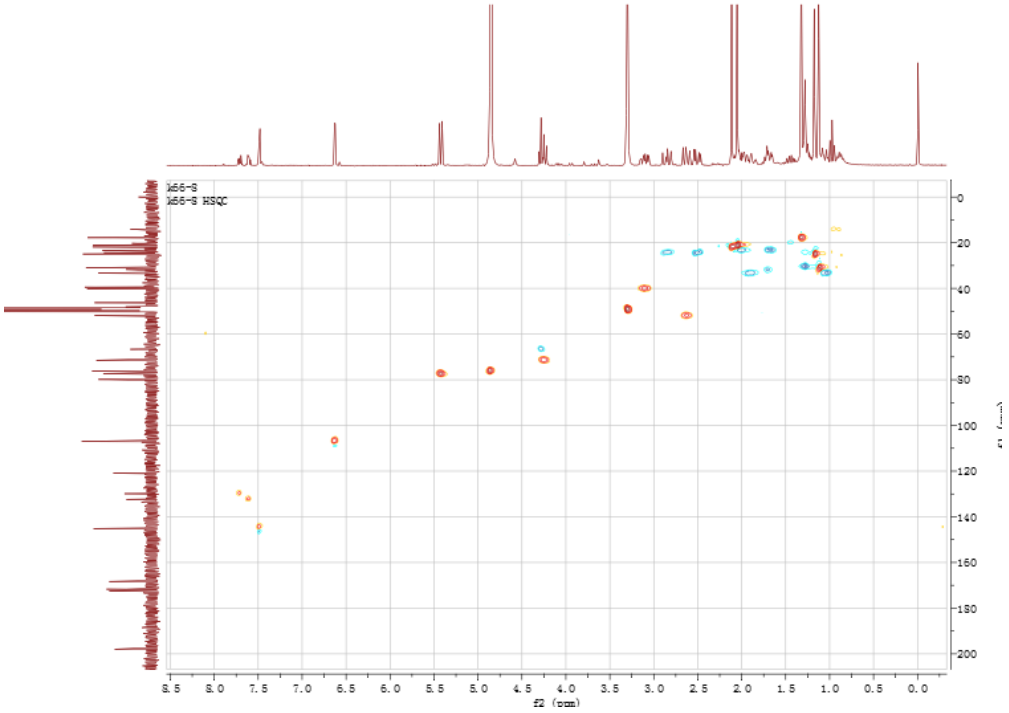


Figure S6. HMBC spectrum (CD_3OD) of compound **1**.

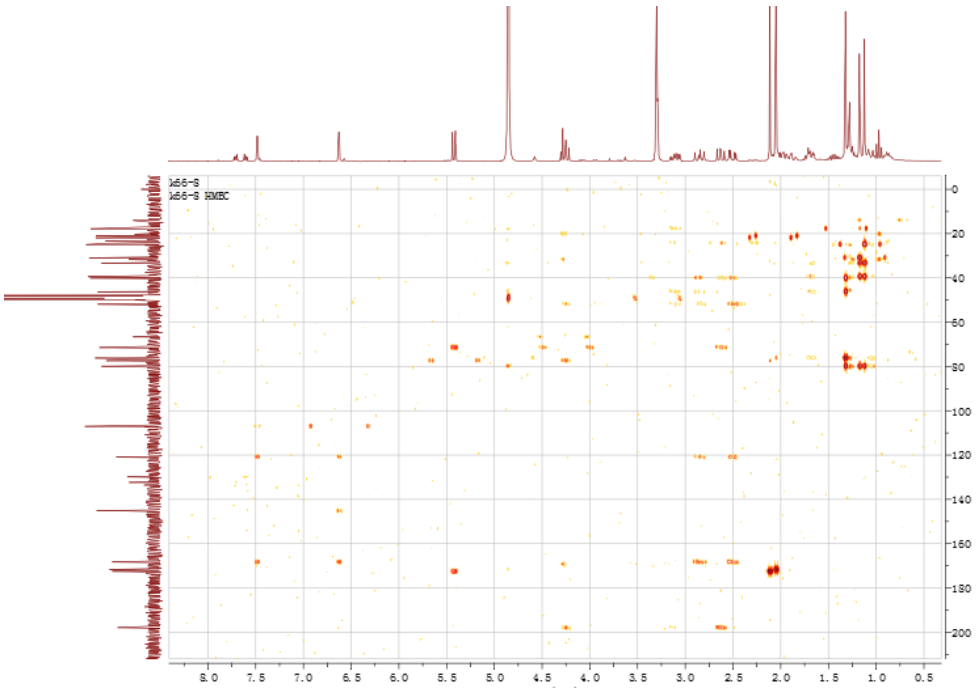


Figure S7. NOESY spectrum (CD_3OD) of compound **1**.

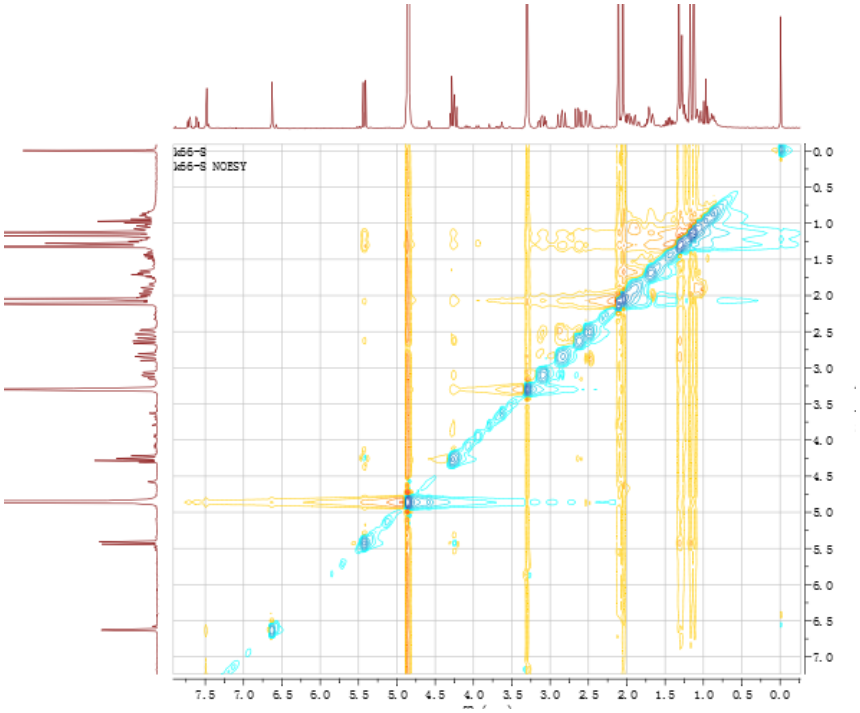


Figure S8. ^1H NMR spectrum (CD_3OD, 300 MHz) of compound **2**.

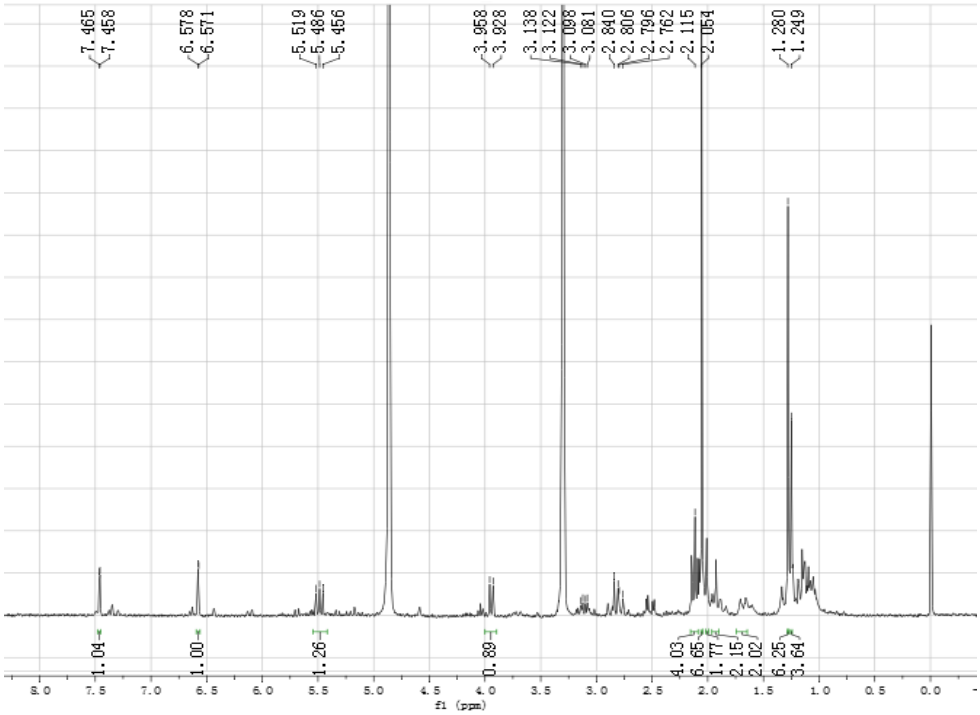


Figure S9. ^{13}C NMR spectrum (CD_3OD, 75 MHz) of compound **2**.

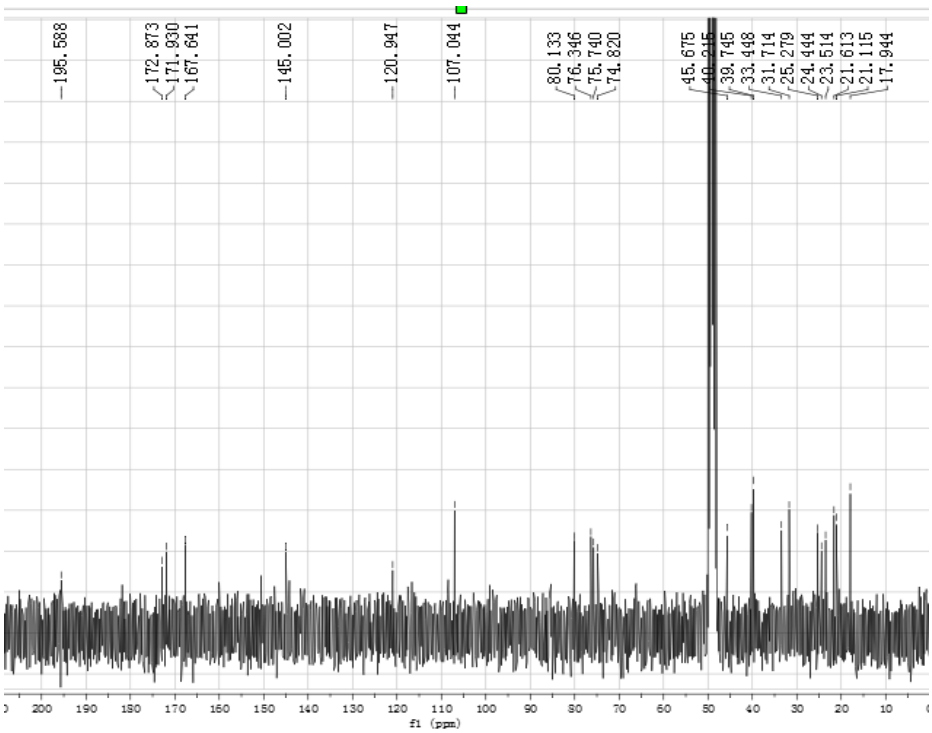


Figure S10. DEPT spectrum (CD_3OD, 75 MHz) of compound **2**.

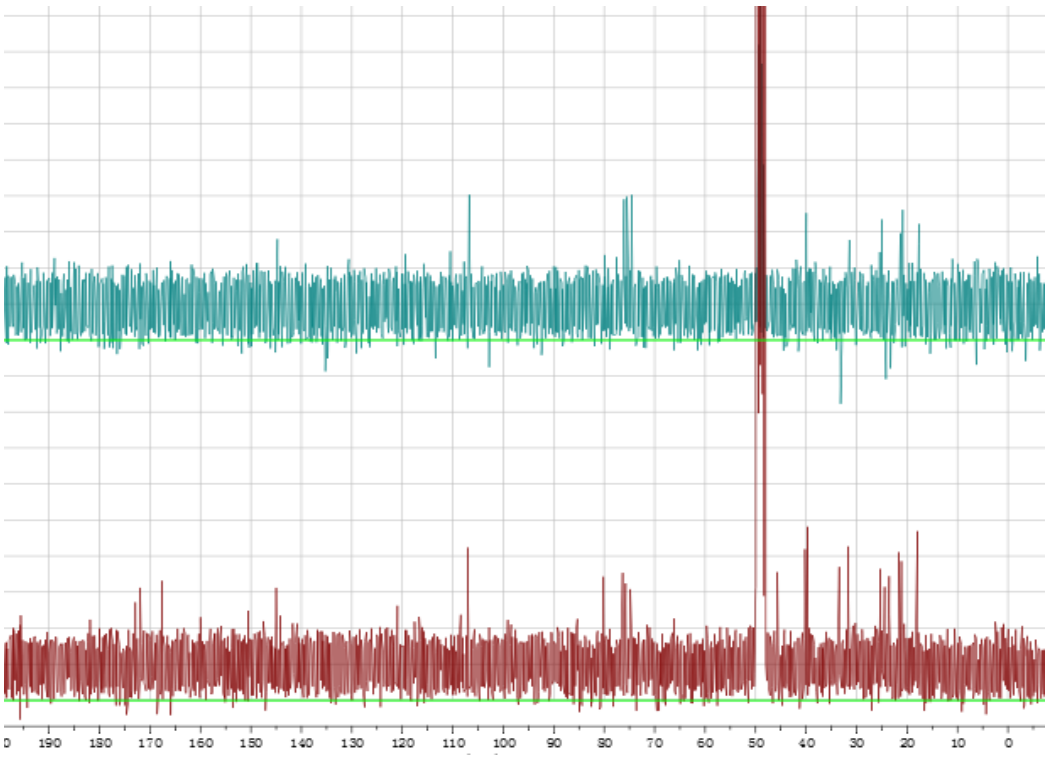


Figure S11. $^{1}H\square^{1}H$ COSY spectrum (CD_3OD) of compound **2**.

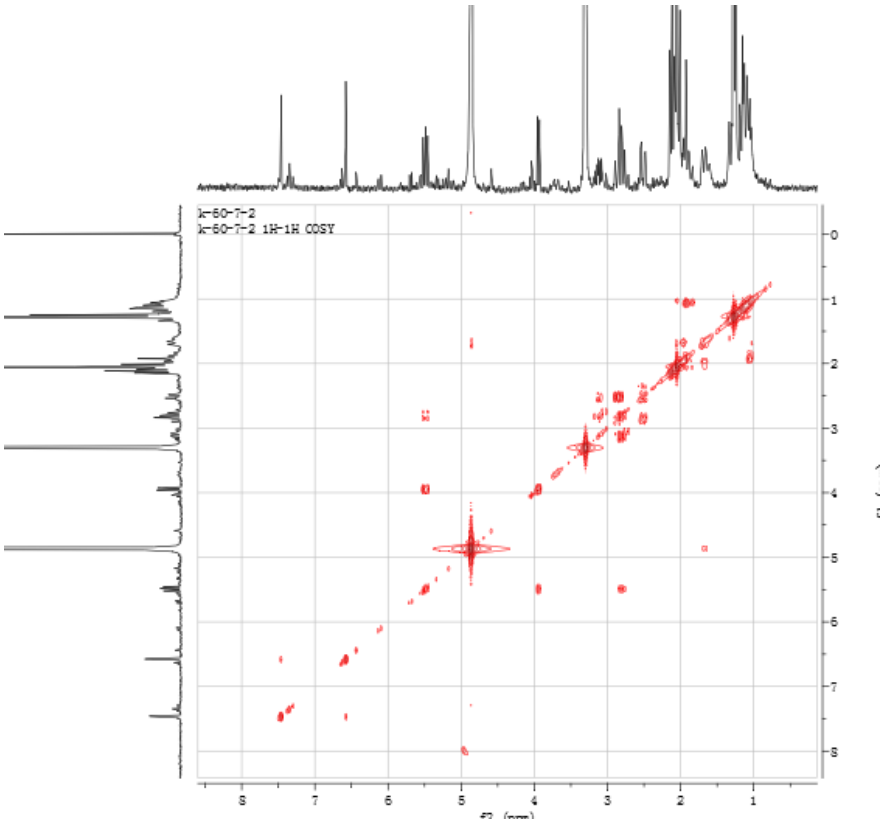


Figure S12. HSQC spectrum (CD_3OD) of compound **2**.

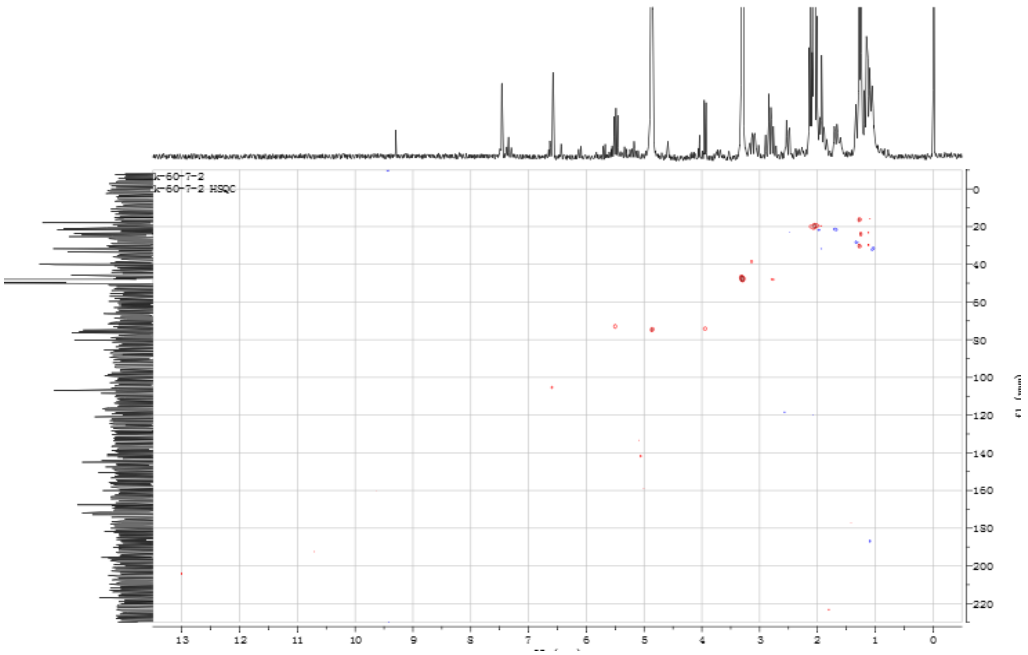


Figure S13. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of compound **3**.

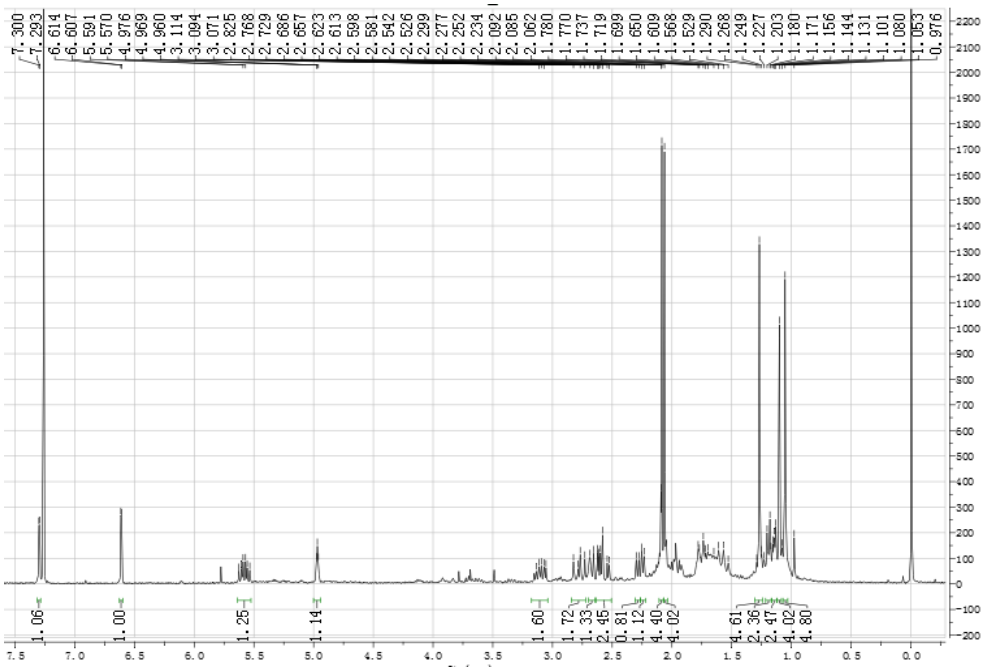


Figure S14. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of compound **3**.

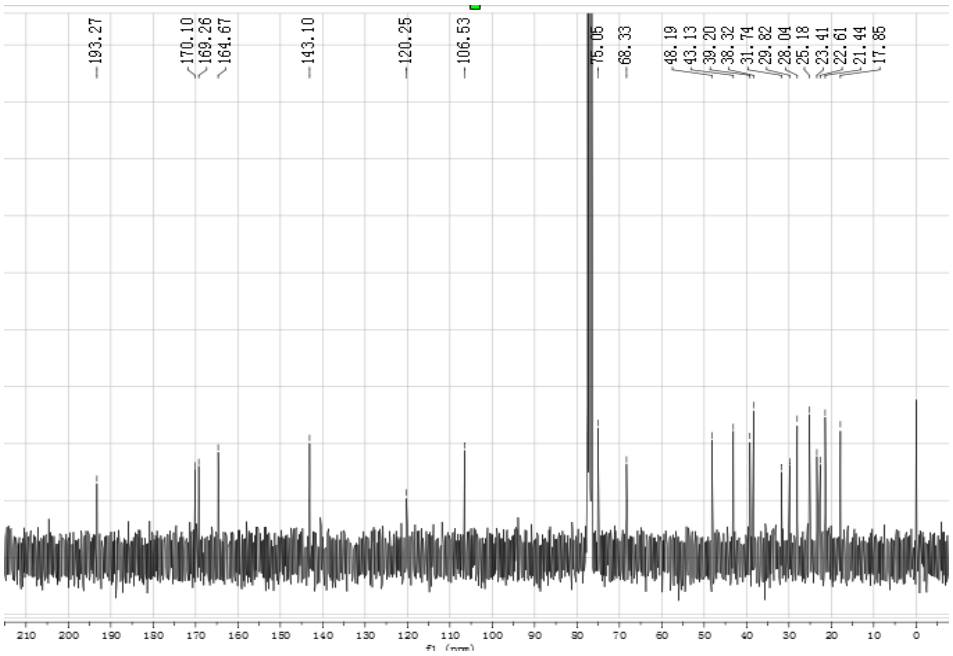


Figure S15. DEPT spectrum ($CDCl_3$, 75 MHz) of compound **3**.

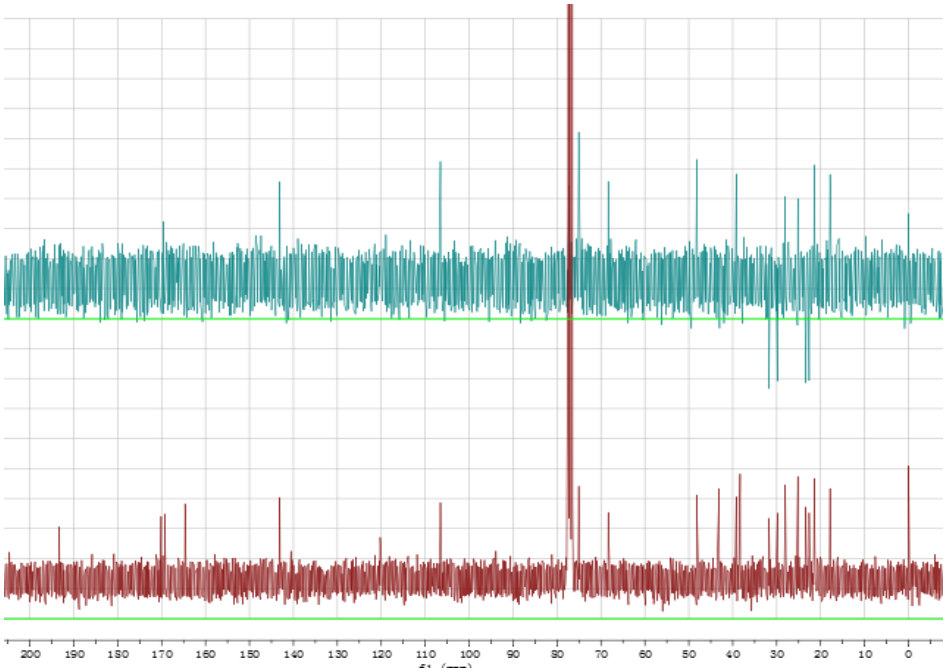


Figure S16. ^1H□^1H COSY spectrum ($CDCl_3$) of compound **3**.

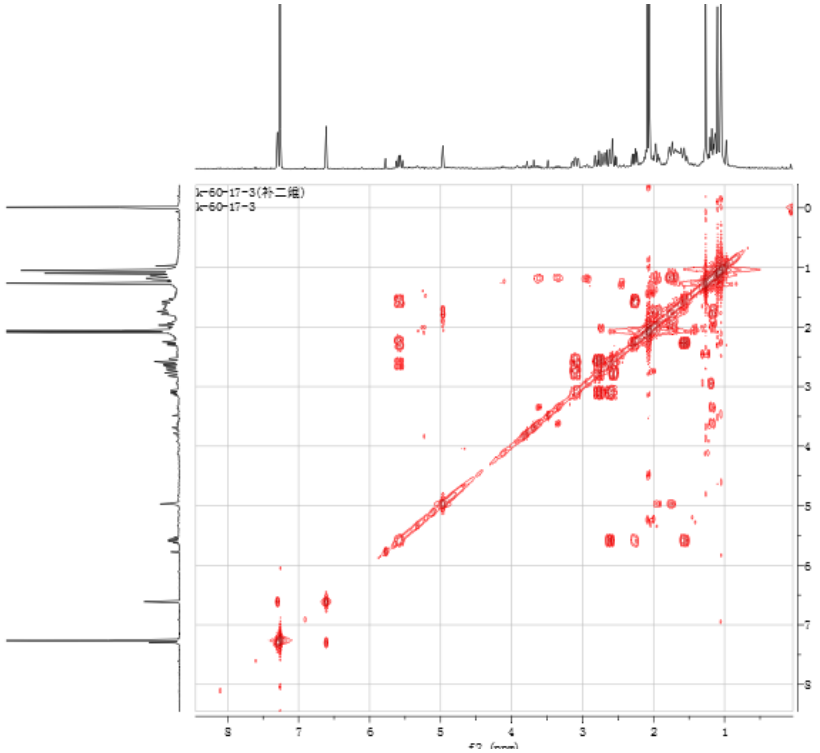


Figure S17. HSQC spectrum ($CDCl_3$) of compound **3**.

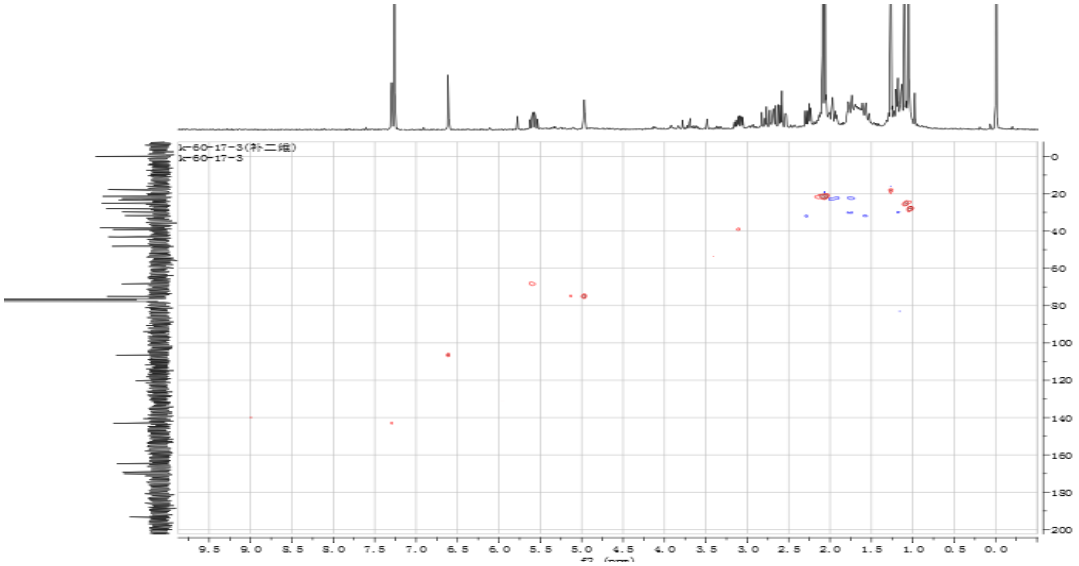


Figure S18. HMBC spectrum ($CDCl_3$) of compound **3**.

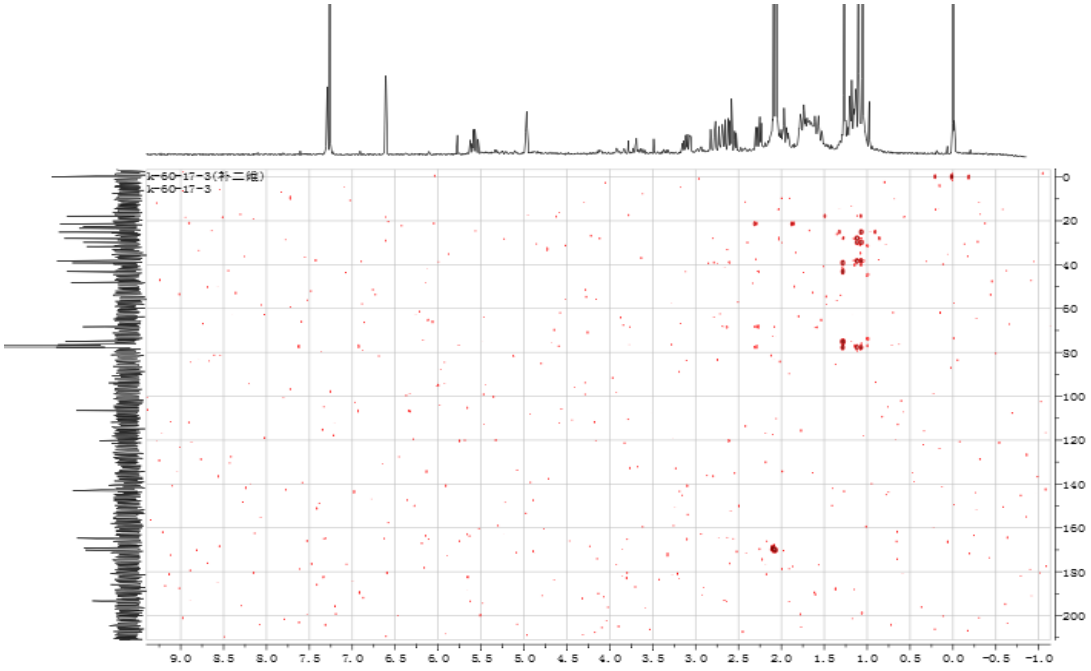


Figure S19. NOESY spectrum ($CDCl_3$) of compound **3**.

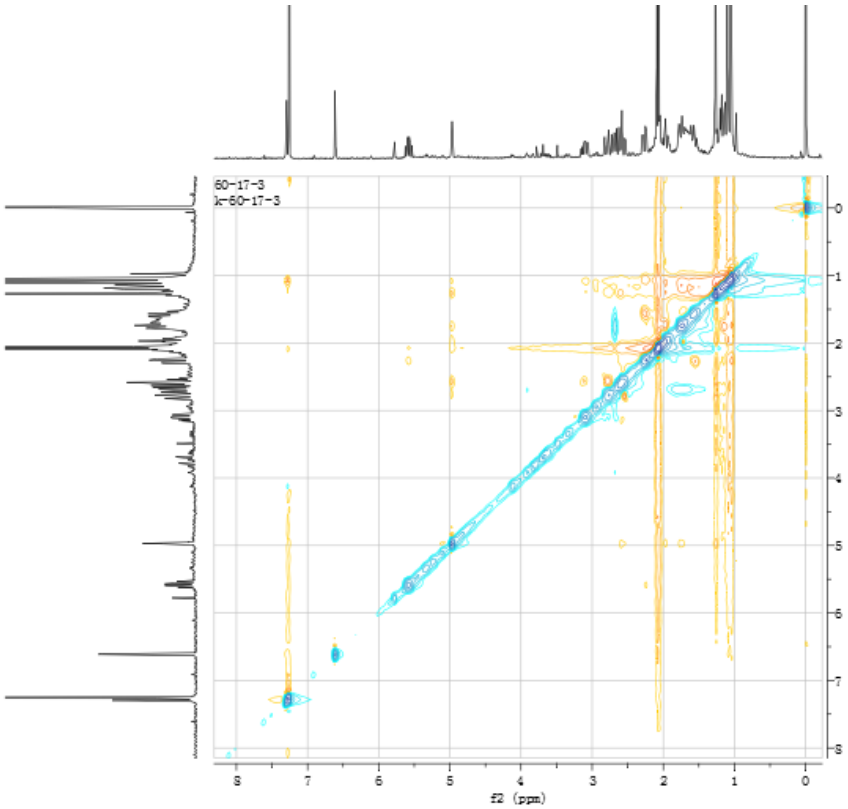


Figure S20. ^1H NMR spectrum (CD_3OD, 300 MHz) of compound **4**.

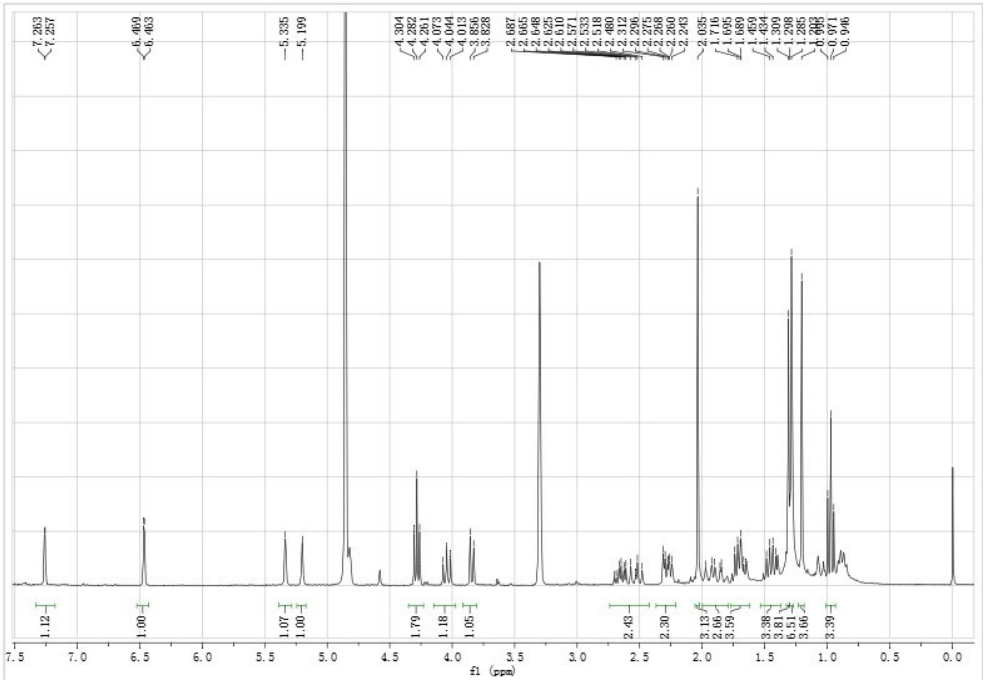


Figure S21. ^{13}C NMR spectrum (CD_3OD, 75 MHz) of compound **4**.

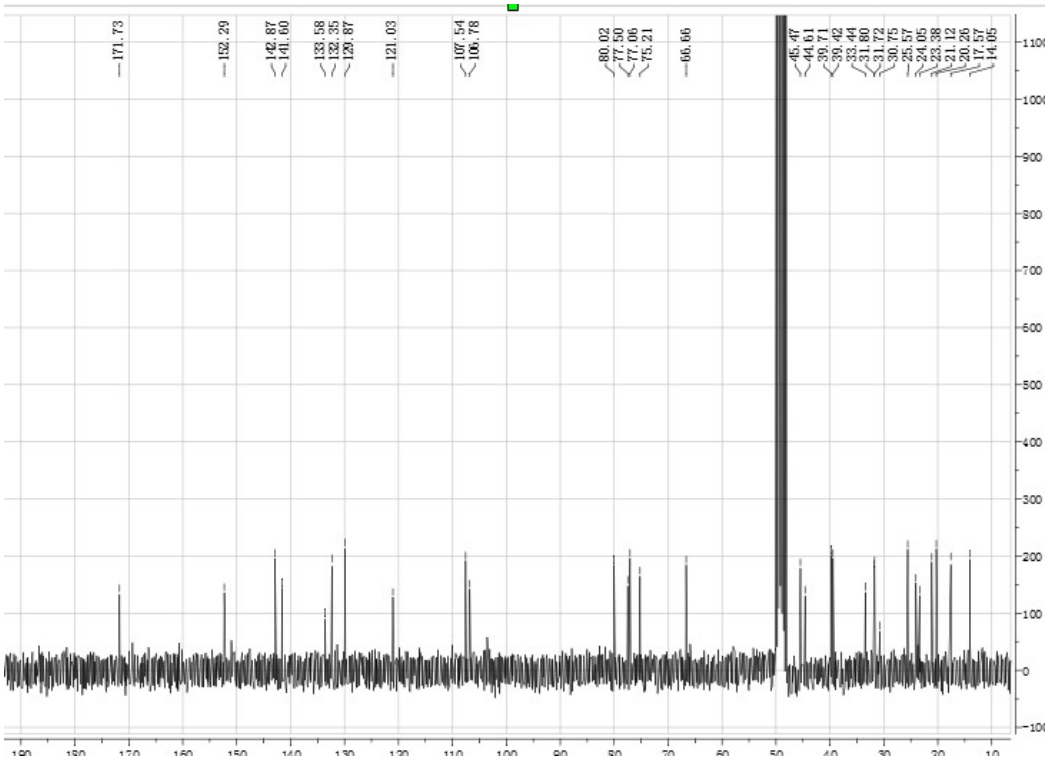


Figure S22. DEPT spectrum (CD_3OD, 75 MHz) of compound **4**.

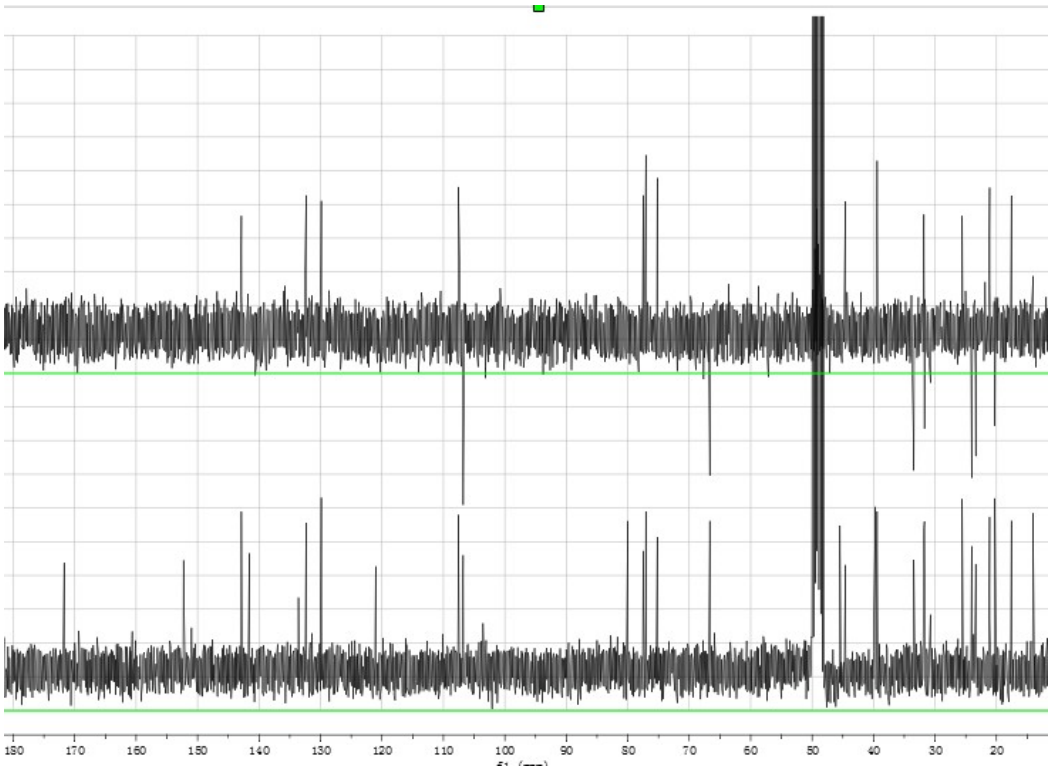


Figure S23. $^{1}H\square^{1}H$ COSY spectrum (CD_3OD) of compound **4**.

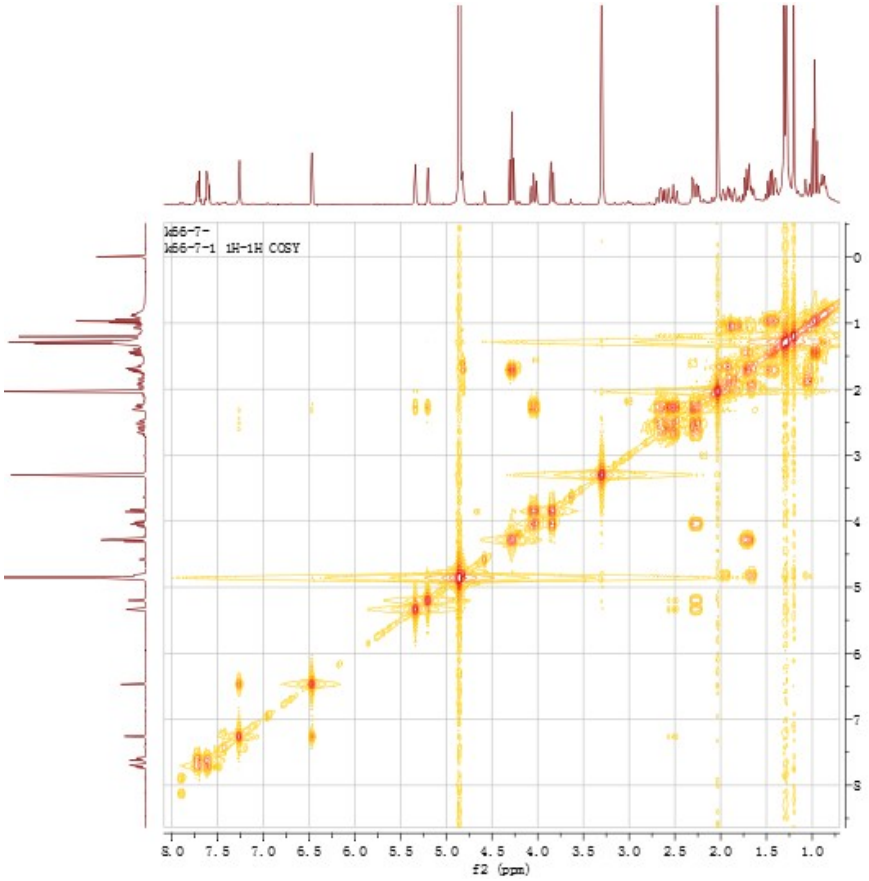


Figure S24. HSQC spectrum (CD_3OD) of compound **4**.

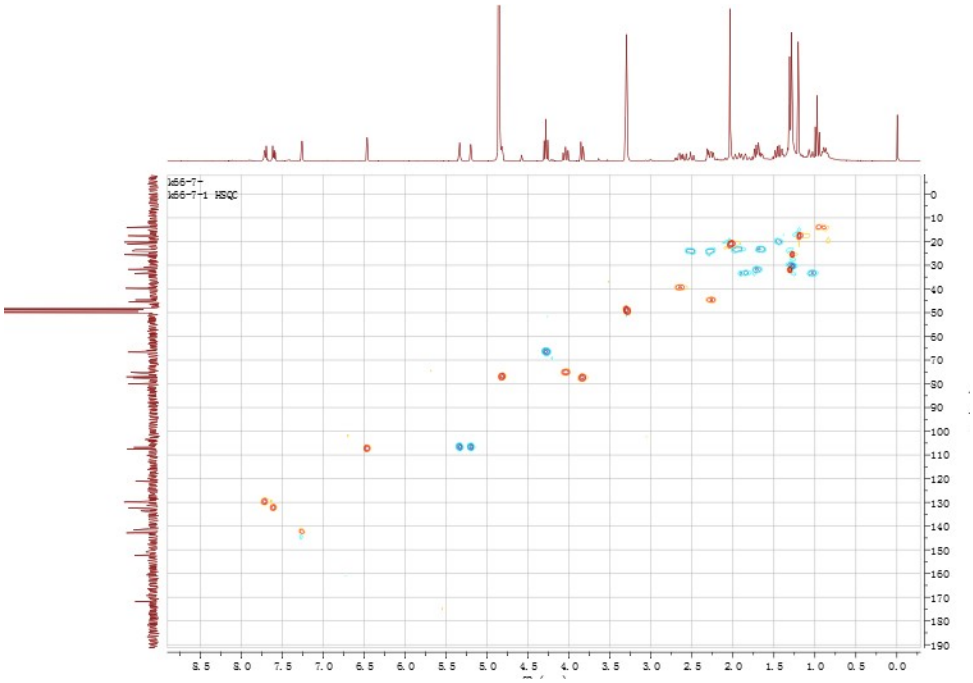


Figure S25. HMBC spectrum (CD_3OD) of compound **4**.

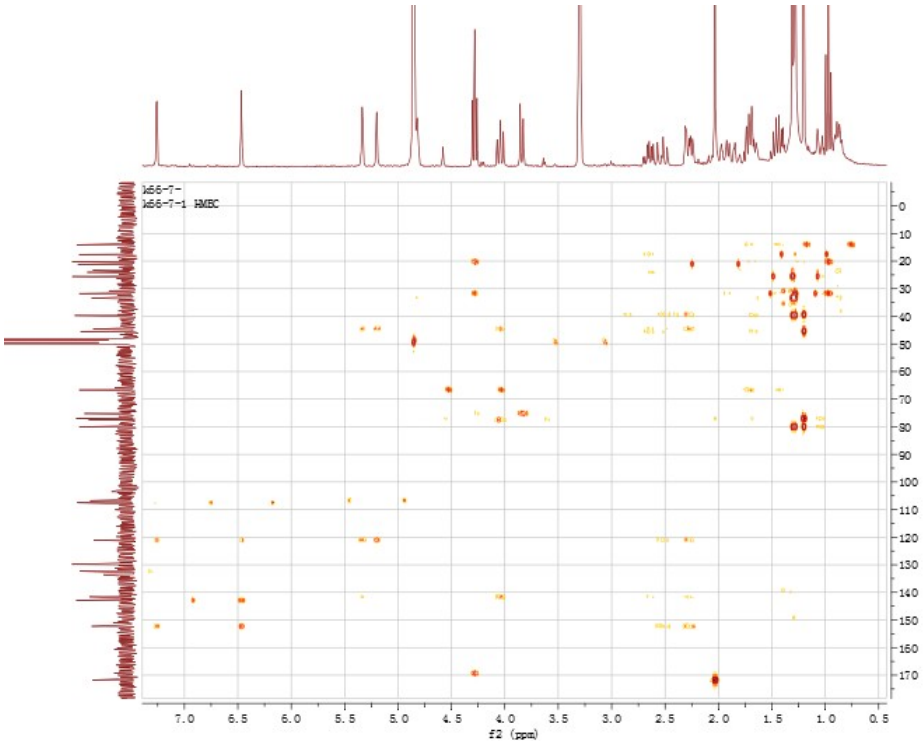


Figure S26. NOESY spectrum (CD_3OD) of compound **4**.

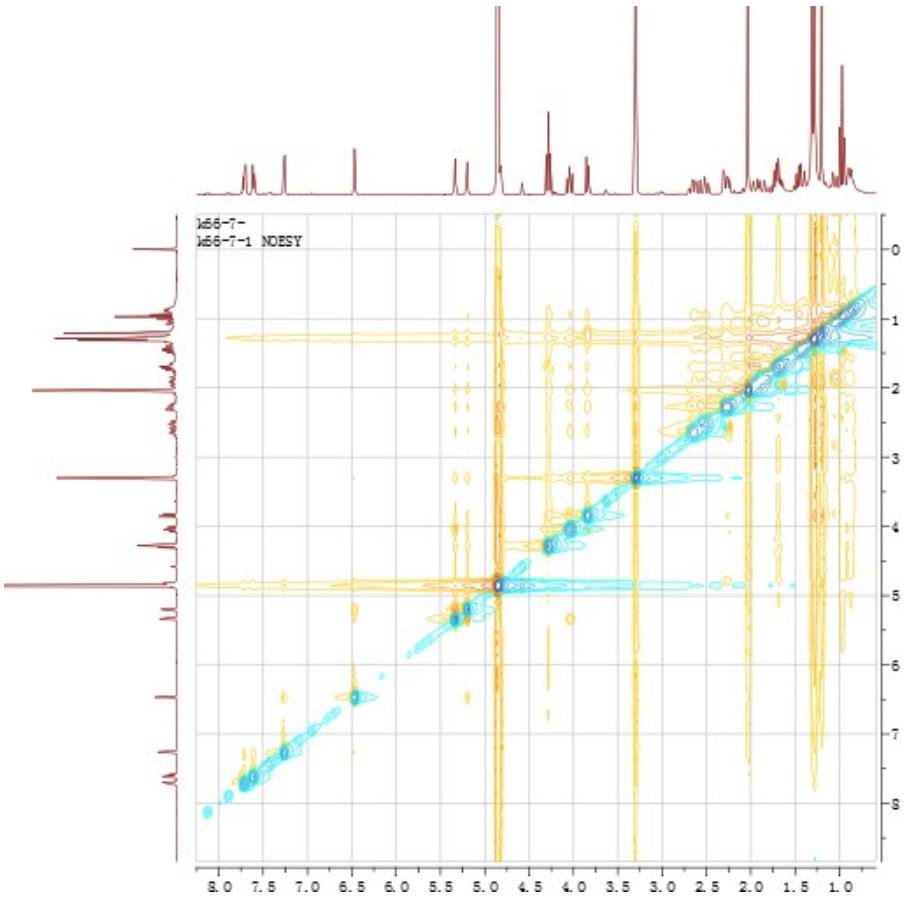


Figure S27. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of compound **5**.

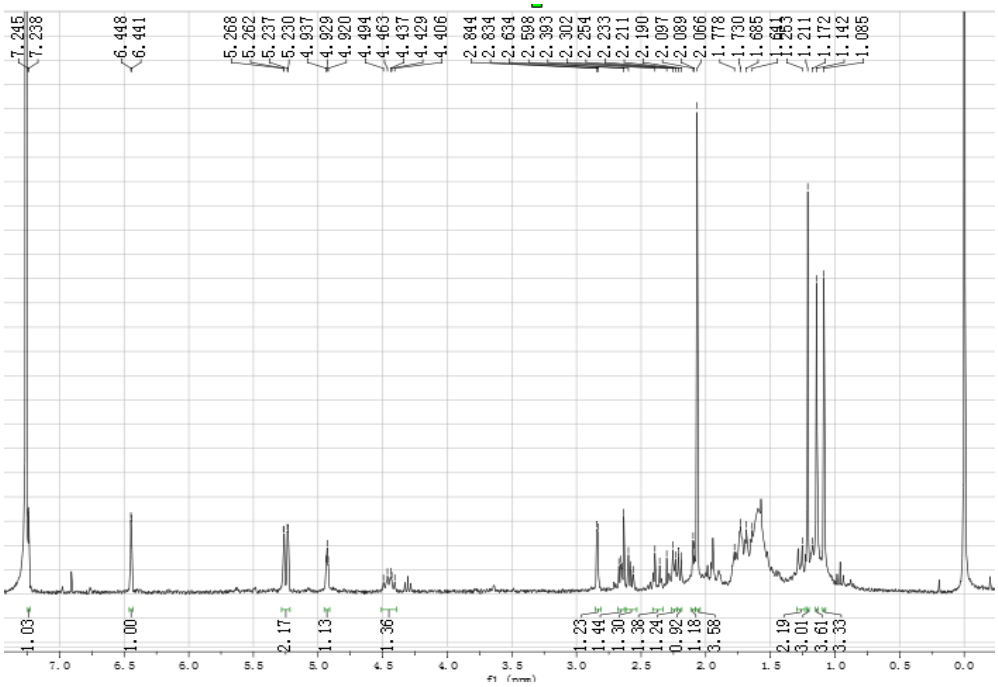


Figure S28. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of compound **5**.

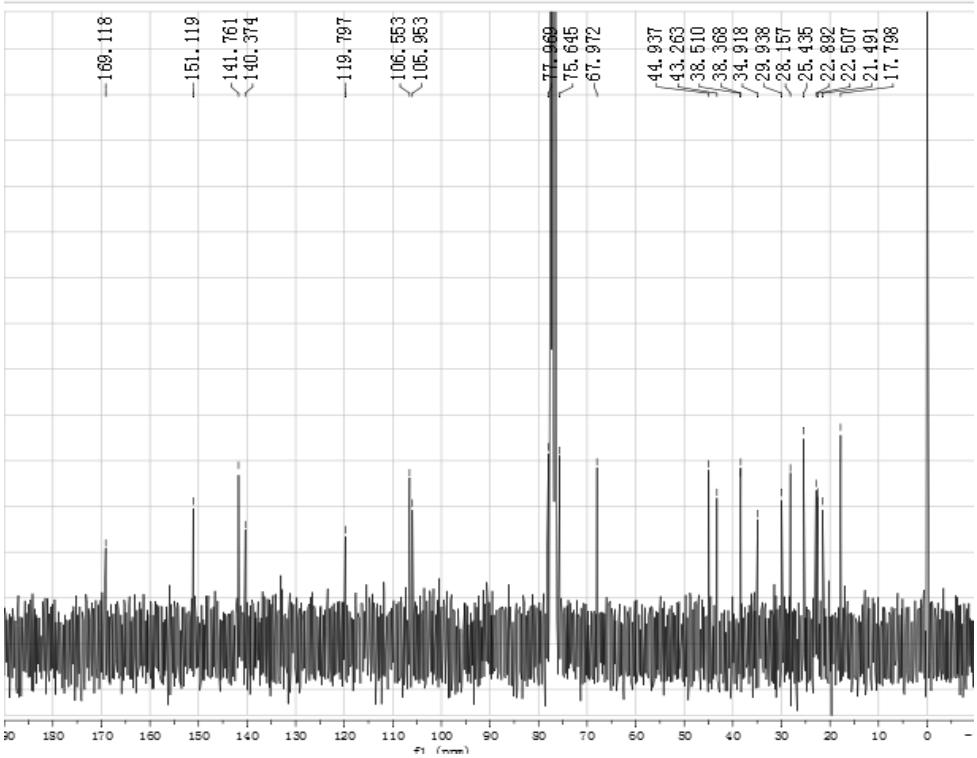


Figure S29. DEPT spectrum ($CDCl_3$, 75 MHz) of compound **5**.

Figure S30. ^1H NMR spectrum ($CDCl_3$, 300 MHz) of compound **6**.

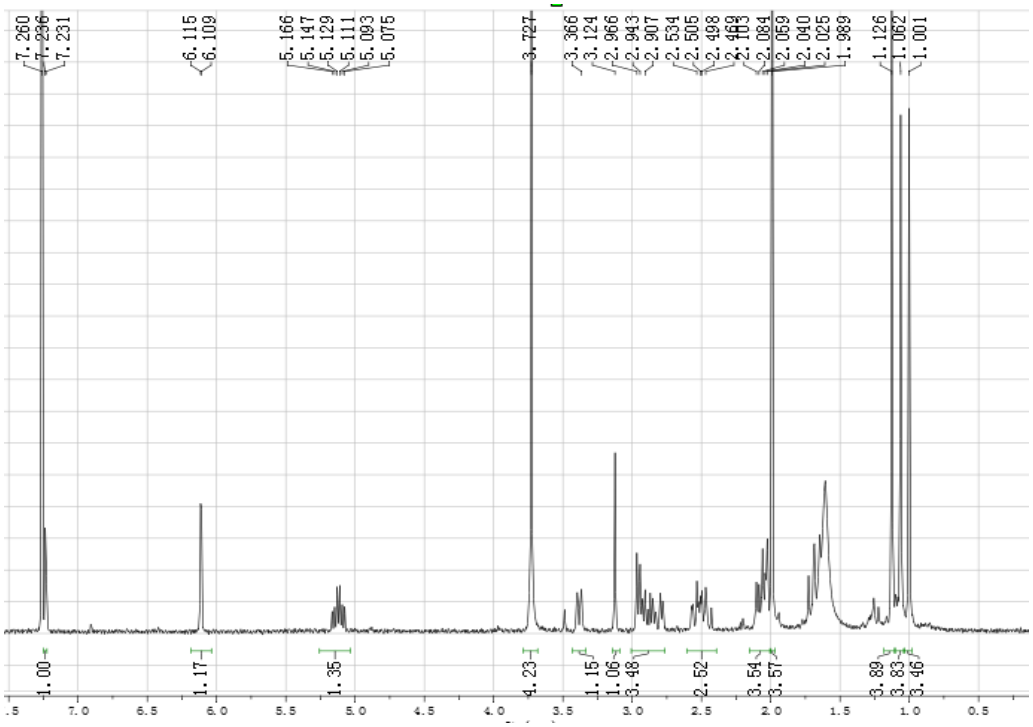


Figure S31. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of compound **6**.

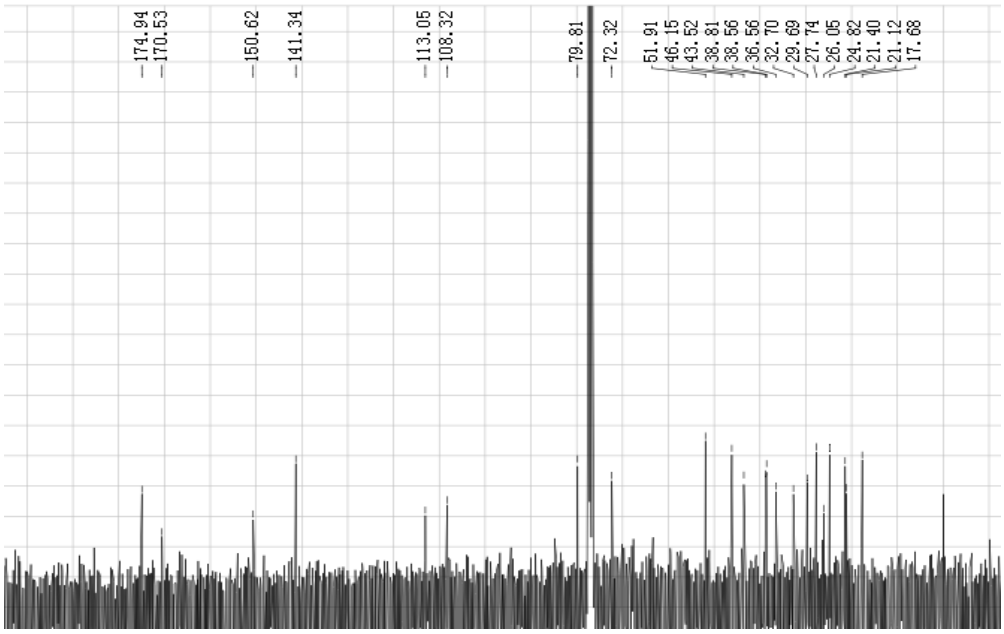


Figure S32. DEPT spectrum ($CDCl_3$, 75 MHz) of compound **6**.

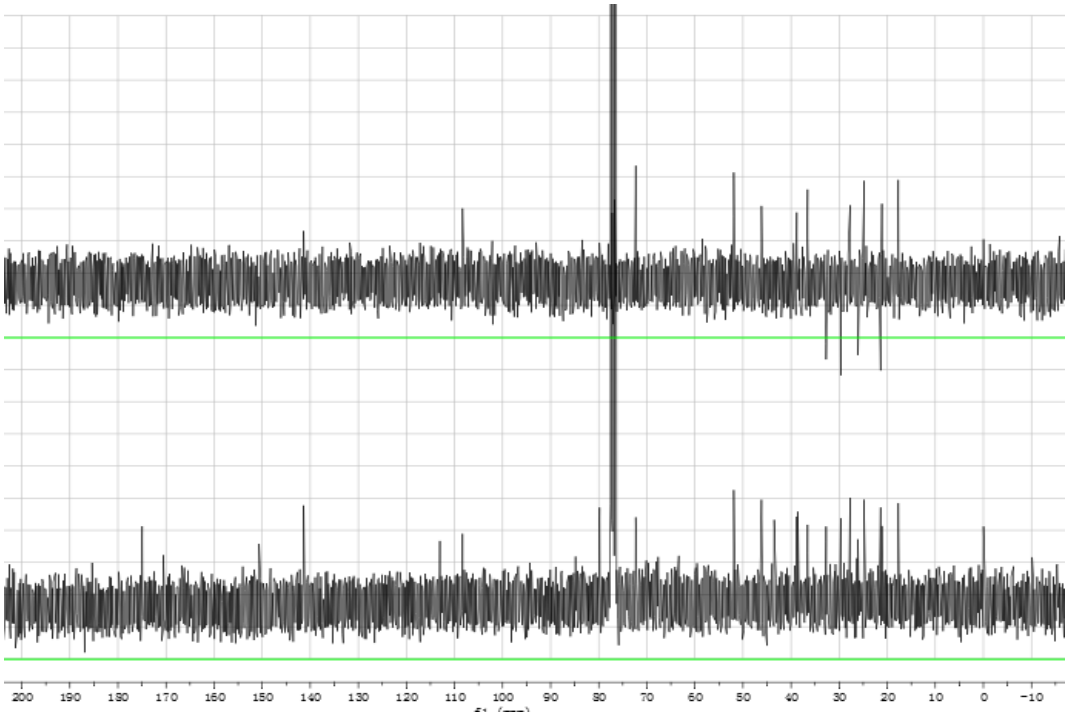


Figure S33. $^{1}H\square^{1}H$ COSY spectrum ($CDCl_3$) of compound **6**.

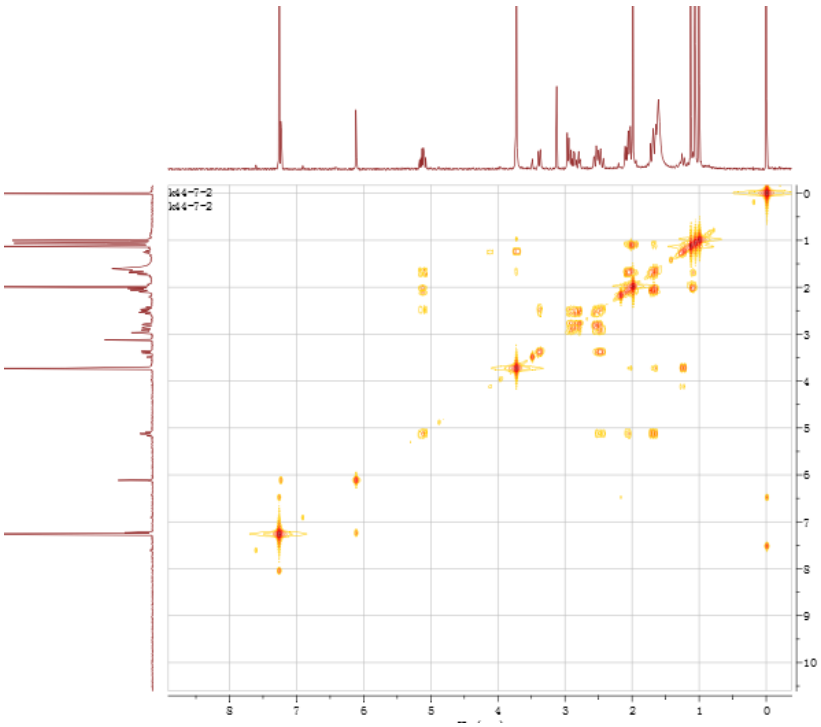


Figure S34. HSQC spectrum ($CDCl_3$) of compound **6**.

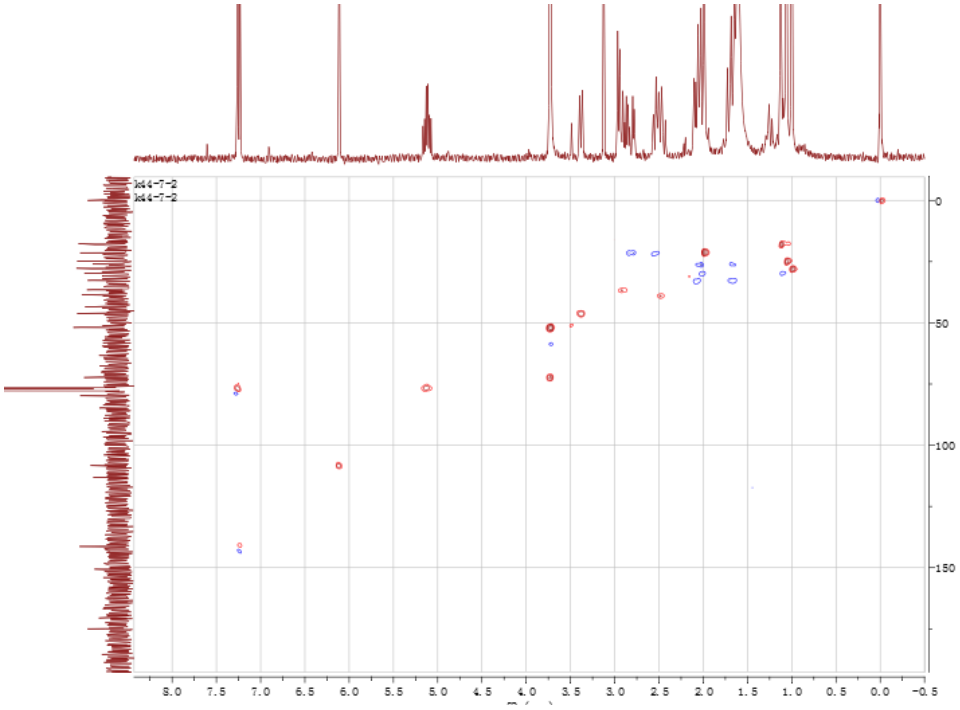


Figure S35. HMBC spectrum ($CDCl_3$) of compound **6**.

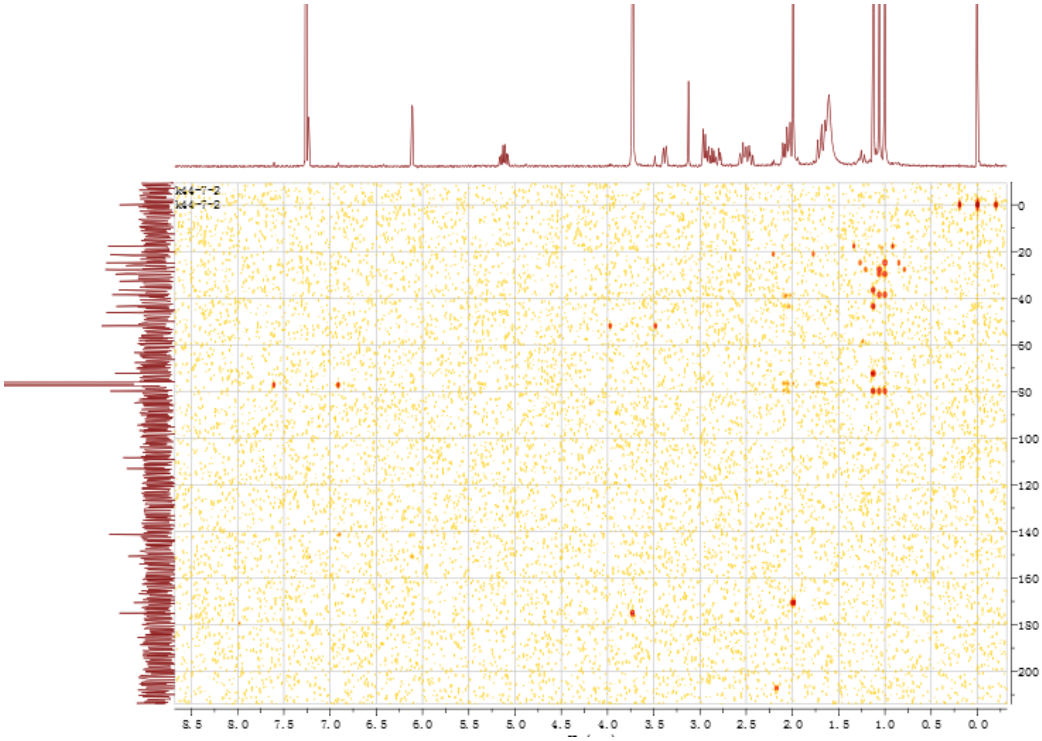


Figure S36. ^1H NMR spectrum (CD_3OD, 300 MHz) of compound **7**.

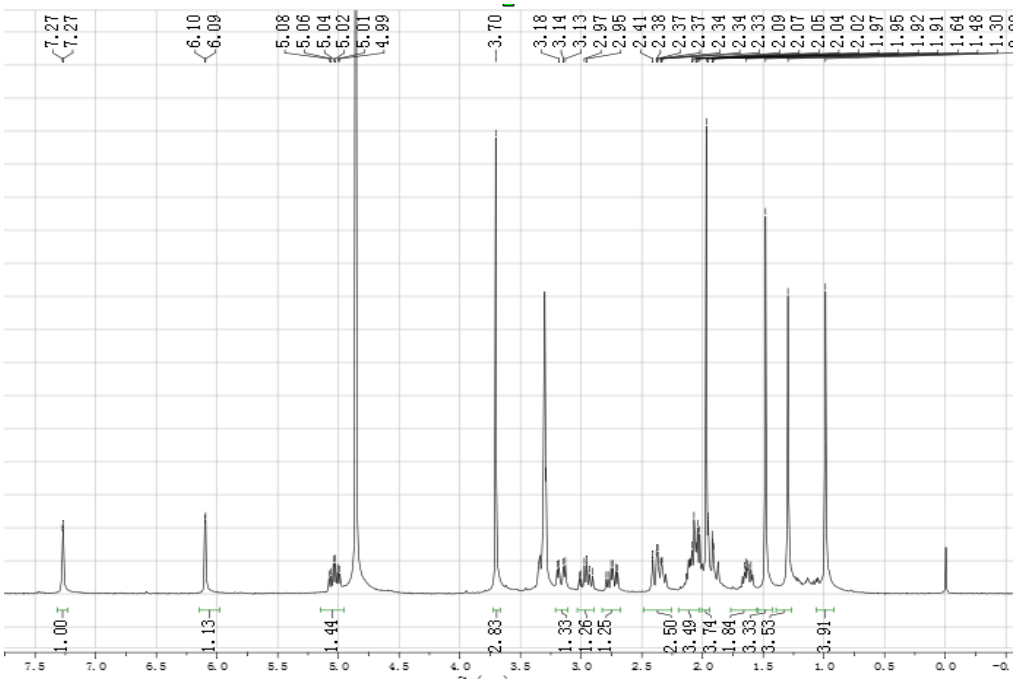


Figure S37. ^{13}C NMR spectrum (CD_3OD, 75 MHz) of compound **7**.

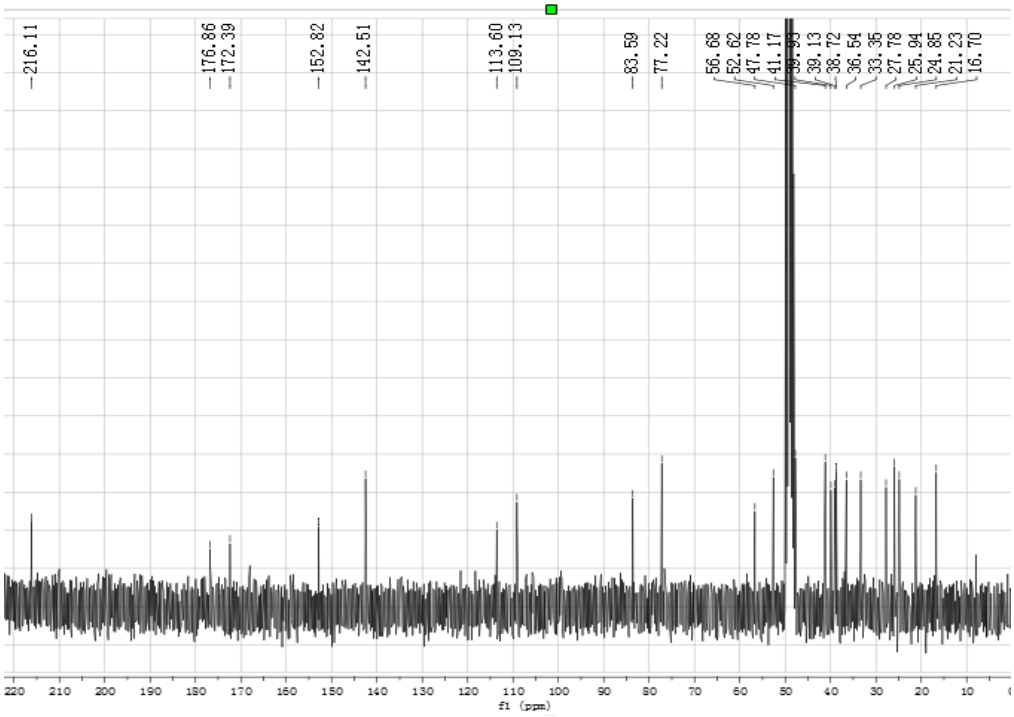


Figure S38. DEPT spectrum (CD_3OD, 75 MHz) of compound**7**.

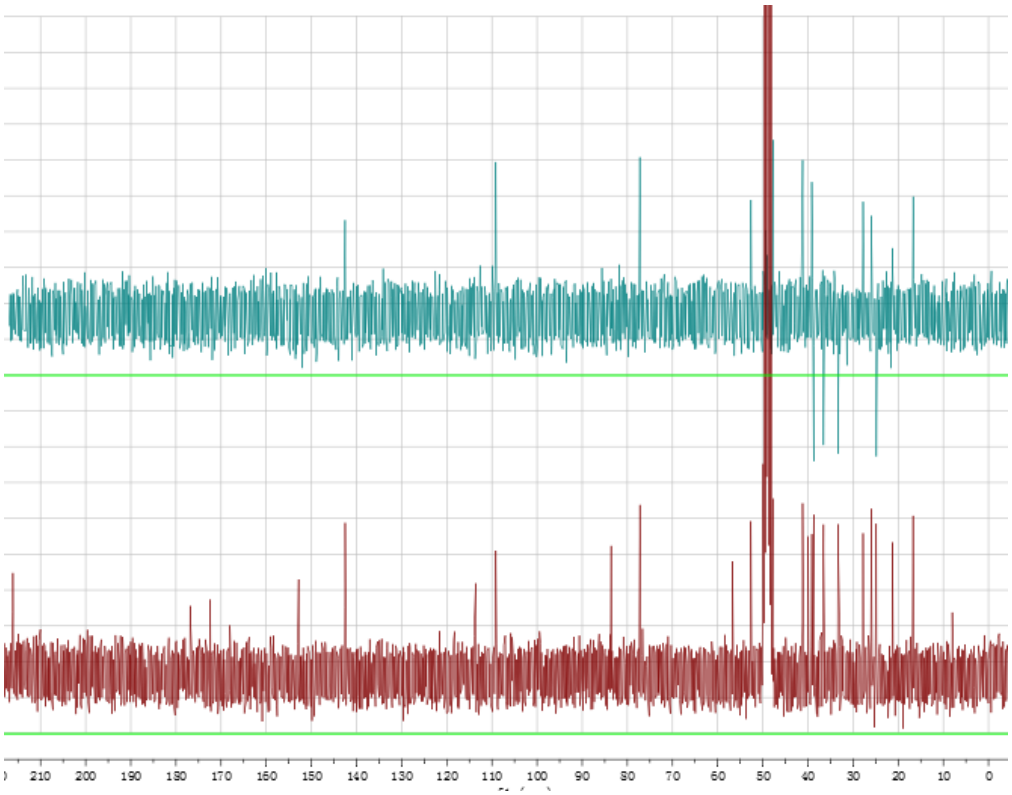


Figure S39. $^{1}H\square^{1}H$ COSY spectrum (CD_3OD) of compound **7**.

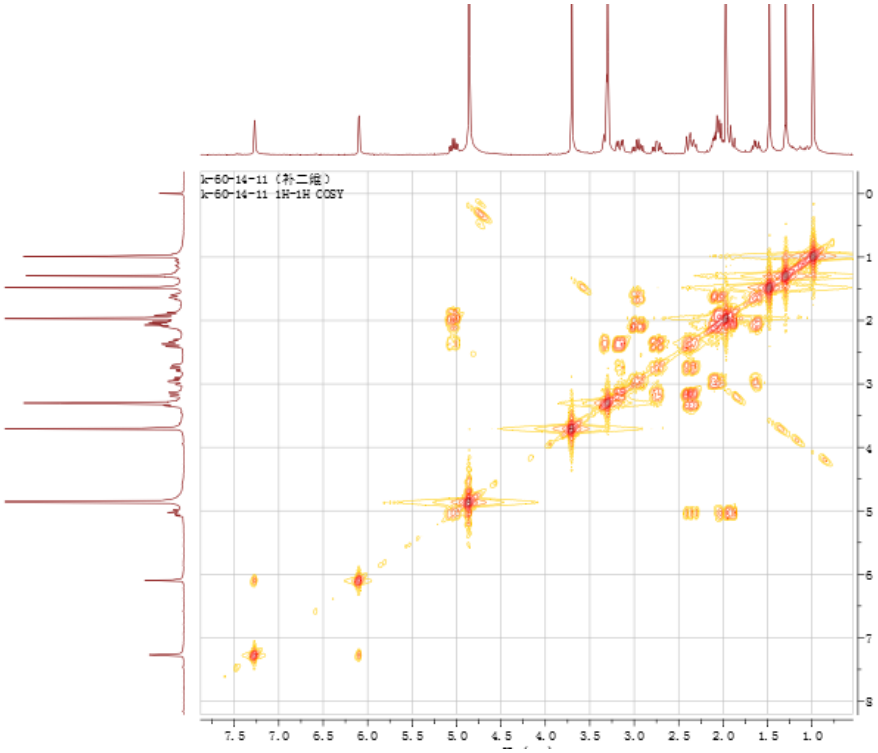


Figure S40. HSQC spectrum (CD_3OD) of compound **7**.

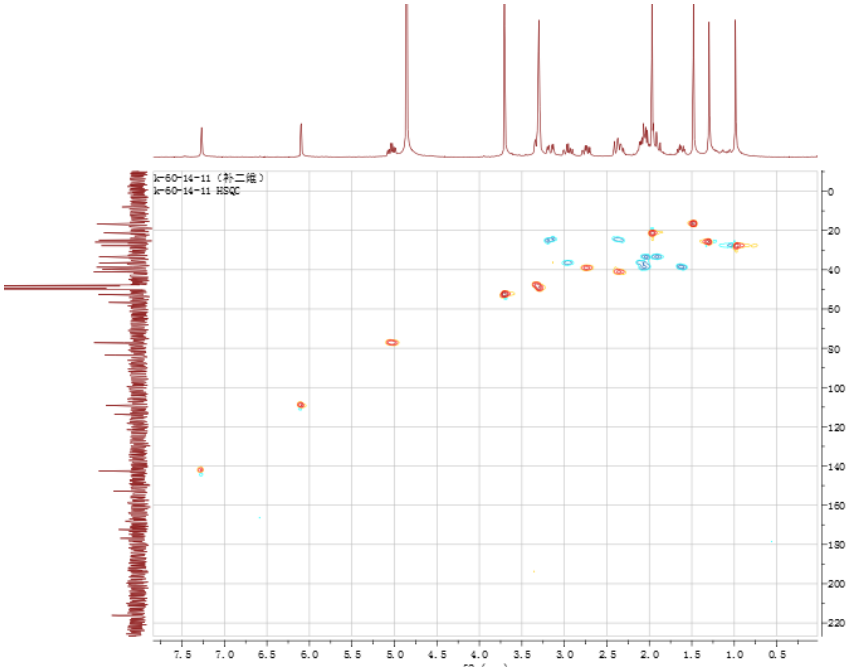


Figure S41. HMBC spectrum (CD_3OD) of compound **7**.

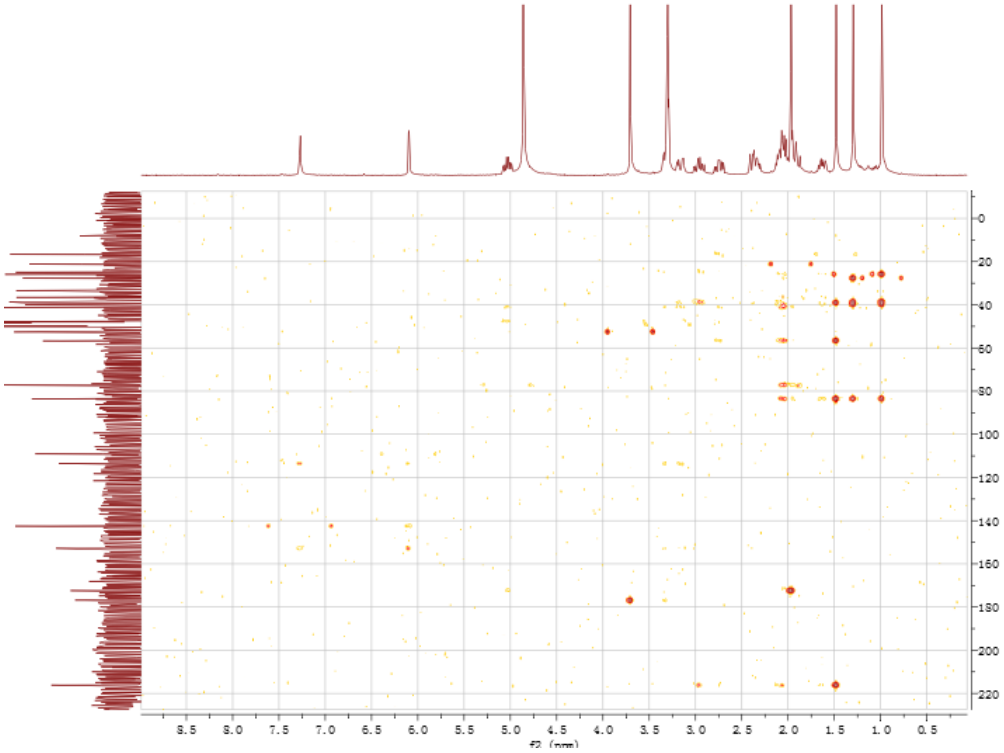


Figure S42. NOESY spectrum (CD_3OD) of compoun7.

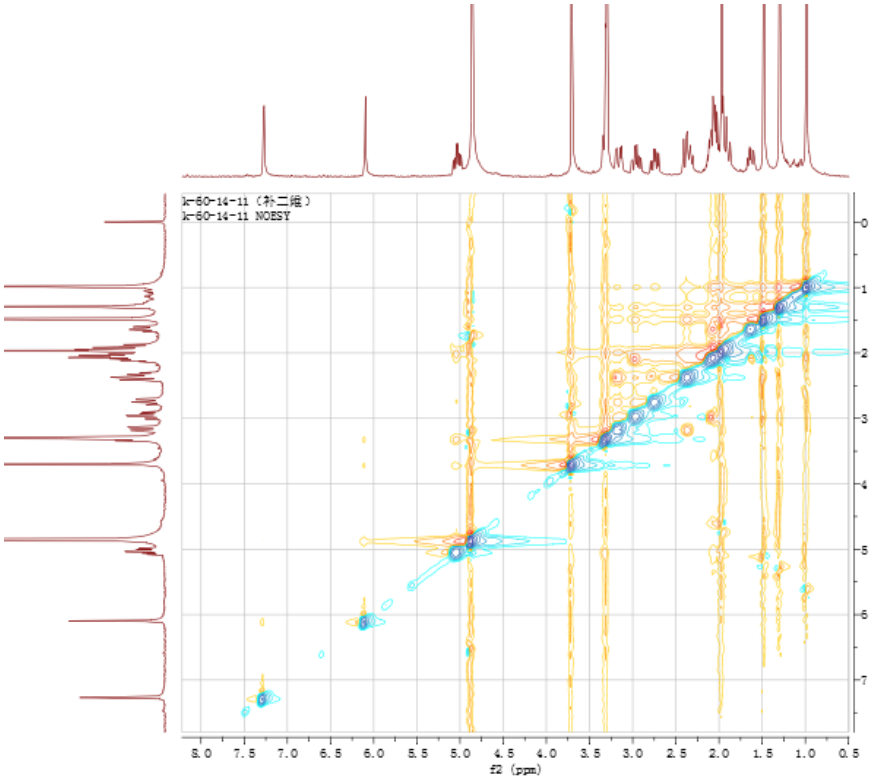


Figure S43. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of compound **8**.

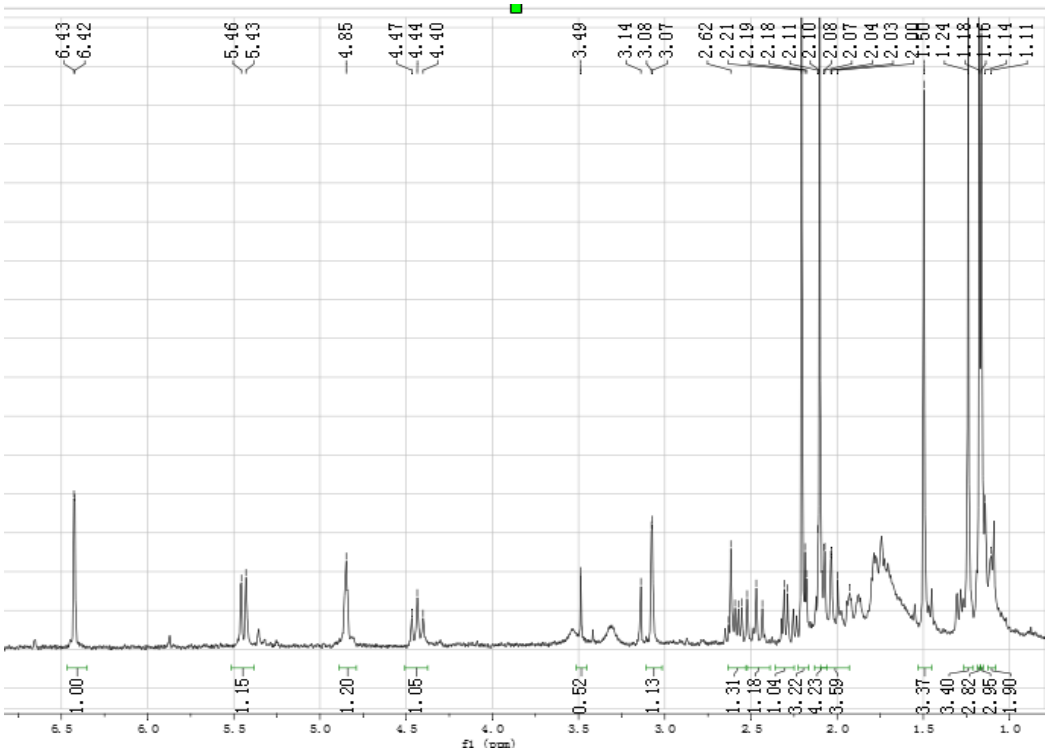


Figure S44. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of compound **8**.

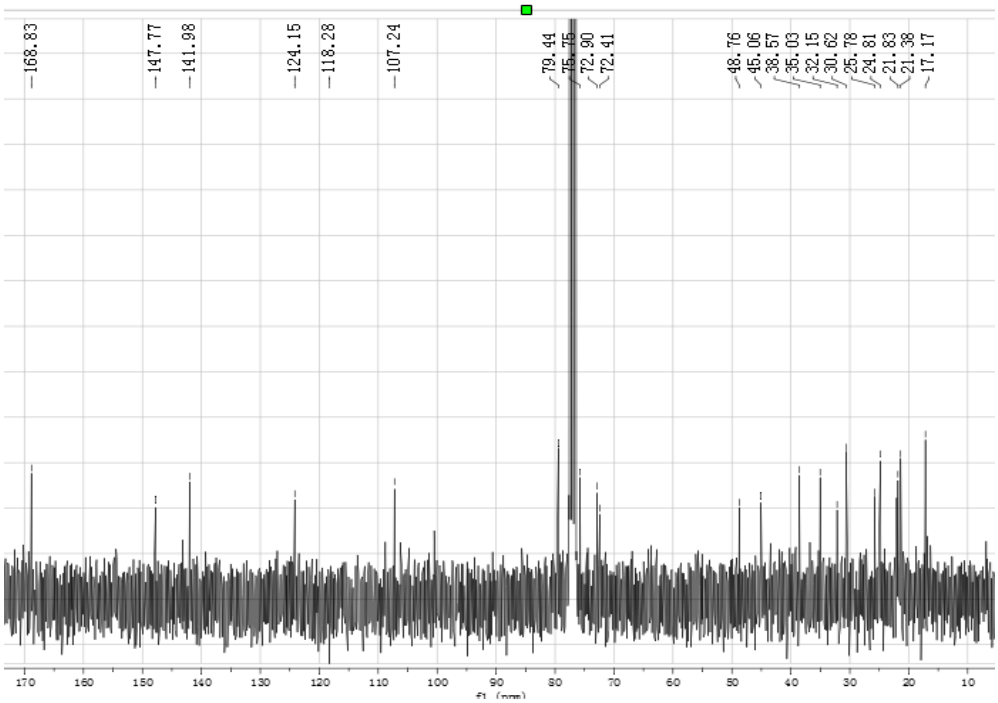


Figure S45. DEPT spectrum ($CDCl_3$, 75 MHz) of compound **8**.

Figure S46. ^1H□^1H COSY spectrum ($CDCl_3$) of compound **8**.

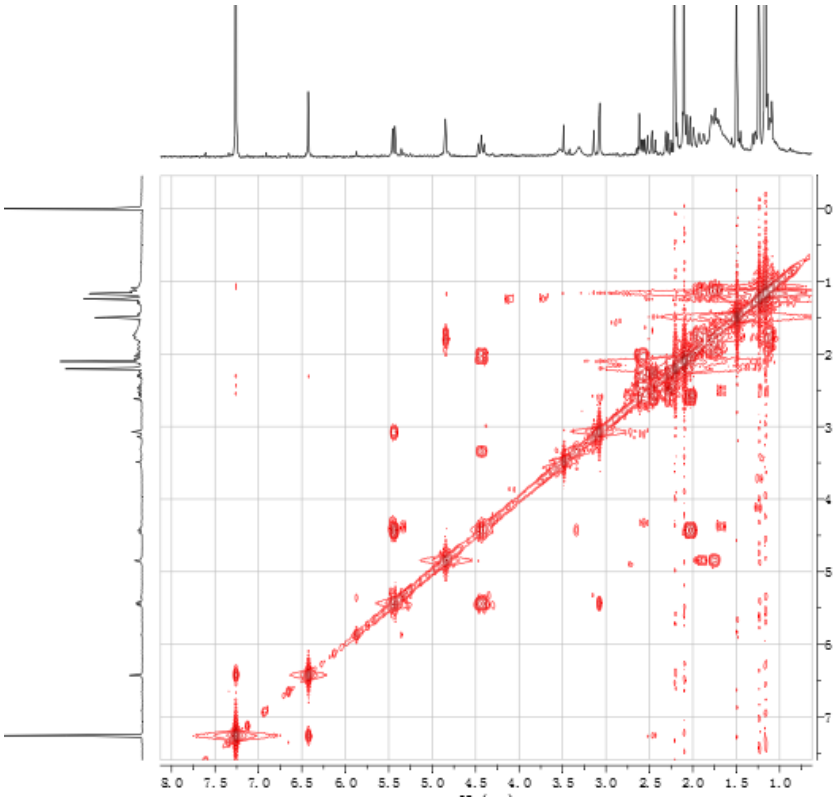


Figure S47. HSQC spectrum ($CDCl_3$) of compound **8**.

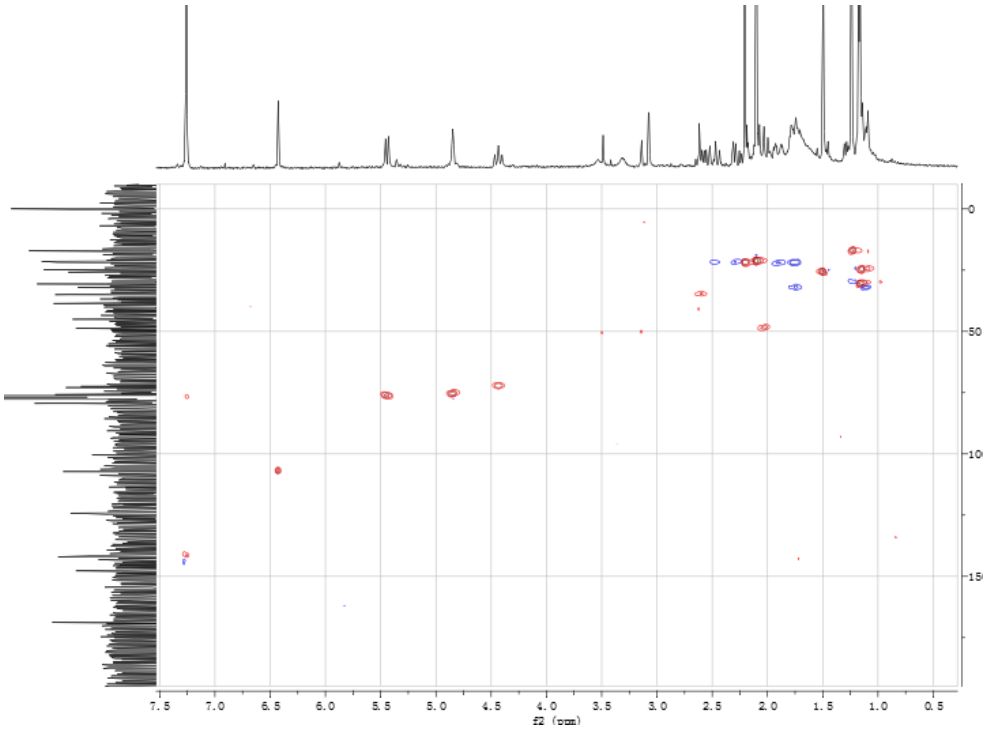


Figure S48. HMBC spectrum ($CDCl_3$) of compound **8**.

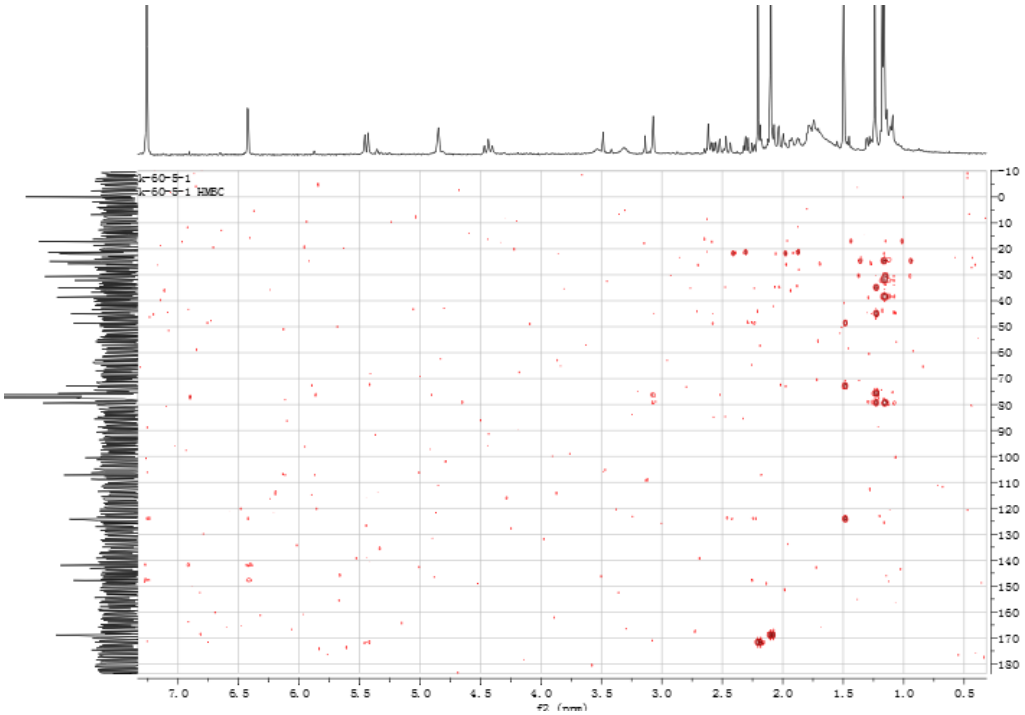


Figure S49. NOESY spectrum ($CDCl_3$) of compound **8**.

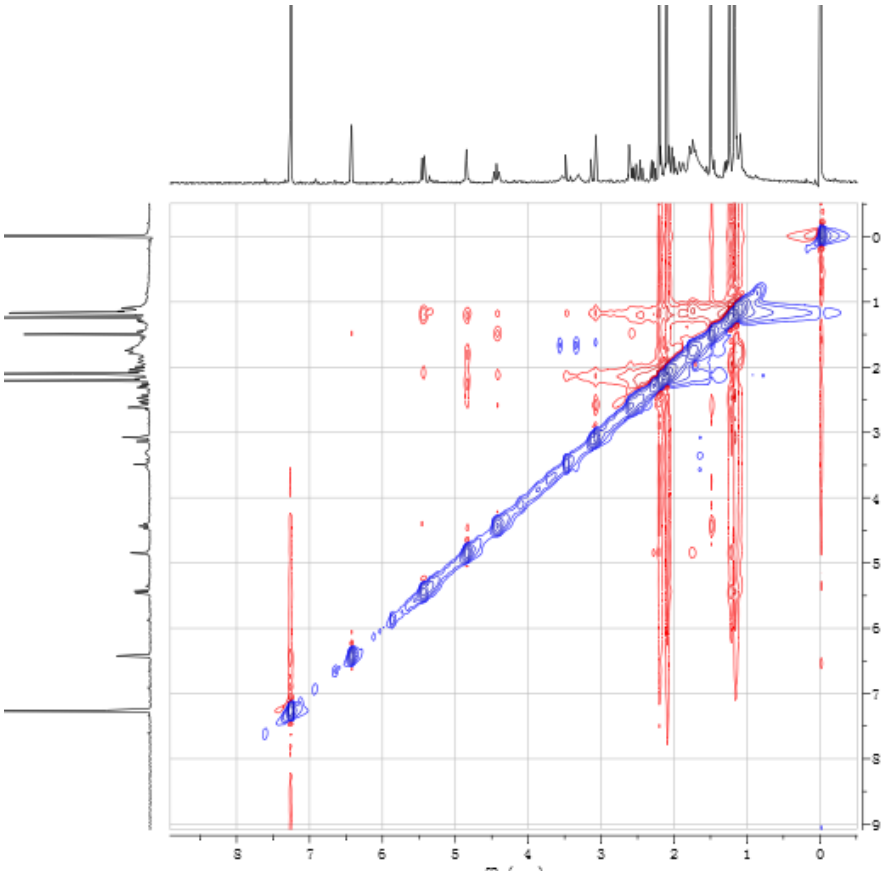


Figure S50. ^1H NMR spectrum (CD_3COCD_3, 300 MHz) of compound **9**.

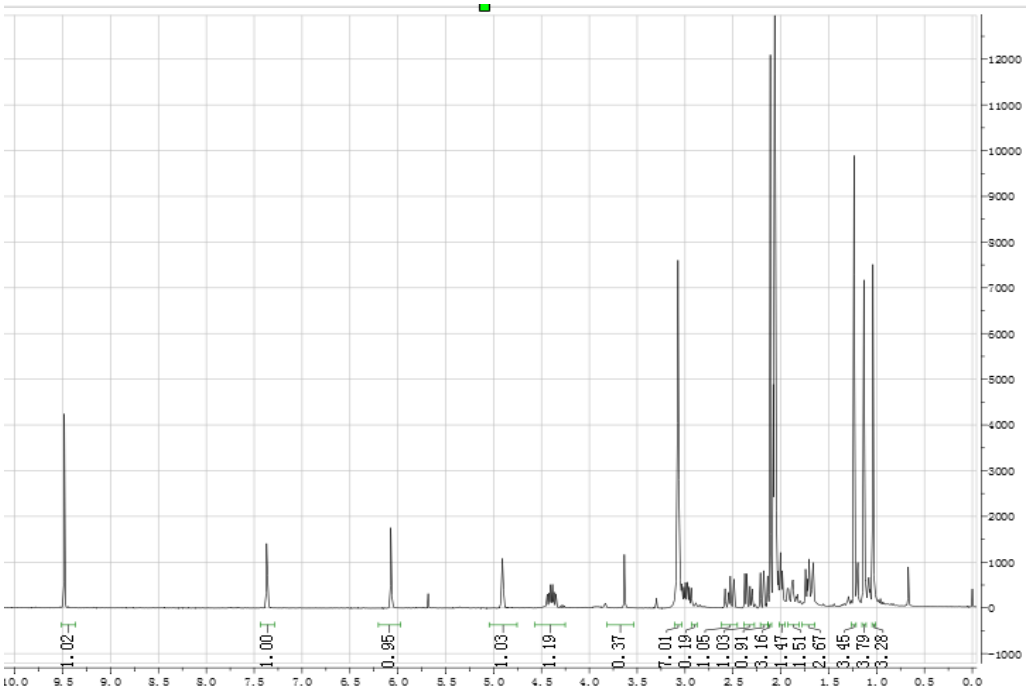


Figure S51. ^{13}C NMR spectrum (CD_3COCD_3, 75 MHz) of compound **9**.

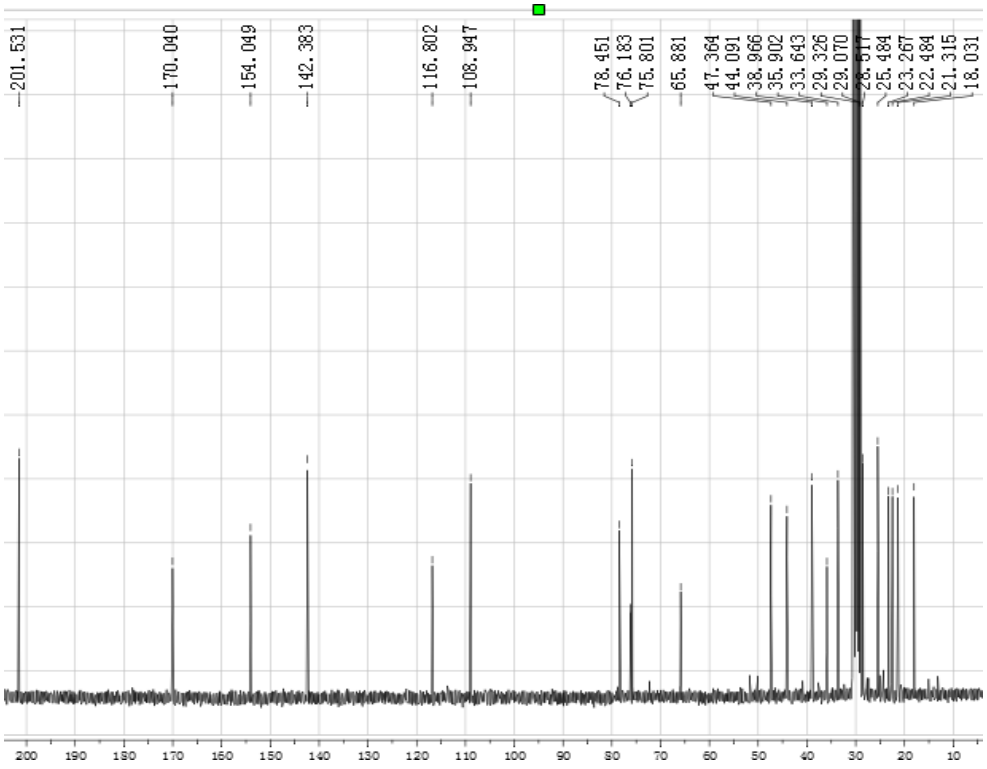


Figure S52. DEPT spectrum (CD_3COCD_3, 75 MHz) of compound **9**.

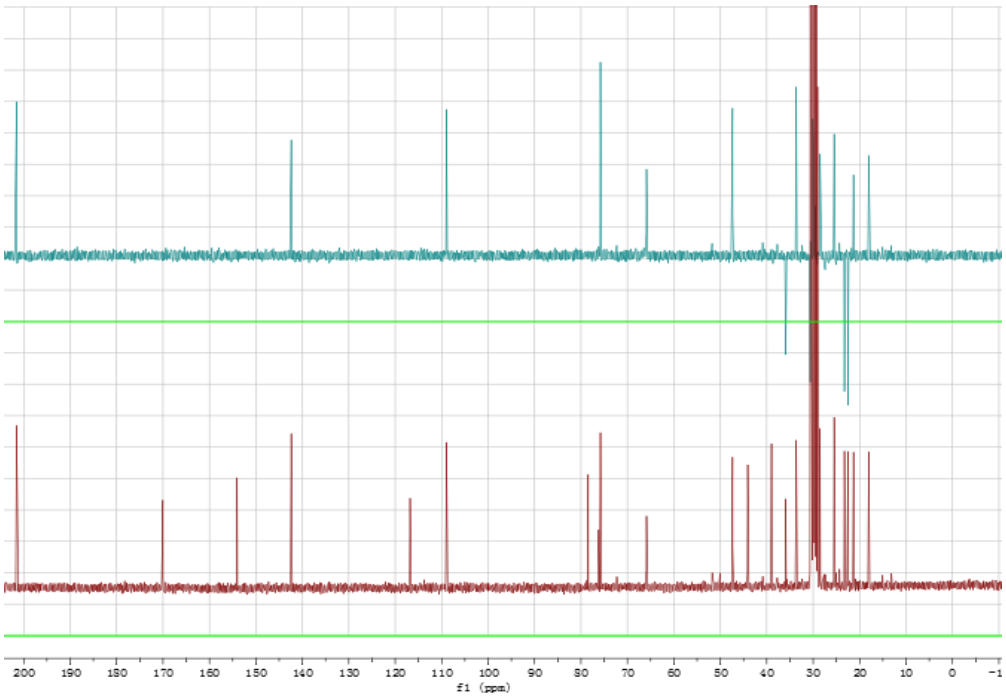


Figure S53. $^{1}H\square^{1}H$ COSY spectrum (CD_3COCD_3) of compound **9**.

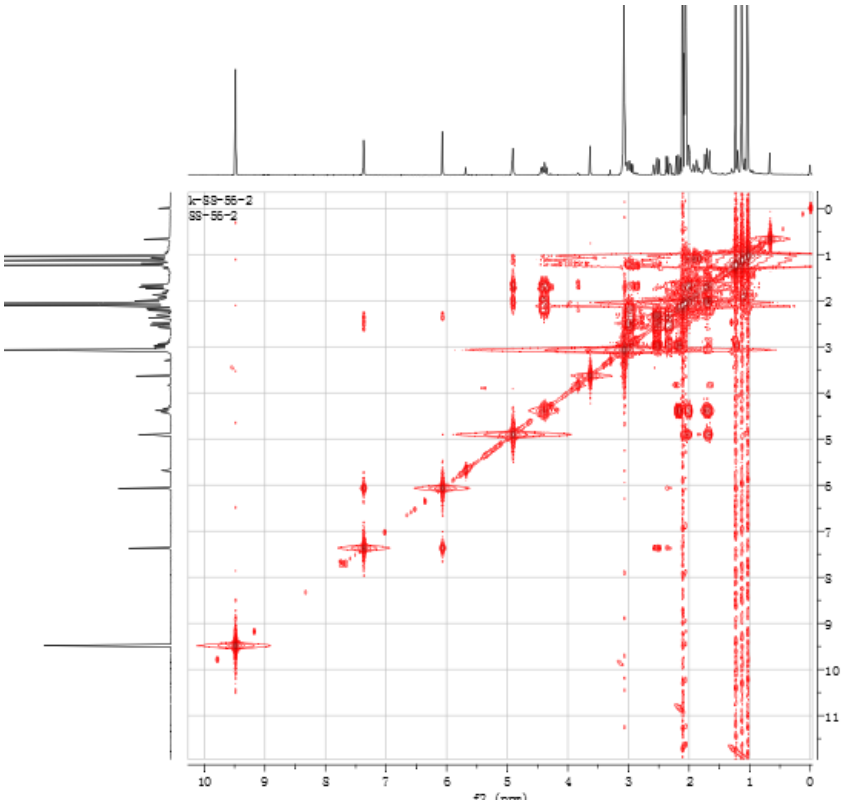


Figure S54. HSQC spectrum (CD_3COCD_3) of compound **9**.

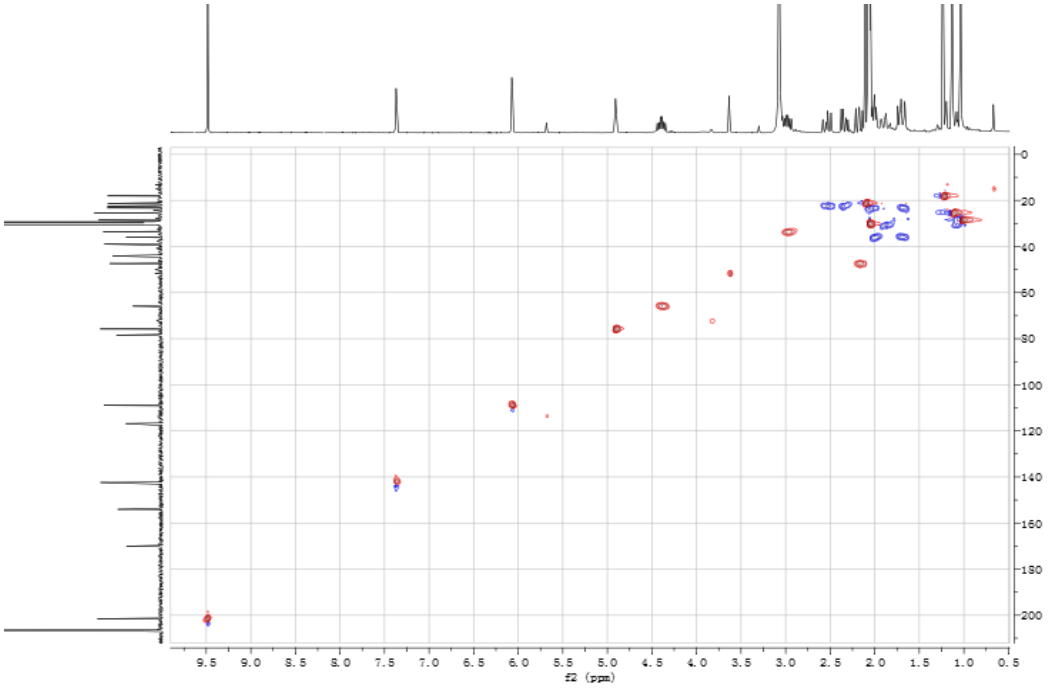


Figure S55. HMBC spectrum (CD_3COCD_3) of compound **9**.

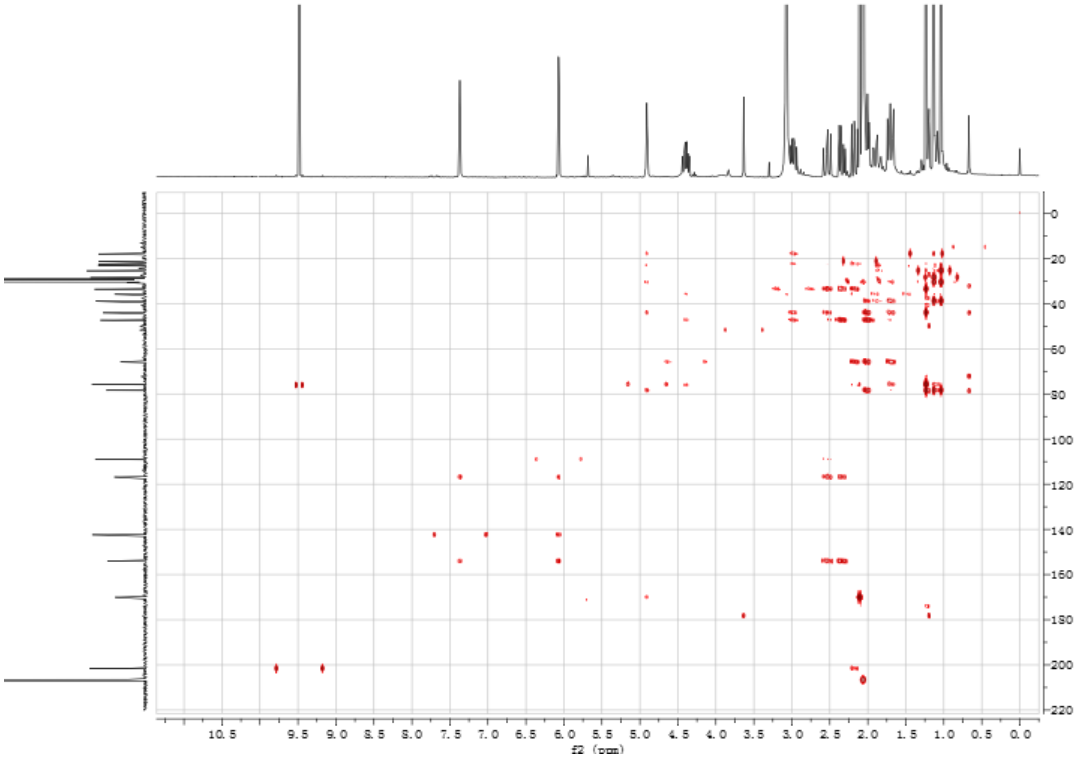


Figure S56. NOESY spectrum (CD_3COCD_3) of compound **9**.

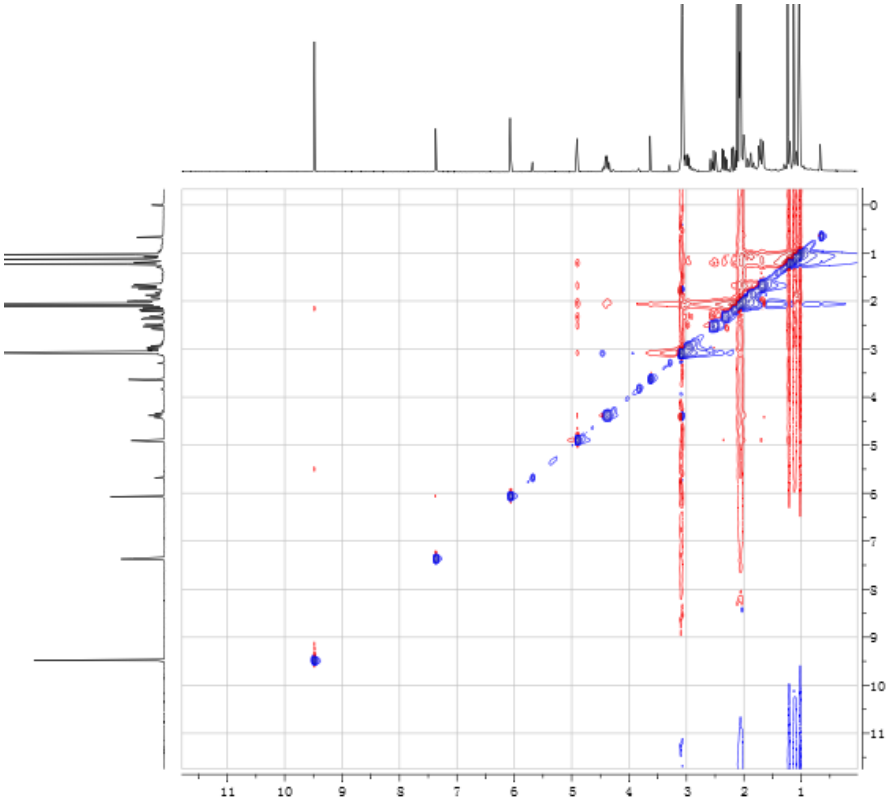


Figure S57. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of compound **10**.

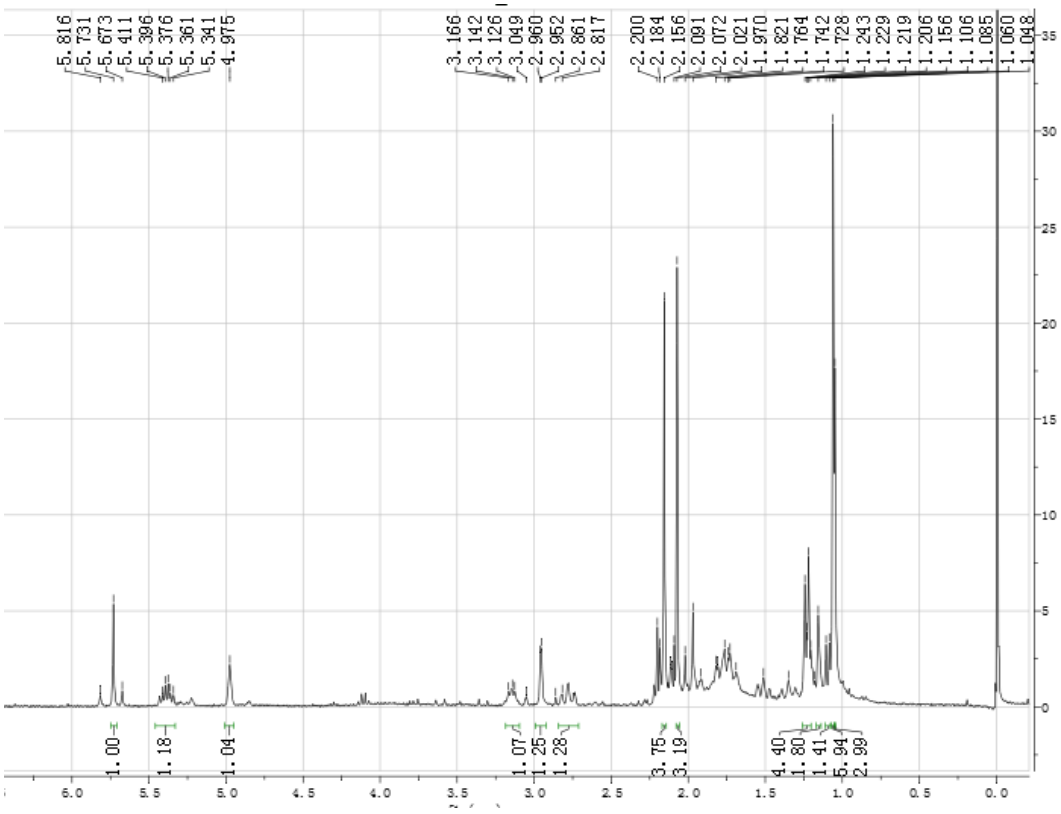


Figure S58. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of compound **10**.

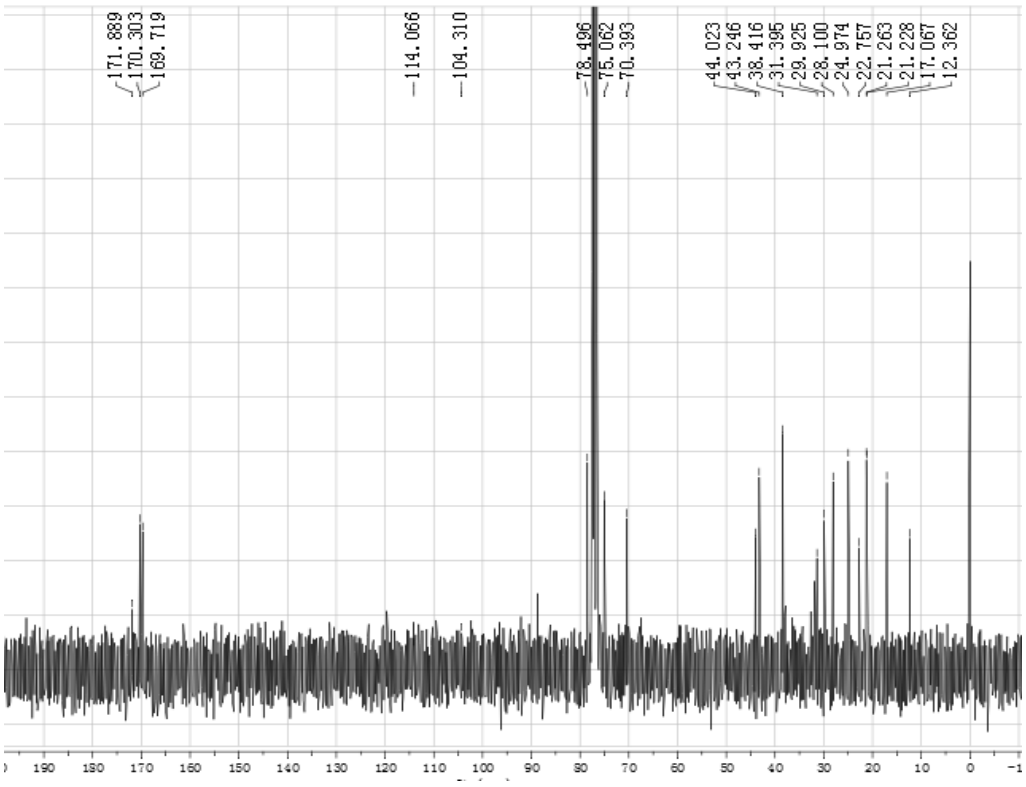


Figure S59. DEPT spectrum ($CDCl_3$, 75 MHz) of compound **10**.

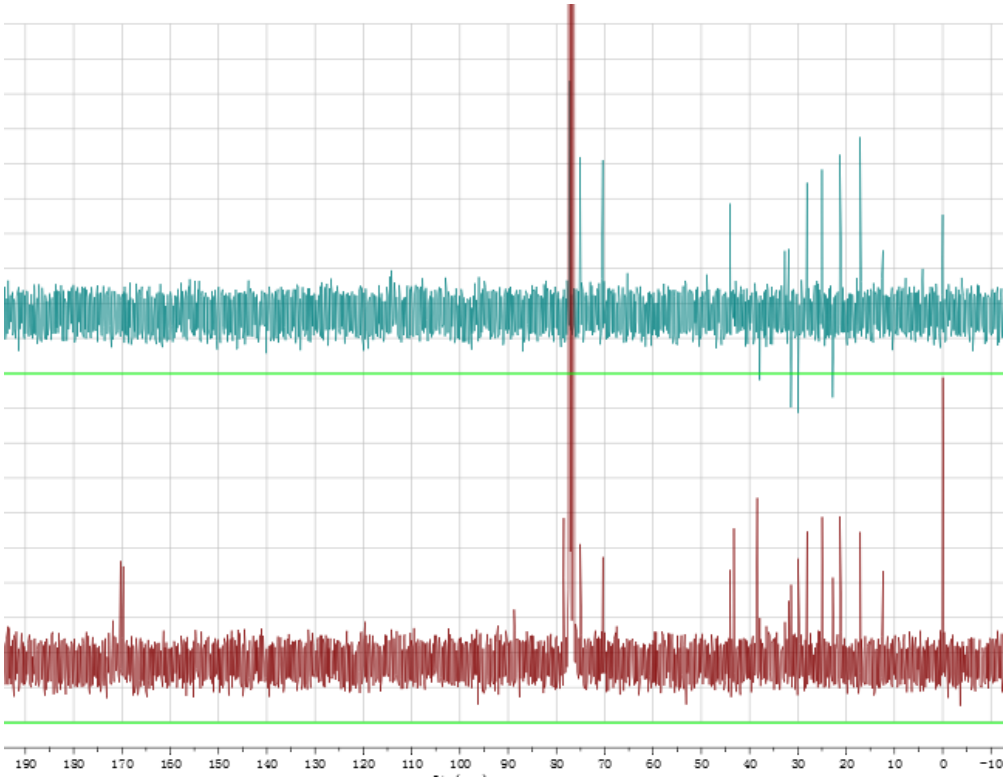


Figure S60. ^1H□^1H COSY spectrum ($CDCl_3$) of compound **10**.

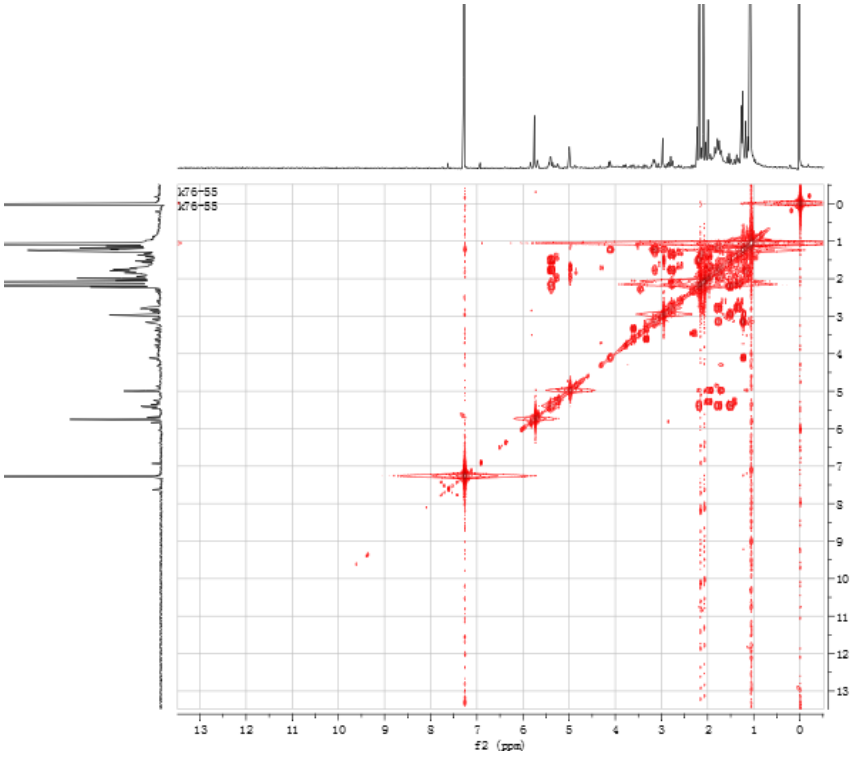


Figure S61. HSQC spectrum ($CDCl_3$) of compound **10**.

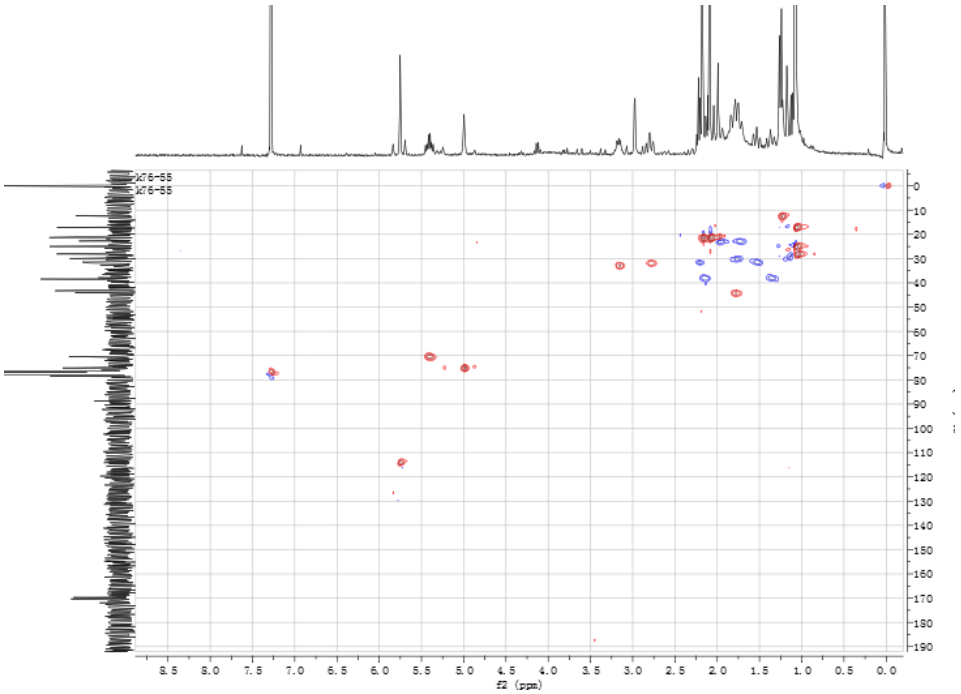


Figure S62. HMBC spectrum ($CDCl_3$) of compound **10**.

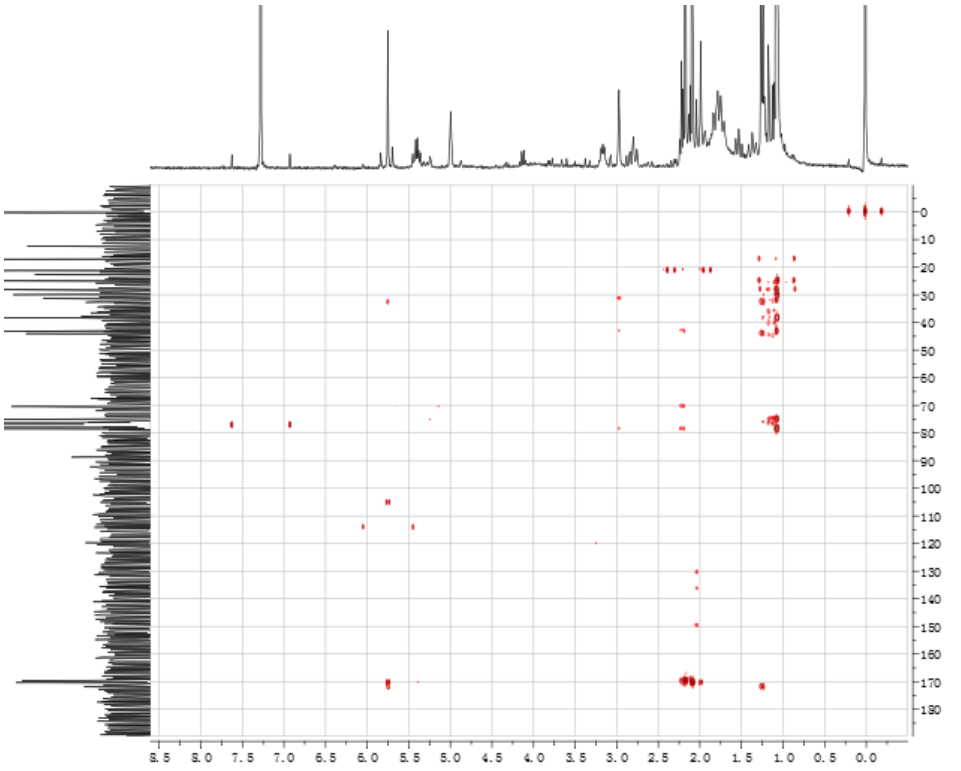


Figure S63. NOESY spectrum ($CDCl_3$) of compound **10**.

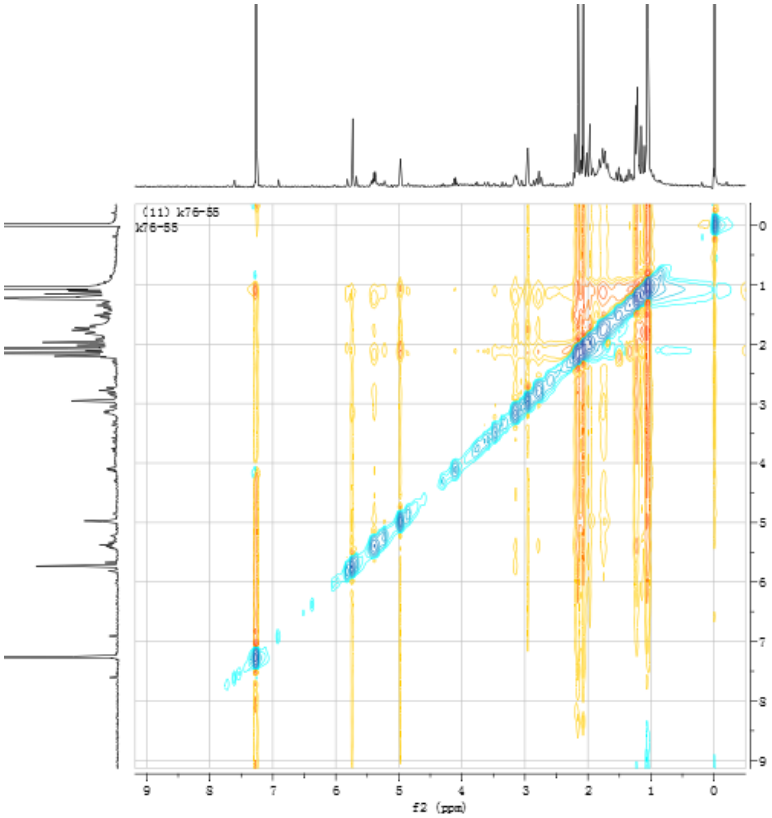


Figure S64. ^1H NMR spectrum ($CDCl_3$, 300 MHz) of compound **11**.

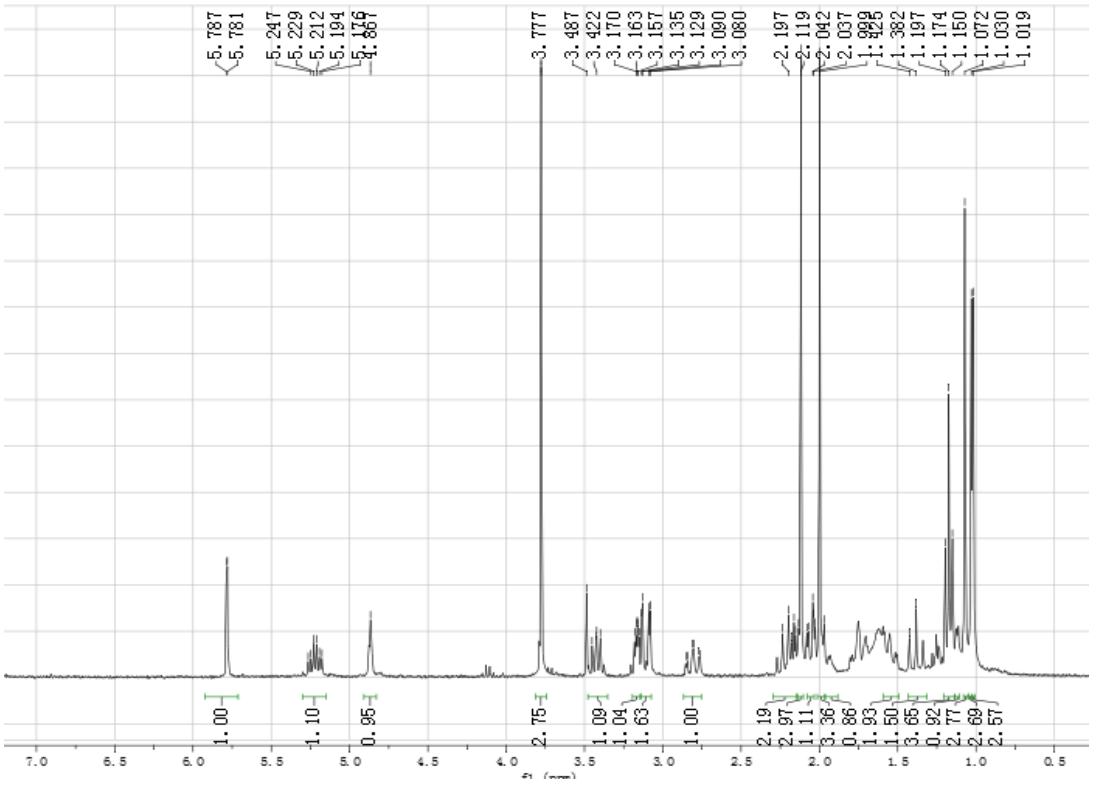


Figure S65. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of compound **11**.

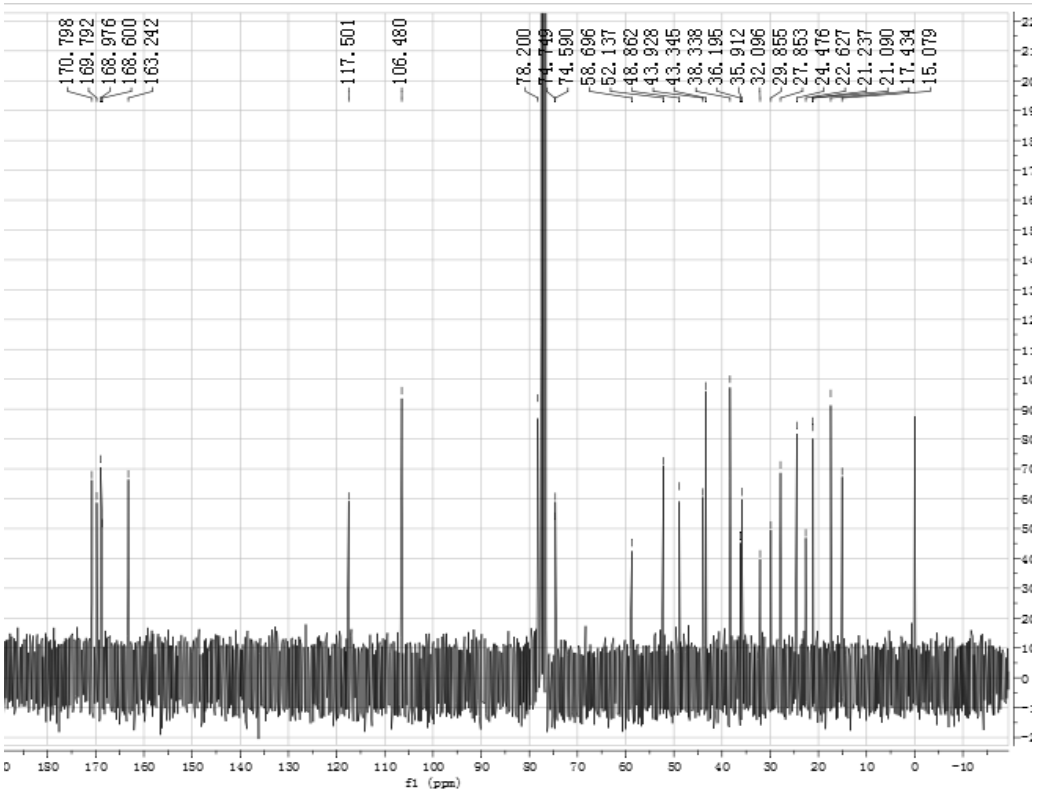


Figure S66. DEPT spectrum ($CDCl_3$, 75 MHz) of compound **11**.

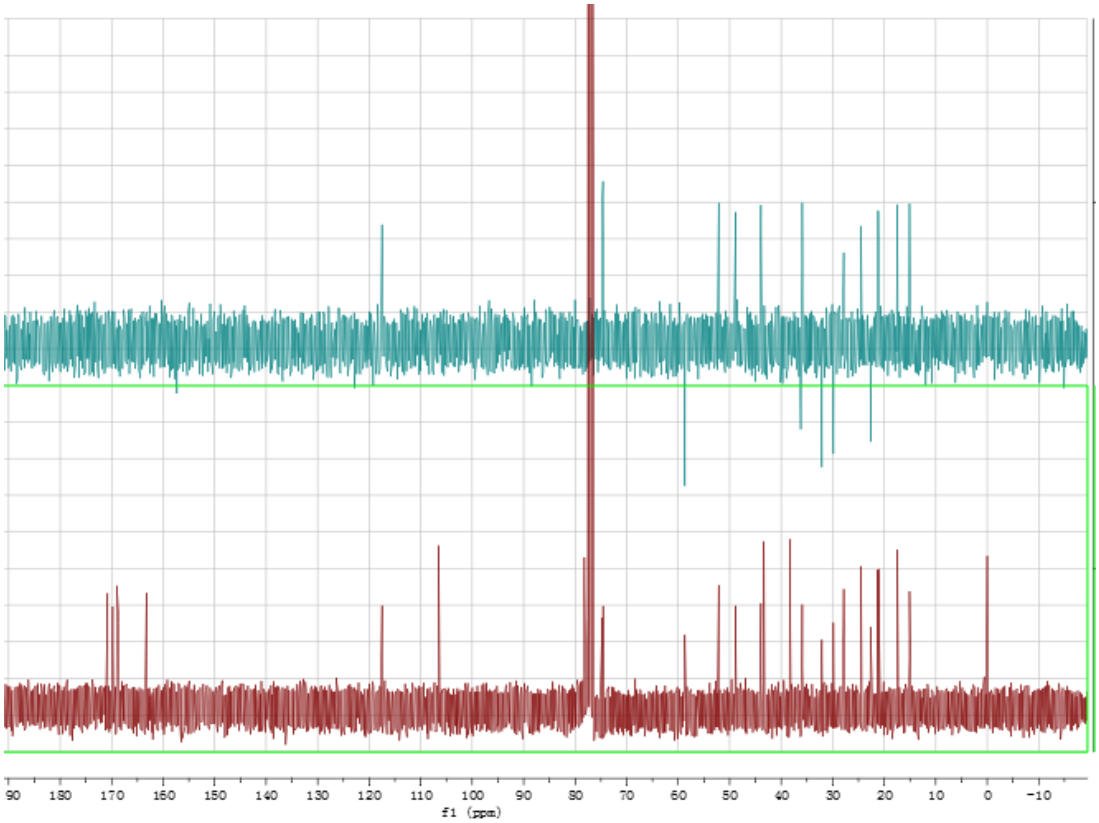


Figure S67. $^{1}H\square^{1}H$ COSY spectrum ($CDCl_3$) of compound **11**.

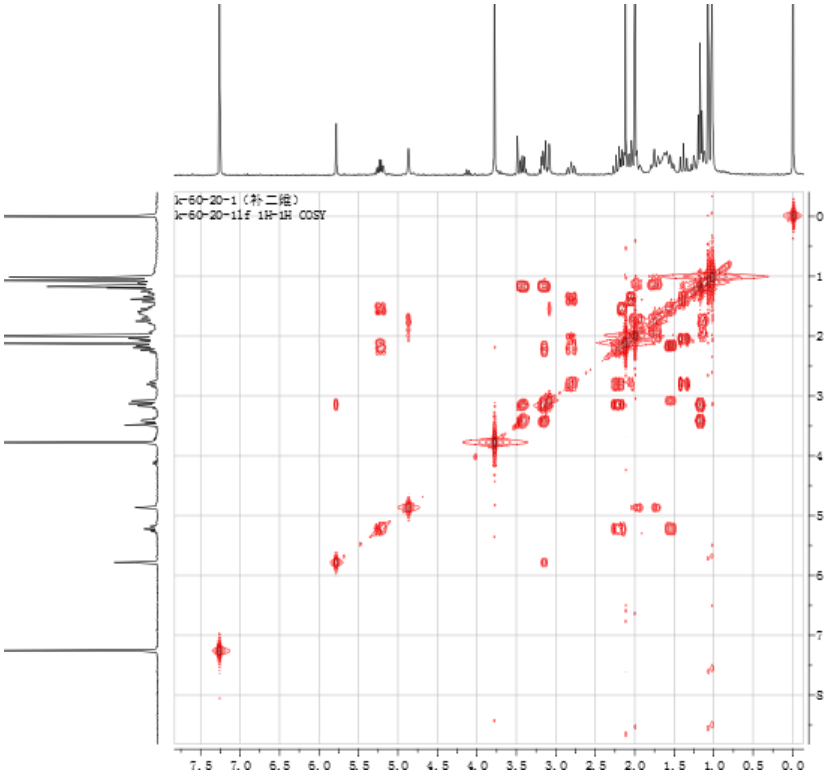


Figure S68. HSQC spectrum ($CDCl_3$) of compound **11**.

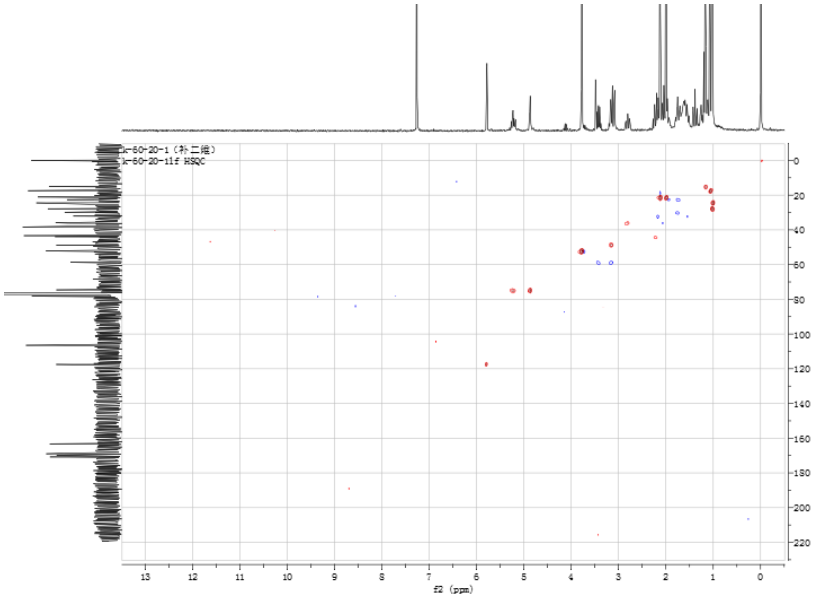


Figure S69. HMBC spectrum ($CDCl_3$) of compound **11**.

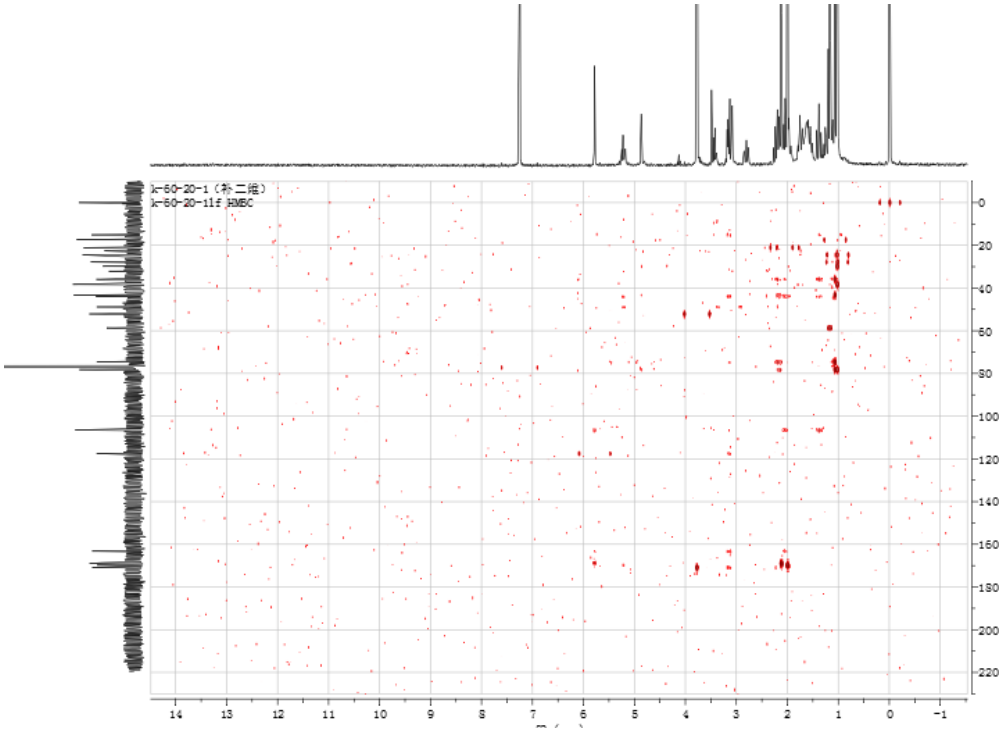
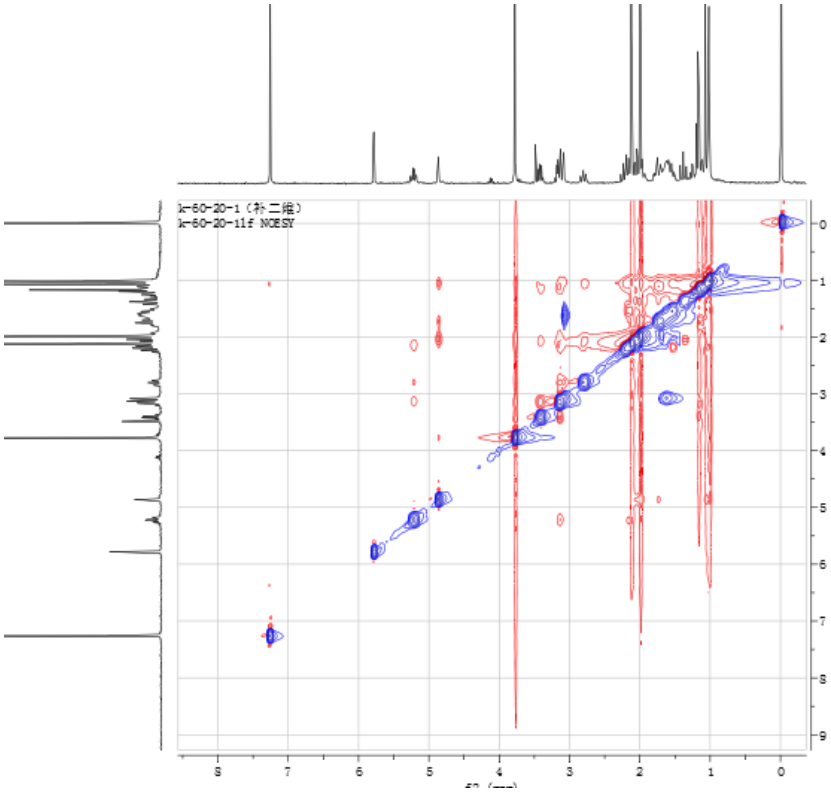


Figure S70. NOESY spectrum ($CDCl_3$) of compound **11**.



COX-2 inhibition by diterpenoids from the seeds of *Caesalpinia minax*

Compound **1-23** was evaluated for COX-2 inhibitory activity using an enzyme immunoassay (EIA) kit (catalog no. 560131, Cayman Chemical, Ann Arbor, MI) according to the manufacturer's instructions. Briefly, reactions mixtures were prepared Tris–HCl buffer and COX-2, and the reaction was initiated by the addition of arachidonic acid. After 2 min, the reaction was terminated by adding HCl, and PGE2 was quantitated by an ELISA method. The test compound was dissolved in DMSO and final concentration was 4 μM. Following transfer to a 96-well plate coated with a mouse anti-rabbit IgG, the tracer prostaglandin acetylcholine esterase and primary antibody (mouse anti PGE2) were added. Plates were then incubated at room temperature overnight, reaction mixtures were removed, and wells were washed. Ellman's reagent was added to each well and the plate was incubated for about 60 min, until the control wells yielded an OD = 0.3-0.8 at 412 nm. Results were expressed as a percentage relative to a control (solvent-treated samples). All determinations were performed in duplicate, and values generally agreed within 10%.

After evaluation at 4.0 μM, the most potent compounds **23** and **16** were further tested at a series concentration. The dose dependent inhibition rate was shown in Fig. S71. The IC_{50} values 2.4±0.1μM and 3.2±0.2 for **23** and **16**, respectively were calculated from the curves. Compounds **23** and **16** with a lactone ring are stronger than other tetracyclic furanoditerpenoids. The most potent tetracyclic furanoditerpenoid is compound **1** with an inhibition rate 67.8% at 4.0 μM and IC_{50}=3.5±0.2μM.

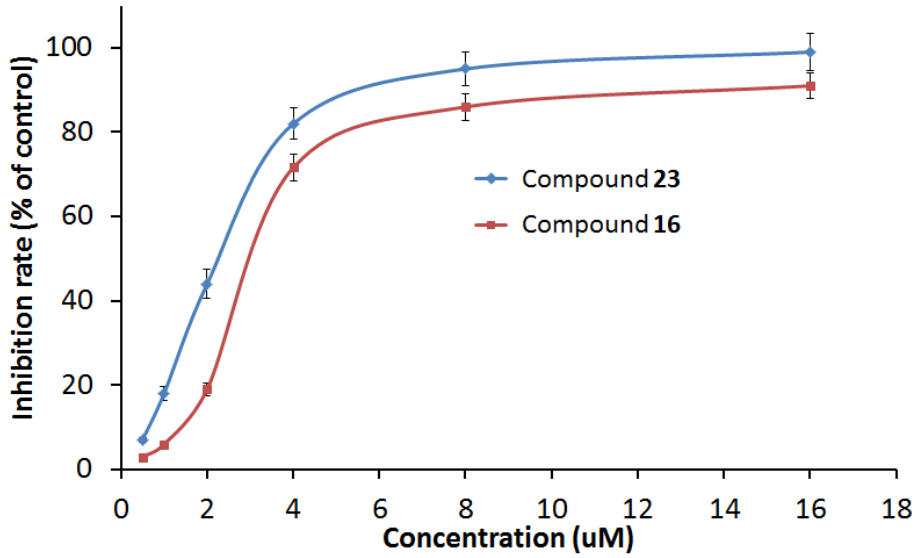


Figure S71. Dose-dependent curves for the inhibition of COX-2 by compounds 23 and 16.