

Supporting Information

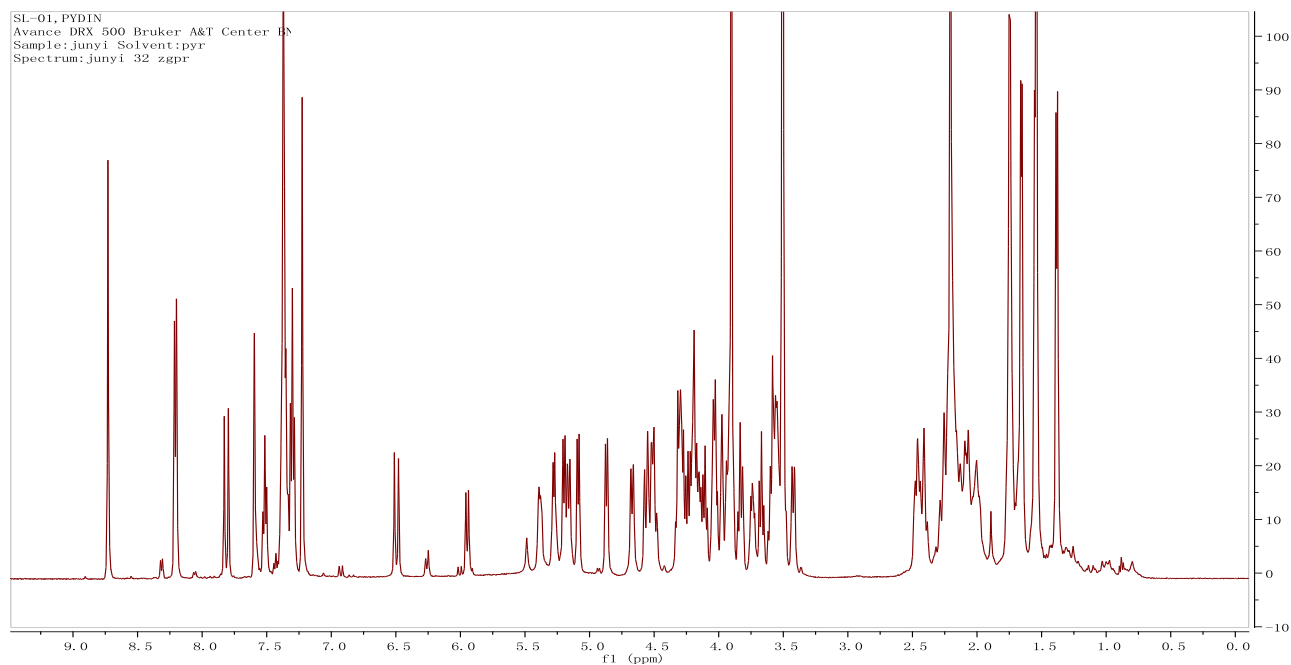


Figure S1. ^1H -NMR (500 MHz) spectrum of **1** in Pyridine- d_5 .

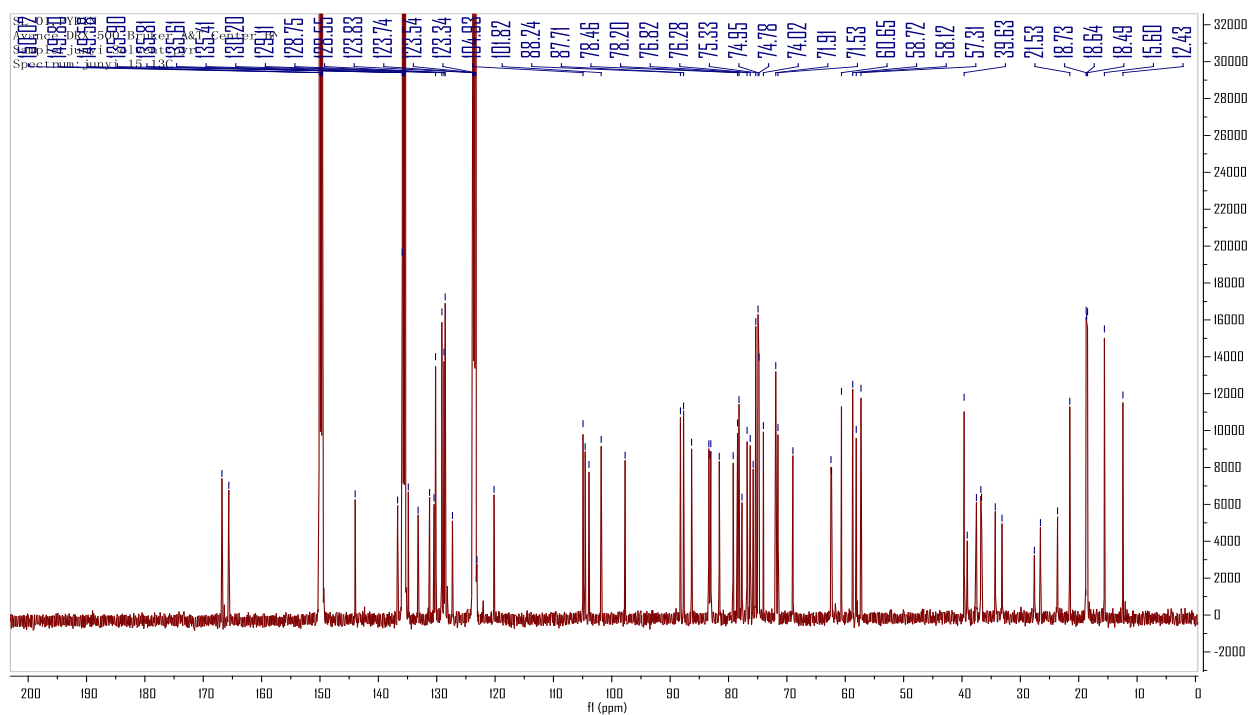


Figure S2. ^{13}C -NMR (125 MHz) spectrum of **1** in Pyridine- d_5 .

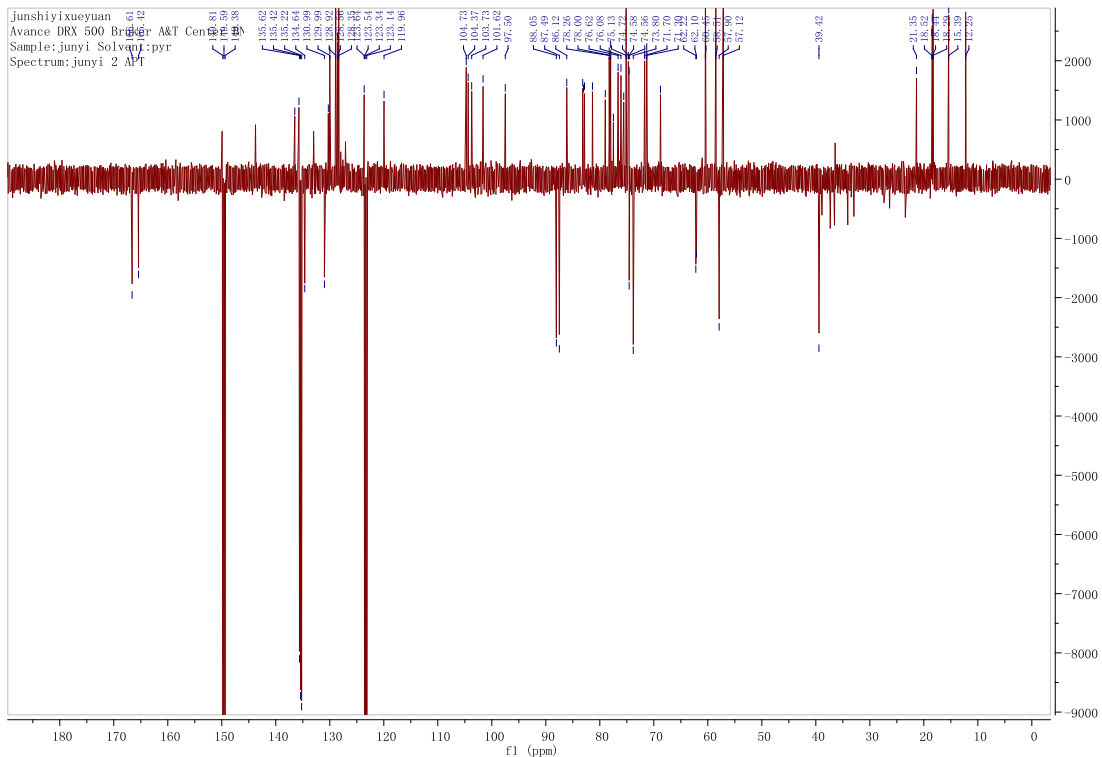


Figure S3. APT (500 MHz) spectrum of **1** in Pyridine-*d*₅.

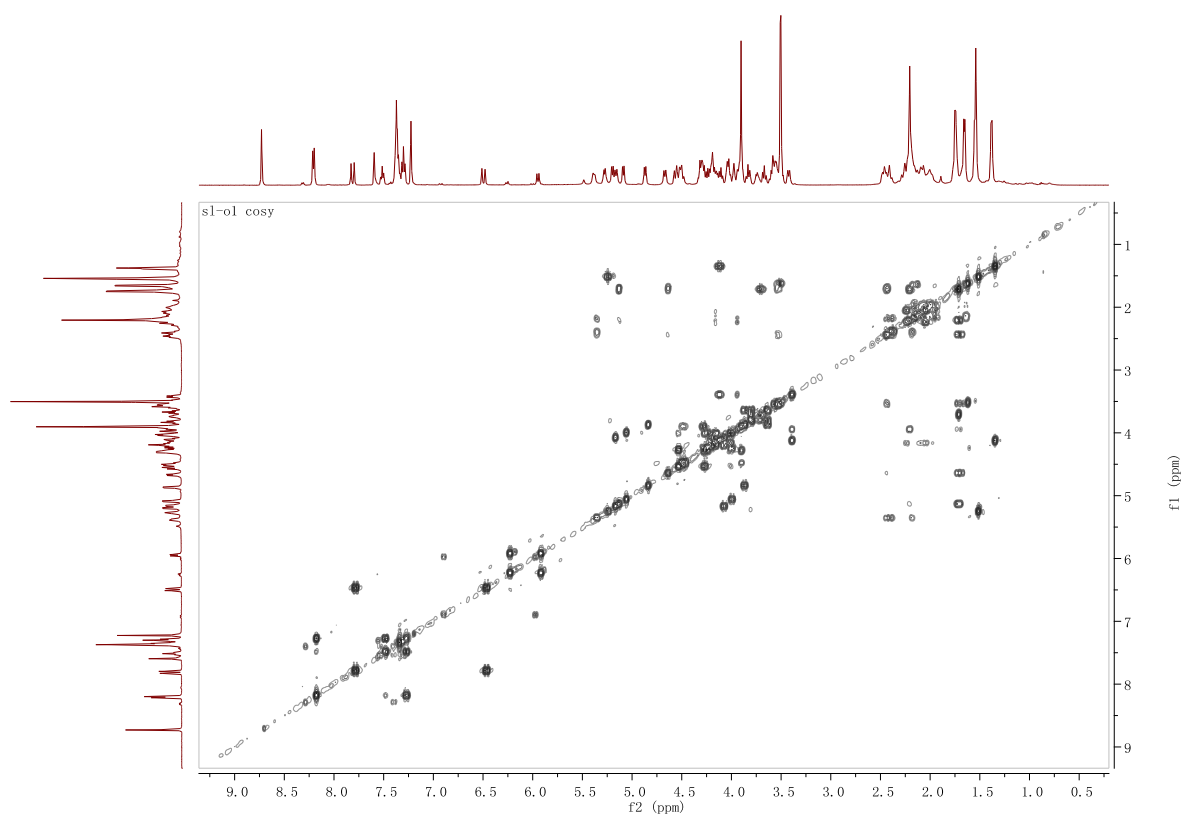


Figure S4. COSY (500 MHz) spectrum of **1** in Pyridine-*d*₅.

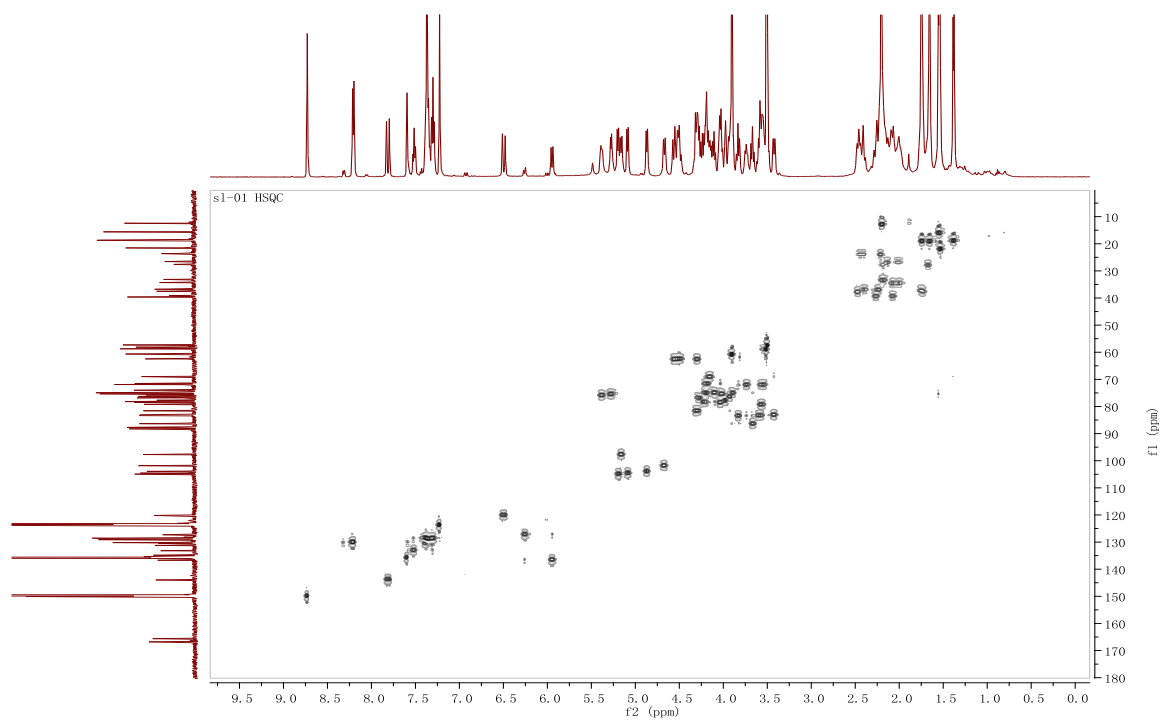


Figure S5. HSQC (500 MHz) spectrum of **1** in Pyridine-*d*₅.

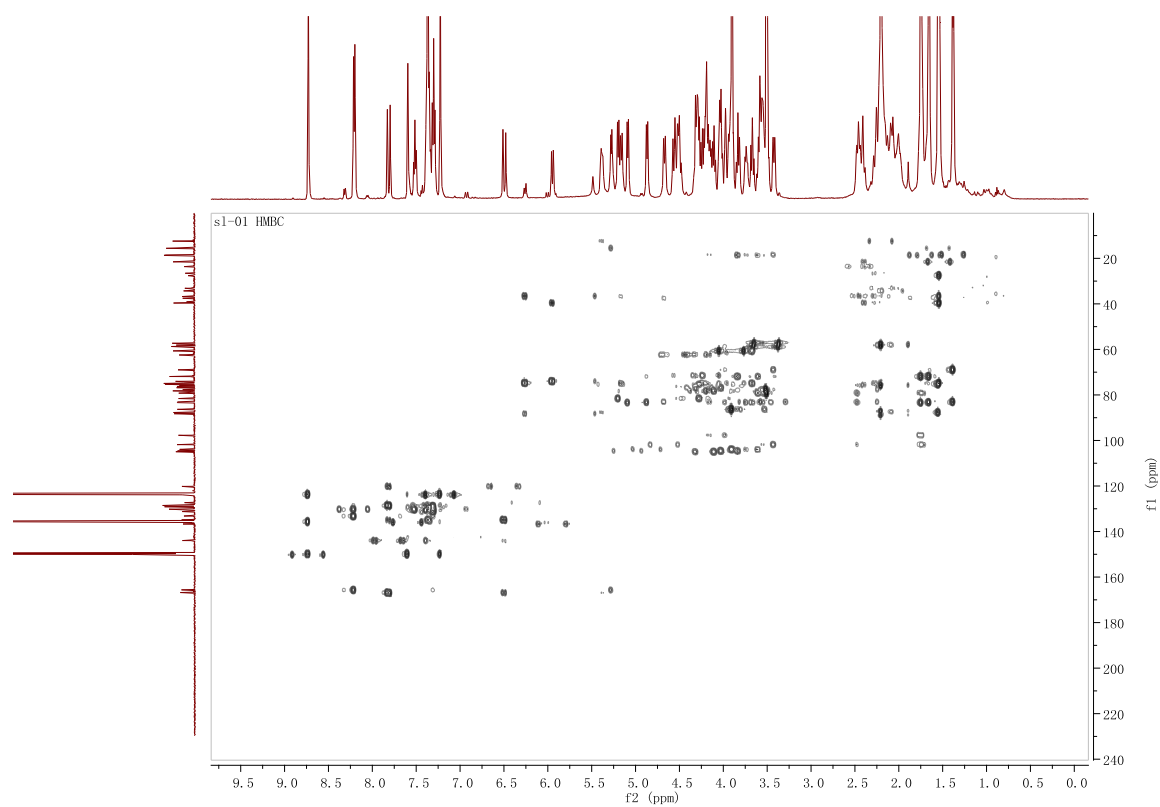


Figure S6. HMBC (500 MHz) spectrum of **1** in Pyridine-*d*₅.

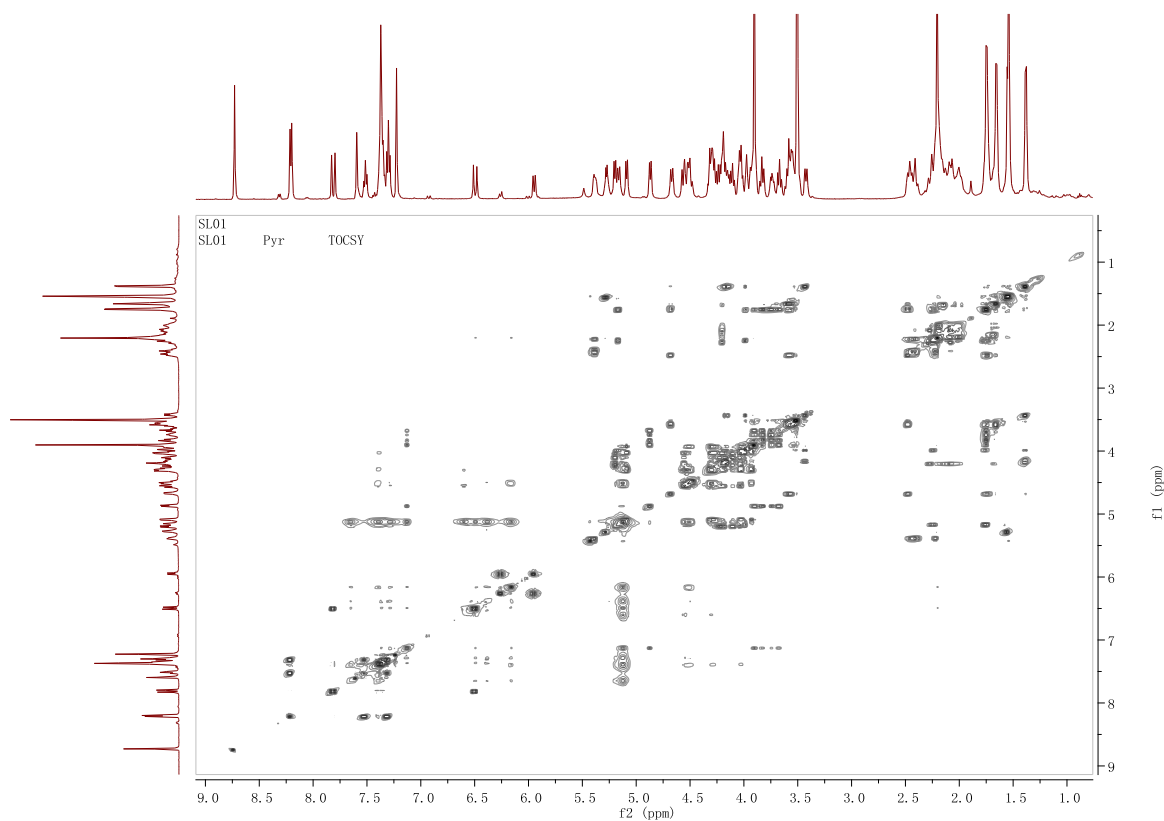


Figure S7. TOCSY (500 MHz) spectrum of **1** in Pyridine-*d*₅.

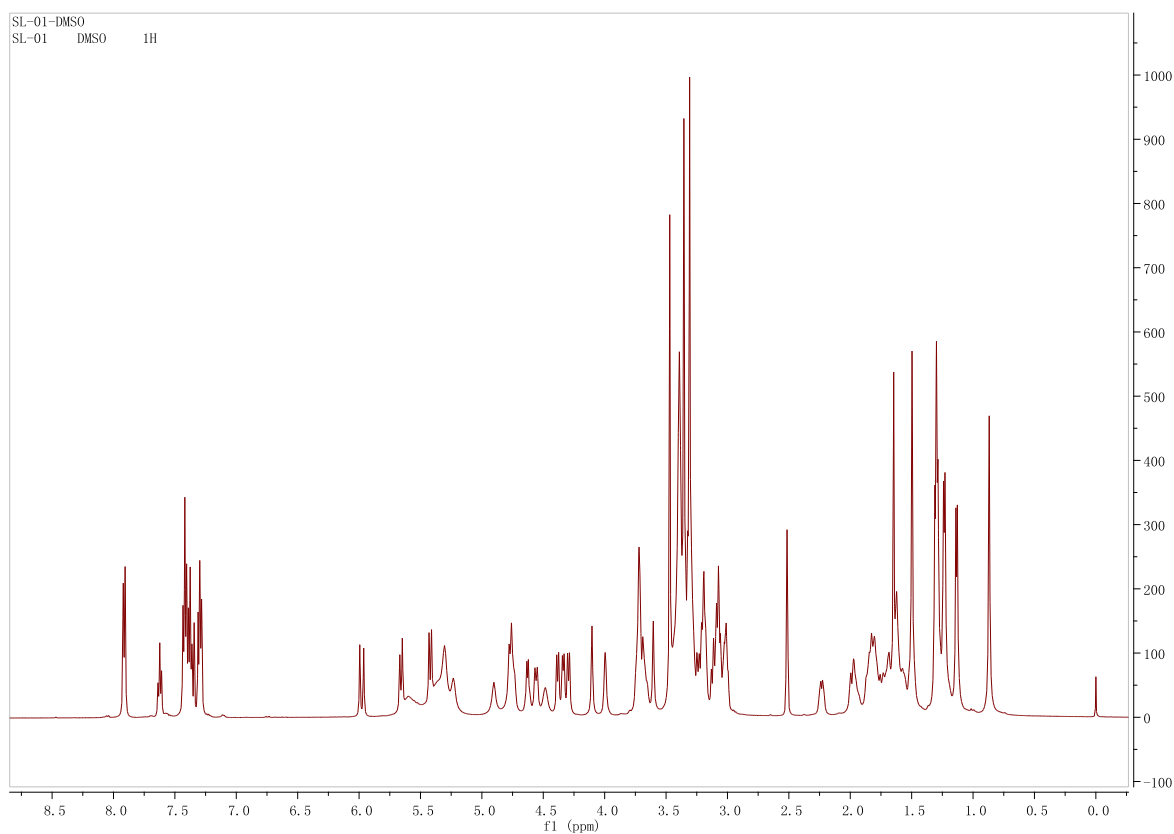


Figure S8. ¹H-NMR (500 MHz) spectrum of **1** in DMSO-*d*₆.

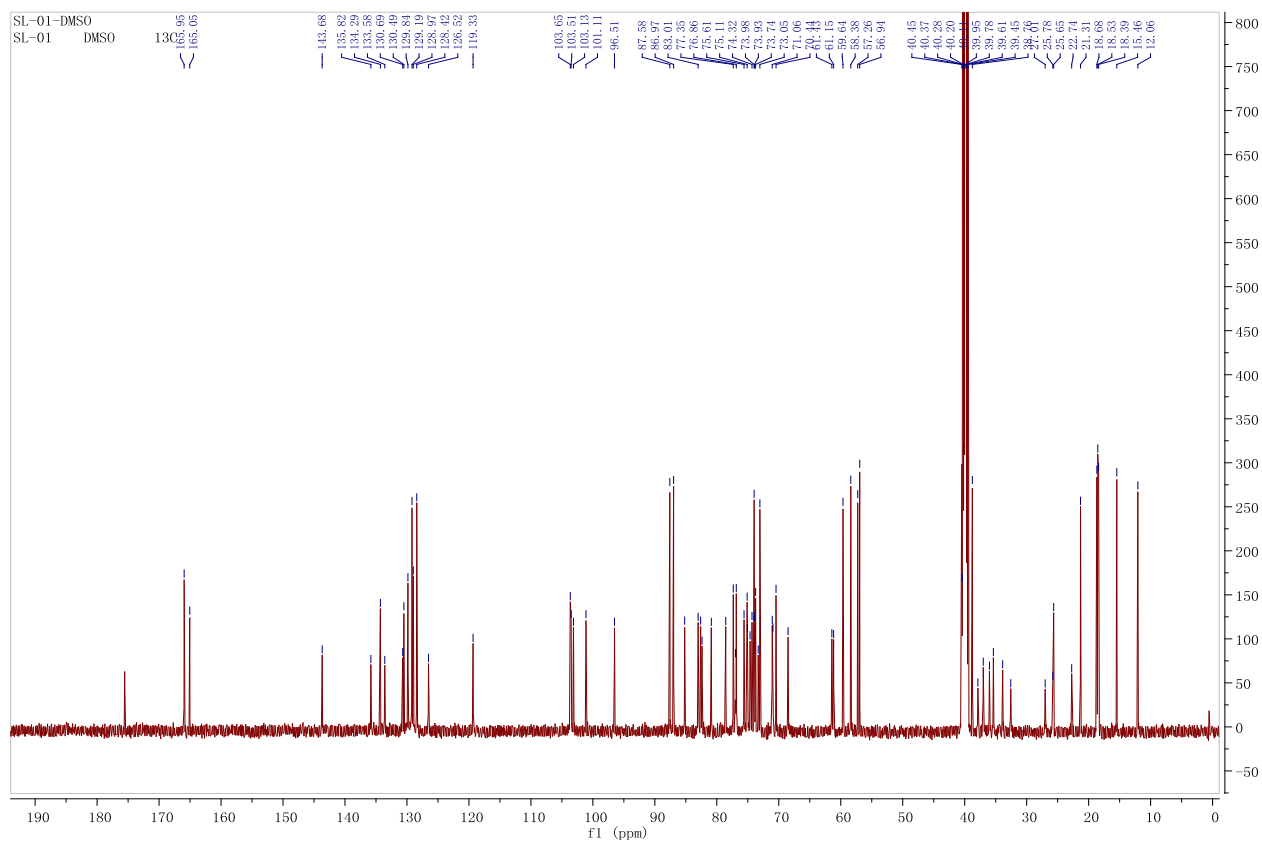


Figure S9. ¹³C-NMR (125 MHz) spectrum of **1** in DMSO-*d*₆.

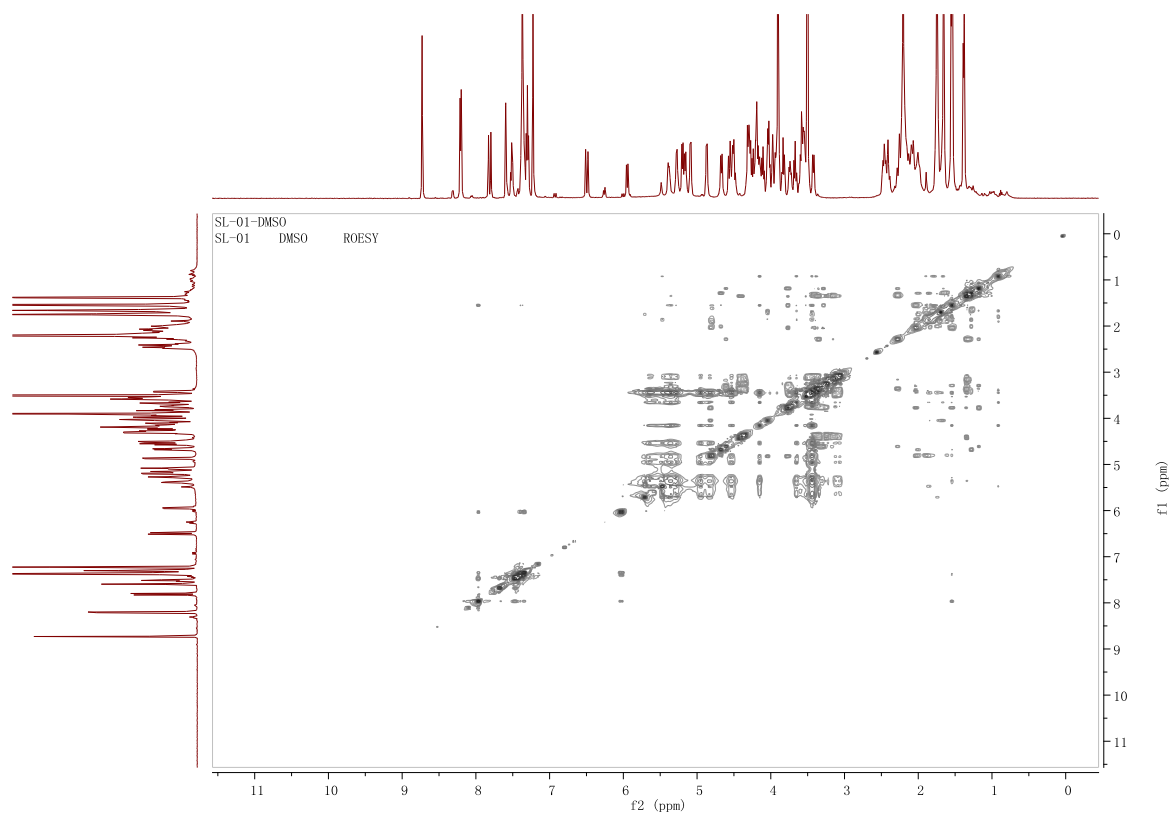


Figure S10. ROESY (500 MHz) spectrum of **1** in DMSO-*d*₆.

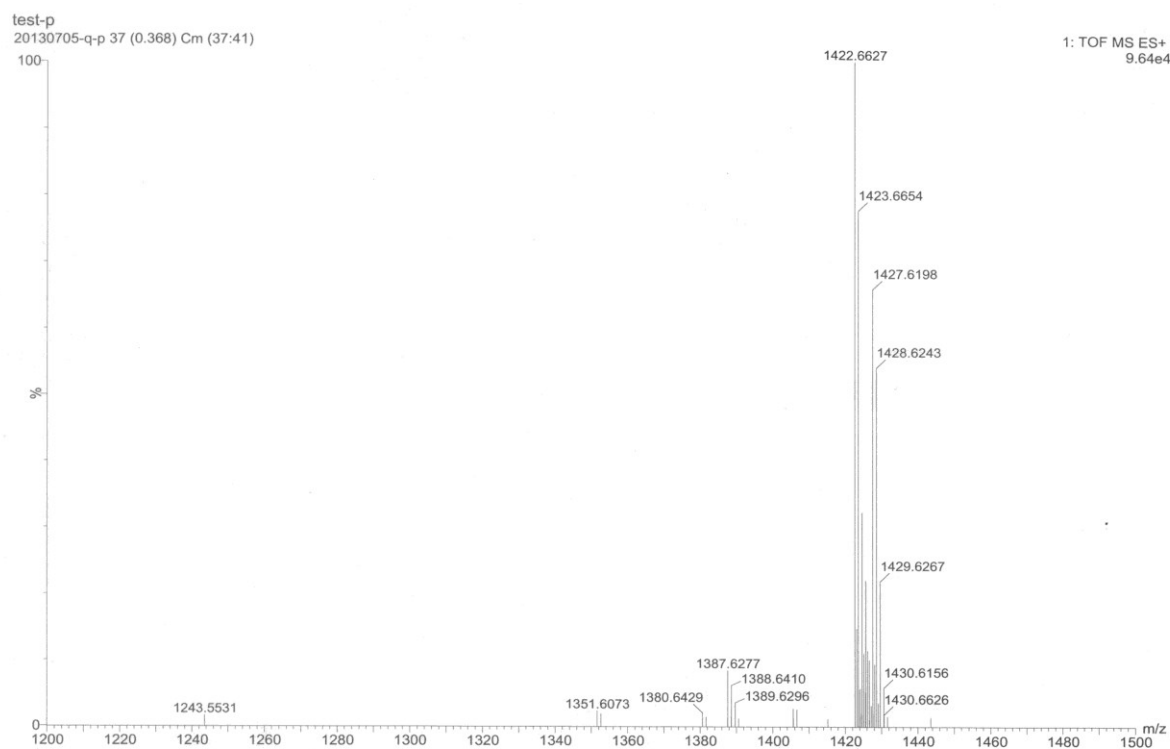


Figure S11. HRESIMS spectrum of **1**.

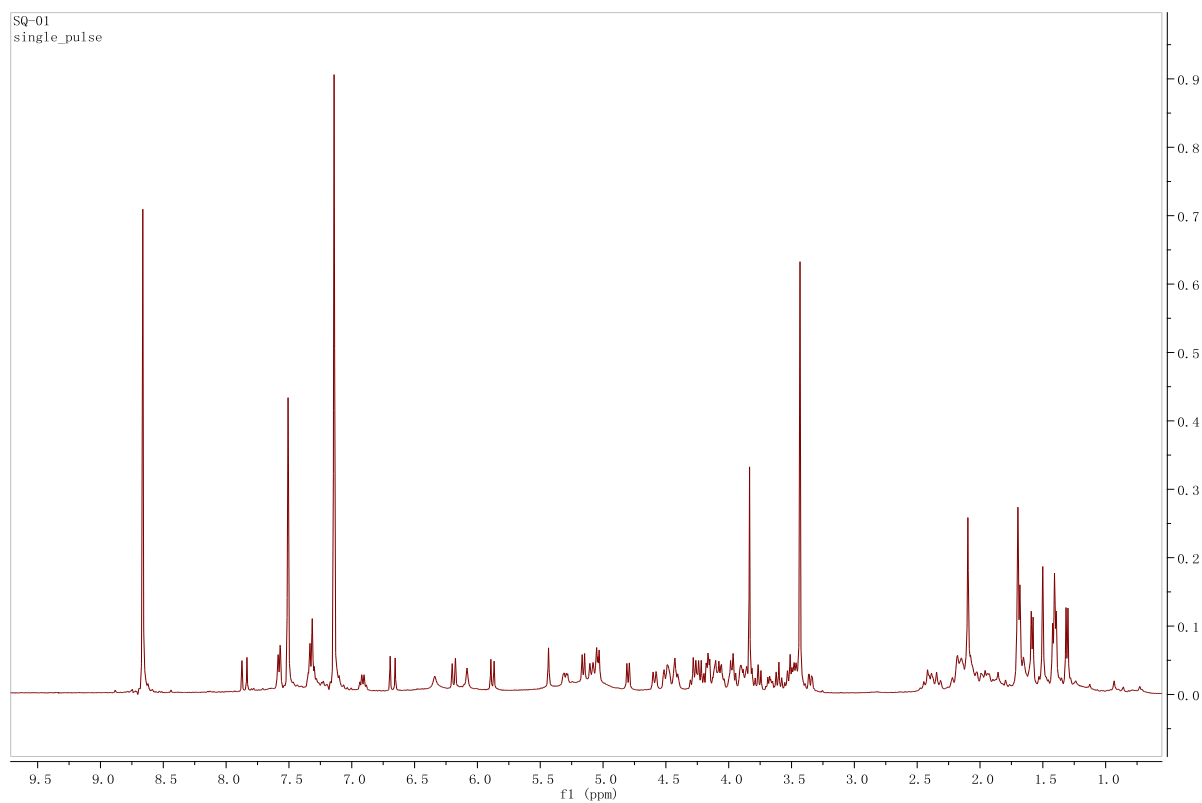


Figure S12. ^1H -NMR (400 MHz) spectrum of **2** in Pyridine- d_5 .

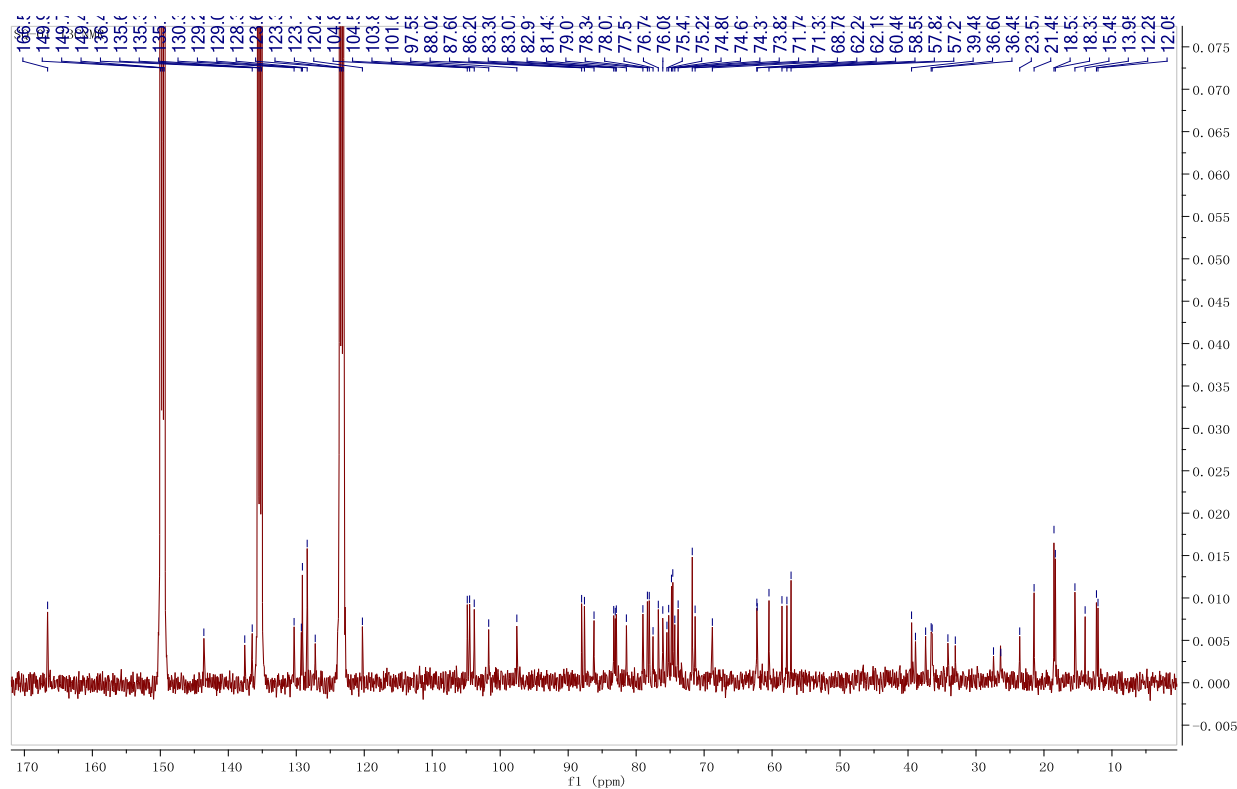


Figure S13. ¹³C-NMR (100 MHz) spectrum of **2** in Pyridine-*d*₅.

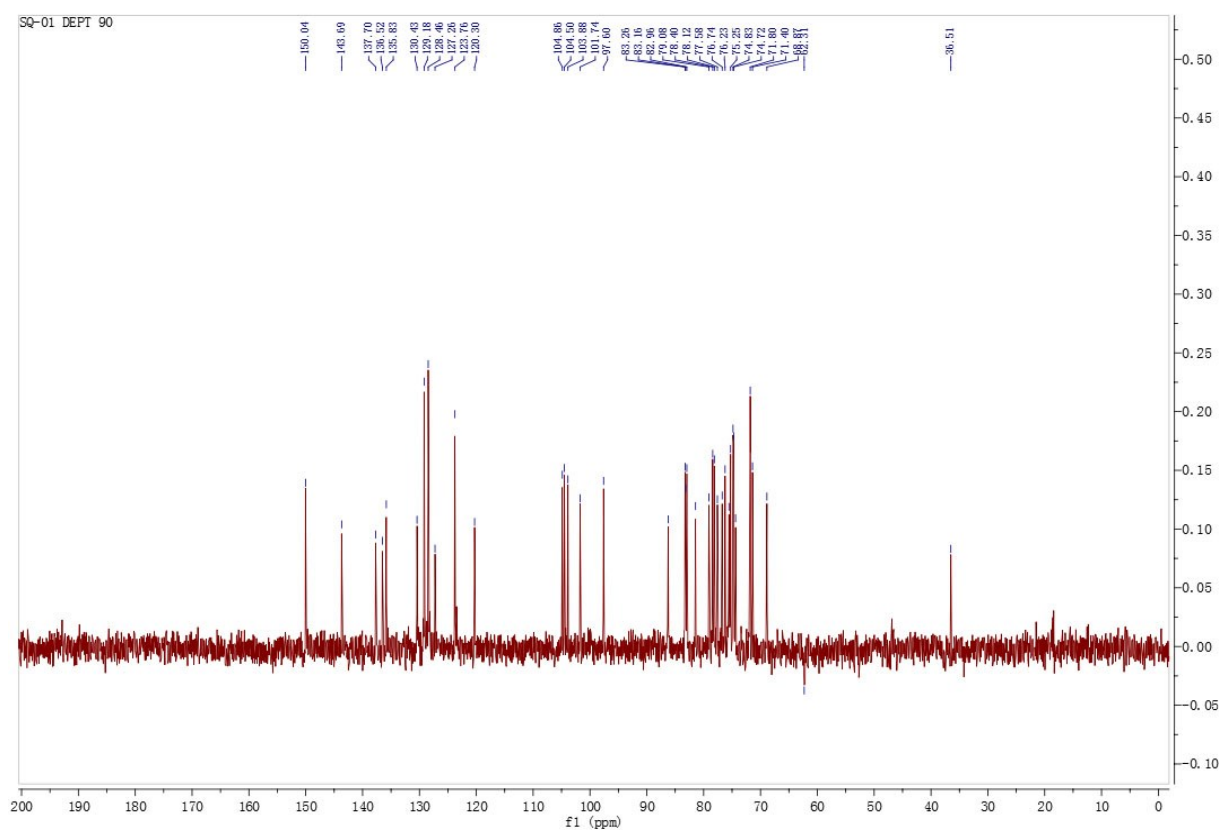


Figure S14. DEPT (θ = 90°) (400 MHz) spectrum of **2** in Pyridine-*d*₅.

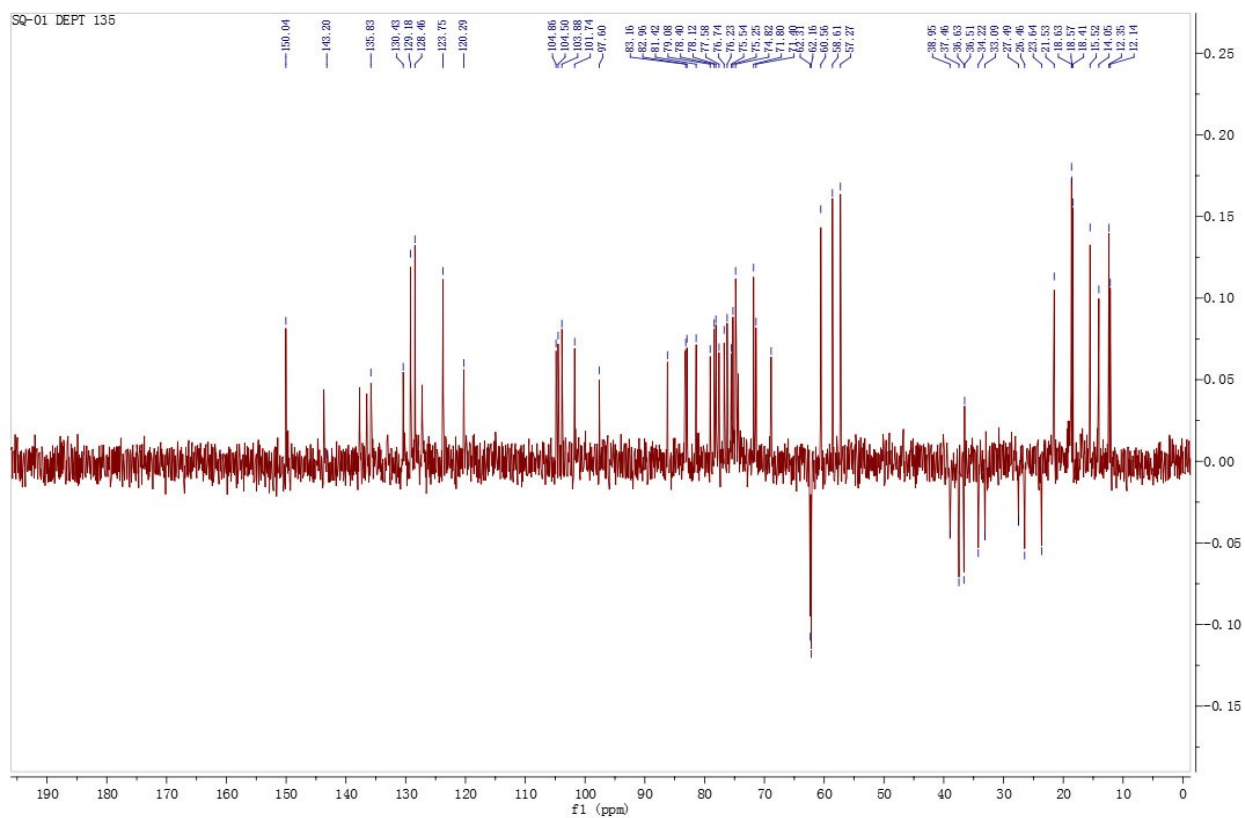


Figure S15. DEPT ($\theta = 135^\circ$) (400 MHz) spectrum of **2** in Pyridine-*d*₅.

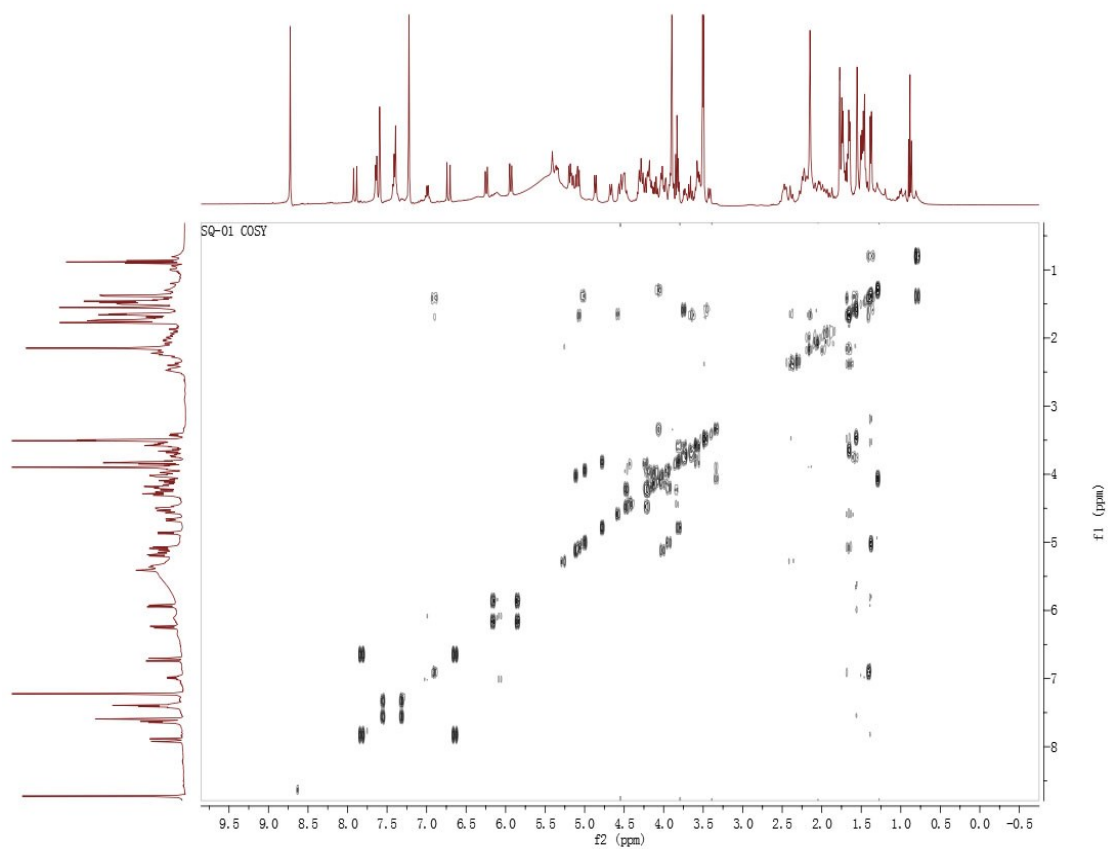


Figure S16. COSY (400 MHz) spectrum of **2** in Pyridine-*d*₅.

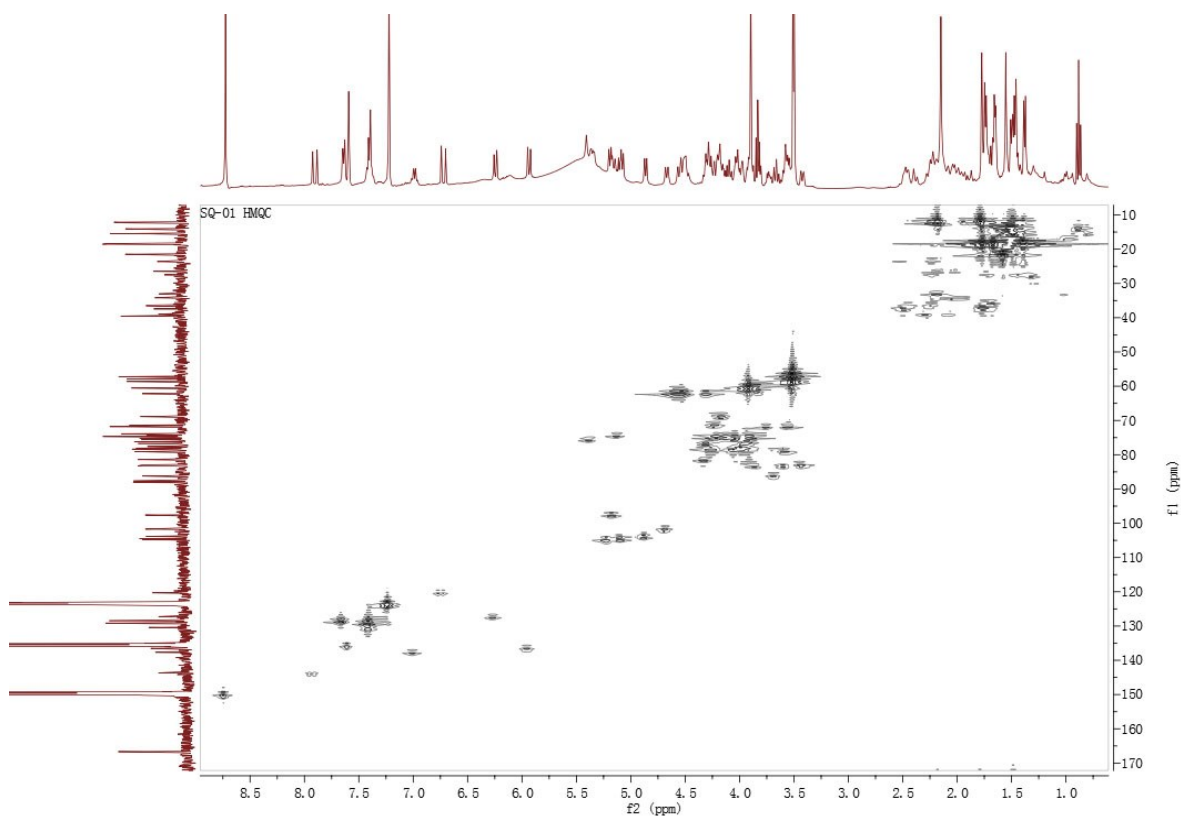


Figure S17. HMBC spectrum of **2** in Pyridine-*d*₅.

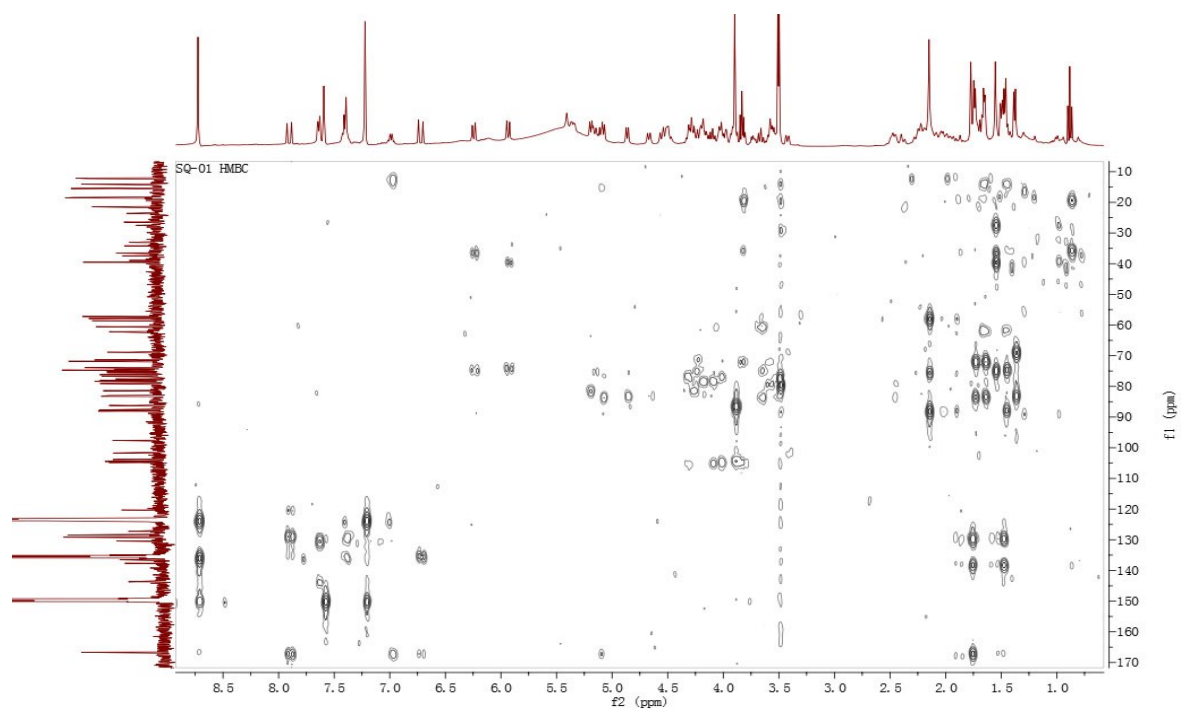


Figure S18. HMBC spectrum of **2** in Pyridine-*d*₅.

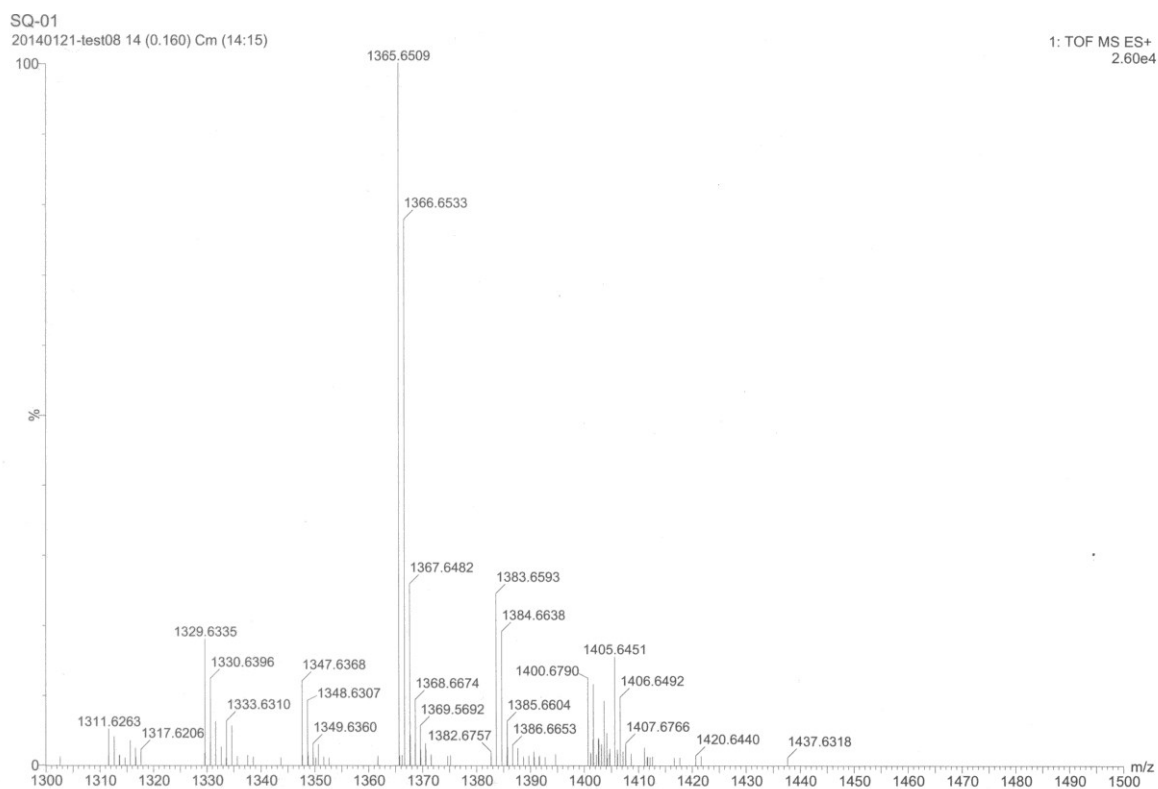


Figure S19. HRESIMS spectrum of **2**.

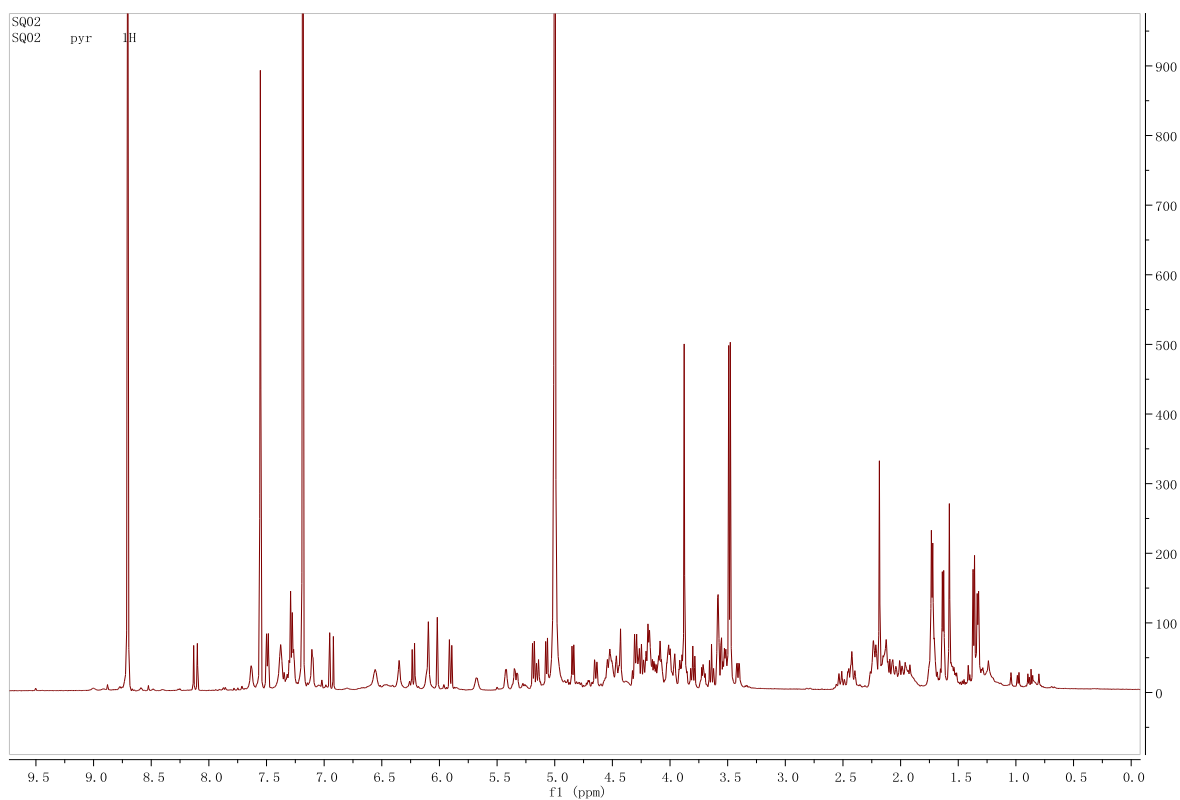


Figure S20. ^1H -NMR (500 MHz) spectrum of **3** in Pyridine- d_5 .

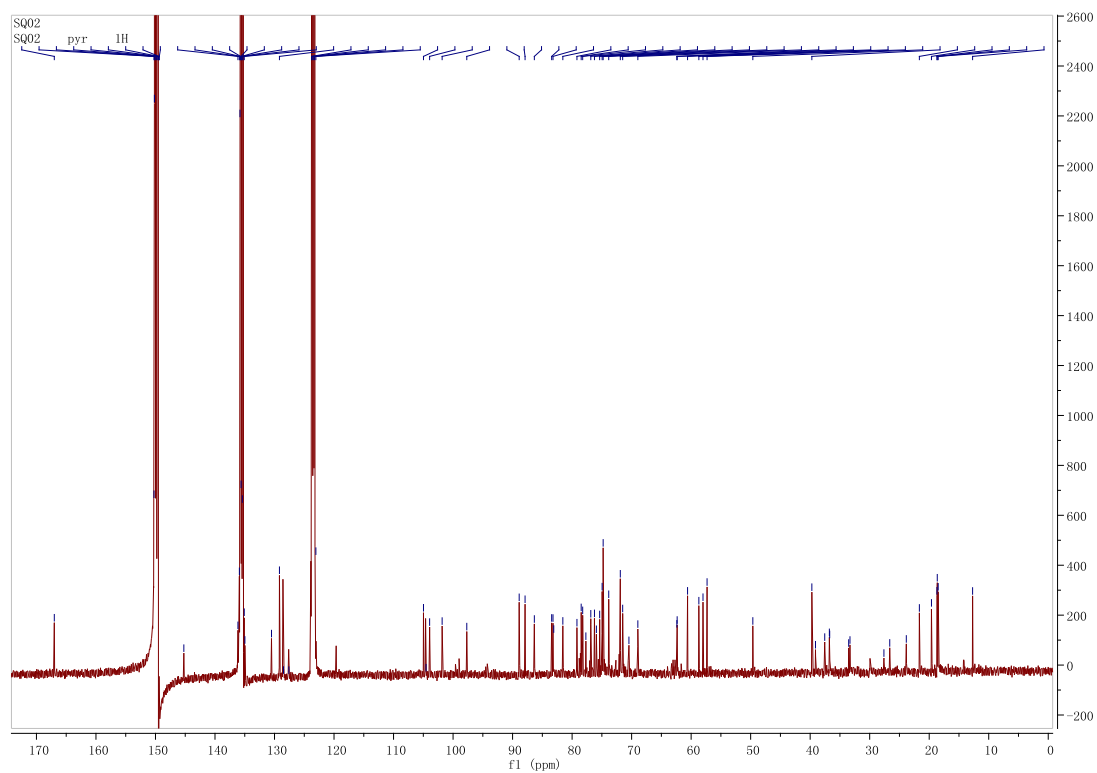


Figure S21. ^{13}C -NMR (125 MHz) spectrum of **3** in $\text{Pyridine-}d_5$.

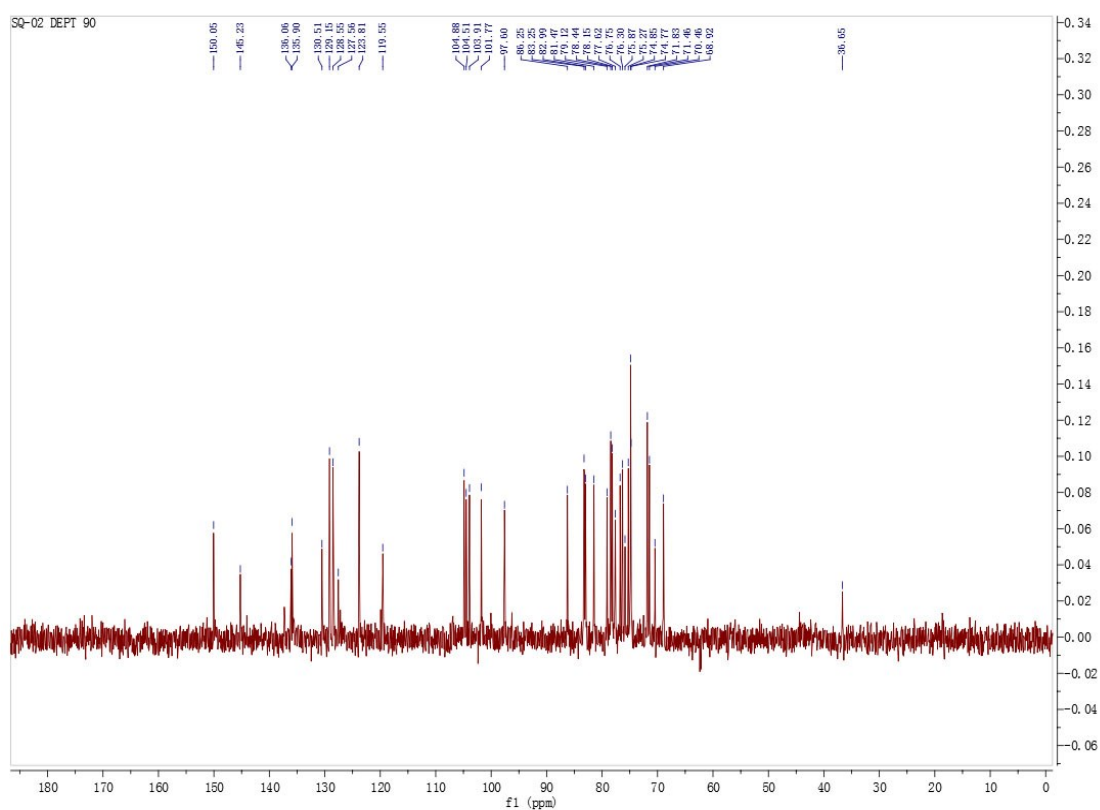


Figure S22. DEPT ($\theta = 90^\circ$) (400 MHz) spectrum of **3** in $\text{Pyridine-}d_5$.

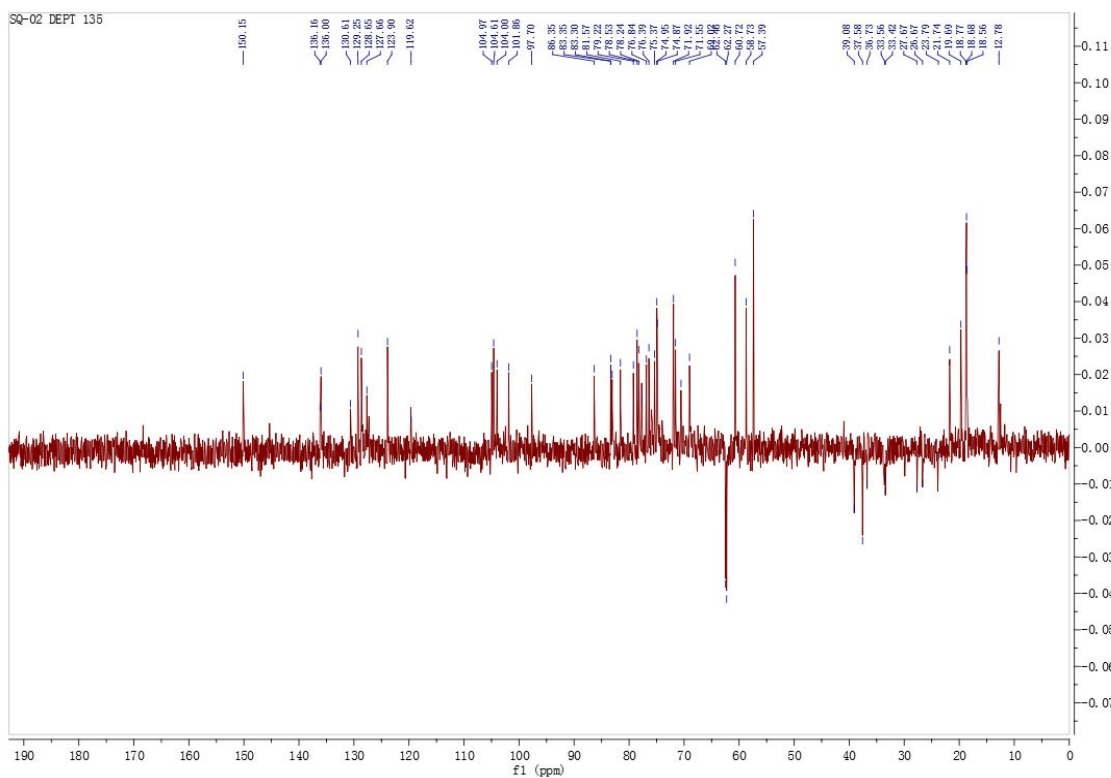


Figure S23. DEPT ($\theta = 135^\circ$) (400 MHz) spectrum of **3** in Pyridine-*d*₅.

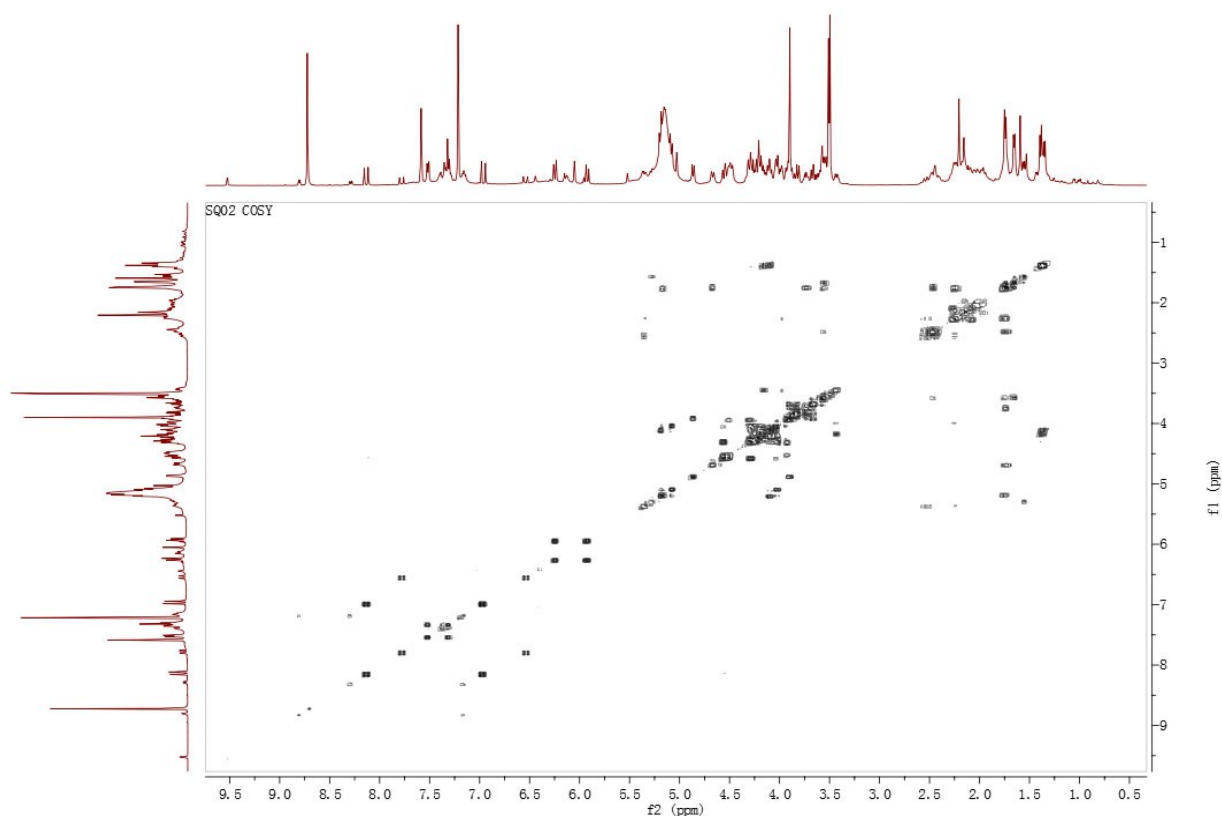


Figure S24. COSY (400 MHz) spectrum of **3** in Pyridine-*d*₅.

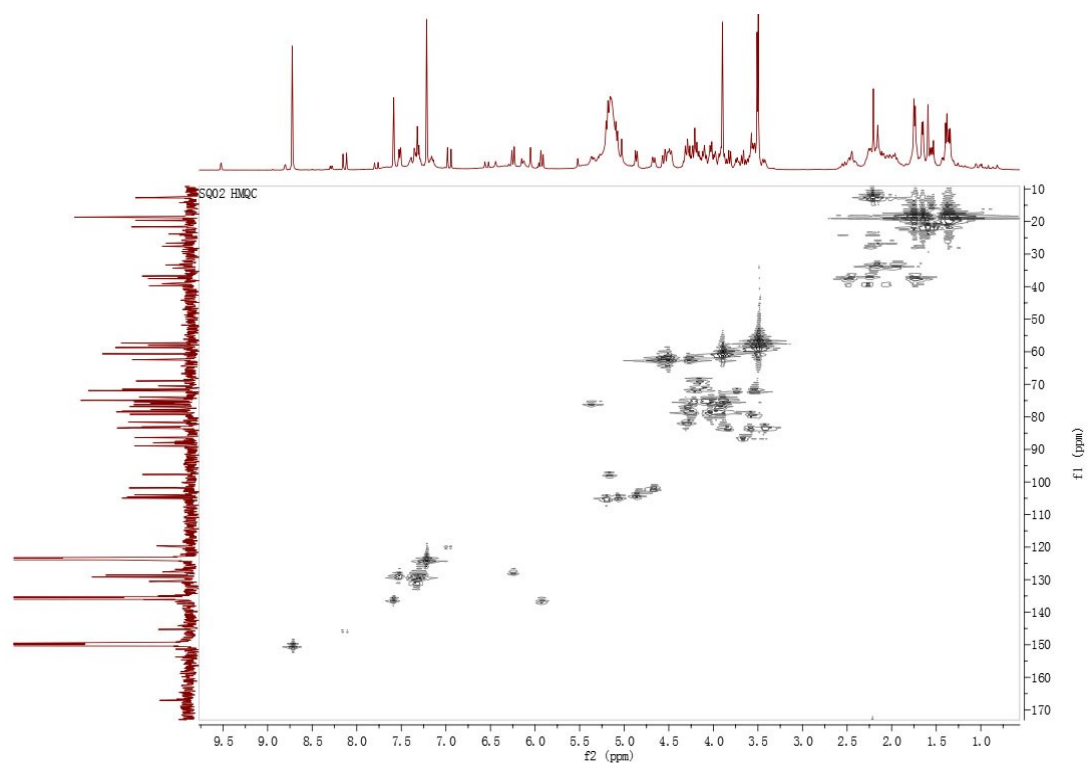


Figure S25. HMQC spectrum of **3** in Pyridine-*d*₅.

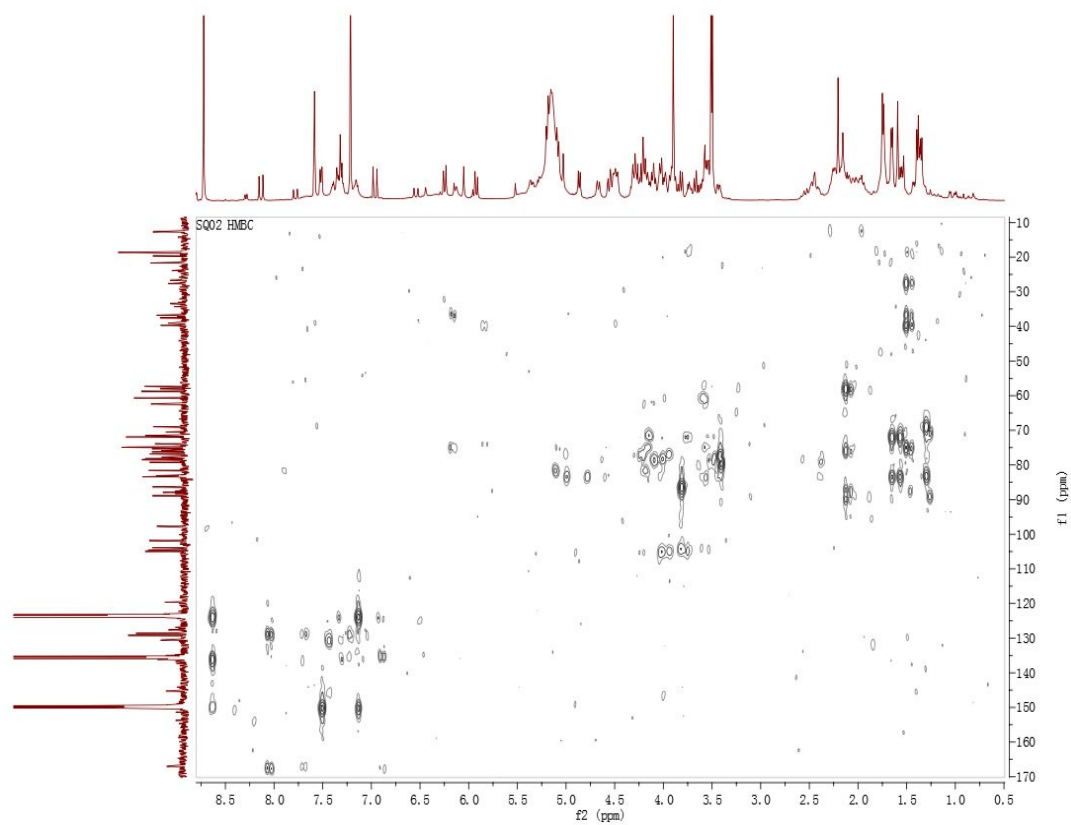


Figure S26. HMBC spectrum of **3** in Pyridine-*d*₅.

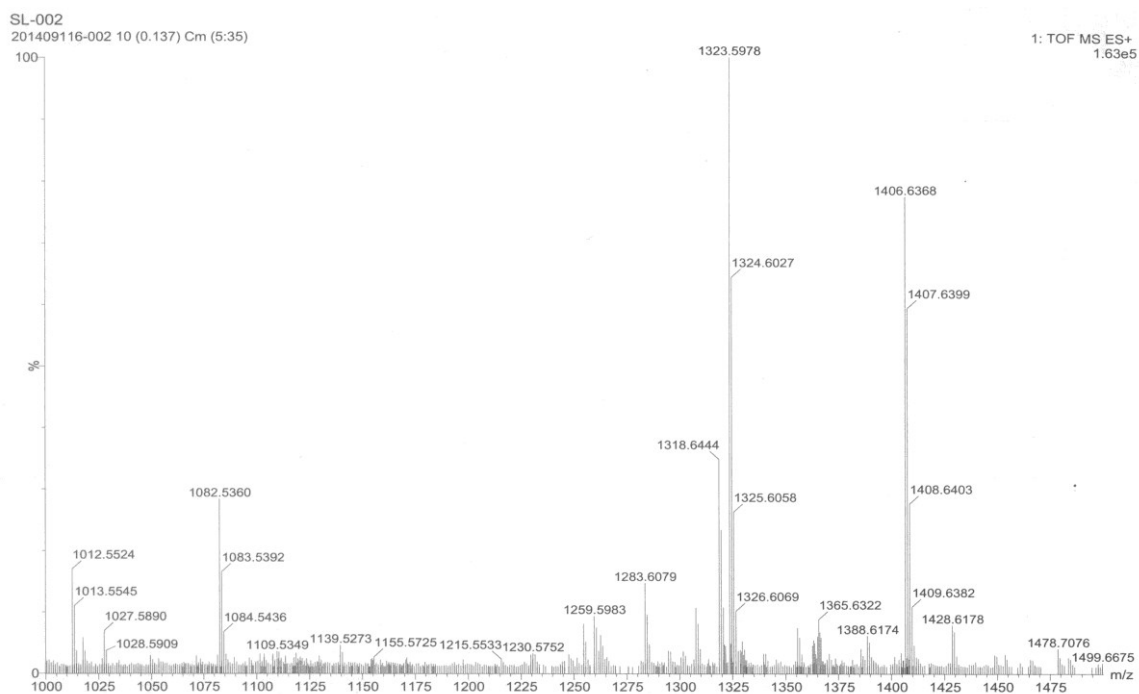


Figure S27. HRESIMS spectrum of **3**.

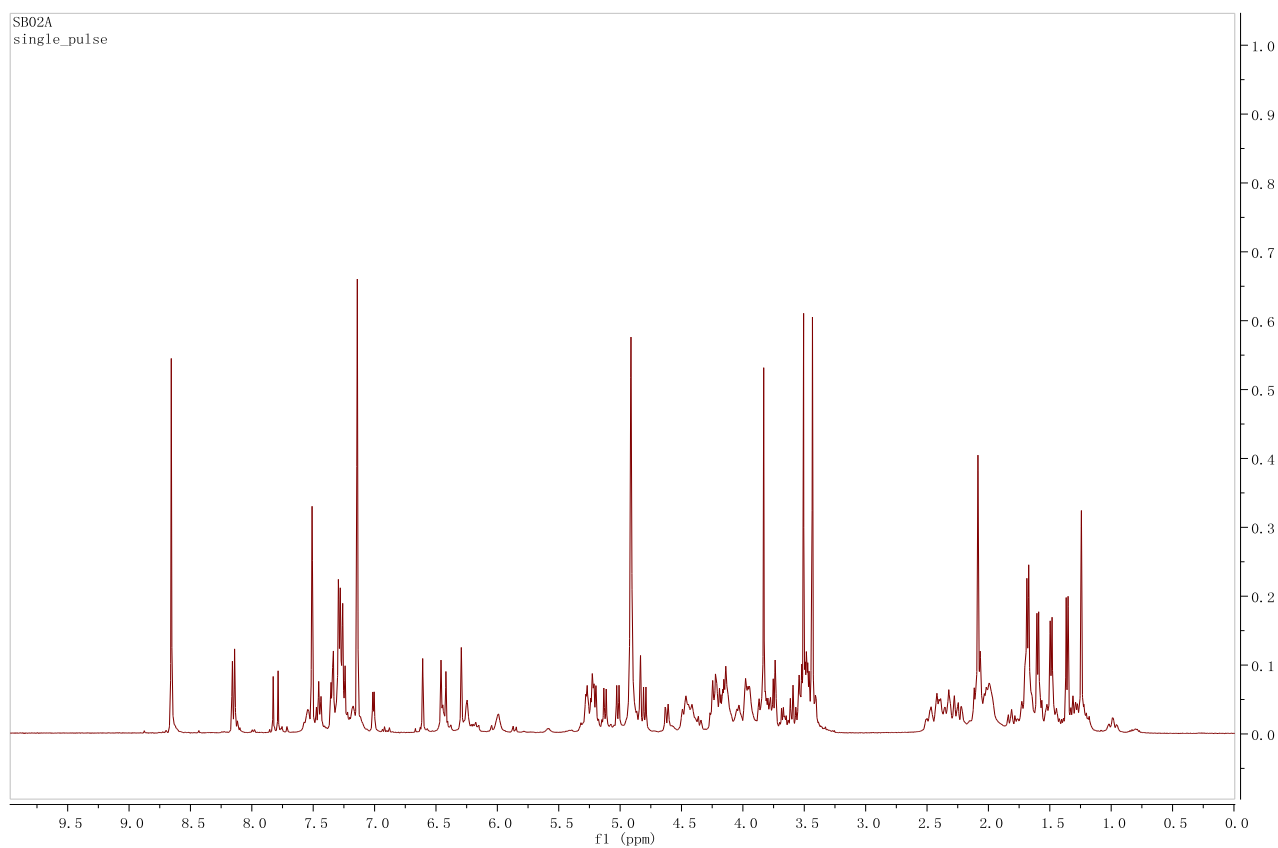


Figure S28. ^1H -NMR (400 MHz) spectrum of **4** in Pyridine- d_5 .

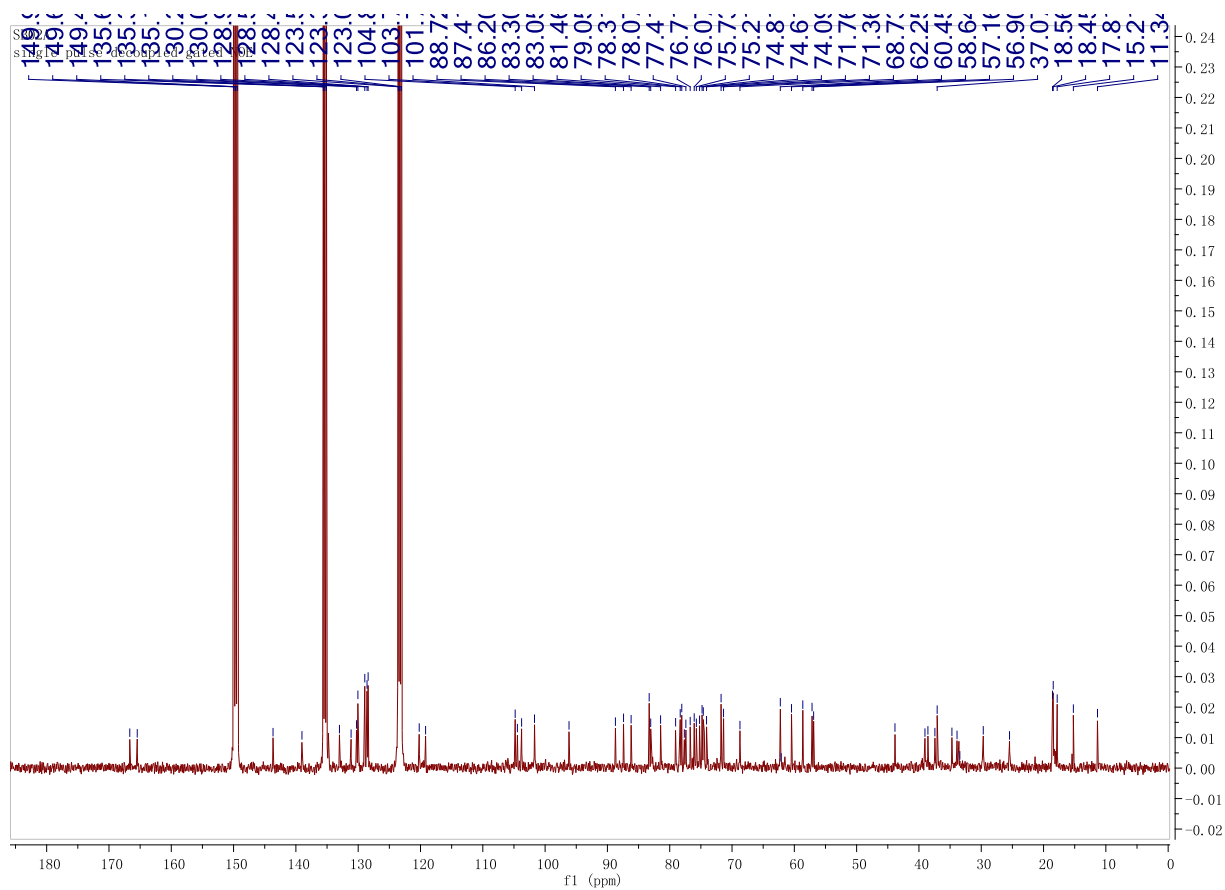


Figure S29. ^{13}C -NMR (100 MHz) spectrum of **4** in Pyridine- d_5 .

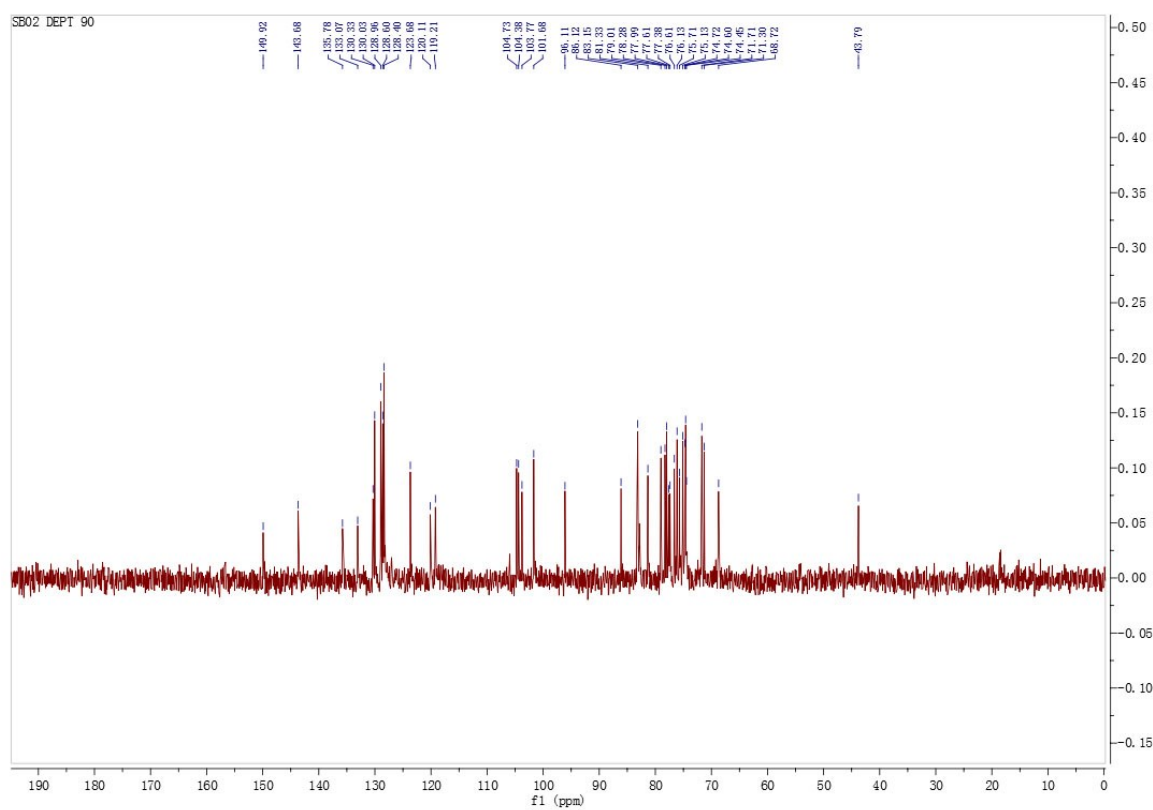


Figure S30. DEPT ($\theta = 90^\circ$) (400 MHz) spectrum of **4** in Pyridine- d_5 .

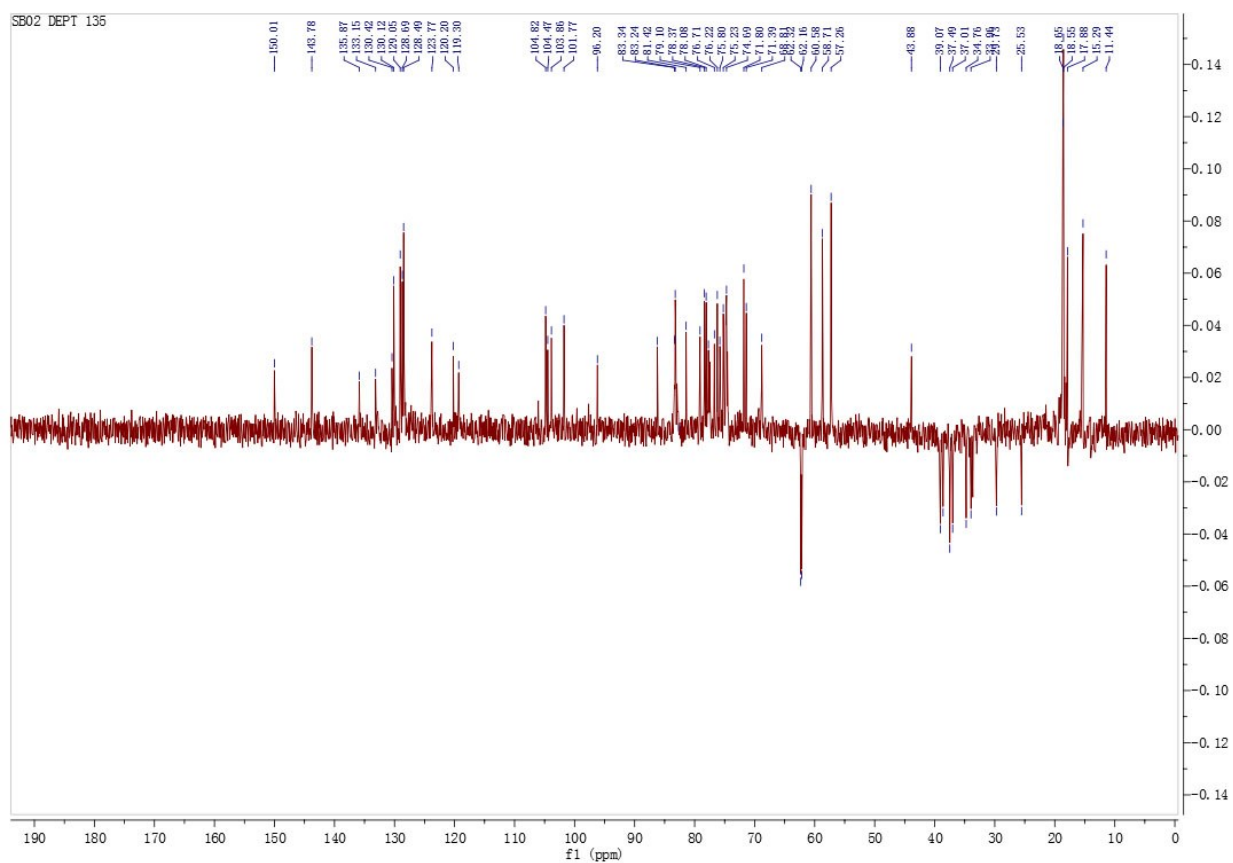


Figure S31. DEPT ($\theta = 135^\circ$) (400 MHz) spectrum of **4** in Pyridine- d_5 .

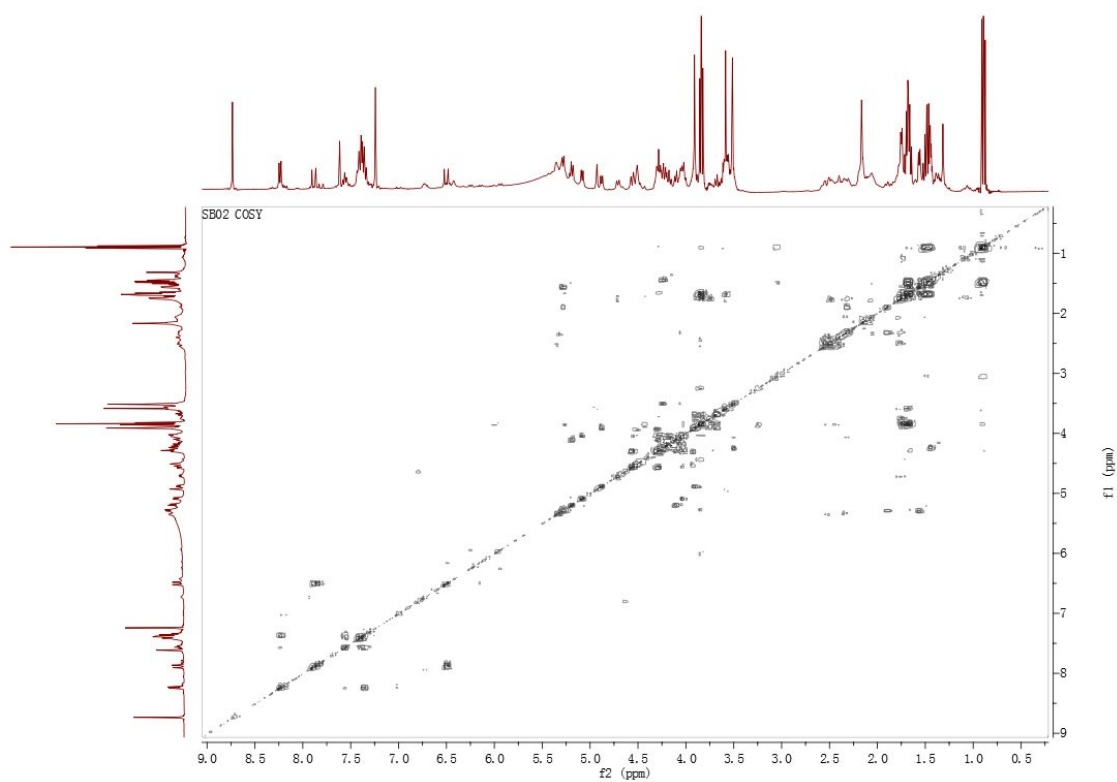


Figure S32. COSY (400 MHz) spectrum of **4** in Pyridine- d_5 .

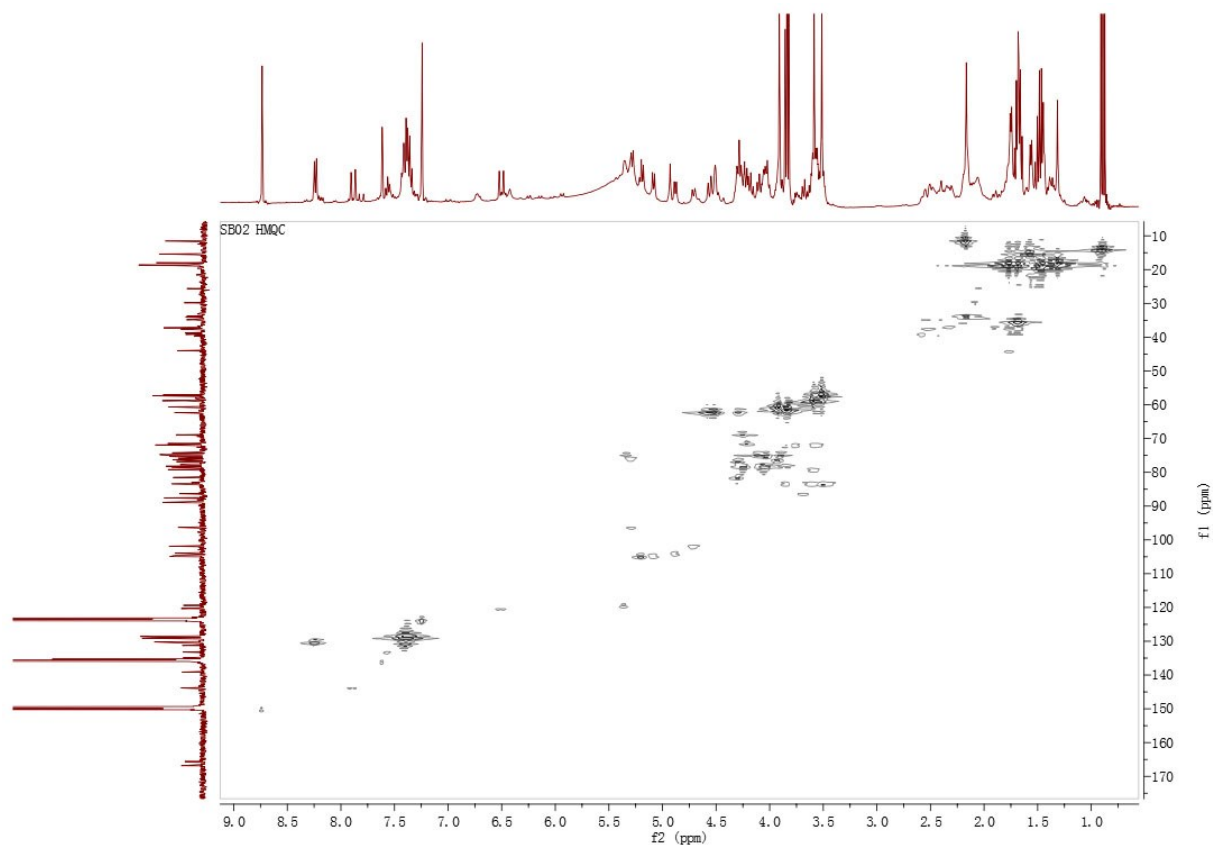


Figure S33. HMQC spectrum of **4** in Pyridine-*d*₅.

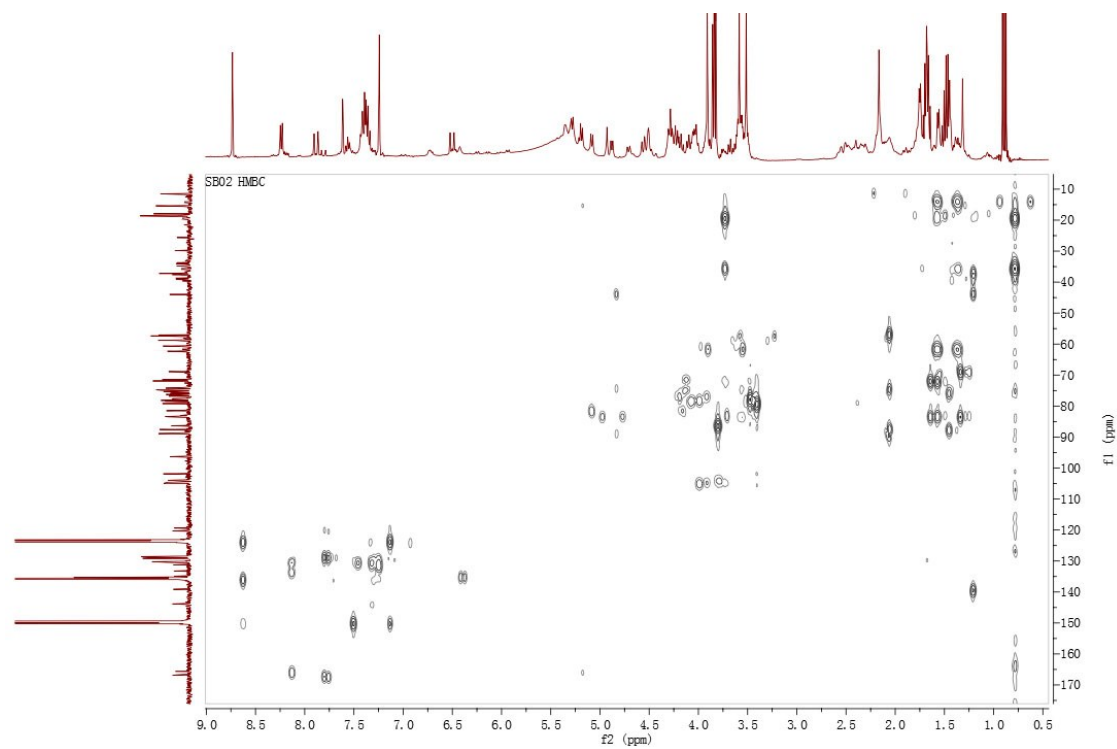


Figure S34. HMBC spectrum of **4** in Pyridine-*d*₅.

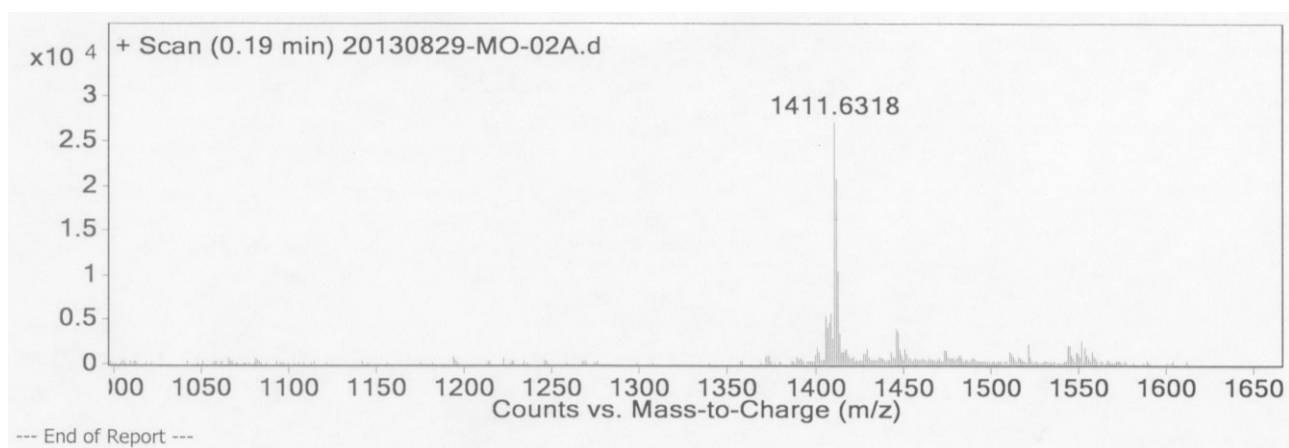


Figure S35. HRESIMS spectrum of **4**.

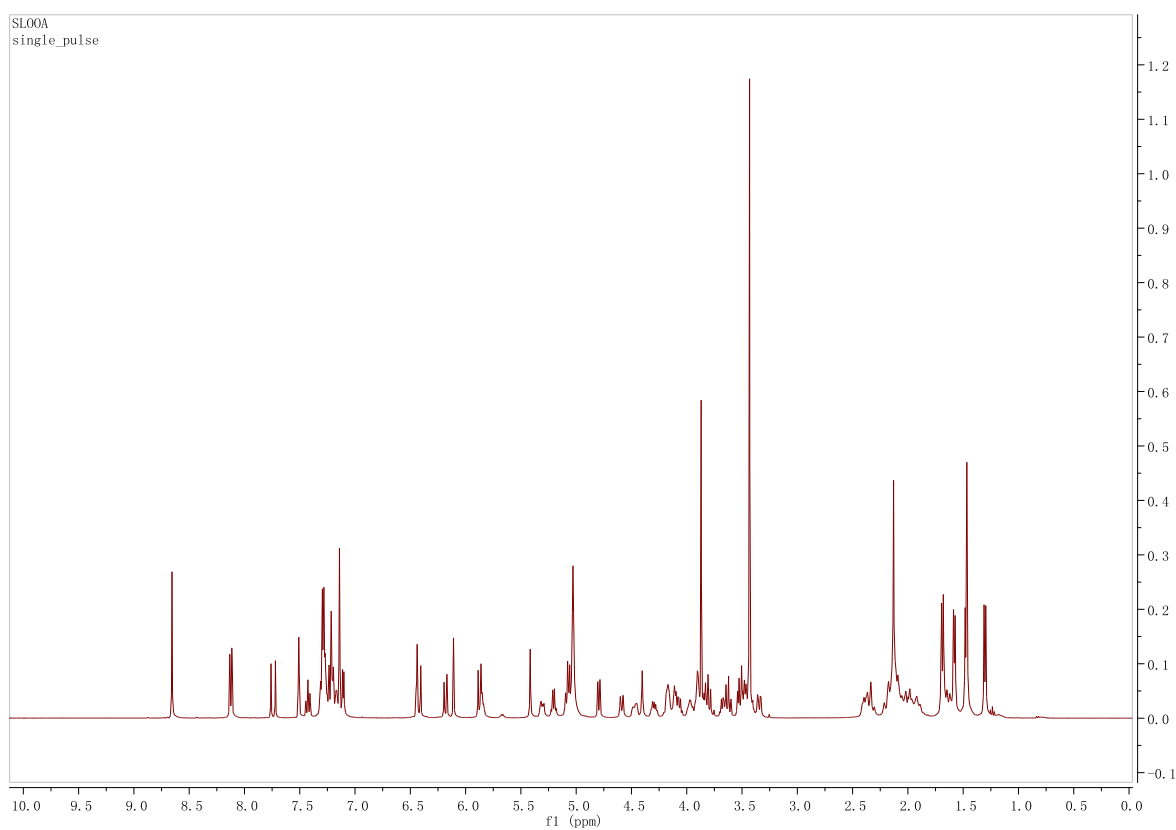


Figure S36. ¹H-NMR (400 MHz) spectrum of **5** in Pyridine-*d*₅.

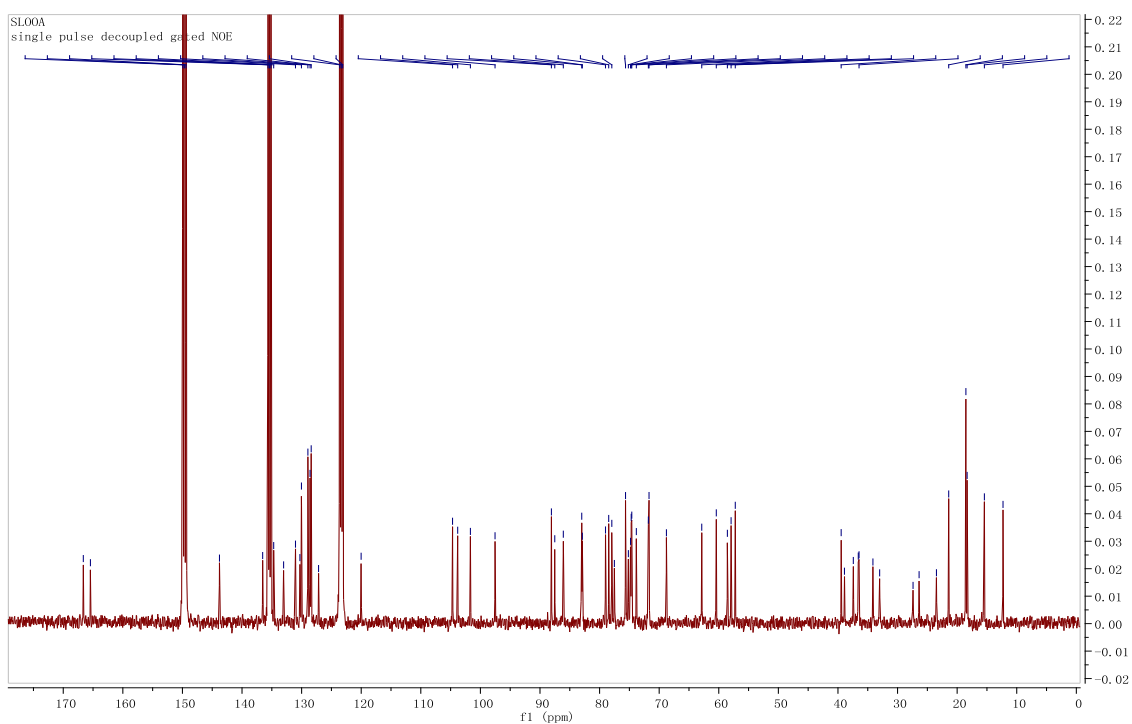


Figure S37. ^{13}C -NMR (100 MHz) spectrum of **5** in $\text{Pyridine-}d_5$.

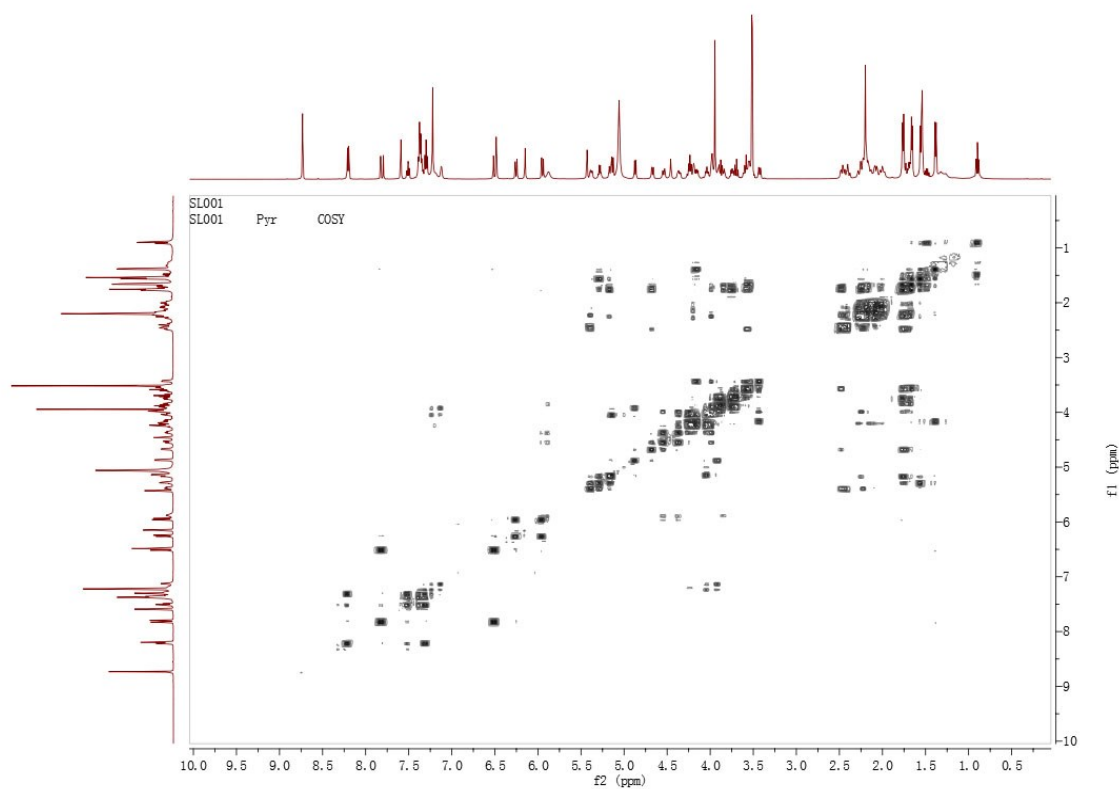


Figure S38. COSY (500 MHz) spectrum of **5** in $\text{Pyridine-}d_5$.

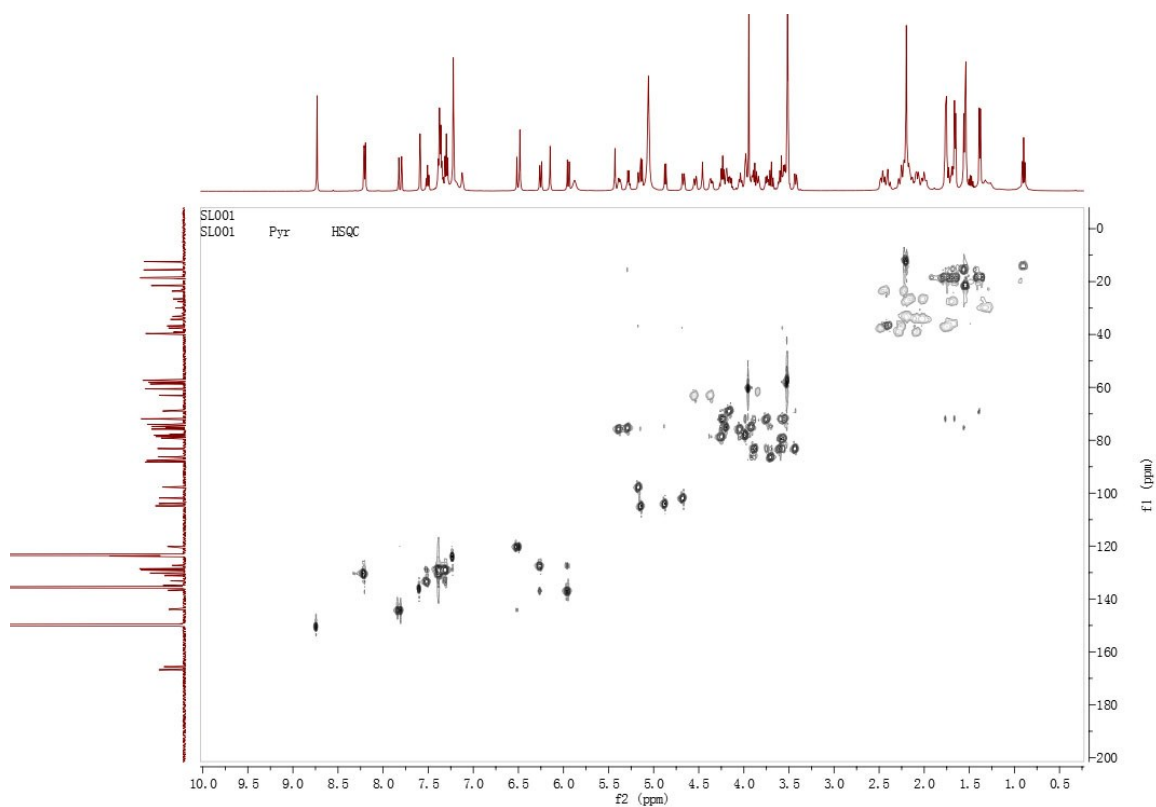


Figure S39. HMQC spectrum of **5** in Pyridine-*d*₅.

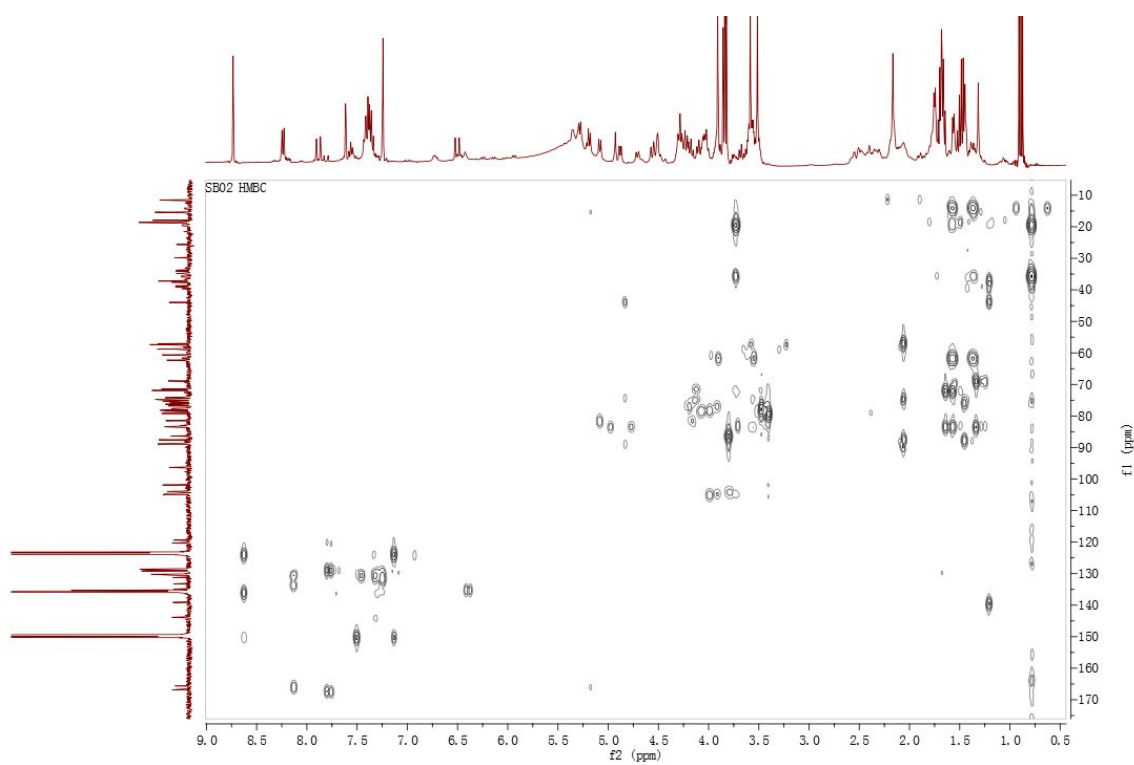


Figure S40. HMBC spectrum of **5** in Pyridine-*d*₅.

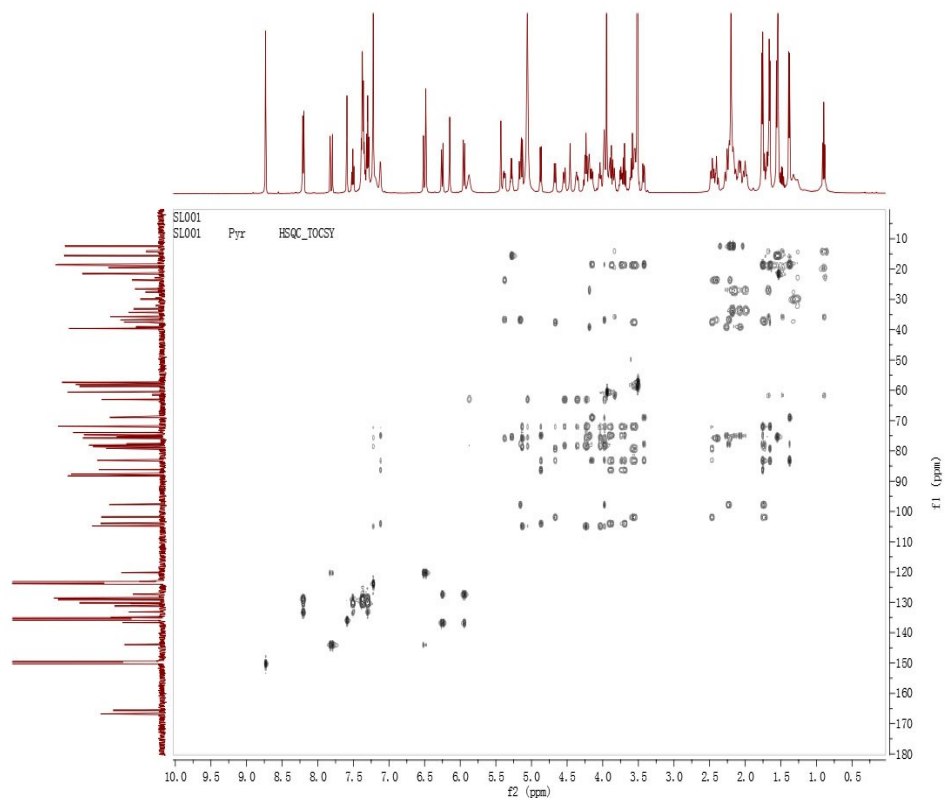


Figure S41. HMQC-TOCSY spectrum of **5** in Pyridine-*d*₅.

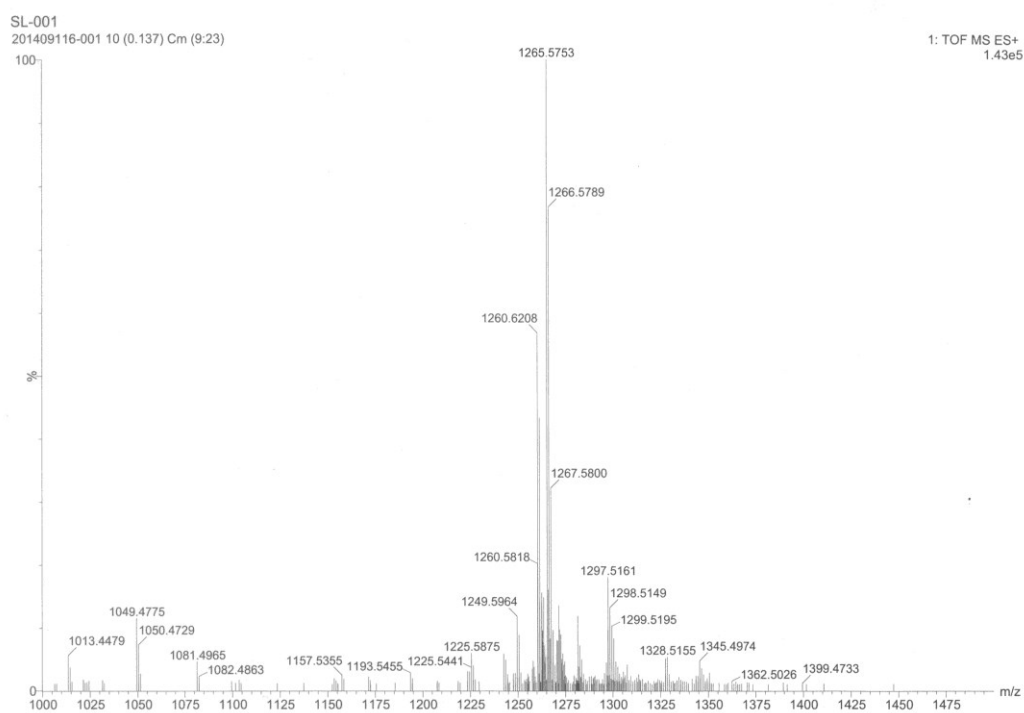


Figure S42. HRESIMS spectrum of **5**.

Table S1. ^{13}C -NMR (100 MHz) of the aglycones of compounds **1–3** and gymnepregosides E, A, C (in Pyridine- d_5).

NO.	δ_{C}					
	1 ^(a)	gymnepregosides E	2	gymnepregosides A	3	gymnepregosides C
1	27.6 (t)	27.6	27.5 (t)	27.7	27.6 (t)	27.9
2	26.5 (t)	26.6	26.5 (t)	26.5	26.5 (t)	26.9
3	74.9 (d)	74.9	74.9 (d)	74.8	74.9 (d)	75.0
4	39.0 (t)	39.1	39.0 (t)	39.1	39.0 (t)	39.3
5	74.7 (s)	74.8	74.7 (s)	74.7	74.8 (s)	75.0
6	136.7 (d)	136.7	136.6 (d)	136.7	136.1 (d)	136.3
7	127.3 (d)	127.3	127.3 (d)	127.4	127.6 (d)	127.7
8	74.0 (s)	74.0	74.0 (s)	74.0	73.8 (s)	74.1
9	36.6 (d)	36.9	36.5 (d)	37.0	36.6 (d)	37.1
10	39.6 (s)	39.6	39.6 (s)	39.6	39.6 (s)	39.9
11	23.6 (t)	23.7	23.7 (t)	23.6	23.6 (t)	24.1
12	75.8 (d)	75.8	75.6 (d)	75.9	75.9 (d)	76.1
13	58.1 (s)	58.1	57.9 (s)	58.0	58.1 (s)	58.3
14	88.2 (s)	88.3	88.1 (s)	88.1	88.9 (s)	89.1
15	33.1 (t)	33.2	33.1 (t)	33.1	33.3 (t)	33.6
16	34.3 (t)	34.3	34.2 (t)	34.2	33.5 (t)	33.8
17	87.7 (s)	87.7	87.7 (s)	87.8	87.9 (s)	88.1
18	12.4 (q)	12.5	12.3 (q)	12.1	12.7 (q)	12.9
19	21.5 (q)	21.5	21.5 (q)	21.4	21.6 (q)	21.9
20	75.3 (d)	78.4	74.4 (d)	74.4	70.4 (d)	70.7
21	15.6 (q)	15.6	15.5 (q)	15.5	19.6 (q)	19.9
Cinnamoyl moiety						
1'	166.8 (s)	166.8	166.7 (s)	166.8	167.0 (s)	167.1
2'	120.1 (d)	120.2	120.3 (d)	120.4	119.6 (d)	119.8
3'	143.9 (d)	144.0	143.7 (d)	143.8	145.2 (d)	145.4
4'	134.8 (s)	134.9	134.8 (s)	134.9	134.9 (s)	135.1
5',9'	128.5 (d)	128.6	128.5 (d)	128.6	128.6 (d)	128.7
6',8'	129.1 (d)	129.1	129.2 (d)	129.3	129.2 (d)	129.4
7'	130.4 (d)	130.4	130.5 (d)	130.5	130.5 (d)	130.6
(E)-2-Methyl-2-butenoyl or benzoyl moiety						
1''	165.6 (s)	165.5	166.7 (s)	166.8		
2''	131.2 (d)	131.2	129.4 (s)	129.5		
3''	130.2 (d)	130.2	137.7 (d)	137.7		
4''	128.7 (d)	128.8	14.1 (q)	14.0		
5''	133.2 (d)	133.2	12.2 (q)	12.3		
6''	128.7 (d)	128.8				
7''	130.2 (d)	130.2				

^(a) Measured at 125 MHz.