Supplementary Materials

Reductive Metabolism of Ellagitannins in the Young Leaves of *Castanopsis sieboldii*

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Table S1. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR Data for **9u** and **10o** (δ in ppm, J in Hz, Measured in pyridine-*d5*)

		9u		**10o**	
	position	^{1}H	^{13}C	^{1}H	^{13}C
triterpene	1	2.21 (dd, 12.7, 4.9)	47.5	2.27 (dd, 13.0, 4.6)	48.0
		1.25 (m)		1.37 (m)	
	2	4.23 (m)	68.3	4.47 (m)	66.5
	3	3.42 (d, 9.0)	78.6	5.40 (d, 9.5)	79.1
	4		48.9		48.6
	5	1.41 (m)	57.40	1.54 (m)	57.3
	6	2.45 (m)	20.0	2.46 (d, 13.2)	19.9
		1.62 (m)		1.66 (m)	
	7	1.57 (m)	33.05	1.50 (m)	32.5
		1.25 (m)		1.24 (m)	
	8		39.7		39.4
	9	1.70 (m)	47.6	1.76 (m)	47.6
	10		38.1		38.2
	11	1.95 (m)	24.0	1.95 (2H, m)	24.1
	12	5.37 (m)	125.8	5.37 (t, 3.4)	122.5
	13		138.6		144.3
	14		42.4		42.0
	15	2.41 (m)	28.7	2.34 (td,13.9, 4.6)	28.4
		1.09 (m)		1.09 (m)	
	16	2.03 (m)	24.6	2.06 (td, 13.7, 3.8)	23.3
				2.00 (m)	
	17		48.3		46.9
	18	2.49 (d, 11.0)	53.1	3.18 (dd, 13.7, 5.1)	41.6
	19	1.38 (m)	39.3	1.72 (m)	46.1
				1.21 (m)	
	20	0.88 (m)	39.1		30.8
	21	1.34 (m)	30.8	1.37 (m)	34.0
				1.09 (m)	
	22	1.92 (m)	36.8	1.77 (2H, m)	32.6
		1.69 (m)			
	23	6.04 (d, 11.2)	71.4	5.54 (d, 11.5)	69.7
		3.73 (d, 11.2)		3.82 (d, 11.5)	
	24	5.31 (d, 11.2)	62.6	5.46 (d, 11.7)	61.8
		4.40 (m)		4.33 (d, 11.5)	
	25	0.87 (3H, s)	16.7	0.96 (3H, s)	16.5
	26	1.05 (3H, s)	17.5	1.02 (3H, s)	17.3
	27	1.12 (3H, s)	23.8	1.30 (3H, s)	26.2
	28		176.2		176.4
	29	0.92 (d, 6.4)	17.4	0.91 (3H, s)	33.1
	30	0.90 (d, 7.1)	21.3	0.89 (3H, s)	23.6
glucose	1	6.26 (d, 8.1)	95.8	6.34 (d, 8.3)	95.9
	2	4.20 (t, 8.3)	74.2	4.21 (t, 8.3)	74.3
	3	4.28 (t, 8.9)	78.9	4.28 (t, 8.8)	79.0
	4	4.36 (m)	71.1	4.37 (t, 9.0)	71.0
	5	4.02 (m)	79.3	4.03 (m)	79.5
	6	4.44 (m)	62.20	4.47 (m)	62.2
				4.42 (dd, 11.7, 4.5)	
HHDP	1,1'		116.5 (2C)		116.7 (2C)
	2,2'		127.5, 127.8		127.4, 126.8
	3,3'	7.16 (s), 7.29 (s)	107.3, 108.36	7.08 (s), 7.56 (s)	107.5, 108.6
	4,4'		146.8, 146.6		146.8, 145.91
	5,5'		137.8, 137.7		137.8 (2C)
	6,6'		146.19, 146.24		145.94 (2C)
	7,7'		169.6, 169.8		169.0, 169.6
galloyl	1				121.4
	2,6			8.03 (s)	111.9
	3,5				146.3
	4				141.6
	CO				167.4
	1'				
	2',6'				
	3',5'				
	4'				
	CO				

Table S2. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR Data for **11o** and **12o** (δ in ppm, J in Hz, Measured in pyridine-*d5*)

		11o		**12o**	
	position	^{1}H	^{13}C	^{1}H	^{13}C
triterpene	1	2.23 (dd, 4.5 ,12.8)	47.82	2.28 (m)	48.4
		1.37 (m)		1.36 (m)	
	2	4.12 (m)	65.3	4.47 (m)	66.5
	3	5.74 (d, 10.3)	84.8	5.38 (m)	79.0
	4		47.80		48.4
	5	1.18 (m)	50.8	1.52 (m)	57.5
	6	2.04 (m)	20.7	2.40 (m)	19.9
		1.75 (m)		1.59 (m)	
	7	1.22 (m)	33.3	1.52 (m)	32.7
		1.01 (m)		1.17 (m)	
	8		39.9		39.4
	9	1.75 (m)	48.5	1.73 (m)	47.6
	10		38.8		38.0
	11	1.93 (2H, m)	23.9	1.95 (m)	24.0
	12	5.40 (m)	122.3	5.37 (m)	122.6
	13		144.2		143.9
	14		42.2		42.2
	15	2.17 (m)	28.1	2.18 (m)	28.2
		1.08 (m)		1.16 (m)	
	16	2.02 (m)	23.5	2.08 (m)	24.6
		1.91 (m)			
	17		47.0		47.0
	18	3.15 (dd, 4.9, 13.9)	41.7	3.16 (dd, 13.6, 5.3)	41.7
	19	1.68 (m)	46.2	1.73 (m)	46.1
		1.19 (m)		1.22 (m)	
	20		30.7		30.6
	21	1.33 (m)	34.0	1.37 (m)	34.0
		1.05 (m)		1.11 (m)	
	22	1.82 (m)	32.5	1.81 (m)	32.6
		1.75 (m)		1.76 (m)	
	23	5.51 (d, 11.2)	69.6	5.54 (d, 11.5)	69.7
		4.15 (d, 11.0)		3.78 (d, 11.5)	
	24	5.48 (m)	63.1	5.41 (m)	61.8
		4.48 (m)		4.32 (m)	
	25	1.12 (3H, s)	17.7	0.94 (3H,s)	16.7
	26	1.05 (3H, s)	17.5	0.96 (3H, s)	17.3
	27	1.14 (3H, s)	26.0	1.21 (3H, s)	26.0
	28		176.4		176.3
	29	0.87 (3H, s)	33.1	0.91 (3H, s)	33.1
	30	0.84 (3H, s)	23.59	0.88 (3H, s)	23.6
glucose	1	6.32 (d, 7.8)	95.82	6.39 (d, 8.3)	95.4
	2	4.22 (t, 8.4)	74.14	4.30 (m)	72.3
	3	4.27 (t, 8.8)	78.91	6.15 (t, 9.3)	80.10
	4	4.37 (t, 9.0)	71.1	4.55 (t, 9.3)	68.90
	5	4.06 (m)	79.4	4.04 (m)	79.1
	6	4.42 (m)	62.3	4.41 (dd, 3.2, 6.8)	61.7
		4.47 (m)			
HHDP	1,1'		116.3, 116.56		116.7 (2C)
	2,2'		126.6, 127.2		127.4, 126.8
	3,3'	7.14 (s), 6.90 (s)	106.7, 108.0	7.07 (s), 7.53 (s)	107.6, 108.6
	4,4'		146.7, 146.5		146.8, 145.9
	5,5'		137.57, 137.8		137.8, 137.9
	6,6'		146.0, 146.4		146.0 (2C)
	7,7'		169.9, 169.8		169.00, 169.5
galloyl	1		121.74		121.3
	2,6	7.93 (s)	110.4	8.01 (s)	111.9
	3,5		147.4		146.5
	4		140.8		141.5
	CO		168.0		167.3
	1'				121.6
	2',6'			7.86 (s)	110.5
	3',5'				147.4
	4'				140.7
	CO				167.2

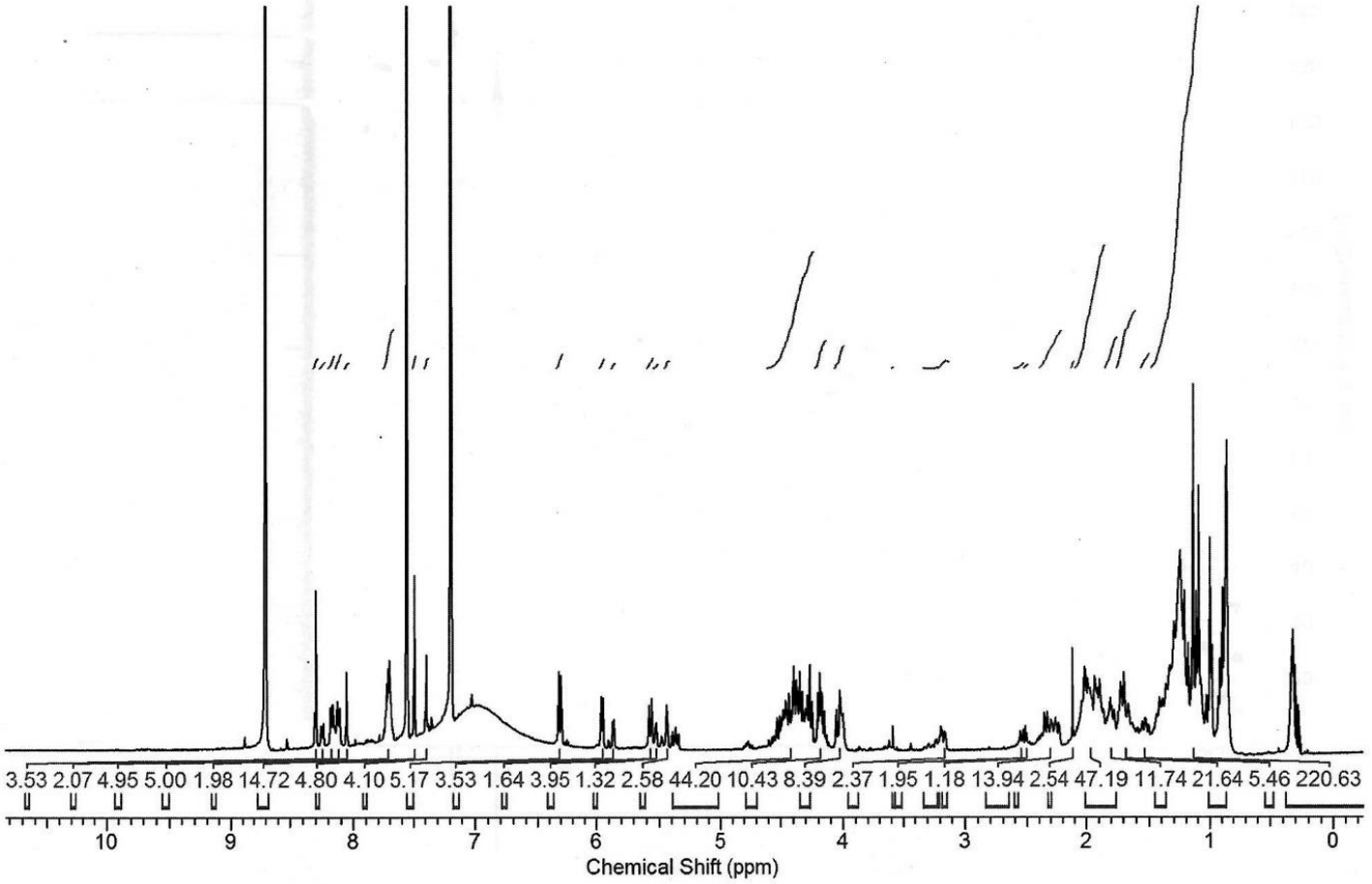


Figure S1. ^{1}H NMR spectrum of **1o** (pyridine-d_5, 500 MHz)

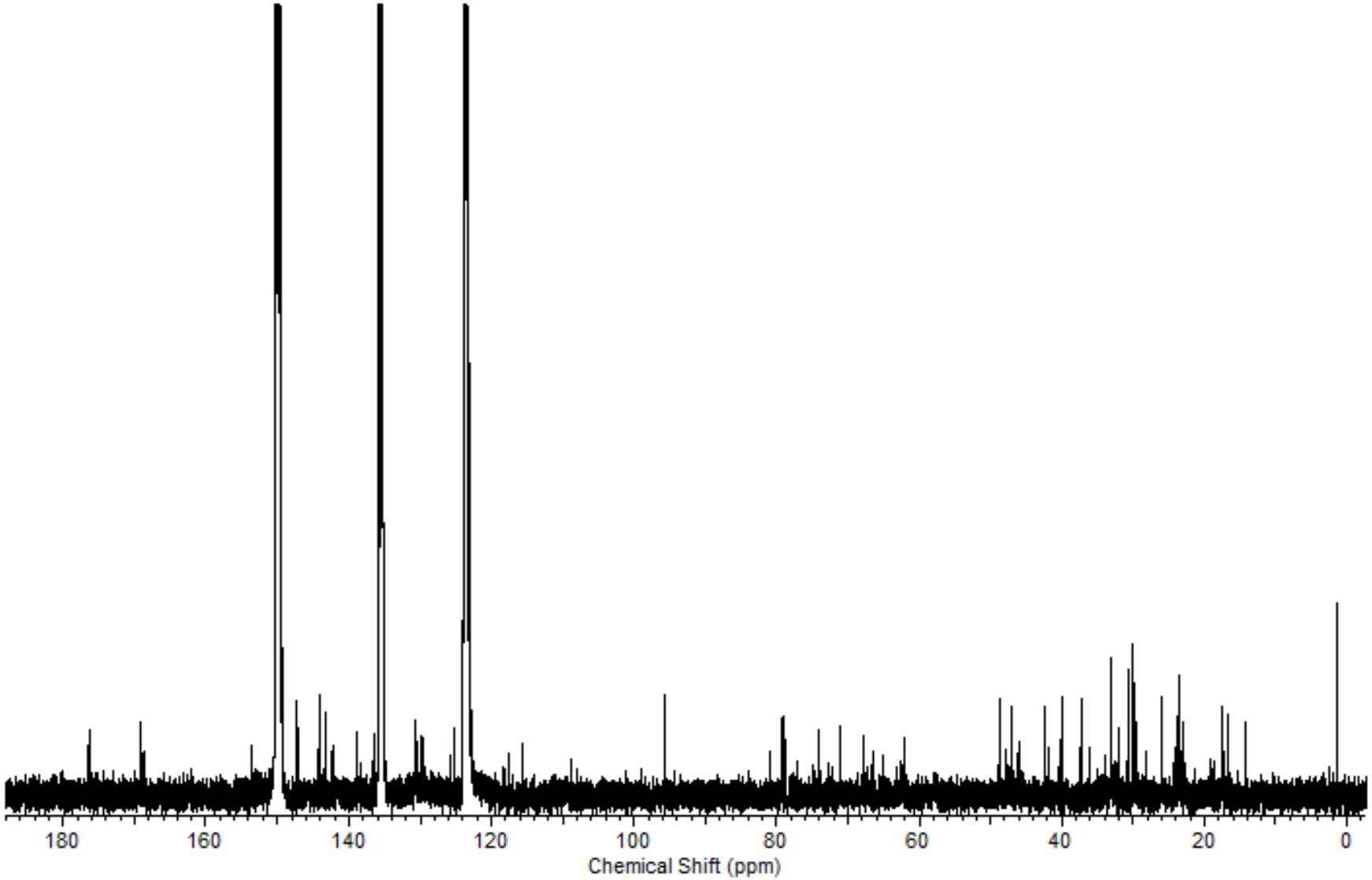


Figure S2. ^{13}C NMR spectrum of **1o** (pyridine-d_5, 126 MHz)

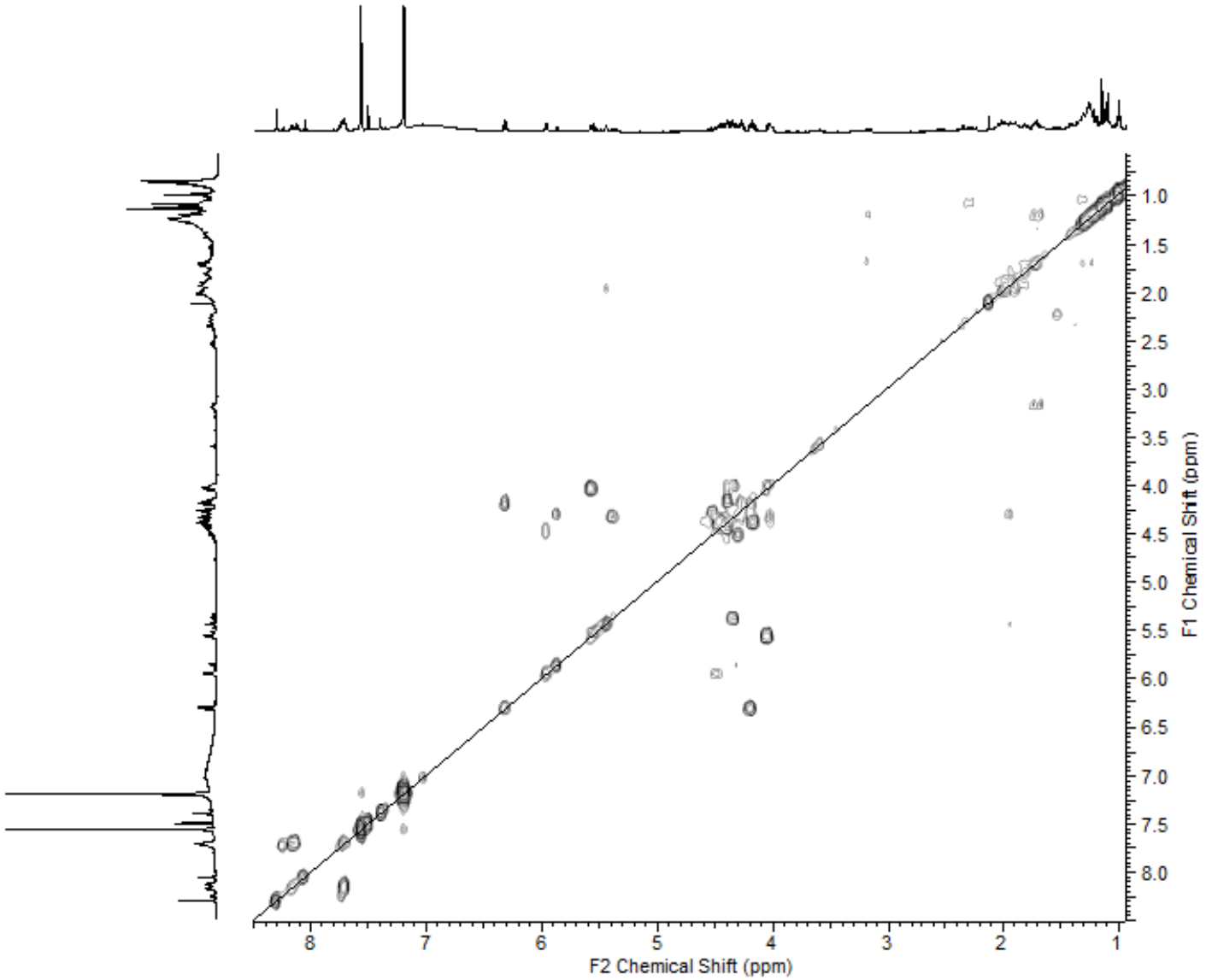


Figure S3. ^{1}H-^{1}H COSY spectrum of **1o** (pyridine-d_5, 500 MHz)

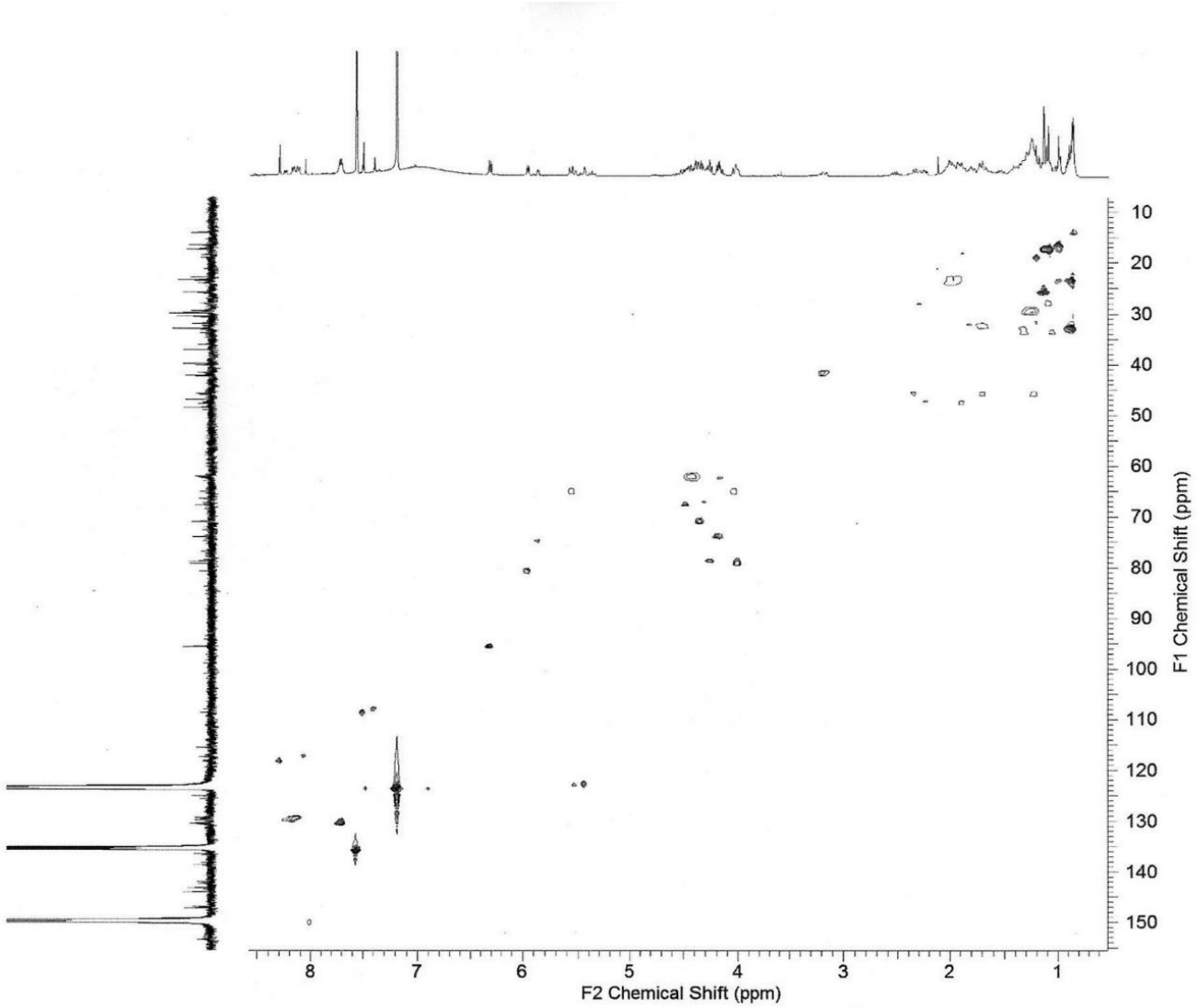


Figure S4. HSQC spectrum of **1o** (pyridine-d_5)

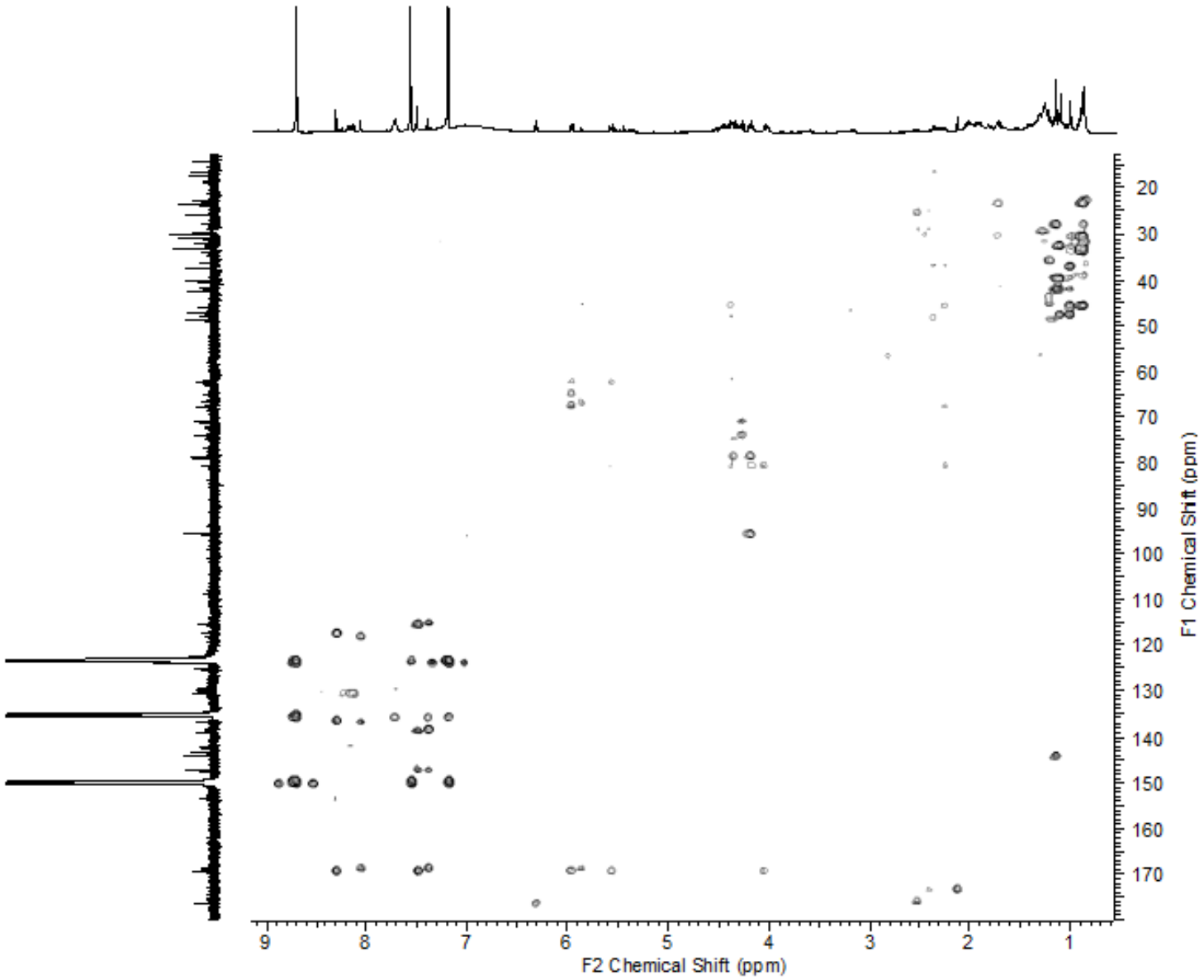


Figure S5. HMBC spectrum of **1o** (pyridine-d_5)

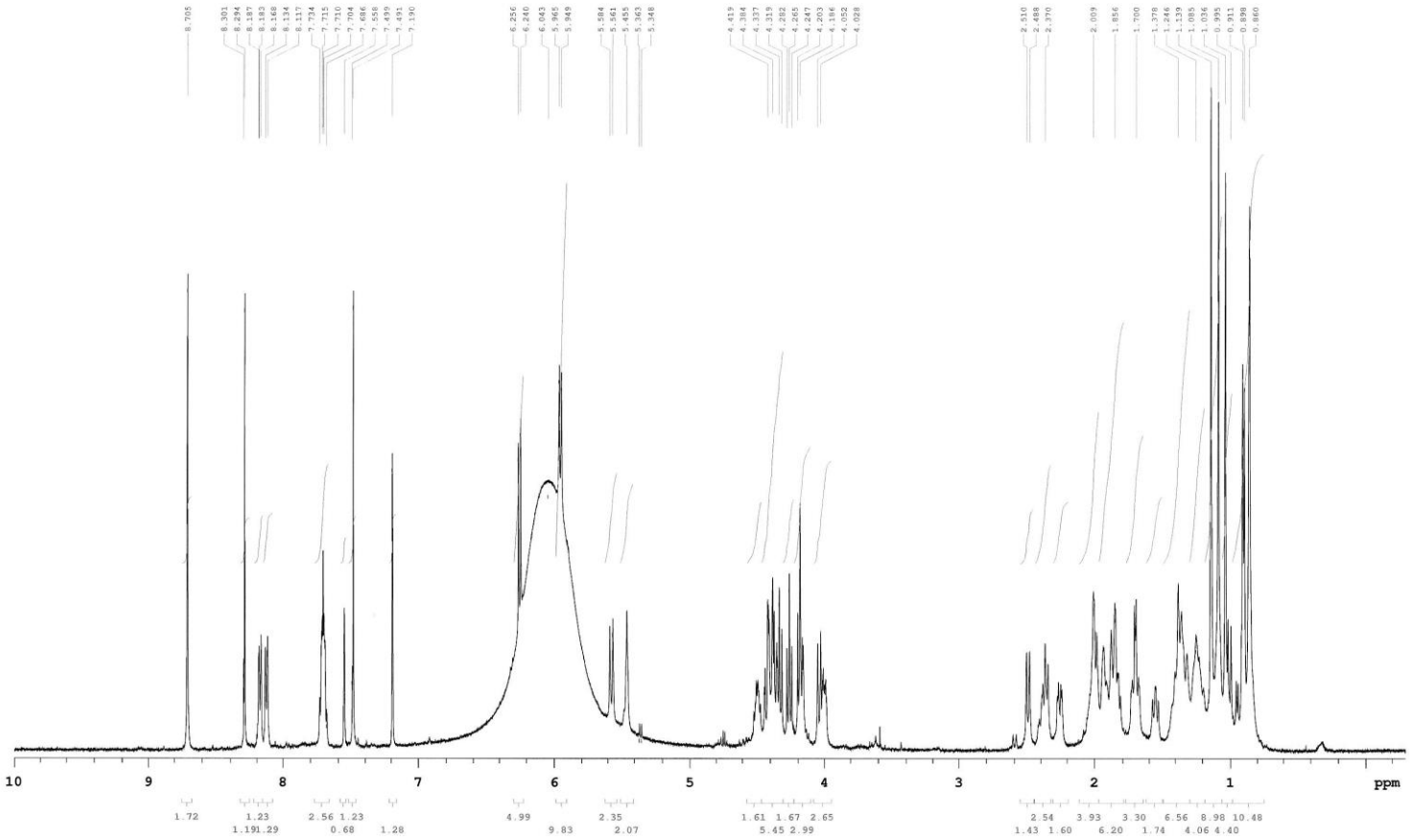


Figure S6. ^{1}H NMR spectrum of **1u** (pyridine-d_5, 500 MHz)

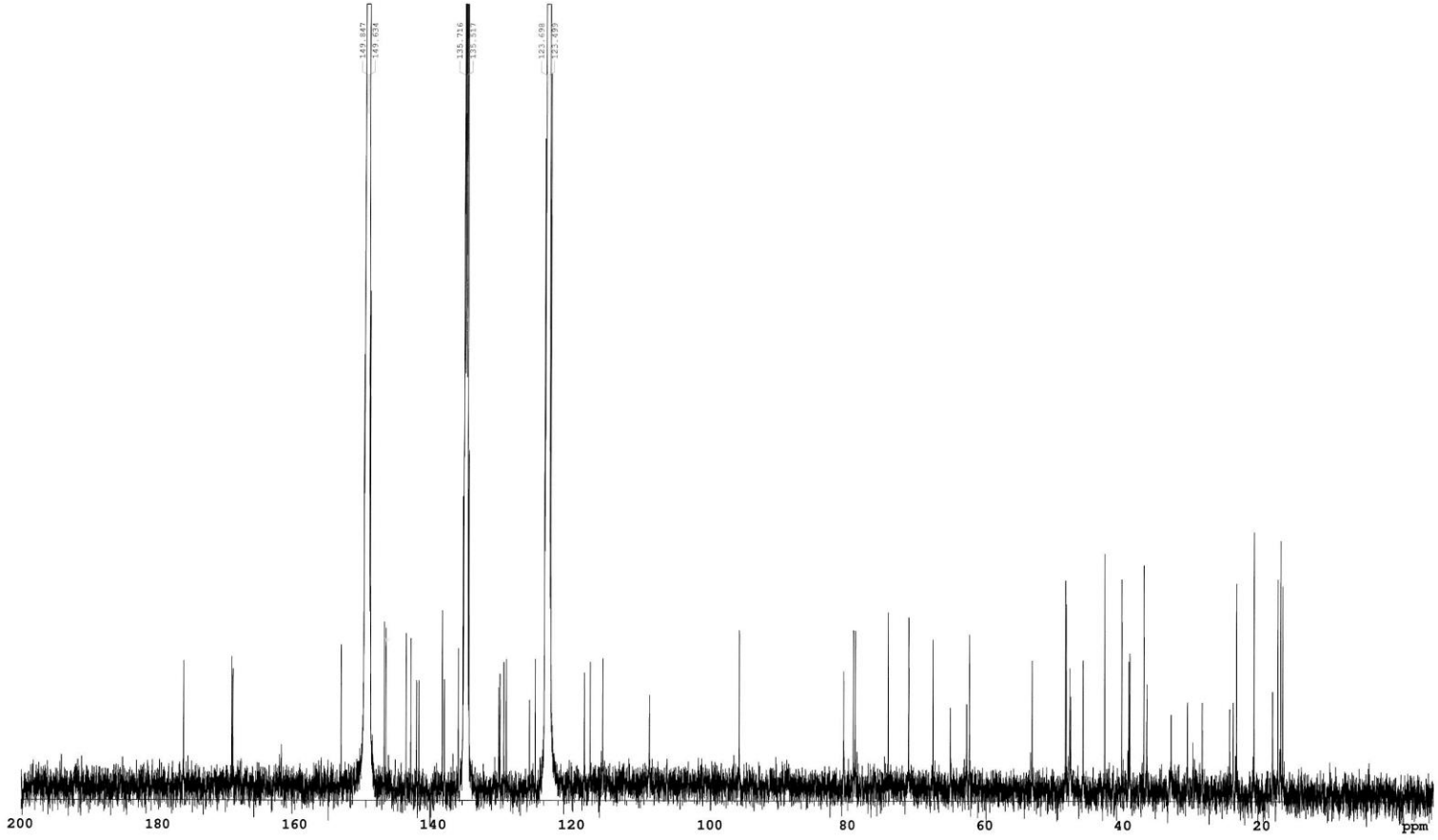


Figure S7. ^{13}C NMR spectrum of **1u** (pyridine-d_5, 126 MHz)

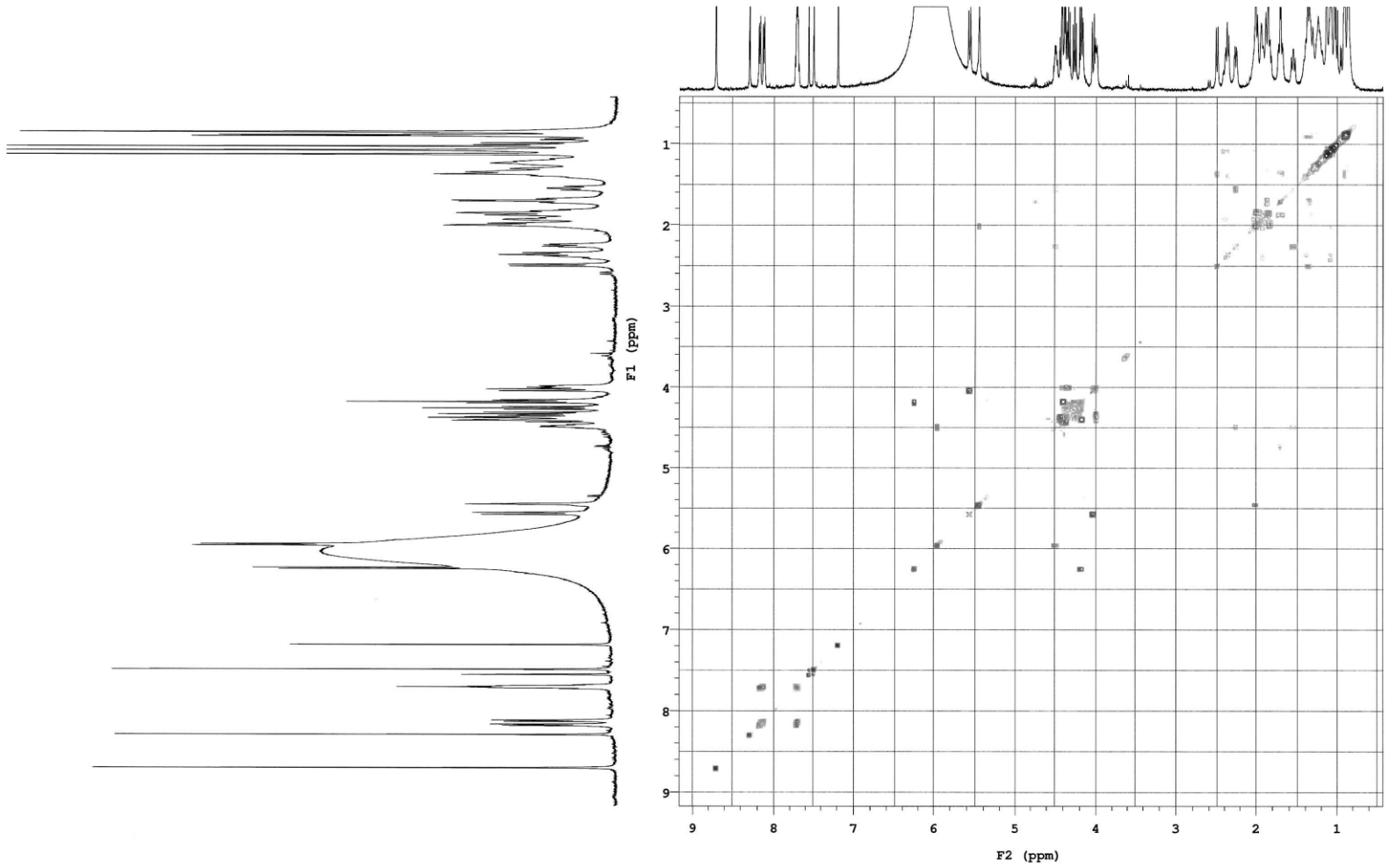


Figure S8. ^{1}H-^{1}H COSY spectrum of **1u** (pyridine-d_5, 500 MHz)

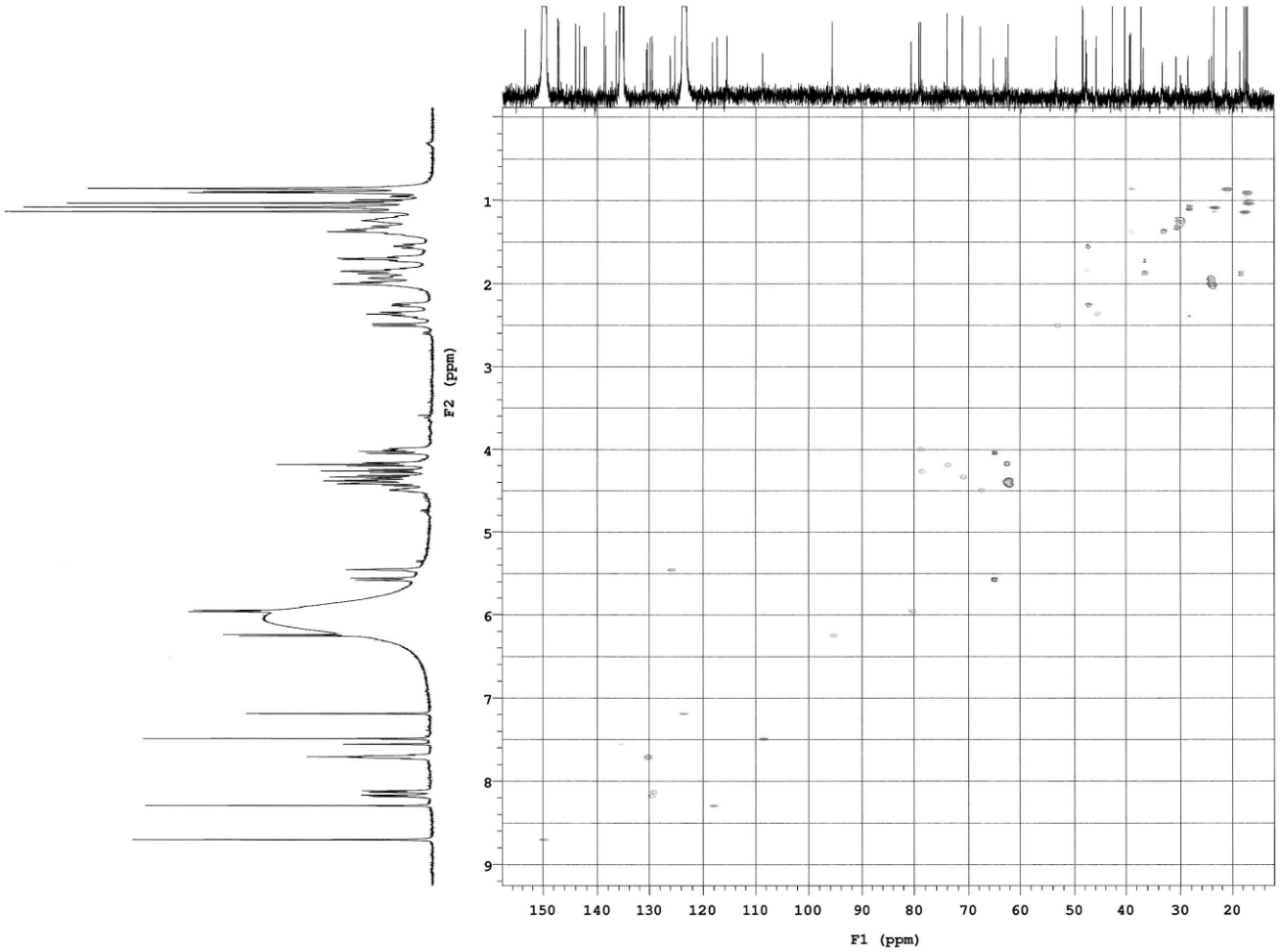


Figure S9. HSQC spectrum of **1u** (pyridine-d_5)

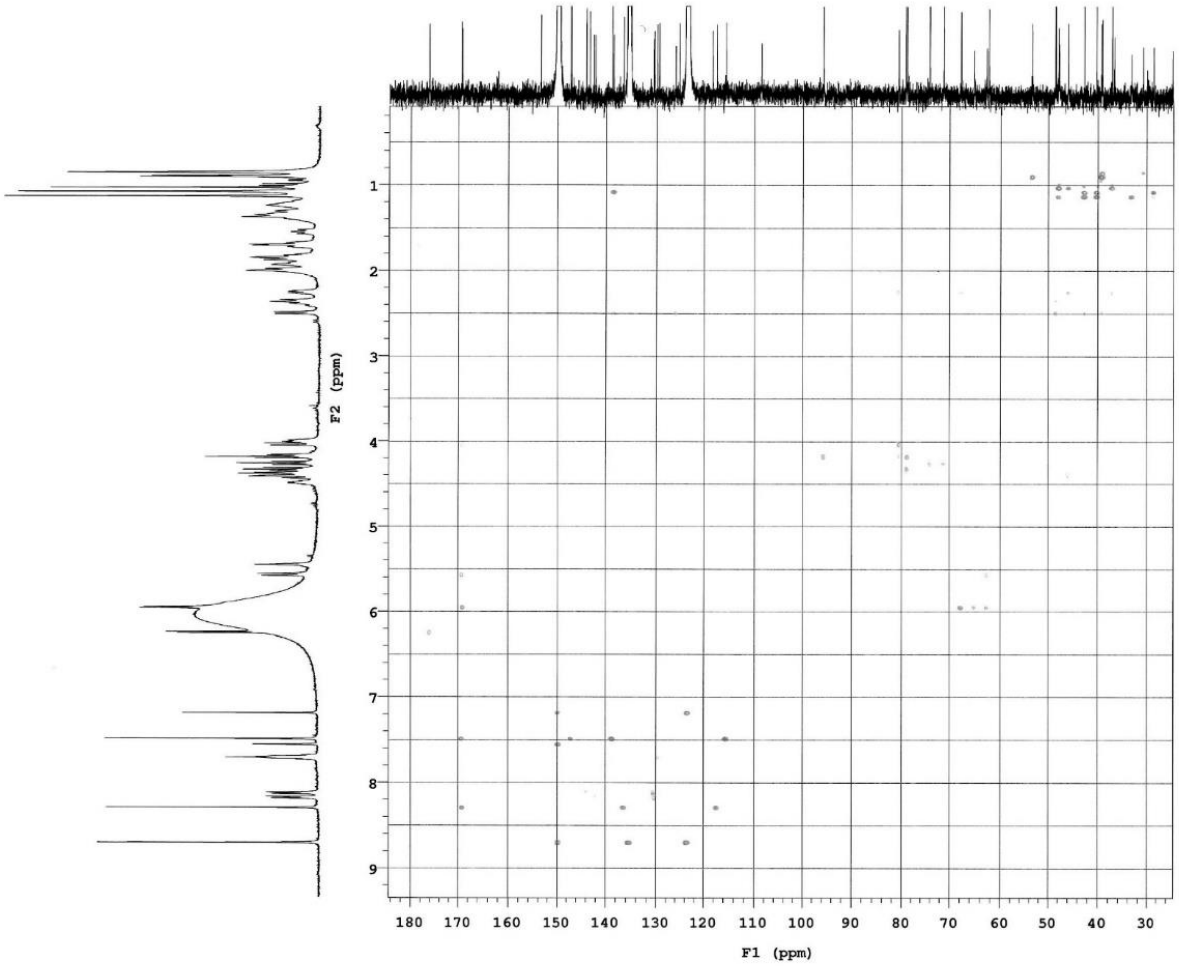


Figure S10. HMBC spectrum of **1u** (pyridine-d_5, 500 MHz)

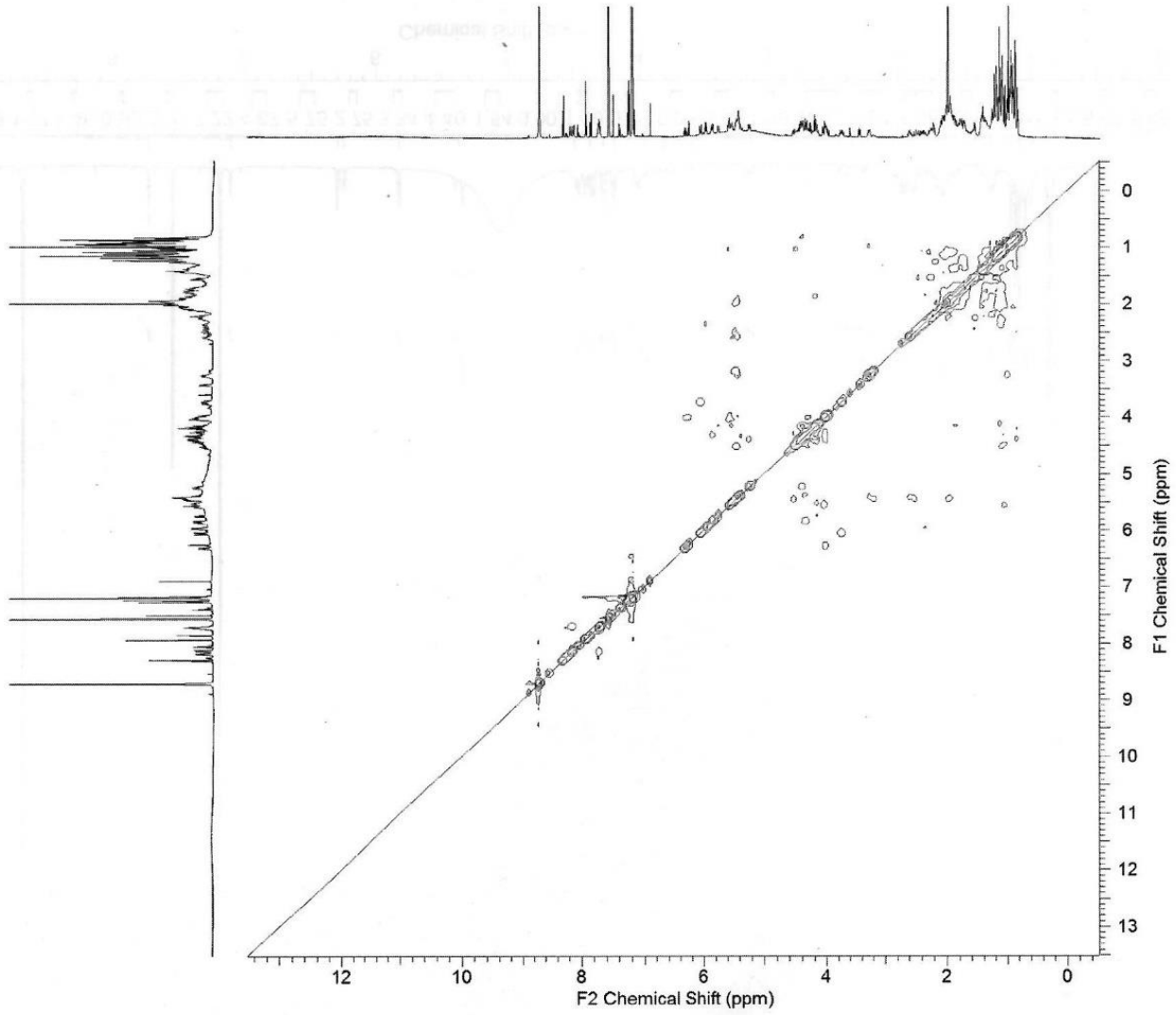


Figure S11. NOESY spectrum of **1o,u** (pyridine-d_5, 500 MHz)

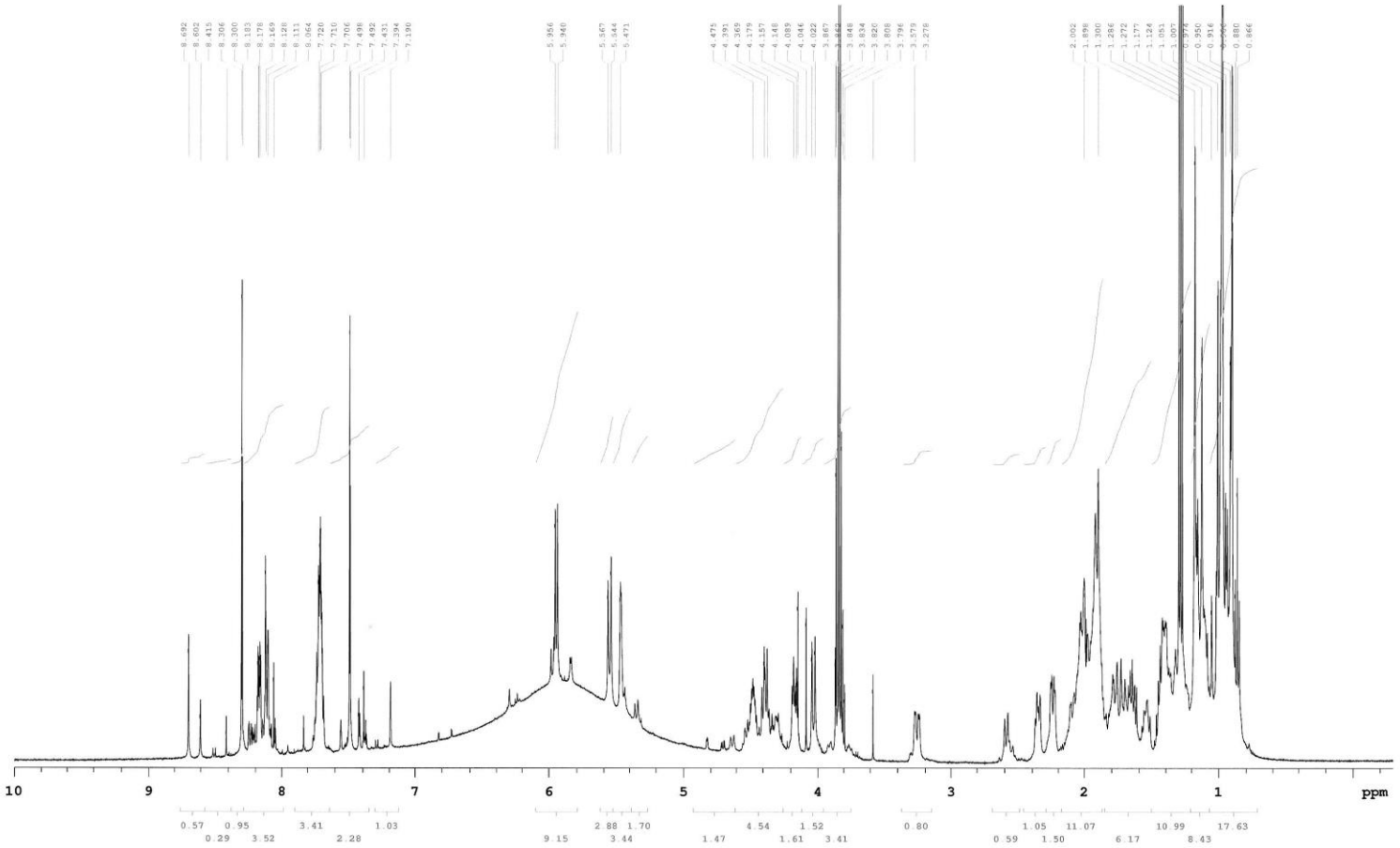


Figure S12. ^{13}H NMR spectrum of **2** (pyridine-d_5, 500 MHz)

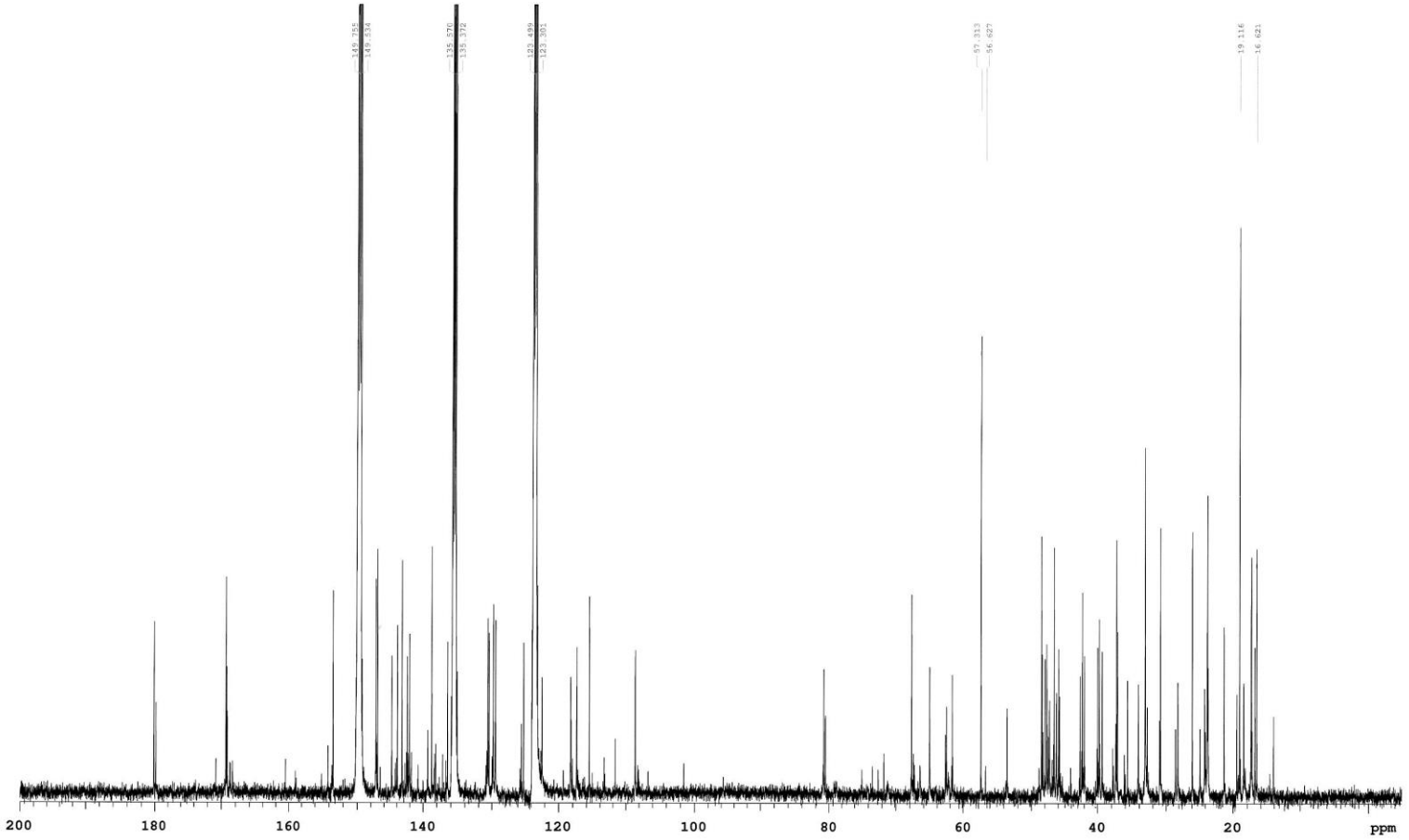


Figure S13. ^{13}C NMR spectrum of **2** (pyridine-d_5, 126 MHz)

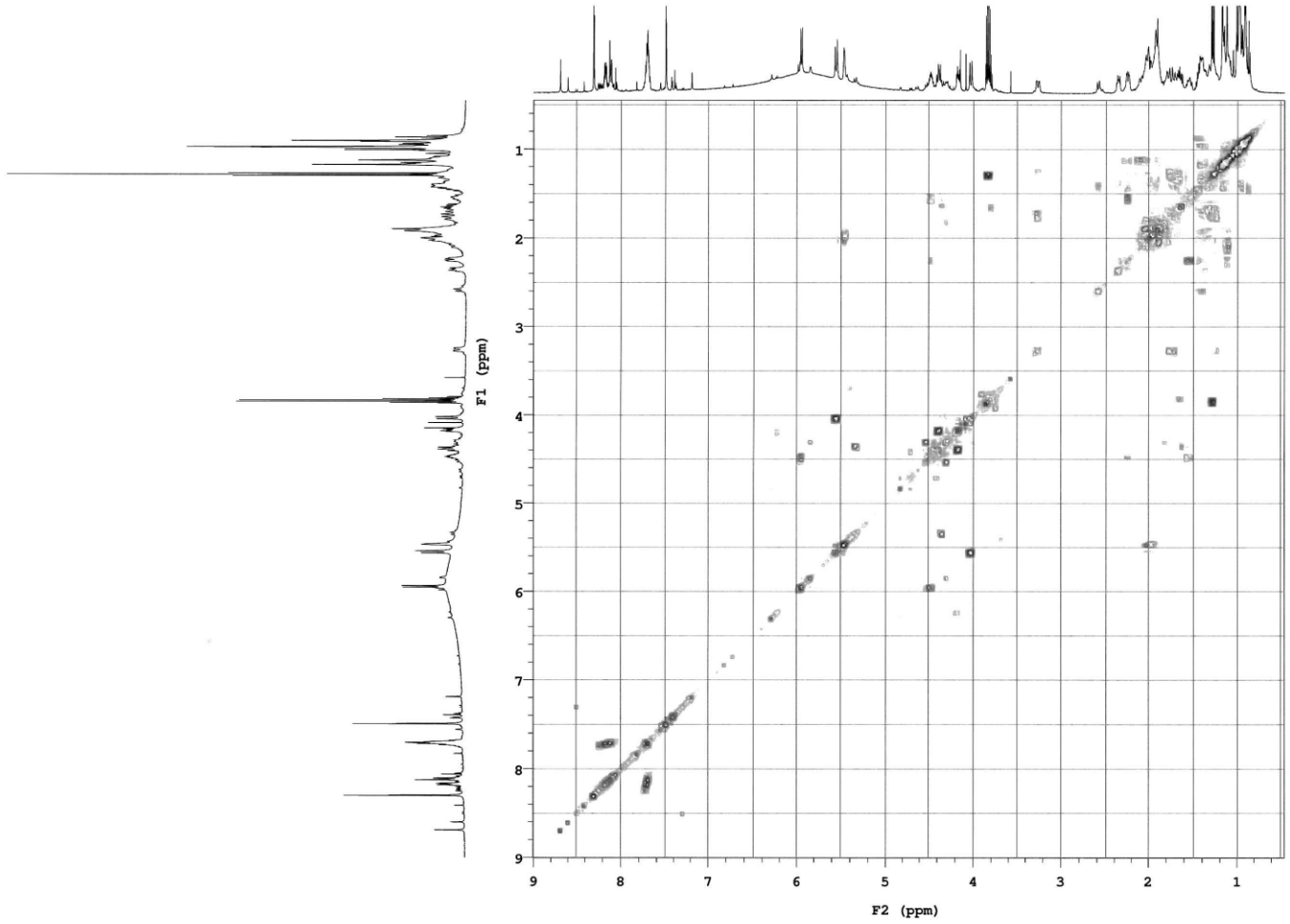


Figure S14. ^{1}H-^{1}H COSY spectrum of **2** (pyridine-d_5, 500 MHz)

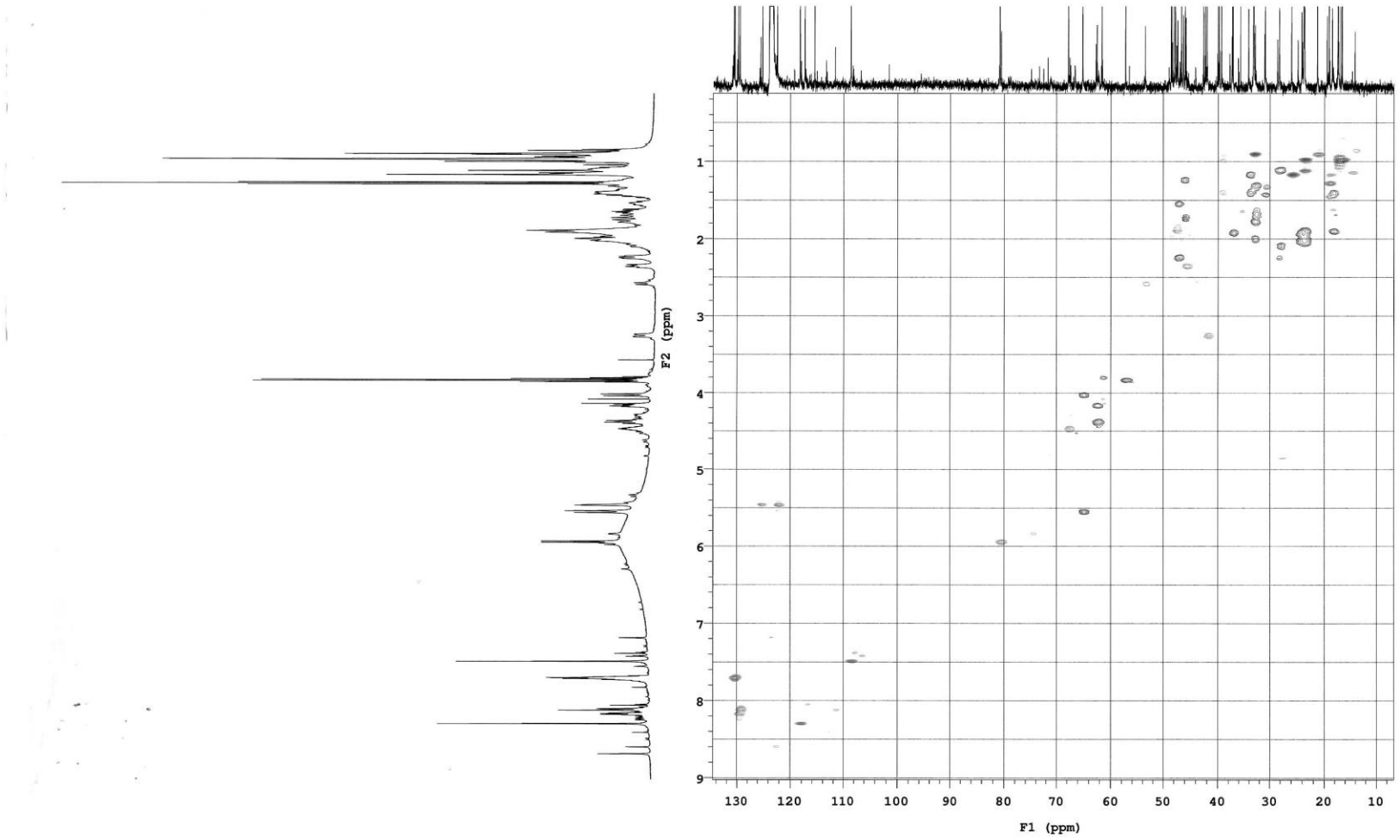


Figure S15. HSQC spectrum of **2** (pyridine-d_5)

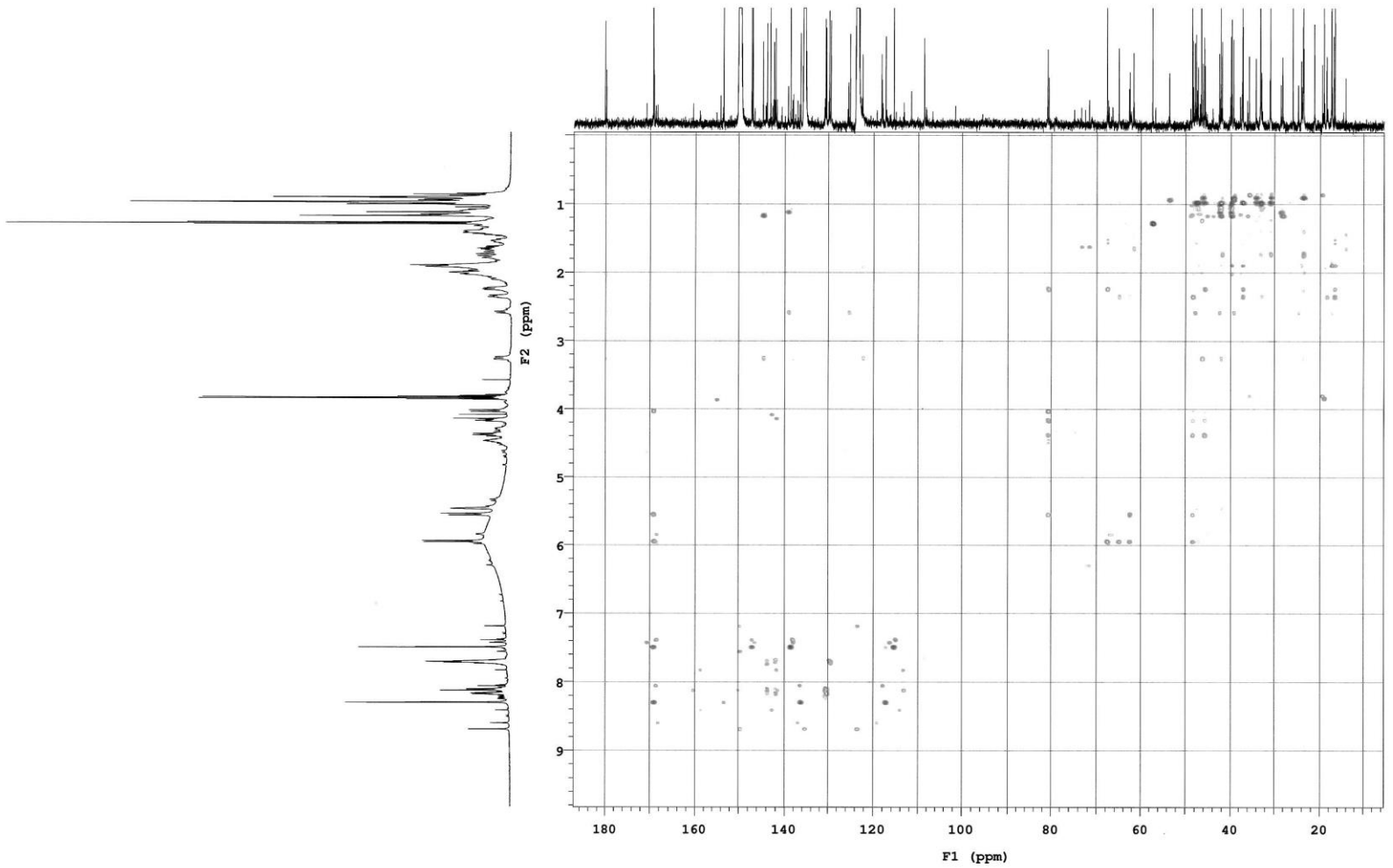


Figure S16. HMBC spectrum of **2** (pyridine-d_5)

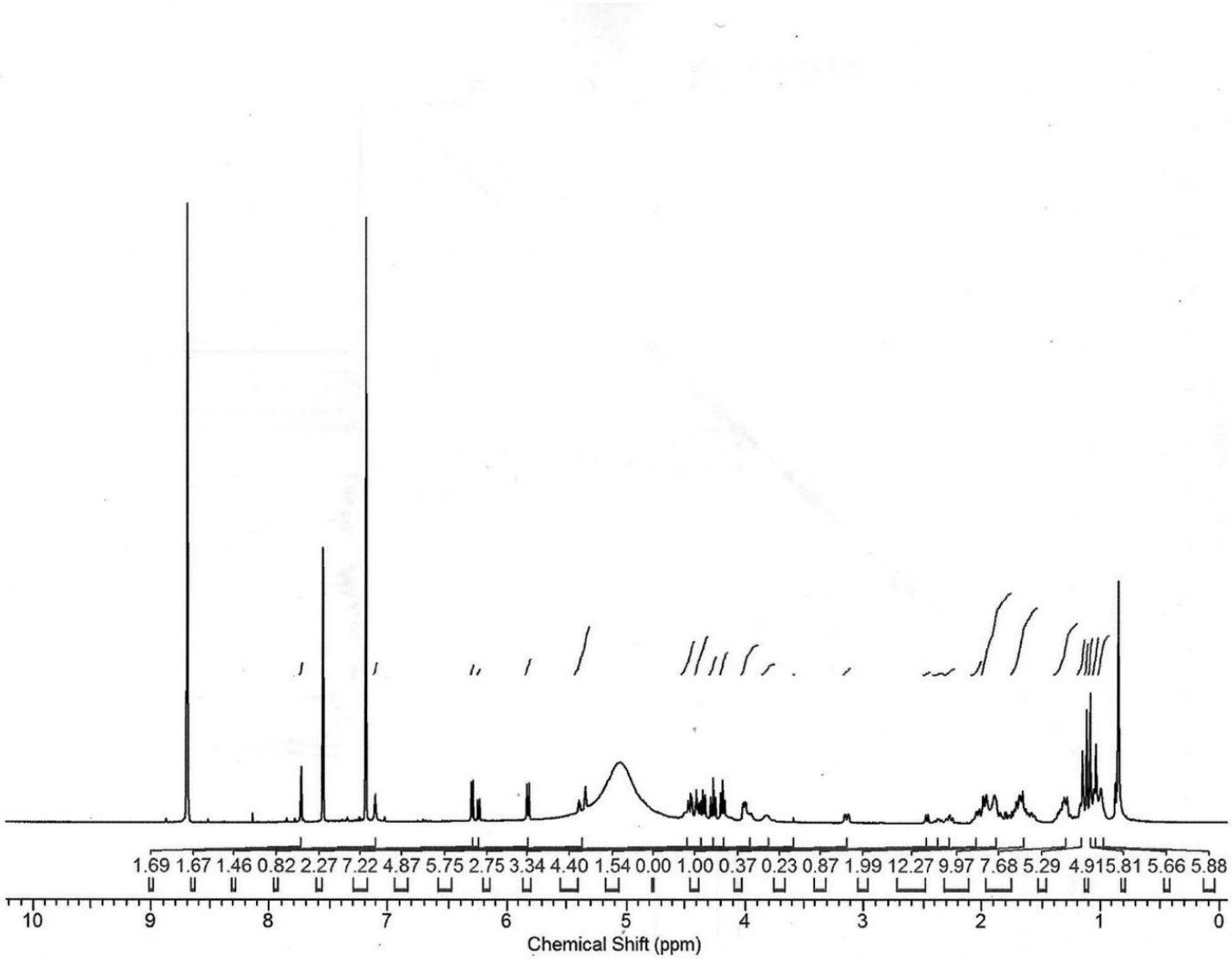


Figure S17. ^{1}H NMR spectrum of **4** (pyridine-d_5, 500 MHz)

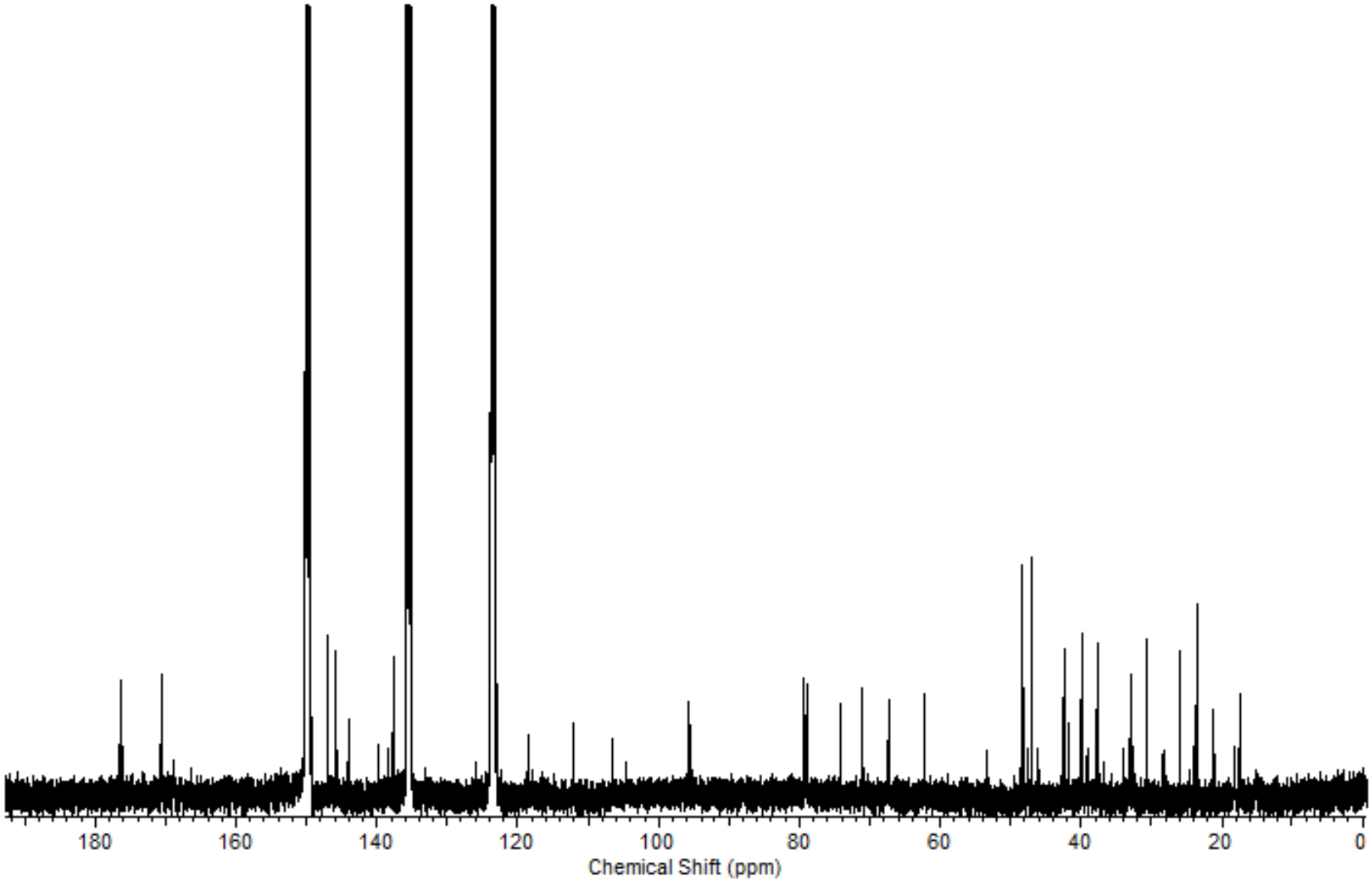


Figure S18. ^{13}C NMR spectrum of **4** (pyridine-d_5, 126 MHz)

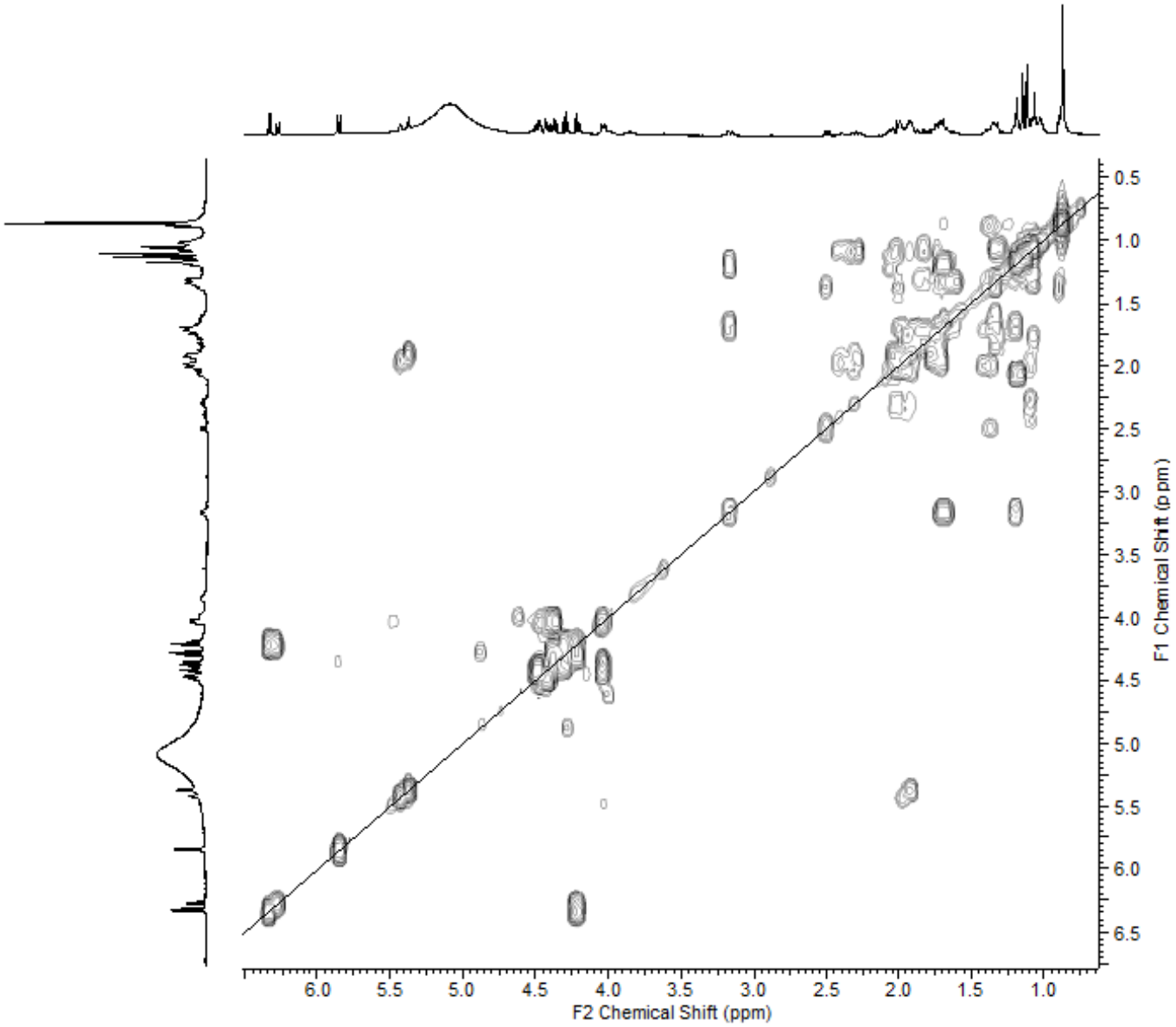


Figure S19. ^{1}H-^{1}H COSY spectrum of **4** (pyridine-d_5, 500 MHz)

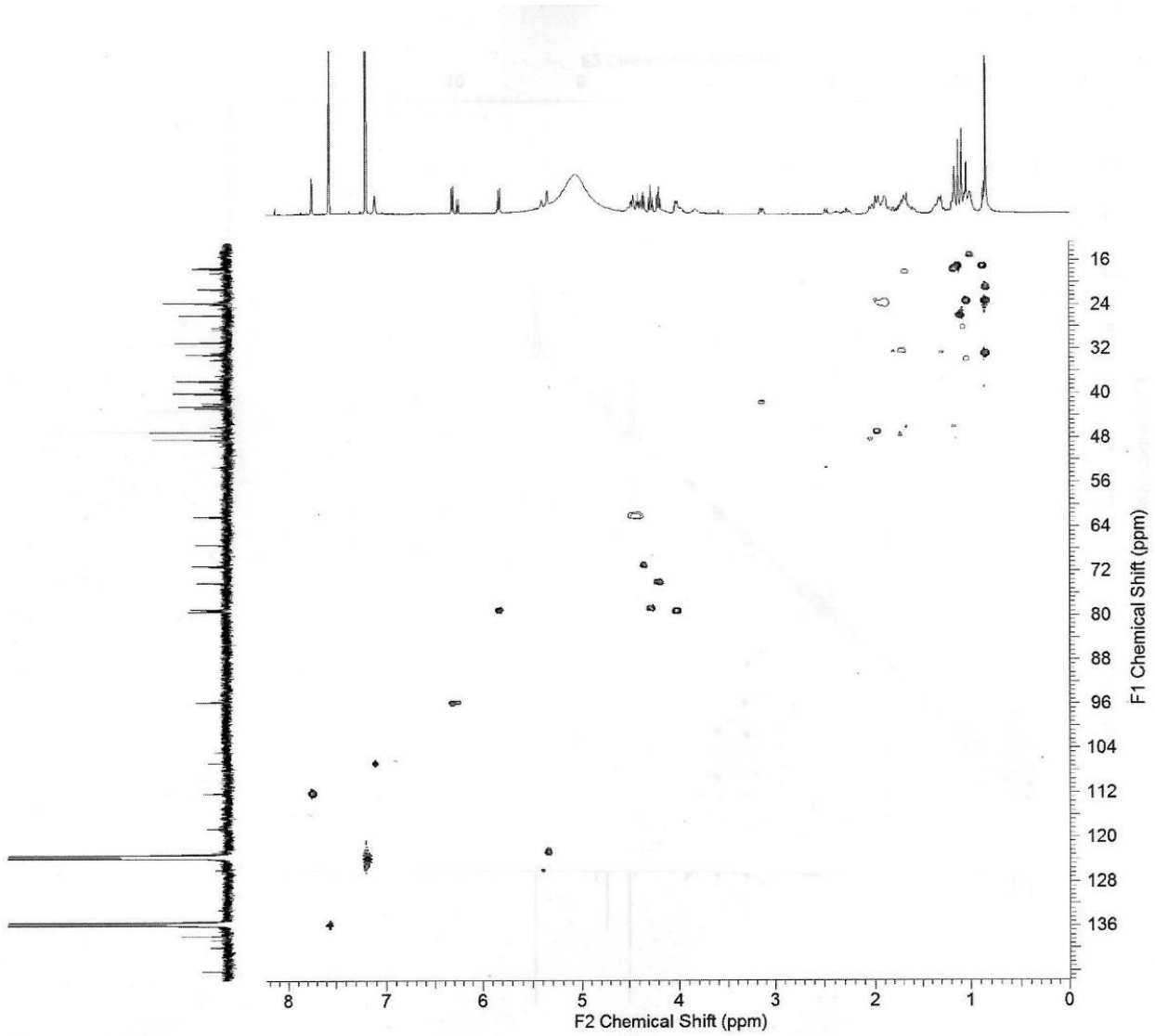


Figure S20. HSQC spectrum of **4** (pyridine-d_5)

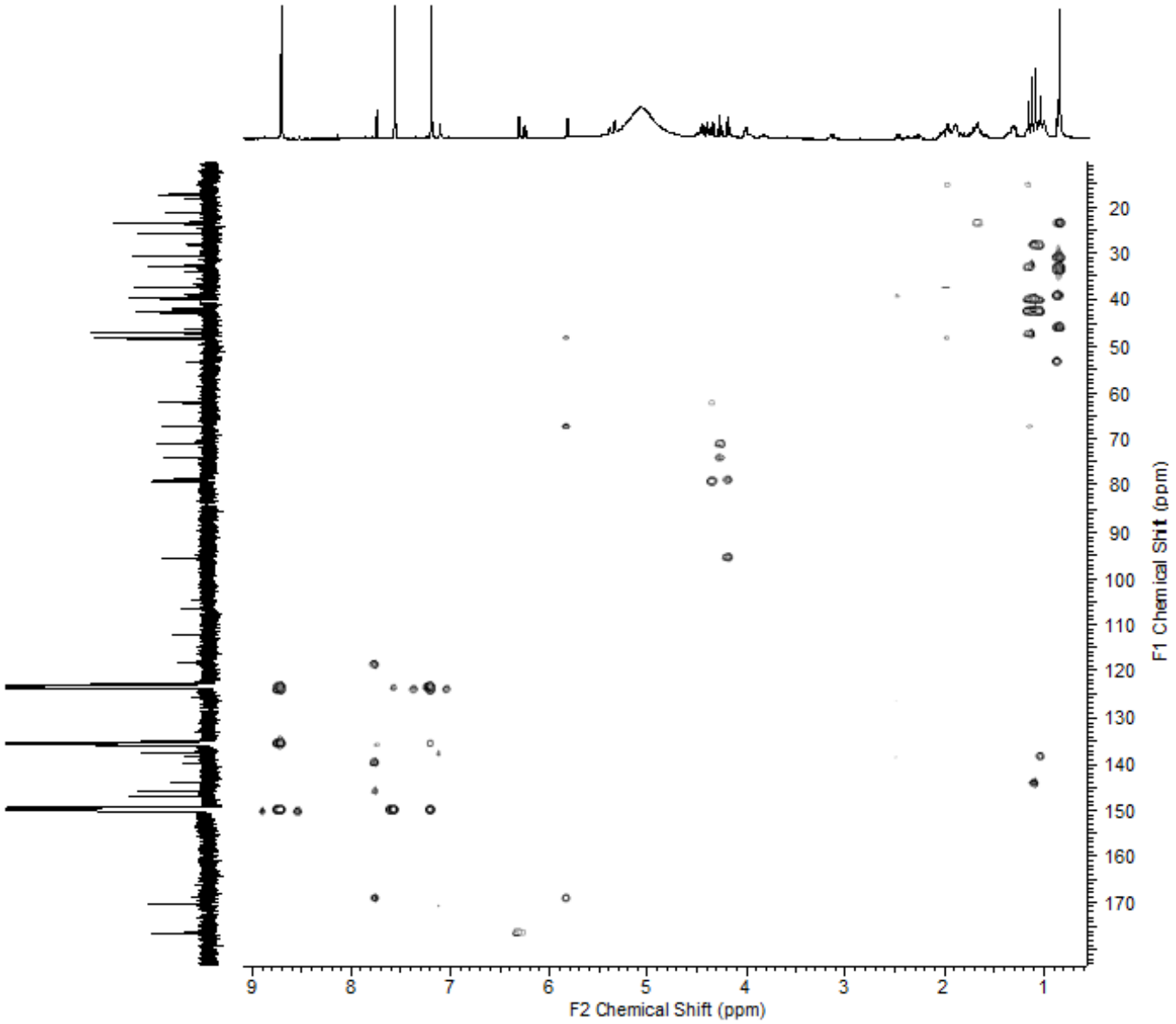


Figure S21. HMBC spectrum of **4** (pyridine-d_5)

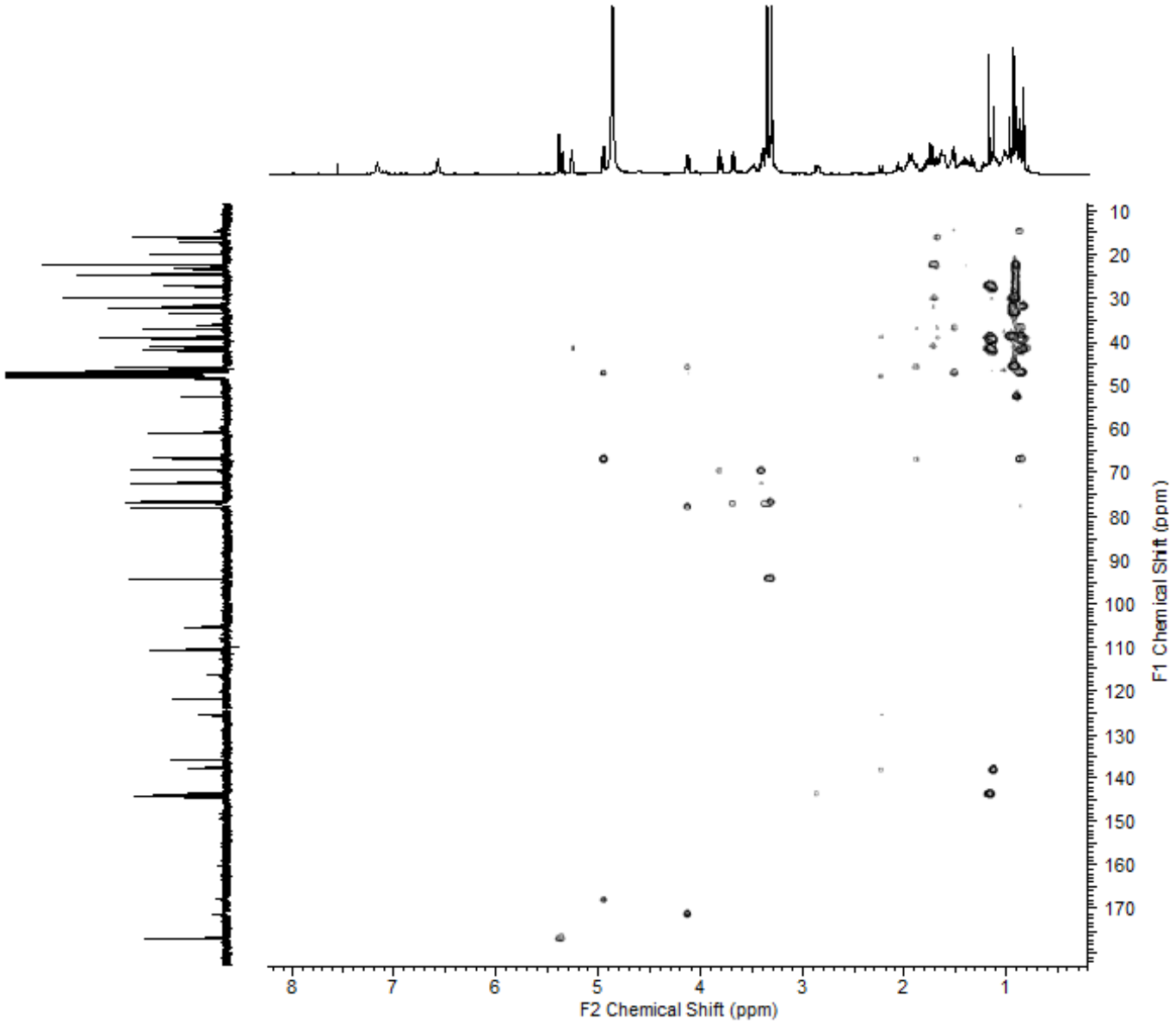


Figure S22. HMBC spectrum of **4** (CD_3OD, 500 MHz)

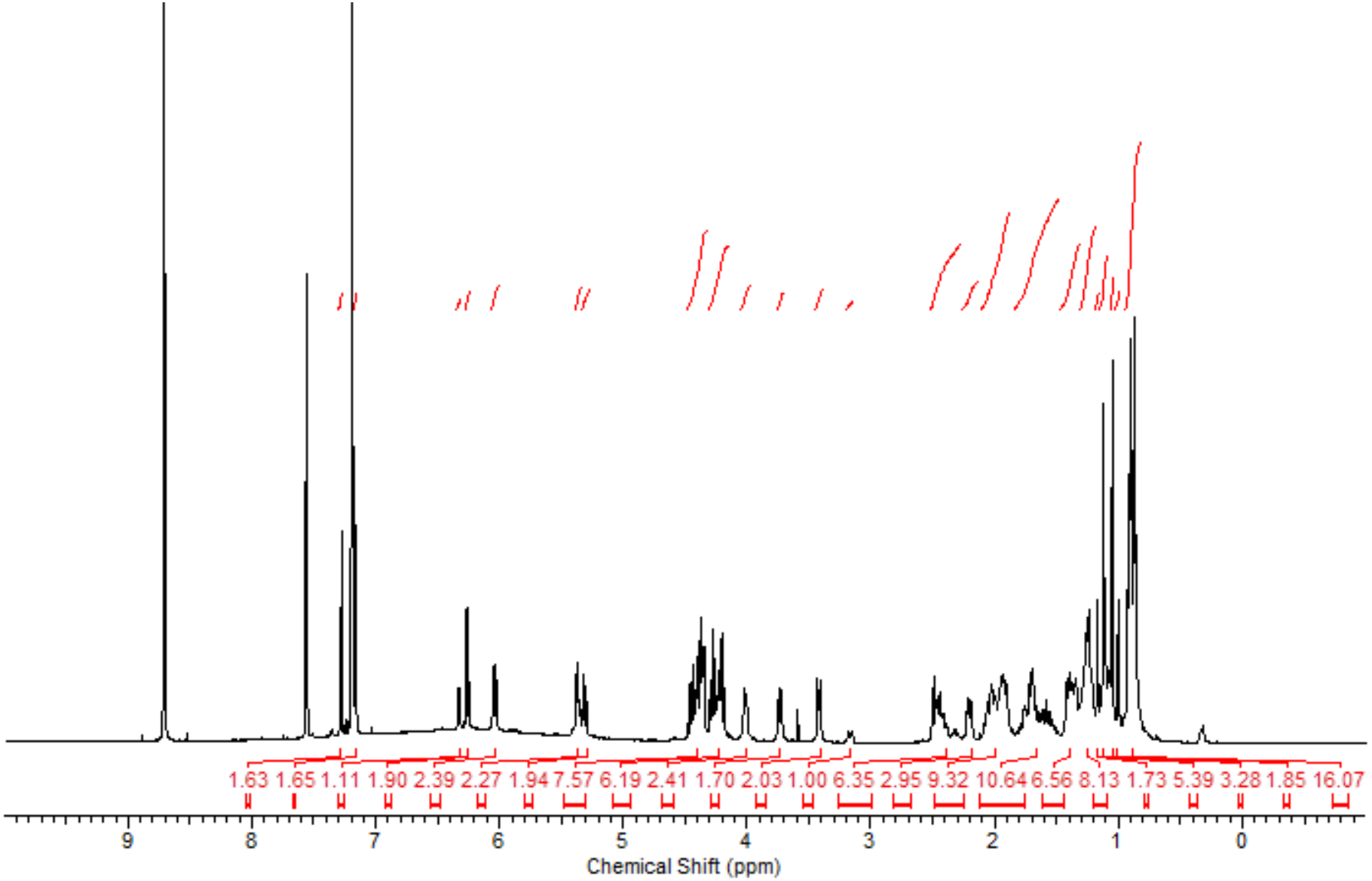


Figure S23. ^{1}H NMR spectrum of **9** (pyridine-d_5, 500 MHz)

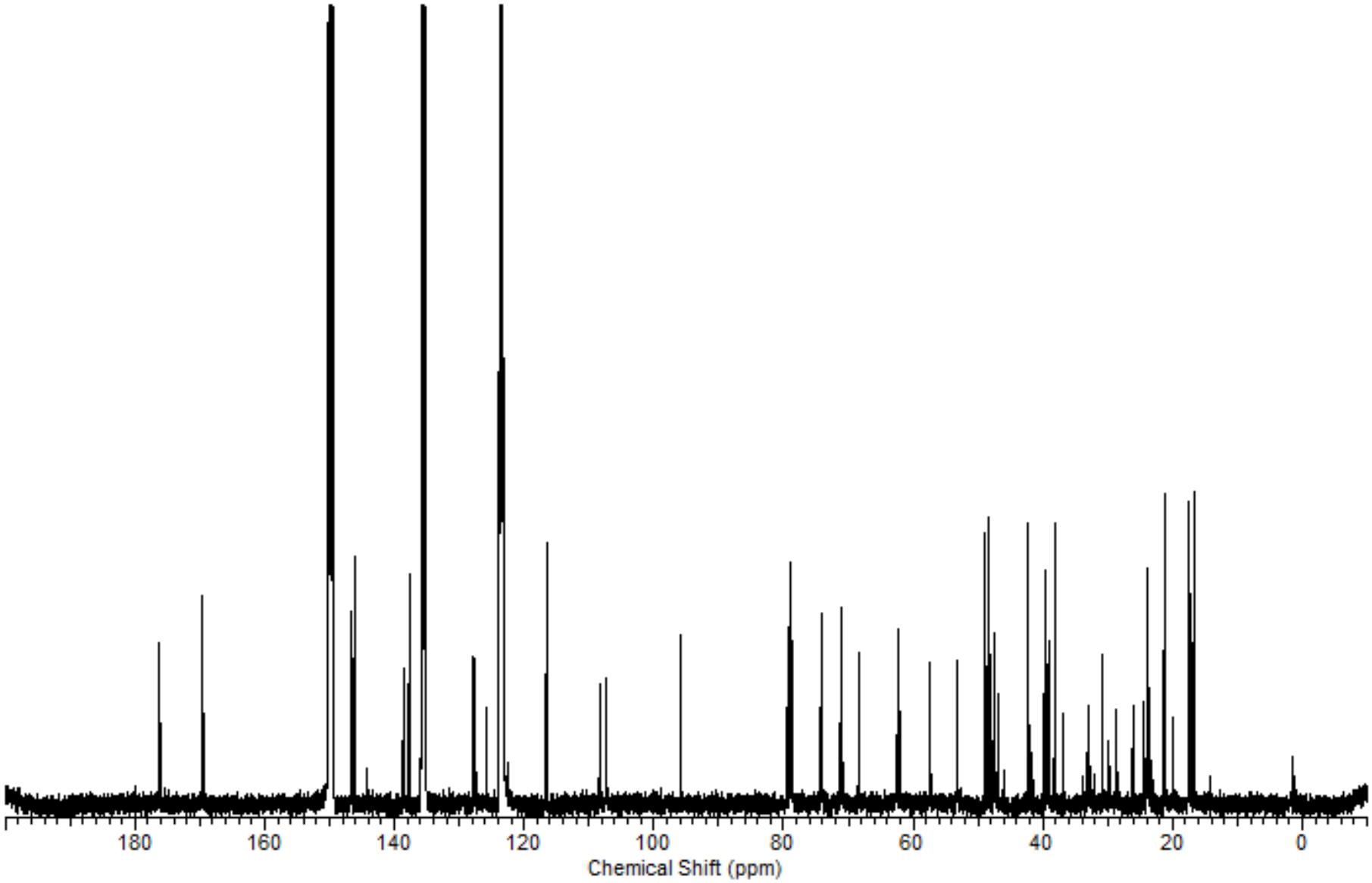


Figure S24. ^{13}C NMR spectrum of **9** (pyridine-d_5, 126 MHz)

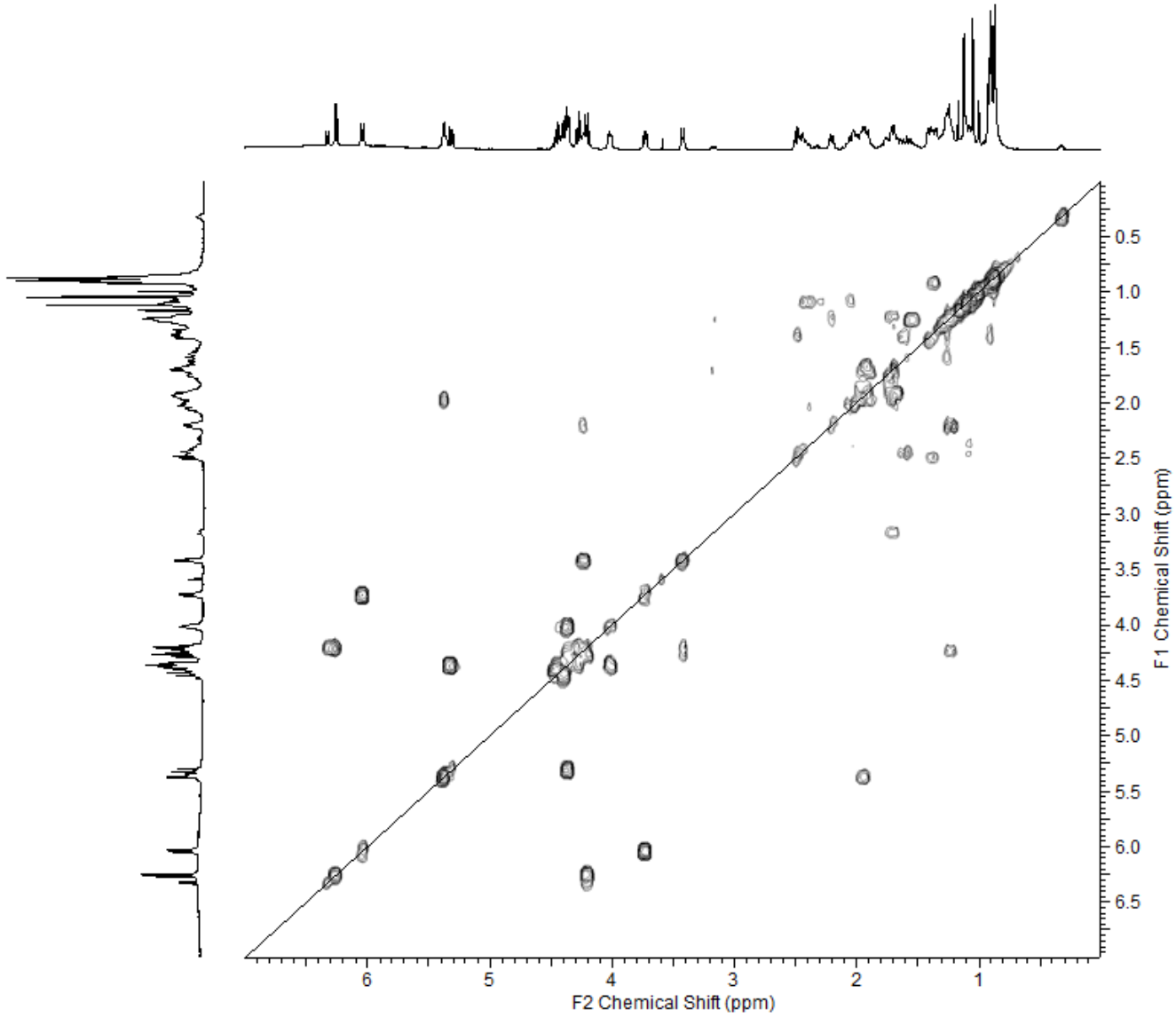


Figure S25. ^{1}H-^{1}H COSY spectrum of **9** (pyridine-d_5, 500 MHz)

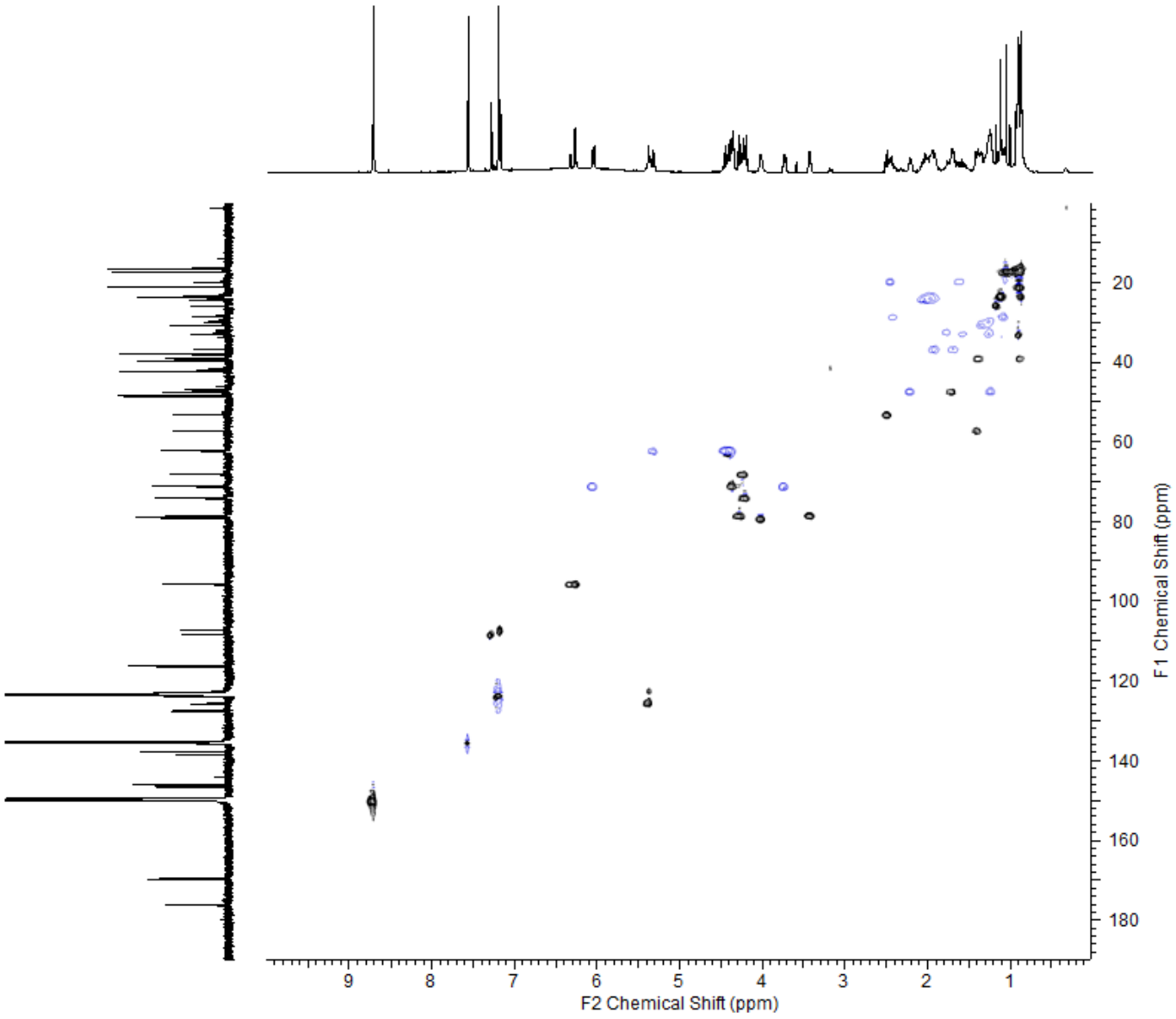


Figure S26. HSQC spectrum of **9** (pyridine-d_5)

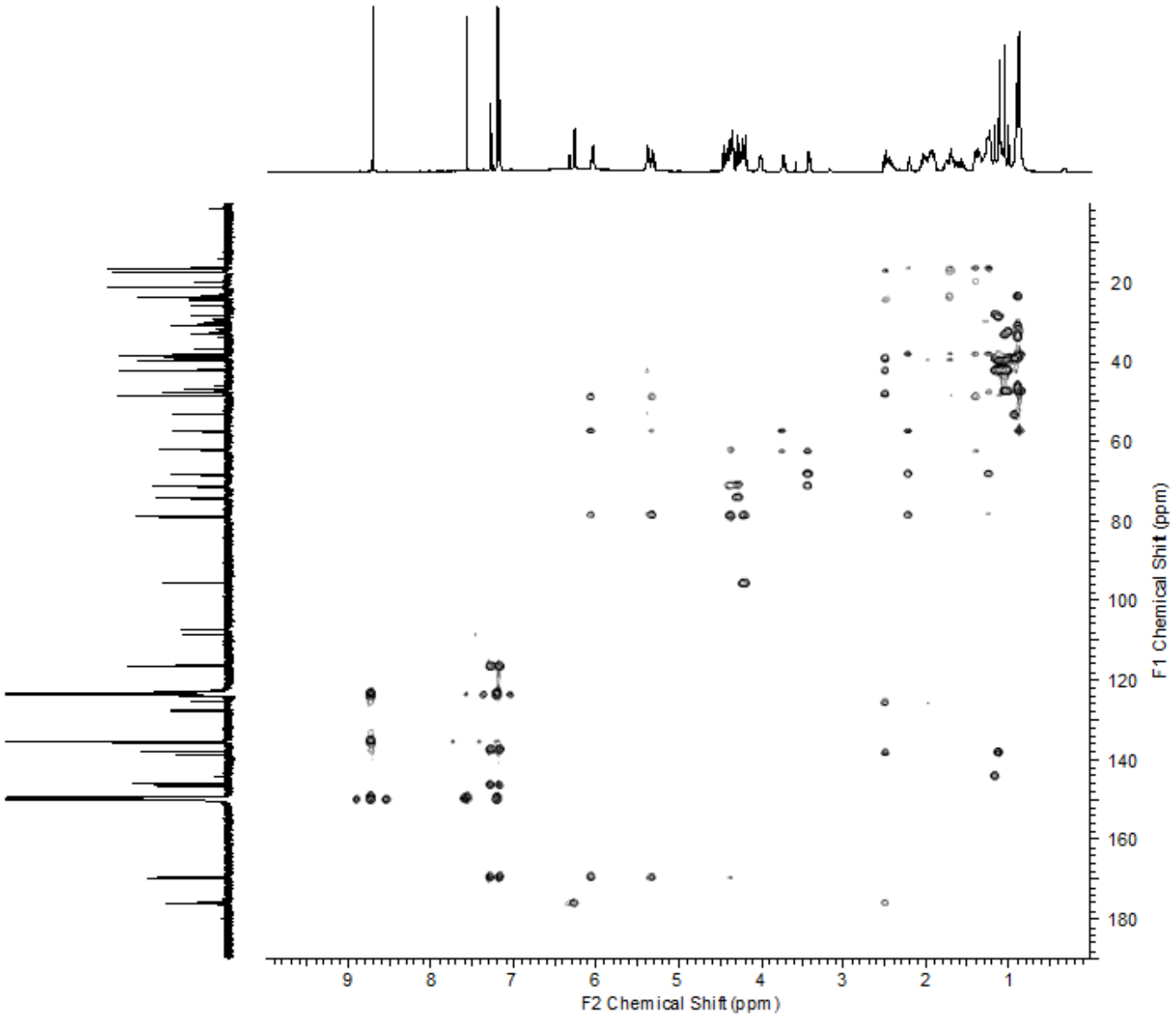


Figure S27. HMBC spectrum of **9** (pyridine-d_5)

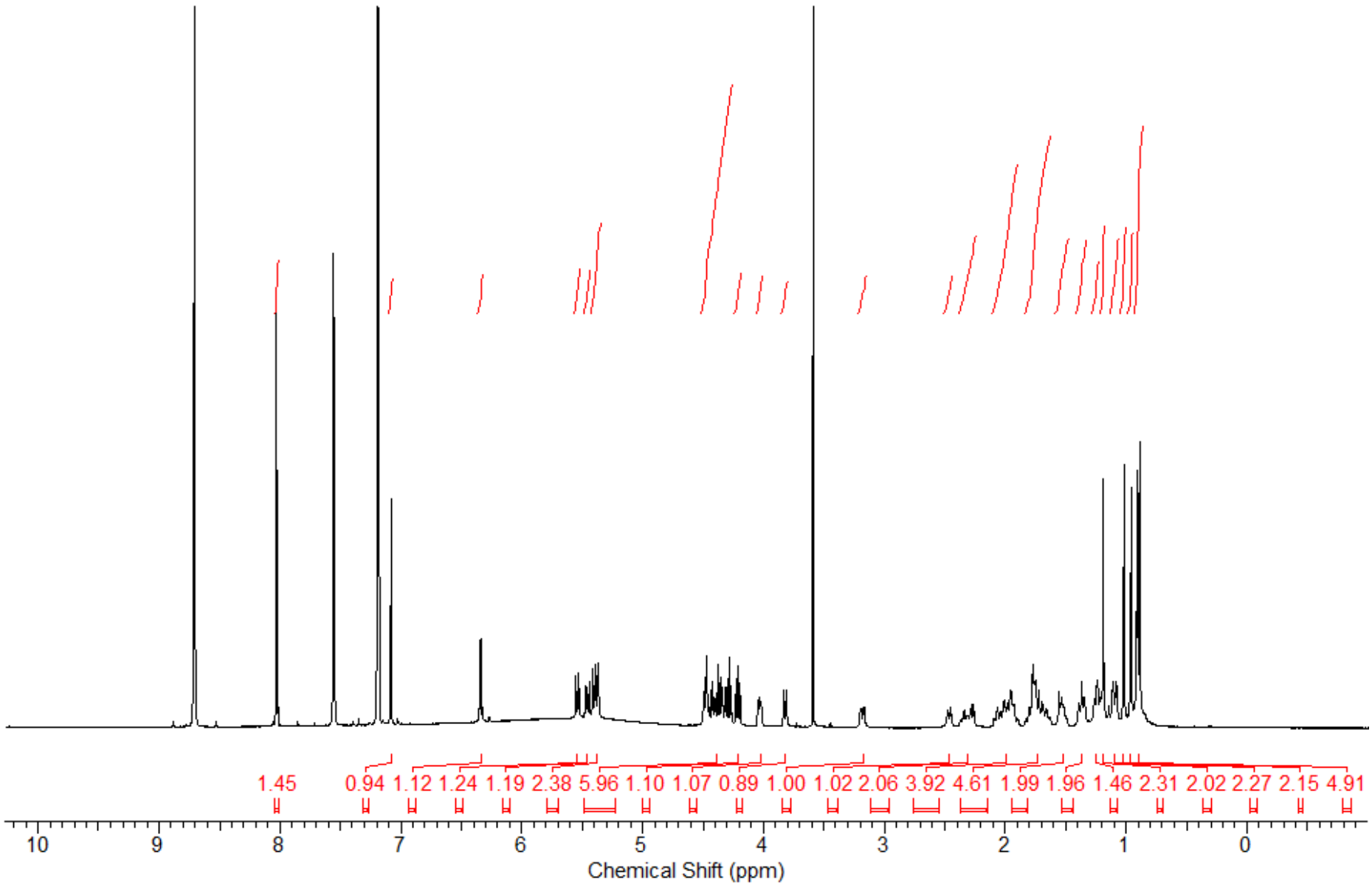


Figure S28. ^{1}H NMR spectrum of **10** (pyridine-d_5, 500 MHz)

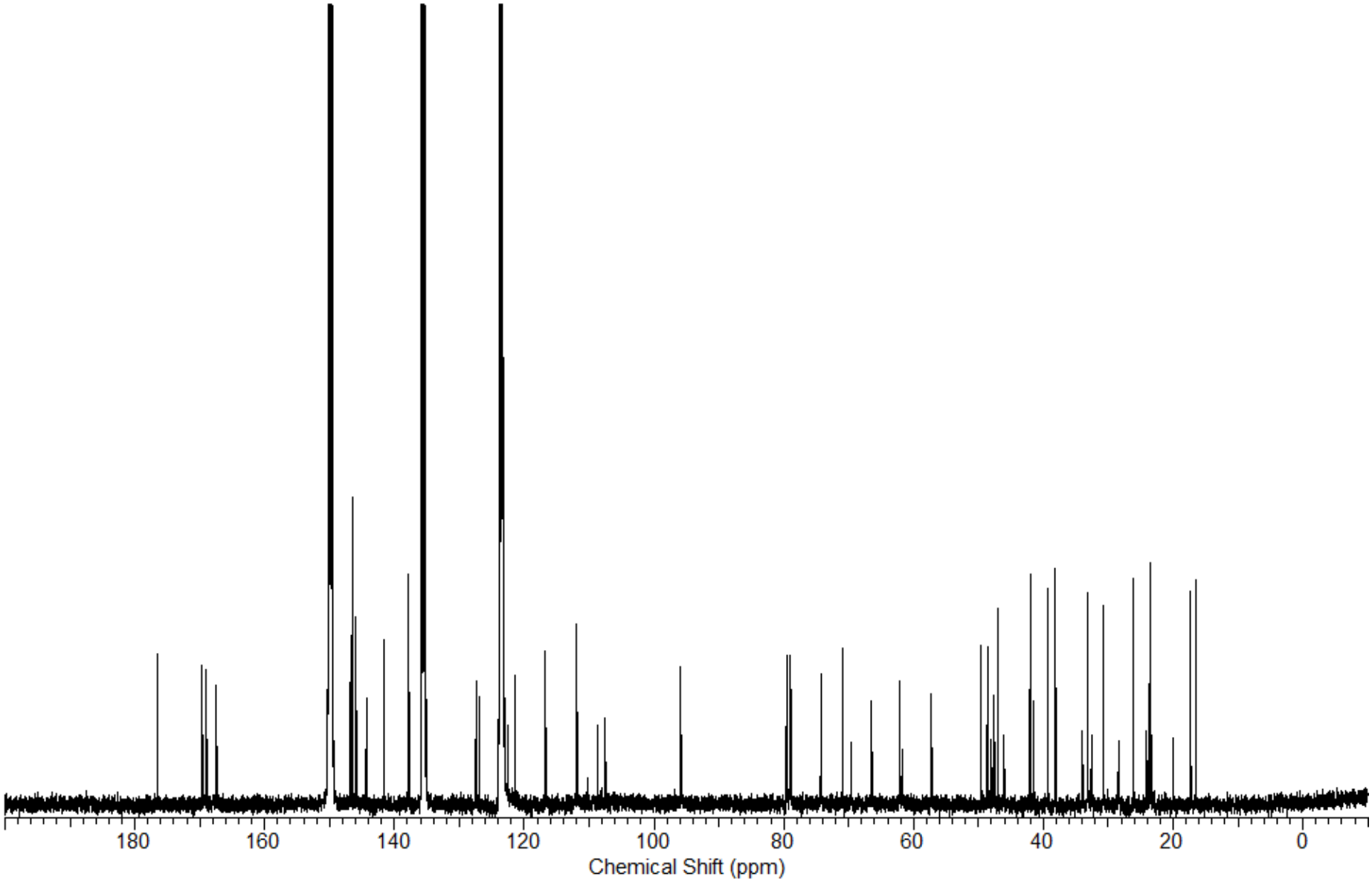


Figure S29. ^{13}C NMR spectrum of **10** (pyridine-d_5, 126 MHz)

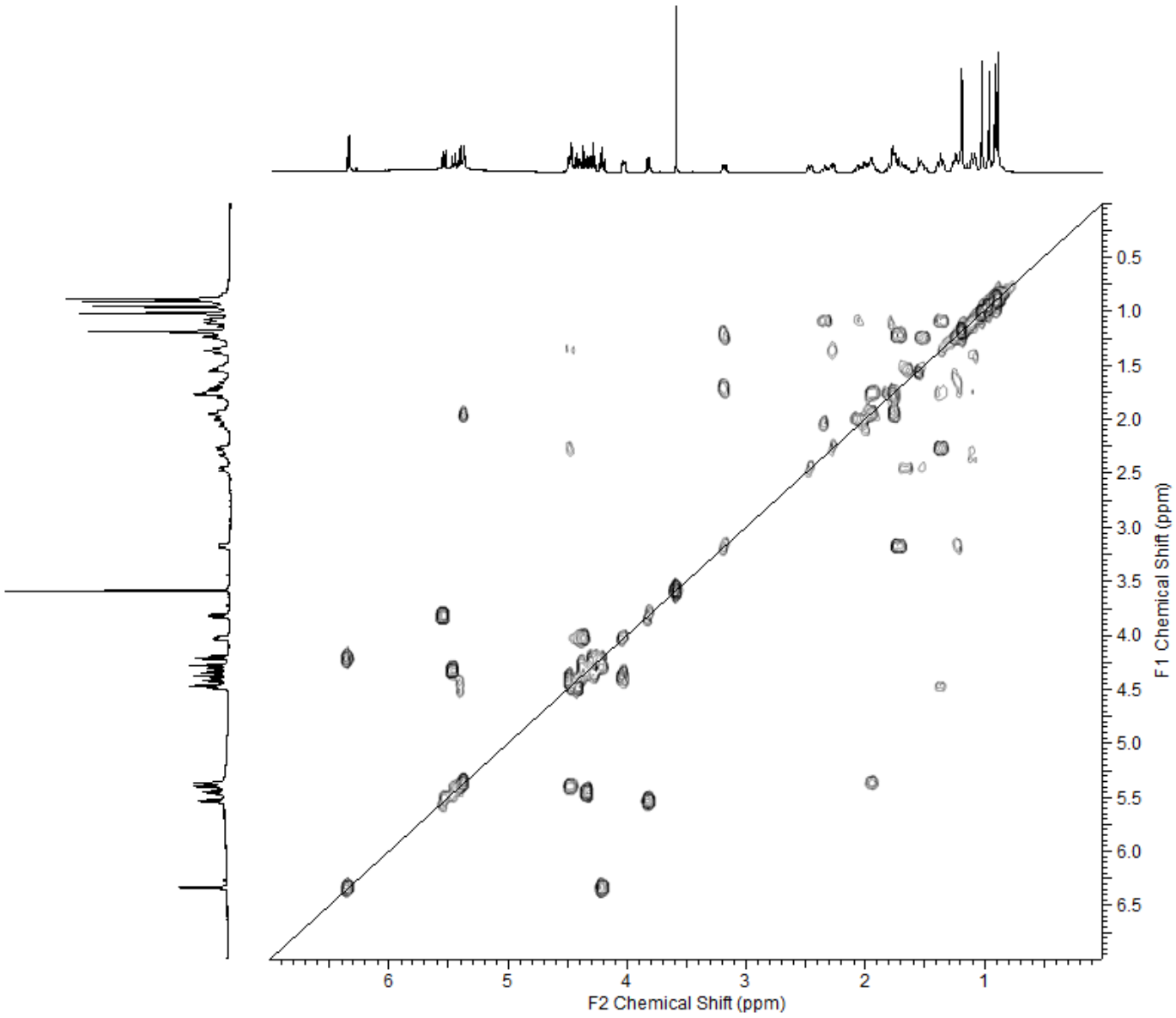


Figure S30. ^{1}H-^{1}H COSY spectrum of **10** (pyridine-d_5, 500 MHz)

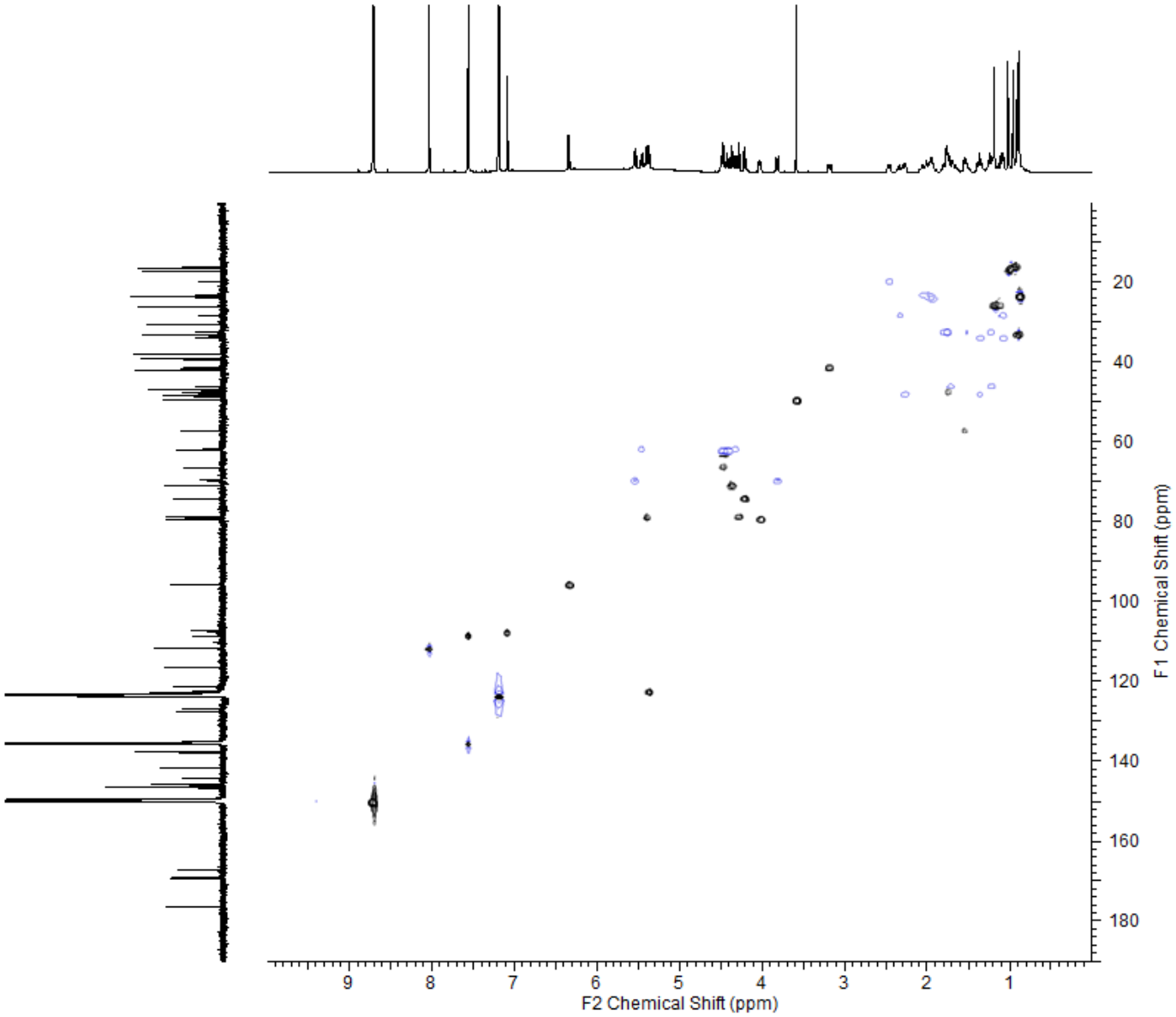


Figure S31. HSQC spectrum of **10** (pyridine-d_5)

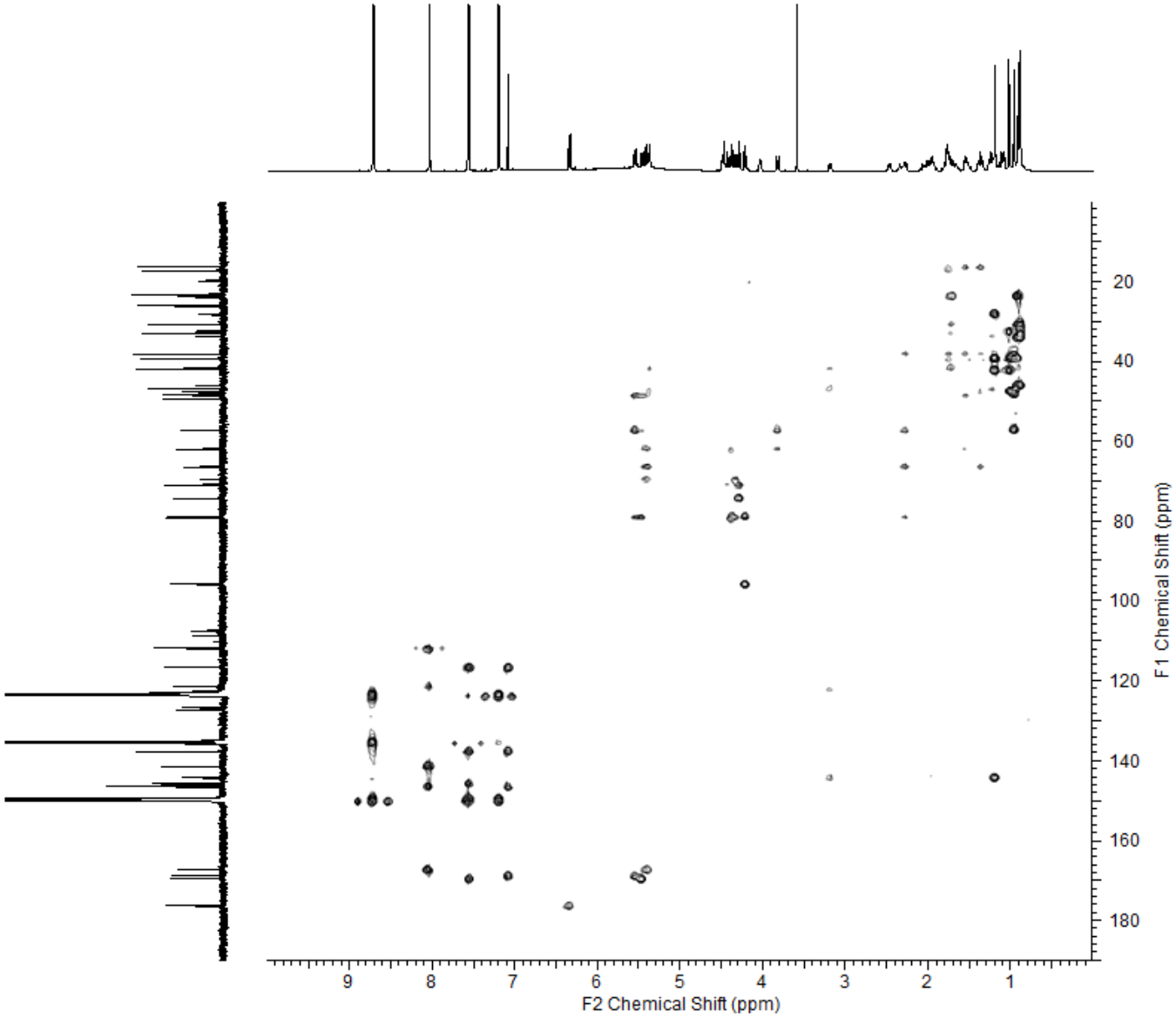


Figure S32. HMBC spectrum of **10** (pyridine-d_5)

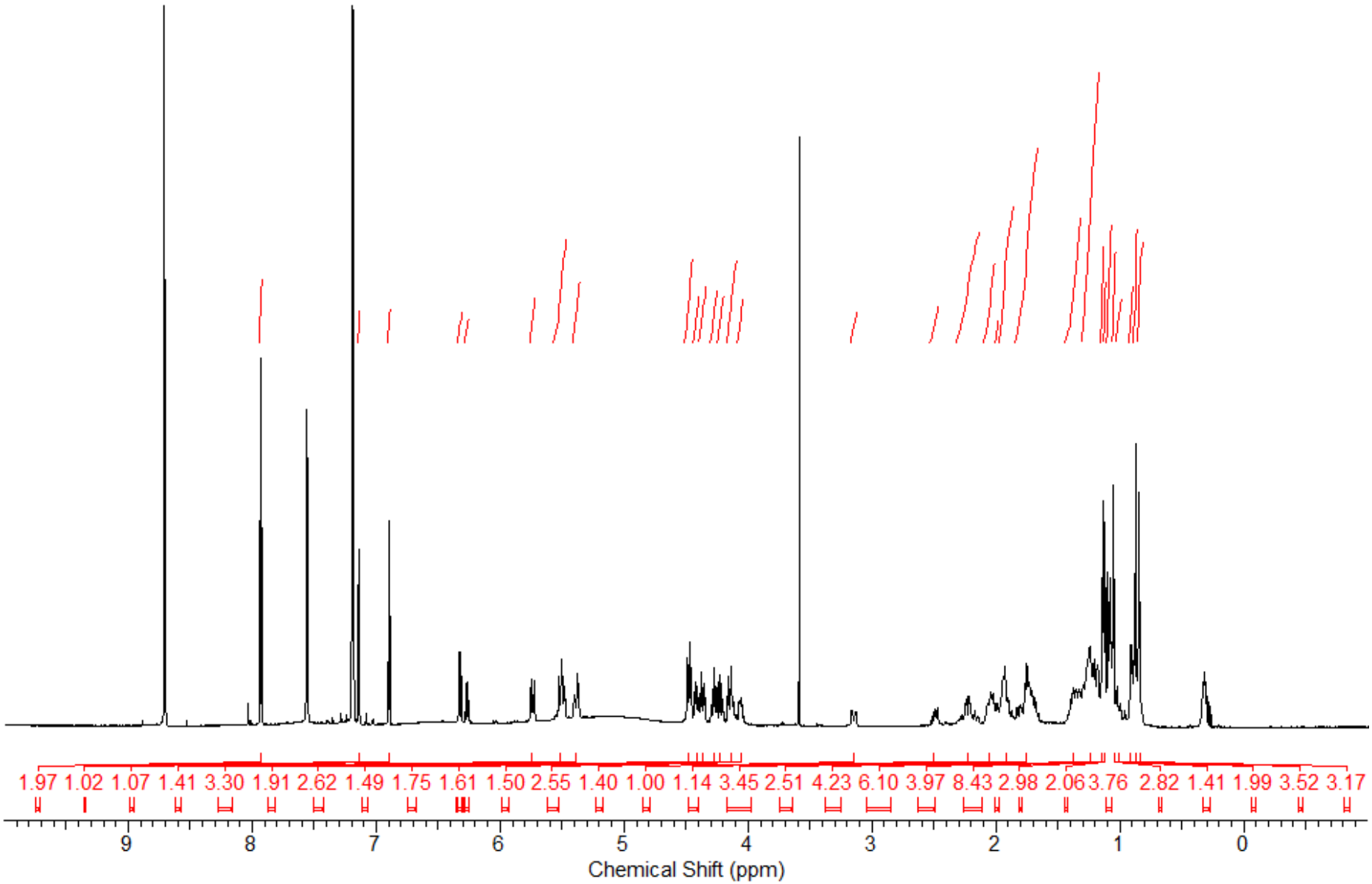


Figure S33. ^{1}H NMR spectrum of **11** (pyridine-d_5, 500 MHz)

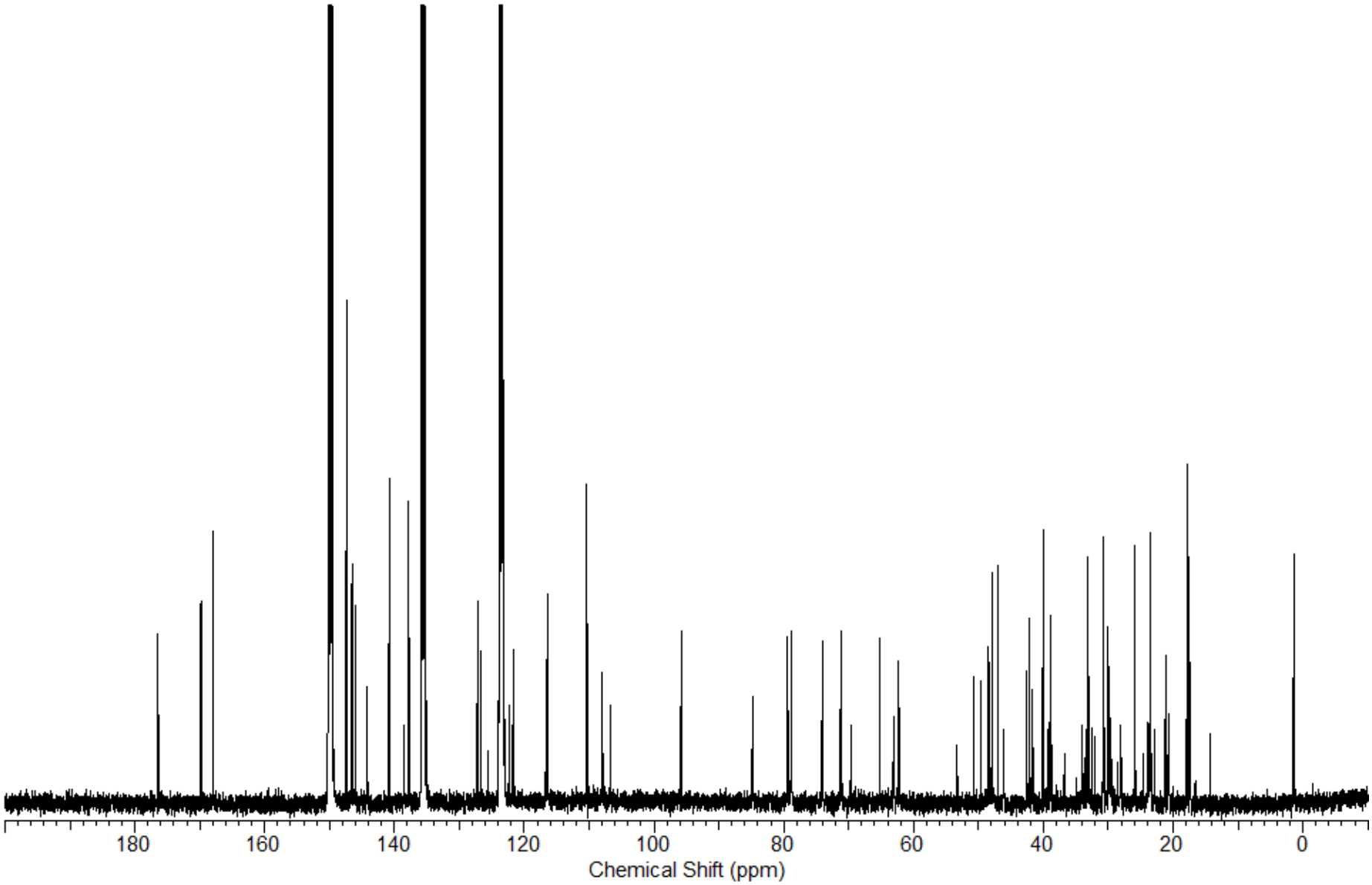


Figure S34. ^{13}C NMR spectrum of **11** (pyridine-d_5, 126 MHz)

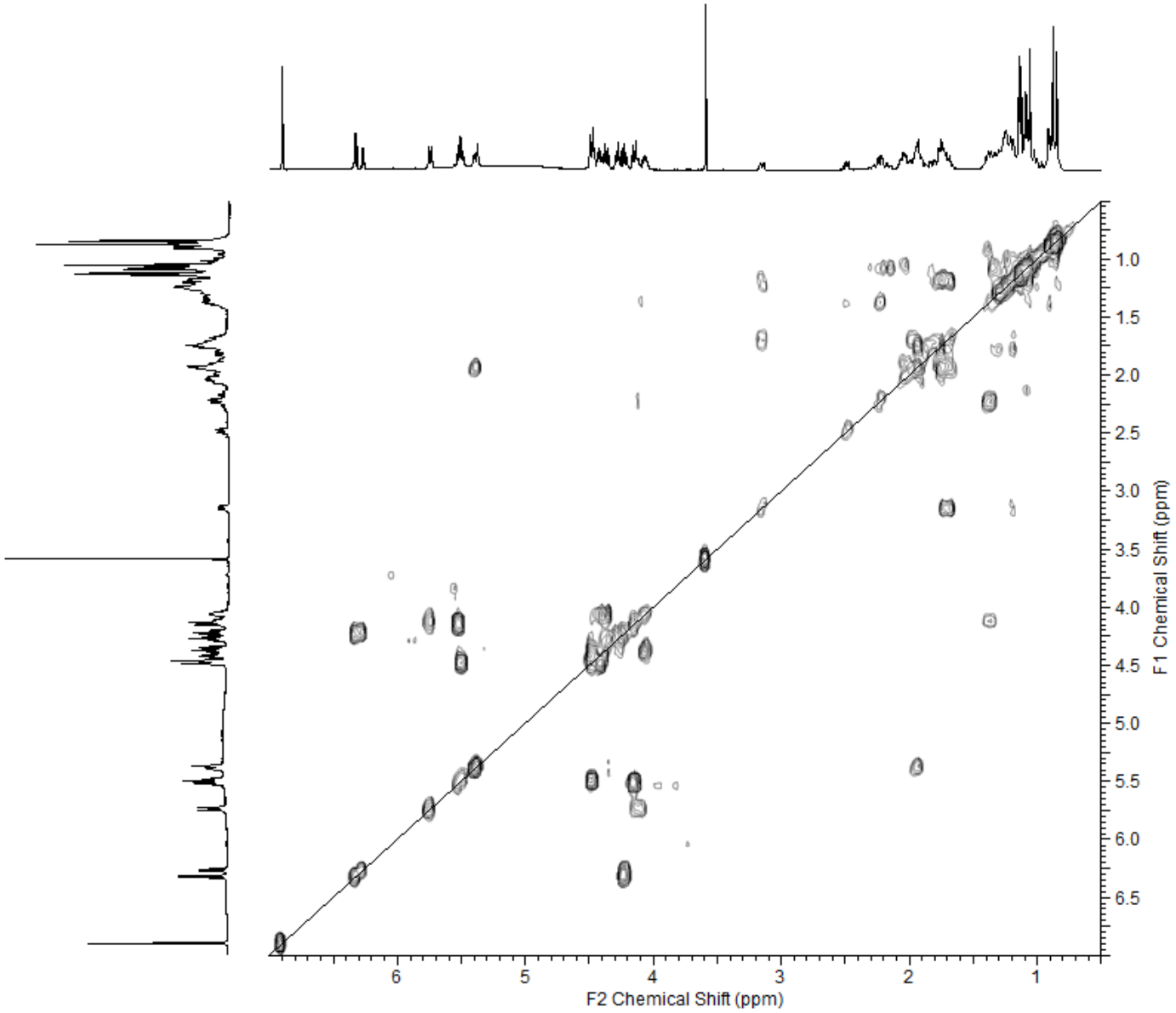


Figure S35. ^{1}H-^{1}H COSY spectrum of **11** (pyridine-d_5, 500 MHz)

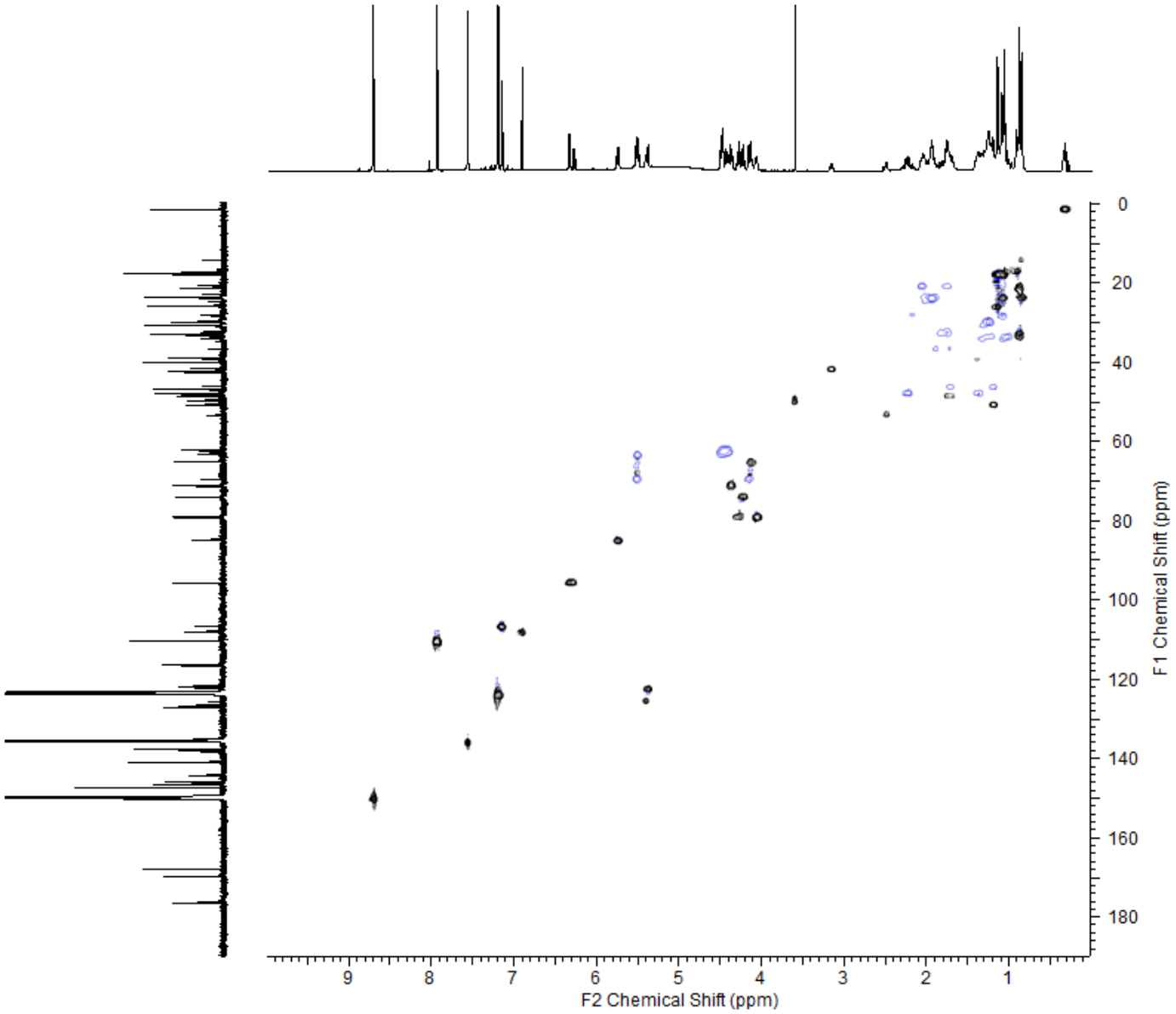


Figure S36. HSQC spectrum of **11** (pyridine-d_5)

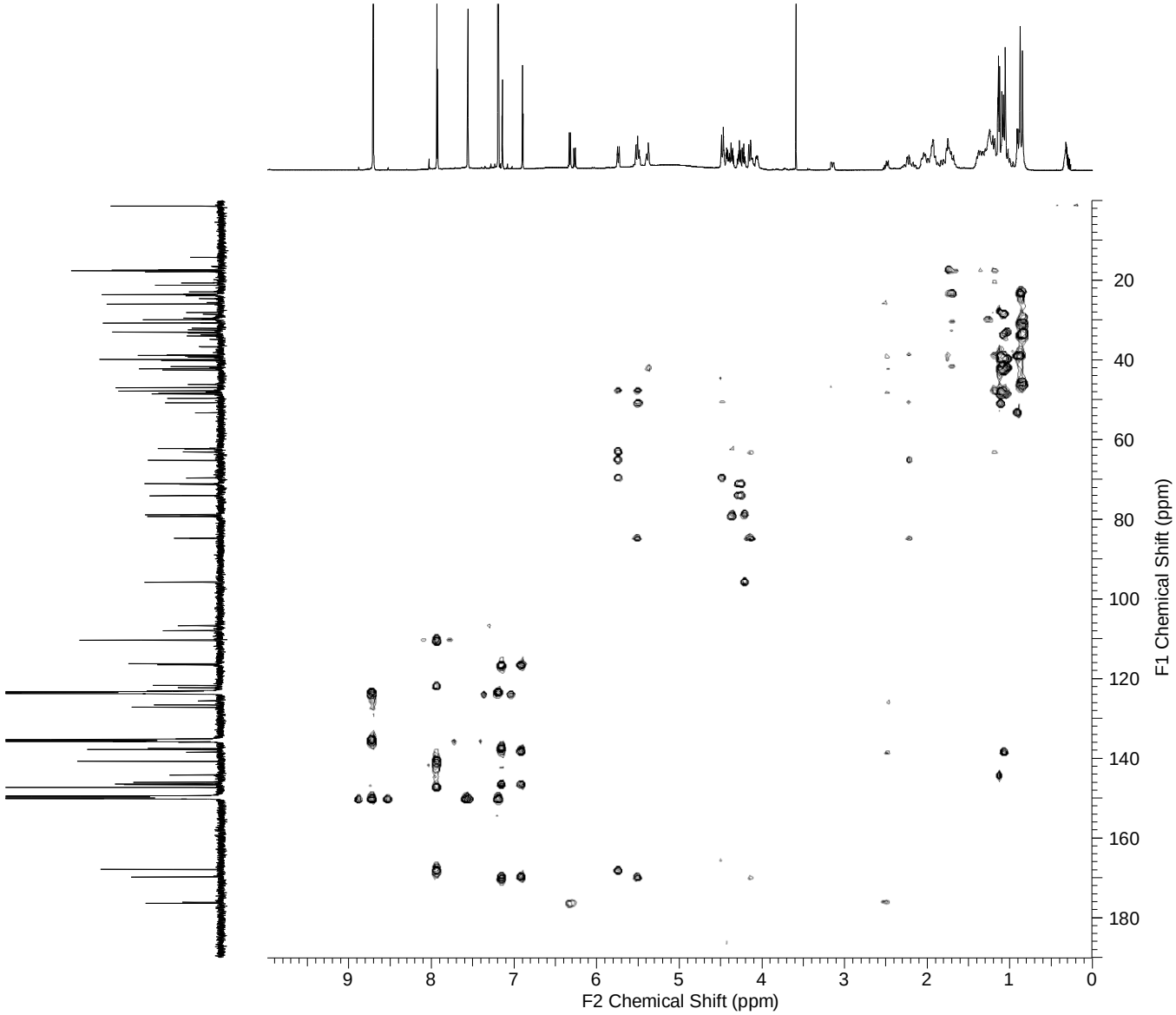


Figure S37. HMBC spectrum of **11** (pyridine-d_5)

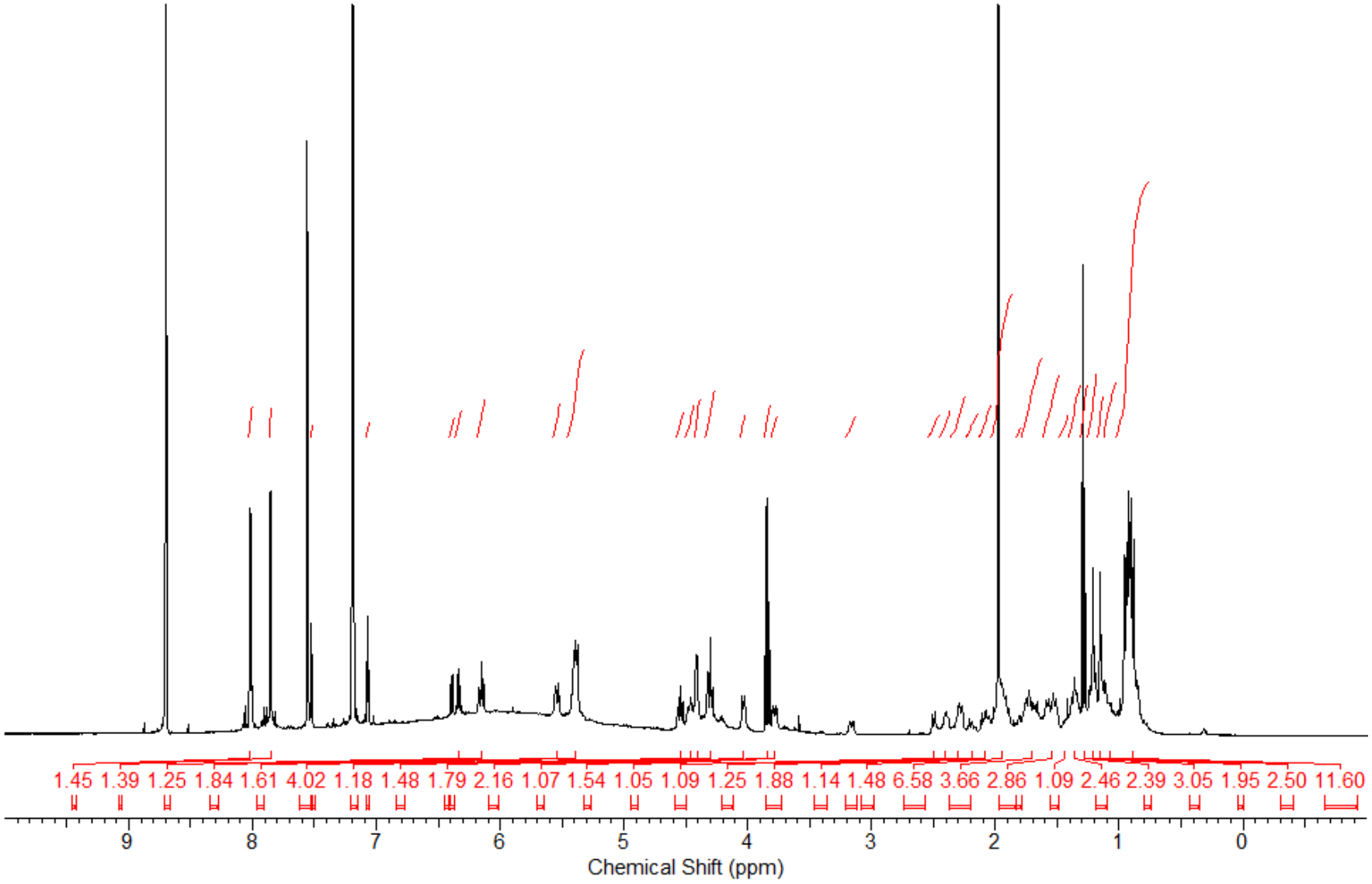


Figure S38. ^{1}H NMR spectrum of **12** (pyridine-d_5, 500 MHz)

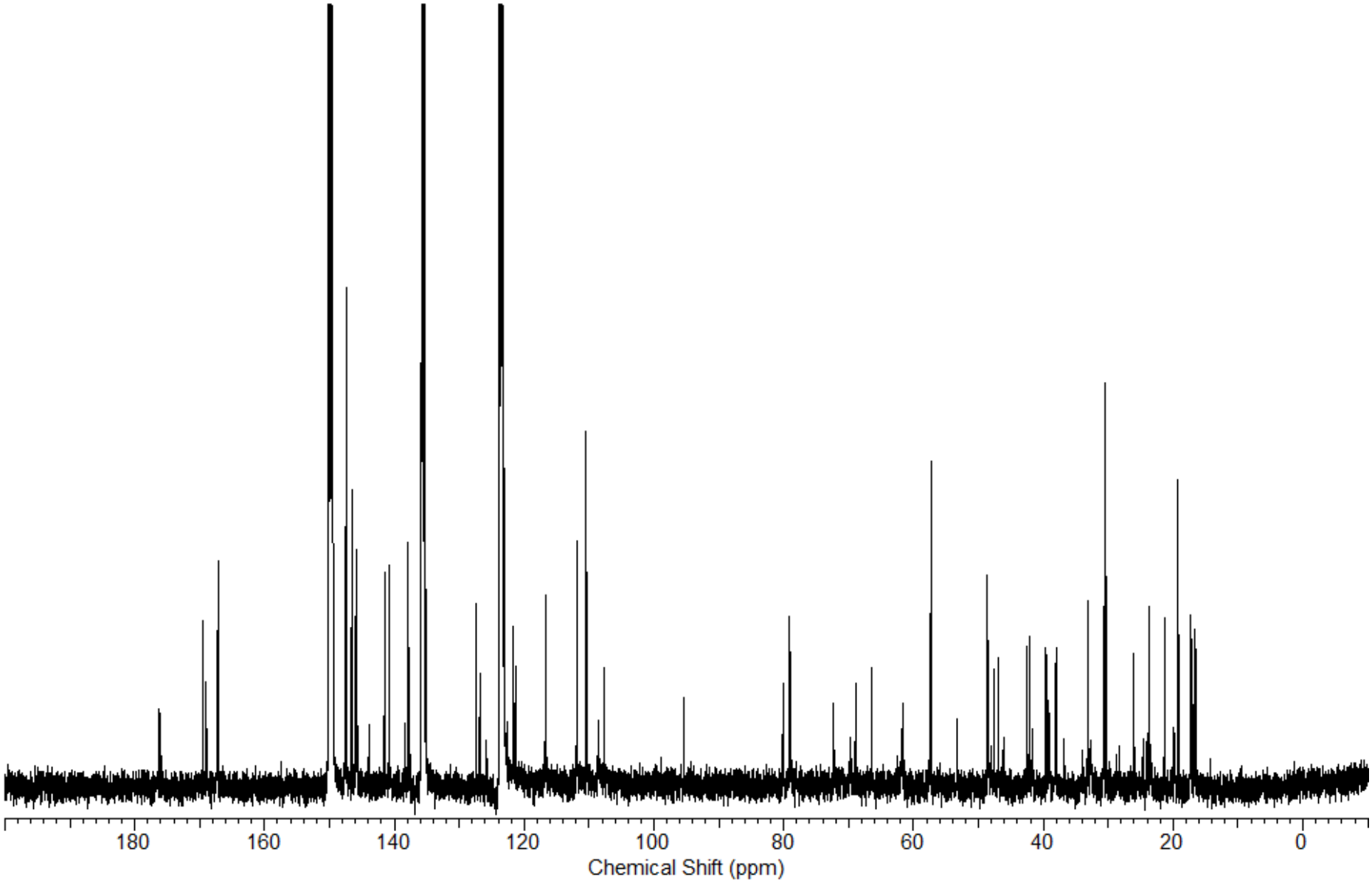


Figure S39. ^{13}C NMR spectrum of **12** (pyridine-d_5, 126 MHz)

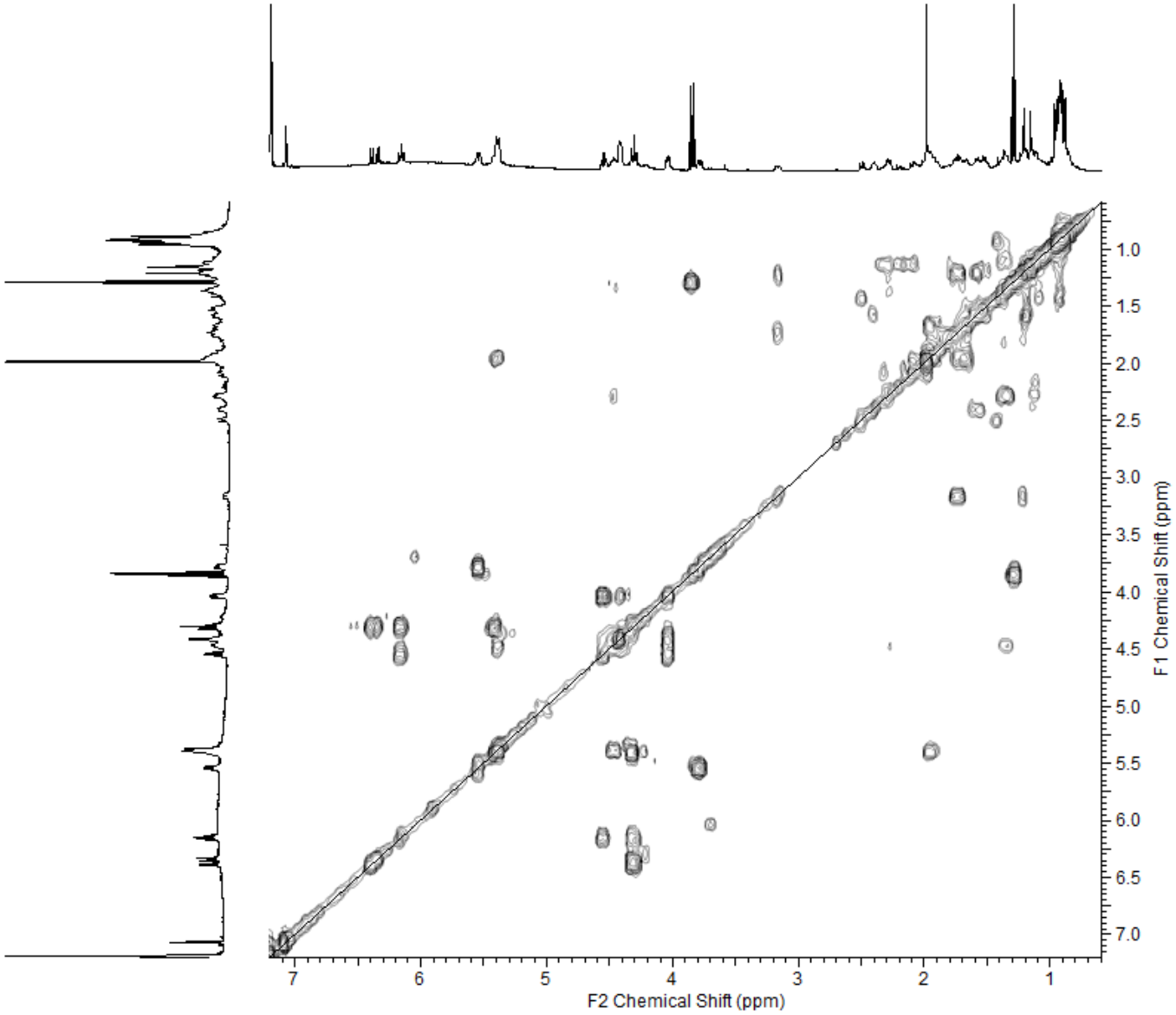


Figure S40. ^{1}H-^{1}H COSY spectrum of **12** (pyridine-d_5, 500 MHz)

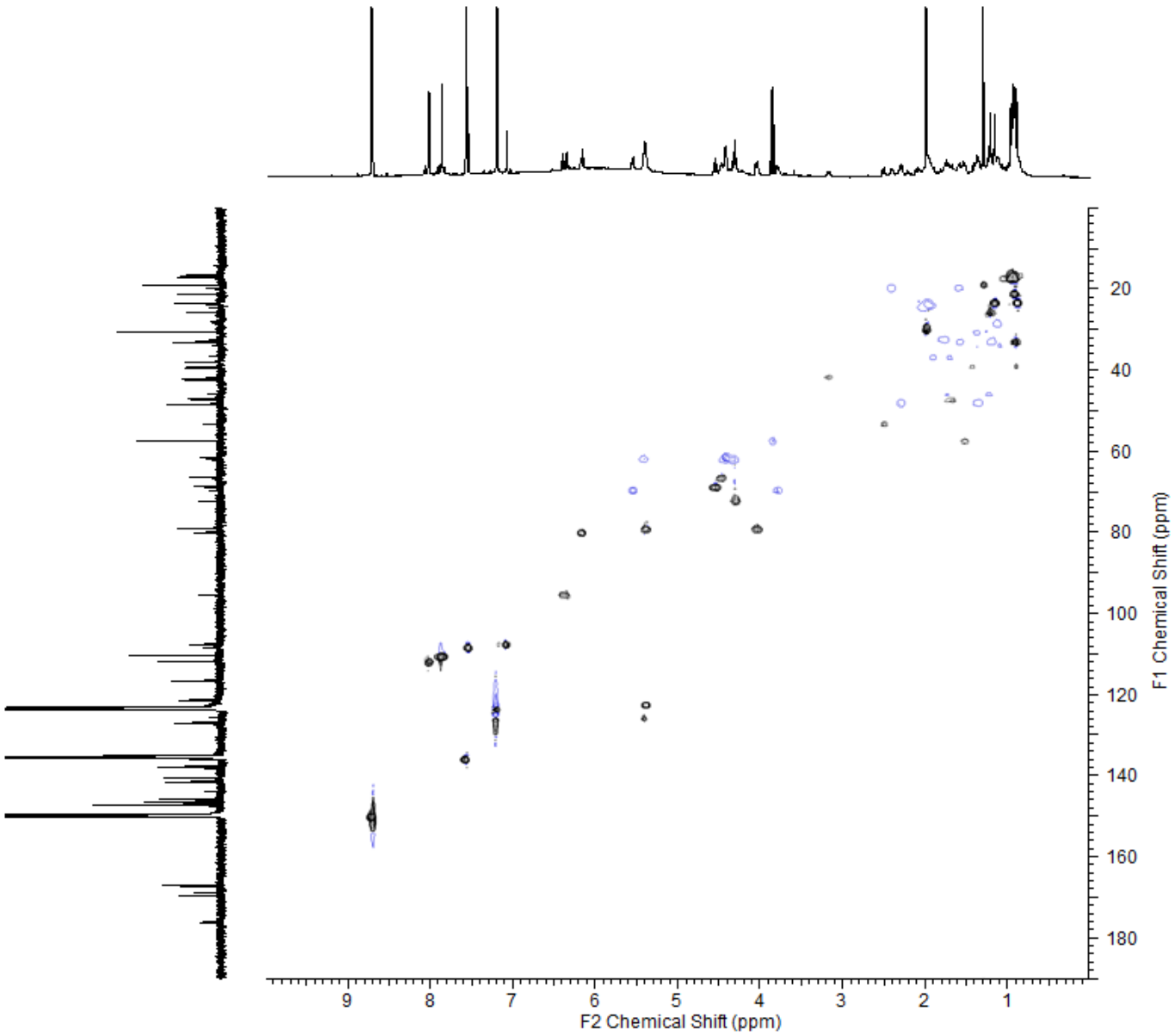


Figure S41. HSQC spectrum of **12** (pyridine-d_5)

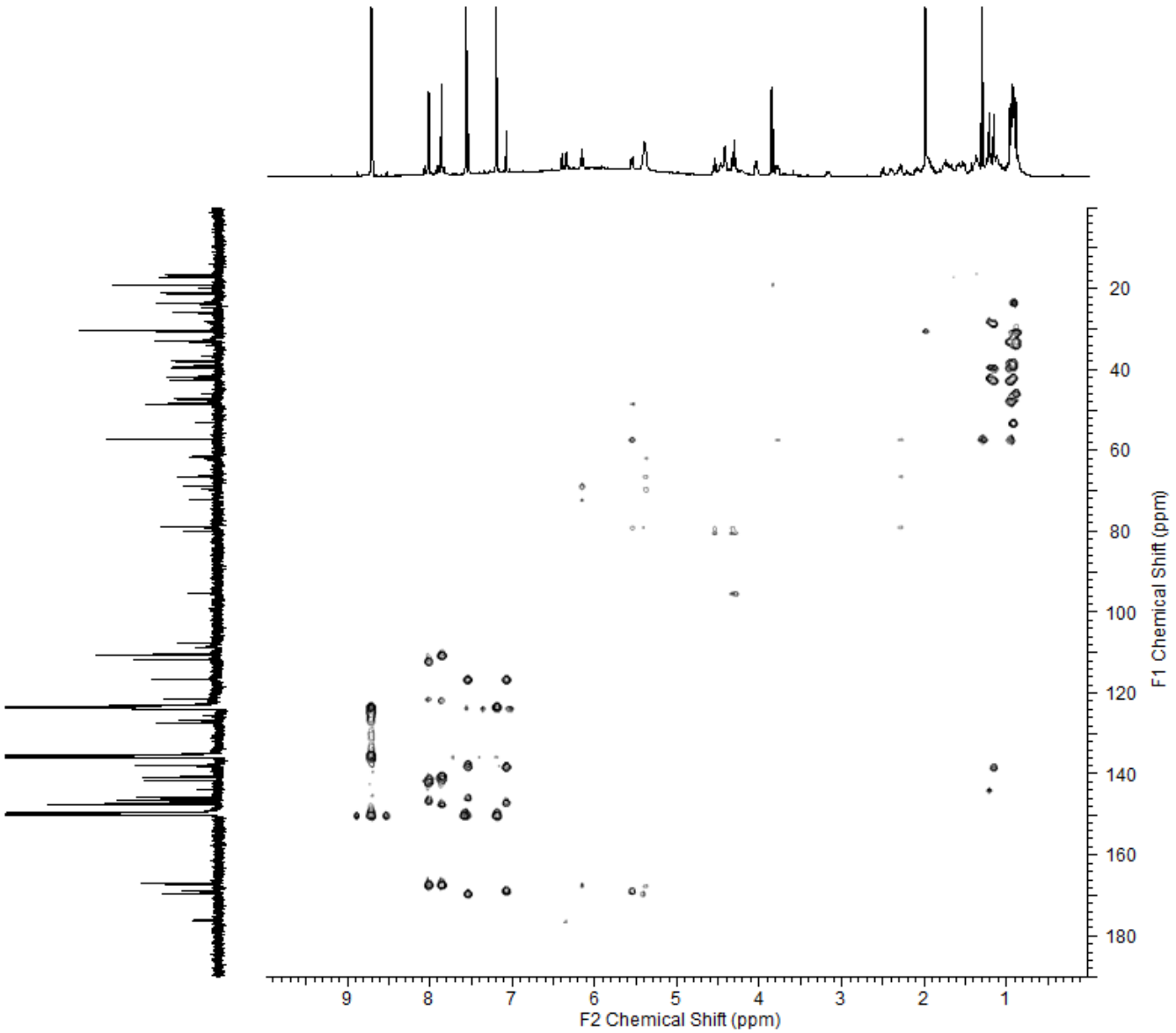


Figure S42. HMBC spectrum of **12** (pyridine-d_5)

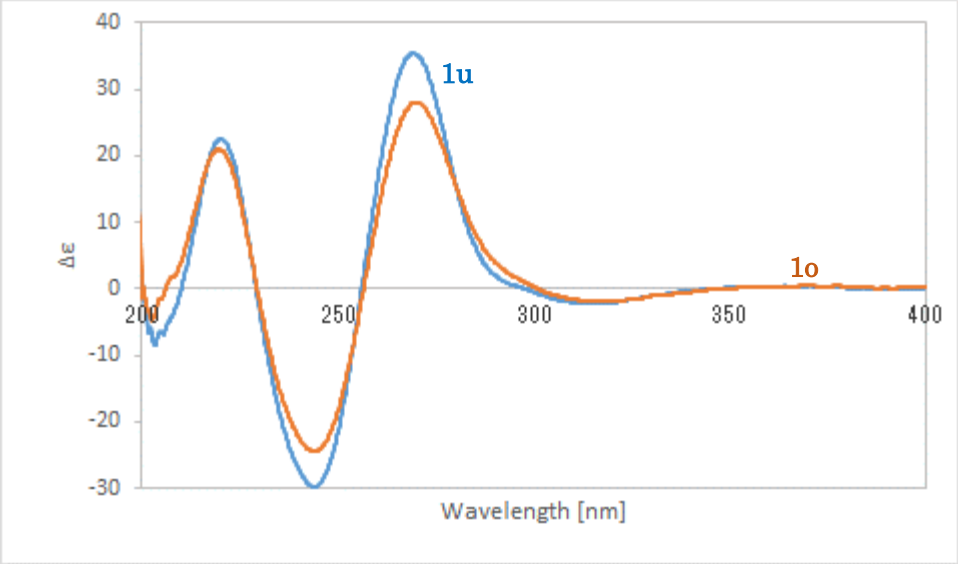


Figure S43. Experimental ECD spectra of **1o** and **1u**

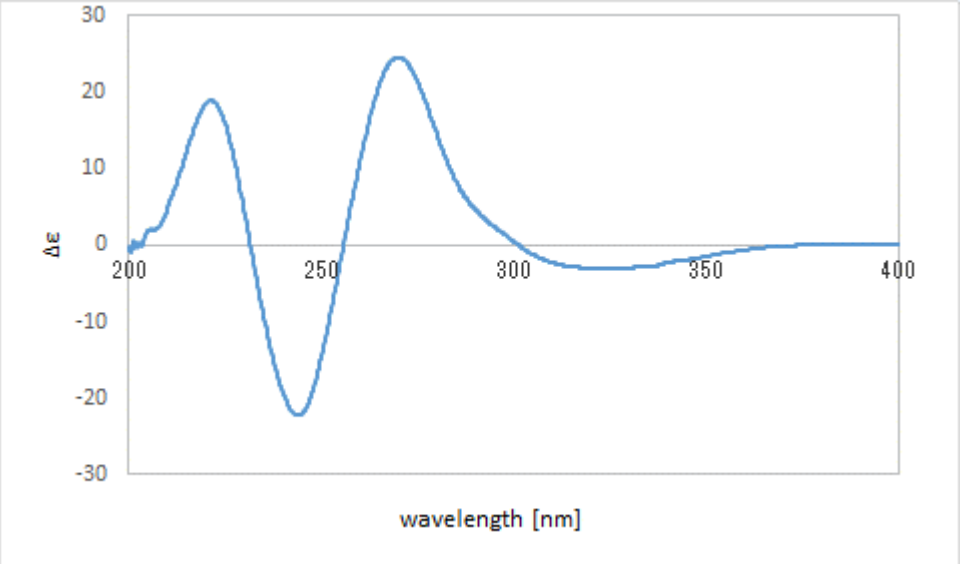
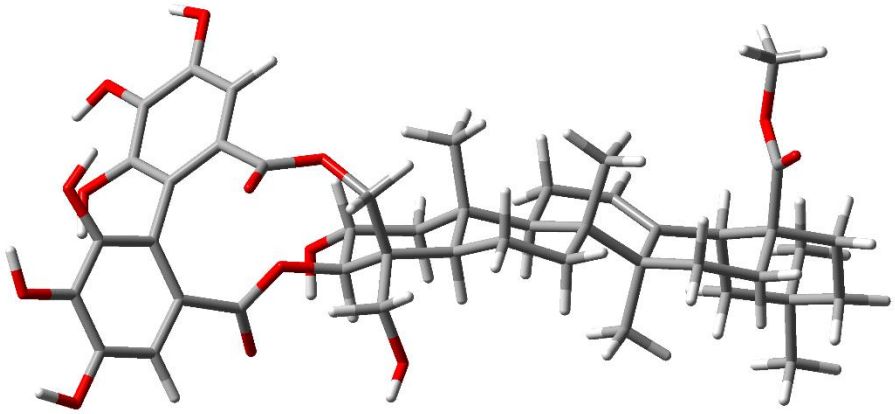
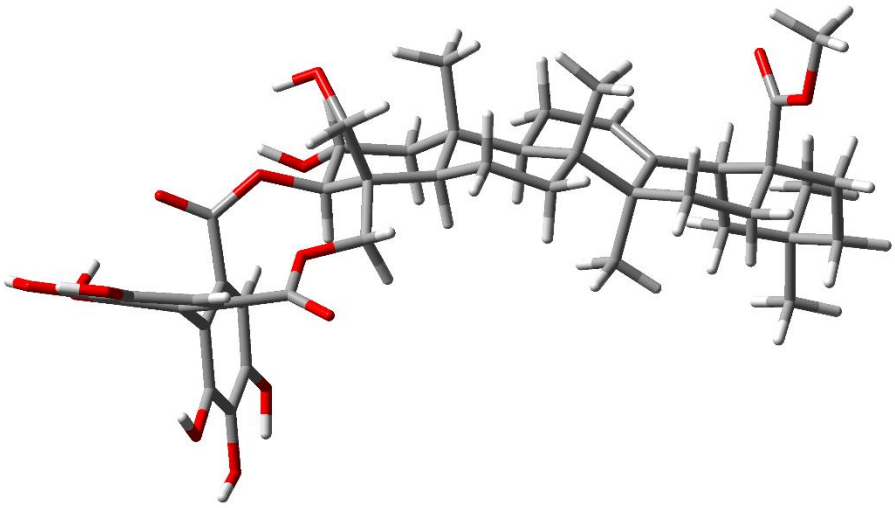


Figure S44. Experimental ECD spectra of **2o**,**u**

Figure S45. Lowest-energy conformers of 3,24-(*R*)-HHDP ester of methyl 2α,3β,23,24-tetrahydroxyolean-12-en-28-oate (**4'oA**) and 3,23-(*R*)-HHDP ester of methyl 2α,3β,23,24-tetrahydroxyolean-12-en-28-oate (**4'oB**) at the B3LYP/6-31G(d,p) level in pyridine.



4'oA (3,24-(*R*)-HHDP ester**)**



4'oB (3,23-(*R*)-HHDP ester**)**

Table S3. Calculated ^{1}H NMR chemical shifts of **4'oA**.

	calculated[a]																		experimental[b]
Position	**4oA-1**	**4oA-2**	**4oA-3**	**4oA-4**	**4oA-5**	**4oA-6**	**4oA-7**	**4oA-8**	**4oA-9**	**4oA-10**	**4oA-11**	**4oA-12**	**4oA-13**	**4oA-14**	**4oA-15**	**4oA-16**	**4oA-17**	averaged-**4oA**[c]	averaged-**4oA** (corrected)[d]	**4o**
1	2.11	2.12	2.01	1.99	2.03	2.01	2.05	1.97	2.04	2.18	2.04	2.09	2.15	2.14	1.95	2.01	2.00	2.07	2.03	2.02
	0.89	0.89	0.89	0.91	0.93	0.94	0.97	0.87	1.04	0.98	0.97	0.93	0.98	0.93	0.89	1.03	0.91	0.91	0.82	1.16
2	3.95	3.96	3.42	3.39	3.49	3.46	3.53	3.33	4.20	3.89	3.53	4.03	3.89	4.23	3.32	4.20	3.45	3.76	3.78	4.17
3	5.38	5.39	4.20	4.21	5.15	5.15	4.96	4.49	5.65	4.98	4.98	5.39	4.97	5.45	4.50	5.63	4.21	5.08	5.15	5.82
5	1.75	1.76	1.41	1.38	1.85	1.82	1.18	1.39	1.79	1.19	1.19	1.76	1.18	1.79	1.41	1.80	1.39	1.64	1.58	1.97
6	1.53	1.52	2.96	2.94	1.71	1.70	1.46	2.86	1.57	1.48	1.47	1.54	1.49	1.56	2.87	1.57	2.98	1.86	1.80	1.66
	1.54	1.54	1.64	1.61	1.54	1.52	1.54	1.63	1.55	1.56	1.56	1.54	1.58	1.58	1.65	1.56	1.60	1.56	1.50	1.34
7	1.82	1.82	1.80	1.83	1.78	1.80	1.72	1.83	1.83	1.75	1.69	1.80	1.75	1.83	1.83	1.83	1.84	1.81	1.75	1.59
	1.44	1.43	1.40	1.46	1.41	1.45	1.43	1.45	1.44	1.44	1.39	1.45	1.42	1.47	1.44	1.43	1.46	1.43	1.36	1.30
9	1.85	1.83	1.79	1.77	1.83	1.81	1.74	1.76	1.86	1.80	1.77	1.86	1.82	1.87	1.80	1.87	1.77	1.82	1.77	1.73
11	2.17	2.17	2.08	2.06	2.11	2.10	2.07	2.04	2.18	2.14	2.08	2.18	2.14	2.21	2.06	2.16	2.06	2.13	2.09	1.89
12	5.87	5.92	5.87	5.85	5.89	5.90	5.84	5.86	5.93	5.90	5.87	5.85	5.84	5.88	5.79	5.89	5.85	5.88	5.98	5.34
15	2.01	1.72	1.90	1.64	1.91	1.63	1.62	1.66	1.65	1.63	1.88	2.00	1.90	1.98	1.89	1.97	1.64	1.83	1.77	2.27
	1.18	1.26	1.14	1.23	1.14	1.22	1.22	1.22	1.26	1.21	1.13	1.16	1.13	1.15	1.15	1.22	1.24	1.20	1.12	1.05
16	2.06	2.18	2.01	2.17	2.02	2.14	2.17	2.17	2.12	2.12	2.01	2.05	2.01	2.06	2.05	2.07	2.18	2.10	2.06	1.97
	1.77	1.78	1.76	1.78	1.75	1.78	1.78	1.78	1.79	1.77	1.77	1.77	1.75	1.80	1.79	1.79	1.78	1.77	1.72	1.89
18	3.19	3.21	3.18	3.23	3.18	3.24	3.27	3.26	3.24	3.28	3.22	3.20	3.22	3.20	3.21	3.21	3.23	3.21	3.21	3.13
19	1.81	1.82	1.81	1.81	1.82	1.83	1.80	1.76	1.80	1.75	1.83	1.80	1.75	1.80	1.83	1.86	1.81	1.81	1.76	1.63
	1.23	1.27	1.18	1.27	1.18	1.26	1.27	1.26	1.27	1.26	1.21	1.24	1.23	1.25	1.25	1.24	1.27	1.24	1.16	1.16
21	1.52	1.53	1.53	1.54	1.53	1.51	1.53	1.56	1.51	1.54	1.52	1.52	1.51	1.54	1.50	1.50	1.54	1.53	1.46	1.30
	1.36	1.35	1.38	1.25	1.38	1.30	1.25	1.33	1.31	1.28	1.34	1.35	1.29	1.34	1.27	1.33	1.25	1.34	1.26	1.04
22	1.74	1.72	1.74	1.71	1.74	1.71	1.71	1.75	1.76	1.72	1.70	1.75	1.72	1.76	1.69	1.72	1.71	1.73	1.67	1.63
23	3.56	3.55	3.47	3.44	3.54	3.54	4.65	3.50	3.46	4.16	4.66	3.61	4.17	3.68	3.51	3.46	3.44	3.61	3.62	
	3.69	3.68	3.99	3.99	4.00	3.97	3.40	4.13	3.68	3.30	3.44	3.71	3.30	3.76	4.16	3.68	4.00	3.77	3.79	
24	4.58	4.58	5.34	5.33	5.15	5.16	5.32	5.25	4.53	4.97	5.31	4.61	4.98	4.62	5.24	4.52	5.29	4.87	4.93	
	4.15	4.17	4.71	4.70	4.43	4.42	4.58	4.65	4.17	4.62	4.59	4.12	4.61	4.18	4.65	4.18	4.68	4.35	4.39	
25	1.31	1.33	0.86	0.86	0.87	0.88	0.84	0.85	1.37	1.32	0.83	1.30	1.29	1.37	0.85	1.35	0.84	1.14	1.06	1.12
26	0.99	1.03	0.89	0.92	0.89	0.94	0.91	0.92	1.06	1.01	0.86	0.98	0.95	1.03	0.87	1.02	0.92	0.97	0.88	1.16
27	1.26	1.26	1.22	1.24	1.20	1.22	1.23	1.24	1.27	1.25	1.20	1.25	1.22	1.26	1.25	1.27	1.25	1.24	1.17	1.09
29	0.99	0.99	0.99	0.99	0.99	0.99	0.98	0.96	0.98	0.97	1.01	0.99	0.97	0.99	0.99	1.00	0.99	0.99	0.90	0.84
30	1.05	1.00	1.05	1.02	1.05	1.02	1.02	1.00	1.02	1.01	1.06	1.05	1.04	1.06	1.06	1.03	1.02	1.03	0.95	0.84
HHDP 3	7.49	7.49	7.74	7.73	7.75	7.74	7.81	7.62	7.74	7.62	7.81	7.14	7.61	7.22	7.62	7.71	7.67	7.59	7.75	7.72
HHDP 3'	7.35	7.36	7.06	7.07	6.98	6.98	7.05	7.11	7.38	7.51	7.04	7.09	7.50	7.53	7.12	7.36	6.84	7.23	7.38	7.08

[a] *Calculated using the GIAO method at the mPW1PW91/6-311+G(2d,p) level in pyridine (PCM).* [b] *Measured in pyridine-d_5.* [c] *Averaged according to the Boltzmann distribution theory at 298 K based on relative Gibbs free energies.* [d] *Linearly corrected for the experimental data.*

Table S4. Calculated ^{1}H NMR chemical shifts of **4'oB**.

	calculated[a]																				experimental[b]
Position	**4oB-1**	**4oB-2**	**4oB-3**	**4oB-4**	**4oB-5**	**4oB-6**	**4oB-7**	**4oB-8**	**4oB-9**	**4oB-10**	**4oB-11**	**4oB-12**	**4oB-13**	**4oB-14**	**4oB-15**	**4oB-16**	**4oB-17**	**4oB-18**	**4oB-19**	averaged-**4oB**[c]	averaged-**4oB** (corrected)[d]	**4o**
1	2.29	2.26	2.21	2.27	2.20	2.21	2.15	2.20	2.19	2.09	2.24	2.32	2.30	2.16	2.17	2.17	2.38	2.26	2.22	2.23	2.18	2.02
	1.19	1.19	1.19	1.20	1.19	1.19	1.19	1.22	1.19	1.23	1.16	1.19	1.20	1.15	1.20	1.11	0.98	1.16	1.15	1.19	1.15	1.16
2	4.62	4.44	4.50	4.46	4.44	4.66	4.51	4.54	4.46	4.61	4.30	4.29	4.68	4.49	4.54	4.14	4.21	4.44	4.50	4.51	4.43	4.17
3	5.17	5.21	5.13	5.19	5.20	5.08	5.13	5.16	5.20	5.09	5.06	5.08	5.17	5.09	5.16	4.98	4.93	5.15	5.09	5.15	5.07	5.82
5	1.12	1.17	1.18	1.17	1.15	1.12	1.17	1.19	1.16	1.11	1.06	1.10	1.13	1.17	1.18	1.01	1.19	1.16	1.18	1.15	1.12	1.97
6	1.63	1.50	1.51	1.51	1.52	1.63	1.53	1.52	1.54	1.65	2.03	2.02	1.64	1.54	1.54	1.92	1.51	1.51	1.52	1.58	1.54	1.66
	1.21	1.31	1.33	1.35	1.32	1.22	1.33	1.40	1.35	1.22	1.42	1.43	1.23	1.35	1.38	1.60	1.43	1.36	1.34	1.31	1.27	1.34
7	1.68	1.65	1.65	1.66	1.61	1.68	1.63	1.68	1.63	1.53	1.44	1.47	1.69	1.63	1.66	1.52	1.67	1.66	1.65	1.64	1.60	1.59
	1.43	1.39	1.40	1.40	1.31	1.43	1.32	1.41	1.34	1.36	1.28	1.33	1.44	1.34	1.39	1.33	1.38	1.40	1.41	1.38	1.35	1.30
9	1.83	1.81	1.79	1.83	1.83	1.80	1.80	1.79	1.86	1.89	1.85	1.84	1.84	1.79	1.82	1.85	1.75	1.82	1.77	1.82	1.78	1.73
11	2.19	2.14	2.11	2.15	2.13	2.17	2.11	2.13	2.16	2.21	2.19	2.21	2.19	2.11	2.14	2.16	2.14	2.14	2.11	2.15	2.10	1.89
12	5.90	5.87	5.86	5.88	5.79	5.90	5.78	5.89	5.81	5.75	5.81	5.88	5.91	5.78	5.84	5.78	5.92	5.87	5.86	5.86	5.76	5.34
15	1.70	1.66	1.66	1.67	1.87	1.71	1.85	1.68	1.90	2.08	1.88	1.63	1.71	1.84	1.86	1.90	1.65	1.66	1.67	1.74	1.70	2.27
	1.19	1.20	1.21	1.19	1.05	1.20	1.05	1.21	1.04	1.04	1.05	1.17	1.20	1.06	1.08	1.05	1.22	1.20	1.22	1.15	1.12	1.05
16	2.15	2.14	2.14	2.14	2.02	2.15	2.01	2.15	2.03	2.05	2.00	2.16	2.15	2.02	2.05	2.01	2.14	2.14	2.14	2.11	2.06	1.97
	1.80	1.78	1.79	1.77	1.72	1.80	1.72	1.76	1.75	1.75	1.72	1.82	1.78	1.73	1.79	1.73	1.76	1.77	1.79	1.77	1.73	1.89
18	3.23	3.21	3.21	3.21	3.20	3.22	3.20	3.23	3.23	3.17	3.18	3.24	3.21	3.20	3.22	3.19	3.24	3.18	3.21	3.21	3.15	3.13
19	2.15	2.11	2.10	2.13	2.11	2.14	2.09	2.12	2.13	2.21	2.16	2.20	2.16	2.10	2.13	2.18	2.12	2.13	2.10	2.13	2.08	1.63
	1.19	1.20	1.21	1.19	1.05	1.20	1.05	1.21	1.04	1.04	1.05	1.17	1.20	1.06	1.08	1.05	1.22	1.20	1.22	1.15	1.12	1.16
21	1.53	1.52	1.52	1.53	1.47	1.53	1.46	1.52	1.47	1.46	1.47	1.51	1.54	1.46	1.50	1.47	1.52	1.54	1.53	1.51	1.47	1.30
	1.30	1.29	1.29	1.30	1.32	1.30	1.31	1.32	1.31	1.31	1.33	1.29	1.30	1.31	1.30	1.33	1.33	1.30	1.29	1.30	1.27	1.04
22	1.69	1.69	1.69	1.67	1.71	1.69	1.69	1.67	1.68	1.72	1.70	1.70	1.68	1.69	1.67	1.71	1.70	1.67	1.69	1.69	1.65	1.63
23	3.20	3.55	3.54	3.47	3.55	3.23	3.56	3.52	3.44	3.24	3.19	3.20	3.20	3.53	3.49	3.22	3.51	3.46	3.51	3.41	3.35	
	4.48	5.01	5.13	5.56	5.02	4.47	5.10	5.57	5.61	4.48	5.30	5.32	4.82	5.18	5.61	5.67	5.54	5.53	5.17	5.03	4.95	
24	3.74	3.58	3.61	3.62	3.59	3.74	3.62	3.63	3.64	3.76	4.12	4.13	3.83	3.62	3.65	3.99	3.61	3.62	3.61	3.68	3.61	
	3.70	4.41	4.41	4.45	4.41	3.69	4.41	4.45	4.43	3.71	4.02	4.00	3.79	4.39	4.43	3.91	4.40	4.43	4.39	4.18	4.11	
25	1.48	0.98	0.97	1.02	0.94	1.49	0.93	1.00	0.98	1.43	1.20	1.27	1.50	0.93	0.99	1.18	1.01	1.00	0.97	1.14	1.10	1.12
26	1.05	0.85	0.85	0.86	0.77	1.03	0.77	0.87	0.77	0.77	0.79	0.87	1.05	0.78	0.81	0.82	0.92	0.85	0.85	0.88	0.85	1.16
27	1.24	1.21	1.21	1.21	1.18	1.23	1.19	1.21	1.22	1.22	1.17	1.19	1.24	1.19	1.22	1.18	1.19	1.20	1.21	1.21	1.18	1.09
29	0.98	0.97	0.97	0.97	0.98	0.98	0.98	0.97	0.99	0.99	0.97	0.98	0.98	0.98	0.98	0.98	0.98	0.97	0.97	0.98	0.95	0.84
30	1.02	1.01	1.01	1.01	1.06	1.02	1.06	1.01	1.06	1.08	1.06	1.02	1.01	1.06	1.05	1.06	1.00	1.01	1.01	1.03	1.00	0.84
HHDP 3	7.71	7.76	7.79	7.85	7.74	7.82	7.80	8.22	7.80	7.84	7.51	7.49	7.83	7.64	8.17	7.37	8.07	7.71	7.63	7.79	7.67	7.72
HHDP 3'	7.53	7.58	7.62	7.57	7.59	7.54	7.63	7.57	7.57	7.54	7.51	7.50	7.36	7.58	7.58	8.13	7.59	7.41	7.56	7.57	7.46	7.08

[a] Calculated using the GIAO method at the mPW1PW91/6-311+G(2d,p) level in pyridine (PCM). [b] Measured in pyridine-d_5. [c] Averaged according to the Boltzmann distribution theory at 298 K based on relative Gibbs free energies. [d] Linearly corrected for the experimental data.

Table S5. Calculated ^{13}C NMR chemical shifts of **4'oA**.

	calculated[a]																		experimental[b]
Position	**4oA-1**	**4oA-2**	**4oA-3**	**4oA-4**	**4oA-5**	**4oA-6**	**4oA-7**	**4oA-8**	**4oA-9**	**4oA-10**	**4oA-11**	**4oA-12**	**4oA-13**	**4oA-14**	**4oA-15**	**4oA-16**	**4oA-17**	averaged-**4oA**[c]	averaged-**4oA** (corrected)[d]	**4o**
1	45.5	45.5	44.7	44.6	44.7	44.6	44.1	44.7	45.8	45.1	44.0	45.5	45.1	45.4	44.5	45.7	44.5	45.1	46.8	48.3
2	68.4	68.4	67.7	67.6	67.4	67.4	67.5	68.2	67.3	67.6	67.6	68.4	67.6	68.3	68.1	67.3	67.4	68.0	69.0	67.4
3	77.4	77.4	81.2	81.2	79.7	79.7	84.4	80.5	75.1	84.0	84.4	77.5	84.1	78.2	80.3	75.1	81.5	79.0	79.7	79.1
4	48.5	48.5	50.4	50.2	49.6	49.7	47.8	49.7	48.6	48.7	47.9	48.5	48.7	48.6	49.9	48.5	50.1	49.0	50.5	48.3
5	44.0	44.1	55.5	55.6	44.2	44.2	52.2	55.6	44.1	50.8	52.1	44.0	50.7	44.0	55.5	44.0	55.4	47.2	48.8	47.0
6	16.0	16.0	16.9	16.9	15.7	15.6	16.7	16.8	16.3	16.9	16.7	16.0	16.9	16.0	16.8	16.3	16.9	16.2	18.8	18.2
7	30.0	30.7	30.2	31.3	29.9	30.9	31.3	31.2	30.9	31.5	30.3	30.0	30.5	30.3	30.4	29.9	31.2	30.5	32.6	32.7
8	41.0	40.7	40.2	40.1	40.5	40.2	40.2	40.3	40.7	40.7	39.9	41.1	40.6	41.0	40.1	40.7	40.1	40.6	42.4	39.9
9	45.1	45.2	45.8	45.8	45.9	45.9	45.7	45.9	45.3	45.5	45.7	44.9	45.5	45.0	45.9	45.3	45.7	45.4	47.1	47.5
10	39.1	39.2	39.0	39.0	38.5	38.7	38.6	39.0	38.9	39.9	38.6	39.2	39.8	39.3	39.1	38.6	38.9	39.0	40.9	37.7
11	22.4	22.3	22.4	22.4	22.4	22.4	22.4	22.4	22.3	22.0	22.4	22.4	22.0	22.4	22.4	22.4	22.4	22.4	24.7	24.0
12	127.4	127.8	127.0	127.3	127.2	127.4	127.4	127.6	127.8	127.9	127.0	127.3	127.5	127.6	126.7	127.5	127.3	127.4	126.6	122.7
13	150.5	149.6	150.5	149.6	150.4	149.6	149.5	149.5	149.9	149.9	150.3	150.8	150.6	150.6	150.5	150.2	149.7	150.1	148.6	144.1
14	42.9	43.7	43.6	43.8	43.7	44.1	43.7	43.7	44.2	43.9	43.7	42.8	43.3	43.4	43.5	43.4	43.7	43.5	45.2	42.2
15	24.8	25.5	24.3	25.3	24.3	25.3	25.4	25.2	25.0	25.3	24.4	24.7	24.4	24.6	24.5	24.6	25.4	25.0	27.2	28.1
16	20.7	21.3	20.6	21.4	20.6	21.5	21.4	21.3	21.4	21.5	20.7	20.7	20.7	20.7	20.8	20.8	21.4	21.0	23.4	23.4
17	48.7	48.2	48.6	48.0	48.6	47.9	47.8	48.4	48.4	48.1	48.0	48.5	48.5	48.6	48.2	49.2	48.0	48.4	49.9	47.0
18	41.5	41.1	41.2	41.2	41.3	41.0	41.1	41.1	41.3	41.2	41.3	41.4	41.6	41.6	41.5	41.4	41.2	41.3	43.1	41.7
19	43.1	43.2	43.8	42.9	43.8	43.1	43.0	42.9	42.8	42.9	43.6	43.0	42.8	43.0	43.0	43.4	42.9	43.2	44.9	46.1
20	31.4	31.1	31.2	31.2	31.1	31.1	31.2	31.8	31.3	31.1	31.1	31.4	31.0	31.1	31.3	31.1	31.1	31.2	33.3	30.7
21	31.1	31.3	30.8	31.5	30.8	31.3	31.6	31.7	31.4	31.4	30.8	31.1	31.1	31.2	31.1	30.9	31.5	31.2	33.2	33.9
22	31.0	30.7	31.1	31.0	31.1	30.8	30.8	30.8	31.0	30.7	31.0	31.0	30.9	31.0	31.1	31.0	30.9	30.9	33.0	33.0
23	60.1	60.1	69.0	69.0	56.8	56.8	71.2	68.9	60.0	73.4	71.2	60.2	73.5	60.3	68.9	60.0	69.3	62.7	63.8	62.2
24	60.3	60.4	71.2	71.4	70.4	70.4	72.9	70.1	60.9	62.1	72.9	59.9	62.2	59.8	70.0	60.9	71.4	64.7	65.7	62.4
25	10.3	10.3	11.3	11.3	11.5	11.5	10.8	11.2	10.3	10.9	11.0	10.4	10.9	10.5	11.3	10.3	11.2	10.7	13.4	17.5
26	12.6	13.3	12.5	13.2	12.5	13.2	13.3	13.3	13.7	13.6	12.4	12.5	12.7	12.8	12.3	12.9	13.2	12.9	15.6	17.7
27	20.9	20.4	20.7	20.2	20.7	20.2	20.1	20.1	20.5	20.3	20.6	21.0	20.8	20.7	20.8	20.9	20.2	20.6	23.0	25.9
28	184.0	183.9	183.9	183.8	183.9	183.9	183.8	183.9	184.0	183.7	183.8	184.0	183.7	183.9	183.7	184.0	183.8	183.9	181.4	176.4
29	28.5	28.5	28.6	28.3	28.6	28.4	28.2	28.3	28.3	28.3	28.6	28.4	28.3	28.4	28.3	28.4	28.3	28.4	30.6	33.0
30	18.7	18.6	18.7	18.6	18.7	18.6	18.6	18.6	18.6	18.6	18.7	18.7	18.7	18.7	18.7	18.7	18.6	18.6	21.1	23.6
HHDP-1	110.5	110.5	116.8	116.6	116.8	116.6	116.5	113.9	111.3	110.4	116.7	117.3	110.3	117.5	114.1	111.2	120.7	113.2	112.8	118.4
HHDP-1'	109.3	109.1	116.0	116.1	115.8	115.9	115.9	116.6	110.3	110.4	116.0	116.9	110.3	119.4	116.5	110.1	118.6	112.4	112.0	118.0
HHDP-2	128.0	128.0	125.5	125.5	125.8	125.9	126.1	124.6	126.9	127.5	126.0	126.5	127.5	127.1	124.5	127.0	125.0	126.9	126.1	
HHDP-2'	131.2	131.2	124.7	124.5	125.1	124.8	124.3	123.7	131.7	129.8	124.7	129.4	129.6	128.9	124.1	131.8	124.7	128.5	127.6	
HHDP-3	111.7	111.7	113.3	113.4	113.0	113.2	113.7	110.7	113.3	113.3	113.7	107.2	113.2	110.0	110.5	113.3	112.5	112.2	111.9	112.1
HHDP-3'	107.5	107.5	104.3	104.3	104.0	104.0	104.0	106.9	107.3	108.7	104.2	104.0	108.7	110.0	106.9	107.3	101.7	106.3	106.1	106.6
HHDP-4	146.6	146.6	146.6	147.1	146.6	147.0	147.1	144.0	146.3	146.5	146.7	143.1	146.6	143.1	143.9	146.3	145.9	146.4	145.0	145.7
HHDP-4'	147.3	147.2	145.8	145.9	145.8	145.9	145.9	145.3	146.8	147.1	145.8	143.4	147.1	145.6	145.1	147.0	143.2	146.5	145.1	145.9
HHDP-5	135.9	136.0	141.1	141.8	141.1	141.5	141.7	137.2	136.4	136.7	141.0	135.8	136.8	135.7	137.2	136.3	140.9	137.9	136.8	139.8
HHDP-5'	135.6	135.5	135.0	135.5	134.7	135.4	135.4	135.4	134.6	136.2	135.0	135.2	136.3	140.0	134.8	134.9	135.5	135.5	134.4	137.7
HHDP-6	143.2	143.3	146.0	146.1	146.1	146.2	146.0	146.2	143.0	143.3	145.8	146.6	143.4	143.3	146.1	142.8	144.5	144.4	143.1	147.1
HHDP-6'	144.0	143.9	143.9	143.7	143.8	144.1	143.6	143.7	143.0	143.6	143.6	146.5	143.6	143.7	143.5	143.3	146.9	143.9	142.6	146.9
HHDP-7	173.6	173.7	174.3	174.4	174.7	174.7	175.0	173.6	170.9	174.6	174.9	175.4	174.8	174.7	173.7	171.0	175.7	174.0	171.8	168.9
HHDP-7'	173.9	173.9	178.5	178.6	179.3	179.2	179.1	174.4	174.0	175.8	179.0	174.1	175.8	173.8	174.3	174.0	178.1	175.8	173.5	170.7

[a] Calculated using the GIAO method at the mPW1PW91/6-311+G(2d,p) level in pyridine (PCM). [b] Measured in pyridine-d_5. [c] Averaged according to the Boltzmann distribution theory at 298 K based on relative Gibbs free energies. [d] Linearly corrected for the experimental data.

Table S6. Calculated ^{13}C NMR chemical shifts of **4'oB**.

	calculated[a]																				experimental[b]
Position	**4oB-1**	**4oB-2**	**4oB-3**	**4oB-4**	**4oB-5**	**4oB-6**	**4oB-7**	**4oB-8**	**4oB-9**	**4oB-10**	**4oB-11**	**4oB-12**	**4oB-13**	**4oB-14**	**4oB-15**	**4oB-16**	**4oB-17**	**4oB-18**	**4oB-19**	averaged-**4oB**[c]	averaged-**4oB** (corrected)[d]	**4o**
1	42.1	41.4	44.3	41.2	41.3	45.1	44.2	44.8	41.0	45.1	41.8	42.0	42.1	44.3	44.6	40.7	44.6	41.3	44.5	42.8	43.9	48.3
2	68.7	67.5	67.7	67.5	67.5	69.0	67.7	67.9	67.5	68.7	67.5	67.6	68.6	68.0	67.9	67.7	68.7	67.6	67.9	68.0	68.4	67.4
3	92.7	91.2	88.5	90.1	91.4	89.4	88.6	87.2	90.2	89.4	90.4	90.4	91.3	88.5	87.2	89.0	89.6	89.8	88.3	90.2	90.0	79.1
4	48.7	47.7	47.5	47.6	47.6	48.6	47.4	47.7	47.4	48.6	47.2	47.4	48.1	47.4	47.6	47.9	48.7	47.5	47.5	47.9	48.9	48.3
5	51.8	53.1	52.4	52.9	52.7	51.5	52.2	52.3	52.8	51.2	52.4	52.8	51.6	52.2	52.4	51.8	52.2	52.9	52.5	52.3	53.2	47.0
6	18.3	17.1	17.2	17.1	17.2	18.4	17.3	17.1	17.0	18.7	19.6	19.7	18.0	17.2	17.1	19.8	17.2	17.0	17.2	17.6	19.5	18.2
7	31.6	31.3	31.2	31.4	29.8	31.6	29.9	31.4	29.8	28.8	30.2	31.5	31.6	29.9	30.4	30.1	31.4	31.4	31.2	30.9	32.4	32.7
8	40.9	40.4	40.4	40.5	40.0	40.9	40.1	40.5	40.4	40.8	40.0	40.1	40.9	40.2	40.6	40.0	40.3	40.6	40.5	40.5	41.7	39.9
9	45.3	46.5	46.2	46.6	46.4	45.2	46.2	46.4	46.6	45.7	46.7	46.7	45.4	46.2	46.3	47.0	46.2	46.6	46.3	46.1	47.1	47.5
10	38.4	38.6	38.3	38.5	38.5	38.2	38.3	38.2	38.5	38.0	38.3	38.6	38.5	38.2	38.1	38.8	38.8	38.6	38.3	38.4	39.6	37.7
11	22.7	22.5	22.4	22.5	22.5	22.7	22.5	22.4	22.6	22.9	22.4	22.3	22.7	22.5	22.6	22.3	22.2	22.5	22.4	22.6	24.2	24.0
12	127.6	127.1	127.0	127.4	126.6	127.5	126.6	127.5	126.9	127.0	126.8	127.1	127.9	126.5	127.1	126.6	127.4	127.3	127.0	127.2	125.9	122.7
13	149.6	149.3	149.5	149.5	150.3	149.6	150.3	149.6	150.2	150.8	150.2	149.5	149.6	150.3	150.2	150.4	149.9	149.6	149.5	149.8	147.9	144.1
14	43.8	43.4	43.3	43.5	42.6	43.8	42.8	43.5	42.8	42.7	42.3	43.1	44.0	42.9	43.1	42.5	43.6	43.5	43.3	43.3	44.4	42.2
15	25.5	25.7	25.6	25.7	24.6	25.5	24.6	25.6	24.6	24.7	24.7	25.3	25.5	24.6	24.6	24.5	25.5	25.6	25.6	25.3	26.9	28.1
16	21.6	21.6	21.6	21.6	20.5	21.6	20.6	21.5	20.7	20.4	20.4	21.3	21.5	20.6	20.8	20.5	21.5	21.5	21.6	21.3	23.0	23.4
17	48.1	47.9	47.9	47.6	48.3	48.1	48.2	47.5	48.1	47.8	48.1	47.8	47.8	48.2	47.9	48.3	47.4	47.6	47.9	48.0	49.0	47.0
18	41.3	41.0	41.0	41.2	41.3	41.2	41.3	41.2	41.3	41.5	41.3	40.9	41.4	41.3	41.4	41.3	41.2	41.1	41.0	41.2	42.4	41.7
19	42.8	43.0	43.0	43.2	43.0	42.8	42.9	43.3	42.8	42.6	43.3	43.0	43.0	42.9	43.0	43.2	43.4	43.2	43.0	43.0	44.1	46.1
20	31.6	31.7	31.7	31.4	31.5	31.6	31.6	31.2	31.8	31.9	31.4	31.8	31.4	31.7	31.7	31.4	31.2	31.4	31.7	31.6	33.0	30.7
21	31.4	31.4	31.3	31.3	30.9	31.3	31.0	31.3	30.9	30.8	30.9	31.4	31.4	31.0	31.0	30.9	31.4	31.3	31.3	31.2	32.7	33.9
22	30.7	30.7	30.7	30.9	30.9	30.7	30.9	30.9	30.9	31.0	31.1	30.8	30.9	30.9	30.7	31.0	30.7	30.9	30.7	30.8	32.3	33.0
23	71.0	73.4	72.8	72.9	73.4	71.0	72.9	73.0	72.7	71.0	68.6	68.6	71.3	72.4	72.8	68.8	73.3	72.6	72.3	72.2	72.5	62.2
24	58.3	63.4	63.4	63.8	63.4	58.3	63.4	63.8	63.8	58.3	59.3	59.4	58.7	63.4	63.8	56.3	63.4	63.7	63.4	61.7	62.3	62.4
25	10.6	11.8	11.6	11.9	11.7	10.4	11.5	11.7	11.9	10.3	10.8	11.0	10.4	11.5	11.7	11.7	11.6	11.8	11.6	11.3	13.3	17.5
26	13.6	12.6	12.6	12.5	11.4	13.5	11.6	12.6	11.5	12.0	10.8	12.2	13.5	11.7	11.8	11.3	12.9	12.5	12.6	12.5	14.5	17.7
27	20.0	20.1	20.2	20.3	20.7	20.0	20.7	20.3	21.0	22.2	20.7	20.1	20.2	20.7	20.8	20.8	20.4	20.3	20.2	20.4	22.1	25.9
28	183.8	183.8	183.8	183.6	183.5	183.8	183.4	183.7	183.6	183.9	183.5	183.8	183.7	183.4	183.6	183.4	183.8	183.7	183.8	183.7	180.8	176.4
29	28.3	28.3	28.3	28.3	28.3	28.3	28.3	28.3	28.3	28.3	28.3	28.3	28.3	28.3	28.3	28.3	28.3	28.3	28.3	28.3	29.8	33.0
30	18.7	18.7	18.7	18.6	18.8	18.7	18.8	18.6	18.8	18.9	18.8	18.7	18.6	18.8	18.8	18.8	18.6	18.6	18.7	18.7	20.5	23.6
HHDP-1	114.2	114.3	114.0	116.2	114.4	113.9	114.2	115.9	115.9	114.5	113.9	114.1	115.4	117.3	115.7	114.6	116.2	119.2	117.4	114.8	113.9	118.0
HHDP-1'	115.8	115.5	116.1	113.4	115.5	116.0	115.9	113.6	113.5	116.0	115.9	115.9	113.3	120.3	113.6	117.7	113.5	118.0	120.3	115.4	114.5	118.4
HHDP-2	126.2	126.6	127.3	123.8	126.4	126.5	127.0	124.2	123.8	126.3	126.8	127.1	124.6	127.1	124.2	127.8	123.9	124.0	127.2	126.0	124.8	
HHDP-2'	127.9	128.1	127.9	125.8	128.0	127.9	128.0	126.0	125.6	127.9	128.6	128.5	126.6	127.0	125.8	119.6	125.8	124.1	126.9	127.3	126.0	
HHDP-3	107.0	107.3	107.2	108.7	107.2	107.2	107.2	109.4	108.5	107.0	106.4	106.2	108.6	104.8	109.1	106.8	108.9	106.1	105.0	107.5	106.8	106.6
HHDP-3'	111.8	112.4	112.5	110.4	112.4	111.8	112.5	110.2	110.6	111.8	111.2	111.2	109.2	111.6	110.5	113.4	110.5	108.8	111.6	111.6	110.8	112.1
HHDP-4	145.7	146.0	145.7	145.0	145.8	145.6	145.7	145.0	144.9	145.4	145.8	145.7	144.9	143.1	144.9	142.8	144.8	142.4	143.1	145.4	143.6	145.7
HHDP-4'	147.2	147.1	146.9	143.8	147.1	147.1	147.0	143.6	144.1	147.3	147.0	147.0	144.1	145.8	143.9	145.7	143.6	143.4	145.8	146.2	144.4	145.9
HHDP-5	134.6	134.8	134.2	135.6	134.8	134.2	134.2	135.0	135.5	134.1	134.5	134.7	135.1	134.0	135.0	134.3	135.1	135.5	134.2	134.7	133.2	137.7
HHDP-5'	140.1	139.9	140.1	136.6	140.0	140.2	140.2	136.4	136.8	140.6	139.6	139.7	136.5	139.9	136.7	138.5	136.4	136.5	139.8	139.2	137.6	139.8
HHDP-6	143.3	143.2	142.7	143.5	143.2	142.9	142.7	143.1	143.3	143.4	143.3	143.8	143.5	145.3	143.0	145.5	143.2	146.3	145.5	143.3	141.6	146.9
HHDP-6'	145.6	145.5	145.5	145.3	145.6	145.6	145.7	145.4	145.4	146.0	145.6	145.5	145.8	144.3	145.4	143.2	145.2	145.6	144.3	145.5	143.7	147.1
HHDP-7	178.1	178.1	178.9	174.3	178.1	178.6	178.9	174.4	174.2	178.5	178.4	178.3	173.5	178.5	174.4	172.5	175.1	174.0	178.5	177.3	174.6	170.7
HHDP-7'	171.4	170.6	170.2	170.1	170.6	171.3	170.4	170.3	170.0	171.3	171.7	171.6	171.4	170.7	170.2	171.0	170.5	170.6	170.7	170.7	168.3	168.9

[a] Calculated using the GIAO method at the mPW1PW91/6-311+G(2d,p) level in pyridine (PCM). [b] Measured in pyridine-d_5. [c] Averaged according to the Boltzmann distribution theory at 298 K based on relative Gibbs free energies. [d] Linearly corrected for the experimental data.

Figure S46. Correlation plots of experimental ^{1}H NMR chemical shifts versus corresponding calculated ^{1}H NMR chemical shifts of **4'o**.

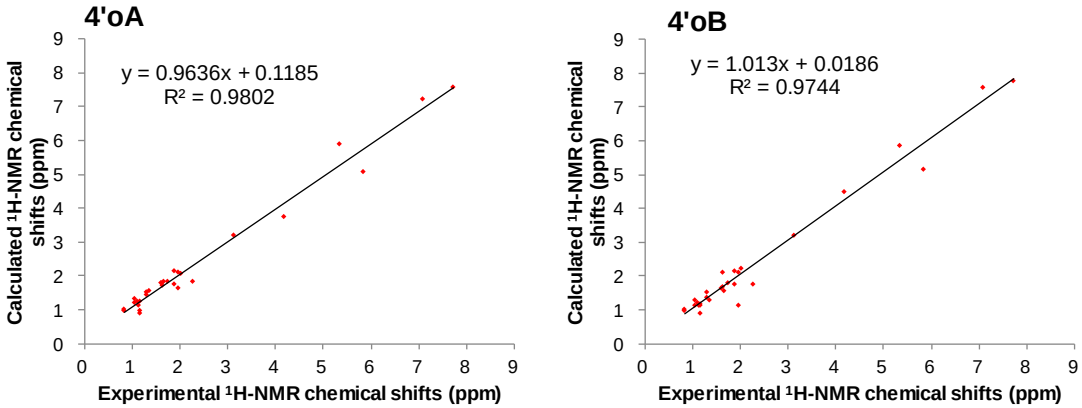


Figure S47. Correlation plots of experimental ^{13}C NMR chemical shifts versus corresponding calculated ^{13}C NMR chemical shifts of **4'o**.

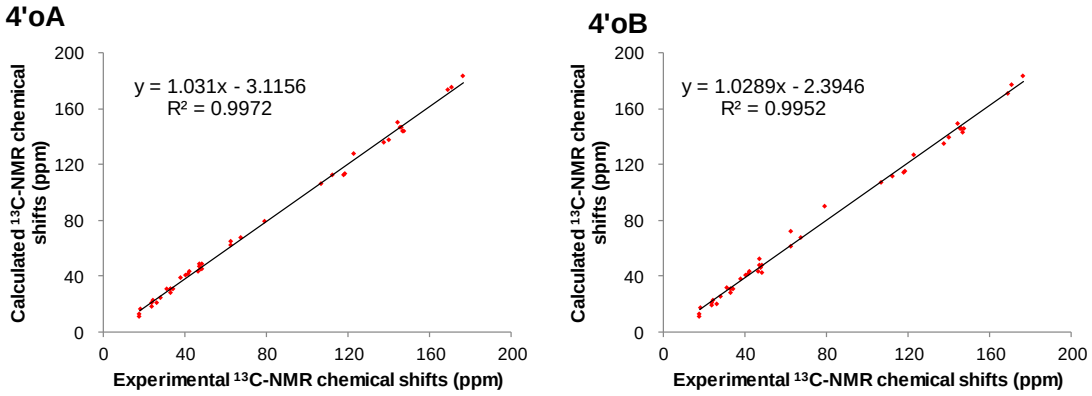


Table S7. The DP4+ probability analysis of **4'o**.

	4'oA	**4'oB**
sDP4+ (^{1}H)	48.77%	51.23%
sDP4+ (^{13}C)	100.00%	0.00%
sDP4+ (^{1}H + ^{13}C)	100.00%	0.00%
uDP4+ (^{1}H)	0.58%	99.42%
uDP4+ (^{13}C)	99.90%	0.10%
uDP4+ (^{1}H + ^{13}C)	85.66%	14.34%
DP4+ (^{1}H)	0.55%	99.45%
DP4+ (^{13}C)	100.00%	0.00%
DP4+ (^{1}H + ^{13}C)	100.00%	0.00%

Cartesian coordinates of the lowest-energy conformer of **4'oA** (**4'oA-1**) at the B3LYP/6-31G(d,p) level in pyridine (PCM).

C	1.50017600	0.42996600	1.09983100
C	1.93986700	-0.84574500	0.38158400
C	1.30883400	-1.09715400	-1.01920800
C	-0.24758100	-0.95309100	-0.85650800
C	-0.75792700	0.35462500	-0.16542300
C	-0.02803900	0.47625300	1.20080500
C	-1.05354800	-1.24658100	-2.13403400
C	-2.51799100	-1.53565100	-1.77671300
C	-3.22262900	-0.38821800	-1.00830800
C	-2.29724900	0.14041200	0.14474500
C	-0.45262200	1.63360600	-0.98196700
C	-4.58194200	-0.91318700	-0.32429100
C	-5.21297900	0.24060400	0.48013000
C	-4.44823300	1.21135500	0.99879100
C	-2.95999400	1.34753500	0.83722000
C	-5.56246900	-1.44622600	-1.41345600
C	-7.03512300	-1.52514100	-0.98388900
C	-7.56358800	-0.17360400	-0.46365900
C	-6.71793300	0.27375000	0.76454200
C	-9.07979200	-0.24770300	-0.09564800
C	-9.37533900	-1.03401400	1.18674300
C	-8.58661600	-0.52173400	2.41249700
C	-7.08396200	-0.52357700	2.04543800
C	-3.54704200	0.73394300	-2.02973000
C	-9.06001400	0.88501900	2.83183700
C	-8.81205000	-1.47986400	3.59616000
C	-4.33091300	-2.09395800	0.66178000
C	6.26093400	-2.65438200	0.93068600
C	5.59315000	-1.43659100	0.75646900
C	6.24469400	-0.32690300	0.15748800
C	7.56218300	-0.52889400	-0.29379300
C	8.21538500	-1.75786900	-0.15134100
C	7.56728200	-2.82344100	0.47774900
C	5.73141300	1.08439000	0.10751300
C	4.75885400	1.59105400	-0.78534600
C	4.36009200	2.92970200	-0.74622800
C	4.93965100	3.80994300	0.16582000
C	5.89458500	3.33401700	1.06817500
C	6.27331100	1.98833000	1.04339600
O	8.31818600	0.44356200	-0.88673900
O	7.19806600	1.64889200	1.99021600
O	6.41856800	4.22154500	1.96359800
O	4.56449600	5.11694200	0.18413600
C	4.08887900	0.65642600	-1.73343200
O	2.74246600	0.84896300	-1.71524500
O	4.65045100	-0.18129500	-2.40847800
C	4.15459700	-1.45174400	1.16839800
O	3.72354100	-2.02220900	2.15547500
C	1.65411300	-2.56093600	-1.40562900
C	1.91352000	-0.23396000	-2.18237300
O	3.38519200	-0.84872000	0.24483100
O	1.04422000	-3.46472500	-0.49272500
O	2.10978700	0.52261000	2.38956300
O	9.48823600	-1.96029400	-0.59710100
O	8.19420500	-4.02052700	0.63421200
C	-7.51235600	0.84794500	-1.61052700
O	-7.60817500	0.56664600	-2.79168600
O	-7.44336000	2.12344200	-1.17840200
C	-7.49778300	3.13831300	-2.19987000
H	1.87639400	1.29674900	0.55433300
H	1.66932600	-1.70487900	1.00352200
H	-0.50590600	-1.75910000	-0.15718600
H	-0.29692000	1.40756000	1.70894200
H	-0.34746200	-0.34540300	1.85734000
H	-0.98686200	-0.41779500	-2.84790200
H	-0.65240900	-2.12351500	-2.65163200
H	-3.07987300	-1.76207900	-2.68993500
H	-2.51900600	-2.45336200	-1.18106900
H	-2.28029800	-0.66574700	0.88586500
H	-0.81252600	1.58557400	-2.01018100
H	0.61889900	1.83223700	-1.03135800
H	-0.91079600	2.51084300	-0.51781500

H	-4.93036100	2.00485400	1.57136500
H	-2.50960500	1.51214800	1.82434100
H	-2.76779200	2.27473300	0.27946600
H	-5.23015500	-2.44209700	-1.72769500
H	-5.52371400	-0.81822300	-2.30371600
H	-7.17525300	-2.28382400	-0.20796600
H	-7.63611100	-1.84226500	-1.84177500
H	-6.96752700	1.31776000	0.96945000
H	-9.46185300	0.77371700	0.01285900
H	-9.62061100	-0.69124500	-0.93993500
H	-9.13769300	-2.09460000	1.03379500
H	-10.45297800	-0.98878400	1.39057000
H	-6.50035000	-0.10503400	2.87473200
H	-6.76517700	-1.56617800	1.94917400
H	-4.15982000	1.52545400	-1.59441300
H	-2.63983000	1.19546500	-2.41749100
H	-4.08326300	0.33894700	-2.89598100
H	-8.93139600	1.63180000	2.04359500
H	-8.50033400	1.23242500	3.70769200
H	-10.12257300	0.86927700	3.10024300
H	-8.24587400	-1.15755100	4.47759900
H	-8.49503700	-2.49916100	3.34795900
H	-9.87161000	-1.51663100	3.87484800
H	-3.81695300	-1.78056100	1.57264000
H	-5.28017600	-2.53637800	0.97030800
H	-3.75285300	-2.89788000	0.19909300
H	5.75169400	-3.48689700	1.40112700
H	3.59972900	3.29940500	-1.42347300
H	7.75233800	1.20010800	-1.10786800
H	7.30753500	0.68533200	2.00729800
H	7.01044700	3.74051300	2.56305800
H	5.04897700	5.56047100	0.89841500
H	2.74721300	-2.66276400	-1.39498700
H	1.32021000	-2.75854600	-2.43356500
H	2.52023600	-0.85546000	-2.84327100
H	1.12697800	0.22725400	-2.77659800
H	1.43488900	-4.33695600	-0.63247800
H	2.06713400	-0.35201100	2.80420600
H	9.78714700	-1.15558500	-1.04945600
H	9.07946600	-3.95225100	0.24293900
H	-8.43438600	3.07069800	-2.75749700
H	-6.65955100	3.02977100	-2.89130200
H	-7.43556200	4.08892700	-1.67200800

Cartesian coordinates of the lowest-energy conformer of **4'oB** (**4'oB-1**) at the B3LYP/6-31G(d,p) level in pyridine (PCM).

C	-1.15850000	0.11761900	2.74122700
C	-2.01364900	-0.13011000	1.49169900
C	-1.49878700	-1.24638200	0.52914400
C	0.06252100	-1.05844600	0.33663200
C	0.94190700	-0.81968100	1.60621800
C	0.30309000	0.35592500	2.38922200
C	0.72953100	-2.10965100	-0.57289900
C	2.04539400	-1.54903000	-1.13124800
C	3.07178400	-1.14146000	-0.04280600
C	2.35827700	-0.32421500	1.09461400
C	1.00905700	-2.04917100	2.54075000
C	4.21769000	-0.19318200	-0.65867300
C	5.16067700	0.25513600	0.47719500
C	4.72713600	0.33001700	1.74288900
C	3.35548100	-0.04051100	2.23237300
C	5.00776900	-0.95252600	-1.76785000
C	6.36894900	-0.33832700	-2.12324200
C	7.28487200	-0.22621100	-0.88636400
C	6.60608500	0.67558200	0.18289100
C	8.70112800	0.31570300	-1.25782900
C	8.73247400	1.81306700	-1.58454900
C	8.13757600	2.69550400	-0.46470000
C	6.70881500	2.18371000	-0.16718000
C	3.71999500	-2.44161600	0.50632500
C	9.01963600	2.66369600	0.79998700
C	8.05351900	4.15129400	-0.95826900
C	3.63173500	1.08527400	-1.32862700

C	-3.83964200	2.54459600	1.16543600
C	-4.53119400	1.36762800	0.86402800
C	-5.37464300	1.26826200	-0.25943700
C	-5.48669800	2.39625600	-1.08622100
C	-4.80681600	3.58292800	-0.78955300
C	-3.98592400	3.65942200	0.33850200
C	-6.15654100	0.04604900	-0.64057800
C	-5.70616100	-0.89463100	-1.59666700
C	-6.57560100	-1.85029500	-2.13535300
C	-7.89333200	-1.93207100	-1.68795600
C	-8.31989700	-1.08631300	-0.65552700
C	-7.45534400	-0.11590400	-0.13829900
O	-6.25062400	2.44775800	-2.21729100
O	-7.94321700	0.63605800	0.89901200
O	-9.58177300	-1.25219000	-0.17252900
O	-8.73020100	-2.87341900	-2.20118700
C	-4.25791000	-1.04004100	-1.92355300
O	-3.52070200	-0.87993300	-0.79887300
O	-3.79048000	-1.34918000	-3.00248200
C	-4.49372500	0.18241300	1.76699900
O	-5.51502200	-0.25100300	2.28182900
C	-1.97085500	-2.66884700	0.97108800
C	-2.08975100	-1.01035600	-0.88824000
O	-3.34163900	-0.46443000	2.02909800
O	-2.05791000	-2.90079500	2.37295400
O	-1.63504000	1.28191700	3.42810500
O	-4.90985300	4.69593900	-1.57467100
O	-3.32518100	4.81232300	0.63321700
C	7.55503200	-1.61201100	-0.27898700
O	7.61951400	-1.86584600	0.90940100
O	7.80666100	-2.53824400	-1.22909700
C	8.16395300	-3.85003300	-0.75216900
H	-1.24951400	-0.75248900	3.39701400
H	-2.08592200	0.80871300	0.94042900
H	0.13646400	-0.10652400	-0.21247000
H	0.83852500	0.54501200	3.32417800
H	0.36667900	1.27788200	1.79551800
H	0.90359700	-3.04215900	-0.02596100
H	0.08945700	-2.37495100	-1.41933000
H	2.49928000	-2.28410800	-1.80524800
H	1.78010700	-0.68817800	-1.75235100
H	2.12601100	0.64672400	0.64394000
H	1.42558200	-2.93134400	2.05517800
H	0.01862100	-2.33329300	2.89575200
H	1.62935500	-1.83596900	3.41604800
H	5.42730600	0.65320800	2.51417600
H	2.97883500	0.76311300	2.87765800
H	3.45522200	-0.91414500	2.89185800
H	4.38909700	-1.00230900	-2.67102100
H	5.18791600	-1.98708300	-1.46797500
H	6.24477600	0.65586200	-2.56395300
H	6.85272400	-0.95493200	-2.88641000
H	7.15942700	0.52661900	1.11460500
H	9.38054700	0.11843500	-0.41979400
H	9.08445900	-0.26190300	-2.10616100
H	8.17645100	2.00084100	-2.51231000
H	9.76971000	2.11152900	-1.78455400
H	6.27970800	2.74933600	0.66908800
H	6.08533200	2.41465200	-1.03694800
H	4.60468000	-2.23803500	1.11225600
H	3.02509200	-3.01259000	1.11956500
H	4.02228800	-3.10340500	-0.30953400
H	10.02621900	3.03576400	0.57704600
H	9.12591500	1.66060600	1.22177000
H	8.59311400	3.30397400	1.58045600
H	7.61047100	4.80135900	-0.19504900
H	7.43964000	4.22917900	-1.86283000
H	9.04951300	4.54386800	-1.19402000
H	3.19593400	1.77774200	-0.60578500
H	4.41657500	1.63218400	-1.85398200
H	2.87219600	0.84384500	-2.07666500
H	-3.18523800	2.60606100	2.02769000
H	-6.21618800	-2.56178500	-2.86977500
H	-6.67500900	1.58774300	-2.36038600
H	-7.23893700	0.64790100	1.57938300
H	-9.68222900	-0.65650000	0.58930400

H	-9.57876800	-2.81249100	-1.73465400
H	-2.94747000	-2.85877000	0.51125100
H	-1.27703900	-3.41514100	0.57684300
H	-1.68948300	-0.09151700	-1.32863500
H	-1.86282400	-1.83761000	-1.56266600
H	-2.82065000	-2.39221200	2.68510800
H	-2.41116600	1.02096100	3.94214700
H	-5.50659600	4.49821600	-2.31326300
H	-3.54907100	5.47002600	-0.04409800
H	8.33200500	-4.45101700	-1.64482400
H	7.35471900	-4.27370200	-0.15364800
H	9.07160300	-3.80318600	-0.14649700