

4,5-*Seco*-probotryenols A-C, a new type of sesquiterpenoids from *Stachybotrys bisbyi*

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S1. NMR data of 1–10

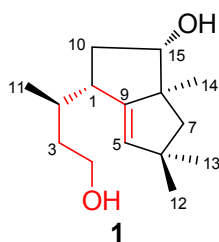


Table S1 1D and 2D NMR data for **1** (CDCl₃)

Position	δ_C^a	$^*\delta_H$ (<i>J</i> in Hz) ^a	¹ H- ¹ H COSY ^a	HMBC ^a	NOESY ^b
1	42.0	2.10 dt (8.4, 8.4)	2, 10a, 10b	2, 3, 5, 9, 11	3a, 3b, 11, 15
2	35.7	1.46	1, 3b, 11	1, 11	14
3	38.1	1.95, a	3b, 4a, 4b	1, 4	1, 11, 5
		1.29, b	2, 3a, 4b	1, 4	1, 11, 5
4	61.3	3.73, a	3a, 4b	2, 3	11
		3.65, br dt (10.4, 7.5), b	3a, 3b, 4a	2, 3	11
5	134.8	5.13, s		1, 6, 7, 8, 9	3a, 3b
6	50.0			5, 6, 8, 9, 12, 13, 14,	
7	53.7	1.65, d (12.8), a (β)	7b	15	12, 15
		1.61, d (12.8), b (α)	7a	5, 6, 8, 9, 12, 13, 14,	13, 14
				15	
8	57.7				
9	151.4				
10	40.9	2.36, ddd (12.8, 8.1, 7.4), a (α)	1, 10b, 15	1, 8, 9, 15	11, 14
		1.60, b (β)	1, 10a, 15	1, 8, 9, 15	11
11	17.9	0.88, d (6.4)	2	1, 2, 3	1, 3a, 3b, 4a, 4b, 10a, 10b
12	31.3	1.05, s		5, 6, 7, 13	7a
13	30.5	1.18, s		5, 6, 7, 12	7b
14	19.9	1.14, s		7, 8, 9, 15	2, 7b, 10a
15	80.9	3.73, dd (10.4, 7.2)	10a, 10b	7, 14	1, 7a

^a The data were recorded with a Bruker AV 400 spectrometer (¹H for 400 MHz, ¹³C for 100 MHz).

^b The data were recorded with a Bruker AV 600 spectrometer (¹H for 600 MHz, ¹³C for 150 MHz).

* The indiscernible signals due to overlap or having complex multiplicity are reported without designating their multiplicity.

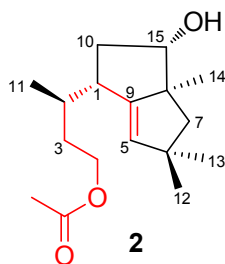


Table S2 1D and 2D NMR data of **2** (^1H for 400 MHz, ^{13}C for 100 MHz in CDCl_3)

Position	δ_{C}	$^*\delta_{\text{H}}$ (J in Hz)	^1H - ^1H COSY	HMBC	NOESY
1	41.7	2.10	2, 10a, 10b	2, 3, 5, 9, 11	3a, 3b, 11, 15
2	35.9	1.45	1, 3b, 11	1	14
3	33.7	1.99, a	3b, 4a, 4b	1, 4	1, 11, 5
		1.34, b	2, 3a, 4a, 4b	1, 4	1, 11, 5
4	63.0	4.15, ddd (10.8, 8.0, 5.3), a	3a, 3b, 4b	2, 3, COCH_3	11
		4.05, dt (10.8, 7.6), b	3a, 3b, 4a	2, 3, COCH_3	11
5	134.9	5.13, s		1, 6, 7, 8, 9	3a, 3b
6	50.0				
7	53.6	1.65, d (12.8), a (β)	7b	5, 6, 8, 9, 12, 13, 14, 15	12, 15
		1.61, d (12.8), b (α)	7a	5, 6, 8, 9, 12, 13, 14, 15	13, 14
8	57.6				
9	151.2				
10	40.9	2.37, ddd (12.8, 8.0, 7.6), a (α)	1, 10b, 15	1, 8, 9, 15	11, 14
		1.59, b (β)	1, 10a, 15	1, 8, 9, 15	11
11	17.7	0.89, d (6.4)	2	1, 2, 3	1, 3a, 3b, 4a, 4b, 10a, 10b
12	31.3	1.05, s		5, 6, 7, 13	7a
13	30.4	1.18, s		5, 6, 7, 12	7b
14	19.9	1.14, s		7, 8, 9, 15	2, 7b, 10a
15	80.8	3.74, dd (10.4, 7.2)	10a, 10b	7, 14	1, 7a
COCH_3	171.2				
COCH_3	21.0	2.04, s		COCH_3	

* The indiscernible signals due to overlap or having complex multiplicity are reported without designating their multiplicity

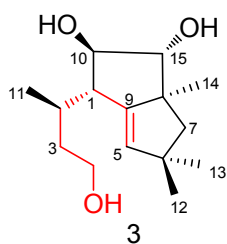


Table S3 1D and 2D NMR data of **3** (^1H for 400 MHz, ^{13}C for 100 MHz in CDCl_3)

Position	δ_{C}	$^*\delta_{\text{H}}$ (J in Hz)	^1H - ^1H COSY	HMBC	ROESY
1	49.6	2.14, t (7.2)	2, 10	2, 3, 5, 8, 9, 10, 11	3a, 3b, 11, 15
2	33.4	1.69	1, 3b, 11	1	14
3	37.2	1.86, a	3b, 4a, 4b	1, 4	1, 11, 5
		1.36, b	2, 3a, 4b	1, 4	1, 11, 5
4	61.0	3.73, a	3a, 4b	2, 3	11
		3.65, br dt (10.3, 7.4), b	3a, 3b, 4a	2, 3	11
5	135.2	5.18, s		1, 6, 7, 8, 9	3a, 3b
6	49.1				
7	54.3	1.68, d (12.4), a (β)	7b	5, 6, 8, 9, 12, 13, 14, 15	12, 15
		1.58, d (12.4), b (α)	7a	5, 6, 8, 9, 12, 13, 14, 15	13, 14
8	56.0				
9	147.7				
10	83.1	4.00, t (7.6)	1, 15	1, 8, 9, 15	14, 11
11	17.9	1.00, d (6.8)	2	1, 2, 3	1, 3a, 3b, 4a, 4b, 10
12	31.4	1.06, s		5, 6, 7, 13	7a
13	30.3	1.15, s		5, 6, 7, 12	7b
14	21.4	1.12, s		7, 8, 9, 15	2, 7b, 10
15	86.8	3.48, d (7.6)	10	7, 8, 10, 14	1, 7a

* The indiscernible signals due to overlap or having complex multiplicity are reported without designating their multiplicity

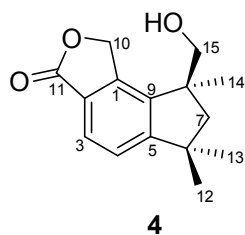


Table S4 1D and 2D NMR data of **4** (^1H for 400 MHz, ^{13}C for 100 MHz in CDCl_3)

Position	δ_{C}	δ_{H} (J in Hz)	^1H - ^1H COSY	HMBC	ROESY
1	143.4				
2	125.2				
3	124.9	7.76, d (8.0)	4	1, 5	
4	123.9	7.27, d (8.0)	3	2, 9	
5	159.5				
6	43.4				
7	51.6	2.11, d (13.6), a (β) 1.87, d (13.6), b (α)	7b 7a	5, 6, 8, 9, 12, 13, 14, 15 5, 6, 8, 9, 12, 13, 14, 15	15 14
8	48.8				
9	141.3				
10	69.5	5.51, d (15.6), a 5.34, d (15.6), b	10b 10a	1, 9, 11 1, 9, 11	
11	171.5				
12	31.2	1.36, s		5, 6, 7, 13	
13	31.9	1.36, s		5, 6, 7, 12	
14	23.8	1.39, s		7, 8, 9, 15	7b
15	70.7	3.71, s		7, 8, 9, 14	7a

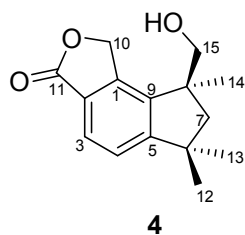


Table S5 1D and 2D data NMR of **4** (^1H for 600 MHz, ^{13}C for 150 MHz in CD_3OD)

Position	δ_{C}	δ_{H} (J in Hz)	^1H - ^1H COSY	HMBC
1	145.3			
2	125.2			
3	125.6	7.72, d (7.8)	4	1, 5, 11
4	125.2	7.38, d (7.8)	3	2, 9
5	161.2			
6	44.4			
7	52.6	2.17, d (13.2), a (β) 1.84, d (13.2), b (α)	7b 7a	5, 6, 8, 9, 12, 13, 14, 15 5, 6, 8, 9, 12, 13, 14, 15
8	50.2			
9	143.5			
10	70.7	5.54, d (15.6), a 5.46, d (15.6), b	10b 10a	1, 2, 9, 11 1, 2, 9, 11
11	173.9			
12	32.3	1.36, s		5, 6, 7, 13
13	31.5	1.36, s		5, 6, 7, 12
14	24.4	1.36, s		7, 8, 9, 15
15	71.1	3.63, d (11.4), a 3.60, d (11.4), b	15b 15a	7, 8, 9, 14 7, 8, 9, 14

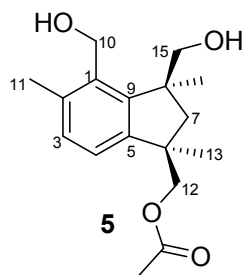


Table S6 1D and 2D NMR data for **5** (CDCl₃)

Position	δ_C^a	δ_H (J in Hz) ^a	¹ H- ¹ H COSY ^a	HMBC ^a	ROESY ^b
1	134.8				
2	137.5				
3	130.4	7.12, d (8.0)	4	1, 5, 11	
4	123.5	7.05, d (8.0)	3	2, 6, 9	
5	147.3				
6	44.4				
7	49.3	2.37, d (13.2), a (β) 1.72, d (13.2), b (α)	7b 7a	5, 6, 8, 9, 12, 13, 14, 15 5, 6, 8, 9, 12, 13, 14, 15	12, 15a, 15b 13, 14
8	50.4				
9	145.1				
10	58.3	4.77, d (11.6), a 4.71, d (11.6), b	10b 10a	1, 2, 9 1, 2, 9	
11	20.9	2.04, s		1, 2, 3	
12	72.4	4.09, s		5, 6, 7, 13, <u>COCH₃</u>	7a
13	27.1	1.34, s		5, 6, 7, 12	7b
14	26.9	1.39, s		7, 8, 9, 15	7b
15	70.9	3.92, d (11.6), a 3.64, d (11.6), b	15b 15a	7, 9, 14 7, 9, 14	7a 7a
<u>COCH₃</u>	171.3				
<u>COCH₃</u>	18.9	2.43, s		<u>COCH₃</u>	

^a The data were recorded with a Bruker AV 400 spectrometer (¹H for 400 MHz, ¹³C for 100 MHz).

^b The data were recorded with a Bruker AV 600 spectrometer (¹H for 600 MHz, ¹³C for 150 MHz)

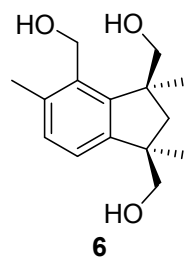
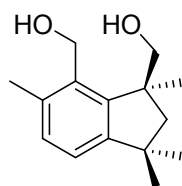


Table S7 1D and 2D NMR data of **6** (^1H for 400 MHz, ^{13}C for 100 MHz in CD_3OD)

Position	δ_{C}	δ_{H} (J in Hz)	^1H - ^1H COSY	HMBC
1	136.0			
2	138.7			
3	131.1	7.08, d (7.6)	4	1, 5, 11
4	124.4	7.01, d (7.6)	3	2, 9, 6
5	149.3			
6	47.5			
7	50.0	2.48, d (13.6), a (β) 1.60, d (13.6), b (α)	7b 7a	5, 6, 8, 9, 12, 13, 14, 15 5, 6, 8, 9, 12, 13, 14, 15
8	51.4			
9	147.2			
10	58.7	4.75, d (11.6), a 4.71, d (11.6), b	10b 10a	1, 2, 9 1, 2, 9
11	19.2	2.40, s		1, 2, 3
12	72.1	3.52, s		5, 6, 7, 13
13	27.5	1.27, s		5, 6, 7, 12
14	27.6	1.41, s		7, 8, 9, 15
15	71.6	3.77, d (11.2), a 3.69, d (11.2), b	15b 15a	7, 8, 9, 14 7, 8, 9, 14



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Table S7 1D and 2D NMR data of **7** (^1H for 400 MHz, ^{13}C for 100 MHz in CDCl_3)

Position	δ_{C}	δ_{H} (J in Hz)
1	134.4	
2	136.4	
3	130.4	7.13, d (8.0)
4	123.0	7.03, d (8.0)
5	152.3	
6	40.8	
7	54.0	2.22, d (12.8), a (β) 1.79, d (12.8), b (α)
8	50.3	
9	144.1	
10	58.7	4.79, d (11.2), a 4.73, d (11.2), b
11	18.9	2.43, s
12	32.2	1.30, s
13	31.1	1.30, s
14	26.3	1.39, s
15	71.0	3.93, d (11.2), a 3.64, d (11.2), b

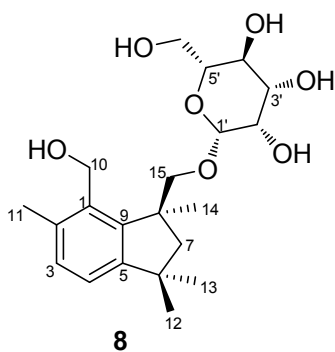


Table S8 1D and 2D NMR data of **8** (^1H for 600 MHz, ^{13}C for 150 MHz in CDCl_3)

Position	δ_{C}	δ_{H} (J in Hz)	^1H - ^1H COSY	HMBC	ROESY
1	135.9				
2	137.5				
3	130.4	7.07, d (7.6)	4	1, 5, 11	
4	122.4	6.97, d (7.6)	3	2, 9	
5	151.1				
6	40.6				
7	55.0	1.92, d (13.6), a (β) 1.84, d (13.6), b (α)	7b 7a	5, 6, 8, 9, 12, 13, 14, 15 5, 6, 8, 9, 12, 13, 14, 15	12, 15 13, 14
8	48.4				
9	145.0				
10	58.7	5.02, d (11.6), a 4.57, d (11.6), b	10b 10a	1, 2, 9 1, 2, 9	
11	19.3	2.41, s		1, 2, 3	
12	32.1	1.25, s		5, 6, 7, 13	7a
13	31.7	1.27, s		5, 6, 7, 12	7b
14	26.9	1.49, s		7, 8, 9, 15	7b
15	78.4	4.06, d (9.4), a 3.45, d (9.4), b	15b 15a	9, 14 9, 14, 1'	7a 7a
1'	100.9	4.42, br s	2'	15, 2'	3', 5'
2'	71.0	4.01, br s	1', 3'	3', 4'	
3'	73.8	3.37, br d (7.4)	2', 4'		1', 5'
4'	66.1	3.74, t (8.3)	3', 5'		
5'	76.1	2.94, br d (8.4)	4', 6a'		1', 3'
6'	60.5	3.65, br d (11.4), a 3.49, d (11.4), b	5', 6b' 6a'		

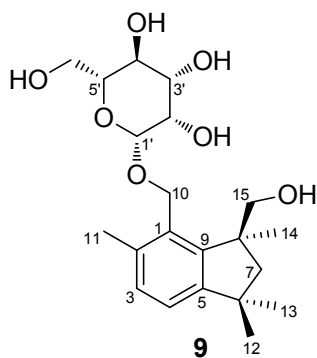


Table S9 1D and 2D NMR data of **9** (^1H for 400 MHz, ^{13}C for 100 MHz in CDCl_3)

Position	δ_{C}	$^*\delta_{\text{H}}$ (J in Hz)	^1H - ^1H COSY	HMBC	NOESY
1	130.7				
2	137.3				
3	130.0	7.06, d (7.6)	4	1, 5, 11	
4	123.3	7.02, d (7.6)	3	2, 9	
5	152.4				
6	40.8				
7	53.1	2.28, d (13.2), a (β) 1.66, d (13.2), b (α)	7b 7a	5, 6, 8, 9, 12, 13, 14, 15 5, 6, 8, 9, 12, 13, 14, 15	12, 15 13, 14
8	50.2				
9	145.5				
10	65.2	5.08, d (10.0), a 4.46, d (10.0), b	10b 10a	1, 2, 9 1, 2, 9	
11	19.2	2.33, s		1, 2, 3	
12	32.3	1.27, s		5, 6, 7, 13	7a
13	31.1	1.27, s		5, 6, 7, 12	7b
14	26.4	1.30, s		7, 8, 9, 15	7b
15	69.8	3.99, d (11.2), a 3.52, d (11.2), b	15b 15a	9, 14 9, 14	7a 7a
1'	100.1	4.49, br s	2'	10, 2'	3', 5'
2'	71.1	3.80, br s	1', 3'	3', 4'	
3'	73.7	3.30	2', 4'		1', 5'
4'	65.7	3.82	3', 5'		
5'	76.2	3.07	4', 6a'		1', 3'
6'	60.7	3.82, a 3.72, d (12.0), b	5', 6b' 6a'		

* The indiscernible signals due to overlap or having complex multiplicity are reported without designating their multiplicity.

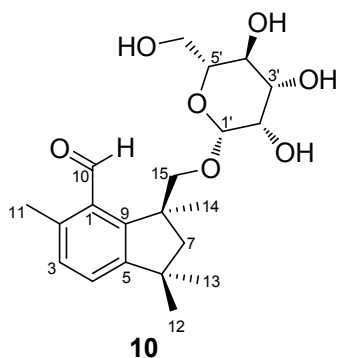


Table S10 1D and 2D NMR data of **10** (^1H for 400 MHz, ^{13}C for 100 MHz in CDCl_3)

Position	δ_{C}	$^*\delta_{\text{H}}$ (J in Hz)	^1H - ^1H COSY	HMBC	ROESY
1	132.8				
2	138.5				
3	131.6	7.10, d (7.6)	4	1, 5, 11	
4	127.4	7.18, d (7.6)	3	2, 9	
5	152.0				
6	41.3				
7	53.8	2.19, d (13.6), a (β) 1.84, d (13.6), b (α)	7b 7a	5, 6, 8, 9, 12, 13, 14, 15 5, 6, 8, 9, 12, 13, 14, 15	12, 15a, 15b 13, 14
8	49.1				
9	148.3				
10	195.8	10.61, s		1, 2	
11	21.2	2.49, s		1, 2, 3	
12	31.3	1.27, s		5, 6, 7, 13	7a
13	32.0	1.29, s		5, 6, 7, 12	7b
14	26.9	1.51, s		7, 8, 9, 15	7b
15	77.5	4.08, d (9.6), a 3.60, d (9.6), b	15b 15a	9, 14 9, 14, 1'	7a 7a
1'	100.7	4.39, br s	2'	15, 2'	3', 5'
2'	70.9	3.93, br s	1', 3'	3', 4'	
3'	73.9	3.47, br d (8.4)	2', 4'		1', 5'
4'	66.6	3.80	3', 5'		
5'	76.0	3.09, br d (8.4)	4', 6a'		1', 3'
6'	61.1	3.80, a 3.72, d (11.2), b	5', 6b' 6a'		

* The indiscernible signals due to overlap or having complex multiplicity are reported without designating their multiplicity

S2. The HPLC analyses of the reaction products (2a and 5a)

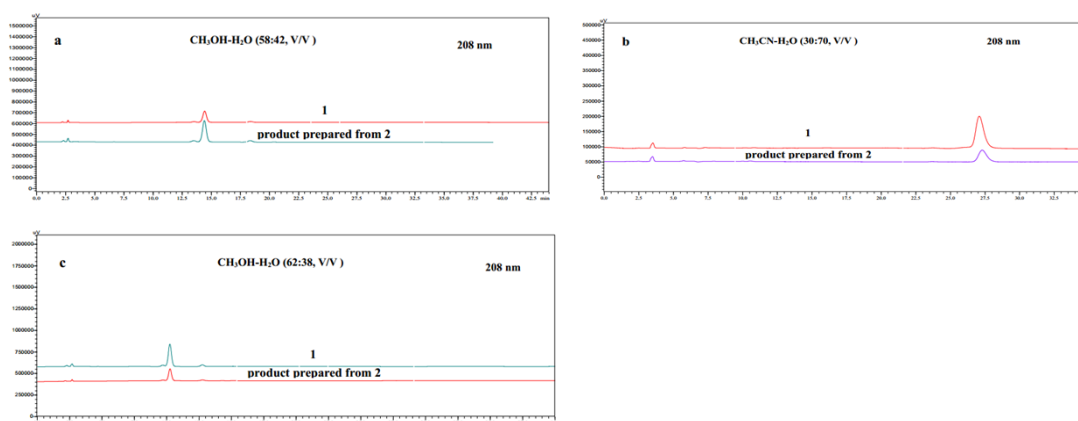


Fig. S1 The product prepared from 2 (2a) and compound 1 were compared by HLPC with three eluting systems (Phenomenex C18 column; 250 × 4.6 mm, 5 μm; **a**: MeOH-H₂O (58:42, v/v); **b**: CH₃CN-H₂O (30:70, v/v); **c**: MeOH-H₂O (62:38, v/v); 1.0 mL/min; 35 °C)

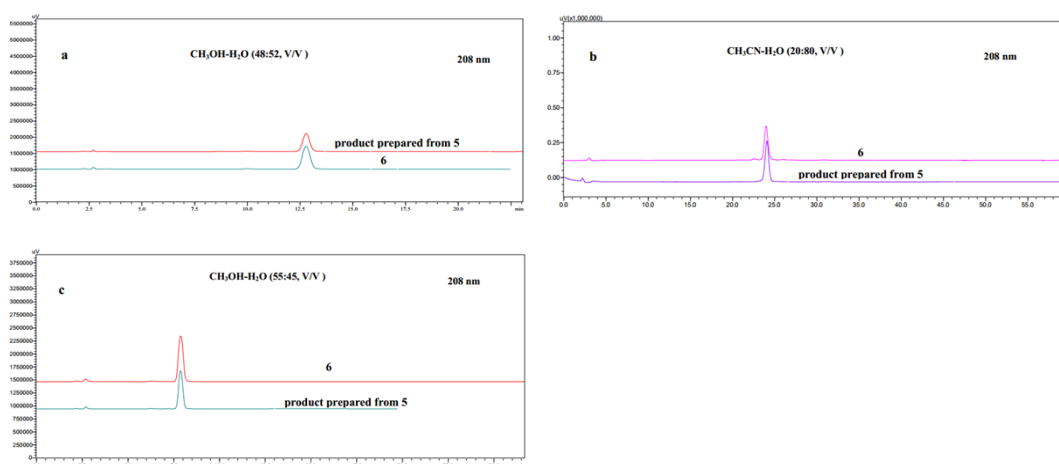
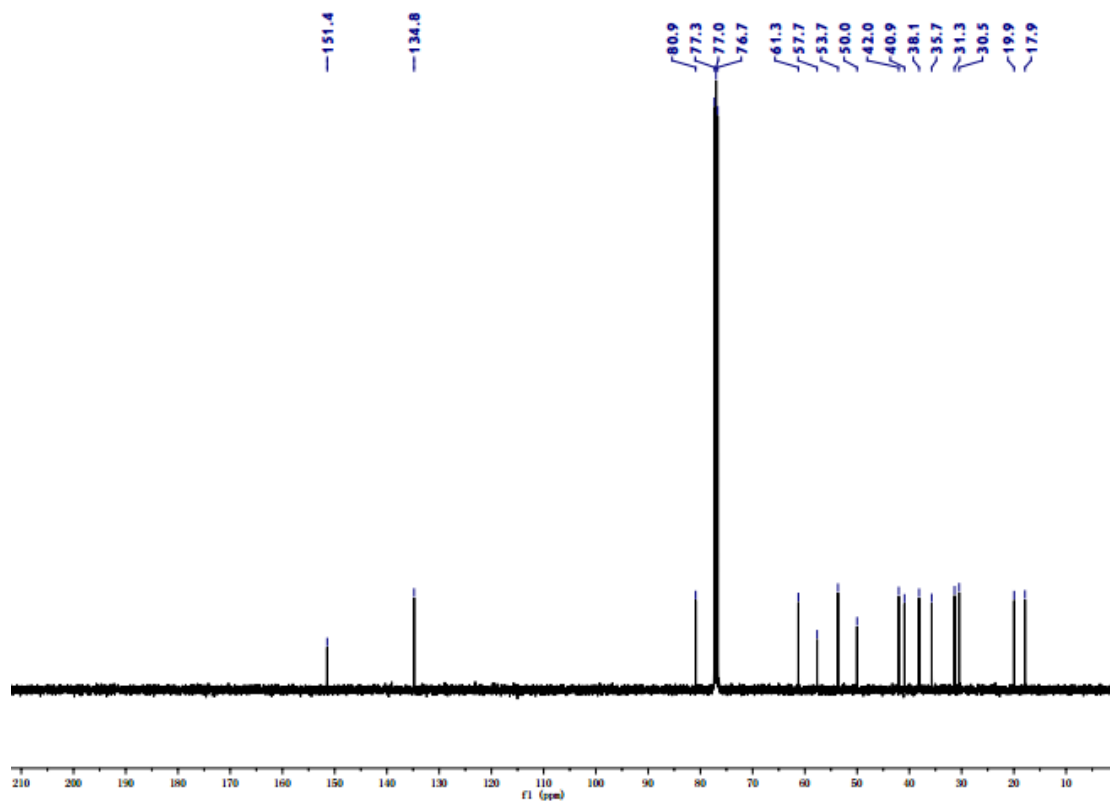
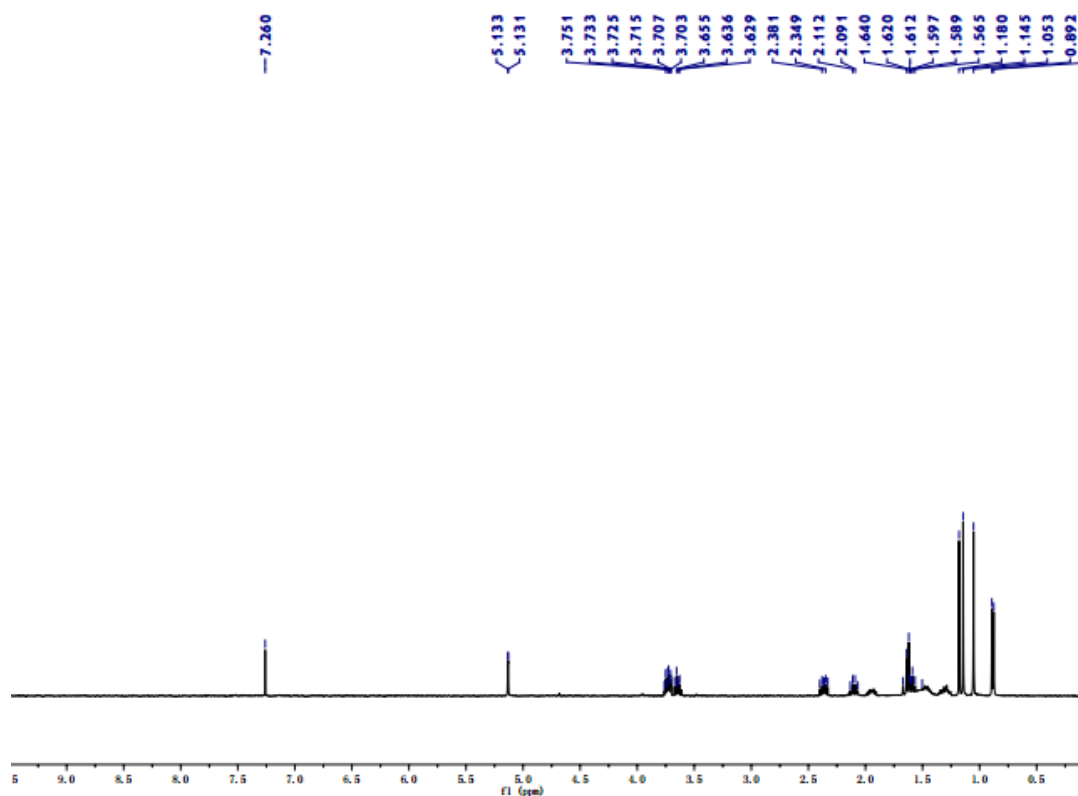
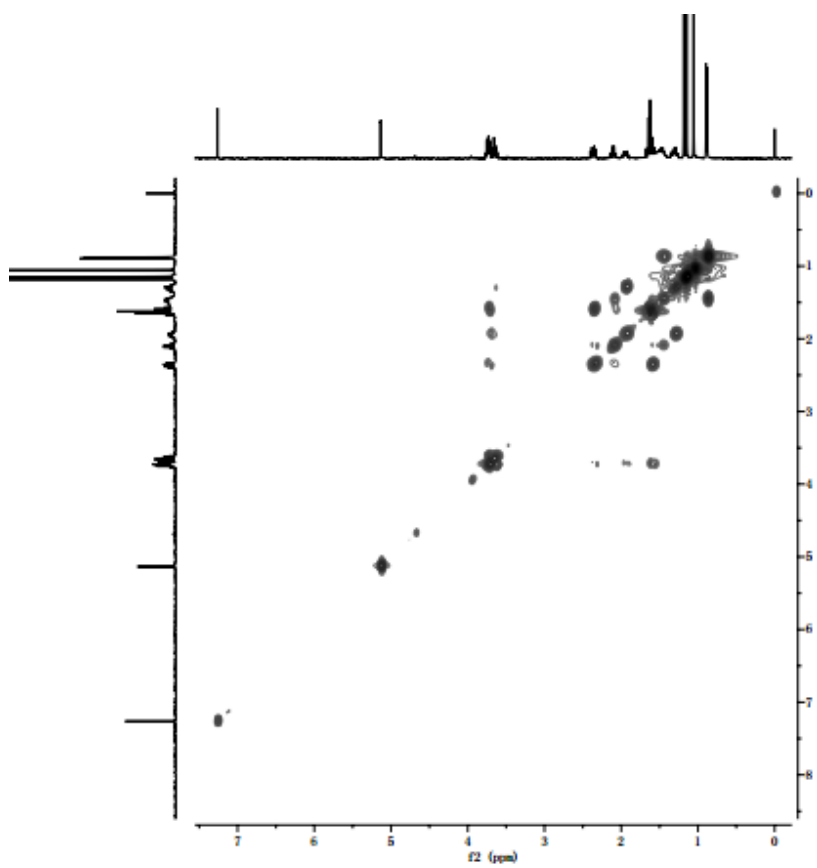


Fig. S2 The product prepared from 5 (5a) and Compound 6 were compared by HLPC with three eluting systems (Phenomenex C18 column; 250 × 4.6 mm, 5 μm; **a**: MeOH-H₂O (48:52, v/v); **b**: CH₃CN-H₂O (20:80, v/v); **c**: MeOH-H₂O (55:45, v/v); 1.0 mL/min; 35 °C)

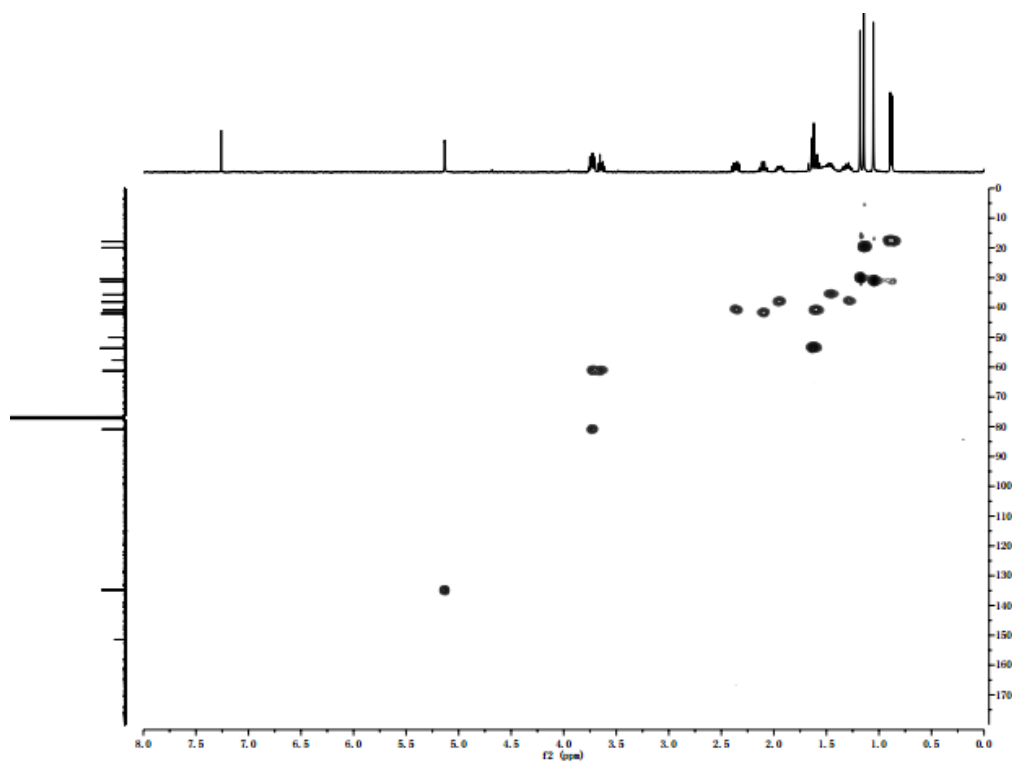
S3. The 1D and 2D NMR spectra of 1–10



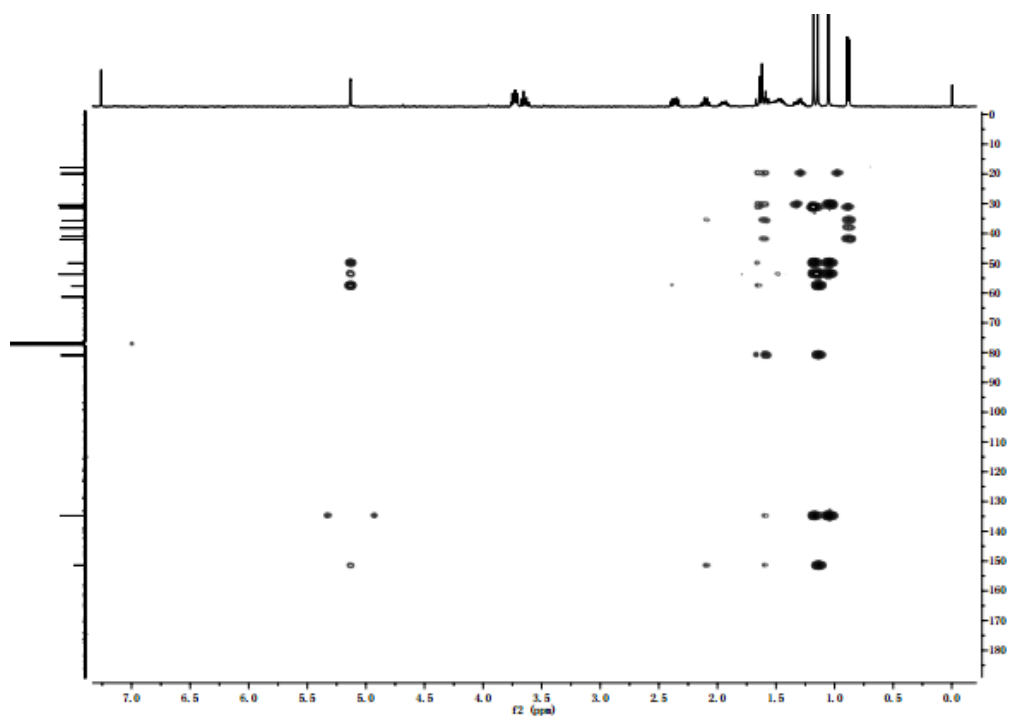
¹³C NMR spectrum of **1** (100 MHz, in CDCl₃)



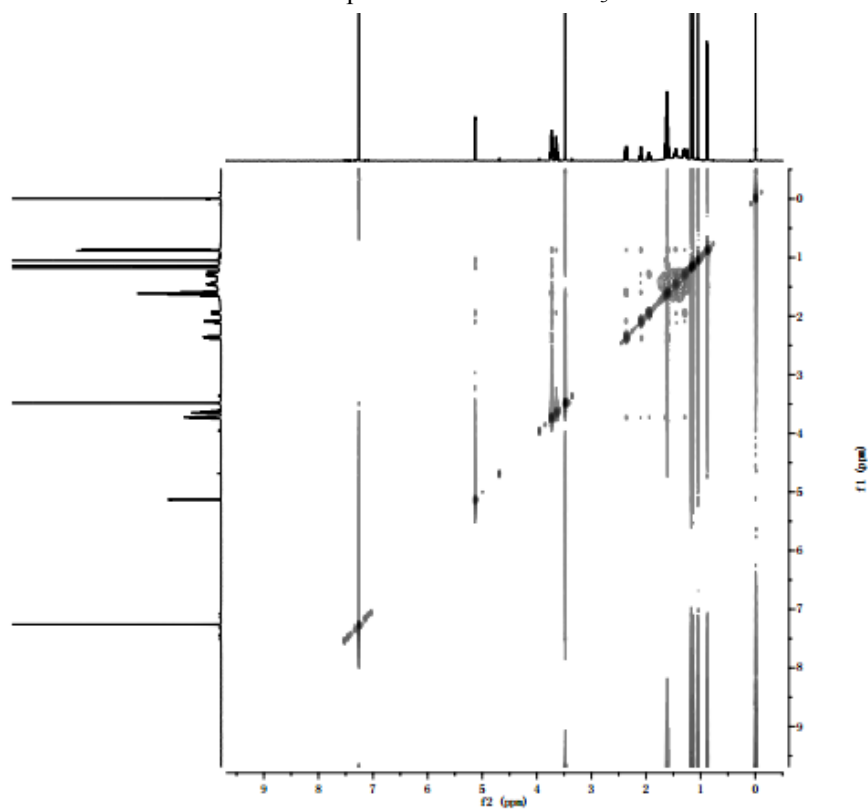
^1H - ^1H COSY spectrum for **1** in CDCl_3



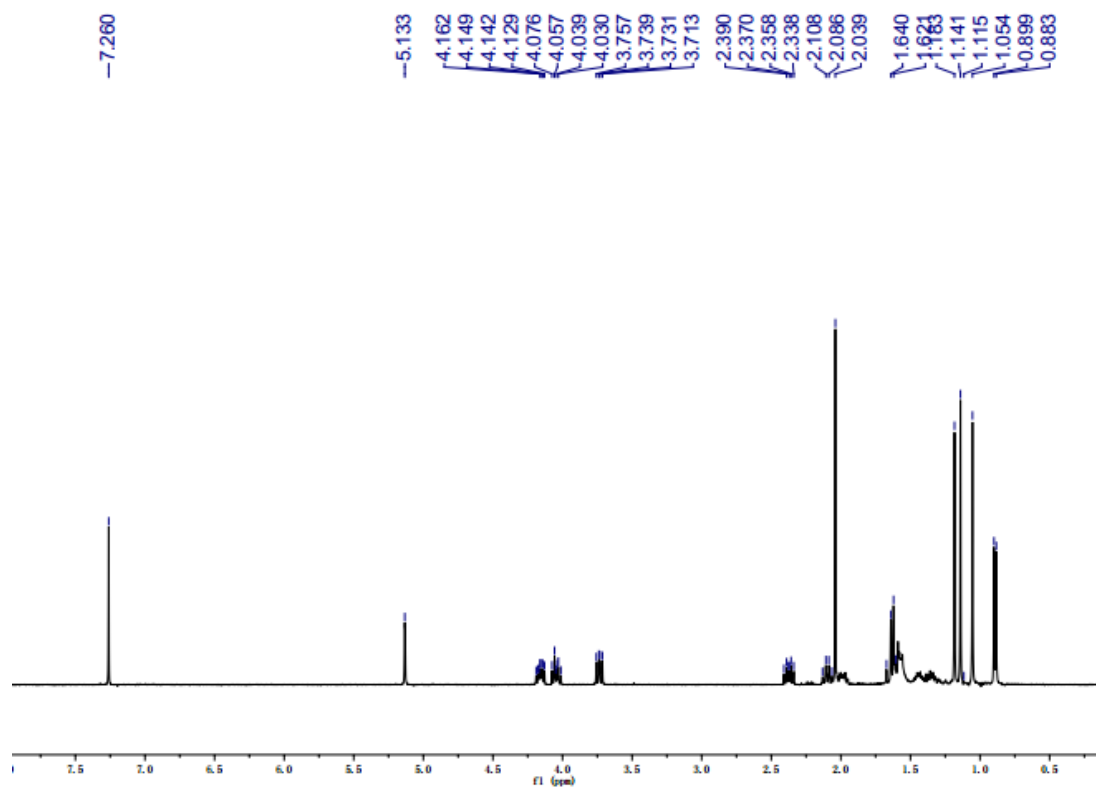
HSQC spectrum for **1** in CDCl_3



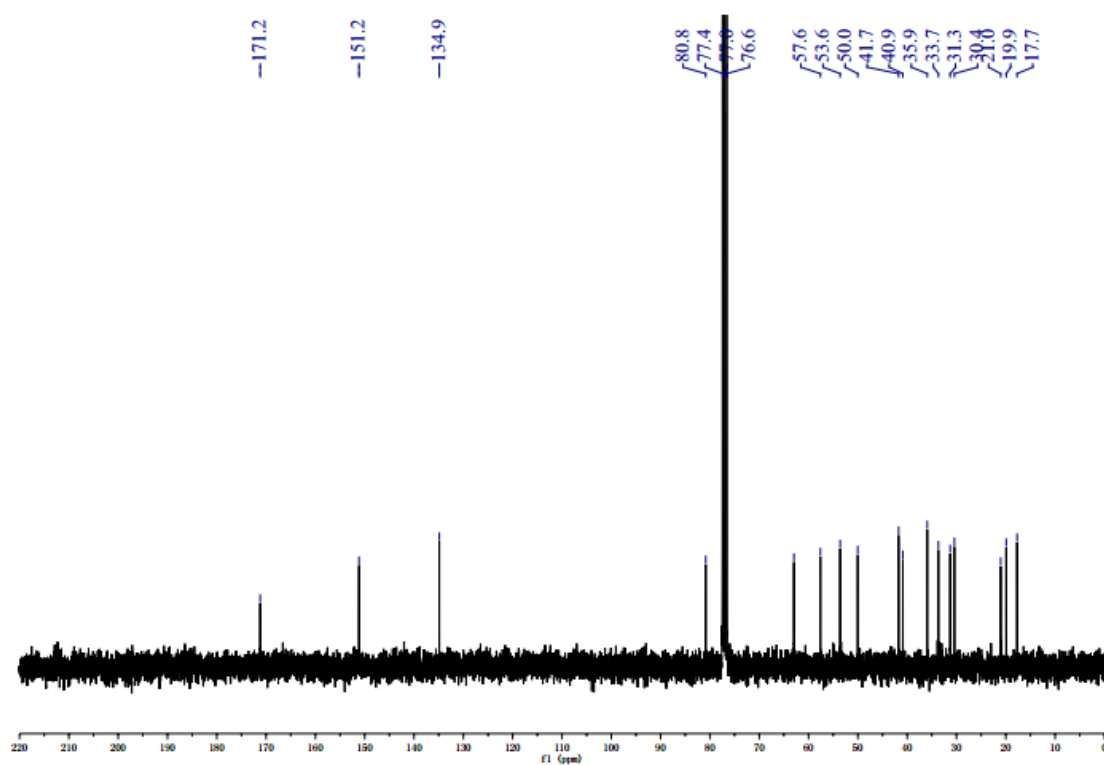
HMBC spectrum for **1** in CDCl₃



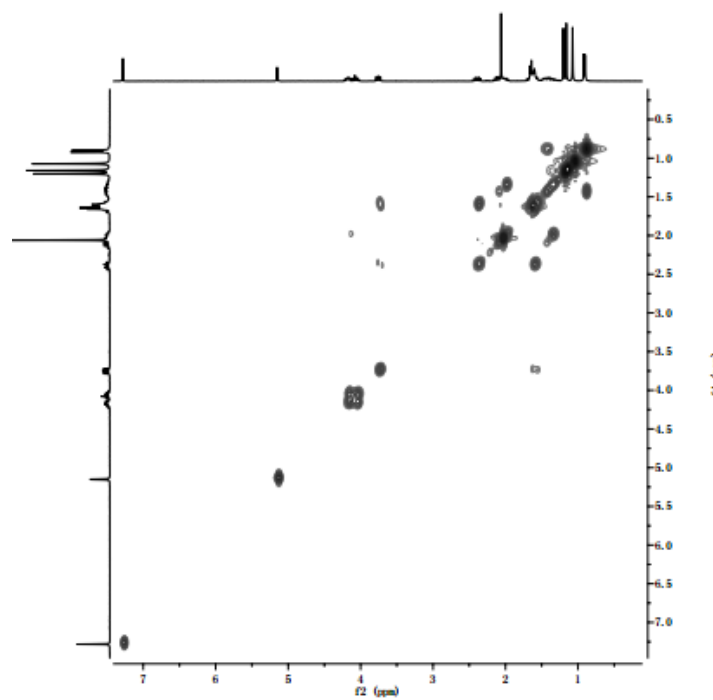
NOESY spectrum for **1** in CDCl₃



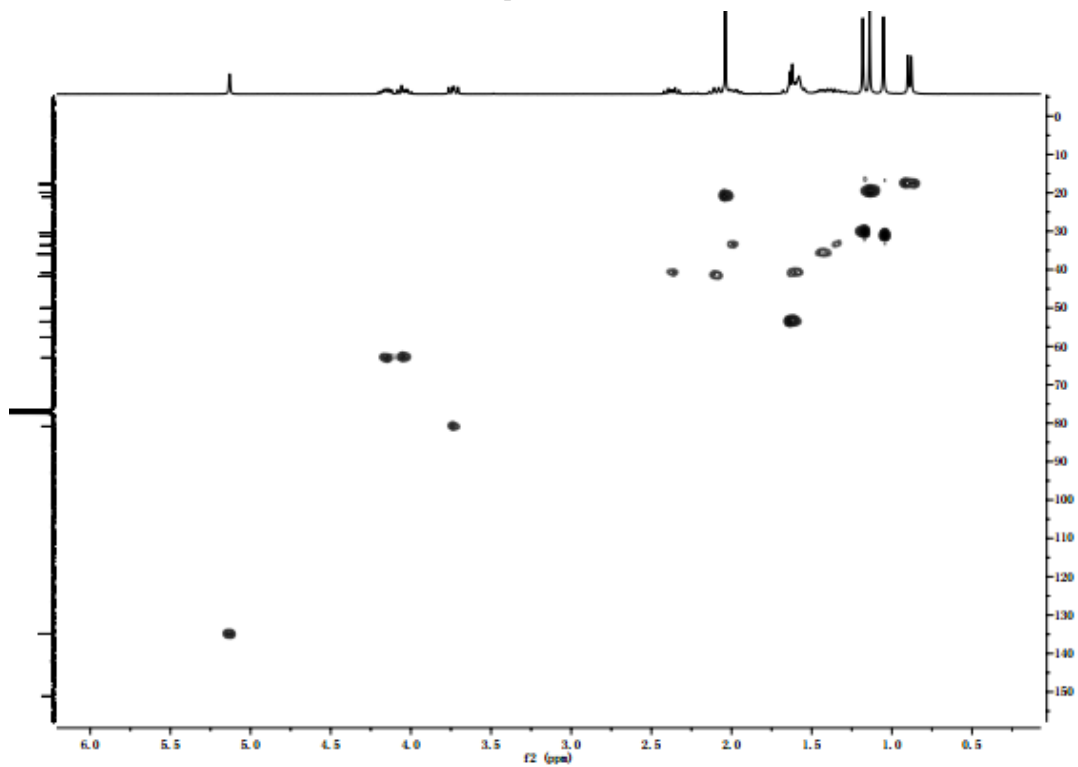
^1H NMR spectrum of **2** (400 MHz, in CDCl_3)



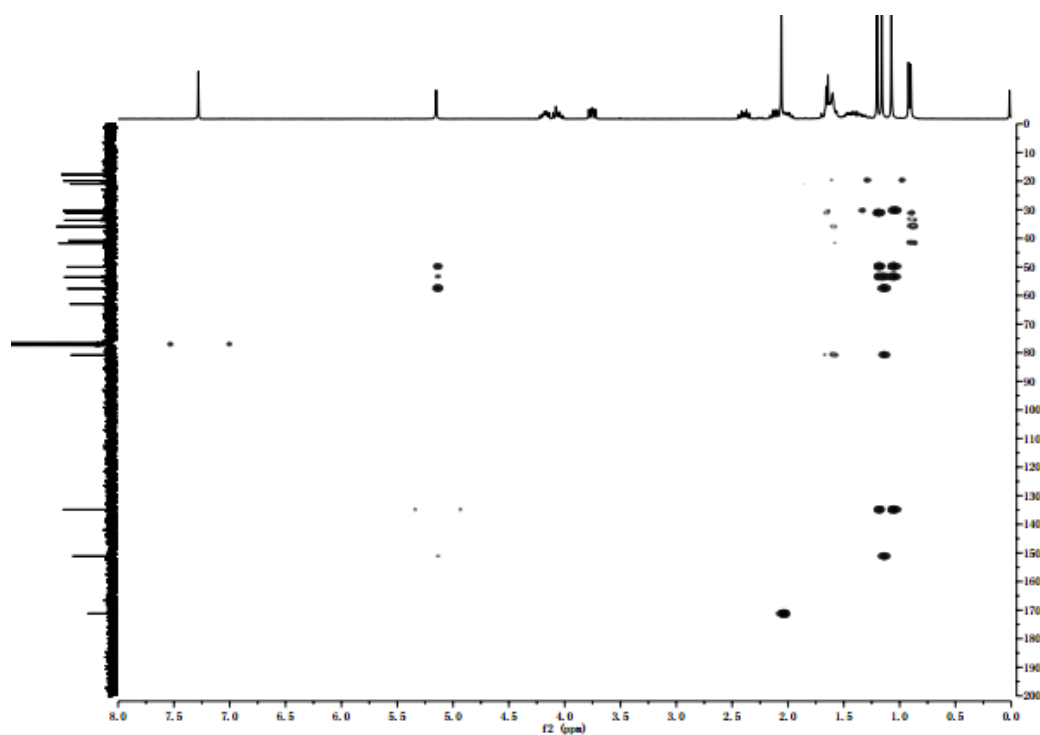
^{13}C NMR spectrum of **2** (100 MHz, in CDCl_3)



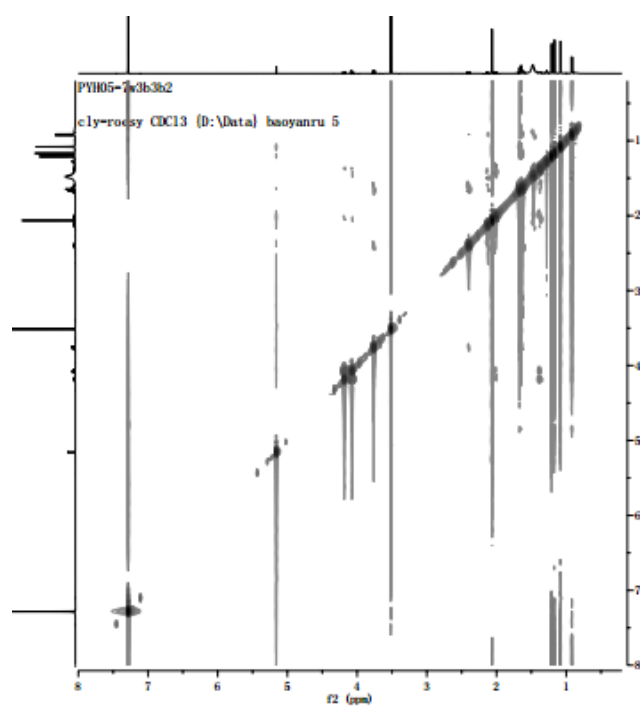
^1H - ^1H COSY spectrum for **2** in CDCl_3



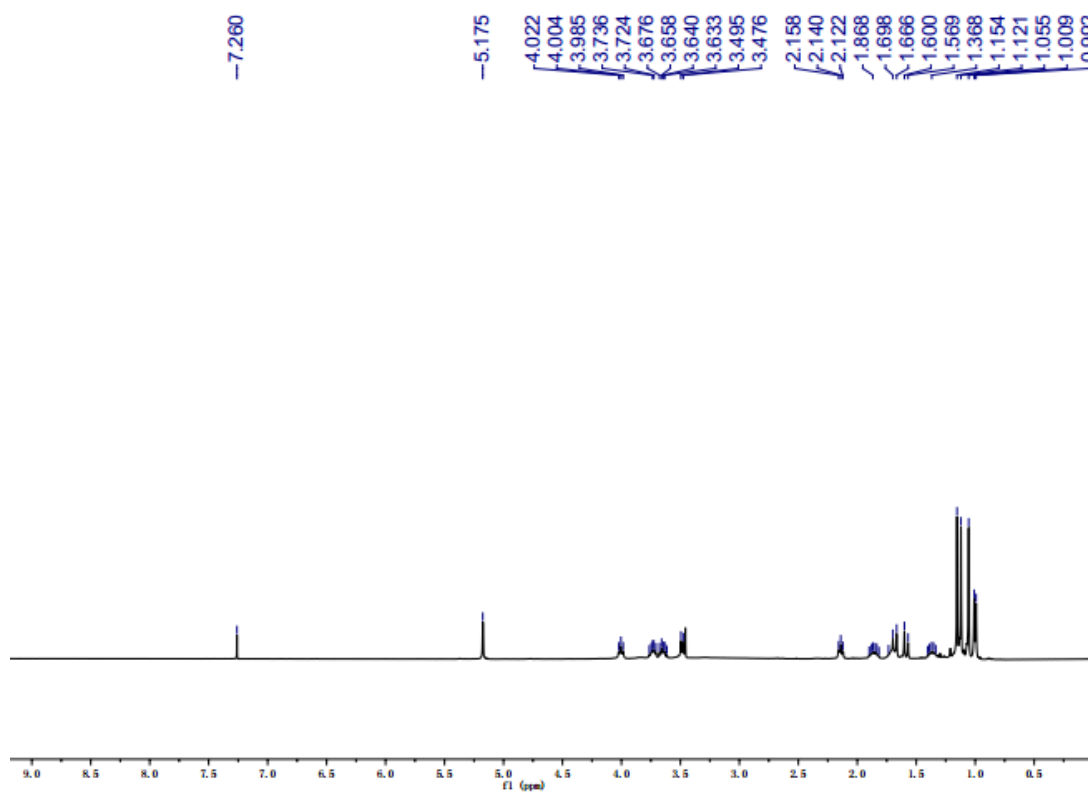
HSQC spectrum for **2** in CDCl_3



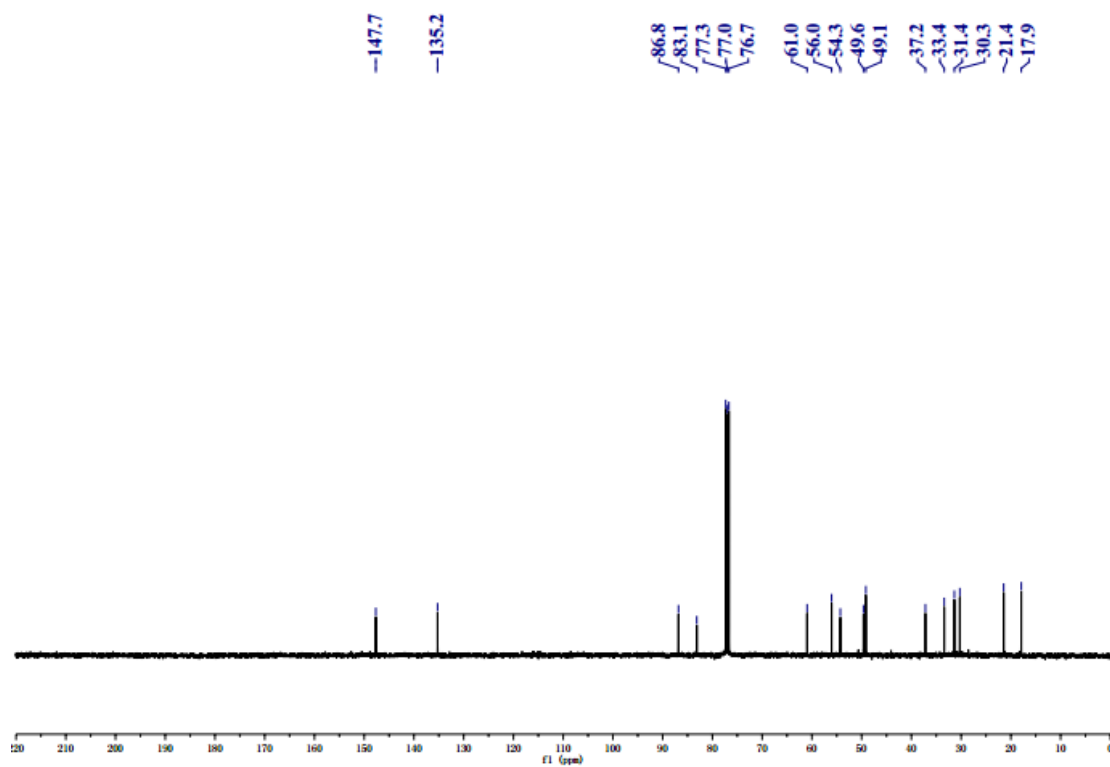
HMBC spectrum for **2** in CDCl_3



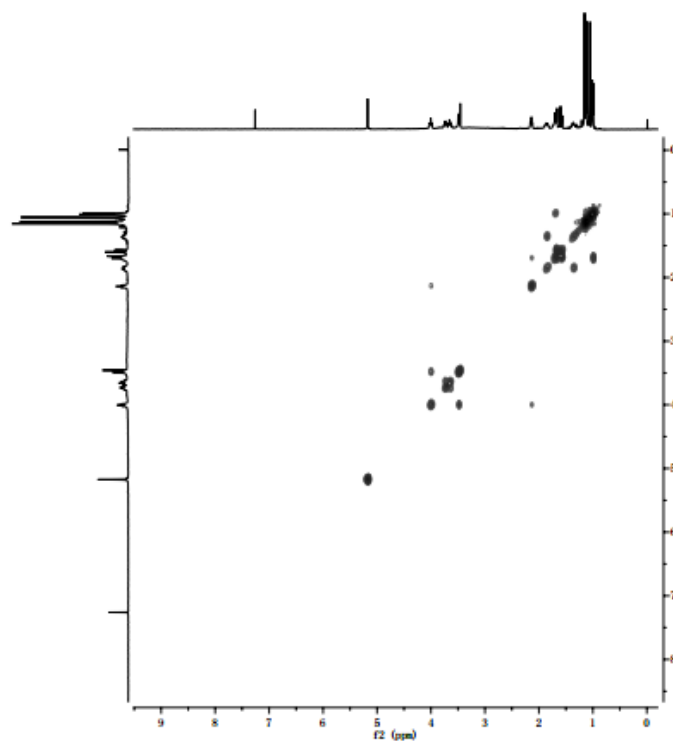
NOESY spectrum for **2** in CDCl_3



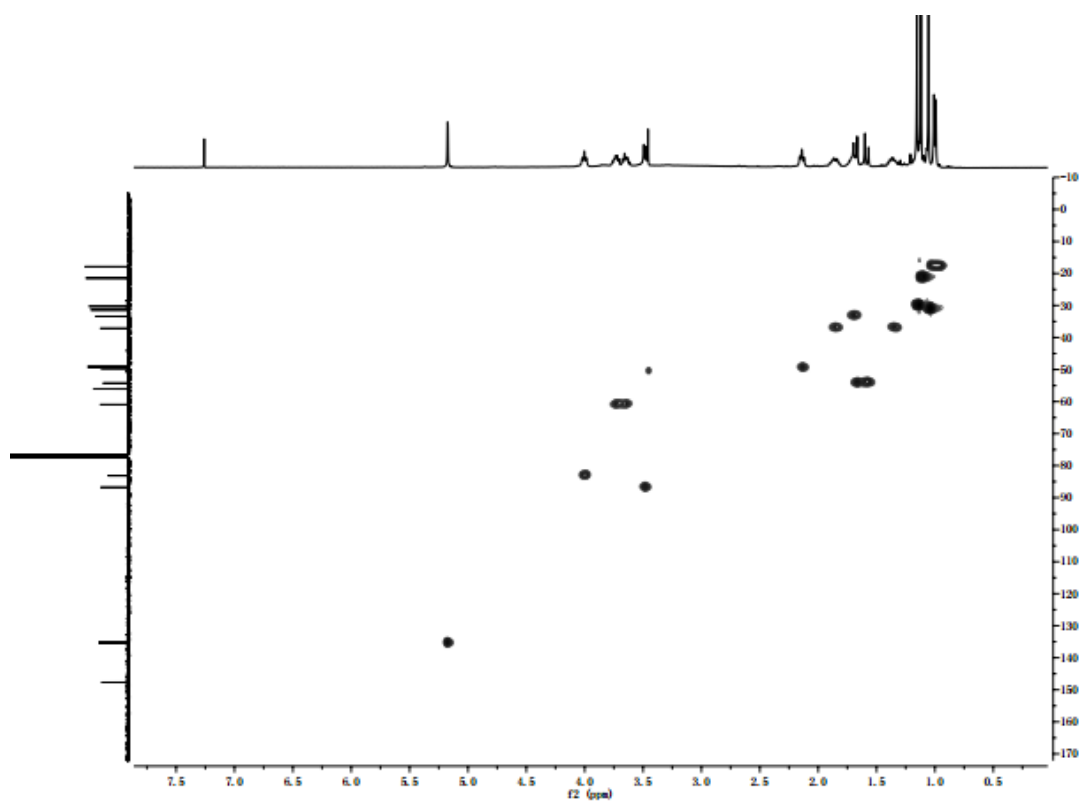
^1H NMR spectrum of **3** (400 MHz, in CDCl_3)



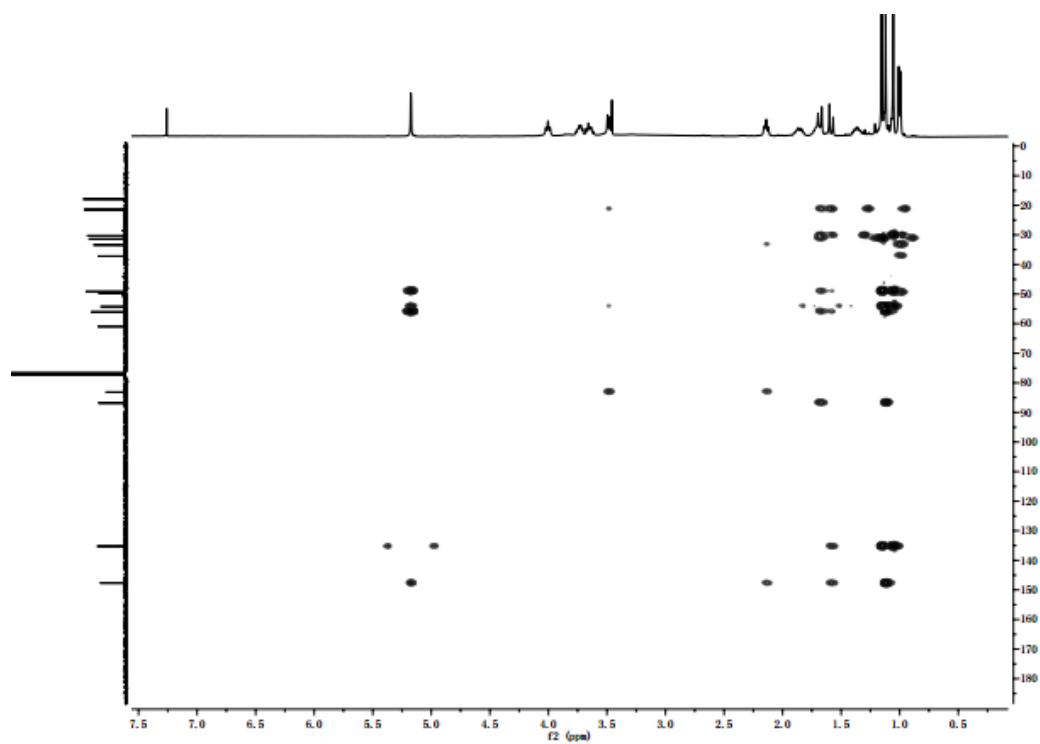
^{13}C NMR spectrum of **3** (100 MHz, in CDCl_3)



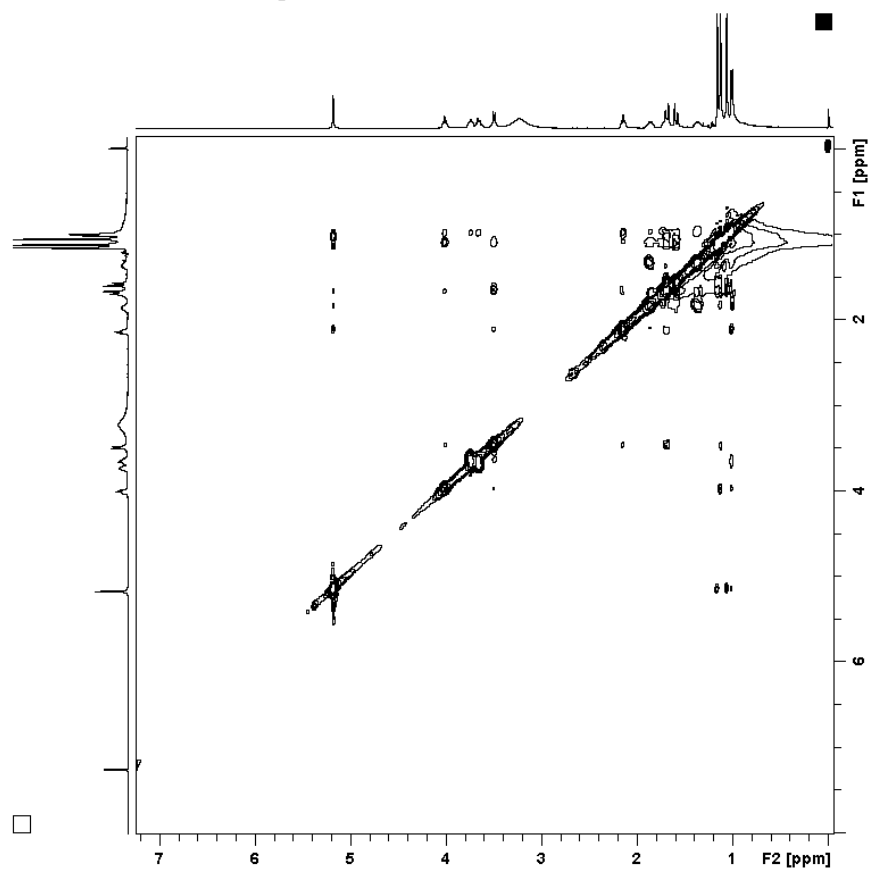
^1H - ^1H COSY spectrum for **3** in CDCl_3



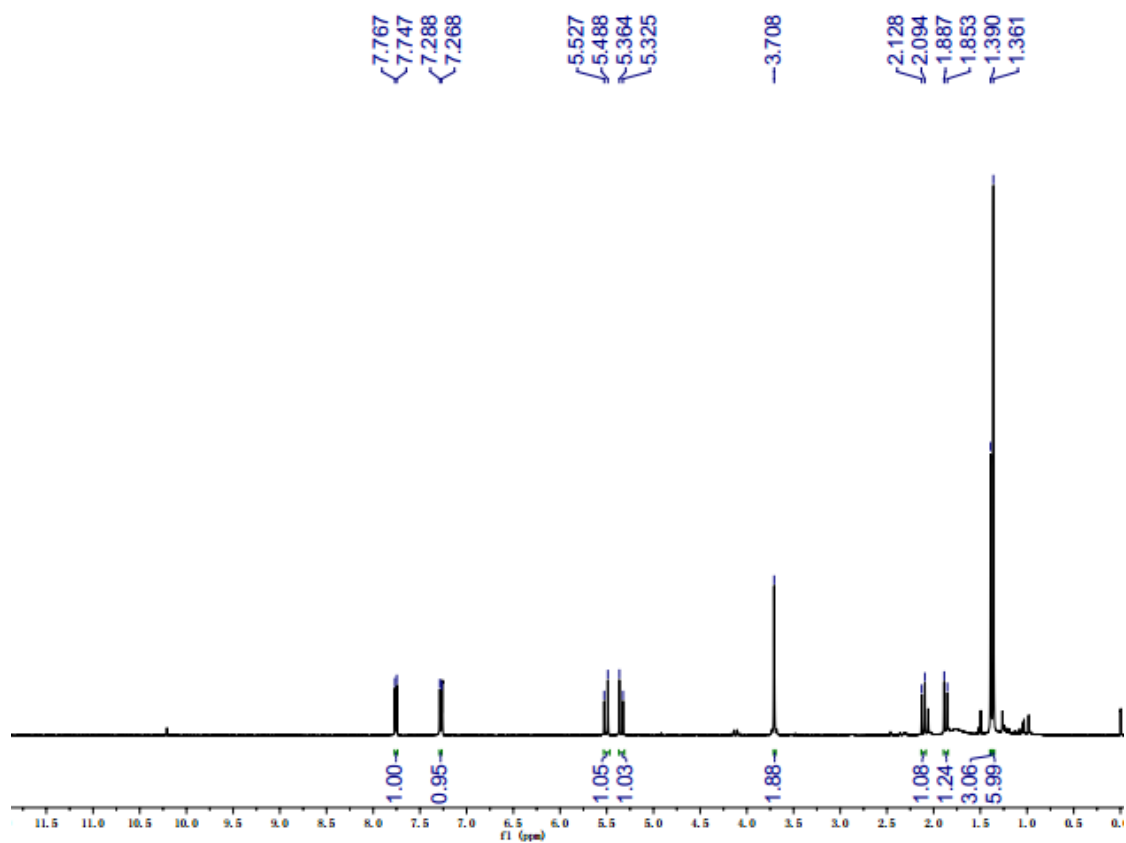
HSQC spectrum for **3** in CDCl_3



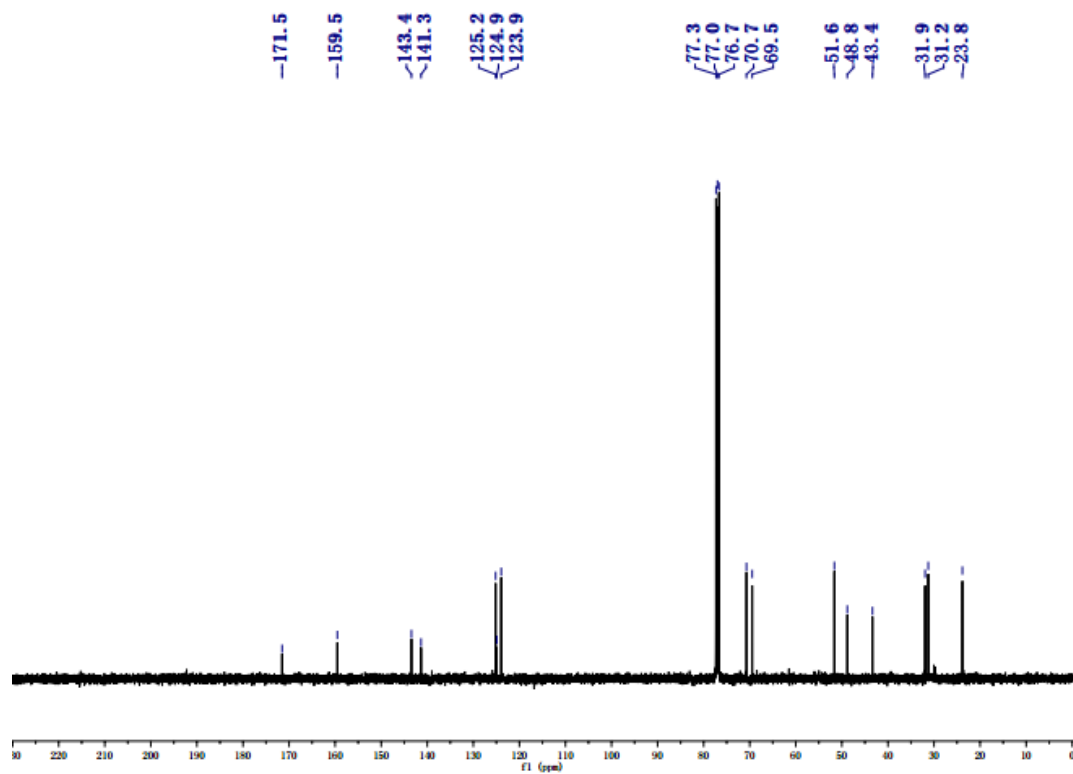
HMBC spectrum for **3** in CDCl_3



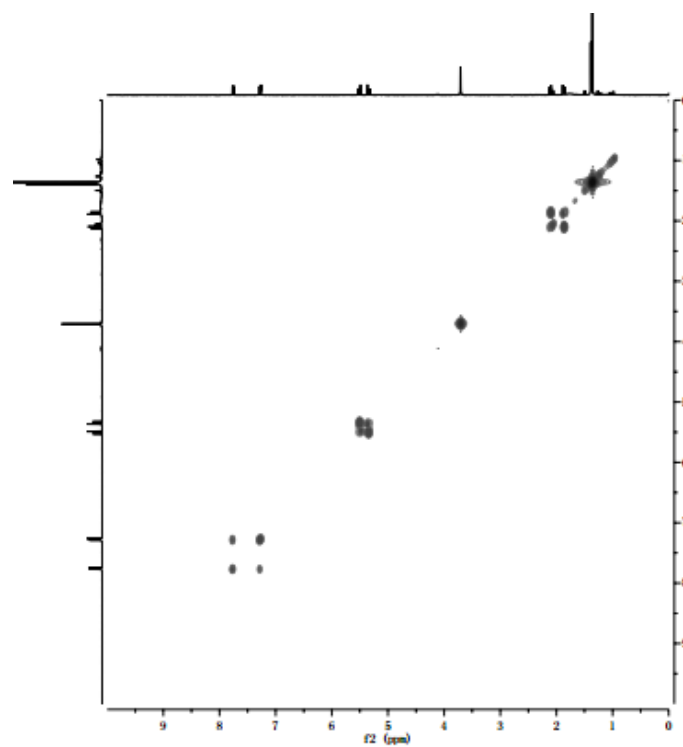
ROESY spectrum for **3** in CDCl_3



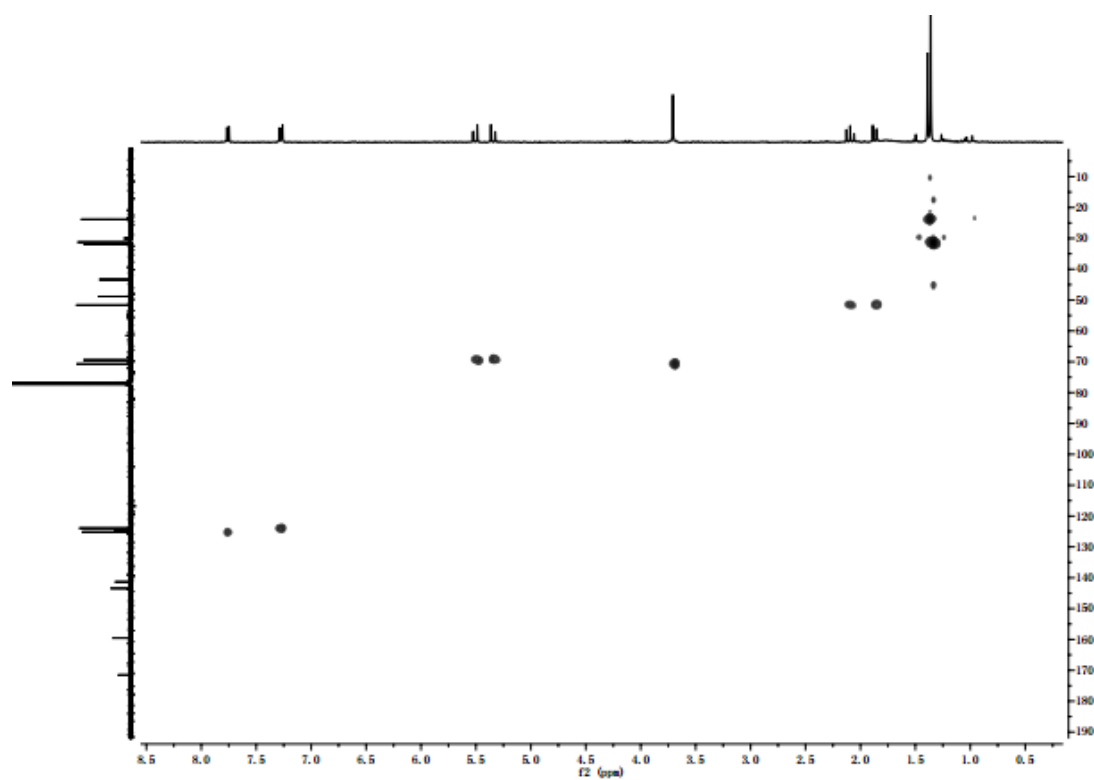
¹H NMR spectrum of **4** (400 MHz, in CDCl₃)



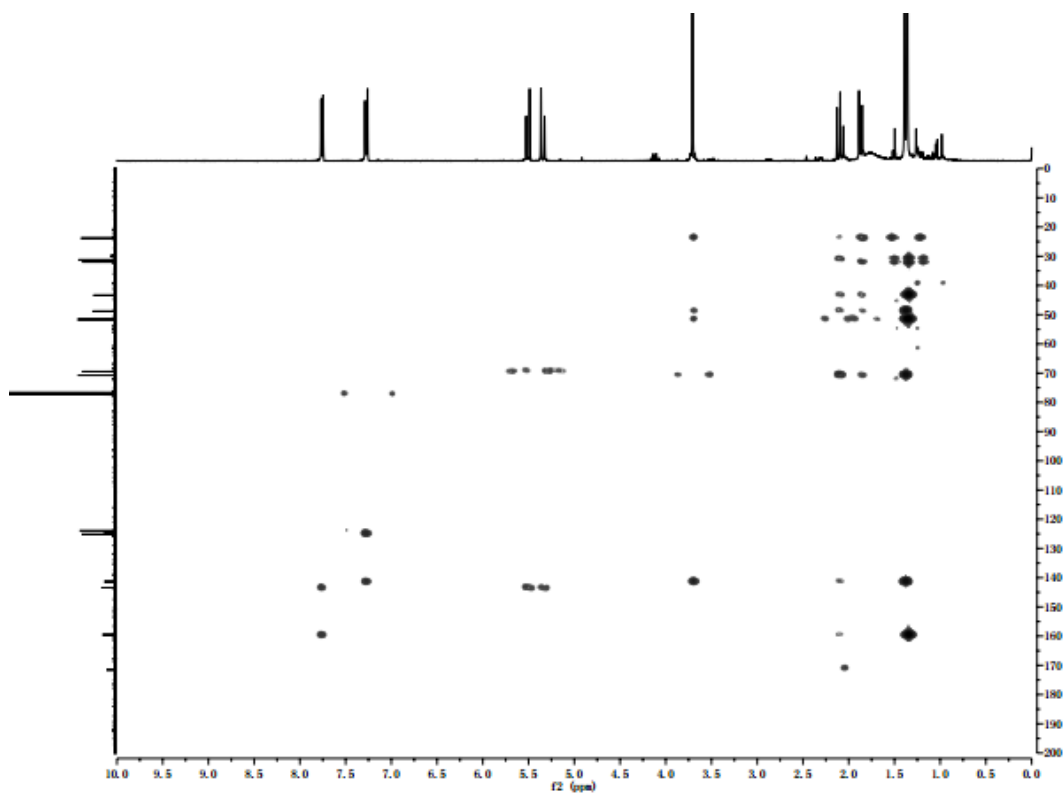
¹³C NMR spectrum of **4** (100 MHz, in CDCl₃)



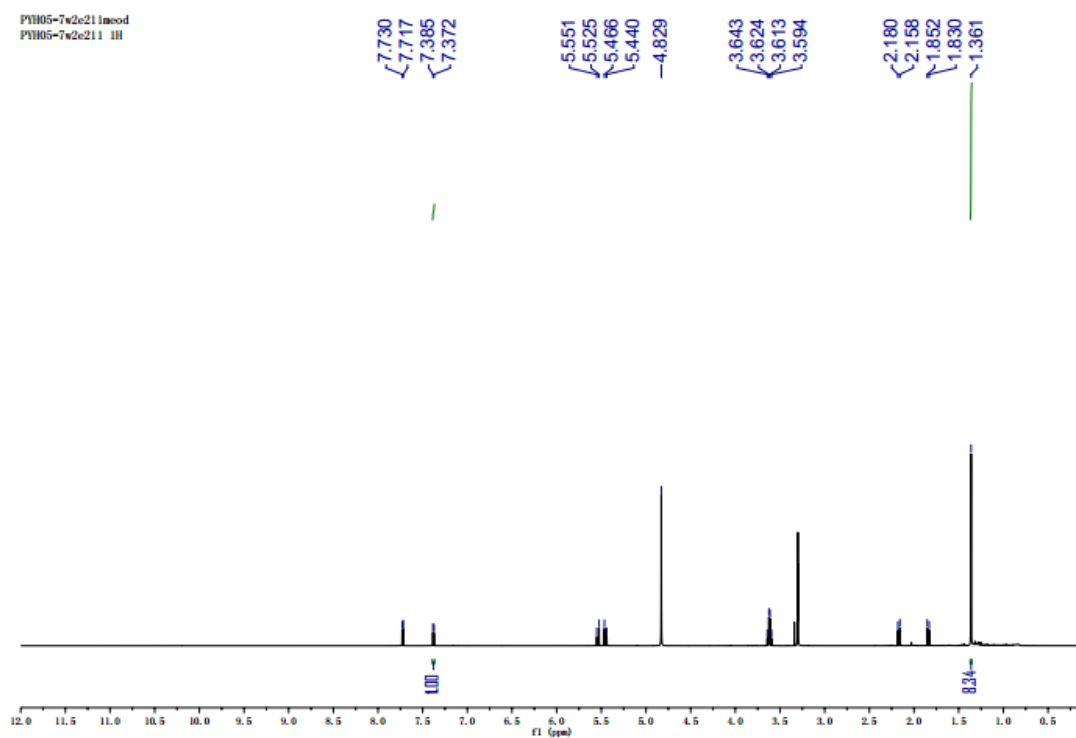
^1H - ^1H COSY spectrum for **4** in CDCl_3



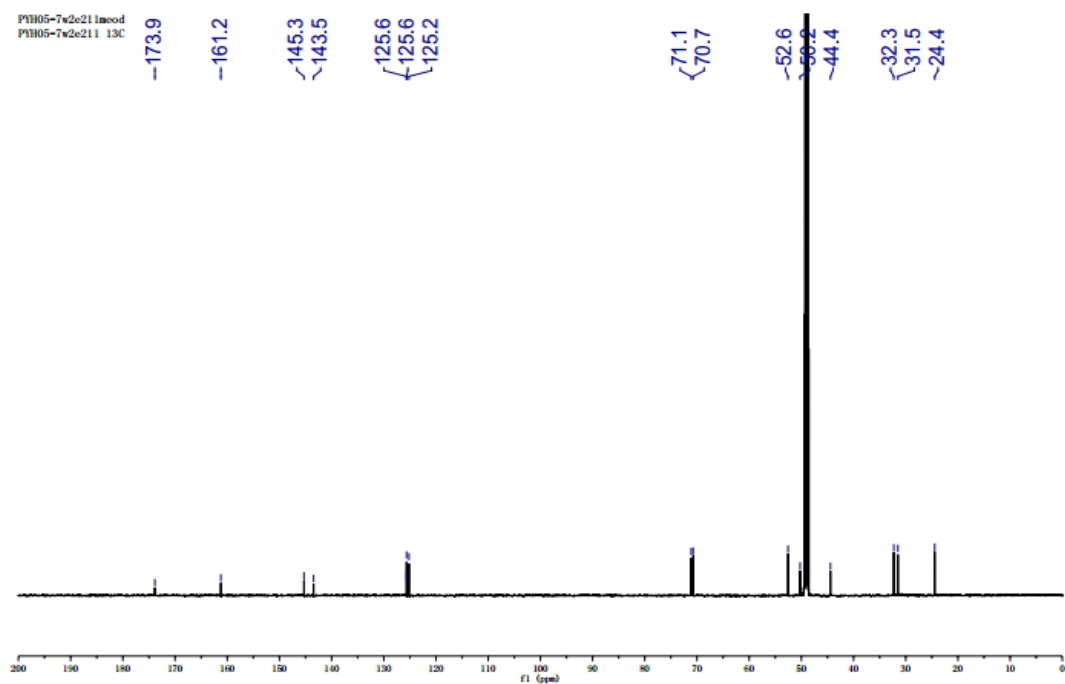
HSQC spectrum for **4** in CDCl_3



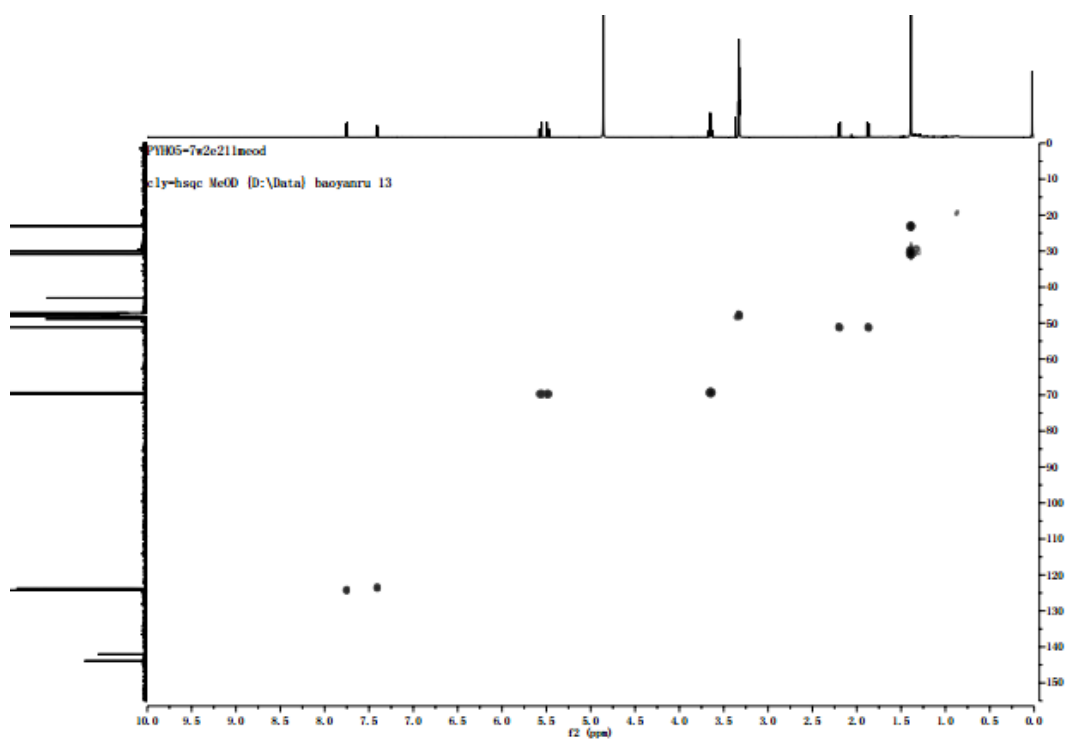
HMBC spectrum for **4** in CDCl_3



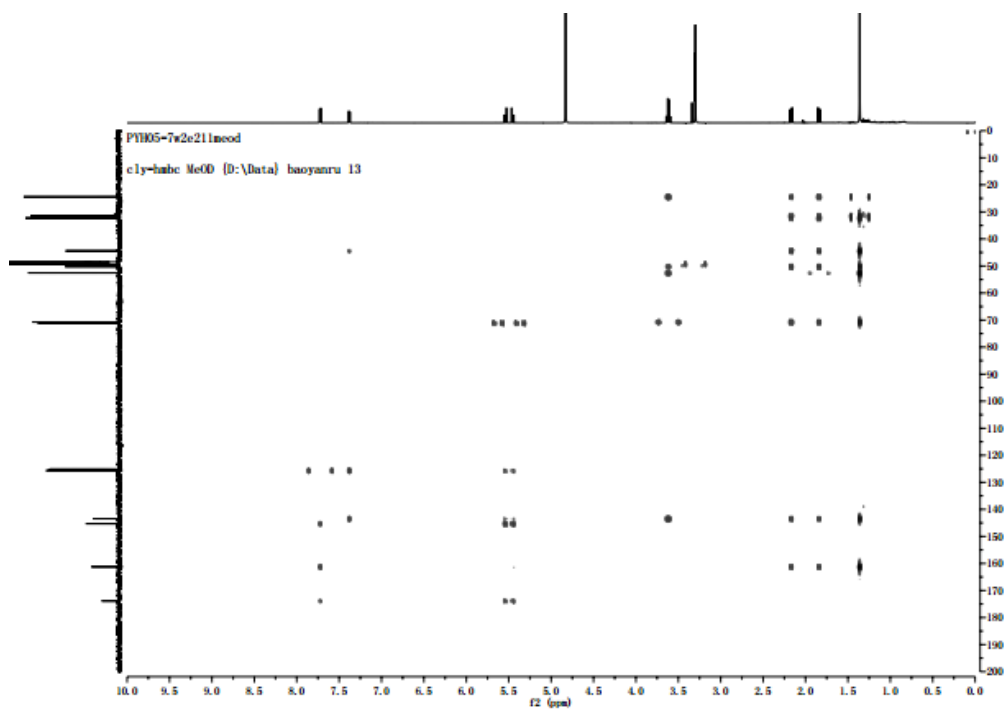
^1H NMR spectrum of **4** (600 MHz, in CD_3OD)



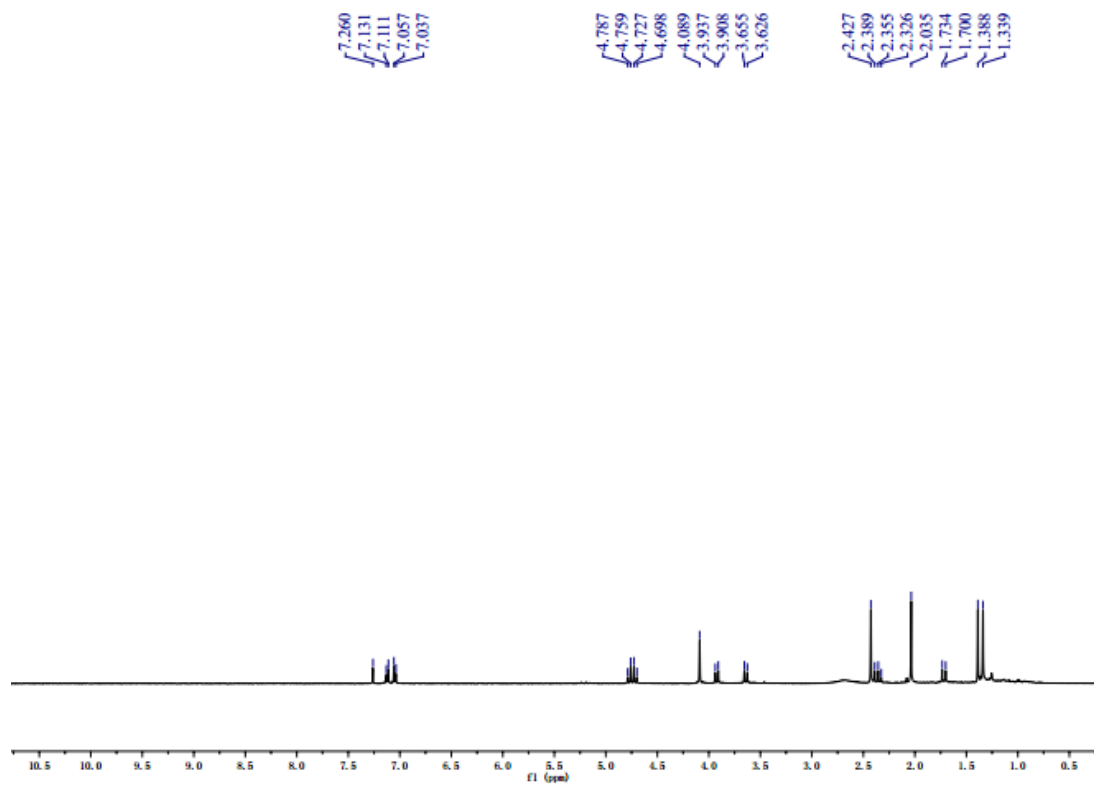
^{13}C NMR spectrum of **4** (150 MHz, in CD_3OD)



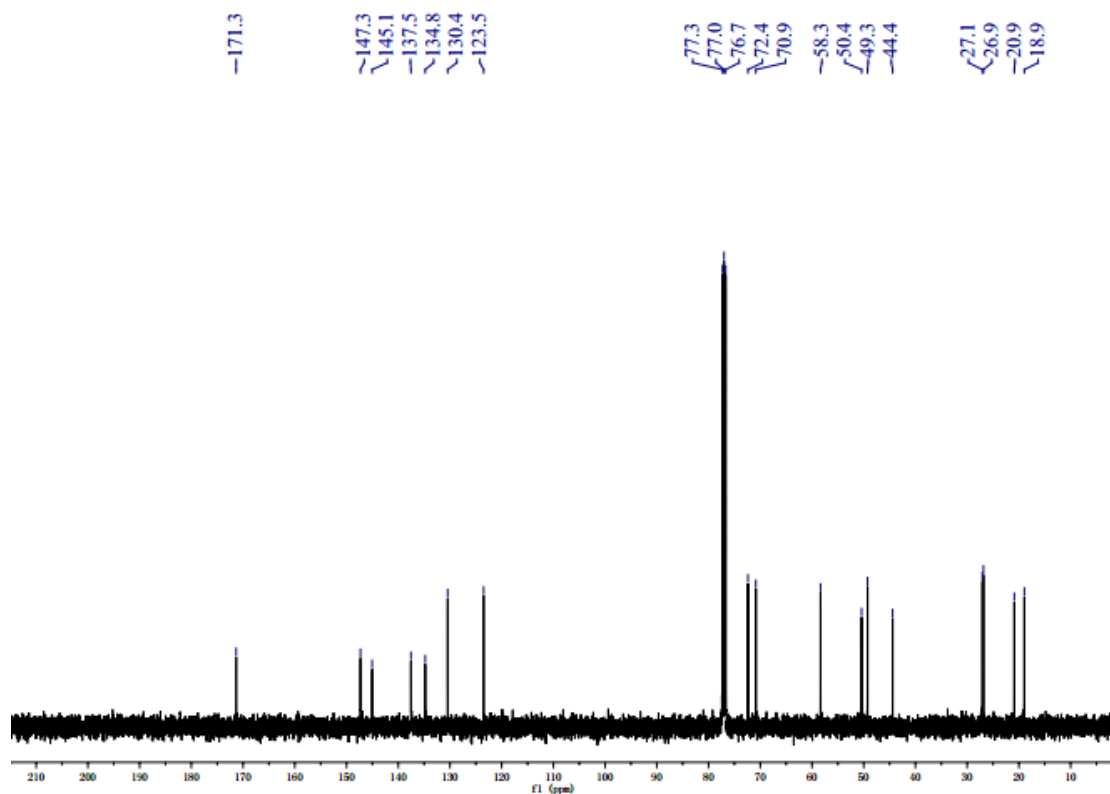
HSQC spectrum for **4** in CD_3OD



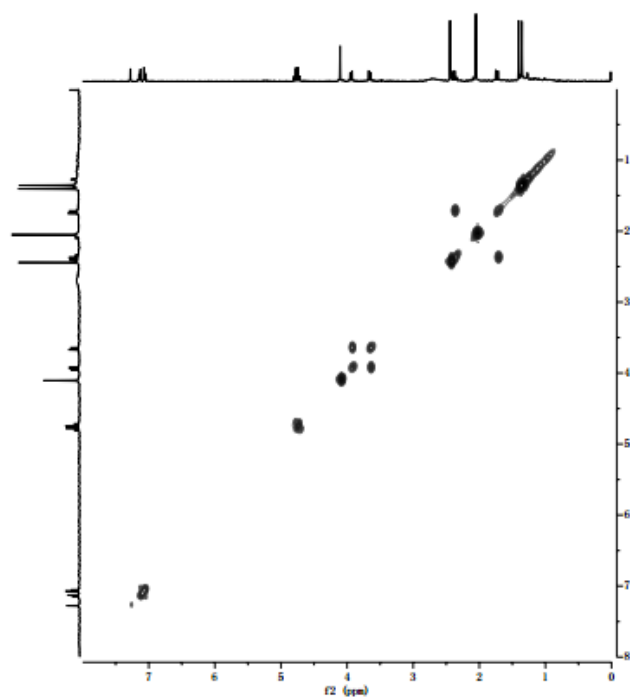
HMBC spectrum for **4** in CD₃OD



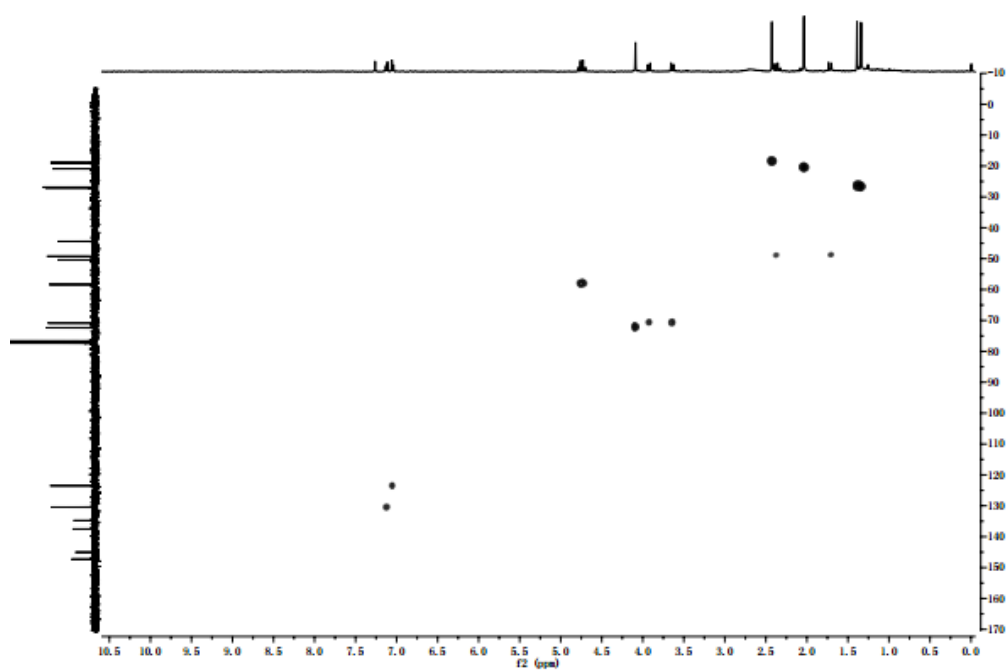
¹H NMR spectrum of **5** (400 MHz, in CDCl₃)



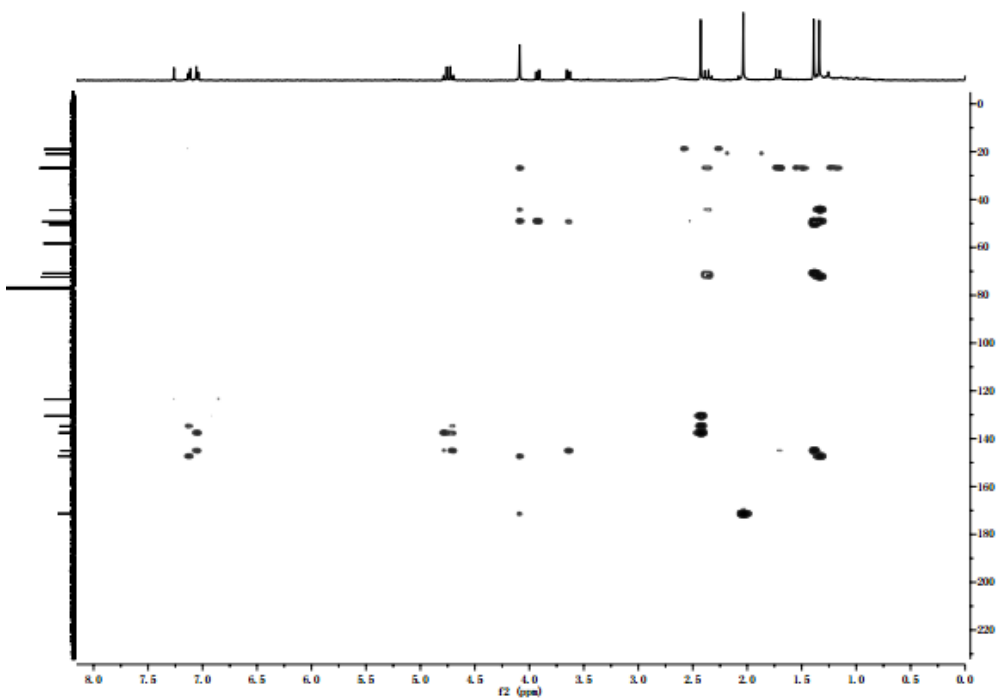
^{13}C NMR spectrum of **5** (100 MHz, in CDCl_3)



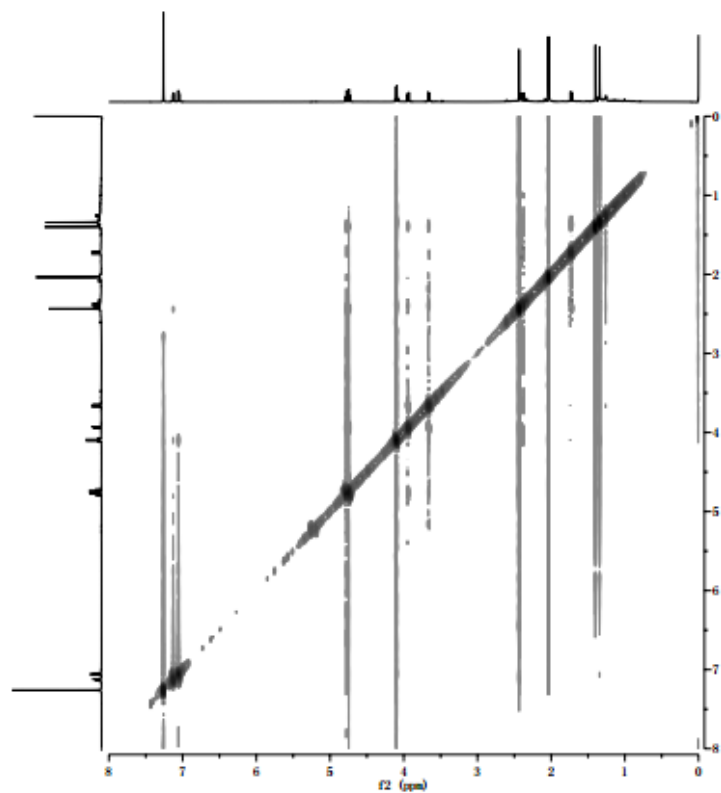
^1H - ^1H COSY spectrum for **5** in CDCl_3



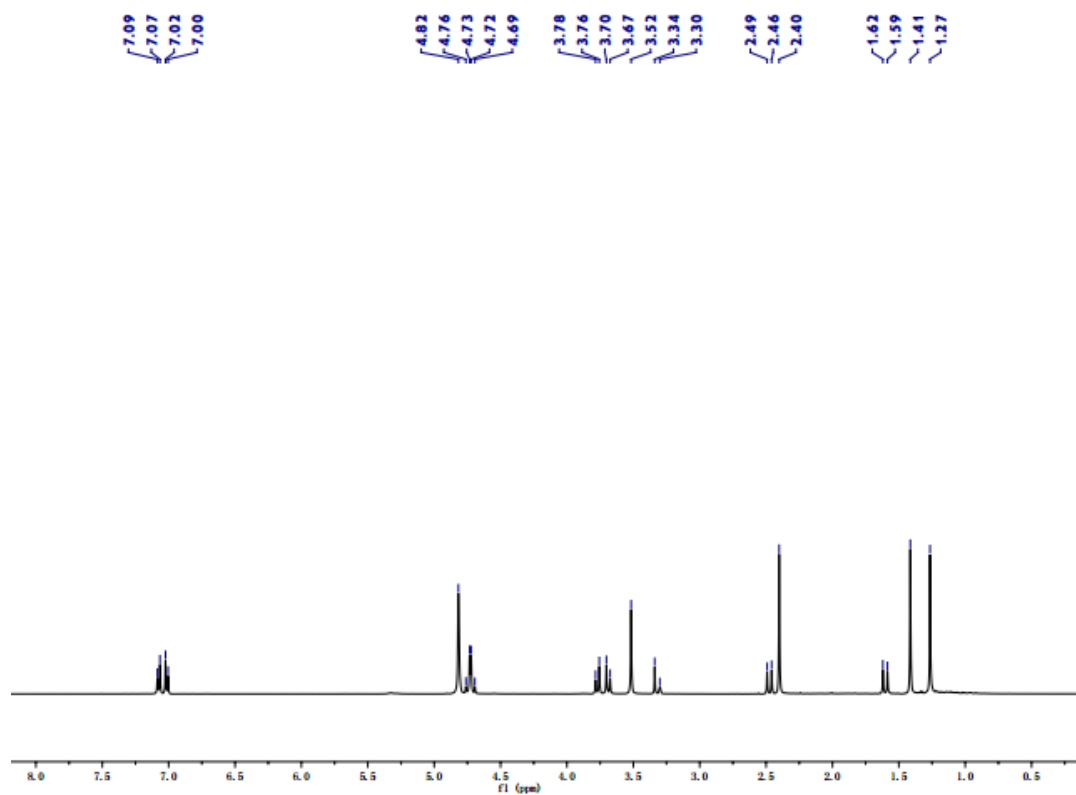
HSQC spectrum for **5** in CDCl₃



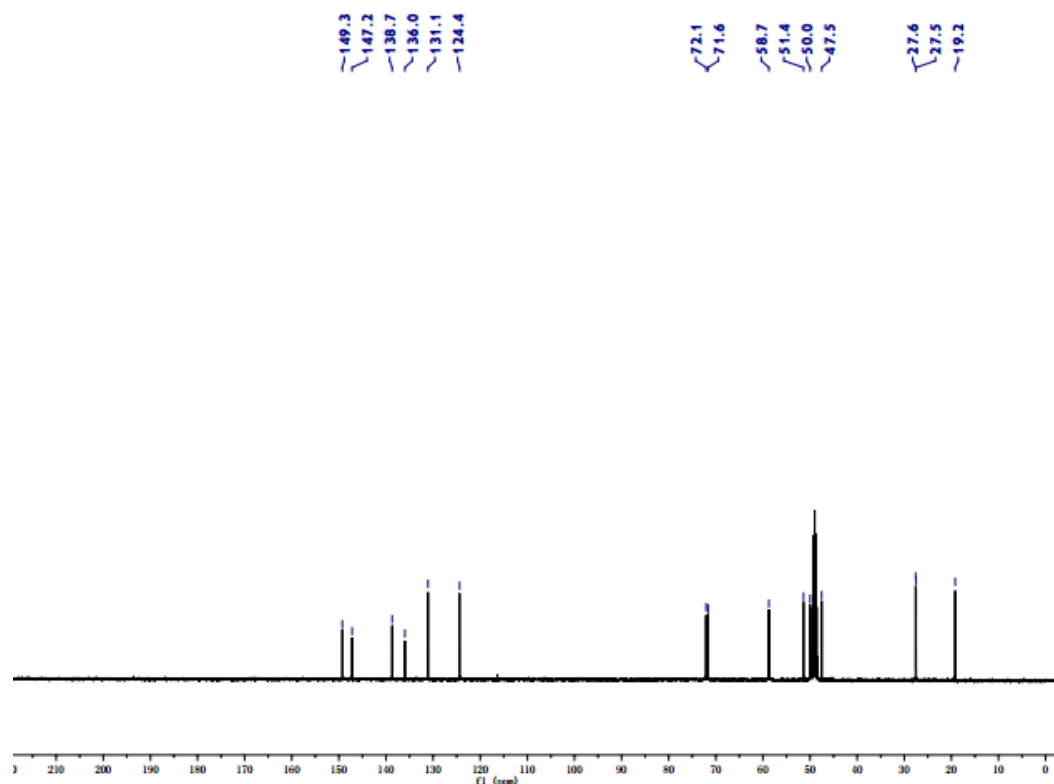
HMBC spectrum for **5** in CDCl₃



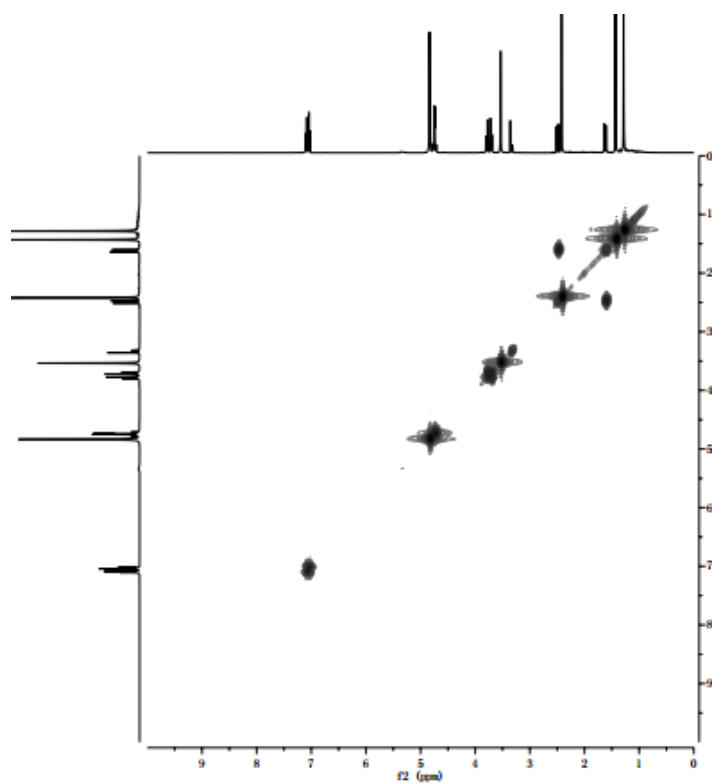
ROESY spectrum for **5** in CDCl_3



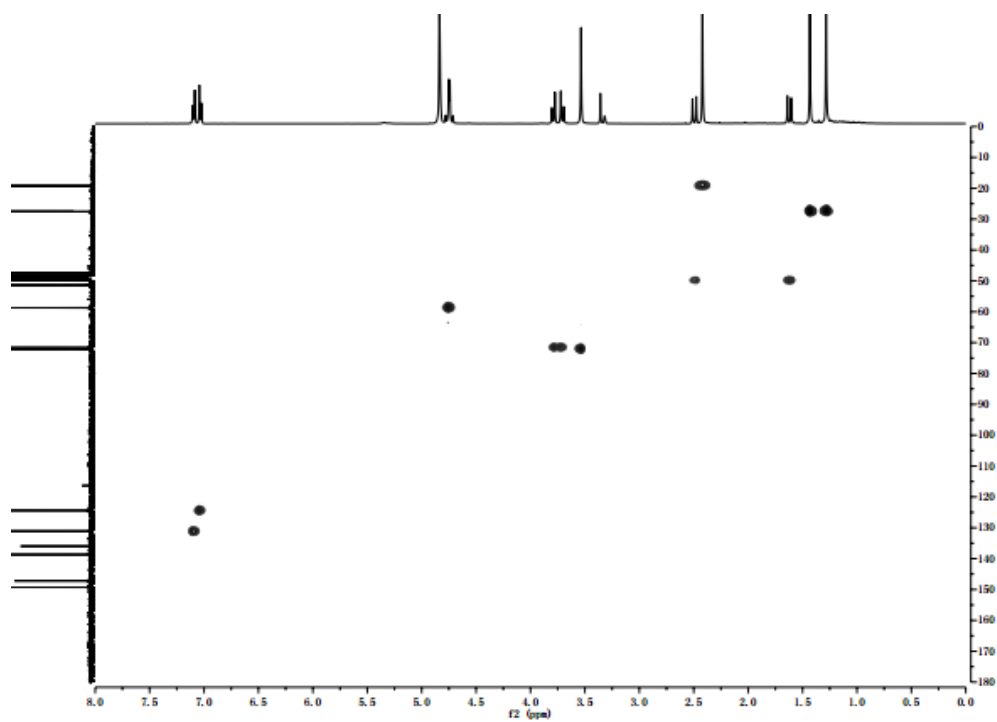
^1H NMR spectrum of **6** (400 MHz, in CD_3OD)



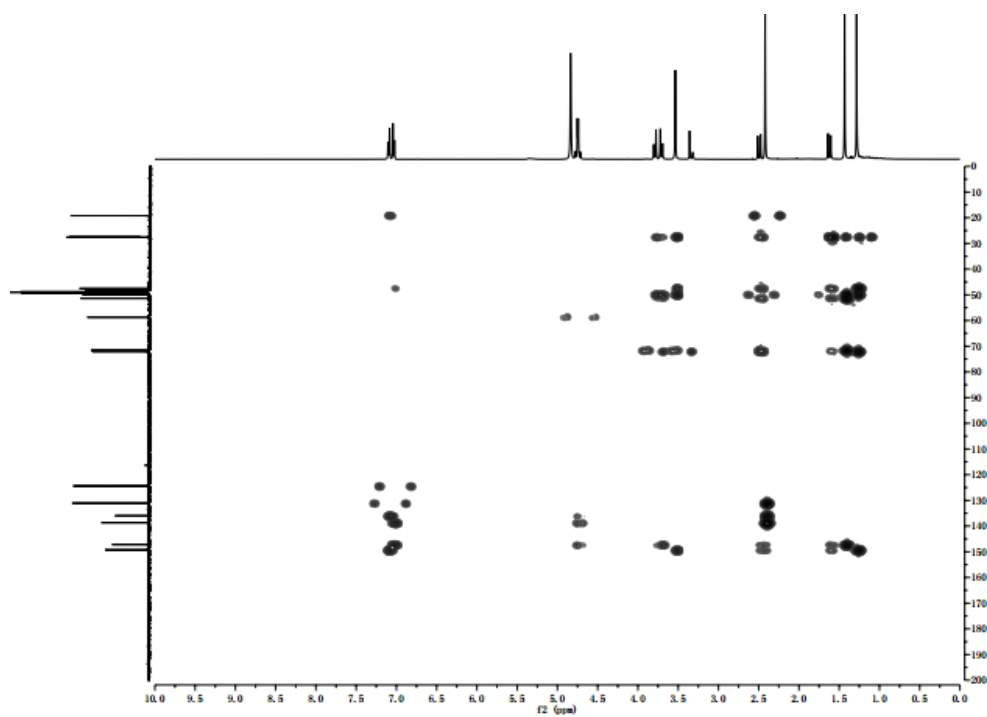
^{13}C NMR spectrum of **6** (100 MHz, in CD_3OD)



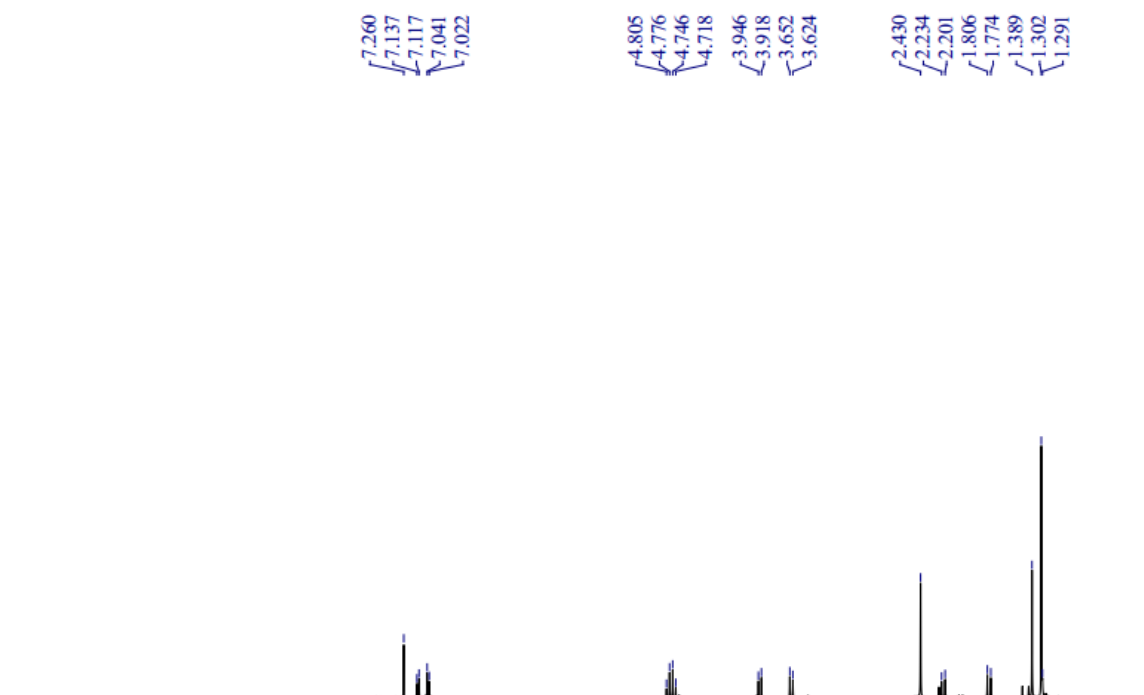
^1H - ^1H COSY spectrum for **6** in CD_3OD



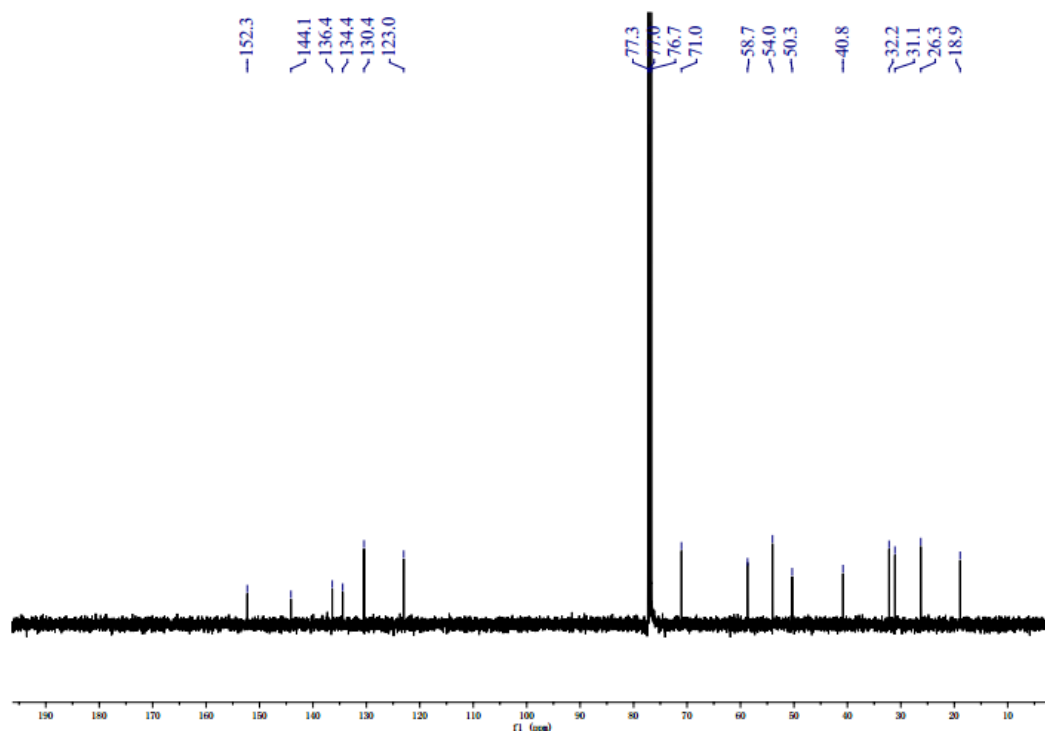
HSQC spectrum for **6** in CD₃OD



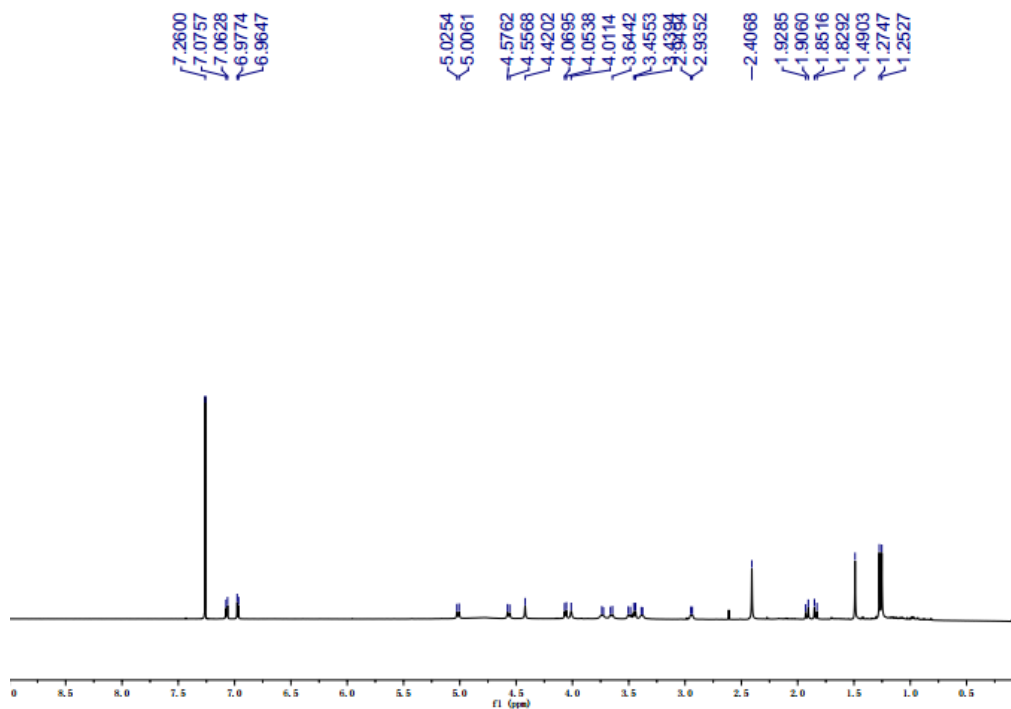
HMBC spectrum for **6** in CD₃OD



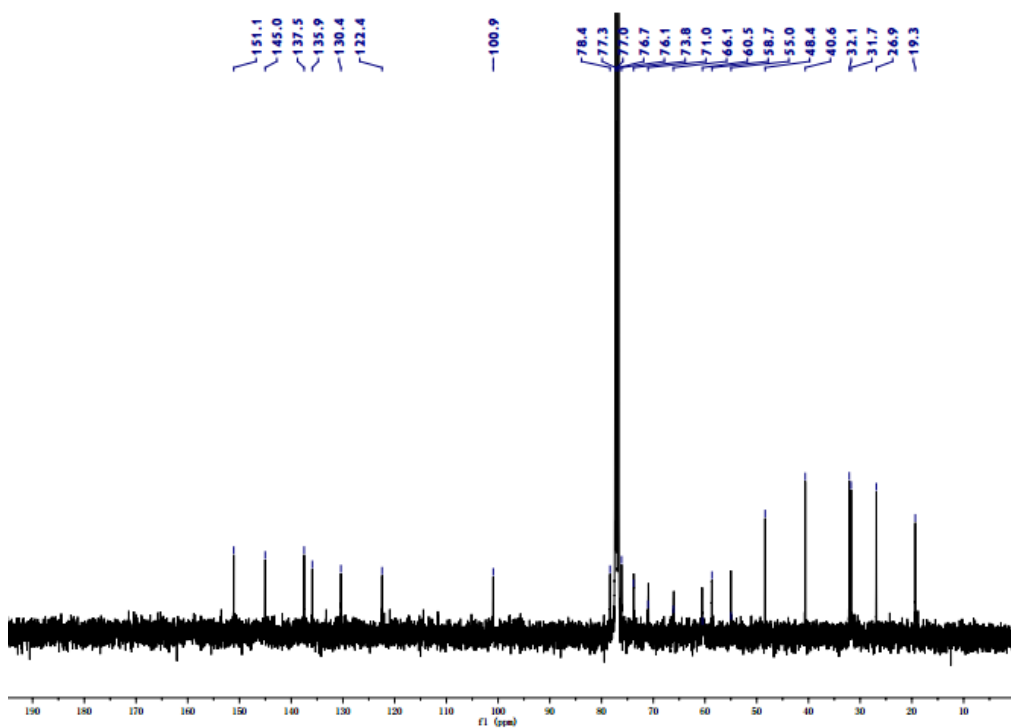
¹H NMR spectrum of 7 (400 MHz, in CDCl₃)



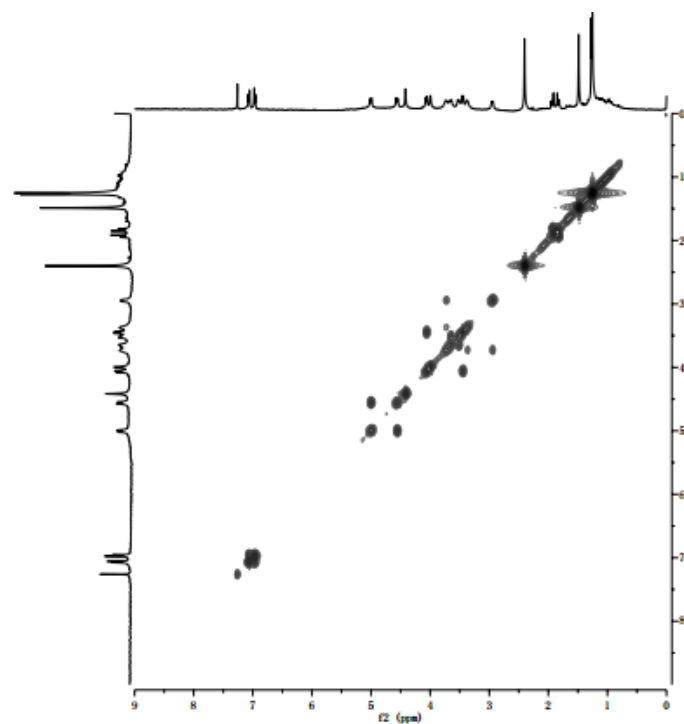
¹³C NMR spectrum of 7 (100 MHz, in CDCl₃)



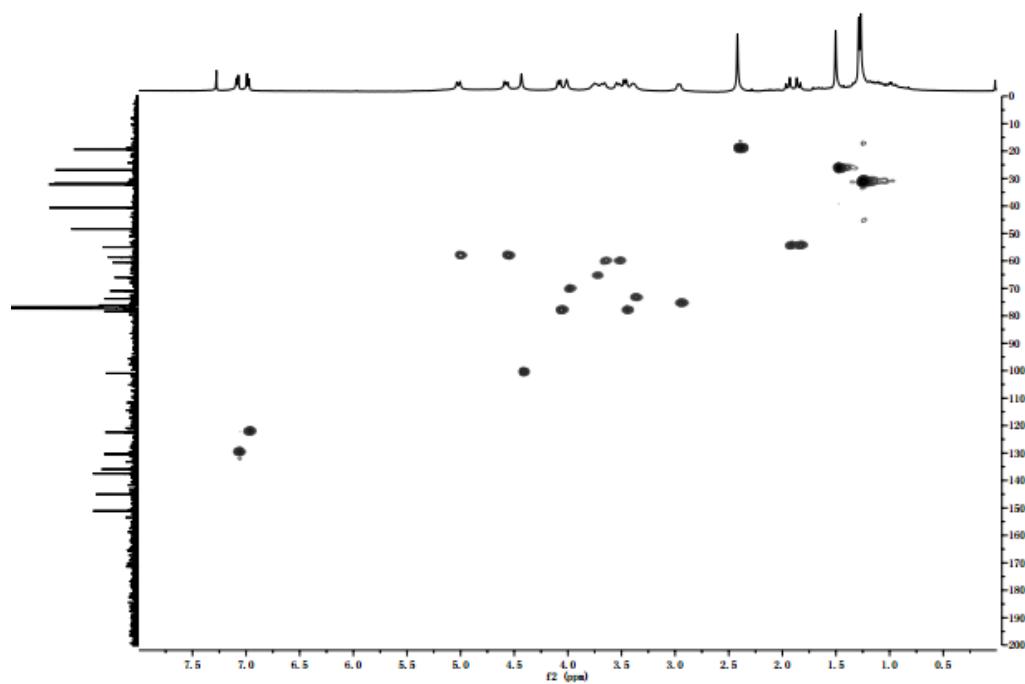
¹H NMR spectrum of **8** (600 MHz, in CDCl₃)



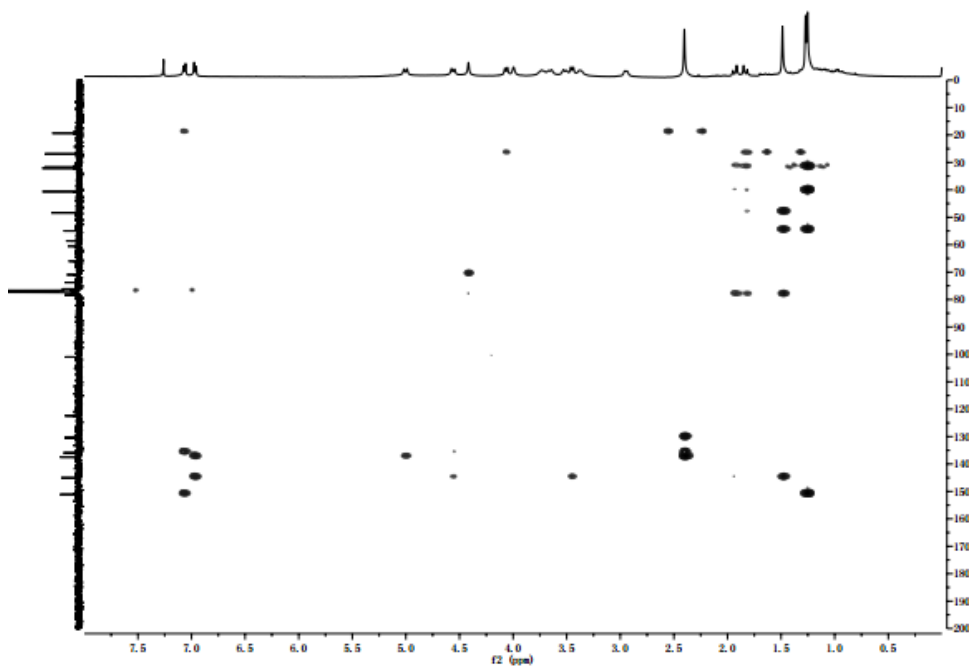
¹³C NMR spectrum of **8** (150 MHz, in CDCl₃)



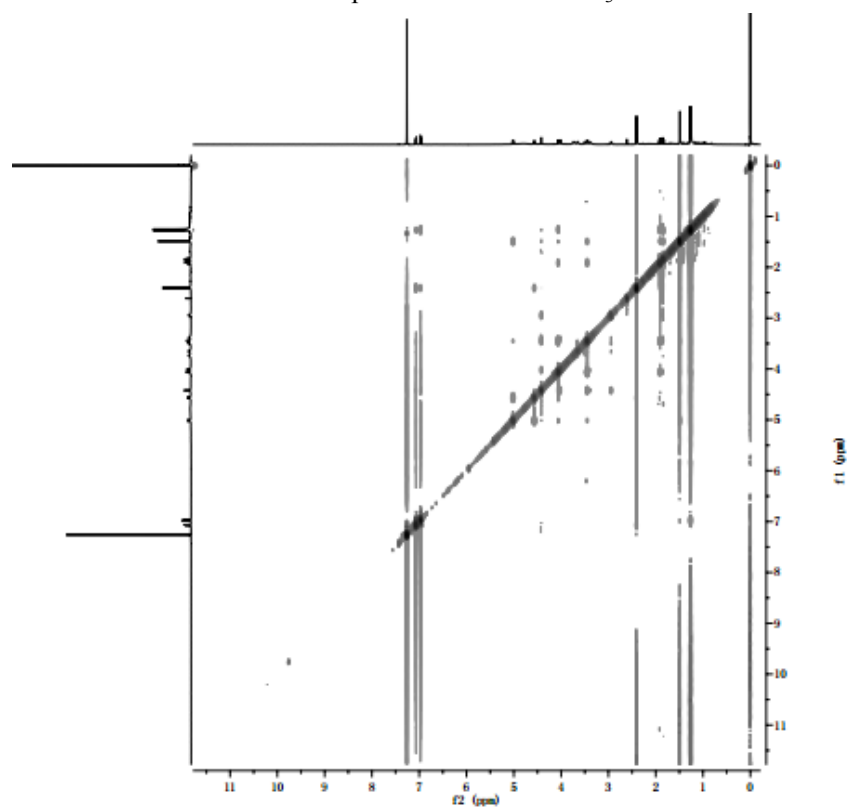
^1H - ^1H COSY spectrum for **8** in CDCl_3



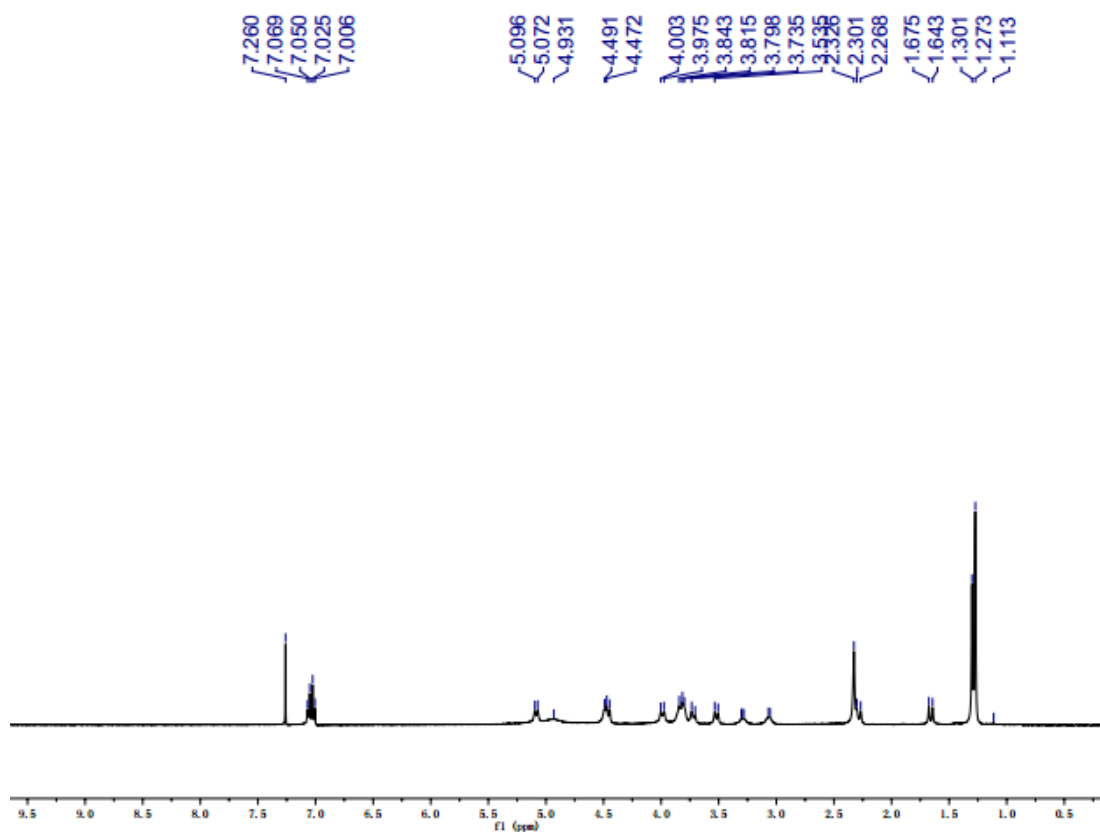
HSQC spectrum for **8** in CDCl_3



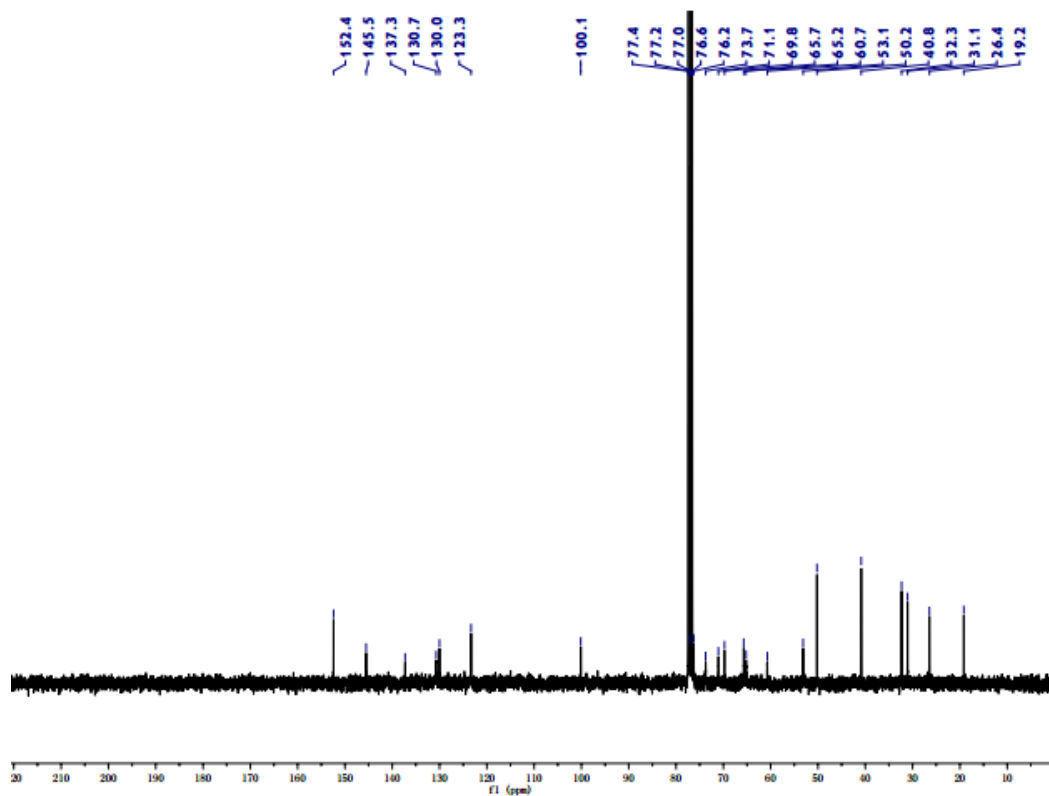
HMBC spectrum for **8** in CDCl_3



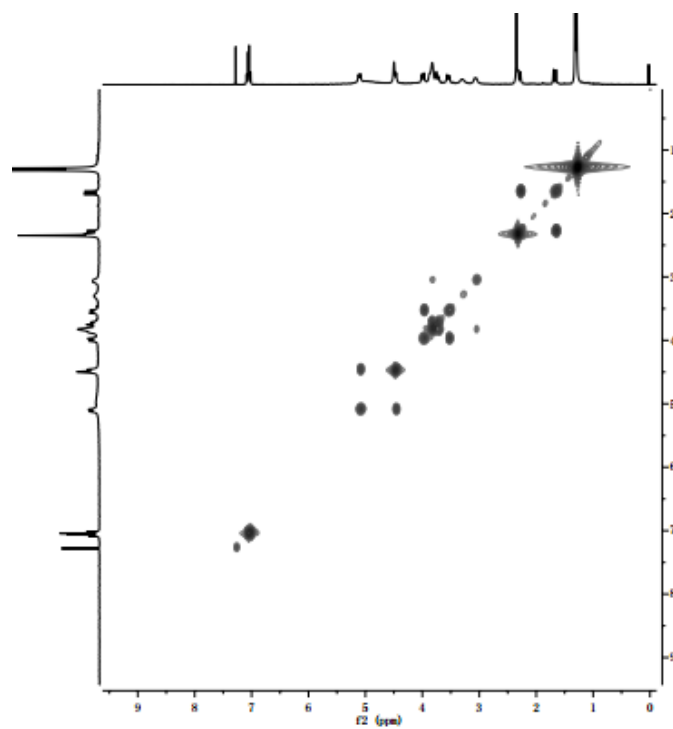
ROESY spectrum for **8** in CDCl_3



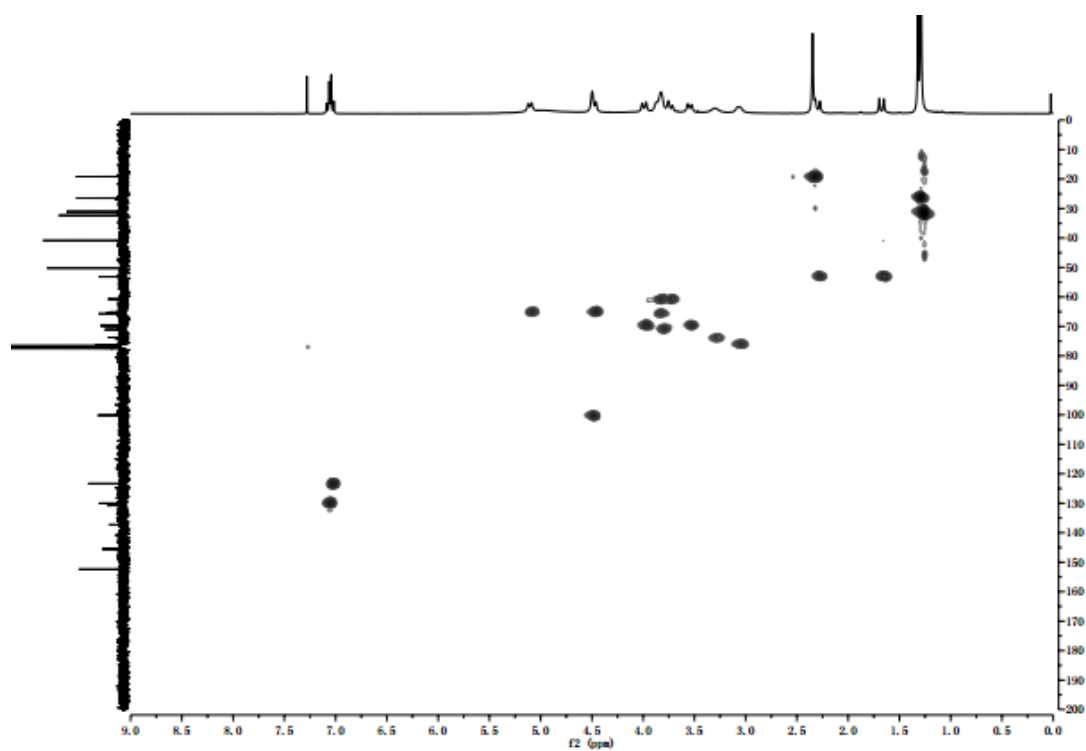
^1H NMR spectrum of **9** (400 MHz, in CDCl_3)



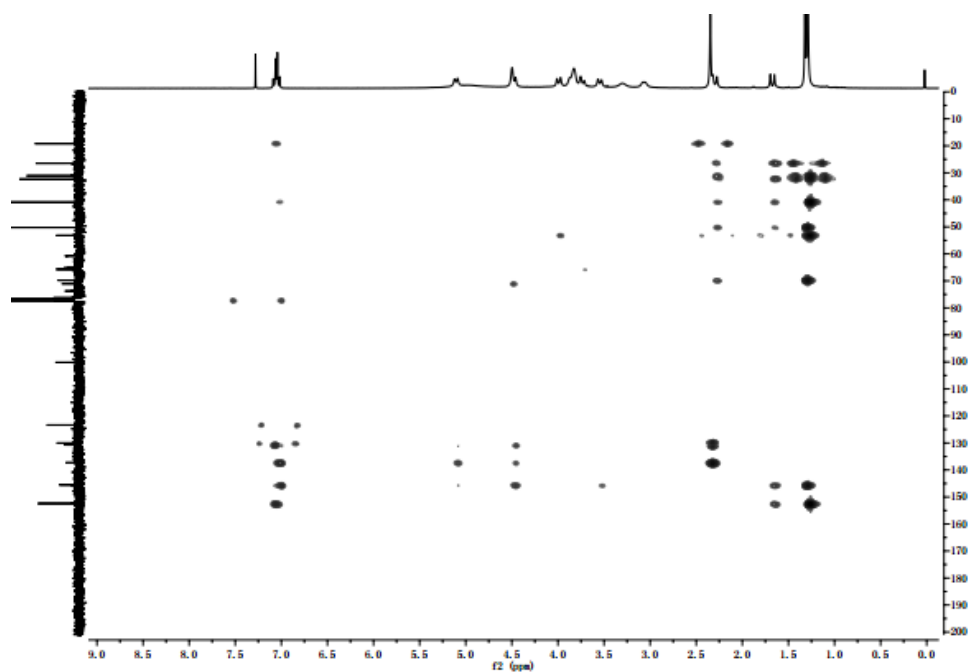
^{13}C NMR spectrum of **9** (100 MHz, in CDCl_3)



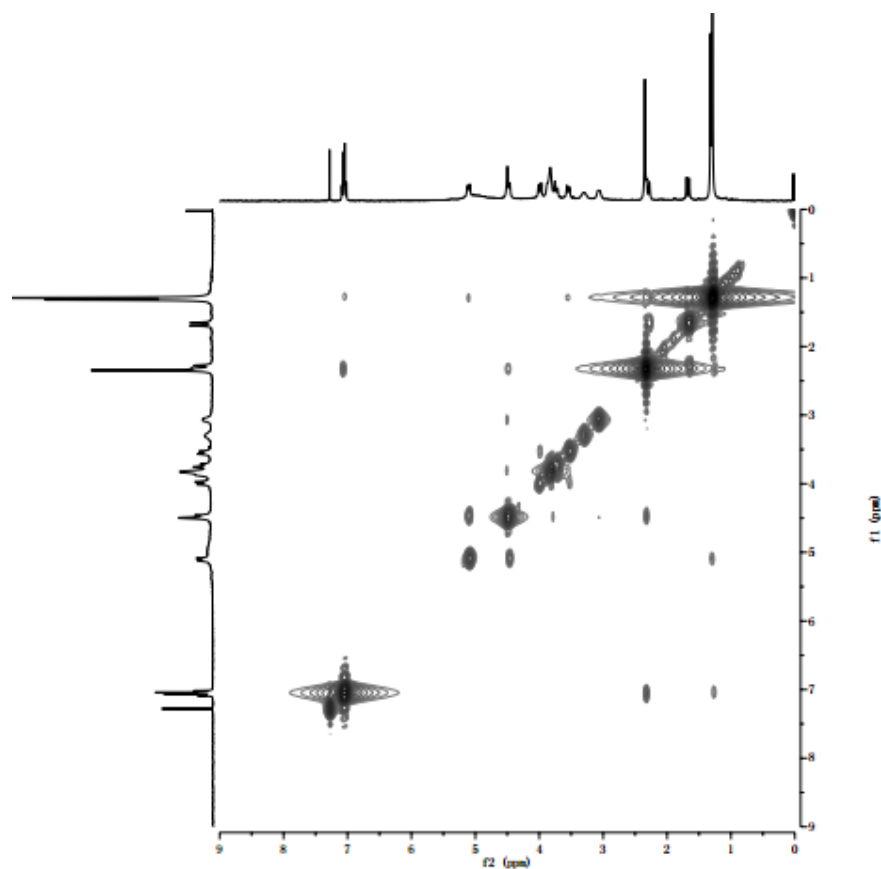
^1H - ^1H COSY spectrum for **9** in CDCl_3



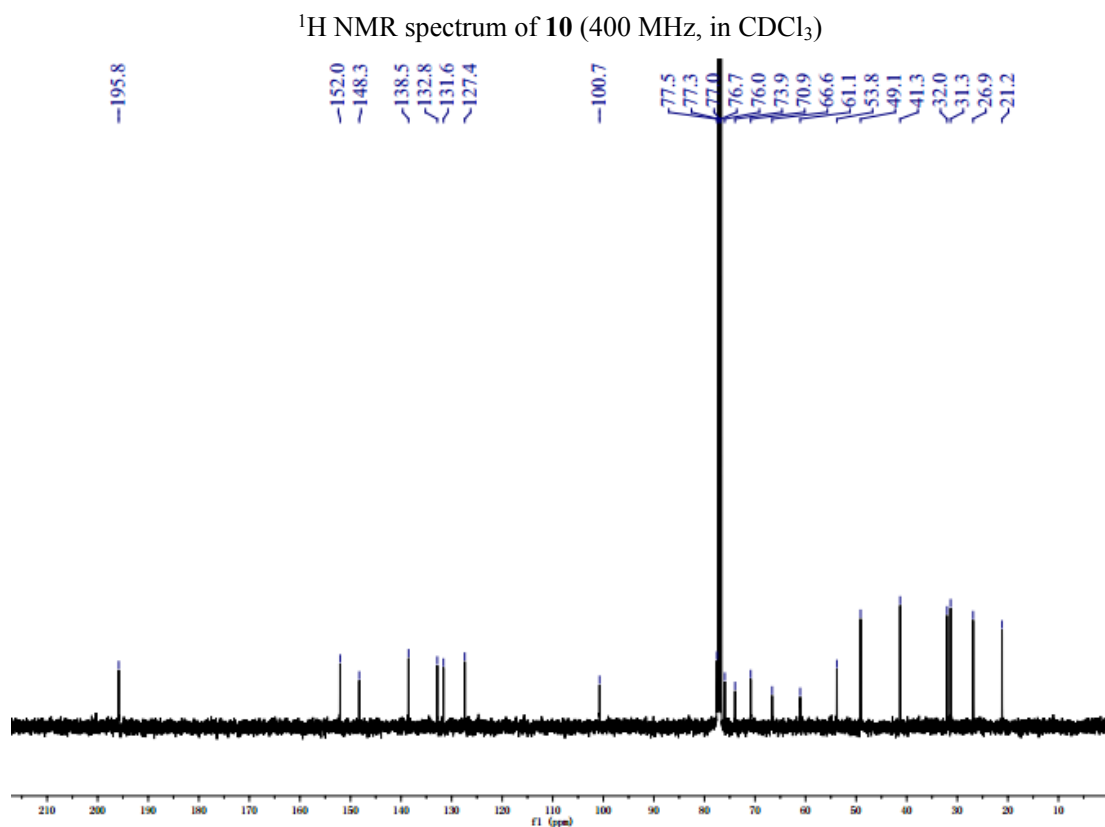
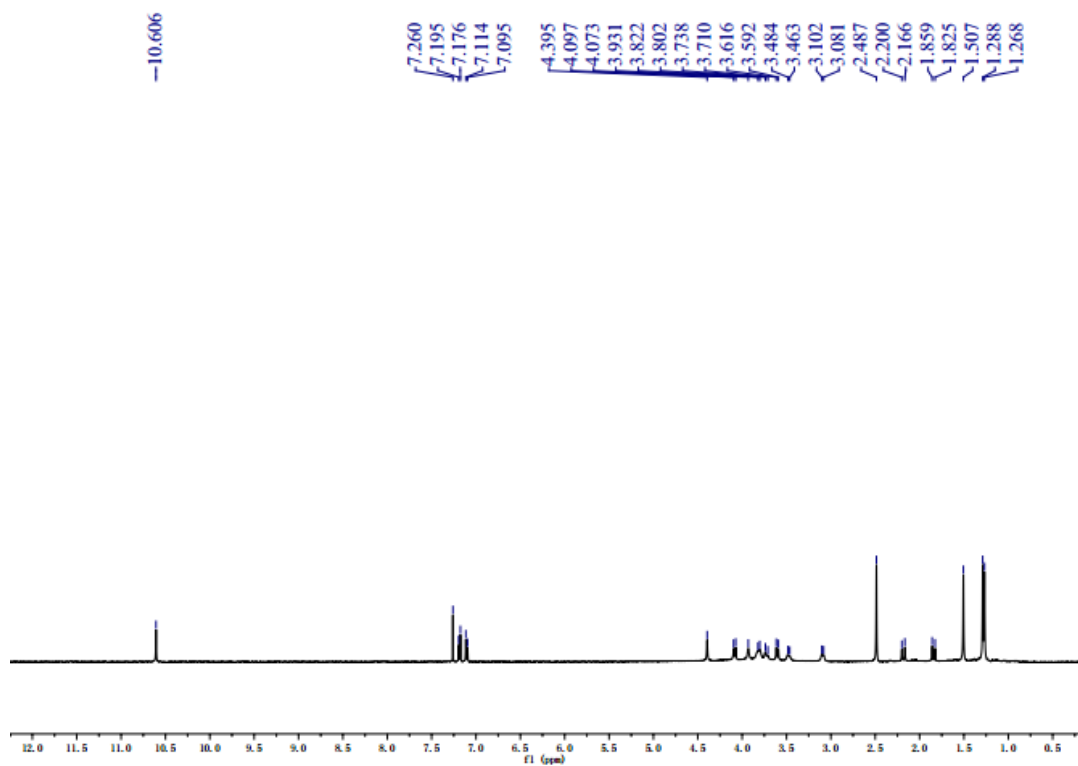
HSQC spectrum for **9** in CDCl_3

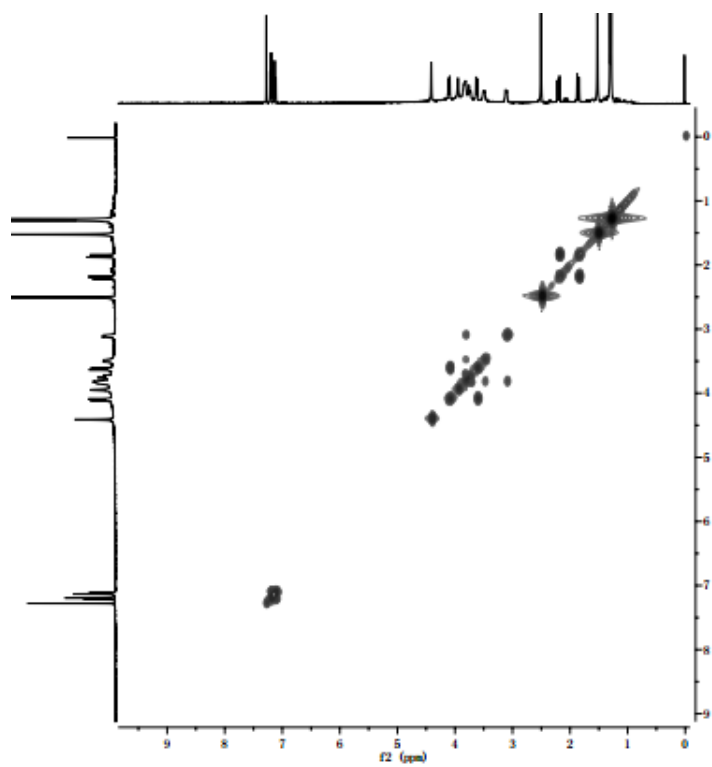


HMBC spectrum for **9** in CDCl_3

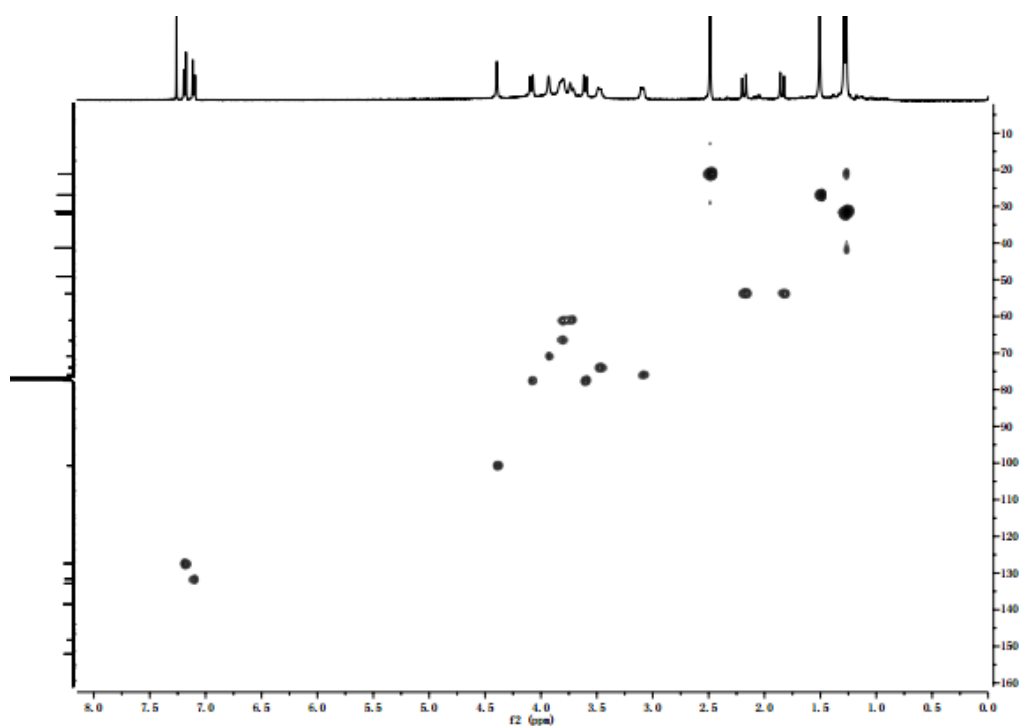


NOESY spectrum for **9** in CDCl_3

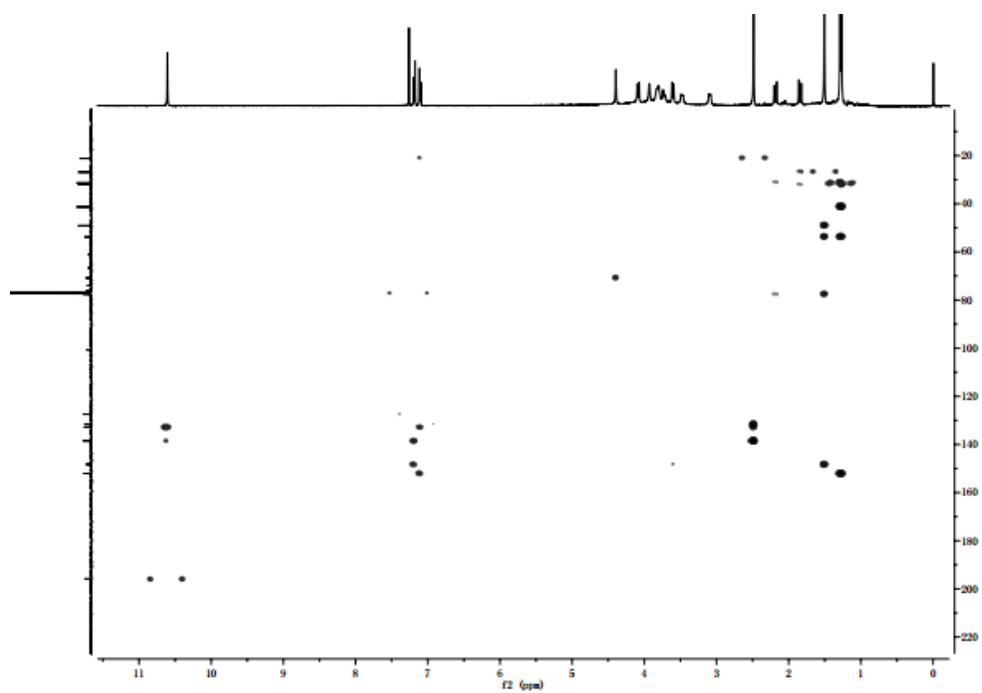




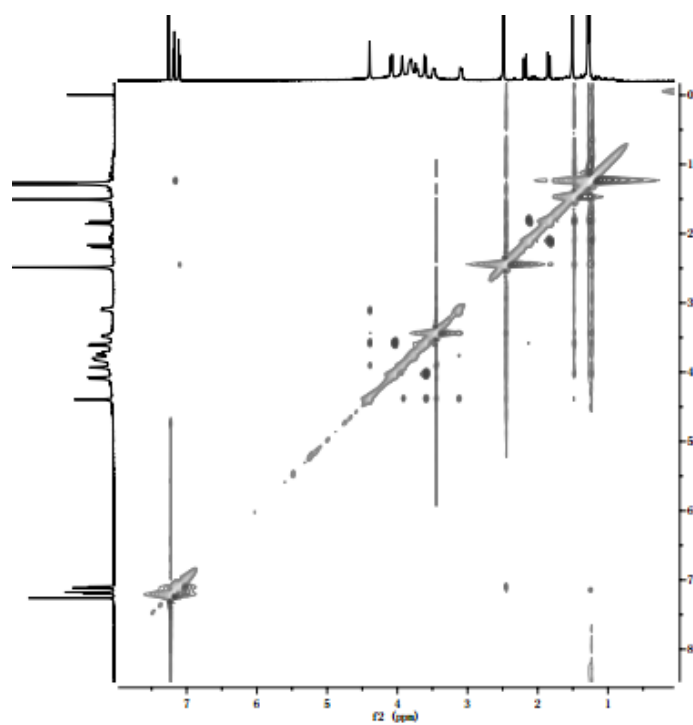
^1H - ^1H COSY spectrum for **10** in CDCl_3



HSQC spectrum for **10** in CDCl_3



HMBC spectrum for **10** in CDCl_3



ROESY spectrum for **10** in CDCl_3