Supplementary Information

Table S1. Complete NMR data of **5** in $CDCl_3$:CD_3OD (3:1).

Position	$\delta^{13}C$	$\delta^{1}H$ (mult, *J* in Hz)	HMBC	COSY
1	39.2	α 0.72 (m)	18.1, 16.0	1.64
		β 1.64 (m)		0.72
2	18.1	β 1.22 (m)		1.42
		α 1.42 (m)		1.22
3	41.7	α 0.98 (ddd, 13.0, 13.0, 3.5)		
		β 1.20 (m)		
4	32.8			
5	56.1	0.76 (brd, 13.0)		
6	18.2	β 1.30 (m)	37.7, 36.6	
		α 1.40 (m)	37.7, 36.6	
7	41.7	α 0.92 (ddd, 12.5, 12.5, 3.0)		1.66
		β 1.66 (ddd, 13.0, 3.0, 3.0)		0.92
8	37.7			
9	50.6	1.32 (m)	37.7, 36.6, 16.7	
10	36.6			
11	25.2	β 1.28 (m)	45.5, 37.7	1.54, 3.60
		α 1.54 (m)	37.7	1.28, 3.60
12	70.2	3.60 (dd 3.0, 3.0)	50.6, 45.5	1.54, 1.28
13	45.5			
14	45.1	1.19 (m)	16.7	
15	30.6	β 1.33 (m)	67.4, 45.5, 45.1, 37.7	1.99
		α 1.99 (ddd 12.0, 8.0, 2.0)	175.5, 67.4, 45.1	1.33, 4.26
16	67.4	4.26 (dd 10.0, 8.0)	175.5, 30.6	5.73, 1.99
17	175.5			
18	83.3	5.06 (brs)	175.5, 110.6, 70.2, 67.4, 45.5, 45.1, 11.6	
19	174.9			
20	110.6	5.73 (brs)	175.5, 174.9, 83.3	4.26
21	32.9	0.67 (s)	41.7, 32.8	
22	20.8	0.65 (s)	56.1, 32.8, 20.8	
23	16.0	0.68 (s)	56.1, 50.6, 39.2, 36.6	
24	16.7	0.72 (s)	50.6, 45.1, 41.7, 37.7	
25	11.6	0.51 (s)	83.3, 70.2, 45.5, 45.1	

Table S2. Complete NMR data of **6** in $CDCl_3$.

Position	$\delta^{13}C$	$\delta^{1}H$ (mult, *J* in Hz)	HMBC	COSY
1	40.1	α 0.75 (ddd, 12.5, 3.5, 3.5)		
		β 1.68 (m)		
2	18.8	β 1.40 (m)		
		α 1.57 (m)		
3	42.2	α 0.95 (ddd, 12.5, 12.5, 3.5)		
		β 1.36 (m)		
4	33.5			
5	56.6	0.82 (m)		
6	18.4	β 1.29 (m)		
		α 1.54 (m)		
7	42.5	α 1.02 (ddd, 13.0, 13.0, 4.0)		1.77
		β 1.77 (ddd, 13.0, 4.0, 3.0)		1.02
8	38.2			
9	61.4	0.87 (m)		
10	37.8			
11	17.2	β 1.38 (m)		
		α 1.60 (m)		
12	40.5	α 1.33 (m)	12.3	
		β 2.03 (m)		
13	41.6			
14	51.6	1.09 (m)	61.4, 41.6, 38.2, 28.0, 12.3	2.19, 1.47
15	28.0	β 1.47 (m)	69.7, 51.6	5.52, 2.19, 1.09
		α 2.19 (ddd, 12.5, 7.0, 2.0)	167.0, 41.6, 69.8	5.52, 1.47, 1.09
16	69.8	5.52 (ddd, 11.5, 7.0, 2.0)	167.0	5.76, 2.19, 1.47
17	167.0			
18	90.0	4.33 (d, 2.0)	173.0, 167.0, 112.4, 41.6, 12.3	5.76
19	173.0			
20	112.4	5.76 (dd, 2.0, 2.0)	173.0, 90.0	5.52, 4.33
21	33.5	0.82 (s)	56.6, 42.2, 33.5, 18.8	
22	21.5	0.78 (s)	42.2, 33.5, 21.5, 18.8	
23	16.5	0.81 (s)	61.4, 56.6, 40.1, 37.8	
24	17.7	0.85 (s)	61.4, 51.6, 38.2	
25	12.3	0.70 (s)	90.0, 51.6, 41.6, 40.5	
16-OAc	170.0			
	21.1	2.16 (s)	170.0	

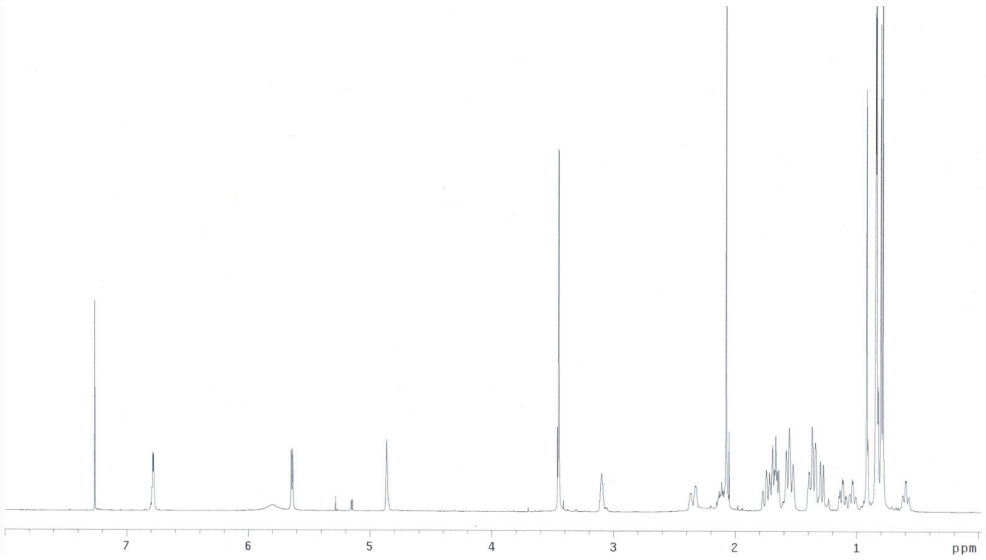
Table S3. Complete NMR data of **7** in $CDCl_3$.

Position	$\delta^{13}C$	$\delta^{1}H$ (mult, *J* in Hz)	HMBC	COSY
1	40.2	α 0.78 (ddd, 12.5, 3.5, 3.50)		
		β 1.69 (m)		
2	18.8	β 1.40 (m)		
		α 1.55 (m)		
3	42.2	α 1.10 (ddd, 13.0, 13.0, 3.5)		
		β 1.35 (m)		
4	33.5			
5	56.7	0.78 (m)		
6	18.5	β 1.40 (m)		
		α 1.54 (m)		
7	42.6	α 1.00 (m)	56.7, 17.7	
		β 1.81 (ddd, 12.5, 3.0, 3.0)	56.7, 17.7	
8	38.2			
9	61.4	0.81 (m)	40.7	
10	37.8			
11	17.2	β 1.33 (m)	61.4, 41.6	
		α 1.59 (m)	38.2	
12	40.7	α 1.34 (m)	12.4	
		β 2.03 (dd, 10.0, 3.0)	90.1, 61.4, 51.9, 12.4	
13	41.6			
14	51.9	1.05 (m)	69.0, 41.6, 38.2	1.45, 2.17
15	31.7	β 1.45 (m)		1.05, 2.17
		α 2.17 (ddd, 12.5, 7.0, 2.5)	171.7, 69.0, 51.9, 41.6	4.49, 1.45, 1.05
16	69.0	4.49 (ddd, 9.3, 7.0, 2.0)	171.7, 111.9, 31.7	5.90, 2.17
17	171.7			
18	90.1	4.29 (brs)	41.6, 12.4	5.90
19	173.5			
20	111.9	5.90 (brs)	173.5, 171.7, 90.1, 69.0	4.49, 4.29
21	33.4	0.83 (s)	56.7, 42.2, 33.5	
22	21.5	0.79 (s)	56.7, 42.2, 33.5, 21.5	
23	16.5	0.81 (s)	61.4, 40.2, 37.8	
24	17.7	0.86 (s)	61.4, 51.9, 38.2	
25	12.4	0.69 (s)	90.1, 51.9, 41.6, 40.7	

Table S4. Complete NMR data of **8** in $CDCl_3$.

Position	$\delta^{13}C$	$\delta^{1}H$ (mult, *J* in Hz)	HMBC	COSY
1	39.8	α 0.60 (m)		1.58
		β 1.58 (m)		0.60
2	18.1	β 1.36 (m)	37.1	1.56, 1.08
		α 1.56 (m)		1.36
3	42.1	α 1.08 (m)		1.36
		β 1.24 (m)	18.1	
4	33.5			
5	56.8	0.87 (m)		
6	18.6	β 1.38 (m)	56.8	1.55
		α 1.55 (m)		1.38
7	40.7	α 0.99 (ddd, 14.5, 12.5, 3.0)		1.68
		β 1.68 (m)	52.8, 37.4	1.26, 0.99
8	37.4			
9	52.8	1.26 (dd, 13.0, 4.0)	37.1	1.71, 1.68
10	37.1			
11	22.3	β 1.71 (m)		1.80, 1.26
		α 1.80 (m)		4.99, 1.71
12	76.3	4.99 (brs)	52.8	1.80
13	41.0			
14	49.4	2.09 (dd, 14.0, 3.5)	41.0	2.34
15	34.3	β 2.34 (dd, 18.0, 14.0)	202.0, 49.4	2.43, 2.09
		α 2.43 (dd, 18.0, 3.5)	202.0, 41.0	2.34
16	202.0			
17	135.4			
18	155.3	6.51 (brs)	202.0, 76.3, 62.1, 49.4, 41.0	4.16
19	62.1	4.16 (brs)	202.0, 155.3, 135.4	6.51
20	33.5	0.83 (s)	56.8, 42.1, 33.5	
21	21.6	0.79 (s)	56.8, 42.1, 33.5, 21.6	
22	16.2	0.80 (s)	52.8, 39.8, 37.1	
23	16.6	0.91 (s)	52.8, 49.4, 40.7, 37.4	
24	19.6	1.11 (s)	76.3, 49.4, 41.0	
OAc	170.8			
	21.5	2.04 (s)	170.8	

Figure S1. ^{1}H-NMR and ^{13}C-NMR Spectra (500 and 125 MHz, $CDCl_3$) of **1**. Compound **1**: pale yellow amorphous solid; ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 6.77 (d, *J* = 3.4 Hz, H-16), 4.84 (brs, H-12), 3.42 (brs, H-19), 3.09 (brs, H-18), 2.32 (ddd, *J* = 20.5, 5.2, 3.4 Hz, H-15), 2.10 (ddd, *J* = 20.5, 9.2, 3.2 Hz, H-15), 2.05 (s, 12-OAc), 1.75 (m, H-11), 1.67 (m, H-7), 1.64 (m, H-14), 1.62 (m, H-11), 1.54 (m, H-1), 1.50 (m, H-2), 1.50 (m, H-6), 1.34 (m, H-2), 1.34 (m, H-3), 1.32 (m, H-6), 1.26 (brd, *J* = 12.5 Hz, H-9), 1.09 (ddd, *J* = 12.5, 12.5, 3.4 Hz, H-3), 1.01 (ddd, *J* = 12.5, 12.5, 3.4 Hz, H-7), 0.90 (s, H-24), 0.83 (s, H-25), 0.81 (s, H-21), 0.80 (m, H-5), 0.78 (s, H-23), 0.76 (s, H-22), 0.57 (ddd, *J* = 12.5, 12.5, 3.4 Hz, H-1); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 171.4 (12-OAc), 168.2 (C-20), 135.5 (C-16), 128.3 (C-17), 74.8 (C-12), 56.5 (C-5), 52.5 (C-9), 50.9 (C-18), 50.8 (C-19), 49.9 (C-14), 42.1 (C-3), 41.6 (C-7), 39.8 (C-1), 37.9 (C-8), 37.5 (C-13), 37.0 (C-10), 33.5 (C-4), 33.4 (C-21), 24.3 (C-15), 22.4 (C-11), 21.5 (C-22), 21.1 (12-OAc), 18.6 (C-2), 18.1 (C-6), 16.4 (C-23), 16.2 (C-24), 15.1 (C-25); (+)-HRFABMS *m/z* 467.2769 $[M + Na]^+$ (calcd for $C_{27}H_{40}O_5Na$, 467.2768).



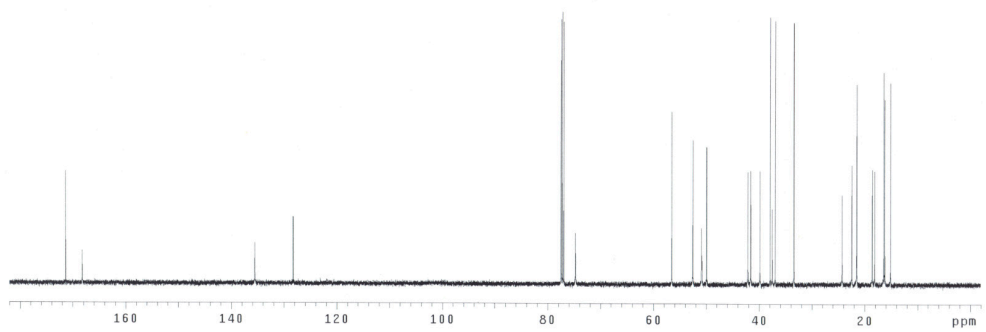


Figure S2. ^{1}H-NMR and ^{13}C-NMR Spectra (500 and 125 MHz, $CDCl_3$) of 2. Compound **2**: pale yellow amorphous solid; ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 5.51 (brs, H-12), 4.61 (d, *J* = 17.0 Hz, H-20), 4.54 (d, *J* = 17.0 Hz, H-20), 2.36 (dd, *J* = 18.0, 3.5 Hz, H-16), 2.28 (dd, *J* = 18.0, 8.5 Hz, H-16), 1.97 (ddd, *J* = 14.5, 3.3, 3.3 Hz, H-11), 1.92 (12-OAc), 1.89 (m, H-15), 1.80 (ddd, *J* = 12.5, 3.0, 3.0 Hz, H-7), 1.65 (m, H-2), 1.58 (dd, *J* = 13.0, 2.0 Hz, H-14), 1.56 (m, H-6), 1.55 (m, H-1), 1.54 (m, H-11), 1.54 (m, H-15), 1.42 (m, H-2), 1.36 (m, H-6), 1.34 (m, H-3), 1.22 (m, H-3), 1.16 (m, H-9), 1.14 (s, H-25), 1.00 (dd, *J* = 12.5, 3.0 Hz, H-7), 0.87 (s, H-24), 0.84 (m, H-5), 0.82 (s, H-21), 0.78 (s, H-23), 0.77 (s, H-22), 0.54 (ddd, *J* = 15.0, 9.0, 3.5 Hz, H-1); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 172.1 (C-19), 170.2 (12-OAc), 160.2 (C-17), 133.1 (C-18), 74.2 (C-12), 71.1 (C-20), 56.8 (C-5), 53.2 (C-9), 51.4 (C-14), 42.2 (C-3), 41.7 (C-7), 39.9 (C-1), 38.7 (C-13), 37.7 (C-8), 37.1 (C-10), 33.5 (C-4), 33.5 (C-21), 25.1 (C-16), 21.5 (C-22), 21.4 (C-11), 21.3 (C-25), 21.1 (12-OAc), 18.6 (C-6), 18.3 (C-2), 17.2 (C-24), 16.9 (C-15), 16.1 (C-23),; (+)-HRFABMS *m/z* 429.3008 $[M + H]^+$ (calcd for $C_{27}H_{41}O_4$, 429.3005).

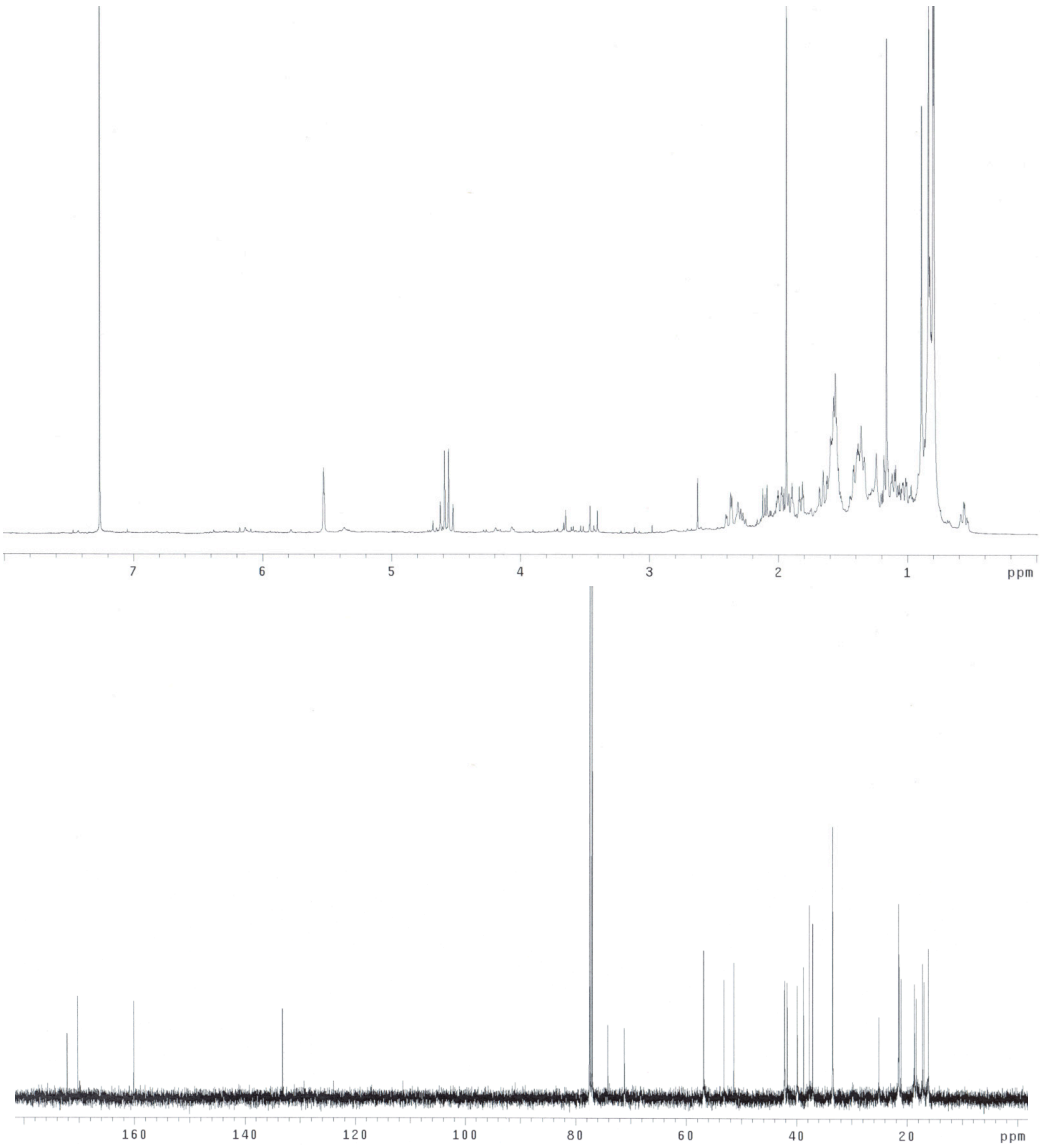


Figure S3. ^{1}H-NMR and ^{13}C-NMR Spectra (500 and 125 MHz, $CDCl_3$) of **3.** Compound **3**: pale yellow amorphous solid; ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 5.77 (brs, H-20), 5.52 (dd, *J* = 10.0, 7.5 Hz, H-16), 4.92 (brs, H-18), 4.85 (brs, H-12), 2.19 (dd, *J* = 10.0, 8.5 Hz, H-15), 2.12 (s, 16-OAc), 2.08 (s, 12-OAc), 1.91 (d, *J* = 16.0 Hz, H-11), 1.77 (d, *J* = 12.5 Hz, H-7), 1.61 (m, H-15), 1.59 (m, H-1), 1.58 (m, H-6), 1.57 (m, H-2), 1.46 (m, H-15), 1.45 (d, *J* = 13.5 Hz, H-14), 1.38 (m, H-6), 1.35 (m, H-2), 1.33 (m, H-3), 1.22 (m, H-9), 1.10 (m, H-3), 1.05 (m, H-7), 0.85 (s, H-24), 0.82 (s, H-21), 0.79 (m, H-5), 0.76 (s, H-22), 0.76 (s, H-23), 0.75 (s, H-25), 0.55 (m, H-1); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 172. 6 (C-19), 169.9 (12-OAc), 169.5 (C-17), 167.5 (16-OAc), 112.9 (C-20), 82.2 (C-18), 74.3 (C-12), 69.2 (C-16), 56.6 (C-5), 52.3 (C-9), 47.0 (C-14), 44.0 (C-13), 42.1 (C-7), 42.0 (C-3), 39.9 (C-1), 38.2 (C-8), 37.0 (C-10), 33.4 (C-21), 33.4 (C-4), 27.7 (C-15), 21.7 (C-11), 21.5 (12-OAc), 21.5 (C-22), 21.0 (16-OAc), 18.6 (C-2), 18.3 (C-6), 17.2 (C-24), 16.3 (C-23), 12.1 (C-25). (+)-LRFABMS *m/z* 487 [$(M + H)^+$].

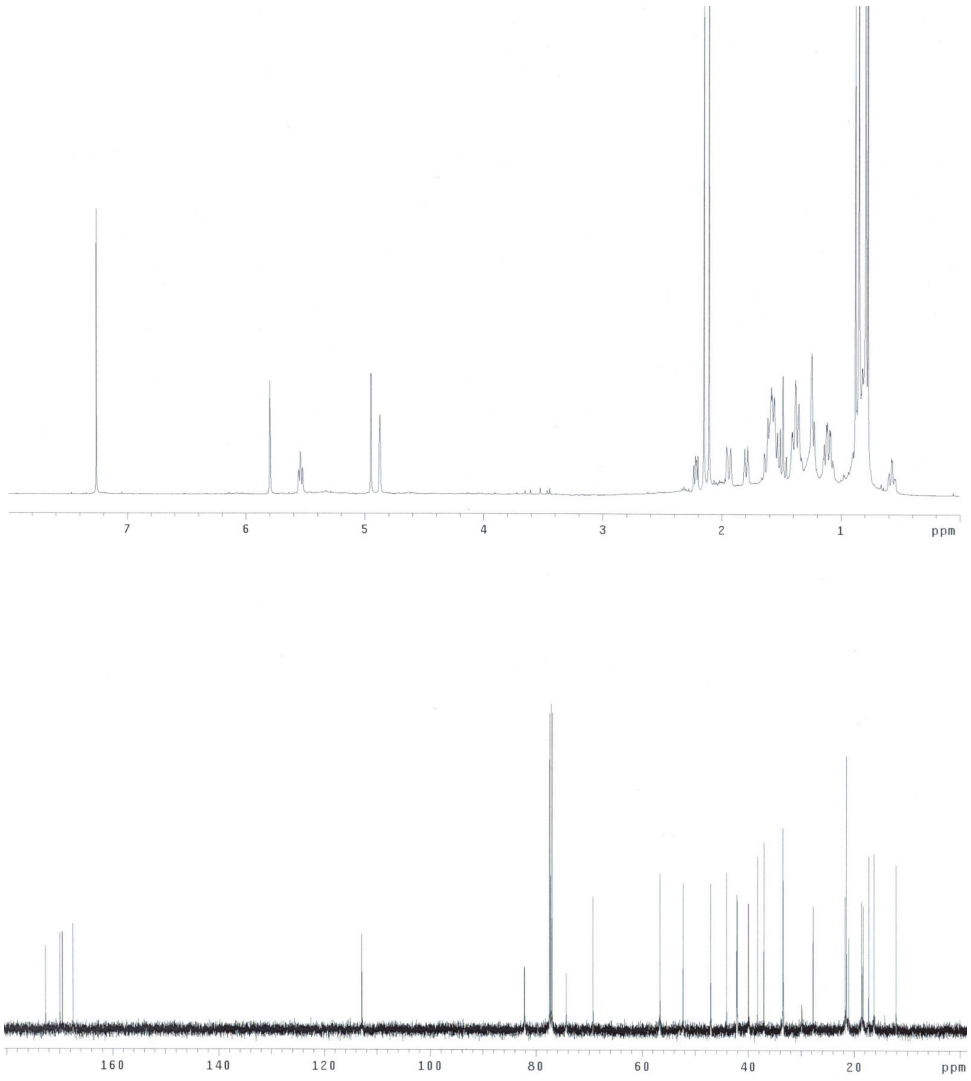


Figure S4. ^{1}H-NMR and ^{13}C-NMR Spectra (500 and 125 MHz, $CDCl_3$) of **4**. Compound **4**: pale yellow amorphous solid; ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 5.90 (brs, H-20), 4.89 (brs, H-18), 4.84 (brs, H-12), 4.49 (dd, *J* = 10.0, 6.0 Hz, H-16), 2.17 (dd, *J* = 11.0, 6.0 Hz, H-15), 2.08 (s, 12-OAc), 1.88 (brd, *J* = 15.5 Hz, H-11), 1.81 (brd, *J* = 12.5, 3.0, 3.0 Hz, H-7), 1.59 (m, H-11), 1.57 (m, H-1), 1.55 (m. H-2), 1.55 (m, H-6), 1.48 (ddd, *J* = 11.0, 11.0, 10.0 Hz, H-15), 1.39 (brd, *J* = 11.0 Hz, H-14), 1.37 (m, H-2), 1.36 (m, H-6), 1.35 (m, H-3), 1.20 (d, *J* = 12.5 Hz, H-9), 1.06 (m, H-3), 1.03 (m, H-7), 0.86 (s, H-24), 0.82 (s, H-21), 0.80 (m, H-5), 0.77 (s, H-22), 0.77 (s, H-23), 0.72 (s, H-25), 0.54 (dd, *J* = 13.0, 12.5 Hz); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 173.7 (C-19), 173.2 (C-17), 169.7 (12-OAc), 112.2 (C-20), 82.4 (C-18), 74.5 (C-12), 68.2 (C-16), 56.7 (C-5), 52.3 (C-9), 47.1 (C-14), 44.0 (C-13), 42.2 (C-7), 42.1 (C-3), 39.9 (C-1), 38.1 (C-8), 37.0 (C-10), 33.4 (C-21), 33.4 (C-4), 31.1 (C-15), 21.8 (C-11), 21.5 (C-22), 21.5 (12-OAc), 18.6 (C-2), 18.4 (C-6), 17.3 (C-24), 16.3 (C-23), 12.2 (C-25). (+)-HRFABMS *m*/*z* 445.2951 $[M + H]^+$ (calcd for $C_{27}H_{41}O_5$, 445.2954).

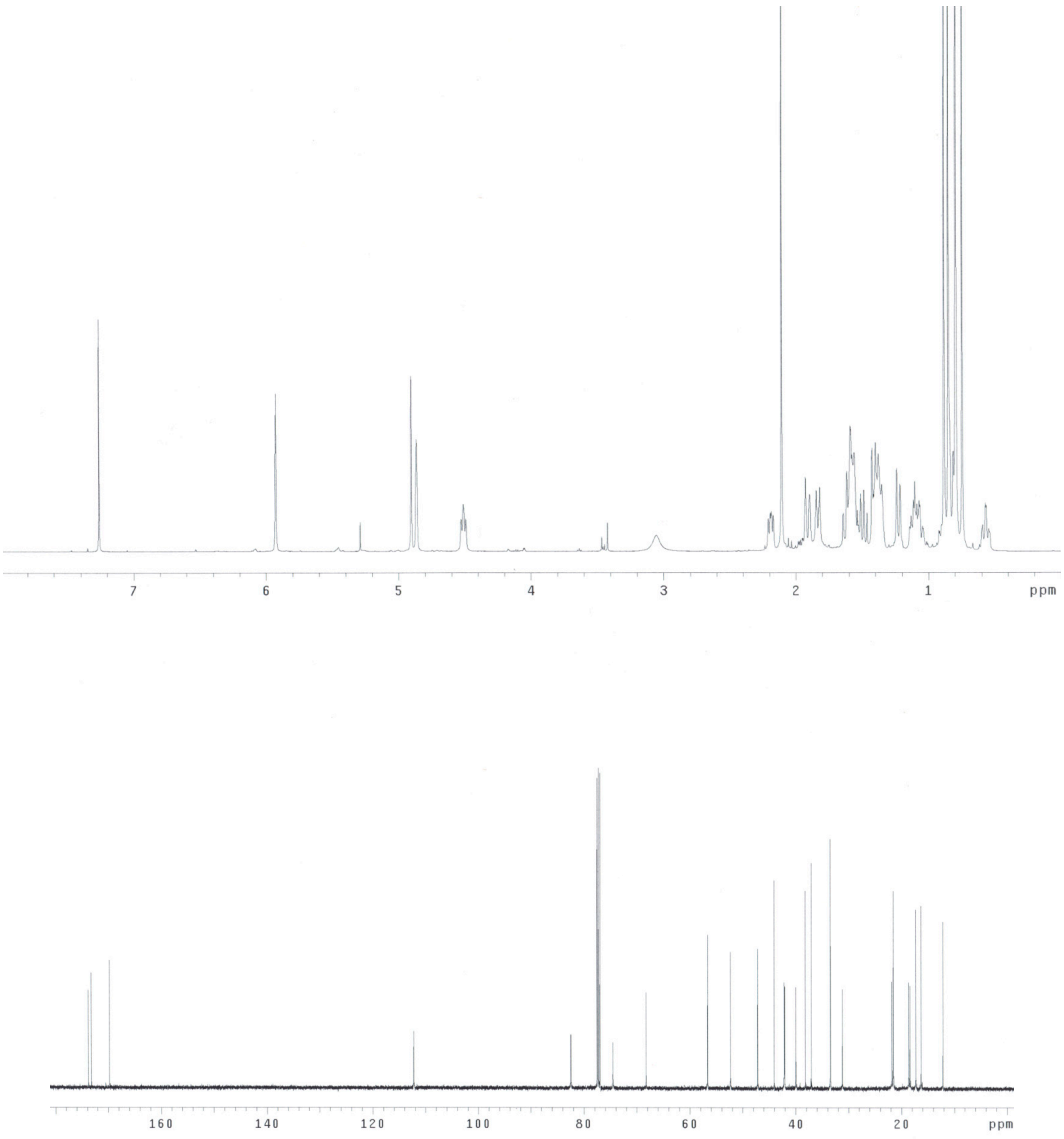


Figure S5. ^{1}H-NMR and ^{13}C-NMR Spectra (500 and 125 MHz, $CDCl_3$:CD_3OD (3:1)) of **5**.

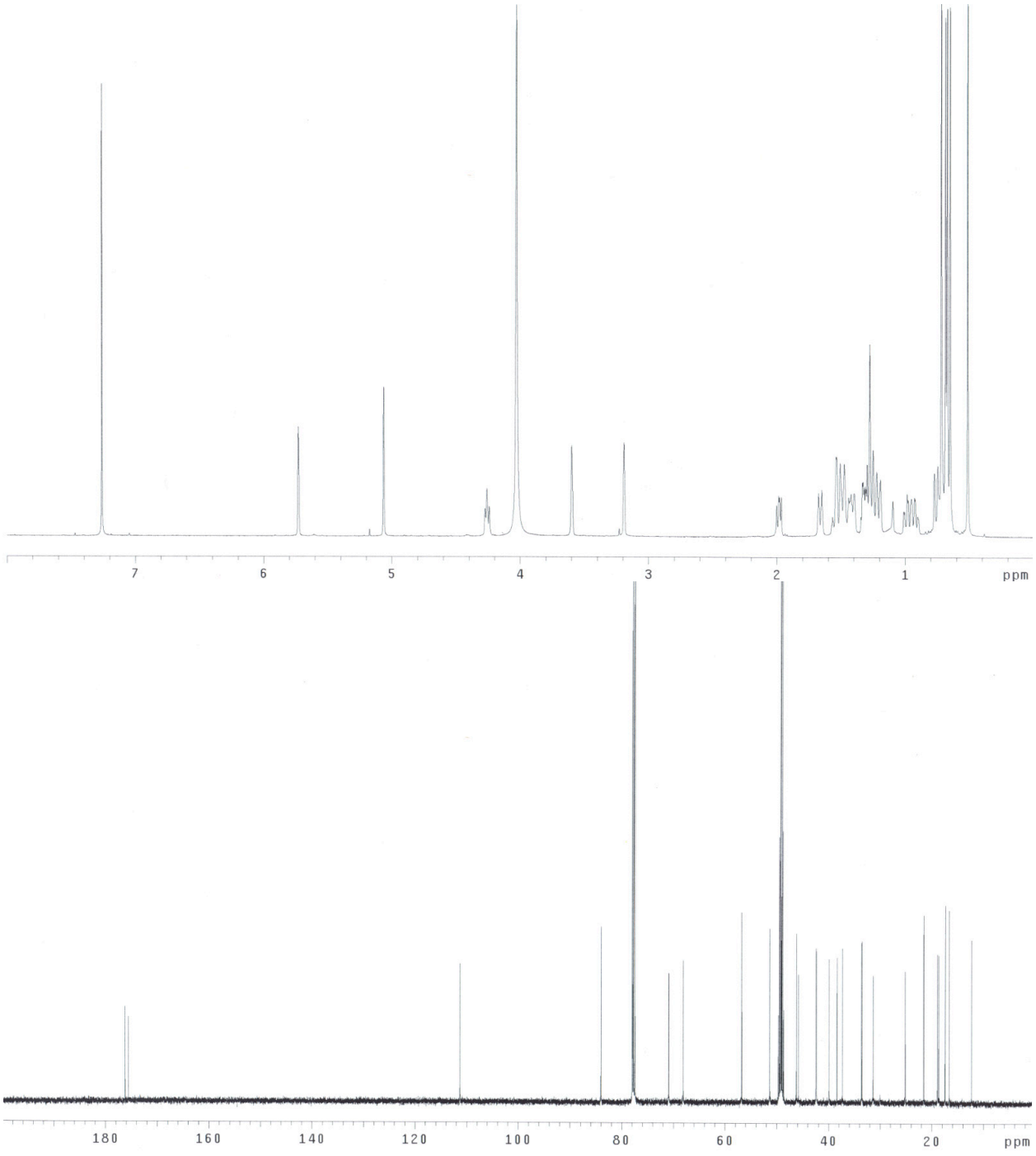
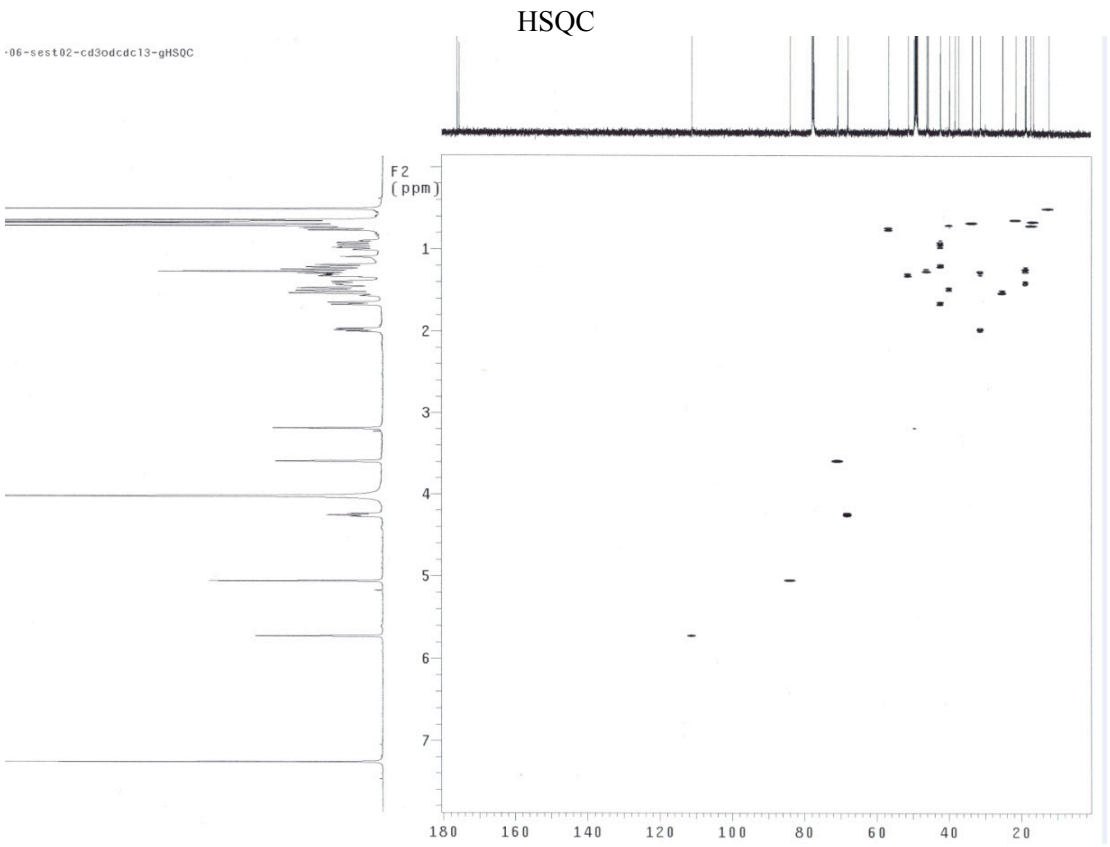


Figure S6. HSQC and HMBC Spectra ($CDCl_3$:CD_3OD (3:1)) of **5**.



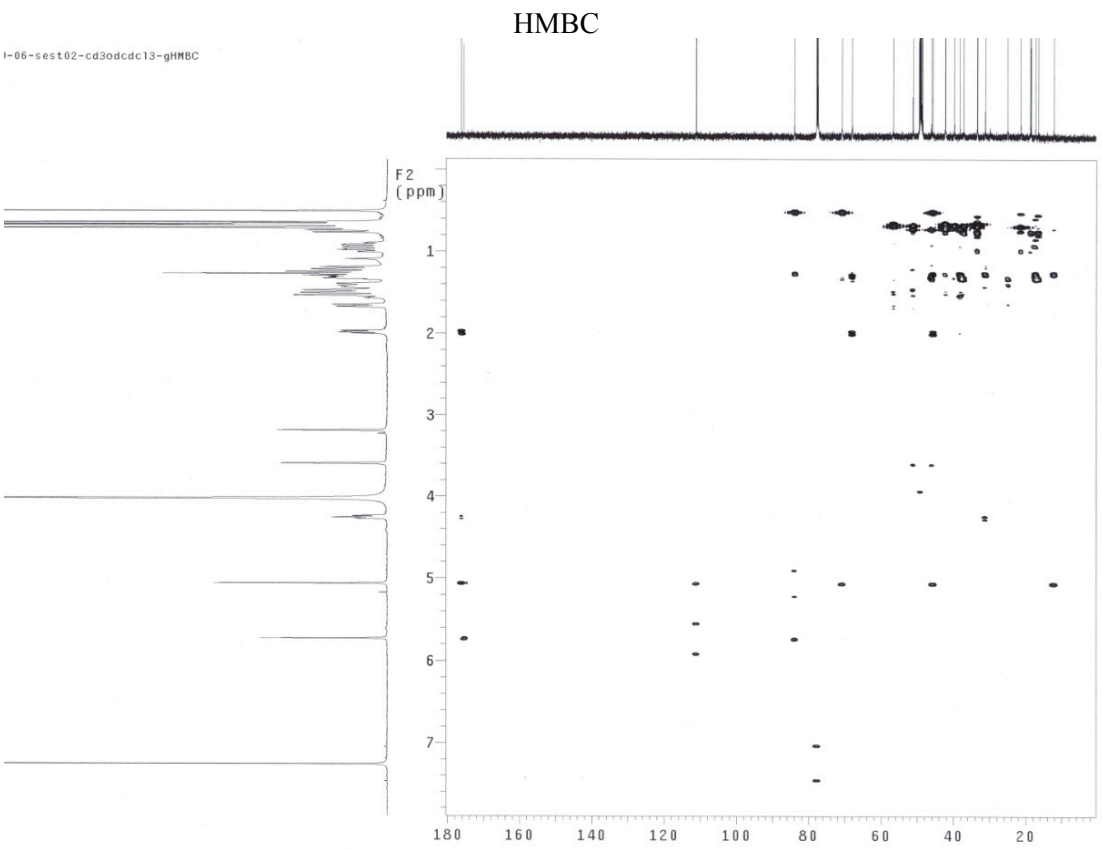
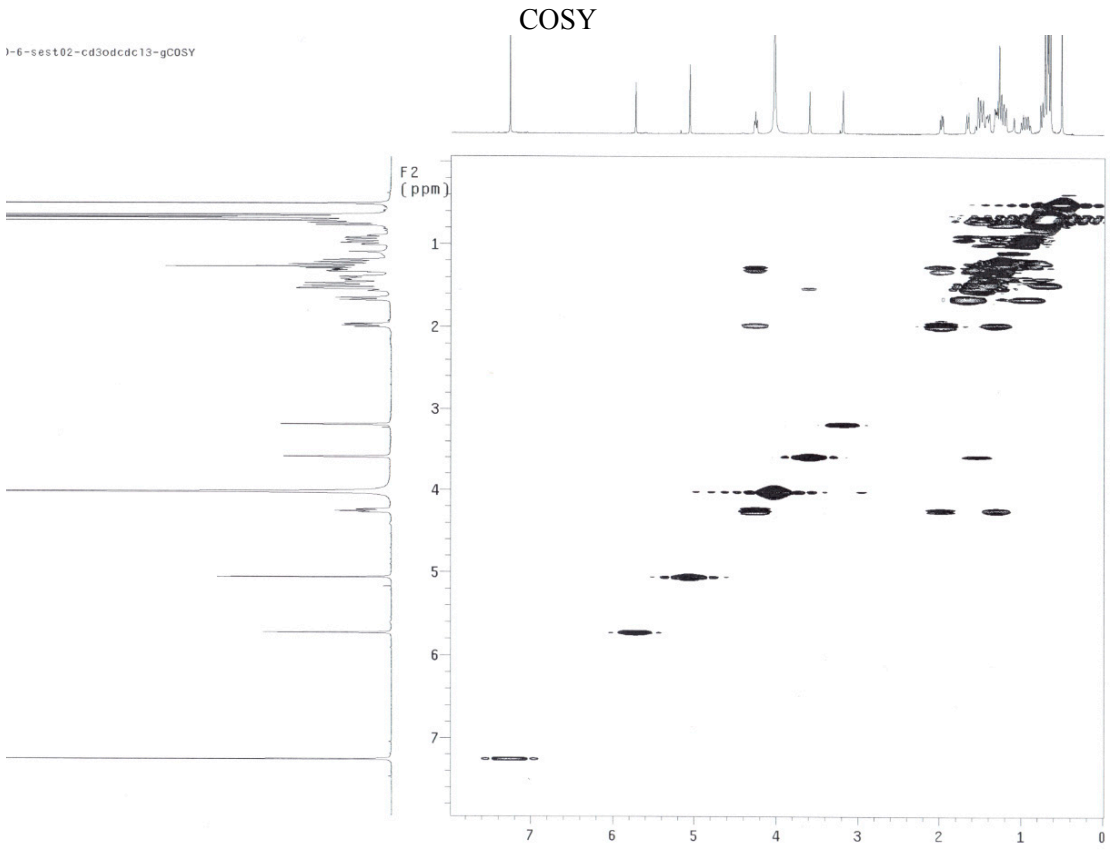


Figure S7. COSY and NOESY Spectra ($CDCl_3$:CD_3OD (3:1)) of **5**.



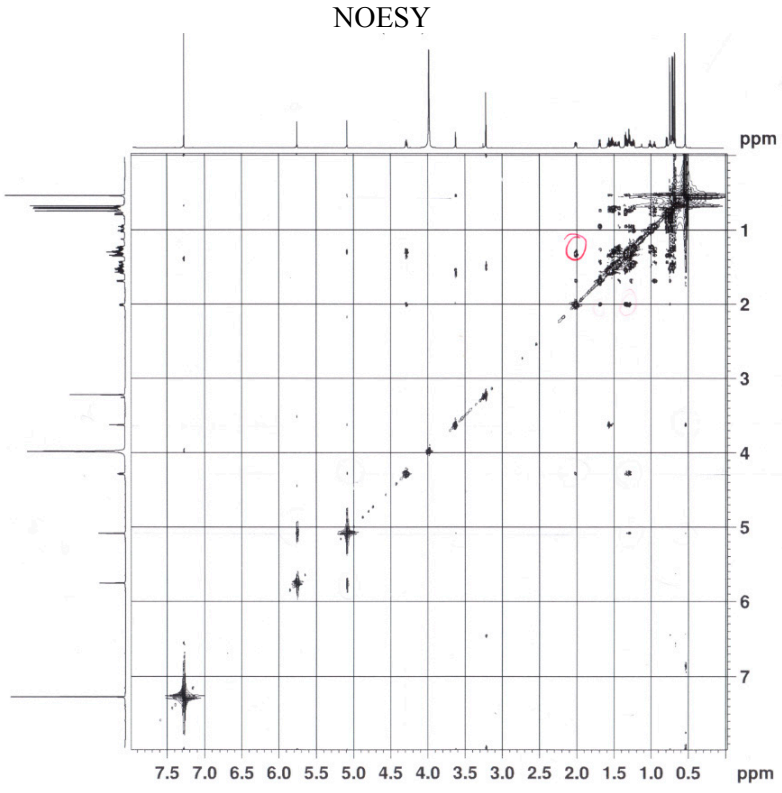


Figure S8. ^{1}H-NMR and ^{13}C-NMR Spectra (500 MHz and 125 MHz, $CDCl_3$) of **6**.

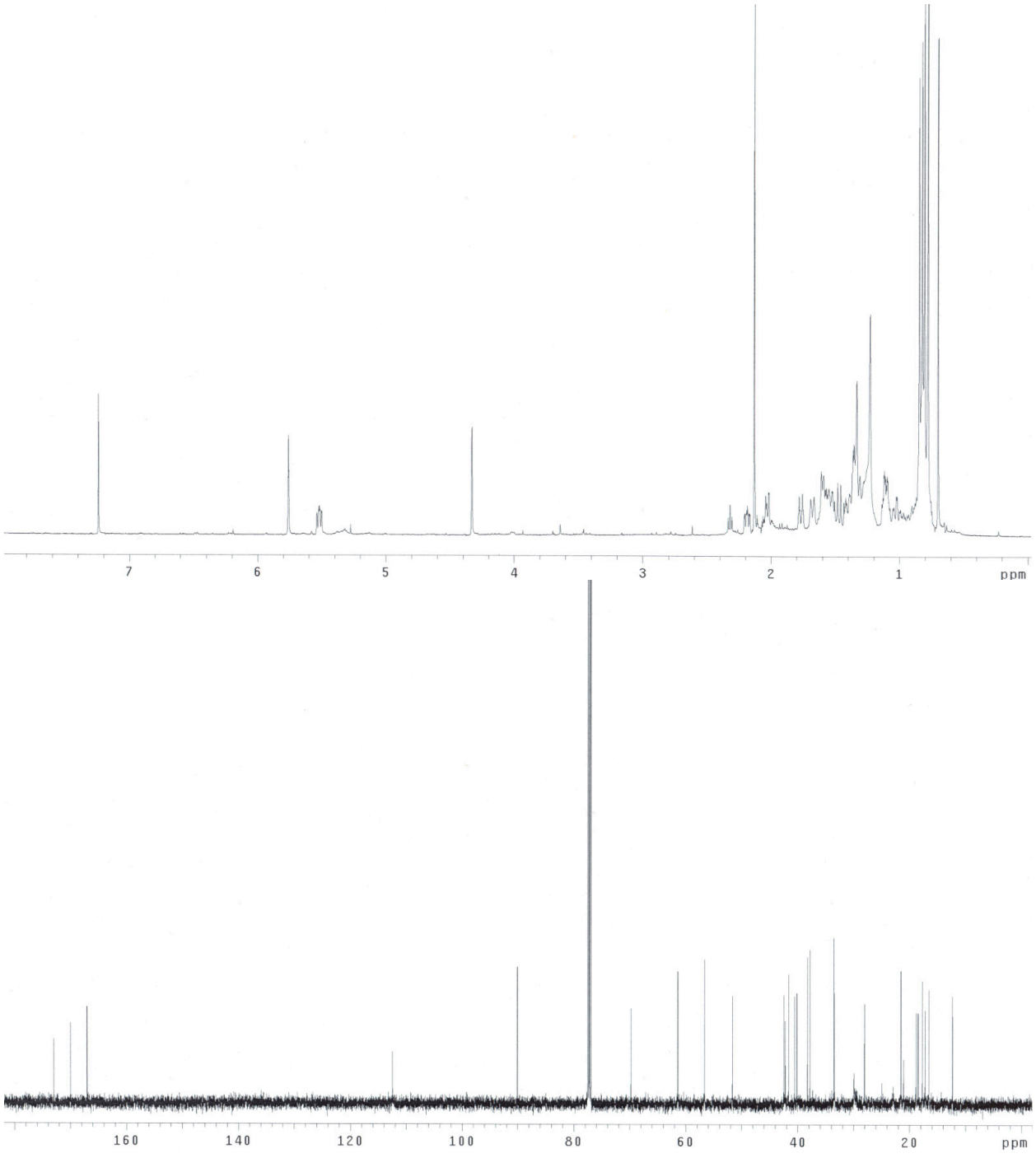
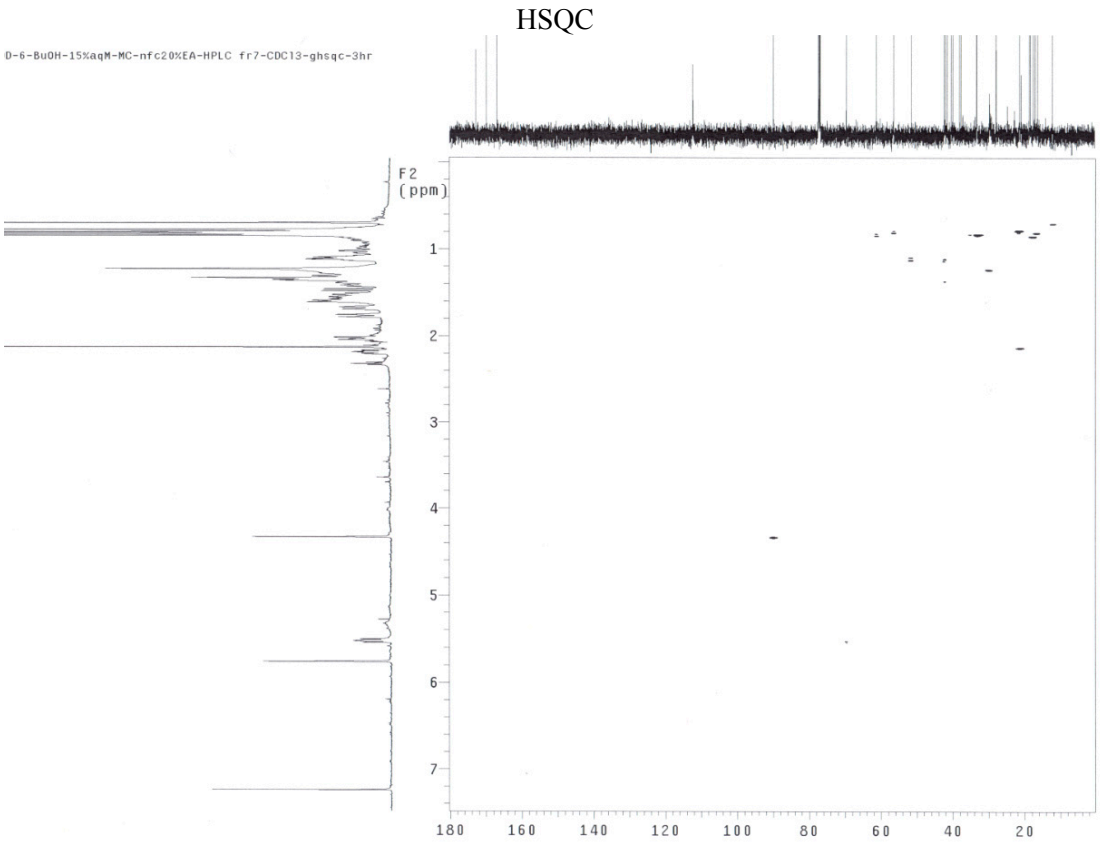


Figure S9. HSQC and HMBC Spectra ($CDCl_3$) of **6**.



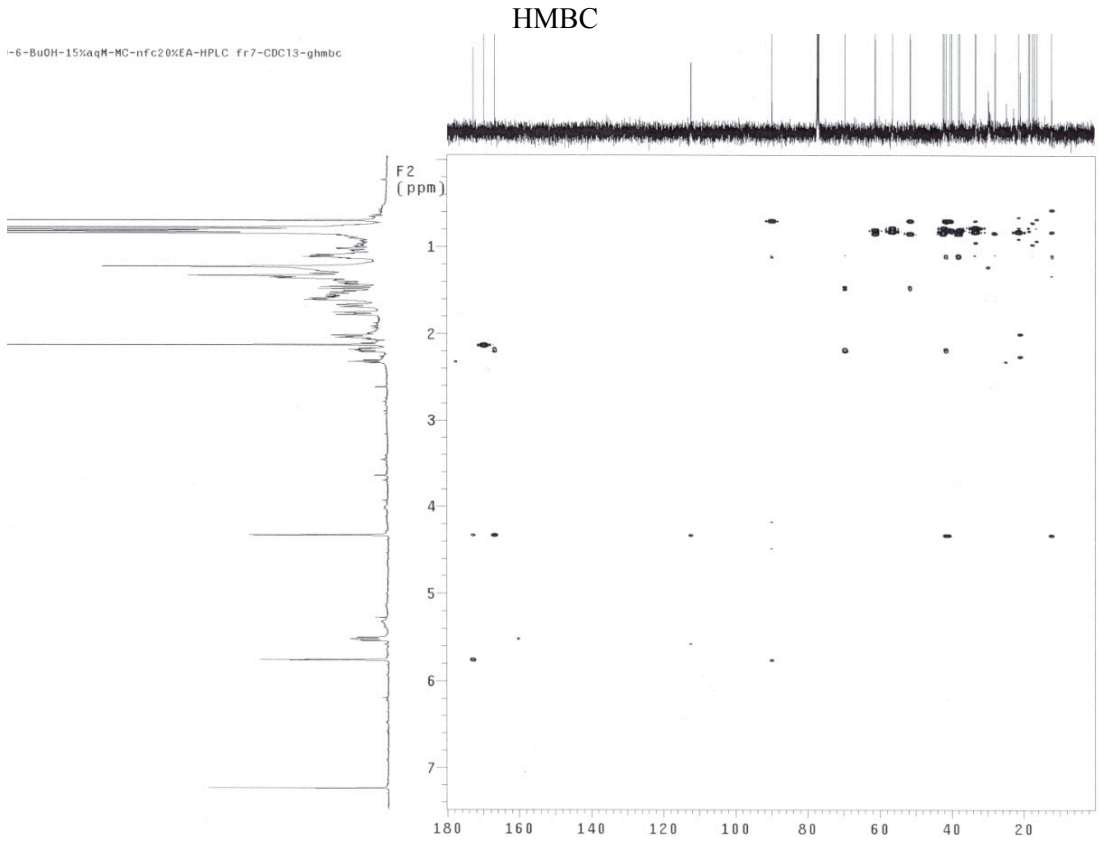
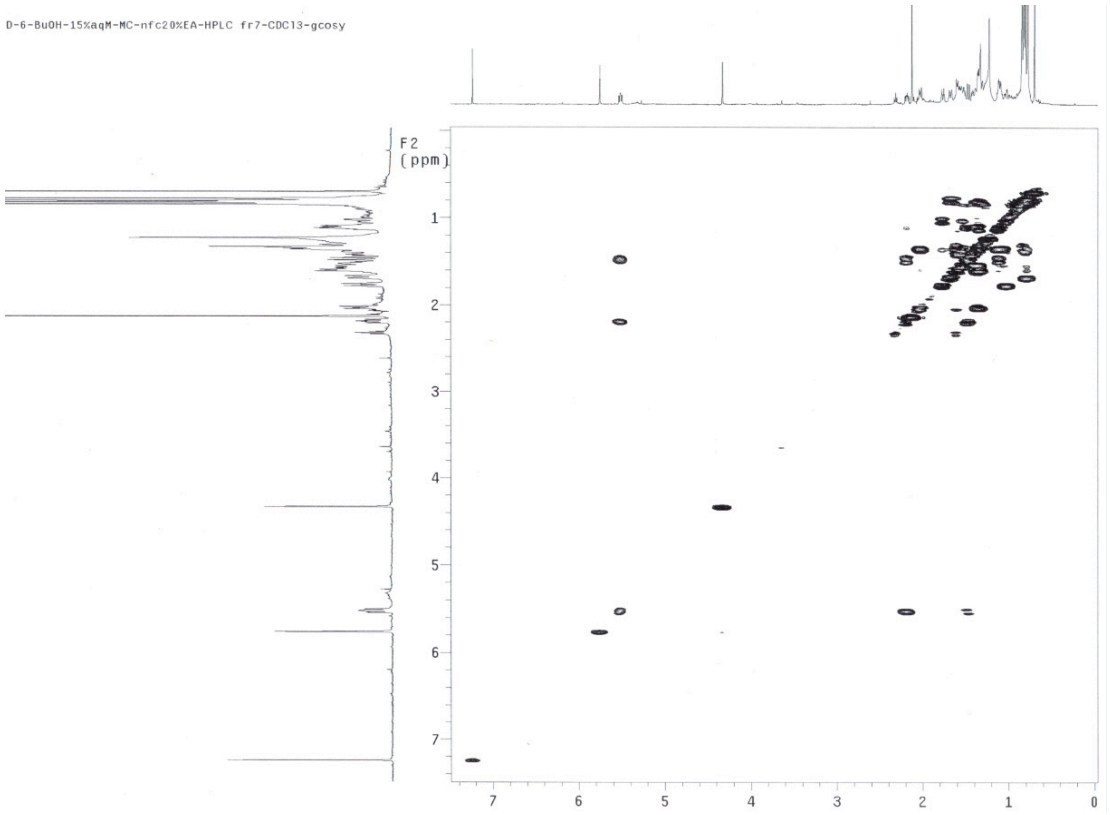


Figure S10. COSY and NOESY Spectra ($CDCl_3$) of **6**.

COSY



NOESY

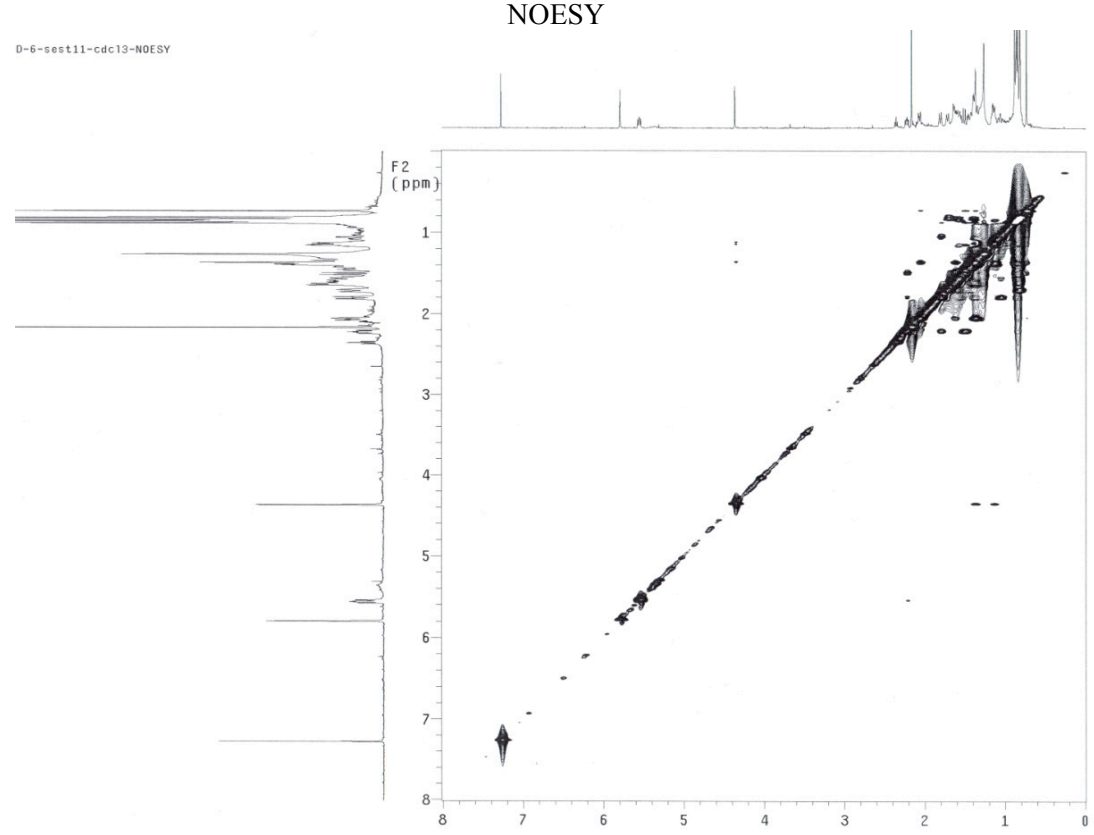


Figure S11. ^{1}H-NMR and ^{13}C-NMR Spectra (500 and 125 MHz, $CDCl_3$) of **7**.

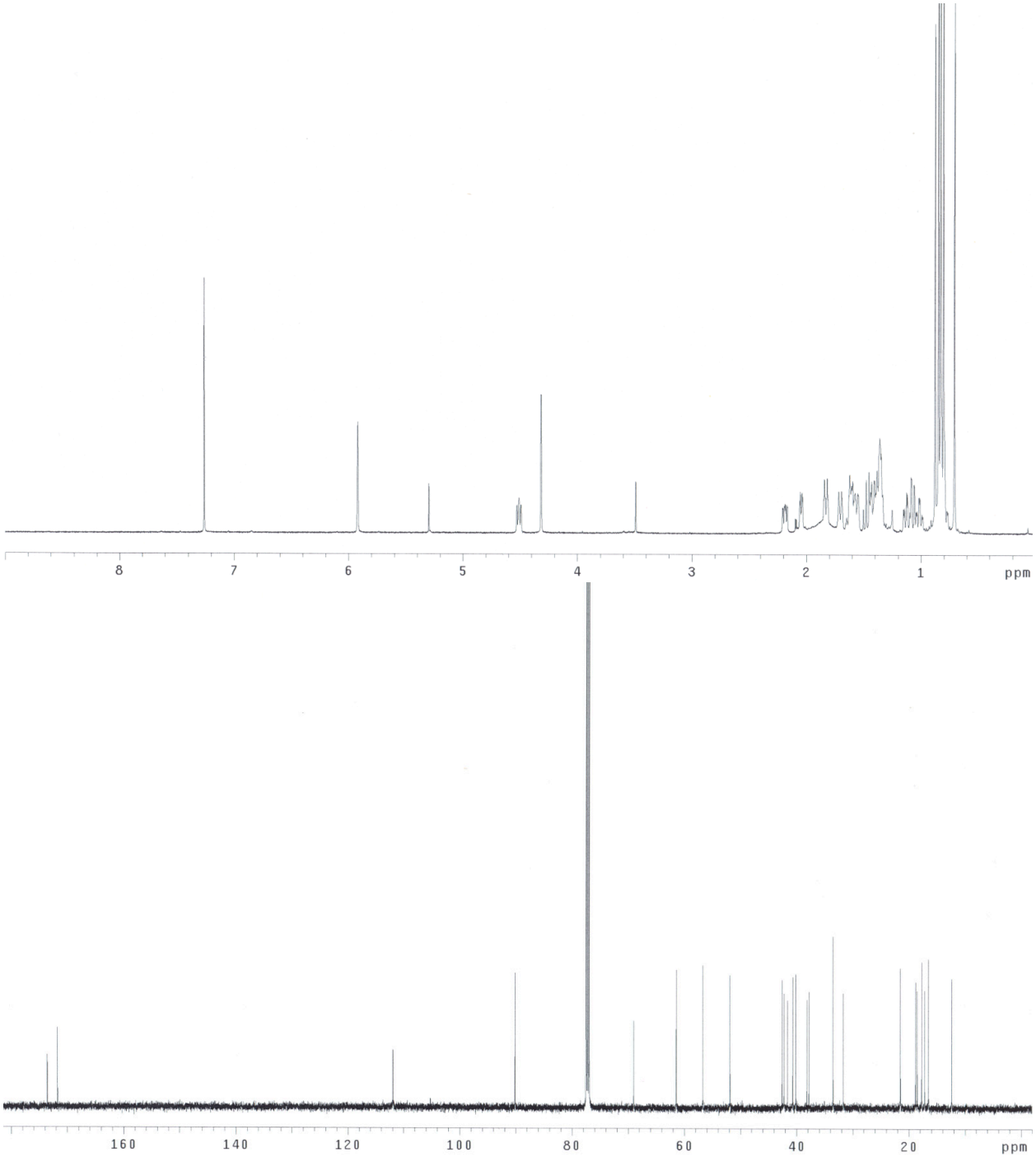


Figure S12. HSQC and HMBC Spectra ($CDCl_3$) of **7**.

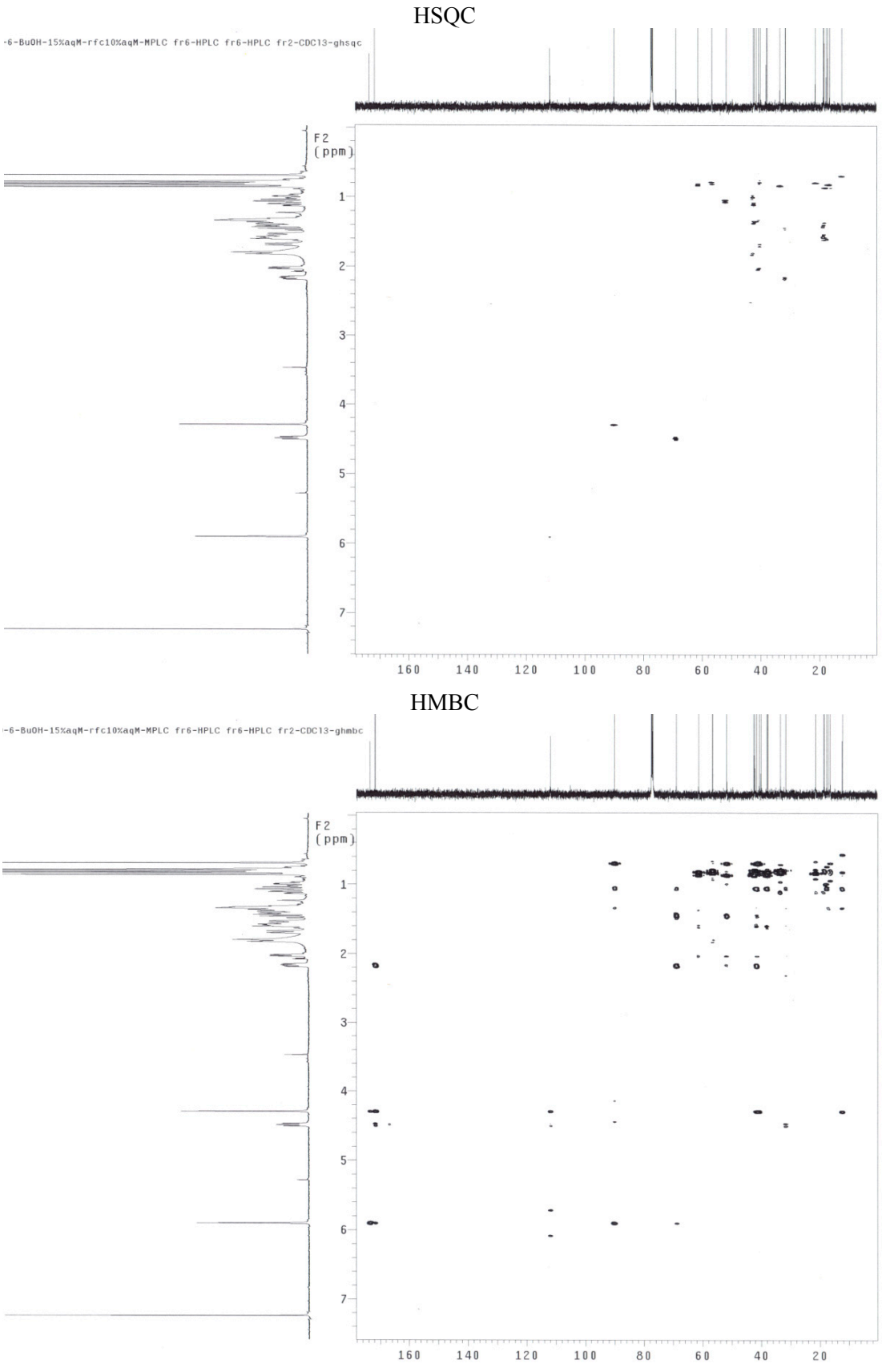


Figure S13. COSY and NOESY Spectra ($CDCl_3$) of **7**.

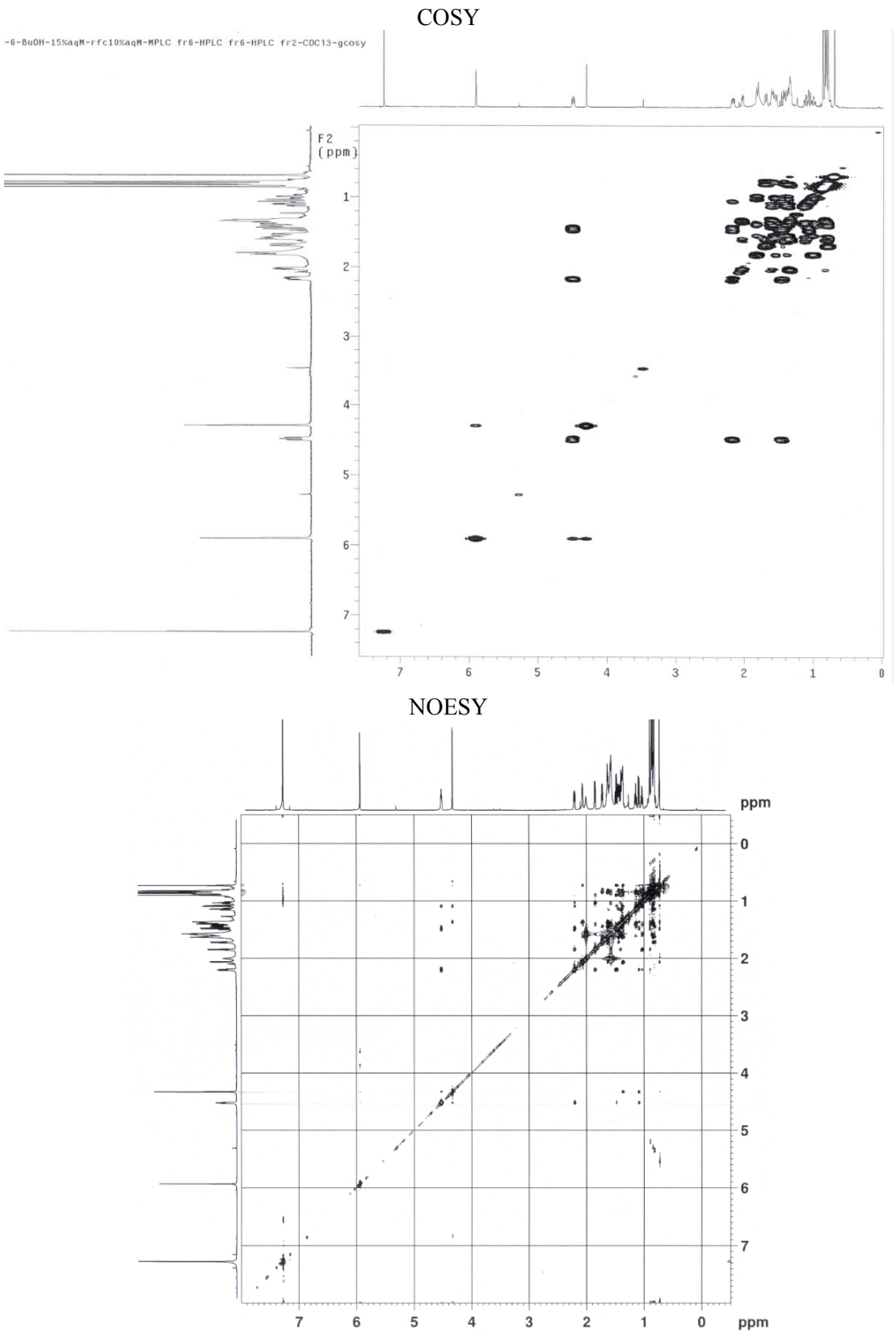


Figure S14. ^{1}H-NMR and ^{13}C-NMR Spectra (500 and 125 MHz, $CDCl_3$) of **8**.

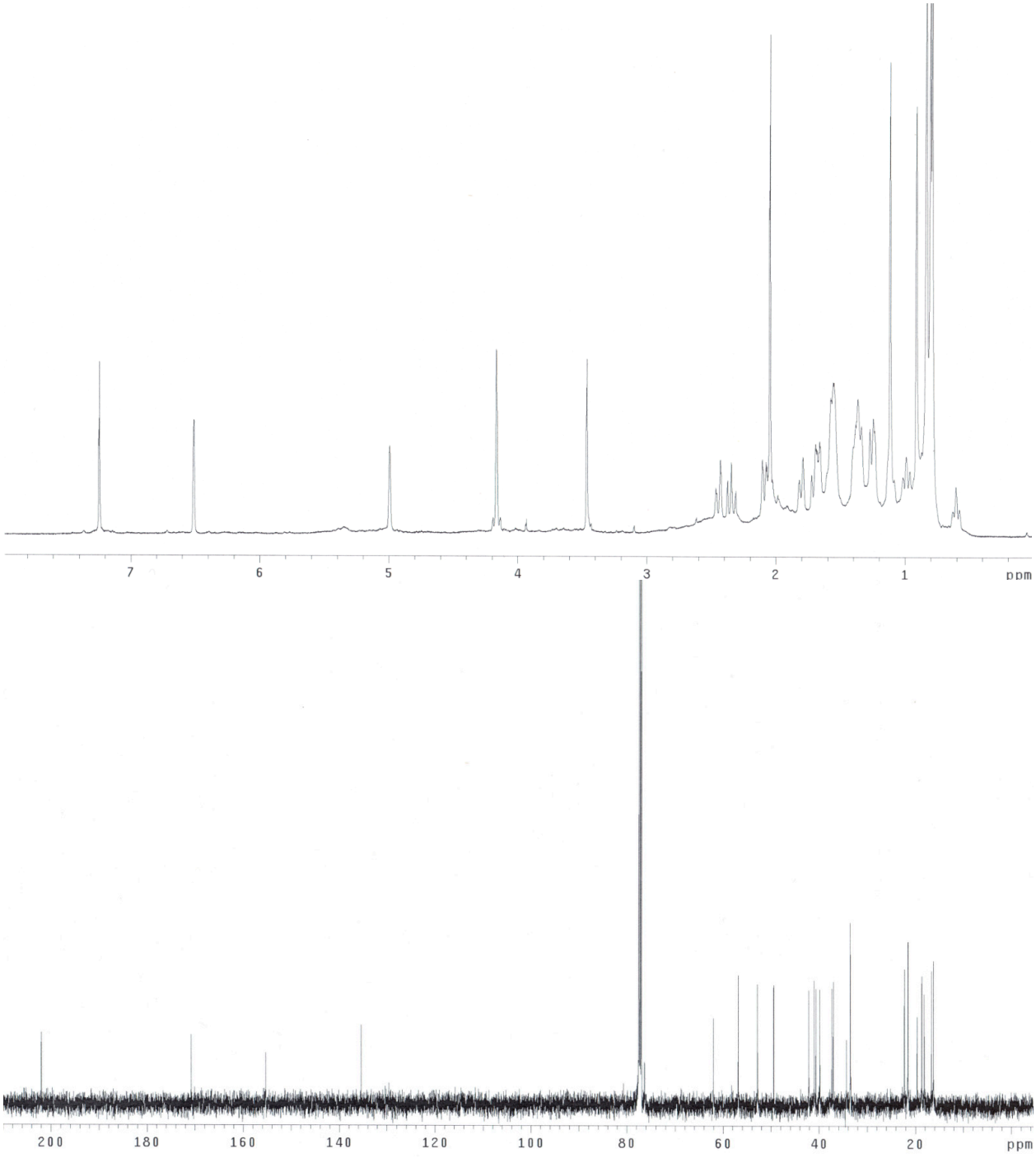


Figure S15. HSQC and HMBC Spectra ($CDCl_3$) of **8**.

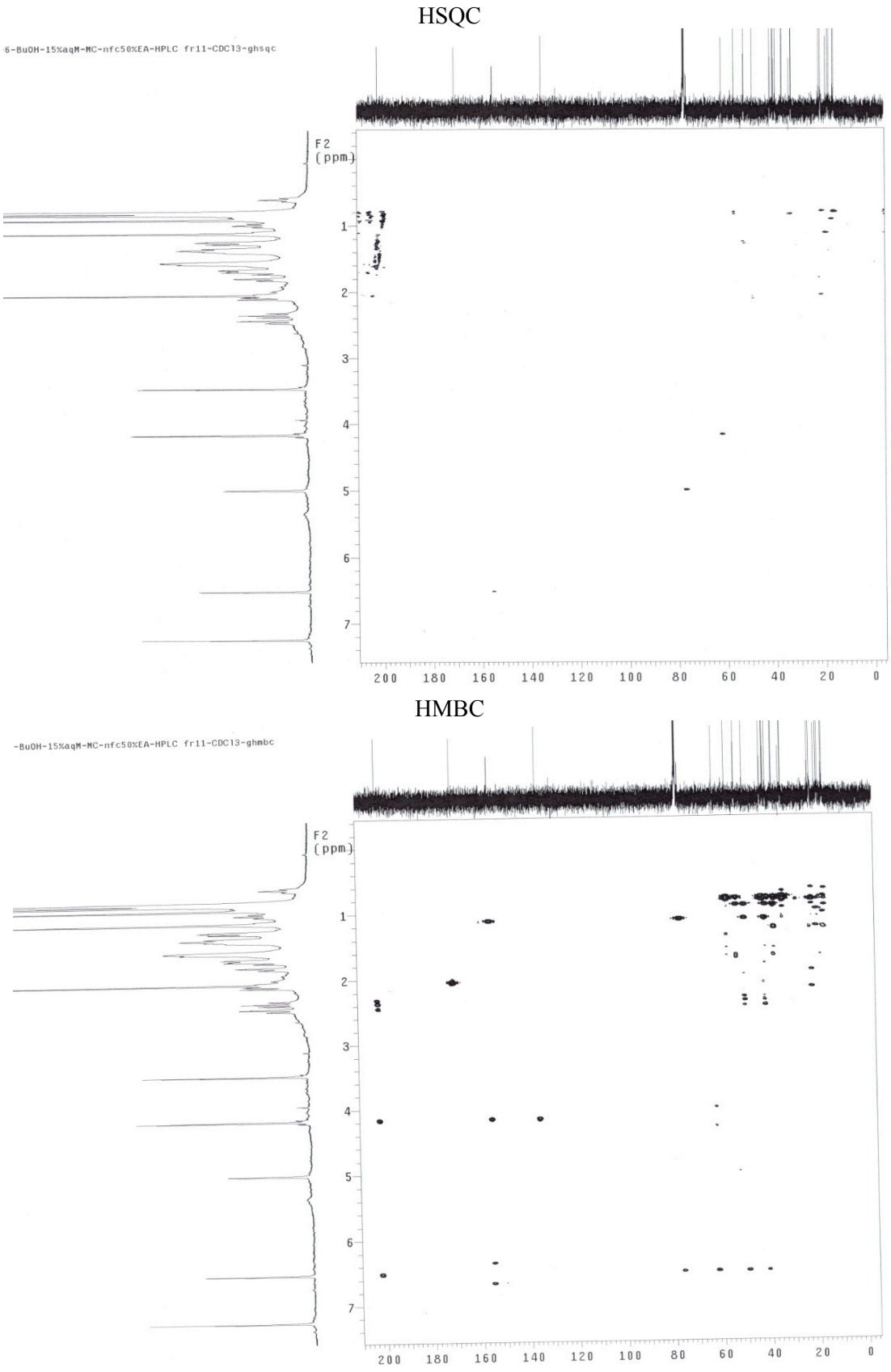
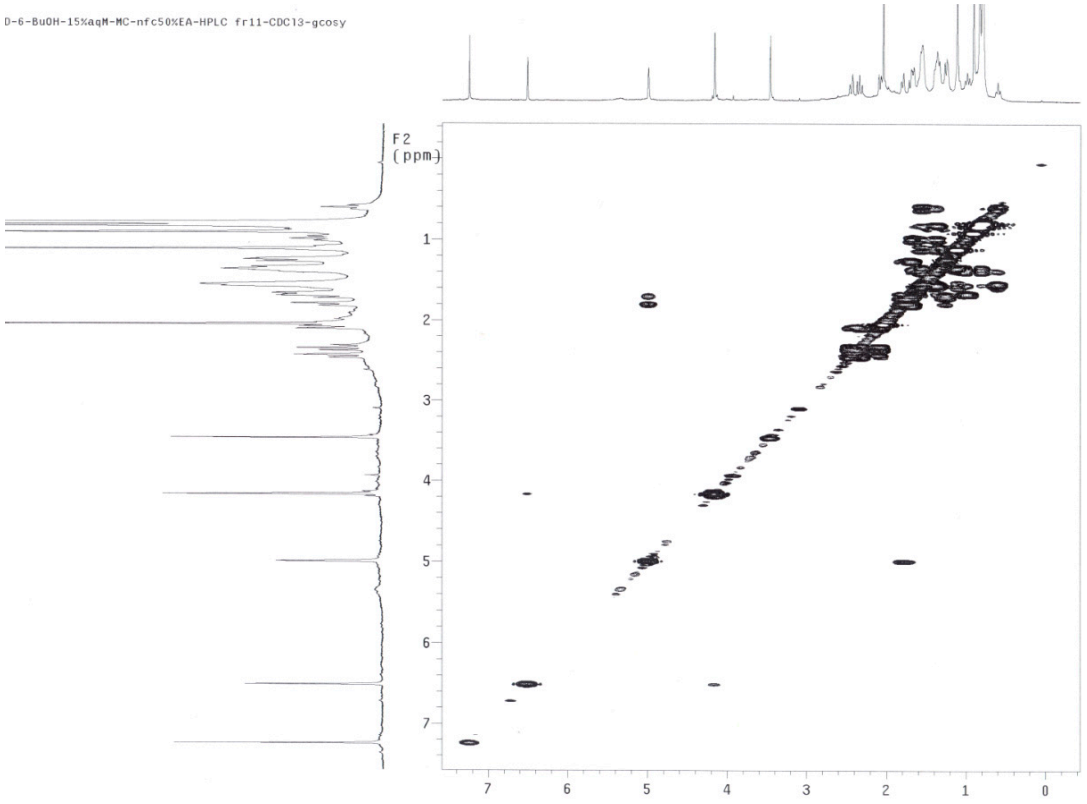


Figure S16. COSY and NOESY Spectra ($CDCl_3$) of **8**.

COSY



NOESY