Electronic Supplementary Information

New prenylated coumarins from the stems of *Toddalia asiatica*

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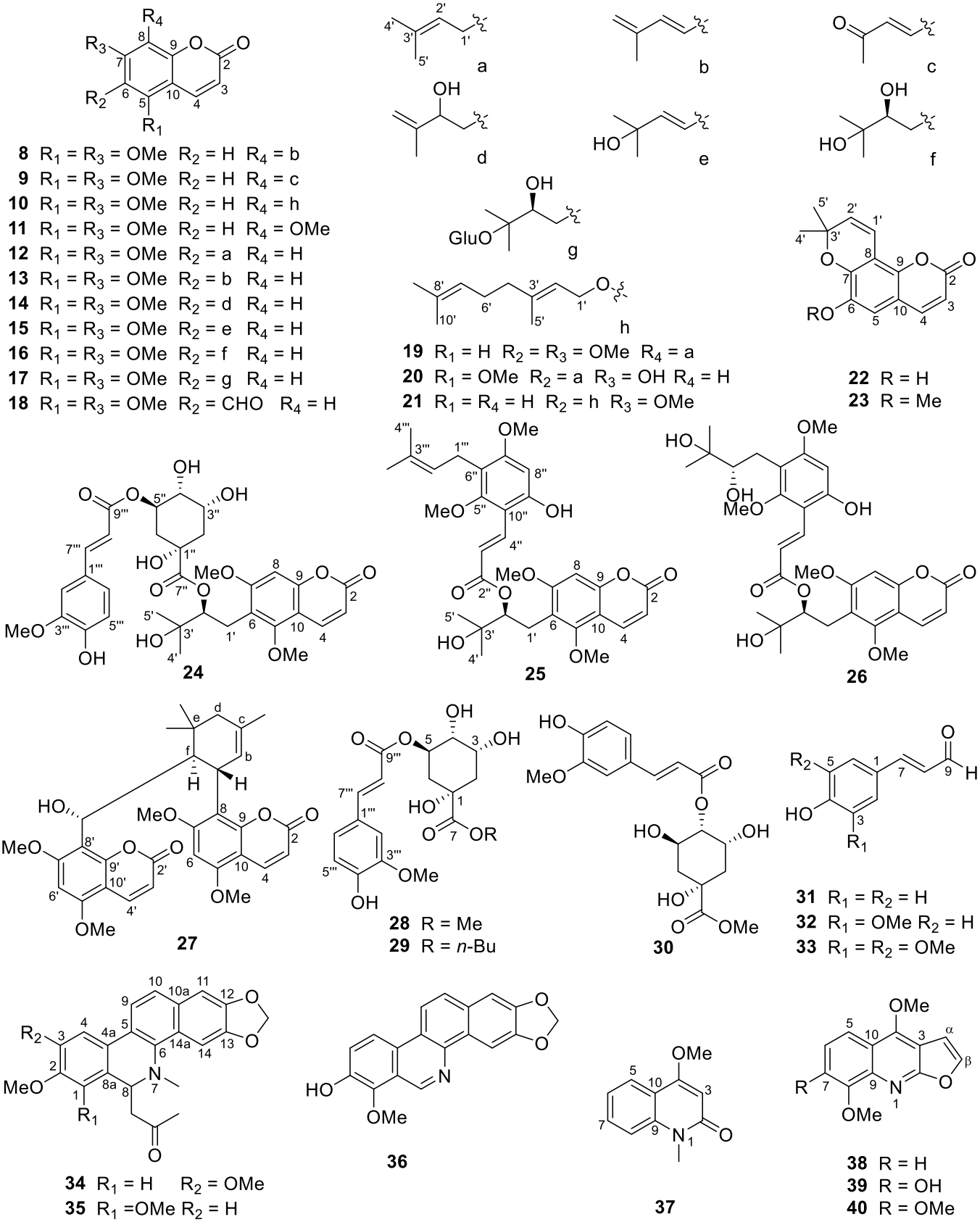


Fig. S1.1. Known compounds (**8**–**40**) from the stem of *Toddalia asiatica*

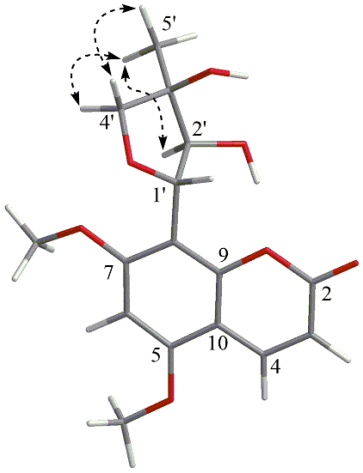


Fig. S1.2. Key NOE correlations of compound **2**

Table S2.1. ^{1}H NMR spectroscopic data of **8**, **9**, **11–16**, and **18–23** in $CDCl_3$ (400 MHz, *J* in Hz, δ in ppm)

position	**8**	**9**	**11**	**12**	**13**	**14**	**15**	**16**	**18**	**19**	**20**	**22**	**23**
3	6.14, d (9.6)	6.18, d (9.7)	6.16, d (9.7)	6.21, d (9.6)	6.25, d (9.7)	6.18, d (9.6)	6.25, d (9.7)	6.23, d (9.6)	6.30, d (9.7)	6.28, d (9.5)	6.22, d (9.6)	6.22, d (9.4)	6.24, d (9.4)
4	7.96, d (9.6)	7.97, d (9.7)	7.98, d (9.7)	7.86, d (9.6)	7.92, d (9.7)	7.81, d (9.6)	7.91, d (9.7)	7.83, d (9.6)	7.96, d (9.7)	7.58, d (9.5)	7.90, d (9.6)	7.53, d (9.4)	7.57, d (9.4)
5										6.77, s		6.83, s	6.76, s
6	6.30, s	6.32, s	6.34, s										
8				6.60, s	6.63, s	6.58, s	6.62, s	6.63, s	6.66, s		6.81, s		
1′	7.36, d (16.6)	7.92, d (16.6)		3.34, d (6.9)	6.65, d (16.5)	2.91, dd (13.6, 4.2) 2.82, dd (13.6, 8.6)	6.75, d (16.5)	2.90, dd (13.7, 2.4) 2.74, dd (13.7, 10.3)	10.42, s	3.53. d (7.3)	3.42, d (6.8)	6.79, d (10.1)	6.87, d (10.0)
2′	6.79, d (16.6)	7.23, d (16.6)		5.12, t (6.9)	7.25, d (16.5)	4.25, dd (8.6, 4.2)	6.69, d (16.5)	3.59, ddd (10.3, 4.6, 2.4)		5.20, t (7.2)	5.22, t (6.8)	5.68, d (10.1)	5.74, d (10.0)
4′	5.13, br.s 5.06, br.s	2.40, s		1.67, s	5.12, s 5.11, s	4.88, s 4.76, s	1.44, s	1.29, s		1.64, s	1.73, s	1.45, s	1.51, s
5′	2.01, s			1.76, s	2.00, s	1.79, s	1.44, s	1.27, s		1.82, s	1.82, s	1.45, s	1.51, s
5-OMe	3.95, s	3.99, s	3.91, s	3.81, s	3.79, s	3.83, s	3.78, s	3.86, s	3.97, s		3.83, s		
6-OMe										3.87, s			3.88, s
7-OMe	3.93, s	3.98, s	3.96, s	3.87, s	3.92, s	3.85, s	3.90, s	3.88, s	3.98, s	3.87, s			
8-OMe			3.91, s					2′-OH, 2.63, d (4.6) 4′-OH, 2.38, br.s					

Table S2.2. ^{13}C NMR spectroscopic data of **8**, **9**, **11–16**, and **18–23** in $CDCl_3$ (100 MHz, δ in ppm)

position	**8**	**9**	**11**	**12**	**13**	**14**	**15**	**16**	**18**	**19**	**20**	**22**	**23**
2	161.1, C	160.5, C	161.0, C	161.4, C	161.2, C	161.0, C	161.2, C	161.1, C	160.4, C	161.3, C	162.3, C	161.6, C	161.4, C
3	110.8, CH	111.4, CH	111.4, CH	112.3, CH	112.8, CH	112.5, CH	112.9, CH	112.8, CH	113.7, CH	114.8, CH	111.8, CH	115.2, CH	115.3, CH
4	138.7, CH	138.7, CH	138.9, CH	139.1, CH	139.0, CH	138.9, CH	139.0, CH	138.9, CH	138.5, CH	143.5, CH	139.8, CH	144.1, CH	143.9, CH
5	155.6, C	158.4, C	156.2 C	155.3, C	155.7, C	156.1, C	155.7, C	156.1, C	159.7, C	107.1, CH	155.8, C	111.5, CH	108.6, CH
6	90.4, CH	90.3, CH	91.5, CH	120.4, C	116.7, C	117.5, C	116.2, C	118.0, C	115.4, C	147.5, C	118.7, C	143.9, C	146.6, C
7	161.2, C	163.2, C	148.8, C	161.8, C	161.7, C	161.7, C	161.6, C	161.6, C	160.0, C	149.9, C	160.0, C	141.9, C	145.8, C
8	107.2, C	104.7, C	130.2, C	95.5, CH	95.7, CH	95.5, CH	95.6, CH	95.8, CH	96.0, CH	124.5, C	100.0, CH	109.5, C	110.4, C
9	153.4, C	155.0, C	152.5, C	154.8, C	154.9, C	155.0, C	155.0, C	155.1, C	165.1, C	150.7, C	154.4, C	143.4, C	145.0, C
10	103.8, C	103.9, C	104.1, C	107.2, C	107.7, C	107.1, C	107.7, C	107.3, C	108.1, C	114.6, C	107.2, C	112.1, C	111.5, C
1′	135.6, CH	131.9, CH		22.8, CH_2	118.3, CH	30.2, CH_2	115.5, CH	26.2, CH_2	187.6, CH	22.8, CH_2	23.0, CH_2	113.3, CH	113.3, CH
2′	117.1, CH	129.9, CH		122.3, CH	137.0, CH	75.1, CH	143.1, CH	78.1, CH		121.4, CH	121.6, CH	130.7, CH	131.0, CH
3′	143.3, C	200.1, C		132.1, C	143.1, C	147.5, C	71.6, C	73.0, C		132.7, C	134.6, C	78.8, C	78.1, C
4′	117.0, CH_2	27.7, CH_3		25.8, CH_3	117.9, CH_2	110.4, CH_2	30.0, CH_3	26.3, CH_3		25.8, CH_3	25.9, CH_3	28.1, CH_3	28.1, CH_3
5′	18.4, CH_3			18.0, CH_3	18.4, CH_3	17.9, CH_3	30.0, CH_3	23.7, CH_3		18.0, CH_3	18.1, CH_3	28.1, CH_3	28.1, CH_3
5-OMe	55.9, CH_3	56.27, CH_3	61.8, CH_3	63.2, CH_3	62.1, CH_3	63.2, CH_3	61.9, CH_3	63.3, CH_3	64.8, CH_3		63.4, CH_3		
6-OMe										56.1, CH_3			56.6, CH_3
7-OMe	56.0, CH_3	56.34, CH_3	56.6, CH_3	56.2, CH_3	56.3, CH_3	56.1, CH_3	56.3, CH_3	56.4, CH_3	56.8, CH_3	61.1, CH_3			
8-OMe			56.2, CH_3										

Table S2.3. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectroscopic data of **10**, **17**, and **21** (J in Hz, δ in ppm)

	10[a]		**17**[b]		**21**[a]			**10**[a]		**17**[b]		**21**[a]	
position	δ_H, multi. (J in Hz)	δ_C, type	δ_H, multi. (J in Hz)	δ_C, type	δ_H, multi. (J in Hz)	δ_C, type	position	δ_H, multi. (J in Hz)	δ_C, type	δ_H, multi. (J in Hz)	δ_C, type	δ_H, multi. (J in Hz)	δ_C, type
2		160.9, C		163.3, C		161.5, C	1′	4.59, d (7.2)	70.0, CH_2	2.90, dd (13.6, 10.1) 2.76, dd (13.6, 2.6)	27.1, CH_2	4.65, d (6.3)	66.3, CH_2
3	6.12, d (9.7)	111.2, CH	6.22, d (9.6)	112.5, CH	6.21, d (9.4)	113.3, CH	2′	5.57, br.t (7.5)	119.9, CH	3.83, dd (13.6, 2.6)	77.4, CH	5.44, br.t (5.7)	118.5, CH
4	7.94, d (9.7)	138.8, CH	8.00, d (9.6)	141.2, CH	7.58, d (9.4)	143.4, CH	3′		142.5, C		81.9, C		142.0, C
5		152.4, C		157.6, C	6.77, s	108.2, CH	4′	1.65, s	16.5, CH_3	1.37, s	21.8, CH_3	1.72, s	16.8, CH_3
6	6.31, s	91.5, CH		120.2, C		146.7, C	5′	2.01, m	39.7, CH_2	1.37, s	23.9, CH_3	2.05, m	39.5, CH_2
7		156.7, C		163.6, C		149.9, C	6′/1″	2.01, m	26.6, CH_2	4.59, d (7.7)	98.6, CH	2.05, m	26.2, CH_2
8		128.9, C	6.72, s	96.3, CH	6.82, s	101.2, CH	7′/2″	5.03, br.t (6.8)	124.0, CH	3.23, dd (9.2, 7.7)	75.1, CH	5.02, br.t (6.9)	123.7, CH
9		149.3, C		156.1, C		152.2, C	8′/3″		131.7, C	3.41, m	78.0, CH		131.9, C
10		104.0, C		108.3, C		111.3, C	9′/4″	1.65, s	25.8, CH_3	3.31, m	71.6, CH	1.60, s	25.6, CH_3
5-OMe	3.89, s	56.1, CH_3	3.91, s	63.9, CH_3			10′/5″	1.57, s	17.8, CH_3	3.33, m	77.8, CH	1.55, s	17.7, CH_3
7-OMe	3.94, s	56.6, CH_3	3.91, s	56.7, CH_3	3.86, s	56.4, CH_3	6″			3.82, m 3.66, m	62.6, CH_2		

[a] In $CDCl_3$; [b] In CD_3OD.

Table S2.4. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectroscopic data of **24** (J in Hz, δ in ppm)

position	**24**[a]		**24**[b]	
	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)	δ_C, type
2		163.0, C		161.1, C
3	6.10, d (9.5)	112.9, CH	6.22, d (9.6)	112.9, CH
4	7.86, d (9.5)	140.7, CH	7.71, d (9.6)	138.7, CH
5		157.6, C		156.0, C
6		117.9, C		116.3, C
7		163.6, C		162.0, C
8	6.61, s	96.4, CH	6.54, s	95.7, CH
9		156.4, C		155.2, C
10		108.2, C		107.0, C
1′a	3.19, t (12.3)	24.4, CH_2	3.17, dd (13.4 11.0)	23.5, CH_2
1′b	2.90, d (13.6)		2.90, dd (13.4, 2.4)	
2′	5.27, d (11.1)	80.1, CH	5.20, dd (11.0, 2.4)	79.6, CH
3′		72.9, C		72.2, C
4′	1.30, s	25.9, CH_3	1.35, s	25.3, CH_3
5′	1.24, s	26.4, CH_3	1.26, s	27.0, CH_3
1″		76.9, C		76.3, C
2″a	1.78, d (14.2)	37.9, CH_2	1.95, m	36.6, CH_2
2″b	1.95, d (14.2)		1.95, m	
3″	4.06, br. s	71.5, CH	4.15, br. s	70.7, CH
4″	3.58, d (9.3)	73.8, CH	3.57, d (9.5)	73.6, CH
5″	5.22, m	71.6, CH	5.26, ddd (11.3, 9.5, 4.4)	70.6, CH
6″a	2.00, m	39.5, CH_2	1.95, m	38.7, CH_2
6″b	1.46, t (12.0)		1.95, m	
7″		174.2, C		172.6, C
1‴		127.6, C		126.7, C
2‴	7.18, s	111.7, CH	7.05, d (1.8)	109.7, CH
3‴		149.3, C		146.1, C
4‴		150.7, C		148.5, C
5‴	6.81, d (8.0)	116.5, CH	6.87, d (8.2)	114.9, CH
6‴	7.05, d (8.0)	124.2, CH	7.01, dd (8.2, 1.8)	123.6, CH
7‴	7.56, d (15.9)	146.9, CH	7.57, d (15.8)	147.1, CH
8‴	6.25, d (15.9)	115.5, CH	6.22, d (15.8)	114.8, CH
9‴		168.5, C		167.6, C
5-OMe	3.85, s	63.7, CH_3	3.86, s	63.4, CH_3
7-OMe	3.85, s	56.8, CH_3	3.81, s	56.4, CH_3
3‴-OMe	3.90, s	56.5, CH_3	3.90, s	56.1, CH_3

[a] In CD_3OD; [b] In $CDCl_3$.

Table S2.5. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectroscopic data of **25** and **26** in $CDCl_3$ (J in Hz, δ in ppm)

position	**25**		**26**	
	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)	δ_C, type
2		161.6, C		161.6, C
3	6.13, d (9.6)	112.3, CH	6.09, d (9.6)	112.1, CH
4	7.75, d (9.6)	139.1, CH	7.74, d (9.6)	139.3, CH
5		156.2, C		156.3, C
6		117.0, C		117.1, C
7		162.2, C		162.3, C
8	6.53, s	95.6, CH	6.49, s	95.5, CH
9		155.3, C		155.2, C
10		107.1, C		107.1, C
1′a	2.95, dd (13.6, 2.5)	24.1, CH_2	2.93, dd (13.3)	24.2, CH_2
1′b	3.17, dd (13.6, 10.2)		3.14, t (13.3)	
2′	5.29, dd (10.2, 2.5)	78.3, CH	5.29, d (10.0)	78.5, CH
3′		73.0, C		72.9, C
4′	1.38, s	25.3, CH_3	1.37, s	25.3, CH_3
5′	1.34, s	26.9, CH_3	1.33, s	26.8, CH_3
2″		168.6, C		168.7, C
3″	6.60, d (16.2)	117.0, CH	6.59, d (16.1)	117.9, CH
4″	7.75, d (16.2)	137.3, CH	7.66, d (16.0)	137.1, CH
5″		159.4, C		159.8, C
6″		116.2, C		112.8, C
7″		160.7, C		160.4, C
8″	6.19, s	95.9, CH	6.15, s	96.2, CH
9″		156.5, C		157.7, C
10″		108.4, C		108.5, C
1‴a	3.22, d (6.7)	22.6, CH_2	2.57, q (11.6)	25.8, CH_2
1‴b			2.78, t (11.6)	
2‴	5.10, t (6.4)	123.4, CH	3.50, m	78.8, CH
3‴		131.3, C		73.2, C
4‴	1.65, s	25.9, CH_3	1.26, s	26.1, CH_3
5‴	1.74, s	17.9, CH_3	1.25 s	23.9, CH_3
5-OMe	3.86, s	63.5, CH_3	3.84, s	63.4, CH_3
7-OMe	3.84, s	56.4, CH_3	3.81, s	56.4, CH_3
5″-OMe	3.59, s	61.7, CH_3	3.59, s	61.7, CH_3
7″-OMe	3.76, s	55.7, CH_3	3.65, s	55.8, CH_3

Table S2.6. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectroscopic data of **27** in $CDCl_3$ (*J* in Hz, δ in ppm)

position	**27**	position	**27**
	δ_H, multi. (*J* in Hz)		δ_C, type
3	5.88, d (9.5)	2/2′	160.8 and 160.8, C
4	7.70, d (9.5)	3/3′	108.8 and 109.1, CH
6	6.07, s	4/4′	138,7 and 138.7, CH
3′	5.74, d (9.6)	5/5′	161.7 and 162.1, C
4′	7.56, d (9.6)	6/6′	89.7 and 90.6, CH
6′	6.06, s	7/7′	155.4 and 152.6, C
a	3.54, d (10.3)	8/8′	111.8 and 113.0, C
b	4.76, br. s	9/9′	154.7 and 154.9, C
d	2.26, d (16.6)	10/10′	102.9 and 102.7, C
	1.58, d (16.6)		
f	3.13, dd (10.3, 8.3)	a	50.5, CH
g	5.35, d (8.3)	b	122.0, CH
c-Me	1.59, s	c	131.5, C
e-Me × 2	1.35 and 1.13, each s	d	47.5, CH_2
5/7/5′/7′-OMe	4.03, 3.93, 3.78, and 3.76, each s	e	35.1, C
		f	33.0, CH
		g	67.6, CH
		c-Me	20.8, CH_3
		e-Me × 2	23.7 and 31.9, CH_3
		5/7/5′/7′-OMe	56.2, 55.8, 55.7, and 55.5, CH_3

Table S2.7. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectroscopic data of **28–30** (*J* in Hz, δ in ppm)

position	**28**[a]		**29**[b]		**30**[a]	
	δ_H, multi. (*J* in Hz)	δ_C, type	δ_H, multi. (*J* in Hz)	δ_C, type	δ_H, multi. (*J* in Hz)	δ_C, type
1		75.9, C		75.8, C		76.4, C
2	2.15, dd (13.4, 8.6) 2.04, dd (13.4, 6.4)	37.95, CH_2	2.21, dd (14.7, 2.3) 2.08, dd (14.7, 92.)	37.2, CH_2	2.10–2.19, m	42.1, CH_2
3	4.17, m	70.5, CH	4.20, m	70.8, CH	4.21, dd (9.1, 4.3)	65.7, CH
4	3.76, dd (7.8, 3.1)	72.7, CH	3.69, dd (9.8, 2.9)	74.1, CH	4.79, dd (8.7, 3.1)	78.5, CH
5	5.39, ddd (9.5, 7.8, 3.1)	72.1, CH	5.39, ddd (12.3, 9.8, 4.1)	70.9, CH	4.30, m	69.0, CH
6	2.23, dd (9.5, 3.8)	38.04, CH_2	2.31, dd (12.3, 4.1) 1.92, t (12.3)	38.9, CH_2	1.98–2.03, m	38.4, CH_2
7		175.4, C		174.3, C		175.7, C
1′		168.3, C		167.6, C		168.9, C
2′	6.33, d (15.9)	116.5, CH	6.30, d (15.9)	115.2, CH	6.41, d (15.9)	116.5, CH
3′	7.61, d (15.9)	147.0, CH	7.63, d (15.9)	145.9, CH	7.65, d (15.9)	147.0, CH
4′		127.6, C		127.0, C		127.8, C
5′	7.19, s	111.7, CH	7.01, s	109.6, CH	7.16, d (1.9)	111.7, CH
6′		149.4, C		147.0, C		149.4, C
7′		150.7, C		148.3, C		150.6, C
8′	6.83, d (8.1)	115.4, CH	6.90, d (8.1)	114.9, CH	6.77, d (8.2)	115.6, CH
9′	7.08, d (8.1)	124.1, CH	7.04, dd (8.1)	123.4, CH	7.05, dd (8.2, 1.9)	124.1, CH
7-OMe/-O-*n*-Bu	3.72, s	53.0, CH_3	4.18, m 1.65, m 1.37, m 0.94, t (7.2)	66.5, CH_2 30.6, CH_2 19.1, CH_2 13.8, CH_3	3.71, s	53.0, CH_3
6′-OMe	3.90, s	56.5, CH_3	3.90, s	56.1, CH_3	3.85, s	56.4, CH_3

[a] In CD_3OD; [b] In $CDCl_3$.

Table S2.8. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectroscopic data of **31–33** (*J* in Hz, δ in ppm)

position	**31**[a]		**32**[a]	**33**[b]	
	δ_H, multi. (*J* in Hz)	δ_C, type	δ_H, multi. (*J* in Hz)	δ_H, multi. (*J* in Hz)	δ_C, type
1		127.0, C			125.7, C
2	7.55, d (8.2)	132.0, CH	7.26, s	6.81, s	105.7, CH
3	6.86, d (8.2)	117.1, CH			147.5, C
4		162.5, C			138.1, C
5	6.86, d (8.2)	117.1, CH	6.85, d (8.2)		147.5, C
6	7.55, d (8.2)	132.0, CH	7.18, d (8.2)	6.81, s	105.7, CH
7	7.60, d (15.9)	156.0, CH	7.60, d (15.6)	7.38, d (15.7)	153.4, CH
8	6.63, dd (15.9, 7.9)	126.4, CH	6.65, dd (15.6, 7.8)	6.61, dd (15.7, 7.7)	126.9, CH
9	9.58, d (7.9)	196.2, CH	9.57, d (7.8)	9.66, d (7.7)	193.6, C
3/5-OMe				3.94, s	56.5, CH_3
4-OMe			3.92, s		

[a] In CD_3OD; [b] In $CDCl_3$.

Table S2.9. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectroscopic data of **34–36** (*J* in Hz, δ in ppm)

position	**34**[a]		**35**[a]		**36**[b]	
	δ_H, multi. (*J* in Hz)	δ_C, type	δ_H, multi. (*J* in Hz)	δ_C, type	δ_H, multi. (*J* in Hz)	δ_C, type
1	6.86, s	100.5, CH		145.7, C		143.9, C
2		148.3, C		152.3, C		149.1, C
3		147.6, C	6.96, d (8.5)	100.8, CH	8.49, d (8.9)	124.8, CH
4	7.31, s	106.3, CH	7.54, d (8.5)	118.9, CH	7.85, d (8.9)	119.7, CH
4a		123.5, C		139.5, C		128.0, C
5		126.9, C		128.4, C		121.5, C
6		131.0, C		131.2, C		140.6, C
8	4.55, dd (8.7, 5.8)	60.1, CH	5.05, dd (11.5, 3.4)	61.1, CH	9.19, s	146.9, CH
8a		123.5, C		123.4, C		123.1, C
9	7.70, d (8.5)	119.6, CH	7.71, d (8.5)	119.9, CH	8.57, d (8.9)	119.5, CH
10	7.50, d (8.5)	124.0, CH	7.48, d (8.5)	124.0, CH	7.99, d (8.9)	124.0, CH
10a		127.2, C		127.5, C		130.3, C
11	7.10, s	104.4, CH	7.10, s	104.5, CH	7.47, s	105.4, CH
12		149.0, C		148.3, C		149.4, C
13		148.7, C		147.7, C		149.4, C
14	7.57, s	110.4, CH	7.51, s	111.7, CH	7.58, s	102.9, CH
14a		123.3, C		123.4, C		130.2, C
8-acetonyl	2.70, dd (15.8, 8.7); 2.32, dd (15.8, 5.8)	48.4, CH_2 208.1, C 31.6, CH_3	2.57, dd (14.5, 11.5); 2.26, dd (14.5, 3.4)	47.0, CH_2 207.7, C 31.2, CH_3		
	1.97, s		2.06, s			
1-OMe			3.96, s	55.1, CH_3	4.12, s	62.0, CH_3
2-OMe	3.93, s	56.1, CH_3	3.92, s	56.0, CH_3		
3-OMe	3.98, s	56.1, CH_3				
-OCH_2O-	6.03, d (1.3); 6.02, d (1.3)	101.1, CH_2	6.04, s	101.2, CH_2	6.14, s	102.3, CH_2
-*N*Me	2.67, s	42.5, CH_3	2.64, s	43.0, CH_3		

[a] In $CDCl_3$; [b] In pyridine-d_6.

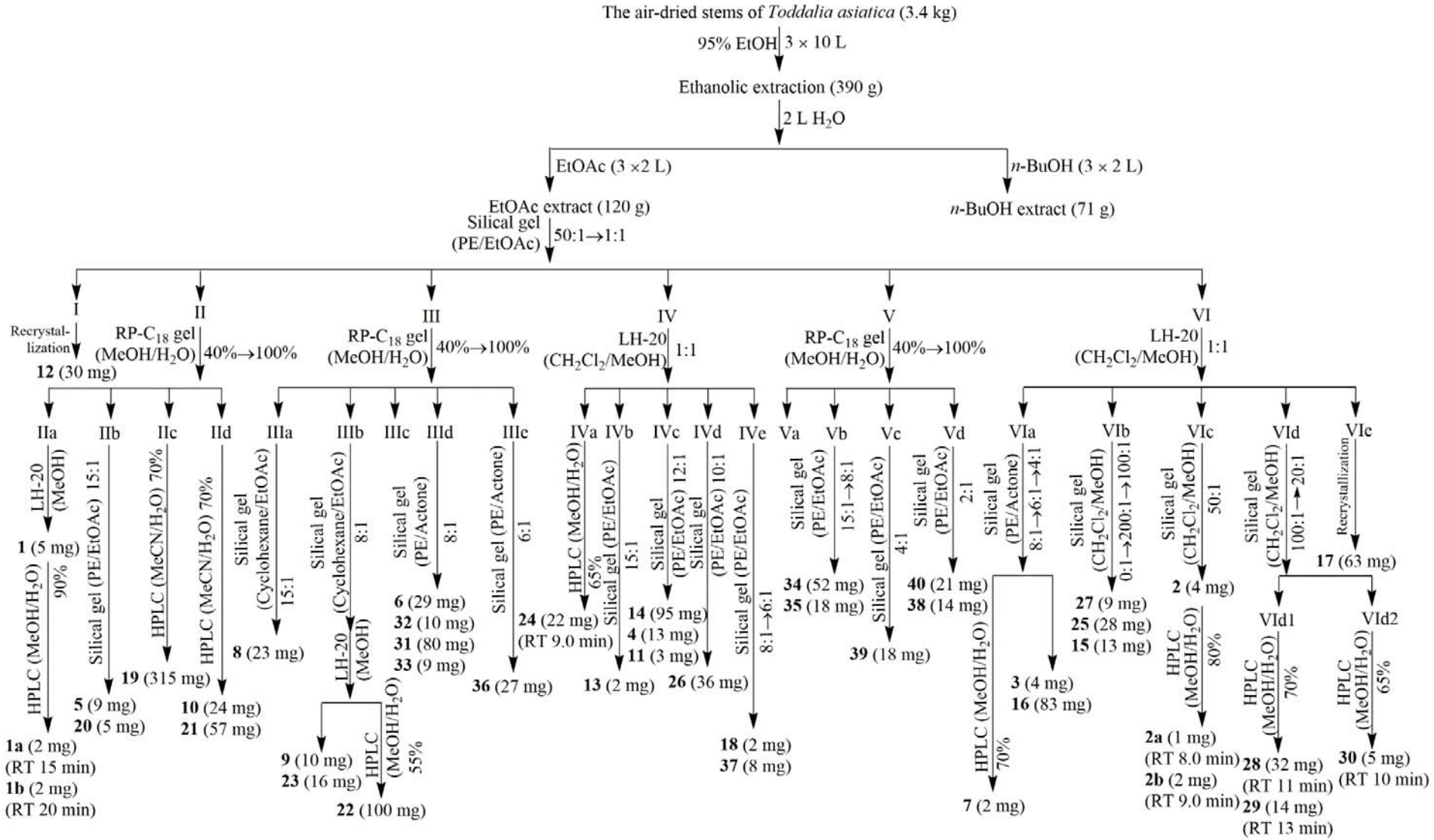
Table S2.10. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectroscopic data of **37–40** in $CDCl_3$ (*J* in Hz, δ in ppm)

position	**37**		**38**		**39**		**40**	
	δ_H, multi. (*J* in Hz)	δ_C, type	δ_H, multi. (*J* in Hz)	δ_C, type	δ_H, multi. (*J* in Hz)	δ_C, type	δ_H, multi. (*J* in Hz)	δ_C, type
2		164.0, C		163.3, C		164.2, C		164.2, C
3	6.03, s	96.6, CH		119.8, C		114.5, C		114.8, C
4		162.8, C		157.0, C		157.6, C		157.6, C
5	7.33, d (8.5)	131.3, CH	7.83, dd (8.6, 1.2)	114.2, CH	7.96, d (9.2)	118.9, CH	7.96, d (9.3)	118.3, CH
6	7.57, t (7.8)	121.8, CH	7.34, dd (8.6, 7.6)	123.5, CH	7.17, d (9.2)	114.7, CH	7.20, d (9.3)	112.1, CH
7	7.22, t (7.6)	123.5, CH	7.04, dd (7.6, 1.2)	107.8, CH		138.7, C		141.8, C
8	7.96, d (7.9)	114.2, CH		154.7, C		140.7, C		141.0, C
9		139.8, C		137.6, C		149.2, C		152.4, C
10		116.6, C		104.0, C		101.8, C		102.1, C
α			7.62, d (2.8)	144.0, CH	7.57, d (2.8)	142.8, CH	7.54, d (2.9)	143.1, CH
β			7.05, d (2.8)	104.6, CH	7.05, d (2.8)	104.9, CH	7.01, d (2.9)	104.8, CH
4-OMe	3.94, s	55.9, CH_3	4.42, s	59.1, CH_3	4.42, s	59.1, CH_3	4.40, s	59.2, CH_3
7-OMe							4.00, s	56.8, CH_3
8-OMe			4.07, s	56.1, CH_3	4.20, s	62.1, CH_3	4.09, s	61.8, CH_3
N-Me	3.66, s	29.0, CH_3						

S3. Experimental and computational section

S3.1. Experimental section Extraction and isolation

See Scheme S3.1.



Scheme S3.1. Flow chart for the isolation of chemical constituents from *Toddalia asiatica*

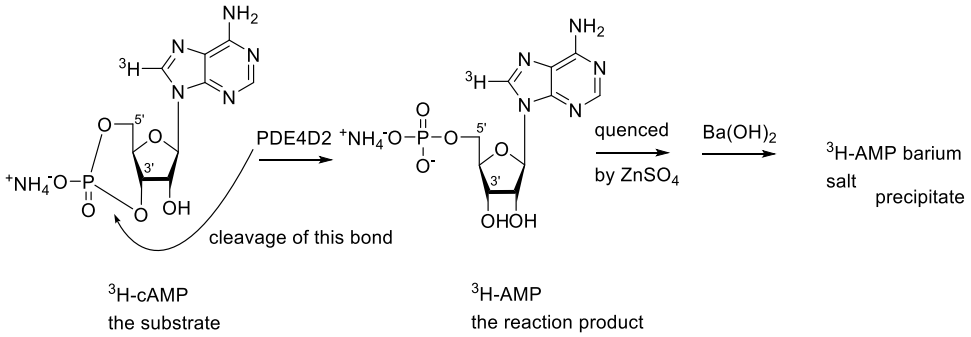
S3.2. Experimental section PDE4D inhibitory screening assays

S3.2.1. Expression and purification of PDE4D2 protein

The cDNAs for expression of human PDE4D2 (catalytic domain, residues 86–413) were subcloned into the expression vector pET15b. All these resultant plasmids were transformed into E. coli strain BL21 (Codonplus) for over expression. The *E. coli* cells carrying these plasmids were grown in LB medium at 37 °C to OD_{600} = 0.7, and then 0.1 mM isopropyl β-D-thiogalactopyranoside was added for further growth at 16 °C for 20–40 h. The recombinant protein was purified by Ni-NTA column (Qiagen). The purity of PDE4D2 protein was greater than 95% as shown by SDS-PAGE. A typical batch of purification yielded over 50 mg of PDE4D2 (catalytic domain) from 1 L cell culture.

S3.2.2. Enzymatic assay.

The enzymatic activities of PDE4D catalytic domain and the inhibition of PDE4D by extracted compounds were assayed by using ^{3}H-cAMP as substrates (20000–30000 cpm/assay) and the reactions were occured in mixture containing 50 mM Tris/HCl (pH 7.5), 10 mM $MgCl_2$, 0.5 mM DTT at room temperature (25 °C) for 15 min. The reactions were terminated by addition of 0.2 M $ZnSO_4$ and $Ba(OH)_2$. The reaction product ^{3}H-AMP was precipitated out, while unreacted ^{3}H-cAMP remained in the supernatant. The mechanism was illustrated as shown below (Scheme S3.2). Radioactivity in the supernatant was measured in 2.5 mL Ultima Gold liquid scintillation cocktails (PerkinElmer) by a PerkinElmer 2910 liquid scintillation counter. Each measurement was repeated at least three times. The IC_{50} values were calculated by nonlinear regression. As a reference compound, rolipram purchased from Sigma was measured its IC_{50} value before other assays.



Scheme S3.2. The mechanism of enzymatic assay

S3.3. Computational section ECD and specific optical rotation calculations

S3.3.1. ECD calculations of compounds 1a/1b and 2a/2b.

The absolute configurations of the two enantiomer pairs **1a/1b** and **2a/2b** were determined by quantum chemical TDDFT calculations of their theoretical ECD spectra. Firstly, geometry of (1′*S*,2′*S*,3′*R*)**-1** was

extracted from the single crystal X-ray data and directly used for further ECD calculation. For (1′*S*,2′*S*,3′*R*)-**2**, conformational analysis was carried out via Monte Carlo searching using molecular mechanism with MMFF94 force field in the Spartan 08 program.[1] In a relative energy window of 0–2 Kcal/mol, the results showed 10 lowest energy conformers (Fig. S4.1). The conformers were then reoptimized using DFT at the B3LYP/6-31+G(d) level in vacuum in the Gaussian 09 program.[2] The B3LYP/6-31+G(d) harmonic vibrational frequencies were further calculated to confirm their stability. In the Gaussian 09 software, the energies, oscillator strengths, and rotational strengths of the first 60 electronic excitations were then calculated using the TDDFT methodology at the B3LYP/6-311++G(2d,2p) level in vacuum. The ECD spectra were simulated by the overlapping Gaussian function (σ = 0.35 eV for (1′*S*,2′*S*,3′*R*)-**1**, 0.20 eV for (1′*S*,2′*S*,3′*R*)-**2**),[3] in which velocity rotatory strengths of the first 24 exited states for (1′*S*,2′*S*,3′*R*)-**1** and the first 8 exited states for (1′*S*,2′*S*,3′*R*)-**2** were adopted. Theoretical ECD spectra for the corresponding enantiomers were obtained by directly reverse the calculated ones.

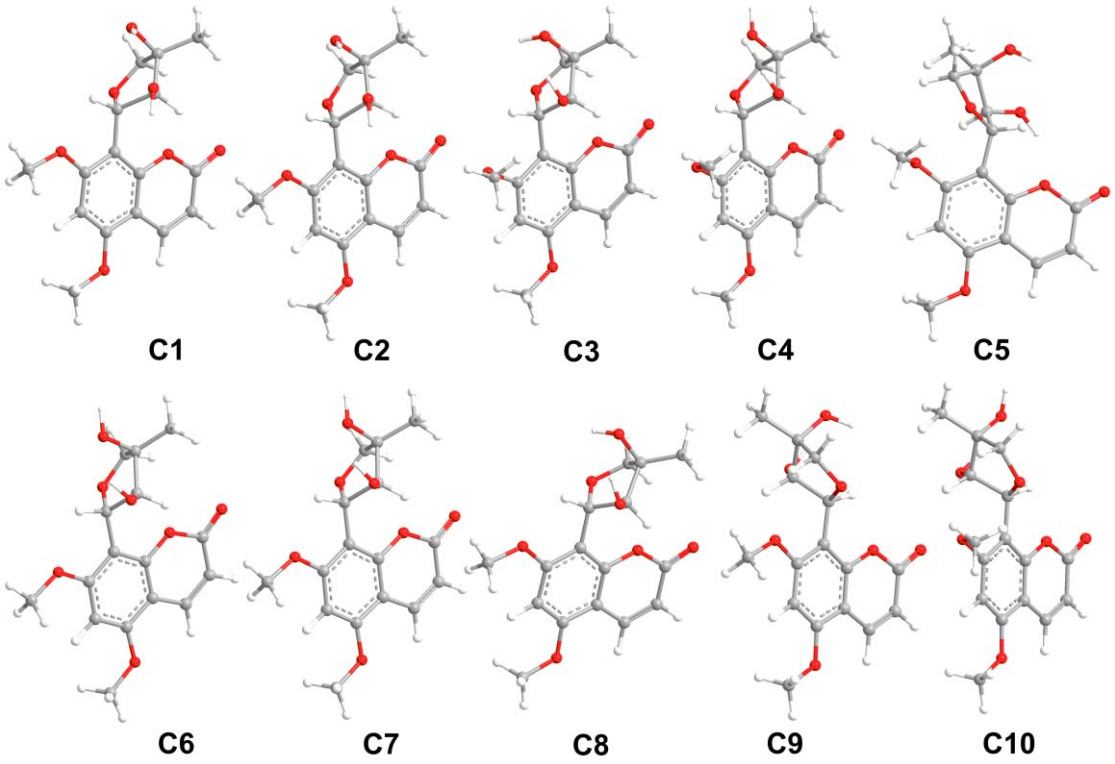


Fig. S4.1. B3LYP/6-311+G(d) optimized lowest energy 3D conformers of (1′*S*,2′*S*,3′*R*)-**2**.

References:

1. *Spartan 04*; Wavefunction Inc.:Irvine, CA.

2. *Gaussian 09*, Revision A.1, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.;

Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

3. Stephens, P. J.; Harada, N. ECD cotton effect approximated by the Gaussian curve and other methods. *Chirality* **2010**, *22*, 229–233.

S3.3.1.1. ECD simulation:

ECD spectrum of each conformation is simulated according to the overlapping Gaussian functions expressed as:

$$\Delta\varepsilon(E)=\frac{1}{2.296\times10^{-39}\sqrt{\pi}\sigma}\sum_{i}^{A}\Delta E_i R_i e^{[-(E-\Delta Ei)^2/\sigma^2]}$$

Where σ is half the bandwidth at 1/e peak height and expressed in energy units. The parameters ΔE_i and R_i are the excitation energies and rotational strengths for the transition i, respectively.

The above function is converted to Δε, λ (wavelength) correlations as:

$$\Delta\varepsilon(\lambda)=\frac{1}{2.296\times10^{-39}\sqrt{\pi}\sigma}\sum_{i}^{A}\Delta E_i R_i e^{[-(1240/\lambda-\Delta Ei)^2/\sigma^2]}$$

and then simulation was accomplished by using the Excel 2003 and the Origin 7.0 software.

To get the final spectra, all the simulated spectra of conformations of each compound were averaged according to their energy and the Boltzmann distribution theory expressed as:

$$\frac{N_i^*}{N}=\frac{g_i e^{-\varepsilon_i/k_BT}}{\sum g_i e^{-\varepsilon_i/k_BT}}$$

S3.3.1.2. Energy analysis for (1′*S*,2′*S*,3′*R*)-2:

conf.	Gibbs free energy (298.15 K)			conf.	Gibbs free energy (298.15 K)		
	G (Hartree)	ΔG (Kcal/mol)	Boltzmann Distribution		G (Hartree)	ΔG (Kcal/mol)	Boltzmann Distribution
C1	-1146.832558	0.606802	0.104	**C6**	-1146.833198	0.205196	0.205
C2	-1146.832557	0.60743	0.104	**C7**	-1146.833194	0.207706	0.204
C3	-1146.831399	1.334086	0.030	**C8**	-1146.833525	0	0.289
C4	-1146.83088	1.659764	0.018	**C9**	-1146.831593	1.212349	0.037
C5	-1146.82963	2.444151	0.005	**C10**	-1146.829691	2.405873	0.005

S3.3.1.3. Calculated ECD data for (1′*S*,2′*S*,3′*R*)-1 X-ray structure:

No	Excitation energies(eV)	Rotatory Strengths*	No	Excitation energies(eV)	Rotatory Strengths*	No	Excitation energies(eV)	Rotatory Strengths*
1	3.7067	2.5637	21	6.0479	11.6477	41	6.6213	1.3237
2	4.1742	19.9063	22	6.0541	-13.9444	42	6.676	3.7782

3	4.3714	-3.5691	23	6.0769	4.7948	43	6.7172	2.3166
4	4.5105	-2.0817	24	6.0924	0.2614	44	6.7247	0.4681
5	4.5318	-1.9576	25	6.1234	-33.8698	45	6.7478	-2.479
6	4.8536	3.3484	26	6.1515	-2.7032	46	6.7702	6.194
7	5.0315	0.4589	27	6.258	2.4915	47	6.7768	-3.1458
8	5.2128	6.0406	28	6.2992	-3.4222	48	6.7937	0.2315
9	5.292	0.0208	29	6.315	6.4559	49	6.8227	-21.5017
10	5.4211	-5.6085	30	6.3722	4.5226	50	6.8445	-16.6135
11	5.4772	14.6515	31	6.3961	-3.1884	51	6.8522	34.1974
12	5.4985	-0.3638	32	6.4048	0.4349	52	6.872	0.0005
13	5.5535	-10.2574	33	6.4395	-2.3141	53	6.9003	-0.3028
14	5.6163	-0.3068	34	6.4554	-0.2532	54	6.9282	0.0833
15	5.6725	2.8844	35	6.4686	-2.9328	55	6.938	-1.698
16	5.775	-6.0008	36	6.4988	-0.9568	56	6.949	-2.4052
17	5.8806	-1.0049	37	6.5377	8.5687	57	6.9553	-2.0742
18	5.9075	1.1876	38	6.5524	1.0871	58	6.983	1.7599
19	5.9344	-1.276	39	6.5943	0.2364	59	7.0021	-2.7786
20	6.0086	40.5267	40	6.6055	-1.8271	60	7.0261	-4.8095

* R(velocity) 10**-40 erg-esu-cm

S3.3.1.4. Calculated ECD data for (1′*S*,2′*S*,3′*R*)-2 structure:

State	C1		C2		C3	
	Excitation energies(eV)	Rotatory Strengths*	Excitation energies(eV)	Rotatory Strengths*	Excitation energies(eV)	Rotatory Strengths*
1	3.7078	4.394	3.7079	4.3681	3.7336	-3.7381
2	4.0721	0.816	4.0722	0.8137	4.1248	-38.6348
3	4.241	-0.0746	4.2411	-0.0776	4.323	2.1085
4	4.5491	-1.4434	4.5491	-1.4394	4.5517	3.6832
5	4.796	-16.6292	4.7962	-16.581	4.8607	0.3209
6	4.8675	7.4354	4.8676	7.4209	5.0422	-8.2073
7	4.9303	-0.5061	4.9302	-0.5134	5.1819	5.6209
8	5.1051	-3.918	5.1051	-3.8952	5.3076	-1.611
9	5.1704	2.7825	5.1709	2.7677	5.4394	-9.8737
10	5.2019	-1.0395	5.2022	-1.0984	5.5855	-1.5293
11	5.307	-4.8133	5.3071	-4.7905	5.6003	-0.2631
12	5.3891	19.3662	5.3891	19.4315	5.6658	-25.6994
13	5.4801	-5.52	5.4803	-5.6054	5.6756	6.0741
14	5.5445	-15.4188	5.5445	-15.4213	5.6916	-3.0596
15	5.6081	14.7973	5.6083	14.759	5.7284	-6.5104
16	5.6682	-11.4741	5.6685	-11.4095	5.7787	19.6138
17	5.6975	7.5719	5.6976	7.4651	5.9435	-0.5224
18	5.737	-16.8969	5.7373	-16.8024	5.9699	2.3561
19	5.8455	1.7923	5.8442	1.7824	6.0155	4.7493
20	5.8601	-4.9011	5.8602	-4.9689	6.0359	1.3252
21	5.9191	-36.4767	5.9193	-36.195	6.0491	-15.8535
22	5.9285	6.0534	5.9285	5.811	6.0776	8.9783

23	5.9515	14.4251	5.9517	14.4367	6.089	4.0268
24	5.9726	-7.3544	5.973	-7.2674	6.2083	3.402
25	6.0361	-0.6015	6.0361	-0.5959	6.2374	-9.1388
26	6.0577	12.6017	6.0575	12.3405	6.2497	2.1771
27	6.0744	10.1564	6.0743	10.3517	6.2799	14.5538
28	6.1263	-20.0248	6.1264	-19.9978	6.2948	-2.5113
29	6.1758	3.6438	6.1761	3.6844	6.3127	11.5758
30	6.2171	12.3233	6.2176	12.4982	6.3357	-2.5014
31	6.2241	-3.0485	6.2244	-3.1998	6.4514	-12.5162
32	6.2347	0.3466	6.2347	0.3406	6.4635	7.2236
33	6.26	20.7578	6.2601	20.4356	6.4819	1.0341
34	6.2722	-5.2625	6.2723	-5.1587	6.4891	-13.8615
35	6.3632	3.0738	6.3633	3.1158	6.5037	6.7488
36	6.4035	7.7916	6.4036	7.7186	6.536	0.8232
37	6.4367	-1.2104	6.4369	-1.1968	6.5591	5.5103
38	6.4507	15.1876	6.4509	15.0887	6.5712	-6.1086
39	6.4732	0.5946	6.4735	0.6901	6.5891	6.9782
40	6.4835	3.9205	6.4837	3.913	6.6087	-2.2937
41	6.4967	-2.0078	6.497	-2.0534	6.6441	18.0535
42	6.5134	-3.2344	6.5135	-3.2422	6.6659	0.2479
43	6.5728	5.8997	6.5732	5.9291	6.68	23.3526
44	6.5981	-0.2783	6.5981	-0.2924	6.7183	4.5225
45	6.6228	6.4836	6.6229	6.3049	6.7365	-6.9888
46	6.6465	26.5772	6.6466	26.6468	6.7644	10.2845
47	6.6742	2.5702	6.6744	3.643	6.782	-4.1049
48	6.6794	-33.9351	6.6795	-36.8024	6.7892	-2.9083
49	6.6809	15.6216	6.681	18.4612	6.8167	4.6995
50	6.6944	11.5258	6.6944	11.0755	6.8526	11.9254
51	6.7042	-5.1946	6.7042	-5.4948	6.865	3.7756
52	6.7306	-7.5448	6.7306	-7.5173	6.8684	-3.5595
53	6.7563	-8.0985	6.7565	-8.268	6.9307	-3.5026
54	6.7739	-13.5214	6.7741	-13.3926	6.9468	-9.0557
55	6.7961	-9.2939	6.7962	-9.3263	6.9698	-5.7051
56	6.8041	1.7911	6.8042	1.914	6.9885	3.5014
57	6.8054	-5.2389	6.8054	-5.3037	6.9915	-1.0122
58	6.8267	-1.2532	6.8267	-1.2662	7.0302	3.7536
59	6.8391	6.3465	6.8393	6.3029	7.045	3.5283
60	6.8875	1.6126	6.888	1.5841	7.0703	-1.3416

* R(velocity) 10**-40 erg-esu-cm

State	**C4**		**C5**		**C6**	
	Excitation energies(eV)	Rotatory Strengths*	Excitation energies(eV)	Rotatory Strengths*	Excitation energies(eV)	Rotatory Strengths*
1	3.7085	-3.514	3.651	2.4267	3.6742	1.33
2	4.119	-32.9258	4.0673	-37.446	4.0915	-1.8159
3	4.2306	-1.7278	4.267	7.6891	4.3142	-0.9275

4	4.5404	3.2231	4.5629	11.233	4.5762	-0.7898
5	4.8802	-7.0961	4.7512	2.4781	4.7904	-10.5902
6	5.0315	5.6521	4.9747	12.2661	4.8576	-0.0359
7	5.1473	0.785	5.0807	-6.2038	4.9376	5.8627
8	5.2672	-7.6002	5.1273	-0.1227	5.2256	-10.701
9	5.3474	3.8388	5.274	3.5851	5.3108	15.8048
10	5.4711	3.2639	5.3716	3.2415	5.3437	-3.6773
11	5.5486	-4.1242	5.5452	-4.5514	5.3564	1.934
12	5.555	0.0619	5.5538	17.8064	5.4646	1.1741
13	5.5607	-4.2763	5.604	-8.6202	5.5394	2.2238
14	5.6636	-20.4122	5.6333	29.0246	5.5544	9.2564
15	5.6764	2.8055	5.7023	-36.4165	5.5708	-15.2823
16	5.7363	29.9101	5.7938	-2.5371	5.6919	17.747
17	5.7684	-3.8714	5.8408	14.2133	5.7432	-0.9154
18	5.8616	-33.9866	5.9329	-8.2211	5.7932	-5.5338
19	5.8999	0.1087	5.9697	-3.7557	5.8214	-6.0716
20	5.9327	-9.4468	6.0464	1.911	5.8322	3.6219
21	5.9615	15.9279	6.0741	-0.0558	5.8888	-10.749
22	6.0688	15.8947	6.1006	25.8871	5.8995	-38.6668
23	6.0743	17.2106	6.129	12.976	5.9385	5.5336
24	6.0889	-19.7726	6.1573	-3.581	5.9564	-18.562
25	6.1586	2.4086	6.1926	1.3399	6.0639	-11.3635
26	6.1988	-0.0495	6.236	-5.2848	6.0871	35.0178
27	6.2278	-5.0773	6.2636	-1.2257	6.127	7.4273
28	6.2446	-0.1346	6.3241	-1.7726	6.1405	-3.327
29	6.3036	-27.817	6.3466	-4.178	6.166	-9.3266
30	6.3152	0.2213	6.3963	6.5885	6.2213	-6.7139
31	6.3512	3.6166	6.4057	-18.3005	6.2605	-4.3412
32	6.4135	-1.8313	6.4246	4.7365	6.269	15.2972
33	6.4235	-7.7322	6.4639	1.2077	6.2948	-11.1205
34	6.4478	13.9014	6.4899	-5.4674	6.3017	0.253
35	6.4557	5.1389	6.5068	-5.8346	6.3261	4.1266
36	6.4798	0.8625	6.5259	-11.1897	6.3872	2.8931
37	6.5029	-1.2888	6.55	-7.0257	6.3913	10.6113
38	6.5189	2.3526	6.57	-7.6863	6.4185	-2.6096
39	6.5377	0.1776	6.6006	-6.9598	6.4453	-1.7223
40	6.5919	1.8561	6.6335	-0.8938	6.4752	1.5474
41	6.5956	5.7283	6.65	1.8051	6.5693	-1.3428
42	6.5996	-4.1	6.6556	14.7775	6.5988	8.2449
43	6.6473	0.58	6.6866	-7.3623	6.6072	6.4936
44	6.6519	30.6208	6.6956	17.0798	6.6148	-2.992
45	6.6708	17.3161	6.7219	18.3212	6.6238	-2.757
46	6.6908	12.2862	6.7258	17.3413	6.6405	3.6799
47	6.7016	-20.3669	6.7458	7.6969	6.6669	7.7919
48	6.7256	2.2887	6.7777	8.9954	6.6837	2.7743
49	6.7417	20.4269	6.7947	-4.0492	6.6889	-28.2587

50	6.7802	3.6266	6.826	1.117	6.7066	12.957
51	6.7957	-2.0403	6.8567	-0.5831	6.7327	-0.3001
52	6.8205	-1.1446	6.8758	2.2734	6.7413	10.8422
53	6.8444	-0.3642	6.8937	-7.7457	6.7556	-9.6125
54	6.877	-3.6255	6.9016	-13.0431	6.7696	1.1753
55	6.8808	0.1507	6.9317	-3.5005	6.7862	-0.9209
56	6.8872	2.2675	6.9378	6.1446	6.7914	3.2843
57	6.8949	3.0842	6.961	-5.6298	6.8131	4.176
58	6.9037	-1.7329	6.9742	-4.776	6.8162	-3.7466
59	6.9403	-1.0293	6.9769	-4.8891	6.8419	-0.7496
60	6.9443	-8.9045	6.9838	-0.0441	6.8704	0.36

* R(velocity) 10**-40 erg-esu-cm

State	**C7**		**C8**		**C9**	
	Excitation energies(eV)	Rotatory Strengths*	Excitation energies(eV)	Rotatory Strengths*	Excitation energies(eV)	Rotatory Strengths*
1	3.674	1.2733	3.6968	-0.0046	3.7835	-5.0144
2	4.0915	-1.7938	4.1101	-2.1346	4.1429	7.419
3	4.3139	-0.9437	4.3779	-1.3072	4.5053	3.5508
4	4.5763	-0.7933	4.5854	0.1539	4.6152	-1.4061
5	4.7902	-10.5854	4.7756	-8.4816	4.8531	1.0048
6	4.8577	-0.0371	4.9022	-0.1311	4.8722	-0.2378
7	4.9376	5.8782	4.9551	2.4261	5.047	-2.3826
8	5.2259	-10.7481	5.3467	-2.3555	5.2974	-11.7288
9	5.3107	15.8878	5.3649	-0.4509	5.3344	6.3912
10	5.3438	-3.6692	5.4067	-1.7689	5.3433	7.7194
11	5.3566	1.9346	5.4292	2.324	5.3693	-5.4594
12	5.4646	1.1993	5.5053	9.9094	5.5726	5.6256
13	5.5391	2.1428	5.5576	-11.5183	5.745	-5.2635
14	5.5543	9.4913	5.6641	-0.3129	5.7573	-6.5827
15	5.5706	-15.4471	5.7452	1.0206	5.7763	22.1753
16	5.6922	17.7148	5.7516	-3.4459	5.8078	12.0983
17	5.7432	-0.8789	5.8561	-1.4755	5.8251	3.8935
18	5.7932	-5.5453	5.8643	-7.4749	5.8438	-17.763
19	5.8214	-6.0596	5.8865	1.1675	5.8595	-3.0495
20	5.8323	3.6155	5.9221	14.4445	5.8777	-1.3401
21	5.8888	-10.9846	5.9348	-25.5283	5.8815	-3.0902
22	5.8994	-38.4529	5.9598	-1.4342	5.9557	-12.3327
23	5.9386	5.5182	5.9897	-1.9213	5.9615	-4.8421
24	5.9563	-18.4333	6.0614	2.8907	6.0916	-12.9527
25	6.0641	-11.2654	6.09	-3.4974	6.1383	-8.575
26	6.0869	34.5643	6.1415	7.191	6.1505	8.3401
27	6.1272	7.4332	6.2107	-4.935	6.1845	7.6998
28	6.1408	-3.1144	6.2442	-1.8069	6.2281	3.1352
29	6.1661	-9.326	6.2631	3.4389	6.2414	-0.0488
30	6.2214	-6.5228	6.2755	9.7057	6.2528	10.7459
31	6.2601	-4.6921	6.2803	-0.1994	6.2965	-5.2493

32	6.269	15.5603	6.3034	3.452	6.3119	2.9344
33	6.2949	-11.1101	6.3715	0.9883	6.3313	-12.2065
34	6.3016	0.2517	6.3875	-0.32	6.3678	19.1166
35	6.3263	4.1125	6.4403	4.7041	6.4172	-3.3785
36	6.3874	3.0171	6.4522	-1.0608	6.4498	-2.2225
37	6.3917	10.4052	6.4568	0.5514	6.4618	-4.6214
38	6.4187	-2.6794	6.4762	-2.8899	6.5033	-6.5416
39	6.4452	-1.728	6.5341	5.4368	6.5406	3.6696
40	6.4752	1.5431	6.5892	3.3239	6.5472	1.7679
41	6.5697	-1.3475	6.6095	-0.7132	6.5604	2.8413
42	6.5987	8.1979	6.6228	0.3253	6.5879	-2.0421
43	6.6073	6.5149	6.6561	11.5181	6.5989	-9.4611
44	6.6149	-3.0353	6.6689	-5.3599	6.6474	2.2881
45	6.6237	-2.6655	6.6868	5.8695	6.6648	6.1744
46	6.6406	3.6234	6.7056	-11.9277	6.6847	16.3658
47	6.6672	7.8865	6.7143	3.0825	6.6996	5.6125
48	6.6839	2.8098	6.7182	-2.3973	6.7412	-4.1255
49	6.689	-28.4353	6.7228	-5.0768	6.749	-1.4578
50	6.7067	13.1062	6.742	8.7366	6.7577	0.5078
51	6.7328	-0.2248	6.7684	-7.9434	6.7641	-2.9181
52	6.7412	10.6731	6.8017	-6.2782	6.779	-3.7721
53	6.7557	-9.6453	6.8157	2.0868	6.799	-26.2174
54	6.7697	1.1427	6.834	-2.882	6.8057	0.7117
55	6.7863	-0.8998	6.8683	4.1985	6.8167	14.4147
56	6.7914	3.2116	6.8859	0.4595	6.8279	-1.1104
57	6.8132	4.2172	6.913	3.498	6.8392	0.6053
58	6.8161	-3.7476	6.9238	-2.6751	6.9325	1.0631
59	6.8416	-0.7531	6.9388	-1.885	6.9522	-0.8896
60	6.8703	0.3371	6.9424	2.387	6.9538	-4.3608

* R(velocity) 10**-40 erg-esu-cm

State	C10		State	C10		State	C10	
	Excitation energies(eV)	Rotatory Strengths*		Excitation energies(eV)	Rotatory Strengths*		Excitation energies(eV)	Rotatory Strengths*
1	3.7832	-6.6279	21	5.9954	-6.8559	41	6.5353	1.6353
2	4.1065	-32.2884	22	6.0152	2.937	42	6.5455	-17.8715
3	4.4515	8.439	23	6.049	-0.5421	43	6.5575	-21.3085
4	4.5448	-1.5183	24	6.0699	-2.5362	44	6.5736	17.1805
5	4.8947	11.8693	25	6.114	-8.5292	45	6.6098	3.8193
6	5.033	-5.646	26	6.1372	-15.0706	46	6.653	10.9954
7	5.1451	8.5075	27	6.1734	19.5254	47	6.6643	13.3092
8	5.2599	-7.4555	28	6.2019	1.1148	48	6.675	-5.3773
9	5.3097	2.744	29	6.2357	34.5311	49	6.6824	-5.9971
10	5.4246	4.1922	30	6.2567	11.0613	50	6.7194	5.6066
11	5.4583	27.3623	31	6.2825	-0.2045	51	6.7328	12.4773
12	5.5353	1.0681	32	6.3267	-6.9227	52	6.7697	-2.2747
13	5.5763	-9.1966	33	6.3492	34.654	53	6.7882	3.0537

14	5.6753	1.268	34	6.4326	13.8592	54	6.7951	0.4872
15	5.6896	-0.1374	35	6.4497	-4.9857	55	6.8268	-22.6842
16	5.7285	-15.1158	36	6.4623	6.8797	56	6.8361	2.92
17	5.7722	8.7631	37	6.4746	0.4383	57	6.855	-1.3648
18	5.8483	-37.4964	38	6.4849	1.4234	58	6.8947	-6.7773
19	5.8707	-6.4321	39	6.5019	-2.0376	59	6.904	-2.821
20	5.9093	-5.483	40	6.5251	-12.3264	60	6.9075	9.4004

* R(velocity) 10**-40 erg-esu-cm

S3.3.2 Specific optical rotation calculation.

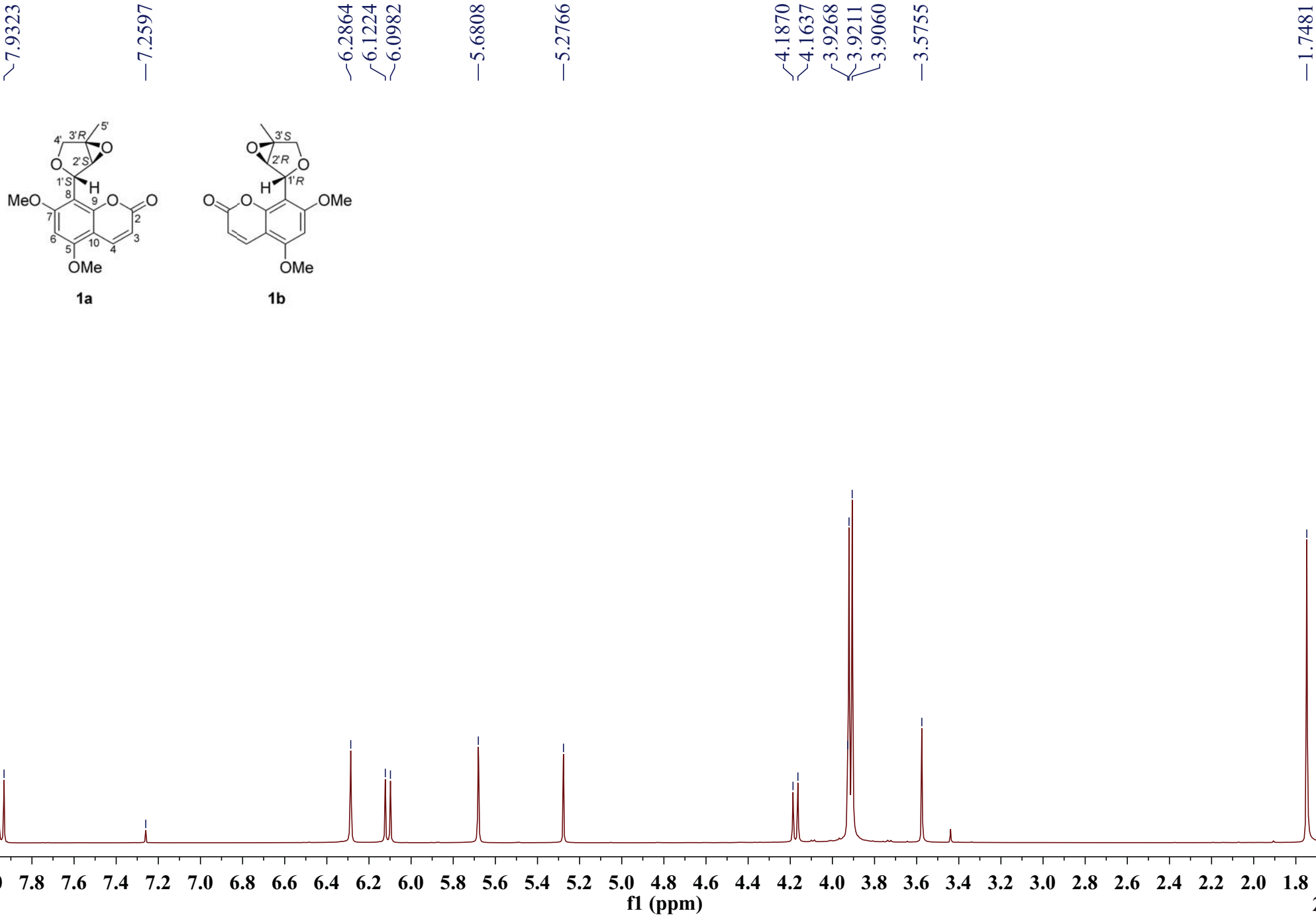
Specific optical rotation for (1′*S*,2′*S*,3′*R*)-**1** was calculated on B3LYP/aug-cc-pVDZ level based on the X-ray geometry. Specific optical rotation for (1′*S*,2′*S*,3′*R*)-**2** was calculated on B3LYP/aug-cc-pVDZ//B3LYP/6-31+G(d) level.

Compound	Specific optical rotation value	Compound	Specific optical rotation value
(1′*S*,2′*S*,3′*R*)-**1**	+95	(1′*S*,2′*S*,3′*R*)-**2**	–117
1a	+61	**2a**	+116
1b	–61	**2b**	–116

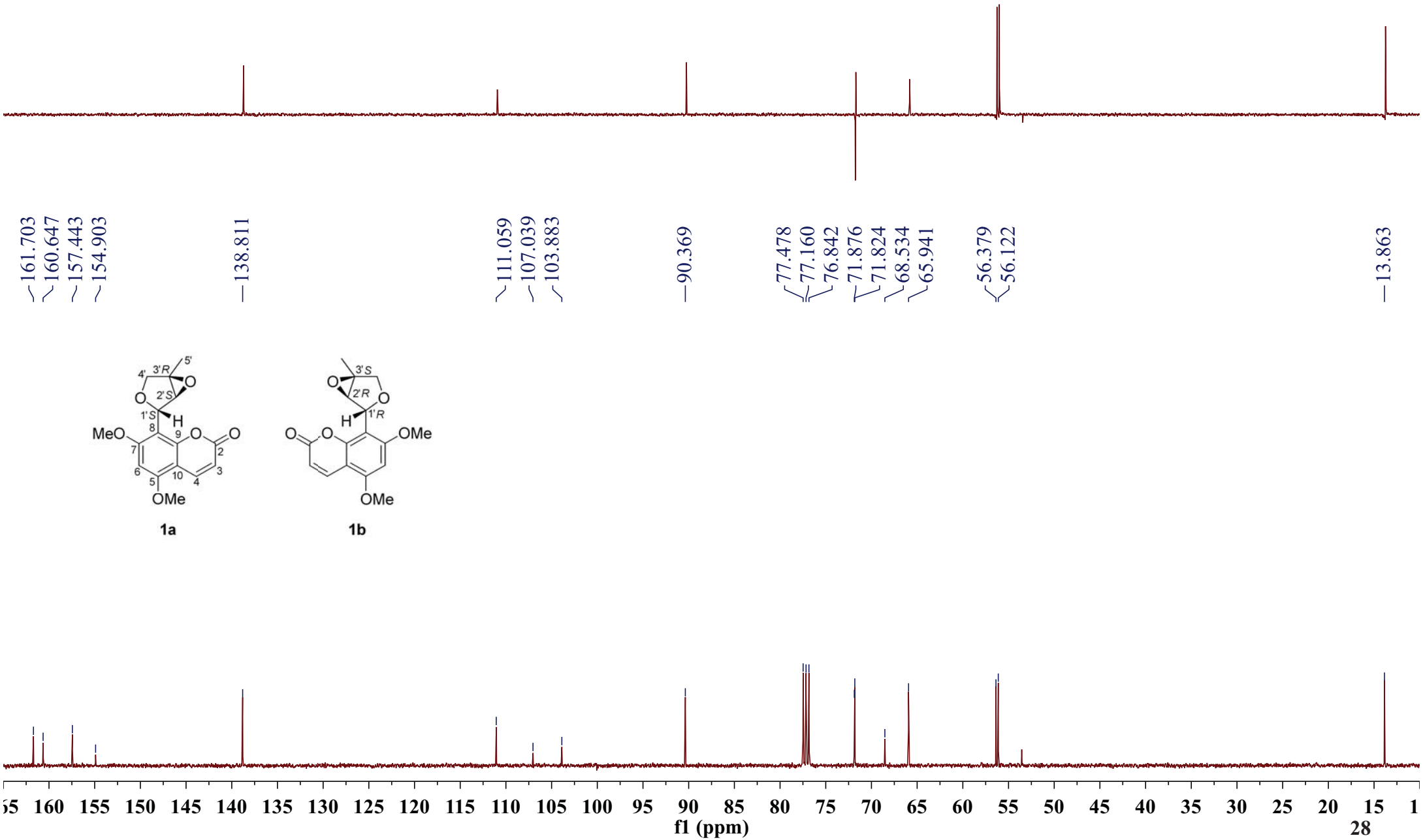
S3.3.2.1 Specific optical rotation values of conformers of (1′*S*,2′*S*,3′*R*)-2

Conf.	Boltzmann Distribution	Specific optical rotation	Conformationally averaged
C1	0.104	–42.15	–116.975
C2	0.104	–42.46	
C3	0.030	–255.87	
C4	0.018	–251.54	
C5	0.005	–5.18	
C6	0.205	–131.37	
C7	0.204	–131.71	
C8	0.289	–134.88	
C9	0.037	–67.71	
C10	0.005	–132.05	

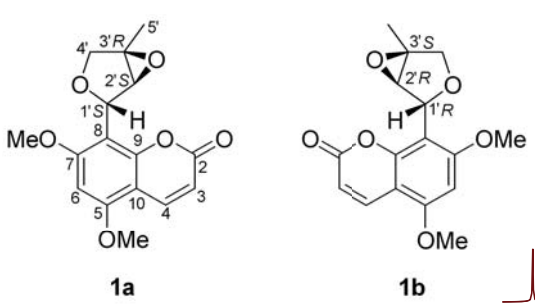
S4.1. ^{1}H NMR spectrum of compound **1**



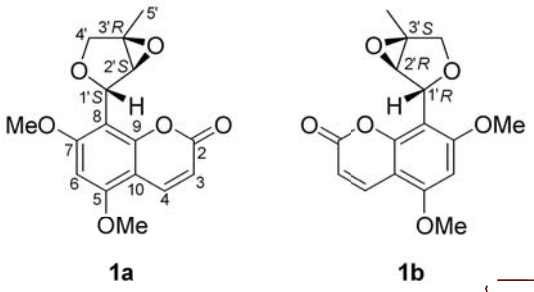
S4.2. ^{13}CNMR and DEPT spectra of compound **1**



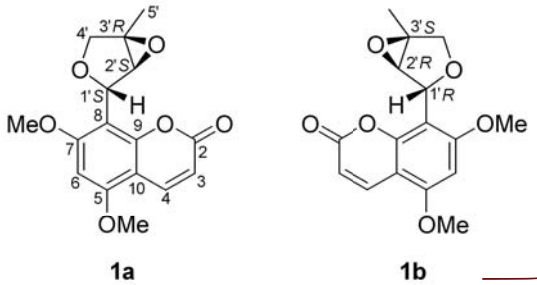
S4.3. HSQC spectrum of compound **1**



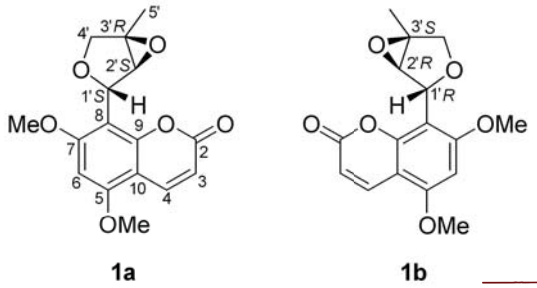
S4.4. ^{1}H-^{1}H COSY spectrum of compound **1**



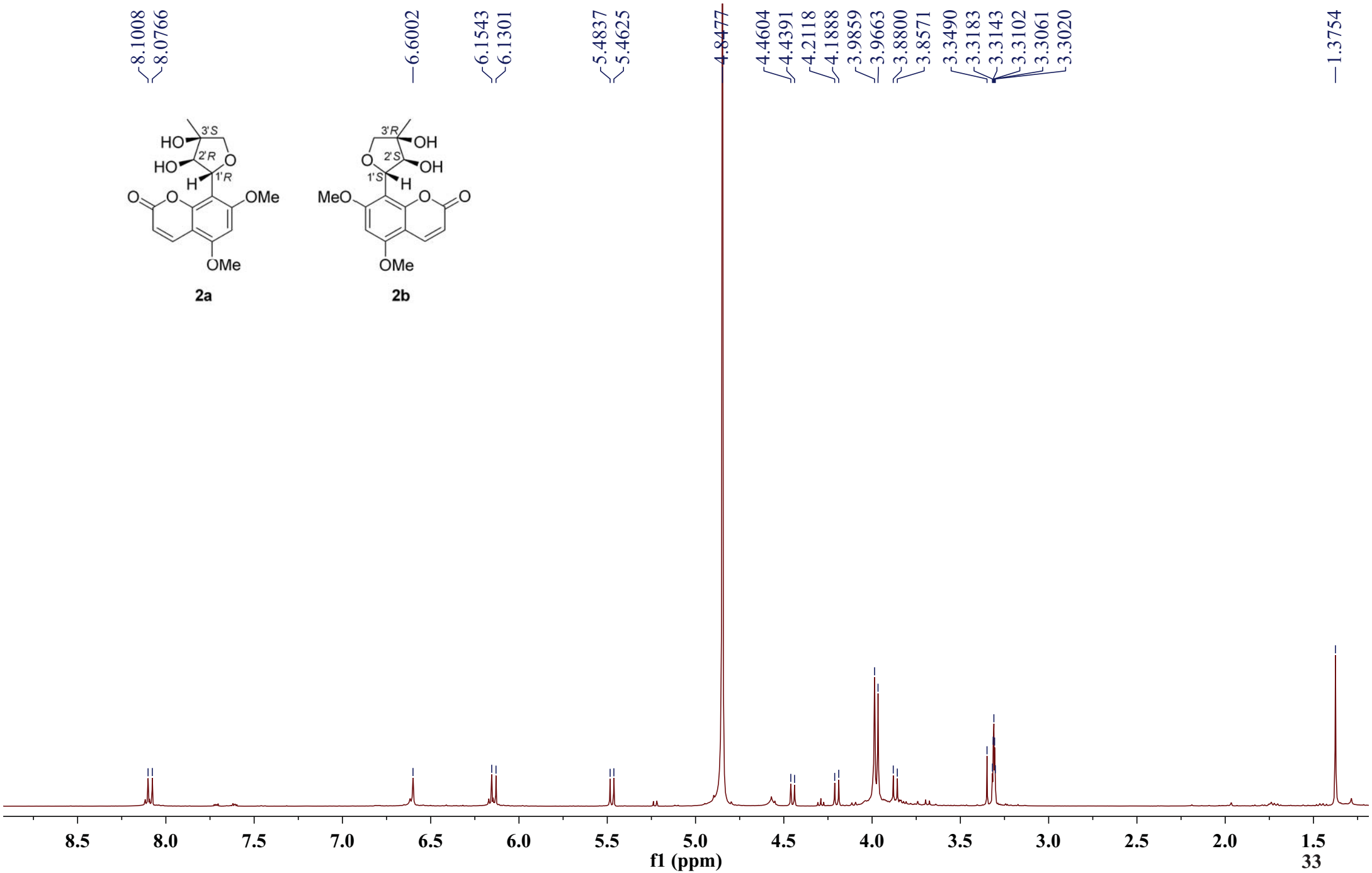
S4.5. HMBC spectrum of compound **1**



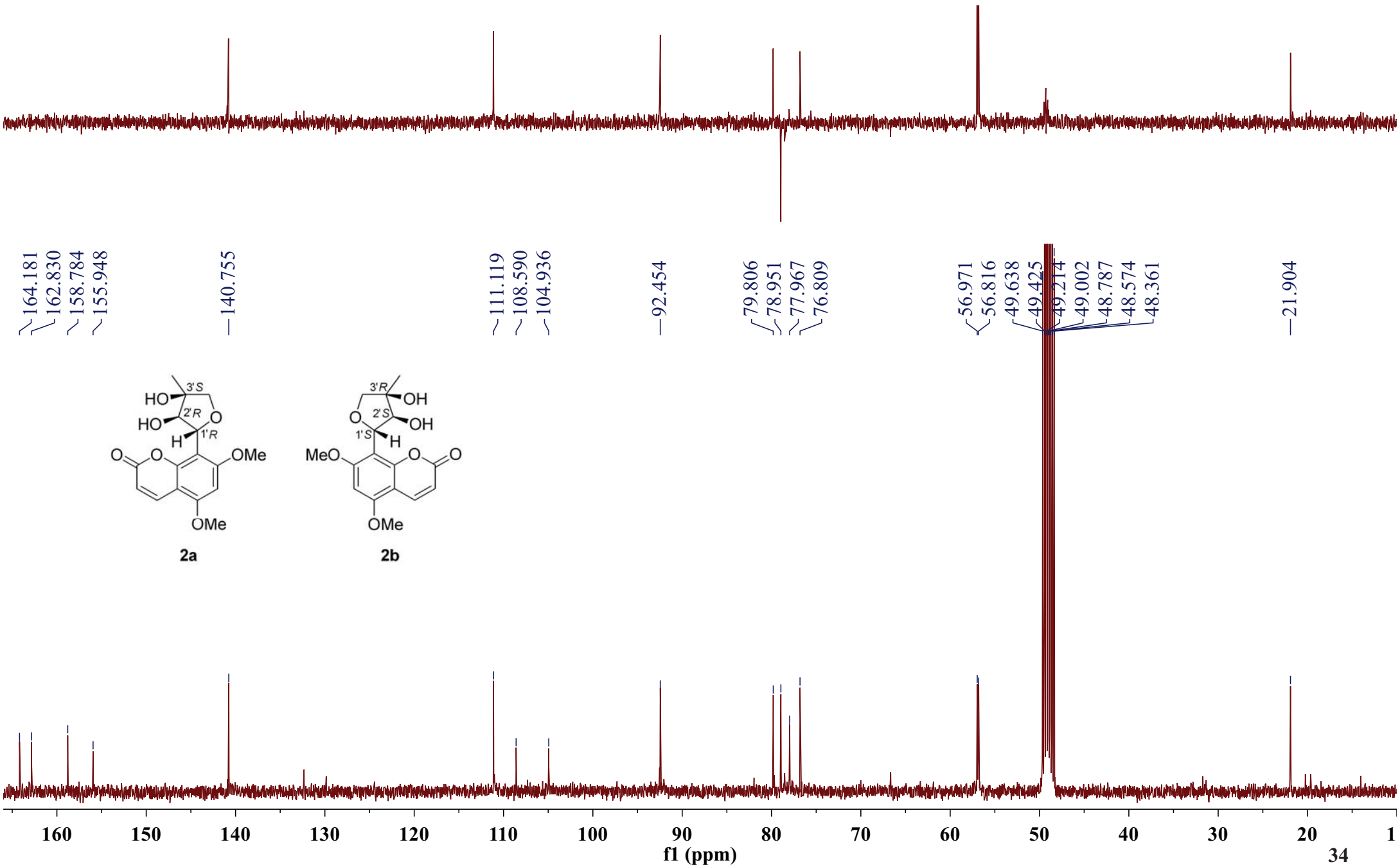
S4.6. NOESY spectrum of compound **1**



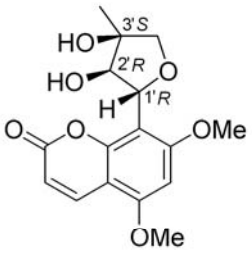
S4.7. ^{1}H NMR spectrum of compound **2**



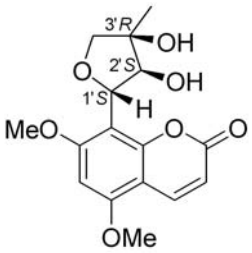
S4.8. ^{13}C NMR and DEPT spectra of compound **2**



S4.9. HSQC spectrum of compound **2**

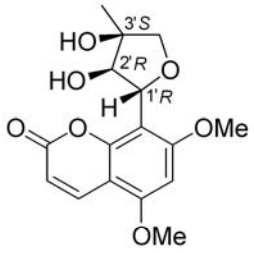


2a

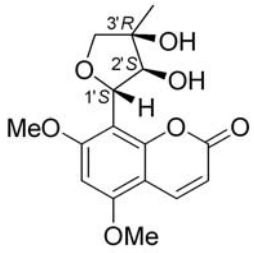


2b

S4.10. ^{1}H-^{1}H COSY spectrum of compound **2**

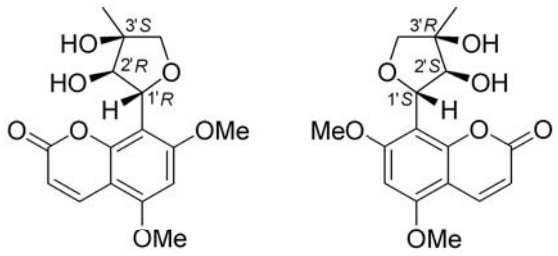


2a



2b

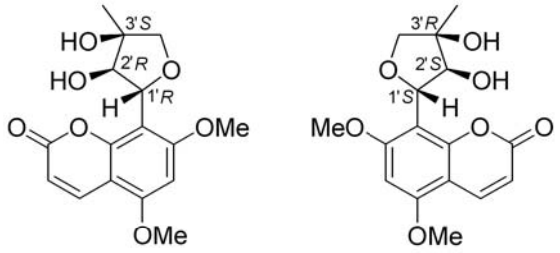
S4.11. HMBC spectrum of compound **2**



2a

2b

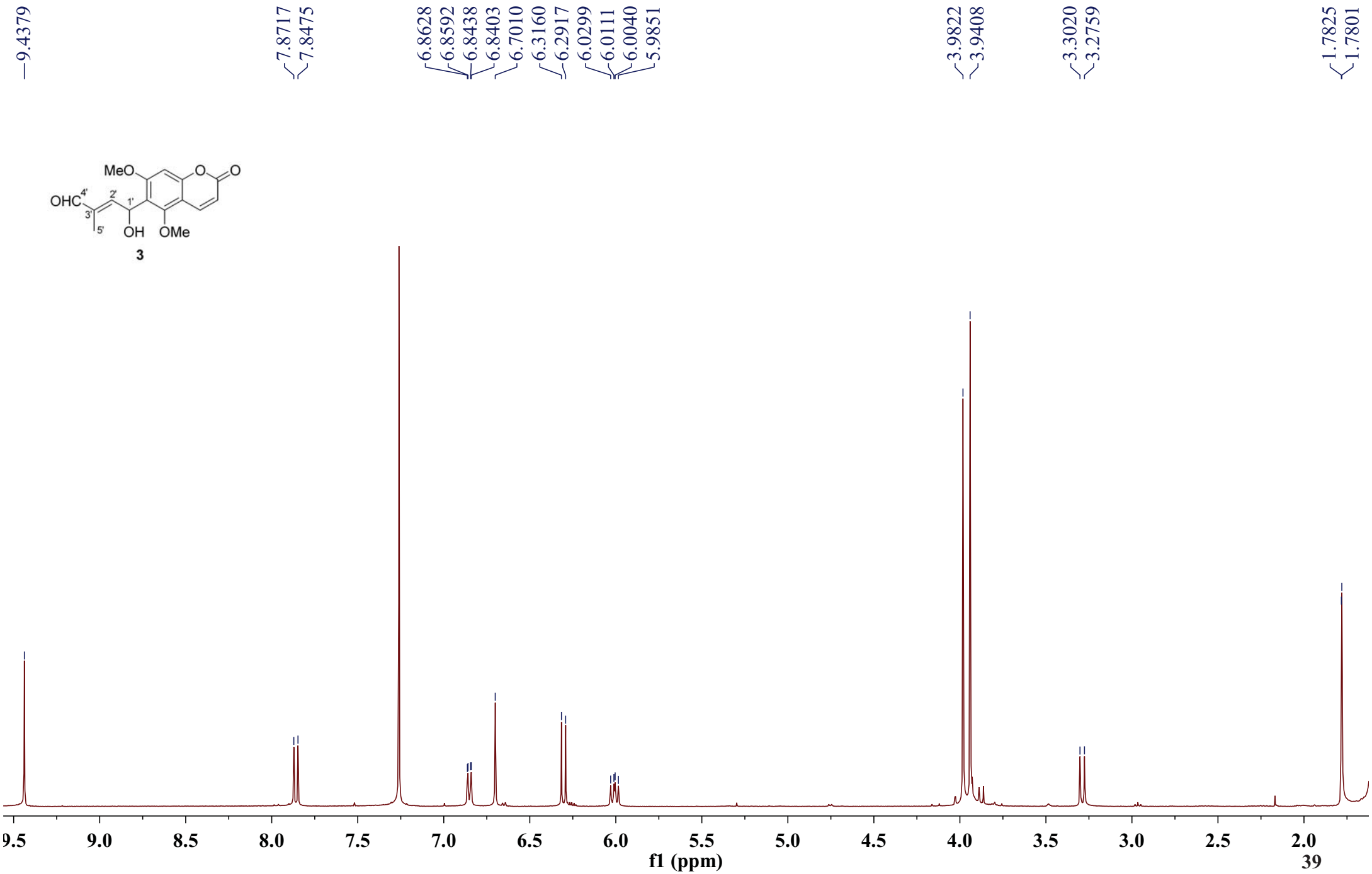
S4.12. NOESY spectrum of compound **2**



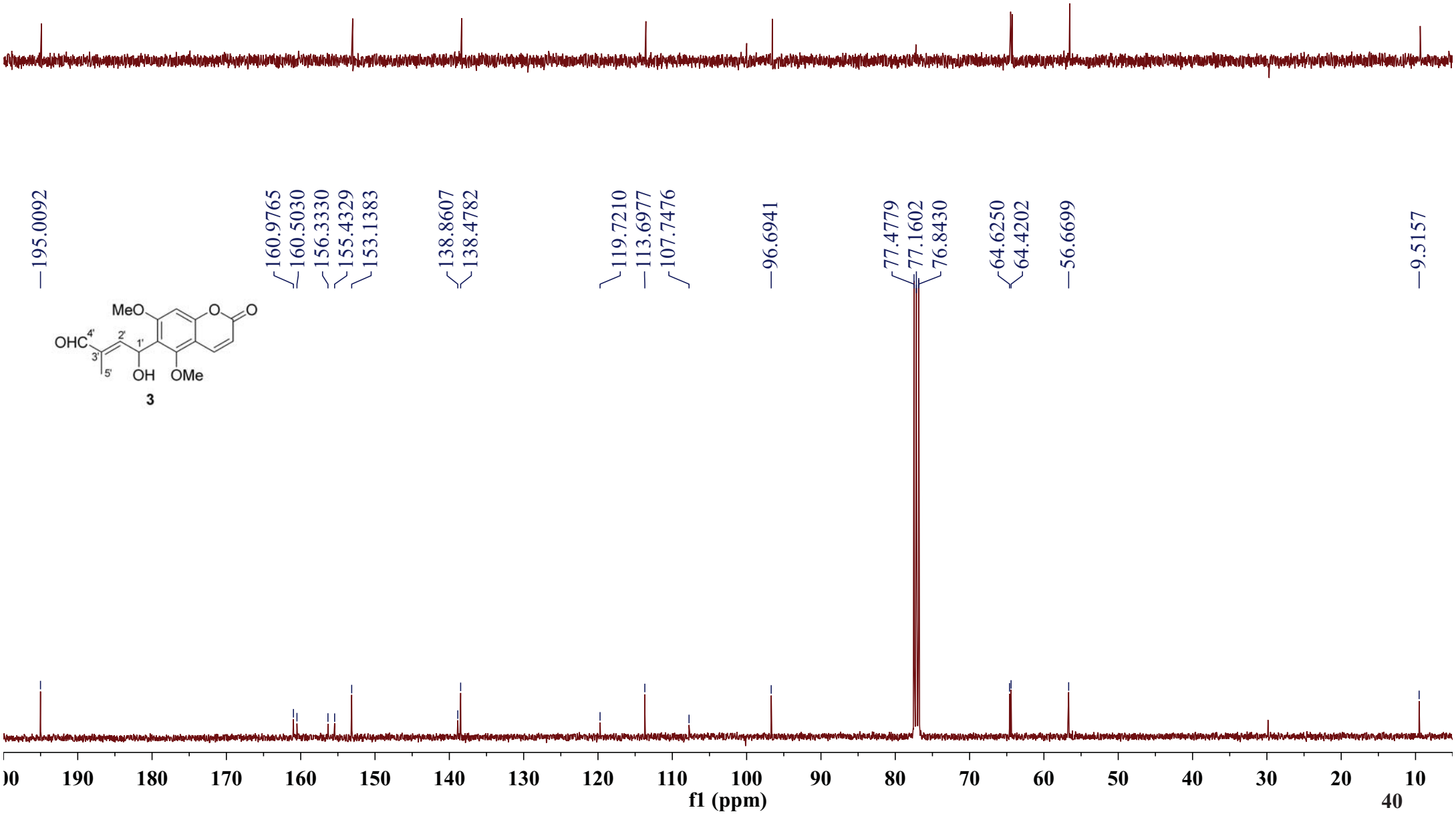
2a

2b

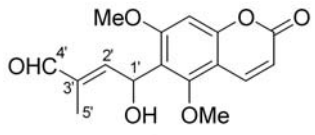
S4.13. ^{1}H NMR spectrum of compound **3**



S4.14. ^{13}C NMR and DEPT spectra of compound **3**

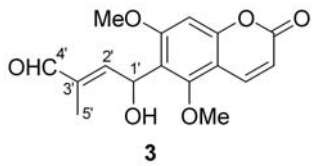


S4.15. HSQC spectrum of compound **3**



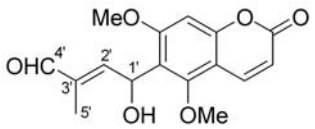
3

S4.16. ^{1}H-^{1}H COSY spectrum of compound **3**



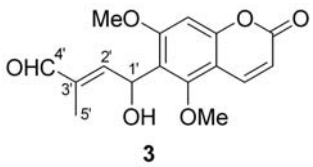
3

S4.17. HMBC spectrum of compound **3**



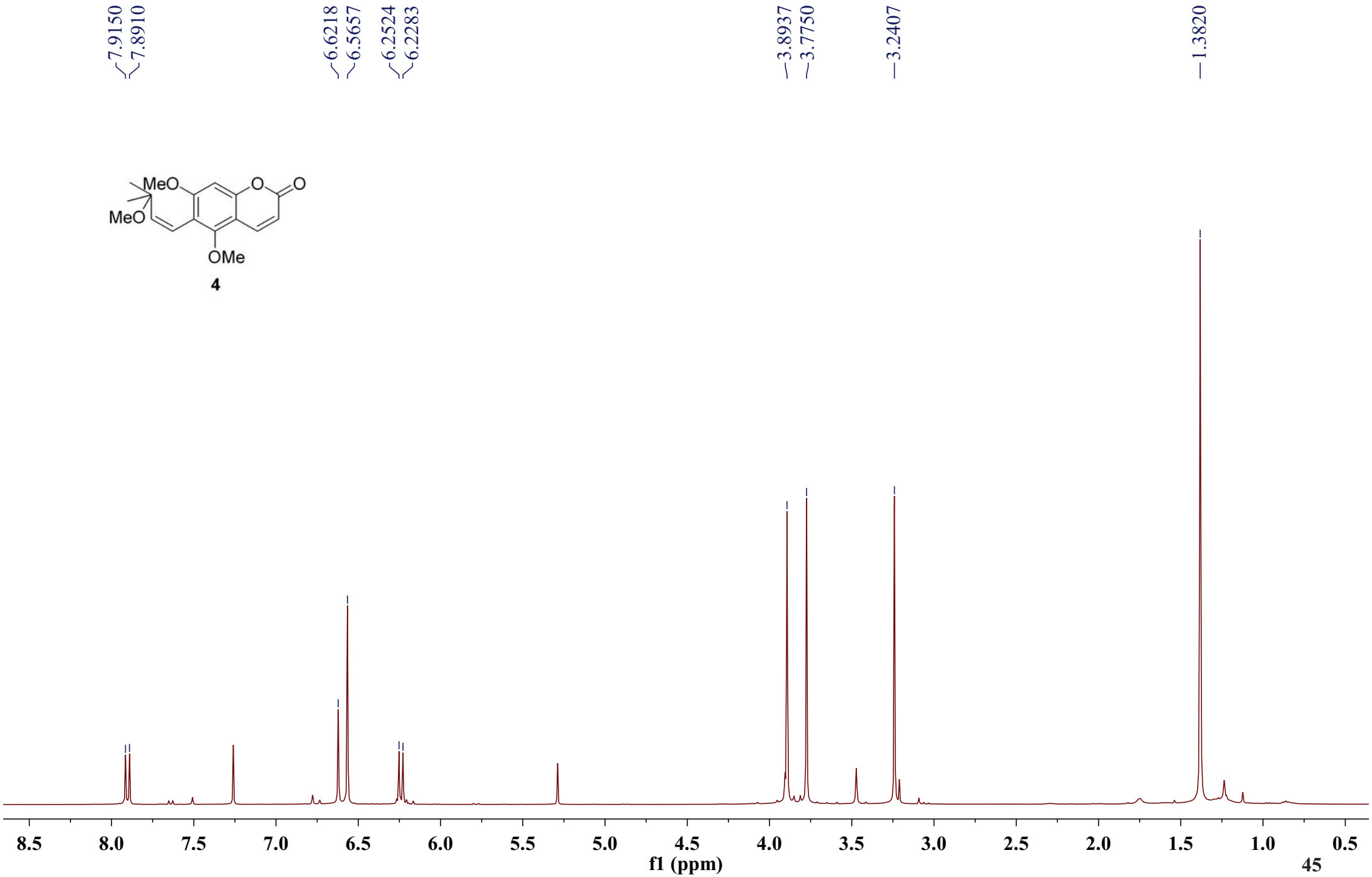
3

S4.18. NOESY spectrum of compound **3**

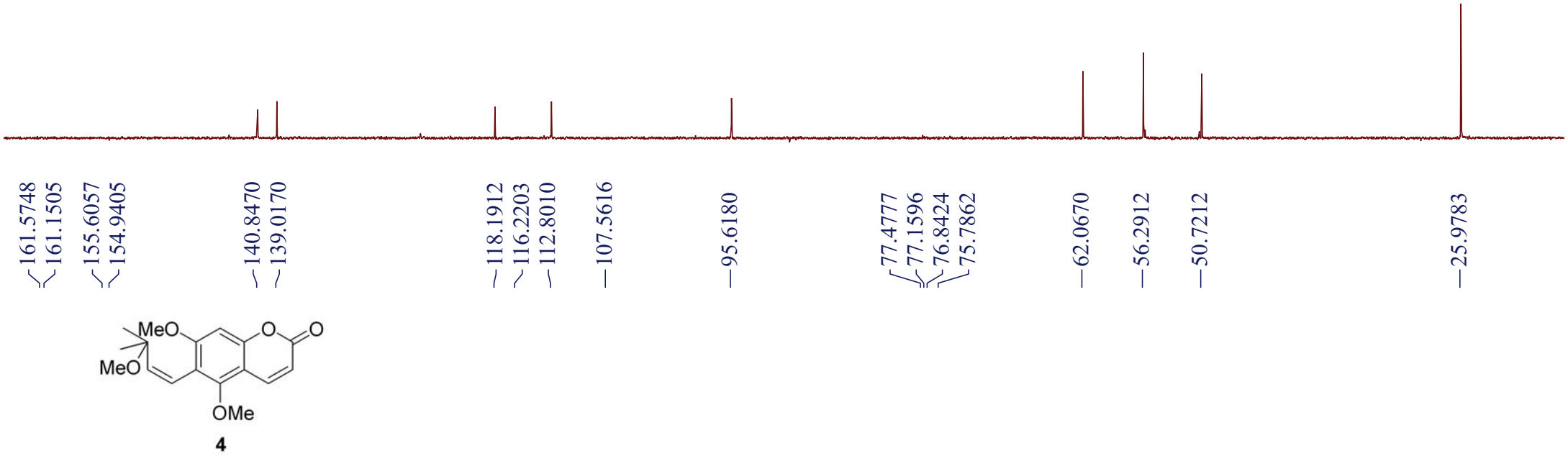


3

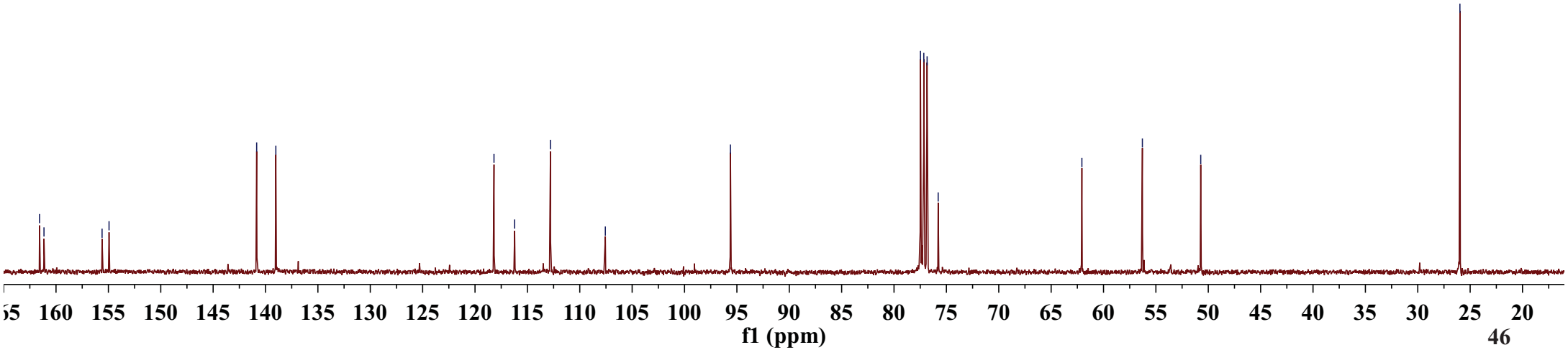
S4.19. ^{1}H NMR spectrum of compound **4**



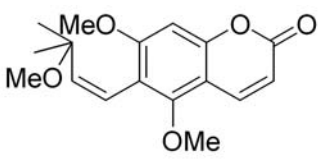
S4.20. ^{13}C NMR and DEPT spectra of compound **4**



4

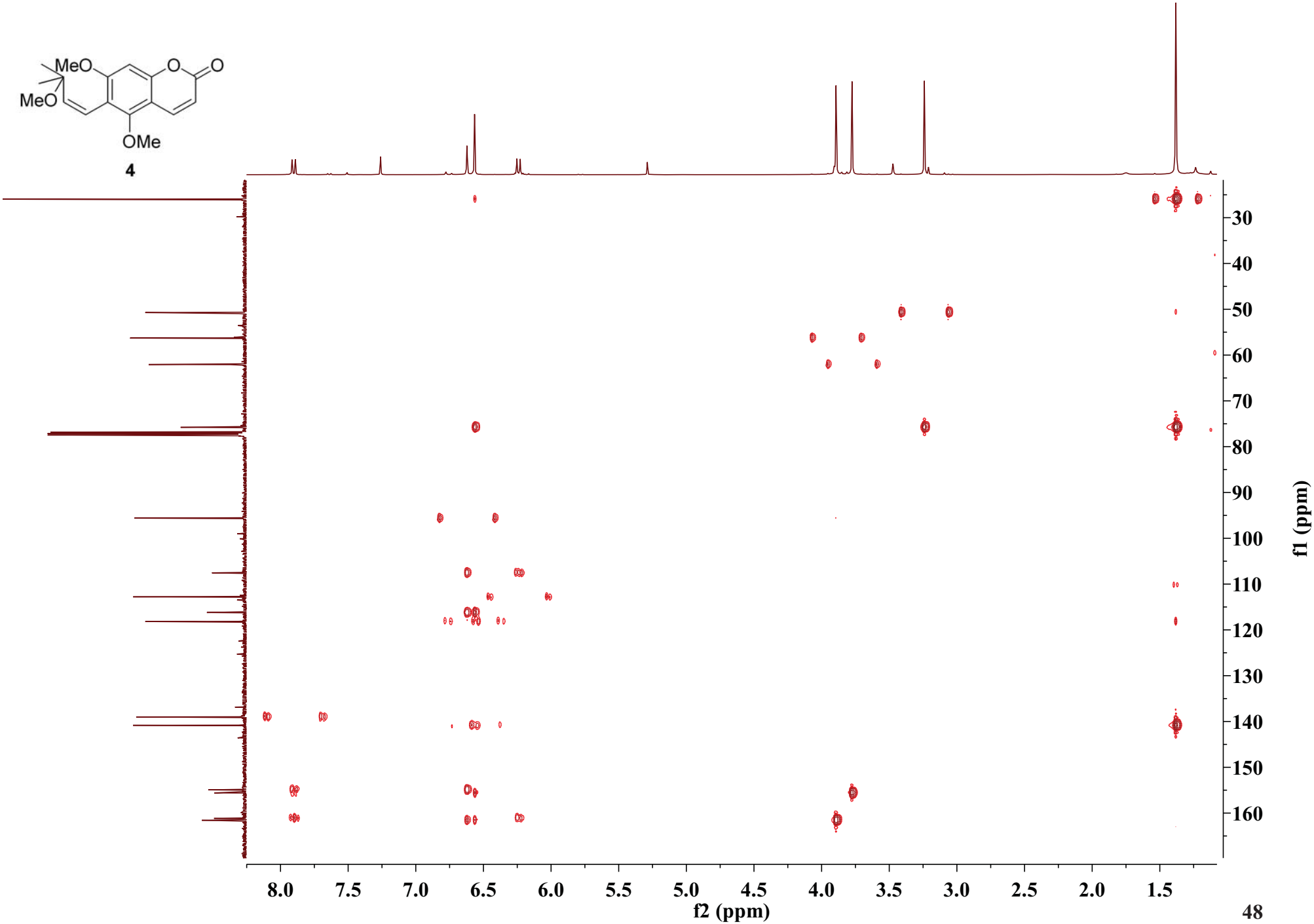


S4.21. HSQC spectrum of compound **4**

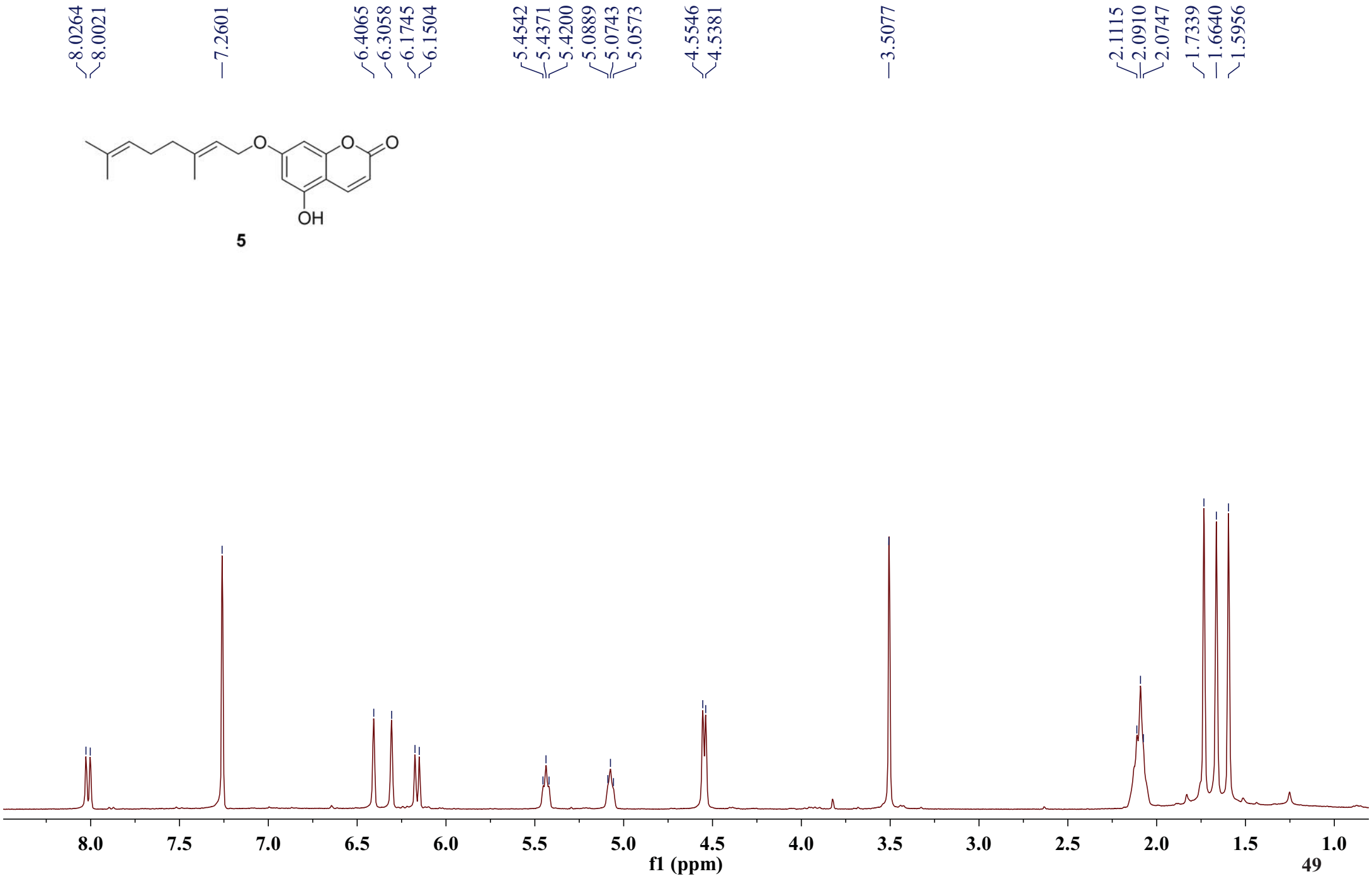


4

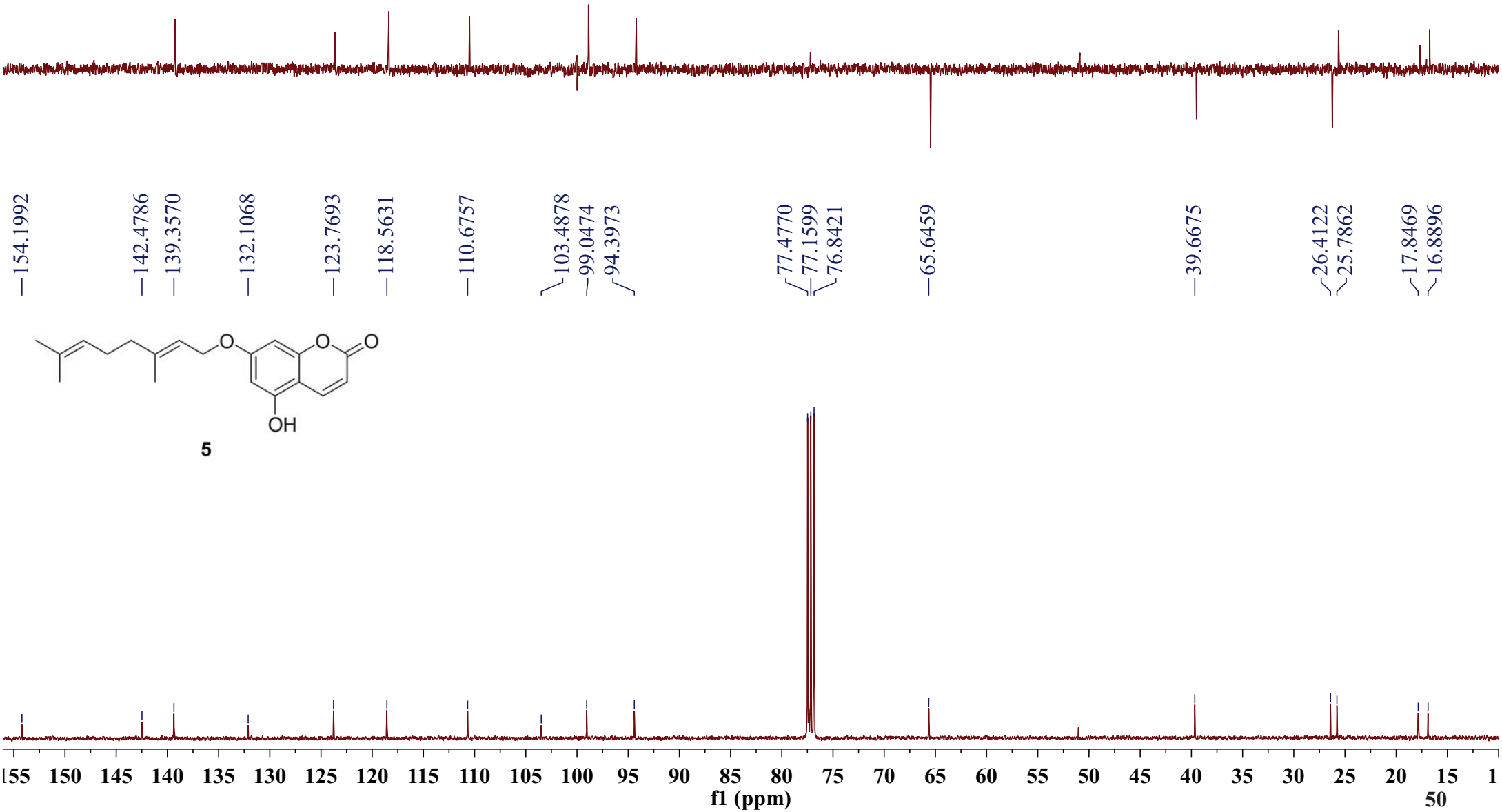
S4.22. HMBC spectrum of compound **4**



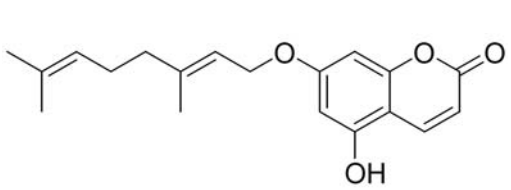
S4.23. ^{1}H NMR spectrum of compound **5**



S4.24. ^{13}C NMR and DEPT spectra of compound **5**

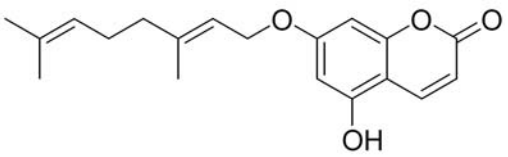


S4.25. HSQC spectrum of compound **5**



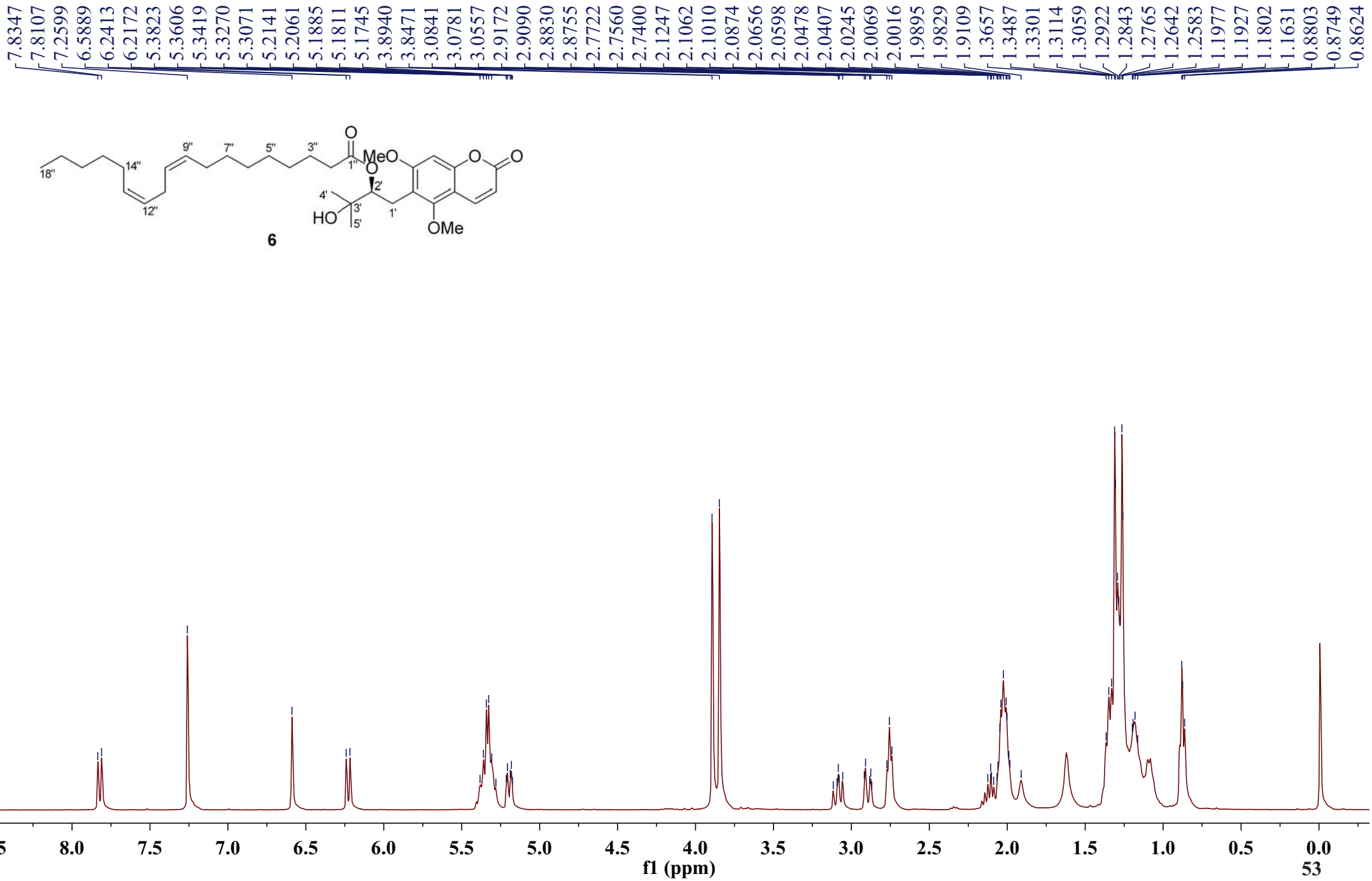
5

S4.26. HMBC spectrum of compound **5**

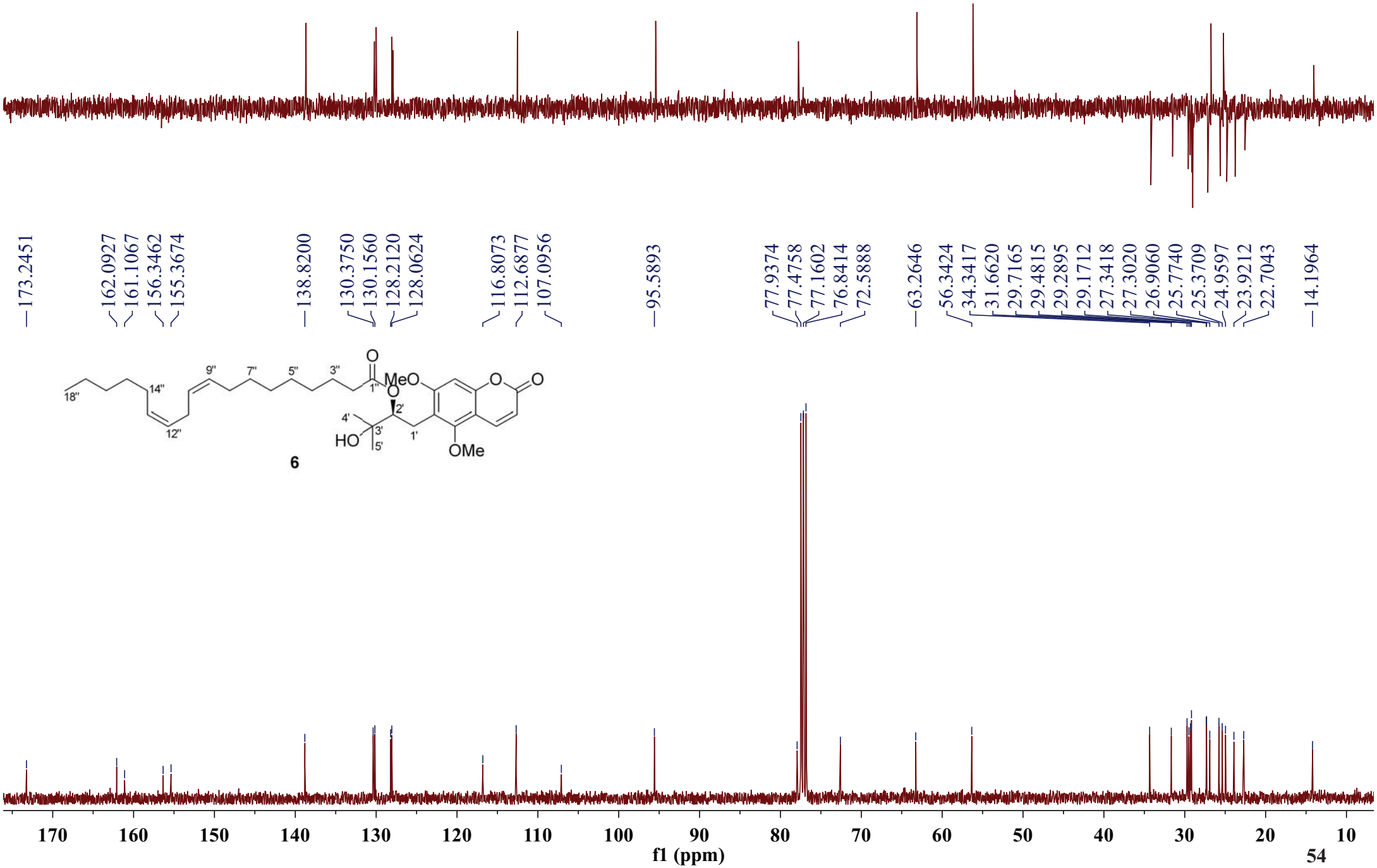


5

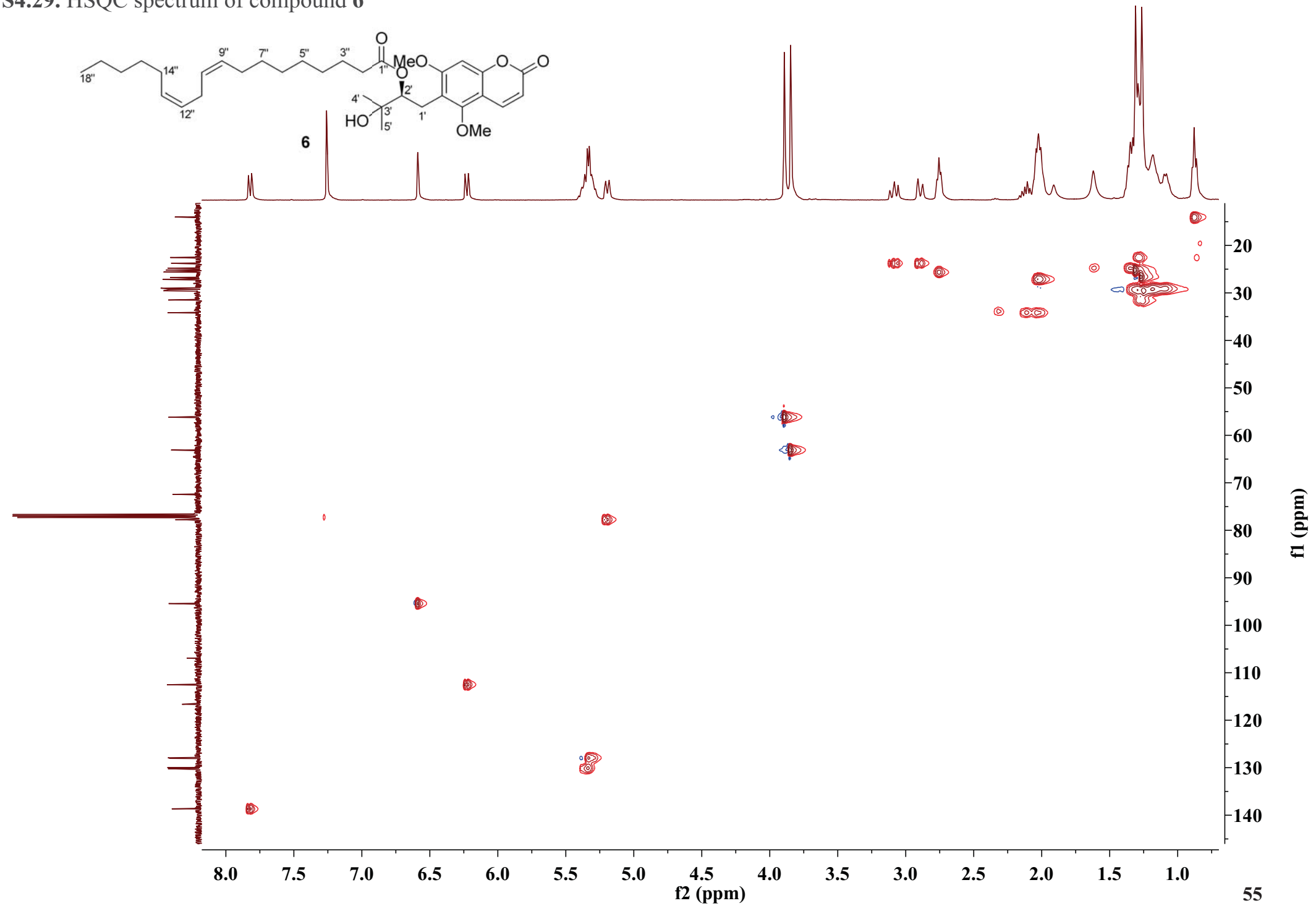
S4.27. ^{1}H NMR spectrum of compound **6**



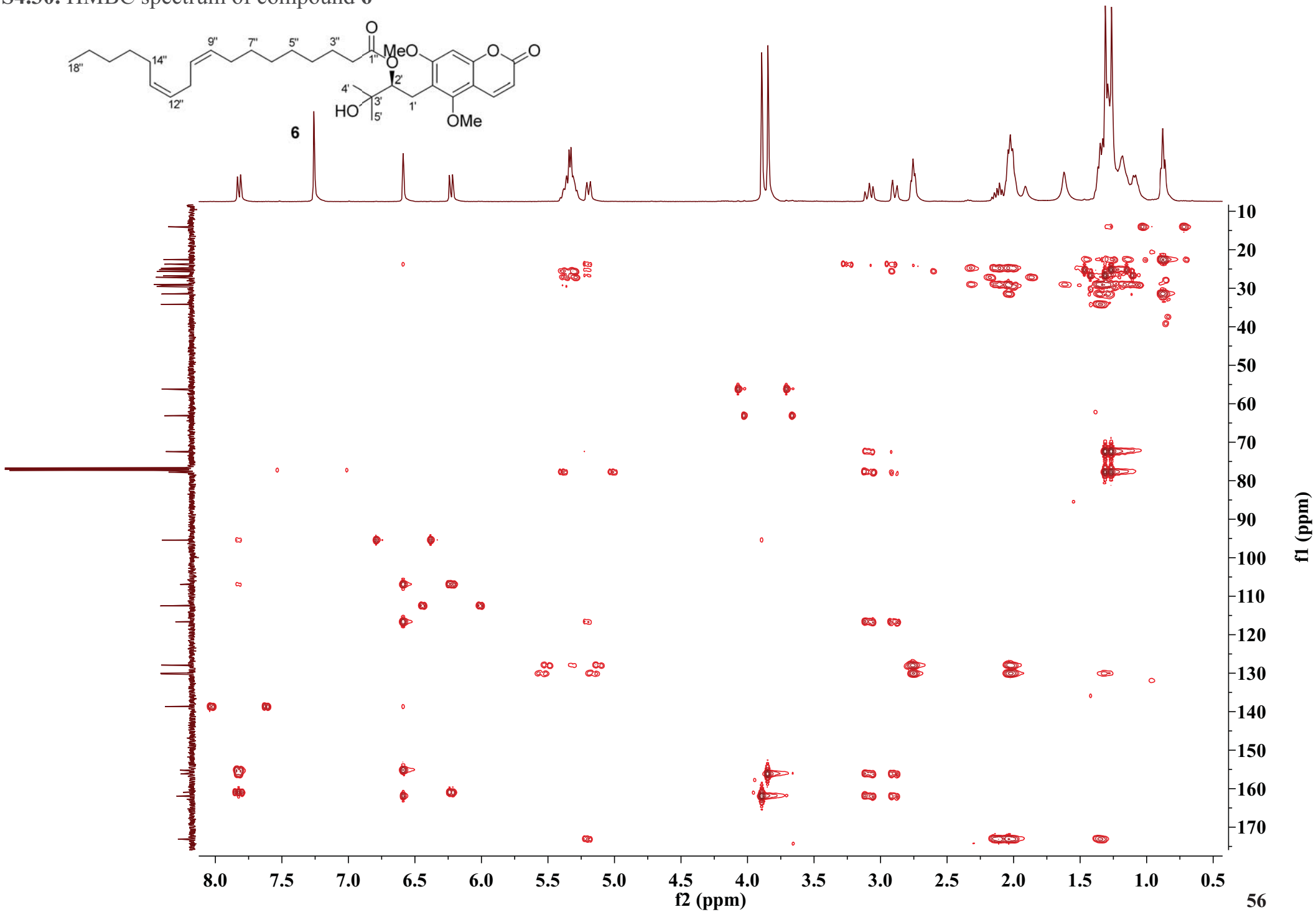
S4.28. ^{13}C NMR and DEPT spectra of compound **6**



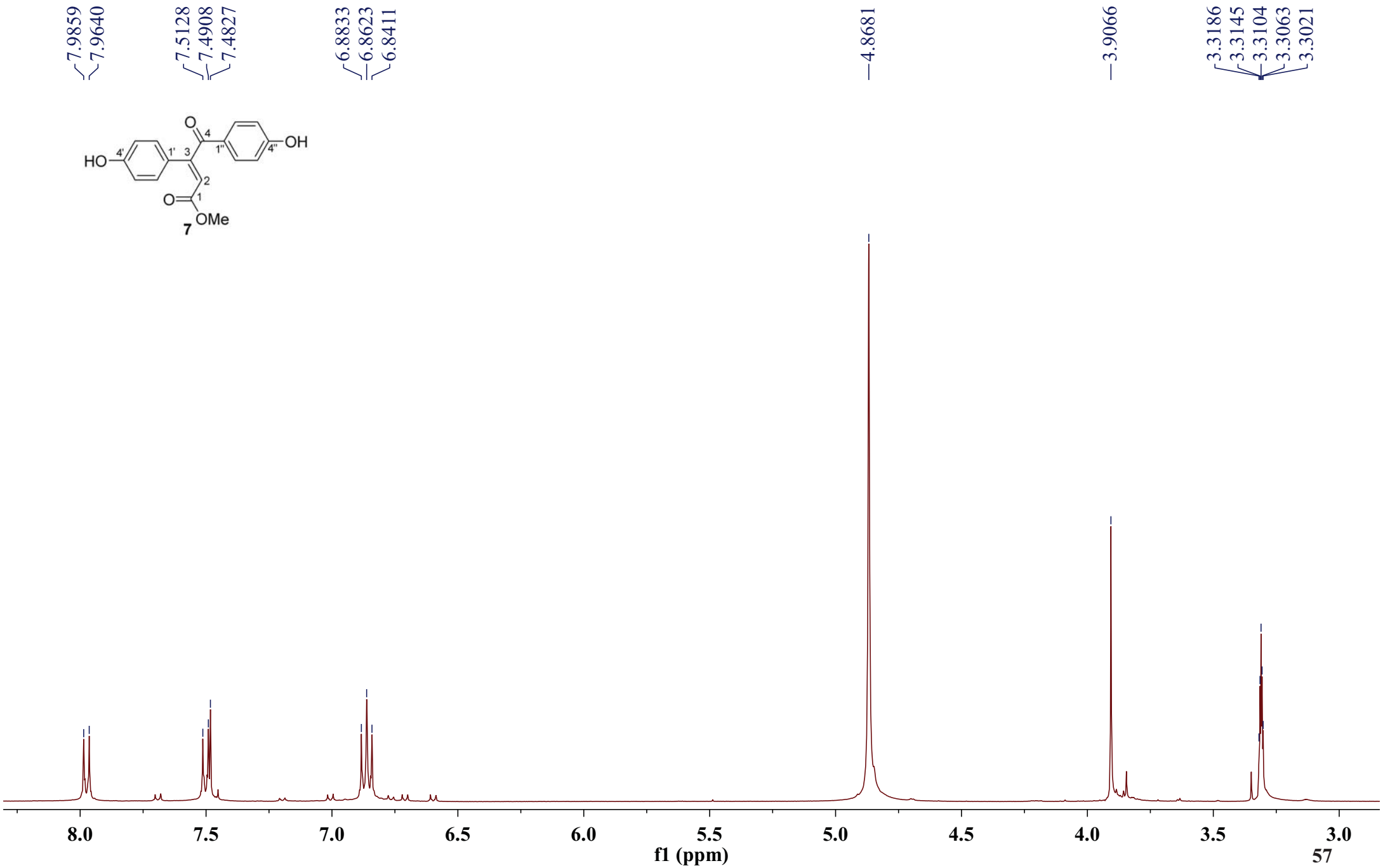
S4.29. HSQC spectrum of compound **6**



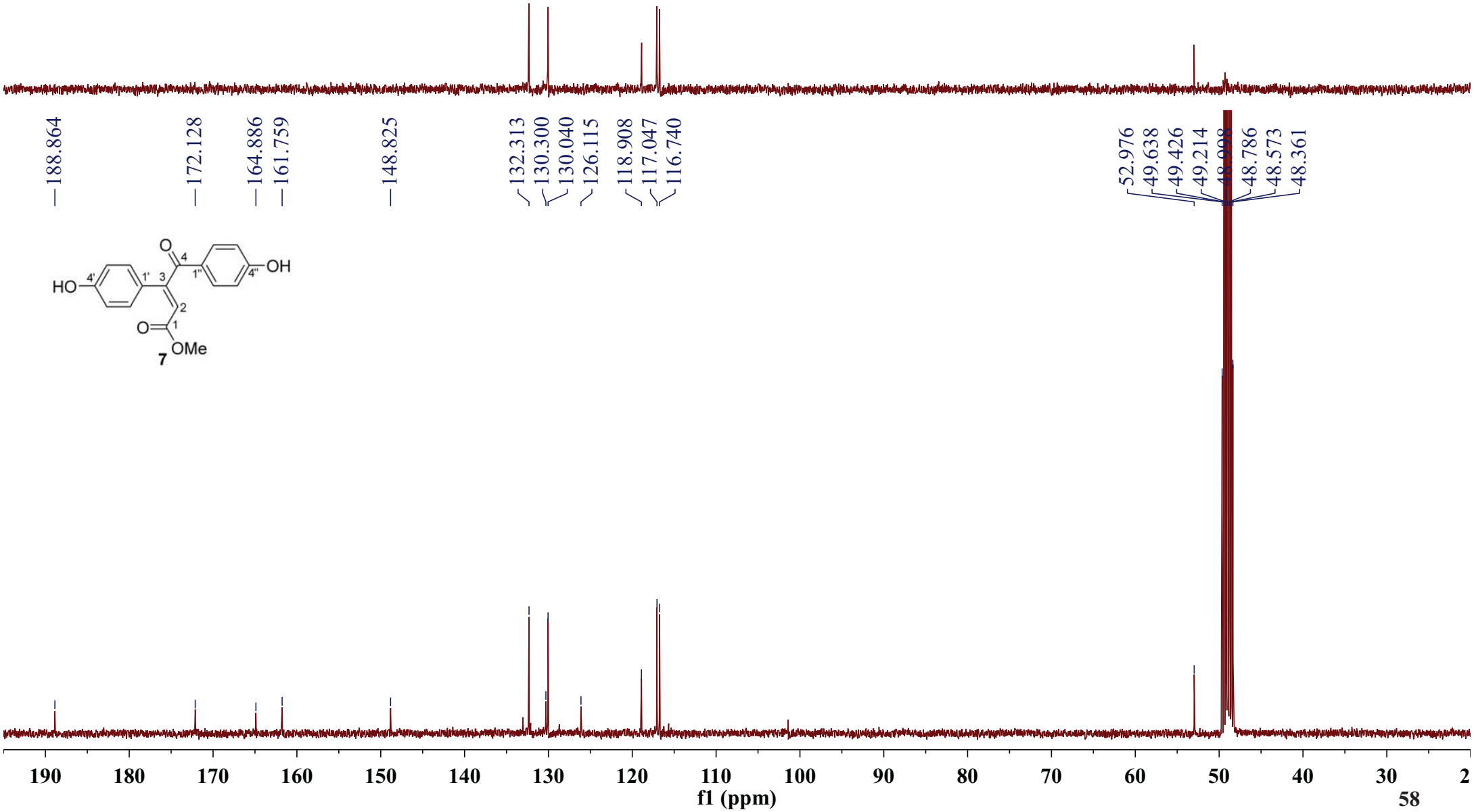
S4.30. HMBC spectrum of compound **6**



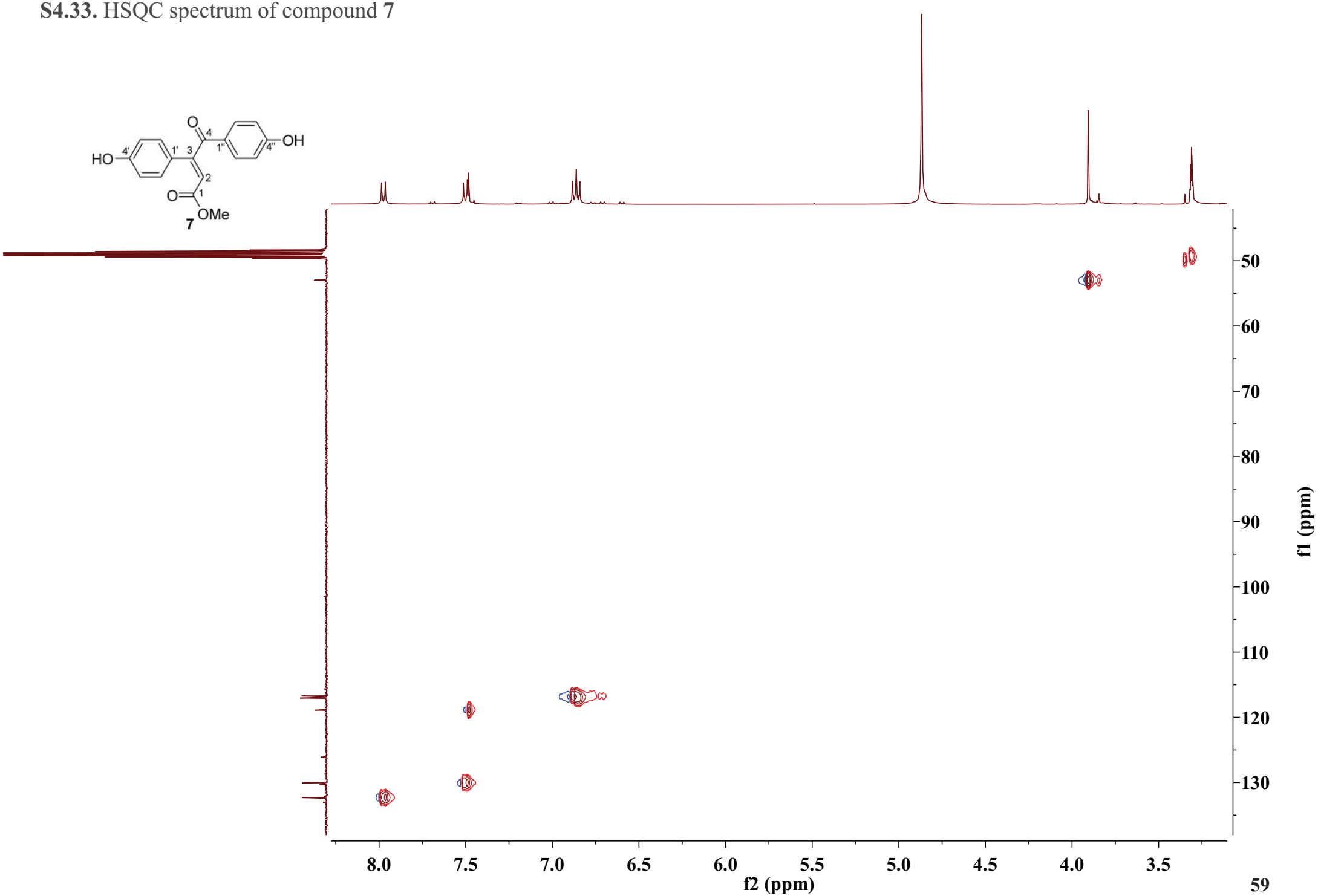
S4.31. ^{1}H NMR spectrum of compound **7**



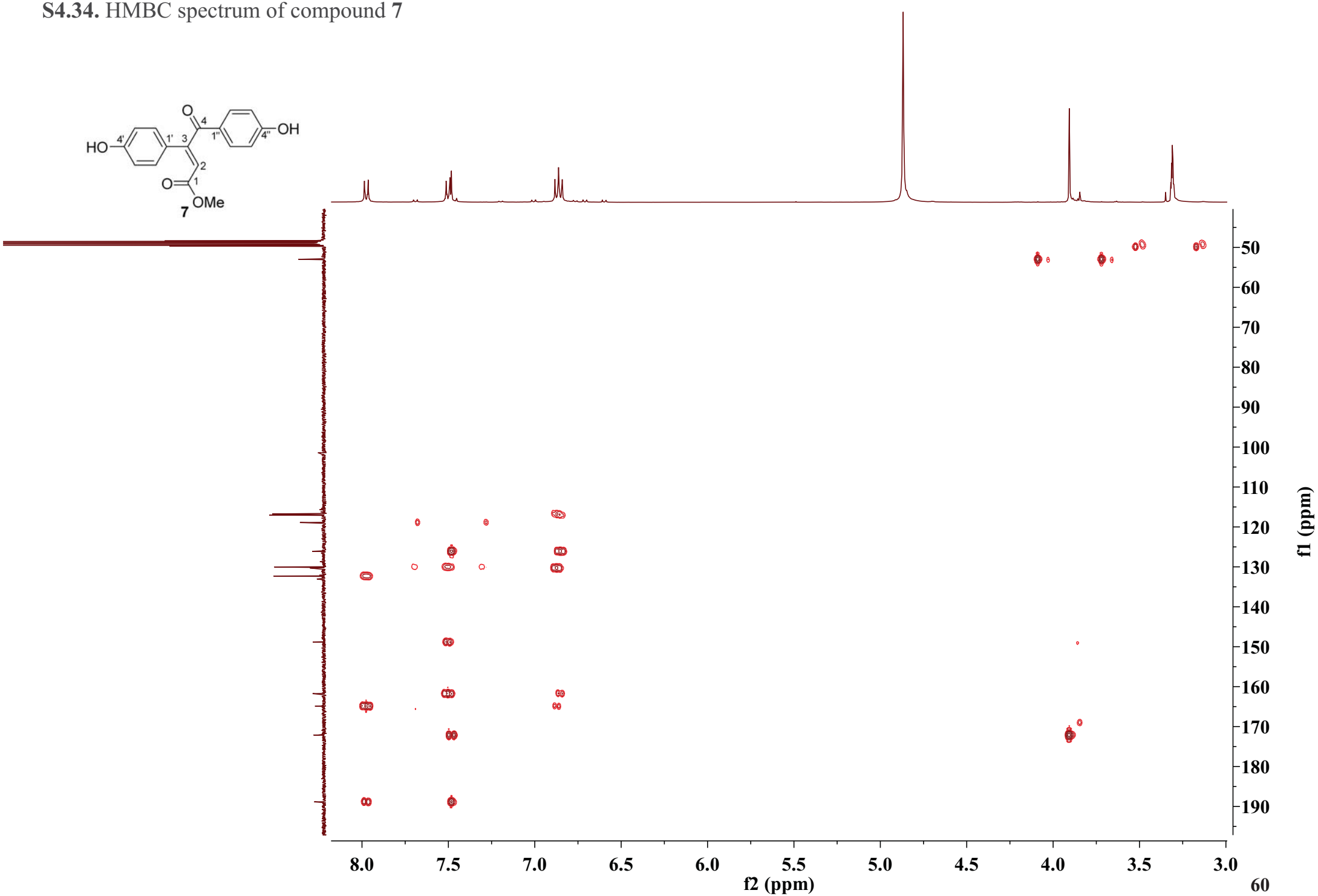
S4.32. ^{13}C NMR and DEPT spectra of compound **7**



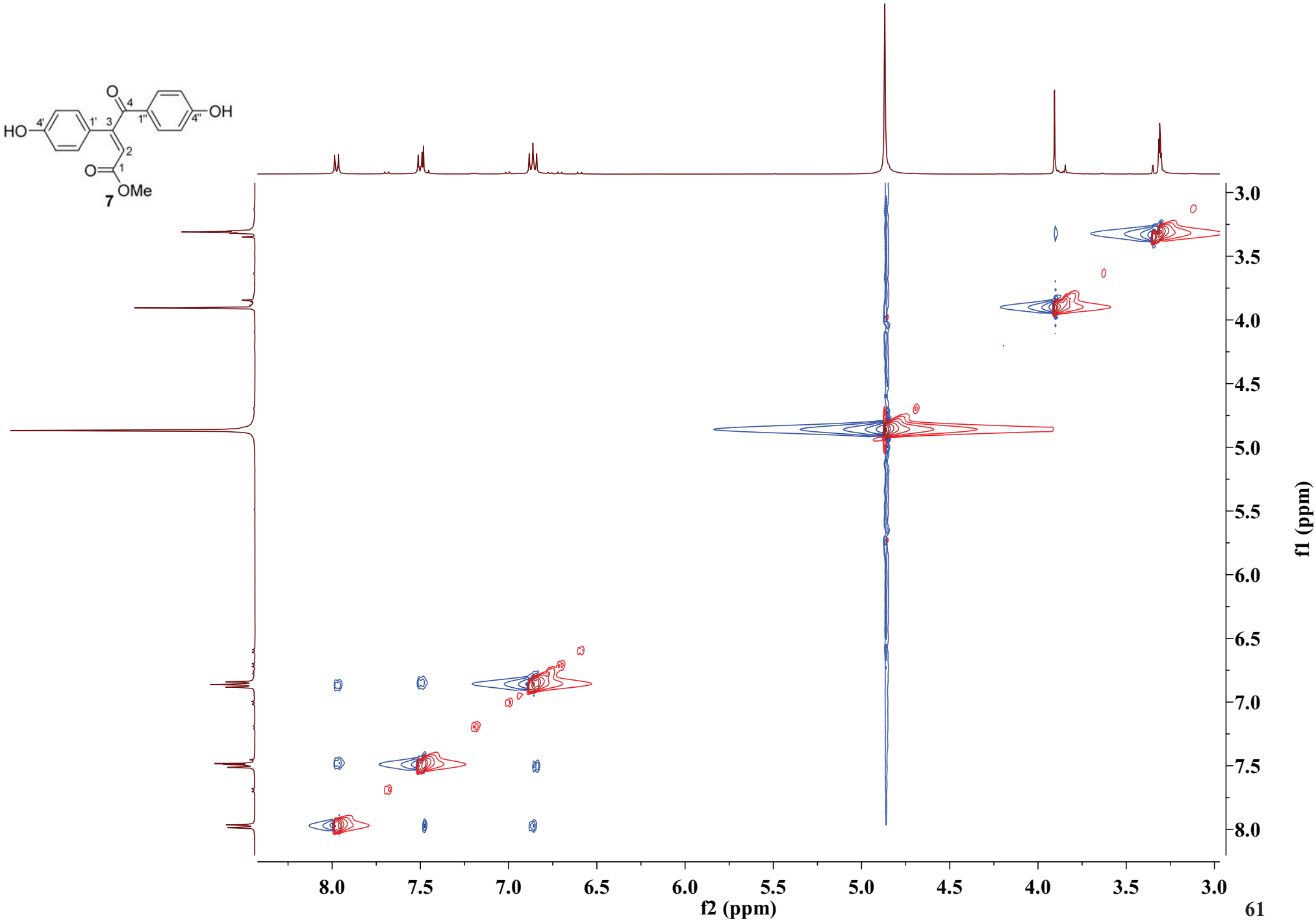
S4.33. HSQC spectrum of compound **7**



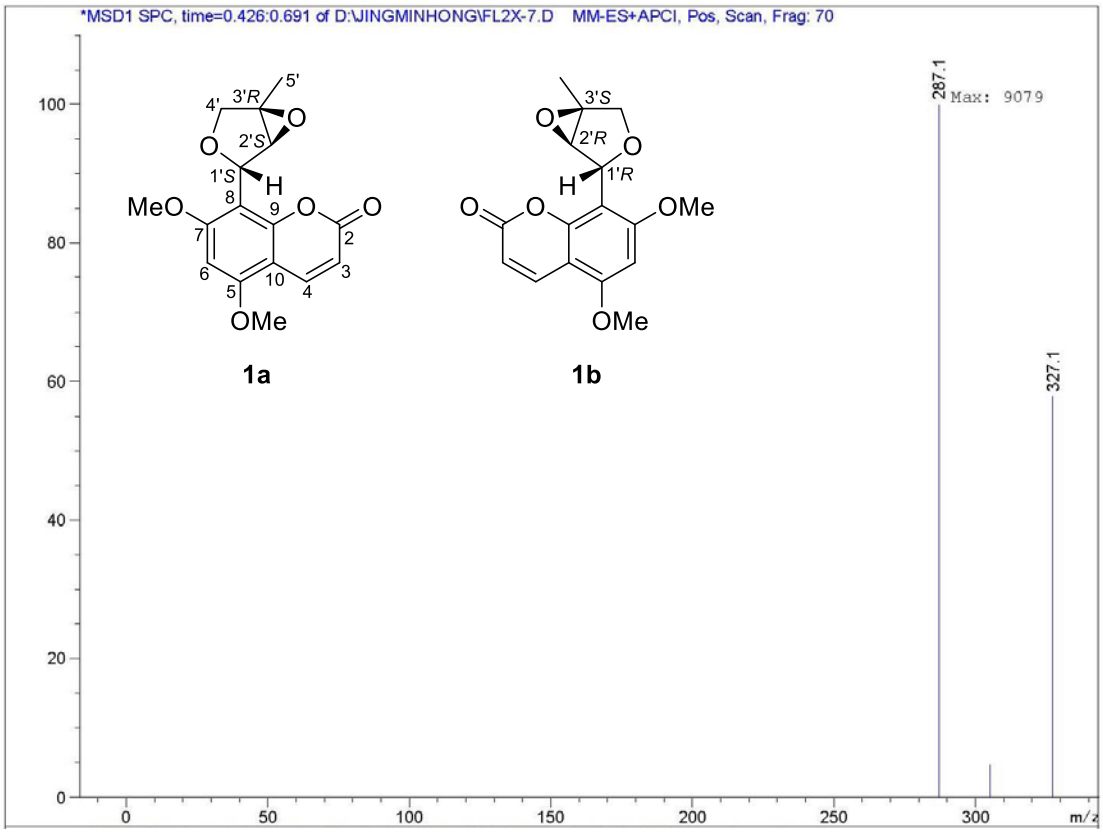
S4.34. HMBC spectrum of compound **7**



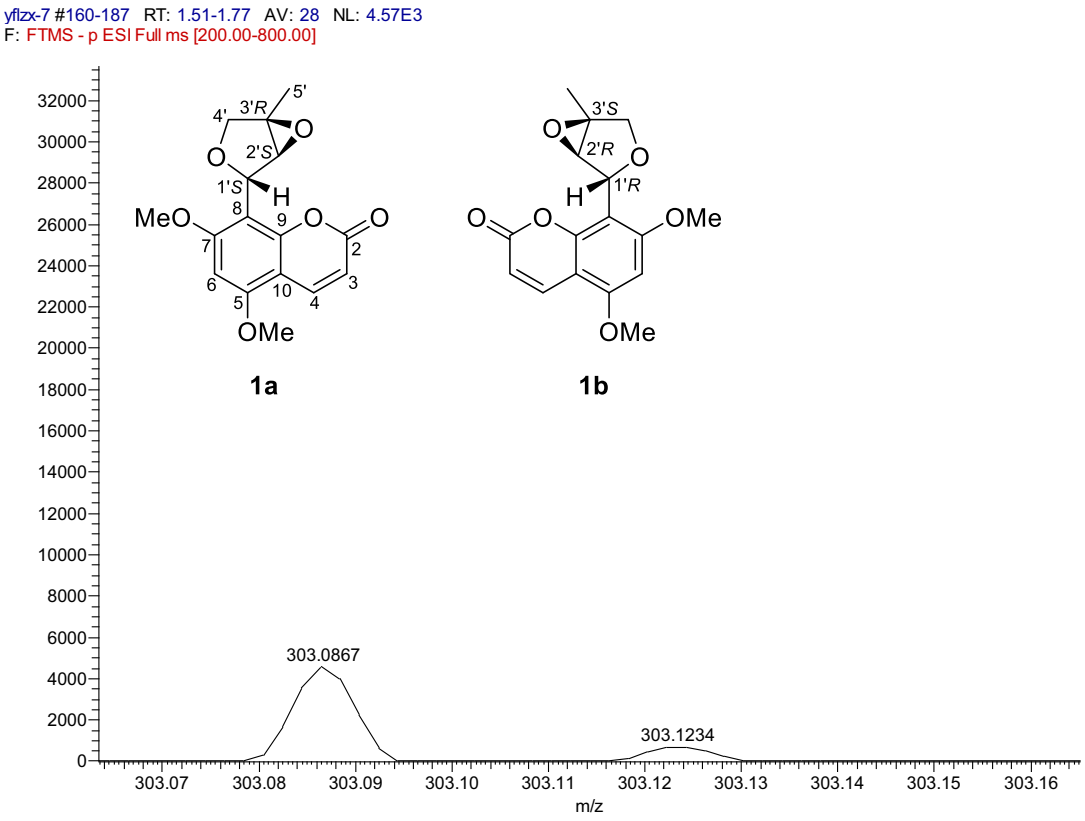
S4.35. NOESY spectrum of compound **7**



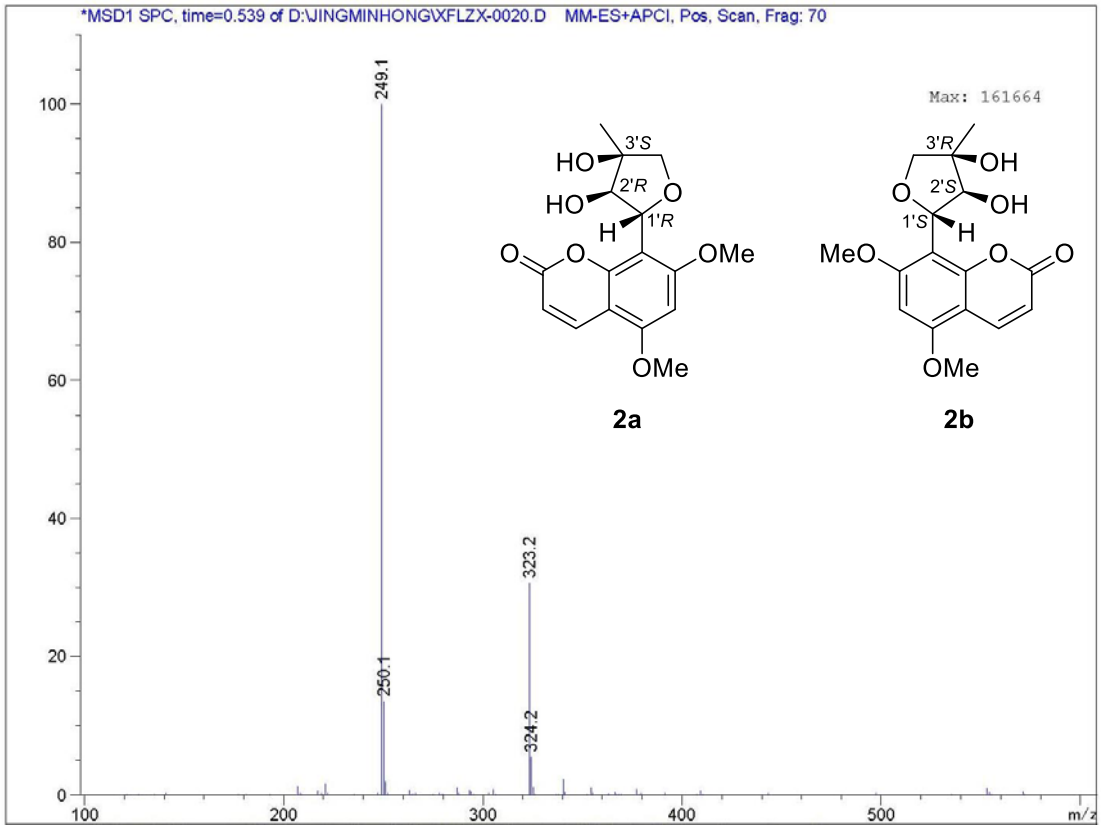
S5.1. ESIMS data of compound **1**



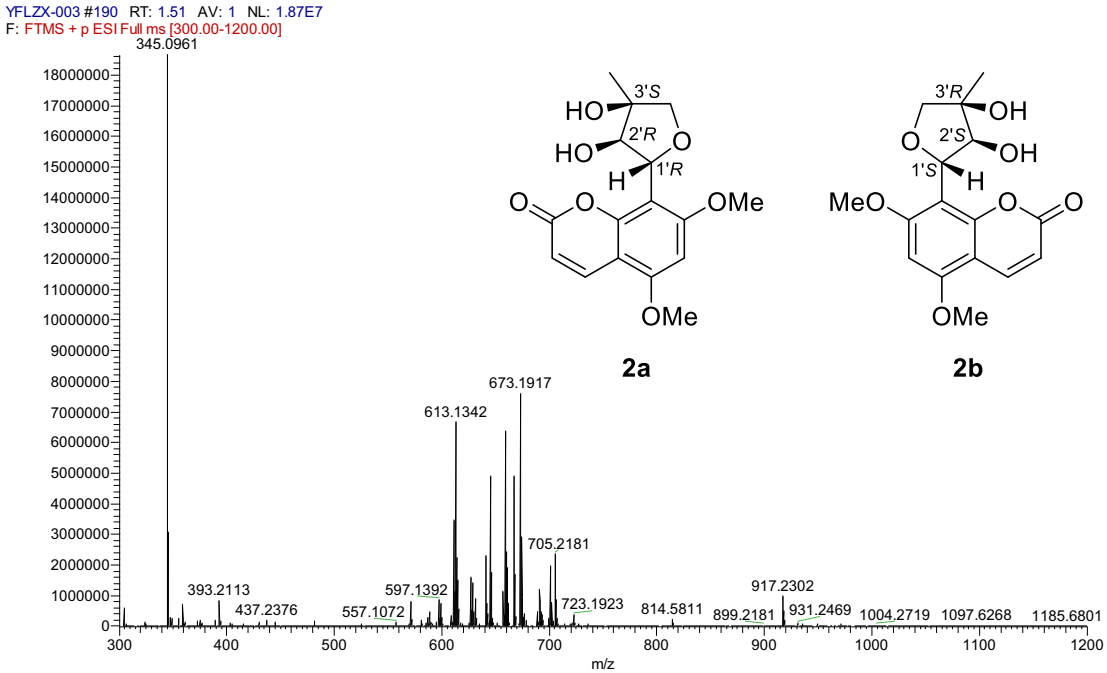
S5.2. HRESIMS data of compound **1**



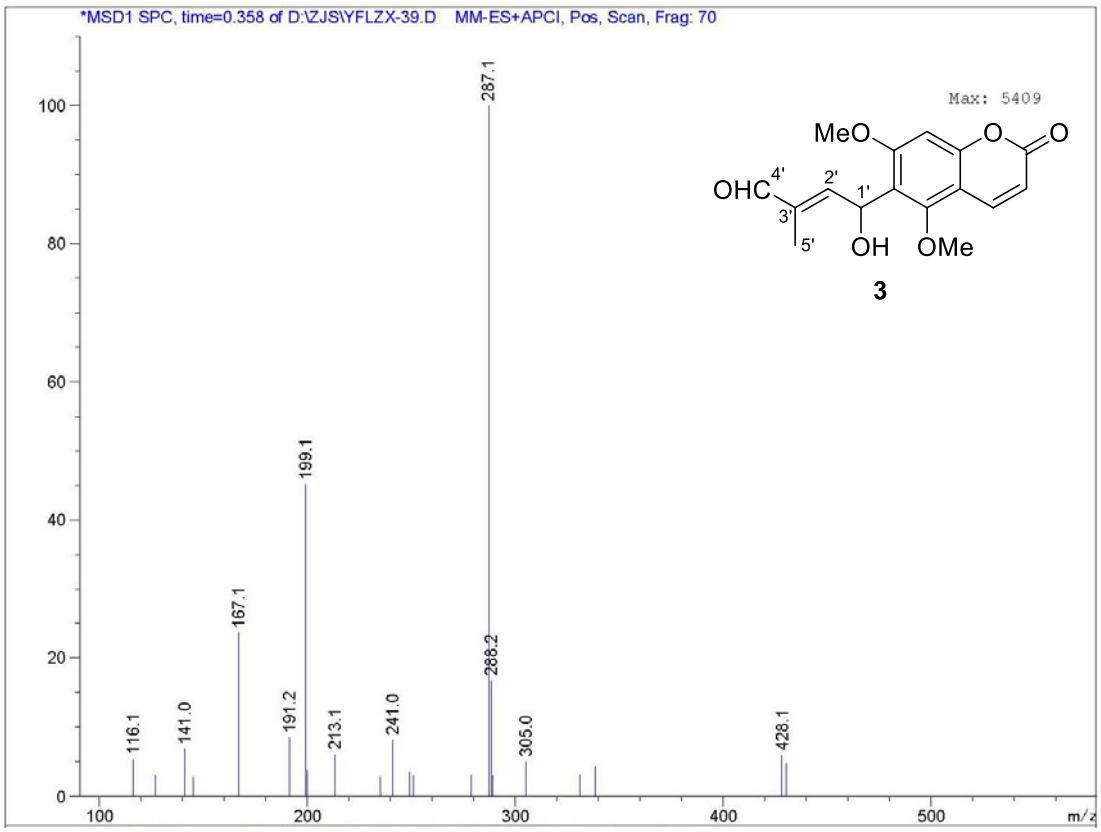
S5.3. ESIMS data of compound **2**



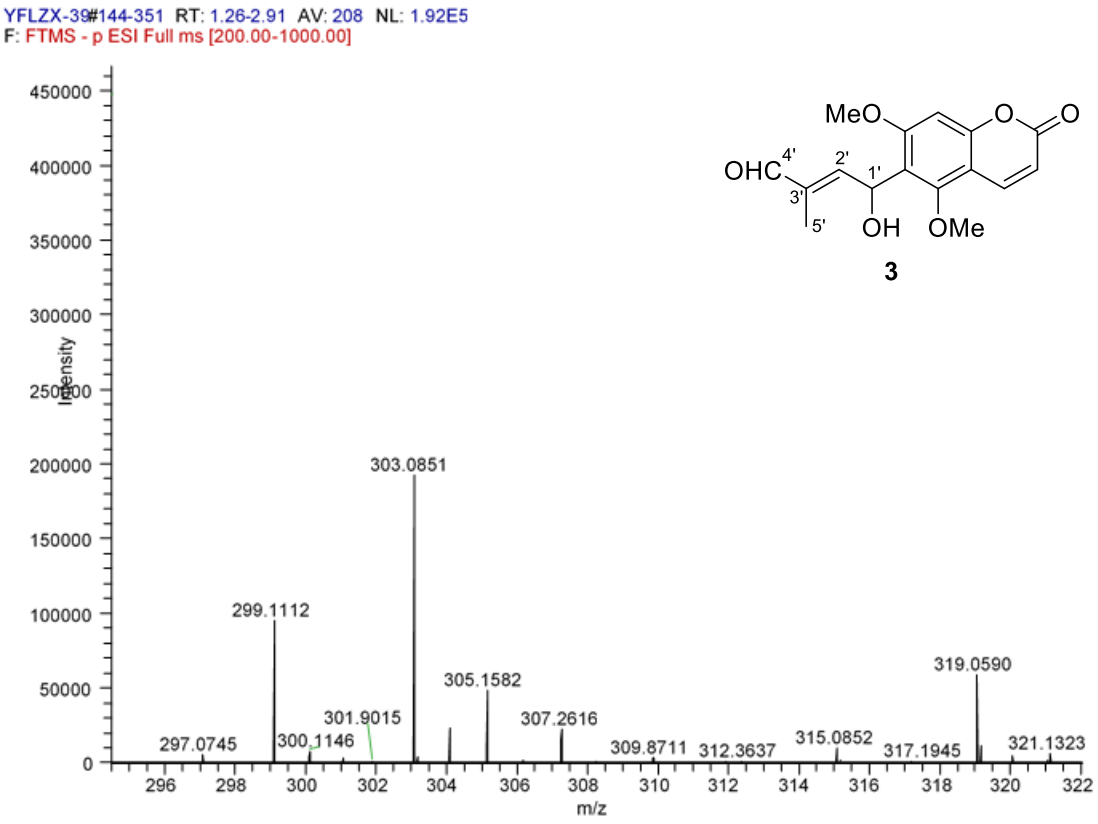
S5.4. HRESIMS data of compound **2**



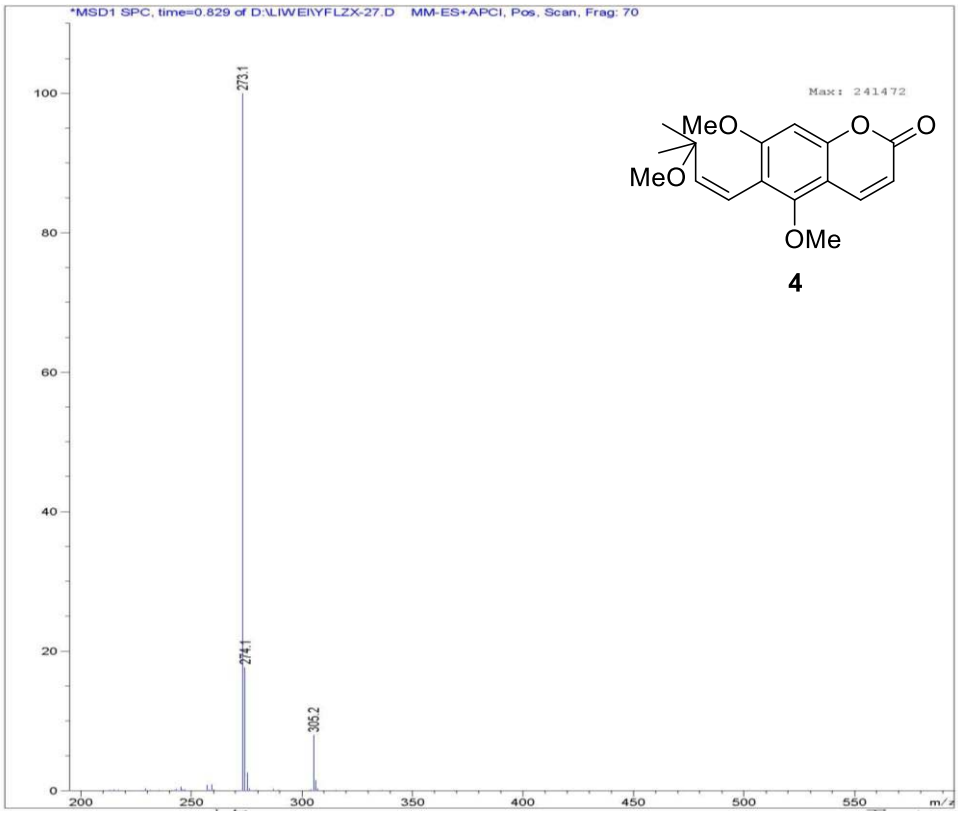
S5.5. ESIMS data of compound **3**



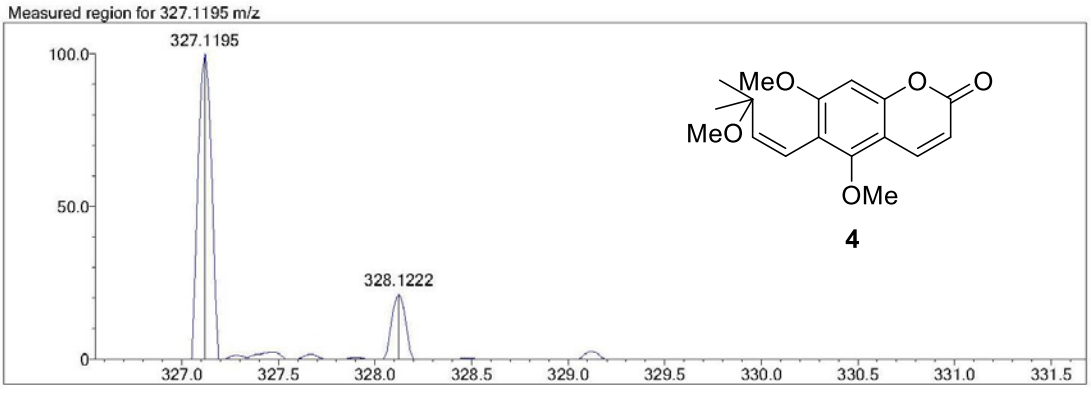
S5.6. HRESIMS data of compound **3**

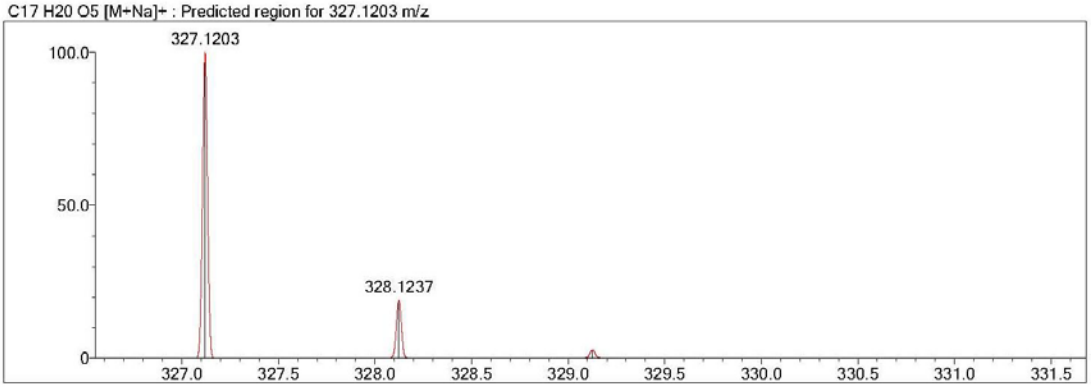


S5.7. ESIMS data of compound **4**



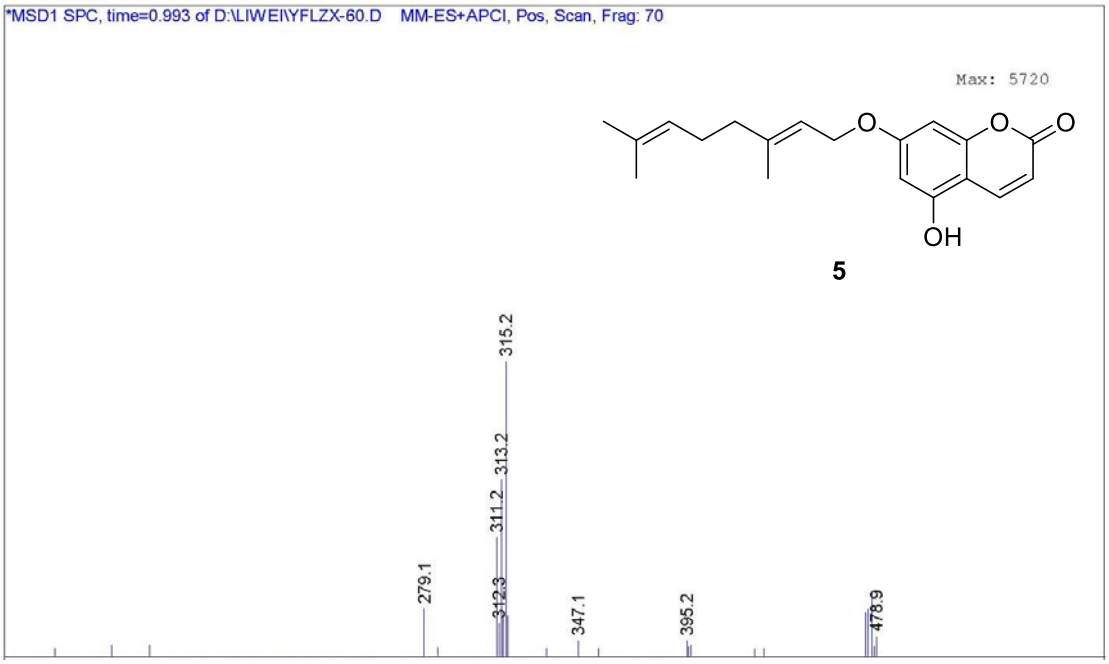
S5.8. HRESIMS data of compound **4**



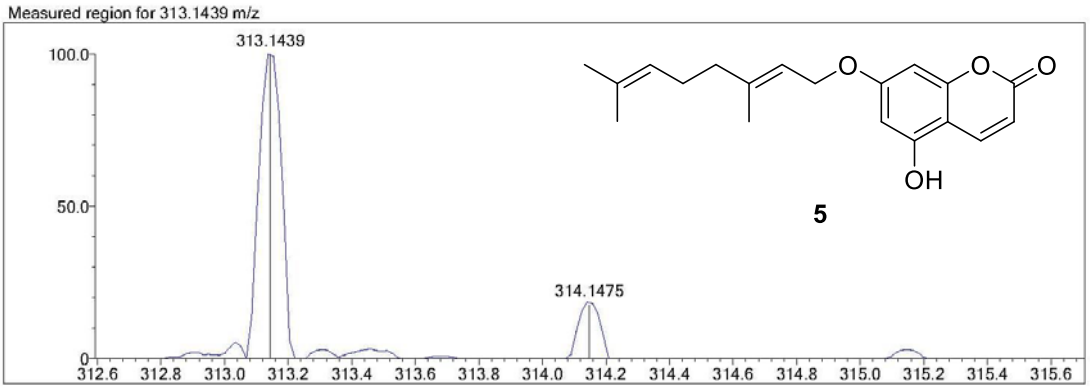


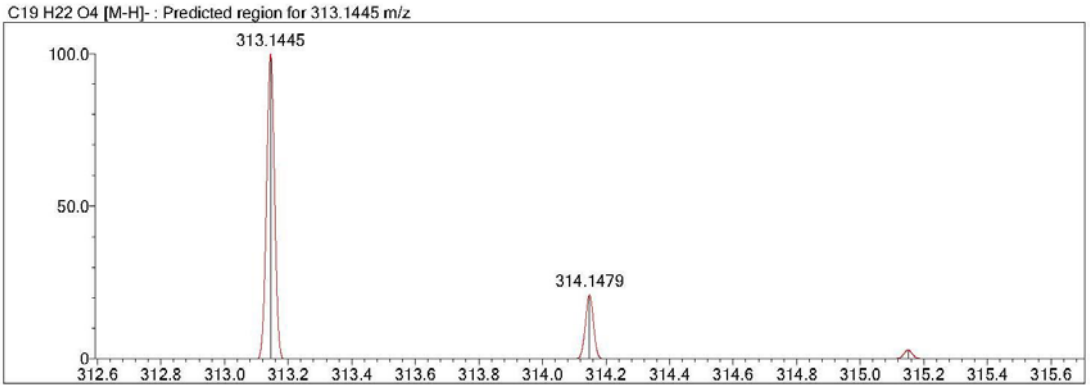
Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	75.82	C17 H20 O5	[M+Na]+	327.1195	327.1203	-0.8	-2.45	78.67	8.0

S5.9. ESIMS data of compound **5**



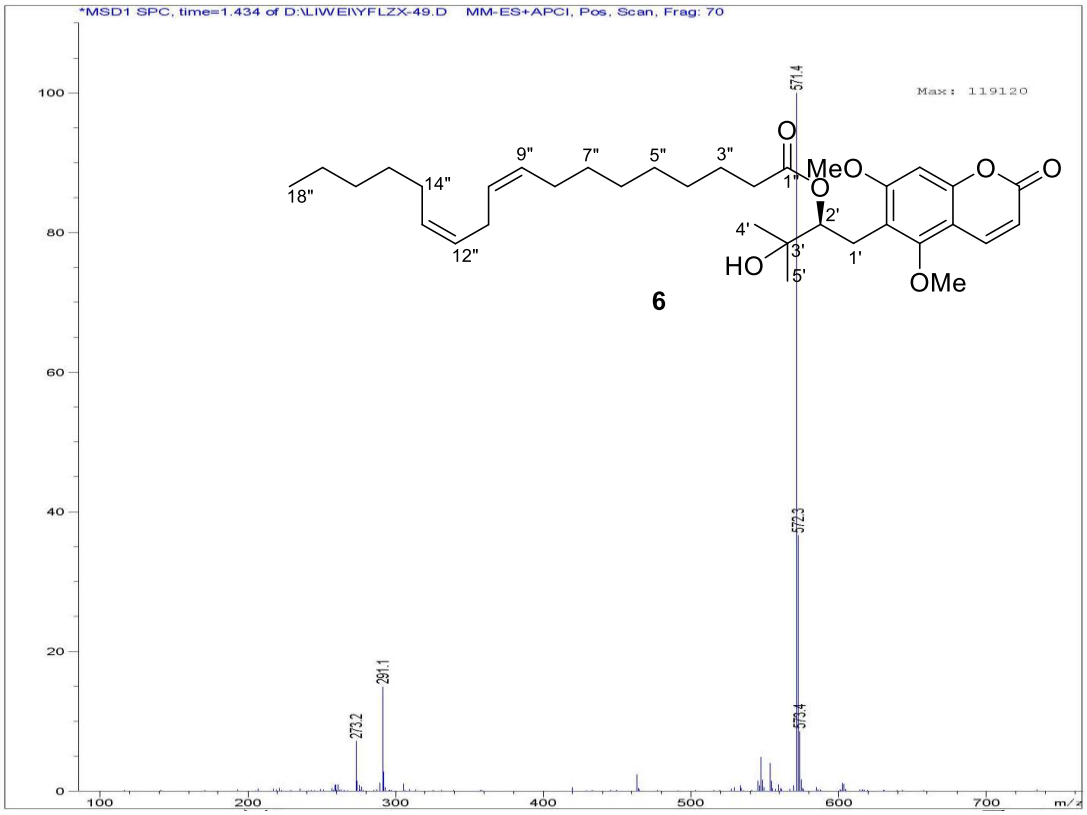
S5.10. HRESIMS data of compound **5**



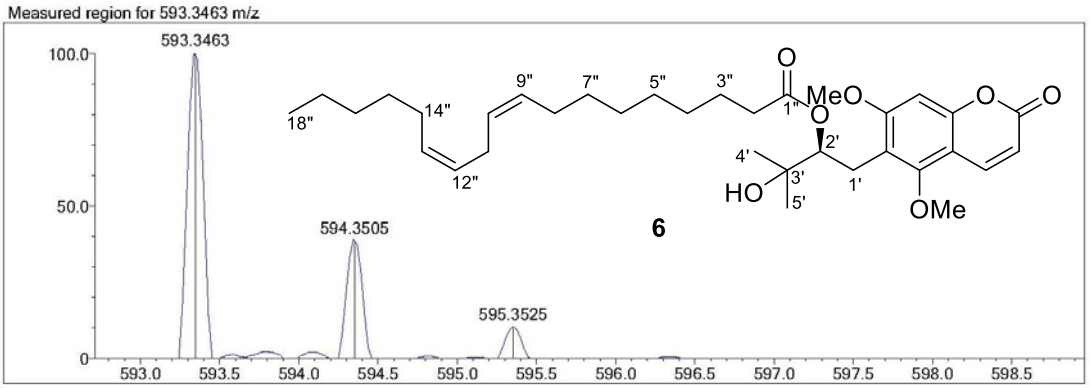


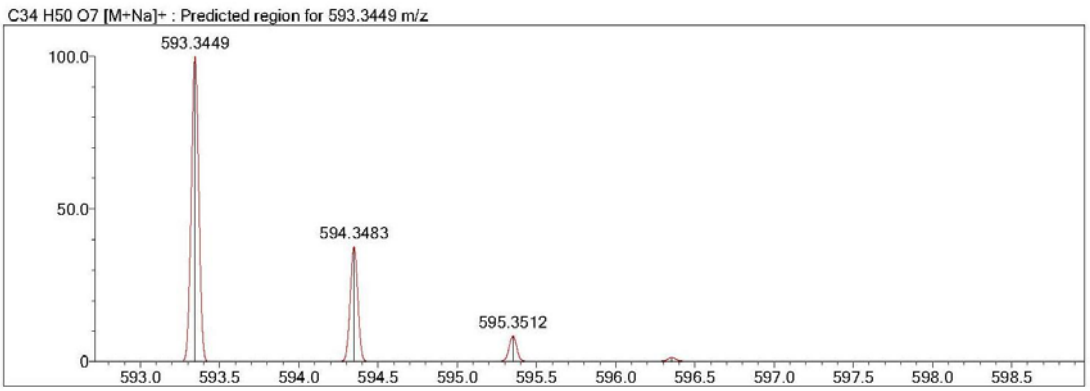
Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
2	77.24	C19 H22 O4	[M-H]-	313.1439	313.1445	-0.6	-1.92	79.06	9.0

S5.11. ESIMS data of compound **6**



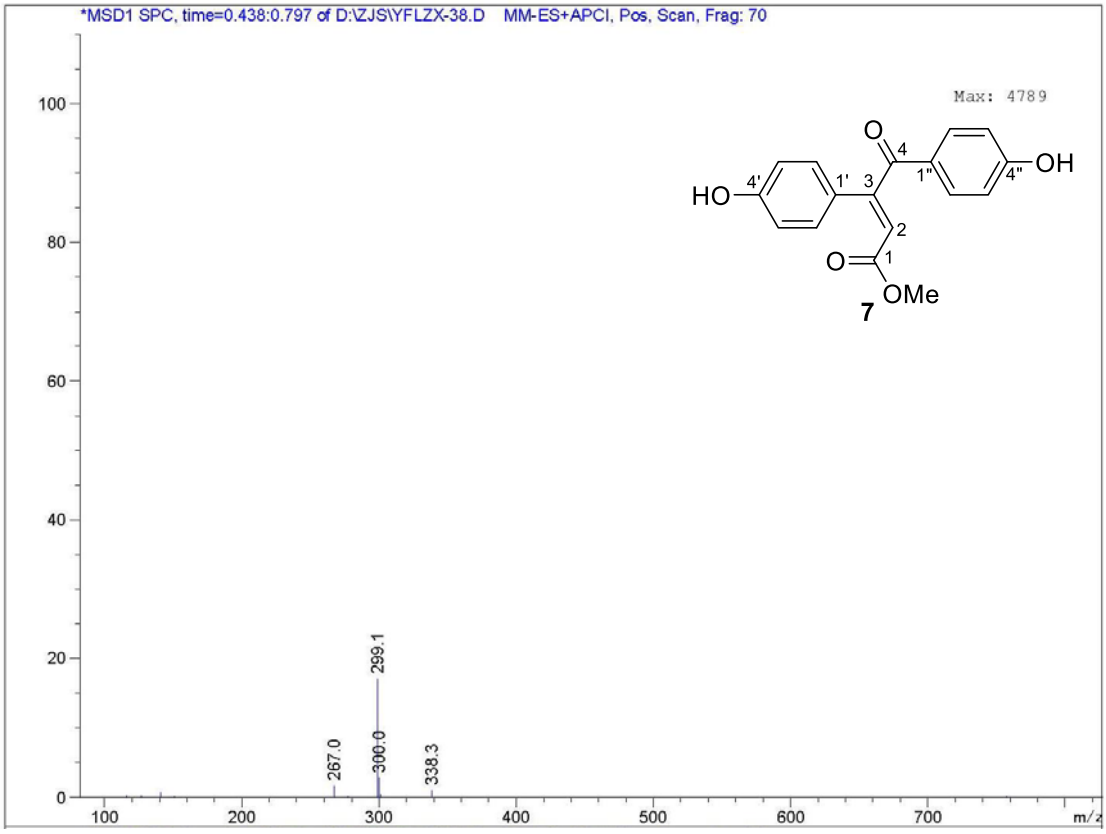
S5.12. HRESIMS data of compound **6**



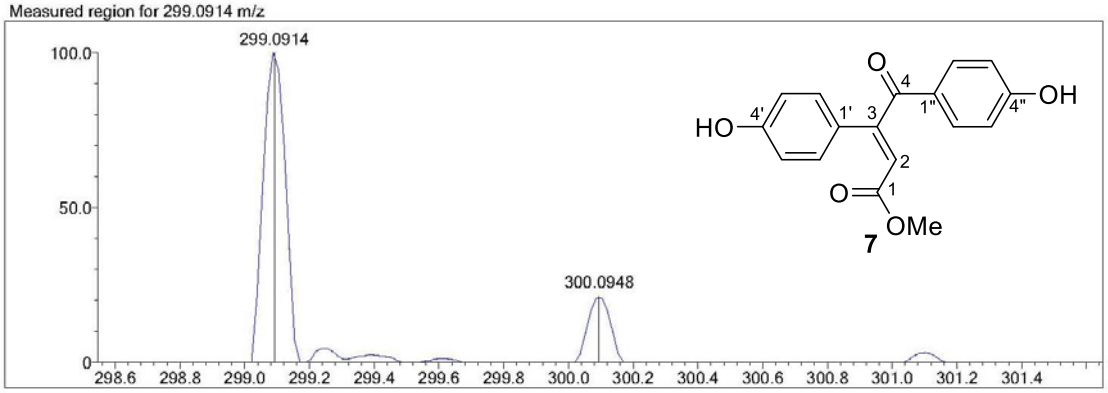


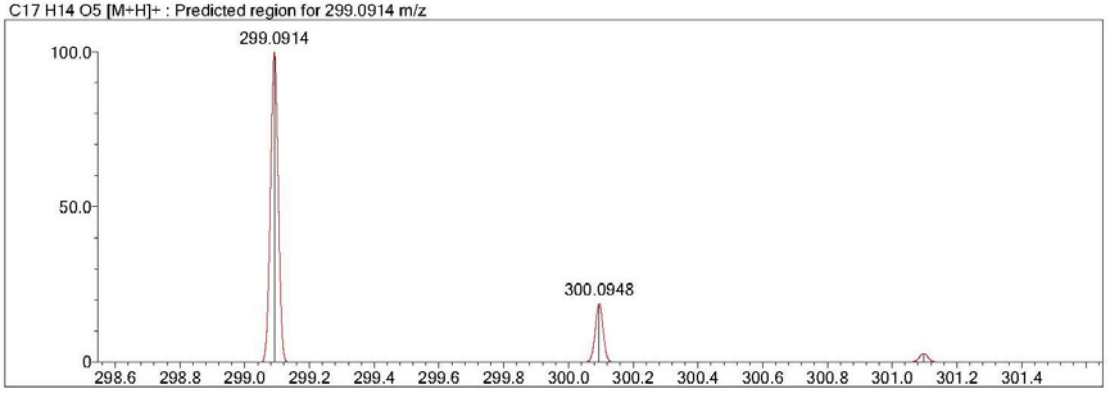
Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	78.90	C34 H50 O7	[M+Na]+	593.3463	593.3449	1.4	2.36	81.68	10.0

S5.13. ESIMS data of compound **7**



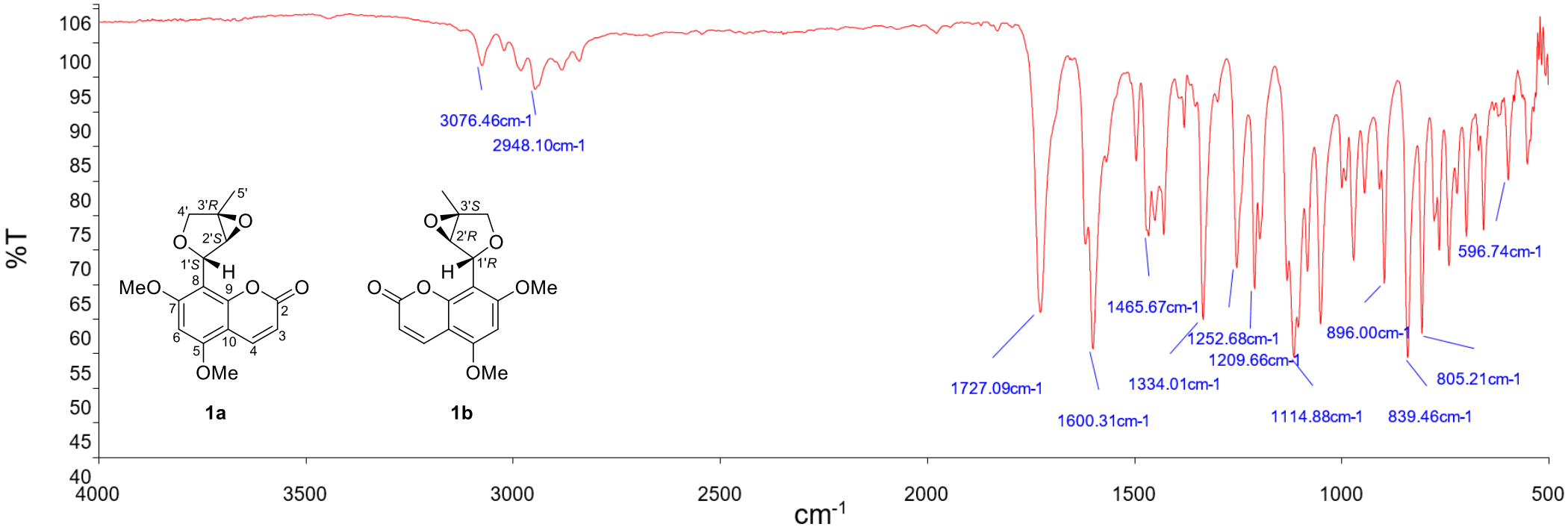
S5.14. HRESIMS data of compound **7**



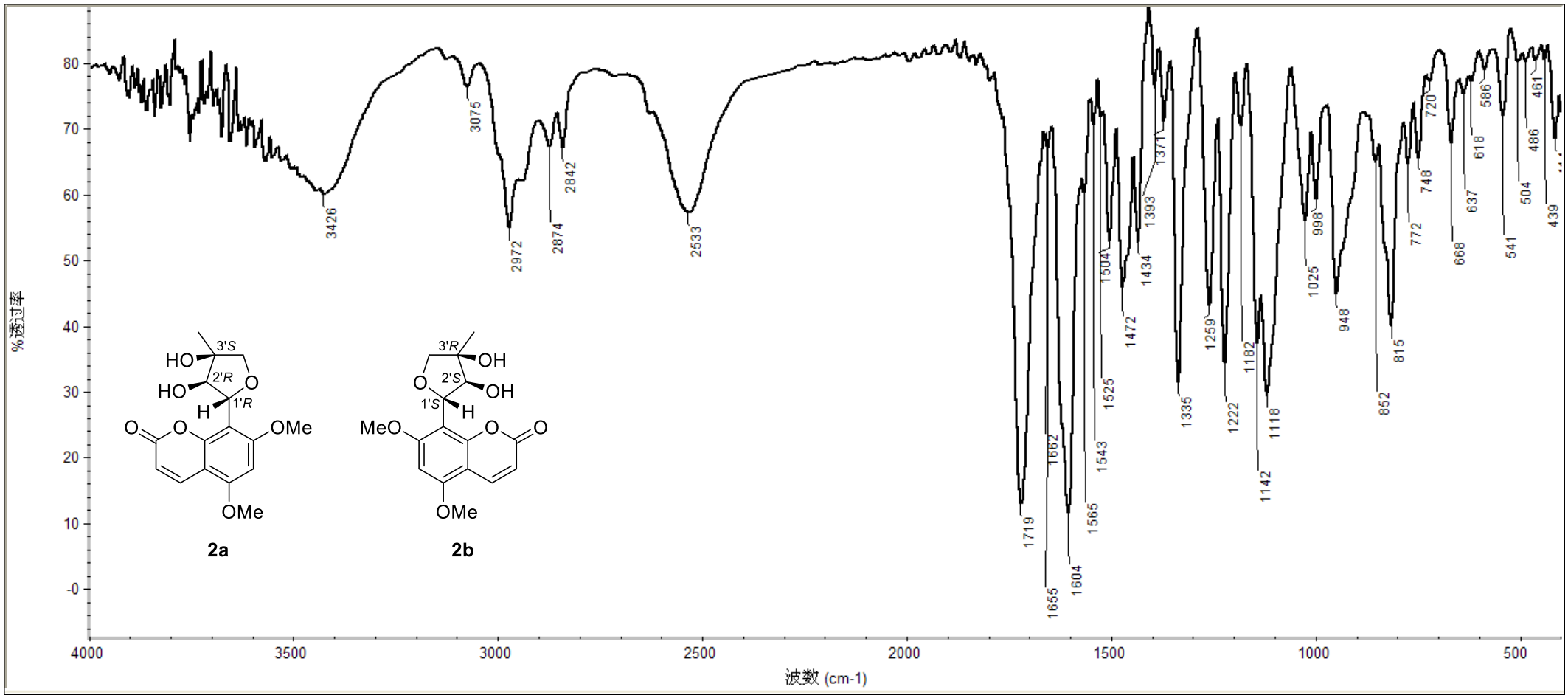


Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	74.74	C17 H14 O5	[M+H]+	299.0914	299.0914	-0.0	0.00	74.74	11.0

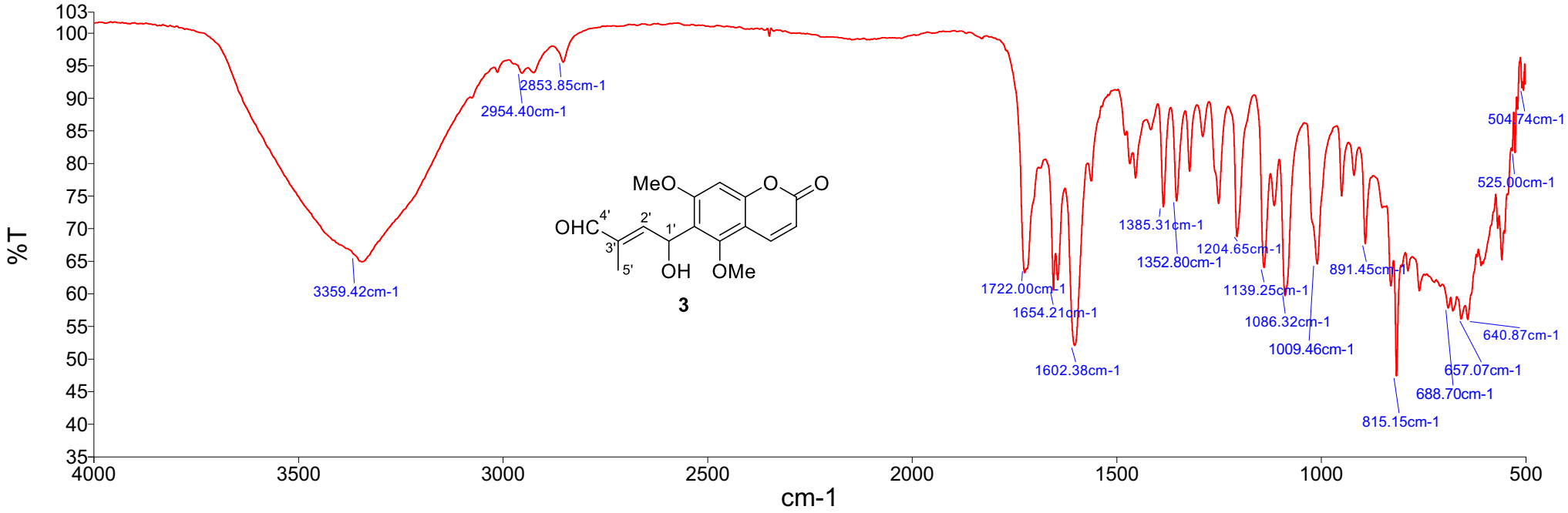
S5.15. IR (KBr disc) spectrum of compound **1**



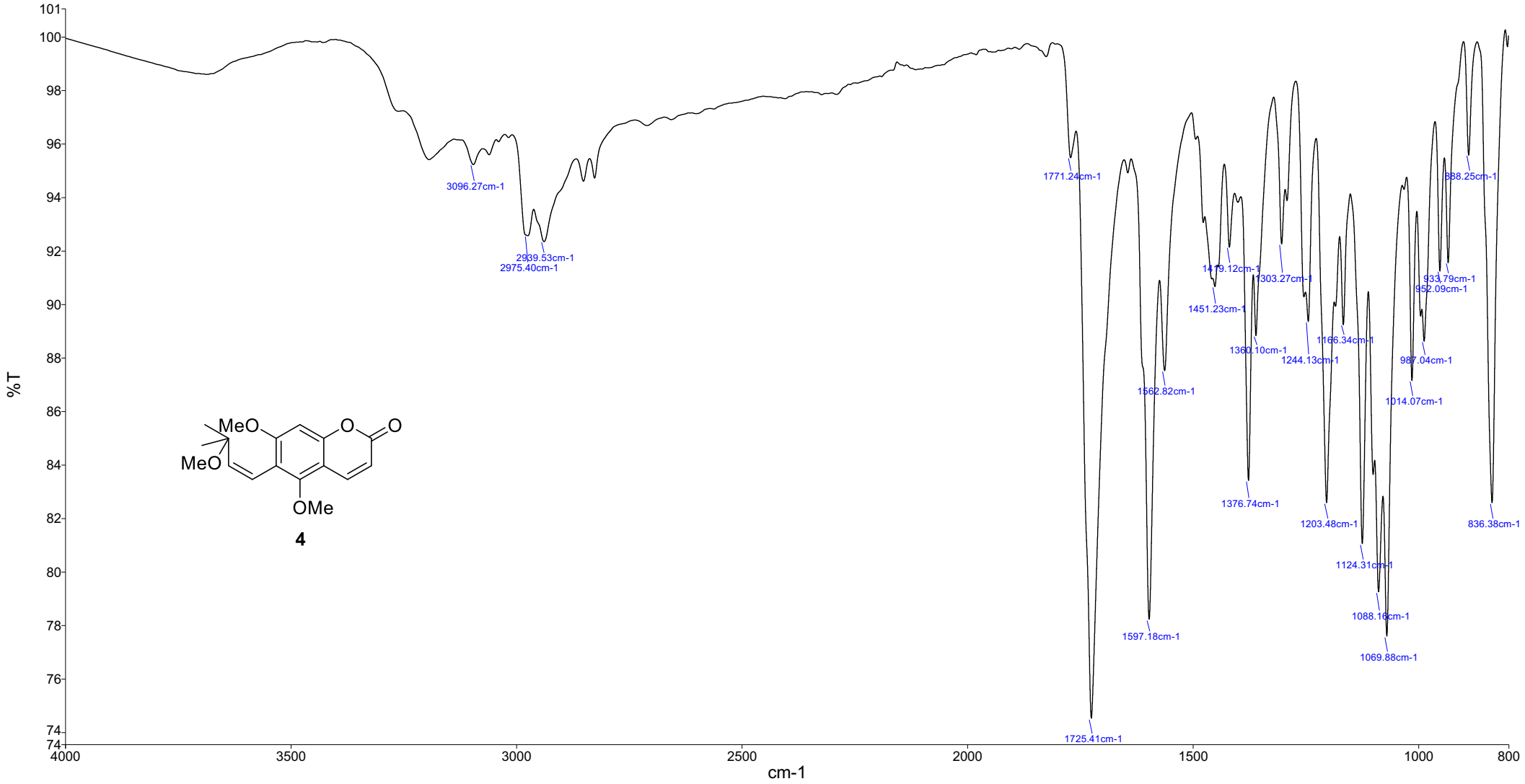
S5.16. IR (KBr disc) spectrum of compound **2**



S5.17. IR (KBr disc) spectrum of compound **3**

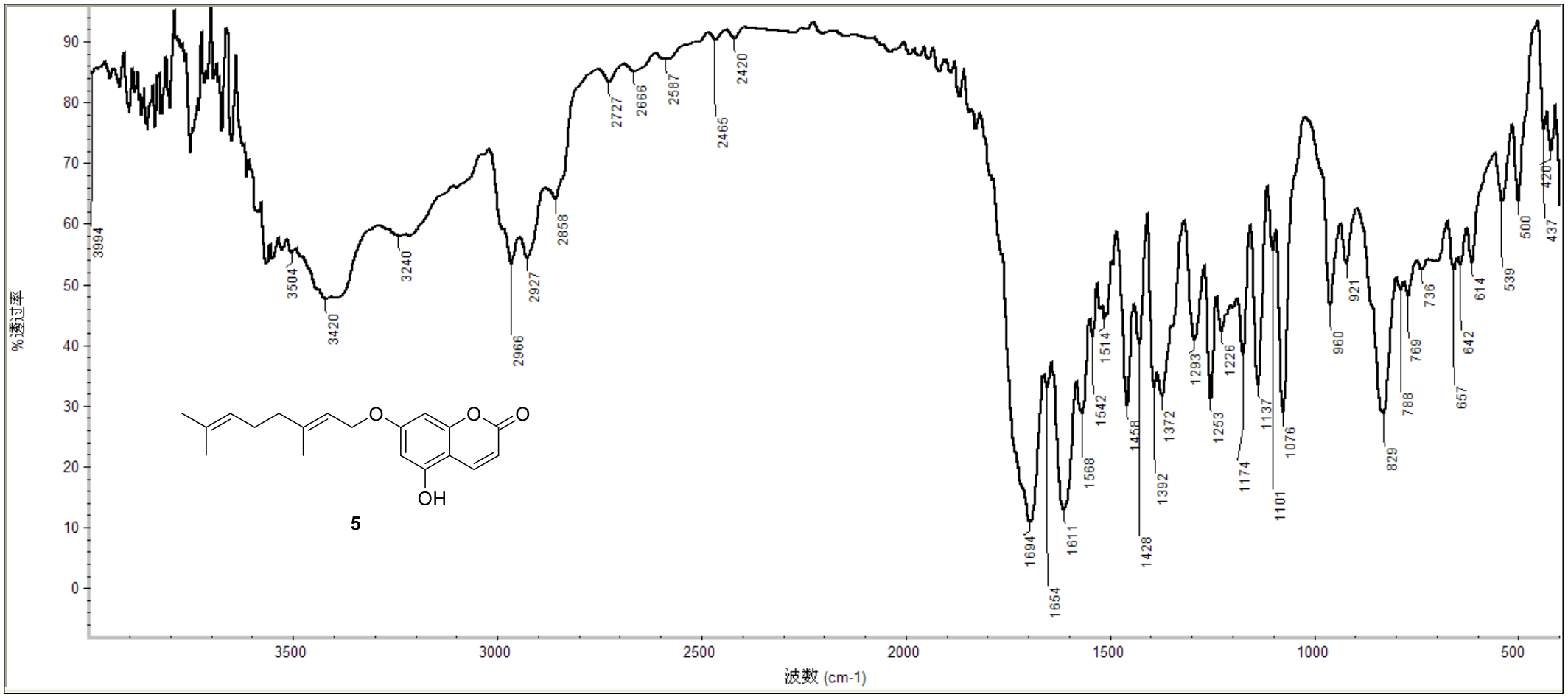


S5.18. IR (KBr disc) spectrum of compound **4**

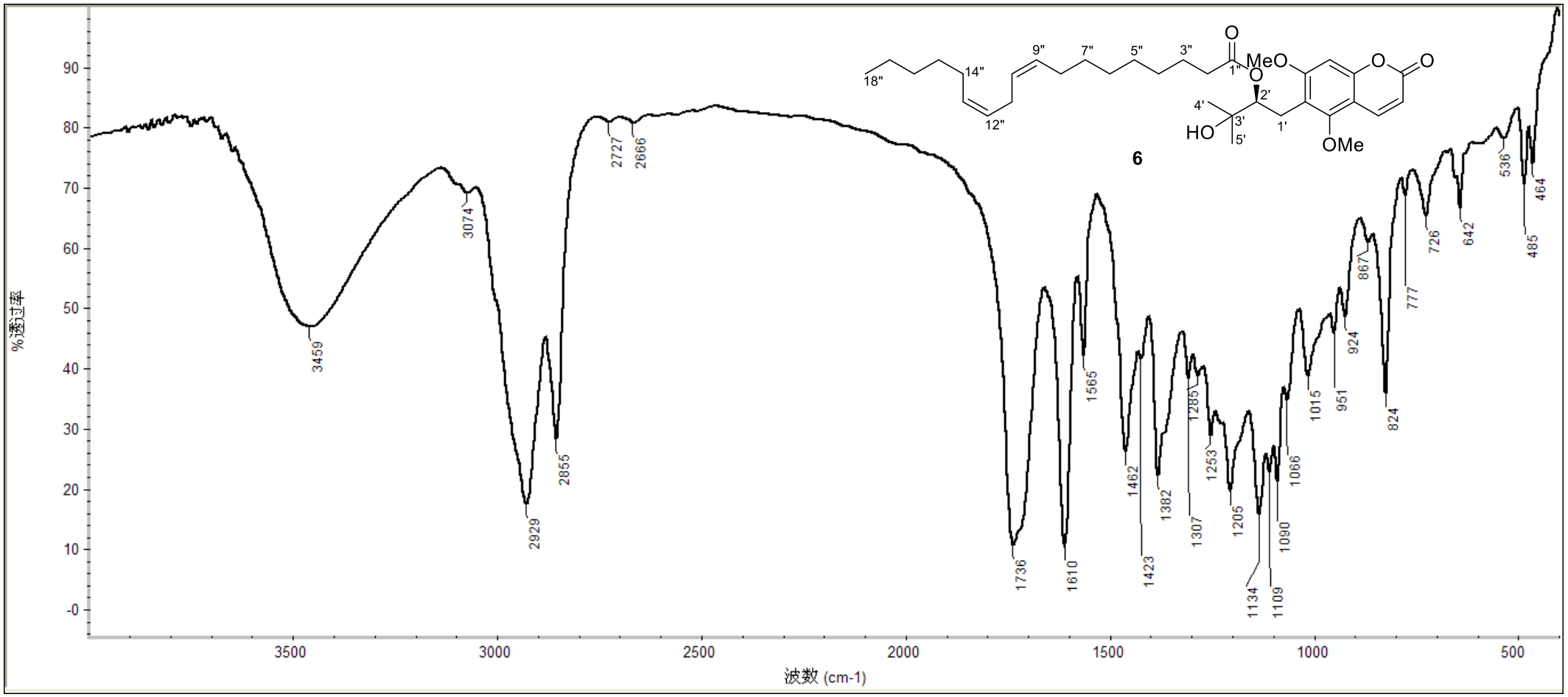


4

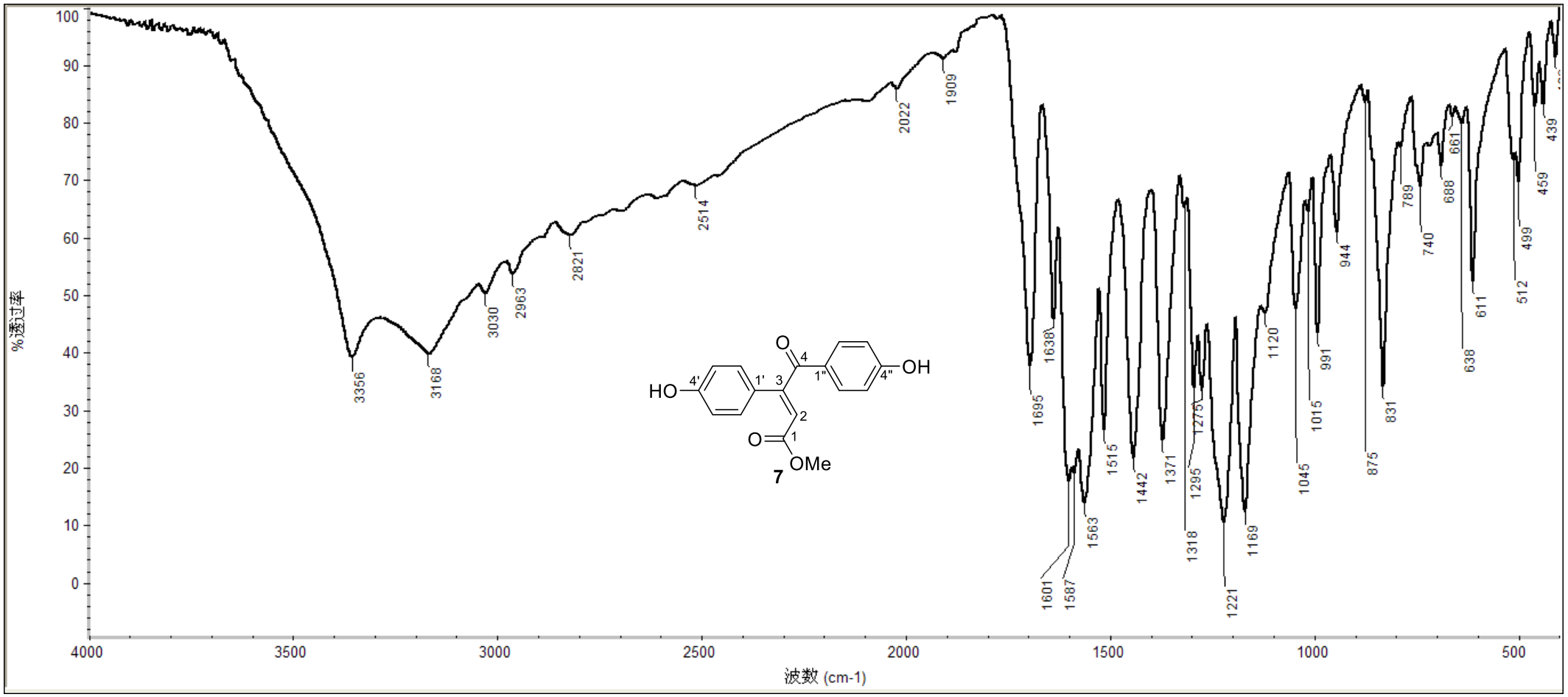
S5.19. IR (KBr disc) spectrum of compound **5**



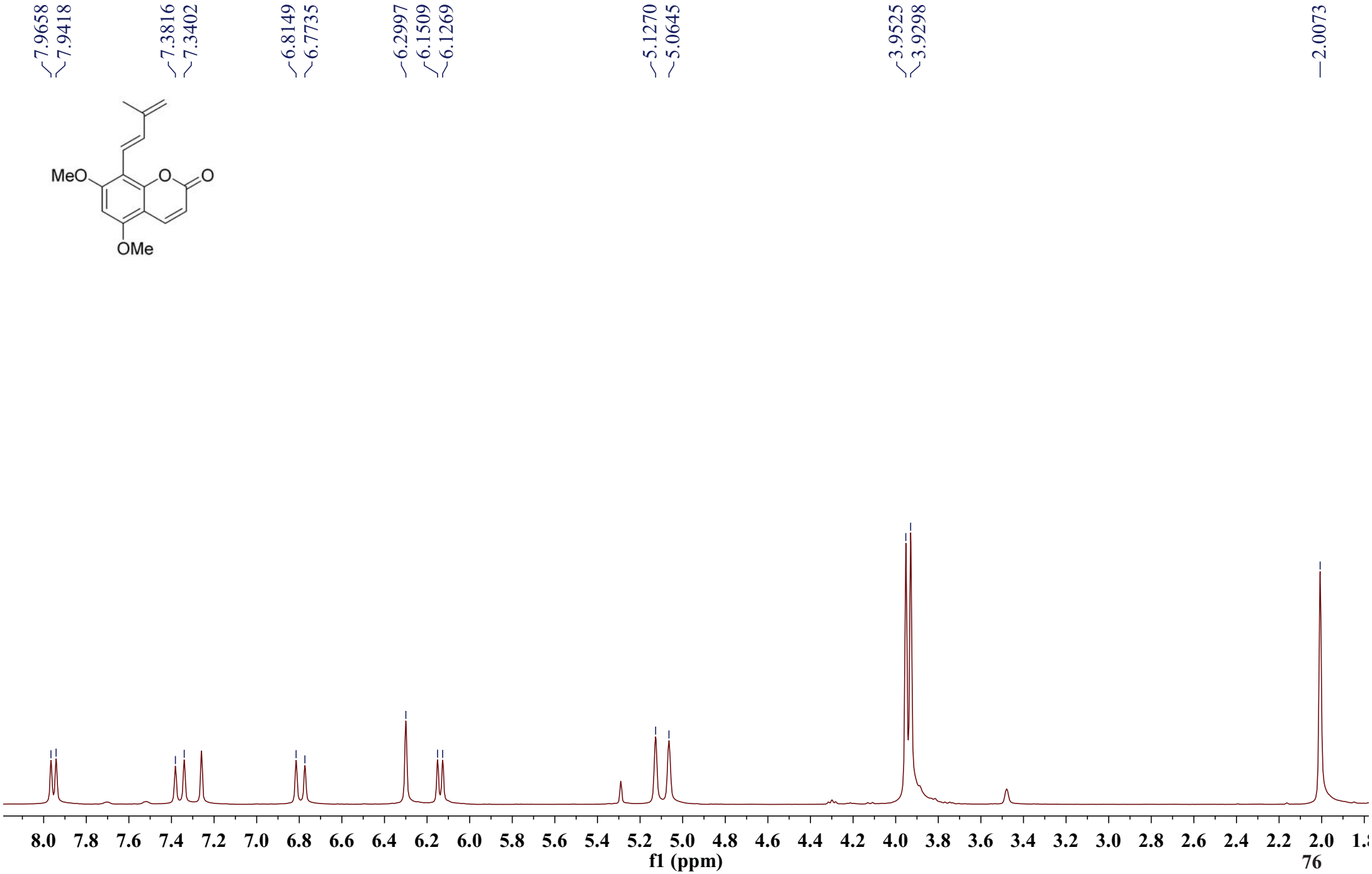
S5.20. IR (KBr disc) spectrum of compound **6**



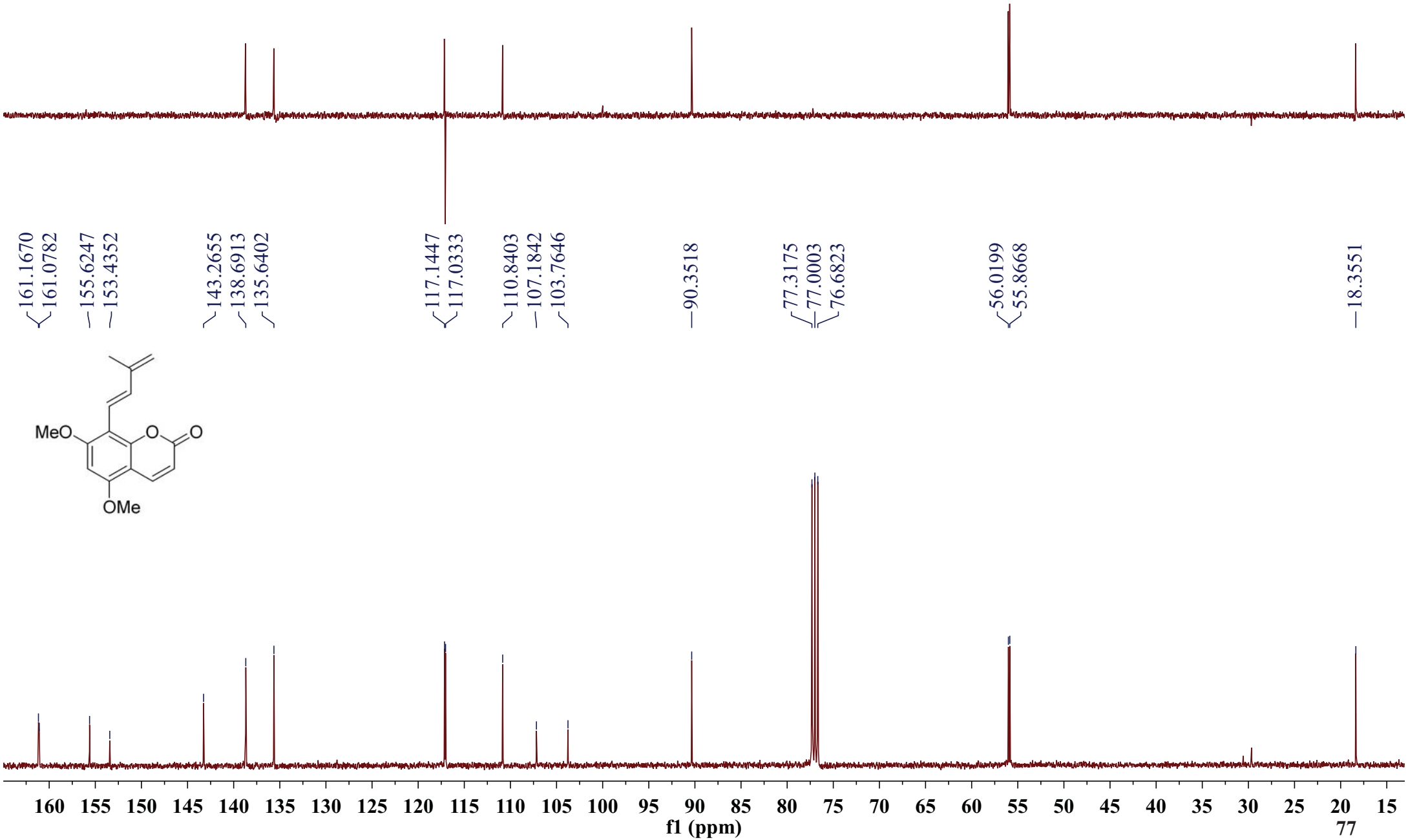
S5.21. IR (KBr disc) spectrum of compound **7**



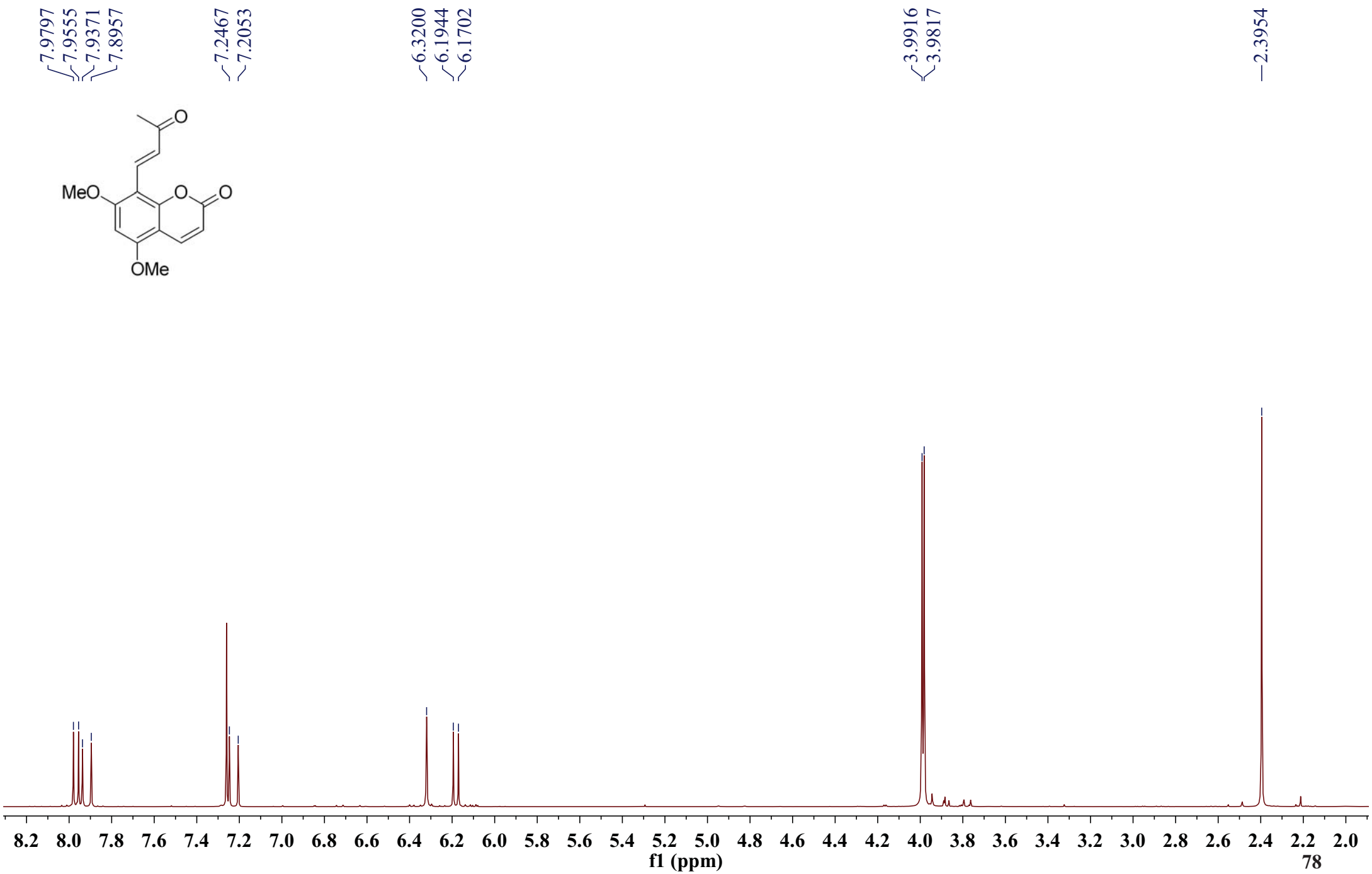
S6.1. ^{1}H NMR spectrum of compound **8**



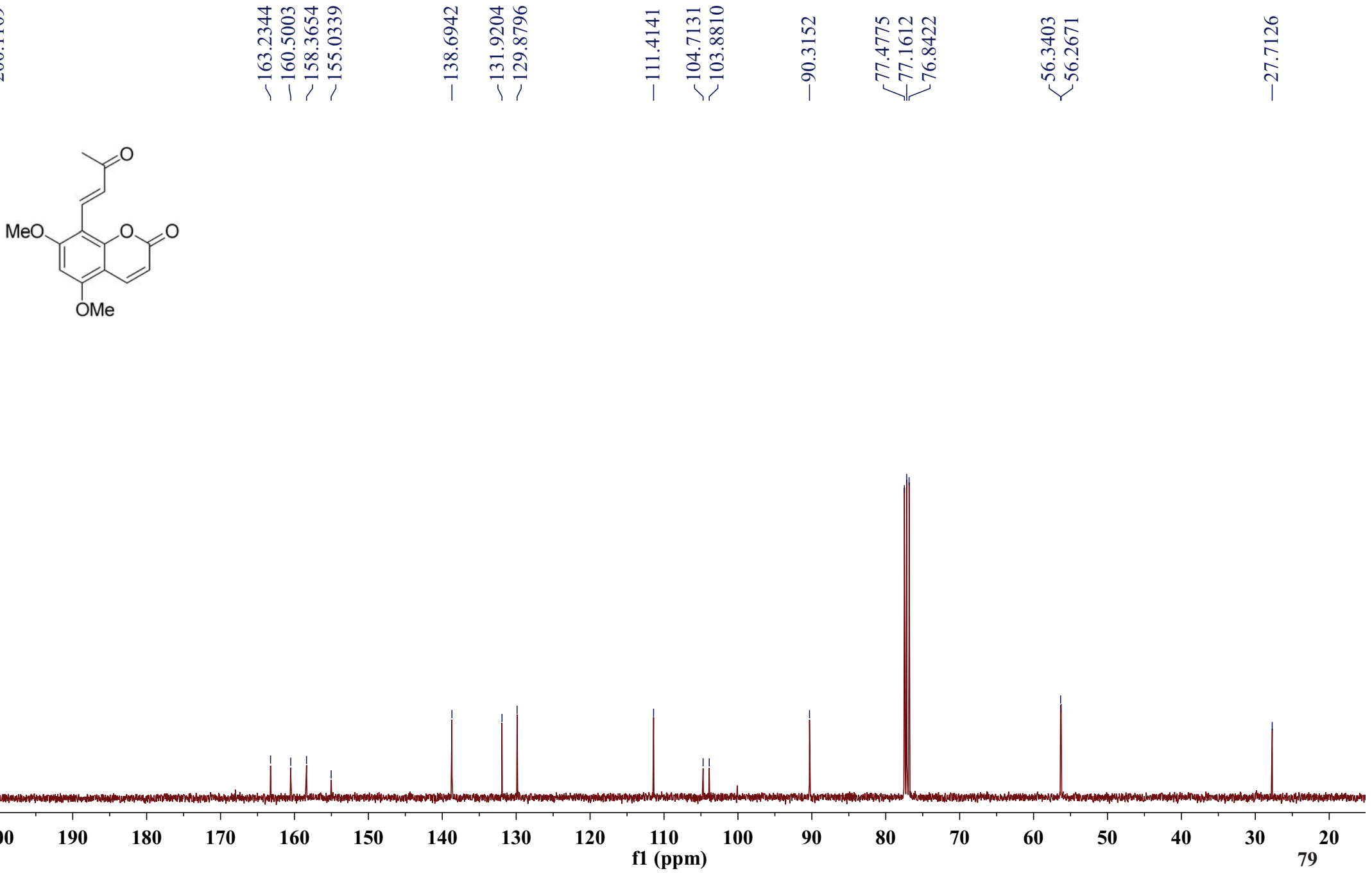
S6.2. ^{13}C NMR and DEPT spectra of compound **8**



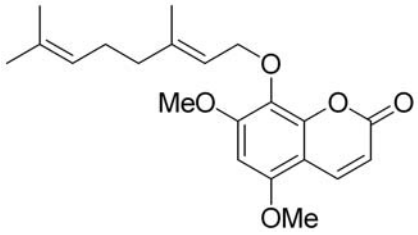
S6.3. ^{1}H NMR spectrum of compound **9**



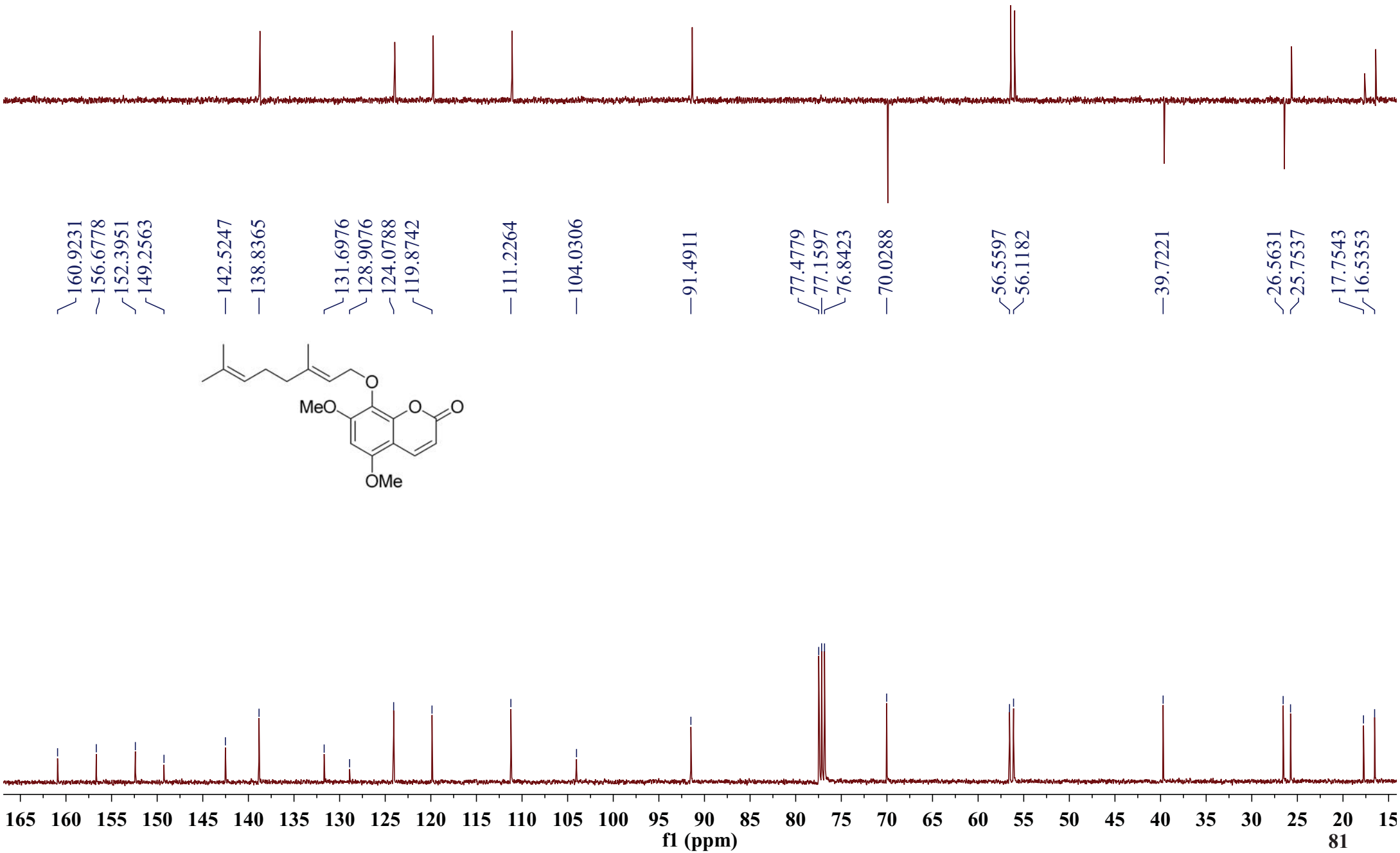
S6.4. ^{13}C NMR spectrum of compound **9**



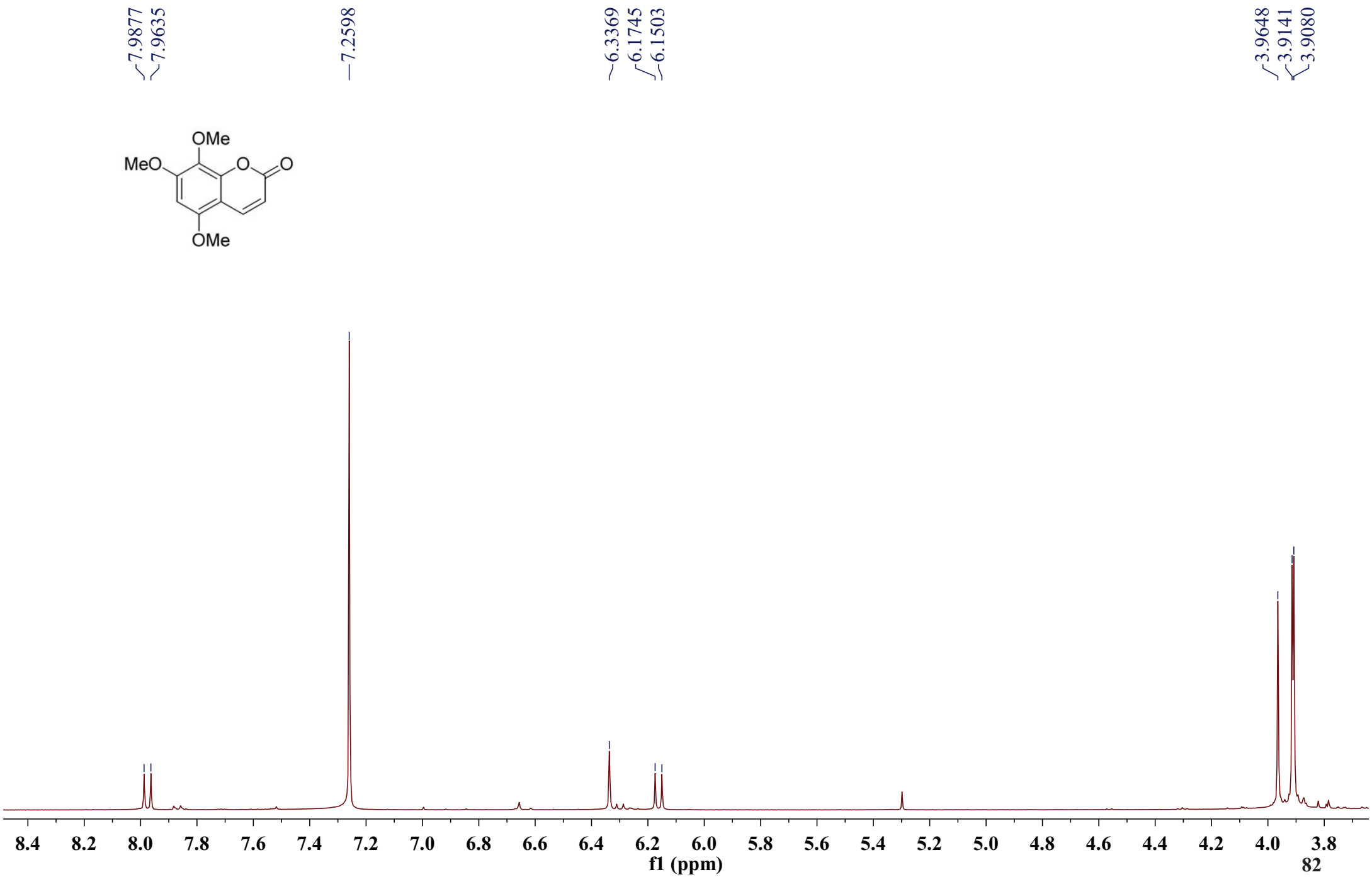
S6.5. ^{1}H NMR spectrum of compound **10**



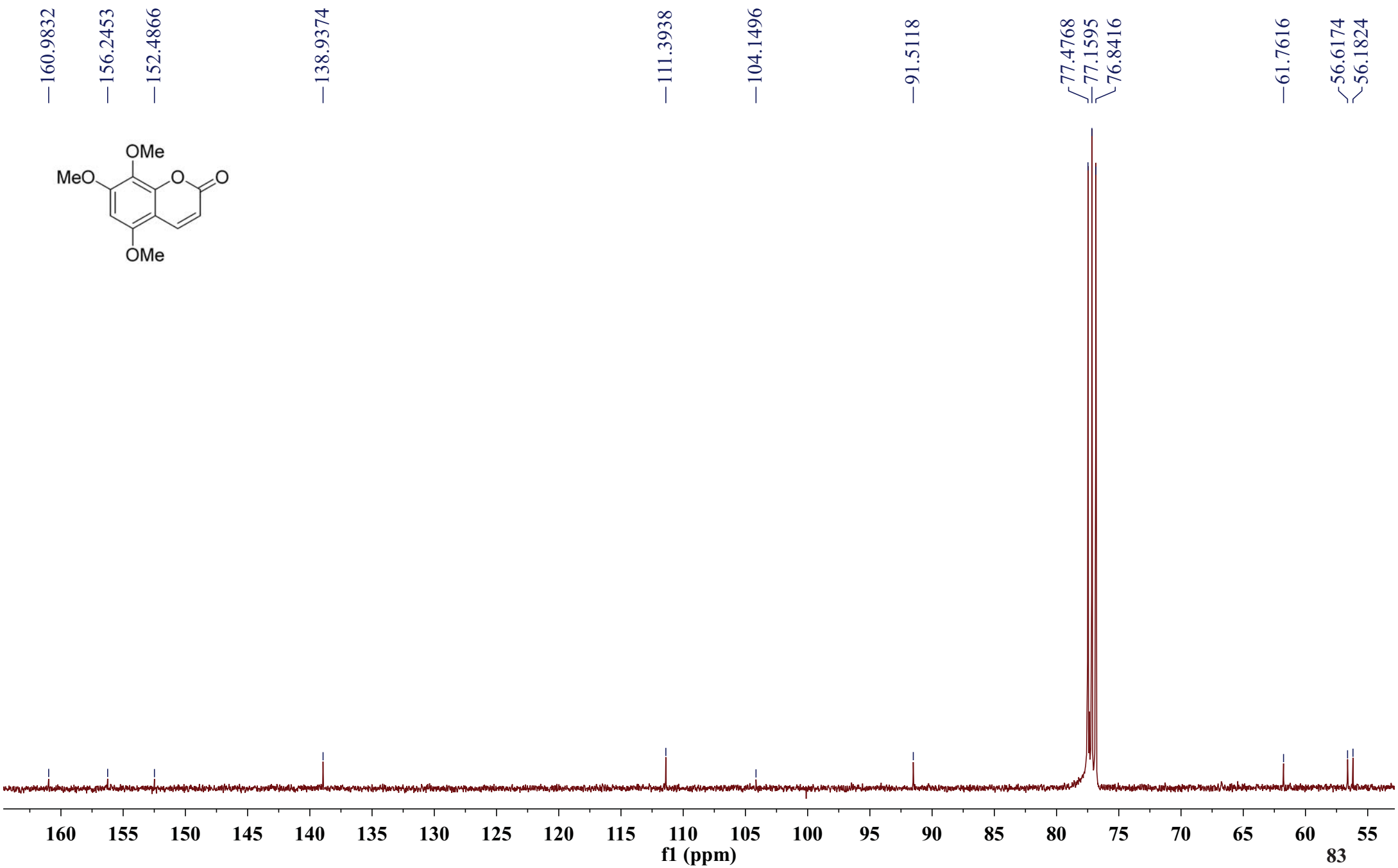
S6.6. ^{13}C NMR and DEPT spectra of compound **10**



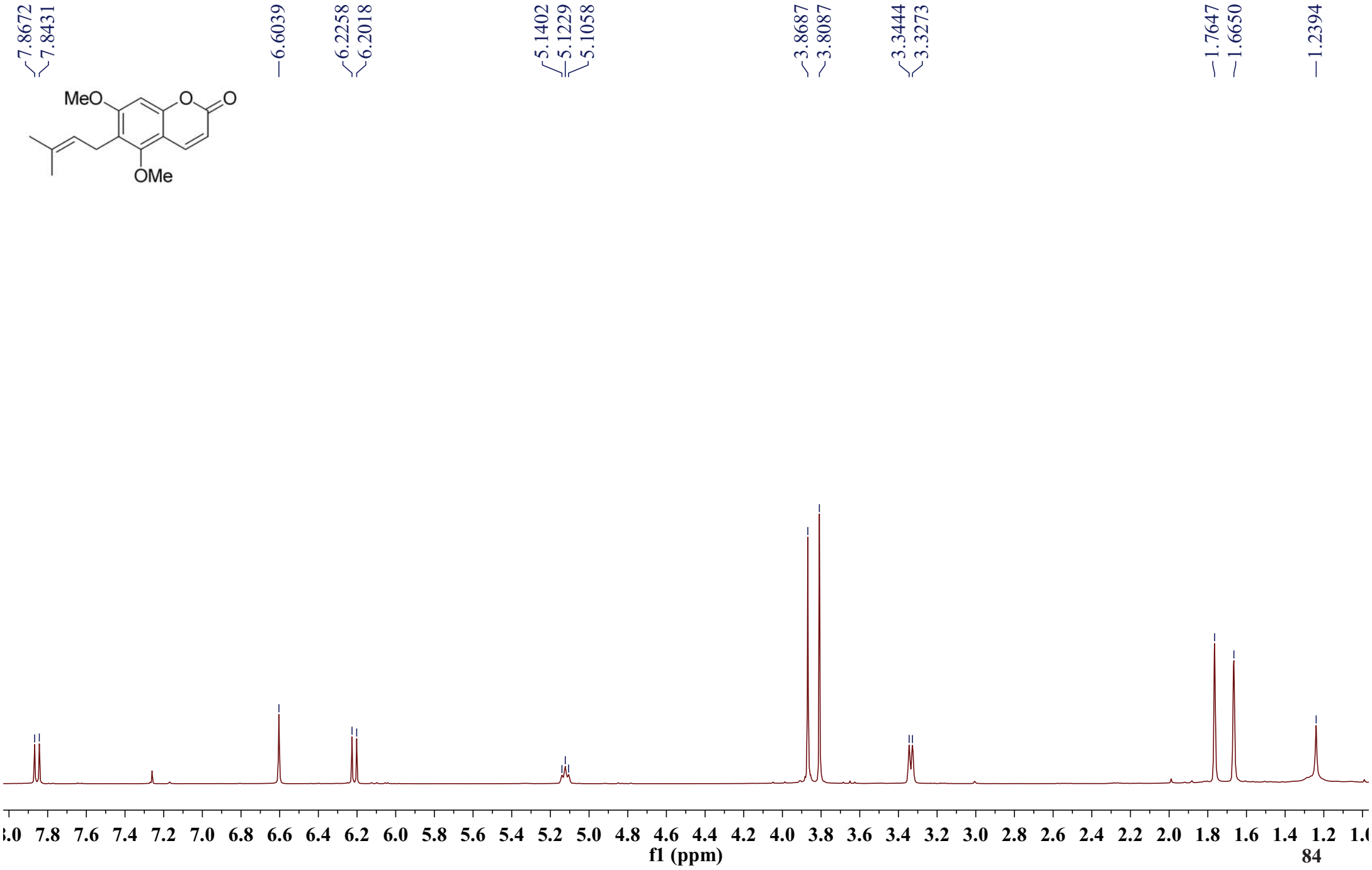
S6.7. ^{1}H NMR spectrum of compound **11**



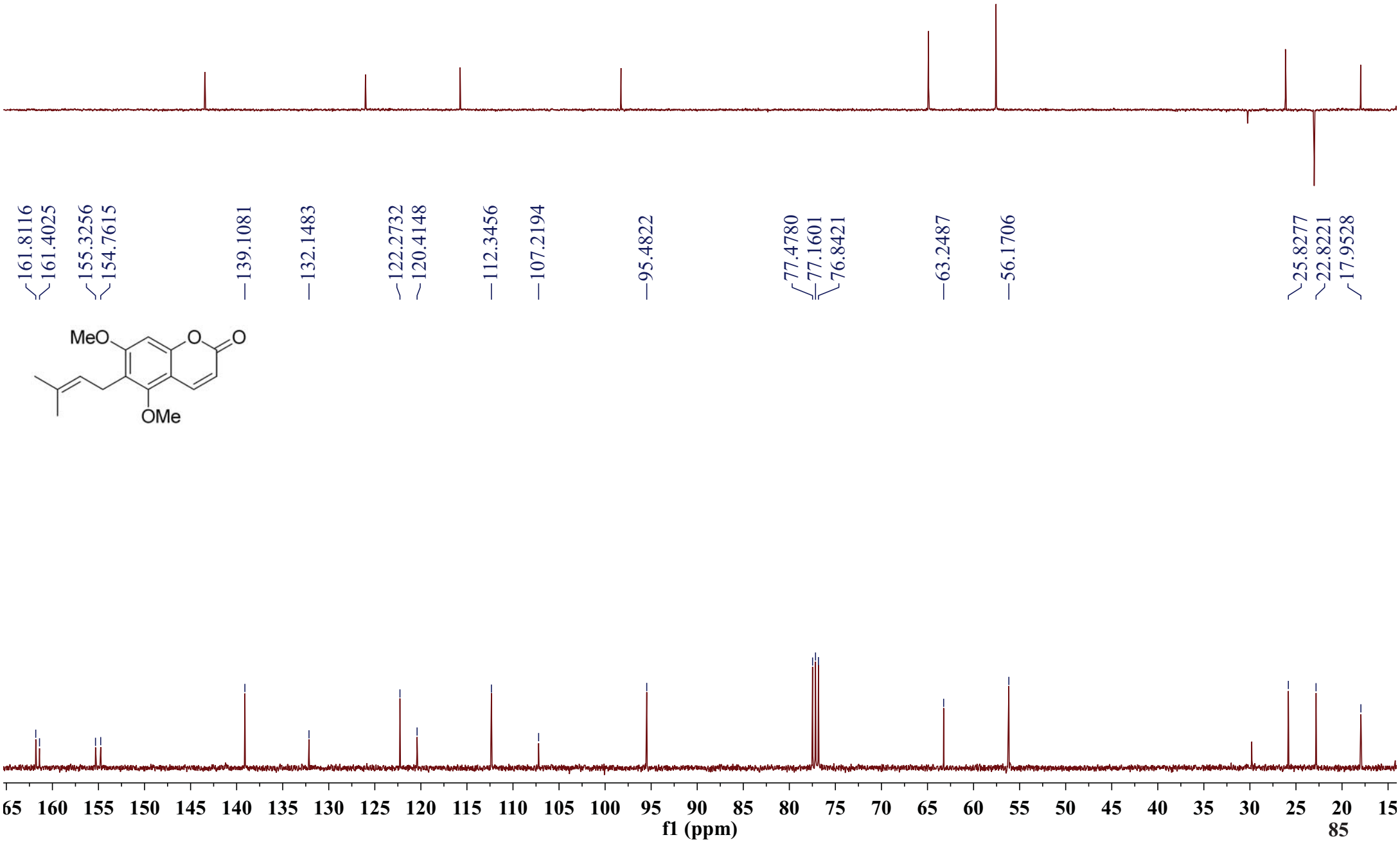
S6.8. ^{13}C NMR spectrum of compound **11**



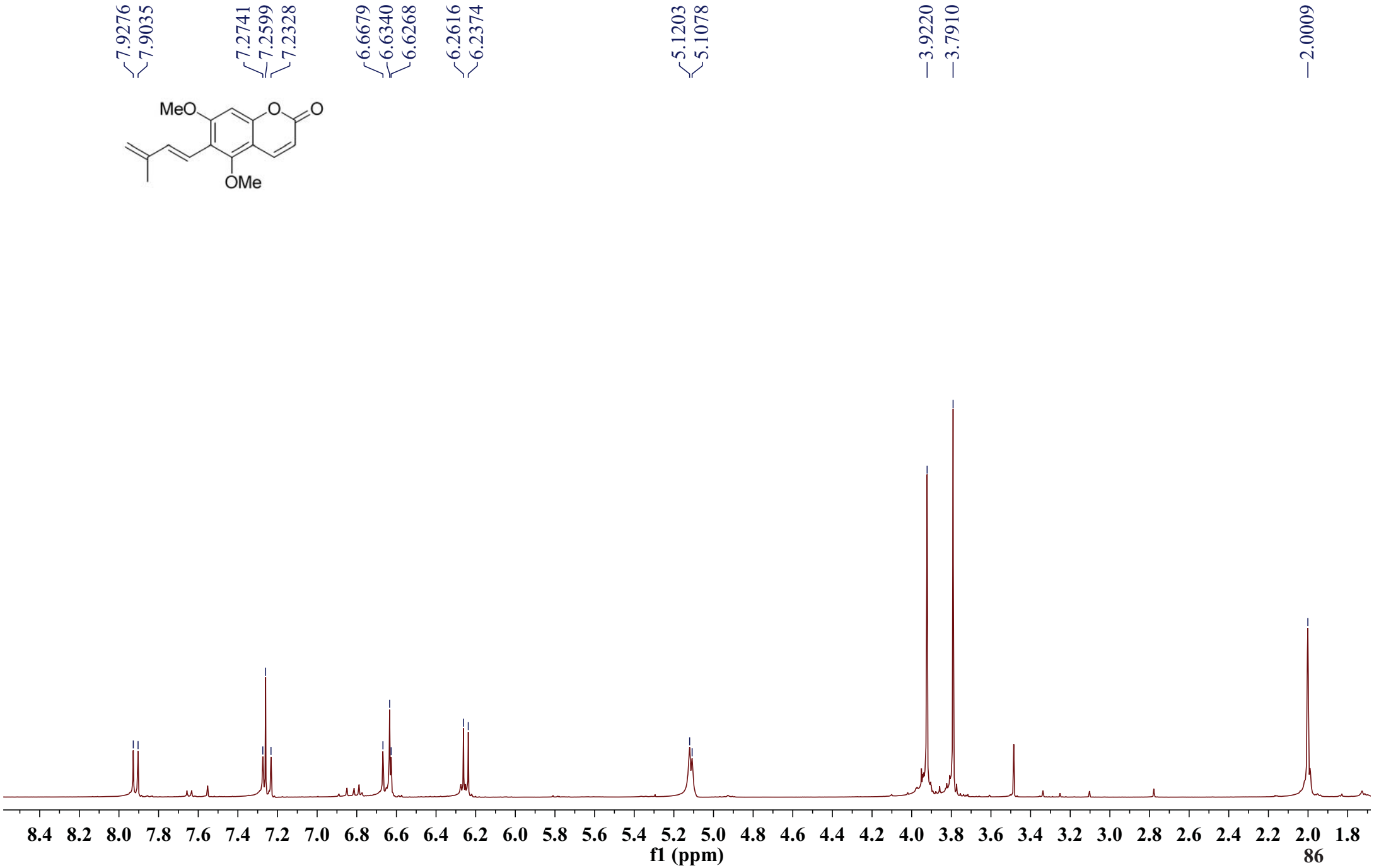
S6.9. ^{1}H NMR spectrum of compound **12**



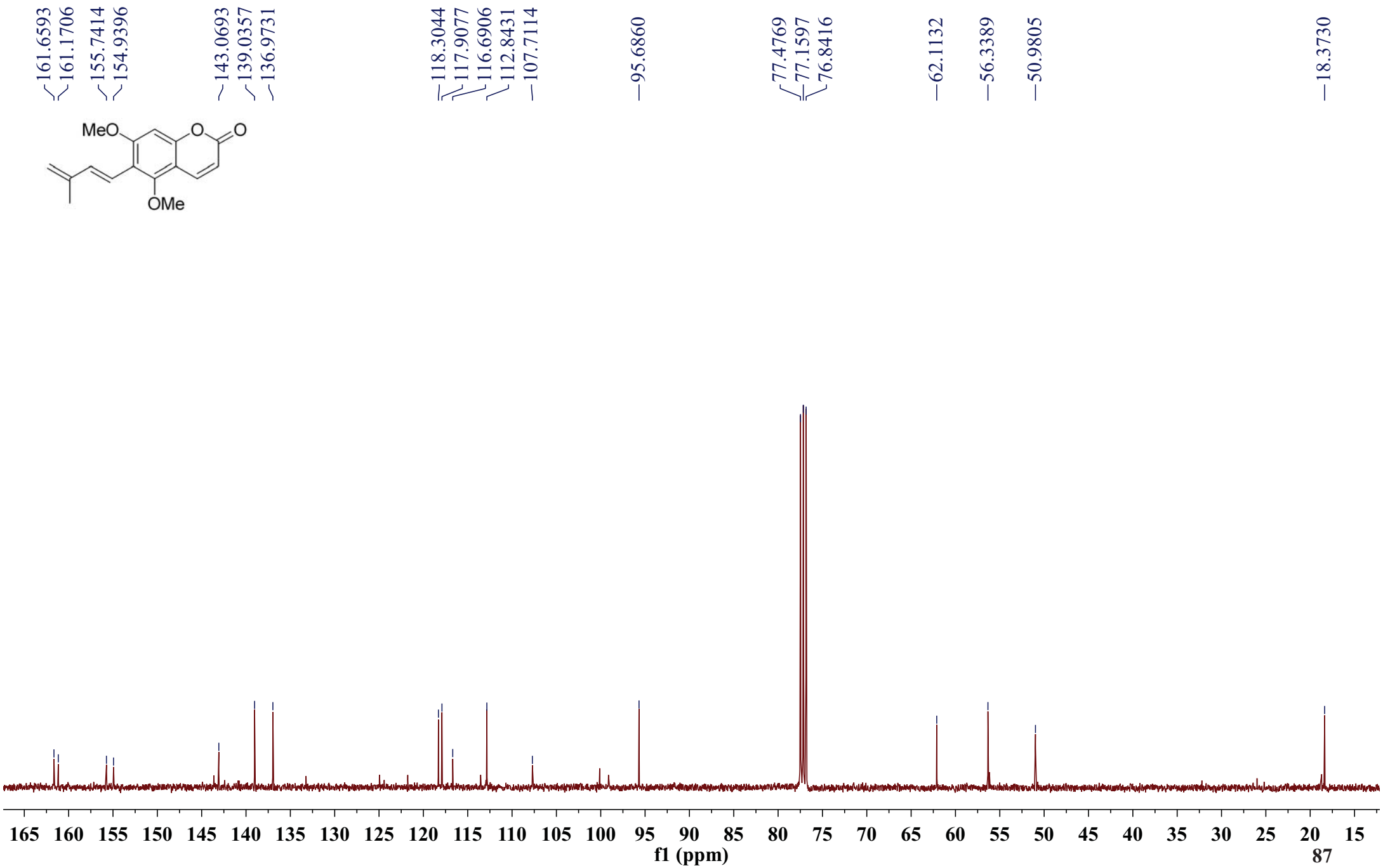
S6.10. ^{13}C NMR and DEPT spectra of compound **12**



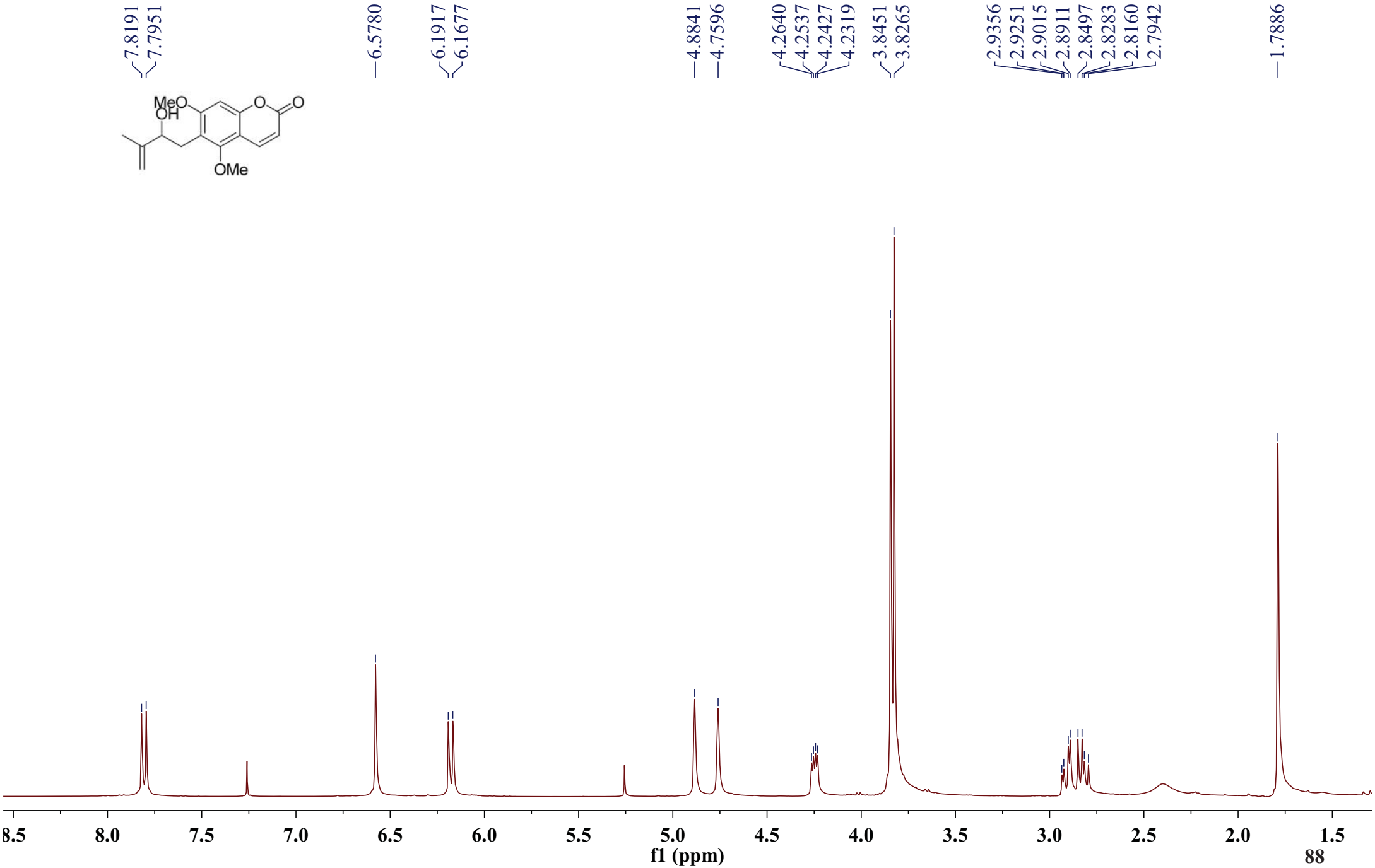
S6.11. ^{1}H NMR spectrum of compound **13**



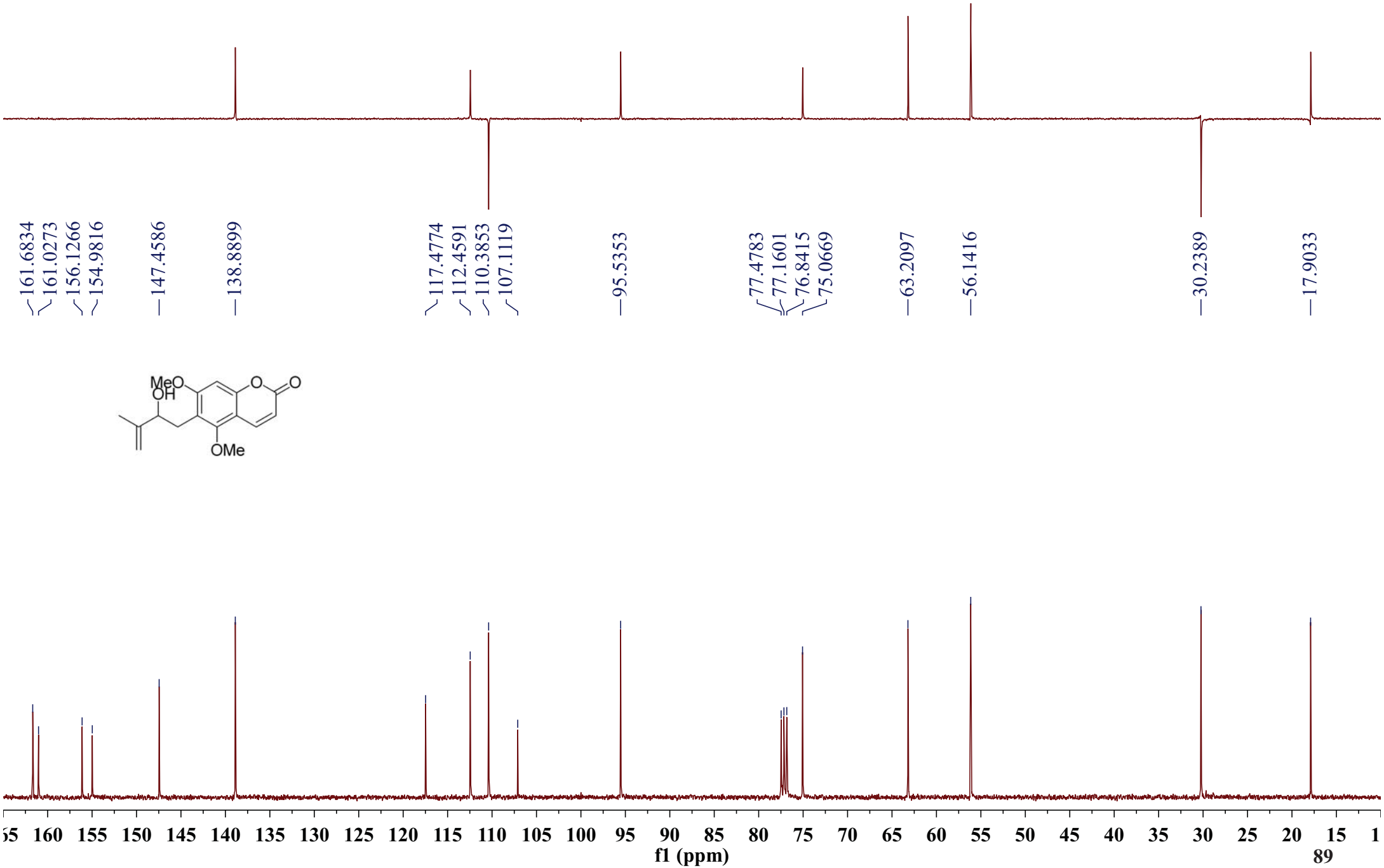
S6.12. ^{13}C NMR spectrum of compound **13**



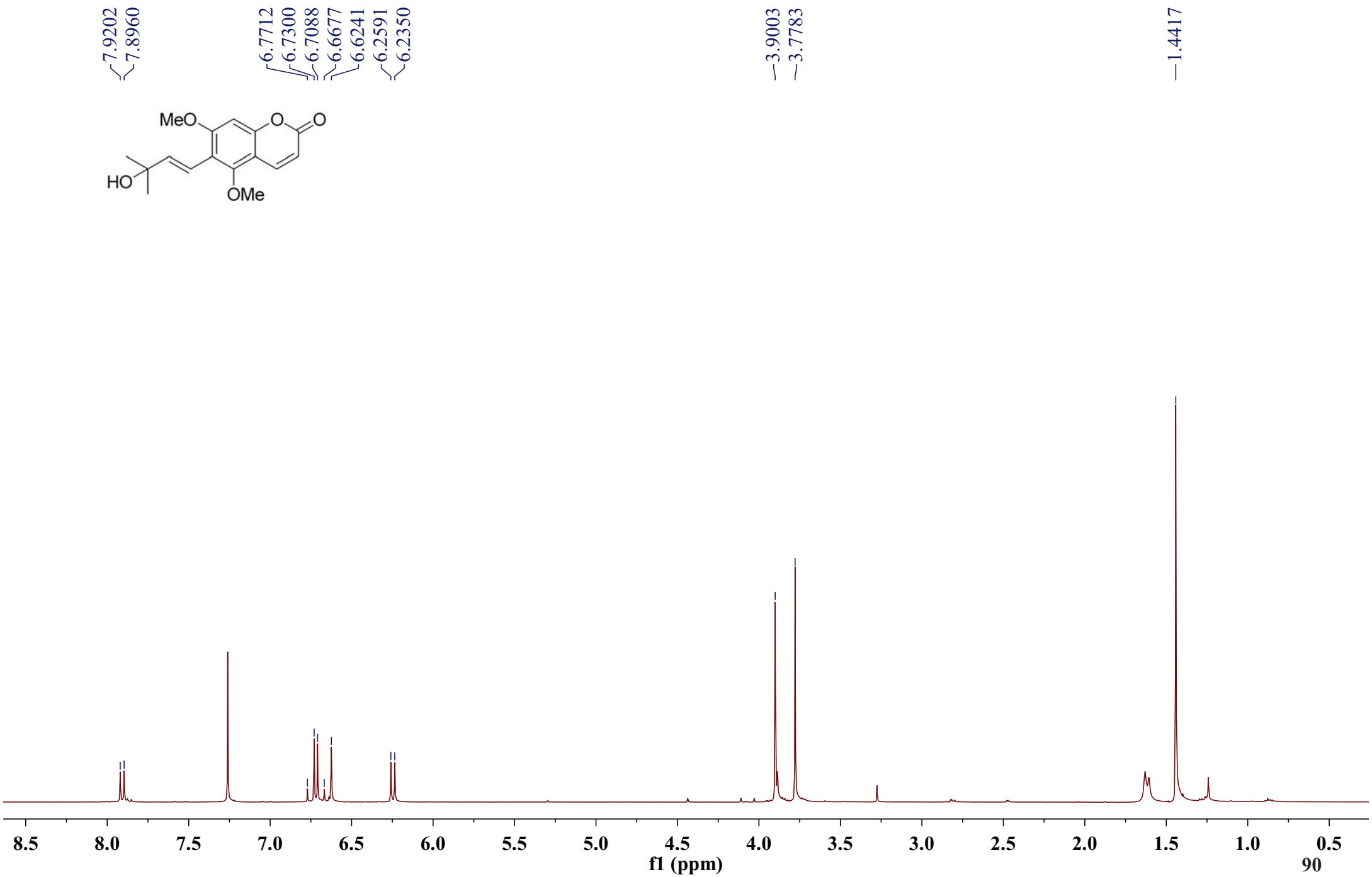
S6.13. ^{1}H NMR spectrum of compound **14**



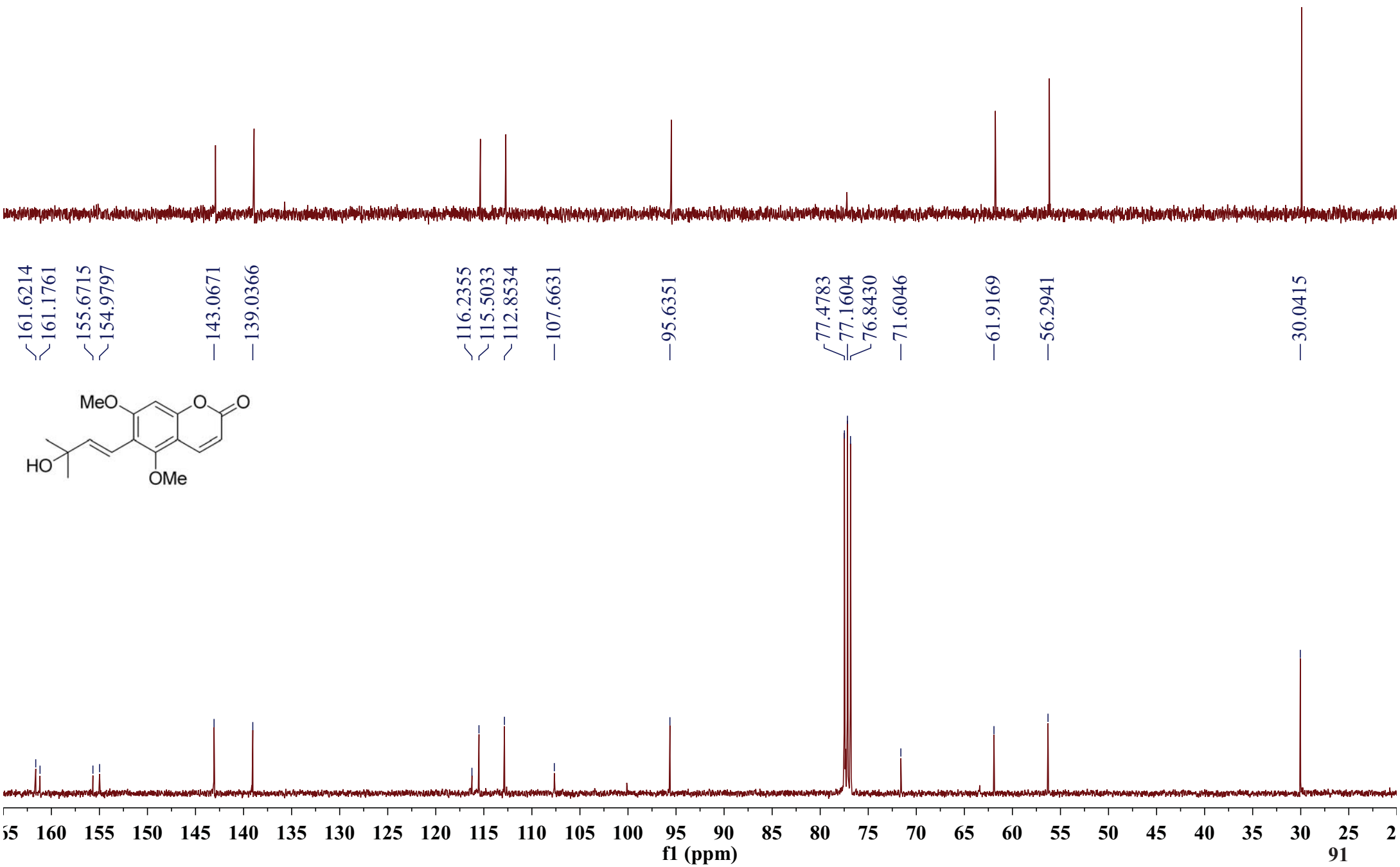
S6.14. ^{13}C NMR and DEPT spectra of compound **14**



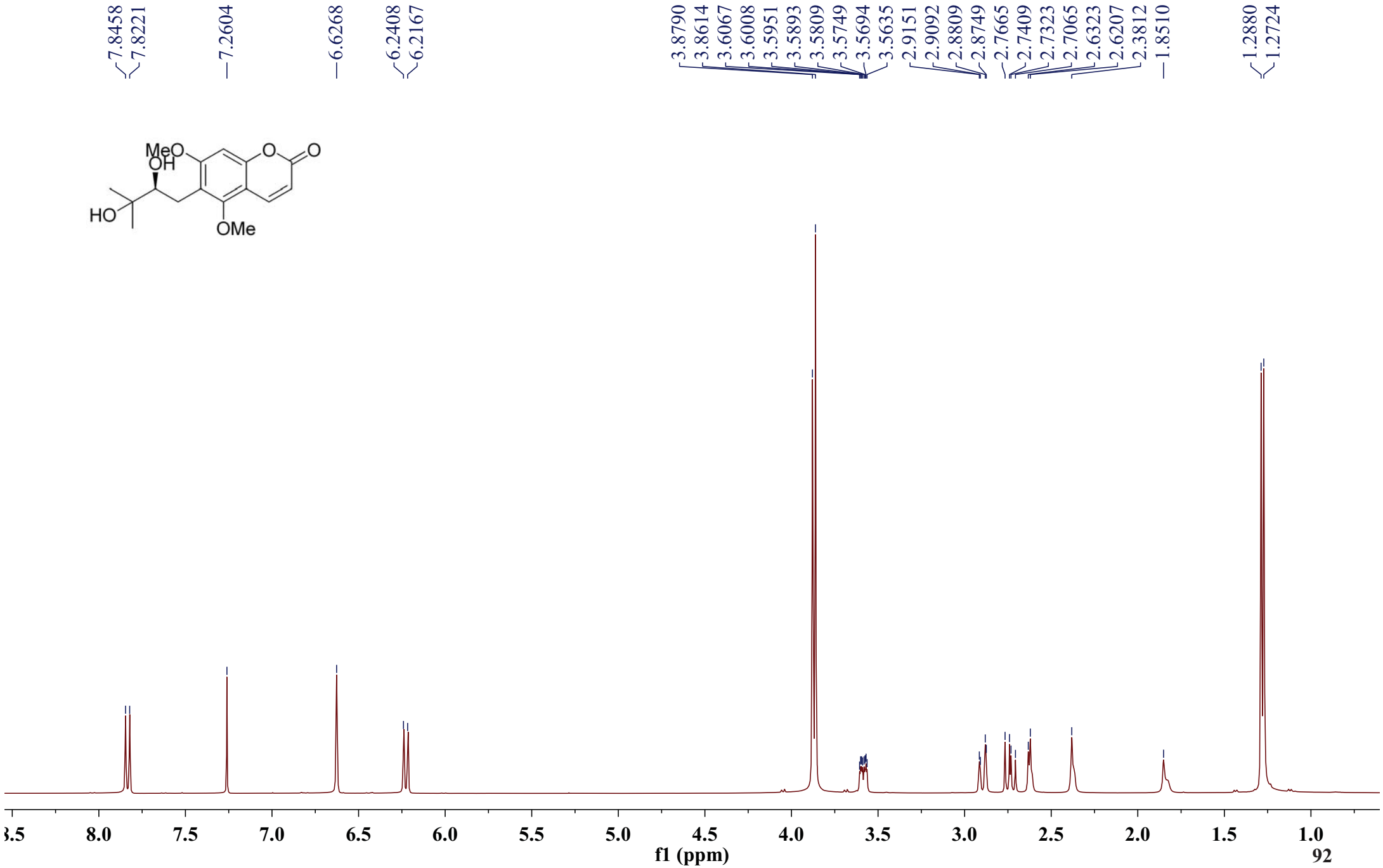
S6.15. ^{1}H NMR spectrum of compound **15**



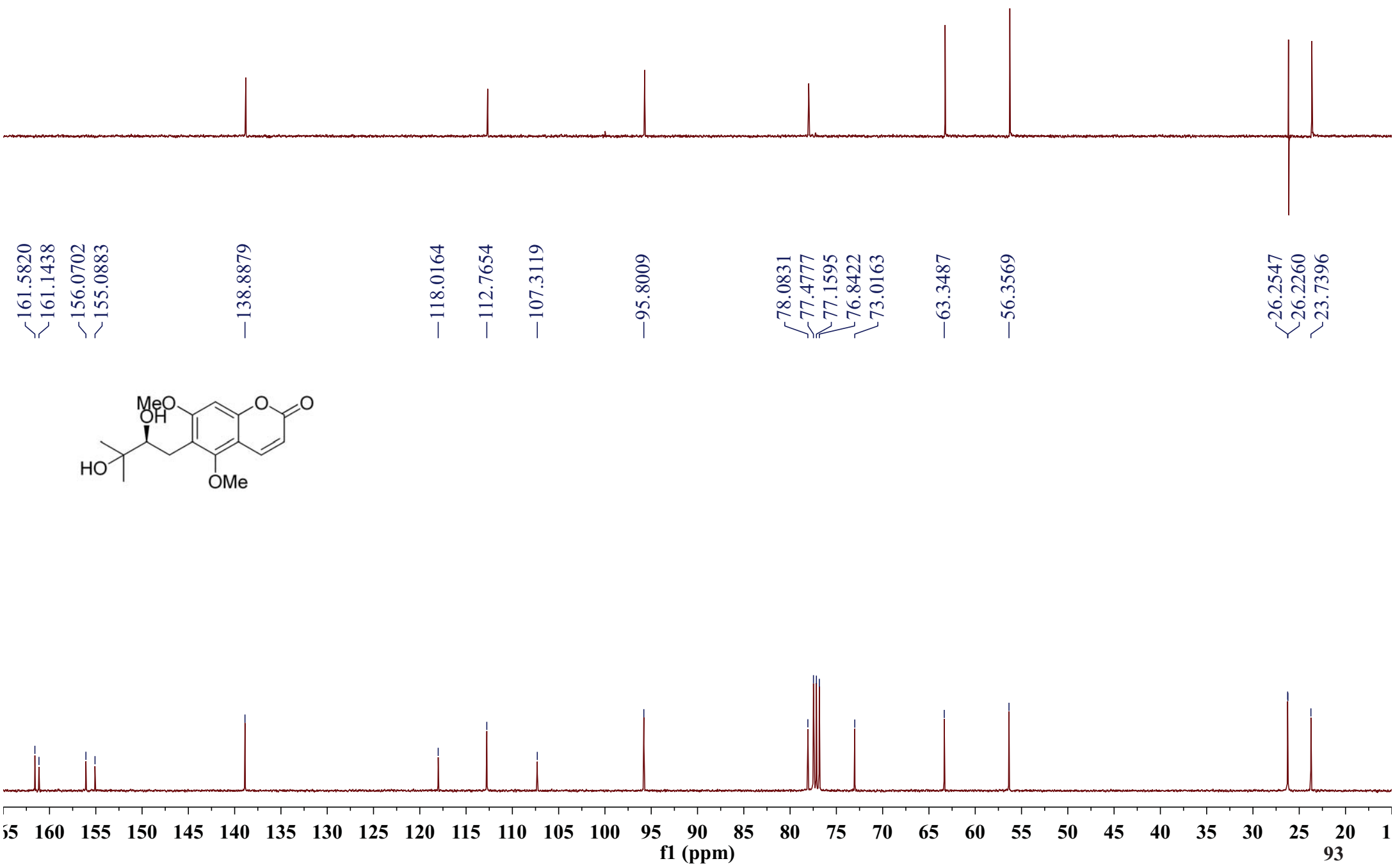
S6.16. ^{13}C NMR and DEPT spectra of compound **15**



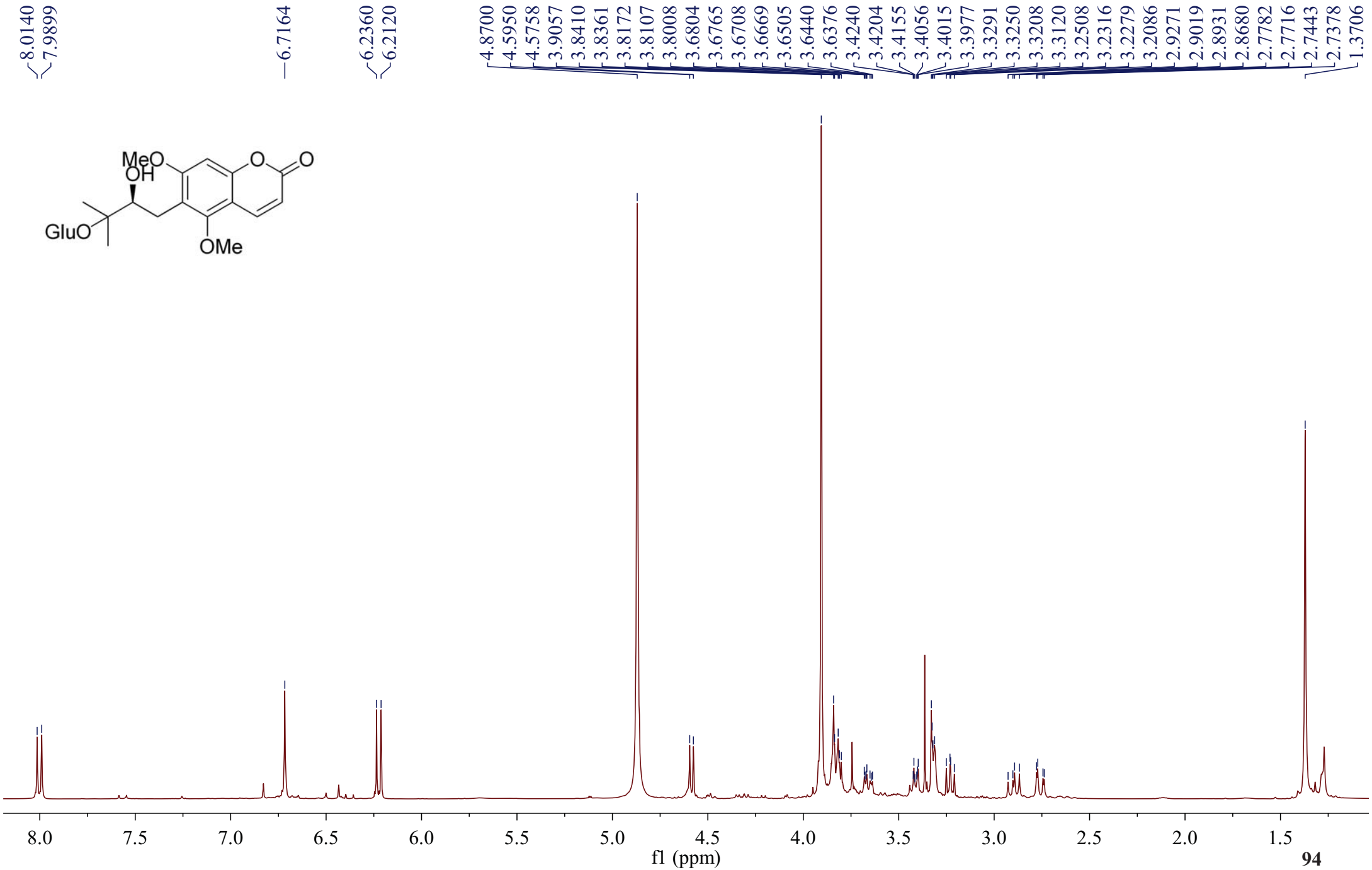
S6.17. ^{1}H NMR spectrum of compound **16**



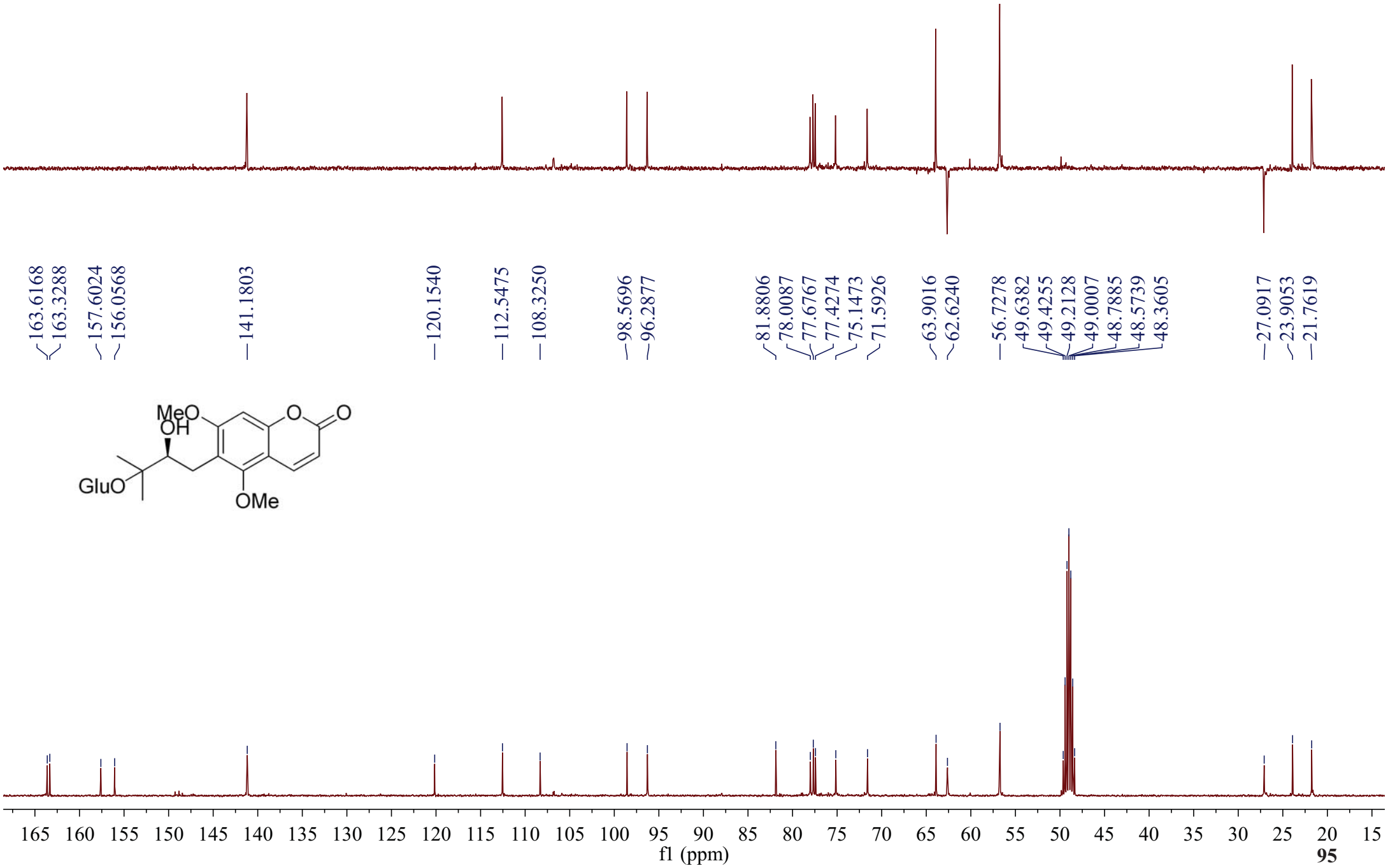
S6.18. ^{13}C NMR and DEPT spectra of compound **16**



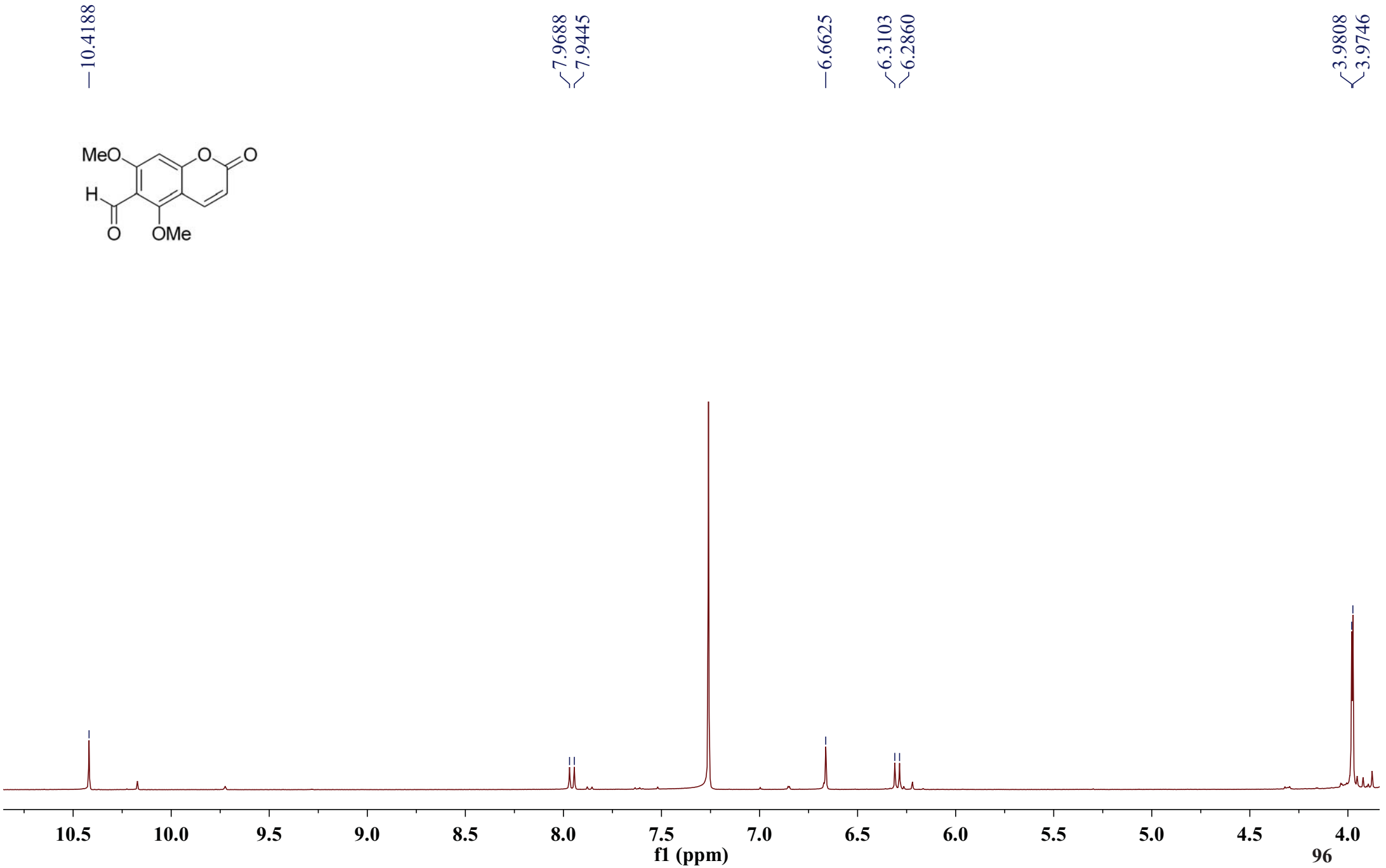
S6.19. ^{1}H NMR spectrum of compound **17**



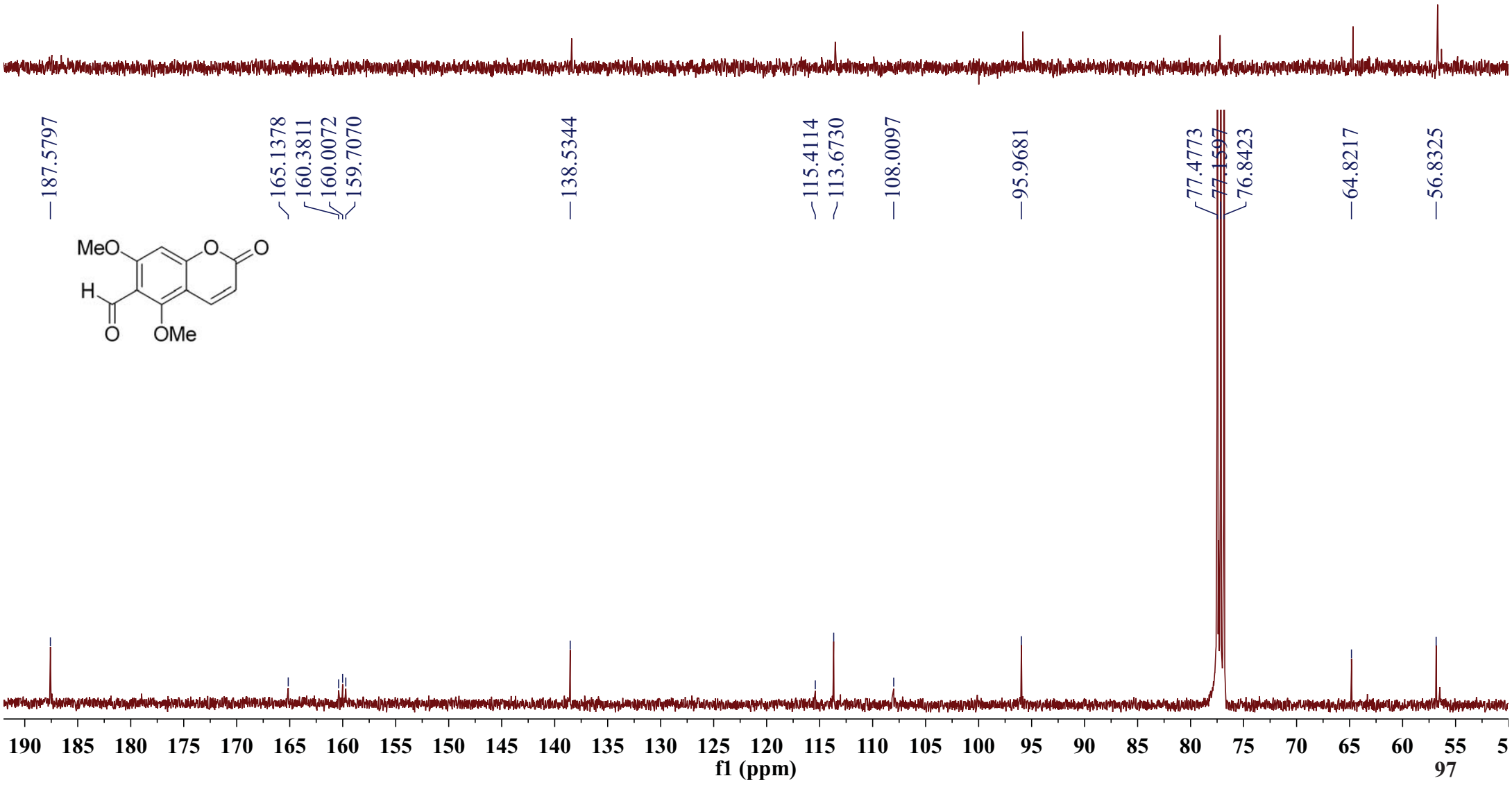
S6.20. ^{13}C NMR and DEPT spectra of compound **17**



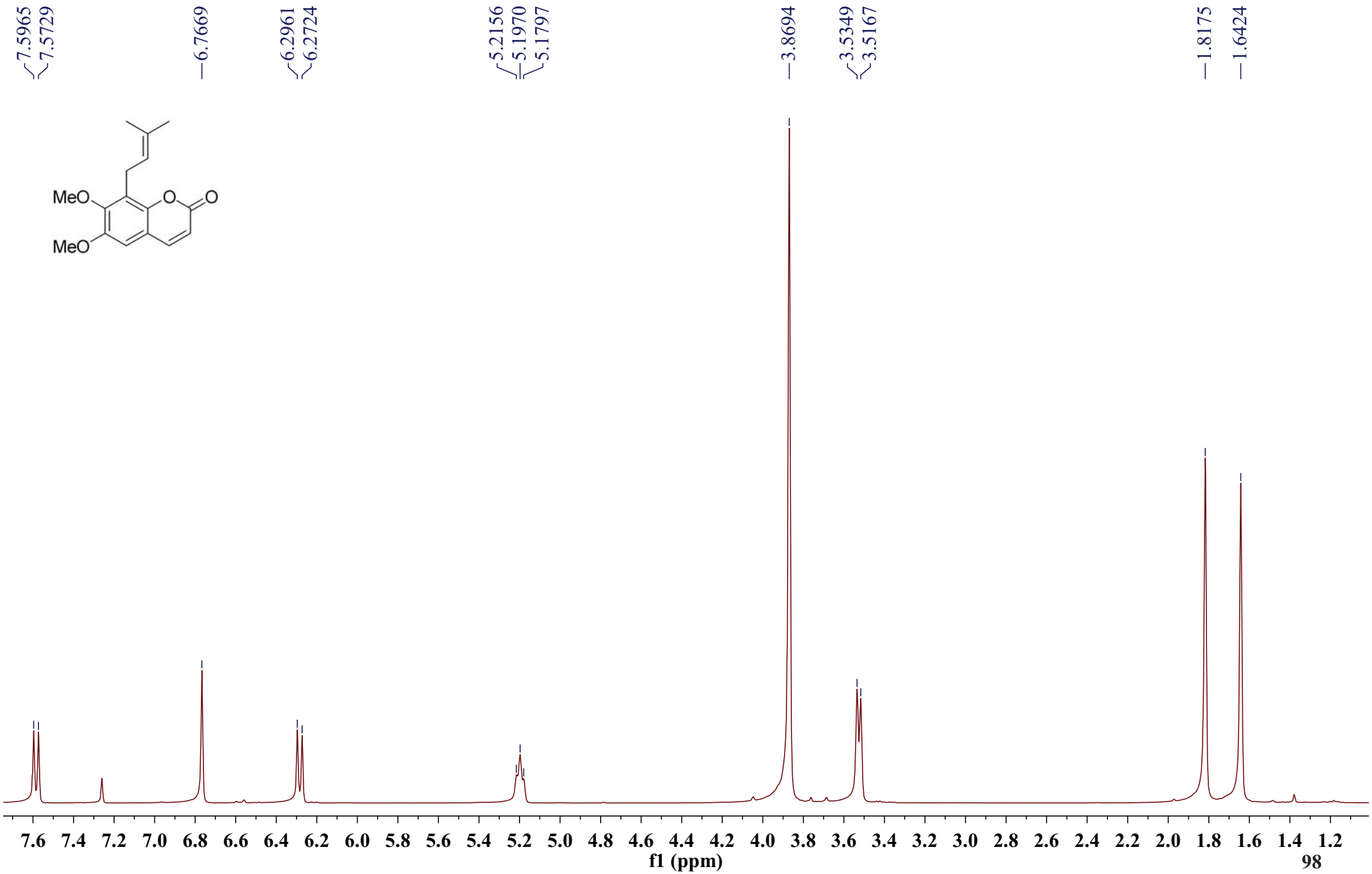
S6.21. ^{1}H NMR spectrum of compound **18**



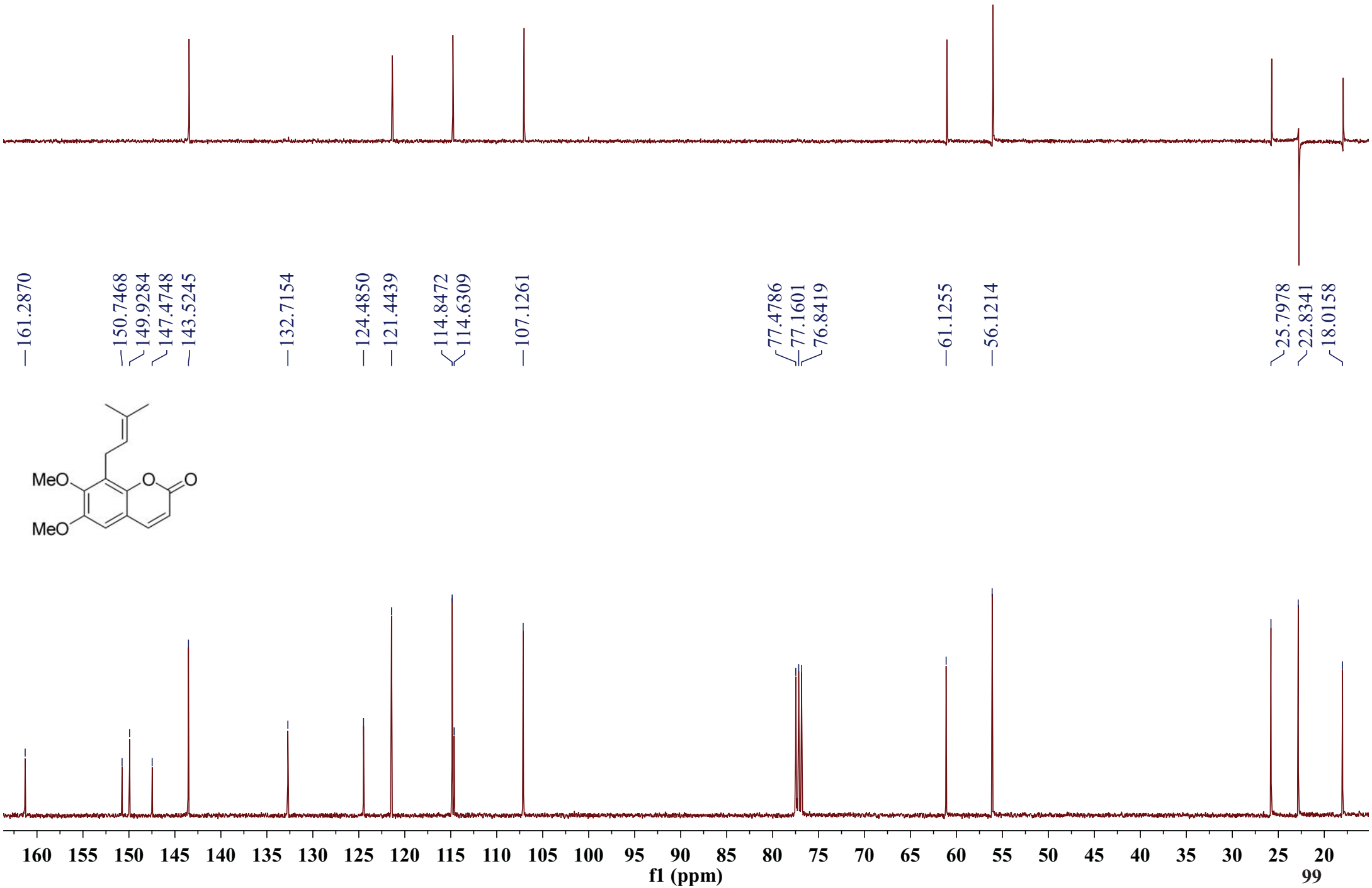
S6.22. ^{13}C NMR and DEPT spectra of compound **18**



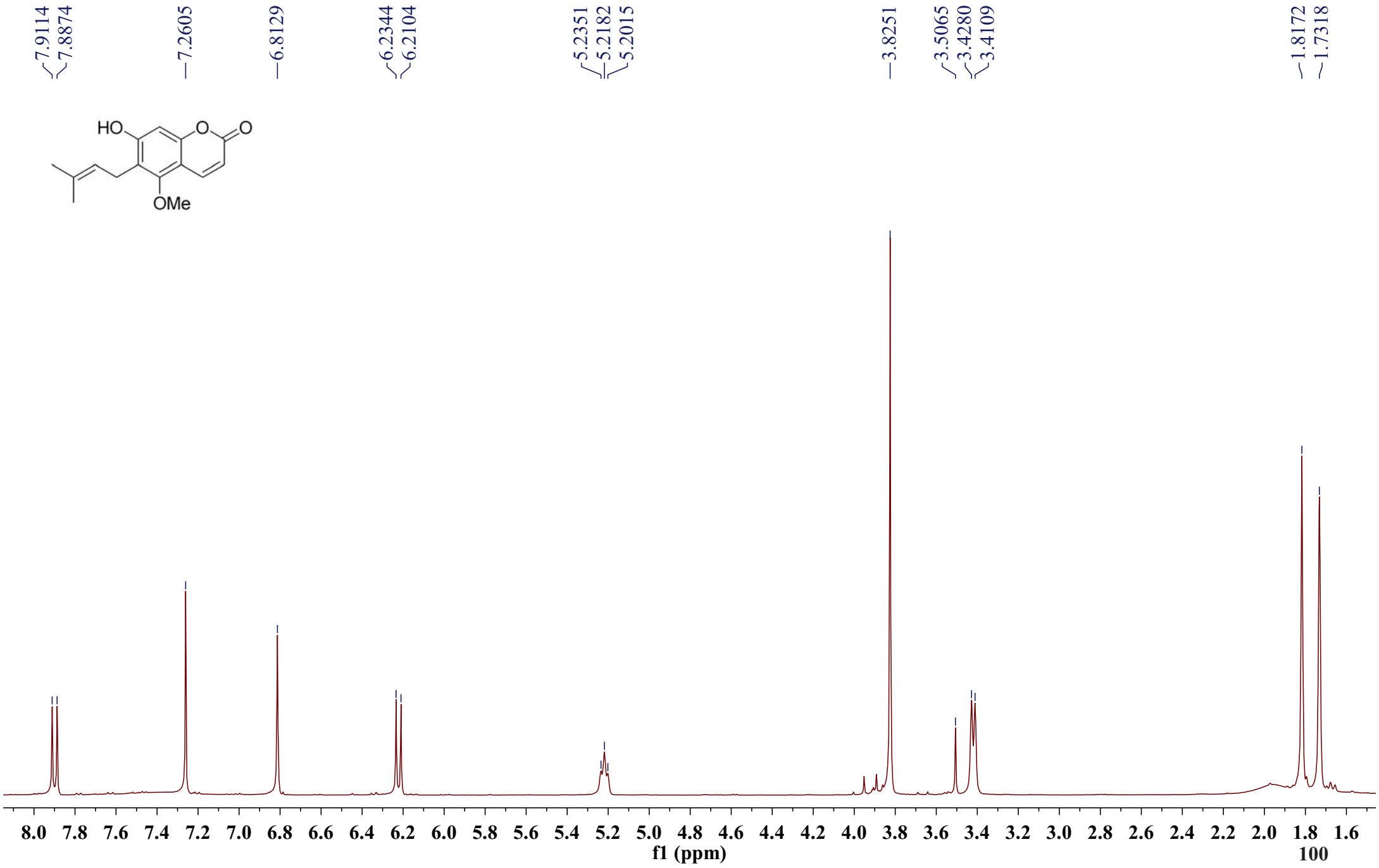
S6.23. ^{1}H NMR spectrum of compound **19**



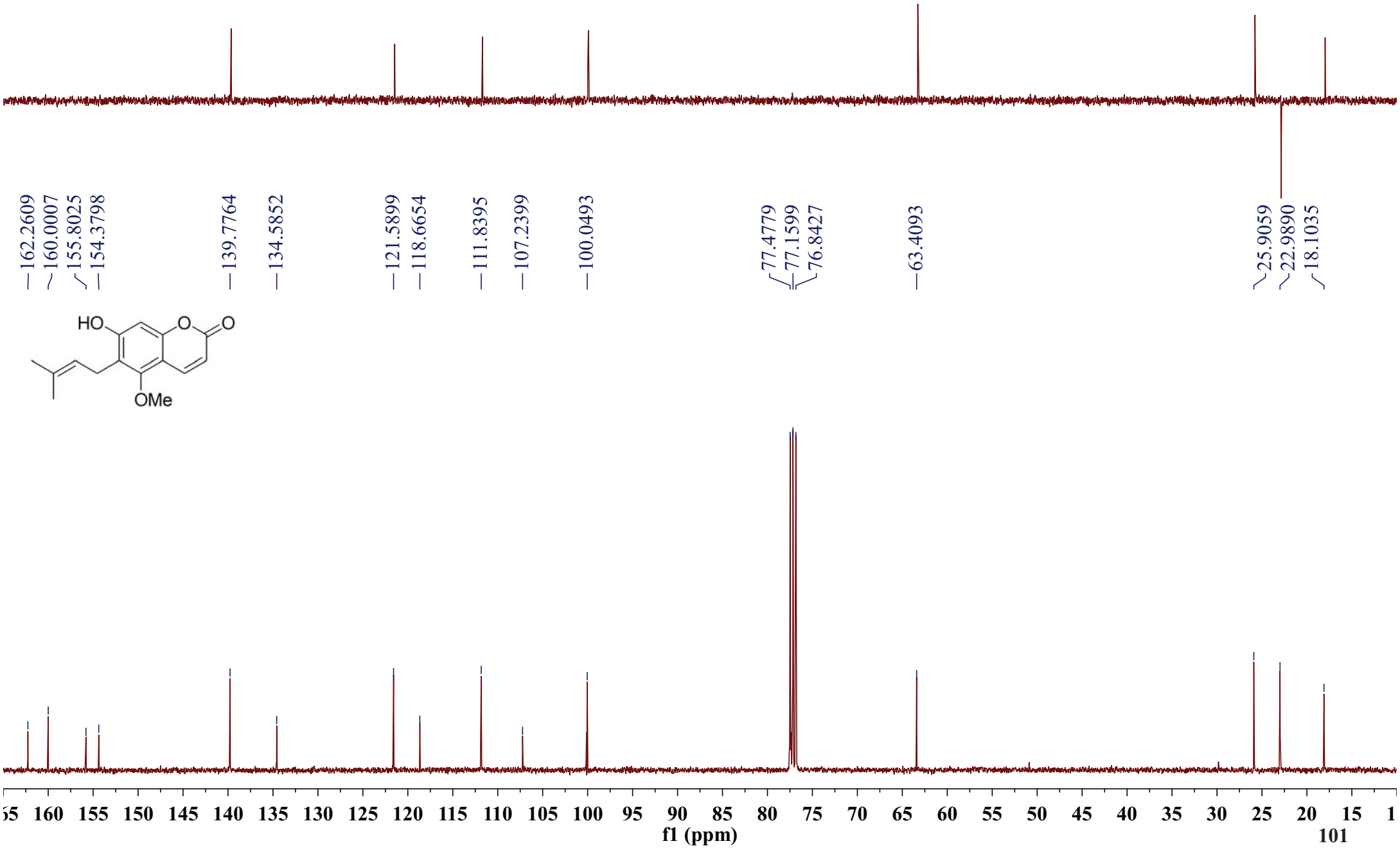
S6.24. ^{13}C NMR and DEPT spectra of compound **19**



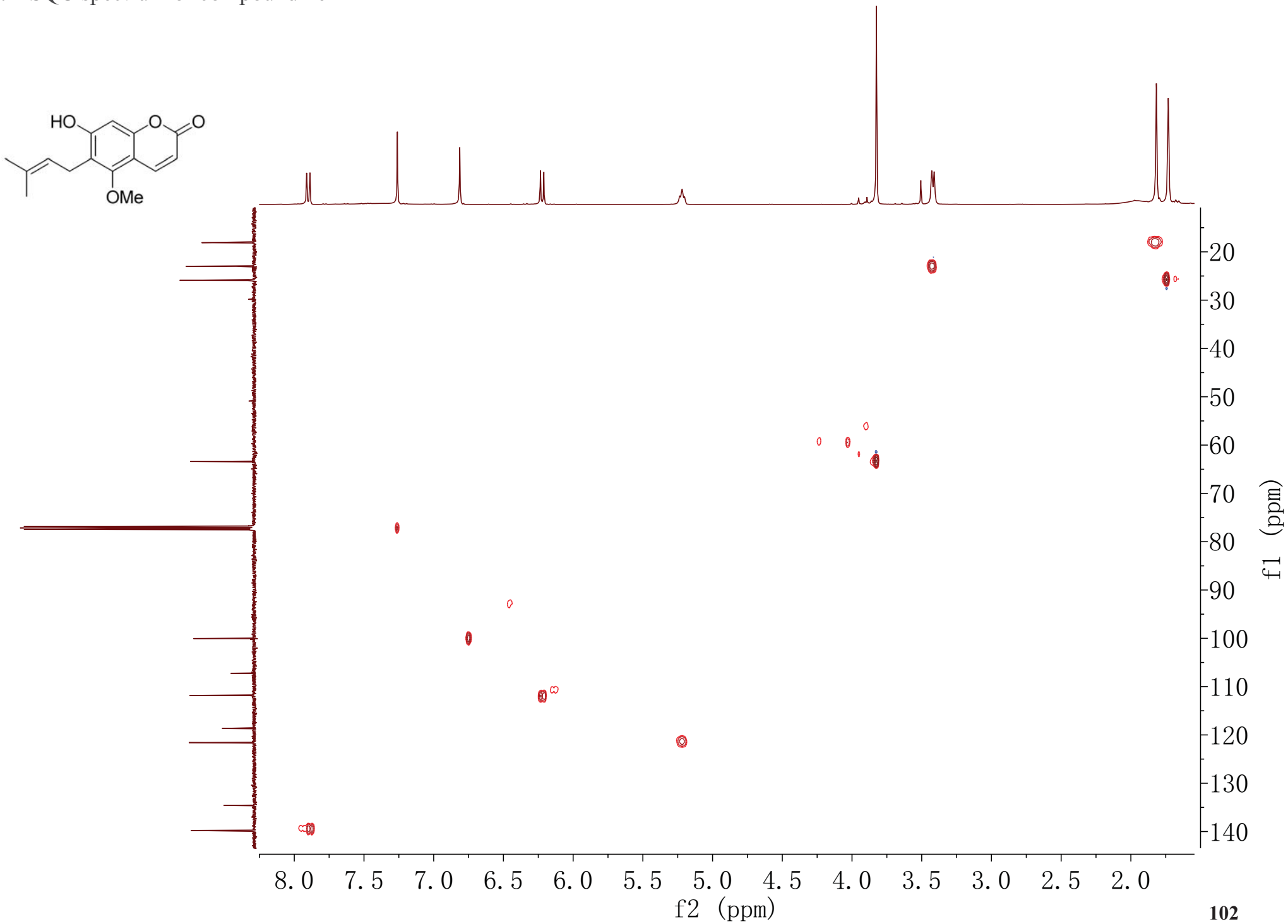
S6.25. ^{1}H NMR spectrum of compound **20**



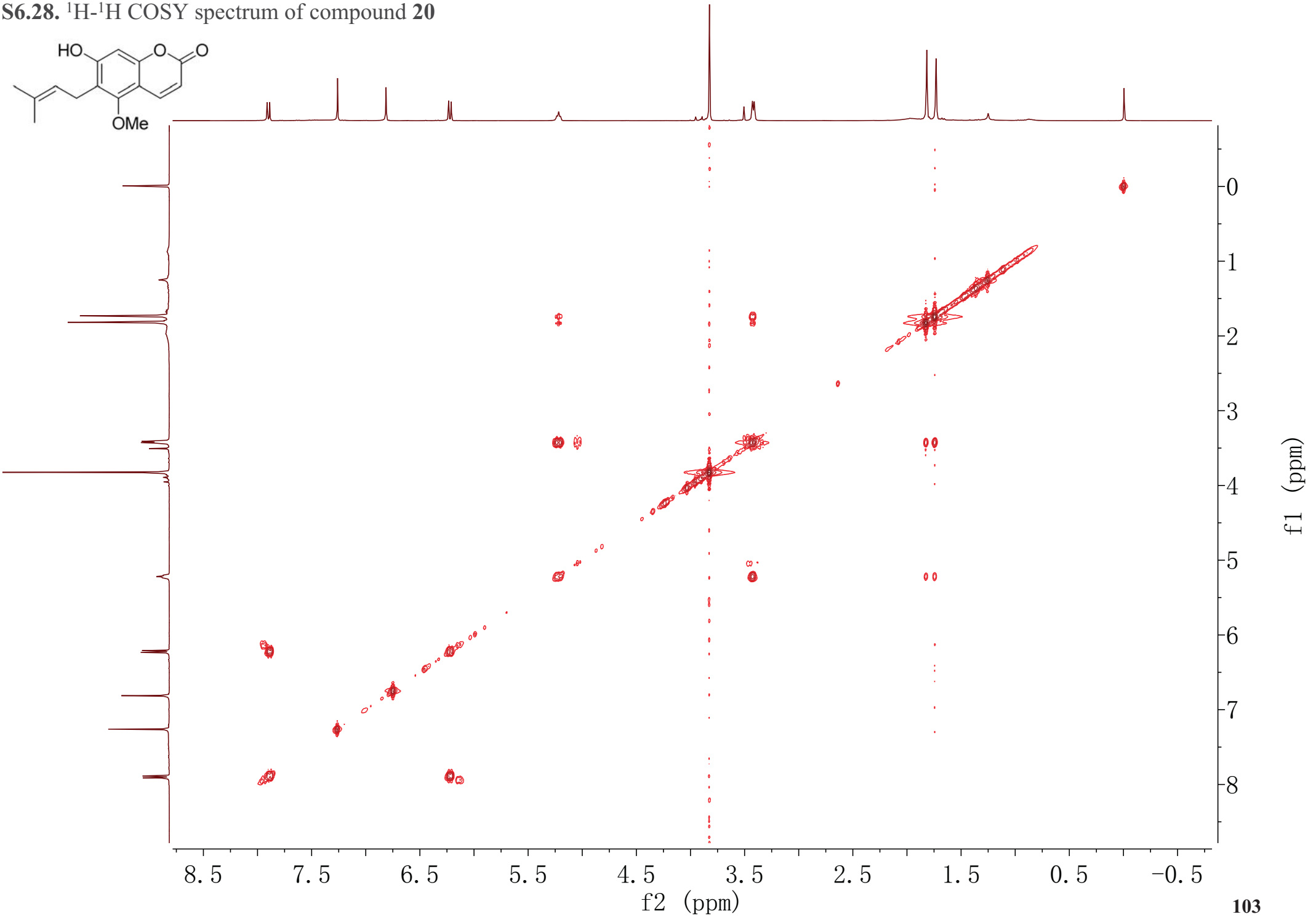
S6.26. ^{13}C NMR and DEPT spectra of compound **20**



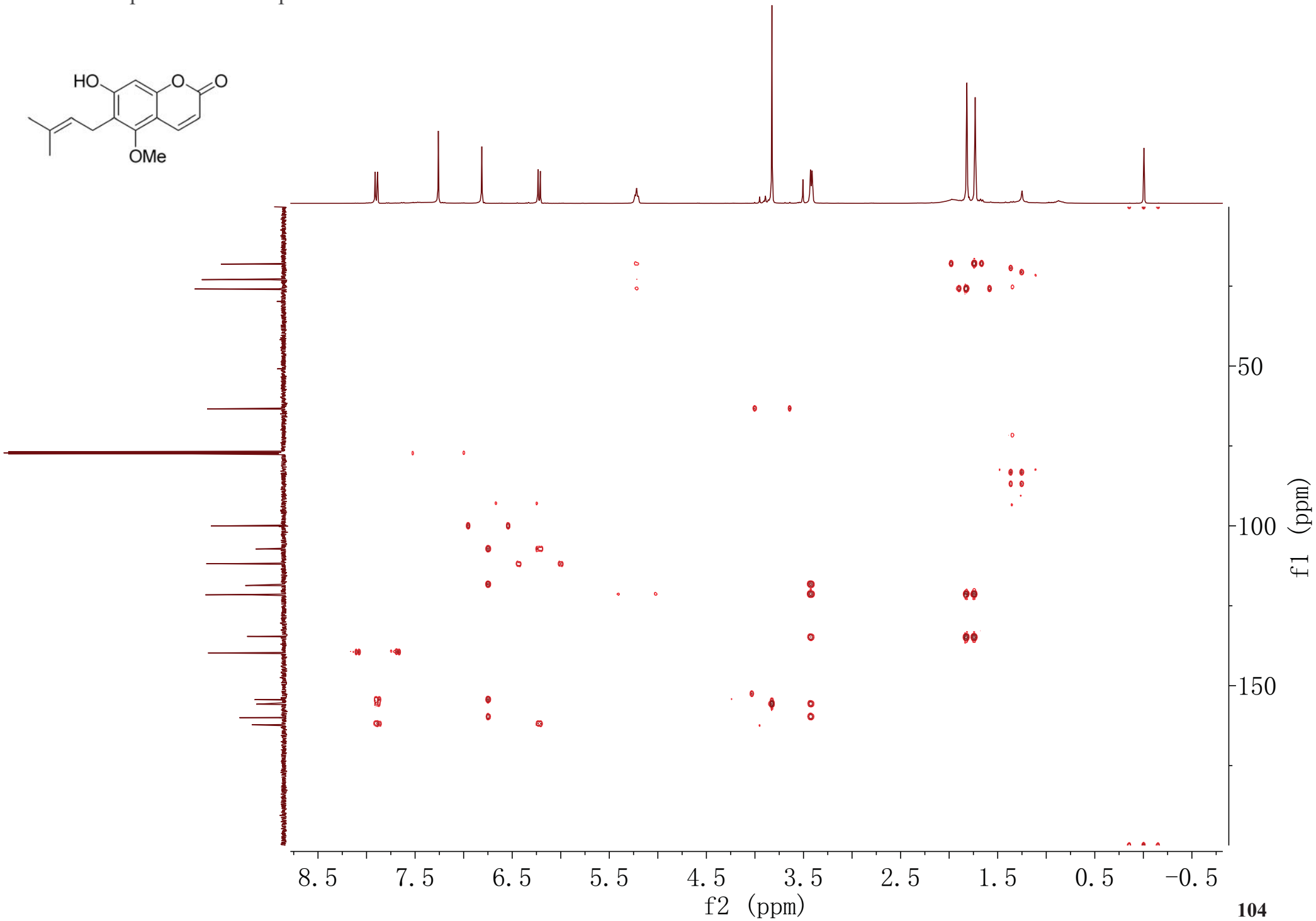
S6.27. HSQC spectrum of compound **20**



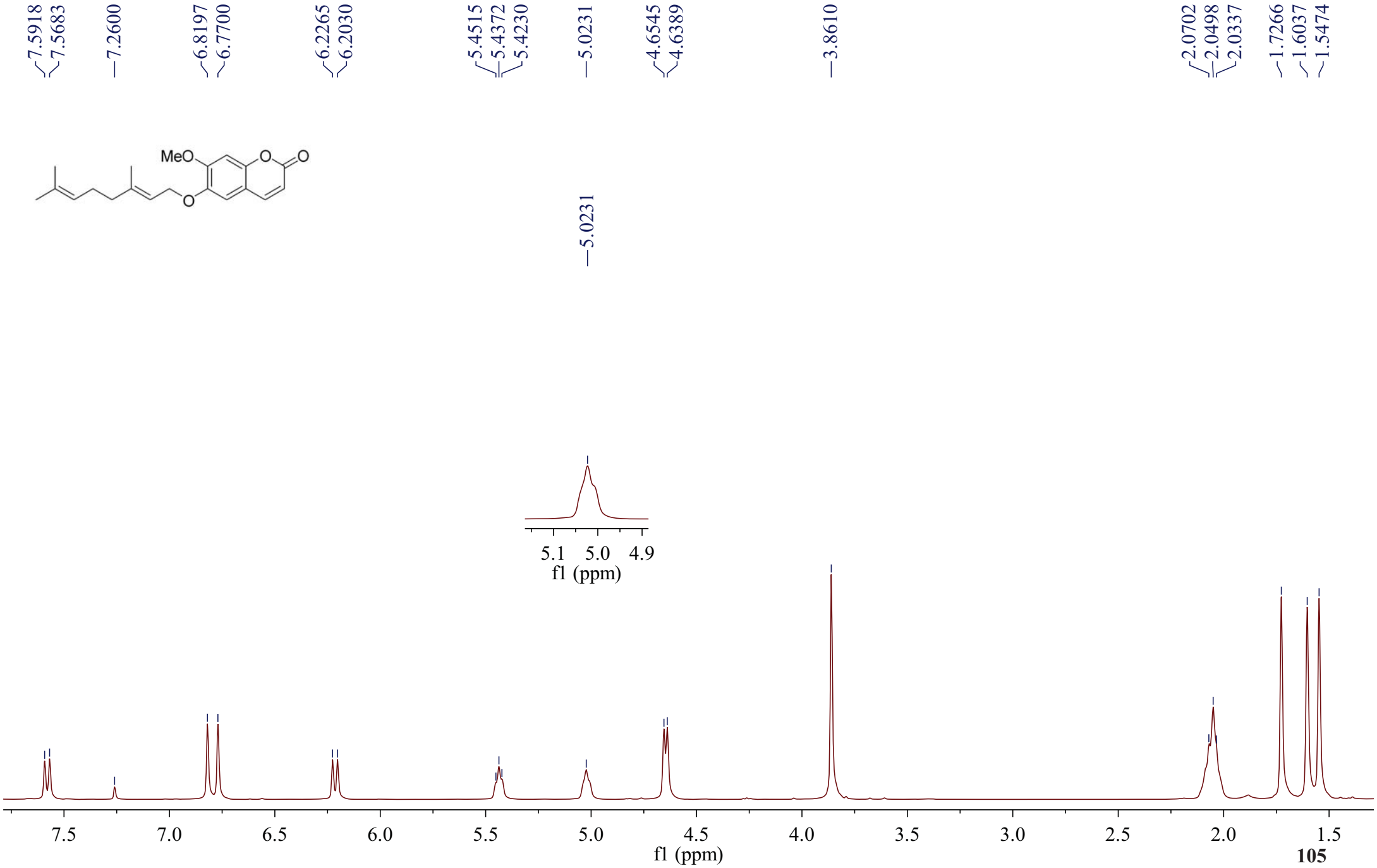
S6.28. ^{1}H-^{1}H COSY spectrum of compound **20**



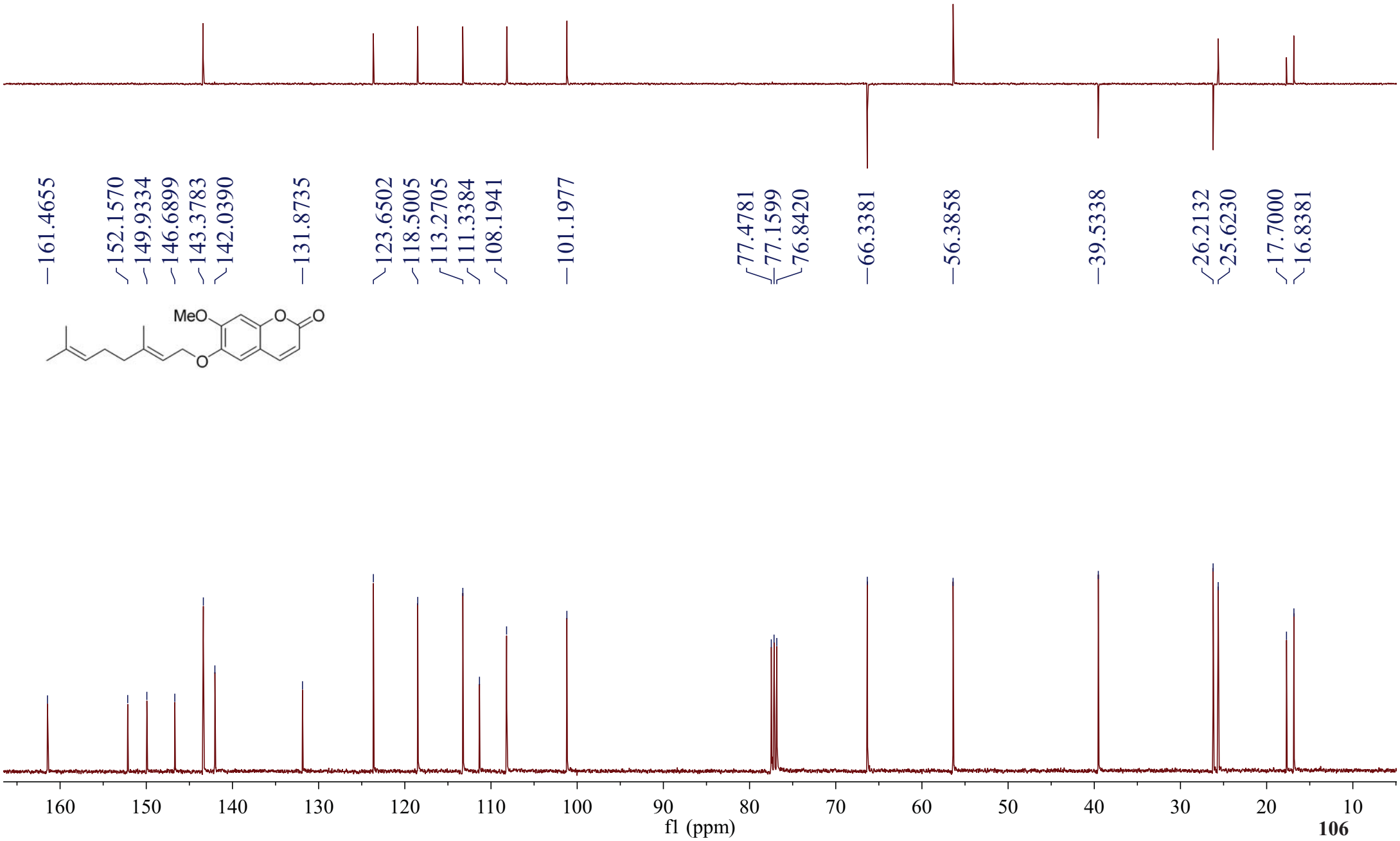
S6.29. HMBC spectrum of compound **20**



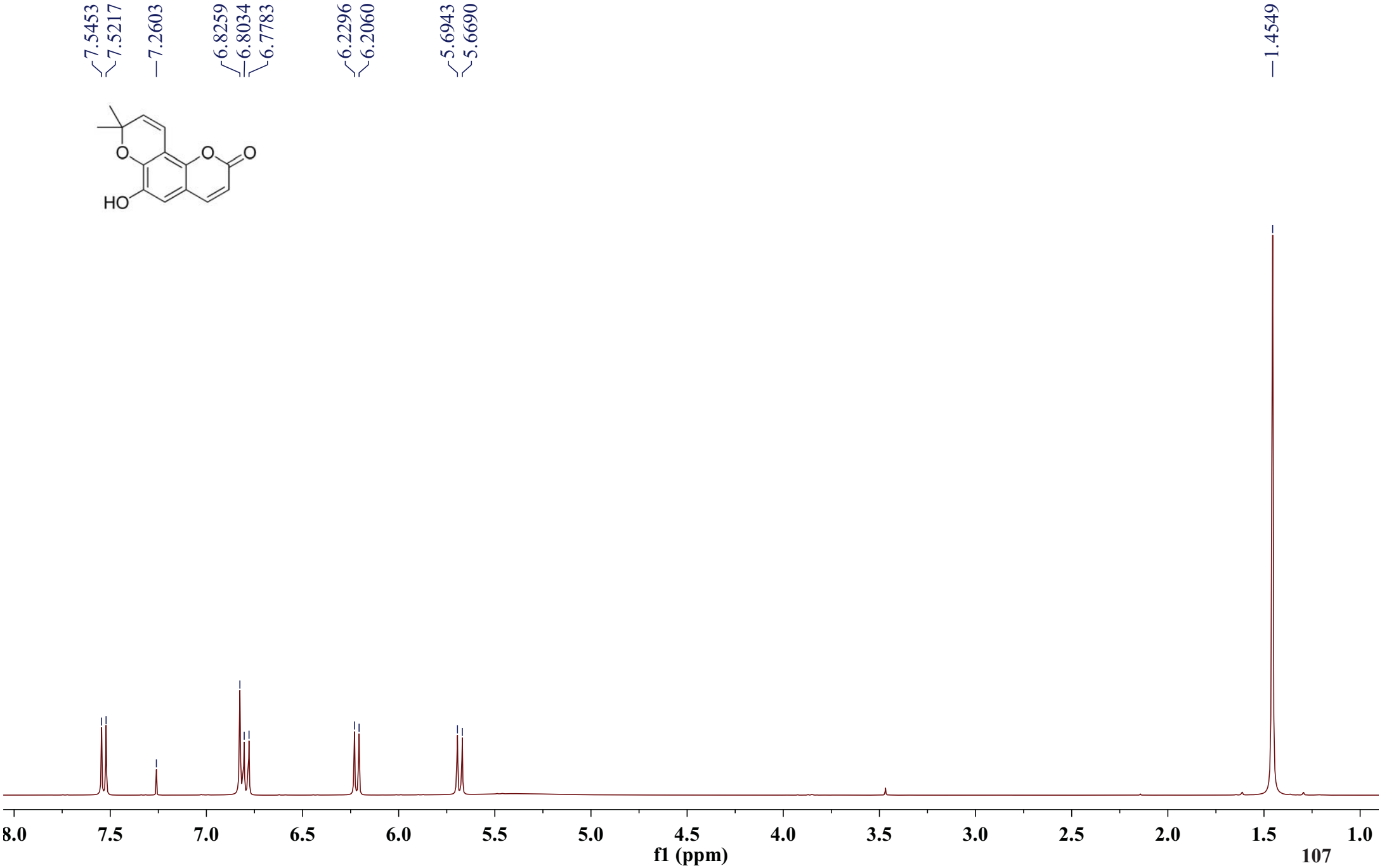
S6.30. ^{1}H NMR spectrum of compound **21**



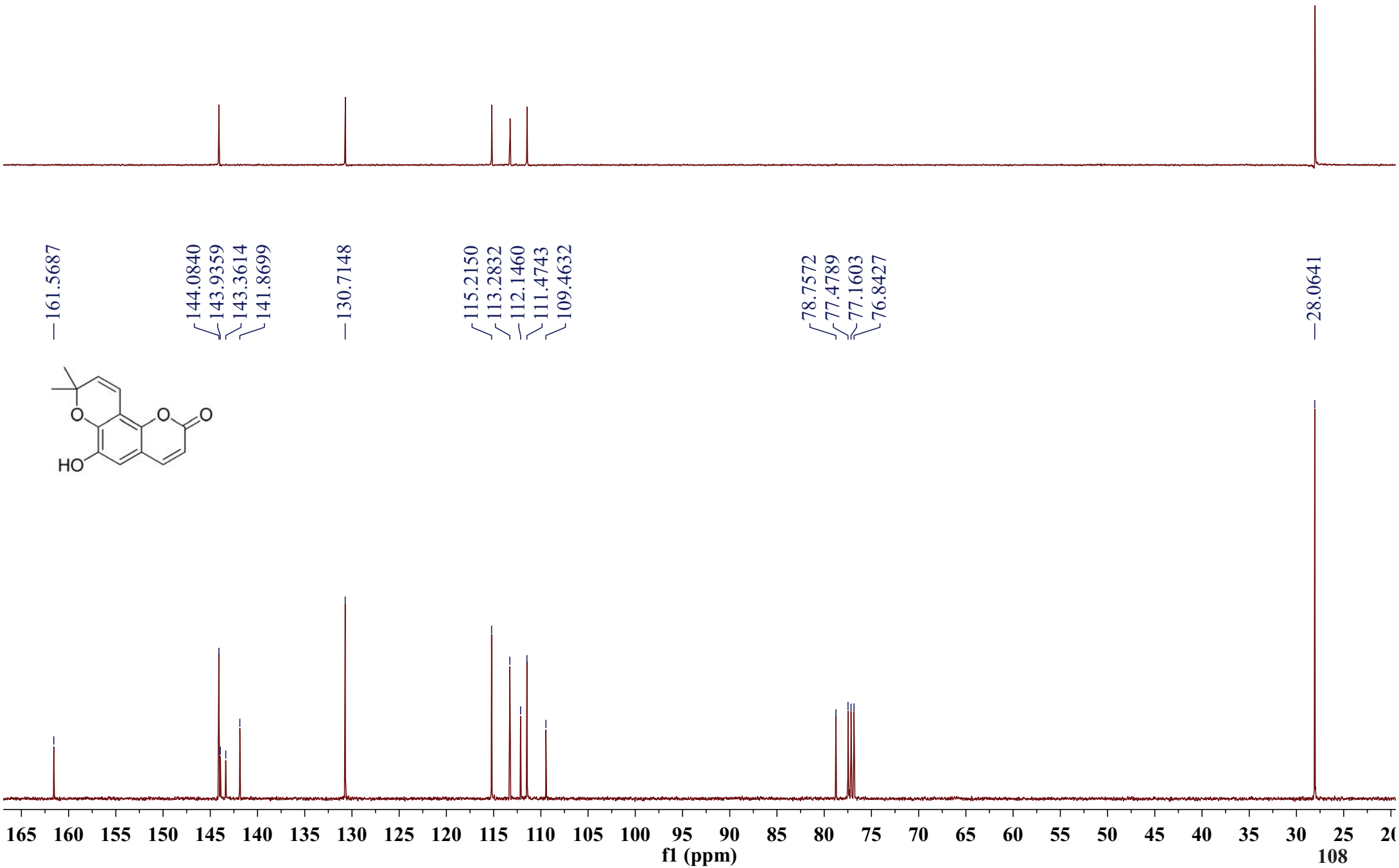
S6.31. ^{13}C NMR and DEPT spectra of compound **21**



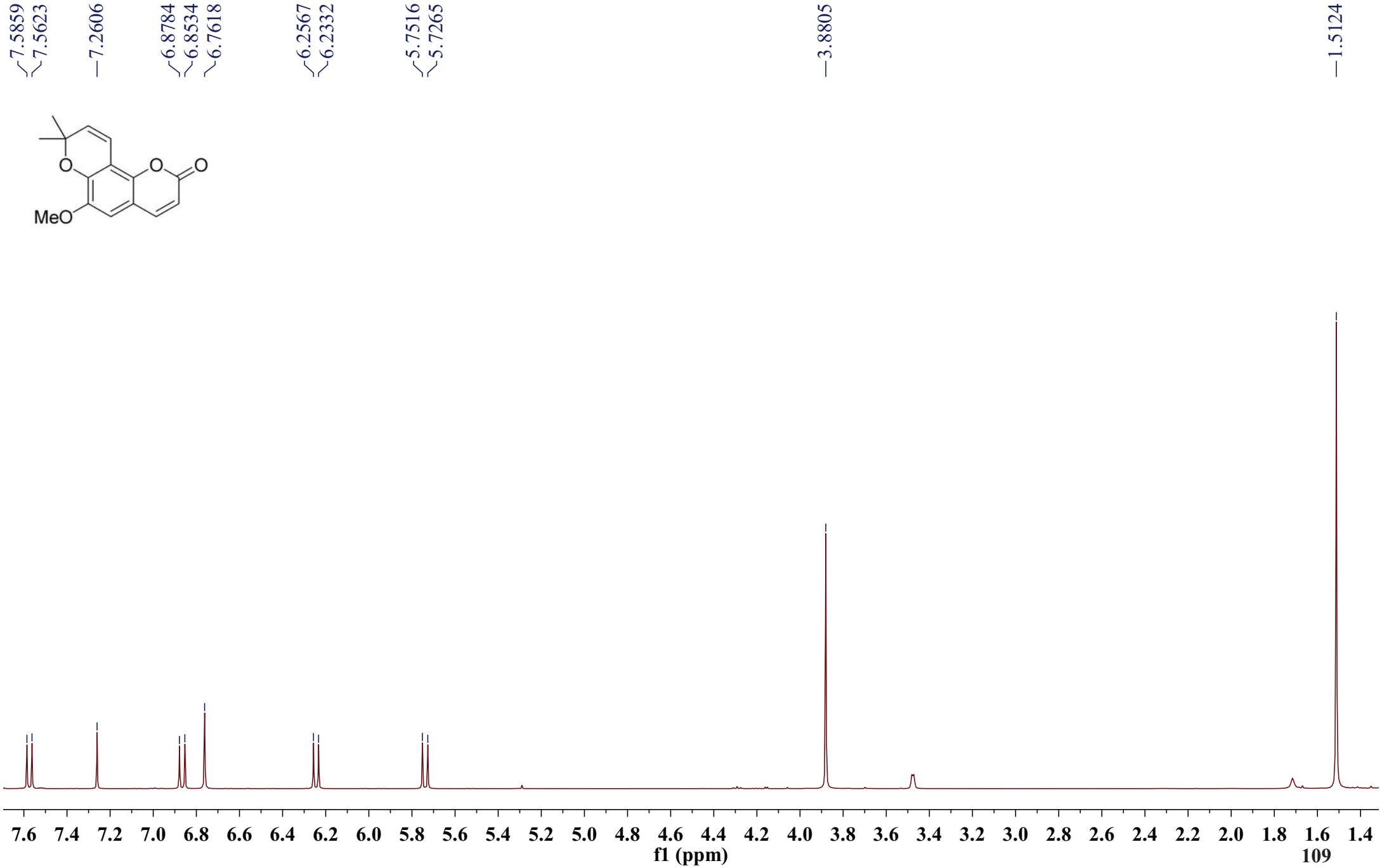
S6.32. ^{1}H NMR spectrum of compound **22**



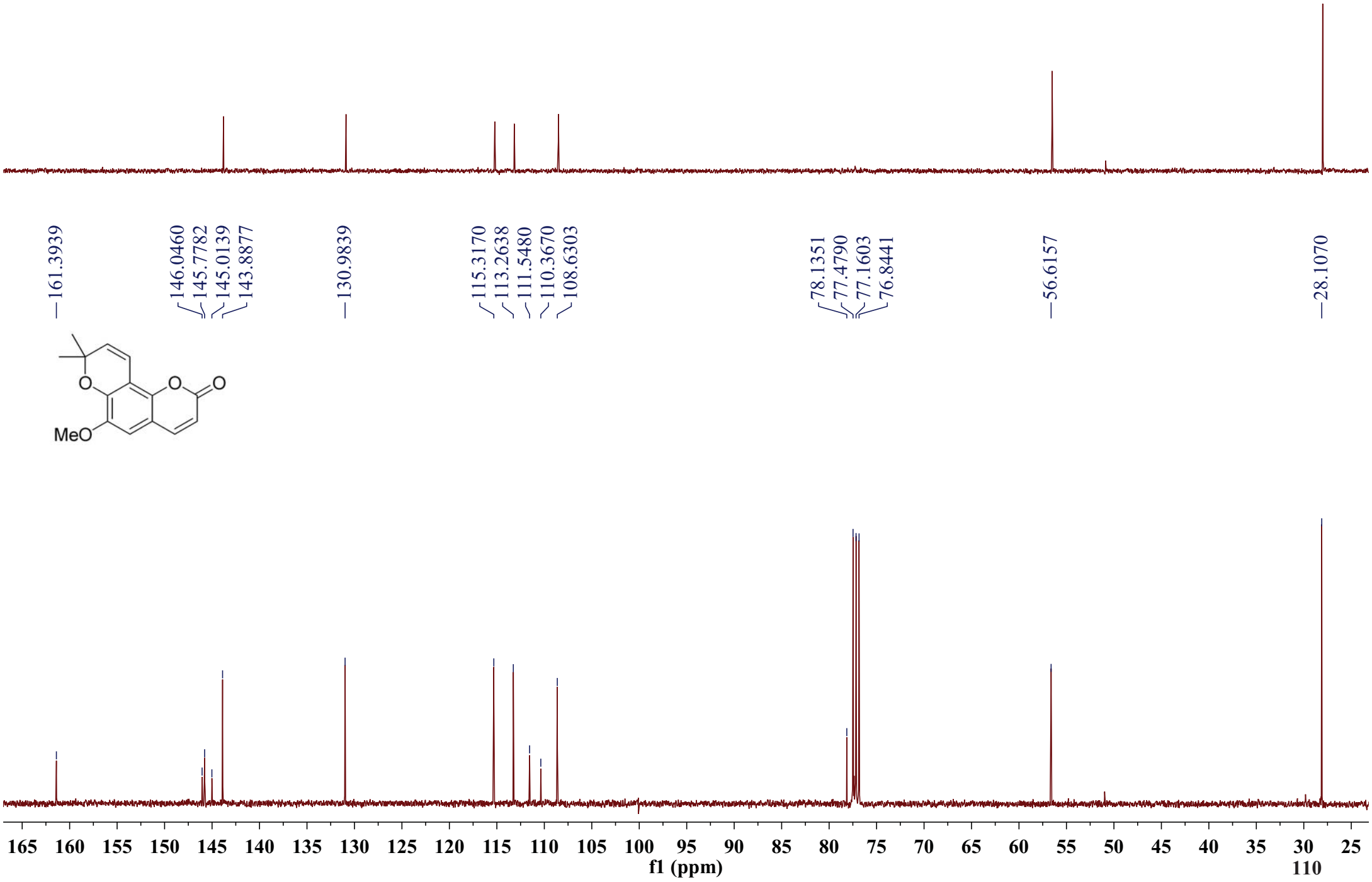
S6.33. ^{13}C NMR and DEPT spectra of compound **22**



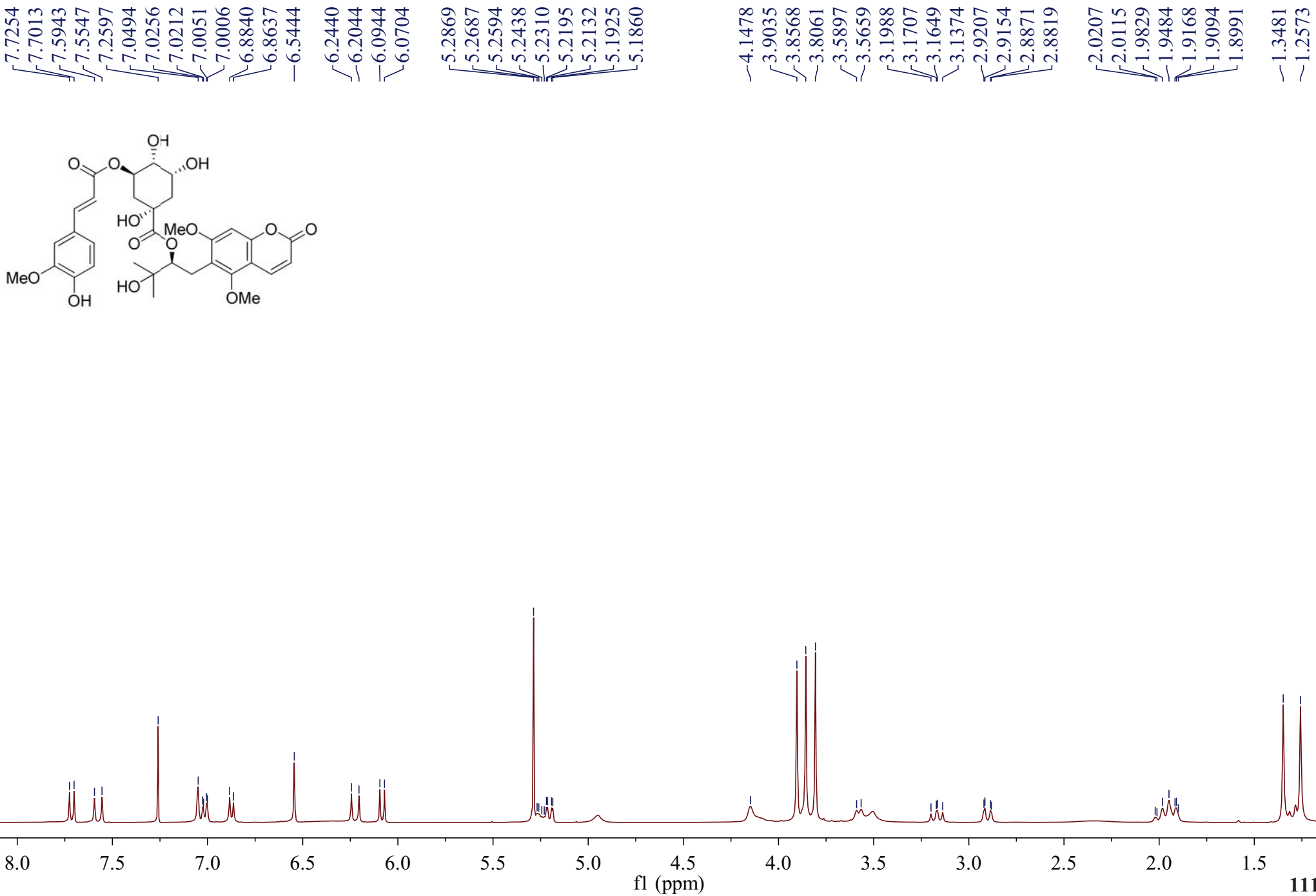
S6.34. ^{1}H NMR spectrum of compound **23**



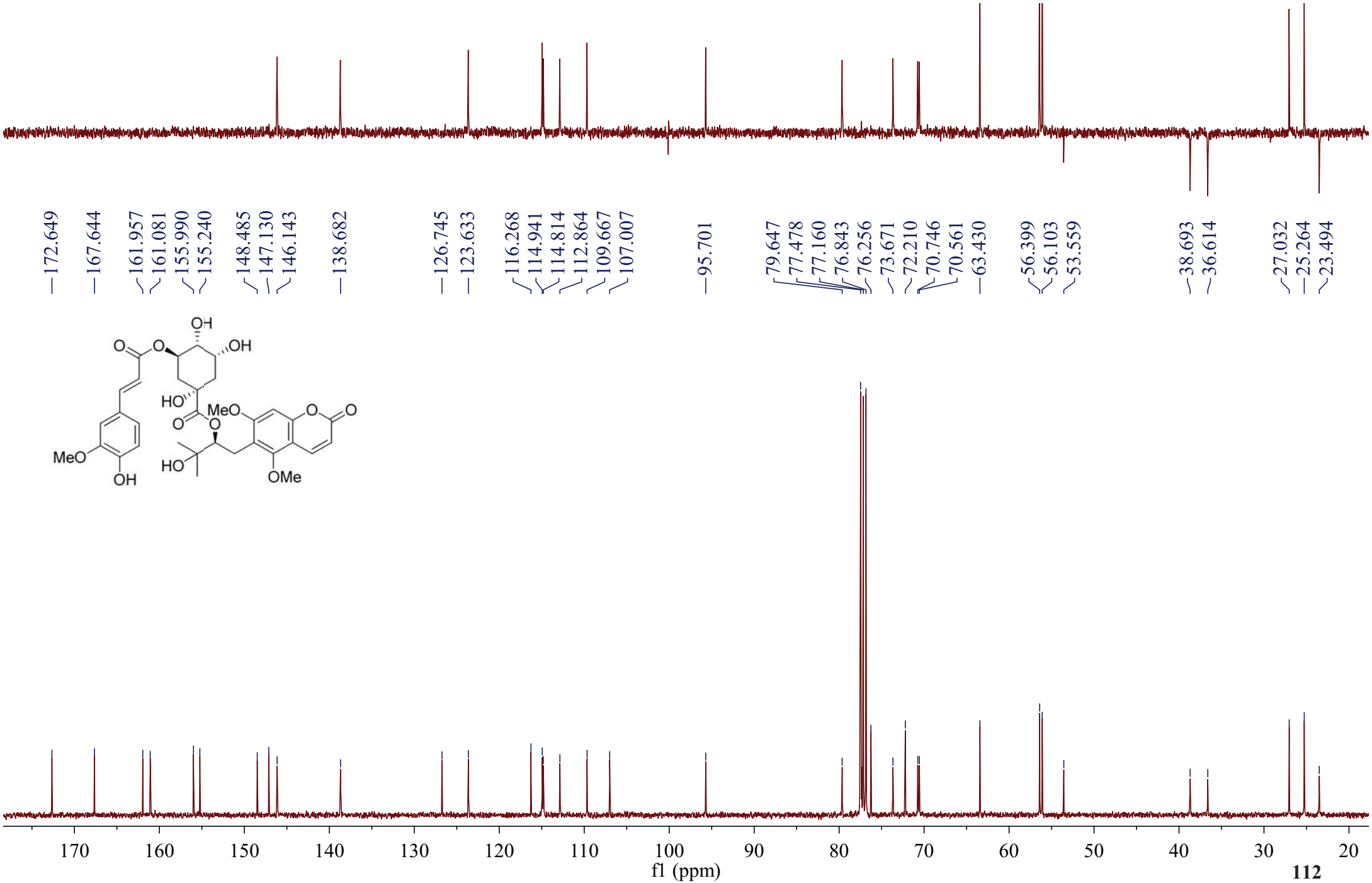
S6.35. ^{13}C NMR and DEPT spectra of compound **23**



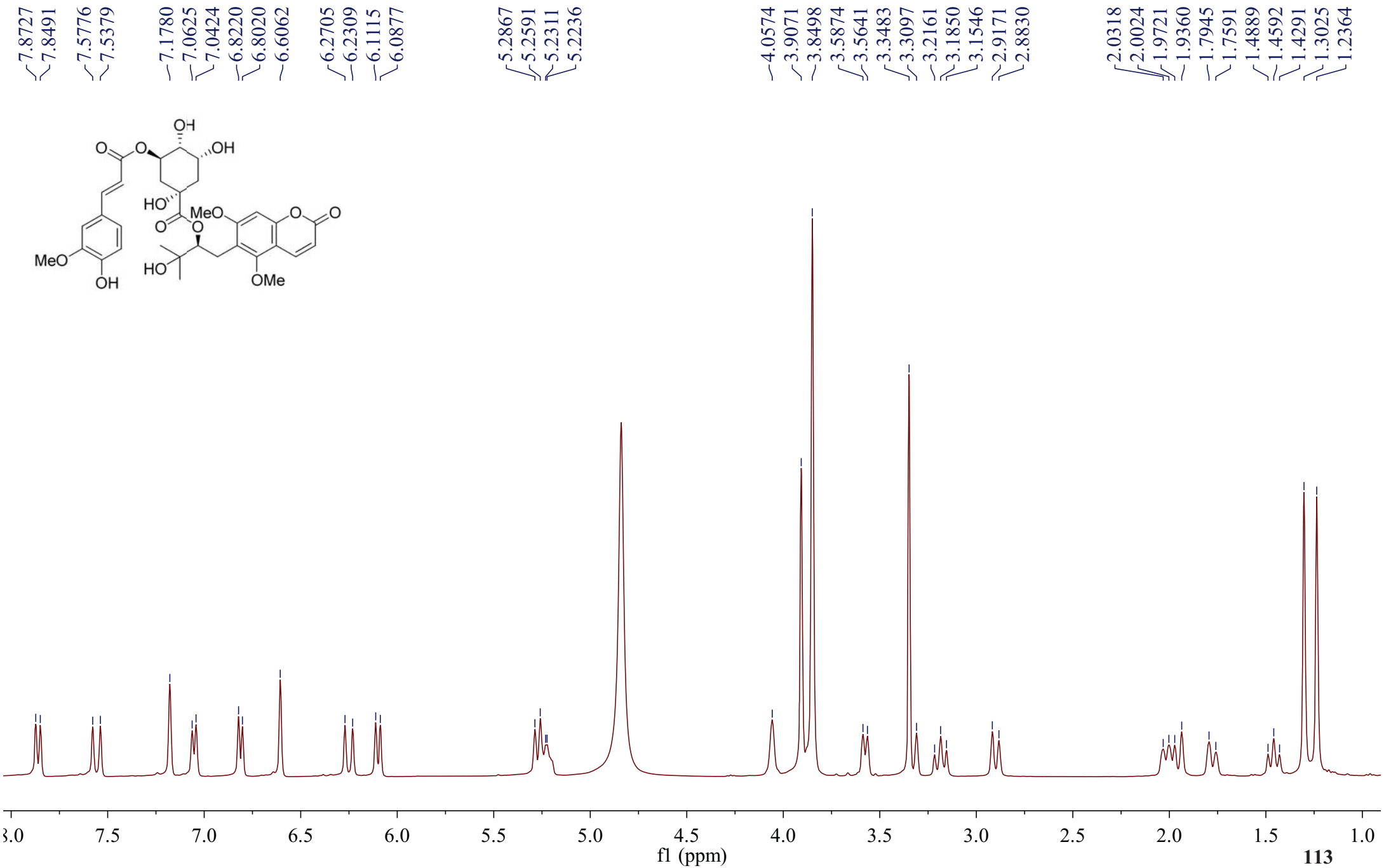
S6.36. ^{1}H NMR spectrum of compound **24**



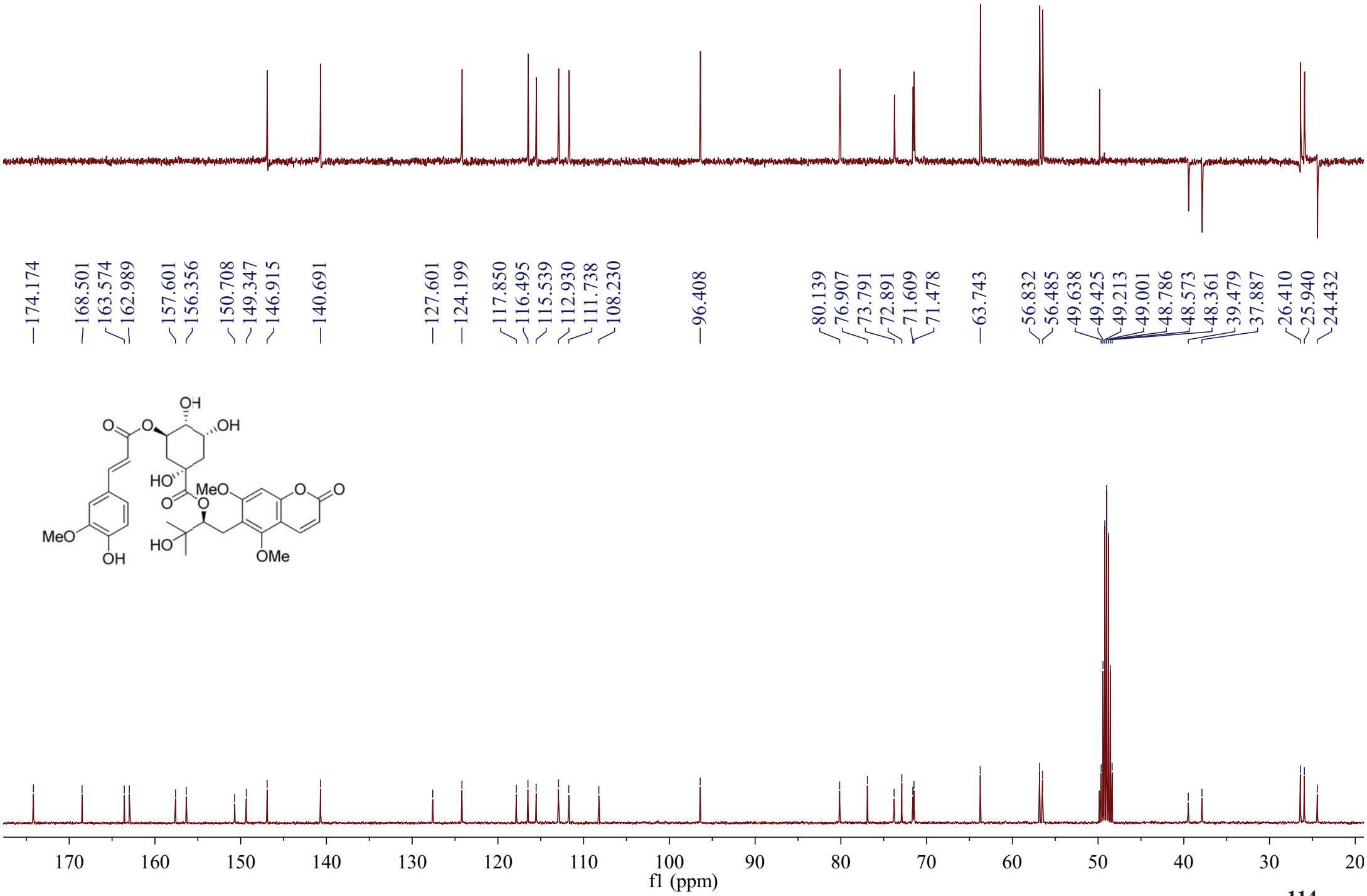
S6.37. ^{13}C NMR and DEPT spectra of compound **24**



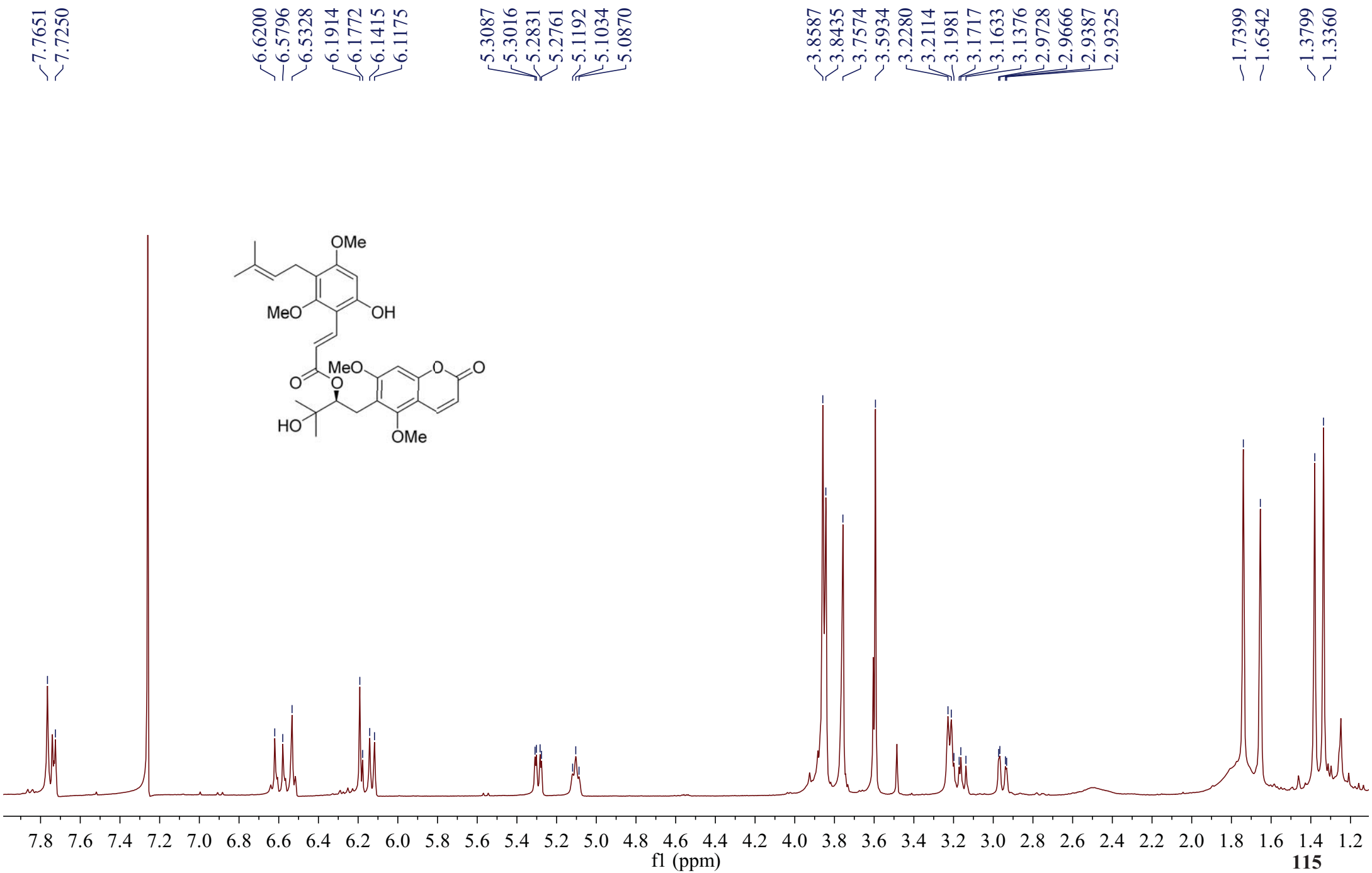
S6.38. ^{1}H NMR spectrum of compound **24**



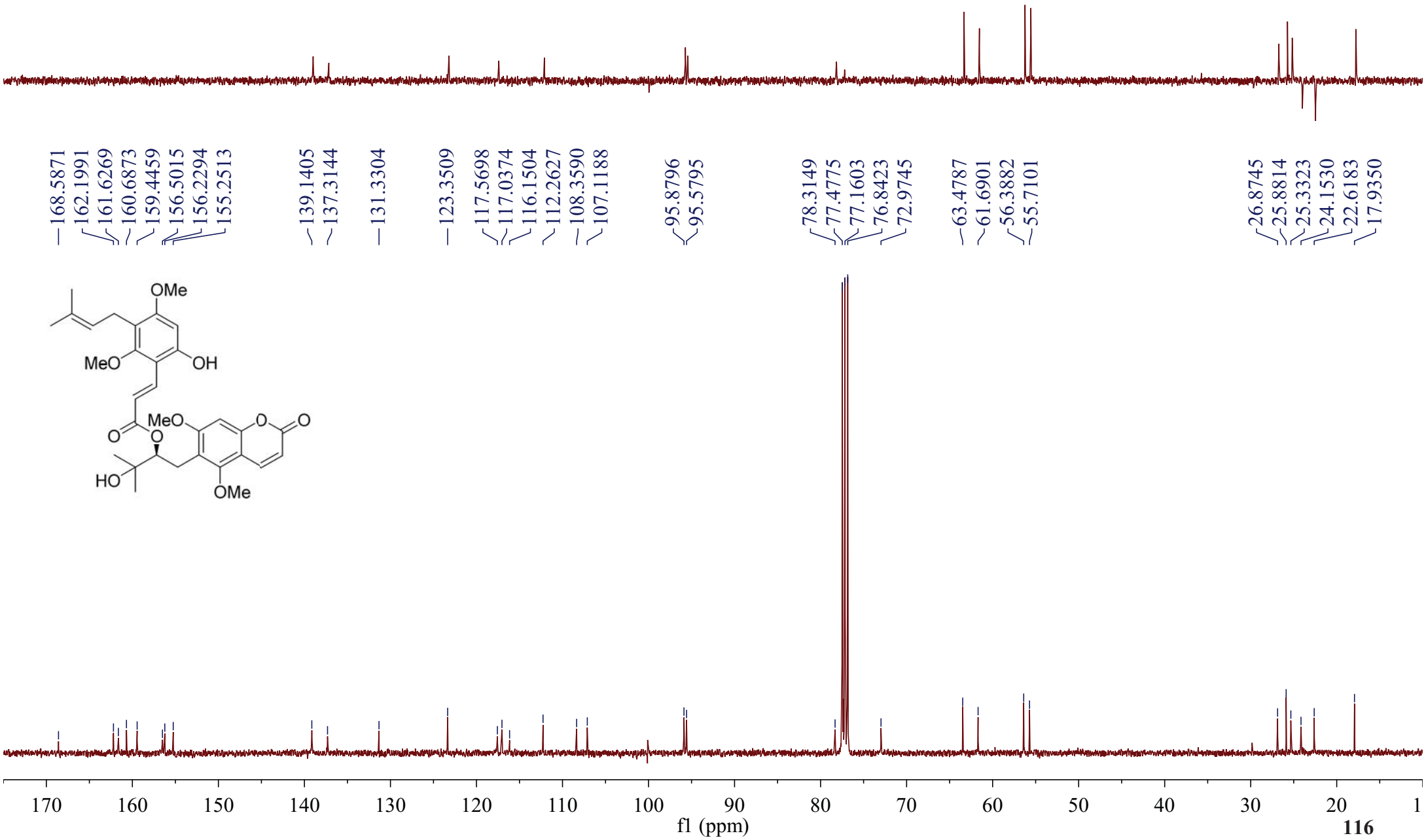
S6.39. ^{13}C NMR and spectra of compound **24**



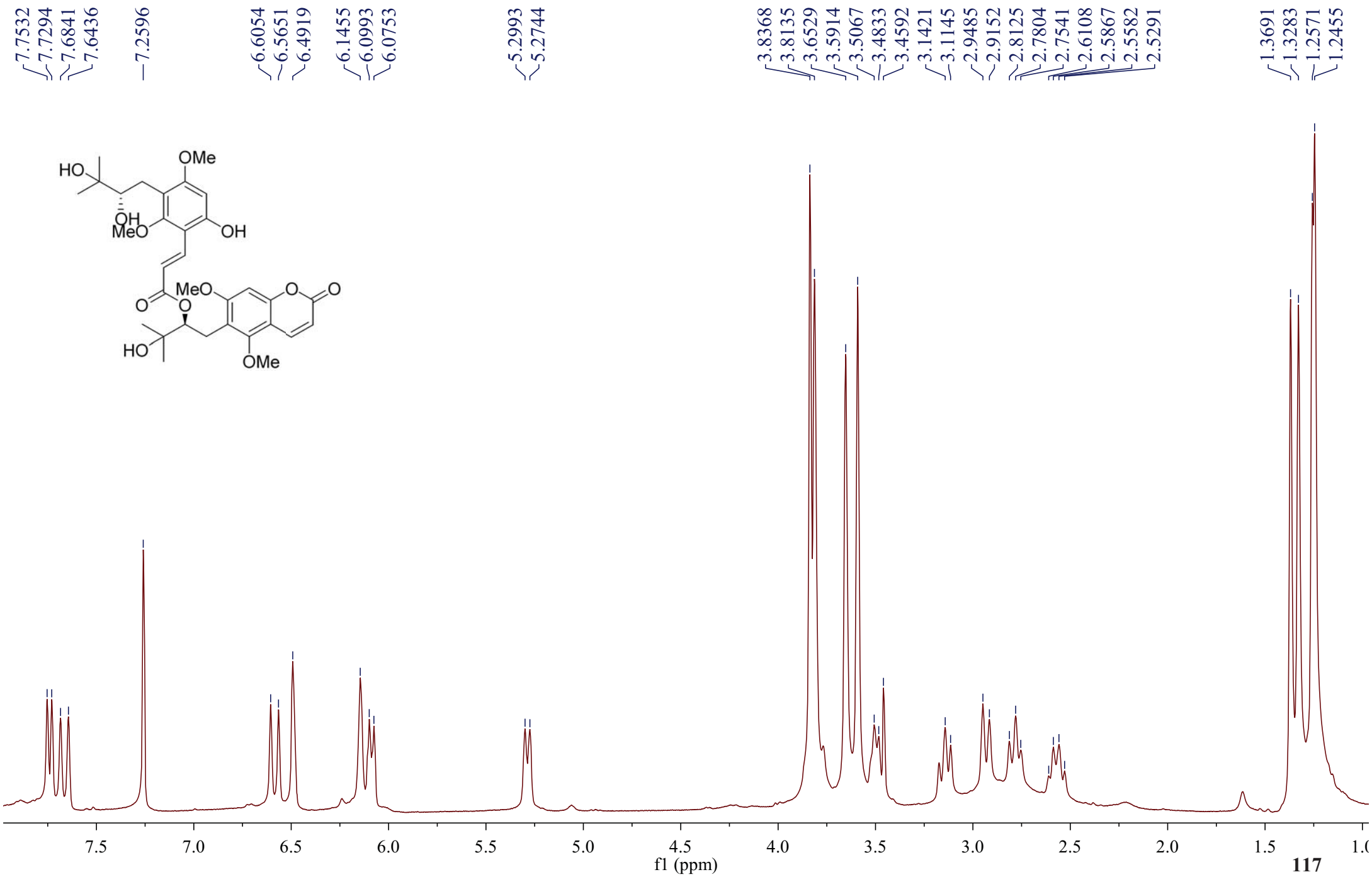
S6.40. ^{1}H NMR spectrum of compound **25**



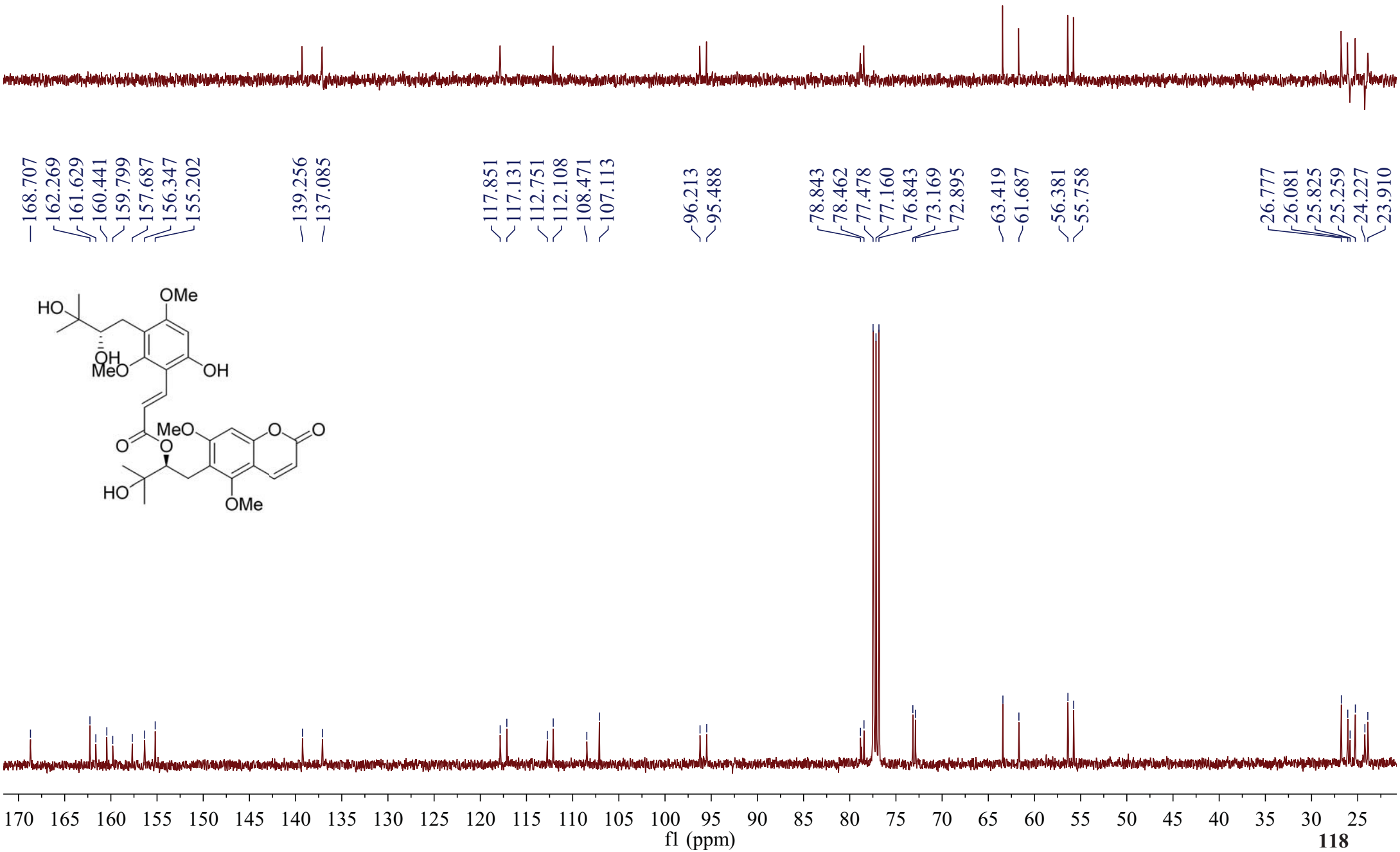
S6.41. ^{13}C NMR and DEPT spectra of compound **25**



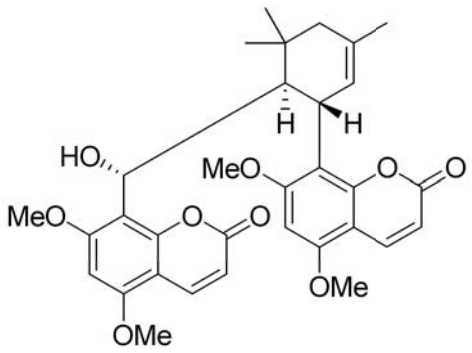
S6.42. ^{1}H NMR spectrum of compound **26**

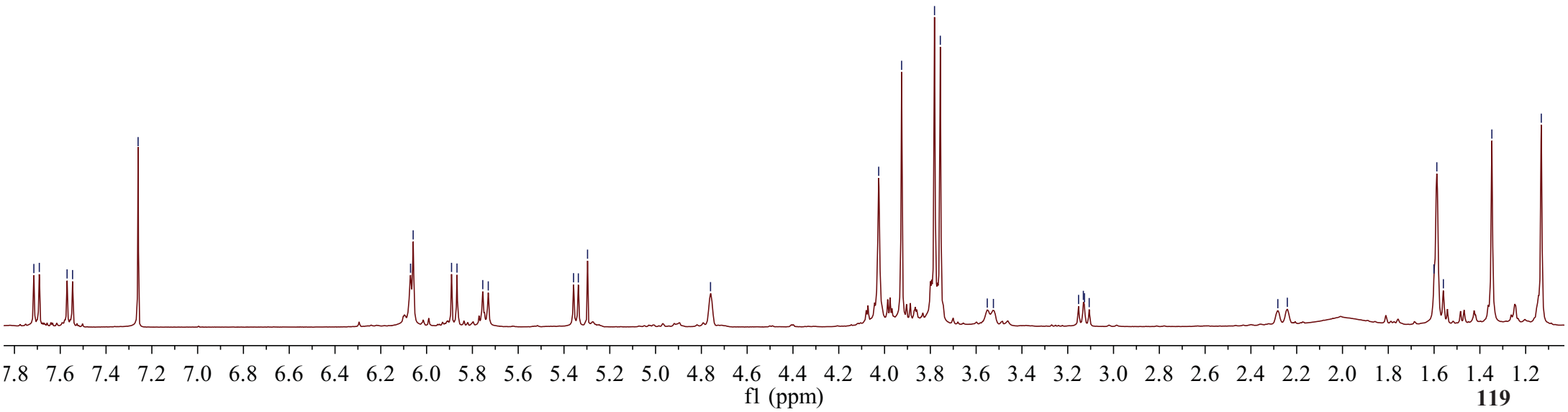


S6.43. ^{13}C NMR and DEPT spectra of compound **26**

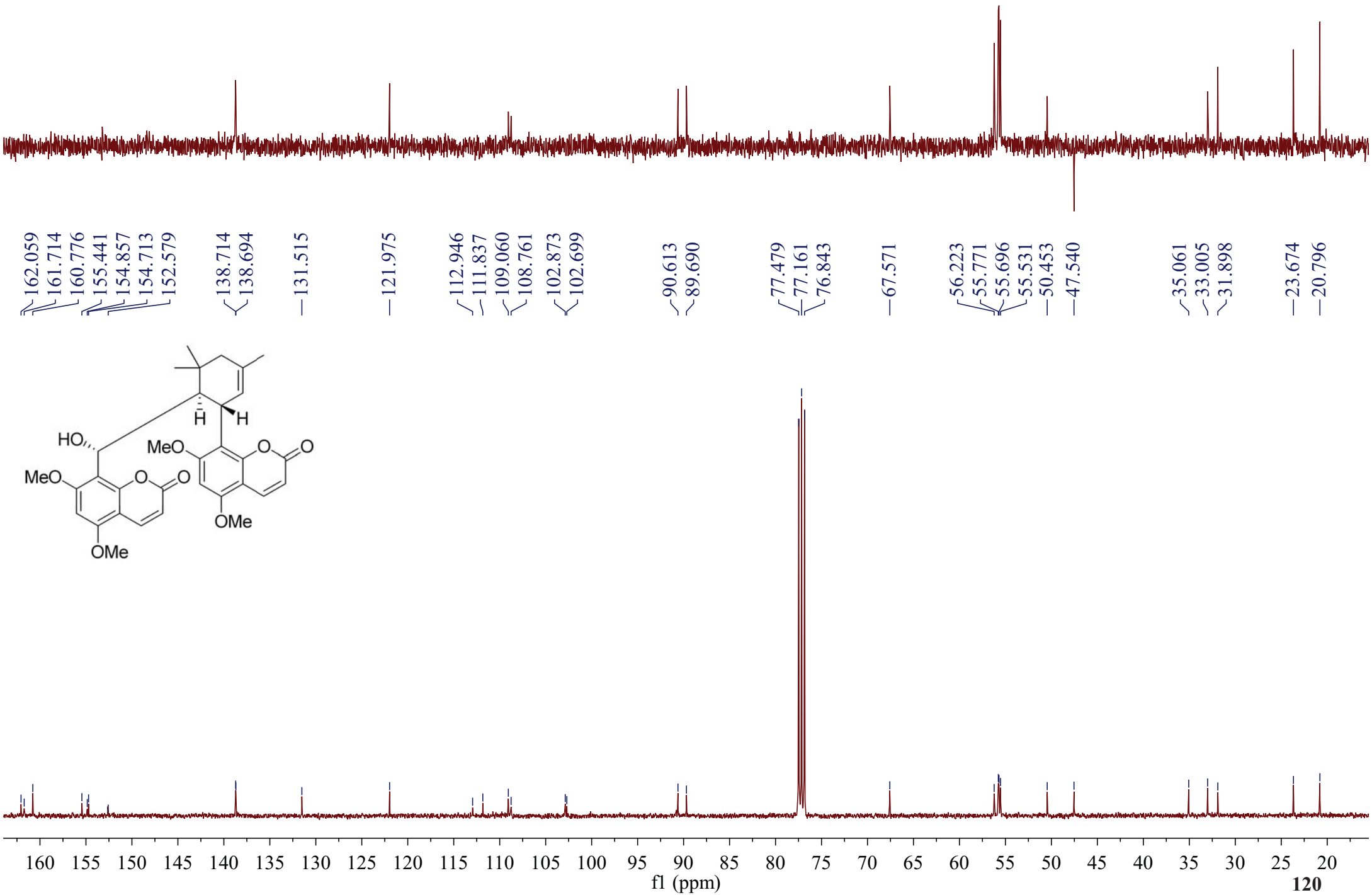


S6.44 ^{1}H NMR spectrum of compound **27**

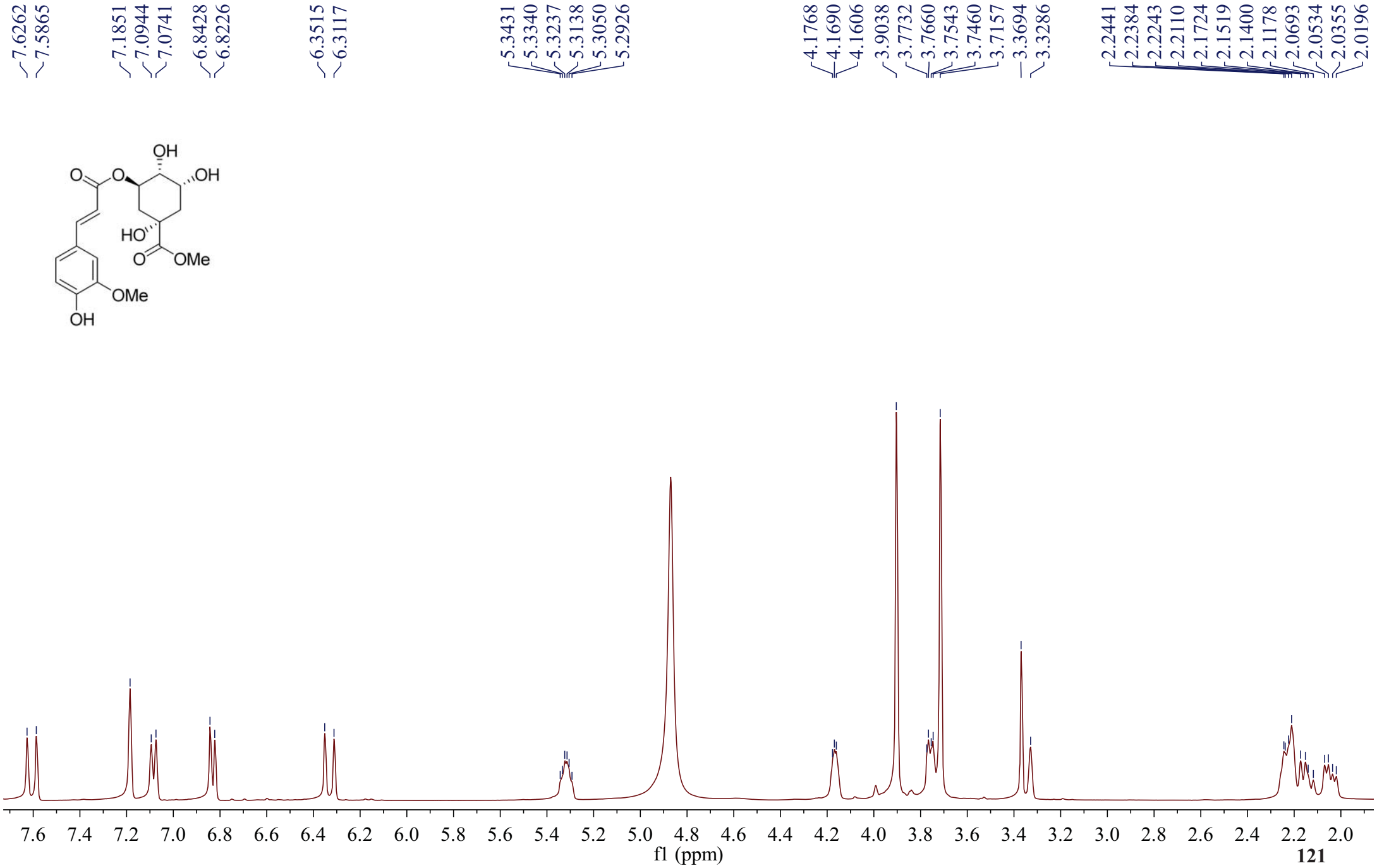




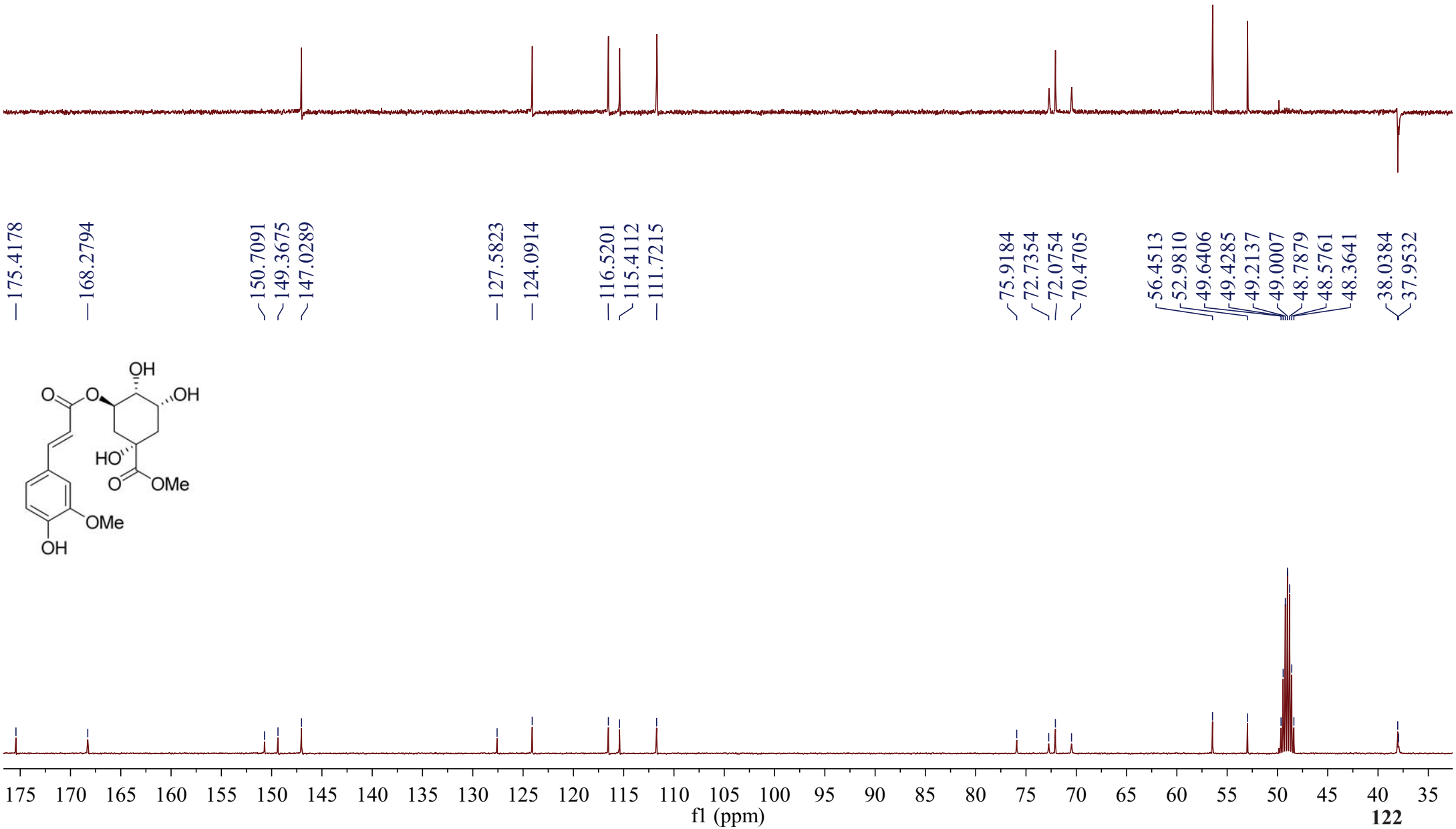
S6.45. ^{13}C NMR and DEPT spectra of compound **27**



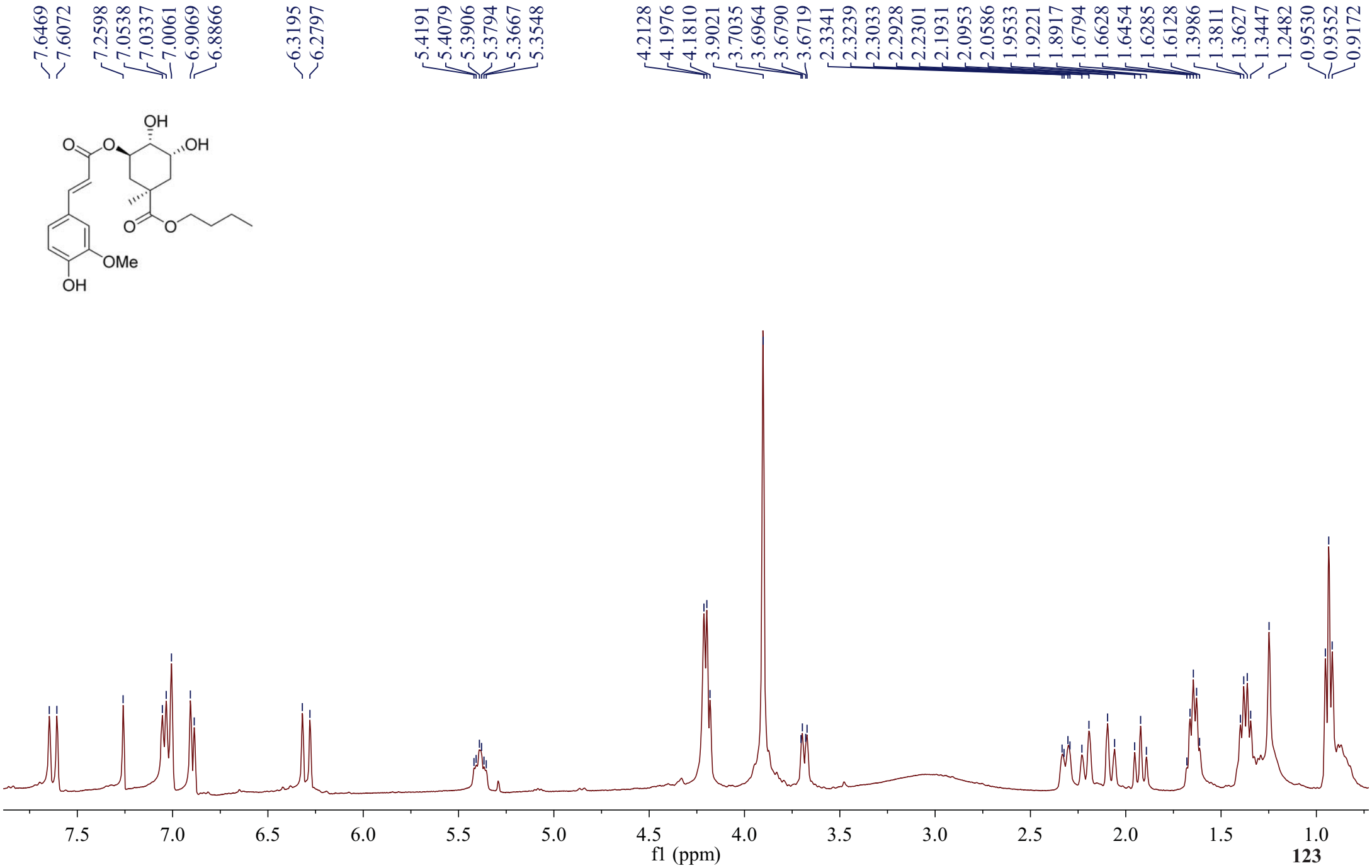
S6.46. ^{1}H NMR spectrum of compound **28**



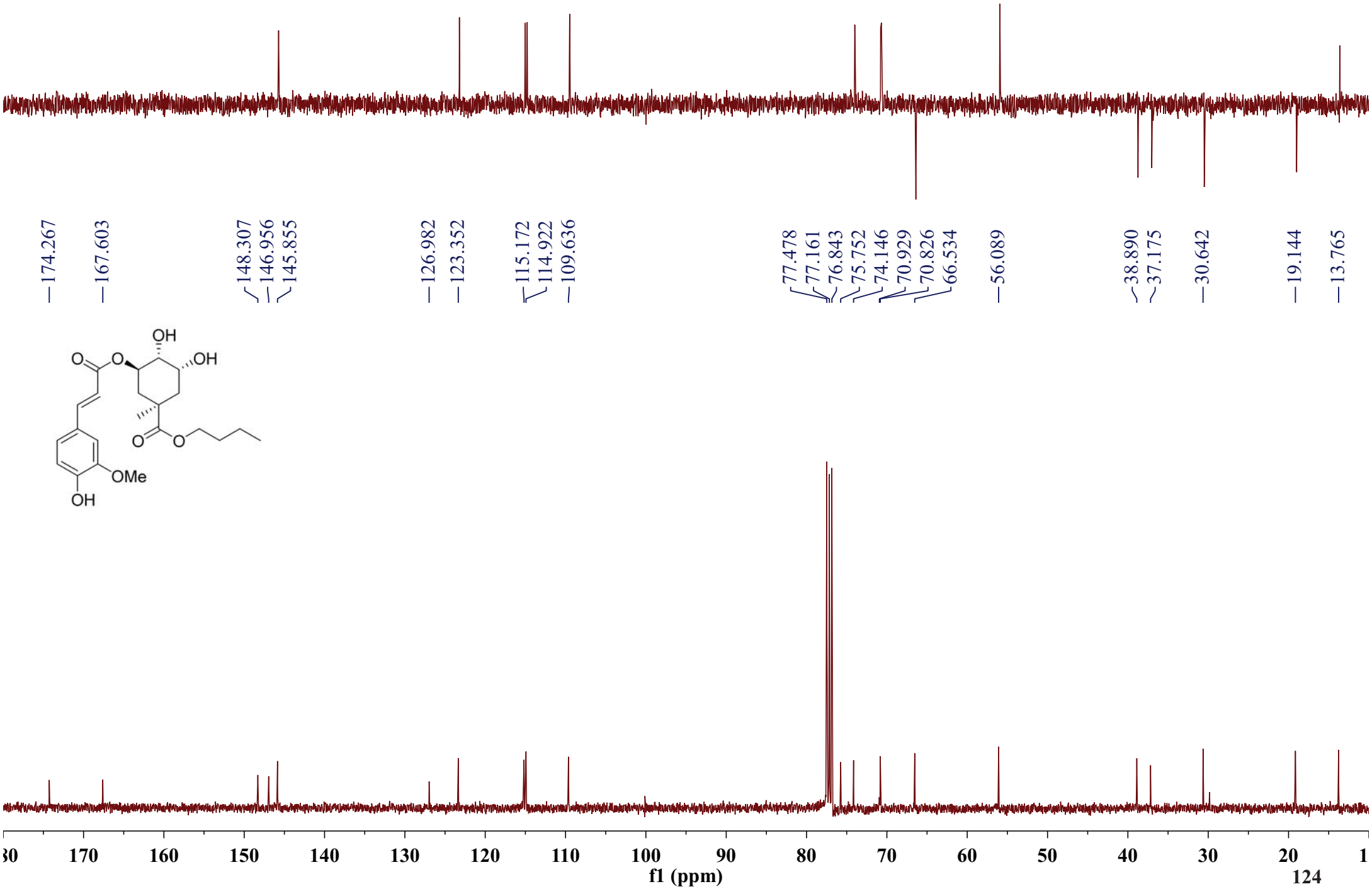
S6.47. ^{13}C NMR and DEPT spectra of compound **28**



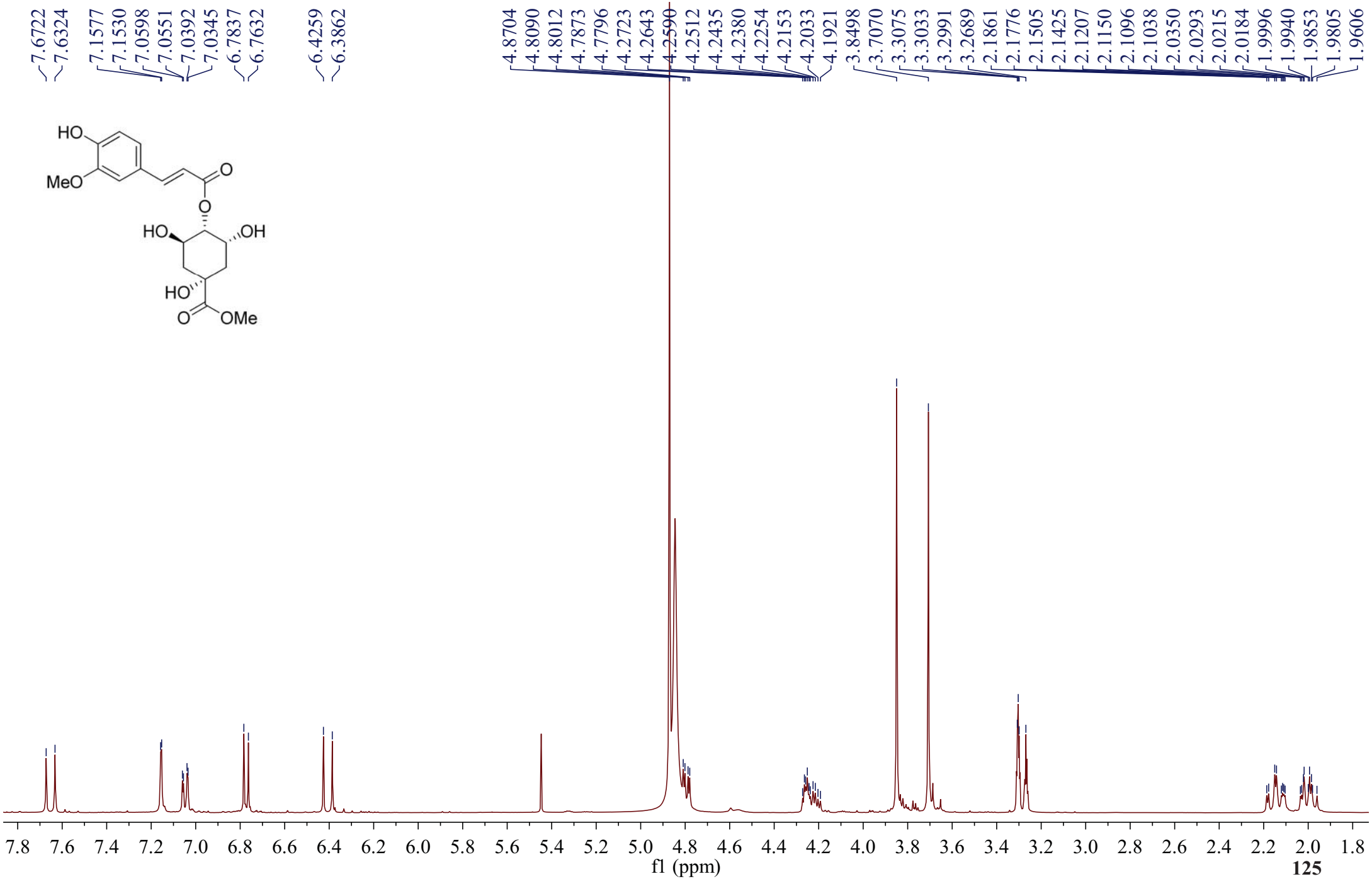
S6.48. ^{1}H NMR spectrum of compound **29**



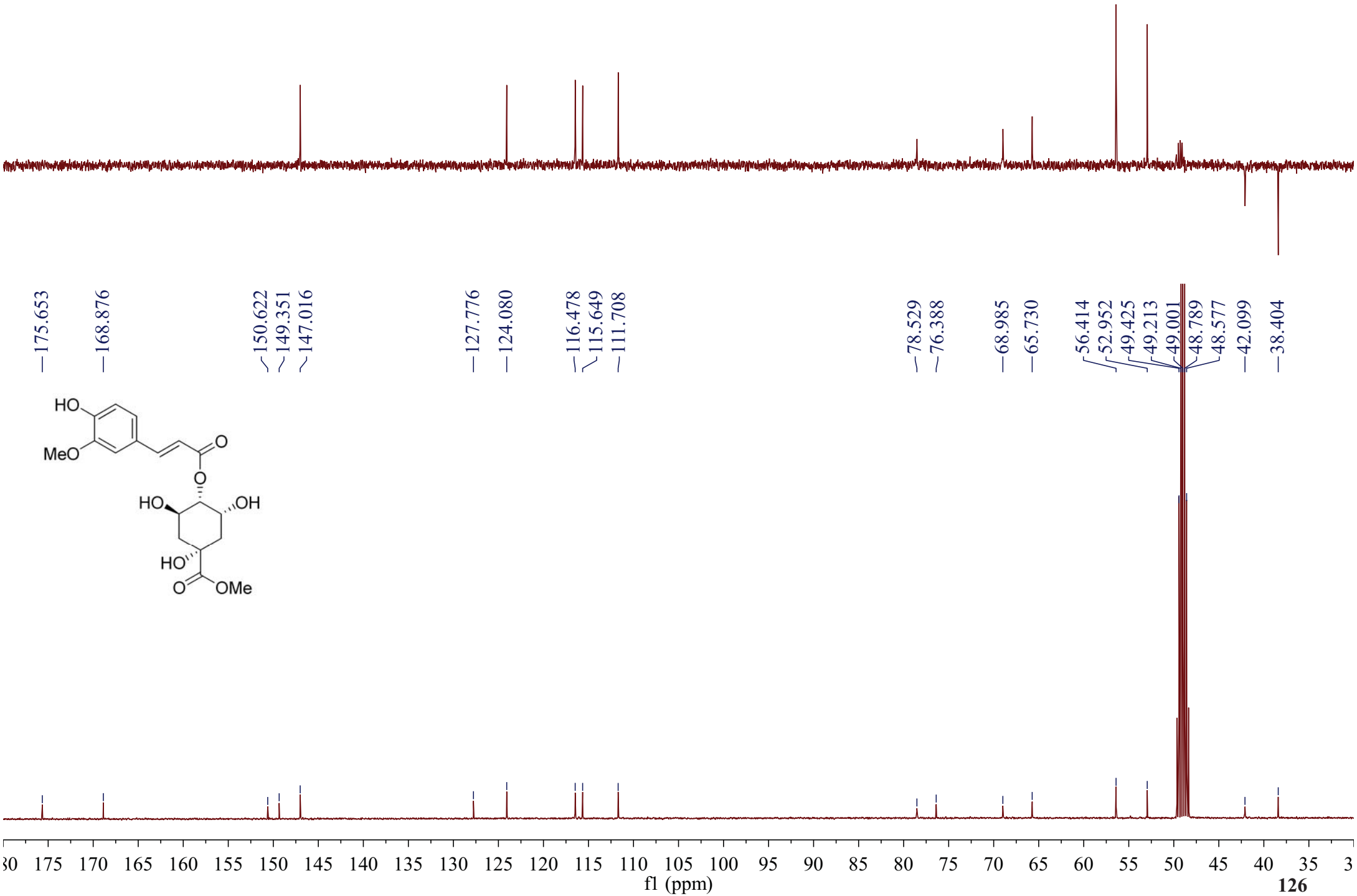
S6.49. ^{13}C NMR and DEPT spectra of compound **29**



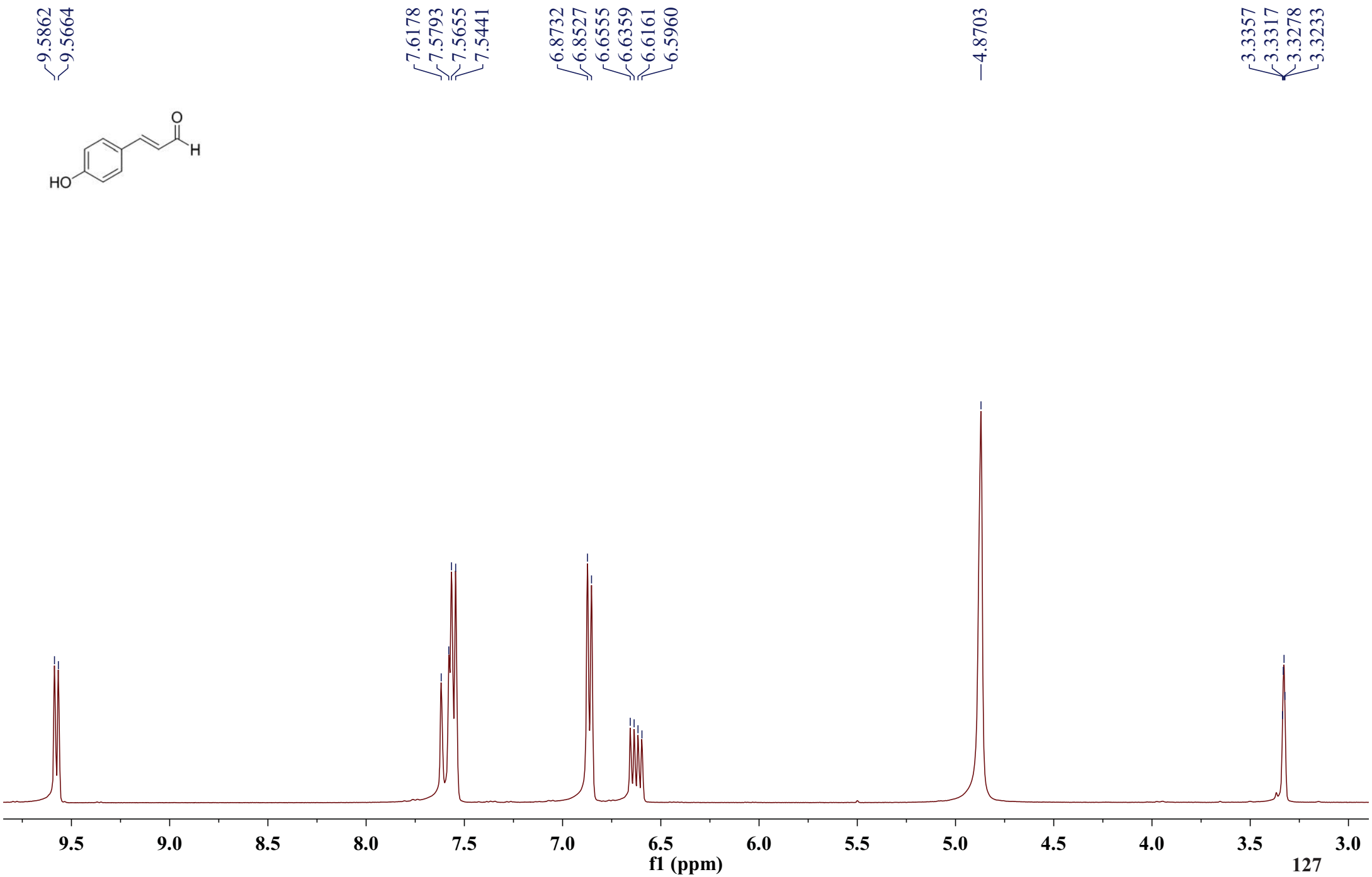
S6.50. ^{1}H NMR spectrum of compound **30**



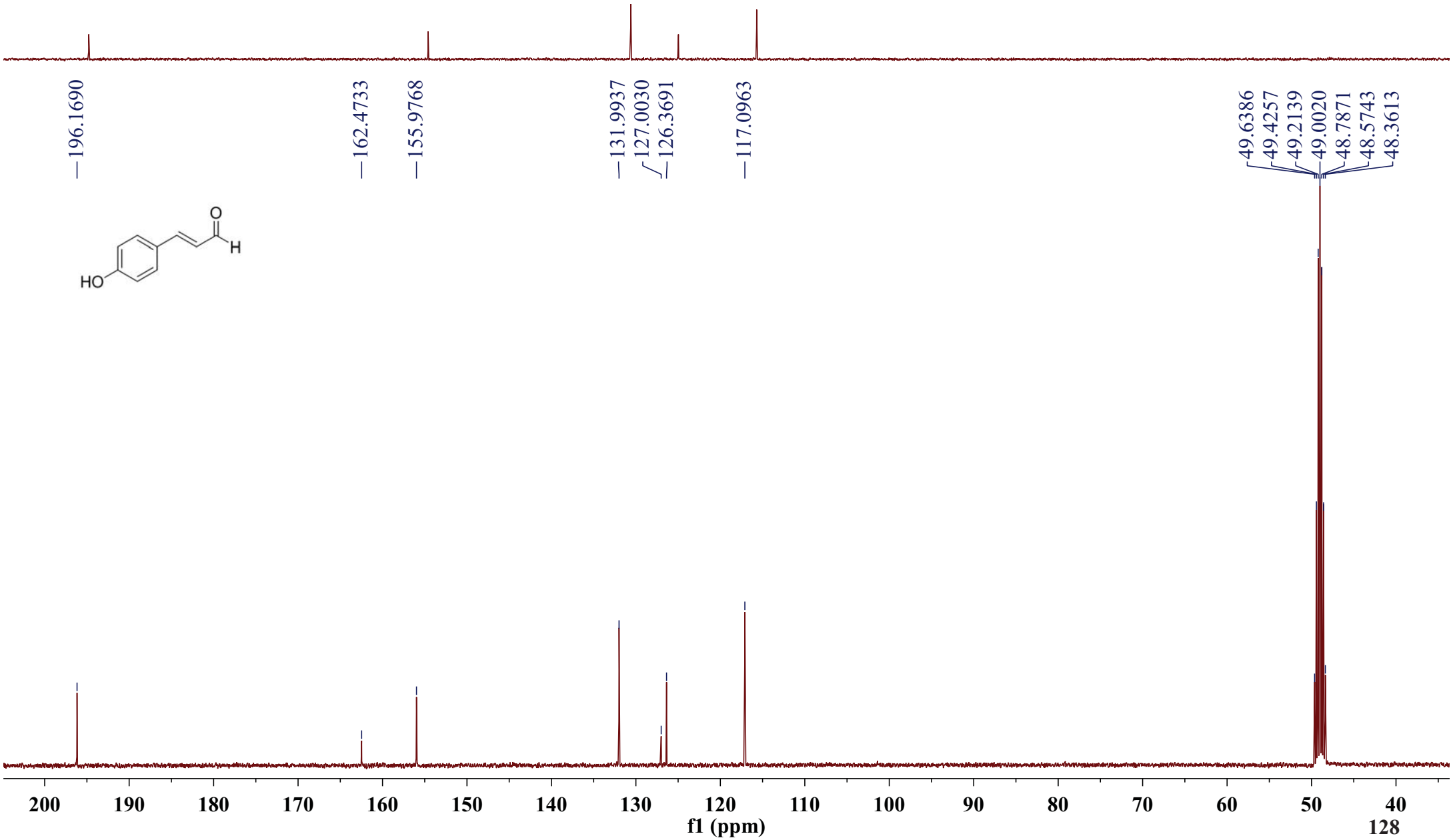
S6.51. ^{13}C NMR and DEPT spectra of compound **30**



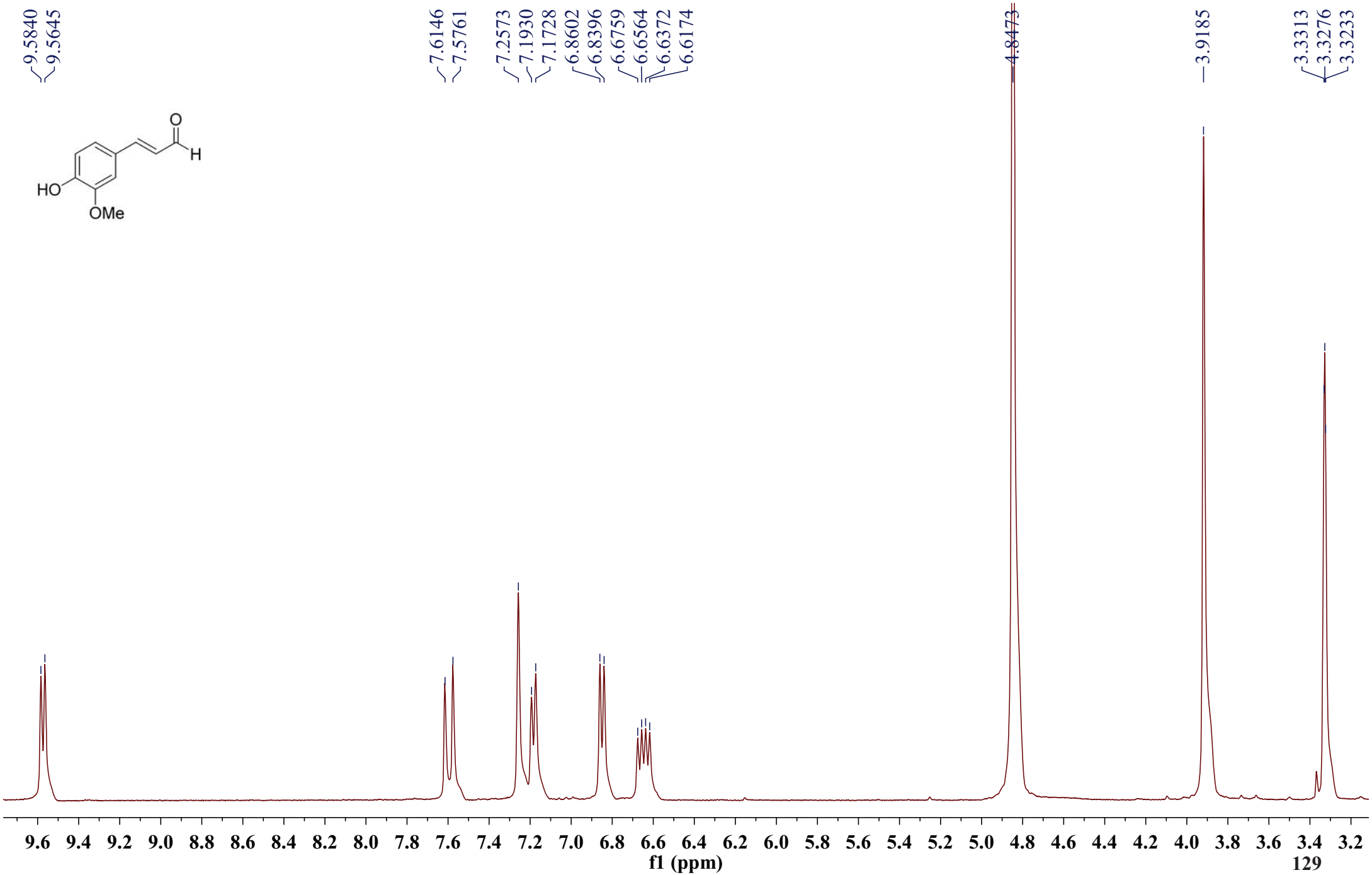
S6.52. ^{1}H NMR spectrum of compound **31**



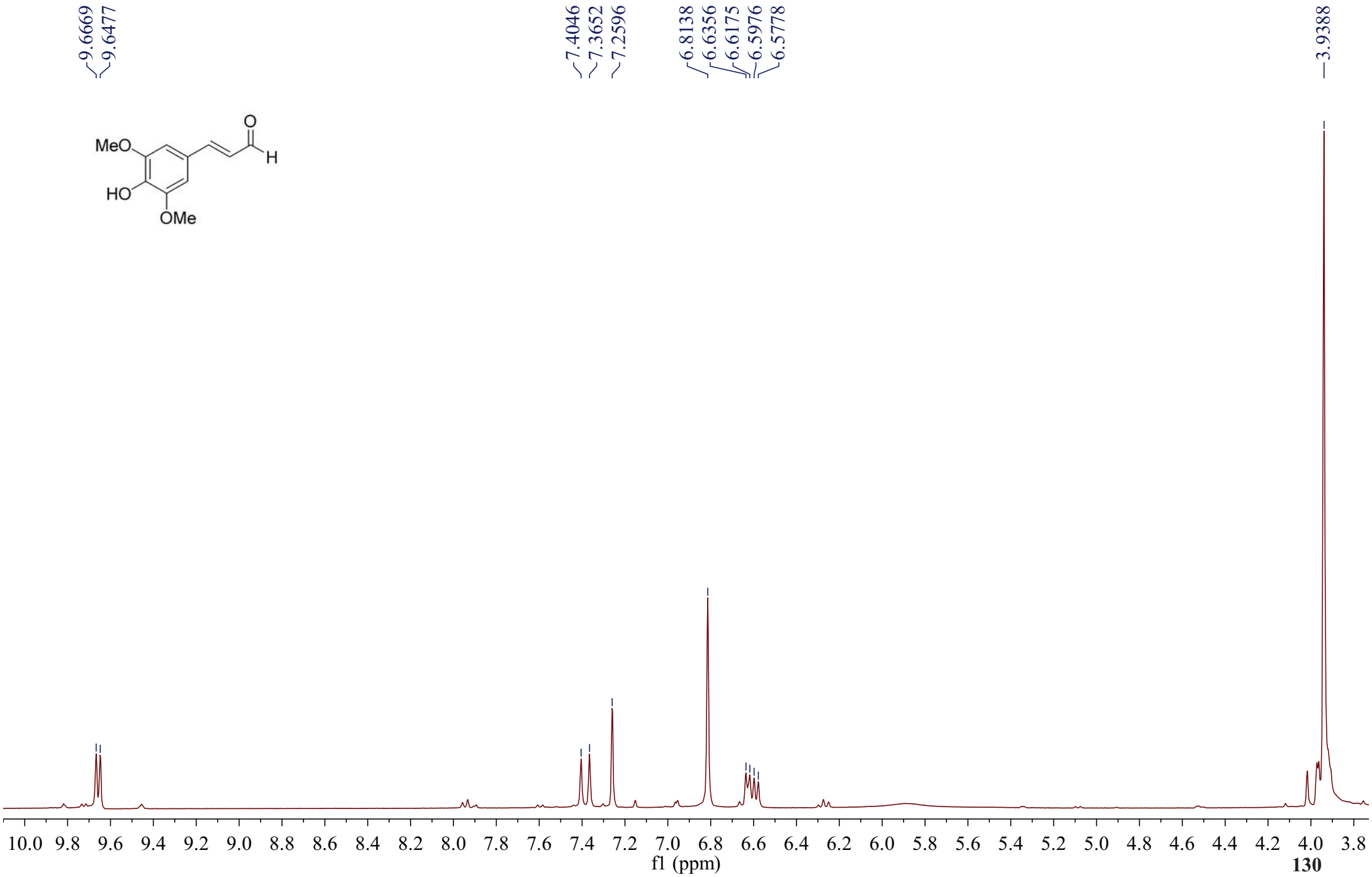
S6.53. ^{13}C NMR and DEPT spectra of compound **31**



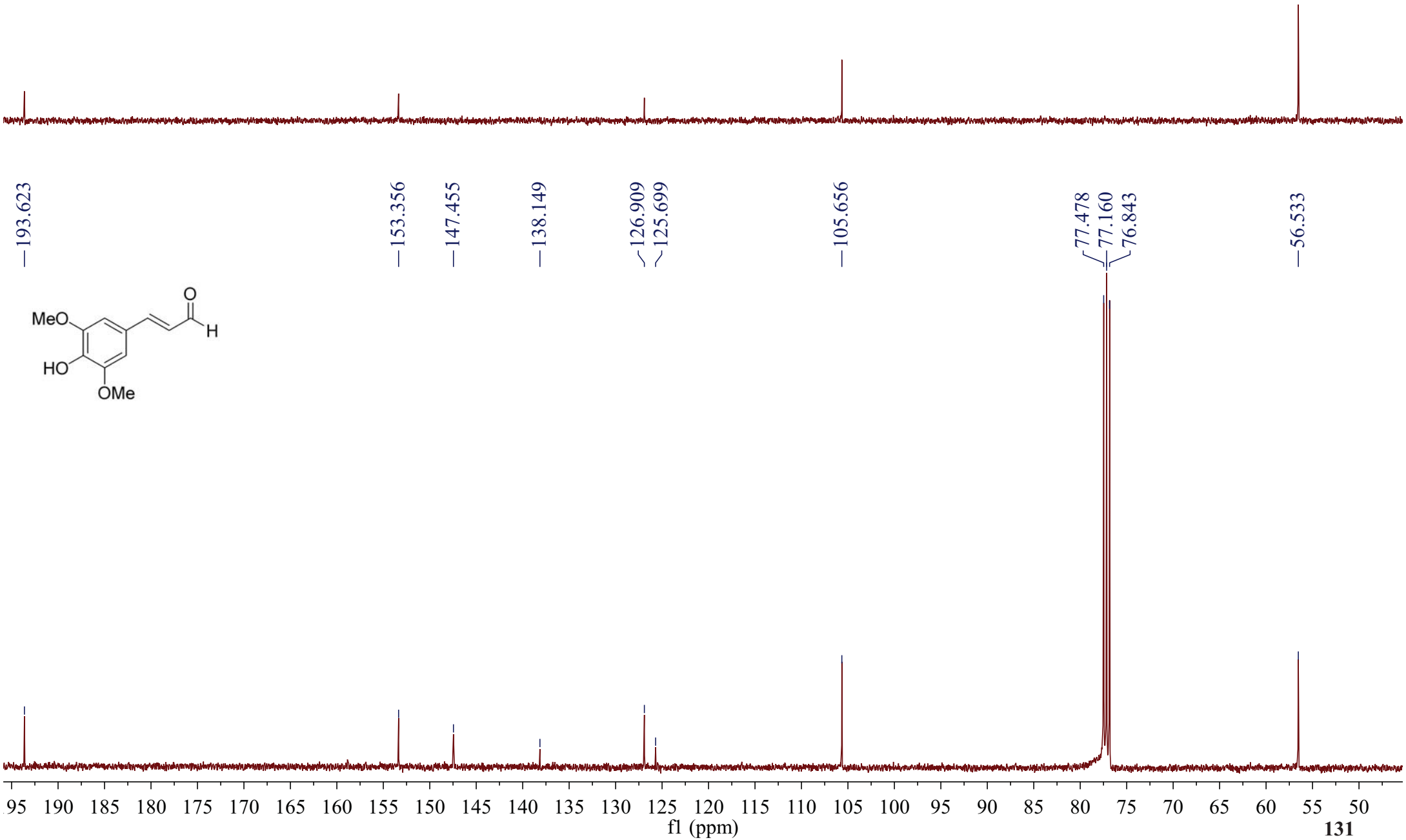
S6.54. ^{1}H NMR spectrum of compound **32**



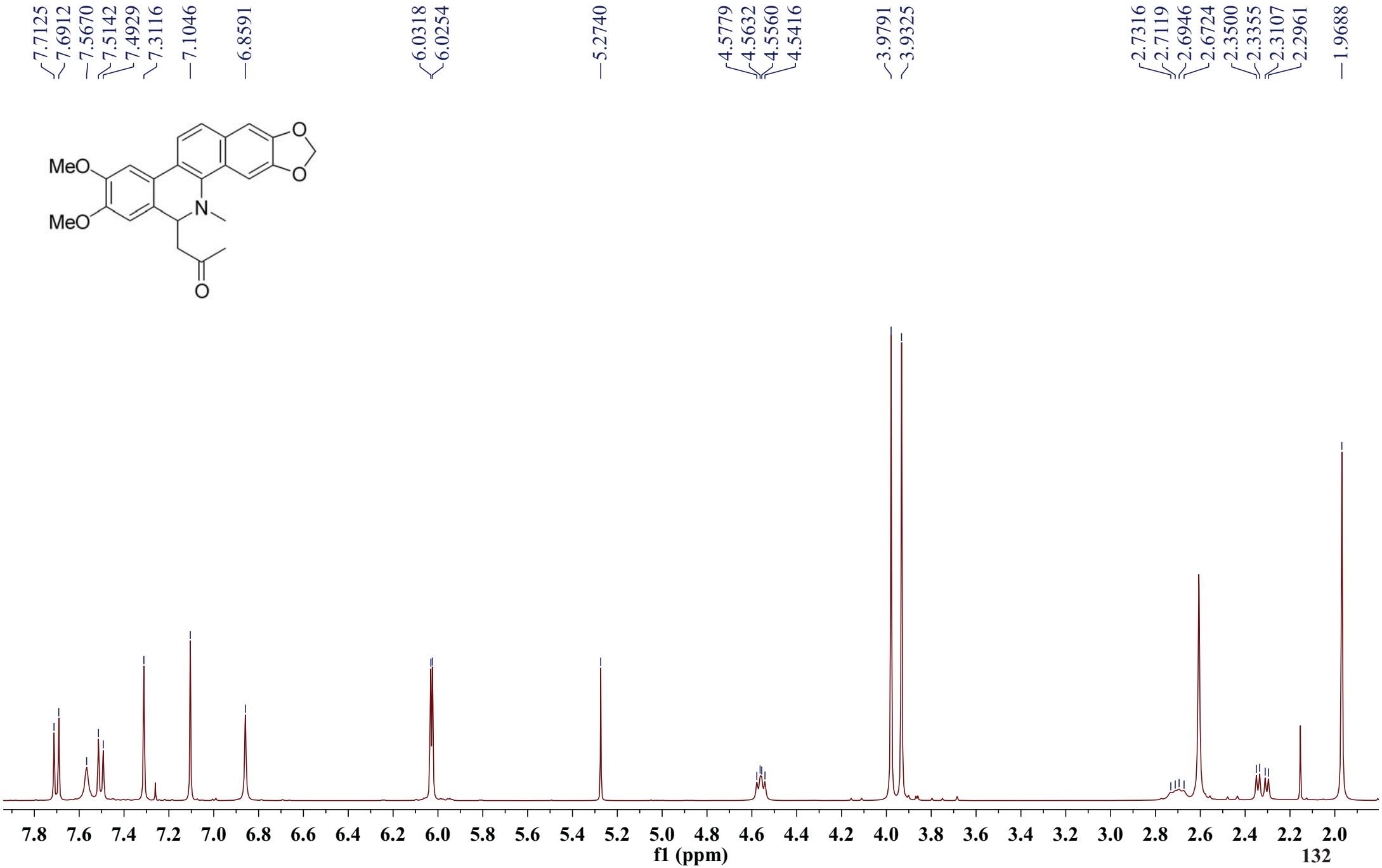
S6.55. ^{1}H NMR spectrum of compound **33**



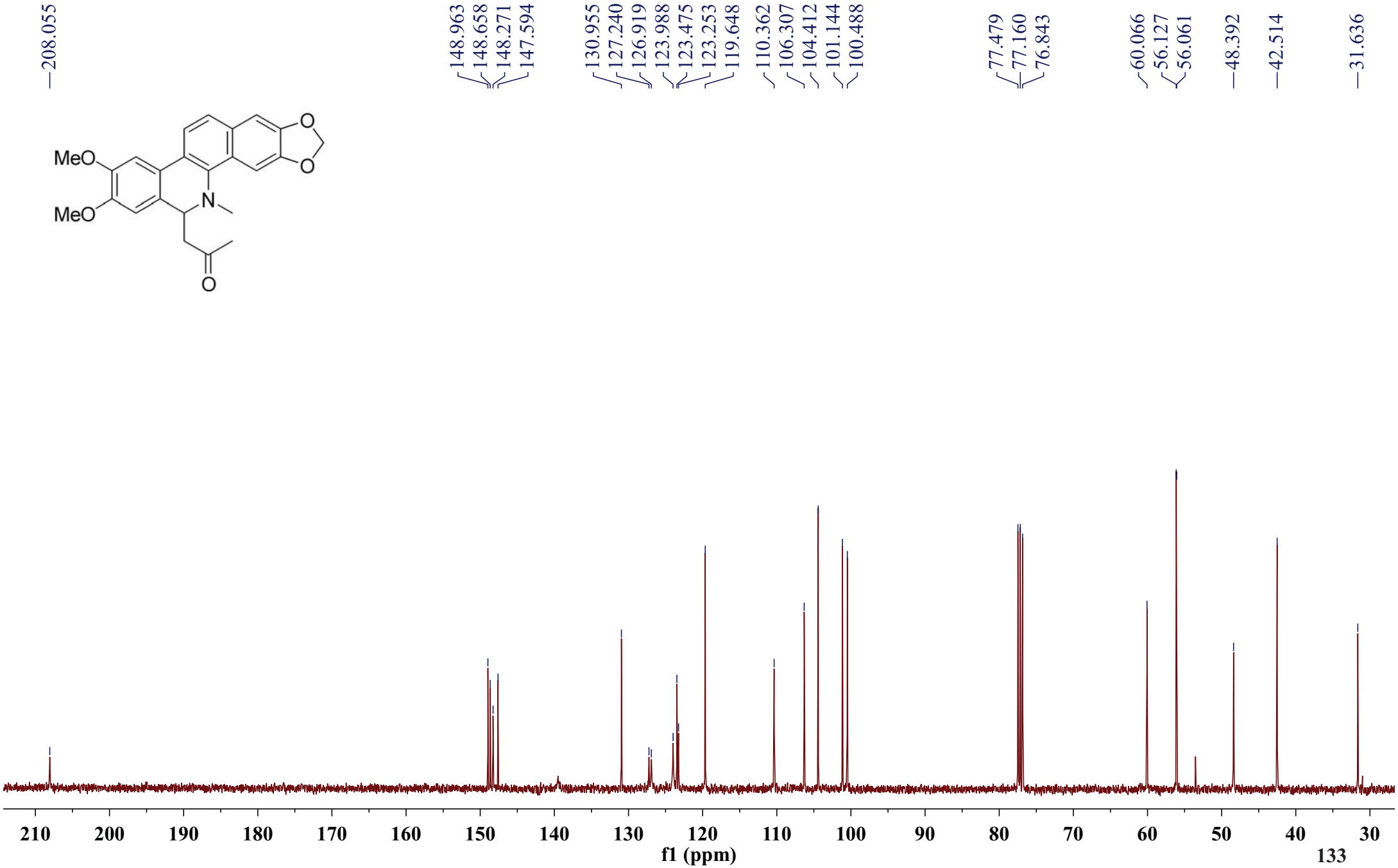
S6.56. ^{13}C NMR and DEPT spectra of compound **33**



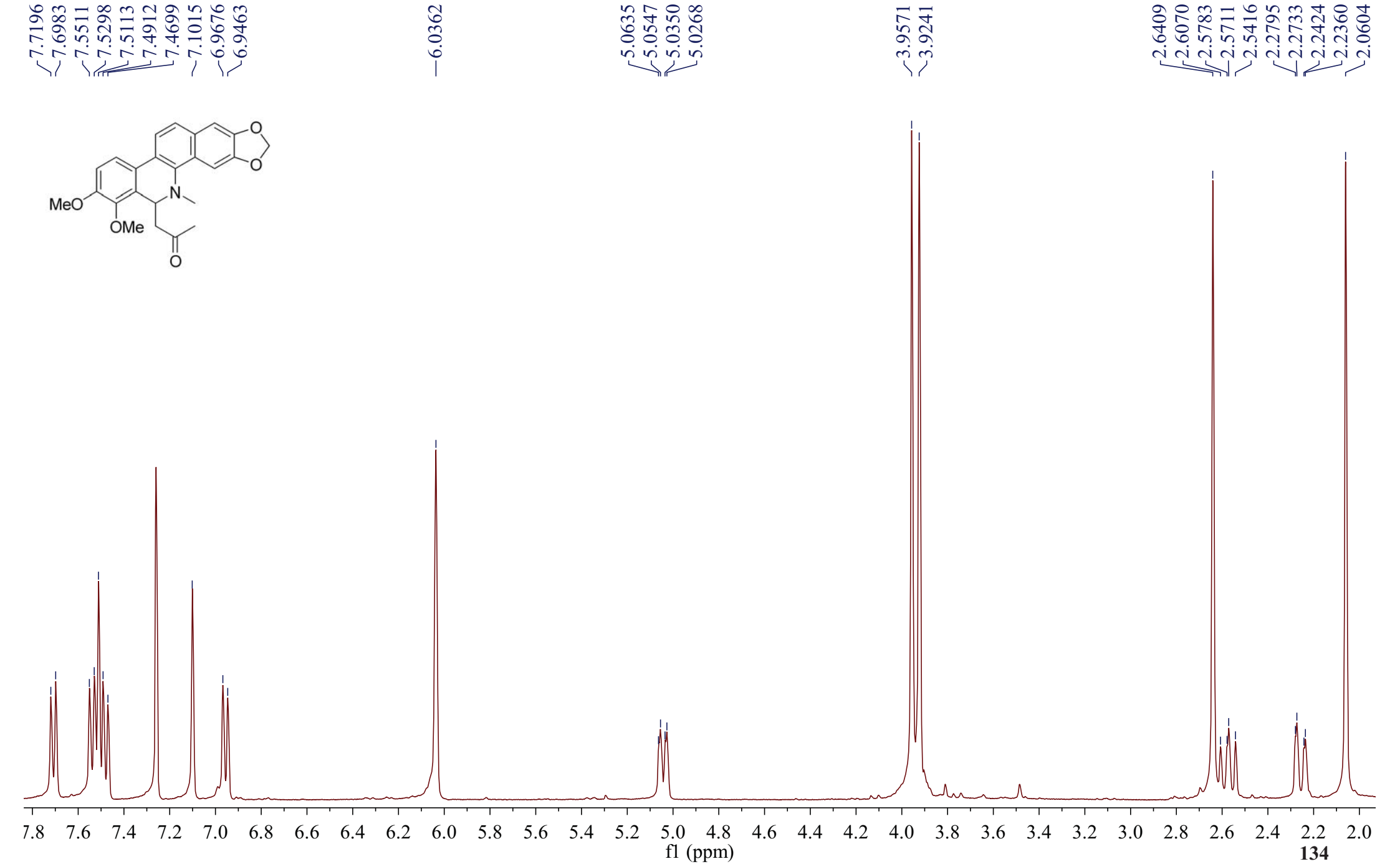
S6.57. ^{1}H NMR spectrum of compound **34**



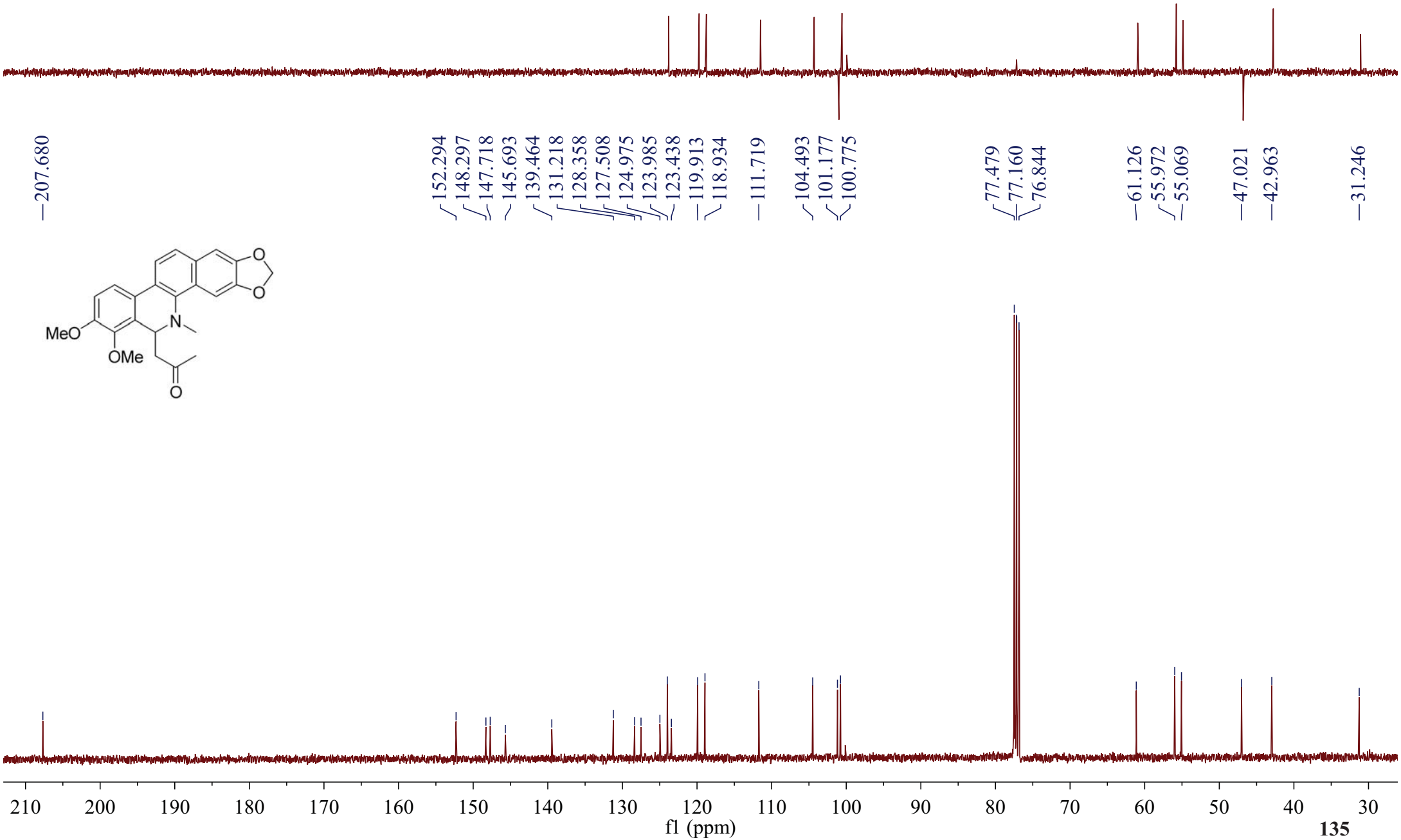
S6.58. ^{13}C NMR spectrum of compound **34**



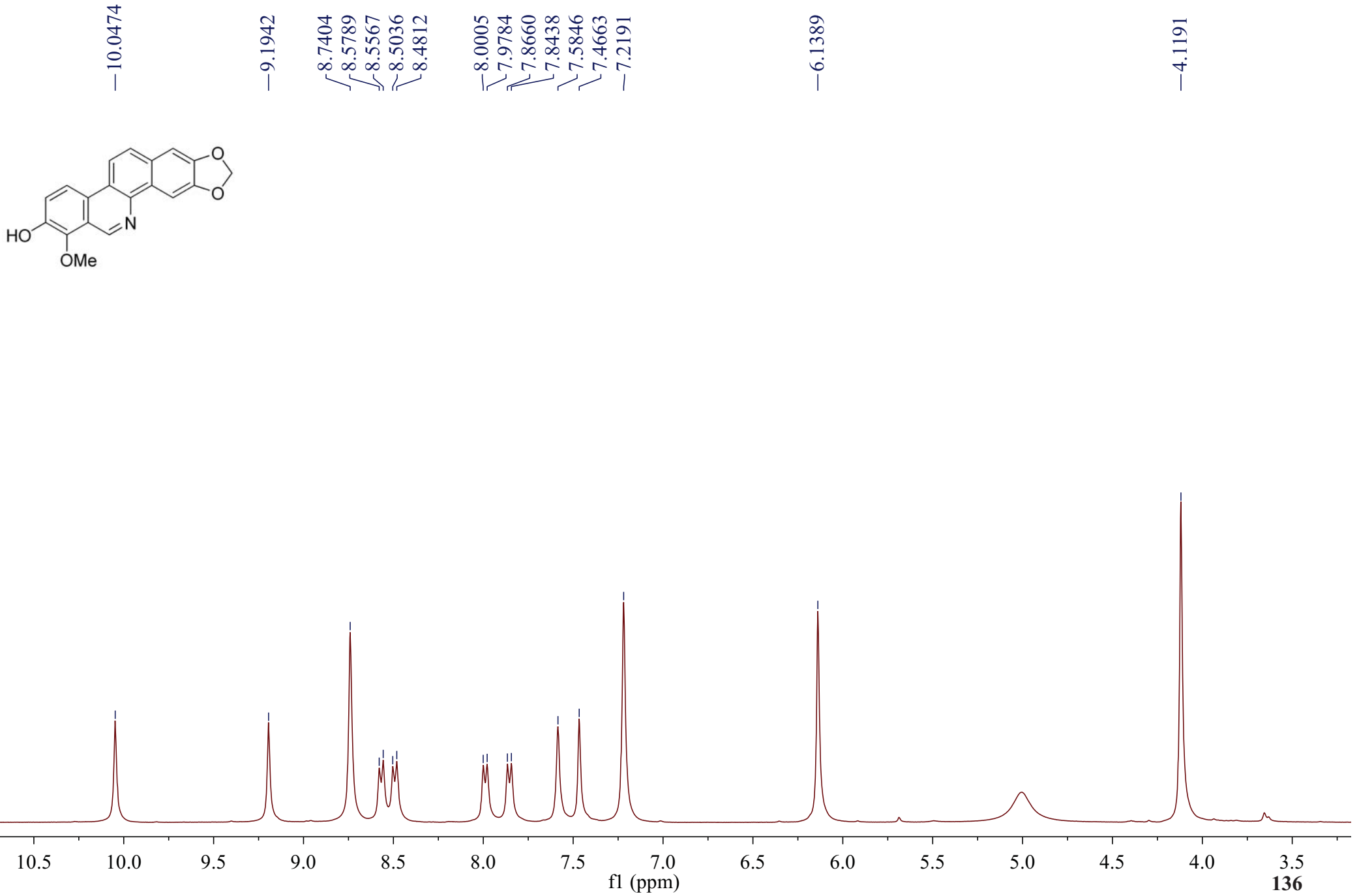
S6.59. ^{1}H NMR spectrum of compound **35**



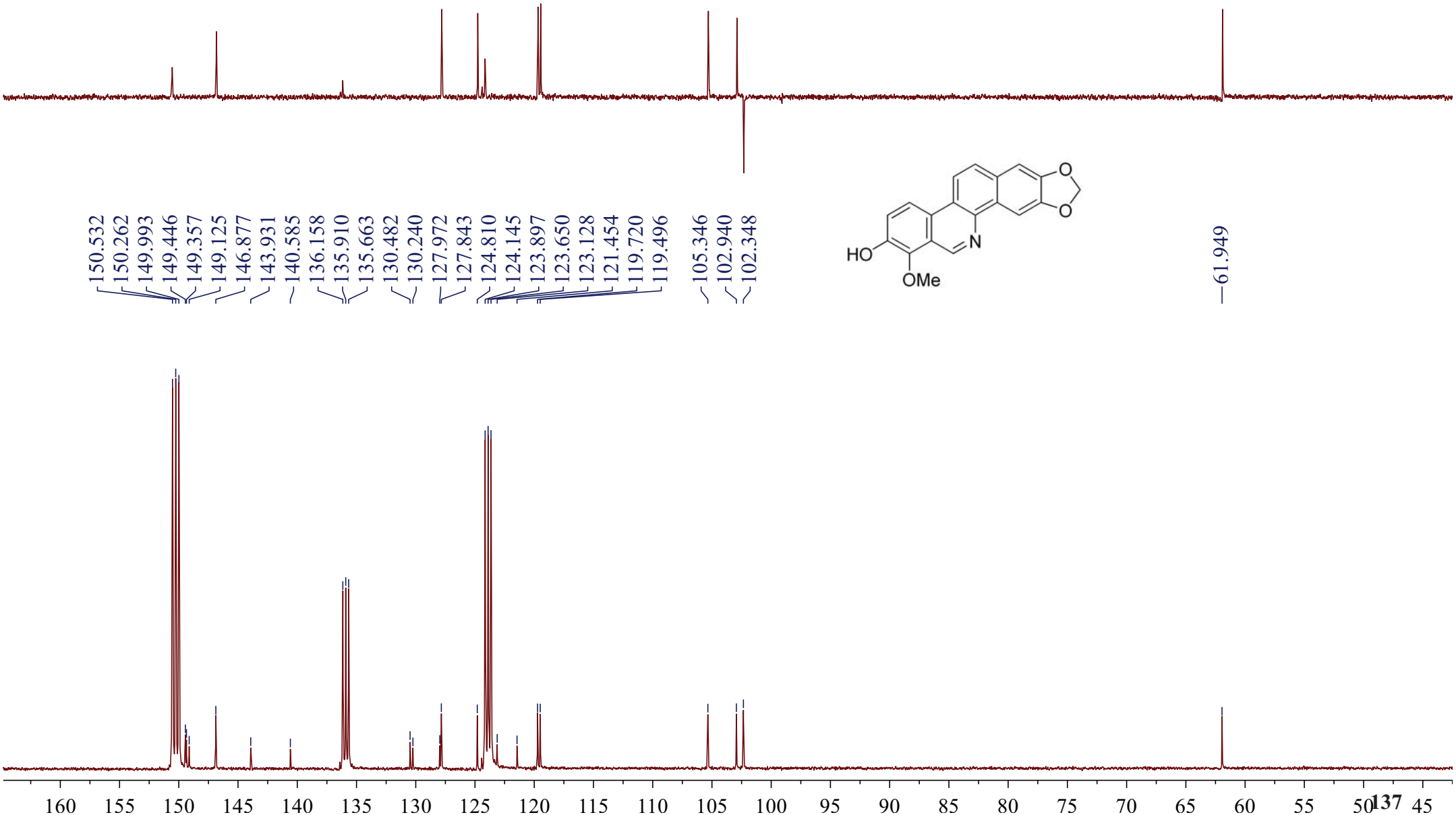
S6.60. ^{13}C NMR and DEPT spectra of compound **35**



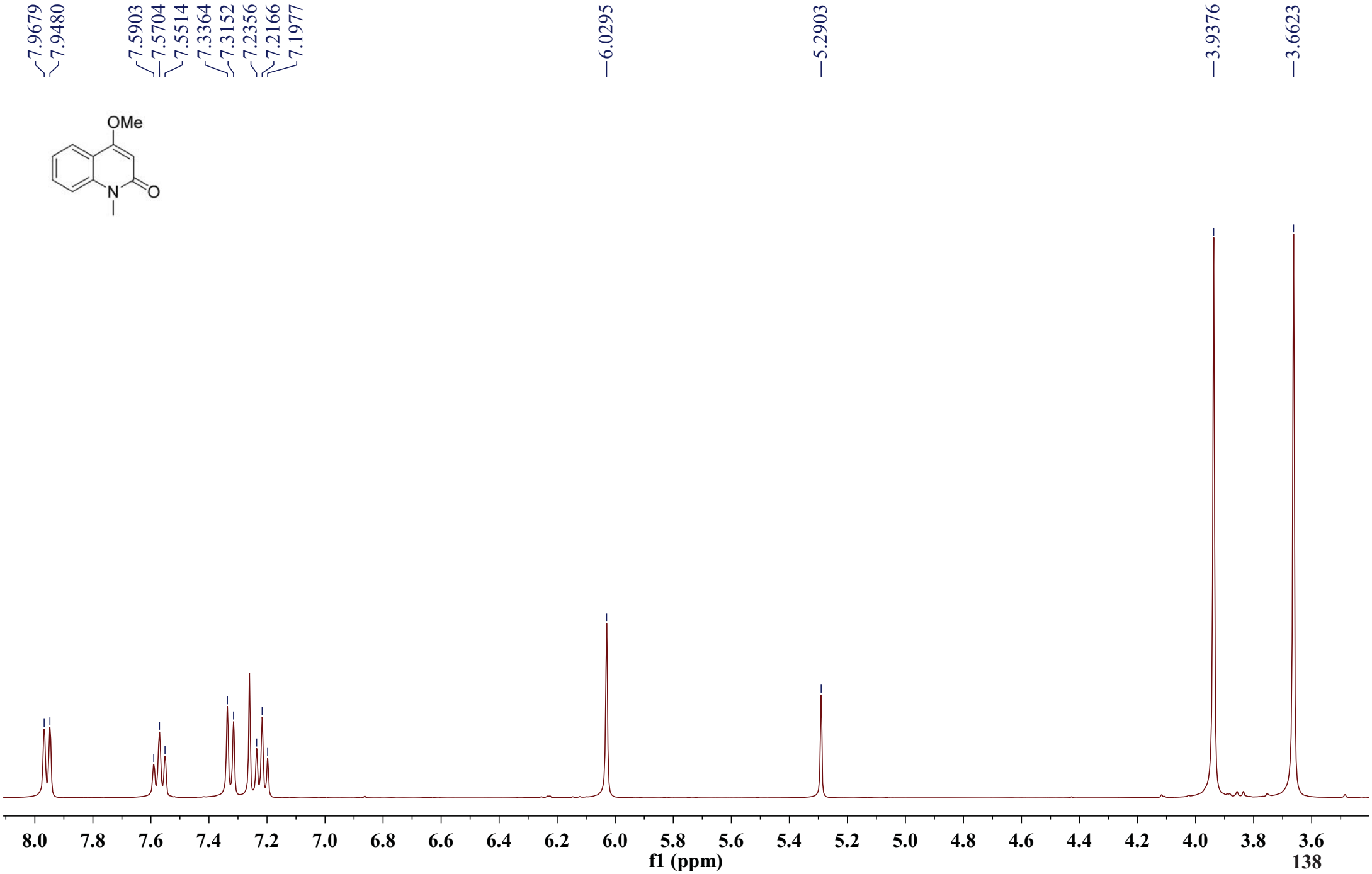
S6.61. ^{1}H NMR spectrum of compound **36**



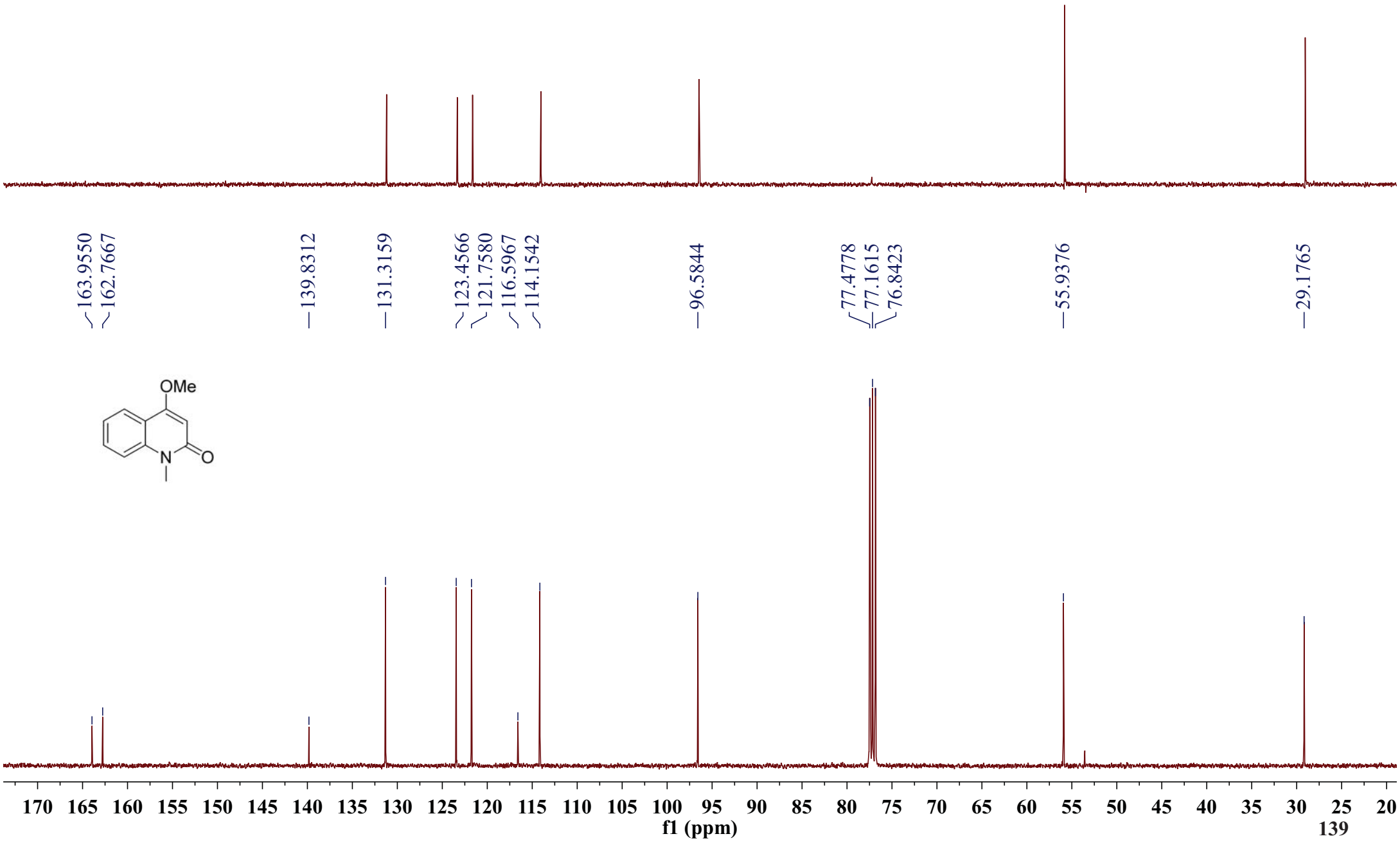
S6.62. ^{13}C NMR and DEPT spectra of compound **36**



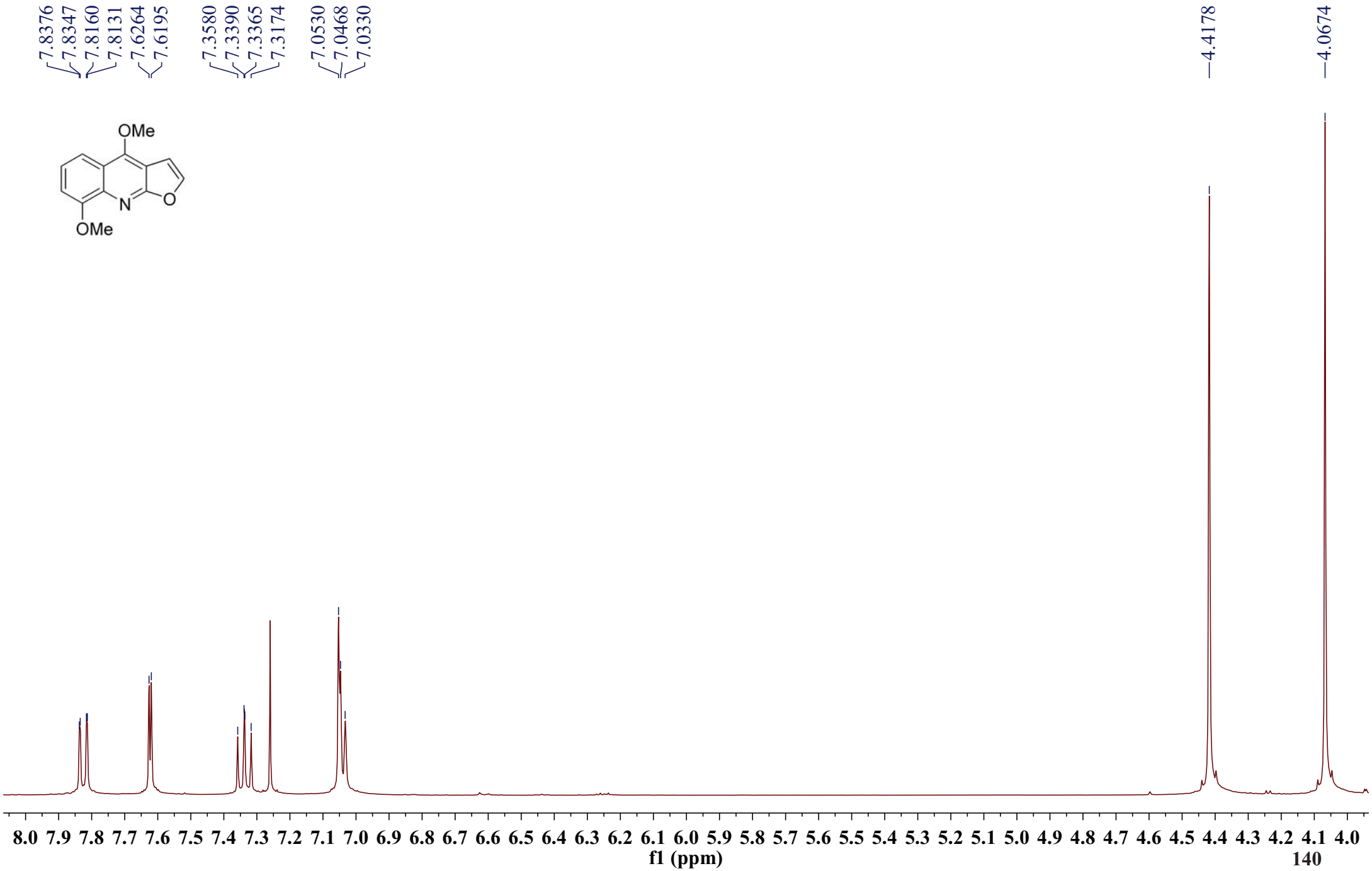
S6.63. ^{1}H NMR spectrum of compound **37**



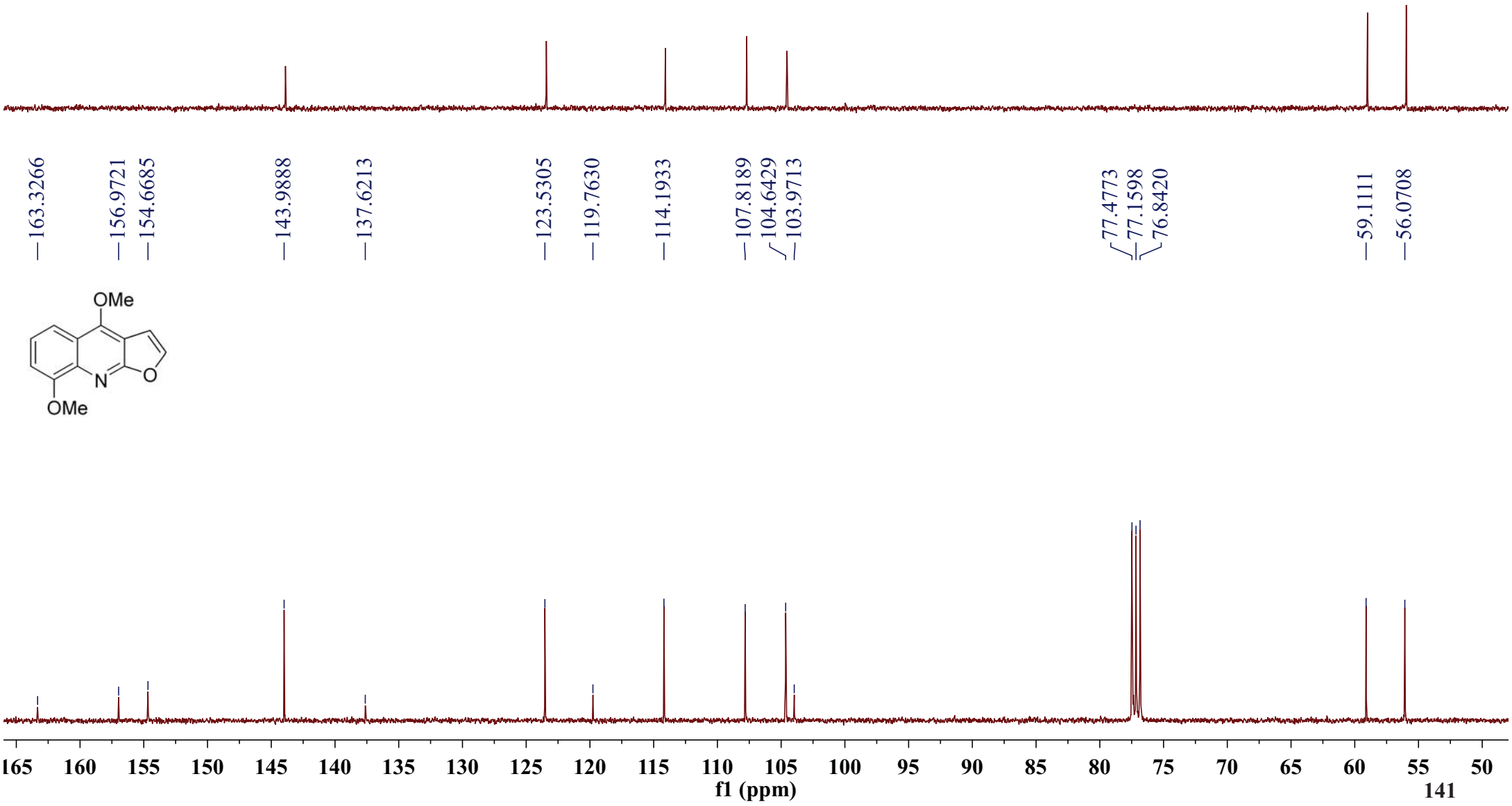
S6.64. ^{13}C NMR and DEPT spectra of compound **37**



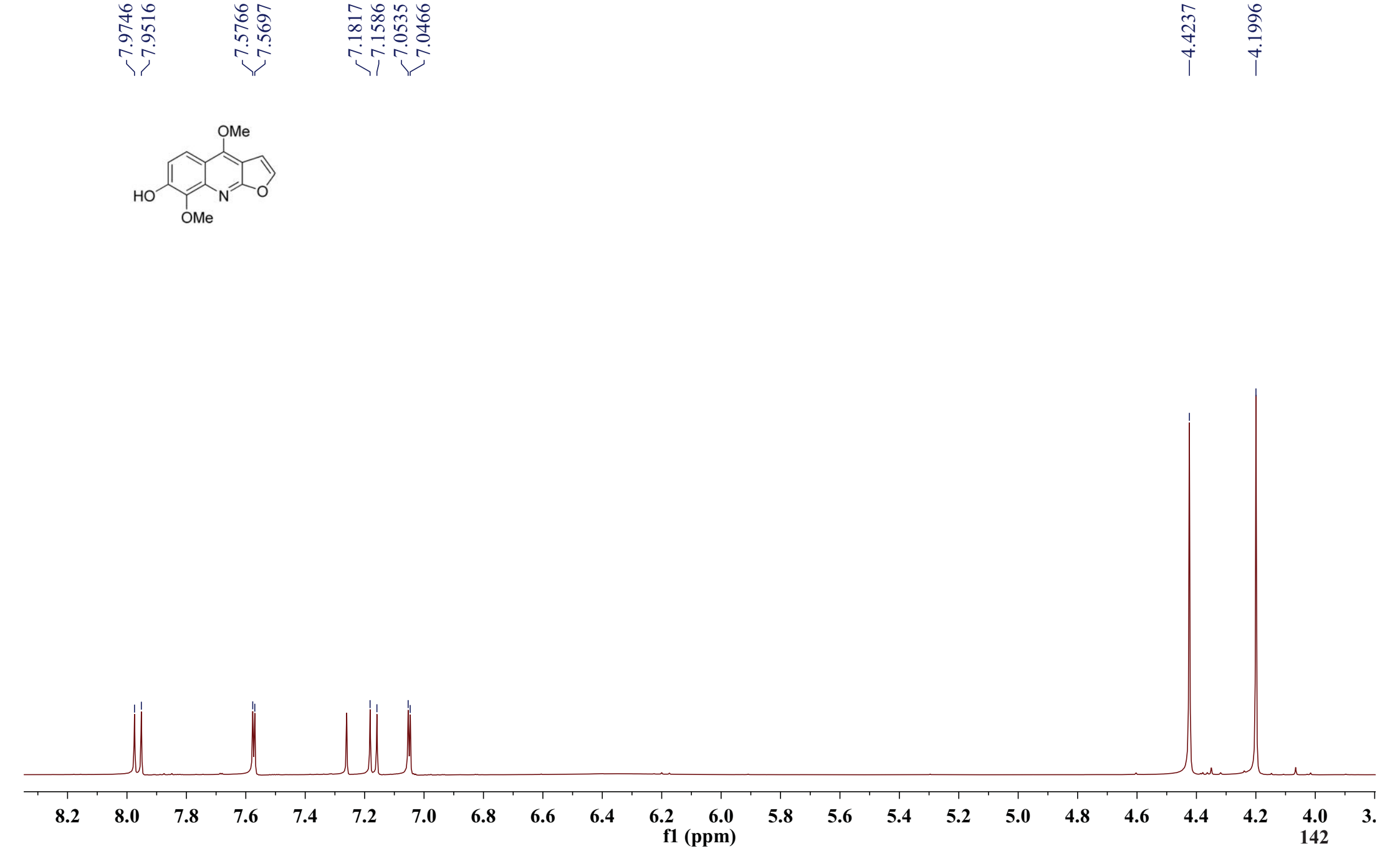
S6.65. ^{1}H NMR spectrum of compound **38**



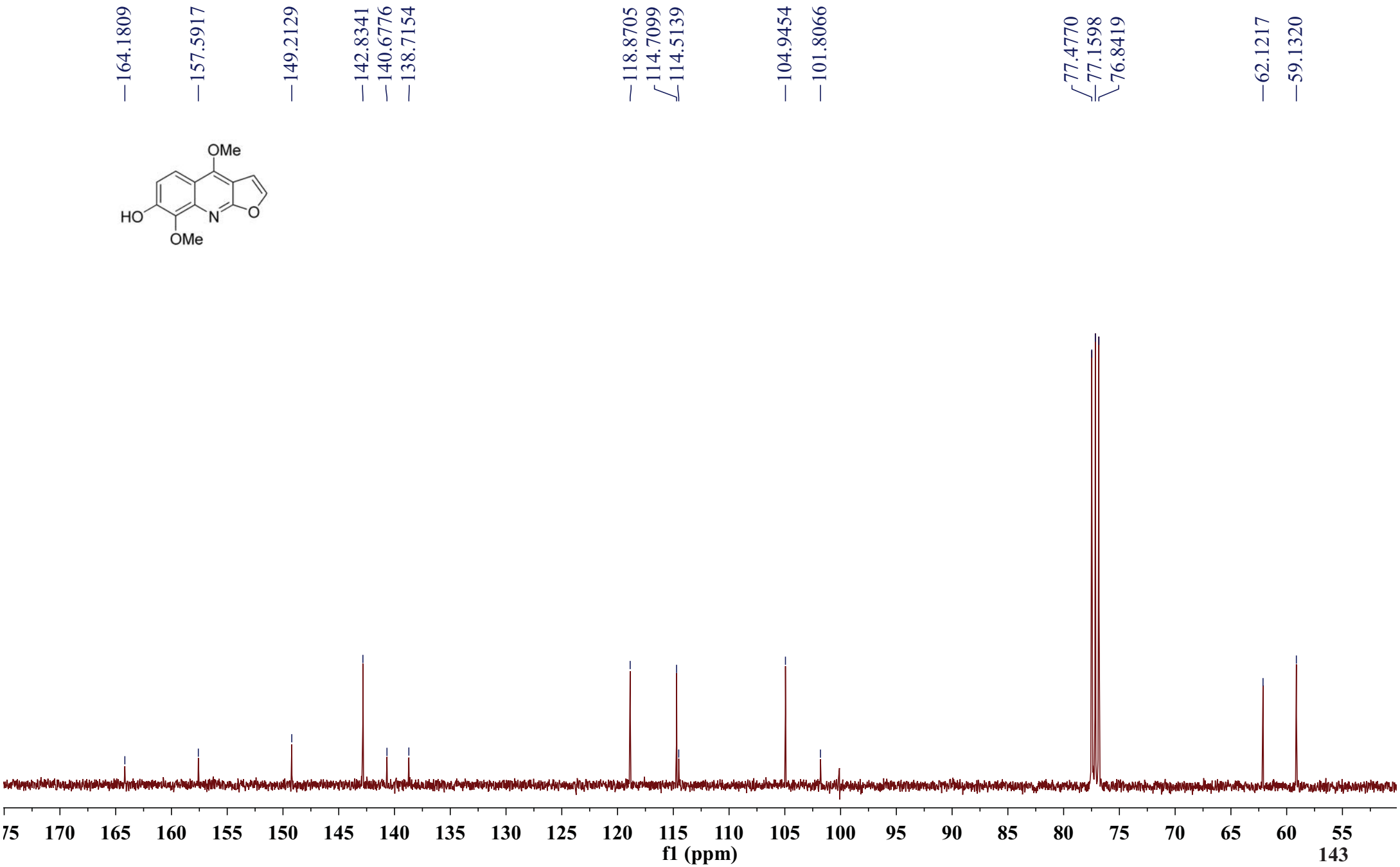
S6.66. ^{13}C NMR and DEPT spectra of compound **38**



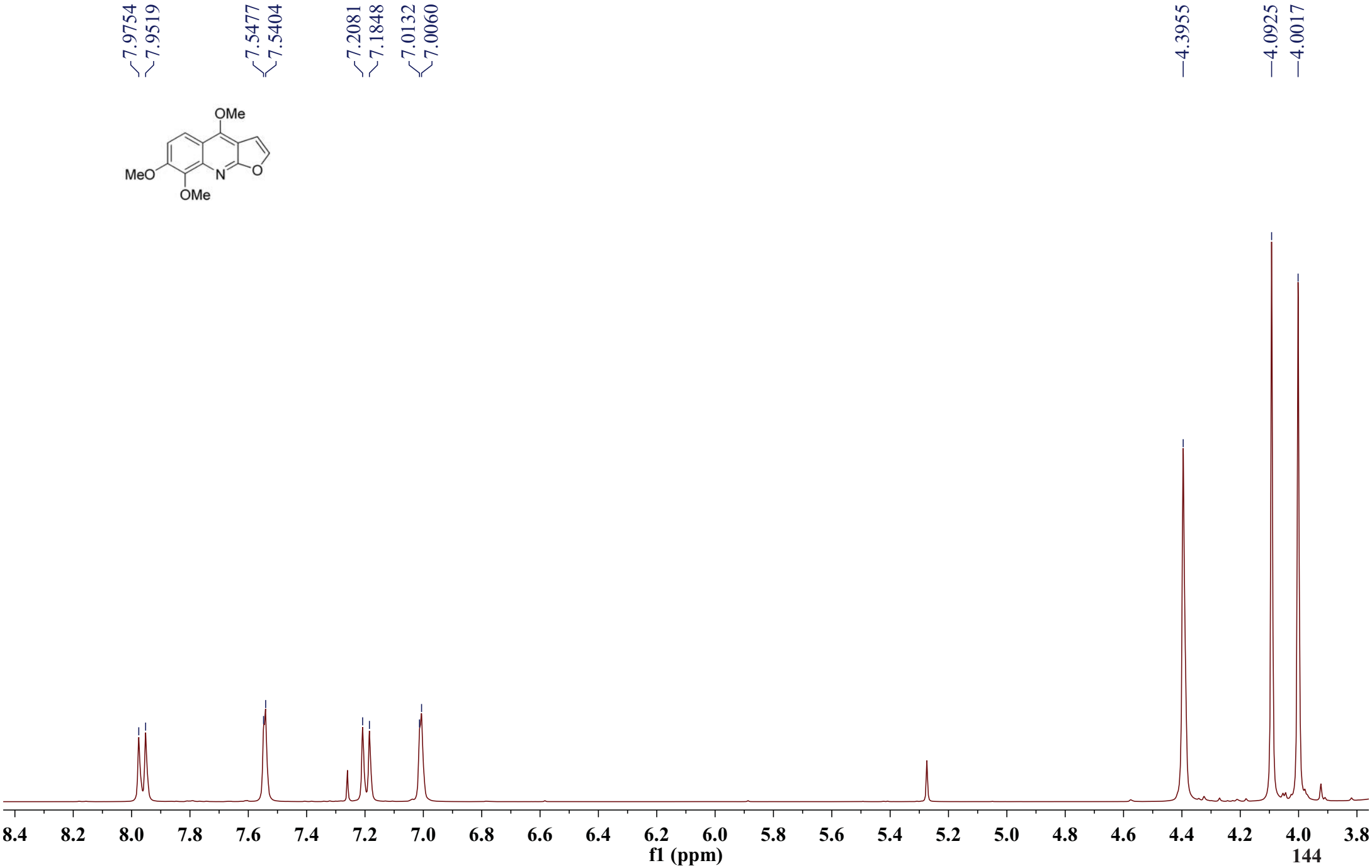
S6.67. ^{1}H NMR spectrum of compound **39**



S6.68. ^{13}C NMR spectrum of compound **39**



S6.69. ^{1}H NMR spectrum of compound **40**



S6.70. ^{13}C NMR spectrum of compound **40**