

## Supporting Information

### Relevance of the deletion of the *Tatri4* gene in the secondary metabolome of *Trichoderma arundinaceum* and its relation with the biocontrol of phytopathogen fungi.

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**Table S1. NMR Spectroscopic data of aspinolide H (12) (<sup>1</sup>H at 500 MHz, <sup>13</sup>C at 125 MHz).**

Position	Proton	$\delta_H$ (Hz)	$\delta^{13}C$	NOESY	HMBC
1	-		169.3		
2	H-2a	2.62 (1H, m)	27.6		
	H-2b	2.39 (1H, m)		H2, H3	
3	H-3a	2.34 (1H, m)	27.3		C4
	H-3b	2.11 (1H, m)		H4, H2, H2'	
4	H-4β	4.34 (1H, t, <i>J</i> = 5.3 Hz)	74.0	H6, H2, H3	
5	H-5β	-	206.6		
6	H-6	3.41 (1H, dd, <i>J</i> = 17.5, 10.5 Hz)	41.5	H4, H6', H8	C5, C7, C8
	H-6'	2.41 (1H, dd, <i>J</i> = 17.5, 3.3 Hz)		H6	C5, C7
7	H-7α	5.64 (1H, dd, <i>J</i> = 11, 9.3 Hz)	69.7	H9	
8	H-8β	5.11 (1H, t, <i>J</i> = 9.8 Hz)	73.8	H6, H10	C7, C9
9	H-9α	4.51 (1H, dq, <i>J</i> = 11.6, 6.1 Hz)	70.4	H7, H10	
10	H-10	1.19 (3H, d, <i>J</i> = 6.1 Hz)	17.0	H9, H8	C8, C9
1'	-	-	172.5		
2'	H-2'	2.3 (2H, m)	36.0		
3'	H-3'	1.63 (2H, sext, <i>J</i> = 7.3 Hz)	18.25		C1', C4', C2'
4'	H-4'	0.94 (3H, t, <i>J</i> = 7.3 Hz)	13.7		C2', C3'
<u>CH<sub>3</sub>CO</u>		1.98 (3H, s)	20.9		
CH <sub>3</sub> COO			169.1		

**Table S2.** NMR Spectroscopic data of aspinolide I (13) (<sup>1</sup>H at 500 MHz, <sup>13</sup>C at 125 MHz).

Position	Proton	$\delta_{\text{H}}$ (Hz)	$\delta^{13}\text{C}$	NOESY	HMBC
1	-		169.2		
2	H-2	2.64 (1H, ddd, $J = 17.9, 13.2, 3.3$ Hz)	27.8		C1
	H-2'	2.38 (1H, m)			C1
3	H-3	2.12 (1H, m)	27.2		C1, C4, C5
	H-3'	2.00 (1H, m)			C2
4	H-4β	4.36 (1H, d, $J = 6.2$ Hz)	74.0	H6, H6', H2, H3	C2, C3, C5
5	H-5β	-	206.7		
6	H-6	3.43 (1H, dd, $J = 17.4, 10.5$ Hz)	41.5	H6', H8	C5, C7, C8
	H-6'	2.41 (1H, dd, $J = 17.4, 1.7$ Hz)			C4, C5, C7, C8
7	H-7α	5.73 (1H, ddd, $J = 10.5, 9.8, 1.7$ Hz)	69.2	H9α, H6'	C5, CO-R, C8
8	H-8β	5.2 (1H, t, $J = 9.8$ Hz)	73.8	H6, H10	C6, C7, C9, C10, C1'
9	H-9α	4.55 (1H, dq, $J = 10.1, 6.1$ Hz)	70.6	H7α, H10	C1, C7, C8, C10
10	H-10	1.20 (3H, d, $J = 6.1$ Hz)	17.0	H8	C8, C9
1'	-	-	165.0		
2'	H-2'	5.82 (1H, dq, $J = 15.5, 1.7$ Hz)	121.6		C1', C4'
3'	H-3'	7.02 (1H, dq, $J = 15.5, 7.0$ Hz)	146.8		C1', C4'
4'	H-4'	1.90 (3H, dd, $J = 7, 1.7$ Hz)	18.21		C2', C3'
<u>CH<sub>2</sub>CH<sub>2</sub>CH=CH(CH<sub>2</sub>)<sub>n</sub>CH<sub>2</sub>CO</u>		0.88 (3H, t, $J = 6.5$ Hz),	14.12		
R-CH=CH-(CH <sub>2</sub> ) <sub>n</sub> CH <sub>2</sub> CO-		1.54-1.21,	22.7, 24.8, 27.1, 28.9-30, 31.9		
R-CH=CH-(CH <sub>2</sub> ) <sub>n</sub> CH <sub>2</sub> CO-		2.15 (2H, m)	34.31, 172.29		
R-CH=CH-(CH <sub>2</sub> ) <sub>n</sub> CH <sub>2</sub> CO-		5.33 (2H, m)	130, 129.6		

**Table S3. NMR Spectroscopic data of aspinolide J (14) ( $^1\text{H}$  at 600 MHz,  $^{13}\text{C}$  at 150 MHz).**

Position	Proton	$\delta_{\text{H}}$ (Hz)	$\delta^{13}\text{C}$	NOESY	HMBC
1	-		176.4		
2	H-2	2.05 (1H, dd, $J= 15.7, 11.7$ Hz)	32.7	H2'	C1, C3, C4
	H-2'	2.45 (1H, ddd, $J=15.7, 9.6, 1.4$ Hz)		H2	C1, C3, C4
3	H-3	1.77 (1H, ddd, $J=13.7, 9.6, 3.0$ Hz)	27.4	H3', H2	C1, C2, C5
	H-3'	2.27 (1H, m)			C1, C2, C4, C5
4	H-4 $\beta$	3.63 (1H, dt, $J= 11.2, 3.0$ Hz)	75.6	H2 , H3, H5, H6	
5	H-5 $\beta$	4.51 (1H, s (br))	73.4	H4, H6	C3, C4, C6
6	H-6 $\beta$	5.55 (1H, dd, $J=15.9, 1.9$ Hz)	130.8	H4, H5, H8	C5, C7, C8
7	H-7 $\alpha$	5.65 (1H, ddd, $J= 15.9, 8.4, 2.5$ Hz)	131.8		C5, C6
8	H-8 $\beta$	3.88 (1H, t, $J=8.8$ Hz)	79.3	H6, H10	C6, C9, C10
9	H-9 $\alpha$	4.9 (1H, dq, $J=8.8, 6.4$ Hz)	74.7	H10	C1, C8
10	H-10	1.42 (3H, d, $J=6.4$ Hz)	16.8	H8, H9	C8, C9

**Table S4. NMR Spectroscopic data of arundinolide A (15) (<sup>1</sup>H at 500 MHz, <sup>13</sup>C at 125 MHz).**

Position	Proton	$\delta_{\text{H}}$ (Hz)	$\delta^{13}\text{C}$	NOESY	HMBC
1	-	-	177.3		
2	H-2 $\alpha$	2.60 (1H, ddd, $J = 18, 10.1, 6$ Hz)	28.4		C-1, C3, C4
	H-2 $\beta$	2.48 (1H, ddd, $J = 18, 10.1, 7.6$ Hz)			C1, C3, C4
3	H-3 $\alpha$	2.21 (1H, m)	21.0		C1, C2, C4, C5
	H-3 $\beta$	2.12 (1H, m)			C1, C4, C5
4	H-4 $\alpha$	4.51 (1H, m)	81.5		
5	H-5 $\alpha$	4.54 (1H, m)	71.7		
6	H-6	5.75 (1H, ddd, $J = 15.7, 5, 1.2$ Hz)	131.2	H8, H5	C5, C7, C8
7	H-7	5.96 (1H, ddd, $J = 15.7, 7, 1.5$ Hz)	127.7	H8, H5	C5, C6, C8
8	H-8	5.24 (1H, ddt, $J = 7, 3.9, 0.9$ Hz)	77.2	H6, H7, H9, H10	C1', C6, C7, C10
9	H-9	3.98 (1H, qd, $J = 6.5, 3.9$ Hz)	69.0	H8, H10	C7, C10
10	H-10	1.18 (3H, d, $J = 6.5$ Hz)	18.3	H8, H9	C8, C9
1'	-	-	165.6		
2'	H-2'	5.88 (1H, dq, $J = 15.6, 1.7$ Hz)	122.3	H4'	C1'
3'	H-3'	7.02 (1H, dq, $J = 15.6, 6.9$ Hz)	145.9	H2', H4'	C1', C4'
4'	H-4'	1.90 (3H, dd, $J = 6.9, 1.7$ Hz)	18.1		C1', C2', C3'

**Table S5.** NMR Spectroscopic data of arundinolide B (16) (<sup>1</sup>H at 500 MHz, <sup>13</sup>C at 125 MHz).

Position	Proton	$\delta_{\text{H}}$ (Hz)	$\delta^{13}\text{C}$	NOESY	HMBC
1	-		177.2		
2	H-2 $\alpha$	2.61 (1H, ddd, $J = 18.0, 10.1, 6$ Hz)	28.5		C-1, C-4
	H-2 $\beta$	2.50 (1H, ddd, $J = 18.0, 10.1, 7.7$ Hz)			C-1
3	H-3 $\alpha$	2.22 (1H, m)	21.0		
	H-3 $\beta$	2.14 (1H, m)			
4	H-4 $\alpha$	4.52 (1H, m)	81.6		
5	H-5 $\alpha$	4.55 (1H, m)	71.8		
6	H-6	5.78 (1H, ddd, $J = 15.5, 5.1, 1.4$ Hz)	129.0		C-5, C-7, C-8
7	H-7	5.91 (1H, ddd, $J = 15.5, 5.7, 1.4$ Hz)	131.1		C-5, C-6, C-8
8	H-8	4.28 (1H, m)	73.9		
9	H-9	4.99 (1H, qd, $J = 6.5, 3.2$ Hz)	73.2		
10	H-10	1.21 (3H, d, $J = 6.5$ Hz)	14.6		C-8, C-9
1'	-	-	173.6		
2'	H-2'	2.31 (2H, t, $J = 7.4$ Hz)	36.3		C-3', C-4'
3'	H-3'	1.66 (2H, sext, $J = 7.4$ Hz)	18.5		C-2', C-4'
4'	H-4'	0.96 (3H, t, $J = 7.4$ Hz)	13.6		C-3', C-2'

**Table S6. NMR Spectroscopic data of trichoarundinal A (17) (<sup>1</sup>H at 500 MHz, <sup>13</sup>C at 125 MHz).**

Position	Proton	$\delta_{\text{H}}$ (Hz)	$\delta^{13}\text{C}$	NOESY	HMBC
1	-		95.8		C1-OH, H-2, H-3, H-5, H-6, H-7, H-9
2	H-2 $\alpha$	1.77 (1H, m (superimposed))	36.1		C1, C3
	H-2 $\beta$	1.64 (1H, m)			
3	H-3 $\alpha$	1.85 (1H, m (superimposed))	26.3		C1, C2
	H-3 $\beta$	1.78 (1H, m (superimposed))			C1, C2
4	H-4 $\beta$	3.64 (1H, m)	70.9	H2, H3, H5, H6	
5	H-5 $\beta$	3.74 (1H, dt, $J$ = 6.1, 2.9 Hz)	72.9	H4, H7 $\beta$ , H6	C1, C3, C4, C6, C7
6	H-6 $\beta$	1.76 (1H, ddd, 13.5, 4.6, 2.9 Hz)	42.2		C1
7	H-7 $\alpha$	2.08 (1H, ddd, $J$ = 13.5, 12.2, 11.1 Hz)	27.5		C1, C6, C8, C9
	H-7 $\beta$	1.92 (1H, m (superimposed))			C1, C6, C8, C9
8	H-8 $\beta$	4.58 (1H, ddd, $J$ = 11.1, 9.8, 4.9 Hz)	73.3	H7 $\beta$ , H6, H10	C1', C9, C10
9	H-9 $\alpha$	4.12 (1H, dq, $J$ = 9.8, 6.2 Hz)	68.2	C1-OH, H7 $\alpha$ , H10	C-1, C7, C8
10	H-10	1.15 (3H, d, $J$ = 6.2 Hz)	17.9	H9, H8	C8, C9
1'	-		165.7		
2'	H-2'	5.84 (1H, dq, $J$ = 15.5, 1.7 Hz)	122.5	H4'	C4'
3'	H-3'	6.99 (1H, dq, $J$ = 15.5, 7 Hz)	145.3	H2', H4'	C1', C4'
4'	H-4'	1.89 (3H, dd, $J$ = 7, 1.7 Hz)	18.0		C2', C3'
C1-OH		3.22 (1H, s)	-		C-1, C-6
C5-OH		3.19 (1H, d, $J$ = 7.0 Hz)	-		C-5, C-6

**Table S7. NMR Spectroscopic data of trichoarundinal B (18) (<sup>1</sup>H at 500 MHz, <sup>13</sup>C at 125 MHz).**

Position	Proton	$\delta_H$ (Hz)	$\delta^{13}C$	NOE	HMBC
1	-		96.6		
2	H-2	2.09 (1H, tt, $J = 14.2, 3.8$ Hz)	22.9		
	H-2	1.77 (1H, m)			
3	H-3	3.67 (1H, t, $J = 2.9$ Hz)	72.0	H-2, H2', H-5	C1, C4
4	H-4	1.64 (1H, m)	27.4		
	H-4	1.96 (1H, m)			
5	H-5 $\beta$	3.91 (1H, s(br))	70.5	H-3, H4, H6 $\beta$ , H7 $\beta$	C1, C6
6	H-6 $\beta$	2.19 (1H, ddd, 13.5, 3.8, 2.5 Hz)	37.6		
7	H-7 $\alpha$	2.01 (1H, ddd, $J = 13.5, 12, 11$ Hz)	27.2		C1
	H-7 $\beta$	1.93 (1H, m (superimposed))			C1
8	H-8 $\beta$	4.59 (1H, ddd, $J = 11, 9.8, 5$ Hz)	73.4	H-6, H7 $\beta$ , H10	C1', C10, C9
9	H-9 $\alpha$	4.13 (1H, dq, $J = 9.8, 6.2$ Hz)	68.4	H7 $\alpha$ , H10, <u>HO</u> -C1	C8
10	H-10	1.17 (3H, d, $J = 6.2$ Hz)	17.9		
1'	-		165.7		
2'	H-2'	5.84 (1H, dq, $J = 15.5, 1.7$ Hz)	122.5		C1', C4'
3'	H-3'	6.99 (1H, dq, $J = 15.5, 7$ Hz)	145.3		C1', C4'
4'	H-4'	1.89 (3H, dd, $J = 7, 1.7$ Hz)	18.0	H3', H2'	
C1-OH		3.91 (1H, s)	-		
C3-OH		2.27 (1H, s(br))			
C5-OH		2.31 (1H, s(br))	-		

**Table S8. NMR Spectroscopic data of compound (19) (<sup>1</sup>H at 500 MHz, <sup>13</sup>C at 125 MHz).**

Position	Proton	$\delta_{\text{H}}$ (Hz)	$\delta^{13}\text{C}$	NOESY	HMBC
1	-				
2	H-2	5.90 (1H, dq, $J = 15.5, 1.7$ Hz)			
3	H-3	7.04 (1H, dq, $J = 15.5, 7.0$ Hz)			
4	H-4	1.89 (3H, dd, $J = 7.0, 1.7$ Hz)		H2, H3	
1'	H-1'a	3.91 (1H, dd, $J = 12.2, 5.0$ Hz)		H2', H4'	
	H-1'b	3.83 (1H, dd, $J = 12.2, 3.8$ Hz)			
2'	H-2'β	4.8 (1H, td, $J = 5.0, 3.8$ Hz)		H4'	
3'	H-3'	4.1 (1H, qd, $J = 6.5, 5.0$ Hz)		H4'	
4'	H-4'	1.24 (3H, d, $J = 6.5$ Hz)		H2', H3'	

**Table S9. NMR Spectroscopic data of compound (20) (<sup>1</sup>H at 500 MHz, <sup>13</sup>C at 125 MHz).**

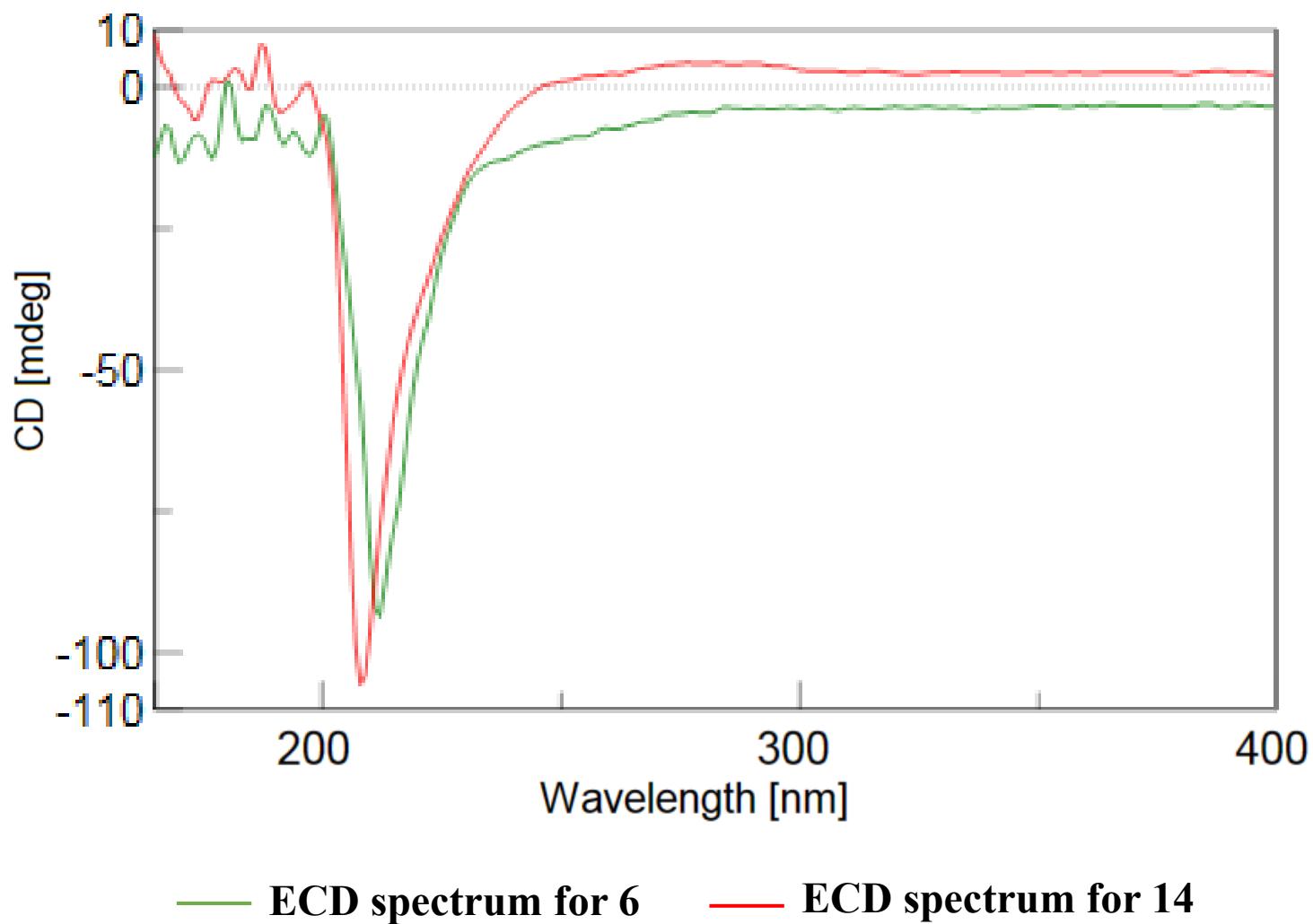
Position	Proton	$\delta_{\text{H}}$ (Hz)	$\delta^{13}\text{C}$	NOE	HMBC
1	-		165.4		
2	H-2	5.86 (1H, dq, $J = 15.5, 1.7$ Hz)	122.1		C1, C4
3	H-3	7.01 (1H, dq, $J = 15.5, 7.0$ Hz)	145.9		C1, C4
4	H-4	1.90 (3H, dd, $J = 7.0, 1.7$ Hz)	18.1	H2, H3	C2, C3
1'	H-1'a	4.28 (1H, dd, $J = 12.0, 3.5$ Hz)	62.1	H2'	C2', C3', <u>COCH<sub>3</sub></u>
	H-1'b	4.20 (1H, dd, $J = 12.0, 6.7$ Hz)		H2'	C2', C3', <u>COCH<sub>3</sub></u>
2'	H-2'β	5.21 (1H, ddd, $J = 6.7, 5.0, 3.5$ Hz)	72.0	H1', H4'	C1, C1', C3', C4'
3'	H-3'	5.11 (1H, qd, $J = 6.5, 5.0$ Hz)	68.7	H4'	C1', C2', C4', <u>COCH<sub>3</sub></u>
4'	H-4'	1.27 (3H, d, $J = 6.5$ Hz)	15.8	H3'	C2', C3'
CH <sub>3</sub> CO	CH <sub>3</sub>	2.04 (6H, s)	21.1, 20.7		
CH <sub>3</sub> CO	-		170.7, 170.0		

**Table S10. NMR Spectroscopic data of compound (21) (<sup>1</sup>H at 500 MHz, <sup>13</sup>C at 125 MHz).**

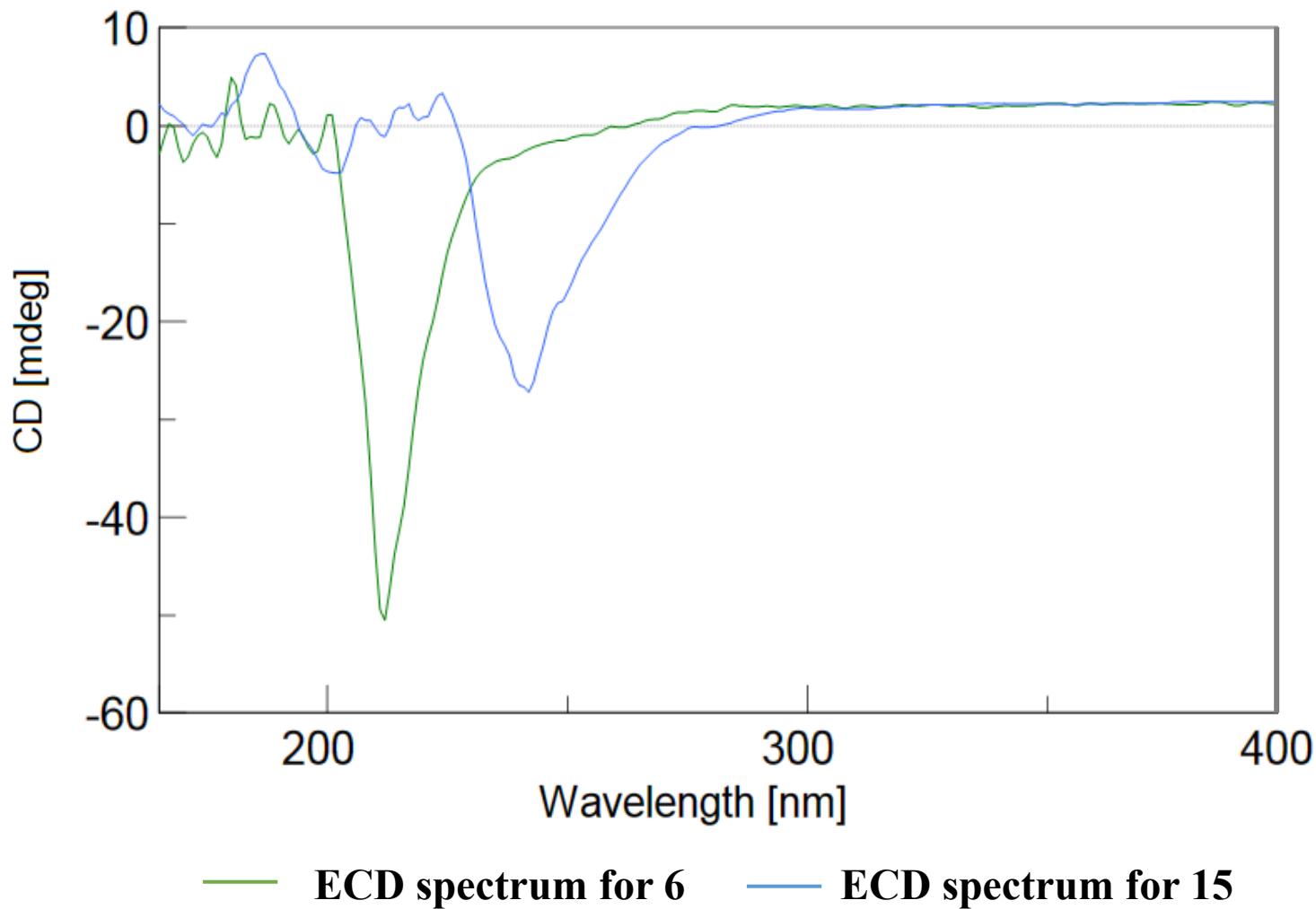
Position	Proton	$\delta_{\text{H}}$ (Hz)	$\delta^{13}\text{C}$	NOE	HMBC
1	-		167.1		
2	H-2	5.90 (1H, dq, $J = 15.5, 1.7$ Hz)	145.3		C1, C4
3	H-3	7.03 (1H, dq, $J = 15.5, 7.0$ Hz)	146.1		C1, C2, C4
4	H-4	1.89 (3H, dd, $J = 7.0, 1.7$ Hz)	18.06	H2, H3	C2, C3
1'	H-1'a H-1'b	4.28 (2H, d(br), $J = 5.0$ Hz)	65.2	H2', H3', H4'	C1, C2', C3'
2'	H-2'β	3.75 (1H, q, $J = 5.0$ Hz)	73.8	H4', H1'	C1', C3', C4'
3'	H-3'	3.84 (1H, dq, $J = 6.4, 5.0$ Hz)	68.4	H4'	C1', C2', C4'
4'	H-4'	1.23 (3H, d, $J = 6.4$ Hz)	18.1	H1', H2', H3'	C2', C3'

**Table S11. NMR Spectroscopic data of compound (22) (<sup>1</sup>H at 500 MHz, <sup>13</sup>C at 125 MHz).**

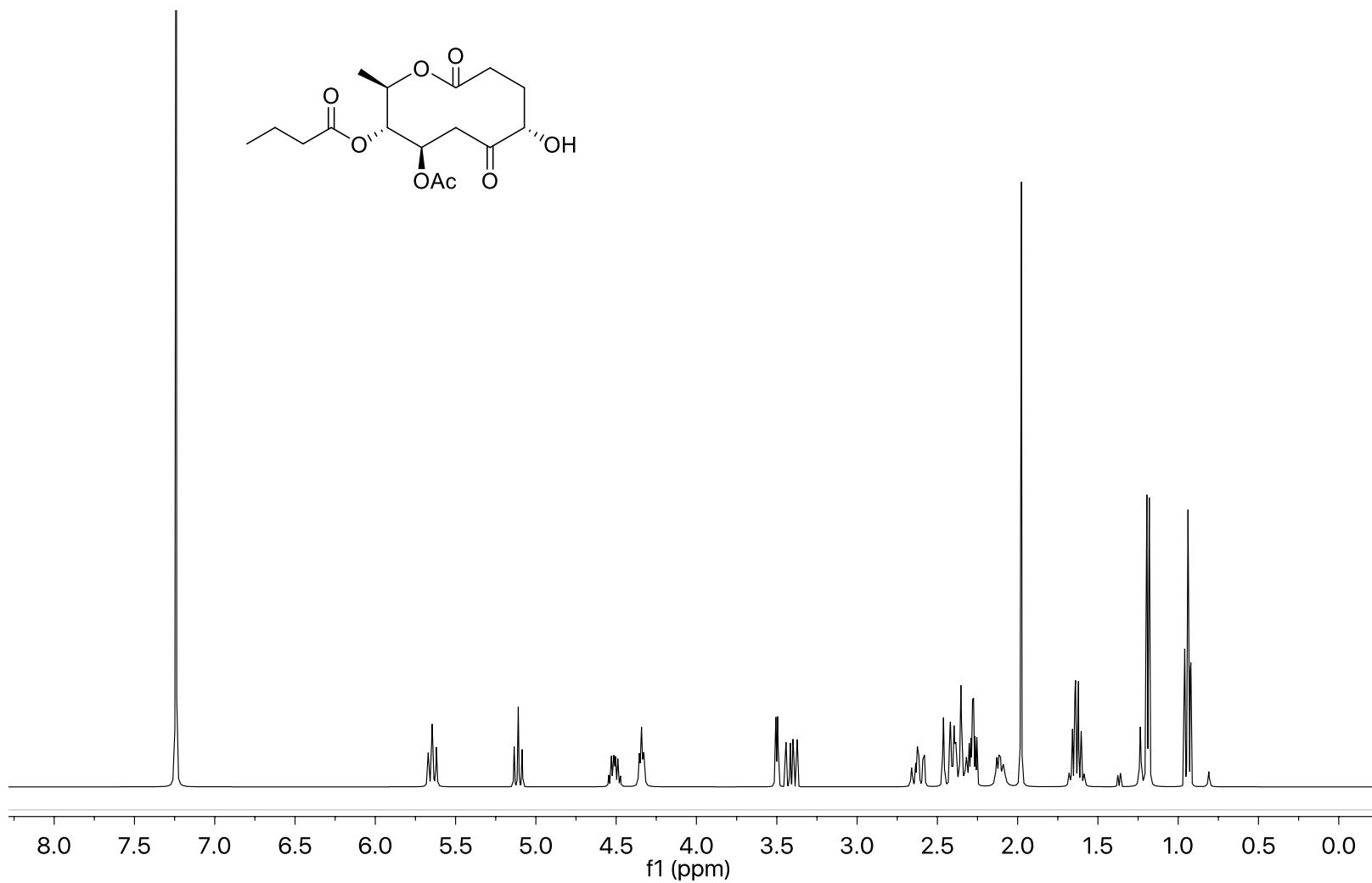
Position	Proton	$\delta_{\text{H}}$ (Hz)	$\delta^{13}\text{C}$	NOE	HMBC
1	-		174.2		
2	H-2	2.35 (1H, t, $J = 7.4$ Hz)	36.0		
3	H-3	1.67 (1H, sext, $J = 7.4$ Hz)	18.4		
4	H-4	0.96 (3H, t, $J = 7.4$ Hz)	13.6		C2, C3
1'	H-1'a H-1'b	4.25 (1H, dd, $J = 11.6, 4.0$ Hz) 4.21 (1H, dd, $J = 11.6, 6$ Hz)	65.3	H2', H4'	C1, C2', C3'
2'	H-2'β	3.75 (1H, q, $J = 5.0$ Hz)	73.7	H1', H4'	C1', C3', C4'
3'	H-3'	3.85 (1H, q, $J = 5.0$ Hz)	68.2	H4'	C1', C2', C4'
4'	H-4'	1.24 (3H, d, $J = 6.5$ Hz)	18.12	H2', H3'	C2', C3'



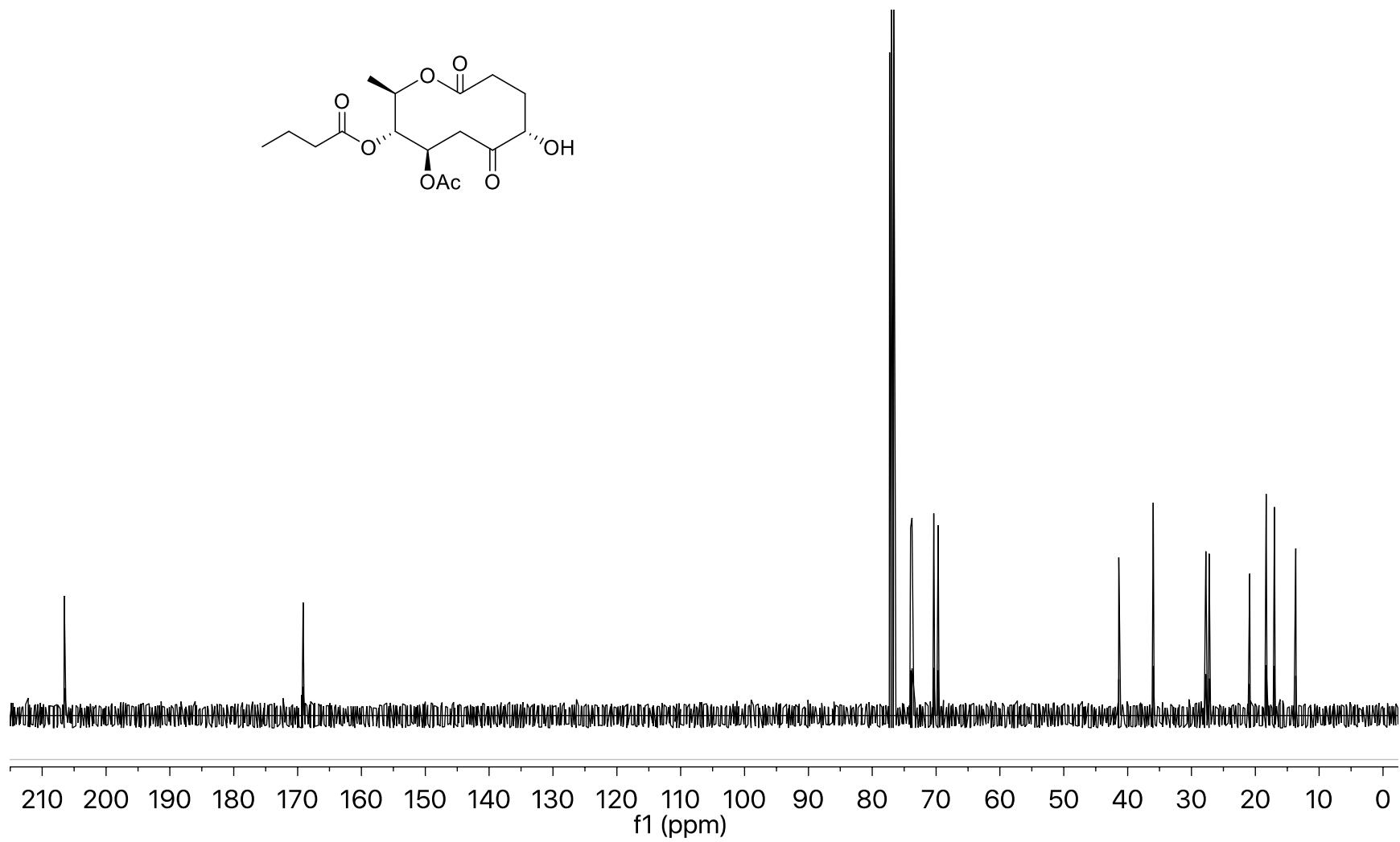
**Figure S1.** *Electronic Circular Dichroism spectra for compounds **6** and **14** in *MeOH**



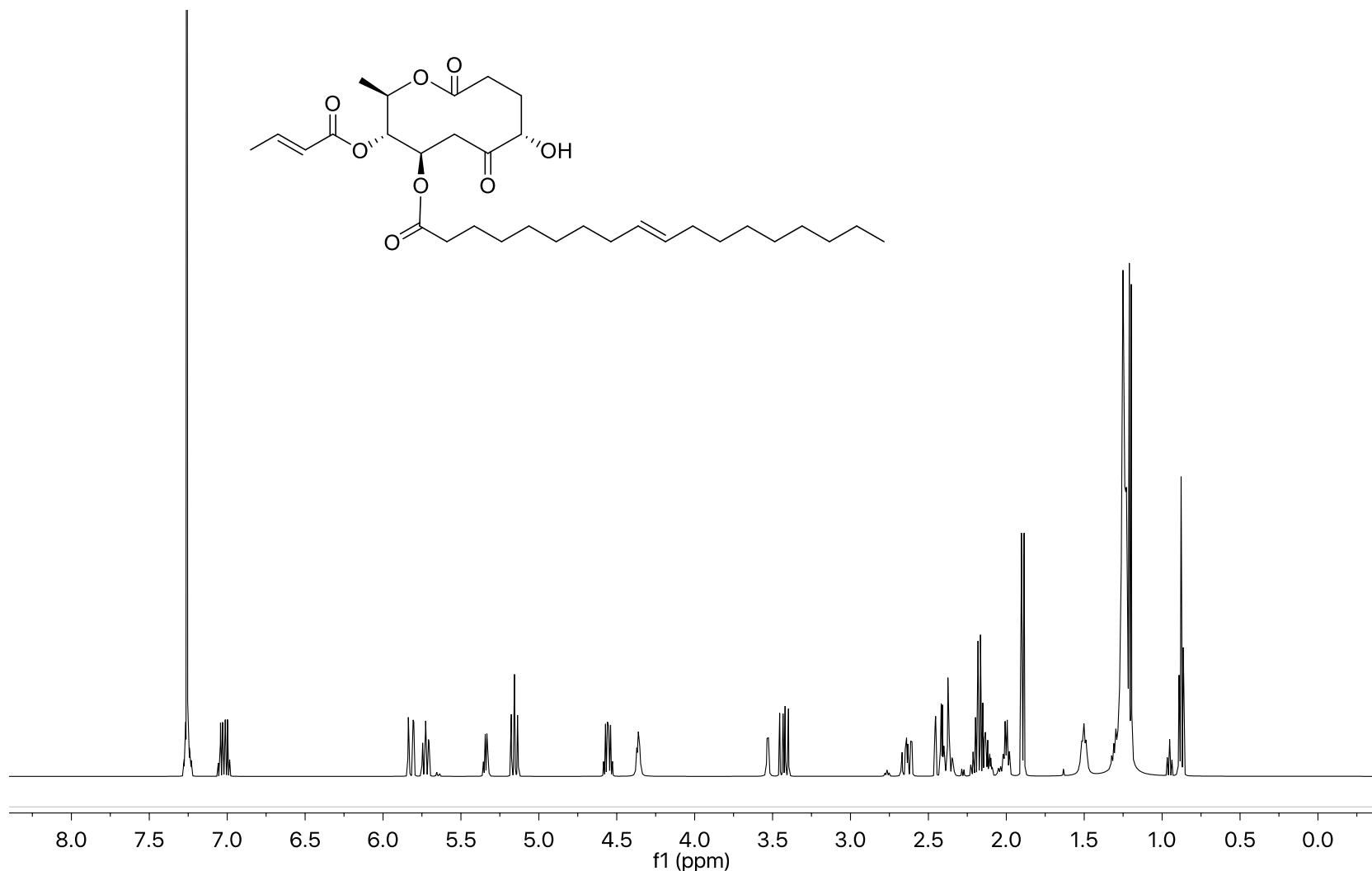
**Figure S2.** Electronic Circular Dichroism spectra for compounds **6** and **15** in MeOH



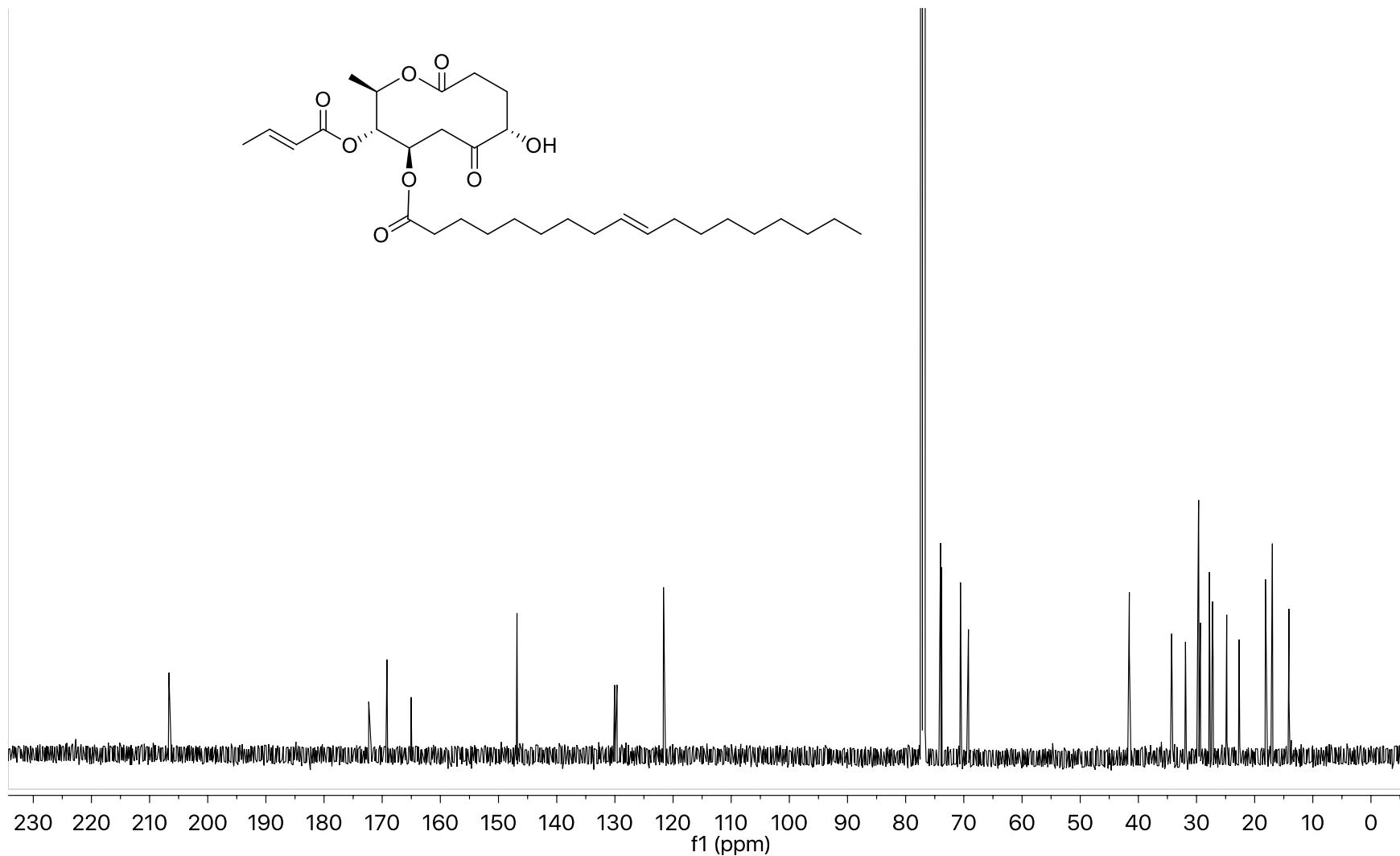
**Figure S3.**  $^1\text{H}$  NMR Spectrum of aspinolide H (12) ( $\text{CDCl}_3$  at 500 MHz)



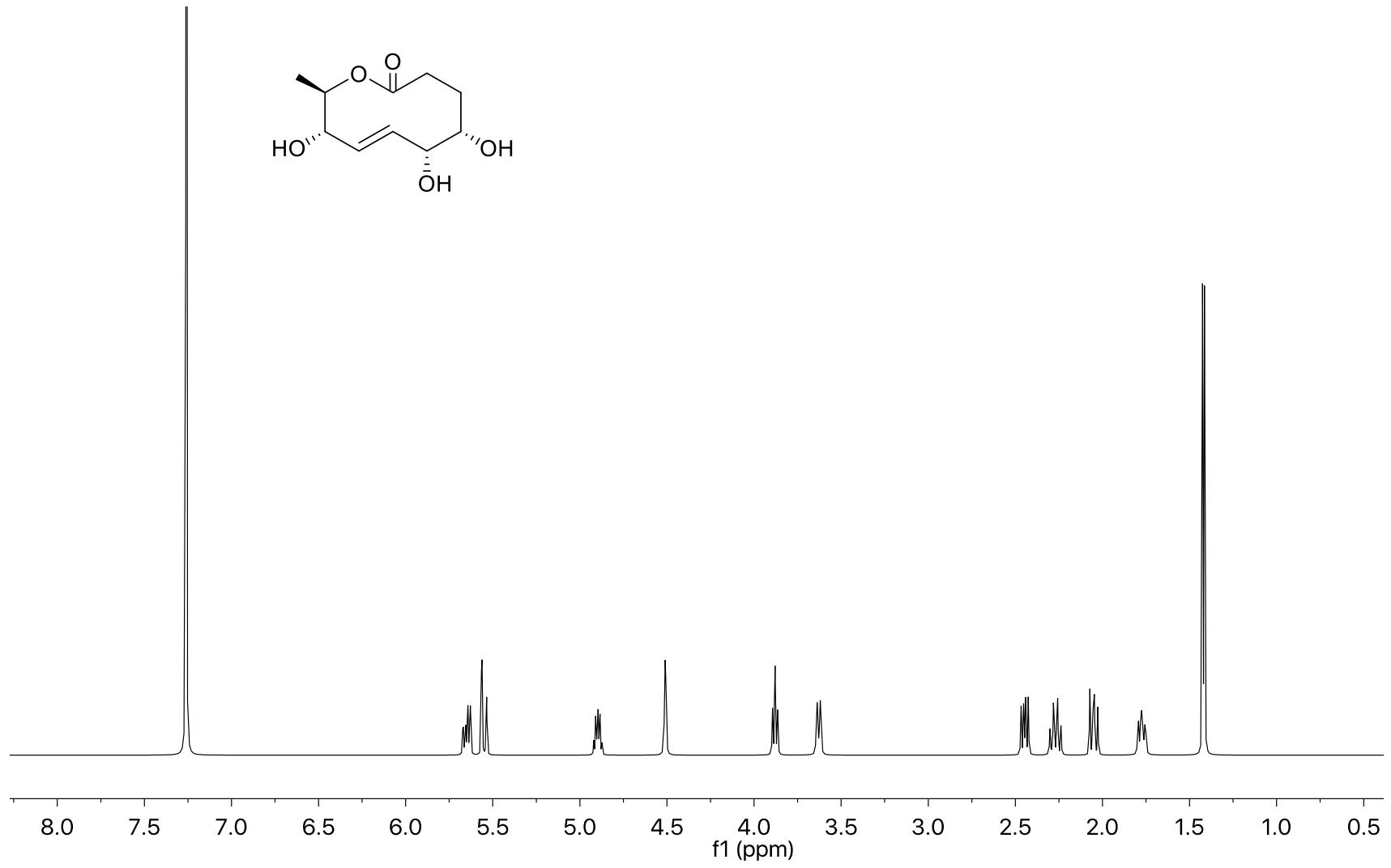
**Figure S4.**  $^1\text{H}$  NMR Spectrum of aspinolide H (**12**) ( $\text{CDCl}_3$  at 500 MHz)



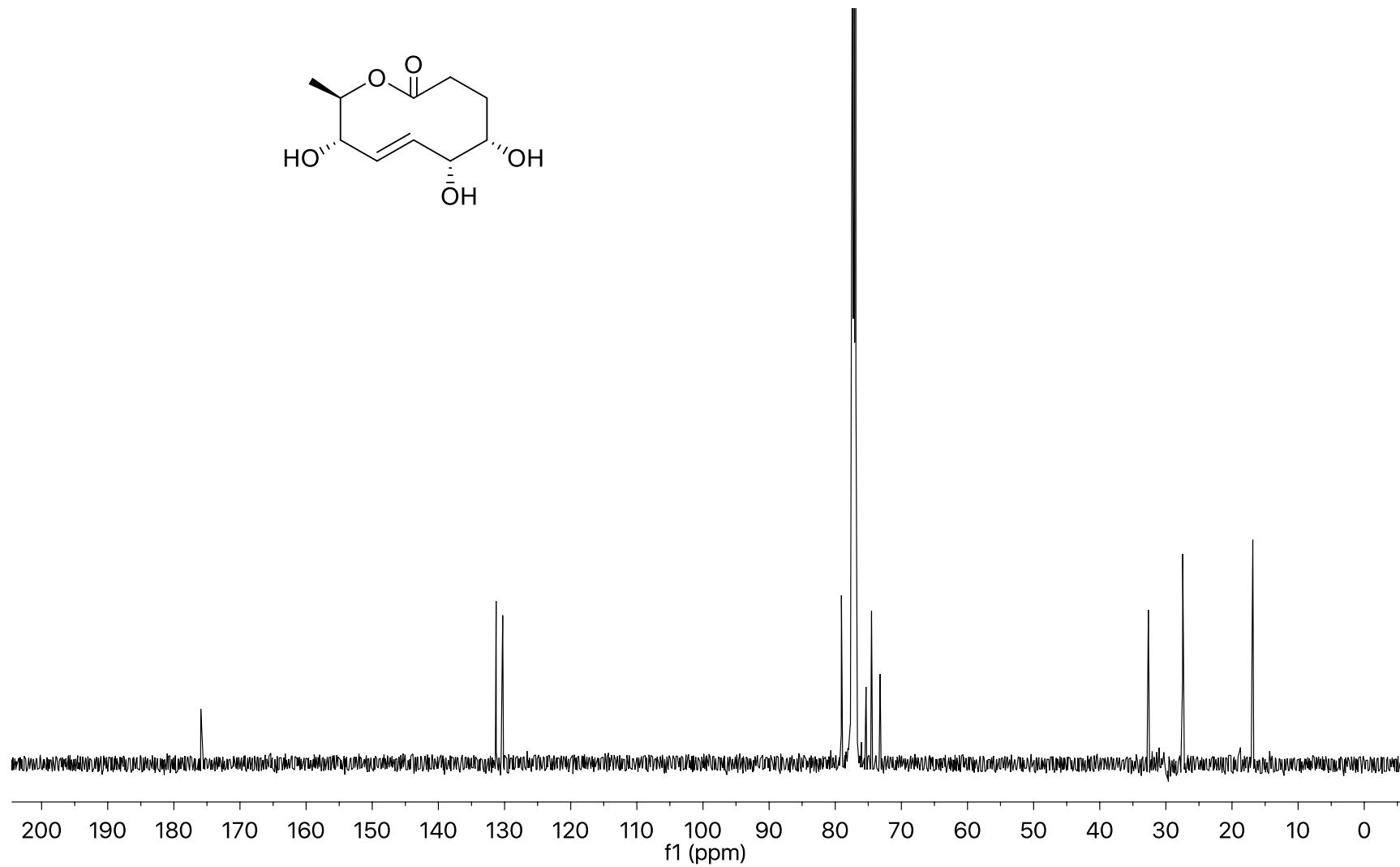
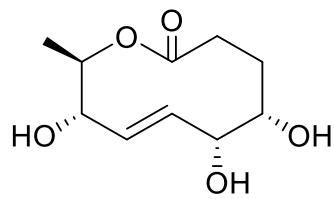
**Figure S5.**  $^1\text{H}$  NMR Spectrum of aspinolide I (**13**) ( $\text{CDCl}_3$  at 500 MHz)



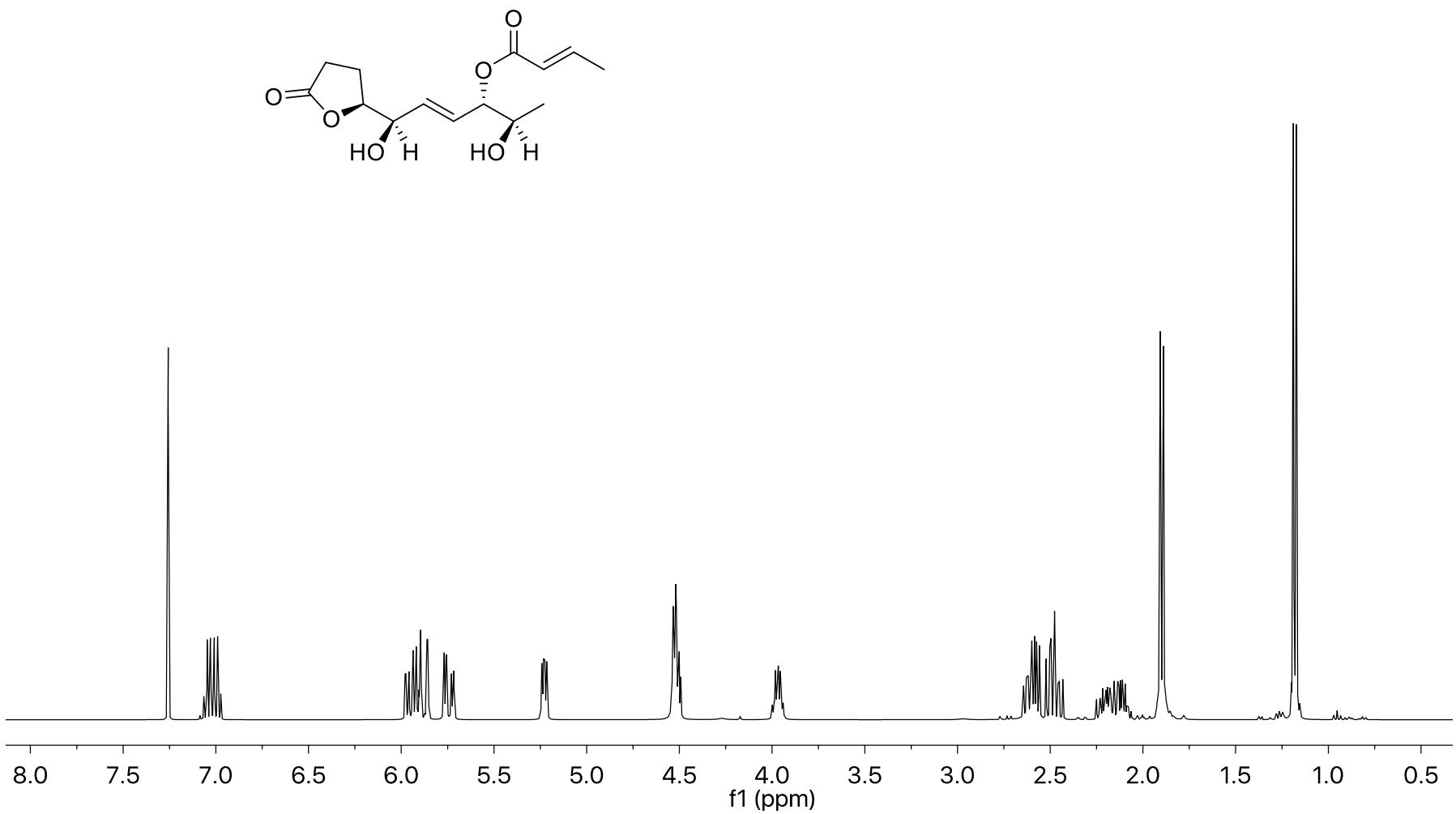
**Figure S6.**  $^{13}\text{C}$  NMR Spectrum of aspinolide I (**13**) ( $\text{CDCl}_3$  at 500 MHz)



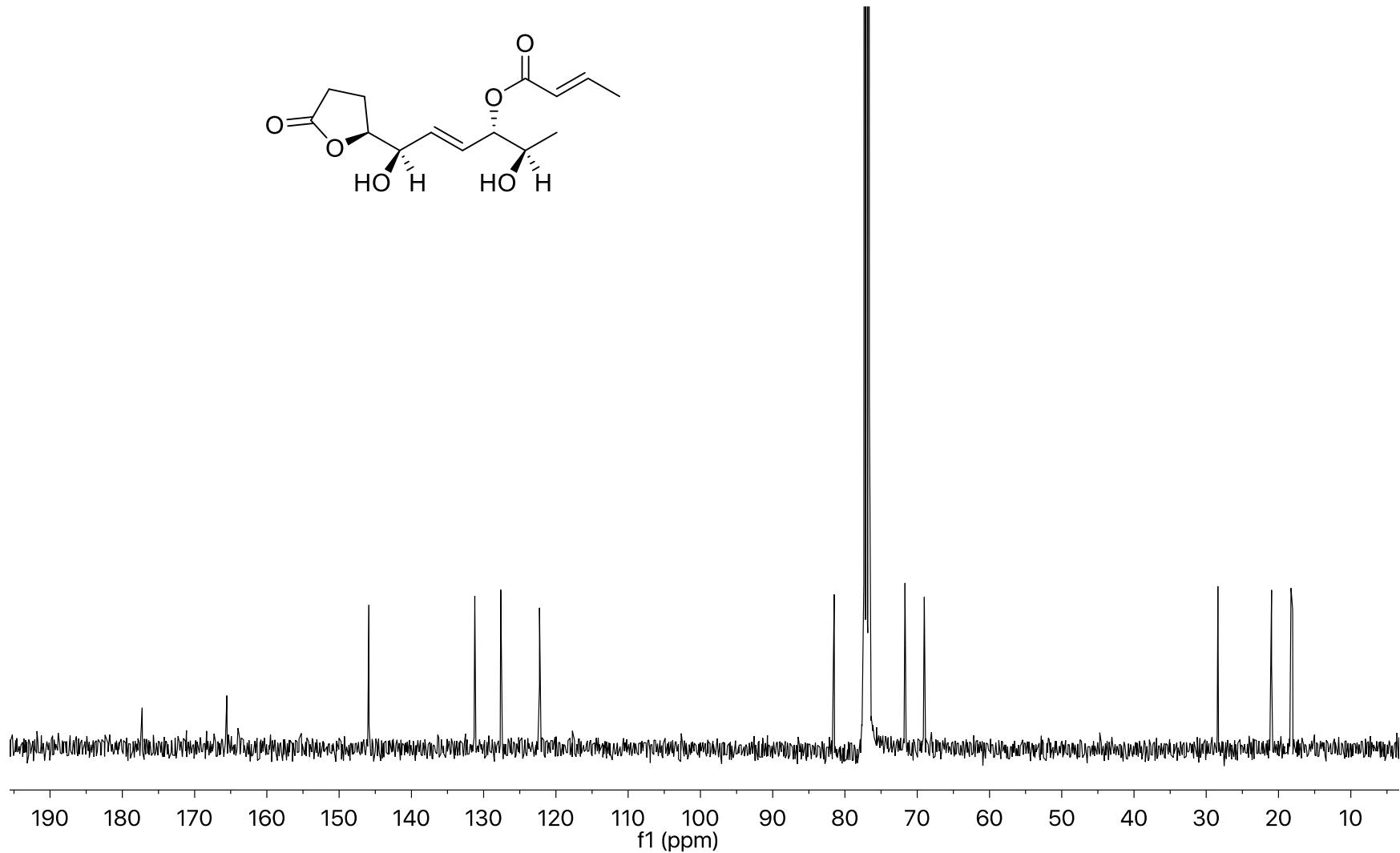
**Figure S7.**  $^1\text{H}$  NMR Spectrum of aspinolide J (**14**) ( $\text{CDCl}_3$  at 500 MHz)



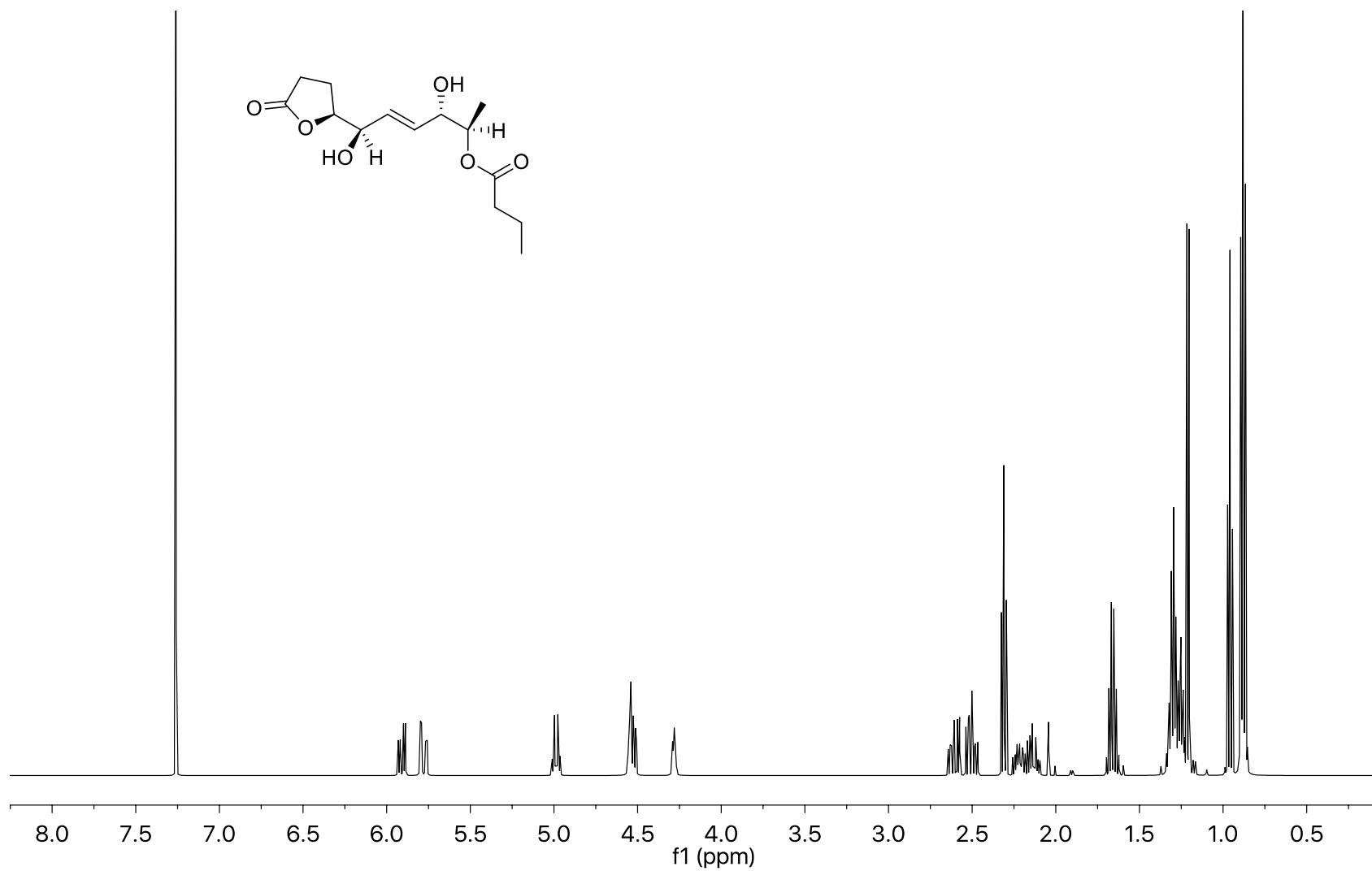
**Figure S8.**  $^{13}\text{C}$  NMR Spectrum of aspinolide J (14) ( $\text{CDCl}_3$  at 500 MHz)



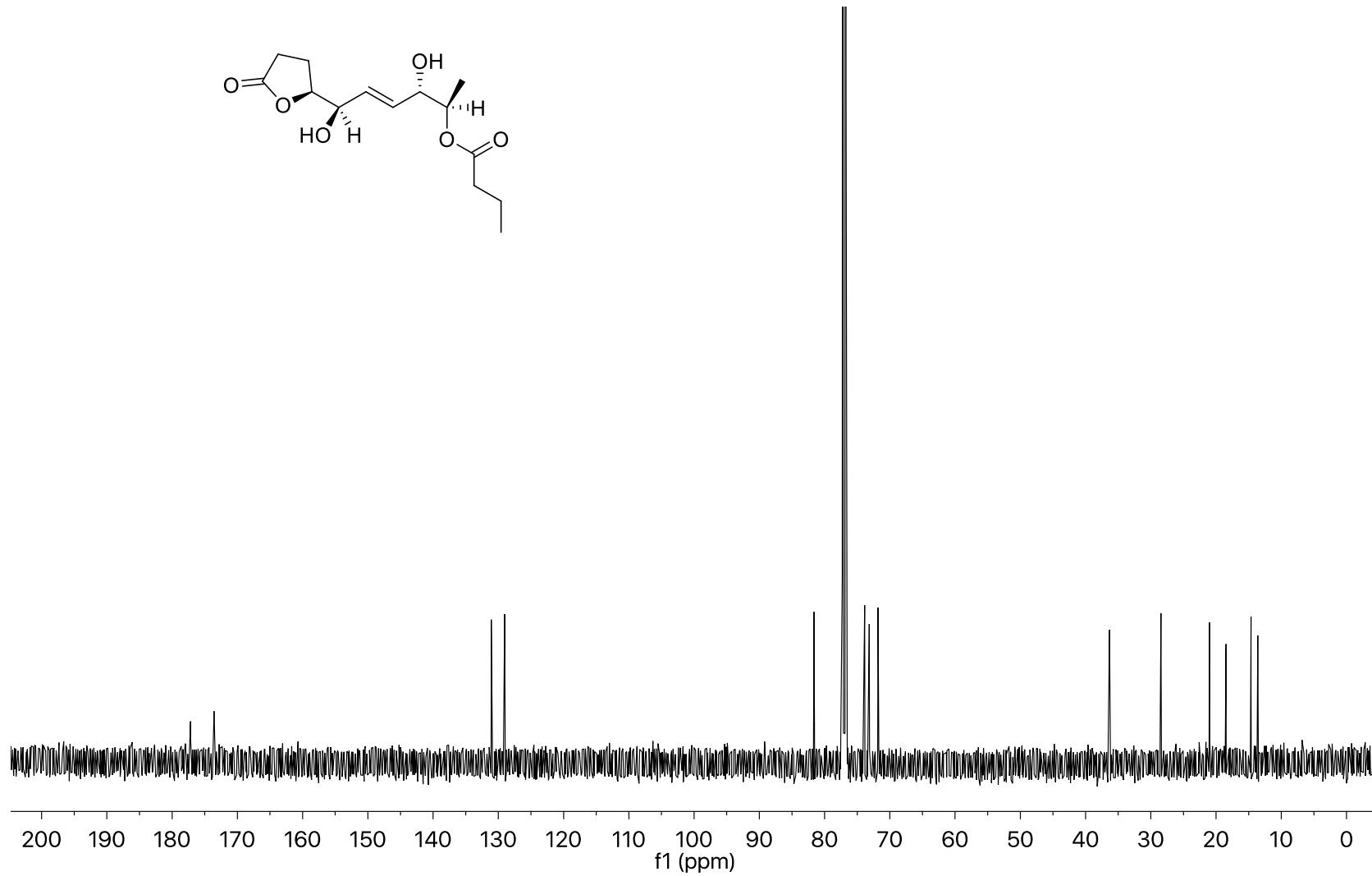
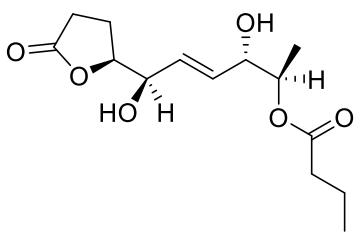
**Figure S9.**  $^1\text{H}$  NMR Spectrum of arundinolide A (15) ( $\text{CDCl}_3$  at 500 MHz)



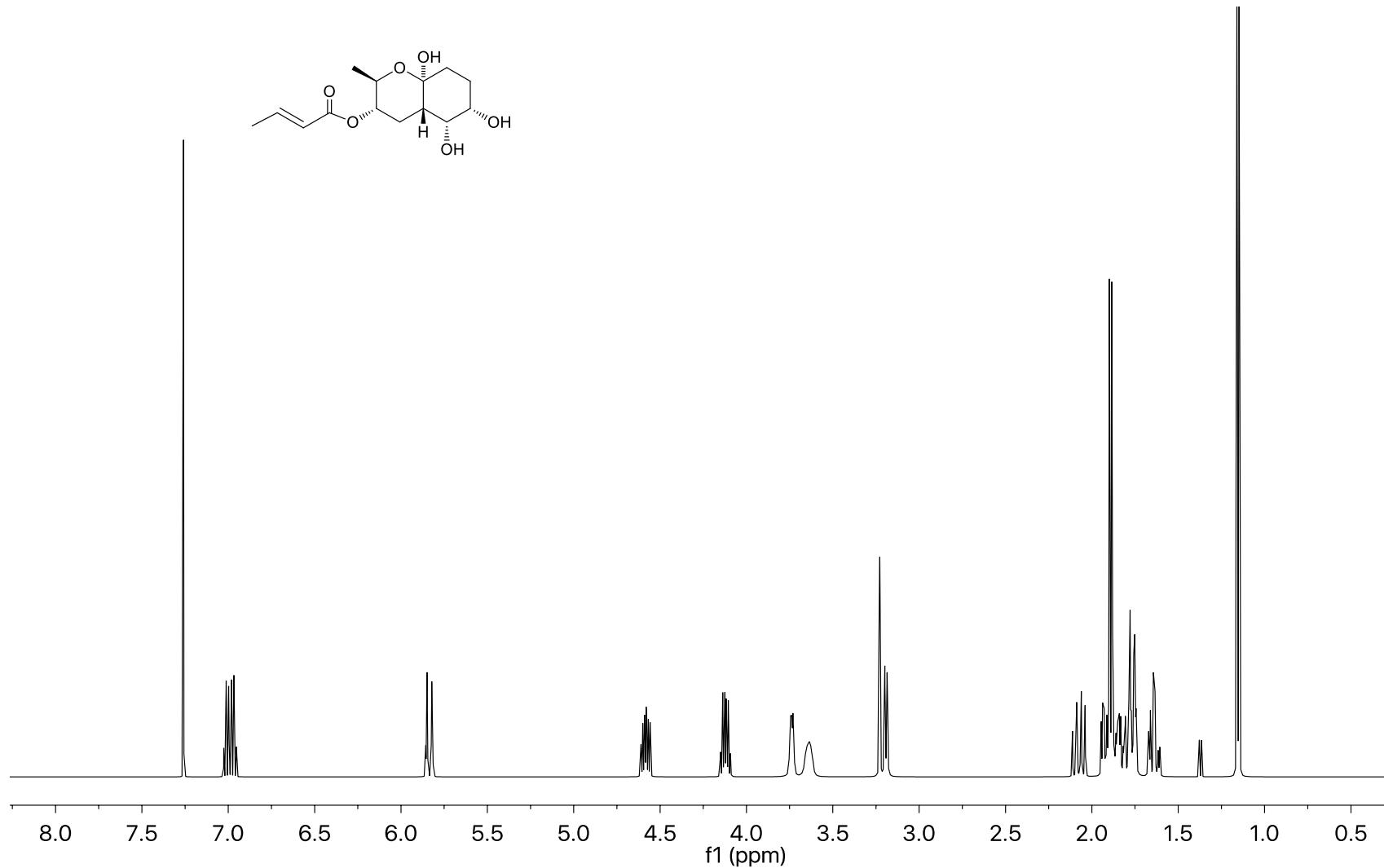
**Figure S10.**  $^{13}\text{C}$  NMR Spectrum of arundinolide A (15) ( $\text{CDCl}_3$  at 500 MHz)



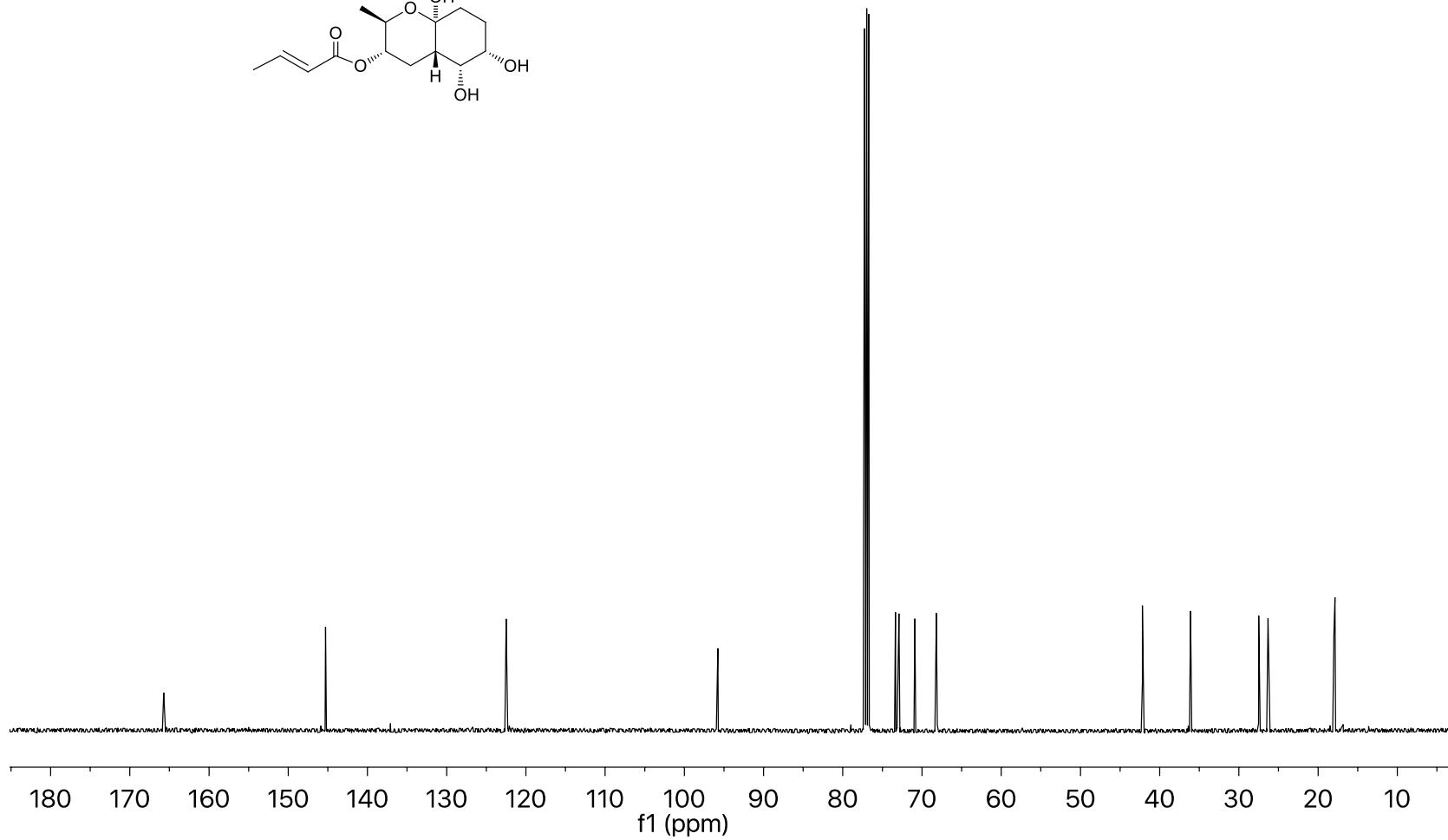
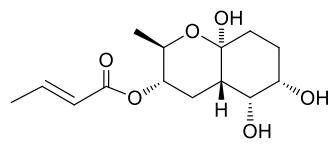
**Figure S11.**  $^1\text{H}$  NMR Spectrum of arundinolide B (**16**) ( $\text{CDCl}_3$  at 500 MHz)



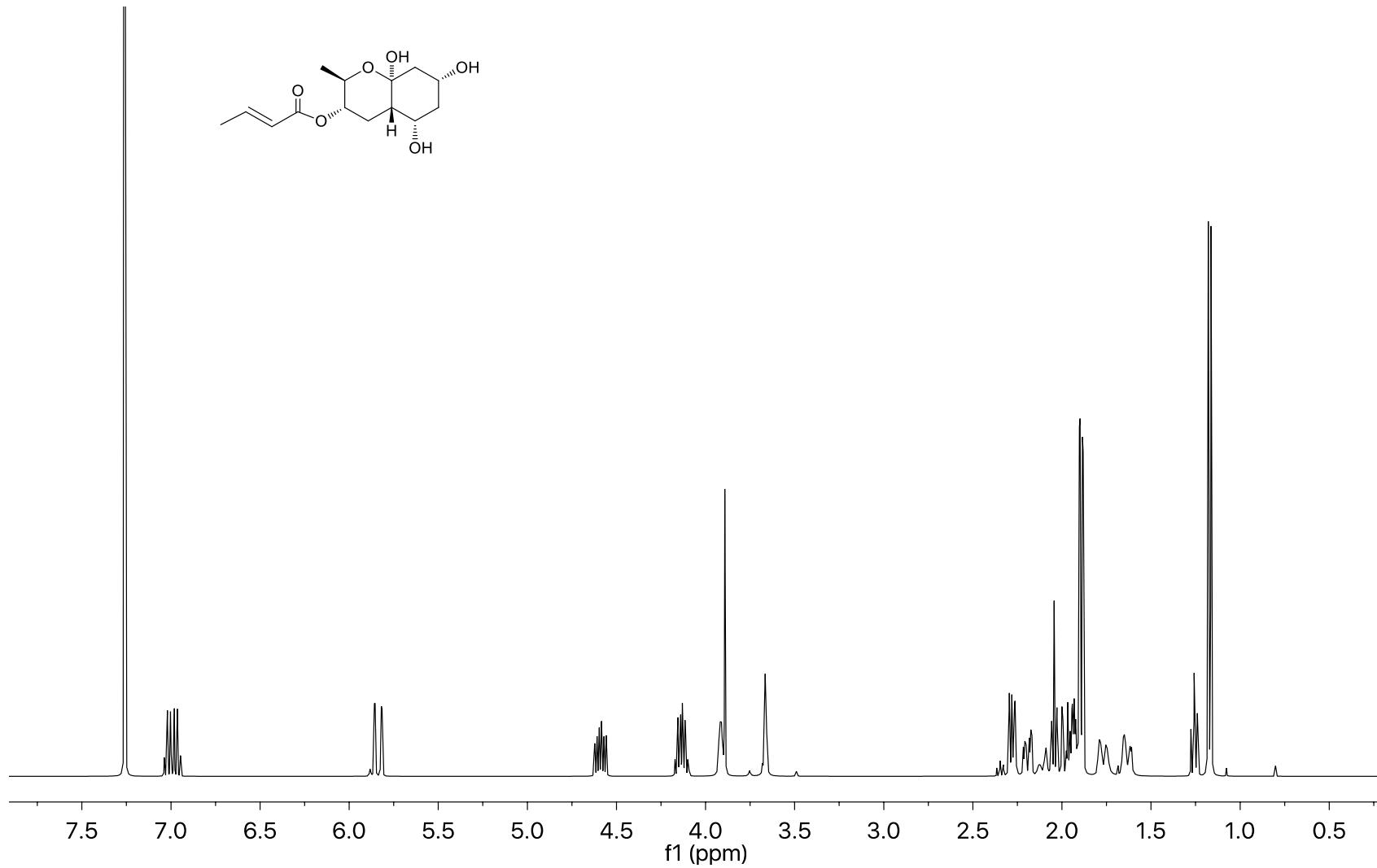
**Figure S12.**  $^{13}\text{C}$  NMR Spectrum of arundinolide B (**16**) ( $\text{CDCl}_3$  at 500 MHz)



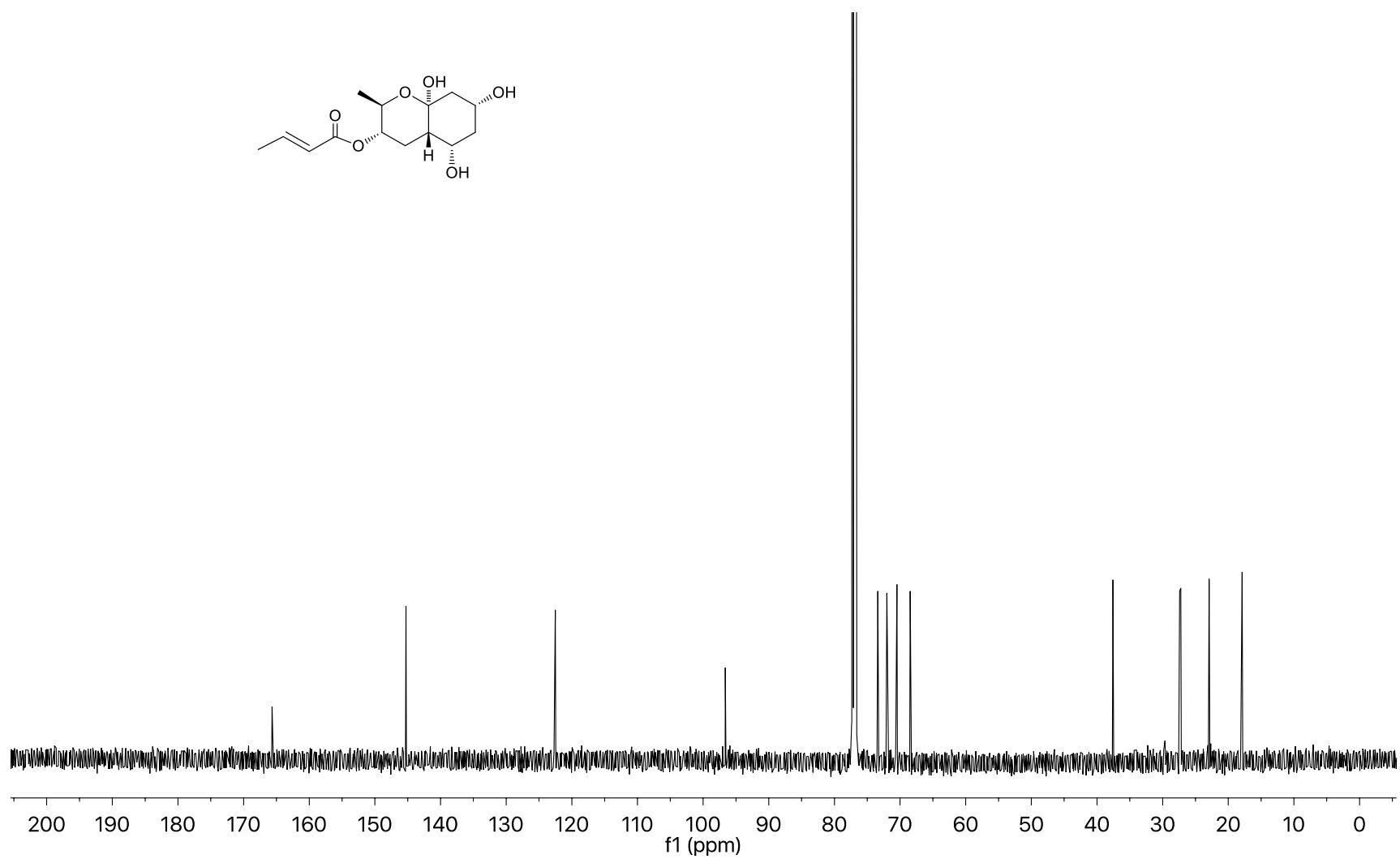
**Figure S13.**  $^1\text{H}$  NMR Spectrum of trichoarundinal A (17) ( $\text{CDCl}_3$  at 500 MHz)



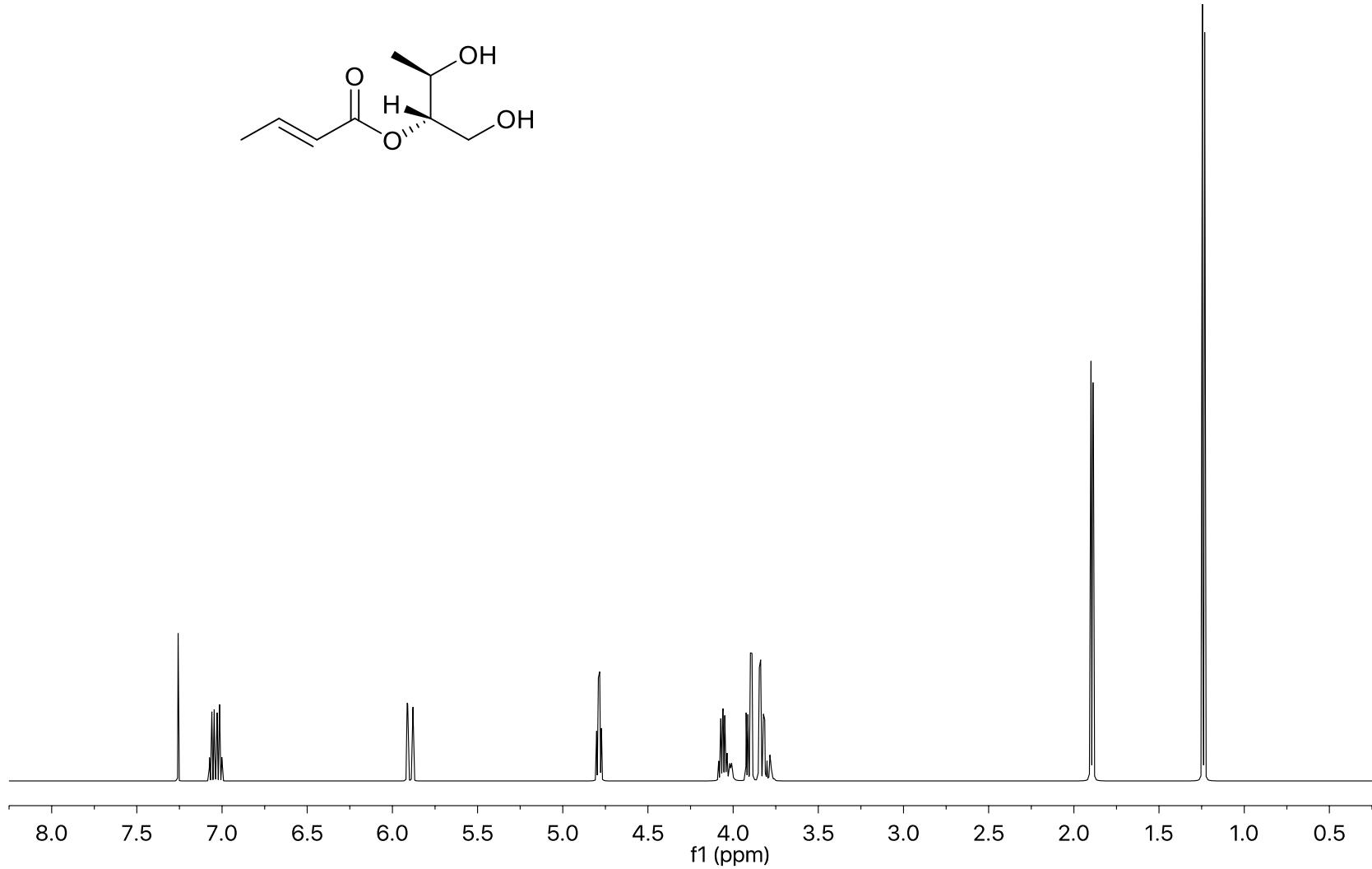
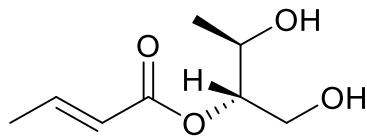
**Figure S14.**  $^{13}\text{C}$  NMR Spectrum of trichoarundinal A (17) ( $\text{CDCl}_3$  at 500 MHz)



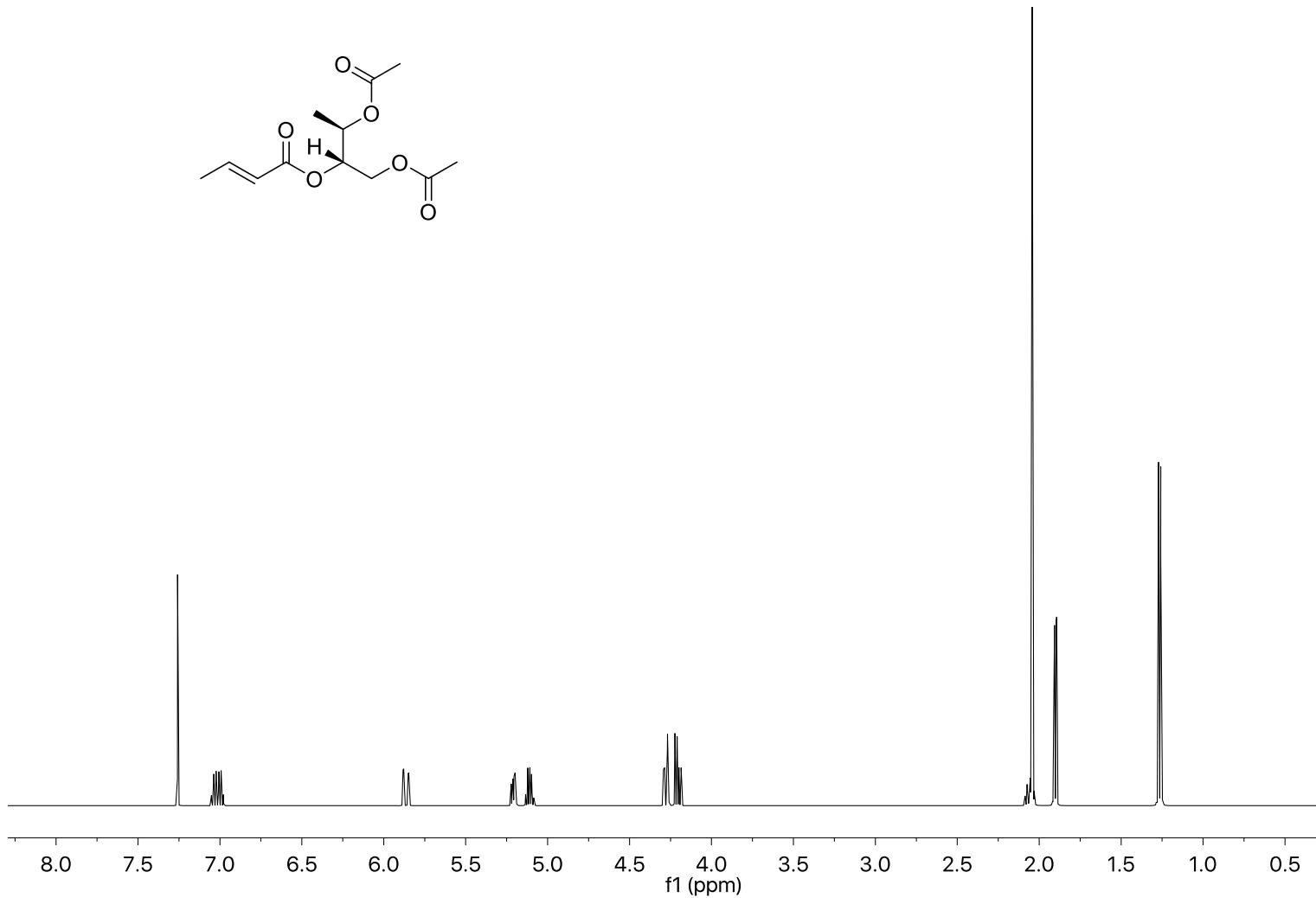
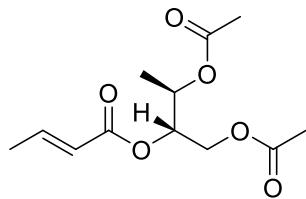
**Figure S15.**  $^1\text{H}$  NMR Spectrum of trichoarundinal B (18) ( $\text{CDCl}_3$  at 500 MHz)



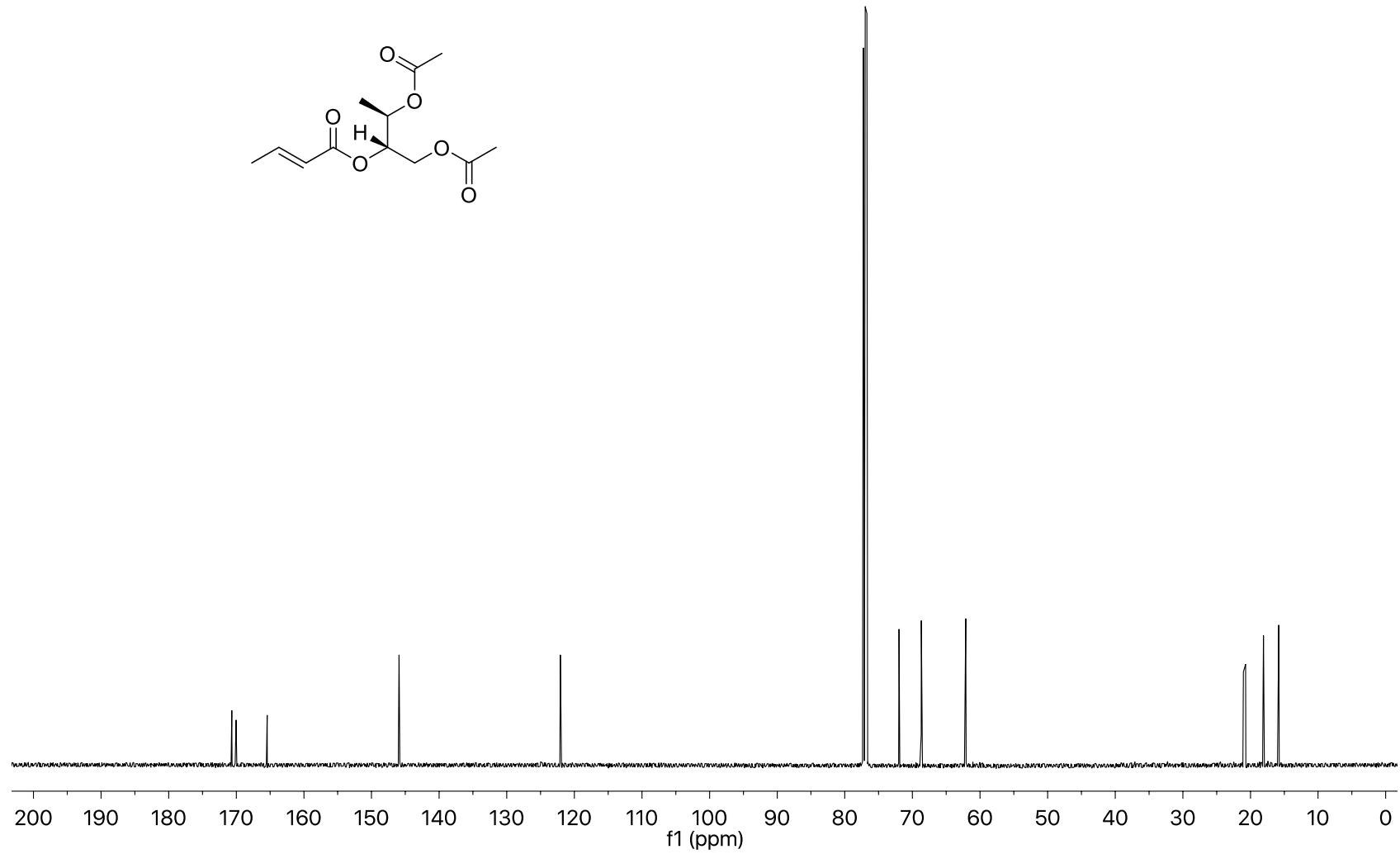
**Figure S16.**  $^{13}\text{C}$  NMR Spectrum of trichoarundinal B (18) ( $\text{CDCl}_3$  at 500 MHz)



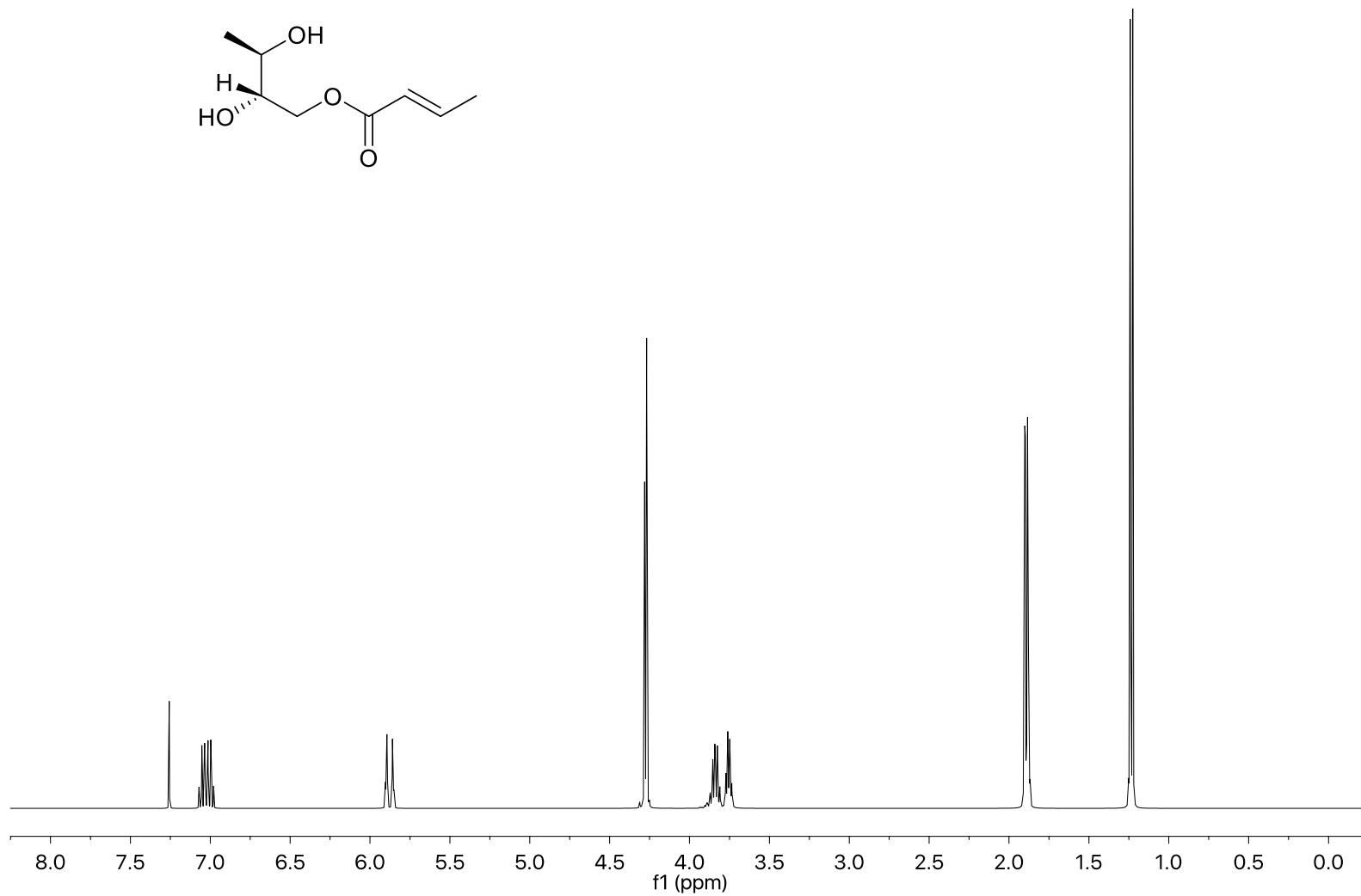
**Figure 17.**  $^1\text{H}$  NMR Spectrum of (E)-(2*S*,3*R*)-1,3-dihydroxybutan-2-yl but-2-enoate (**19**) ( $\text{CDCl}_3$  at 500 MHz)



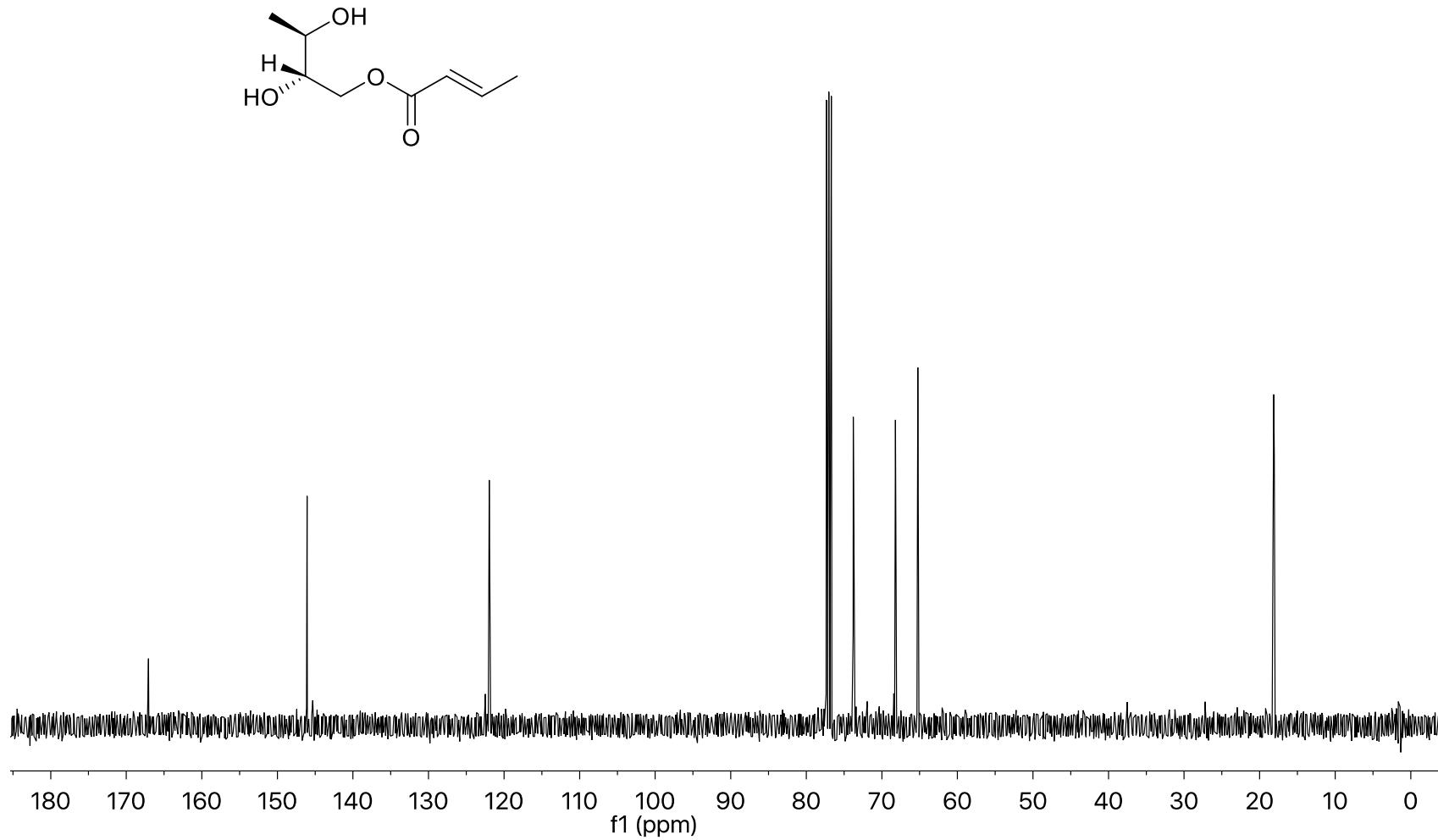
**Figure 18.**  $^1\text{H}$  NMR Spectrum of diacetyl derivative (**20**) (CDCl<sub>3</sub> at 500 MHz)



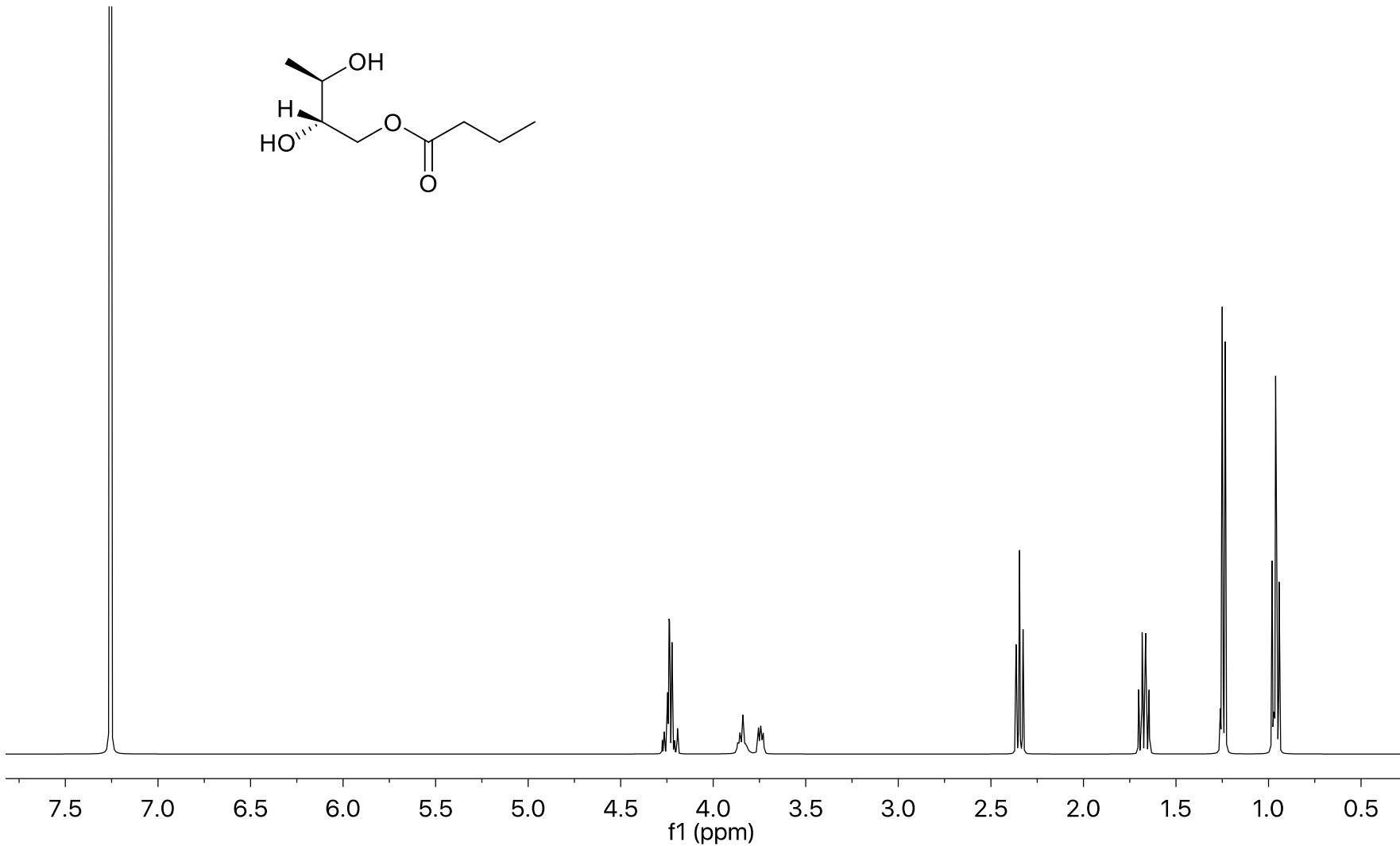
**Figure 19.**  $^{13}\text{C}$  NMR Spectrum of diacetyl derivative (20) (CDCl<sub>3</sub> at 500 MHz)



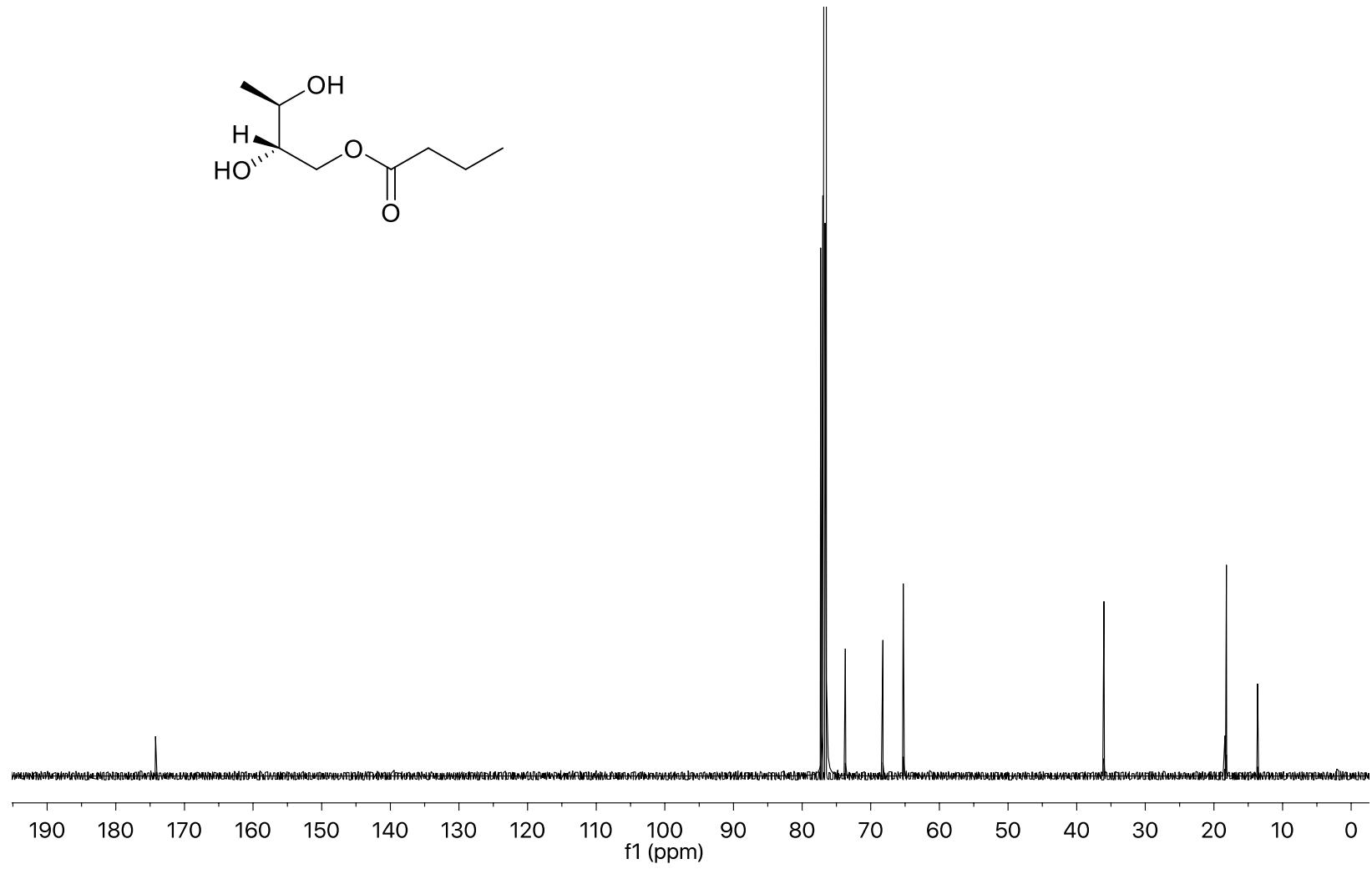
**Figure 20.** <sup>1</sup>H NMR Spectrum of (E)-(2*S*,3*R*)-2',3'-dihydroxybutyl but-2-enoate (**21**) ( $CDCl_3$  at 500 MHz)



**Figure 21.**  $^{13}\text{C}$  NMR Spectrum of (*E*)-(2*S*,3*R*)-2',3'-dihydroxybutyl but-2-enoate (**21**) ( $\text{CDCl}_3$  at 500 MHz)



**Figure 22.**  $^1\text{H}$  NMR Spectrum of  $(2S,3R)$ - $2',3'$ -dihydroxybutyl butyrate (22) ( $\text{CDCl}_3$  at 500 MHz)



**Figure 23.**  $^{13}\text{C}$  NMR Spectrum of  $(2S,3R)$ - $2',3'$ -dihydroxybutyl butyrate (**22**) ( $\text{CDCl}_3$  at 500 MHz)