Supporting Information

Identification of Daphnane Diterpenoids from *Wikstroemia indica* by Liquid Chromatography with Tandem Mass Spectrometry

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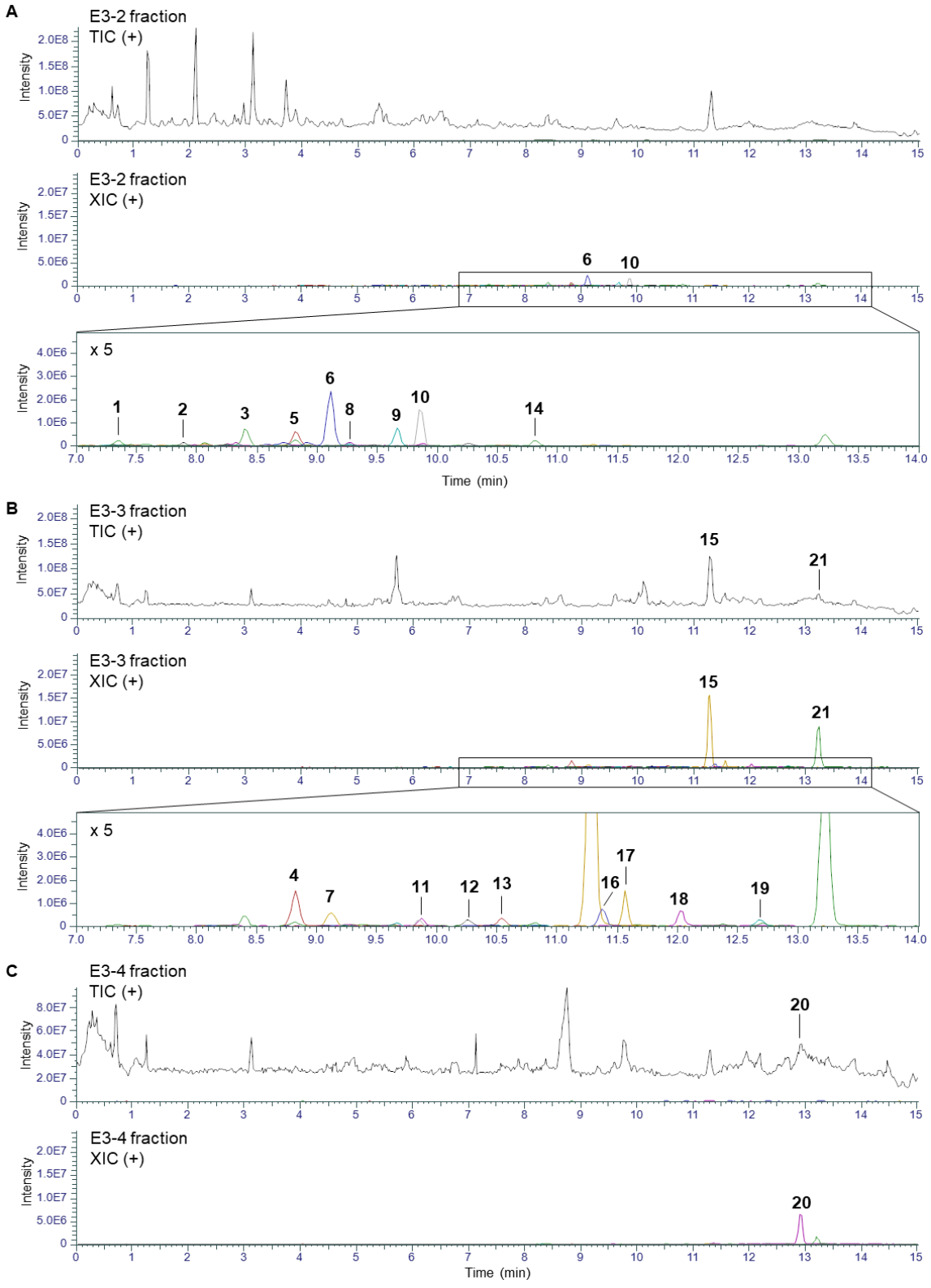


Figure S1. Total ion chromatograms and extracted ion chromatograms in the positive ion mode from the (A) E3-2 fraction, (B) E3-3 fraction, and (C) E3-4 fraction.

Table S1. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR data of compounds **15**, **21**, and **17** ($CDCl_3$).

	15		**17**		**21**	
no.	δ_H (*J* in Hz)	δ_C	δ_H (*J* in Hz)	δ_C	δ_H (*J* in Hz)	δ_C
1	7.59 (1H, dd, 2.5, 1.4)	161.4	7.56 (1H, m)	160.5	7.61 (1H, dd, 2.6, 1.4)	161.2
2		136.6		136.9		136.7
3		209.9		209.5		209.8
4		72.2		72.2		72.3
5	4.23 (1H, s)	72.1	4.23 (1H, s)	72.2	4.23 (1H, s)	72.0
6		60.4		60.4		60.4
7	3.41 (1H, s)	64.4	3.57 (1H, br s)	64.4	3.43 (1H, s)	64.2
8	2.88 (1H, d, 2.5)	36.7	3.57 (1H, d, 2.5)	35.6	2.92 (1H, d, 2.6)	36.7
9		78.7		78.2		79.5
10	3.72 (1H, dq, 2.8, 2.5)	48.2	3.81 (1H, q, 2.5)	47.5	3.79 (1H, dq, 2.9, 2.6)	48.2
11	2.43 (1H, dq, 8.6, 7.2)	34.8	2.47 (1H, q, 7.2)	44.2	2.46 (1H, dq, 8.6, 7.2)	34.9
12	1.62 (1H, d, 14.3)	36.5	5.09 (1H, br s)	78.4	1.66 (1H, d, 14.4)	36.5
	2.19 (1H, dd, 14.3, 8.6)				2.22 (1H, dd, 14.4, 8.6)	
13		84.1		83.8		84.4
14	4.34 (1H, d, 2.5)	81.8	4.80 (1H, d, 2.6)	80.5	4.40 (1H, d, 2.5)	82.0
15		146.3		143.0		146.1
16	4.87 (1H, t, 1.4)	111.1	4.99 (1H, br s)	113.6	4.89 (1H, t, 1.4)	111.3
	5.00 (1H, br s)		5.00 (1H, br s)		5.00 (1H, br s)	
17	1.76 (3H, s)	19.0	1.84 (1H, br s)	18.8	1.78 (3H, s)	18.9
18	1.14 (3H, d, 7.2)	20.3	1.33 (1H, d, 7.2)	18.2	1.17 (3H, d, 7.2)	20.4
19	1.78 (3H, dd, 2.8, 1.4)	9.9	1.77 (1H, m)	9.9	1.79 (3H, dd, 2.9, 1.4)	9.9
20	3.75 (1H, d, 12.6)	65.3	3.75 (1H, dd, 12.5, 4.5)	65.3	3.76 (1H, d, 12.5)	65.0
	3.86 (1H, d, 12.6)		3.95 (1H, dd, 12.5, 5.2)		3.87 (1H, d, 12.5)	
1'		119.4		117.1		116.5
2'	1.93 (2H, m)	34.9	5.65 (1H, d, 15.4)	122.4	5.69 (1H, d, 15.5)	122.8
3'	1.56 (2H, m)	23.5	6.66 (1H, dd, 15.4, 10.6)	135.1	6.68 (1H, dd, 15.5, 10.6)	138.9
4'	1.32 (2H, m)	29.6	6.04 (1H, dd, 15.1, 10.6)	128.6	6.04 (1H, dd, 15.2, 10.6)	134.7
5'	1.25 (2H, m)	29.6	5.85 (1H, dt. 15.1, 7.0)	139.3	5.83 (1H, d, 15.2, 7.2)	128.8
6'	1.25 (2H, m)	29.5	2.08 (2H, q, 7.0)	32.7	2.07 (2H, q, 7.2)	32.7
7'	1.25 (2H, m)	29.3	1.37 (2H, hex, 7.0)	28.7	1.24 (2H, m)	31.9
8'	1.23 (2H, m)	31.9	1.27 (2H, m)	31.3	1.24 (2H, m)	29.6
9'	1.25 (2H, m)	22.7	1.27 (2H, m)	22.5	1.24 (2H, m)	29.5
10'	0.86 (3H, t, 7.0)	14.1	0.87 (3H, t, 6.8)	14.0	1.24 (2H, m)	29.3
11'					1.36 (2H, m)	29.1
12'					1.36 (2H, m)	29.1
13'					1.28 (2H, m)	22.7

14'			0.86 (3H, t, 6.9)	14.1
1"		165.8		
2"	6.35 (1H, d, 15.9)	117.3		
3"	7.62 (1H, d, 15.9)	145.9		
4"		134.1		
5"	7.51 (2H, m)	128.9		
6"	7.37 (2H, m)	128.3		
7"	7.37 (2H, m)	130.6		
8"	7.37 (2H, m)	128.3		
9"	7.51 (2H, m)	128.9		

Table S2. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR data of compounds **12**, **18**, and **20 (**$CDCl_3$).

	12		**18**		**20**	
no.	δ_H (*J* in Hz)	δ_C	δ_H (*J* in Hz)	δ_C	δ_H (*J* in Hz)	δ_C
1	2.97 (1H, t, 12.0)	49.4	2.11 (1H, brt, 9.2)	49.4	2.37 (1H, br t, 11.2)	50.7
2	1.84 (1H, m)	37.6	1.69 (1H, m)	36.9	1.87 (1H, m)	36.3
3	4.91 (1H, d, 4.9)	82.5	3.82 (1H)[a]	79.6	5.06 (1H, 4.9)	83.0
4		79.5		79.3		80.1
5	4.08 (1H, s)	73.7	3.81 (1H)[a]	71.6	4.09 (1H, br s)	73.5
6		60.7		60.0		61.0
7	3.37 (1H, s)	63.5	3.35 (1H, s)	64.4	3.32 (1H, s)	64.2
8	3.04 (1H, d, 2.9)	36.7	2.94 (1H, s)	36.6	2.87 (1H, d, 2.5)	36.8
9		81.4		80.9		81.2
10	3.03 (1H, d, 12.6)	48.2	2.95 (1H, d, 9.2)	48.0	3.08 (1H, d, 11.2)	47.3
11	2.82 (1H, t, 7.7)	41.2	2.49 (1H, dq, 8.3, 7.1)	35.4	2.64 (1H, dq, 8.0, 7.2)	35.3
12	1.96 (1H, m) 2.34 (1H, d, 14.7)	29.6	1.66 (1H, d, 14.1) 2.18 (1H, dd, 14.1, 8.3)	36.3	1.61 (1H, d, 14.0) 2.11 (1H, dd, 14.0, 8.0)	36.5
13		84.5		83.3		83.4
14	4.38 (1H, d, 2.9)	81.4	4.28 (1H, d, 2.6)	82.6	4.25 (1H, d, 2.5)	82.6
15		145.4		146.8		146.8
16	4.94 (1H, t, 1.3) 5.17 (1H, s)	111.9	4.86 (1H, t, 1.5) 4.98 (1H, brs)	110.8	4.83 (1H, t, 1.4) 4.94 (1H, br s)	110.8
17	1.81 (3H, s)	19.0	1.75 (3H, s)	18.9	1.72 (3H, s)	18.9
18	4.35 (1H, t, 10.5) 5.07 (1H, dd, 10.3, 2.0)	67.4	1.37 (3H, d, 7.1)	21.4	1.43 (3H, d, 7.2)	21.3
19	1.20 (3H, d, 6.9)	14.6	1.01 (3H, d, 6.9)	13.9	1.03 (3H, d, 6.6)	14.5
20	3.84 (2H, d, 7.2)	65.9	4.11 (1H, d, 11.7) 4.98 (1H, d, 11.7)	67.9	3.75 (1H, d, 12.2) 3.87 (1H, d, 12.2)	66.2
1'		118.5		119.8		119.7
2'	3.92 (1H, d, 7.5)	70.7	1.81, 1.97 (1H, m)	33.4	1.83, 1.99 (1H, m)	33.6
3'	1.48, 1.61 (1H, m)	28.6	1.60, 1.69 (1H, m)	21.0	1.62, 1.73 (1H, m)	21.0
4'	1.32, 1.67 (1H, m)	24.5	1.27, 1.33 (1H, m)	27.7	1.28, 1.38 (1H, m)	27.8
5'	1.45, 1.57 (1H, m)	19.3	1.27, 1.33 (1H, m)	27.8	1.28, 1.38 (1H, m)	28.0
6'	1.70, 1.88 (1H, m)	28.7	1.24, 1.39 (1H, m)	26.6	1.27, 1.45 (1H, m)	26.7
7'	5.36 (1H, dt, 11.2, 5.0)	73.4	1.15, 1.55 (1H, m)	24.8	1.17, 1.60 (1H, m)	24.7
8'	1.55, 2.00 (1H, m)	27.6	1.31 (2H, m)	37.6	1.39 (2H, m)	38.0
9'	2.39 (1H, m)	28.1	2.37 (1H, m)	29.4	2.54 (1H, m)	29.2
10'	1.26 (3H, d, 7.4)	18.7	0.79 (3H, d, 6.5)	13.0	0.82 (3H, d, 6.9)	12.6
3-Bz-CO		168.2				167.8
3-Bz-1		130.8				129.9
3-Bz-2,6	8.16 (2H, dd, 8.6, 1.5)	130.1			8.02 (2H, dd, 8.0, 1.1)	129.7
3-Bz-3,5	7.35 (2H, t, 7.5)	128.5			7.47 (2H, t, 8.0)	128.7
3-Bz-4	7.53 (1H, tt, 7.5, 1.3)	133.5			7.59 (1H, tt, 8.0, 1.1)	133.5
18-Bz-CO		166.0				
18-Bz-1		129.3				
18-Bz-2,6	8.05 (2H, dd, 8.5, 1.4)	129.6				
18-Bz-3,5	7.44 (2H, t, 7.5)	128.4				
18-Bz-4	7.54 (1H, tt, 7.5, 1.3)	132.8				

20-Bz-CO				166.7
20-Bz-1				129.9
20-Bz-2,6			8.06 (1H, dd, 8.0, 1.4)	129.9
20-Bz-3,5			7.44 (1H, t, 8.0)	128.5
20-Bz-4			7.55 (1H, tt, 8.0, 1.4)	133.2
7'-Bz-CO		166.5		
7'-Bz-1		129.3		
7'-Bz 2,6	8.11 (2H, dd, 8.3, 1.1)	129.6		
7'-Bz 3,5	7.47 (2H, t, 7.5)	128.3		
7'-Bz-4	7.58 (1H, tt, 7.5, 1.3)	133.0		

[a]Overlapping resonances.

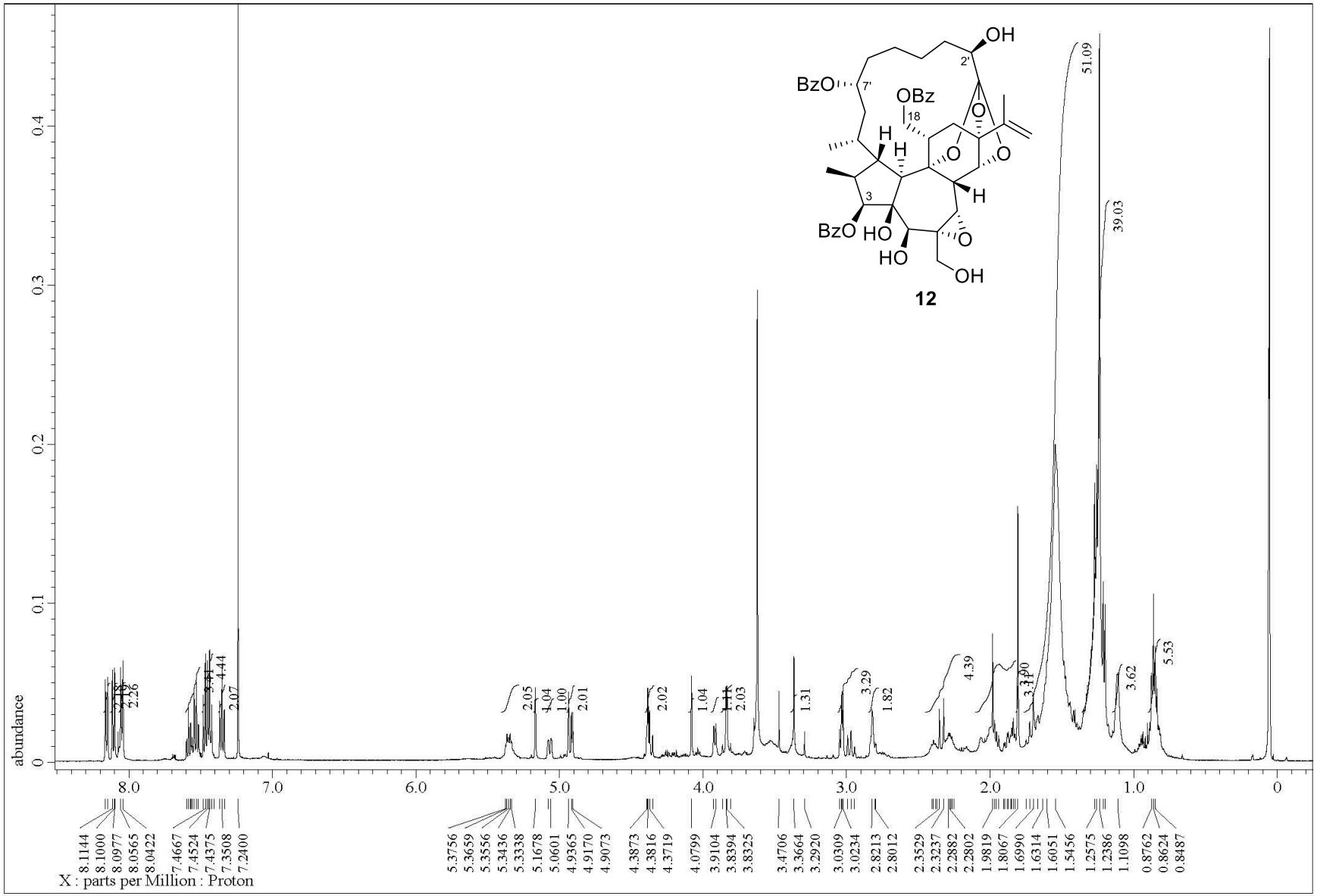


Figure S2. ^{1}H-NMR spectrum of compound **12**.

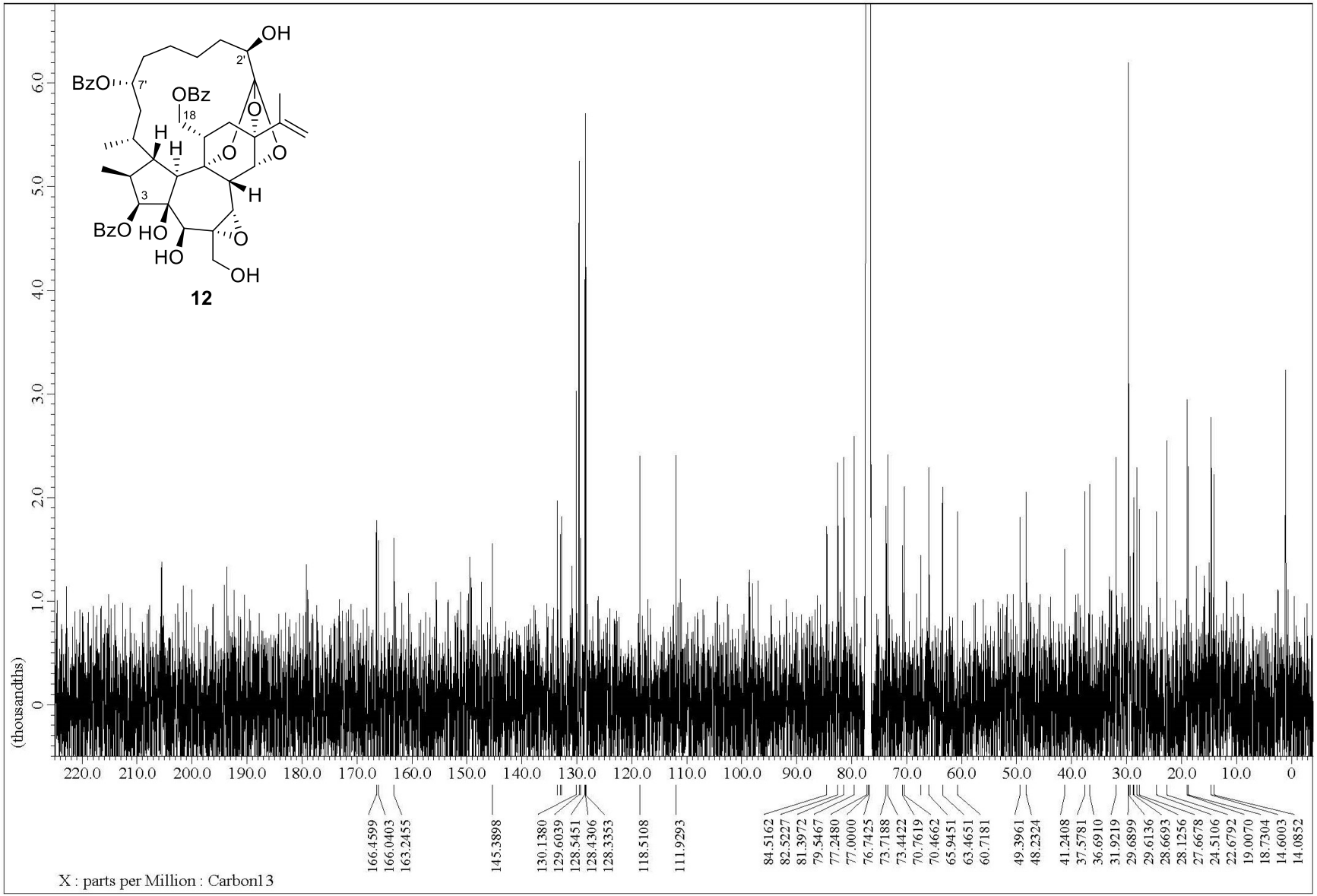


Figure S3. ^{13}C-NMR spectrum of compound **12**.

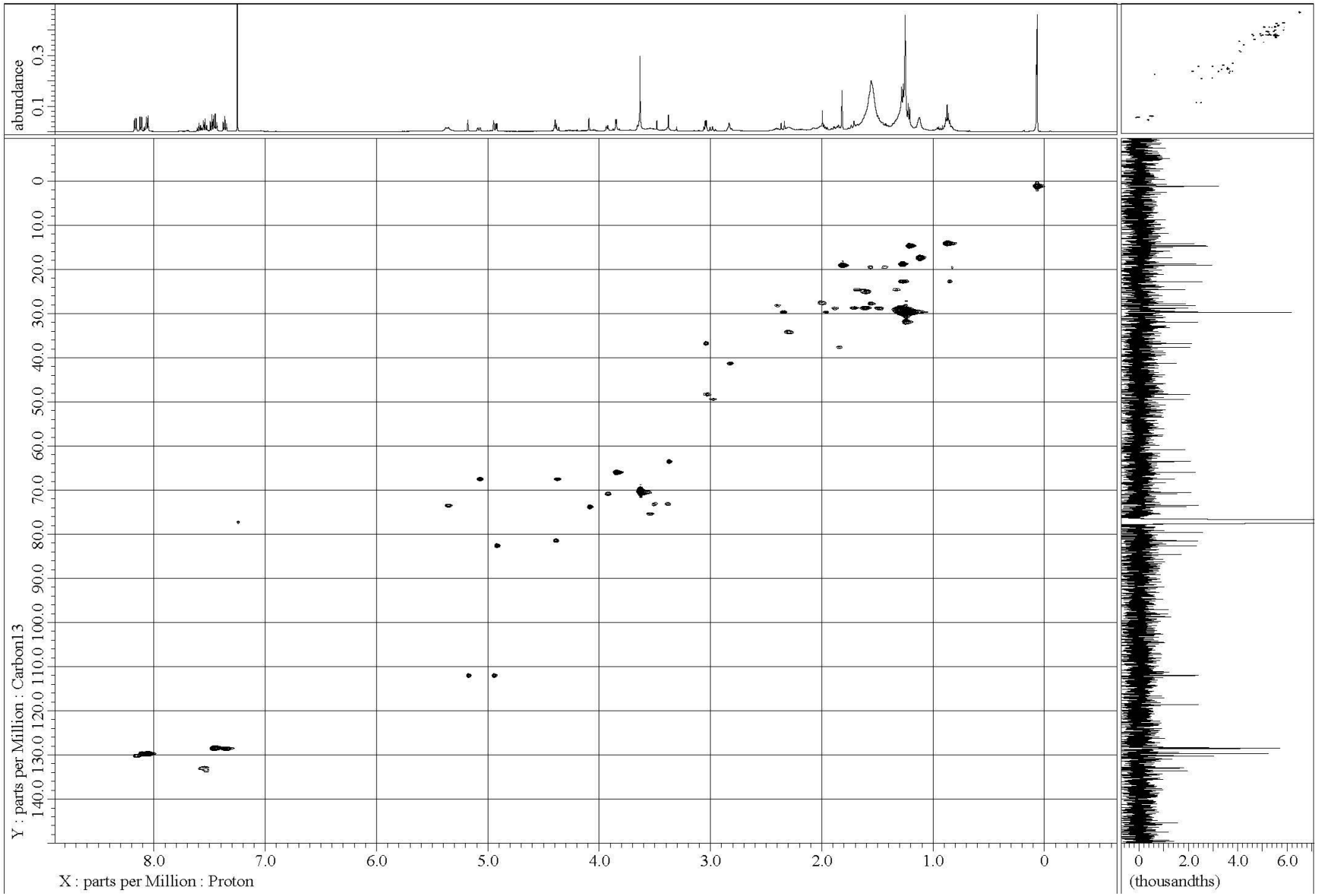


Figure S4. HSQC spectrum of compound **12**.

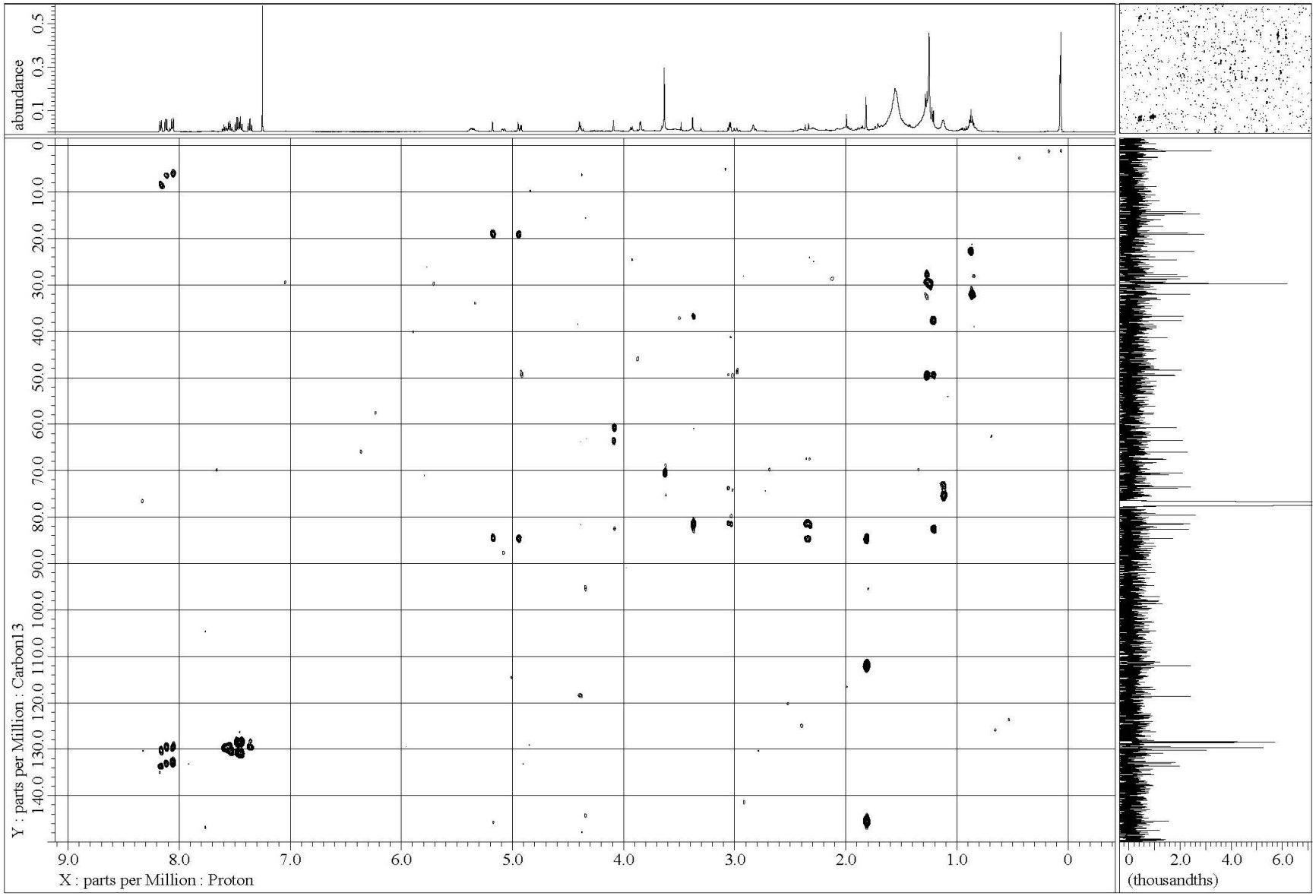
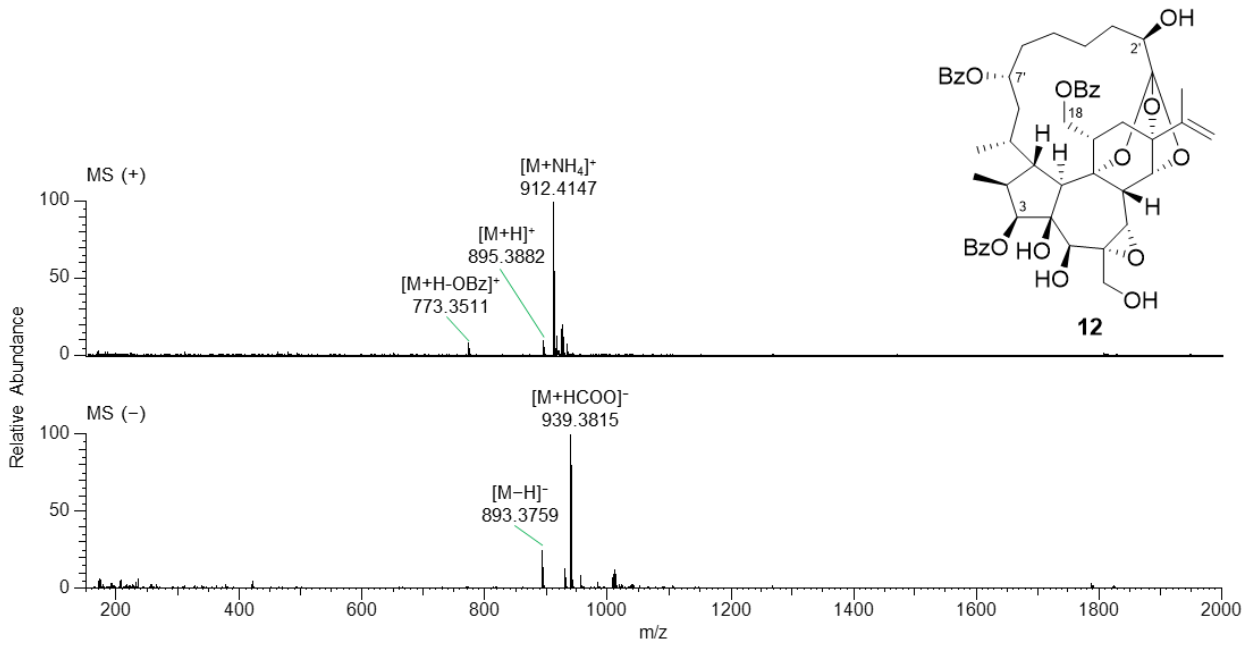


Figure S5. HMBC spectrum of compound **12**.



Peak Mass	Display Formula	Combined Fit	RDB	Delta [ppm]	Theo. mass	Rank	Combined Score	# Matched Iso.	# Missed Iso.	MS Cov. [%]	Pattern Cov. [%]
912.4147	$C_{51}H_{62}O_{14}N$	49.436437522999	21.50	-1.98	912.41648	1	90.91	5	1	93.21	99.93

Fragment Mass

Peak Mass	Display Formula	Combined Fit	RDB	Delta [ppm]	Theo. mass	Rank	Combined Score	# Matched Iso.	# Missed Iso.	MS Cov. [%]	Pattern Cov. [%]
939.3815	$C_{52}H_{59}O_{16}$	53.451450568803	23.50	0.65	939.38086	1	97.55	5	1	100	99.91

Fragment Mass

Figure S6. HRESIMS data of isolated compound **12** in positive ion mode (upper) and negative ion mode (lower).

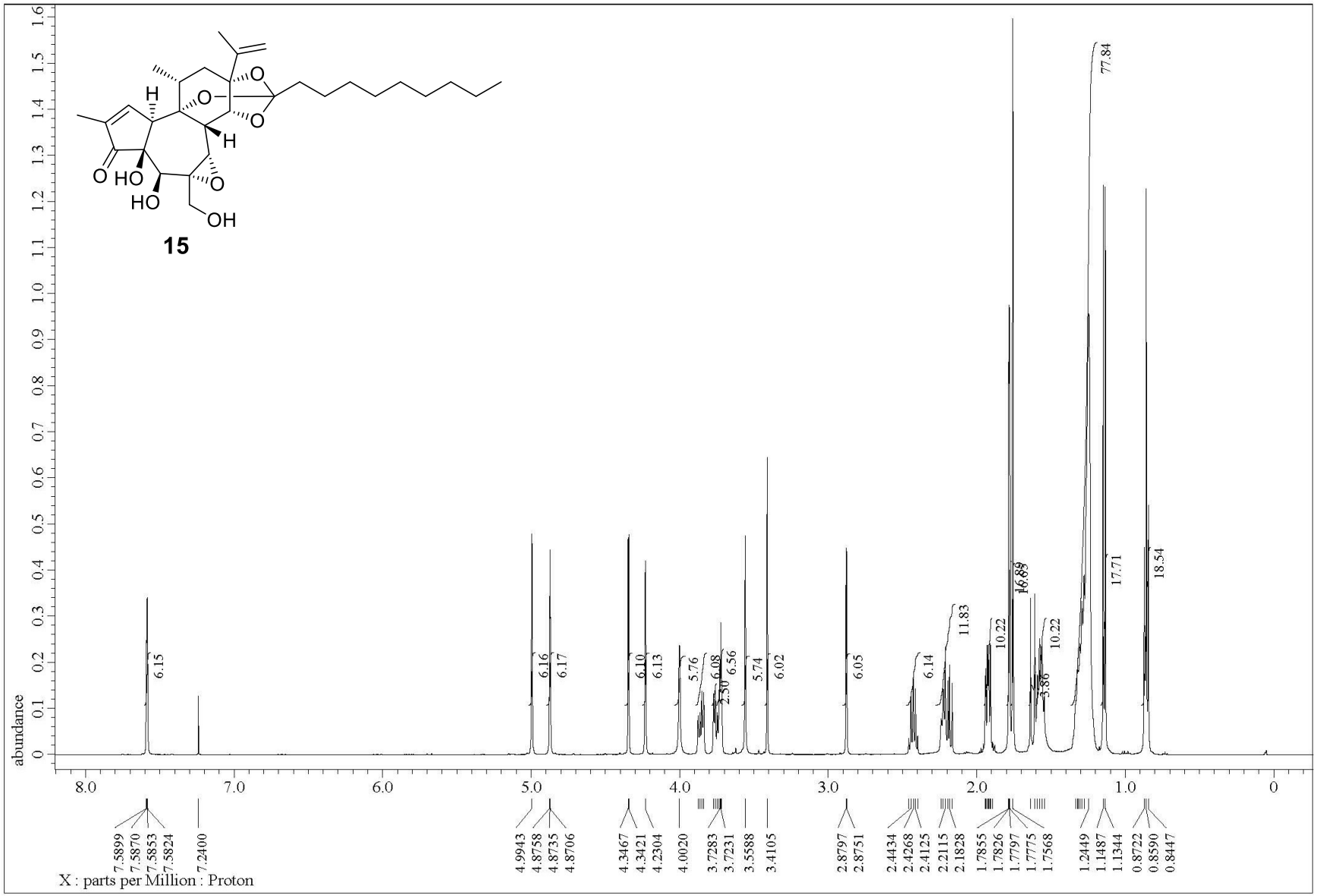


Figure S7. ^{1}H-NMR spectrum of compound **15**.

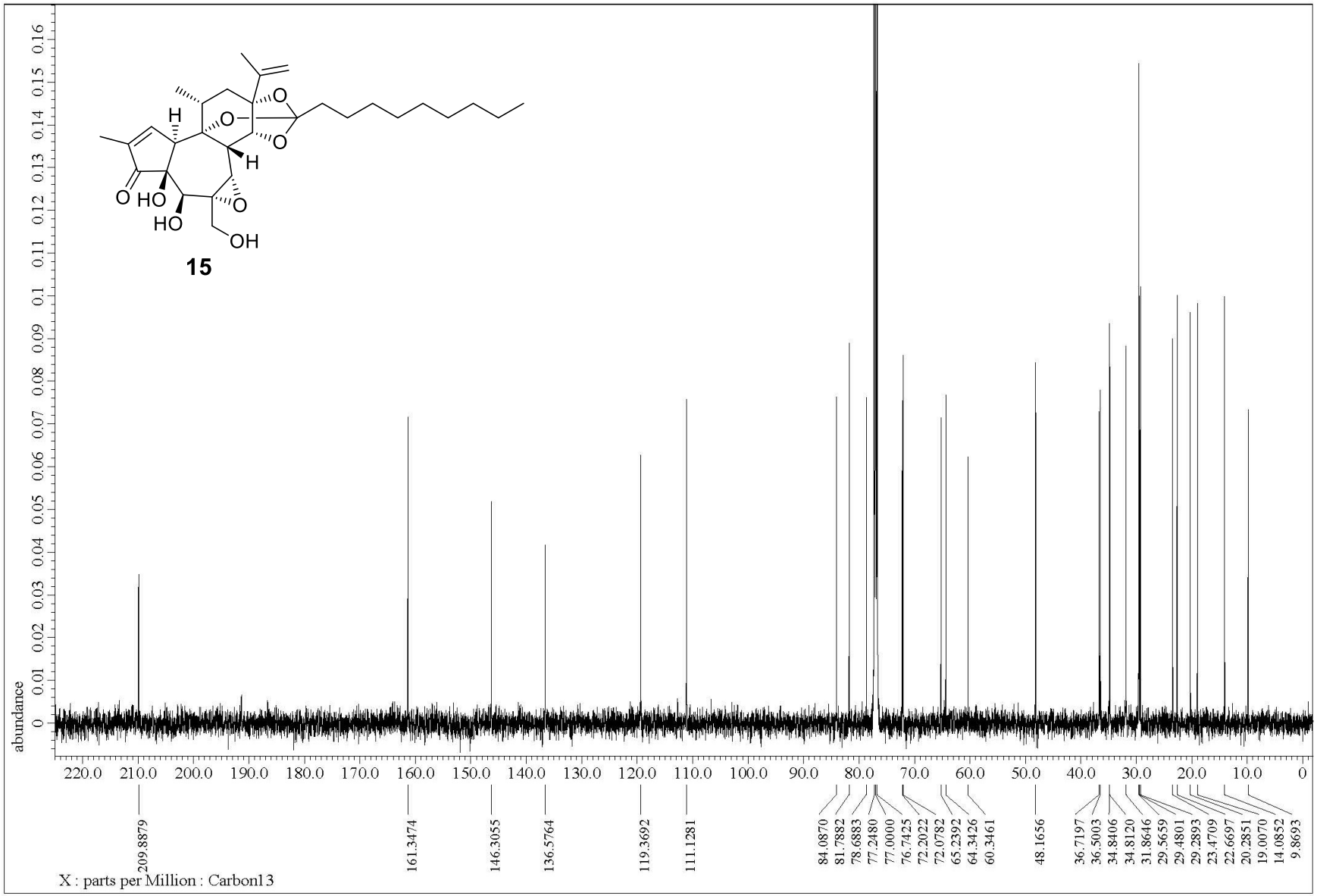
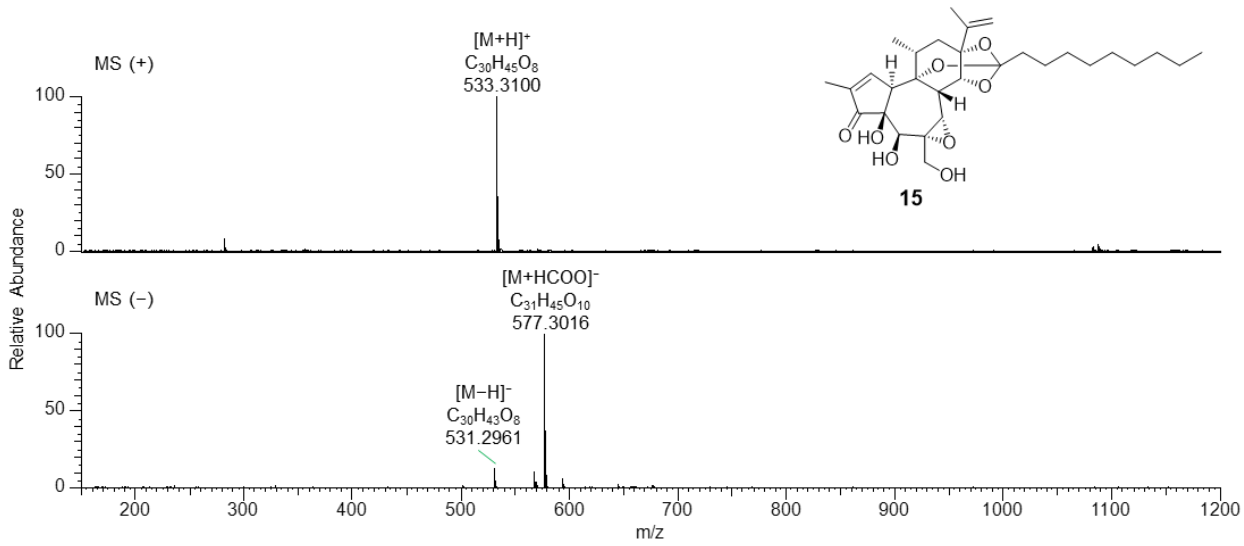


Figure S8. ^{13}C-NMR spectrum of compound **15**.



Peak Mass	Display Formula	Combined Fit	RDB	Delta [ppm]	Theo. mass	Rank	Combined Score	# Matched Iso.	# Missed Iso.	MS Cov. [%]	Pattern Cov. [%]
533.3100	$C_{30}H_{45}O_8$	46.29006226027	28.50	-1.68	533.31089	1	97.03	5	0	99.85	99.91

Fragment Mass

Peak Mass	Display Formula	Combined Fit	RDB	Delta [ppm]	Theo. mass	Rank	Combined Score	# Matched Iso.	# Missed Iso.	MS Cov. [%]	Pattern Cov. [%]
577.3018	$C_{31}H_{45}O_{10}$	83.85757239995	389.50	0.00	577.30182	1	99.15	5	0	100	100

Fragment Mass

Figure S9. HRESIMS data of isolated compound **15** in positive ion mode (upper) and negative ion mode (lower).

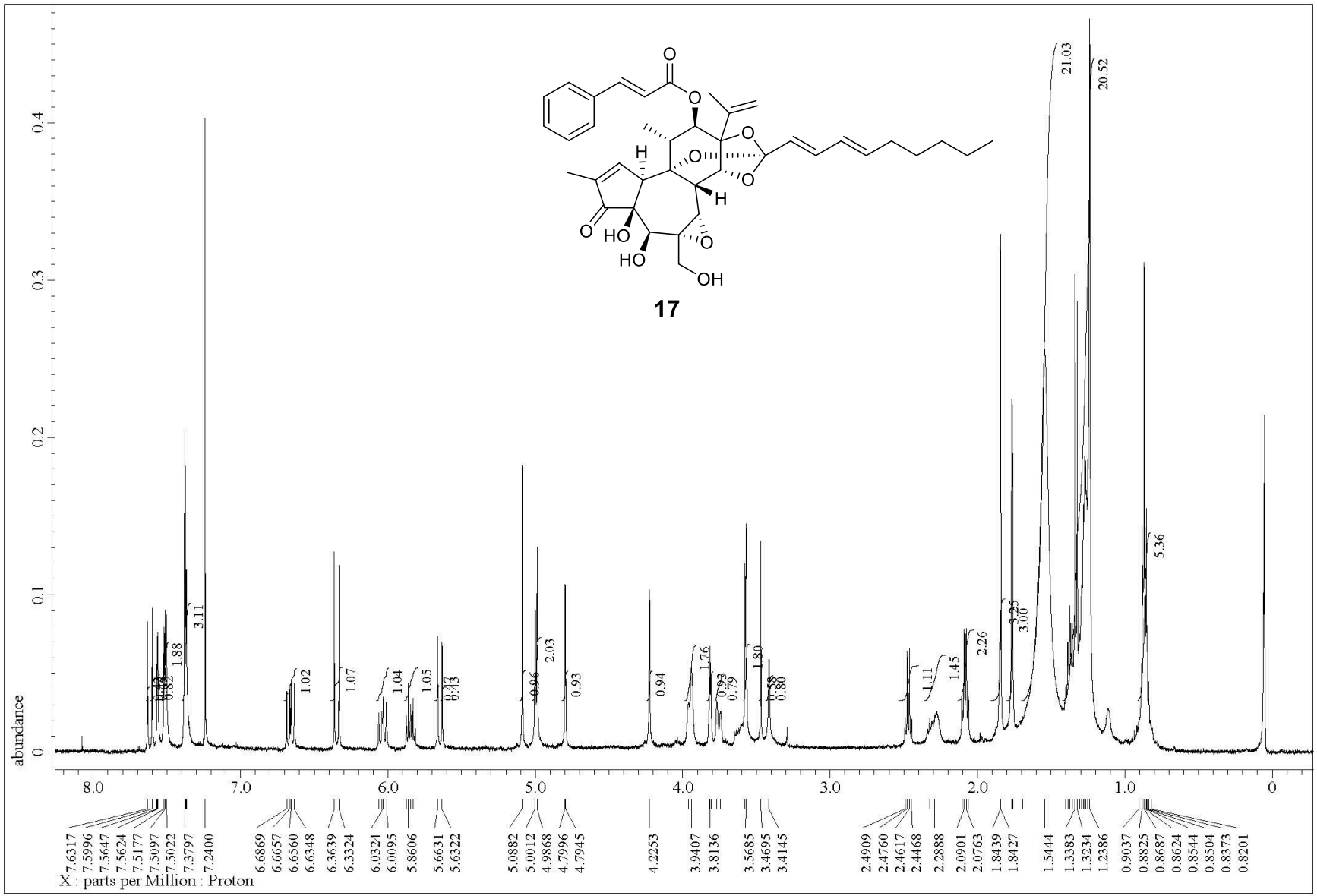


Figure S10. ^{1}H-NMR spectrum of compound **17**.

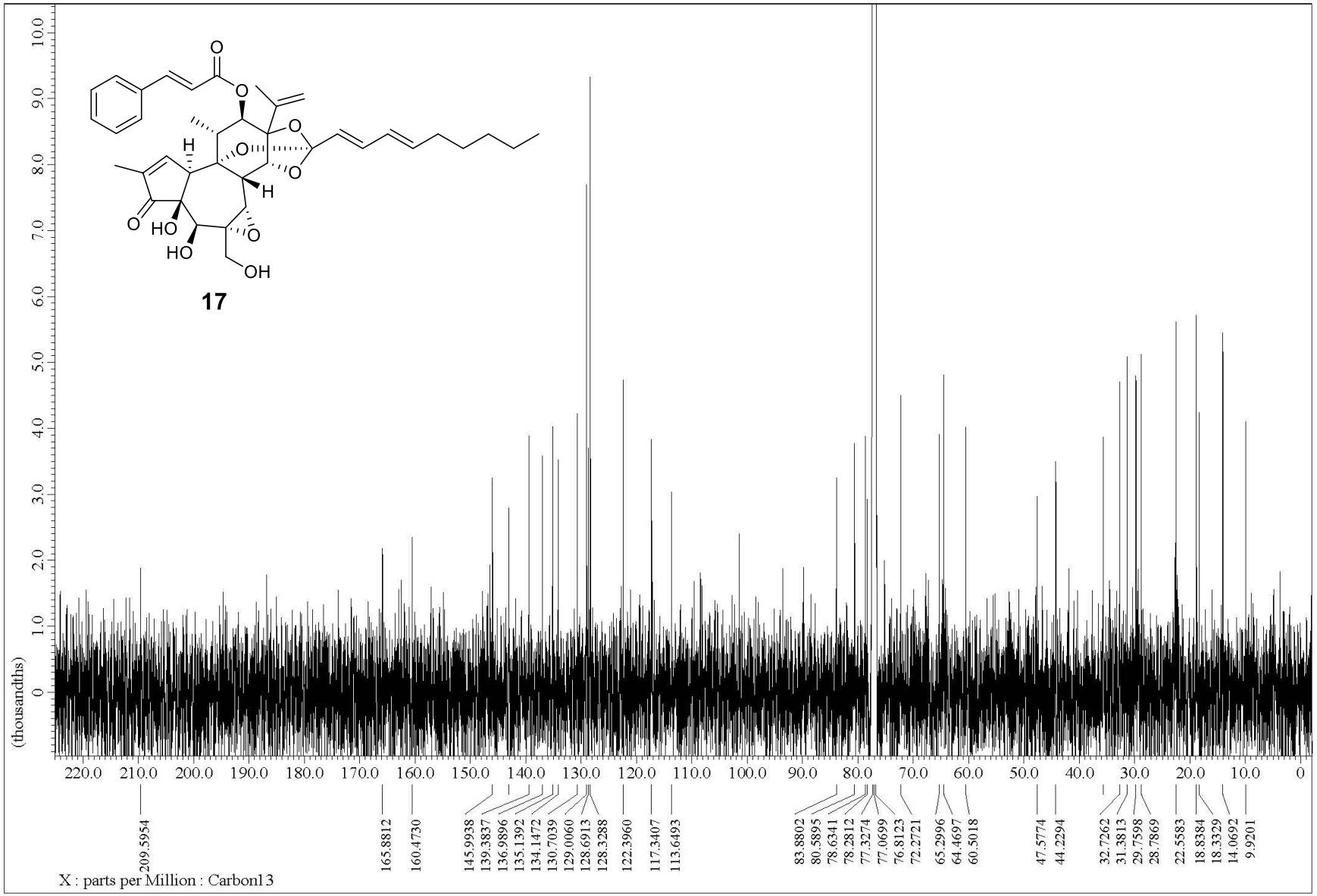
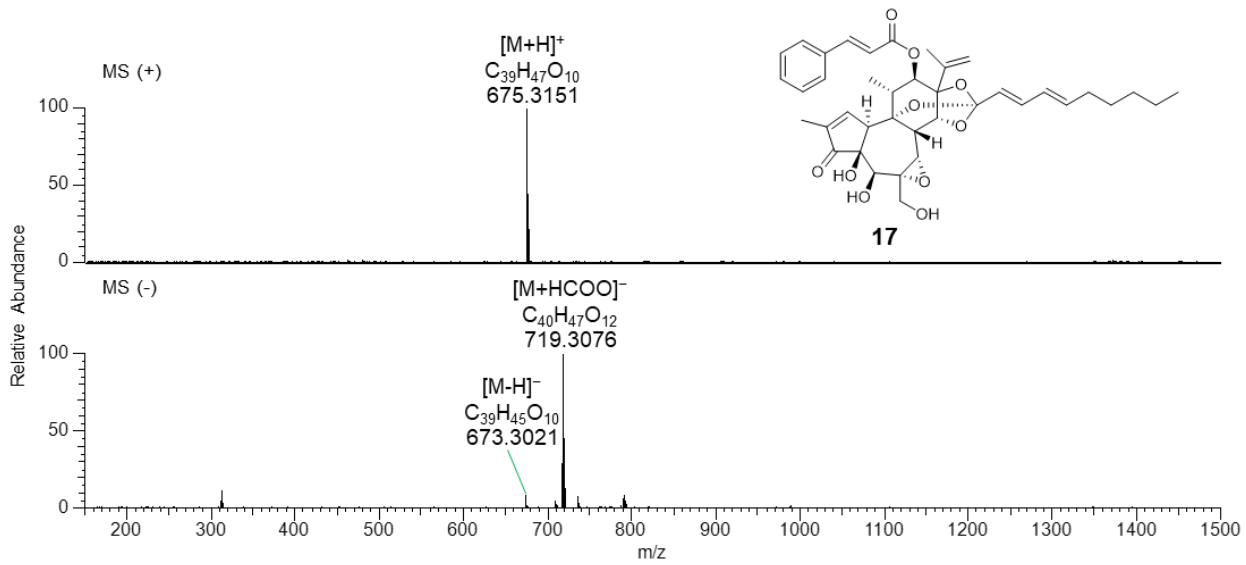


Figure S11. ^{13}C-NMR spectrum of compound **17**.



Peak Mass	Display Formula	Combined Fit	RDB	Delta [ppm]	Theo. mass	Rank	Combined Score	# Matched Iso.	# Missed Iso.	MS Cov. [%]	Pattern Cov. [%]
675.3151	$C_{39}H_{47}O_{10}$	65.996189381113	416.50	-1.85	675.31637	1	98.21	5	0	100	100
Fragment	Mass										
Peak Mass	Display Formula	Combined Fit	RDB	Delta [ppm]	Theo. mass	Rank	Combined Score	# Matched Iso.	# Missed Iso.	MS Cov. [%]	Pattern Cov. [%]
719.3076	$C_{40}H_{47}O_{12}$	61.398730849069	317.50	1.97	719.30620	1	97.88	5	0	99.9	100
Fragment	Mass										

Figure S12. HRESIMS data of isolated compound **17** in positive ion mode (upper) and negative ion mode (lower).

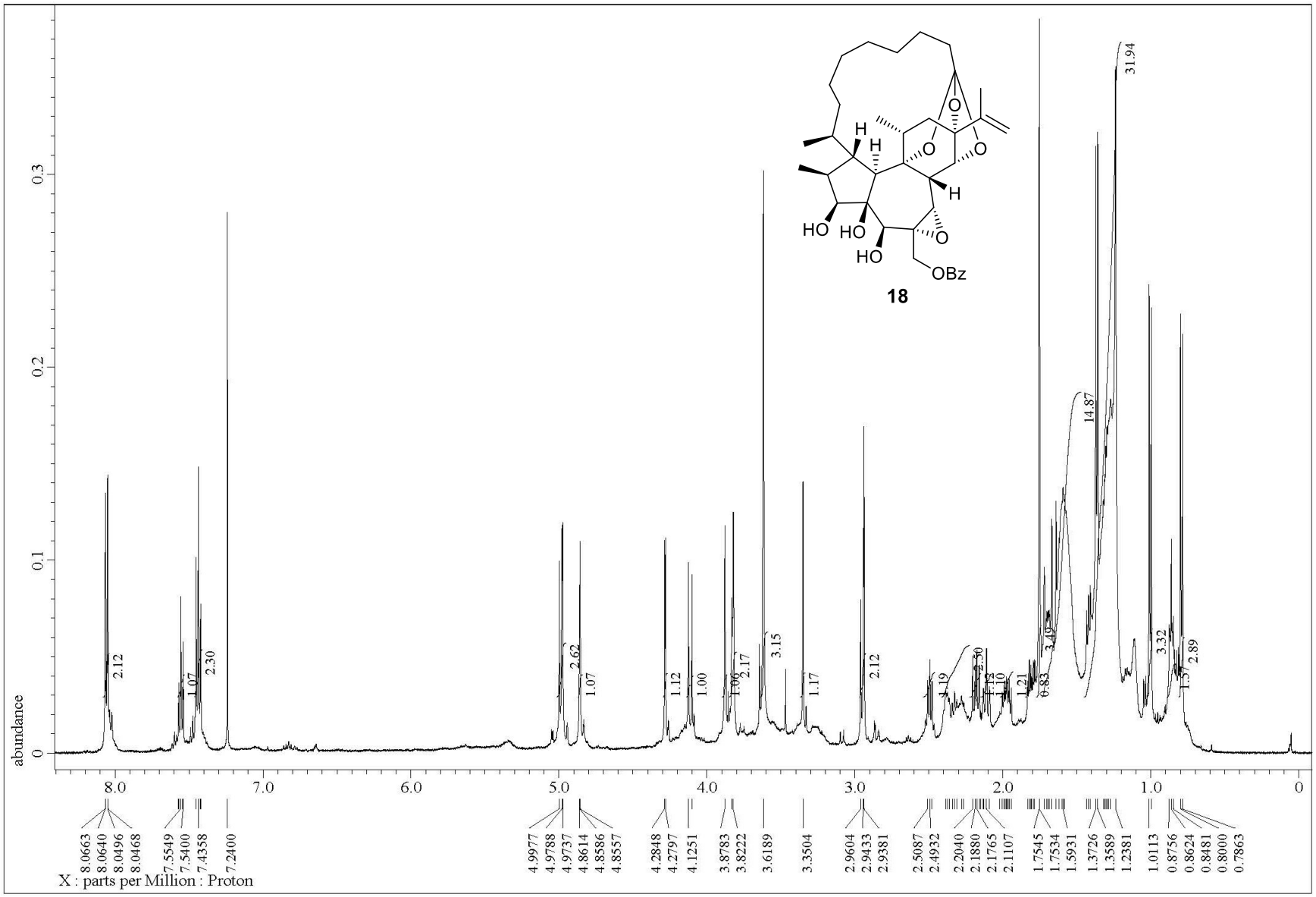


Figure S13. ^{1}H-NMR spectrum of compound **18**.

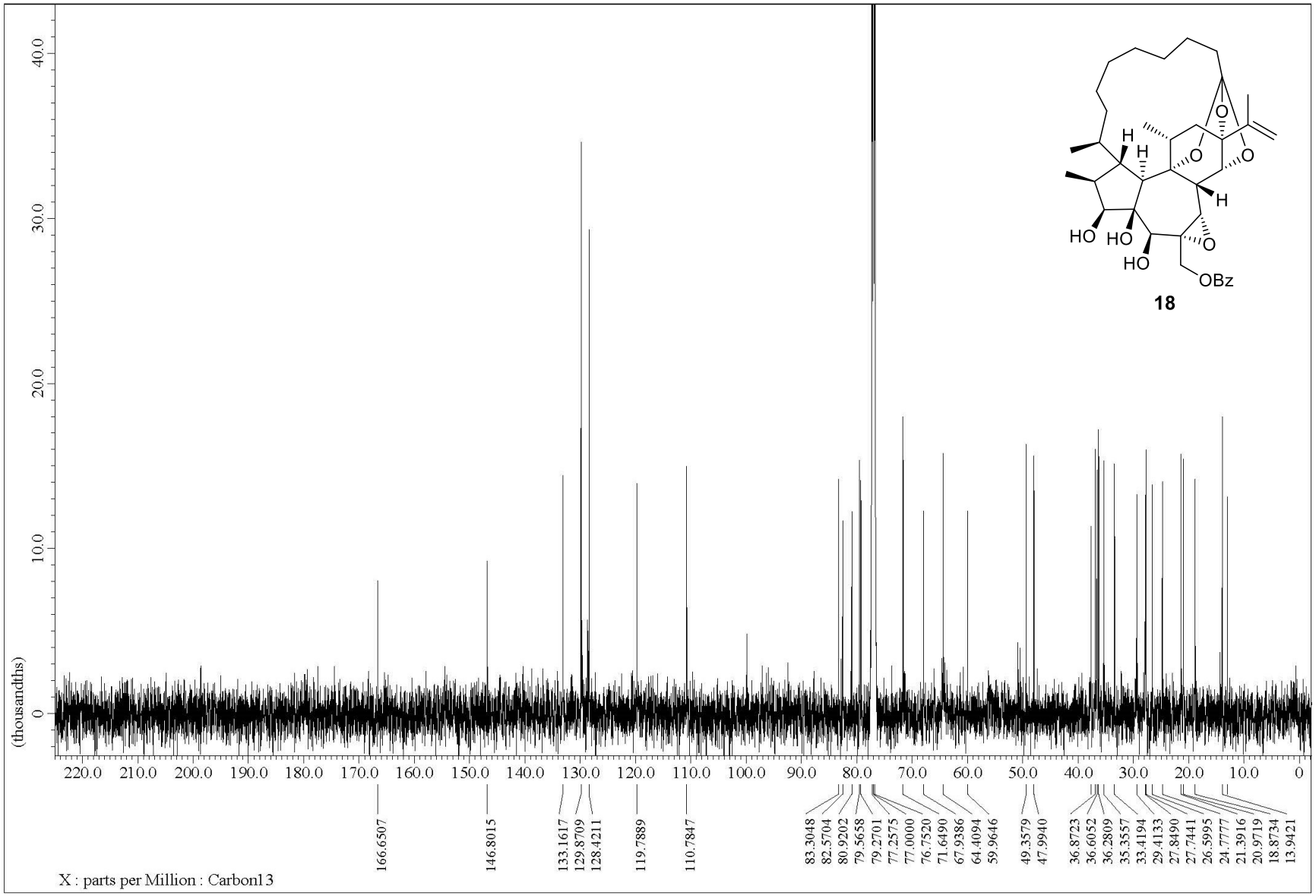
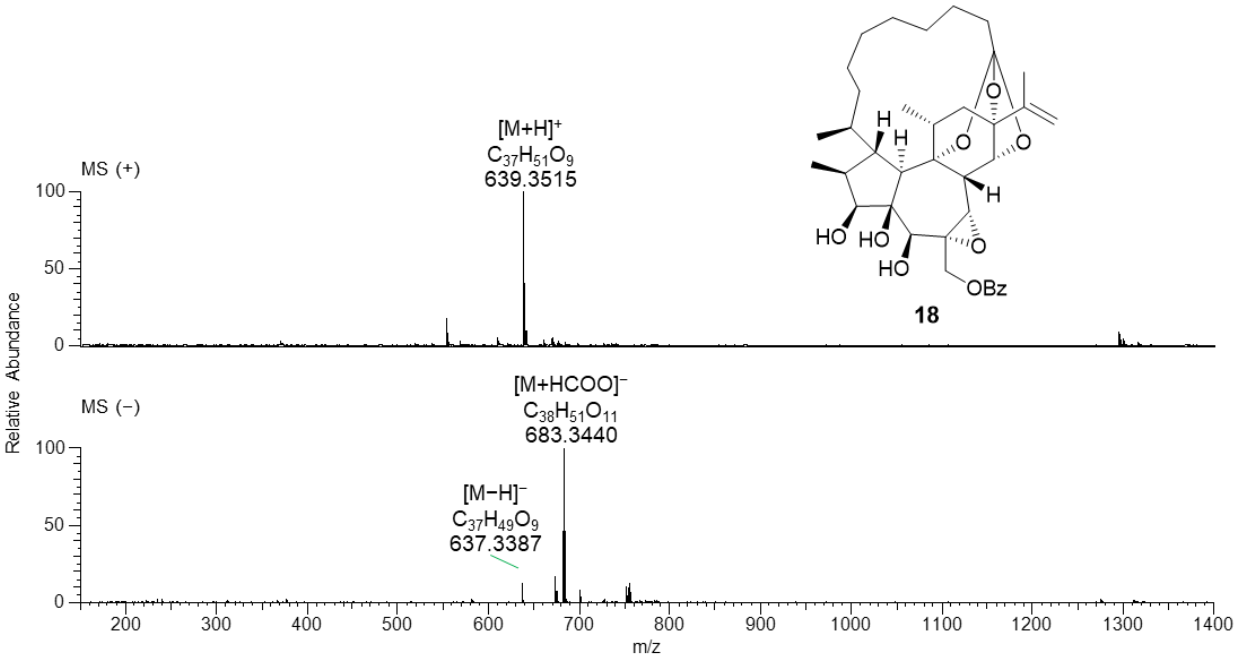


Figure S14. ^{13}C-NMR spectrum of compound **18**.



Peak Mass	Display Formula	Combined Fit	RDB	Delta [ppm]	Theo. mass	Rank	Combined Score	# Matched Iso.	# Missed Iso.	MS Cov. [%]	Pattern Cov. [%]
639.3515	$C_{37}H_{51}O_9$	67.996945725730	212.50	-1.97	639.35276	1	98.32	5	0	100	100
Fragment Mass											
Peak Mass	Display Formula	Combined Fit	RDB	Delta [ppm]	Theo. mass	Rank	Combined Score	# Matched Iso.	# Missed Iso.	MS Cov. [%]	Pattern Cov. [%]
683.3440	$C_{38}H_{51}O_{11}$	67.172842208010	513.50	0.45	683.34369	1	98.27	5	0	100	100
Fragment Mass											

Figure S15. HRESIMS data of compound **18** in positive ion mode (upper) and negative ion mode (lower).

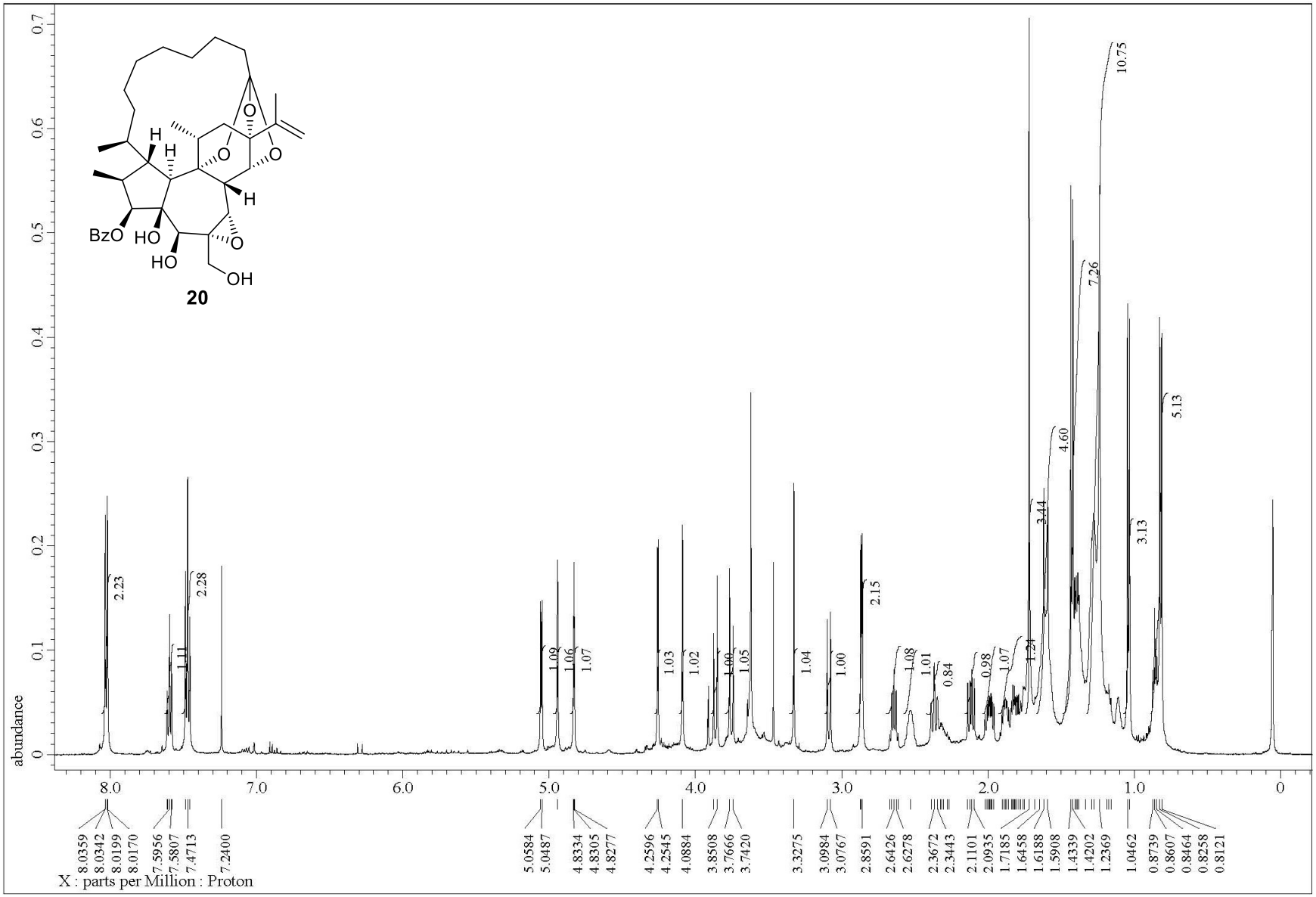


Figure S16. ^{1}H-NMR spectrum of compound **20**.

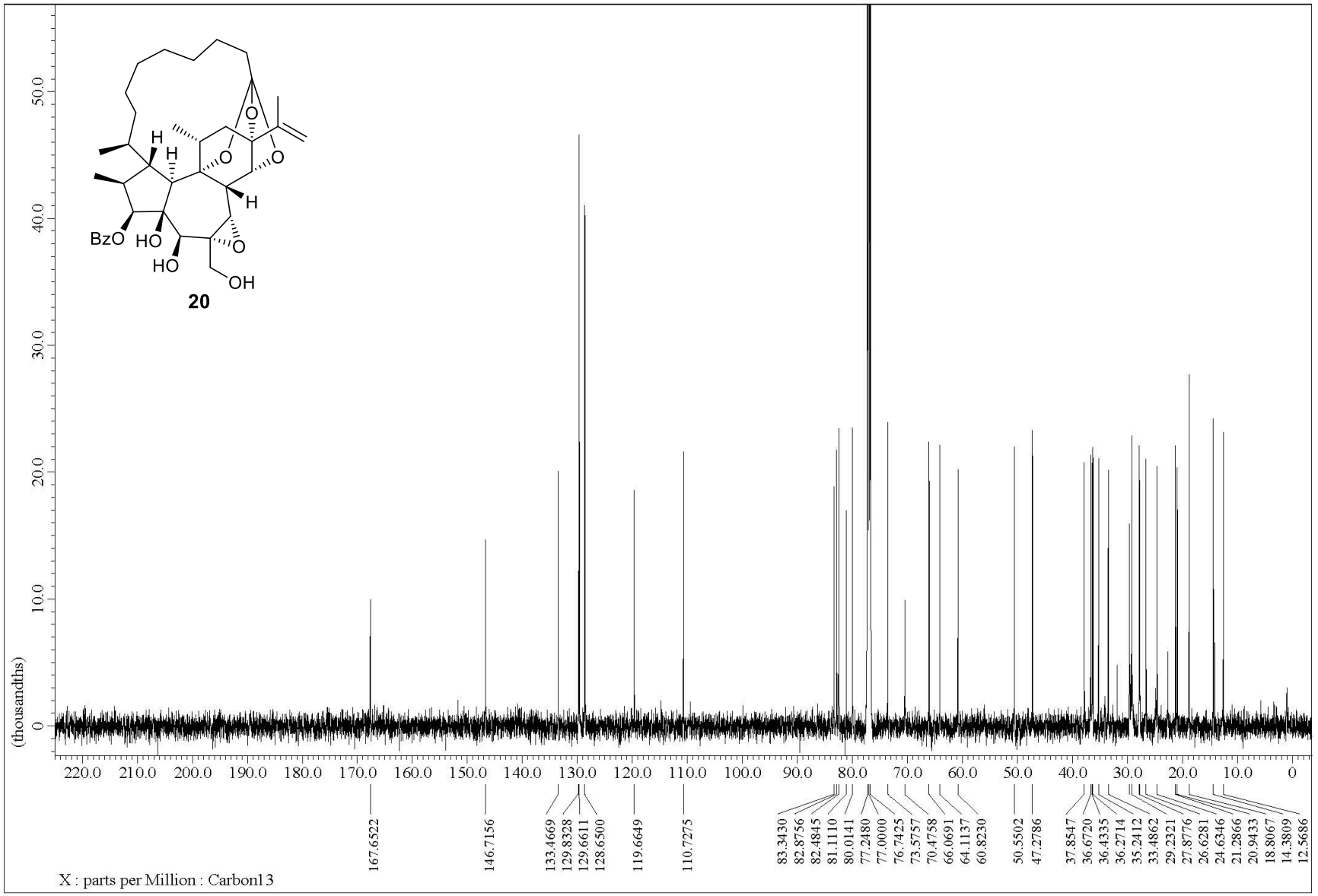
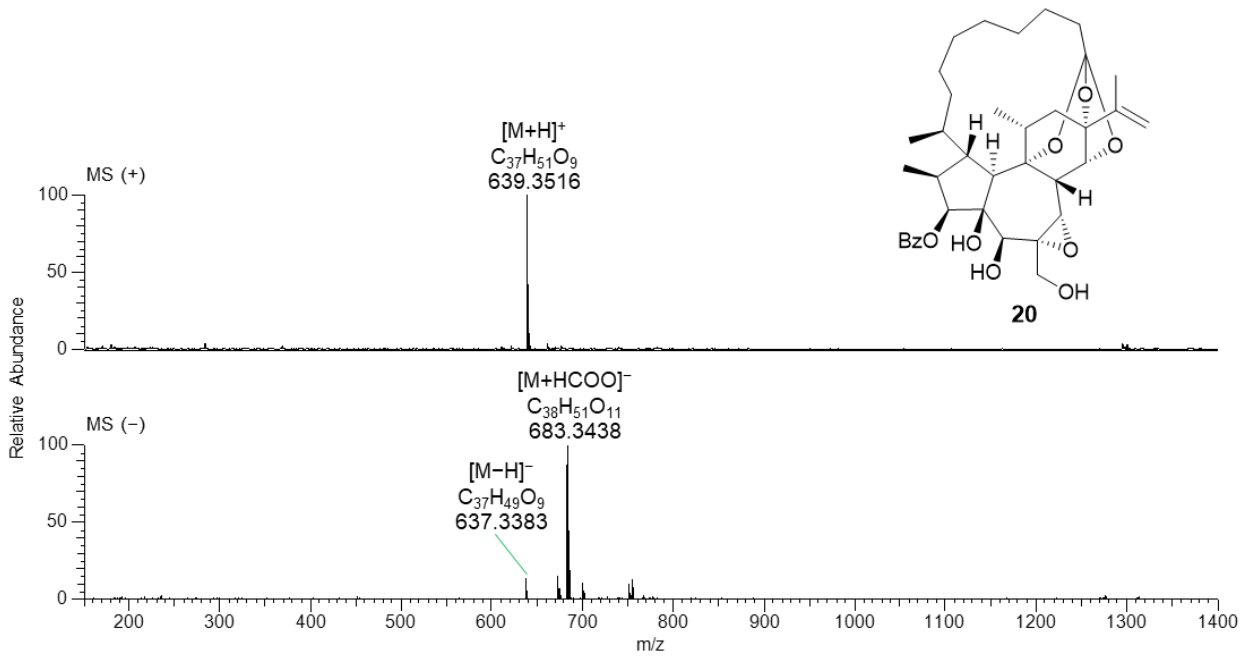


Figure S17. ^{13}C-NMR spectrum of compound **20**.



Peak Mass	Display Formula	Combined Fit	RDB	Delta [ppm]	Theo. mass	Rank	Combined Score	# Matched Iso.	# Missed Iso.	MS Cov. [%]	Pattern Cov. [%]
639.3516	$C_{37}H_{51}O_9$	47.145594127634512.50		-1.87	639.35276	1	97.08	4	1	99.85	99.84
Fragment	Mass										
Peak Mass	Display Formula	Combined Fit	RDB	Delta [ppm]	Theo. mass	Rank	Combined Score	# Matched Iso.	# Missed Iso.	MS Cov. [%]	Pattern Cov. [%]
683.3438	$C_{38}H_{51}O_{11}$	80.368700310610213.50		0.09	683.34369	1	98.97	5	0	100	100
Fragment	Mass										

Figure S18. HRESIMS data of isolated compound **20** in positive ion mode (upper) and negative ion mode (lower).

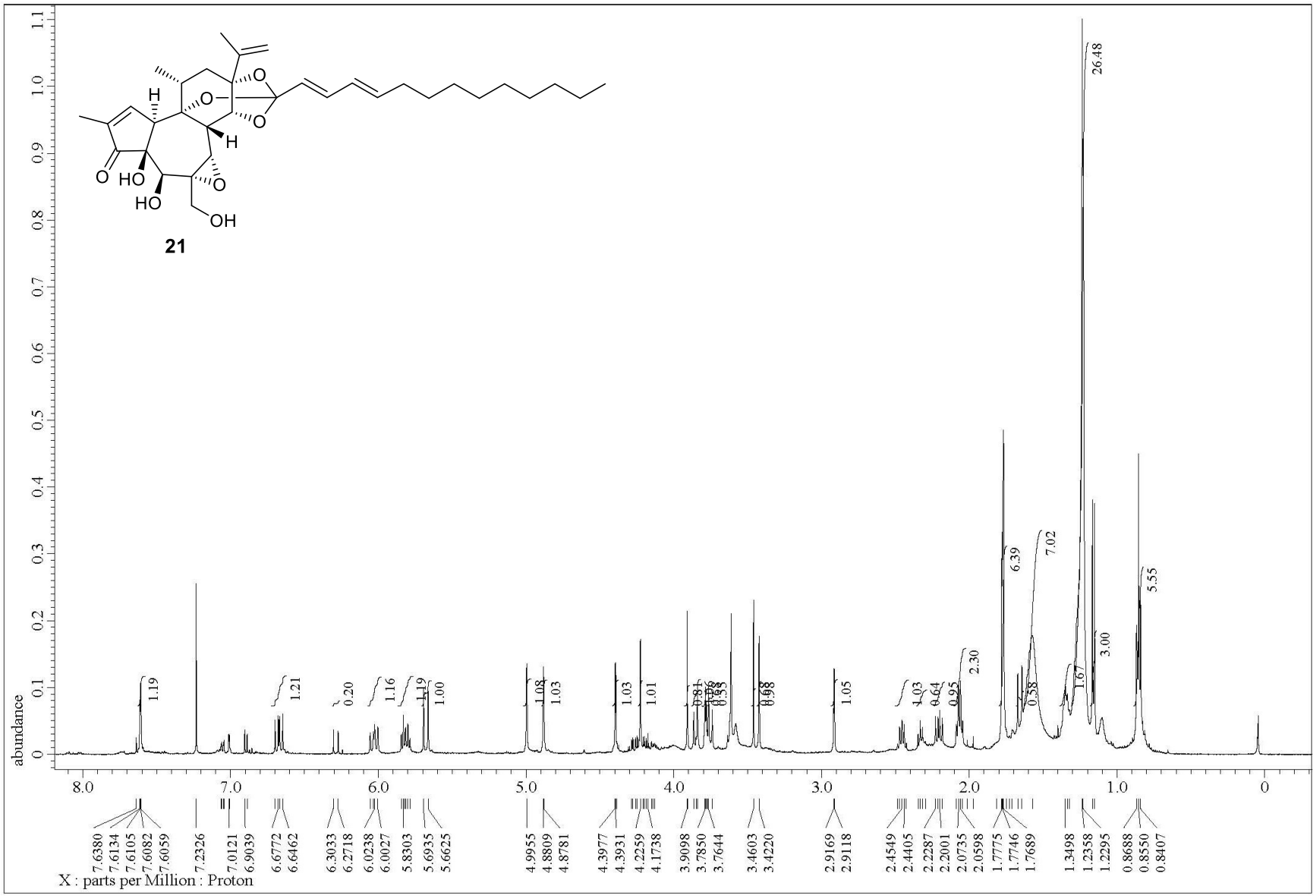


Figure S19. ^{1}H-NMR spectrum of compound **21**.

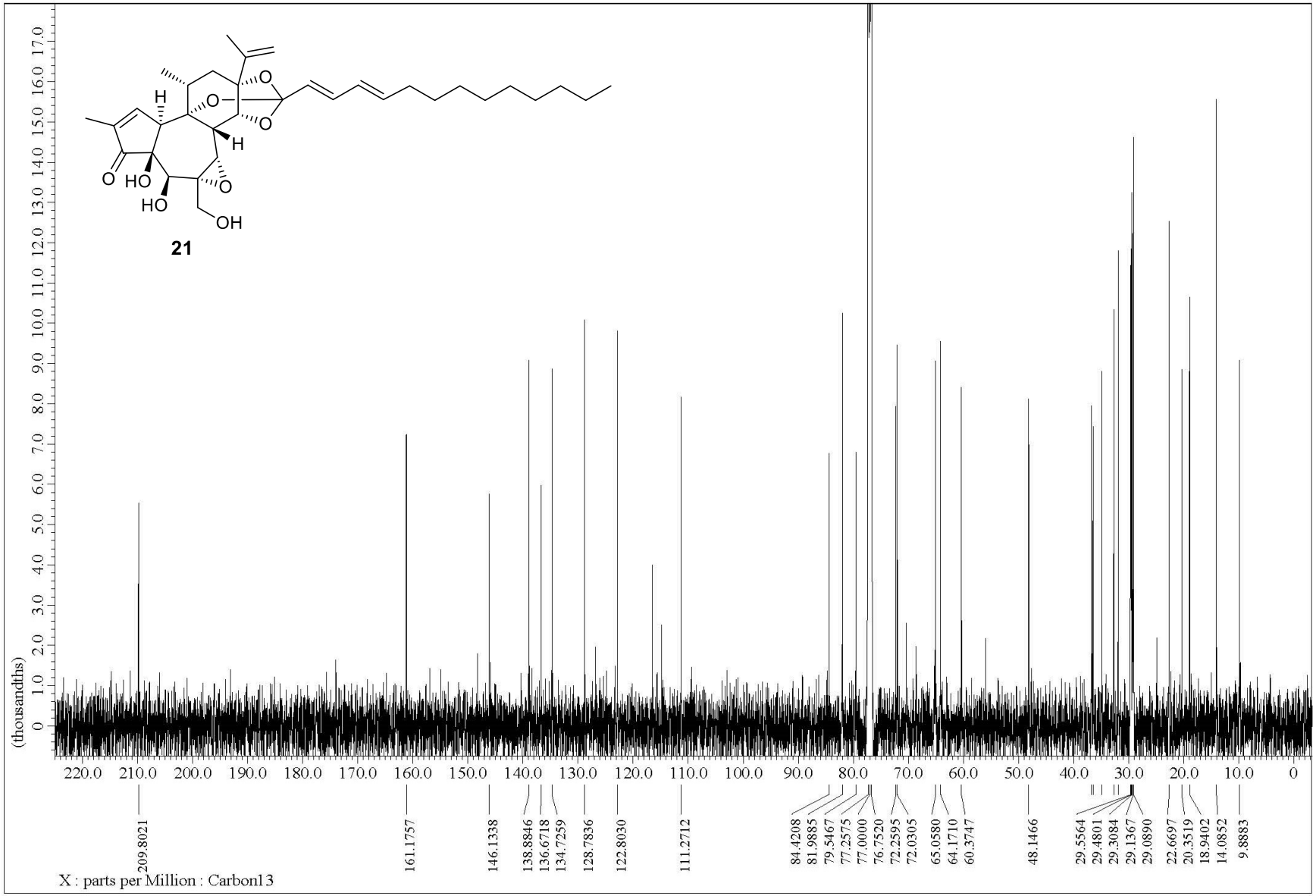
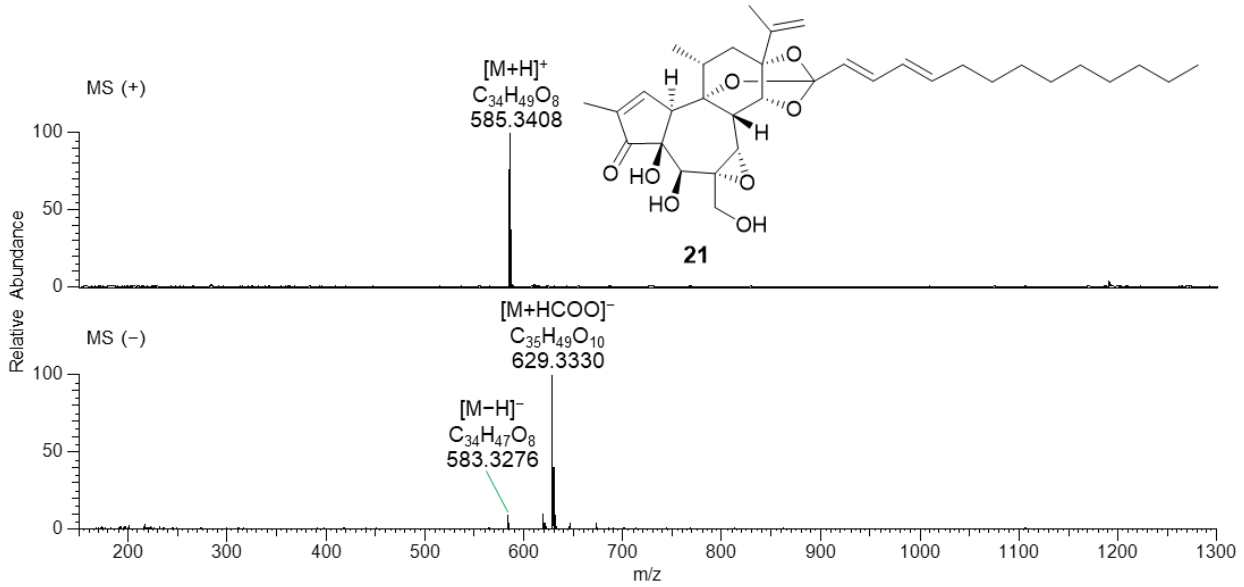


Figure S20. ^{13}C-NMR spectrum of compound **21**.



Peak Mass	Display Formula	Combined Fit	RDB	Delta [ppm]	Theo. mass	Rank	Combined Score	# Matched Iso.	# Missed Iso.	MS Cov. [%]	Pattern Cov. [%]
585.3408	$C_{34}H_{49}O_8$	61.272550619158	510.50	-2.35	585.34219	1	97.93	5	0	99.96	100

Fragment Mass

Peak Mass	Display Formula	Combined Fit	RDB	Delta [ppm]	Theo. mass	Rank	Combined Score	# Matched Iso.	# Missed Iso.	MS Cov. [%]	Pattern Cov. [%]
629.3330	$C_{35}H_{49}O_{10}$	83.416482456887	411.50	-0.18	629.33312	1	98.97	5	0	99.83	100

Fragment Mass

Figure S21. HRESIMS data of compound **21** in positive ion mode (upper) and negative ion mode (lower).

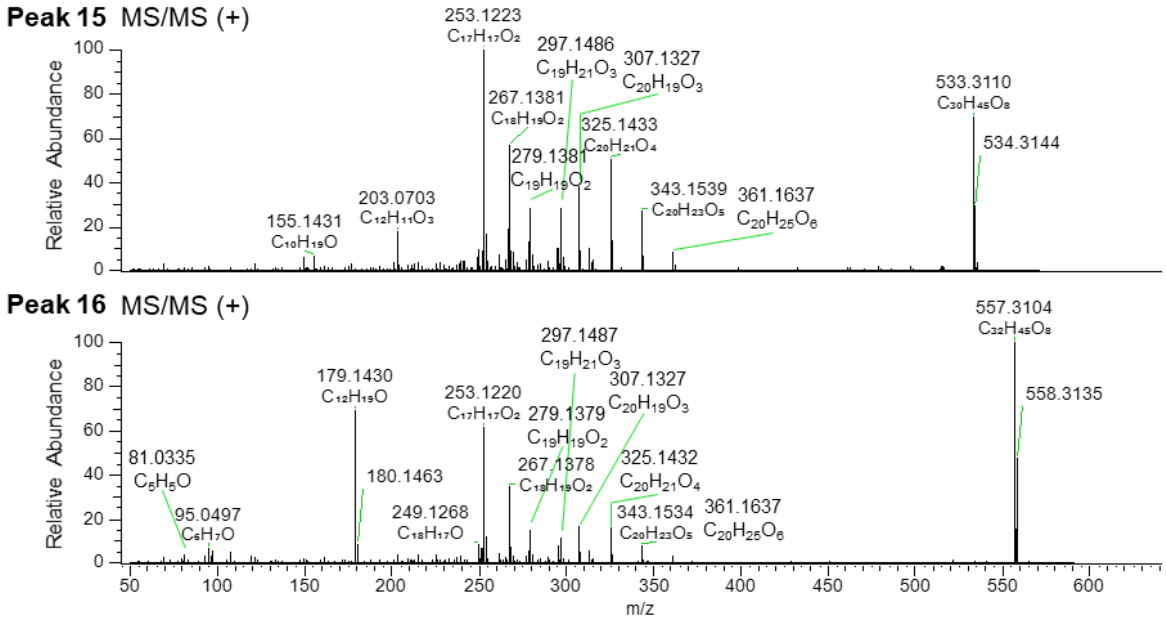


Figure S22. Product ion spectra of peaks **15** and **16** obtained from the protonated molecular ion peak in positive ion mode.

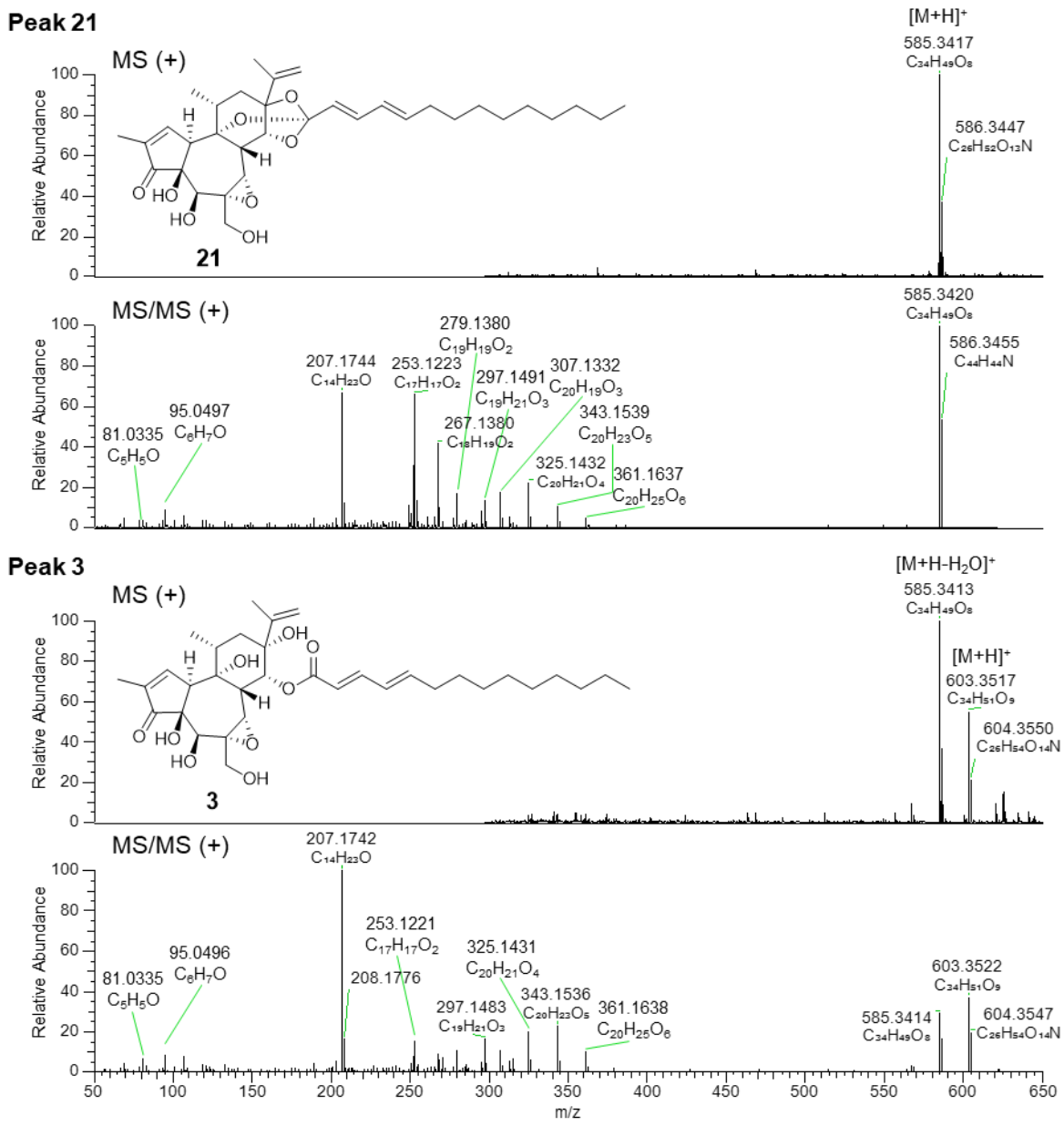


Figure S23. Mass spectra and product ion spectra of peaks **21** and **3** obtained from the protonated molecular ion peak in positive ion mode.

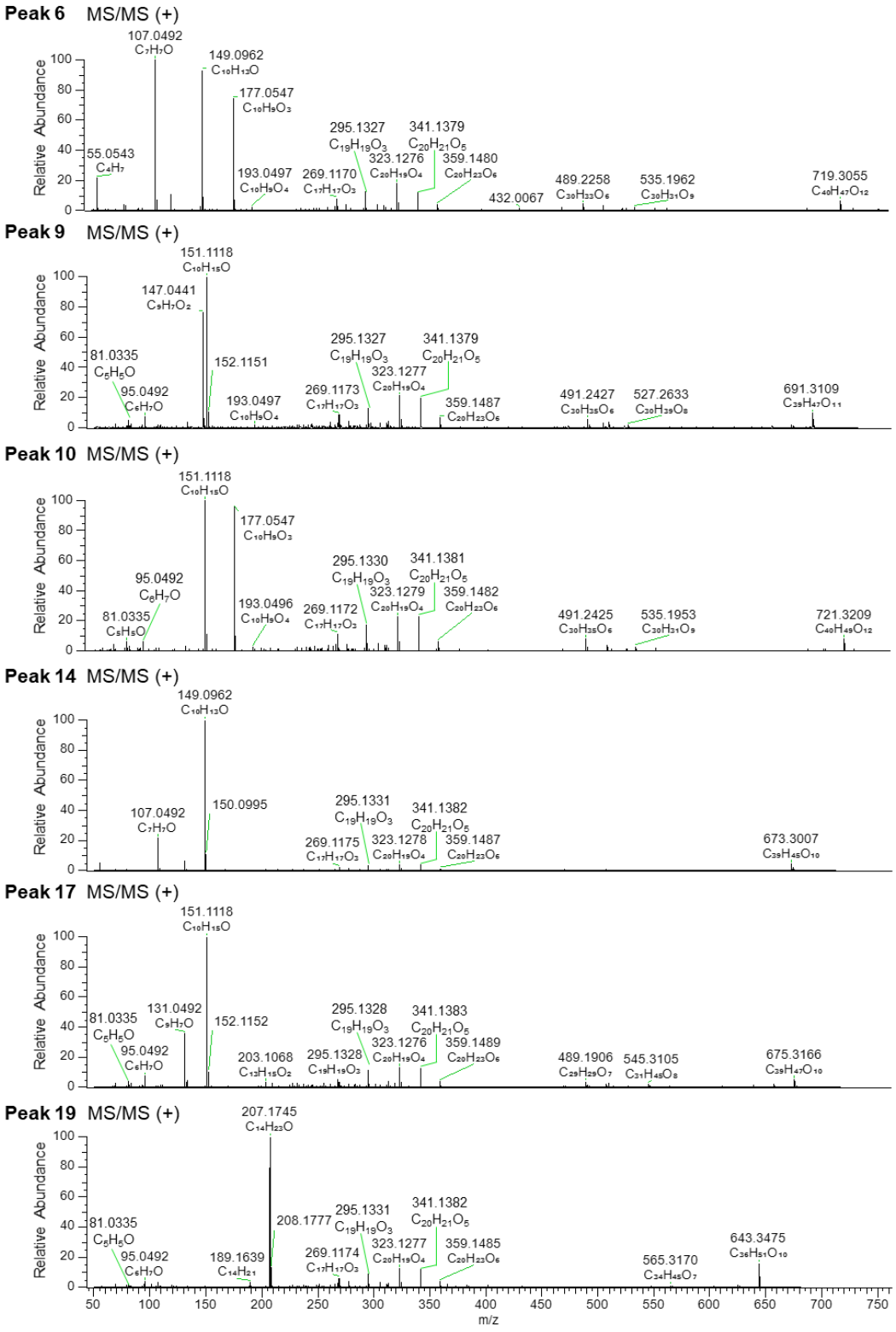


Figure S24. Product ion spectra of peaks **6**, **9**, **10**, **14**, **17**, and **19** obtained from the protonated molecular ion peak in positive ion mode.

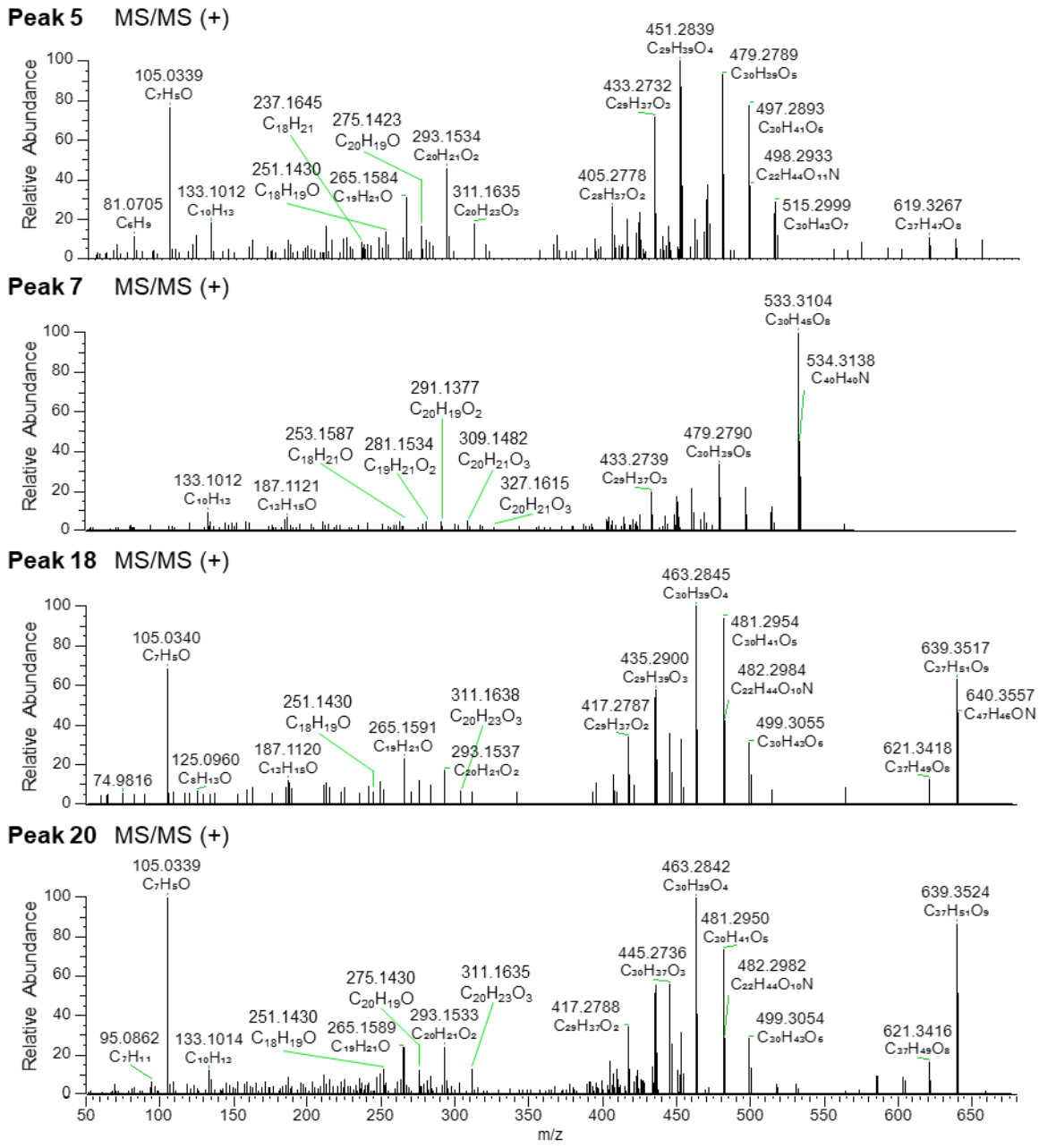


Figure S25. Product ion spectra of peaks **5**, **7**, **18**, and **20** obtained from the protonated molecular ion peak in positive ion mode.

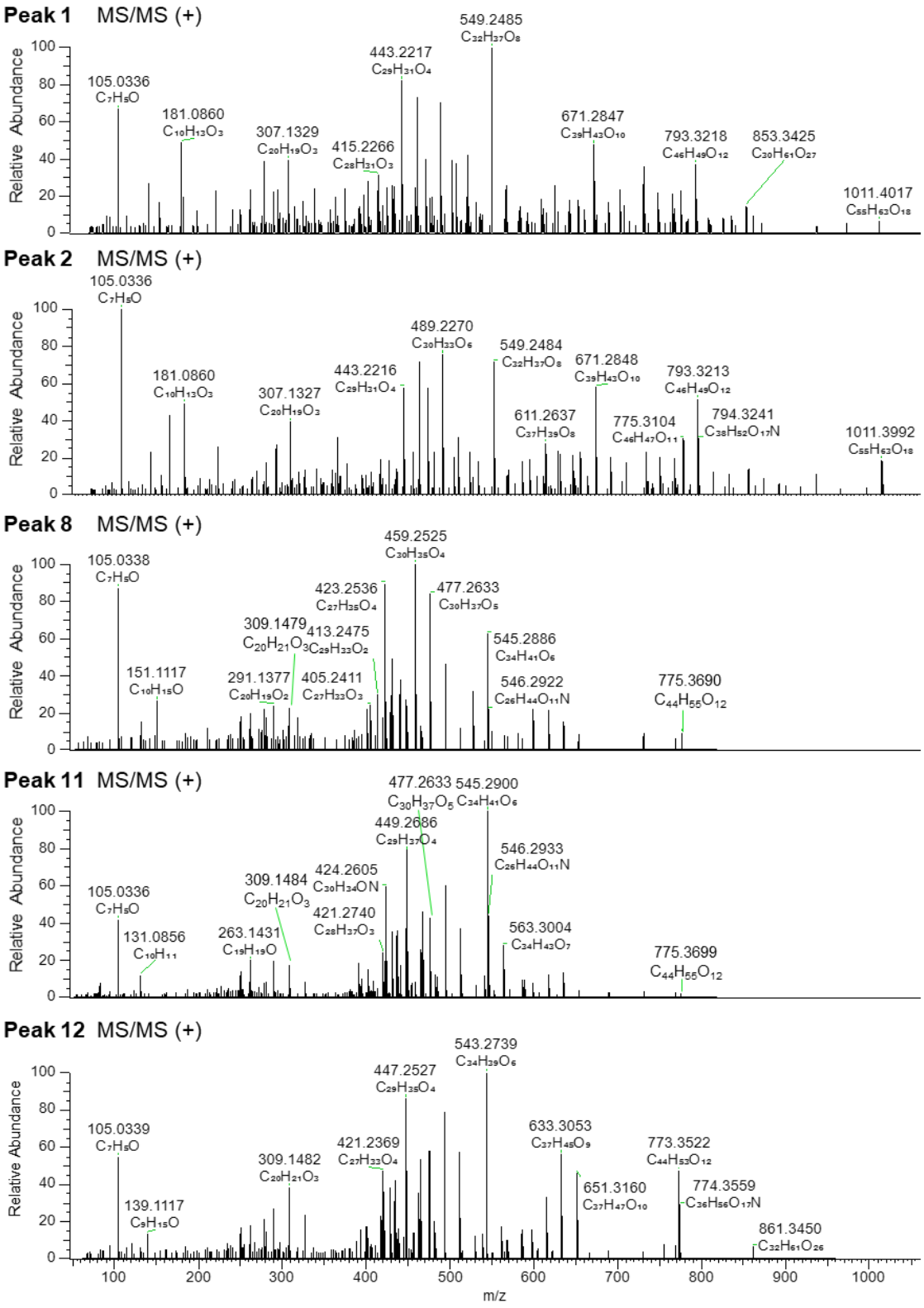


Figure S26. Product ion spectra of peaks **1**, **2**, **8**, and **11** obtained from the protonated molecular ion peak and **12** in obtained from the ammonium adduct ion peak positive ion mode.

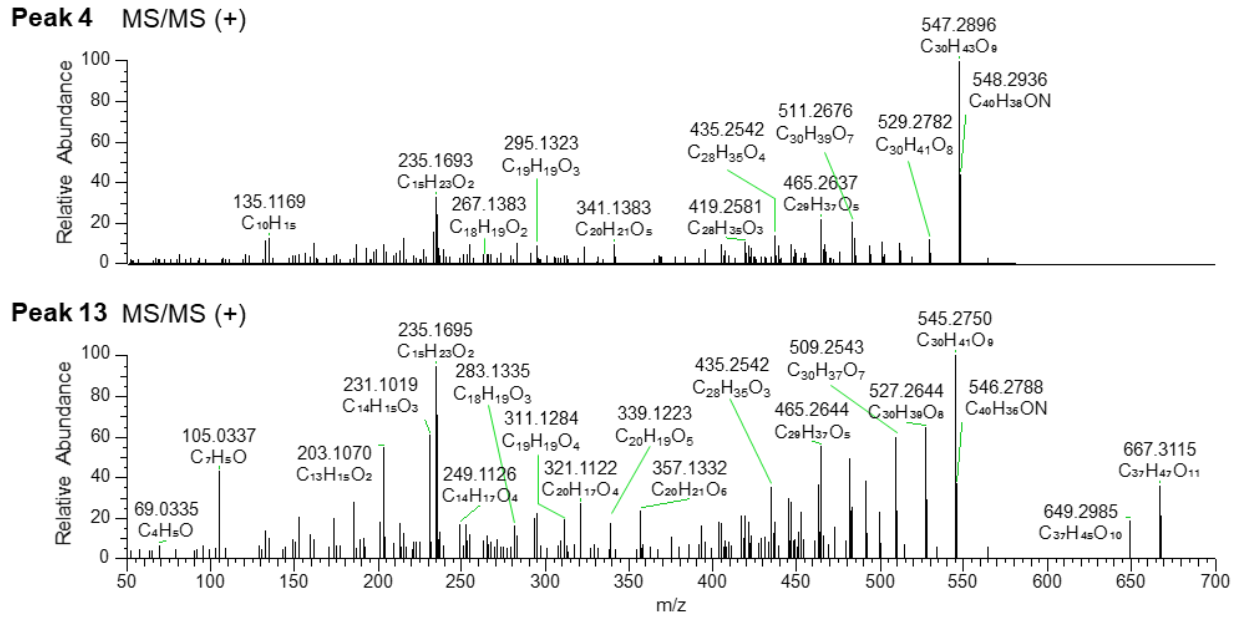


Figure S27. Product ion spectra of peaks **4** and **13** obtained from the protonated molecular ion peak.