

**“Bio-Inspired Enantioselective Total Syntheses of (–)-Viminalins A, B, H, I, N, and
Structural Reassignment of (–)-Viminalin M”**

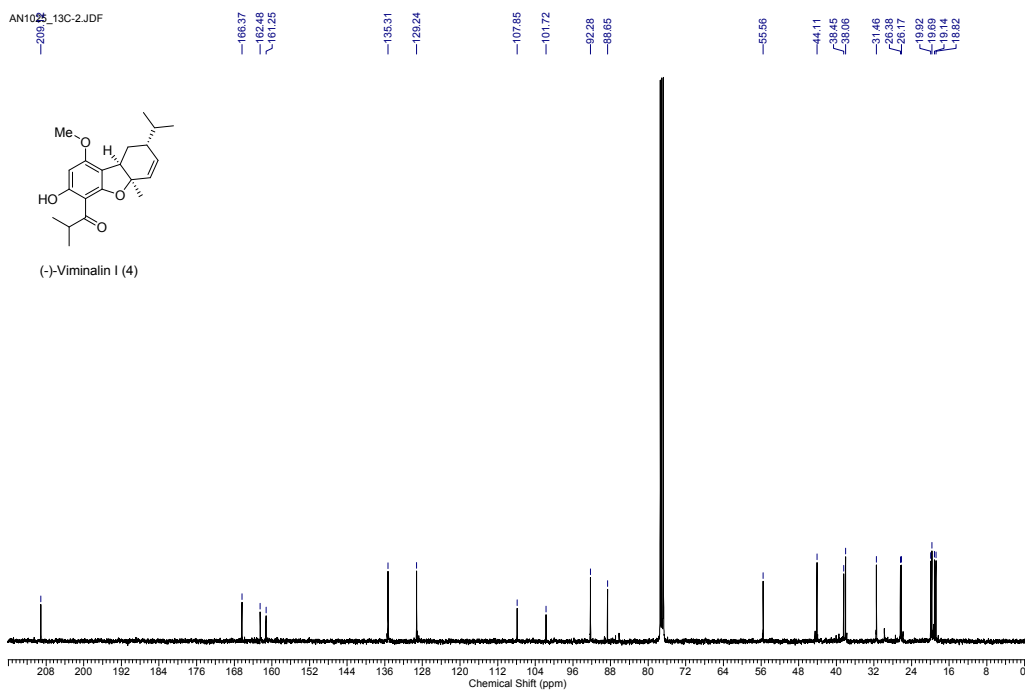
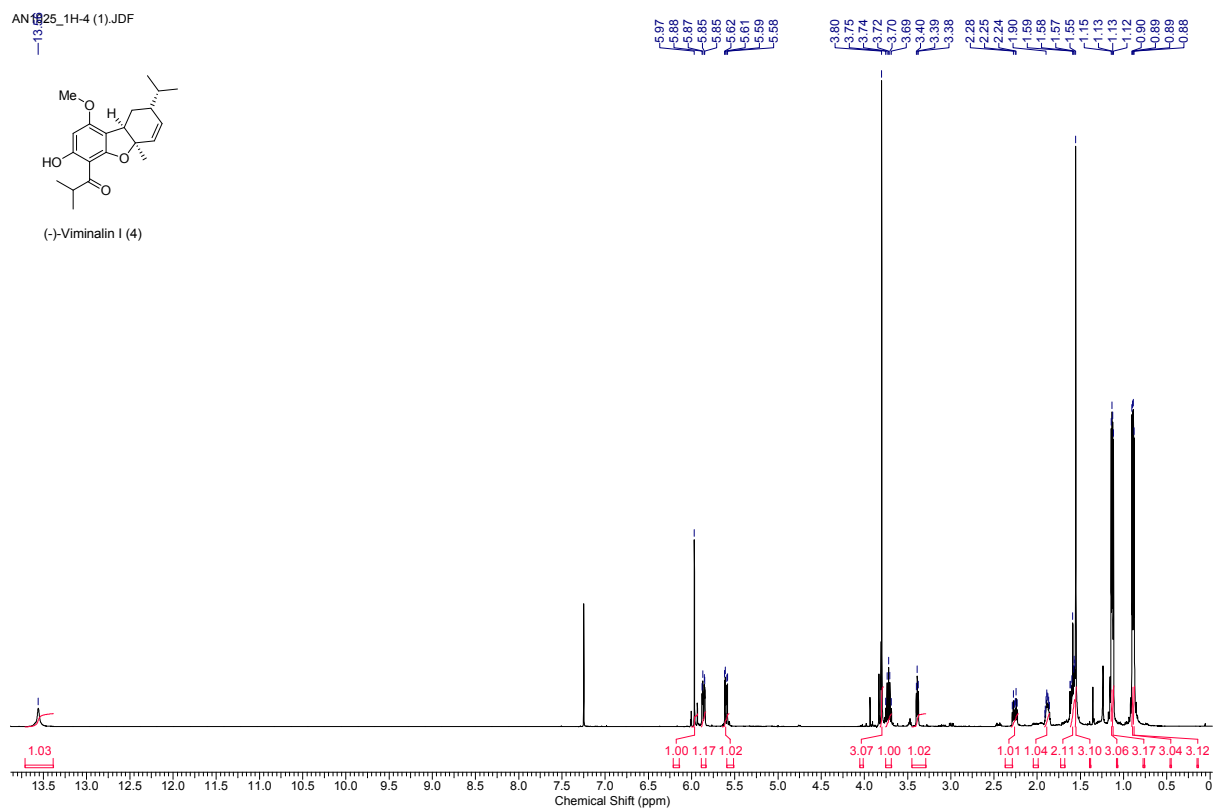
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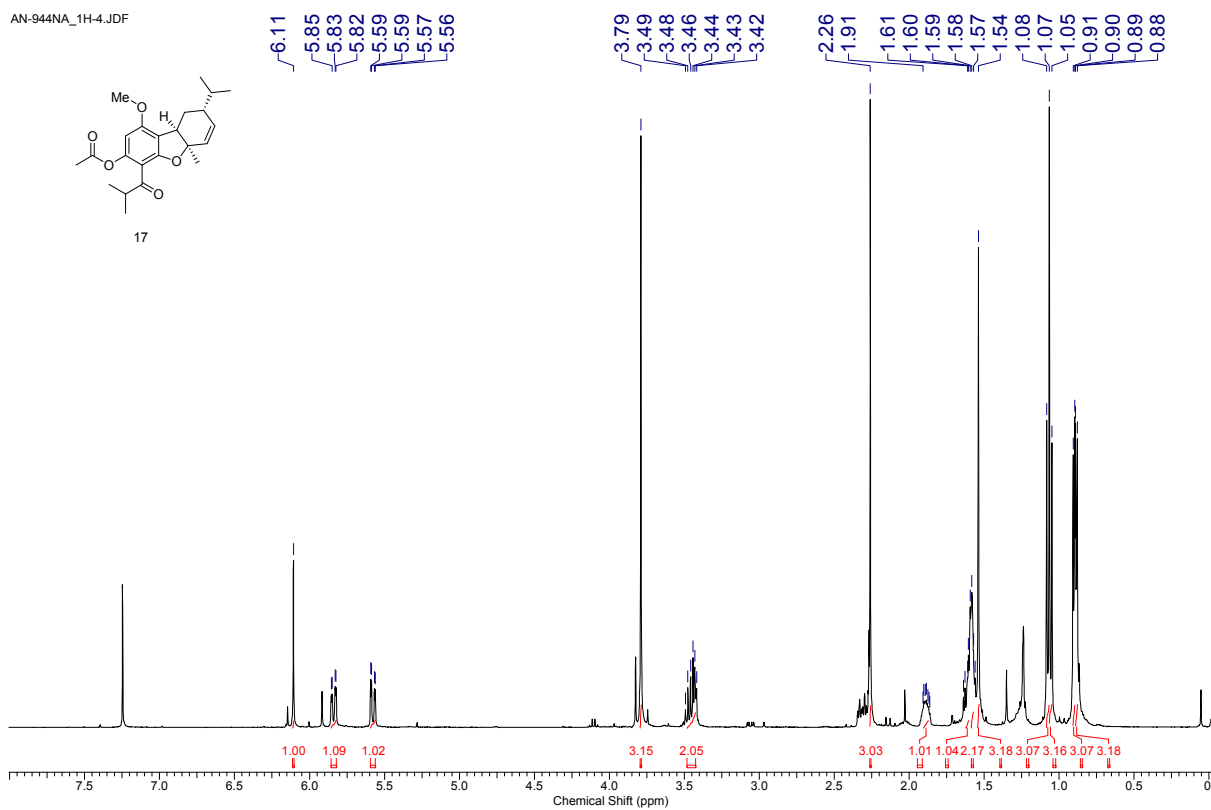
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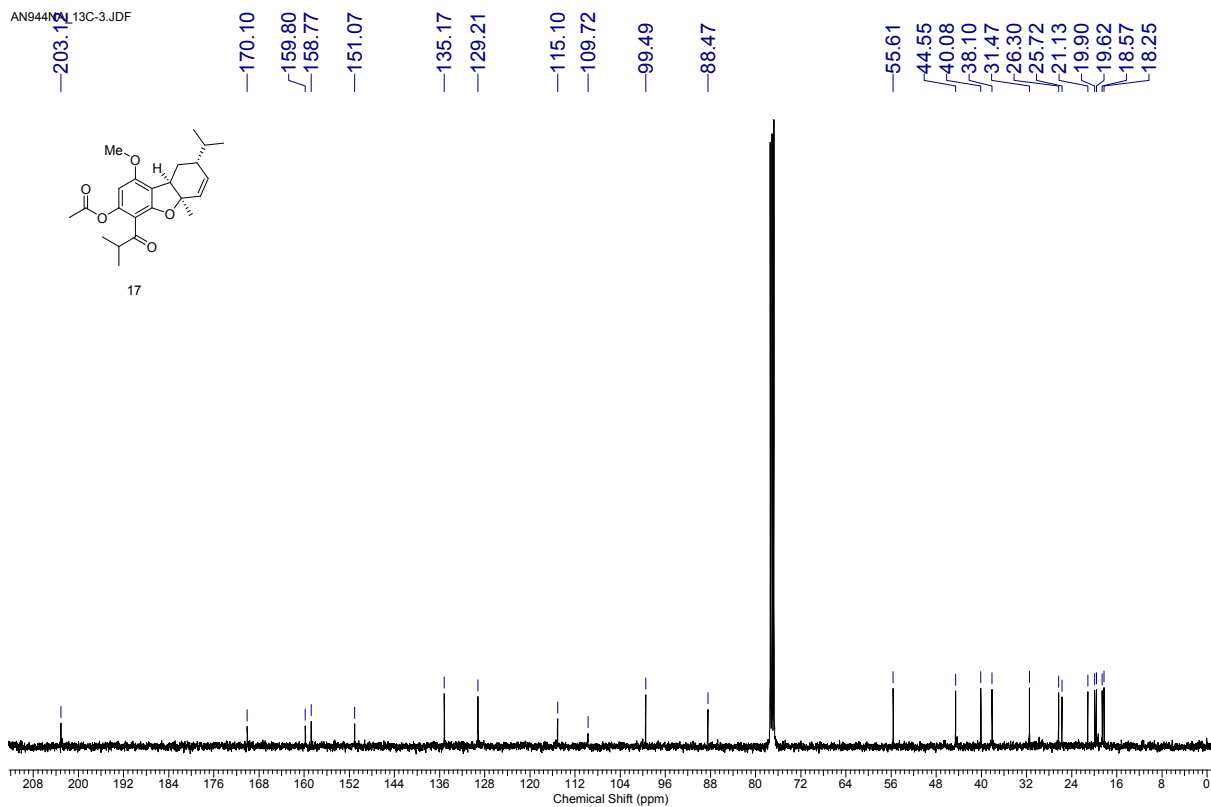
1. NMR Spectras:



AN-944NA_1H-4.JDF

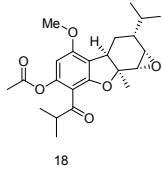
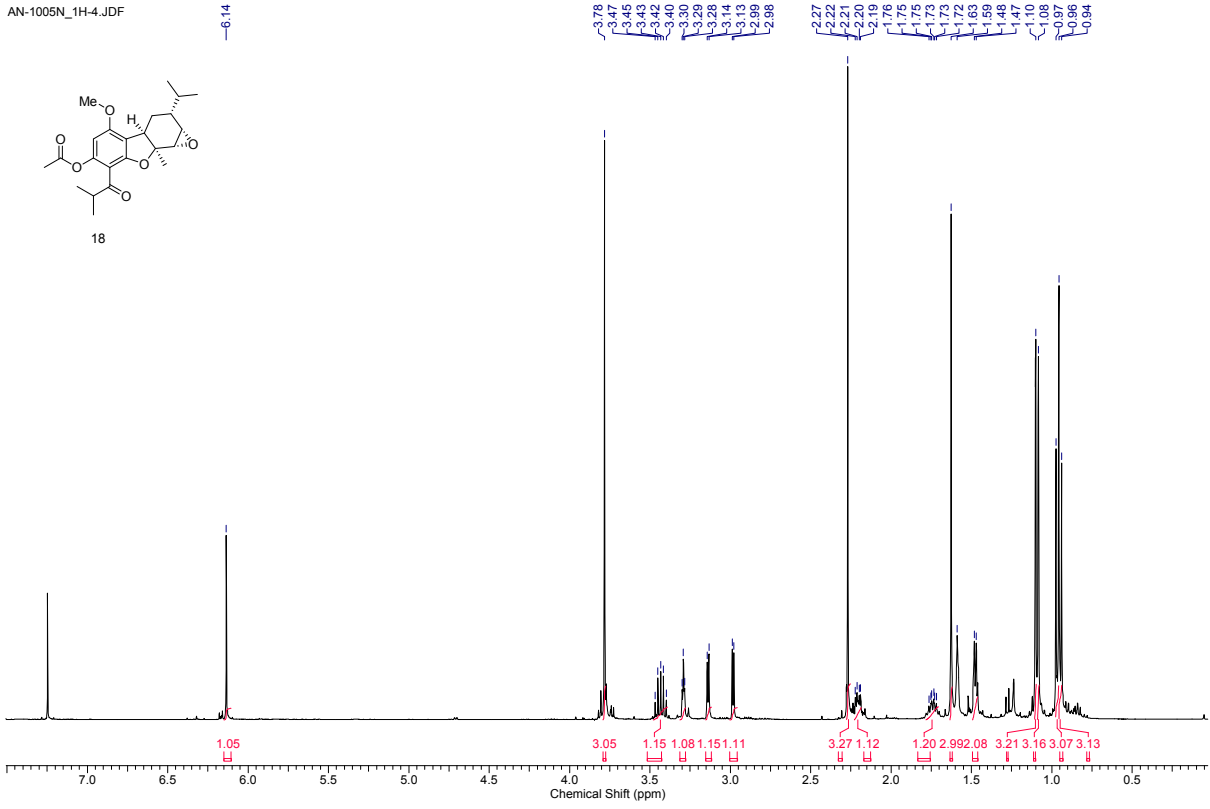


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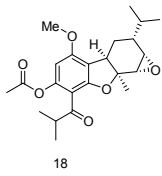
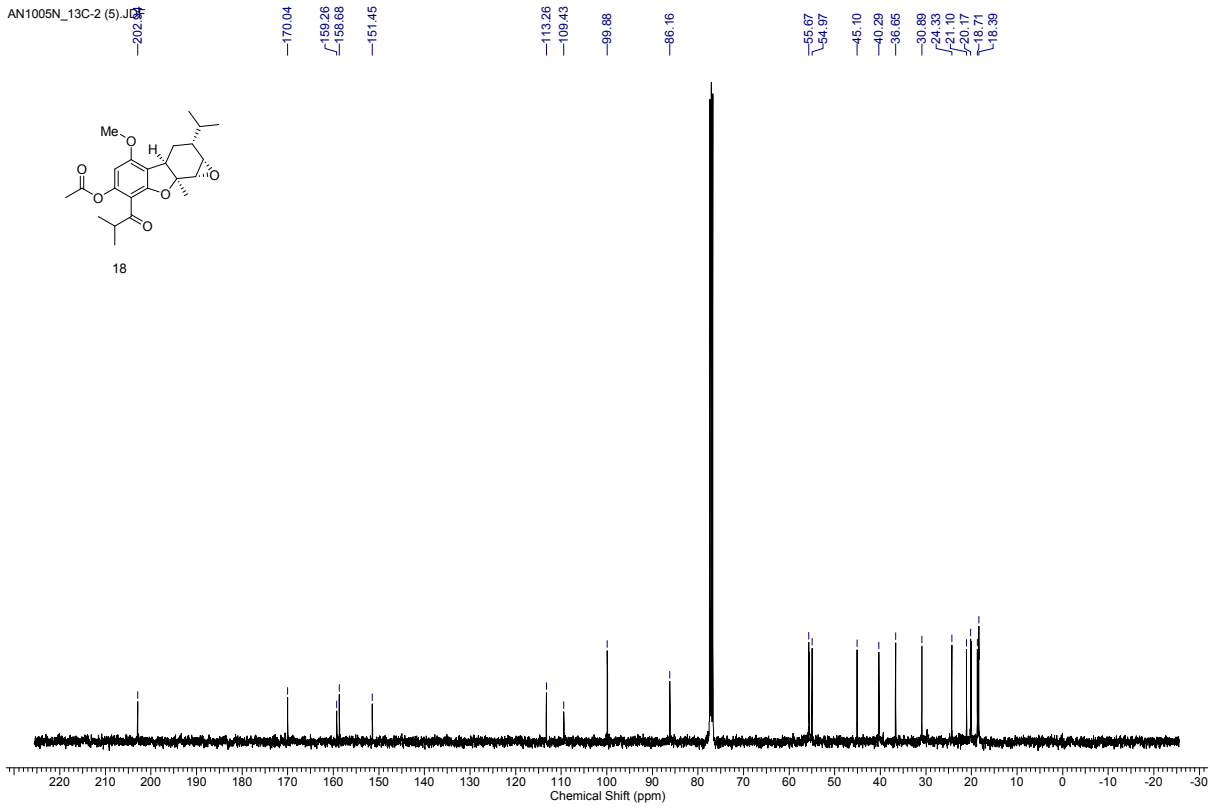
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-6.14

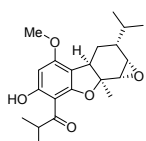


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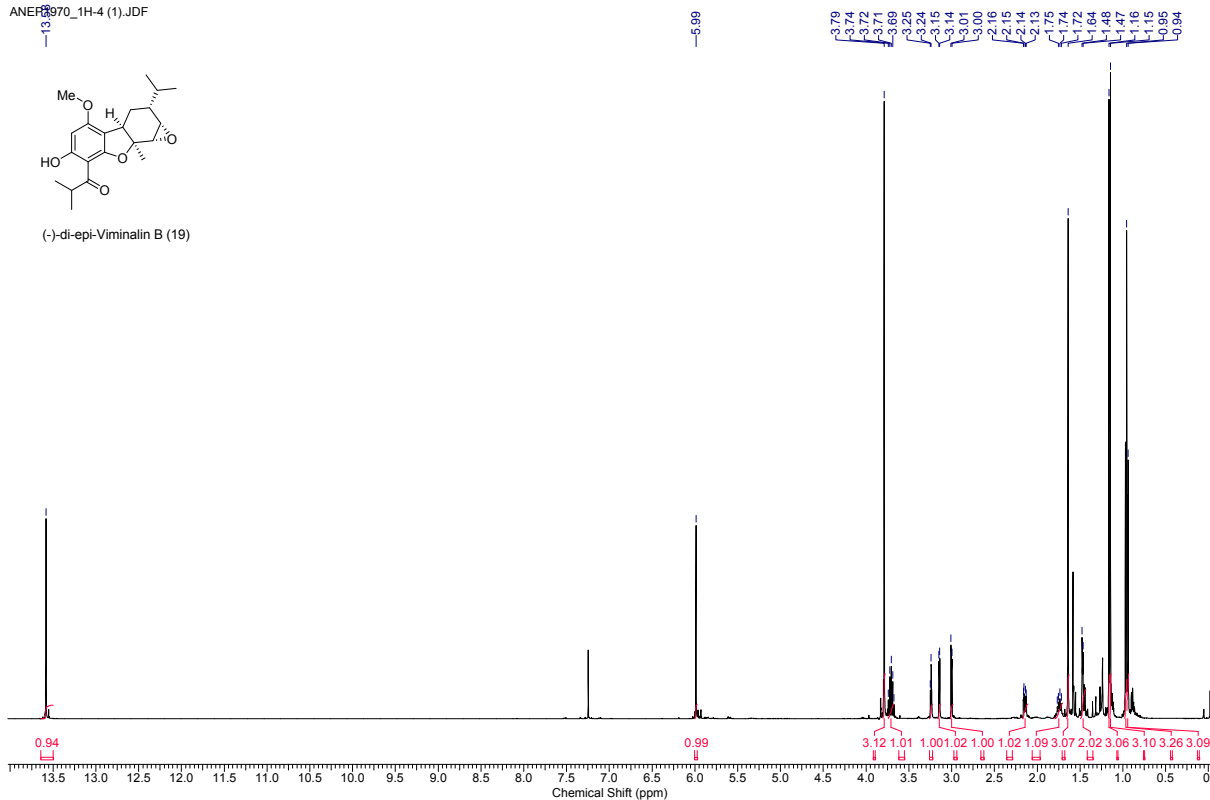
-202.86



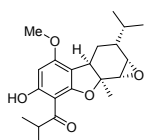
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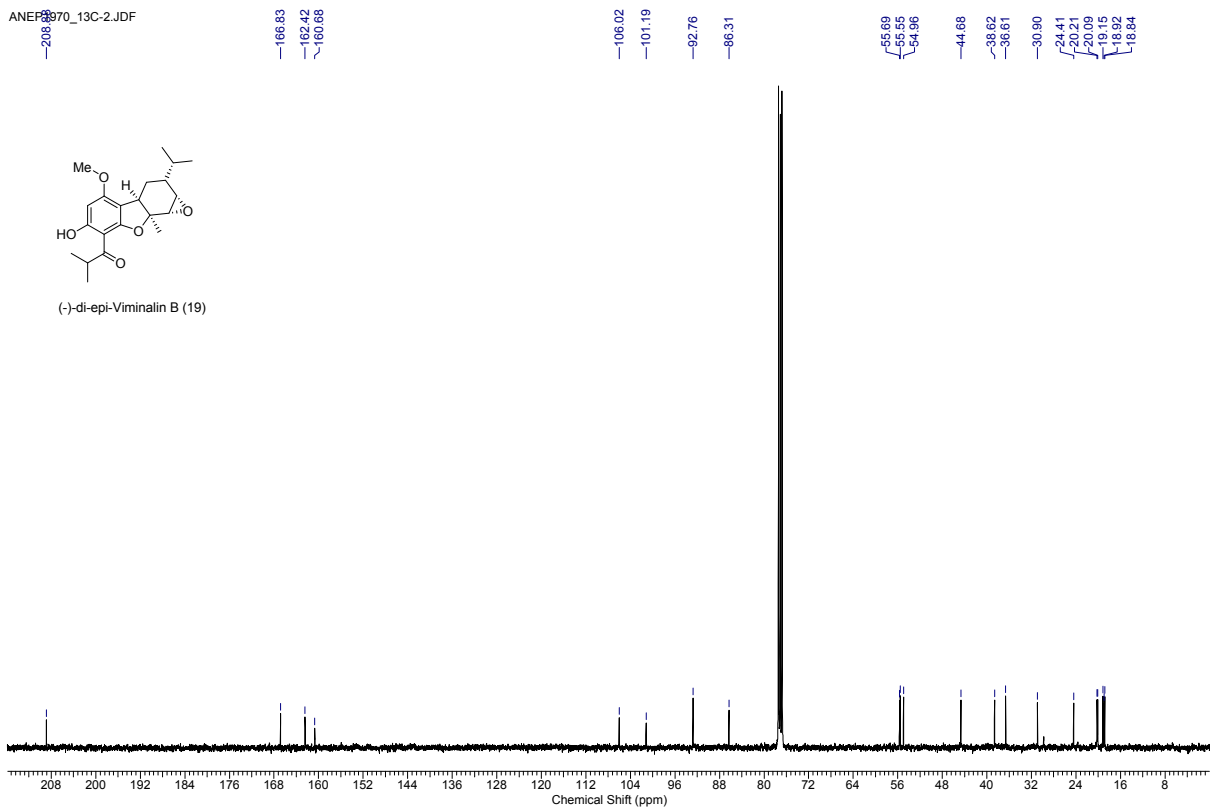
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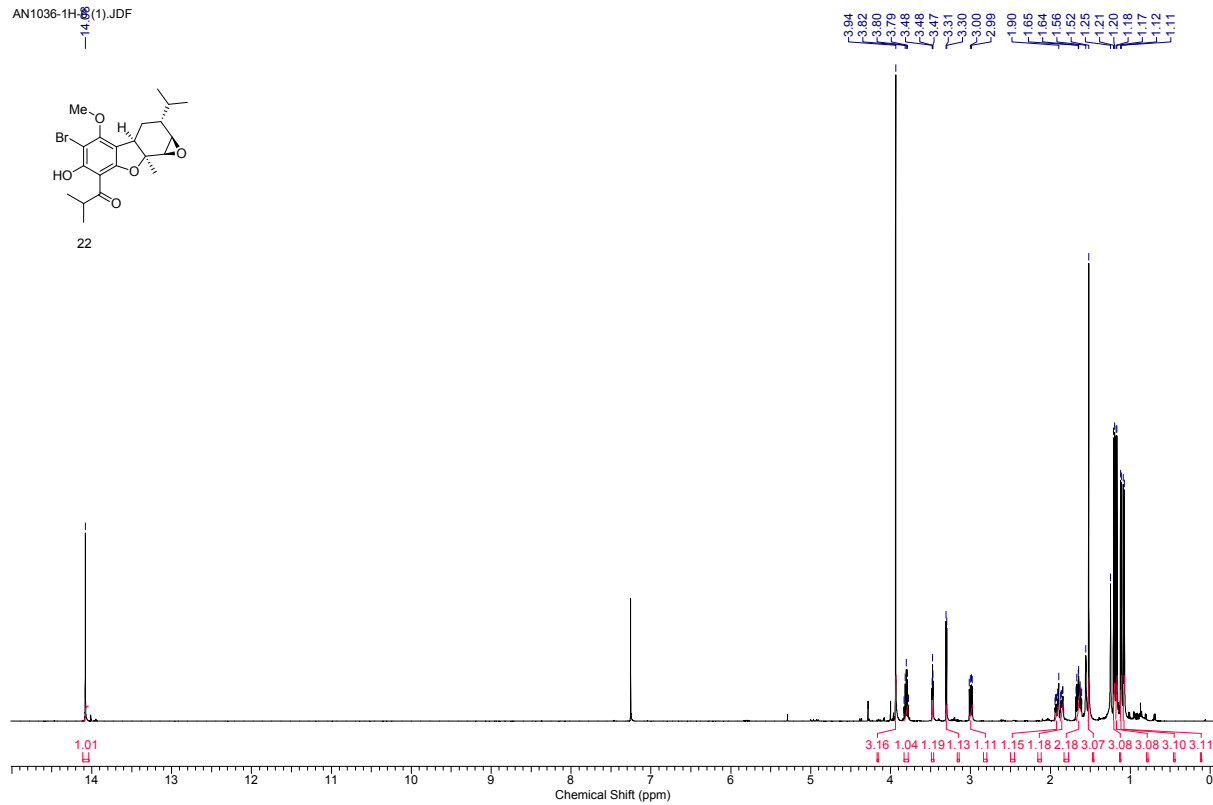
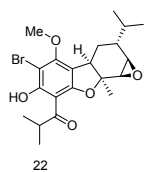
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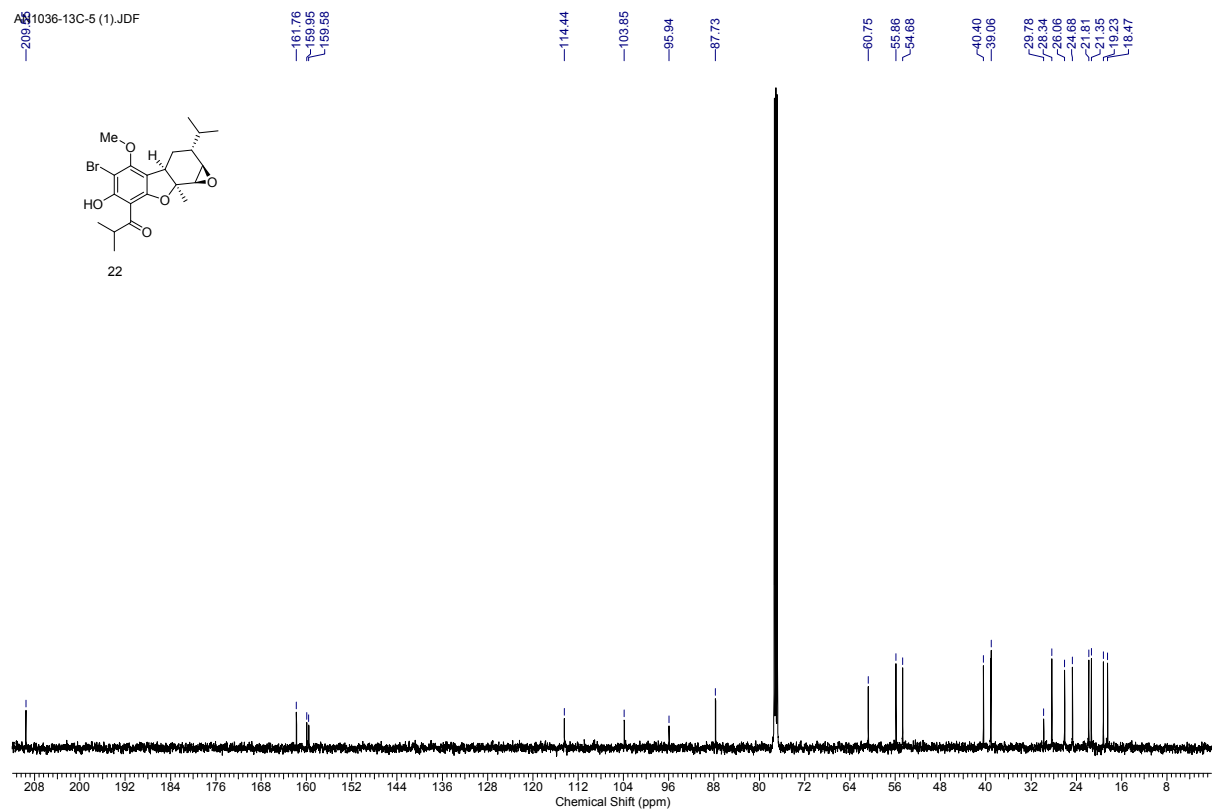
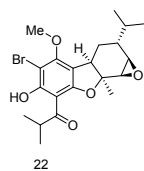
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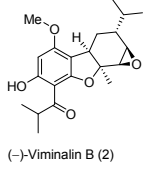
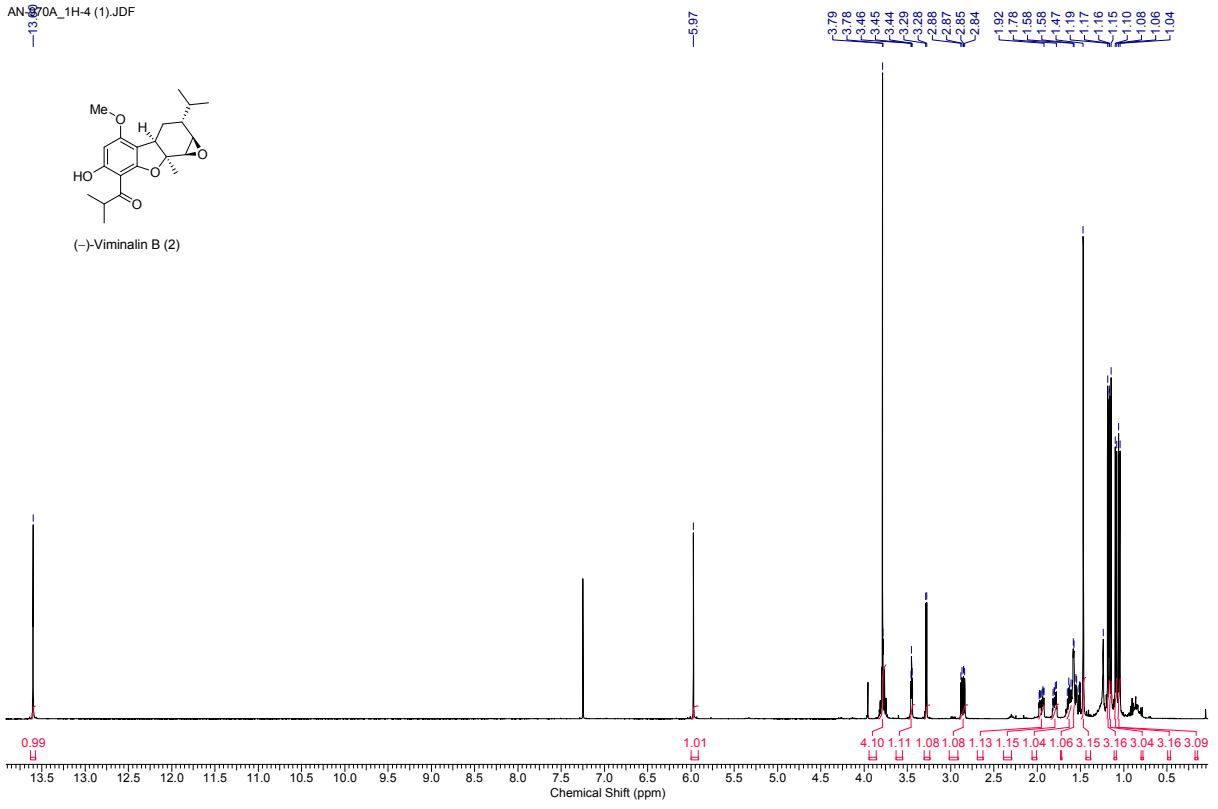
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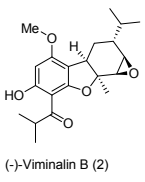
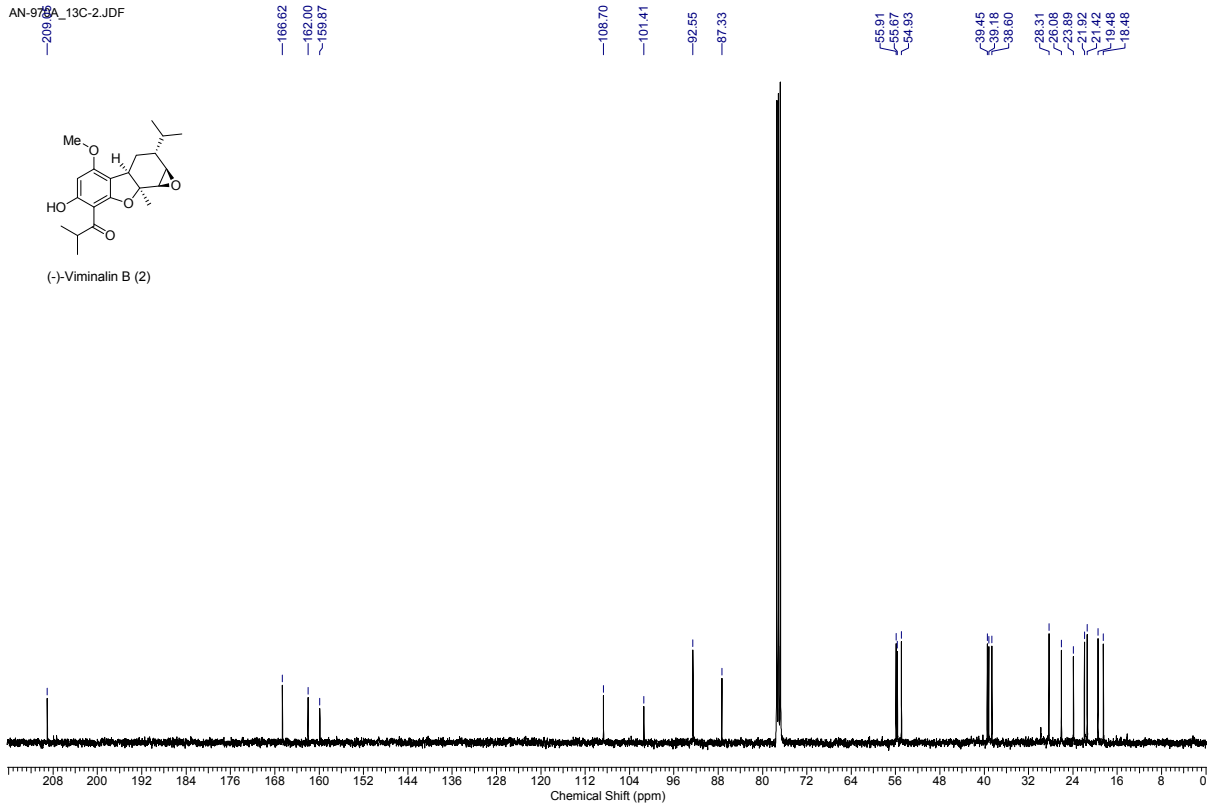
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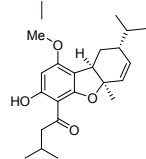
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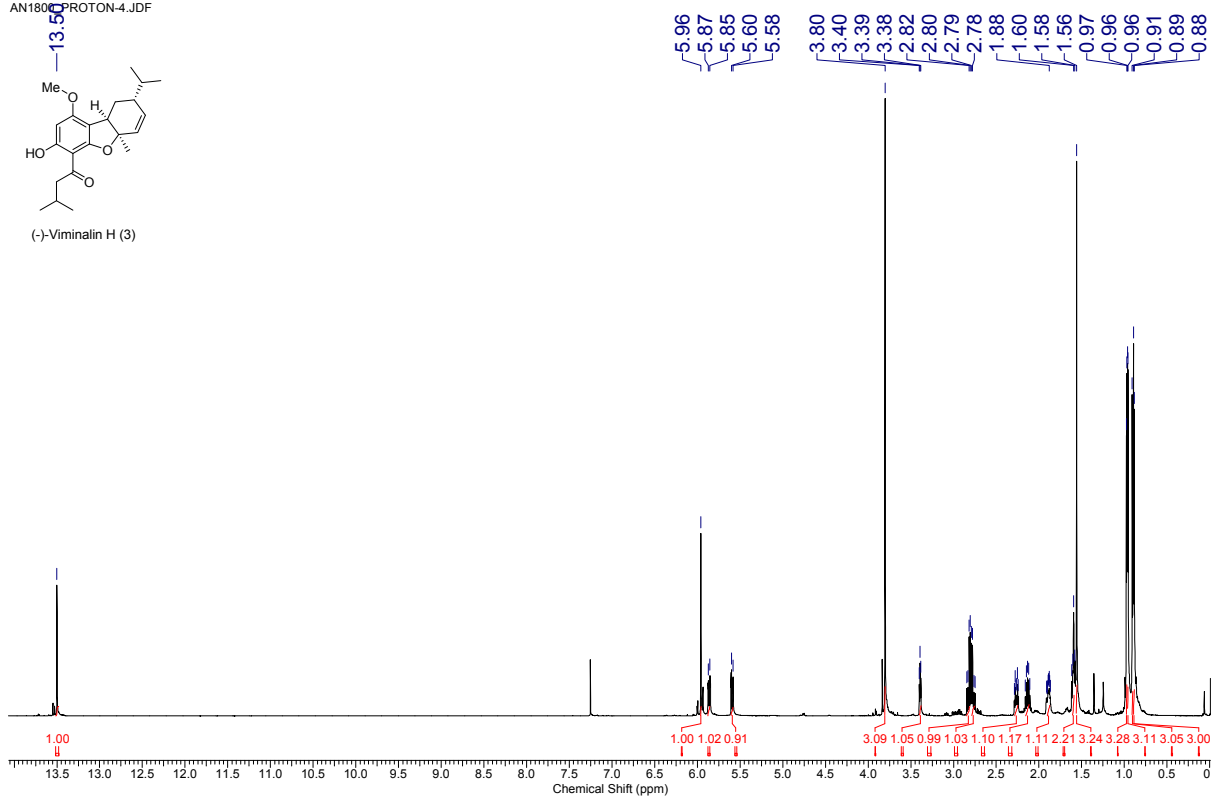
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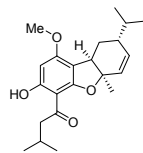
AN1800 PROTON-4.JDF



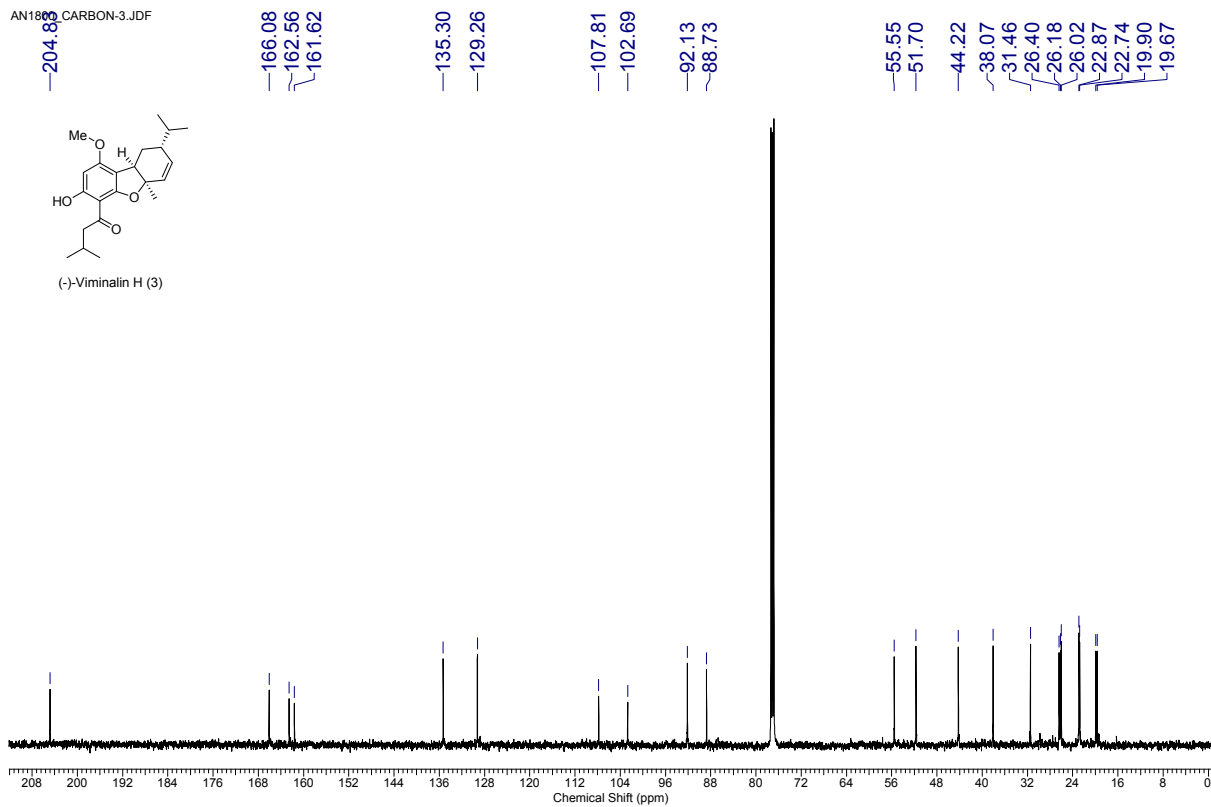
(-)-Viminalin H (3)



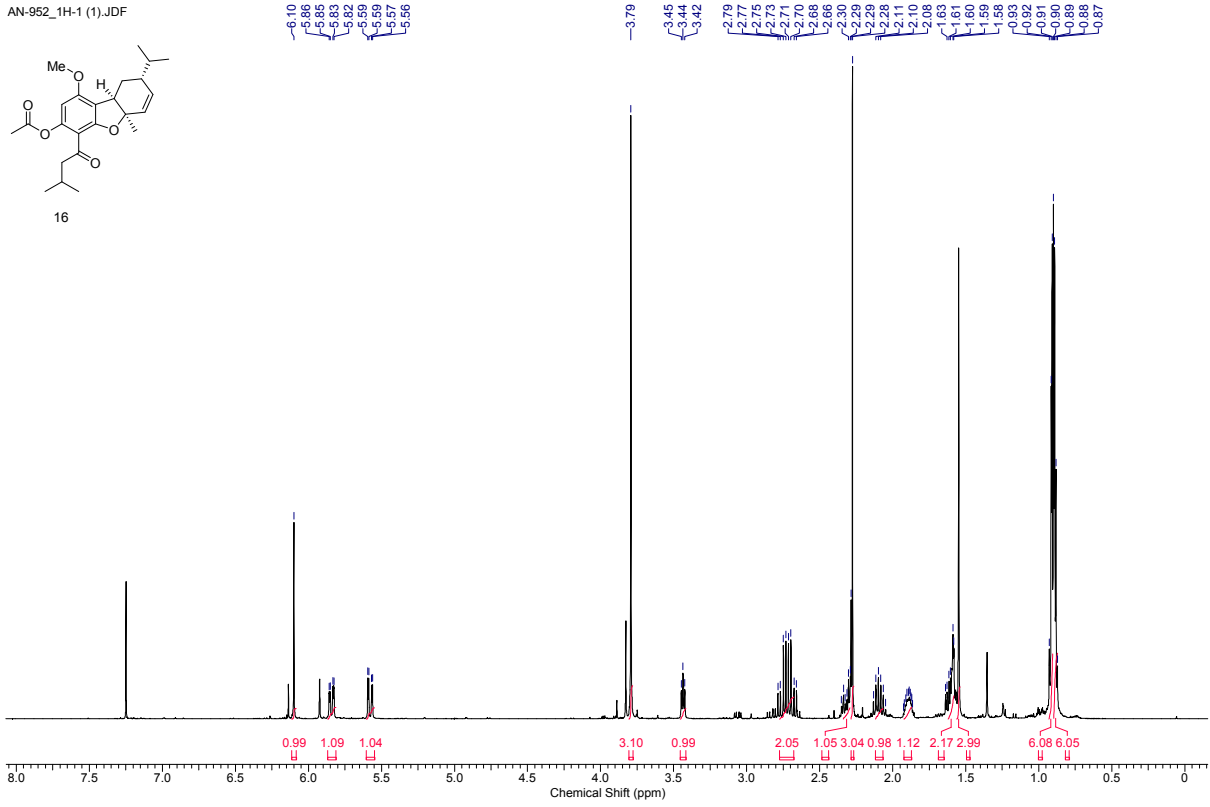
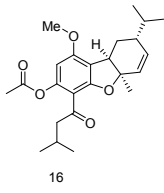
AN1800 CARBON-3.JDF



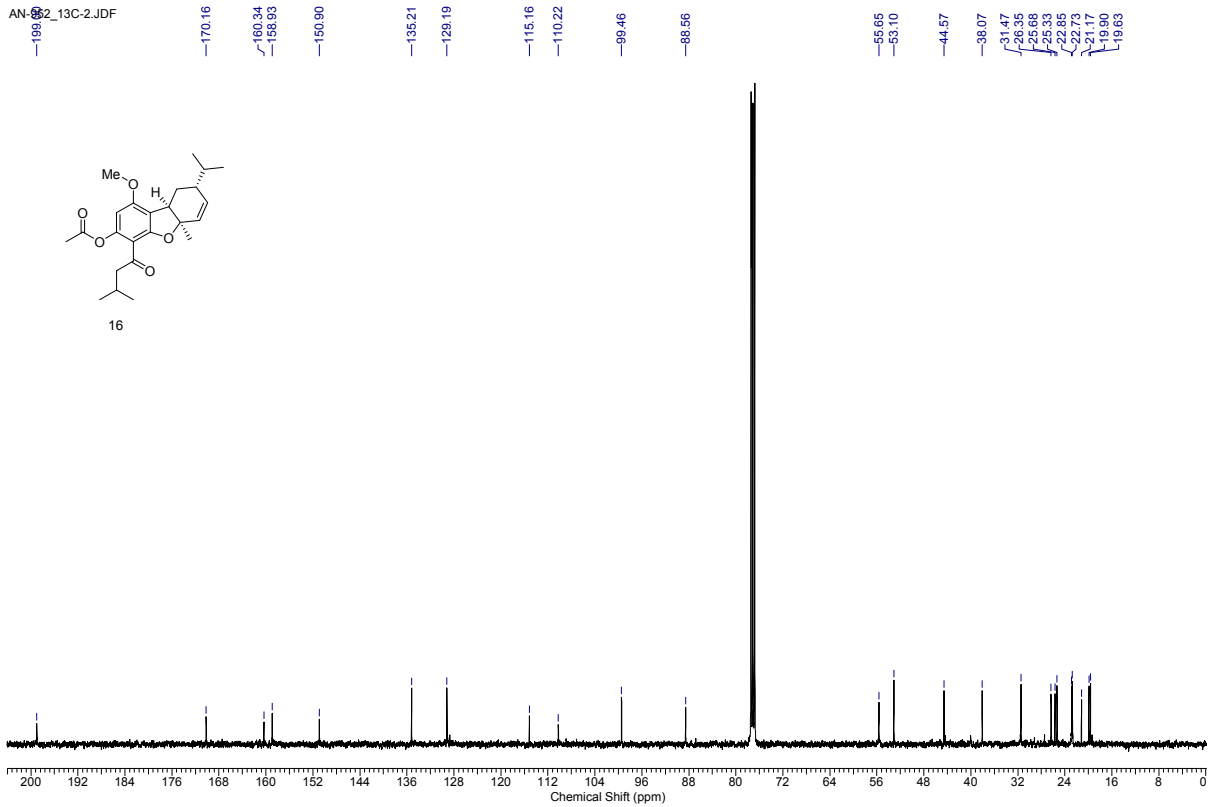
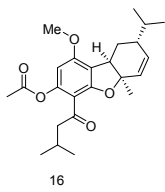
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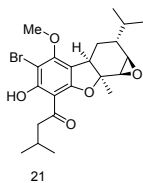
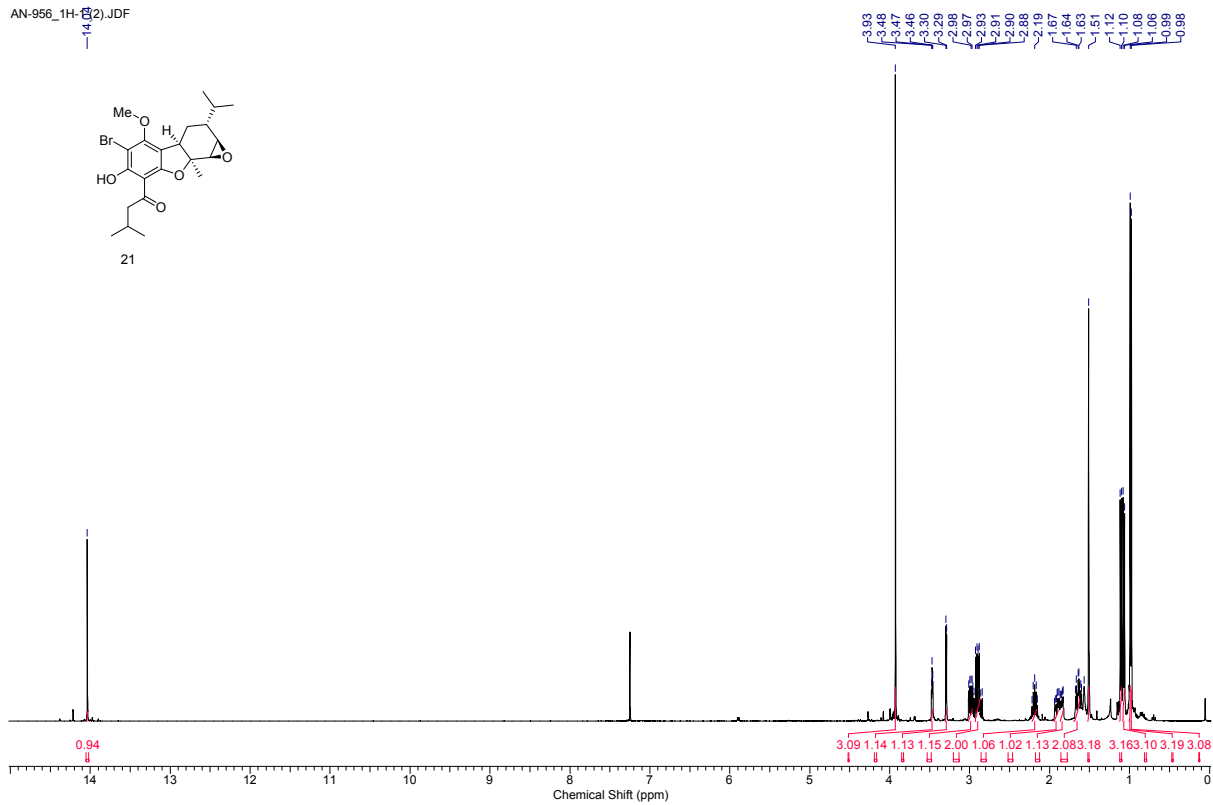
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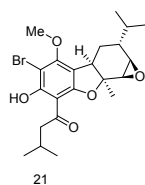
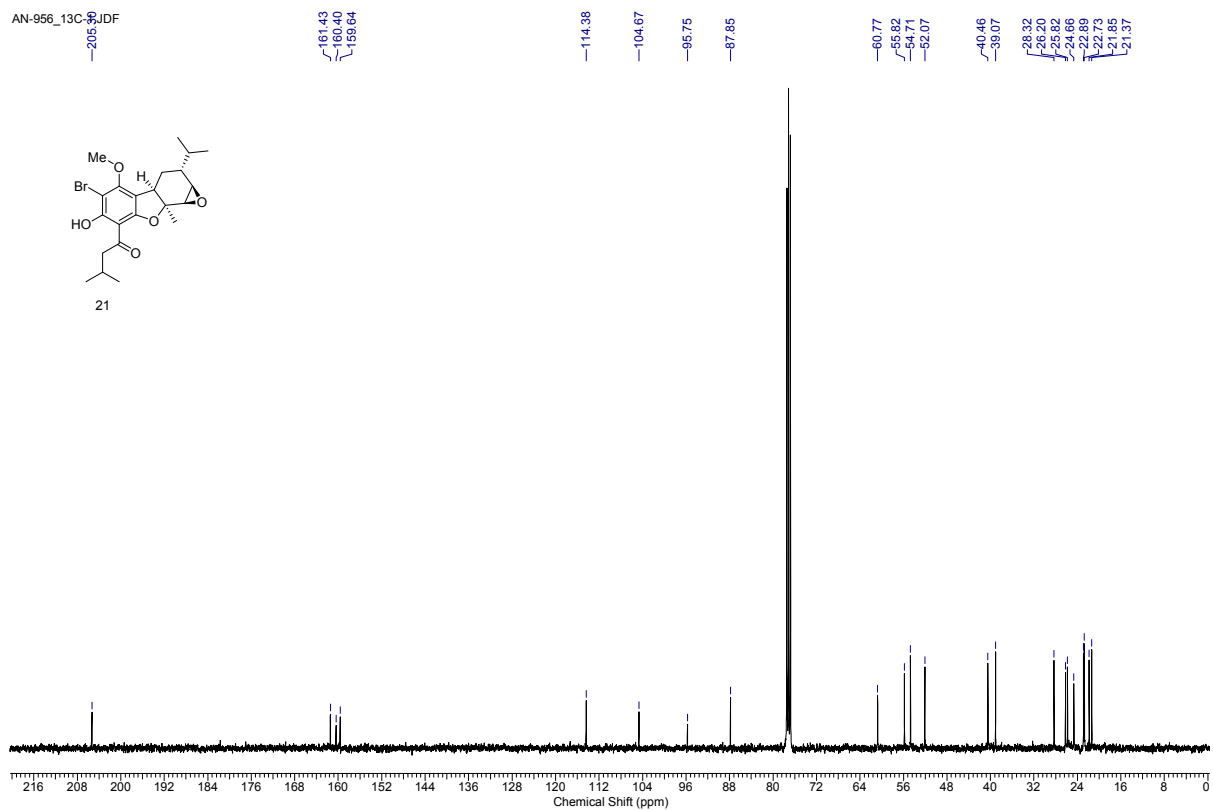
AN-952_13C-2.JDF



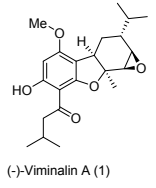
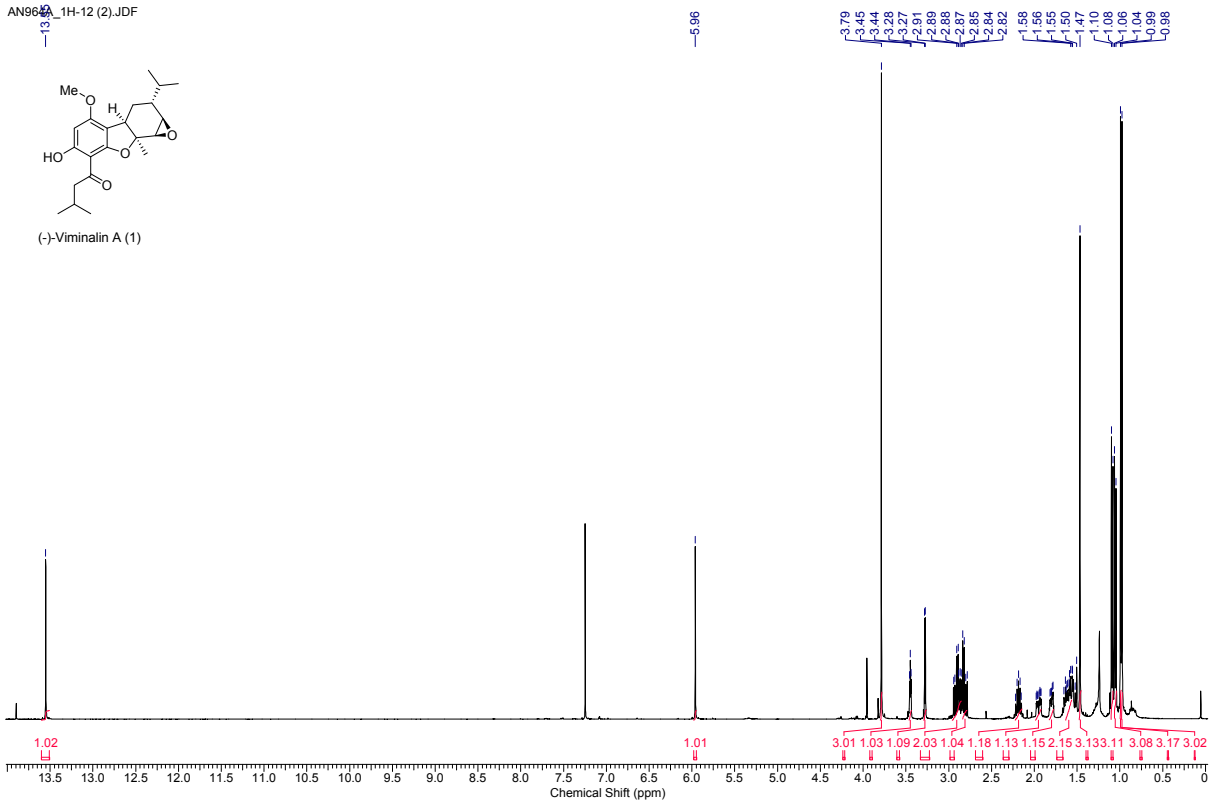
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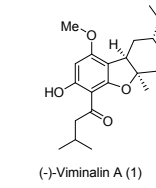
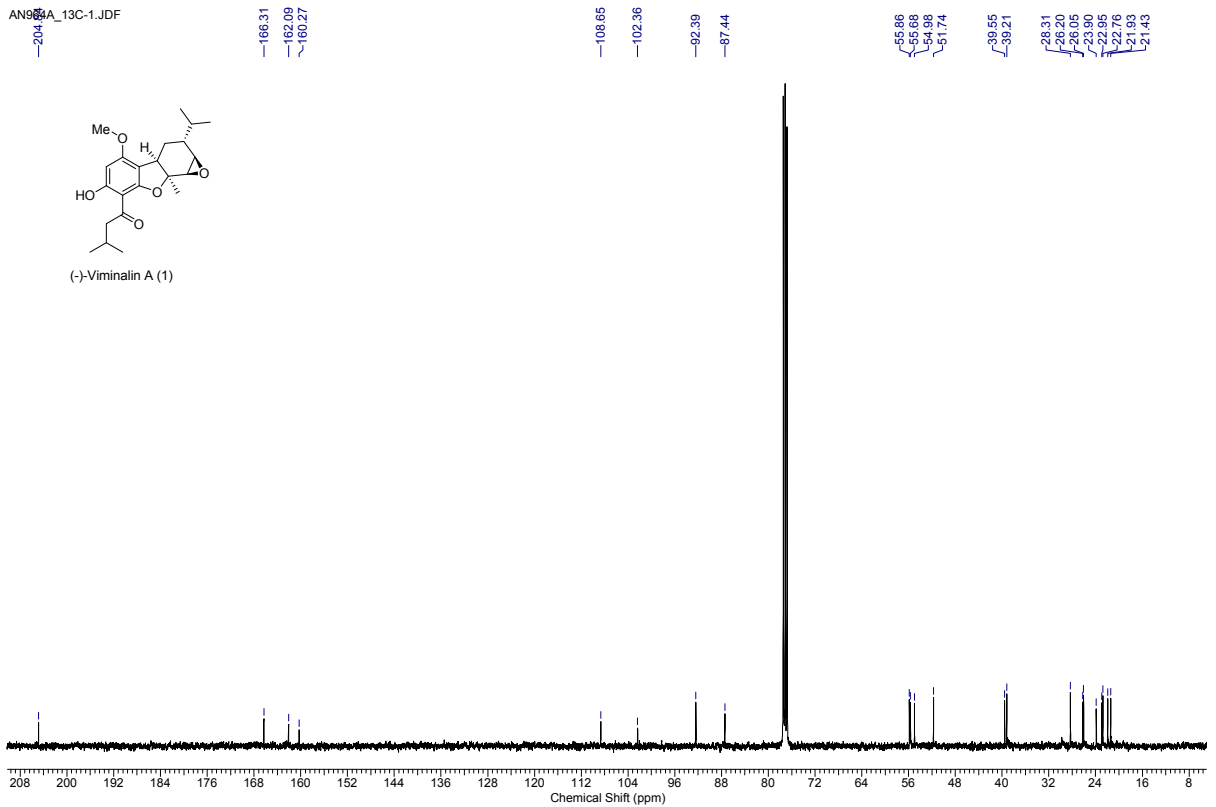
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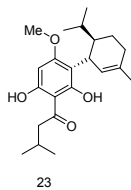
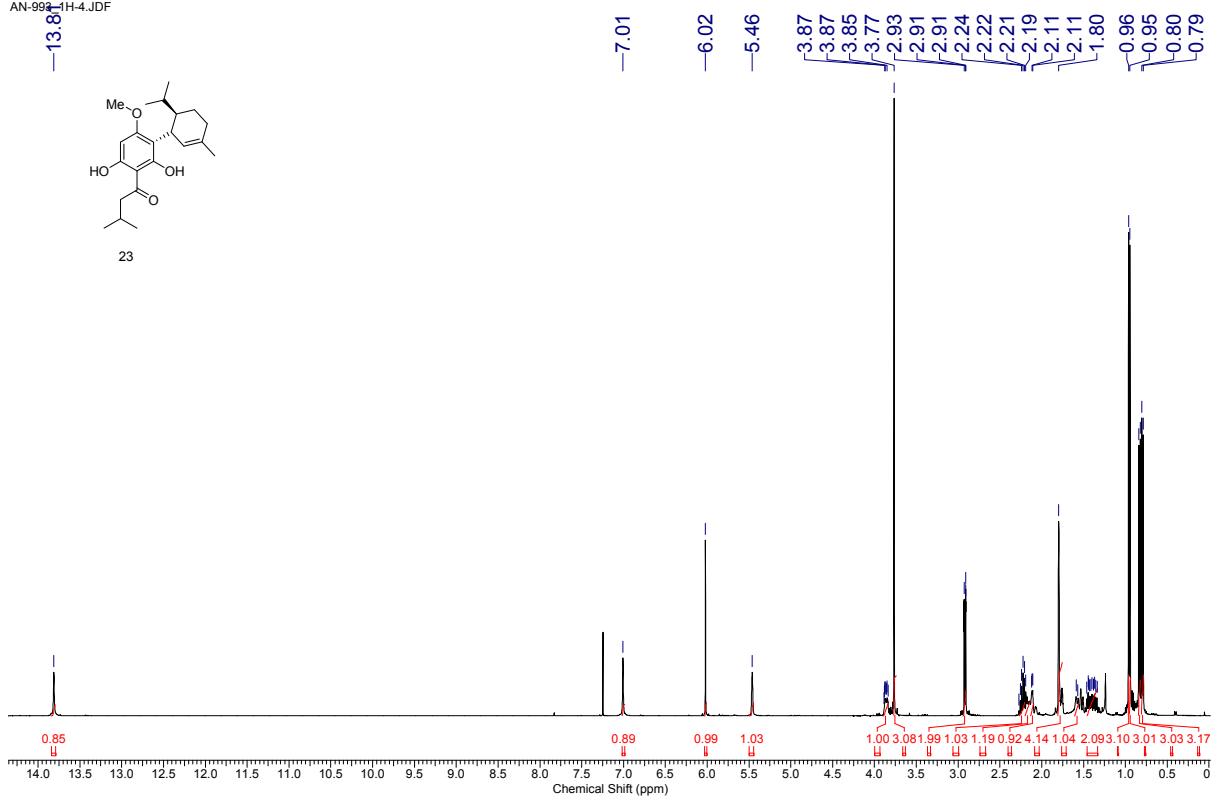
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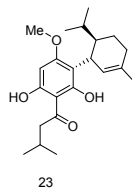
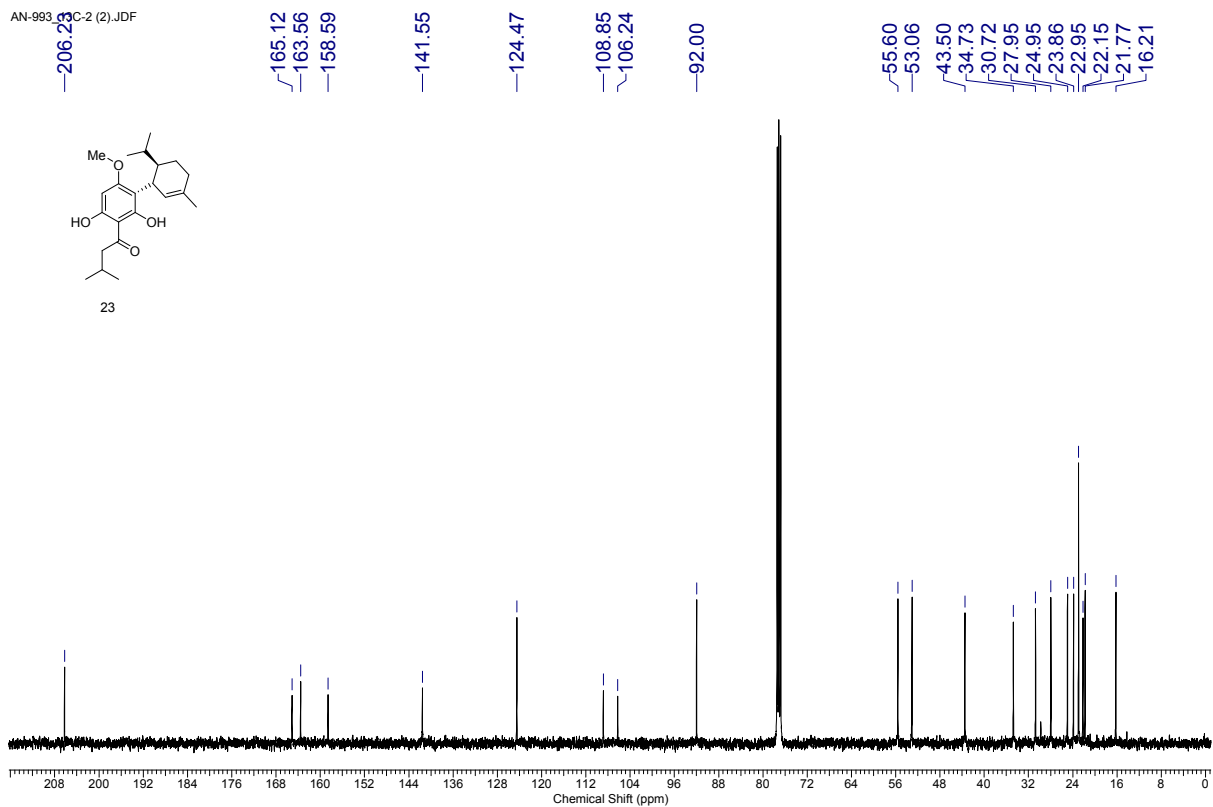
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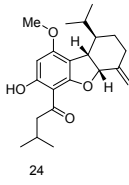
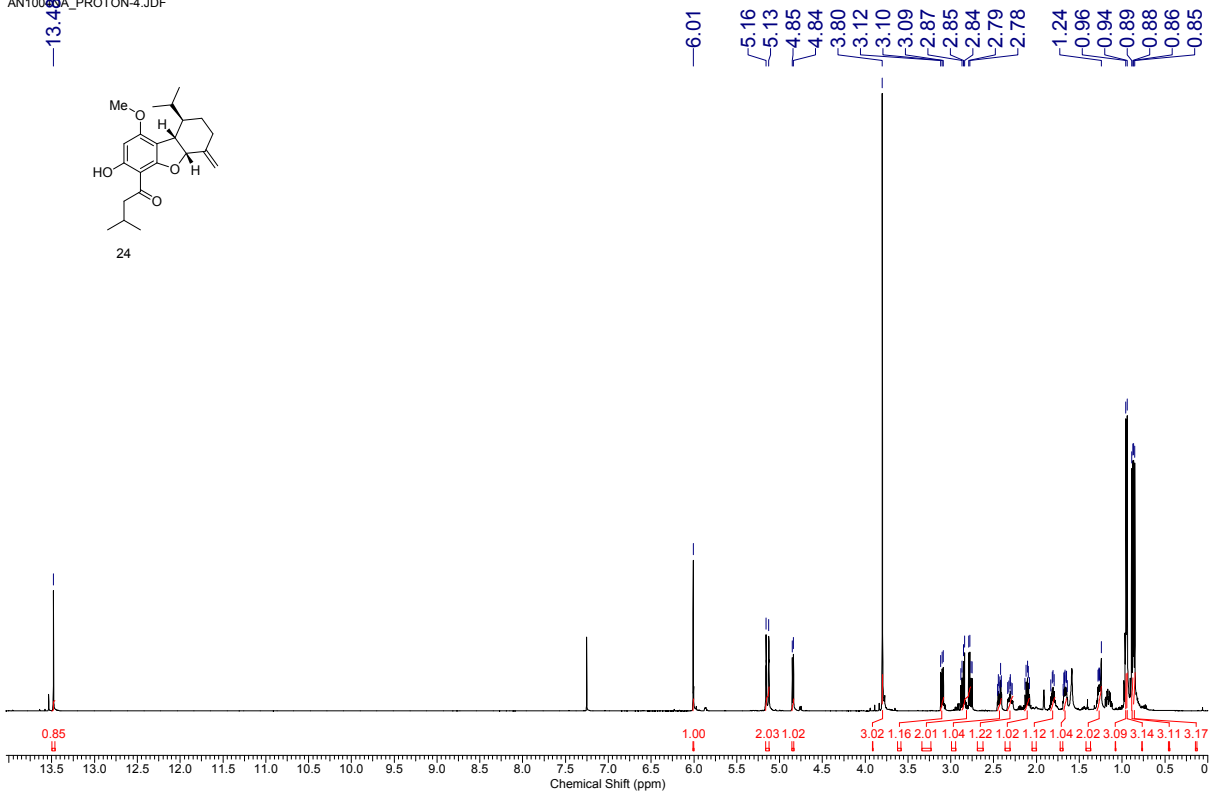
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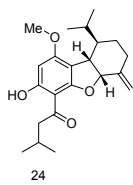
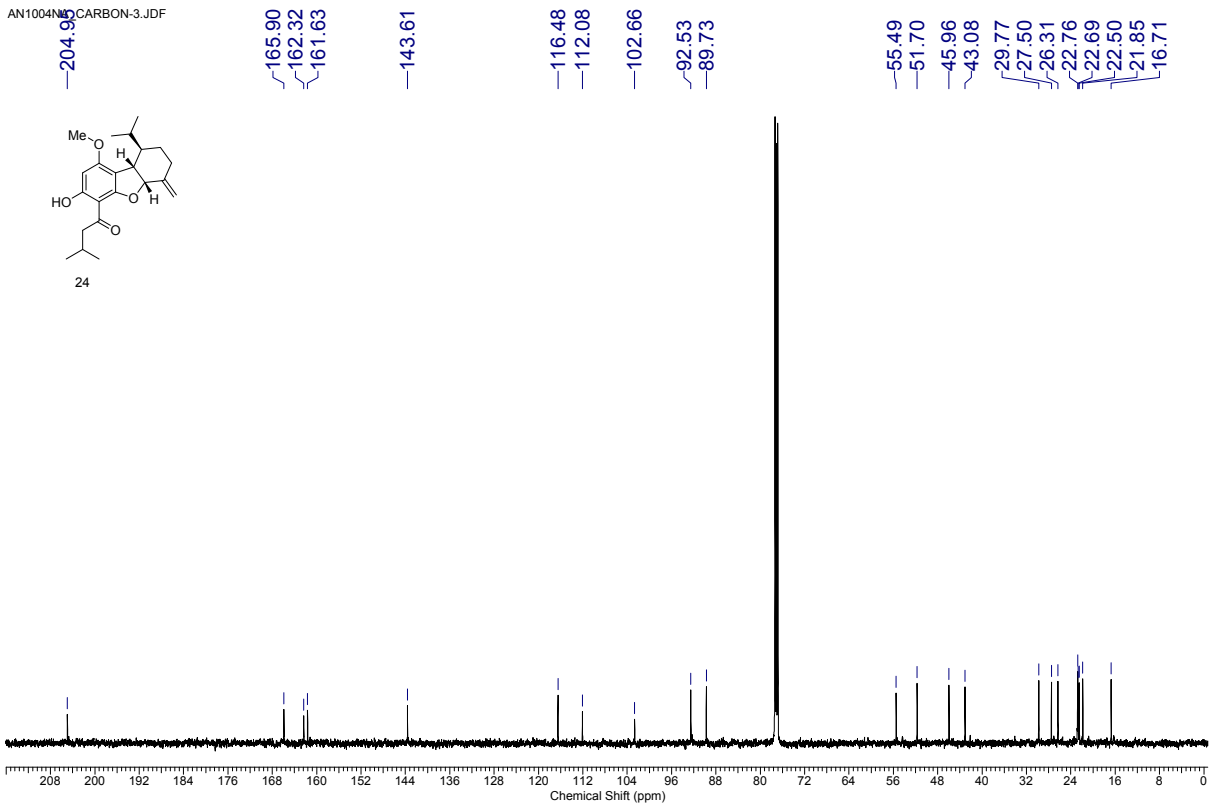
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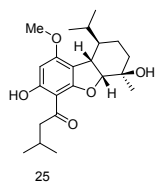
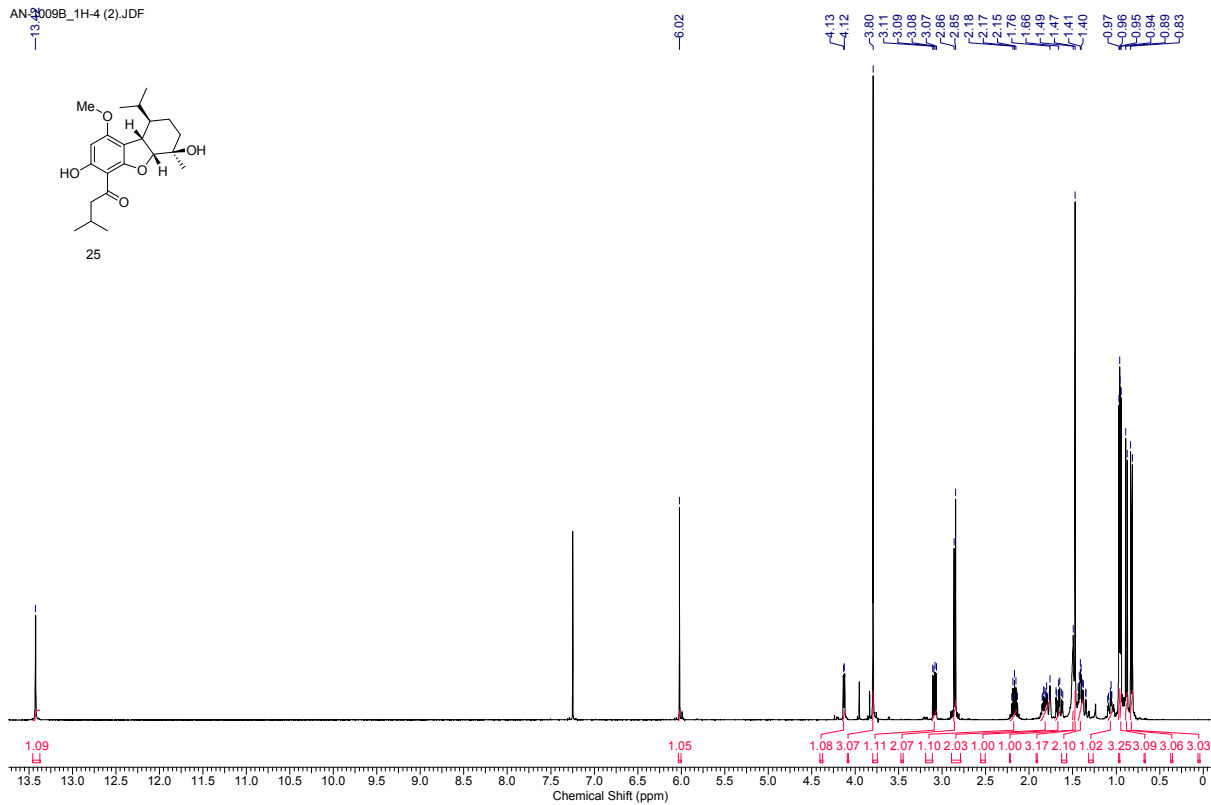
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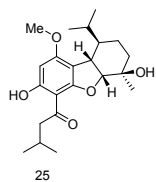
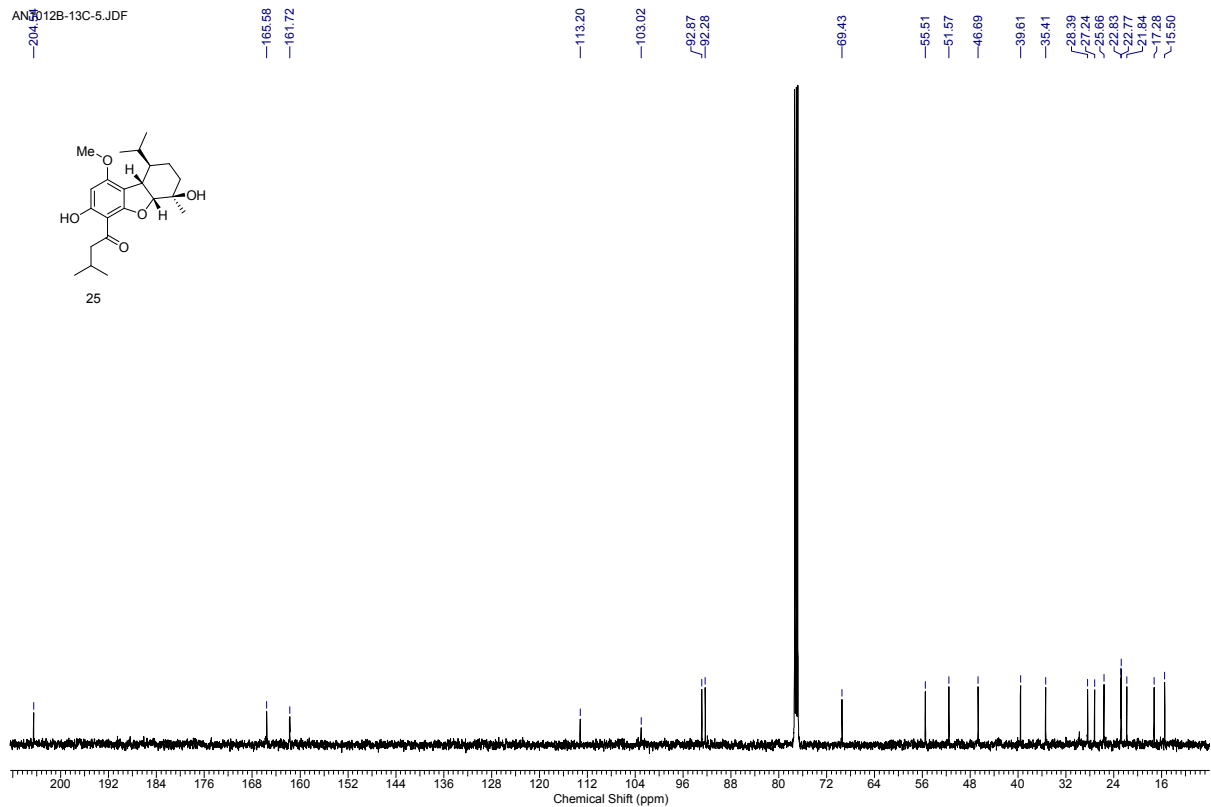
AN1004A_CARBON-3.JDF



AN3009B_1H-4 (2).JDF



AN3012B-13C-5.JDF



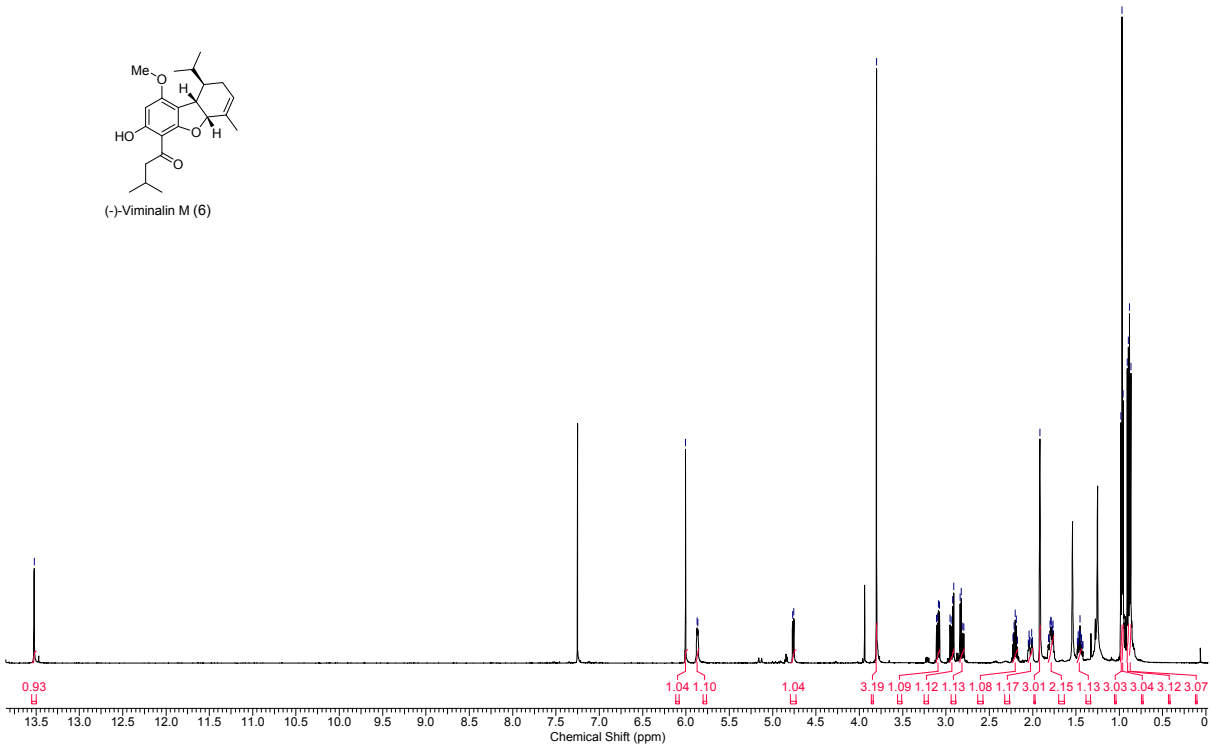
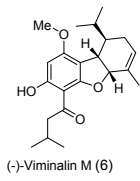
AN 131-1H-4 (1).JDF

13.88

6.01
5.87
5.86

4.77
4.76

3.80
3.10
3.09
3.07
2.95
2.92
2.84
2.82
2.20
2.19
1.92
1.79
1.46
0.98
0.97
0.95
0.91
0.88
0.87



AN 131-13C-5 (2).JDF

204

165.97
162.46
162.34

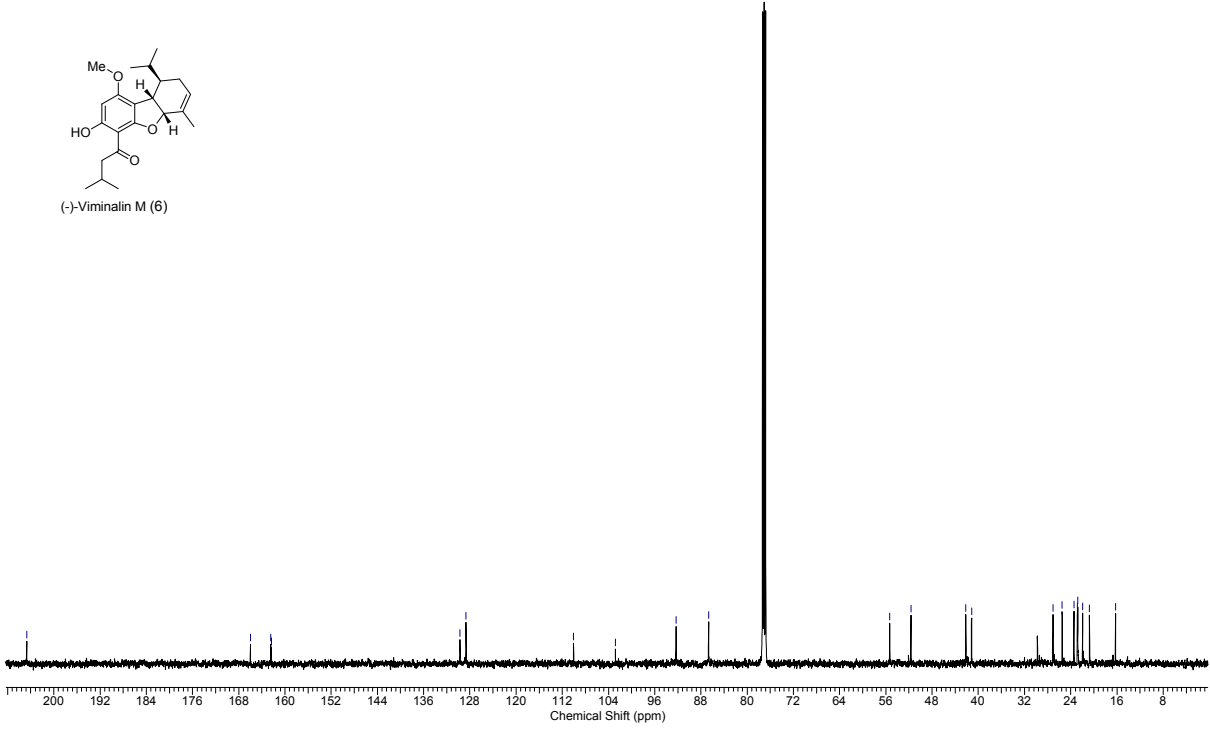
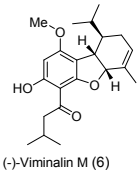
128.71
128.67

110.04
102.81

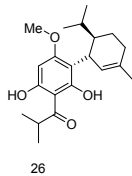
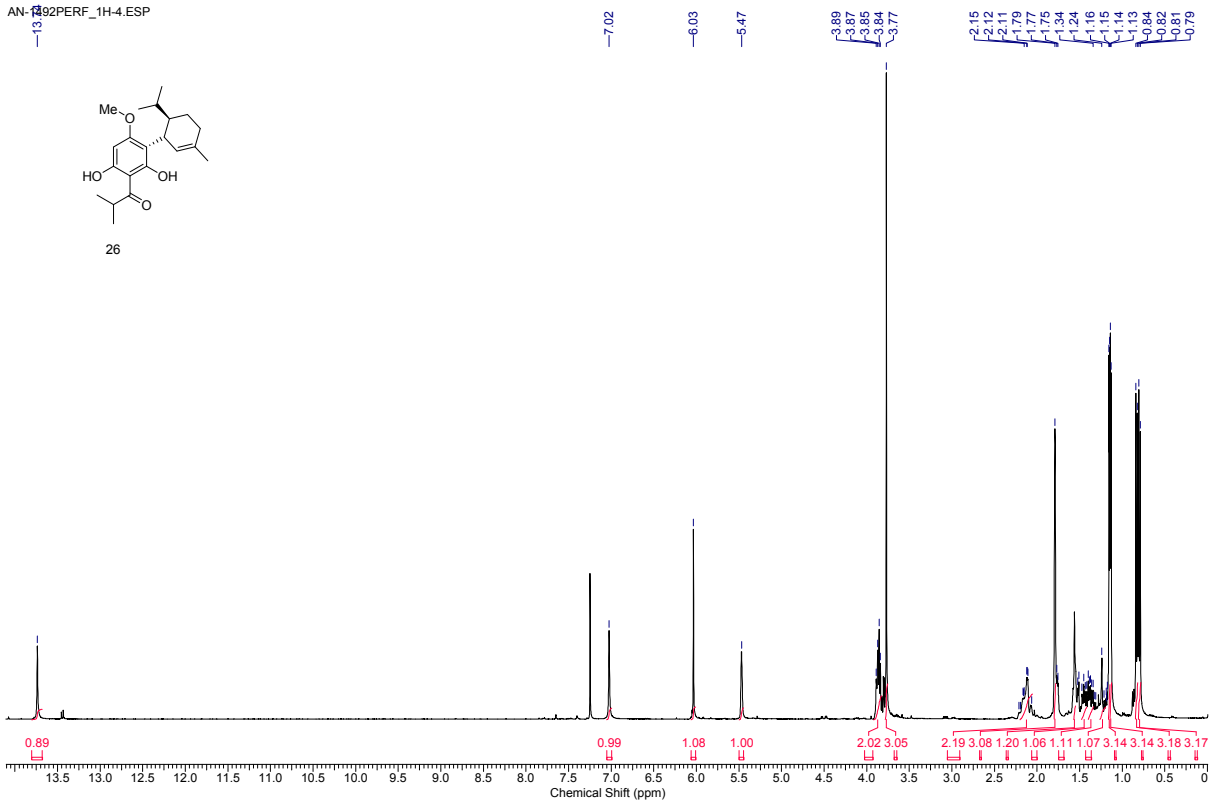
92.30
86.69

55.34
51.66

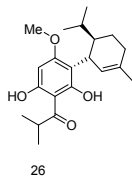
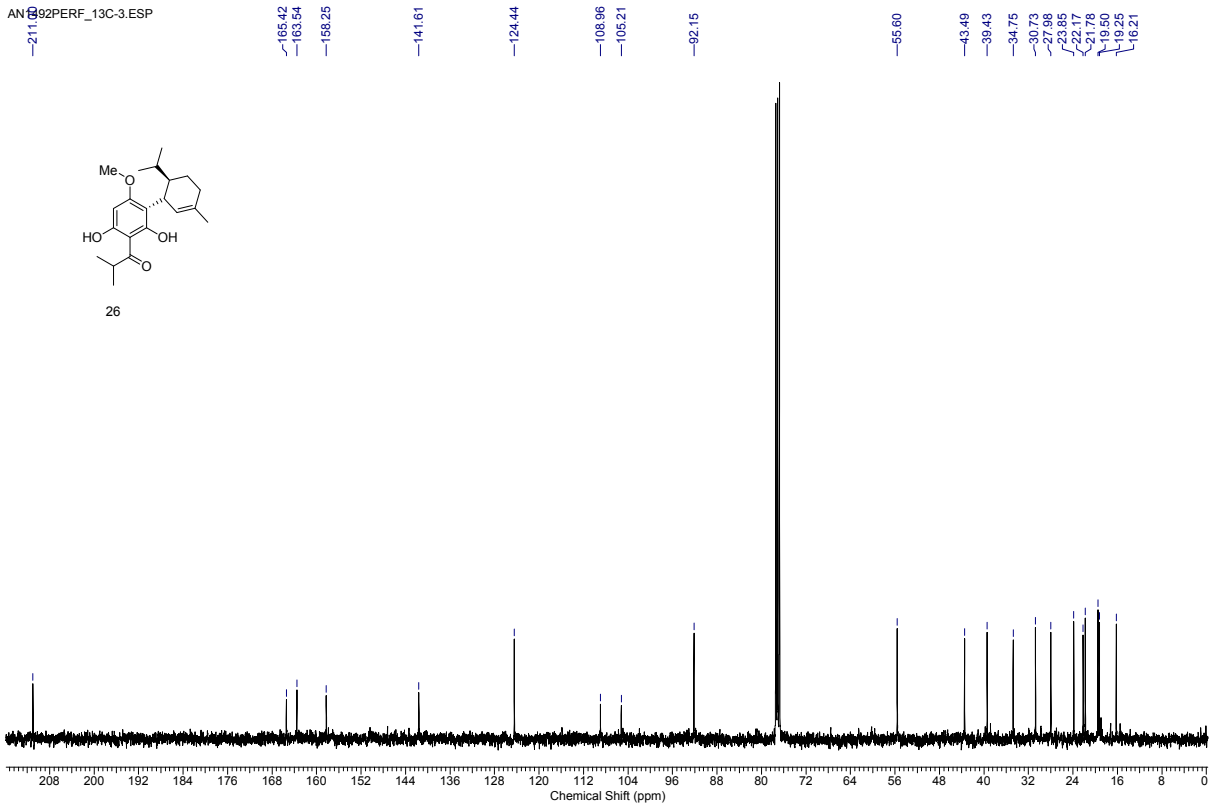
42.17
27.06
26.66
23.45
22.85
22.79
21.96
20.74
16.26



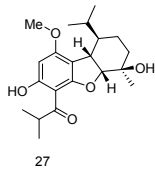
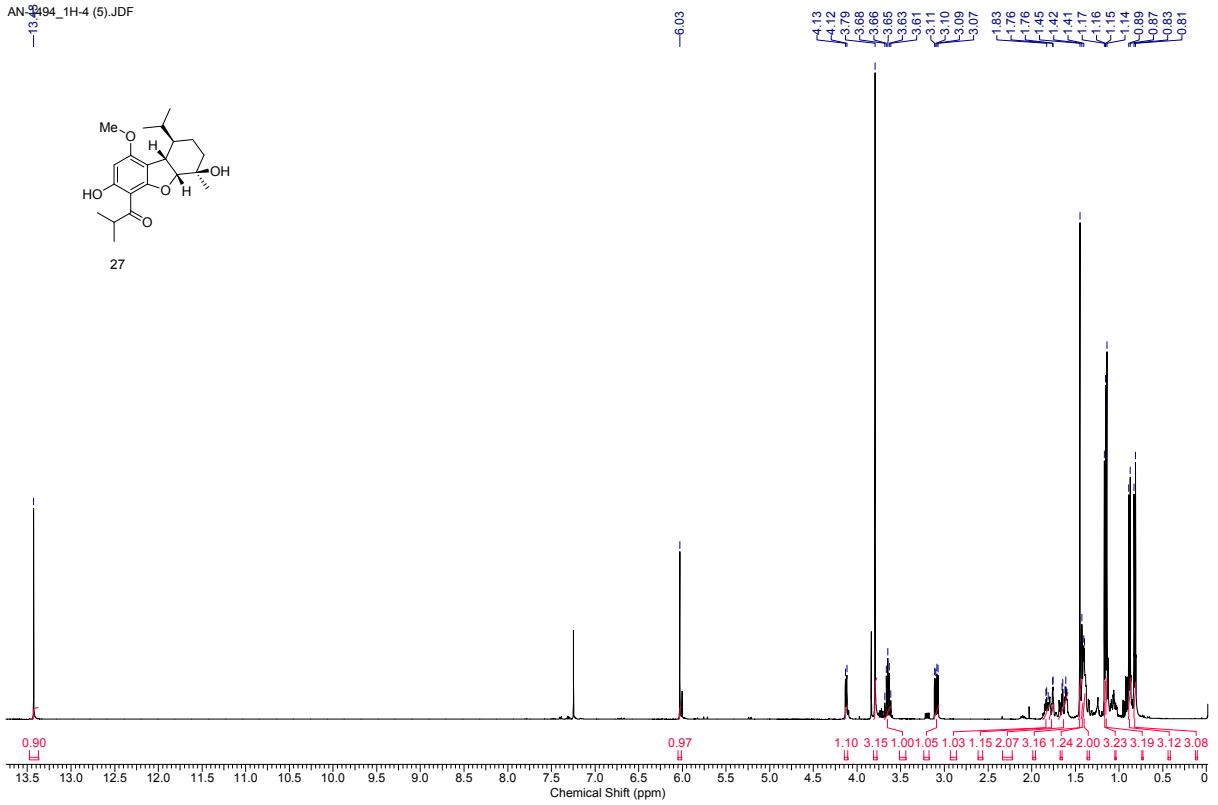
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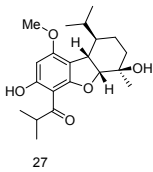
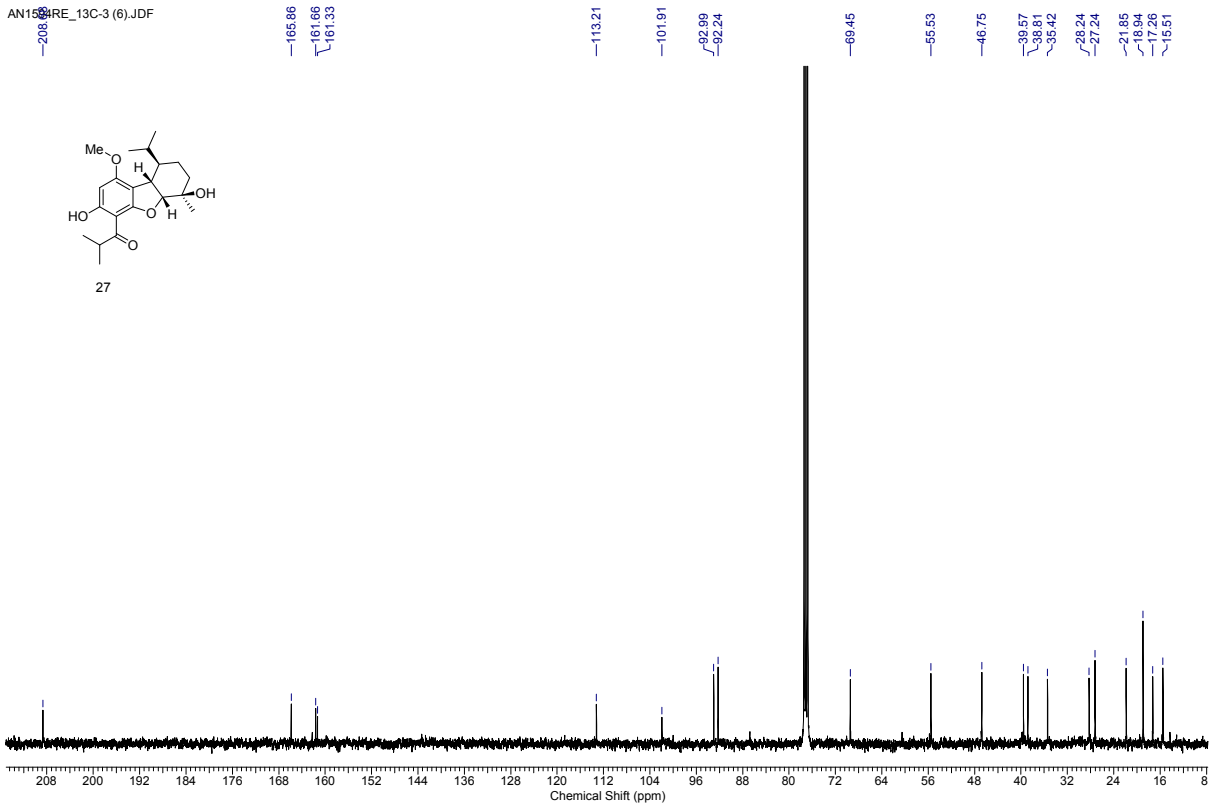
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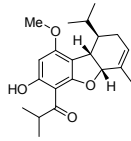
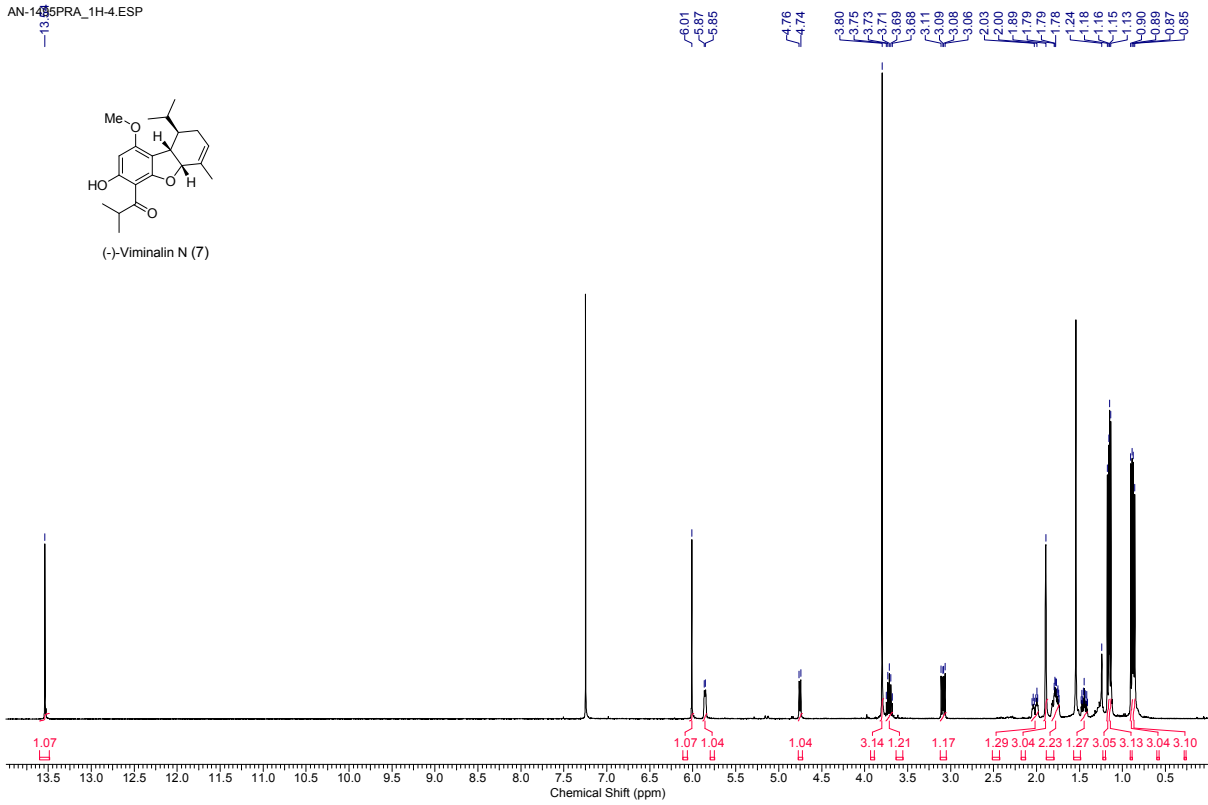
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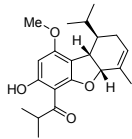
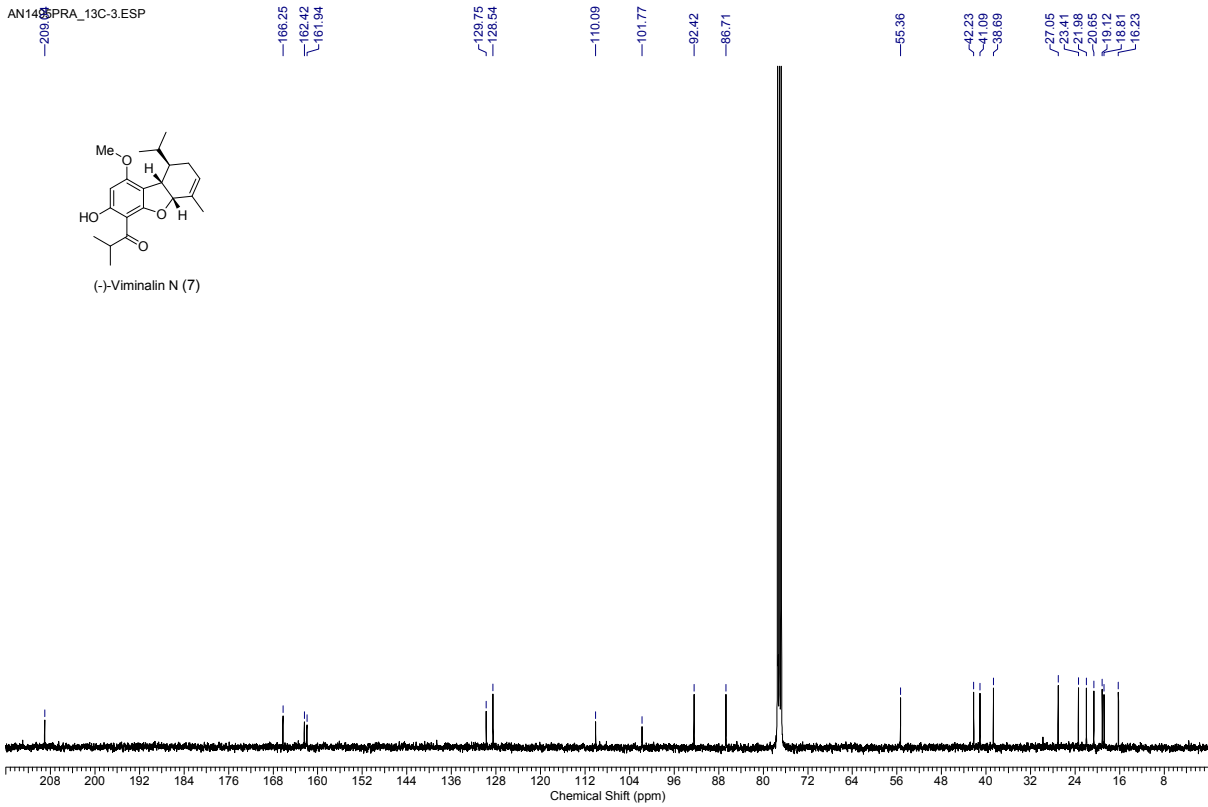
AN15194_13C-3 (6).JDF



AN-1455PRA_1H-4.ESP



AN1455PRA_13C-3.ESP



2. NMR comparison Table:

¹H and ¹³C NMR comparison between natural and synthetic Viminalin A (1)

¹ H-NMR in CDCl ₃		¹³ C-NMR in CDCl ₃	
Natural Viminalin A 500 MHz	Synthetic Viminalin A 400 MHz	Natural Viminalin A 125 MHz	Synthetic Viminalin A 100 MHz
0.99, (d, <i>J</i> = 7.0 Hz)	0.98, (d, <i>J</i> = 7.0 Hz)	204.8	204.8
1.00, (d, <i>J</i> = 7.0 Hz)	0.99, (d, <i>J</i> = 7.0 Hz)	166.4	166.3
1.06, (d, <i>J</i> = 7.0 Hz)	1.05, (d, <i>J</i> = 7.0 Hz)	162.1	162.1
1.11, (d, <i>J</i> = 7.0 Hz)	1.09, (d, <i>J</i> = 7.0 Hz)	160.3	160.3
1.48, (s)	1.47, (s)	108.7	108.7
1.57, (m)	1.56, (m)	102.5	102.4
1.64, (m)	1.63, (m)	92.4	92.4
1.81, (m)	1.83-1.77 (m)	87.5	87.4
1.96, (ddd, <i>J</i> = 14.0, 5.5, 3.0 Hz)	1.95, (ddd, <i>J</i> = 13.7, 5.5, 2.7 Hz)	55.9	55.9
2.20, (m)	2.18, (m)	55.7	55.7
2.82, (dd, <i>J</i> = 14.0, 6.5 Hz)	2.83 (dd, <i>J</i> = 14.0, 6.5 Hz)	55.0	55.0
2.87, (dd, <i>J</i> = 12.5, 5.5 Hz)	2.86 (dd, <i>J</i> = 12.5, 5.5 Hz)	51.7	51.7
2.92, (dd, <i>J</i> = 14.0, 6.5 Hz)	2.93 (dd, <i>J</i> = 14.0, 6.5 Hz)	39.7	39.6
3.28, (d, <i>J</i> = 4.0 Hz)	3.28 (d, <i>J</i> = 4.0 Hz)	39.3	39.2
3.45, (t, <i>J</i> = 4.0 Hz)	3.45 (t, <i>J</i> = 4.0 Hz)	28.4	28.3
3.80, (s)	3.79, (s)	26.2	26.2
5.97, (s)	5.96, (s)	26.1	26.1
13.55, (br. s)	13.55, (s)	24.0	23.9
		22.9	23.0
		22.8	22.8
		21.9	21.9
		21.4	21.4

¹H and ¹³C NMR comparison between natural and synthetic Viminalin B (2)

¹ H-NMR in CDCl ₃		¹³ C-NMR in CDCl ₃	
Natural Viminalin B 500 MHz	Synthetic Viminalin B 400 MHz	Natural Viminalin B 125 MHz	Synthetic Viminalin B 100 MHz
1.06, (d, <i>J</i> = 7.0 Hz)	1.05, (d, <i>J</i> = 6.9 Hz)	209.0	209.1
1.10, (d, <i>J</i> = 7.0 Hz)	1.09, (d, <i>J</i> = 6.9 Hz)	166.7	166.6
1.17, (d, <i>J</i> = 7.0 Hz)	1.15, (d, <i>J</i> = 7.0 Hz)	162.0	162.0
1.19, (d, <i>J</i> = 7.0 Hz)	1.18, (d, <i>J</i> = 7.0 Hz)	160.0	159.9
1.48, (s)	1.47, (s)	108.7	108.7
1.58, (m)	1.58, (m)	101.5	101.4
1.65, (m)	1.64, (m)	92.6	92.5
1.82, (m)	1.84 – 1.75, (m)	87.4	87.3
1.96, (ddd, <i>J</i> = 14.0, 5.5, 3.0 Hz)	1.95, (ddd, <i>J</i> = 14.0, 5.5, 3.0 Hz)	55.9	55.9
2.87, (dd, <i>J</i> = 12.5, 5.5 Hz)	2.86, (dd, <i>J</i> = 12.5, 5.8 Hz)	55.7	55.7
3.29, (d, <i>J</i> = 4.0 Hz)	3.28, (d, <i>J</i> = 4.0 Hz)	55.0	54.9
3.46, (t, <i>J</i> = 4.0 Hz)	3.45, (t, <i>J</i> = 4.0 Hz)	39.7	39.5
3.79, (m)	3.80, (m)	39.4	39.2
3.80, (s)	3.81, (s)	38.6	38.6
5.98, (s)	5.97, (s)	28.5	28.3
13.55, (br. s)	13.60, (s)	26.0	26.1
		24.0	23.9
		21.9	21.9
		21.4	21.4
		19.4	19.5
		18.6	18.5

¹H and ¹³C NMR comparison between natural and synthetic Viminalin H (3)

¹ H-NMR in CDCl ₃		¹³ C-NMR in CDCl ₃	
Natural Viminalin H 500 MHz	Synthetic Viminalin H 500 MHz	Natural Viminalin H 125 MHz	Synthetic Viminalin H 125 MHz
0.90, (d, <i>J</i> = 7.0 Hz)	0.88, (d, <i>J</i> = 7.0 Hz)	204.8	204.8
0.91, (d, <i>J</i> = 7.0 Hz)	0.91, (d, <i>J</i> = 7.0 Hz)	166.1	166.1
0.97, (d, <i>J</i> = 7.0 Hz)	0.96, (d, <i>J</i> = 6.9 Hz)	162.6	162.6
0.97, (d, <i>J</i> = 7.0 Hz)	0.97, (d, <i>J</i> = 6.9 Hz)	161.7	161.6
1.56, (s)	1.56, (s)	135.3	135.3
1.60, (m)	1.60, (m)	129.3	129.3
1.60, (m)	1.60, (m)	107.9	107.8
1.89, (m)	1.91–1.87, (m)	102.8	102.7
2.14, (m)	2.16 – 2.11, (m)	92.2	92.1
2.27, (dt, <i>J</i> = 14.0, 5.0 Hz)	2.27, (dt, <i>J</i> = 13.8, 5.0 Hz)	88.7	88.7
2.78, (dd, <i>J</i> = 14.0, 6.5 Hz)	2.77, (dd, <i>J</i> = 14.0, 6.6 Hz)	55.6	55.5
2.84, (dd, <i>J</i> = 14.0, 6.5 Hz)	2.84, (dd, <i>J</i> = 14.0, 6.6 Hz)	51.7	51.7
3.40, (t, <i>J</i> = 5.0 Hz)	3.39, (t, <i>J</i> = 4.8 Hz)	44.3	44.2
3.81, (s)	3.80, (s)	38.1	38.1
5.61, (dd, <i>J</i> = 10.0, 2.0 Hz)	5.60, (dd, <i>J</i> = 10.2, 2.3 Hz)	31.5	31.5
5.87, (dd, <i>J</i> = 10.0, 2.0 Hz)	5.87, (dd, <i>J</i> = 10.2, 1.9 Hz)	26.4	26.4
5.96, (s)	5.96, (s)	26.3	26.2
13.50, (br. s)	13.50, (s)	26.0	26.0
		22.9	22.9
		22.8	22.7
		19.9	19.9
		19.7	19.7

¹H and ¹³C NMR comparison between natural and synthetic Viminalin I (4)

¹H-NMR in CDCl₃		¹³C-NMR in CDCl₃	
Natural Viminalin I 500 MHz	Synthetic Viminalin I 400 MHz	Natural Viminalin I 125 MHz	Synthetic Viminalin I 100 MHz
0.90, (d, <i>J</i> = 7.0 Hz)	0.88, (d, <i>J</i> = 7.0 Hz)	209.1	209.1
0.91, (d, <i>J</i> = 7.0 Hz)	0.90, (d, <i>J</i> = 7.0 Hz)	166.5	166.4
1.13, (d, <i>J</i> = 7.0 Hz)	1.12, (d, <i>J</i> = 7.0 Hz)	162.5	162.5
1.15, (d, <i>J</i> = 7.0 Hz)	1.14, (d, <i>J</i> = 7.0 Hz)	161.3	161.3
1.56, (s)	1.55, (s)	135.3	135.3
1.60, (m)	1.60, (m)	129.3	129.2
1.61, (m)	1.61, (m)	107.9	107.9
1.89, (m)	1.92 – 1.86, (m)	101.6	101.7
2.27, (dt, <i>J</i> = 14.0, 5.0 Hz)	2.28, (dt, <i>J</i> = 14.0, 5.0 Hz)	92.4	92.3
3.40, (t, <i>J</i> = 5.0)	3.39, (t, <i>J</i> = 4.9)	88.7	88.7
3.73, (m)	3.72, (m)	55.6	55.6
3.81, (s)	3.80, (s)	44.2	44.1
5.61, (dd, <i>J</i> = 10.0, 2.0 Hz)	5.60, (dd, <i>J</i> = 9.8, 2.4 Hz)	38.5	38.5
5.87, (dd, <i>J</i> = 10.0, 2.0 Hz)	5.86, (dd, <i>J</i> = 9.8, 2.4 Hz)	38.2	38.1
5.98, (s)	5.97, (s)	31.5	31.5
13.56, (br. s)	13.56, (s)	26.4	26.4
		26.3	26.2
		19.9	19.9
		19.7	19.7
		19.2	19.1
		18.9	18.8

¹H and ¹³C NMR comparison between natural and synthetic Viminalin M (6)

¹H-NMR in CDCl₃		¹³C-NMR in CDCl₃	
Natural Viminalin M 500 MHz	Synthetic Viminalin M 500 MHz	Natural Viminalin M 125 MHz	Synthetic Viminalin M 125 MHz
0.87, (d, <i>J</i> = 7.0 Hz)	0.87, (d, <i>J</i> = 7.0 Hz)	204.7	204.7
0.90, (d, <i>J</i> = 7.0 Hz)	0.90, (d, <i>J</i> = 7.0 Hz)	166.0	166.0
0.96, (d, <i>J</i> = 7.0 Hz)	0.95, (d, <i>J</i> = 7.0 Hz)	162.5	162.5
0.98, (d, <i>J</i> = 7.0 Hz)	0.98, (d, <i>J</i> = 7.0 Hz)	162.4	162.3
1.45, (tt, <i>J</i> = 11.0, 4.0 Hz)	1.45, (tt, <i>J</i> = 11.0, 4.0 Hz)	129.8	129.7
1.78, (m)	1.76, (m)	128.7	128.7
1.80, (m)	1.82, (m)	110.1	110.0
1.92, (s)	1.92, (s)	102.9	102.8
2.03, (dt, <i>J</i> = 17.0, 4.0 Hz)	2.03, (dt, <i>J</i> = 16.9, 4.0 Hz)	92.4	92.3
2.20, (m)	2.23 – 2.17, (m)	86.7	86.7
2.82, (dd, <i>J</i> = 15.0, 7.0 Hz)	2.82, (dd, <i>J</i> = 15.0, 7.0 Hz)	55.4	55.3
2.93, (dd, <i>J</i> = 15.0, 7.0 Hz)	2.93, (dd, <i>J</i> = 15.0, 7.0 Hz)	51.7	51.7
3.09, (dd, <i>J</i> = 11.0, 7.0 Hz)	3.09, (dd, <i>J</i> = 11.0, 7.0 Hz)	42.2	42.2
3.80, (s)	3.80, (s)	41.2	41.2
4.76, (d, <i>J</i> = 7.0 Hz)	4.76, (d, <i>J</i> = 7.0 Hz)	27.1	27.1
5.87, (d, <i>J</i> = 5.5 Hz)	5.87, (d, <i>J</i> = 6.2 Hz)	25.5	25.5
6.01, (s)	6.01, (s)	23.5	23.4
13.53, (br. s)	13.52, (s)	22.9	22.9
		22.8	22.8
		22.0	22.0
		20.8	20.7
		16.3	16.3

¹H and ¹³C NMR comparison between natural and synthetic Viminalin N (7)

¹H-NMR in CDCl₃		¹³C-NMR in CDCl₃	
Natural viminalin N 600 MHz	Synthetic viminalin N 400 MHz	Natural Viminalin N 150 MHz	Synthetic viminalin N 100 MHz
0.87, (d, <i>J</i> = 7.0 Hz)	0.86, (d, <i>J</i> = 7.0 Hz)	209.1	209.0
0.91, (d, <i>J</i> = 7.0 Hz)	0.90, (d, <i>J</i> = 7.0 Hz)	166.3	166.3
1.15, (d, <i>J</i> = 7.0 Hz)	1.14, (d, <i>J</i> = 7.0 Hz)	162.5	162.4
1.18, (d, <i>J</i> = 7.0 Hz)	1.17, (d, <i>J</i> = 7.0 Hz)	162.0	161.9
1.46, (m)	1.45, (m)	129.8	129.8
1.80, (m)	1.82 - 1.73, (m)	128.6	128.5
1.90, (s)	1.89, (s)	110.1	110.1
2.02, (dt, <i>J</i> = 17.4, 4.1 Hz)	2.02, (dt, <i>J</i> = 17.4, 4.4 Hz)	101.8	101.8
3.10, (dd, <i>J</i> = 11.0, 7.0 Hz)	3.09, (dd, <i>J</i> = 11.0, 7.3 Hz)	92.5	92.4
3.72, (m)	3.71, (m)	86.8	86.7
3.81, (s)	3.80, (s)	55.4	55.4
4.76, (d, <i>J</i> = 7.0 Hz)	4.75, (d, <i>J</i> = 7.3 Hz)	42.3	42.2
5.87, (d, <i>J</i> = 5.5 Hz)	5.86, (d, <i>J</i> = 5.5 Hz)	41.2	41.1
6.02, (s)	6.01, (s)	38.7	38.7
13.54, (br. s)	13.54, (s)	27.1	27.0
		23.5	23.4
		22.0	22.0
		20.7	20.6
		19.2	19.1
		18.9	18.8
		16.3	16.2

3. References:

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