

# Supporting Information

## Enantioselective Total Syntheses of (+)-Hostmanin A, (–)-Linderol A, (+)-Methyllinderatin and Structural Reassignment of Adunctin E

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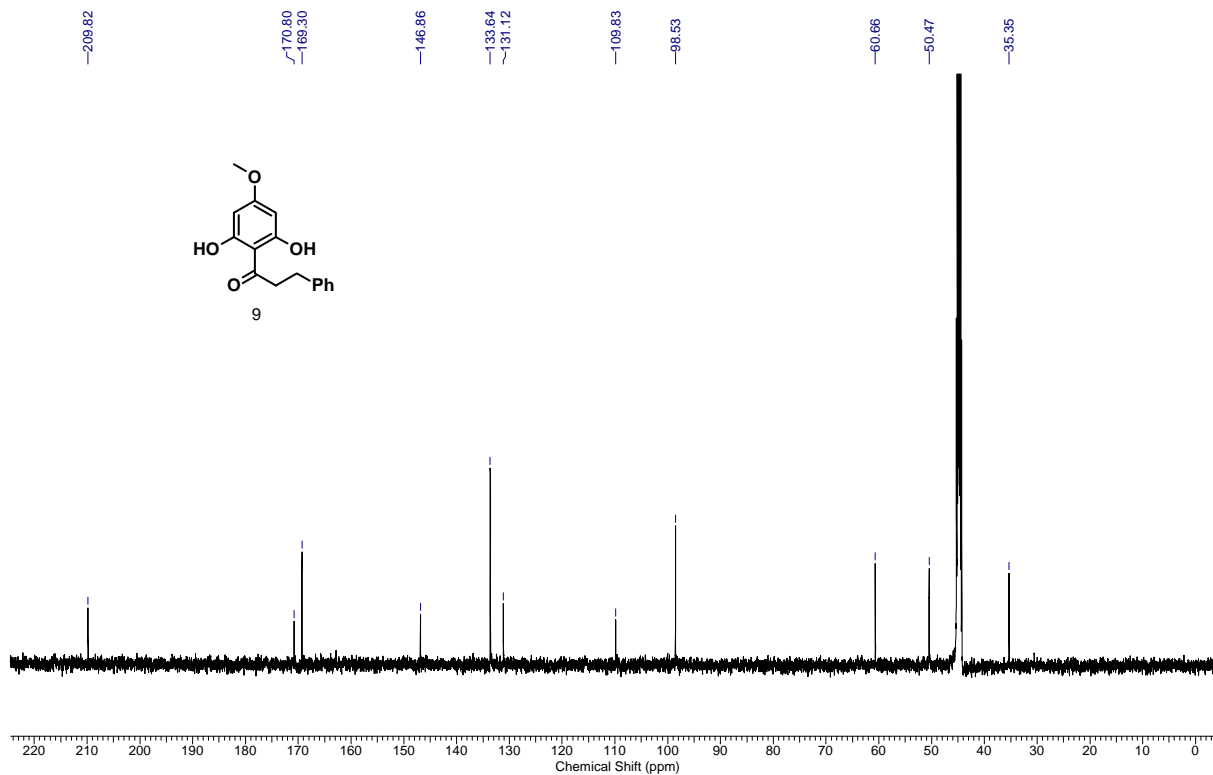
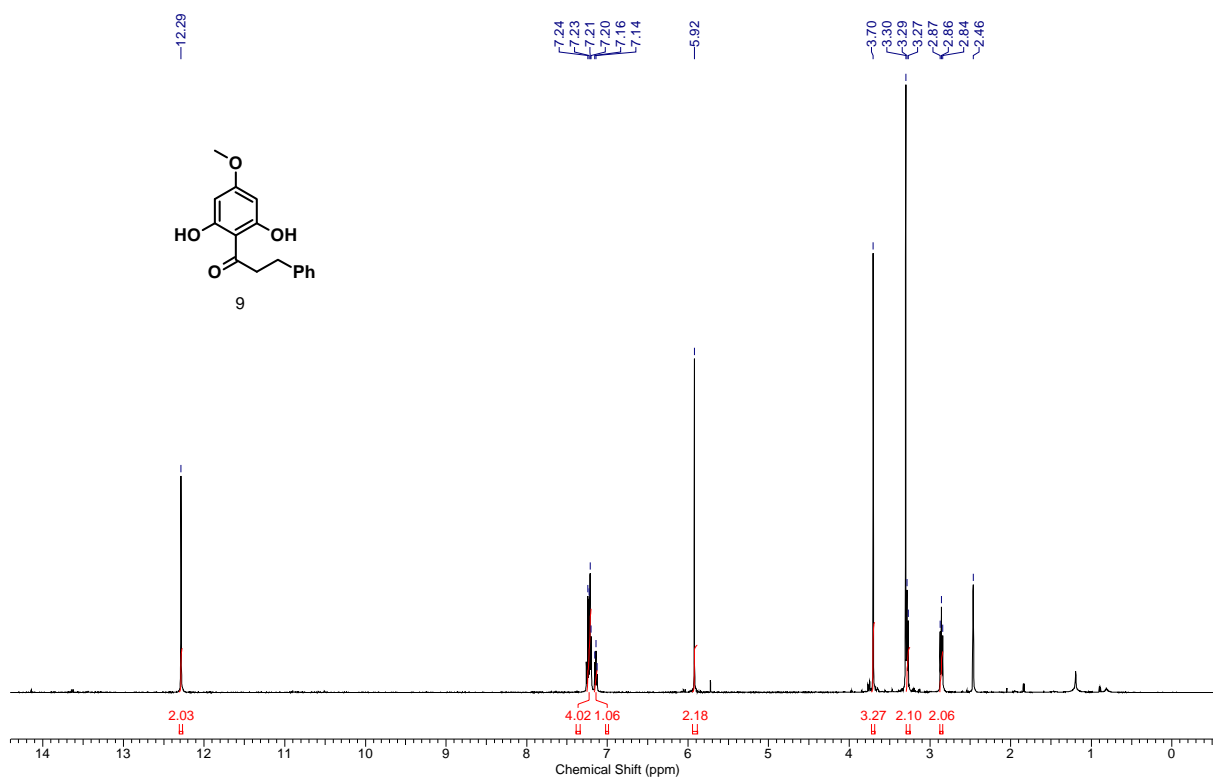
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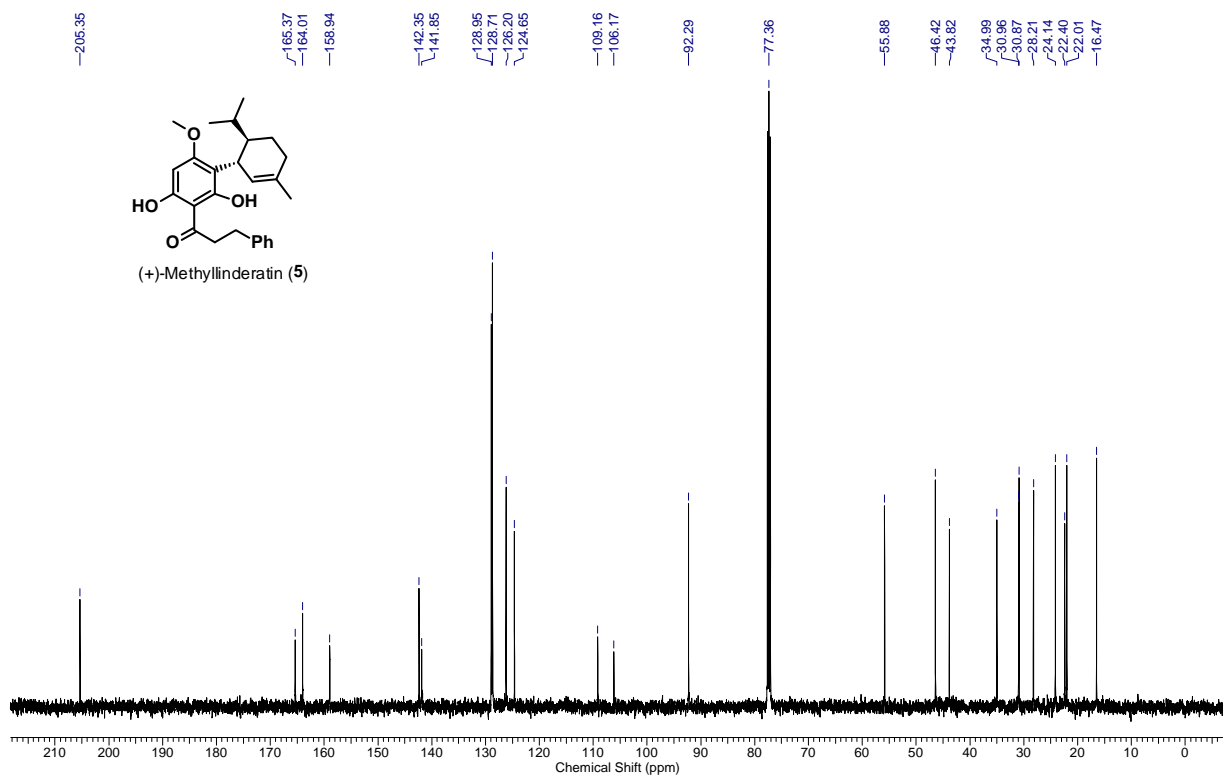
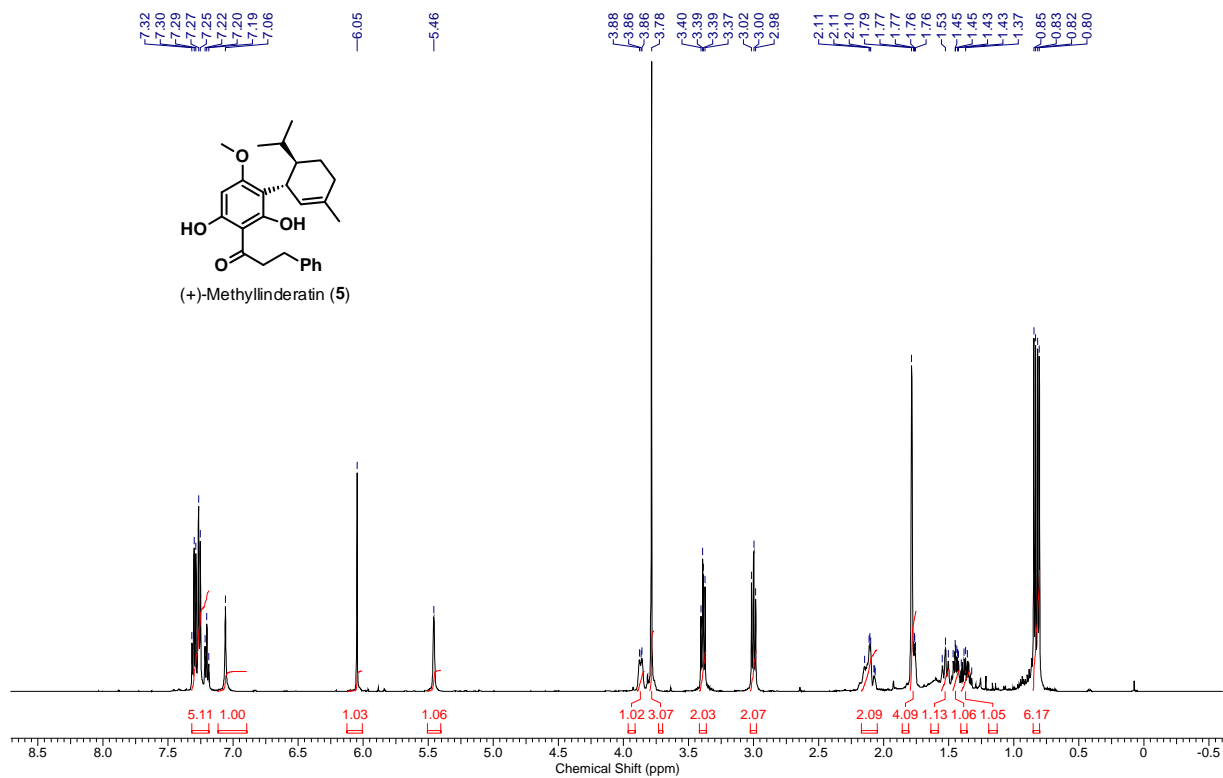
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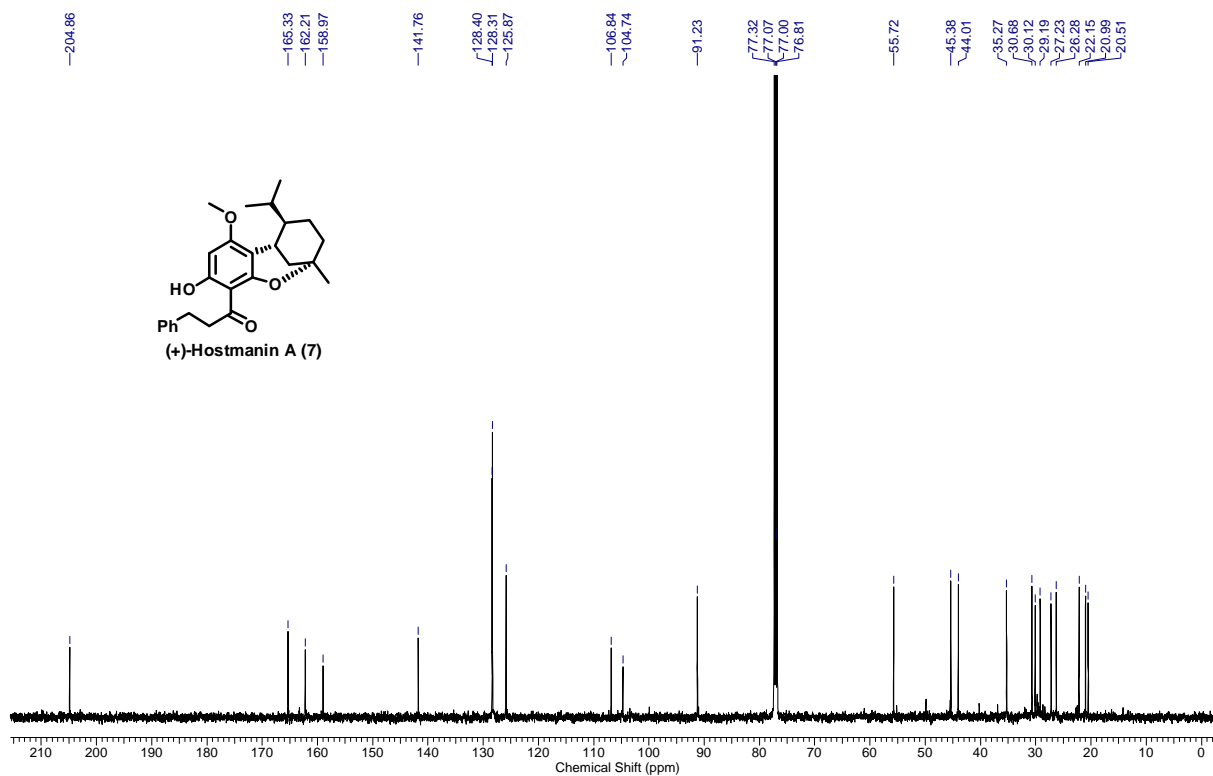
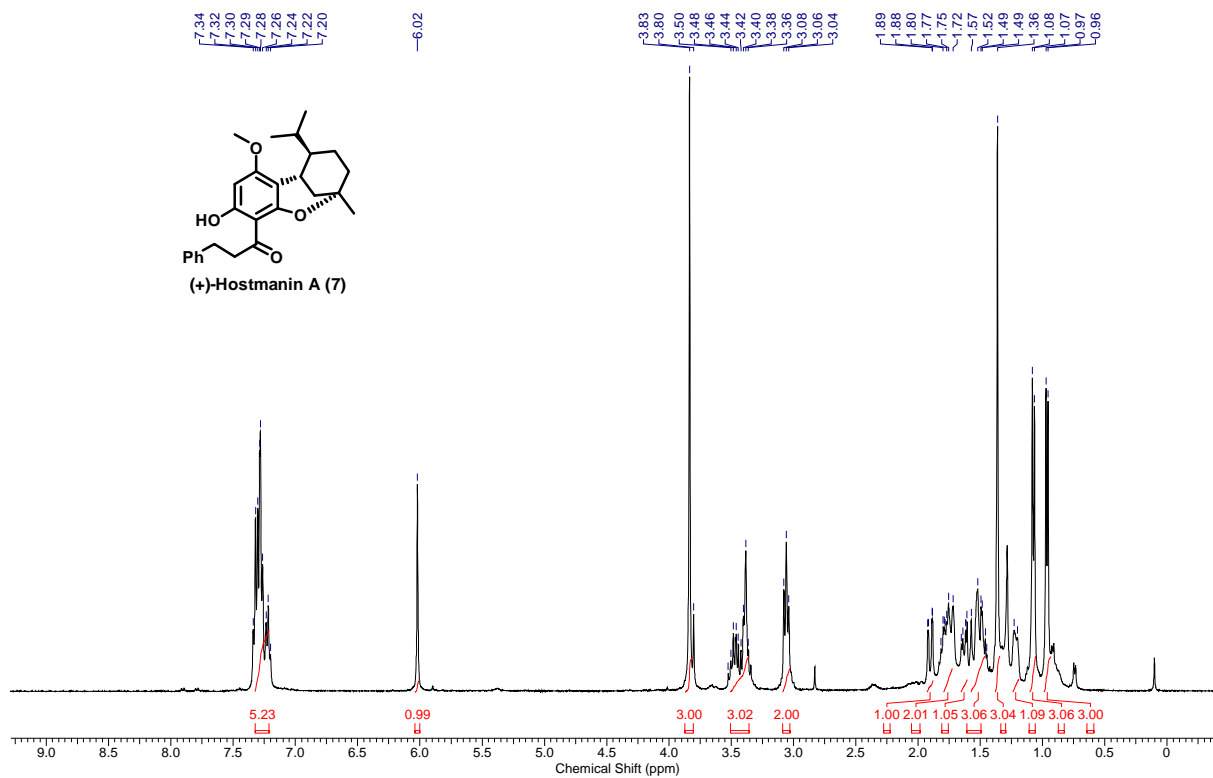
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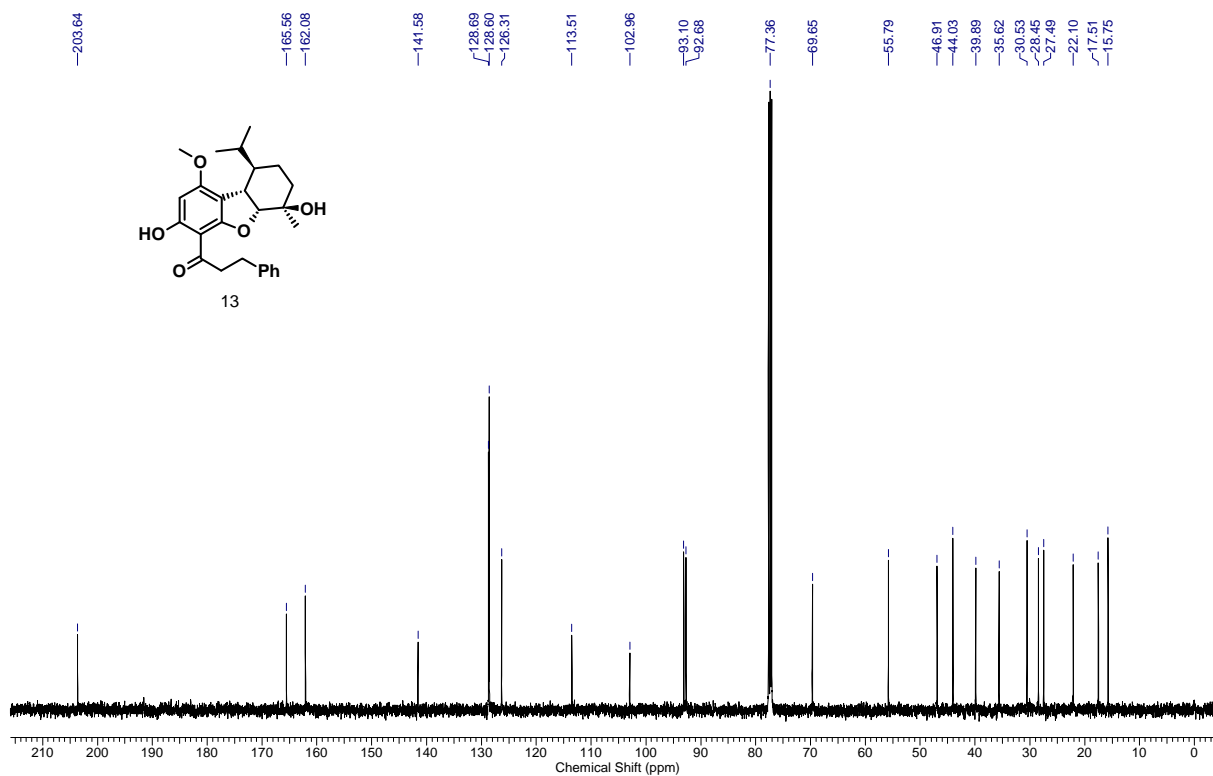
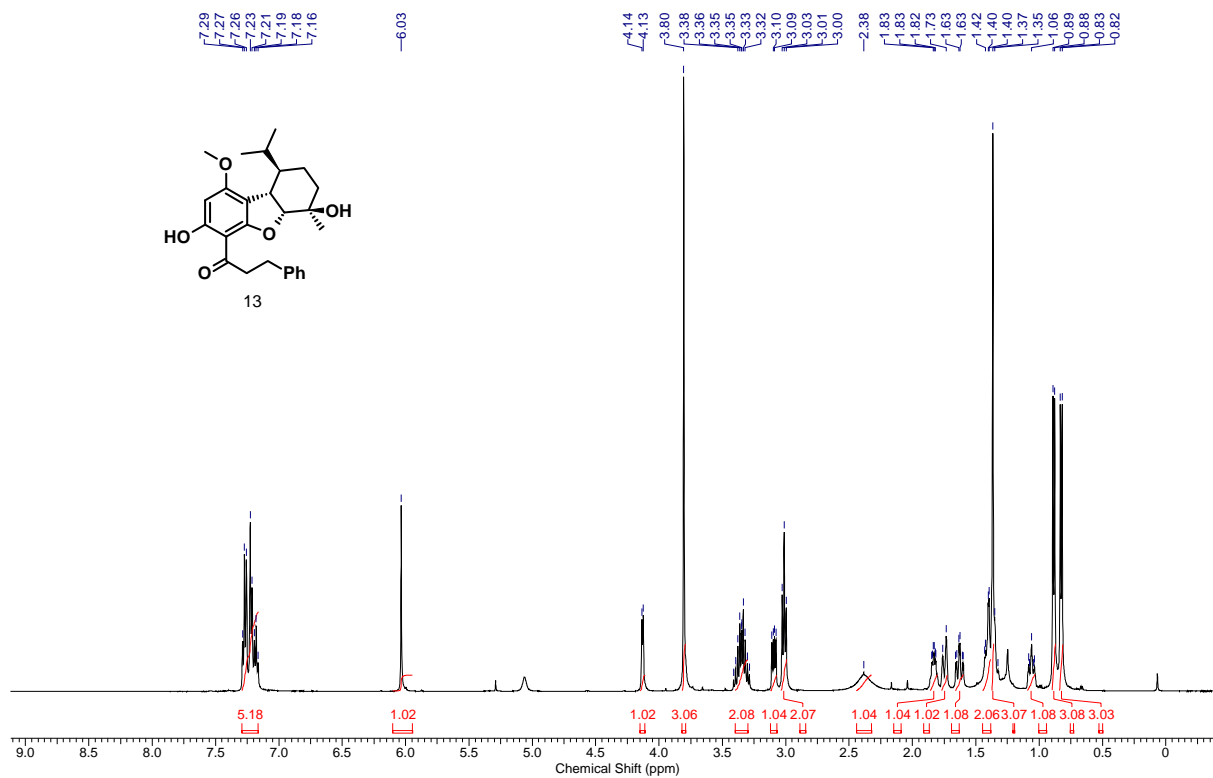
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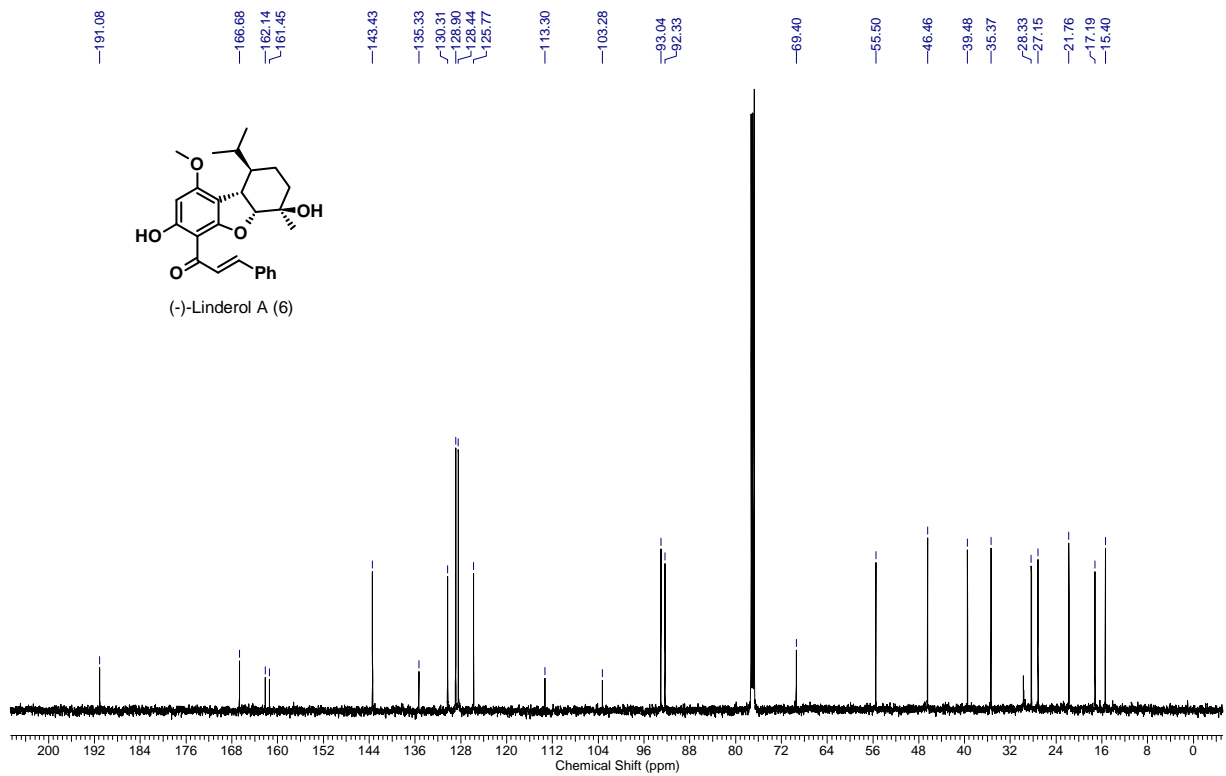
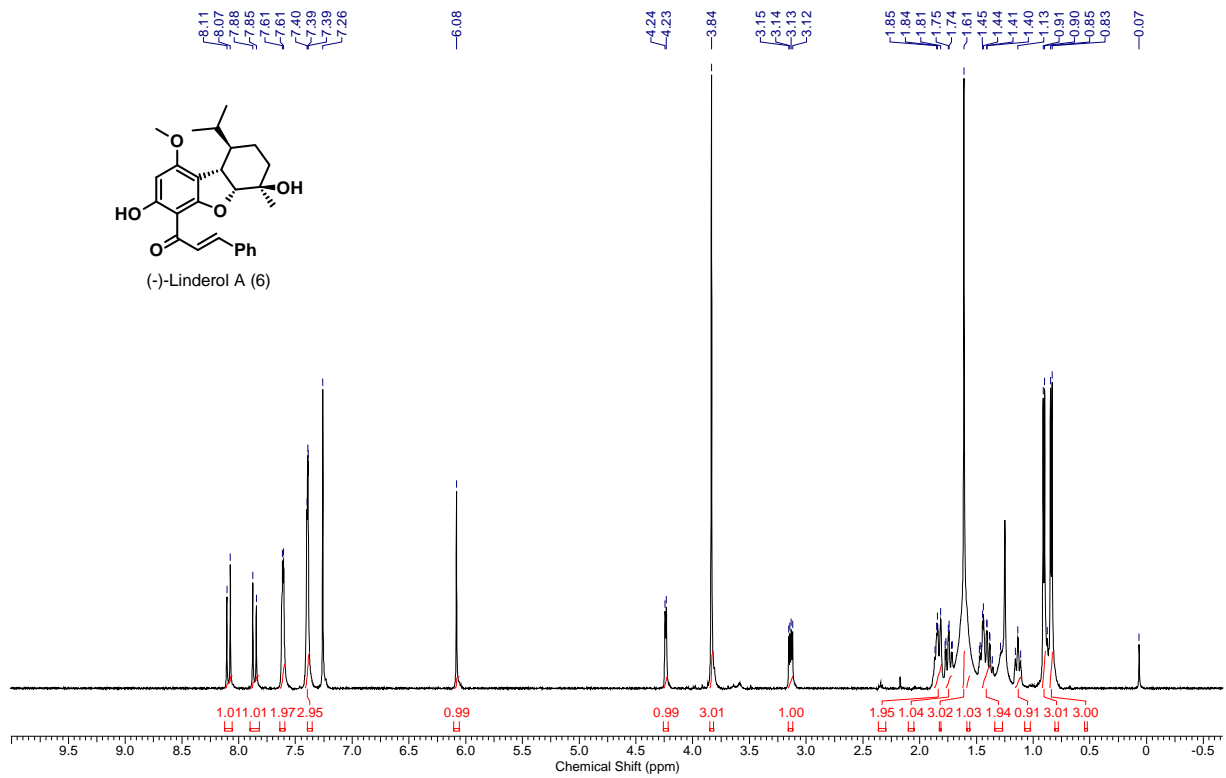
# 1. Spectras:

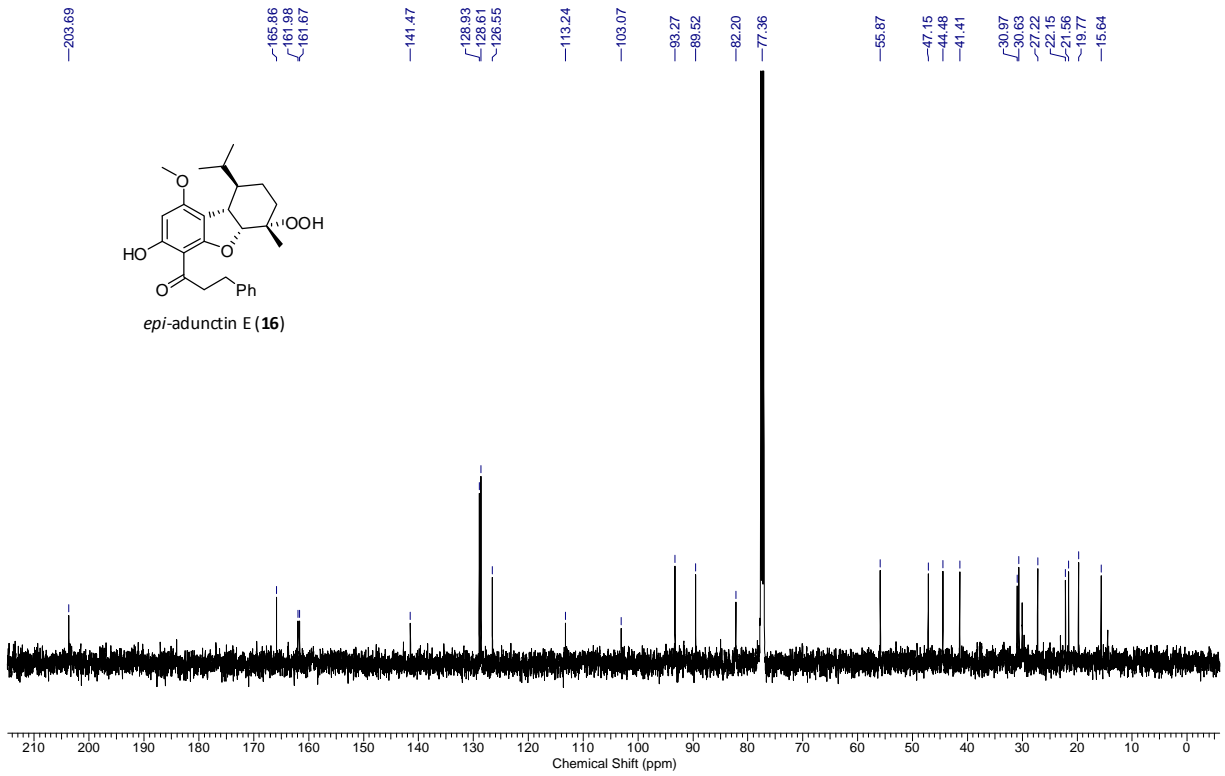
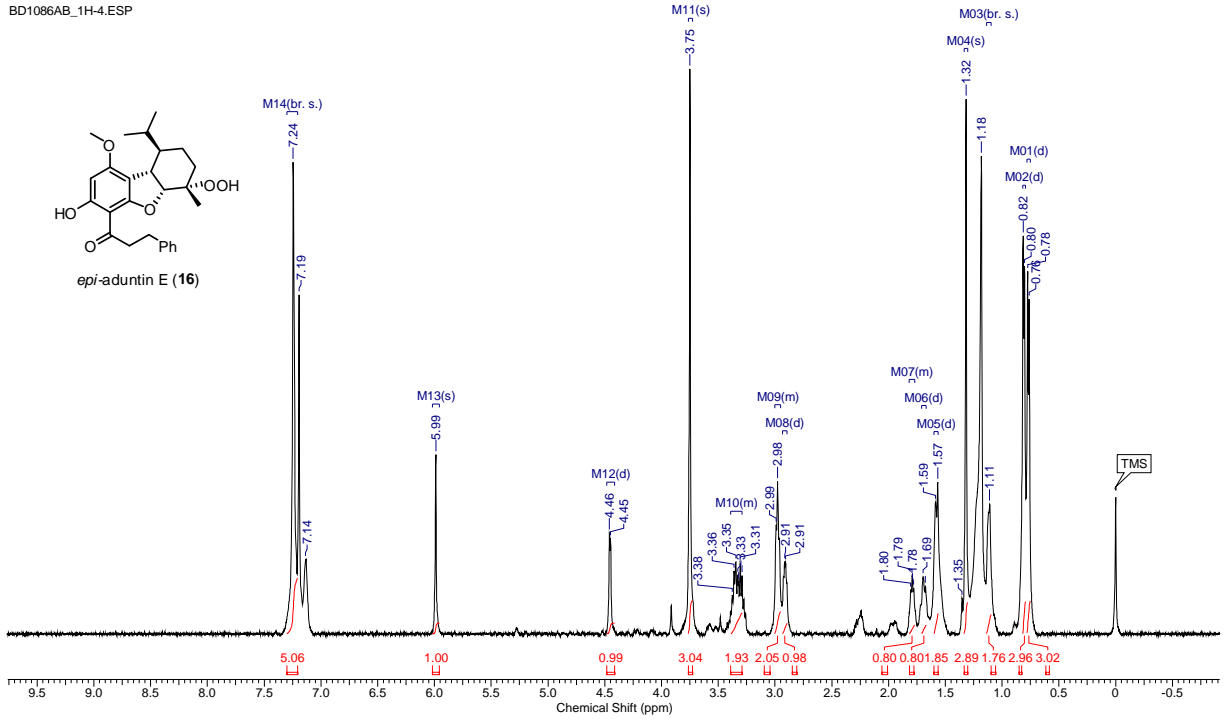




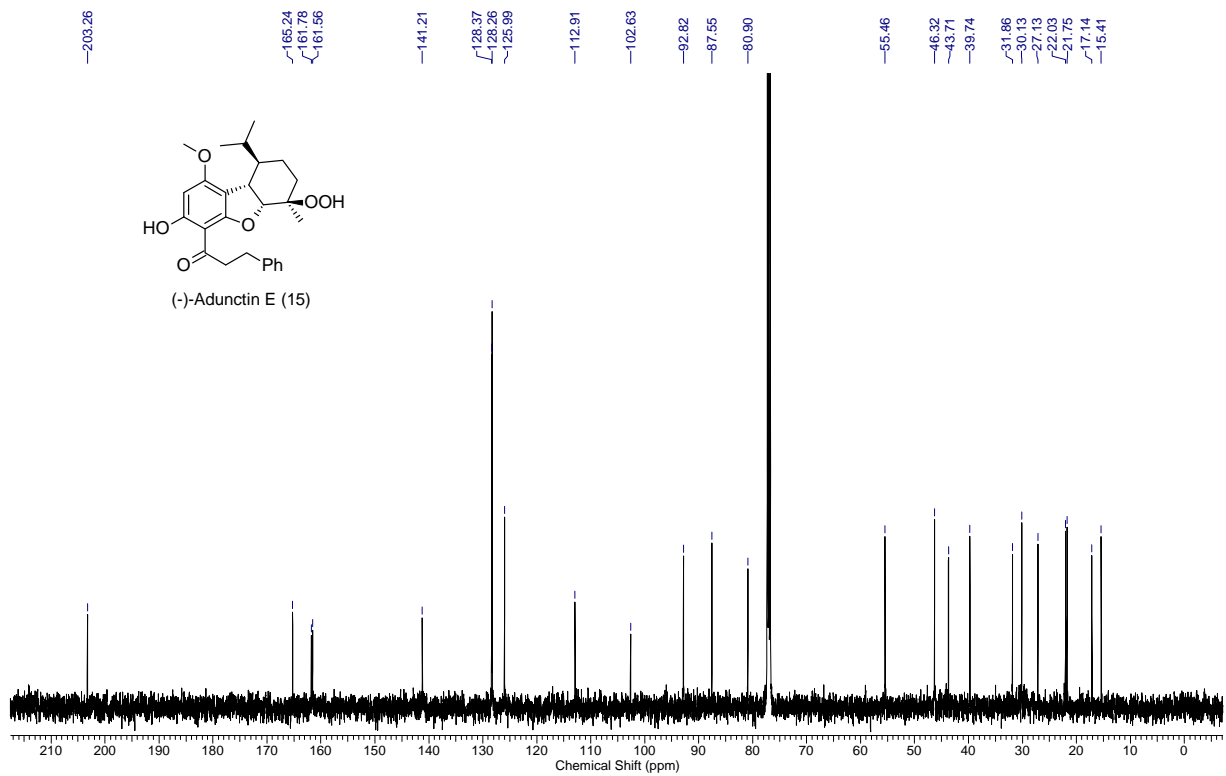
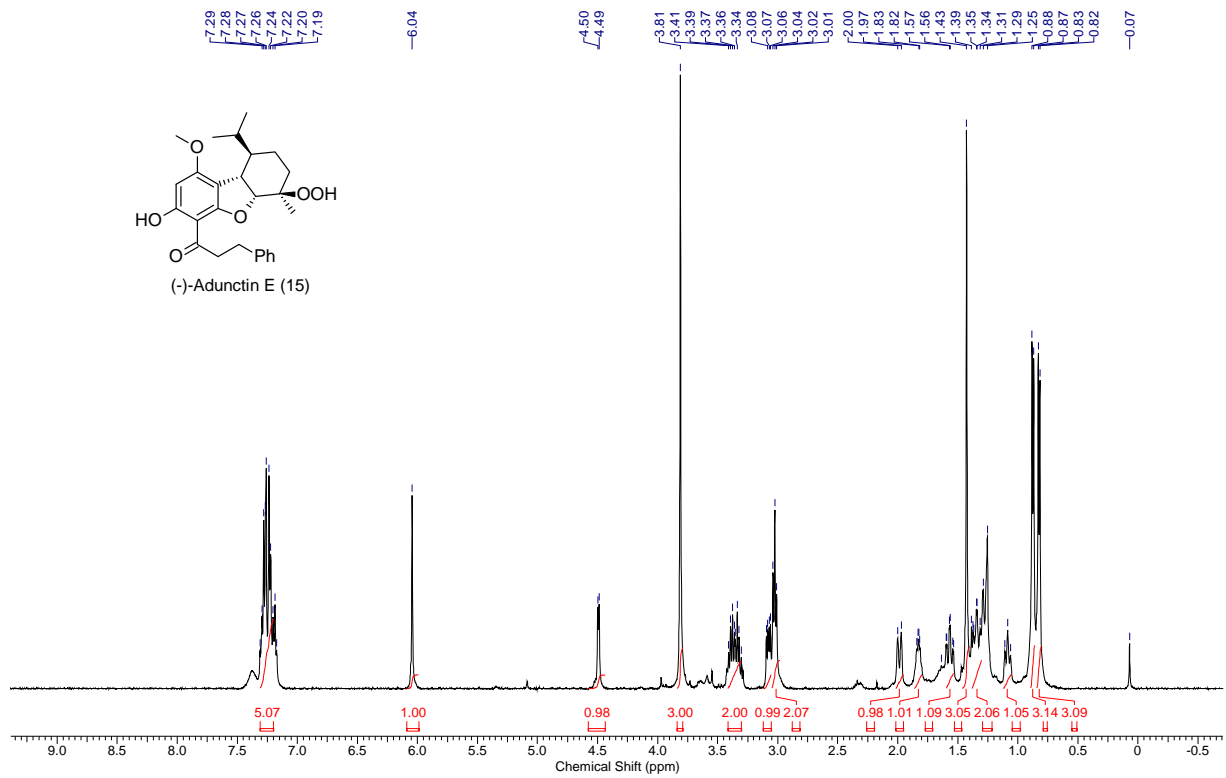






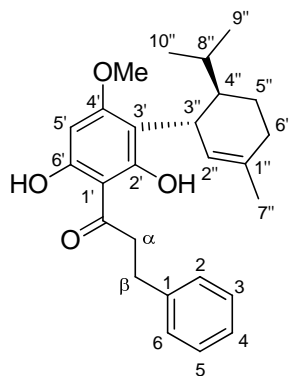






## 2. $^1\text{H}$ and $^{13}\text{C}$ NMR comparison tables

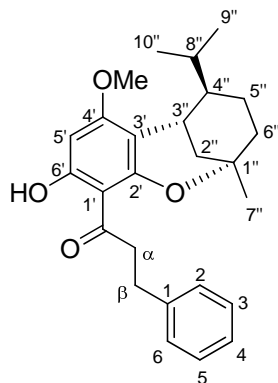
### 2. 1) (+)-Methylinderatin (5):



(+)-Methylinderatin (5)

Position	Natural Methylinderatin (270 MHz, $\text{CDCl}_3$ )	Synthetic Methylinderatin (500 MHz, $\text{CDCl}_3$ )
9',10'- $\text{CH}_3$	0.81, 0.84 (deach, $J=7.4$ Hz)	0.81, 0.84 (deach, $J=8$ Hz)
7''- $\text{CH}_3$	1.79 (s)	1.79 (s)
$\alpha$	3.00 (t, $J=7.4$ Hz)	3.00 (t, $J=7.6$ Hz)
$\beta$	3.39 (t, $J=7.4$ Hz)	3.39 (t, $J=7.6$ Hz)
OCH3	3.79 (s)	3.78 (s)
3''-H	3.87 (br d, $J=10.4$ Hz)	3.87 (br. d, $J=10.6$ Hz)
2''-H	5.46 (s)	5.46 (br. s)
5'-H	6.05 (s)	6.05 (s)
OH (free)	7.05 (s)	7.06 (s)
Ph	7.27 (br. s)	7.32 - 7.19 (m)
OH (chelated )	13.71 (s)	-

## 2.2) (+)-Hostmanin A (7):



(+)-Hostmanin A (7)

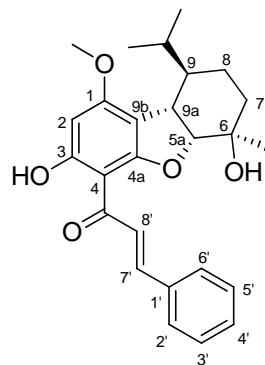
Position	Natural Hostmanin A (500 MHz, CDCl <sub>3</sub> ) <sup>a</sup>	Synthetic Hostmanin A (400 MHz, CDCl <sub>3</sub> )
<b>Dihydrochalcone moiety</b>		
2-H to 6-H	7.21-7.29 (m, 5H)	7.32 - 7.21 (m, 5H)
α-H	3.06 (t, 2H, <i>J</i> =8.0 Hz)	3.06 (t, 2 H, <i>J</i> = 7.8 Hz)
β-H	3.49 (m, 2H)	3.52 - 3.44 (m, 2H)
3'-H	6.02 (s)	6.02 (s)
OH (chelated)	13.90 (s)	-
4-OCH <sub>3</sub>	3.83 (s, 3H)	3.83 (s, 3H)
<b>Monoterpene moiety</b>		
2''-H <sub>a</sub>	1.74 (m)	1.81 - 1.71 (m)
2''-H <sub>b</sub>	1.61 (m)	1.63 (dd, <i>J</i> = 13.7, 4.6 Hz)
3''-H	1.53 (m, 2H)	1.57 - 1.48 (m, 2 H)
4''-H <sub>a</sub>	1.21 (m)	1.24 - 1.19 (m)
5''-H <sub>b</sub>	3.39 (m)	3.42 - 3.36 (m)
6''-H <sub>a</sub>	1.91 (dd, <i>J</i> =13.4, 3.4 Hz)	1.90 (dd, <i>J</i> = 13.3, 2.1 Hz)
6''-H <sub>b</sub>	1.51 (dd, <i>J</i> =13.4, 5.3 Hz)	1.57 - 1.48 (m)
7''-CH <sub>3</sub>	1.36 (s, 3H)	1.36 (s, 3 H)
8''-H	1.78 (m)	1.81 - 1.71 (m)
9''-CH <sub>3</sub>	1.08 (d, 3H, <i>J</i> =6.8Hz)	1.07 (d, 3 H, <i>J</i> = 6.4 Hz)
10''-CH <sub>3</sub>	0.97 (d, 3H, <i>J</i> =6.8Hz)	0.96 (d, 3 H, <i>J</i> = 6.4 Hz)

<sup>a</sup>Multiplicity patterns were unclear due to signal overlapping of hostmanin A (7) and B (8)

Position	Natural Hostmanin A (125 MHz, CDCl <sub>3</sub> )	Synthetic Hostmanin A (125 MHz, CDCl <sub>3</sub> )
C-1	141.8	141.8
C-2	128.3	128.3
C-3	128.4	128.4
C-4	125.8	125.9
C-5	128.4	128.4
C-6	128.3	128.3
C-1'	104.7	104.7
C-2'	165.4	165.3
C-3'	91.2	91.2
C-4'	162.3	162.2
C-5'	106.8	106.8
C-6'	158.9	159.0
C=O	204.9	204.9
C- $\alpha$	45.5	45.4
C- $\beta$	30.7	30.7
OMe	55.7	55.7
C-1''	77.9 <sup>a</sup>	76.8
C-2''	35.3	35.3
C-3''	20.5	20.5
C-4''	44.0	44.0
C-5''	27.2	27.2
C-6''	30.1	30.1
C-7''	29.2	29.2
C-8''	26.3	26.3
C-9''	20.9	21.0
C-10''	22.1	22.1

<sup>a</sup>The C-1'' position of hostmanin B was assigned as 76.7 ppm.

### 2.3) (-)-Linderol A (6):

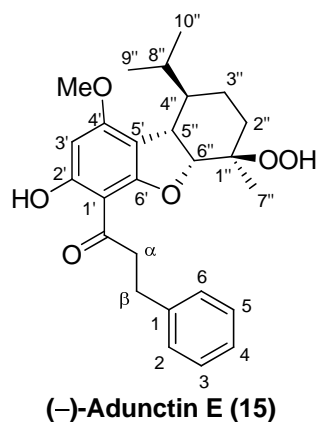


**(-)-Linderol A (6)**

Position	Natural linderol A	Synthetic linderol A (500 MHz, CDCl <sub>3</sub> )
3-OH	13.97 (s)	-
8'	8.09 (d, $J = 15.6$ Hz)	8.09 (d, $J = 15.5$ Hz)
7'	7.86 (d, $J = 15.6$ Hz)	7.86 (d, $J = 15.5$ Hz)
2'-6'	7.61 (m, 2H), 7.39 (m, 3H)	7.61 (d, $J = 4.0$ Hz, 2 H), 7.42 - 7.37 (m, 3 H)
2-H	6.08 (s)	6.08 (s)
5a-H	4.24	4.24 (d, $J = 5.2$ Hz)
1-OCH <sub>3</sub>	3.84 (s)	3.84 (s)
9a-H	3.14	3.14 (dd, $J = 5.4, 11.2$ Hz)
	1.75 (m, 1H)	1.77 - 1.72 (m)
6-CH <sub>3</sub>	1.61 (s)	1.61 (s)
6-OH	1.58 (br)	1.57 (br. s)
	1.35 - 1.48 (m)	1.45 - 1.38 (m)
	1.14 (m, 1H)	1.13 (t, $J = 11.5$ Hz, 1H)
9-CH(CH <sub>3</sub> ) <sub>2</sub>	0.91 (d, $J = 6.8$ Hz) 0.85 (d, $J = 7.0$ Hz)	0.91 (d, $J = 6.3$ Hz, 3 H) 0.84 (d, $J = 6.9$ Hz, 3 H)

Position	Natural Linderol A	Synthetic Lindeol A (125 MHz, CDCl <sub>3</sub> )
C(=O)	191.1	191.1
3	166.7	166.7
1	162.2	162.1
4a	161.5	161.5
7'	143.4	143.4
1' or 4'	135.4	135.3
1' or 4'	130.3	130.3
2', 6'	128.9	128.9
3', 5'	128.4	128.4
8'	125.9	125.8
9b	113.3	113.3
4	103.4	103.3
2	93.1	93.0
5a	92.4	92.3
6	69.4	69.4
	55.5	55.5
	46.5	46.5
	39.5	39.5
7	35.4	35.4
	28.3	28.3
	27.2	27.1
	21.8	21.8
8	17.2	17.2
	15.4	15.4

## 2.4) (-)-Adunctin E (15):

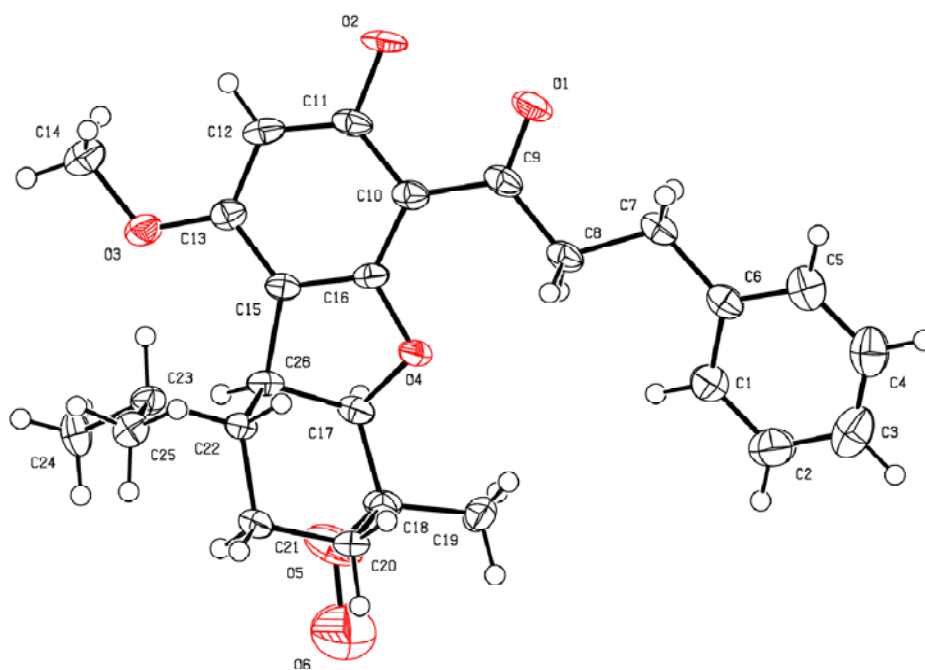


Position	Natural Adunctin E (300 MHz, CDCl <sub>3</sub> )	Adunctin E (500 MHz, CDCl <sub>3</sub> )
<b>Dihydrochalcone moiety</b>		
2-H to 6-H	7.24 (br. m)	7.31 - 7.20 (m)
α-CH <sub>2</sub>	3.38 (m)	3.43 - 3.30 (m)
β-CH <sub>2</sub>	3.02 (t, <i>J</i> = 7.6 Hz)	3.02 (t, <i>J</i> = 7.7 Hz)
3'-H	6.04 (s)	6.04 (s)
OH (chelated)	13.23 (s)	-
4-OCH <sub>3</sub>	3.81 (s)	3.81 (s)
<b>Monoterpene moiety</b>		
2''-H <sub>a</sub>	2.09 (br. m)	2.00 (d, <i>J</i> = 14.9 Hz)
2''-H <sub>b</sub>	1.59 (br. m)	1.62 - 1.54 (m)
3''-H	1.33 (m)	1.38 - 1.30 (m)
4''-H	1.08 (m)	1.08 (t, <i>J</i> = 11.5 Hz)
5''-H <sub>b</sub>	3.07 (dd, <i>J</i> = 11.0, 5.5 Hz)	3.08 (dd, <i>J</i> = 11.5, 5.7 Hz)
6''-H	4.50 (d, <i>J</i> = 5.4 Hz)	4.49 (d, <i>J</i> = 5.2 Hz)
7''-CH <sub>3</sub>	1.43 (s)	1.43 (s)
8''-H	1.83 (m)	1.86 - 1.80 (m)
9''-CH <sub>3</sub>	0.85 (d, <i>J</i> = 6.8 Hz)	0.87 (d, <i>J</i> = 6.9 Hz)
10''-CH <sub>3</sub>	0.83 (d, <i>J</i> = 6.8 Hz)	0.83 (d, <i>J</i> = 6.9 Hz)

Position	Natural adunctin E (75.5 MHz, CDCl <sub>3</sub> )	Synthetic adunctin E (125 MHz, CDCl <sub>3</sub> )
Dihydrochalcone		
C-1	141.2	141.2
C-2, C-6	128.3	128.3
C-4	126.0	126.0
C-3, C-5	128.4	128.4
C- $\alpha$	43.7	43.7
C- $\beta$	30.1	30.1
C=O	203.2	203.3
C-1'	102.7	102.6
C-2'	165.3	165.2
C-3'	92.8	92.8
C-4'	161.8	161.8
C-5'	112.8	112.9
C-6'	161.6	161.6
MeO	55.5	55.5
Monoterpene		
C-1''	80.9	80.9
C-2''	31.8	31.9
C-3''	17.1	17.1
C-4''	46.3	46.3
C-5''	39.8	39.7
C-6''	87.6	87.6
C-7''	22.0	22.0
C-8''	27.1	27.1
C-9''	15.4	15.4
C-10''	21.7	21.8



### 3. X-ray crystallographic data of (-)-adunctin E (15) (compound1):



**Figure 1.** ORTEP diagram of (-)-adunctin E (15). Thermal ellipsoids are drawn at the 50% probability level.

