

## S2 Appendix

### Analytical Data for the Lapachone Family of Metabolites

#### NMR Spectroscopic Data:

- Figure S1**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) spectrum of lapachol (**4**)  
**Figure S2**  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of lapachol (**4**)  
**Figure S3**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) spectrum of dehydro- $\alpha$ -lapachone (**5**)  
**Figure S4**  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of dehydro- $\alpha$ -lapachone (**5**)  
**Figure S5**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) spectrum of  $\alpha$ -lapachone (**6**)  
**Figure S6**  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of  $\alpha$ -lapachone (**6**)  
**Figure S7**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) spectrum of dehydroiso- $\alpha$ -lapachone (**7**)  
**Figure S8**  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of dehydroiso- $\alpha$ -lapachone (**7**)  
**Figure S9** gHSQC ( $^1\text{H}$  500 MHz,  $\text{CDCl}_3$ ) spectrum for dehydroiso- $\alpha$ -lapachone (**7**)  
**Figure S10** gCOSY ( $^1\text{H}$  500 MHz,  $\text{CDCl}_3$ ) spectrum for dehydroiso- $\alpha$ -lapachone (**7**)  
**Figure S11** gHMBC ( $^1\text{H}$  500 MHz,  $\text{CDCl}_3$ ) spectrum for dehydroiso- $\alpha$ -lapachone (**7**)  
**Table S1**  $^1\text{H}$  and  $^{13}\text{C}$  NMR data table for dehydroiso- $\alpha$ -lapachone (**7**) in  $\text{CDCl}_3$

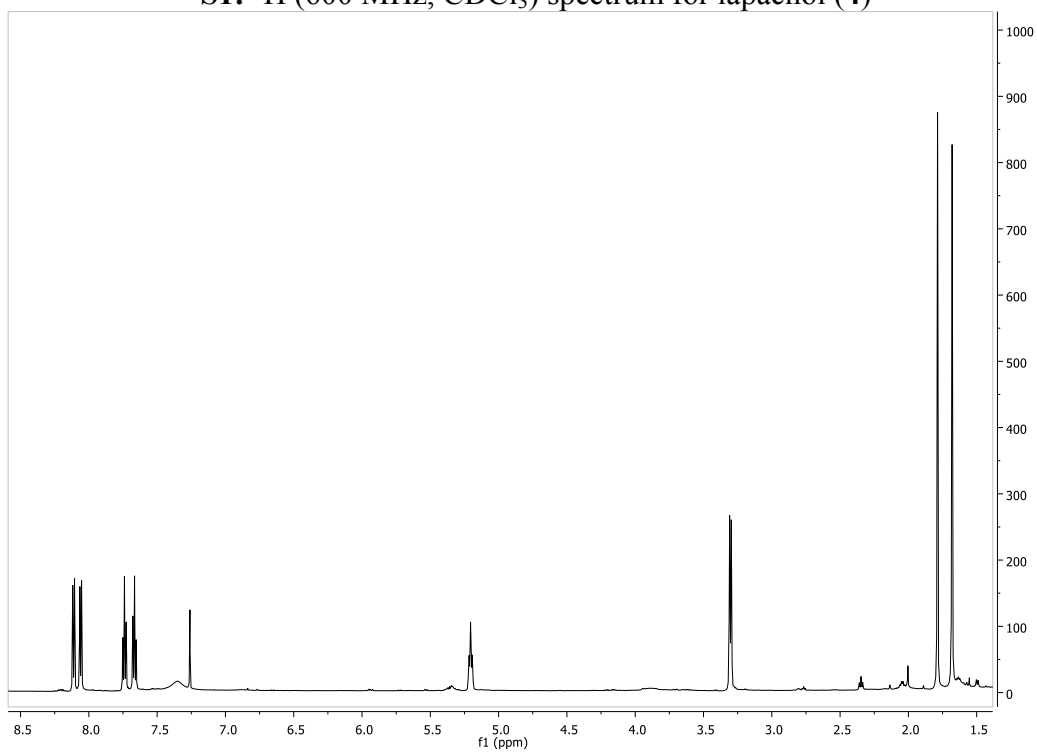
#### HPLC Chromatograms:

- Figure S12** Chiral HPLC of dehydroiso- $\alpha$ -lapachone (**7**)

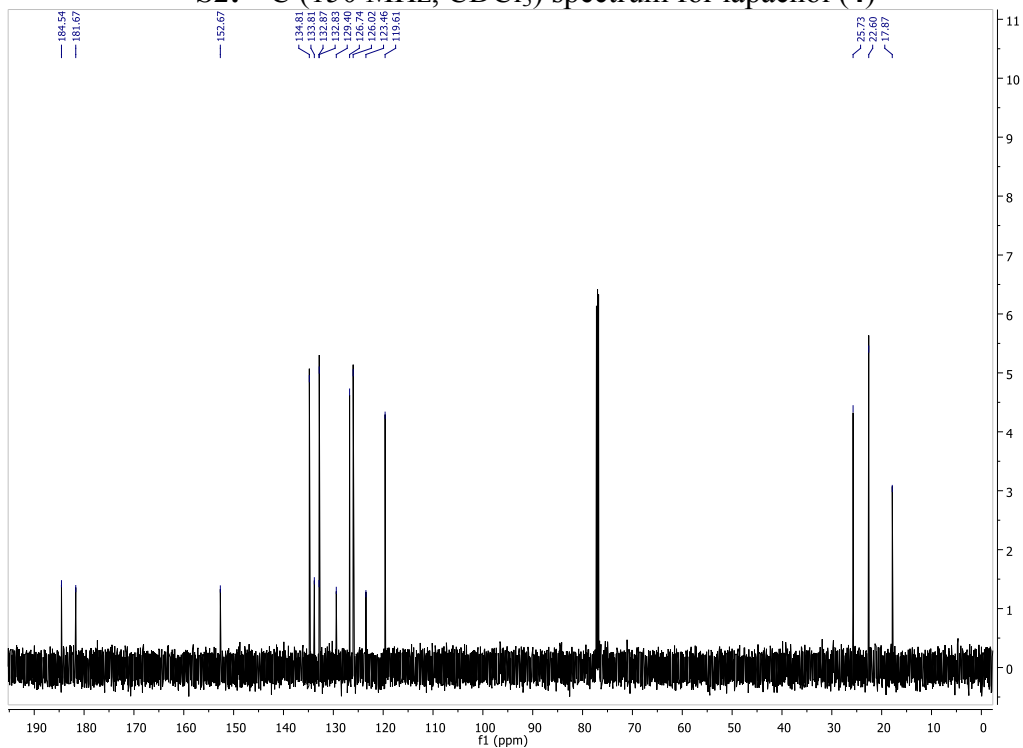
#### HRESIMS Data:

- Figure S13** HRESIMS spectrum for lapachol (**4**)  
**Figure S14** HRESIMS spectrum for dehydro- $\alpha$ -lapachone (**5**)  
**Figure S15** HRESIMS spectrum for  $\alpha$ -lapachone (**6**)  
**Figure S16** HRESIMS spectrum for dehydroiso- $\alpha$ -lapachone (**7**)

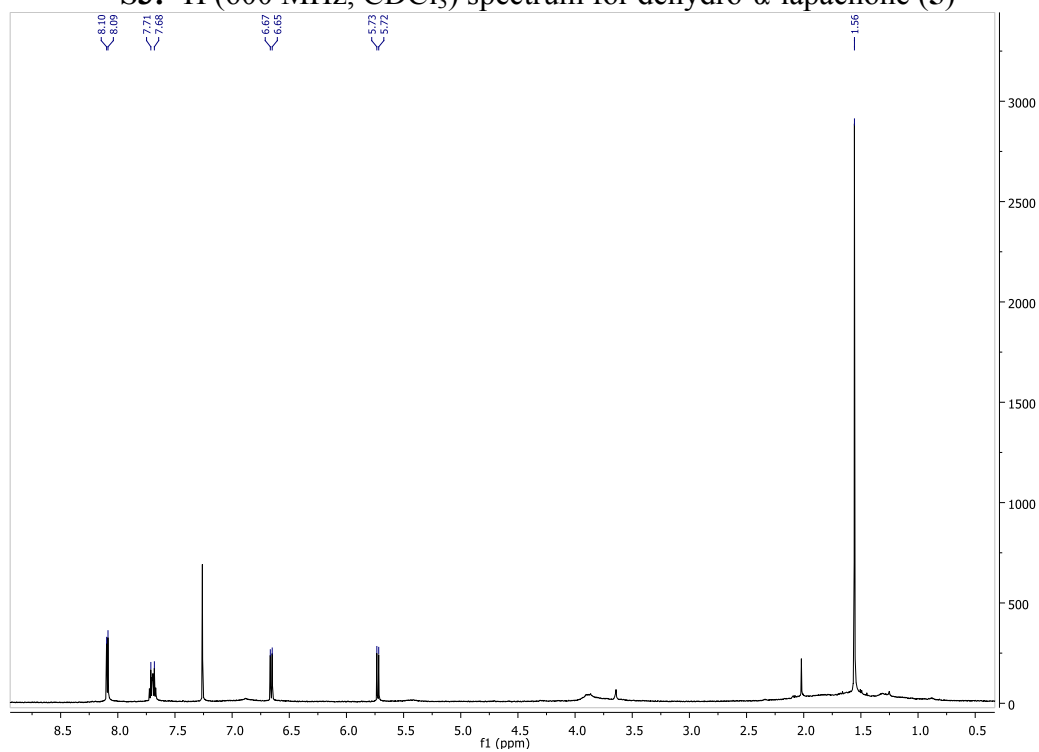
S1:  $^1\text{H}$  (600 MHz,  $\text{CDCl}_3$ ) spectrum for lapachol (4)



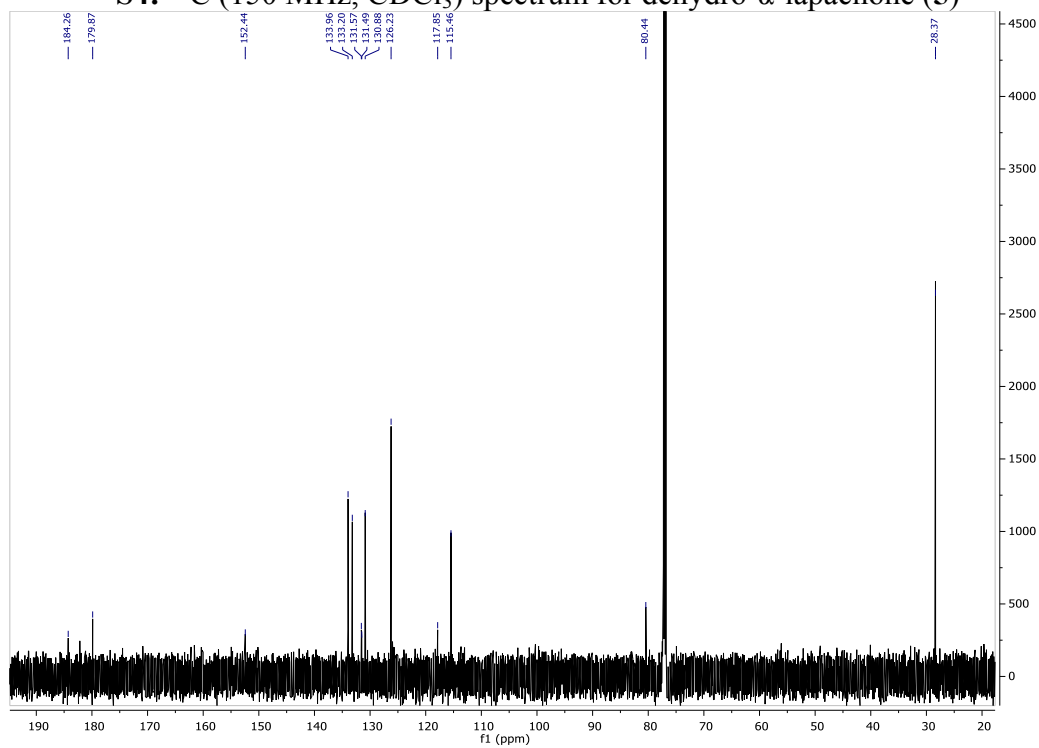
S2:  $^{13}\text{C}$  (150 MHz,  $\text{CDCl}_3$ ) spectrum for lapachol (4)



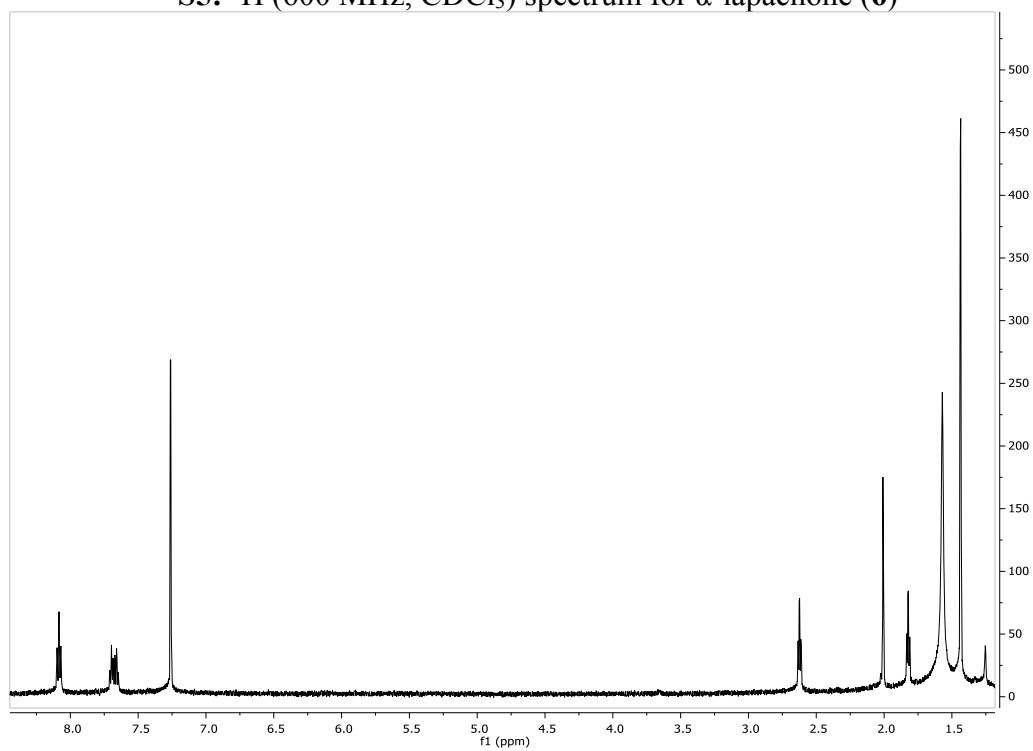
S3:  $^1\text{H}$  (600 MHz,  $\text{CDCl}_3$ ) spectrum for dehydro- $\alpha$ -lapachone (5)



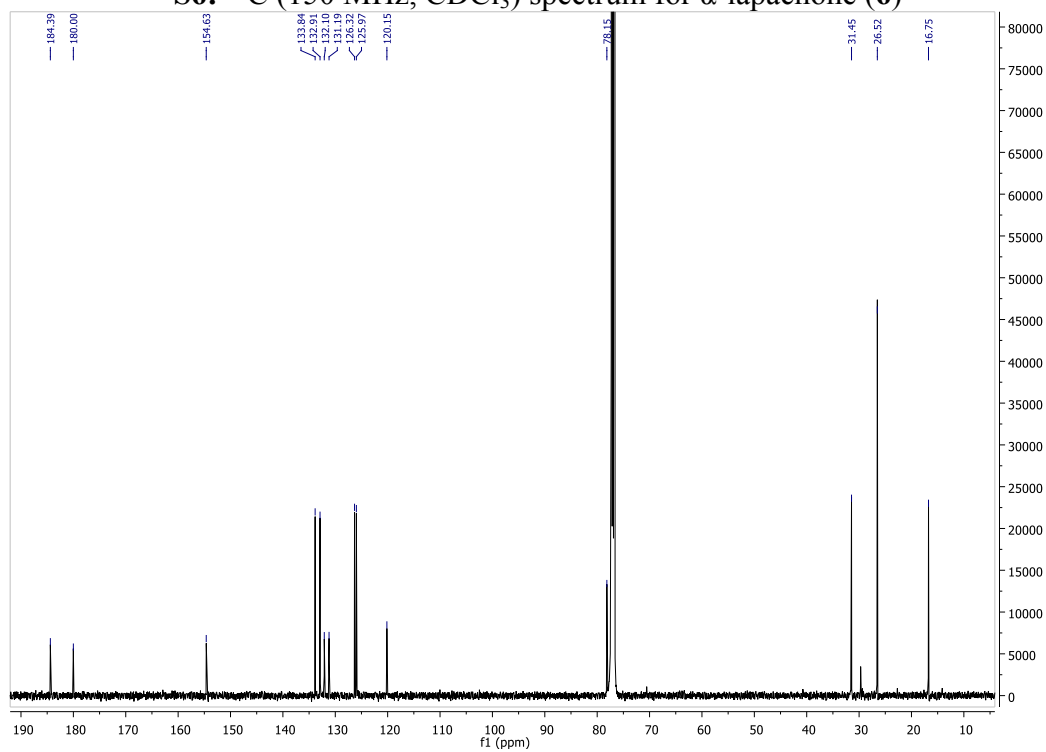
S4:  $^{13}\text{C}$  (150 MHz,  $\text{CDCl}_3$ ) spectrum for dehydro- $\alpha$ -lapachone (5)



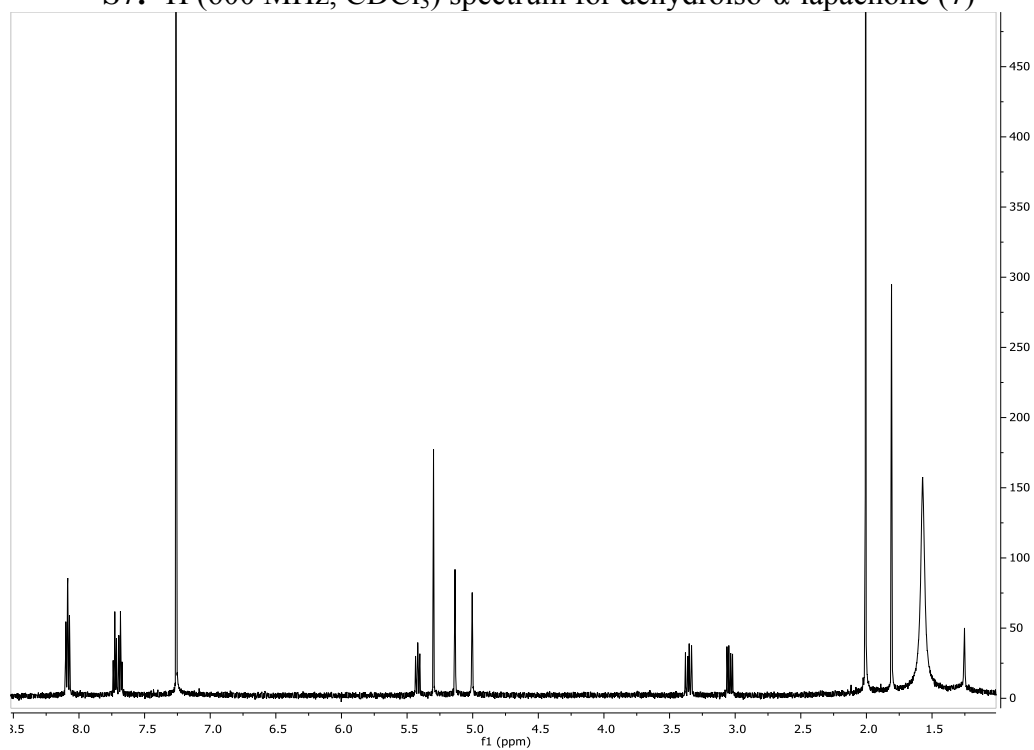
S5:  $^1\text{H}$  (600 MHz,  $\text{CDCl}_3$ ) spectrum for  $\alpha$ -lapachone (6)



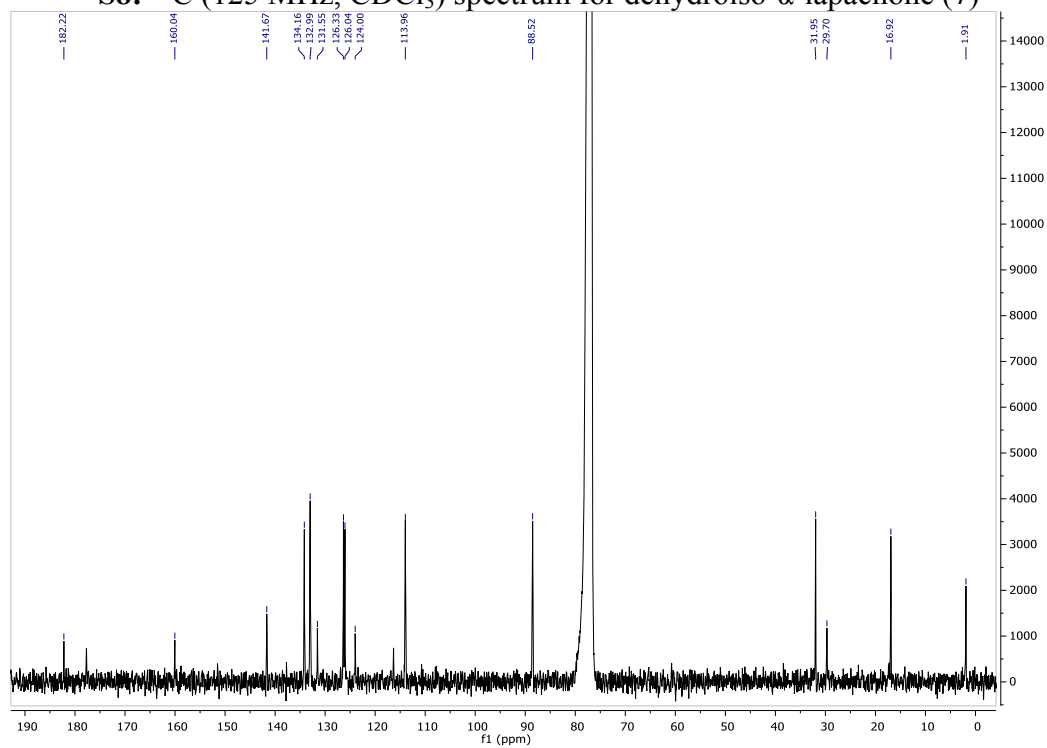
S6:  $^{13}\text{C}$  (150 MHz,  $\text{CDCl}_3$ ) spectrum for  $\alpha$ -lapachone (6)



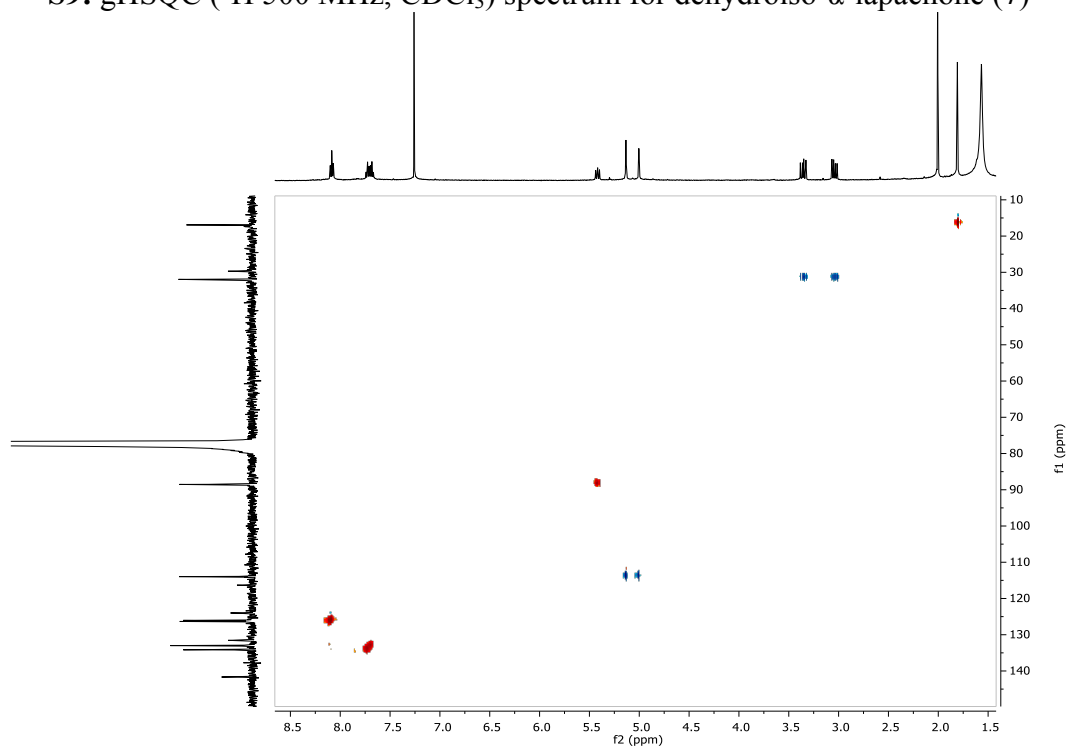
S7:  $^1\text{H}$  (600 MHz,  $\text{CDCl}_3$ ) spectrum for dehydroiso- $\alpha$ -lapachone (7)



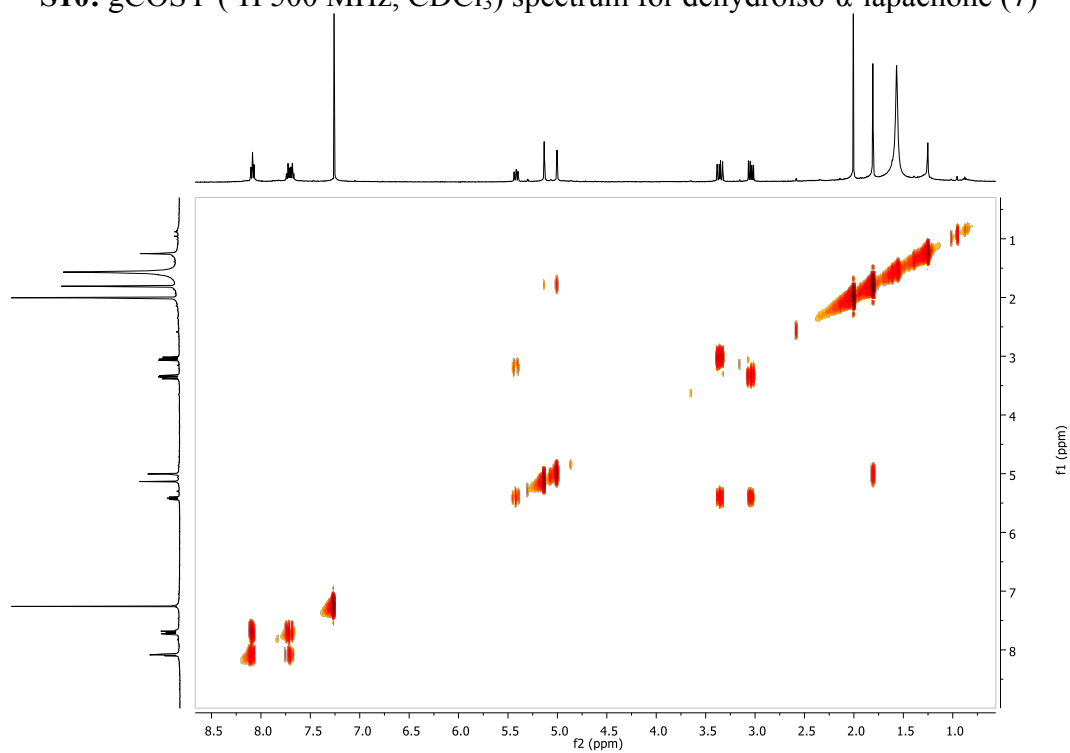
S8:  $^{13}\text{C}$  (125 MHz,  $\text{CDCl}_3$ ) spectrum for dehydroiso- $\alpha$ -lapachone (7)



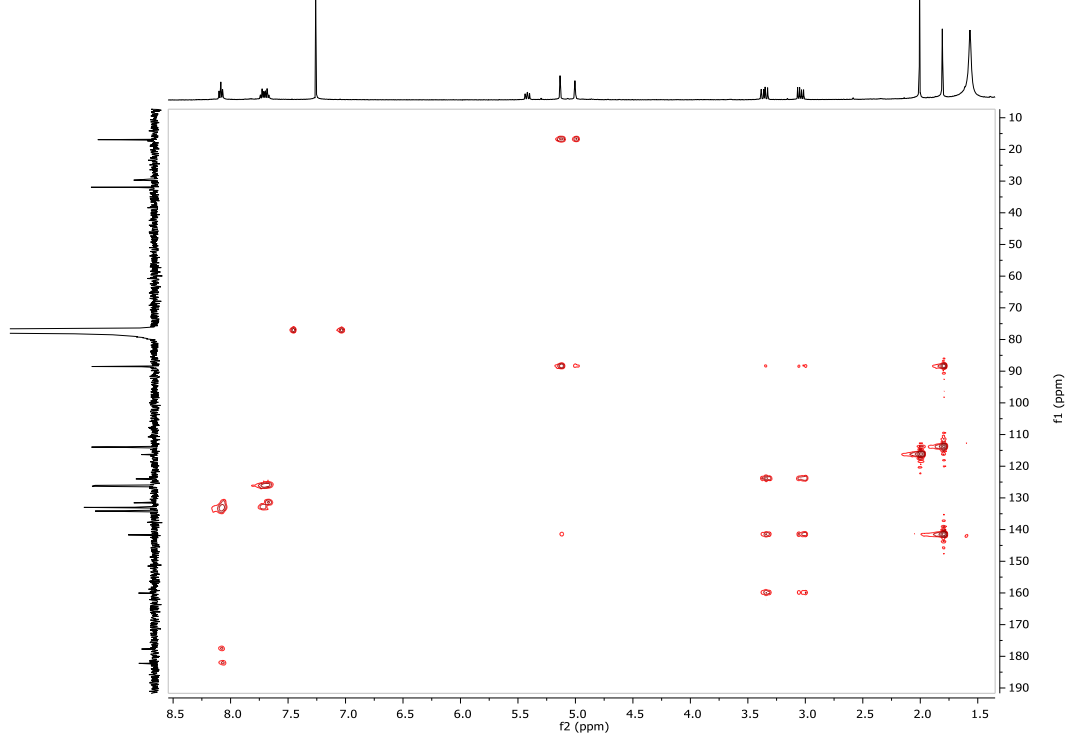
**S9:** gHSQC ( $^1\text{H}$  500 MHz,  $\text{CDCl}_3$ ) spectrum for dehydroiso- $\alpha$ -lapachone (7)



**S10:** gCOSY ( $^1\text{H}$  500 MHz,  $\text{CDCl}_3$ ) spectrum for dehydroiso- $\alpha$ -lapachone (7)



S11: gHMBCAD ( $^1\text{H}$  500 MHz,  $\text{CDCl}_3$ ) spectrum for dehydroiso- $\alpha$ -lapachone (7)

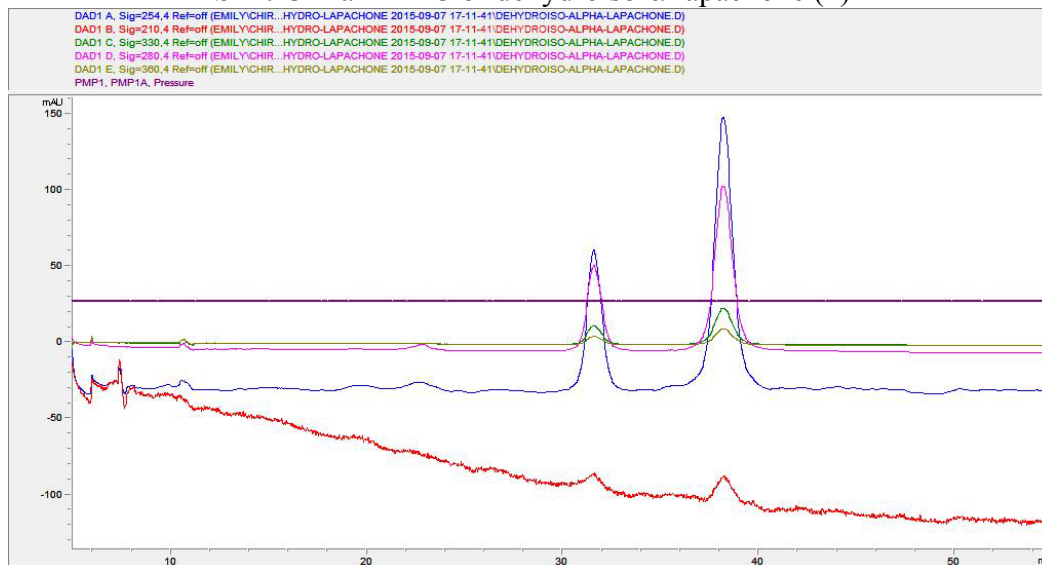


S1:  $^1\text{H}$  and  $^{13}\text{C}$  NMR data table for dehydroiso- $\alpha$ -lapachone (7) in  $\text{CDCl}_3$

position	$\delta_{\text{C}}^{\text{b}}$	$\delta_{\text{H}}$ (J in Hz) <sup>a</sup>	HMBC <sup>a</sup>	COSY <sup>a</sup>
1a	113.9	5.13 (s)	2, 3, 15	15
1b		5.00 (s)	3, 15	15
2	141.6			
3	88.5	5.42 (dd; 10.8, 9.0)	1	4a, 4b
4a	32.0	3.35 (dd; 17.2, 10.8)	2, 5, 6	3, 4b
4b		3.03 (dd; 17.2, 9.0)	2, 3, 5, 6	3, 4a
5	124.0			
6	160.0			
7	177.7			
8	131.6			
9	126.0	8.09 (t; 7.5)	7, 8, 10	10, 11
10	133.0	7.72 (t; 7.5)	9, 11	9/12
11	134.2	7.68 (t; 7.5)	12, 10	9/12
12	126.3	8.09 (t; 7.5)	11, 13, 14	10, 11
13	131.6			
14	182.2			
15	16.9	1.80 (s)	1, 2, 3	1a, 1b

<sup>a</sup>500 MHz for  $^1\text{H}$  NMR, gHMBCAD, gCOSY, <sup>b</sup>125 MHz for  $^{13}\text{C}$  NMR

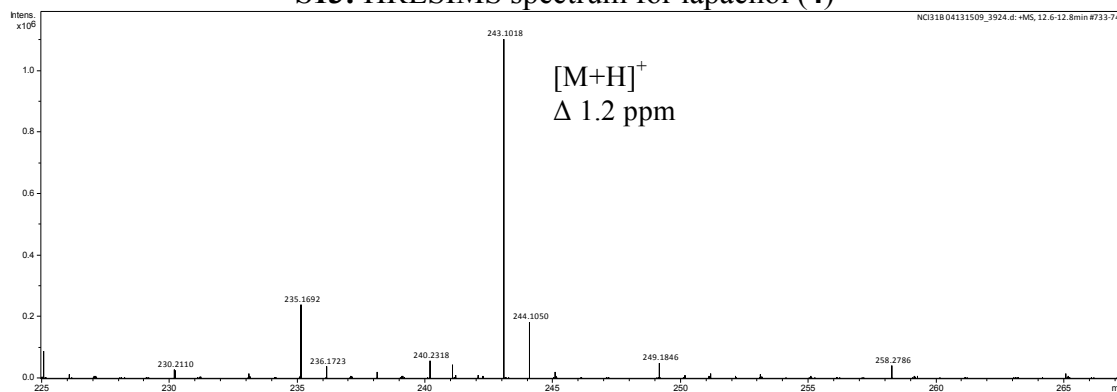
### S12: Chiral HPLC of dehydroiso- $\alpha$ -lapachone (7)



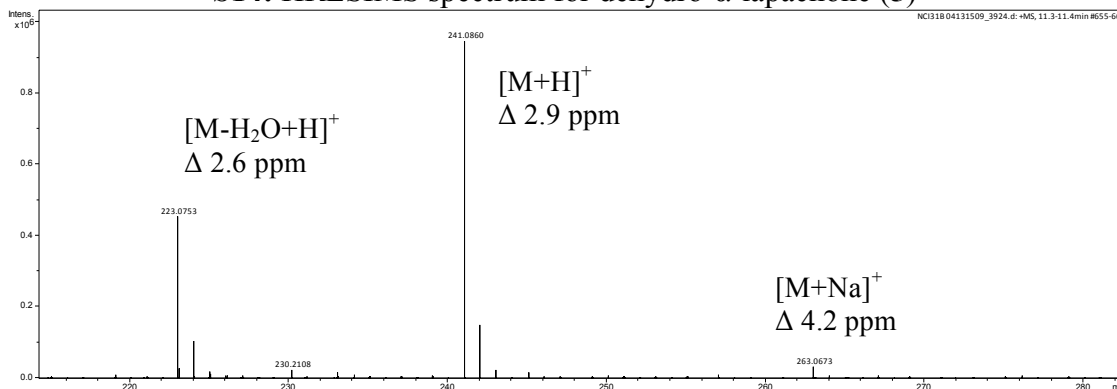
**Figure S12:** Dehydroiso-  $\alpha$ -lapachone (7) is a mixture of enantiomers.

**HPLC Method:** Isocratic gradient using 1% ethanol + 0.1% DEA/hexane + 0.1% DEA with a flow rate of 0.7 mL/min on a Phenomenex Cellulose-4 analytical column (4.6 x 250 mm).

### S13: HRESIMS spectrum for lapachol (4)

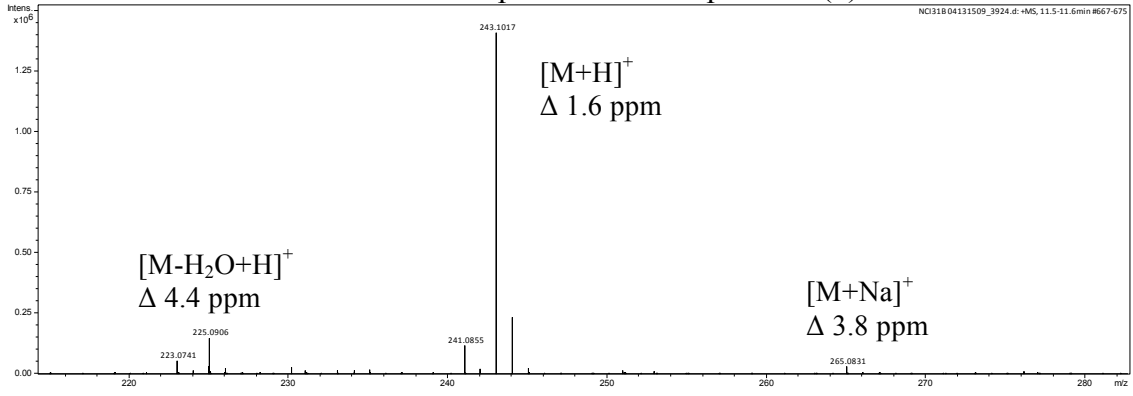


### S14: HRESIMS spectrum for dehydro- $\alpha$ -lapachone (5)





**S15: HRESIMS spectrum for  $\alpha$ -lapachone (6)**



**S16: HRESIMS spectrum for dehydroiso- $\alpha$ -lapachone (7)**

