

Supplementary Figure 4: NMR of ZmCPS4 product, (+)-labda-8,13*E*-dien-15-ol (Compound **12**). Chemical shifts are comparable to the PvCPS1 product from Pelot et. al, 2018 (Pelot K. A., Chen R., Hagelthorn D. M., Young C. A., Addison J. B., Muchlinski A., Tholl D., Zerbe P. (2018). Functional diversity of diterpene synthases in the biofuel crop switchgrass. *Plant Physiol.* doi:10.1104/pp.18.00590). Previous research has shown that class II diTPS yields dephosphorylated products *in vivo* due to the activity of *E. coli* endogenous phosphatases, and thus the structure shown and analyzed here is the resulting alcohol (Zerbe et al., 2013; Zerbe et al., 2015; Pelot et al., 2016; Mafu et al., 2018).

¹³C and ¹H NMR data (201 MHz and 800 MHz, respectively)

Position	δ_C (ppm)	δ_C (ppm)	δ_H (ppm)	δ_H (ppm)	J (Hz)	J (Hz)
	ZmCPS4	PvCPS1	ZmCPS4	PvCPS1	ZmCPS4	PvCPS1
1 a	36.99	36.97	1.19 (m)	1.16 (m)		
b			1.84 (m)	1.82 (dt)		12.7, 2.3
2 a	19.09	19.07	1.51 (dt)	1.48 (dt)	12.8, 3.4	13.9, 3.6
b			1.62 (m)	1.59 (m)		
3 a	41.82	41.80	1.16 (m)	1.15 (m)		
b			1.44 (m)	1.41 (m)		
4	33.34	33.33				
5	51.92	51.90	1.14 (m)	1.12 (dd)		12.8, 2.0
6 a	19.08	19.07	1.42 (m)	1.40 (m)	12.9, 7.2	12.8, 7.5
b			1.67 (dd)	1.64 (dd)		
7 a	33.66	33.64	1.96 (dd)	1.94 (dd)	17.5, 5.8	17.5, 6.4
b			2.06 (m)	2.04 (m)		
8	126.06	126.04				
9	140.16	140.13				
10	39.07	39.05				
11 a	26.79	26.77	2.01 (m)	1.98 (td)		11.8, 5.4
b			2.15 (m)	2.12 (td)		11.8, 4.9
12	40.18	40.16	2.08 (m)	2.05 (m)		
13	140.81	140.79				
14	122.63	122.60	5.46 (m)	5.43 (tq)		7.0, 1.4
15	59.46	59.44	4.19 (d)	4.16 (d)	6.9	7.0
16	16.38	16.36	1.74 (s)	1.71 (s)		
17	19.53	19.51	1.60 (m)	1.58 (s)		
18	33.33	33.32	0.91 (s)	0.88 (s)		
19	21.73	21.70	0.86 (s)	0.83 (s)		
20	20.11	20.09	0.97 (s)	0.94 (s)		



