

Table S1. Media recipes

Media	Composition per litre of media
Water agar (1%)	10 g Agar
Potato Dextrose Agar (PDA)	PDA: 39 g Difco™ dehydrated PDA
Fries (pH 6)	30.0 g sucrose 5.0 g yeast extract 5.0 g ammonium tartrate 1.0 g NH ₄ NO ₃ 1.0 g KH ₂ PO ₄ 0.5 g MgSO ₄ ·7H ₂ O 0.13 g CaCl 0.1 g NaCl If solid media add 15.0 g Agar
Lysogeny Broth (LB)	10.0 g NaCl 10.0 g triptone 5.0 g yeast extract If solid media add 15.0 g Agar
YPD	10 g yeast extract 20.0 g triptone After autoclaving add: 20.0 g glucose
Synthetic dropout media lacking uracil (pH 5.8)	6.7 g Yeast base media (no amino acids) 1.6 g amino acid mix lacking uracil After autoclaving add 30 g glucose If solid media add 15.0 g Bacto Agar

Table S2. List of primers

Name	forward	reverse
Phl	ccctcgttgaccaagaatc	aagttcgtggacacgacct
Leo	gacgtgaccctgttcatca	gagcattcactaggcaacca
Sts01_5flank	ttctggttcggaataagctctt	gagcattcactaggcaa- atttattgtgcgcgttcg
Sts01_3flank	ctaagaaccagttgctccc- tctttgcacctacgattttcc	cattcctgattcctctgtttg
Sts02_5flank	gcgcggaatggtgtaaagt	gagcattcactaggcaa- aaagatgatctcgctgcc
Sts02_3flank	ctaagaaccagttgctccc- tgaaccggcgtaccagttta	accaacacgtcagtgacgac
XW_STS01	atcaactatcaactattaactatatcgtaatacca- atgtcccattcccgccacga	tgtcatttaaattagtgatggtgatggtgatgcac- cacctccacggcagtgacct
XW_STS02_exon1	atcaactatcaactattaactatatcgtaatacca- atggctccgatagatgcatca	gacccatggagaagcacatgactccggacatga agcctttaccaagatcggcatgtc
XW_STS02_exon2	tactttgagtaccgacatgccgatcttggtaaa ggcttcatgtccggagtcatgtg	tgtcatttaaattagtgatggtgatggtgatgcac- acccaaatccttccttcattg
Phleo_qPCR	ggaagttcgtggacacga	gacgtgaccctgttcatca
EIng.f_qPCR	atgatcgacgtttccacc	tcaatagcctcgaggagg
Actin_qPCR	agtcgaagcgtggtatcct	acttggggttgatgggag
SnToxA_qPCR	gtccgtctgtcaacaacatcg	tcagttcccacgagcctatagc

Table S3. NMR data for eudesma-4,11-diene (**1**) (300MHz, CDCl₃).

Chemical shifts (δ) for C (C¹³ NMR) and H (H¹ NMR) and C→H correlation at 2-4 bonds distance (HMBC) are presented.

Carbon number	C δ (ppm)	H δ_a (ppm)	H δ_b (ppm)	HMBC C → H
1 [#]	40.45	1.32	1.5	14
2	19.26	1.57		
3	33.32	1.89	1.99	15
4	124.69	-	-	15
5	135.04	-	-	14, 15
6	30.91	2.54		
7	46.98	1.87	-	13
8	27.83	1.59		
9 [#]	42.44	1.29	1.51	14
10	34.64	-	-	14
11	151.01	-	-	13
12	108.19	4.70	4.72	13
13	21.03	1.75	-	12
14	24.8	1.04	-	
15	19.44	1.61	-	

[#] Data insufficient to distinguish between C1 and C9

Table S4. NMR data for acora-4,9-diene (**4**) (300MHz, CDCl₃).

Chemical shifts (δ) for C (C¹³ NMR) and H (H¹ NMR) and C $\rightarrow$ H correlation at 2-4 bonds distance (HMBC) are presented.

Carbon number	C δ (ppm)	H δ_a (ppm)	H δ_b (ppm)	HMBC C $\rightarrow$ H
1	47.94	-	-	2a, 2b ⁺
2	26.78	1.58*	1.67	3b
3	34.77	1.78	2.09	2a
4	149.09	-	-	2b ⁺ , 15
5	123.97	5.27	-	15
6	29.22	1.98*	-	2a, 2b ⁺ , 14 ⁺
7	28.4	1.83	-	12, 13
8	32.63	1.97	2.18	7, 14 ⁺
9	121.6	5.38	-	14 ⁺
10	134.4	-	-	2a, 2b ⁺ , 14 ⁺
11	55.49	1.65*	-	12, 13
12	21.48	0.81	-	7, 11 ⁺ , 13
13	23.29	0.93	-	12
14	23.99	1.66*	-	
15	15.29	1.6*	-	

*Signals not clear on H NMR, values obtained from HSQC

⁺HMBC correlations with H 2b, H11 and H14 are tentative because signals are too close

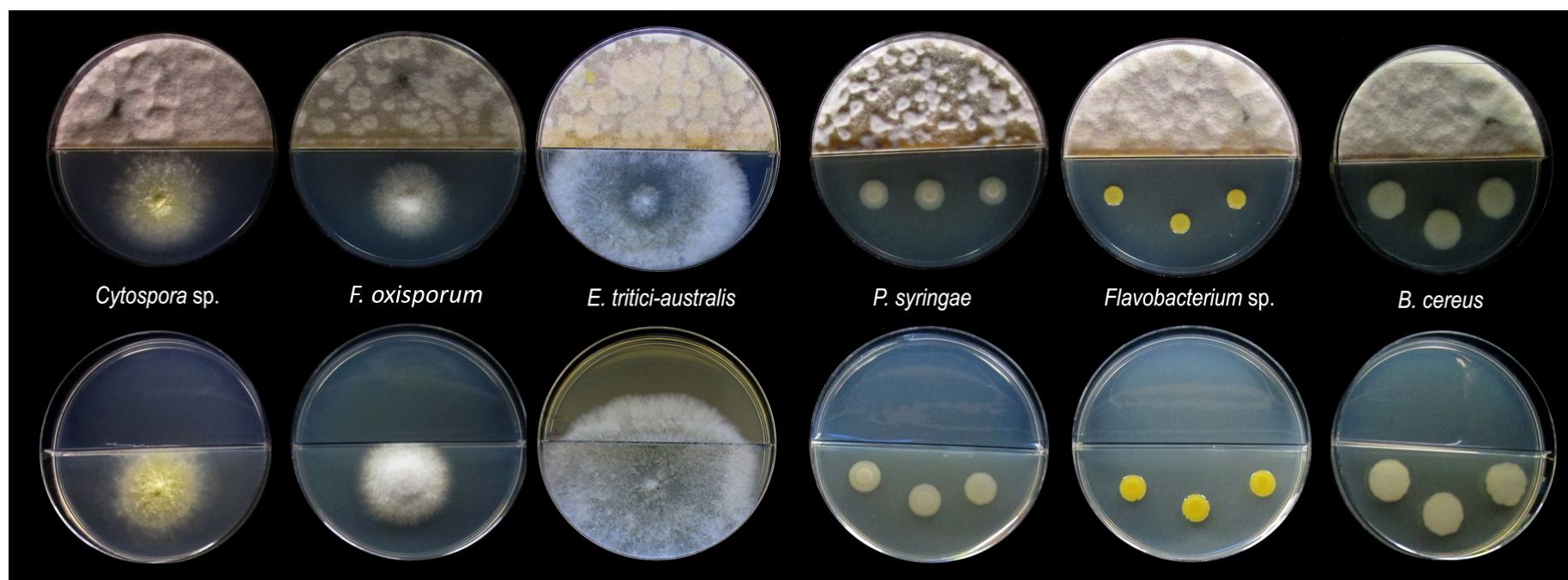


Figure S1. Organisms that showed low or no sensitivity to *P. nodorum* VOCs emitted *in vitro*.

Split plate assay of the effect of VOCs produced by wild type *P. nodorum* (SN15). The top row of plates show effect (or lack of effect) caused by SN15 VOCs over *Cytospora* sp., *Fusarium oxysporum*, *Eutiarosporella tritici-australis*, *Pseudomonas syringae*, *Flavobacterium* sp. and *Bacillus cereus*. The bottom row of plates presents each test organism next to the control, media only: non-inoculated Fries agar.

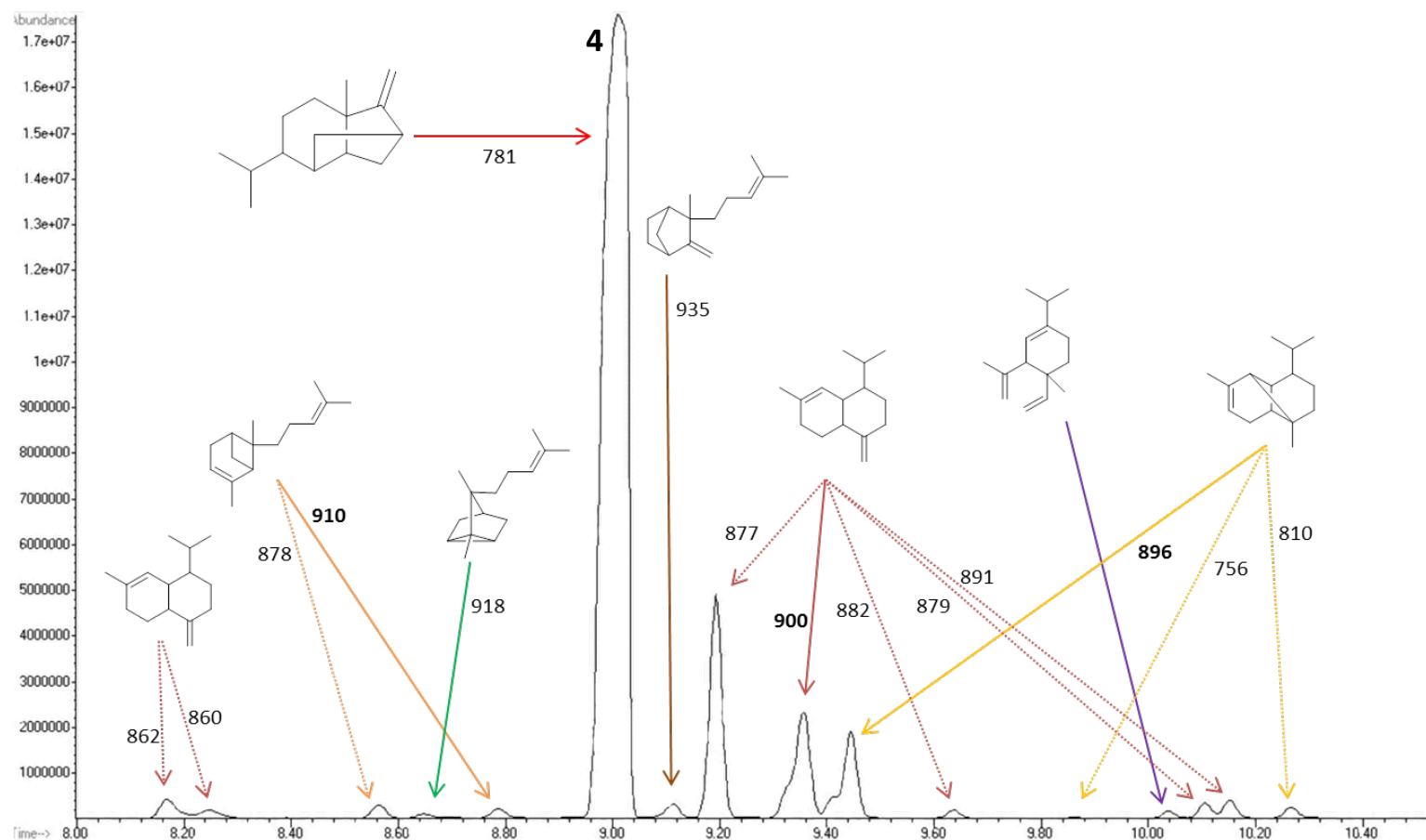


Figure S2. GC-MS from the isolated sesquiterpenes produced by *STS1* expressed in yeast.

The peak corresponding to **4** is marked with its number. The presented structures correspond to the best match within the NIST library. The numbers are the score given by the NIST library (the score could go up to 1000). The proposed structure for **4** is isosativene but did not show a good spectral match to the NIST library as the lower score indicates.

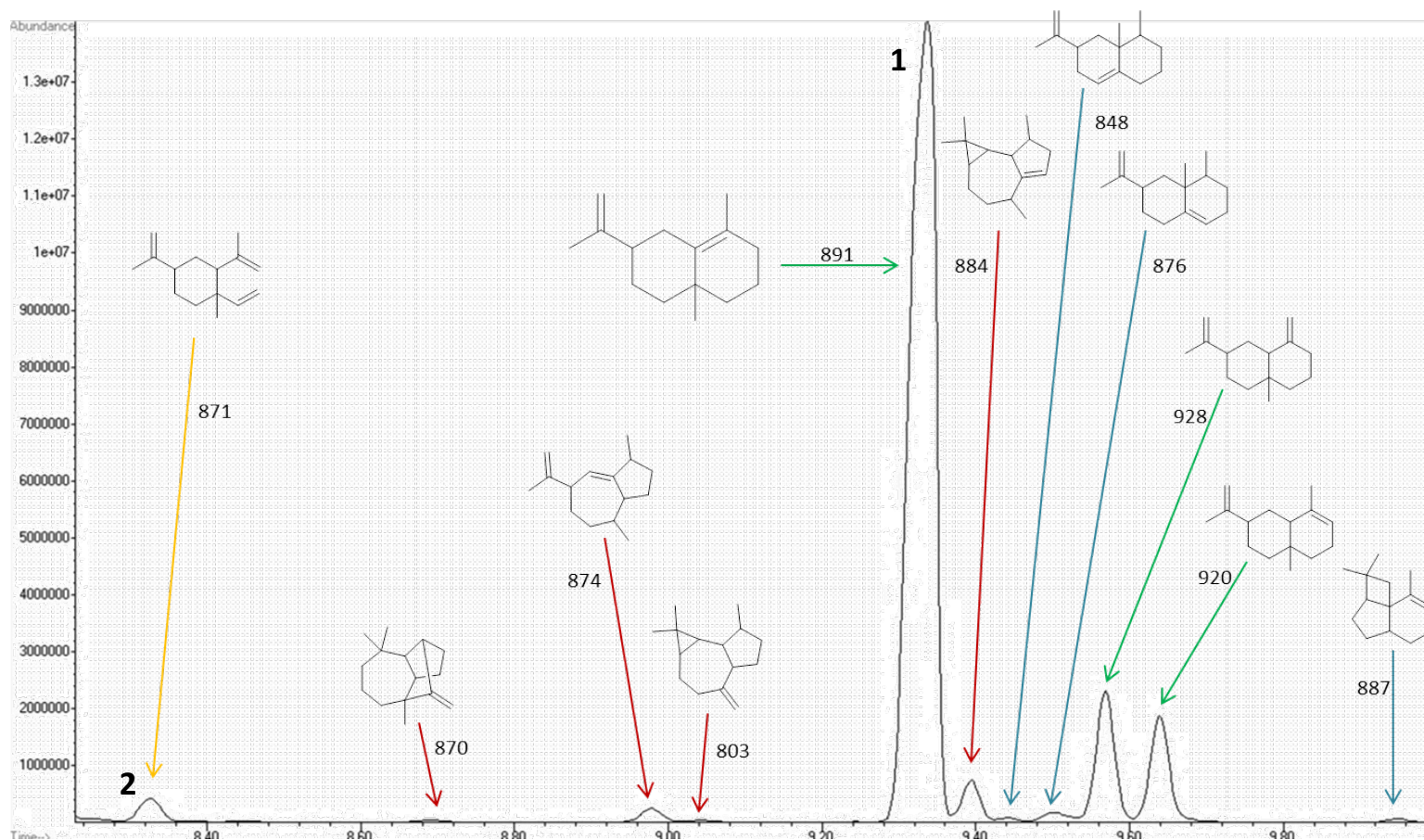


Figure S3. GC-MS from the isolated sesquiterpenes produced by *STS2* expressed in yeast.

The peaks corresponding to **1** and **2** are marked with their number. The presented structures correspond to the best match within the NIST library. The numbers are the score given by the NIST library (the score could go up to 1000).

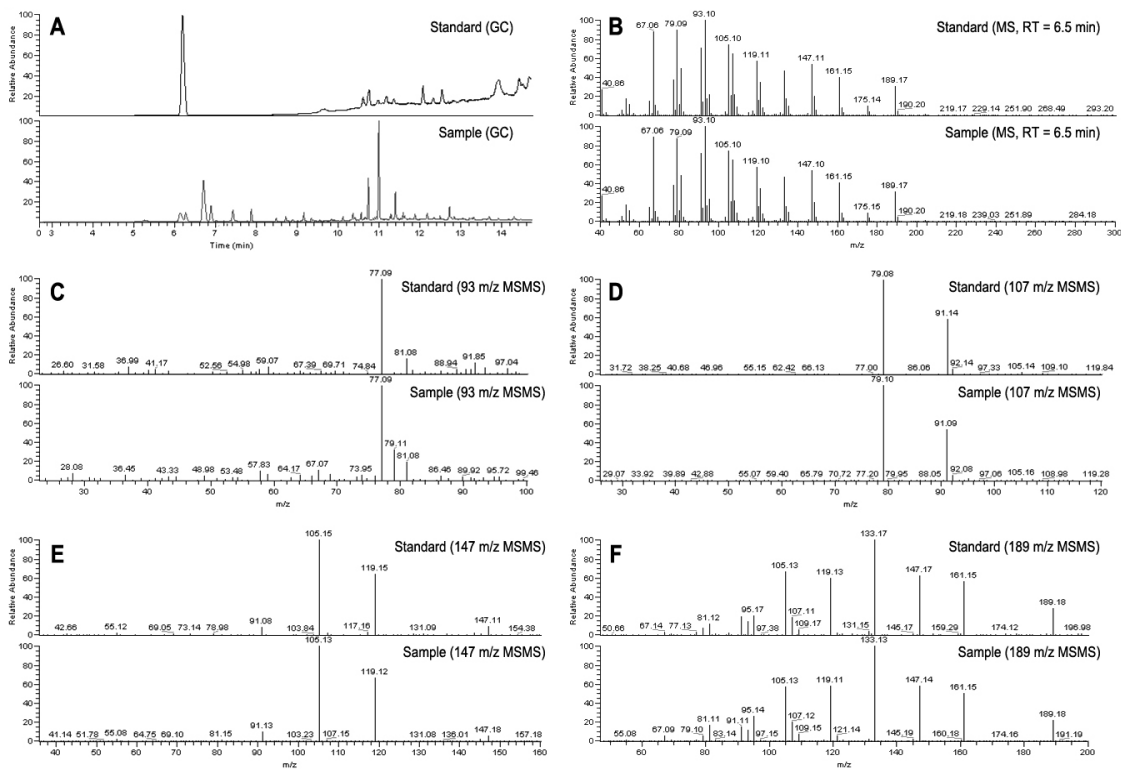


Figure S4. MSMS Identification of β -elemene.

Figure shows the MS chromatogram (A), MS spectrum (B) and MS² spectra of ion 93⁺ (C), 107⁺ (D), 147⁺ (E) and 189⁺ (F). All panels compare acquired data from the spectra (above), and the *P. nodorum* sample (below).

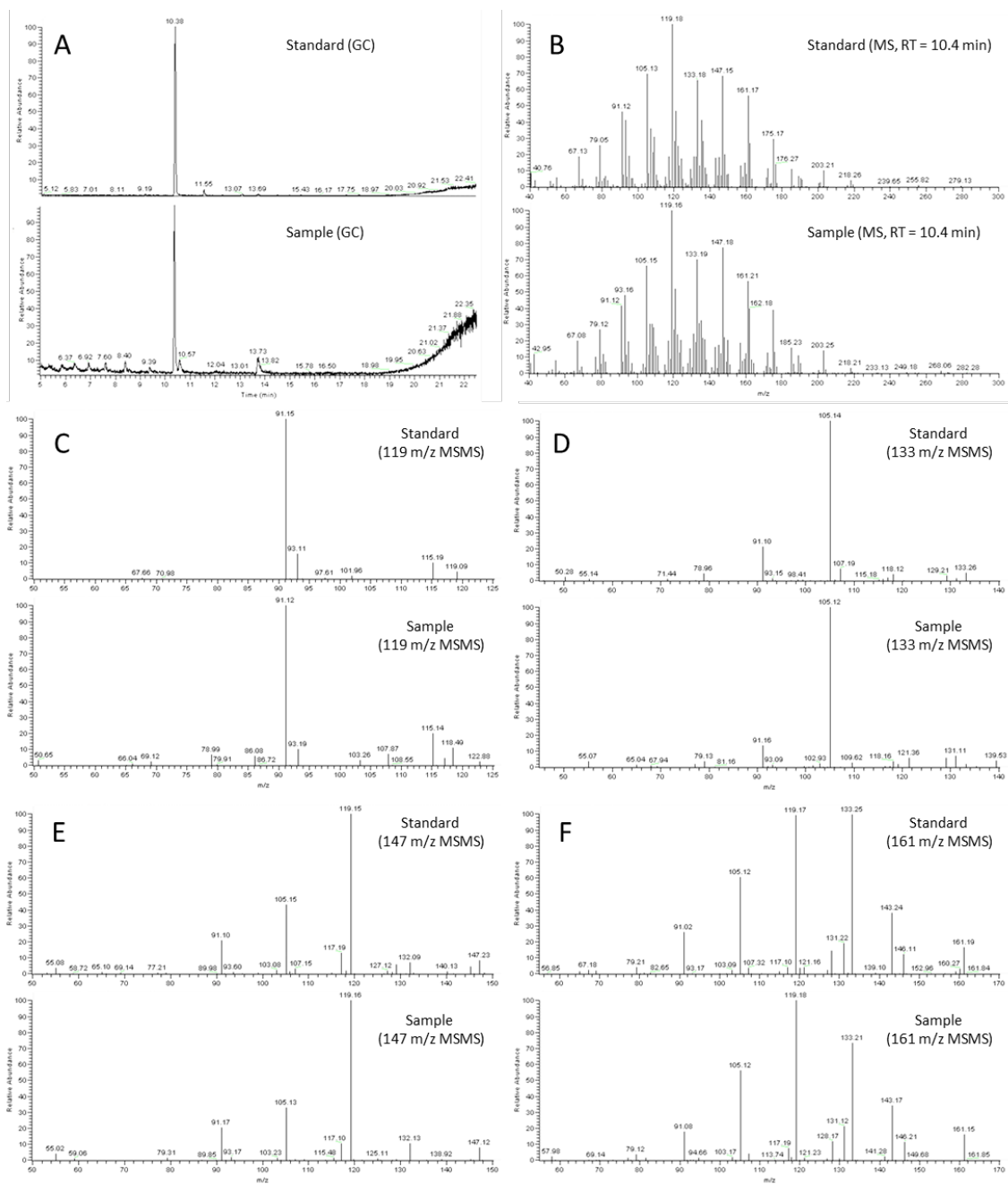


Figure S5. MS/MS Identification of α -cyperone.

Figure shows the MS chromatogram (A), MS spectrum (B) and MS/MS spectra of ion 119⁺ (C), 133⁺ (D), 147⁺ (E) and 161⁺ (F). All panels compare acquired data from the spectra (above), and the purified sample from *P. nodorum* (below).

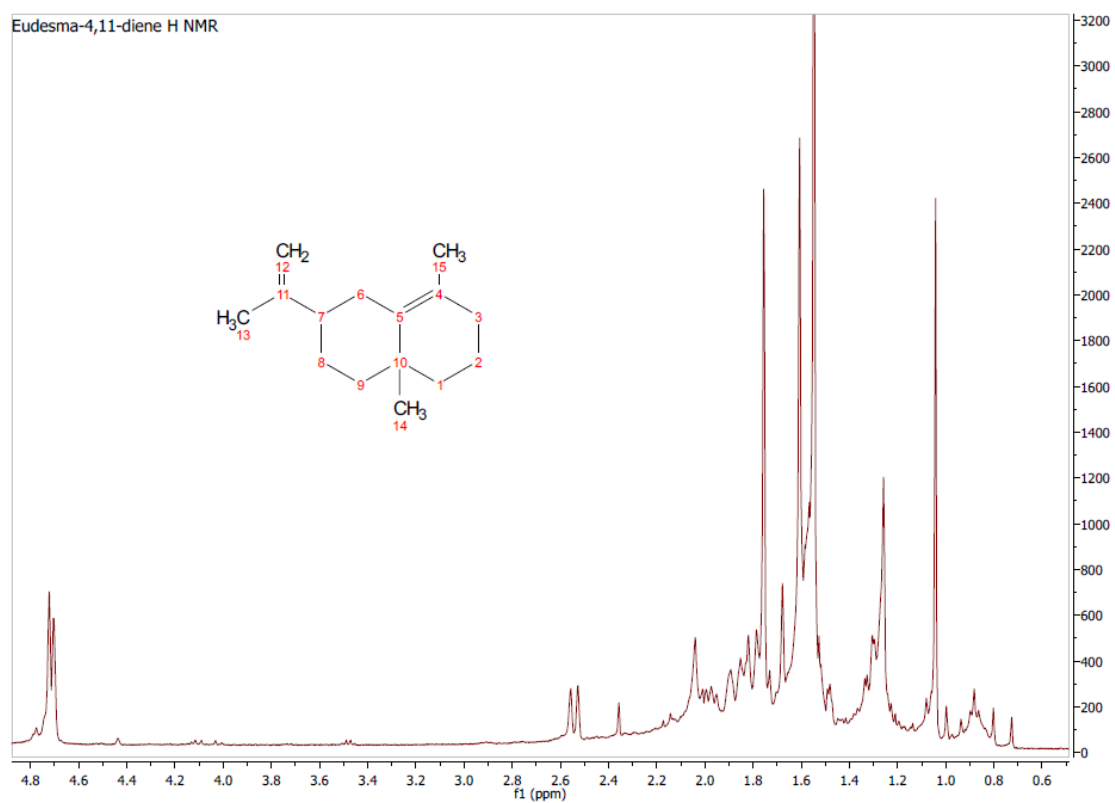


Figure S6. Eudesma-4,11-diene (1) H NMR (300MHz, CDCl₃)

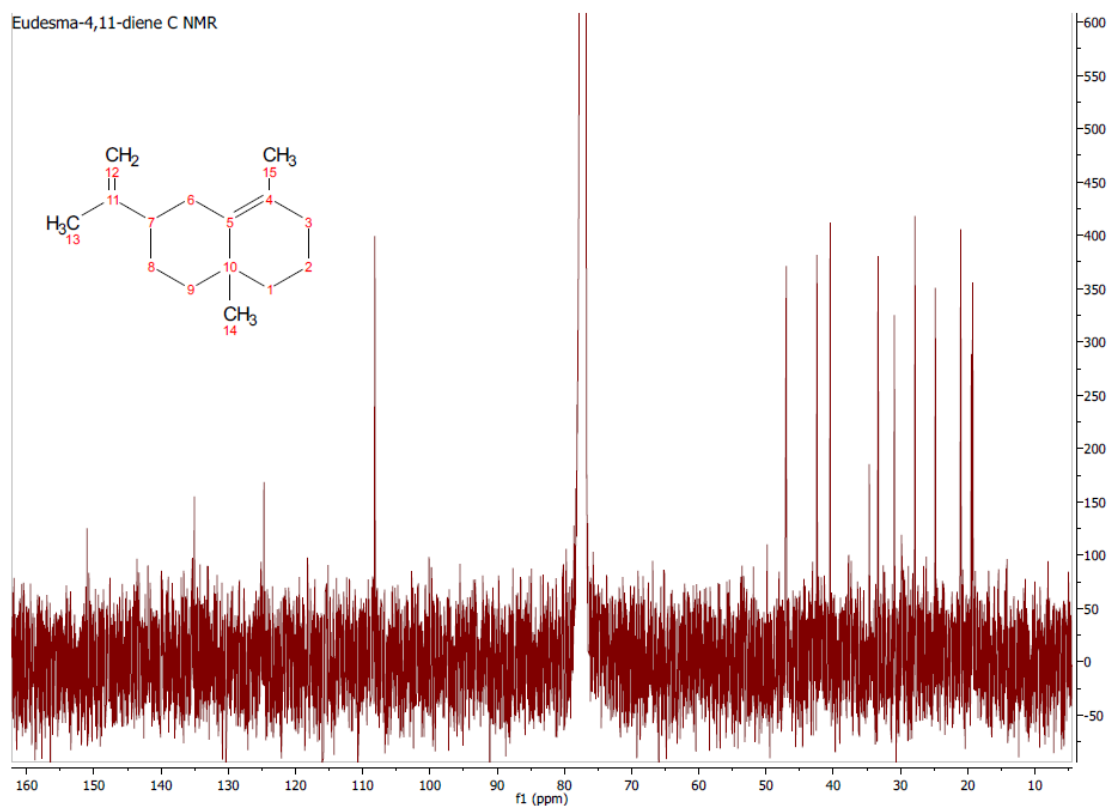


Figure S7. Eudesma-4,11-diene (**1**) C NMR (300MHz, CDCl₃)

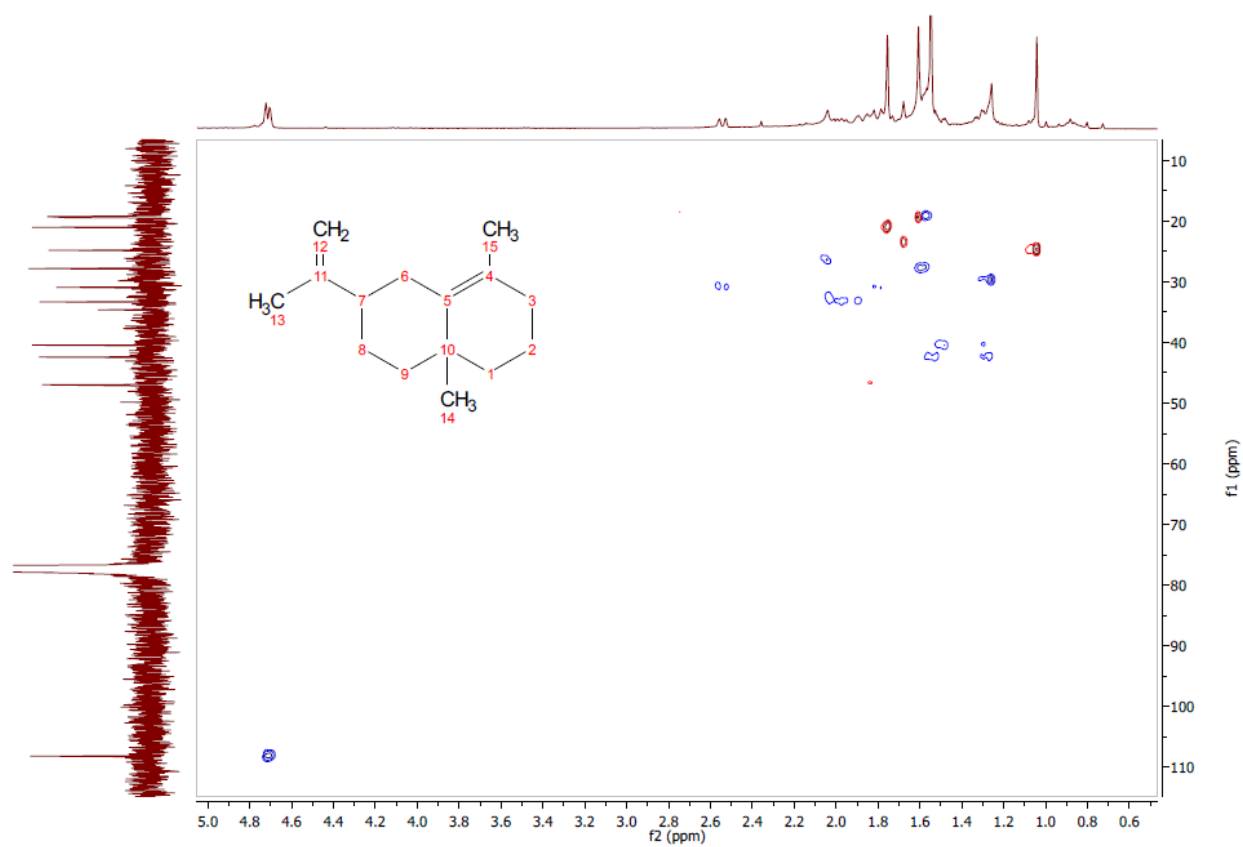


Figure S8. Eudesma-4,11-diene (**1**) HSQC (300MHz, CDCl₃)

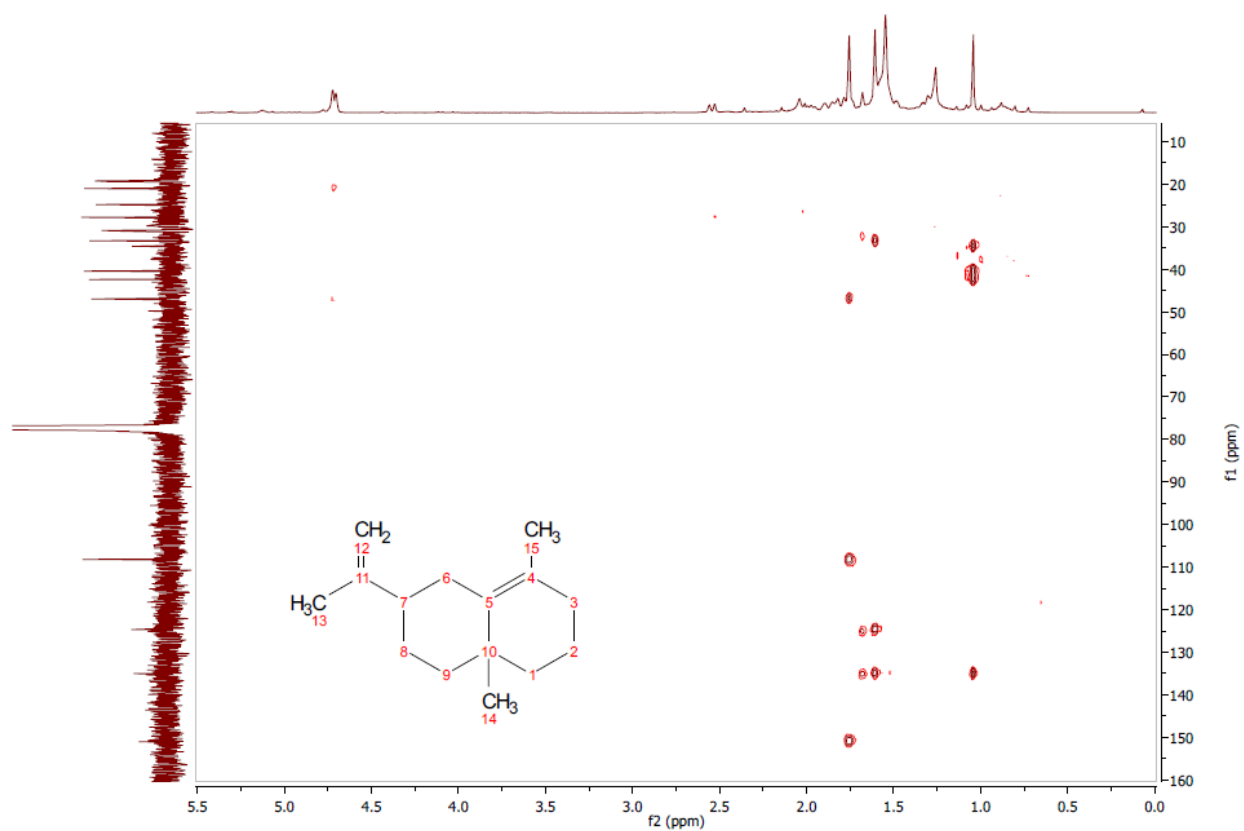


Figure S9. Eudesma-4,11-diene (**1**) HMBC (300MHz, CDCl₃)

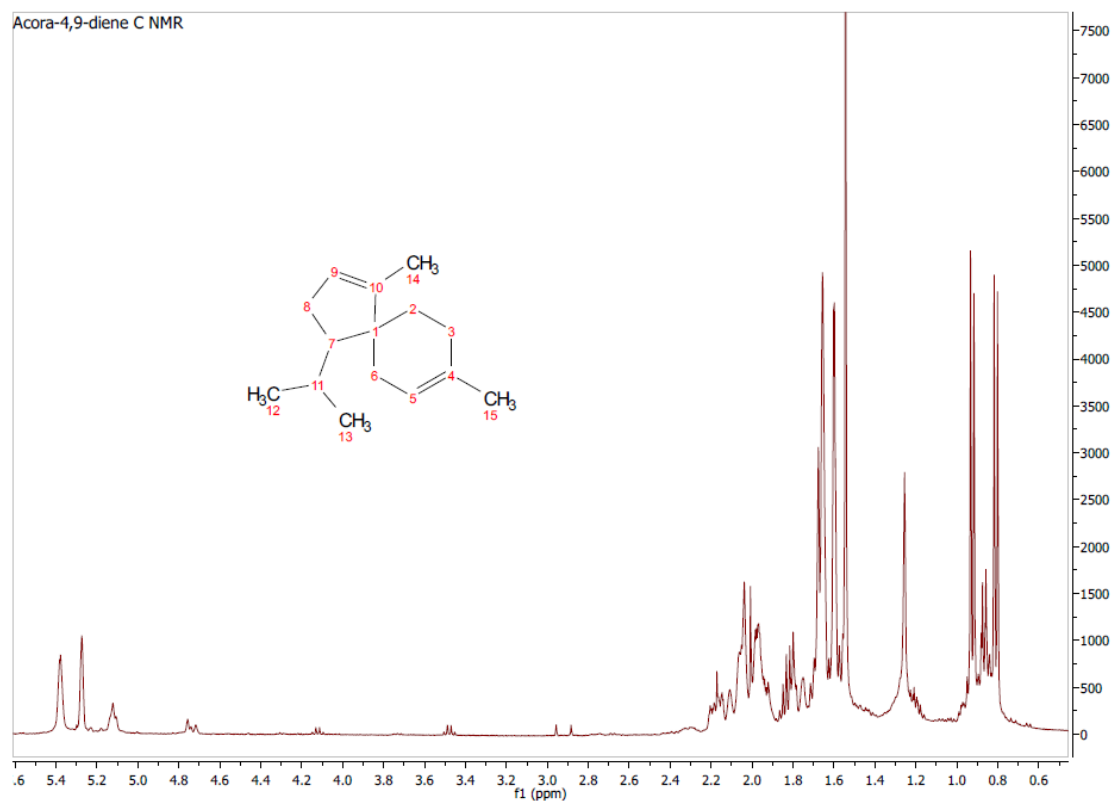


Figure S10. Acora-4,9-diene (**4**) ^1H NMR (300MHz, CDCl_3)

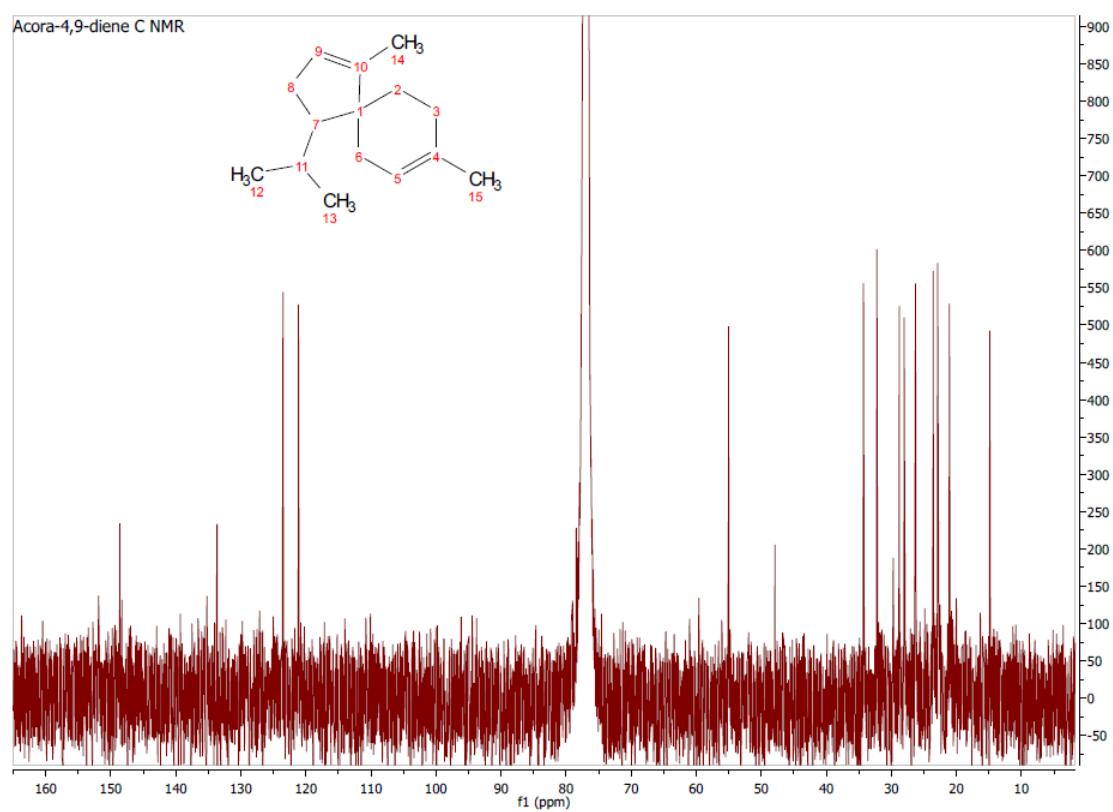


Figure S11. Acora-4,9-diene (**4**) C NMR (300MHz, CDCl₃)

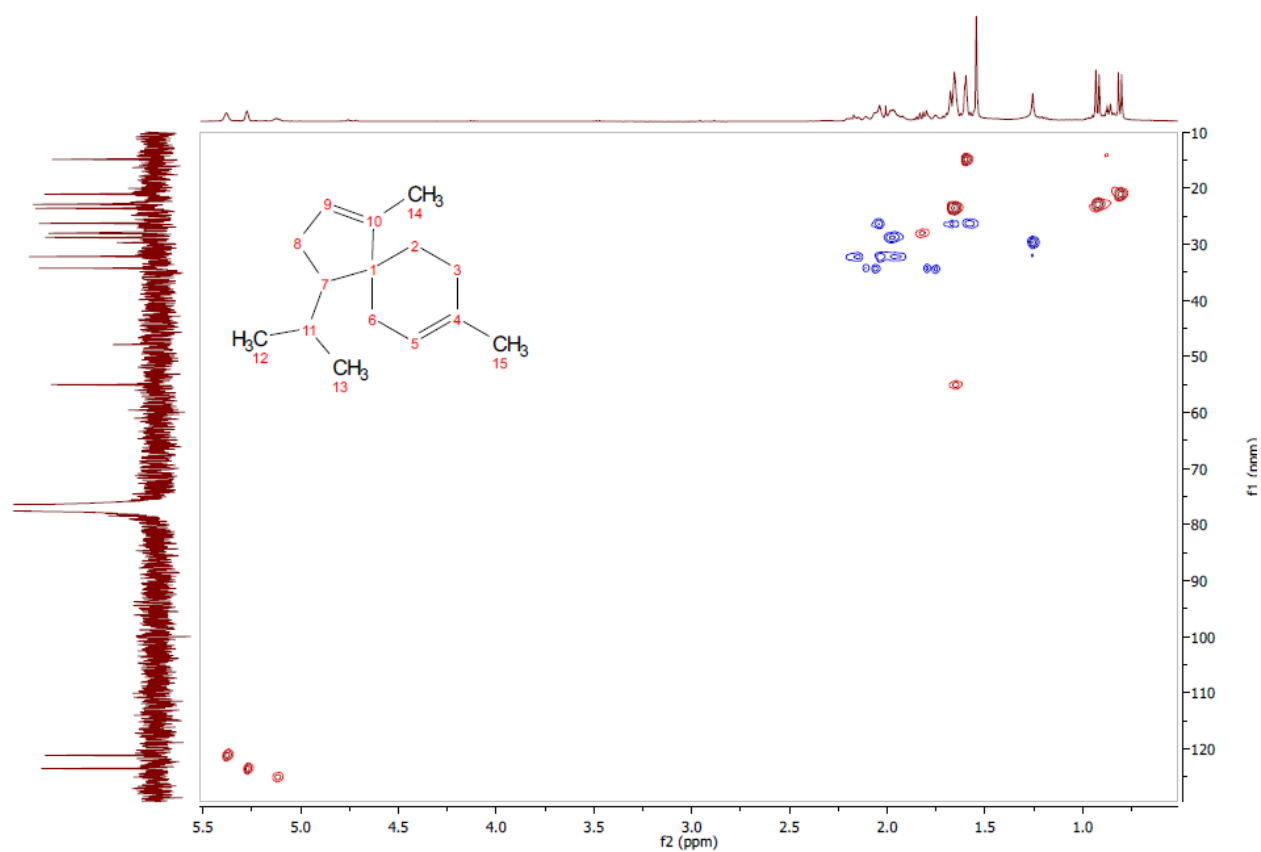


Figure S12. Acora-4,9-diene (**4**) HSQC (300MHz, CDCl_3)

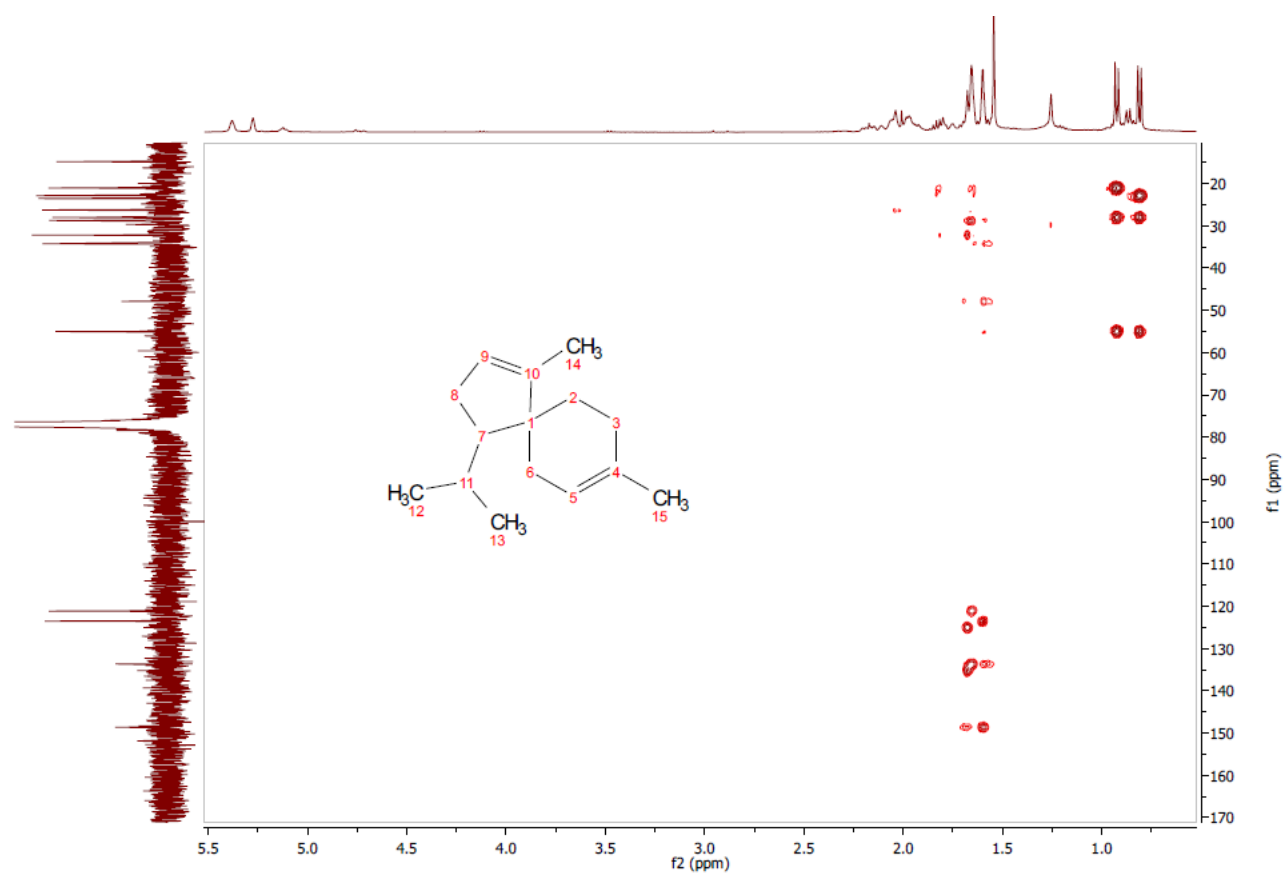


Figure S13. Acora-4,9-diene (**4**) HMBC (300MHz, CDCl₃)



Figure S14. Pathogenicity test of *sts1* and *sts2* on wheat 5 days post inoculation. Two *sts1*, two *sts2* strains and two ectopic mutants were inoculated on wheat cv. Axe. SN15 was used as a positive control and 0.02% tween 20 solution as negative control.

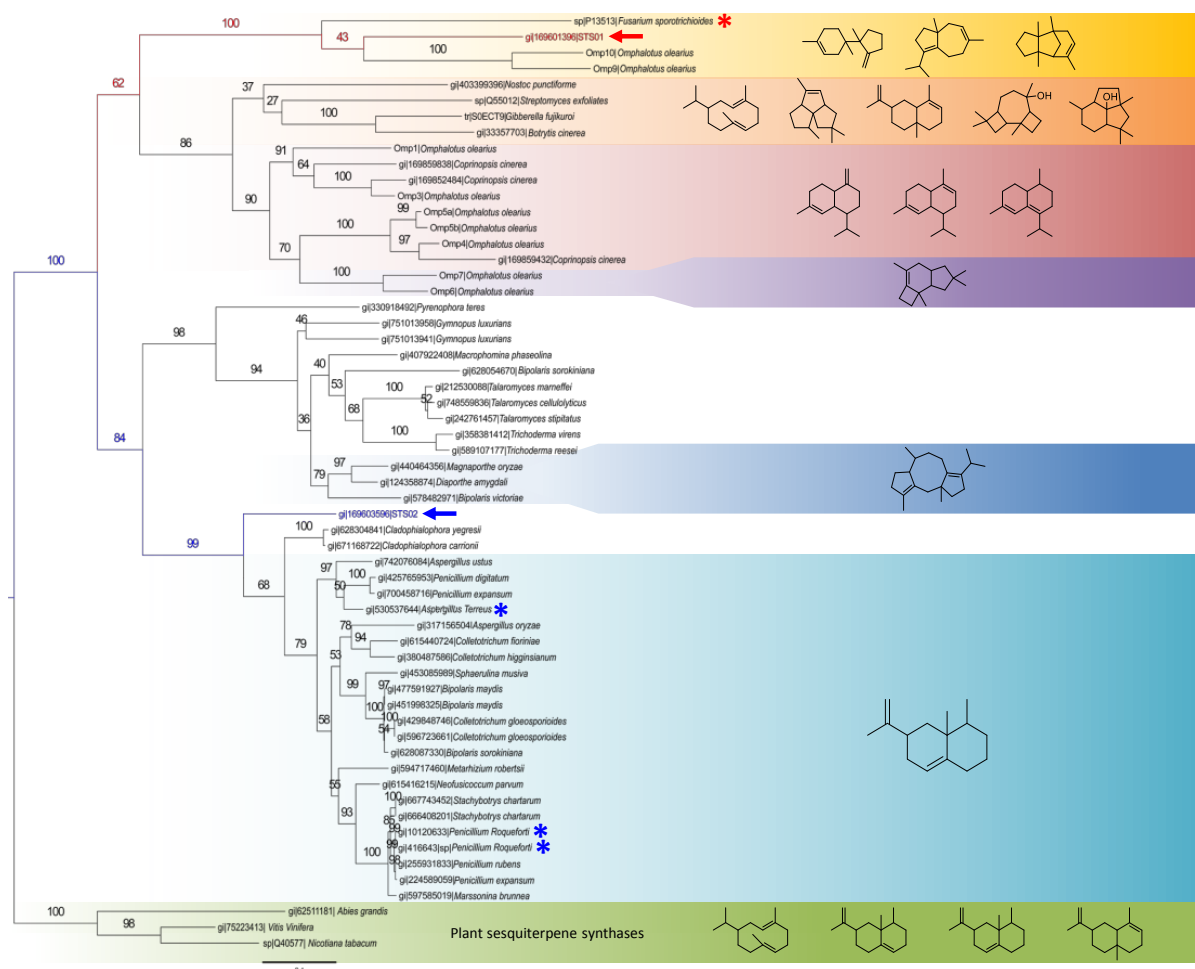


Figure S15. Neighbour joining phylogenetic tree of fungal terpene synthases (plant sesquiterpene synthases as outliers). Red arrow indicates *P. nodorum* Sts1, blue arrow indicates *P. nodorum* Sts2, red asterisk indicates a characterised trichodiene synthase, and blue asterisks indicate characterised aristolochene synthases. The presented chemical structures correspond to some of the reported products of the terpene synthases of each group.