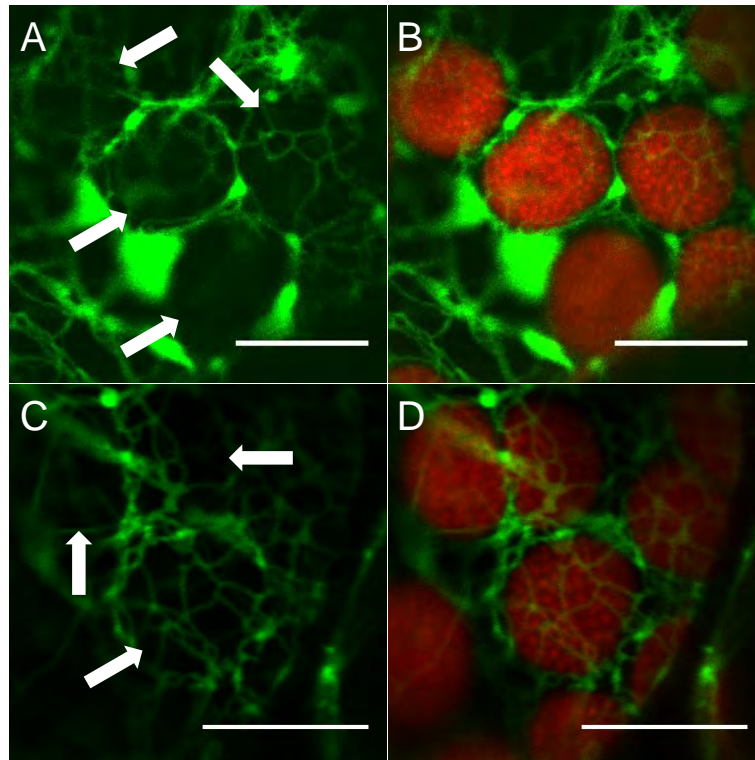


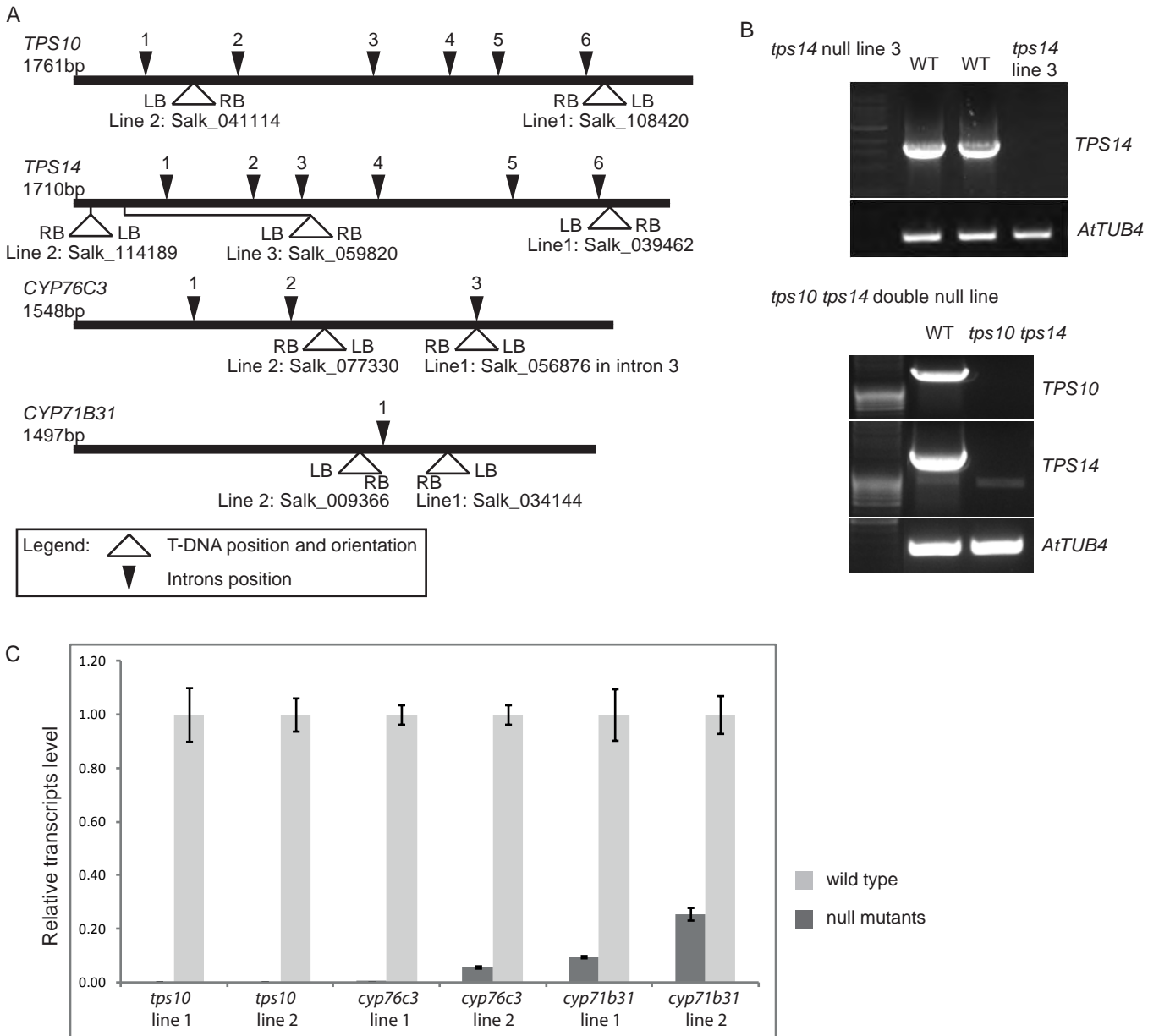
Supplemental Figure 2: Confocal microscopy showing co-localization of CYP76C3 and CYP71B31 with an ER marker.

CYP76C3:eGFP and CYP71B31:eGFP ER were transiently expressed in *N. benthamiana* epidermal cells together with the ER marker mRFP:HDEL and visualized by confocal microscopy. (A) CYP76C3:eGFP, (D) CYP71B31:eGFP, (B and E) mRFP:HDEL, (C and F) merged. Scale bar: 10 μ m.



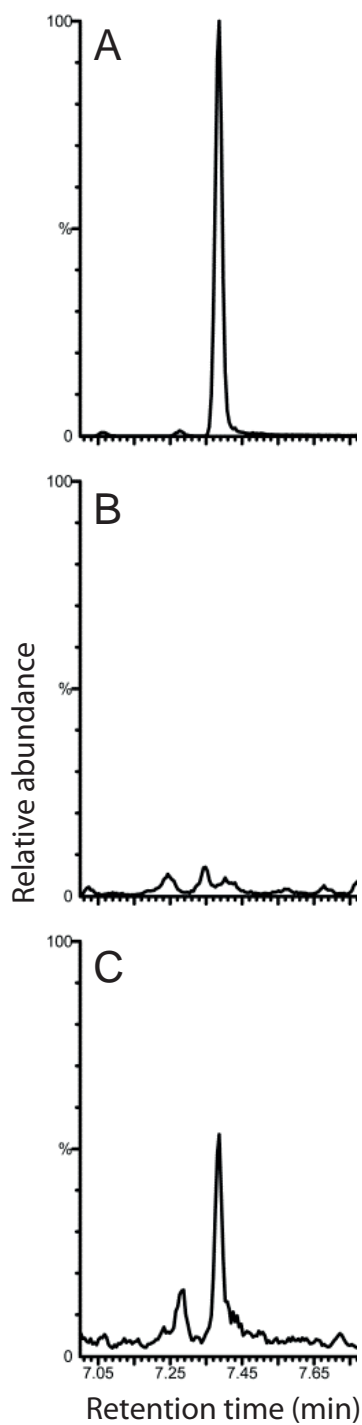
Supplemental Figure 3: Confocal microscopy of CYP71B31:eGFP showing ER membranes encircling the chloroplasts.

Chloroplasts (chlorophyll autofluorescence in plastids stroma) in red. (A and C) CYP71B31:eGFP localized on ER membranes. (B and D) merged with chloroplast autofluorescence. Scale bar: 10 μ m. Arrows (A and C) point to cavities formed by ER in which chloroplasts fit perfectly with region of potential contact between ER and plastid envelope (B and D).



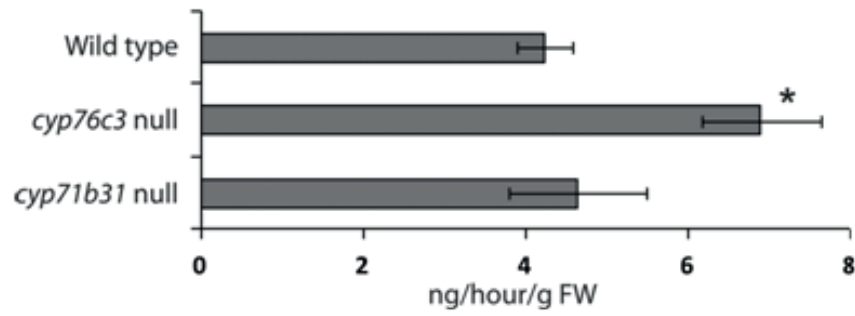
Supplemental Figure 4: Characteristics and validation of the insertion mutants.

(A) Positions of T-DNA in candidate genes for each insertion line tested. (B) RT-PCR on transcripts for insertion mutants *tps14* line 3 and double mutant line *tps10 tps14*. (C) Transcript levels in flowers measured by qRT-PCR for insertion mutants *tps10* lines 1 and 2, *cyp76c3* lines 1 and 2, and *cyp71b31* lines 1 and 2. The T-DNA was not located in TPS14 insertion lines 1 and 2.



Supplemental Figure 5: Linalool emission is absent from flowers of double mutant *tps10 tps14*.

The emitted volatiles of flower bouquets (~60 inflorescences) of wild type and double mutant line *tps10 tps14* were collected for 6 hours and analyzed in GC-MS as described in Methods. (A) Linalool reference, (B) double mutant *tps10 tps14*, (C) wild type. Linalool emission was not affected in single mutant lines *tps10* and *tps14* (data not shown).



Supplemental Figure 6: Linalool emitted by *Arabidopsis* flowers from the P450 insertion mutants.

A small but significant increase of linalool emission is observed with the flowers of *cyp76c3* insertion line. Error bars: SE, n=3. *, $p < 0.05$.

References	RT (min)	Mass	Detected masses			Additional substructures detected							
			[M+H] ⁺	[M+H-H ₂ O] ⁺	[M+H-2H ₂ O] ⁺	mass 1	formula 1	mass 2	formula 2	mass 3	formula 3	mass 4	formula 4
linalool	14.02	154.1352	155.1431	137.1326		153.1275	C10H17O	135.1169	C10H15	123.1170	C9H15	107.0858	C8H11
1,2 epoxy-linalool	11.84	170.1301	171.1380	153.1275	135.1169	123.1170	C9H15	95.0859	C7H11				
8-hydroxylinalool	8.05	170.1301		153.1274	135.1169	109.1015	C8H13	107.0858	C8H11	93.0702	C7H9		
8-oxo-linalool	9.67	168.1145		151.1118	133.1013	123.1170	C9H15	107.0858	C8H11	95.0859	C7H11	93.0702	C7H9
lilac alcohol	10.32	170.1301	171.1380		135.1169	123.1170	C9H15						
lilac alcohol epoxide	7.18	186.1250	187.1329	169.1224	151.1118	123.1170	C9H15						

Compound 1 - RT: 4.52 min			Detected masses			Compound 2 - RT: 6.38 min			Detected masses		
Possible structure	Brut formula	Mass	[M+H] ⁺	[M+H-H ₂ O] ⁺	[M+H-2H ₂ O] ⁺	Possible structure	Brut formula	Mass	[M+H] ⁺	[M+H-H ₂ O] ⁺	[M+H-2H ₂ O] ⁺
8-carboxy-dihydro-linalool	C10H18O3	186.1250		169.1224	151.1118	hydroxy-linalool	C10H18O2	170.1301		153.1275	
6-hydroxy-8-oxo-linalool						lilac alcohol					
epoxy-hydroxy-linalool						1,2- or 6,7- epoxy-linalool					
epoxy-linalool oxide						linalool oxide					
epoxy-8-oxo-dihydro-linalool						8-oxo-dihydro-linalool					
+ hexose (+C6H12O6 - H2O)	C16H28O8	348.1778	349.1858	331.1751		+ hexose (+C6H12O6 - H2O)	C16H28O7	332.1830	333.1908	315.1802	
Additional substructure detected						Additional substructure detected					
	C9H14	122.1090	123.1170				C7H8	92.0621	93.0702		
	C10H12	132.0934	133.1012				C7H10	94.0777	95.0859		
							C8H10	106.0777	107.0858		

Compound 3 - RT: 7.40 min			Detected masses			Compound 4 - RT: 7.44 min			Detected masses		
Possible structure	Brut formula	Mass	[M+H] ⁺	[M+H-H ₂ O] ⁺	[M+H-2H ₂ O] ⁺	Possible structure	Brut formula	Mass	[M+H] ⁺	[M+H-H ₂ O] ⁺	[M+H-2H ₂ O] ⁺
hydroxy-linalool	C10H18O2	170.1301		153.1275	135.1169	hydroxy-linalool	C10H18O2	170.1301	171.1380		
1,2- or 6,7- epoxy-linalool						lilac alcohol					
linalool oxide						linalool oxide					
8-oxo-dihydro-linalool						8-oxo-dihydro-linalool					
+ malonyl hexose (+C9H16O10 - 2H2O)	C19H30O10	418.1833		401.1806		+ hexose (+C6H12O6 - H2O)	C16H28O7	332.1830	333.1908		
Additional substructure detected											
malonyl glucose-H2O	C9H12O8	248.0525	249.0605								

Compound 5 - RT: 7.56 min			Detected masses			Compound 6 - RT: 7.60 min			Detected masses		
Possible structure	Brut formula	Mass	[M+H] ⁺	[M+H-H ₂ O] ⁺	[M+H-2H ₂ O] ⁺	Possible structure	Brut formula	Mass	[M+H] ⁺	[M+H-H ₂ O] ⁺	[M+H-2H ₂ O] ⁺
hydroxy-linalool	C10H18O2	170.1301	171.1380	153.1275		8-carboxy-linalool	C10H16O3	184.1094	185.1173	167.1067	
lilac alcohol						hydroxy-oxo-linalool					
linalool oxide						epoxy-lilac aldehyde					
8-oxo-dihydro-linalool						epoxy-8-oxo-linalool					
+ hexose (+C6H12O6 - H2O)	C16H28O7	332.1828	333.1908								

Compound 7 - RT: 7.67 min			Detected masses			Compound 8 - RT: 7.92 min			Detected masses		
Possible structure	Brut formula	Mass	[M+H] ⁺	[M+H-H ₂ O] ⁺	[M+H-2H ₂ O] ⁺	Possible structure	Brut formula	Mass	[M+H] ⁺	[M+H-H ₂ O] ⁺	[M+H-2H ₂ O] ⁺
hydroxy-linalool	C10H18O2	170.1301	171.1379	153.1275	135.1169	linalool	C10H18O	154.1352	155.1431		
1,2- or 6,7- epoxy-linalool						+ malonyl hexose (+C9H16O10 - 2H2O)	C19H30O9	402.1884	403.1962	385.1856	
linalool oxide						hydroxy-dihydro-linalool	C10H20O2	172.1461		155.1431	
8-oxo-dihydro-linalool						1,2- or 6,7-epoxy-dihydro-linalool					
+ malonyl hexose (+C9H16O10 - 2H2O)	C19H30O10	418.1833	419.1912	401.1806		+ malonyl hexose (+C9H16O10 - 2H2O)	C19H32O10	420.1993	403.1962	385.1856	
Additional substructure detected						Additional substructure detected					
malonyl glucose-H2O	C9H12O8	248.0525	249.0605			malonyl glucose-H2O	C9H12O8	248.0525	249.0605		

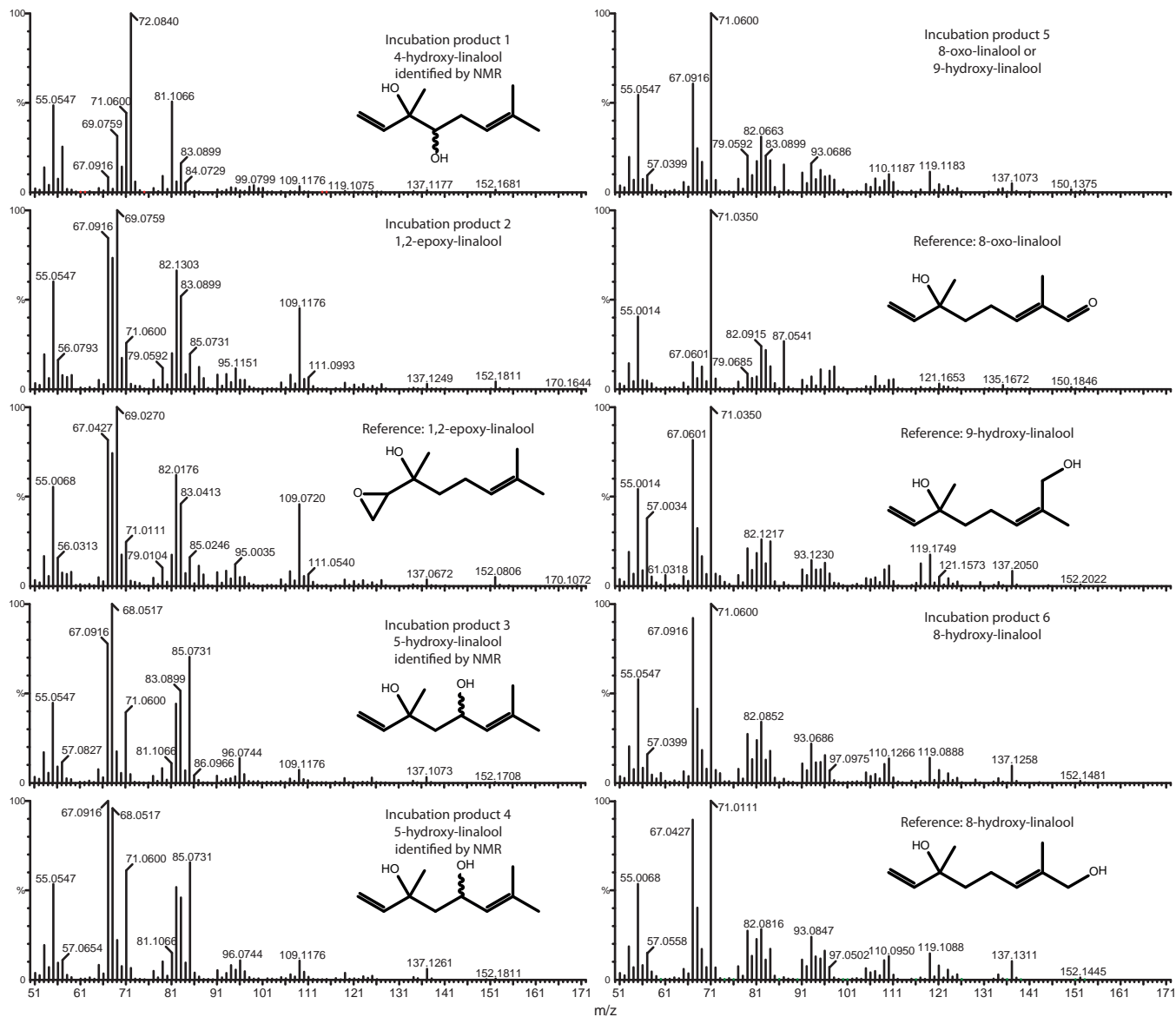
Compound 9 - RT: 8.48 min			Detected masses			Compound 10 - RT: 8.60 min			Detected masses		
Possible structure	Brut formula	Mass	[M+H] ⁺	[M+H-H ₂ O] ⁺	[M+H-2H ₂ O] ⁺	Possible structure	Brut formula	Mass	[M+H] ⁺	[M+H-H ₂ O] ⁺	[M+H-2H ₂ O] ⁺
hydroxy-linalool	C10H18O2	170.1301	171.1380			hydroxy-dihydro-linalool	C10H20O2	172.1461		155.1431	137.1326
lilac alcohol						1,2- or 6,7-epoxy-dihydro-linalool					
linalool oxide						Additional substructure detected					
8-oxo-dihydro-linalool							C7H10	94.0777	95.0859		
+ malonyl hexose (+C9H16O10 - 2H2O)	C19H30O10	418.1833	419.1911	401.1806							

Compound 11 - RT: 8.62 min			Detected masses			Compound 12 - RT: 8.85 min			Detected masses		
Possible structure	Brut formula	Mass	[M+H] ⁺	[M+H-H ₂ O] ⁺	[M+H-2H ₂ O] ⁺	Possible structure	Brut formula	Mass	[M+H] ⁺	[M+H-H ₂ O] ⁺	[M+H-2H ₂ O] ⁺
hydroxy-linalool	C10H18O2	170.1301	171.1380	153.1274	135.1169	hydroxy-dihydro-linalool	C10H20O2	172.1461		155.1431	137.1326
1,2- or 6,7- epoxy-linalool						1,2- or 6,7-epoxy-dihydro-linalool					
linalool oxide						Additional substructure detected					
8-oxo-dihydro-linalool							C7H10	94.0777	95.0859		
+ malonyl hexose (+C9H16O10 - 2H2O)	C19H30O10	418.1833	419.1911	401.1805							

Compound 13 - RT: 10.25 min			Detected masses		
Possible structure	Brut formula	Mass	[M+H] ⁺	[M+H-H ₂ O] ⁺	[M+H-2H ₂ O] ⁺
hydroxy-linalool	C10H18O2	170.1301	171.1379	153.1273	
1,2- or 6,7- epoxy-linalool					
linalool oxide					
8-oxo-dihydro-linalool					

Supplemental Figure 7: Linalool derivatives detected in UHPLC-Orbitrap analysis.

Top lists expected masses of reference compounds, dehydrated forms and derived fragments in ESI+ mode. Bottom lists detected masses of 13 linalool derivatives found in *Arabidopsis* flower methanol extracts and respective putative identification.



Supplemental Figure 8: GC-MS mass spectra of the linalool conversion products and references. Compounds were identified by comparison with authentic references (shown on figure) or by NMR.

Genotyping of *Arabidopsis* null mutant lines

PCR with T-DNA Left Border		
Insertion line	primer 1	primer 2
<i>TPS10</i> line 1	GCGTGGACCGCTTGCTGCAACT (LBb1)	CGTTGTCCGCAAAAAACGTTTCTTAATTG
<i>TPS10</i> line 2	GCGTGGACCGCTTGCTGCAACT (LBb1)	CGATCACAATATTGTGCTACAAGTG
<i>TPS14</i> line 1	GCGTGGACCGCTTGCTGCAACT (LBb1)	GATGTGGAGAAGGCAAGAAGCCAGCCG
<i>TPS14</i> line 2	GCGTGGACCGCTTGCTGCAACT (LBb1)	CCATTCTGGATCTTCTTGACCCGCG
<i>TPS14</i> line 3	GCGTGGACCGCTTGCTGCAACT (LBb1)	GGTTCTTCACGTTCTTCGGATTTGCTTCC
<i>CYP76C3</i> line 1	GCGTGGACCGCTTGCTGCAACT (LBb1)	AGAGCCATCGAGATTCCCGGAC
<i>CYP76C3</i> line 2	GCGTGGACCGCTTGCTGCAACT (LBb1)	AGAGCCATCGAGATTCCCGGAC
<i>CYP71B31</i> line 1	GCGTGGACCGCTTGCTGCAACT (LBb1)	CTTCCTTGTGAAGTGGTTTGC
<i>CYP71B31</i> line 2	GCGTGGACCGCTTGCTGCAACT (LBb1)	GATGTGCCTCGACAGAGTTGCC

PCR over insertion locus		
Insertion line	primer 1	primer 2
<i>TPS10</i> line 1	CGTGATCCCATTCCCTCAAAAAATC	CGTTGTCCGCAAAAAACGTTTCTTAATTG
<i>TPS10</i> line 2	GAGTTCTCTTGATGAATAGCTTGTACG	CGATCACAATATTGTGCTACAAGTG
<i>TPS14</i> line 1	CGAACTCTGGCGAATGGCGTGG	GATGTGGAGAAGGCAAGAAGCCAGCCG
<i>TPS14</i> line 2	GGTTCTTCACGTTCTTCGGATTTGCTTCC	CCATTCTGGATCTTCTTGACCCGCG
<i>TPS14</i> line 3	CCATTCTGGATCTTCTTGACCCGCG	GGTTCTTCACGTTCTTCGGATTTGCTTCC
<i>CYP76C3</i> line 1	TGAAGCTTGGAAAGGTTAACCCG	AGAGCCATCGAGATTCCCGGAC
<i>CYP76C3</i> line 2	TGAAGCTTGGAAAGGTTAACCCG	AGAGCCATCGAGATTCCCGGAC
<i>CYP71B31</i> line 1	CACTGACTTCTCCCCAGAGG	CTTCCTTGTGAAGTGGTTTGC
<i>CYP71B31</i> line 2	CGACCGGCTCCAAAGGGCAAG	GATGTGCCTCGACAGAGTTGCC

Amplification of candidate genes

	Forward primer	Reverse primer
<i>TPS10</i>	GGCTTAAUATGGCCACTCTCTGCAA	GGTTTAAUTCAATCTAAAGGAATCGGATTG
<i>TPS10</i> without plastid transit sequence	GGCTTAAUATGCAGCGTCGTTCTGCG	GGTTTAAUTCAATCTAAAGGAATCGGATTG
<i>TPS14</i>	GGCTTAAUATGGCCTTAATAGCTACC	GGTTTAAUTTACATTAGAGACTTGAGATATTCCG
<i>TPS14</i> without plastid transit sequence	GGCTTAAUATGATCGATGTCATTCAAAGT	GGTTTAAUTTACATTAGAGACTTGAGATATTCCG
<i>CYP76C3</i>	GGCTTAAUATGGACCTCTACTAATTCAAGG	GGTTTAAUTTAATAAGAAGACGATATTGTAGGTTTC
<i>CYP71B31</i>	GGCTTAAUATGTCTATGTTCTAGGTTTGCTC	GGTTTAAUTTATGGAAGAGTTGGTACGAGC

Amplification of promoter of candidate genes

	Forward primer	Reverse primer
Prom. <i>TPS10</i>	GGCTTAAUAGTTCTCGTGTGATTTGATGATAC	GGTTTAAUATTGAATAAATGTATTATTATGCTATACGTAAC
Prom. <i>TPS14</i>	GGCTTAAUCACCATTTCGATTCAATTTTAAG	GGTTTAAUGATGTATGAACTTAAGTTTTGTTTTG
Prom. <i>CYP76C3</i>	GGCTTAAUCTGACTCTTATTGTGGTTTTTGT	GGTTTAAUTGGACGACCACTTTTTCTTTAGG
Prom. <i>CYP71B31</i>	GGCTTAAUCAATGATATGGACGATGACAG	GGTTTAAUGCAAACCTAGGAATATAGATATAATTATTG

Amplification of candidate genes and fusion with eGFP or mRFP

	Forward primer	Reverse primer
<i>TPS10</i>	GGCTTAAUATGGCCACTCTCTGCAA	ATGTGGCGACCGGUACCATCTAAAGGAATCGGATTG
<i>TPS14</i>	GGCTTAAUATGGCCTTAATAGCTACC	ATGTGGCGACCGGUACCCATTAGAGACTTGAGATATTCCG
<i>CYP76C3</i>	GGCTTAAUATGGACCTCTACTAATTCAAGG	ATGTGGCGACCGGUACCATAAGAAGACGATATTGTAGG
<i>CYP71B31</i>	GGCTTAAUATGTCTATGTTCTAGGTTTGCTC	ATGTGGCGACCGGUACCTGGAAGAGTTGGTACGAGC
<i>eGFP</i>	ACCGGTCGCCACAUGGTGAGCAAGGGCGAGG	GGTTTAAUTTAGGCCATGATATAGACGTTGTGG
<i>mRFP</i>	ACCGGTCGCCACAUGGCCTCCTCCGAGGACGTCATC	GGTTTAAUTTAGGCGCCGGTGGAGTGGCG

qRT-PCR and RT-PCR

	Forward primer	Reverse primer
<i>TPS10</i>	ATCGTACAAGCTATTCATCAAGAGGAACT	ACCTAAACCTGTCTCCATCCACC
<i>TPS14</i>	GTCATTGACTCAAGGAGAAATGTCTCAAAC	GCTTCTTGCTTCTCCACATCTTT
<i>CYP76C3</i>	CCCGGAAACATTGACATGAGCGA	ACGATATTGTAGGTTTCTTGACGGGT
<i>CYP71B31</i>	CTTACGATCATCTCATAGCAATGATGTCGG	ATTGTTACTGTTCCAGCGTTTACTCCC
<i>SAND</i> (At2g28390)	GGATTTTCAGTACTCTTCAAGCTA	CTGCCTTGACTAAGTTGACACG
<i>TIP41</i> (At4g34270)	GAAGTGGCTGACAATGGAGTG	ATCAACTCTCAGCCAAAATCG
<i>PP2A</i> (At1g13320)	GACCGAGCCAACTAGGAC	AAAACCTGGTAACTTTTCCAGCA
<i>EXP</i> (At4g26410)	GAGCTGAAGTGGCTTCCATGA	GGTCCGACATACCCATGATCC

Supplemental Table 1: Primers used for genotyping of insertion lines, for amplification of ORFs and 1.5 kb-promoter region of candidate genes, and for qRT-PCR or RT-PCR.

***Arabidopsis* insertion mutant lines**

	SALK line name	Status
<i>tps10</i> line 1	SALK_108420	Homozygous
<i>tps10</i> line 2	SALK_041114	Homozygous
<i>TPS14</i> line 1	SALK_039462	Heterozygous
<i>TPS14</i> line 2	SALK_114189	Heterozygous
<i>tps14</i> line 3	SALK_059820	Homozygous
<i>cyp76c3</i> line 1	SALK_056876	Homozygous
<i>cyp76c3</i> line 2	SALK_077330	Homozygous
<i>cyp71b31</i> line 1	SALK_034144	Homozygous
<i>cyp71b31</i> line 2	SALK_009366	Homozygous
<i>tps10 tps14</i>	Selected after cross fecundation of <i>tps10</i> line 2 and <i>tps14</i> line 3	Homozygous

Supplemental Table 2: Name and status of employed *Arabidopsis* insertion mutant lines.