**SUPPLEMENTARY FIGURE 1. A)** Hierarchical clustering of both ESI+ and ESI- compounds found in non-mycorrhizal (Nm), *F. mosseae* (Fm) and *R. irregularis* (Ri) colonized roots. Samples were collected 8 weeks after inoculation with Fm or Ri. For each treatment, six replicates were injected randomly into the HPLC-QTOF-MS. The signals corresponding to different treatments were compared using the non-parametric Kruskal-Wallis test, and only data with a p<0.1 between groups was used for a supervised analysis. The clustering was performed using the package MarVis Filter from the software MarVis 2.0. B) Venn diagram of combined ESI+ and ESI- compounds obtained from the selected clusters represented in the Figure 2 and table S2. Numbers inside the shared coloured region represents the number of shared differentially accumulated compounds either by Nm-Fm, Nm-Ri or Fm-Ri.



**SUPPLEMENTARY FIGURE 2.** Polyamine phenylpropanoid conjugates (PPCs) and benzylisoquinoline alkaloids (BIAs) differentially accumulated in non-mycorrhizal (Nm), *F. mosseae-*(Fm) and *R. irregularis-*(Ri) colonized roots. For each treatment, six replicates were injected randomly into the HPLC-QTOF MS. Compounds tentatively identified were assigned by a m/z ratio together with their putative names.



**SUPPLEMENTARY TABLE 1**. Shoot and root fresh weight, nitrogen (N) and carbon (C) content, and C/N ratio of non-mycorrhizal (Nm) and mycorrhizal tomato plants eight weeks after inoculation with *F*. *mosseae* (Fm) or *R*. *irregularis* (Ri). Fresh weight data represent the means of ten independent biological replicates  $\pm$  SE. P, N and C content and C/N ratio represent the means of three independent biological replicates each consisting of a pool of roots from three independent plants  $\pm$  SE. Data in the same column not sharing a common letter differ significantly (*p*<0.05) according to Student-Newman-Keuls test.

Treatment	FW Shoot (g)	FW Root (g)	Root : Shoot	Ntotal (g/100g)	Ctotal (g/100g)	C/N
Nm	10,27 ± 1,57 a	4,68 ± 0,66 a	$0,48 \pm 0,03 \text{ a}$	1,91 ± 0,06 a	32,69 ± 0,35 a	$17,17 \pm 0,45 a$
Fm	11,80 ± 0,54 a	6,42 ± 0,43 a	0,54 ± 0,02 a	2,14 ± 0,03 b	30,50 ± 1,21 a	$14,26 \pm 0,47 \text{ b}$
Ri	10,56 ± 0,62 a	5,53 ± 0,48 a	$0,52 \pm 0,02 \text{ a}$	$2,23 \pm 0,22 \text{ ab}$	31,75 ± 2,82 a	$14,29 \pm 0,58 \text{ b}$

## **SUPPLEMENTARY TABLE 2. Identified pathways and compounds found in selected clusters.**

Signals corresponding to different treatments were compared using the non-parametric Kruskal-Wallis test, and only data with a p < 0.1 between groups were used for a supervised analysis. Quantitative values are relative to the sample dry weight and normalized to the lowest amount, and are represented following a colour scale ranging from blue (low) to red (high) accumulation. The signals have been selected following a criteria of maximum colour differences between treatments. Cluster 1 includes signals from the heatmap overrepresented in non-mycorrhizal roots (Nm), Cluster 2 includes signals from the heatmap overrepresented at the same time in both F. mosseae (Fm) and R. irregularis (Ri) colonized roots, Cluster 3 includes signals from the heatmap overrepresented only in Fm colonized roots and Cluster 4 includes signals from the heatmap overrepresented only in Ri colonized roots. The table was built grouping the number of hits provided by the package MarVis Pathway (MarVis 2.0) that were organized by pathways inside each cluster.

	Nm				
	Fm				
	Ri , , , , , , , , , , , , , , , , , , ,	50 60 70	80 90 100 110		
	Nm				
	Fm				
	Ri 2 4 6 6 10 12	14 16		ļ	ļ
		,	v	•	•
	Solanum lycopersicum (tomato)	CLUSTER 1	CLUSTER 2 CI	USTER 3 (	CLUSTER 4
	ABC transporters -	-	14	3	1
	Alanine; aspartate and glutamate metabolism -	-	7	1	2
	Amino acids	-	3	1	1
	Amino sugar and nucleotide sugar metabolism -	-	10	5	1
	Biosynthesis of amino acids -	-	16	9	2
۲ ۲	Cysteine and methionine metabolism -	-	10	1	1
lisn	Aminoacyl-tRNA biosynthesis -	-	3	1	1
abc	Lysine biosynthesis -	-	4	1	1
net	Lysine degradation -	-	4	4	-
p	Glycine; serine and threonine metabolism -	-	8	3	2
Daci	Histidine metabolism -	-	5	6	1
ninc	l ryptophan metabolism -	-	12	8	5
An	Valine: leucine and isoleucine biosynthesis		5	3	-
	Valine: leucine and isoleucine biosynthesis -		2	4	
	Phenylalanine metabolism -		8	-	-
	beta-Alanine metabolism -	-	6	2	1
	Arginine and proline metabolism -		12	5	1
รเ	Linoleic acid metabolism -	-	2	-	16
lipir	alpha-Linolenic acid metabolism -		9	1	-
) XV	Fatty acid degradation -	-	2	-	-
0	Arachidonic acid metabolism -		14	-	1
	Carbon metabolism -	-	9	6	1
~	Citrate cycle (TCA cycle) -	-	4	-	-
lism	Fructose and mannose metabolism -	-	6	-	-
ode	2-Oxocarboxylic acid metabolism -	-	21	8	6
neta	Galactose metabolism -	-	8	1	
_ _	Pentose phosphate pathway -	-	5	4	-
nga	Glycolysis / Glyconeogenesis -	-	3	-	-
õ	Pyruvate metabolism -	-	6	-	-
	Starch and sucrose metabolism -	-	6	-	-
	Glyoxylate and dicarboxylate metabolism -	-	10	3	-
s s	Isoquinoline alkaloid biosynthesis -	2	17	4	-
tive to	Lignans	-	14	4	1
: alc	Phenylpropanoid biosynthesis -	-	7	2	1
olic dei	Flavone and flavonol biosynthesis -	-	3	1	-
ner and	Flavonoid biosynthesis -	-	5	1	2
Ξ	Stilbenoid; diarytheptanoid and gingerol biosynthesis	-	3	2	2
	Limonene and pinene degradation -	-	16		
	Monoterpenoid biosynthesis -	-	14	2	7
	Ubiquinone and other terpenoid-quinone biosynthesis -	-	6	2	1
	Diterpenoid biosynthesis -	6	8	3	-
	Purine metabolism -	-	12	5	2
	Pyrimidine metabolism -		12	6	-
	Nicotinate and nicotinamide metabolism -	-	5	3	1
	Tropane; piperidine and pyridine alkaloid biosynthesis -	-	10	4	1
	Thiamine metabolism -	-	3	-	-
ins	Riboflavin metabolism -	-	3	2	
tam	Vitamin B6 metabolism -	-	7	1	-
i)	Pantothenate and CoA biosynthesis -	1	8	2	1
	Folate biosynthesis -	1	4	1	4
	Plant hormone signal transduction -	-	2	-	-
	Zeatin biosynthesis -	-	6	1	1
	Porphyrin and chlorophyll metabolism -	-	9	2	-
	Propanoate metabolism -	-	3	1	-
	Butanoate metabolism -	-	6	2	-
	Carotenoid biosynthesis -	1	2	-	-
	Glutathione matchelism	-	10	0	5
	Giverolinid metabolism -		5	5	
	Inositol phosphate metabolism -	-	2	-	-
	Ascorbate and aldarate metabolism -	-	7	7	-

Fm

**SUPPLEMENTARY TABLE 3.** HPLC-QTOF-MS library of standards compounds used for identification of metabolites based on exact mass and retention time matching.

			Ionization	Retention time
Compound	Exact mass	Ion mass	mode	(min)
Salicylic Acid	138,032	137,024	ESI-	12,2
Cinamic Acid	148,052	147,045	ESI-	10,5
Indole acetic acid	175,063	174,055	ESI+/ESI-	6,3
Caffeic Acid	180,042	179,035	ESI-	4,0
Jasmonic Acid	210,126	209,118	ESI-	11,1
Abscisic Acid	264,136	263,128	ESI-	9,6
Jasmonate-Isoleucin	323,210	322,202	ESI-	13,4
Ferulic Acid	194,058	193,050	ESI-	5,6
OPDA	292,204	291,196	ESI-	13,0
SAG	300,085	299,077	ESI-	4,1
SGE	300,085	299,077	ESI-	4,1
Chlorogenic acid	354,095	353,087	ESI-	4,4
ABA-Glucoside	426,189	425,181	ESI-	4,9
Camalexin	200,041	201,049	ESI+	11,8
Glycine	750,320	760,398	ESI+	Not retained
Alanine	890,477	900,555	ESI+	0,8
Arginine	174,112	175,120	ESI+	0,5
Asparagine	132,054	133,061	ESI+	0,8
Aspartic Acid	133,038	132,030	ESI-	1,4
Cysteine	121,020	122,028	ESI+	0,8
Glutamine	146,069	147,077	ESI+	0,8
Glutamic acid	147,053	148,061	ESI+	0,8
Histidine	155,070	156,077	ESI+	0,6
Isoleucine	131,095	132,102	ESI+	1,4
Leucine	131,095	132,102	ESI+	1,4
Lysine	146,106	147,113	ESI+	0,6
Methionine	149,051	150,059	ESI+	1,1
Phenylalanine	165,079	166,087	ESI+	2,1
Proline	115,063	116,071	ESI+	0,8
Serine	105,043	106,050	ESI+	0,8
Threonine	119,058	120,066	ESI+	0,8
Tryptophan	204,090	205,098	ESI+	2,6
Tyrosine	181,074	182,082	ESI+	1,2
Valine	117,079	118,087	ESI+	0,9
5-Hydroxyindole-3-acetic				
acid	191,058	192,066	ESI+	3,4
Indole-3-acetamide	174,079	175,087	ESI+	4,1

			Ionization	<b>Retention time</b>
Compound	Exact mass	Ion mass	mode	(min)
N-(3-indoleylacetyl)-L-				
alanine	246,100	247,108	ESI+	8,1
Indole-3-carboxaldehyde	145,053	146,061	ESI+	5,5
Methyl indole-acetate	189,079	190,087	ESI+	10,3
N-[(-)-Jasmonoyl]-				
Methionine (JAMet)	341,160	340,150	ESI-	12,7
Jasmonoyl-L-phenylalanine	357,194	356,186	ESI-	13,3
Jasmonoyl-L-valine				
(JAVal)	309,194	308,186	ESI-	12,5
Indole-3-acetyl-Isoleucine	288,147	289,155	ESI+	12,1
Indole-3-acetyl-L-				
phenylalanine	322,130	323,139	ESI+	12,6
			ESI-/+ (more	
Indole-3-carboxaldehyde	145,053	144,0449/146,0606	neg)	5,3
Indole-3-acetonitrile	156,060	157,077	ESI+	-
Indole-3-acetic acid-L-				
aspartic acid	290,090	289,082	ESI-	9,8
Indole-3-pyruvic acid	203,058	202,0504/204,0661	ESI-/+	-
I3CA methyl ester	175,060	176,071	ESI+	4,0
Indole-3-acetyl-L-				
tryptophan	361,142	360,1348/362,1505	ESI-/+	11,9
Adipic Ac	146,141	145,050	ESI -	3,0
Ketoglutaric Ac	146,021	145,013	ESI -	
Galacturonic Ac,	194,042	193,034	ESI -	1,5
Malic Ac,	134,021	133,014	ESI -	2,1
Folic Ac, (B9)	441,139	440,130	ESI -	4,3?
Fumaric Ac,	116,011	115,016	ESI -	-
Gibberellic Ac,	346,141	345,142	ESI -	5,5
Ascorbic Ac, (C)	176,032	177,060	ESI+	11,5
Maleic Ac,	116,011	115,000	ESI -	-
Nicotinic Ac,	123,032	124,024	ESI+	1,6
p-Aminobenzoic Ac,	137,048	138,050	ESI+	2,7
Pyruvic Ac,	880,160	87,008	ESI -	4,14?
Salicylhydroxamic Ac,	153,043	152,034	ESI -	3,3
Sinapic Ac,	224,069	223,060	ESI -	4,9
Pipecolic Ac,	129,079	128,071	ESI -	0,9
2-Aminoadipic Ac,	161,069	160,061	ESI -	0,9
AMP	347,063	346,050	ESI -	2,6
ADP	427,029	428,030	ESI+	
ATP	506,996	505,987	ESI -	
ATP		508,003	ESI+	
FAD	785,157	786,160	ESI+	-

			Ionization	<b>Retention time</b>
Compound	Exact mass	Ion mass	mode	(min)
NADH	665,120	664,101	ESI -	
Riboflavin (B2)	376,138	377.146,000	ESI+	3,9
Pyridoxal 5-phosphate (B6)	247,025	248,030	ESI+	4,1
Vanillin	152,047	153,050	ESI+	4,2
Quercetin	302,043	301,030	ESI -	10,9
Naringenin	272,069	271,064	ESI -	10,7
Scopoletin	192,042	193,040	ESI+	4,5
Hesperetin	302,079	303,080	ESI+	10,8
6-Benzylaminopurine	225,101	226,108	ESI+	6,2
Kinetin	215,081	216,080	ESI+	4,2
		265,110 (siempre		
Thiamine (B1)	265,110	cargardo)	ESI+	0,5
				2,44 in real
Zeatin (not in the library)	219,112	220,119	ESI+	sample